

PROGRAMA DE PÓS-GRADUAÇÃO EM FÍSICA

ÁREA DE FÍSICA APLICADA

The Grüneisen parameter applied to critical phenomena and experimental investigations of correlated phenomena in molecular conductors

Lucas Cesar Gomes Squillante

**INSTITUTO DE GEOCIÊNCIAS E CIÊNCIAS EXATAS
RIO CLARO - SP**

UNIVERSIDADE ESTADUAL PAULISTA

“Júlio de Mesquita Filho”

Instituto de Geociências e Ciências Exatas

Câmpus de Rio Claro

Lucas Cesar Gomes Squillante

The Grüneisen parameter applied to critical phenomena and experimental investigations of correlated phenomena in molecular conductors

Tese de Doutorado apresentada ao Instituto de Geociências e Ciências Exatas do Câmpus de Rio Claro, da Universidade Estadual Paulista “Júlio de Mesquita Filho”, como parte dos requisitos para obtenção do título de Doutor em Física Aplicada.

Orientador: Prof. Dr. Valdeci Pereira Mariano de Souza

Rio Claro - SP

2023

S773g Squillante, Lucas Cesar Gomes
The Grüneisen parameter applied to critical phenomena and experimental investigations of correlated phenomena in molecular conductors / Lucas Cesar Gomes Squillante. -- Rio Claro, 2023
208 p. : il., tabs., fotos

Tese (doutorado) - Universidade Estadual Paulista (Unesp), Instituto de Geociências e Ciências Exatas, Rio Claro
Orientador: Valdeci Pereira Mariano de Souza

1. Critical phenomena. 2. Grüneisen parameter. 3. strongly correlated electron systems. I. Título.

Sistema de geração automática de fichas catalográficas da Unesp. Biblioteca do Instituto de Geociências e Ciências Exatas, Rio Claro. Dados fornecidos pelo autor(a).

Essa ficha não pode ser modificada.

UNIVERSIDADE ESTADUAL PAULISTA

“Júlio de Mesquita Filho”

Instituto de Geociências e Ciências Exatas

Câmpus de Rio Claro

Lucas Cesar Gomes Squillante

The Grüneisen parameter applied to critical phenomena and experimental investigations of correlated phenomena in molecular conductors

Tese de Doutorado apresentada ao Instituto de Geociências e Ciências Exatas do Câmpus de Rio Claro, da Universidade Estadual Paulista “Júlio de Mesquita Filho”, como parte dos requisitos para obtenção do título de Doutor em Física Aplicada.

Comissão Examinadora

Prof. Dr. Valdeci Pereira Mariano de Souza (orientador)
IGCE / UNESP/Rio Claro (SP)

Prof. Dr. Aniekan Magnus Ukpung
Universidade de KwaZulu Natal / Pietermaritzburg, África do Sul

Prof. Dr. Ricardo Paupitz Barbosa dos Santos
IGCE / UNESP/Rio Claro (SP)

Prof. Dr. Ricardo Egydio de Carvalho
IGCE / UNESP/Rio Claro (SP)

Prof. Dr. Rafael Sá de Freitas
IFUSP / USP/São Paulo (SP)

Conceito: Aprovado.

Rio Claro (SP), 16 de Junho de 2023.

Acknowledgements

I would like to express my profound gratitude to Prof. Dr. Mariano de Souza for the immense support during my entire scientific career and for proposing the research topics investigated in this Thesis, as well as for all his advice and guidance throughout the entire progress of this work. He supported me beyond the academic activities always encouraging me to reach the best version of myself and to flourish my humane personal side in the academic activities and in life. He always saw an inner potential in me that even I didn't know it existed. In a world full of hollowness, superficiality, and lacking true academic mentors, I feel honored and proud to have him as my advisor. For those who know me since I started my undergraduate studies, I once was a non-fully committed student. Today I feel totally different, committed with the academic path and looking forward to become a professor of Physics in a Brazilian university in a near future. In the Talmud it is written that "Whoever saves one life, saves the world entirely" and I feel academically saved! My profound gratitude for you, Prof. Dr. Mariano de Souza!

I cannot express my love and gratitude for my fiancé Mariana Alvarinho Lorizola. She always encouraged me to pursue my dreams and to work hard to achieve my goals. She was also very patient, kind, and lovely during the entire period of the developing and writing of this Thesis. She is the best life partner I would ever imagine having in my life. All the love and affection that came from our relation are somehow spread throughout all chapters of this Thesis in a lovely fashion. Arriving home everyday to find you with a bright smile and our baby cat Frida asking to be petted make me feel loved and my heart warm. I love you, thank you for believing in me! At this point, I recall Robin Williams quote in the role of John Keating in the classical movie "Dead Poets Society" (1989):

"...We don't read and write poetry because it's cute. We read and write poetry because we are members of the human race. And the human race is filled with passion. And medicine, law, business, engineering, these are noble pursuits and necessary to sustain life. But poetry, beauty, romance, love, these are what we stay alive for. To quote from Whitman, "O me! O life!... of the questions of these recurring; of the endless trains of the faithless... of cities filled with the foolish; what good amid these, O me, O life?" Answer: that you are here - that life exists, and identity; that the powerful play goes on and you may contribute a verse. That

the powerful play goes on and you may contribute a verse. What will your verse be? ...”

Thank you for contributing a verse with me in this beautiful journey, my love!

I also would like to thank you my family, my mother Lindalva Gomes and my sister Isis Gomes Marques, for always supporting me in the best way they could, even from a distance. I wish this Thesis will spark love and affection in their lives! If my mother hadn't registered me in English classes when I was a kid, I wouldn't be writing this Thesis in English. Thank you, you are very special to me and I love you both!

I acknowledge all members of the Solid State Physics group, with special thanks to my Ph.D. colleague Isys Mello for all her support throughout the years. Also, I thank everyone from the Physics department at Unesp who supported us during the Ph.D., with special thanks to Leandro Xavier Moreno and Elizabete Pereira das Neves. I also thanks Maria from *Klips Papelaria & Copiadora* who printed all the posters I have presented in conferences for always caring too much about the exceptional printing quality of the posters, contributing to the best poster awards during the Ph.D.

I thank my great friends Renan Vieira Barreto and Vinicius Cavassano Zampier for the time we have lived together. Our home was always filled with nice discussions, celebrations, and a lot of hard work. I remember that we were always working in our manuscripts and projects and it really helped me during the first years of my Ph.D. to live with other people committed with their studies. Special thanks to Renan who really taught me everything I know about training exercises and helped me to get a better shape during the pandemics. Renan always told me what I needed to hear instead of what I wanted to hear, which was very important to me.

Special thanks to one special friend André Kyoshi Fujii Ferrazo who always kindly supported me and encouraged me to do great things. Thank you for all endless philosophical talks, walks at night, and emotional support as well.

I profoundly acknowledge Carlos Eduardo Ortolani Prado de Moura and Cristina Rosa Campos for the amazing support during this Ph.D. period and for making, in particular, this time of my life much lighter and smoother. Thank you both for the enlightenments and emotional support.

I also acknowledge all professors who did not gave me an opportunity and did not believe in my potential. If it weren't by them, I wouldn't be in this lovely academic path I am today.

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

Finally, I thank everyone who directly or indirectly supported me in this Thesis.

Abstract

Critical phenomena are of great interest to the scientific community and can be widely extended to various fields of research, such as classical and quantum phase transitions, caloric effects, and even Biology in brain functionality, for instance. As broadly discussed in the literature, the *smoking-gun* physical quantity to experimentally access both finite-temperature and quantum critical points is the so-called Grüneisen ratio. In this Ph.D. Thesis, a systematic review is performed on the derivation and generalization of the Grüneisen parameter followed by its unprecedented applications to several distinct scenarios, such as magnetic model systems, zero-field quantum phase transitions, the maximization of caloric effects close to *any* critical-end point based on entropy arguments, the here-proposed adiabatic magnetization of a paramagnetic salt, as well as for Cosmology in the frame of the universe expansion. Since this Ph.D. Thesis is a symbiosis between theoretical and experimental results, an experimental investigation of correlated phenomena was carried out for molecular conductors of the $(\text{TMTTF})_2\text{X}$ family, where TMTTF is the base molecule tetramethyltetrathiafulvalene and X a monovalent counter-anion such as PF_6 , SbF_6 , or AsF_6 . Such strongly correlated electron systems are considered suitable ones for the exploration of Mott insulating phase, charge-ordering, spin-Peierls, and superconductivity. In particular, the investigation of a possible multiferroic character in these salts was performed via quasi-static (low-frequency) dielectric constant ε' measurements as a function of temperature where a maximum in ε' as a function of temperature was observed at the corresponding charge-ordering temperature for both hydrogenated and 97.5% deuterated $(\text{TMTTF})_2\text{SbF}_6$ salts. Furthermore, Raman measurements were performed on the 97.5% deuterated $(\text{TMTTF})_2\text{PF}_6$, showing a possible magneto-optical effect on the $\nu_4(a_g)$ vibrational mode of the TMTTF molecule. Yet, fluorescence measurements demonstrated that the fully-hydrogenated $(\text{TMTTF})_2\text{AsF}_6$ presents an expressive fluorescence background, which is roughly five orders of magnitude lower than that for the 97.5% deuterated variant of $(\text{TMTTF})_2\text{PF}_6$.

Keywords: critical phenomena; Grüneisen parameter; strongly correlated electron systems.

Resumo

Fenômenos críticos são de grande interesse para a comunidade científica e podem ser estendidos para várias áreas de pesquisa, como transições de fase clássicas e quânticas, efeitos calóricos e até mesmo na Biologia no contexto da funcionalidade cerebral, por exemplo. É discutido amplamente na literatura que a grandeza física crucial para se acessar experimentalmente tanto pontos críticos a temperatura finita quanto pontos críticos quânticos é a chamada razão Grüneisen. Nesta tese de doutorado, uma revisão sistemática é realizada sobre a derivação e generalização do parâmetro de Grüneisen seguido pelas suas aplicações inéditas para diversos cenários físicos distintos, tais como sistemas modelo para o magnetismo, transições de fase quântica a campo magnético zero, a maximização de efeitos calóricos próximos de qualquer ponto crítico baseado em argumentos de entropia, para a magnetização adiabática de um sal paramagneto proposta nesta tese, bem como para a Cosmologia no contexto da expansão do universo. Uma vez que esta tese de doutorado é uma simbiose entre resultados experimentais e teóricos, uma investigação experimental de efeitos correlacionados em condutores moleculares também foi realizada para os condutores moleculares da família $(\text{TMTTF})_2\text{X}$, onde TMTTF é a molécula base tetrametiltetratíafulvaleno e X um contra-ânion monovalente, tais como PF_6 , SbF_6 ou AsF_6 . Tais sistemas eletrônicos fortemente correlacionados são considerados apropriados para a exploração de isolantes de Mott, fase de carga ordenada, spin-Peierls e até mesmo supercondutividade. Em particular, uma investigação do possível caráter multiferroico destes sais foi realizada utilizando medidas de constante dielétrica quase estática (baixa frequência) ϵ' em função da temperatura onde um máximo de ϵ' foi observado na temperatura de ordenamento de carga correspondente para a variante totalmente hidrogenada e 97,5% deuterada do sal $(\text{TMTTF})_2\text{SbF}_6$. Além disso, experimentos Raman foram realizados na variante 97,5% deuterada do sistema $(\text{TMTTF})_2\text{PF}_6$, onde um possível efeito magneto-óptico no modo vibracional $\nu_4(a_g)$ da molécula TMTTF foi observado. Ainda, experimentos adicionais mostraram que o sistema totalmente hidrogenado $(\text{TMTTF})_2\text{AsF}_6$ apresenta uma expressiva fluorescência, a qual é cerca de cinco ordens de magnitude maior do que a da variante 97,5% deuterada do sistema $(\text{TMTTF})_2\text{PF}_6$.

Palavras-chave: fenômenos críticos; parâmetro de Grüneisen; sistemas eletrônicos fortemente correlacionados.

Contents

1	Introduction	1
2	Theoretical investigations employing the Grüneisen parameter	5
2.1	State of the art	6
2.2	Theoretical background	7
2.2.1	Detailed deduction of the effective Grüneisen parameter . . .	7
2.2.2	The Brillouin-like paramagnet	15
2.2.3	The Friedman equations	20
2.3	Results	27
2.3.1	The magnetic Grüneisen parameter for the Brillouin paramagnet	27
2.3.2	Genuine zero-field quantum phase transitions?	28
2.3.3	Grüneisen parameter and the canonical definition of temperature	33
2.3.4	Adiabatic magnetization in a paramagnetic insulating system	36
2.3.5	Elastocaloric-induced effect adiabatic magnetization	38
2.3.6	Grüneisen parameter and second-order phase transitions . .	48
2.3.7	Generalization of the Grüneisen parameter	52
2.3.8	Maximization of caloric effects	56
2.3.9	Electric Grüneisen parameter and quantum paraelectricity .	59
2.3.10	Grüneisen parameter and the expansion of the universe . . .	62
3	Experimental investigations on the possible multiferroic character of the Fabre salts	74
3.1	Strongly correlated electronic phenomena in the (TMTTF) ₂ X salts	74
3.2	Experimental aspects	83
3.2.1	Principle of work of the Teslatron-PT cryostat	83
3.2.2	Cleaning up of the zeolite trap	90
3.2.3	Pump and purge of the ⁴ He circulation lines	93
3.3	Experimental results	94
3.3.1	Dielectric constant	94
3.3.2	Raman spectra and fluorescence background of the TMTTF salts	96
4	Summary and conclusions	101

5 Perspectives and outlook	103
Bibliography	104
6 Appendices	117
6.1 Absence of a perfect alignment between $\vec{\mu}$ and $\vec{B}$	117
6.2 The impossibility of connecting adiabatic deformations and the concept of negative temperatures	119
6.3 Power down during experiments	122
6.4 Technical aspects	125
6.5 Joint reports	125
6.6 Tutorships	126
6.7 Participation in scientific events	126
6.8 Prizes and awards	127
6.9 Graduate student representative	128
6.10 Published manuscripts as a co-author	129
6.11 Published manuscripts as first author	129
6.12 Fapesp agency divulgation articles	192

“The graveyard is the richest place on Earth, because it is there that you will find all the hopes and dreams that were never fulfilled, the books that were never written, the songs that were never sung, the inventions that were never shared, the cures that were never discovered, all because someone was too afraid to take that first step, keep with the problem, or determined to carry out their dream.”

— Les Brown (1945 -)

1

Introduction

Thermodynamics plays an unquestionable crucial role in Physics covering mathematical descriptions from heat engines [1, 2] to black holes [3], being considered as one of the most relevant fields in Physics in the last centuries [4]. Upon browsing classical Thermodynamics textbooks [1, 2], it is easily noticed that most of its applications are based on industrial machines and this is not a mere coincidence. Indeed, Thermodynamics was the driving intellectual force behind the industrial revolution and all its applications that emerged from this process in the beginning of the nineteenth century [4]. Only in the last decades, Thermodynamics started to play an increasingly key-role in other fields, such as Biology. A few examples lies, for instance, in the description of cell compartmentalization [5] or brain criticality in neural networks [6]. Afterwards, Thermodynamics was employed in modern technology associated with eco-friendly cooling, the so-called caloric effects [7], which refers to the temperature decrease in response to an adiabatic removal of a tuning parameter, which can be pressure or magnetic field, for example. In this context, the *smoking-gun* to explore critical phenomena and caloric effects is the so-called Grüneisen ratio Γ [8, 9], which is defined as the ration between thermal expansivity and the heat capacity at constant pressure. Also, such physical quantity is the appropriate experimental tool to probe quantum critical points [10]. Hence, it becomes evident that Γ is a key quantity in Thermodynamics. This Ph.D. Thesis

is based in two main chapters: a theoretical and an experimental one. At this point, it is worth mentioning that all theoretical topics covered in this Thesis, including the elastocaloric effect, adiabatic magnetization, among others, were possible to be investigated only because of the intense experimental activities and the robust experimental background of the Solid State Physics Laboratory at Unesp - Rio Claro, SP. Thus, in the frame of this Ph.D. Thesis, a theoretical background is reviewed followed by the obtained results regarding modern and cutting-edge applications of Γ .

In the last decades, molecular conductors have been recognized as an appropriate playground for the exploration of correlated phenomena in low-dimensions [11, 12]. A class of systems of particular interest is the $(\text{TMTTF})_2X$, where TMTTF is the base molecule tetramethylnetrathiafulvalene and X a monovalent centrosymmetric counter-anion, such as PF_6 , AsF_6 , and SbF_6 . This electronic system enables the investigation of contemporary aspects in the field of correlated phenomena, like the metal-Mott insulator transition [12] and the charge-ordered phase [11]. It is possible to change the physical properties of such systems either by employing chemical substitution in the base molecules or by applying external hydrostatic pressure [13, 14, 15]. The samples of such systems are single-crystals, which enables the investigation of correlated phenomena in a *clean* environment since no doping is made, i.e., absence of disorder via doping, being only the replacement of the counter-anions X in the electrochemical synthesis performed. In 2018, the so-called Mott-Hubbard ferroelectric phase was investigated in the Fabre salts [16]. A proper comparison between the physical properties of the fully-hydrogenated and the 97.5% deuterated variants of the system $(\text{TMTTF})_2\text{PF}_6$ was performed via systematic quasi-static dielectric constant measurements. It was theoretically predicted that the Mott-Hubbard ferroelectric phase would present magnetoelectric effects [17]. Hence, the investigations regarding possible multiferroic/magnetoelectric effects in these systems is a hot topic nowadays, which is the main focus of the experimental part of this Ph.D. Thesis. After this brief introduction, it is worth mentioning that this Ph.D. Thesis is divided in the following way:

- **Chapter 2:** this chapter is focused on the obtained theoretical results. In the beginning, a theoretical background on the detailed derivation of the effective Grüneisen parameter and its relation with the Grüneisen ratio is presented. After, a brief recapitulation of the fundamental aspects of the Brillouin-like paramagnet is performed, followed by the theoretical results obtained in this Ph.D. regarding zero-field quantum criticality, the relation between the canonical definition of temperature and the magnetic Grüneisen parameter, and caloric effects. Also, a discussion about the Friedmann equations and the Einstein field equations are also presented, as well as the application of the Grüneisen parameter to Cosmology (submitted manuscript). In this context, the following manuscripts were published with the obtained results discussed in this chapter: Physical Review B **100**, 054446 (2019), Scientific Reports **10**, 7981 (2020), Scientific Reports **11**, 9431 (2021), Materials Research Bulletin **142**, 111413 (2021).
- **Chapter 3:** this chapter is dedicated to the experimental results obtained in this Ph.D. Thesis regarding the molecular conductors of the (TMTTF)₂X salts. A brief introduction, motivation, and state-of-the art are presented. Before discussing the results, a compilation of the technical aspects regarding the operation and use of the Teslatron-PT cryostat is included. The experimental results are then presented followed by its discussion.
- **Chapter 4:** here, the summary and conclusions of this Thesis are provided.
- **Chapter 5:** perspectives and outlook are briefly discussed.
- Some appendices are included in the end of the Thesis regarding the non-perfect alinement between the magnetic moment and the external magnetic field, the impossibility of connecting adiabatic deformations and the concept of negative temperatures, power down during experiments, technical aspects like the fixing of a SMB connector, participation in joint reports during the Ph.D. degree, tutorships, attendance to scientific events, prizes and awards,

participation as the graduate student representative, and the full texts of the manuscripts that were published in the frame of this Thesis.

*“Take a good rest, small bird,” he said.
 “Then go in and take your chance like any man or bird
 or fish.”*

— Ernest Hemingway, *The Old Man and the Sea*.

2

Theoretical investigations employing the Grüneisen parameter

Contents

2.1	State of the art	6
2.2	Theoretical background	7
2.2.1	Detailed deduction of the effective Grüneisen parameter	7
2.2.2	The Brillouin-like paramagnet	15
2.2.3	The Friedman equations	20
2.3	Results	27
2.3.1	The magnetic Grüneisen parameter for the Brillouin paramagnet	27
2.3.2	Genuine zero-field quantum phase transitions?	28
2.3.3	Grüneisen parameter and the canonical definition of tem- perature	33
2.3.4	Adiabatic magnetization in a paramagnetic insulating system	36
2.3.5	Elastocaloric-induced effect adiabatic magnetization	38
2.3.6	Grüneisen parameter and second-order phase transitions	48
2.3.7	Generalization of the Grüneisen parameter	52
2.3.8	Maximization of caloric effects	56
2.3.9	Electric Grüneisen parameter and quantum paraelectricity	59
2.3.10	Grüneisen parameter and the expansion of the universe	62

In this chapter, several distinct physical scenarios that were explored using the various definitions of the Grüneisen parameter, namely effective, magnetic,

electric, elastic, and the Grüneisen ratio, are presented, which essentially covers magnetism at ultra low-temperatures, finite-temperature critical points, quantum critical points, caloric effects, and the dark energy problem in modern Cosmology. The obtained results for each topic of research are presented, as well as the published manuscripts that originated from these investigations. Key equations are boxed throughout the text.

2.1 State of the art

During the last four decades, there have been an enormous interest to explore the behaviour of the thermodynamical quantities in the critical regime, i.e., close to a finite-temperature critical point (CP). Particular examples include brain criticality in the frame of neural networks [6] and the onset of unconventional superconductivity [18, 19]. Besides finite-temperature critical points, investigations on quantum critical points have been growing continuously since they can be related to superconductivity [20, 21] or even to quantum Griffiths phases [22], just to mention a few key examples. In this context, the so-called Grüneisen ratio Γ [9, 10], which is given by the ratio between thermal expansivity and the specific heat, plays a fundamental role in exploring critical phenomena, since it quantifies the entropy variation in terms of temperature and the tuning parameter, which can be pressure p or external magnetic field B , for instance. It is well known that upon approaching a finite-temperature CP, Γ is enhanced close to the critical parameters [23]. Over the years, Γ has been employed not only to explore finite-temperature CP [23], but also magnetic-field induced quantum CP [21] and zero-field quantum CP [24, 25, 26]. When the tuning parameter is B , the magnetic Grüneisen parameter Γ_{mag} is the proper quantity to probe, for instance, quantum criticality [10]. Also, Γ_{mag} quantifies the so-called magnetocaloric effect [8], which is the temperature decrease due to an adiabatic removal of B [1]. Hence, this chapter focus on the obtained theoretical results regarding critical phenomena employing the various definitions of Γ .

2.2 Theoretical background

Before starting the discussions of this chapter followed by the obtained results, a theoretical background based on the discussion on Ref. [27] regarding the effective and magnetic Grüneisen parameters, the Grüneisen ratio, and the well-known Brillouin-like paramagnet are provided.

2.2.1 Detailed deduction of the effective Grüneisen parameter

First, it is considered a system where an infinitesimal pressure and temperature variation, namely dp and dT , respectively, can take place as a result of both an infinitesimal entropy variation dS and an infinitesimal strain variation $d\varepsilon$, so that the coupled equations for the differentials can be written as [27]:

$$dp = \left(\frac{\partial p}{\partial \varepsilon} \right)_S d\varepsilon + \left(\frac{\partial p}{\partial S} \right)_\varepsilon dS, \quad (2.1)$$

$$dT = \left(\frac{\partial T}{\partial \varepsilon} \right)_S d\varepsilon + \left(\frac{\partial T}{\partial S} \right)_\varepsilon dS. \quad (2.2)$$

Also, an isotropic compression is considered, so that $\varepsilon = \Delta v/v_0 = (v - v_0)/v_0$, being v the system's volume and v_0 its initial volume. Dividing both sides of Eq. 2.1 by $d\varepsilon$, it reads:

$$\frac{dp}{d\varepsilon} = \left(\frac{\partial p}{\partial \varepsilon} \right)_S + \left(\frac{\partial p}{\partial S} \right)_\varepsilon \frac{dS}{d\varepsilon}, \quad (2.3)$$

$$\frac{dp}{d\varepsilon} = \left(\frac{\partial p}{\partial \varepsilon} \right)_S + \left(\frac{\partial p}{\partial S} \right)_\varepsilon \frac{dS}{d\varepsilon}. \quad (2.4)$$

Assuming an isothermal case, i.e., $dT = 0$, Eq. 2.2 becomes:

$$0 = \left(\frac{\partial T}{\partial \varepsilon} \right)_S d\varepsilon + \left(\frac{\partial T}{\partial S} \right)_\varepsilon dS, \quad (2.5)$$

$$- \left(\frac{\partial T}{\partial S} \right)_\varepsilon dS = \left(\frac{\partial T}{\partial \varepsilon} \right)_S d\varepsilon, \quad (2.6)$$

$$-dS = \frac{\left(\frac{\partial T}{\partial \varepsilon}\right)_S d\varepsilon}{\left(\frac{\partial T}{\partial S}\right)_\varepsilon}, \quad (2.7)$$

$$\frac{dS}{d\varepsilon} = -\frac{\left(\frac{\partial T}{\partial \varepsilon}\right)_S}{\left(\frac{\partial T}{\partial S}\right)_\varepsilon}. \quad (2.8)$$

Replacing Eq. 2.8 in Eq. 2.4, it reads:

$$\frac{dp}{d\varepsilon} = \left(\frac{\partial p}{\partial \varepsilon}\right)_S + \left(\frac{\partial p}{\partial S}\right)_\varepsilon \left[-\frac{\left(\frac{\partial T}{\partial \varepsilon}\right)_S}{\left(\frac{\partial T}{\partial S}\right)_\varepsilon} \right], \quad (2.9)$$

$$\frac{dp}{d\varepsilon} = \left(\frac{\partial p}{\partial \varepsilon}\right)_S - \left(\frac{\partial p}{\partial S}\right)_\varepsilon \left(\frac{\partial S}{\partial T}\right)_\varepsilon \left(\frac{\partial T}{\partial \varepsilon}\right)_S. \quad (2.10)$$

Considering the generalized differential relation for the state functions given by [28]:

$$\left(\frac{\partial x}{\partial z}\right)_g = \left(\frac{\partial x}{\partial y}\right)_g \left(\frac{\partial y}{\partial z}\right)_g. \quad (2.11)$$

Assuming $x = p$, $y = S$, $z = T$, and $g = \varepsilon$ in Eq. 2.11, it reads:

$$\left(\frac{\partial p}{\partial T}\right)_\varepsilon = \left(\frac{\partial p}{\partial S}\right)_\varepsilon \left(\frac{\partial S}{\partial T}\right)_\varepsilon. \quad (2.12)$$

Replacing Eq. 2.12 into Eq. 2.10:

$$\frac{dp}{d\varepsilon} = \left(\frac{\partial p}{\partial \varepsilon}\right)_S - \left(\frac{\partial p}{\partial T}\right)_\varepsilon \left(\frac{\partial T}{\partial \varepsilon}\right)_S. \quad (2.13)$$

Assuming that $dp = (\partial p / \partial \varepsilon)_T d\varepsilon$, Eq. 2.13 becomes:

$$\left(\frac{\partial p}{\partial \varepsilon}\right)_T = \left(\frac{\partial p}{\partial \varepsilon}\right)_S - \left(\frac{\partial p}{\partial T}\right)_\varepsilon \left(\frac{\partial T}{\partial \varepsilon}\right)_S, \quad (2.14)$$

$$\left(\frac{\partial p}{\partial \varepsilon}\right)_T = \left(\frac{\partial p}{\partial \varepsilon}\right)_S - \left(\frac{\partial p}{\partial T}\right)_\varepsilon \left(\frac{\partial T}{\partial \varepsilon}\right)_S. \quad (2.15)$$

The term $(\partial p / \partial \varepsilon)_T$ in Eq. 2.15 can be rewritten based on the definition of $\varepsilon = \Delta v / v_0 = (v - v_0) / v_0$, so that:

$$\left(\frac{\partial p}{\partial \varepsilon}\right)_T = \left[\frac{\partial p}{\partial (\Delta v / v_0)} \right]_T = \left[\frac{\partial p}{\partial v} \frac{\partial v}{\partial (\Delta v / v_0)} \right]_T = v_0 \left(\frac{\partial p}{\partial \Delta v}\right)_T = v_0 \left[\frac{\partial p}{\partial (v - v_0)} \right]_T. \quad (2.16)$$

Considering the case of a compression, v is always lower than v_0 so that $\partial[v - v_0] = -\partial v$ and Eq. 2.16 reads:

$$\left(\frac{\partial p}{\partial \varepsilon}\right)_T = v_0 \left(\frac{\partial p}{\partial (-\partial v)}\right)_T = -v_0 \left(\frac{\partial p}{\partial v}\right)_T. \quad (2.17)$$

The right side of Eq. 2.17 is the definition of the isothermal bulk modulus $\mathcal{B}_T$ [28], so that:

$$\left(\frac{\partial p}{\partial \varepsilon}\right)_T = -v_0 \left(\frac{\partial p}{\partial v}\right)_T = \mathcal{B}_T. \quad (2.18)$$

The same analysis can be made in terms of $(\partial p/\partial \varepsilon)_S$ in Eq. 2.15, so that:

$$\left(\frac{\partial p}{\partial \varepsilon}\right)_S = \mathcal{B}_S, \quad (2.19)$$

where $\mathcal{B}_S$ is the adiabatic bulk modulus [28]. The term $(\partial T/\partial \varepsilon)_S$ in Eq. 2.15 can also be rewritten in terms of $\varepsilon = \Delta v/v_0 = (v - v_0)/v_0$, so that:

$$\left(\frac{\partial T}{\partial \varepsilon}\right)_S = \left[\frac{\partial T}{\partial(\Delta v/v_0)}\right]_S = \left[\frac{\partial T}{\frac{1}{v_0}\partial(\Delta v)}\right]_S = v_0 \left[\frac{\partial T}{\partial(\Delta v)}\right]_S = v_0 \left[\frac{\partial T}{\partial(v - v_0)}\right]_S, \quad (2.20)$$

so that:

$$\left(\frac{\partial T}{\partial \varepsilon}\right)_S = v_0 \left(\frac{\partial T}{\partial v}\right)_S = -v_0 \left(\frac{\partial T}{\partial v}\right)_S. \quad (2.21)$$

Now, replacing Eqs. 2.18, 2.19, and 2.21 into Eq. 2.15, it reads:

$$\mathcal{B}_T = \mathcal{B}_S - \left(\frac{\partial p}{\partial T}\right)_\varepsilon \left[-v_0 \left(\frac{\partial T}{\partial v}\right)_S\right], \quad (2.22)$$

$$(\mathcal{B}_T - \mathcal{B}_S) = \left(\frac{\partial p}{\partial T}\right)_\varepsilon \left(\frac{\partial T}{\partial v}\right)_S v_0. \quad (2.23)$$

Since the condition of a constant v strictly implies in a constant ε as well:

$$\left(\frac{\partial p}{\partial T}\right)_\varepsilon = \left(\frac{\partial p}{\partial T}\right)_v. \quad (2.24)$$

The term $(\partial p/\partial T)_v$ can be rewritten in terms of the well-known relation [28]:

$$\left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_p = -1, \quad (2.25)$$

so that:

$$\left(\frac{\partial p}{\partial T}\right)_v = -\frac{1}{\left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial T}{\partial v}\right)_p}. \quad (2.26)$$

The term $(\partial T/\partial v)_p$ is related to the definition of the thermal expansion coefficient at constant pressure α_p by $(\partial v/\partial T)_p = \alpha_p v_0$ [28], so that $(\partial T/\partial v)_p = 1/(\alpha_p v_0)$ and Eq. 2.26 reads:

$$\left(\frac{\partial p}{\partial T}\right)_v = -\frac{1}{\left(\frac{\partial v}{\partial p}\right)_T \frac{1}{\alpha_p v_0}} = -\frac{\alpha_p v_0}{\left(\frac{\partial v}{\partial p}\right)_T}. \quad (2.27)$$

Following the definition of $\mathcal{B}_T$, the term in Eq. 2.27 $(\partial v/\partial p)_T = -v_0/\mathcal{B}_T$ and thus Eq. 2.27 becomes:

$$\left(\frac{\partial p}{\partial T}\right)_v = -\frac{\alpha_p \mathcal{V}}{-\frac{\mathcal{V}}{\mathcal{B}_T}} = \alpha_p \mathcal{B}_T. \quad (2.28)$$

Now, the term $(\partial T/\partial v)_S$ in Eq. 2.23 can be rewritten employing the relation of Eq. 2.11 considering $x = T$, $y = p$, $z = v$, and $g = S$, so that:

$$\left(\frac{\partial T}{\partial v}\right)_S = \left(\frac{\partial T}{\partial p}\right)_S \left(\frac{\partial p}{\partial v}\right)_S. \quad (2.29)$$

The term $(\partial T/\partial p)_S$ can be rewritten following the relation [28]:

$$\left(\frac{\partial T}{\partial p}\right)_S \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial p}{\partial S}\right)_T = -1, \quad (2.30)$$

$$\left(\frac{\partial T}{\partial p}\right)_S = -\frac{1}{\left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial p}{\partial S}\right)_T}. \quad (2.31)$$

Plugging Eq. 2.31 into Eq. 2.29:

$$\left(\frac{\partial T}{\partial v}\right)_S = -\frac{1}{\left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial p}{\partial S}\right)_T} \left(\frac{\partial p}{\partial v}\right)_S = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p} \left(\frac{\partial p}{\partial v}\right)_S. \quad (2.32)$$

Given the fact that $\alpha_p = (1/v_0)(\partial v/\partial T)_p = (1/v_0)(-\partial S/\partial p)_T$ and the heat capacity at constant pressure $c_p = T(\partial S/\partial T)_p$ [28], Eq. 2.32 becomes:

$$\left(\frac{\partial T}{\partial v}\right)_S = \frac{\alpha_p v_0 T}{c_p} \left(\frac{\partial p}{\partial v}\right)_S. \quad (2.33)$$

Given the definition of $\mathcal{B}_S = -v_0(\partial p/\partial v)_S$ [28], the term in Eq. 2.33 $(\partial p/\partial v)_S = -\mathcal{B}_S/v_0$, so that Eq. 2.33 reads:

$$\left(\frac{\partial T}{\partial v}\right)_S = \frac{\alpha_p \mathcal{V} T}{c_p} \left(-\frac{\mathcal{B}_S}{\mathcal{V}}\right) = -\frac{\alpha_p T \mathcal{B}_S}{c_p}. \quad (2.34)$$

Finally, inserting Eqs. 2.28 and 2.34 in Eq. 2.23, it reads:

$$(\mathcal{B}_T - \mathcal{B}_S) = \alpha_p \mathcal{B}_T \left(-\frac{\alpha_p \mathcal{B}_S T}{c_p} \right) v_0 = -\alpha_p \mathcal{B}_T T \left(\frac{\alpha_p \mathcal{B}_S v_0}{c_p} \right). \quad (2.35)$$

Multiplying both sides of Eq. 2.35 by -1 , it reads:

$$(\mathcal{B}_S - \mathcal{B}_T) = \alpha_p \mathcal{B}_T T \left(\frac{\alpha_p \mathcal{B}_S v_0}{c_p} \right), \quad (2.36)$$

$$\mathcal{B}_S = \mathcal{B}_T + \alpha_p \mathcal{B}_T T \left(\frac{\alpha_p \mathcal{B}_S v_0}{c_p} \right) = \mathcal{B}_T \left[1 + \alpha_p T \left(\frac{\alpha_p \mathcal{B}_S v_0}{c_p} \right) \right], \quad (2.37)$$

$$\frac{\mathcal{B}_S}{\mathcal{B}_T} = 1 + \alpha_p T \left(\frac{\alpha_p \mathcal{B}_S v_0}{c_p} \right). \quad (2.38)$$

Employing the relation for the partial derivatives in Eq. 2.11 assuming $x = p$, $y = T$, $z = S$, and $g = v$, it reads:

$$\left(\frac{\partial p}{\partial S} \right)_v = \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial T}{\partial S} \right)_v. \quad (2.39)$$

Employing the Maxwell relation $(\partial p / \partial S)_v = -(\partial T / \partial v)_S$ [28] and the term $(\partial T / \partial v)_S$ computed in Eq. 2.34, so that, $(\partial p / \partial S)_v = \alpha_p \mathcal{B}_S T / c_p$. The latter can be replaced in Eq. 2.39 together with Eq. 2.28 and the definition of the heat capacity at constant volume $c_v = T(\partial S / \partial T)_v$ [28], i.e., $(\partial T / \partial S)_v = T / c_v$, so that Eq. 2.39 now reads:

$$\frac{\cancel{\alpha_p} \mathcal{B}_S \cancel{\mathcal{T}}}{c_p} = \cancel{\alpha_p} \mathcal{B}_T \frac{\cancel{\mathcal{T}}}{c_v}, \quad (2.40)$$

$$\frac{\mathcal{B}_S}{c_p} = \frac{\mathcal{B}_T}{c_v}, \quad (2.41)$$

which can be rewritten simply as:

$$\frac{\mathcal{B}_S}{\mathcal{B}_T} = \frac{c_p}{c_v}. \quad (2.42)$$

Replacing Eq. 2.42 into Eq. 2.38, it reads:

$$\frac{c_p}{c_v} = 1 + \alpha_p T \left(\frac{\alpha_p v_0}{c_p} \mathcal{B}_S \right) = 1 + \alpha_p T \left(\frac{\alpha_p v_0}{\cancel{c_p}} \frac{\cancel{\mathcal{B}_T}}{c_v} \right) = 1 + \alpha_p T \overbrace{\left(\frac{\alpha_p v_0 \mathcal{B}_T}{c_v} \right)}^{\Gamma_{eff}}. \quad (2.43)$$

The dimensionless physical quantity between parenthesis in Eq. 2.43 is the effective Grüneisen parameter [29, 9]:

$$\boxed{\Gamma_{eff} = \frac{\alpha_p v_0 \mathcal{B}_T}{c_v}}. \quad (2.44)$$

Note that Γ_{eff} is also related to the specific heat ratio, namely $\Gamma_{eff} = (c_p/c_v) - 1$ [30]. It is worth mentioning that Γ_{eff} can be rewritten in terms of the internal energy U . Employing the definition of Γ_{eff} in Eq. 2.44 and, considering $\alpha_p \mathcal{B}_T = (\partial p / \partial T)_v$ [27] and $c_v = (\partial U / \partial T)_v$, we have:

$$\Gamma_{eff} = v_0 \frac{\left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial U}{\partial T}\right)_v} = v_0 \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial U}{\partial T}\right)_v^{-1}. \quad (2.45)$$

Employing the relation from Eq. 2.11, one can write:

$$\left(\frac{\partial p}{\partial U}\right)_v = \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial U}\right)_v = \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial U}{\partial T}\right)_v^{-1}. \quad (2.46)$$

Replacing Eq. 2.46 into Eq. 2.45, it reads [9, 31]:

$$\boxed{\Gamma_{eff} = v_0 \left(\frac{\partial p}{\partial U}\right)_v}. \quad (2.47)$$

Strictly speaking, Γ_{eff} must be computed upon taking into account all the entropy contributions to the system, namely phononic S_{ph} and electronic S_{el} , so that $S_{tot} = S_{ph} + S_{el}$. Rewriting Γ_{eff} upon considering that $(\partial S / \partial \ln v)_T = v_0 \alpha_p \mathcal{B}_T$ and $(\partial S / \partial \ln T)_v = c_v$, Γ_{eff} reads [31]:

$$\Gamma_{eff} = \frac{\left(\frac{\partial S}{\partial \ln v}\right)_T}{\left(\frac{\partial S}{\partial \ln T}\right)_v}. \quad (2.48)$$

Replacing the expression for S_{tot} in Eq. 2.48, we have:

$$\Gamma_{eff} = \frac{\left[\frac{\partial(S_{ph}+S_{el})}{\partial \ln v}\right]_T}{\left[\frac{\partial(S_{ph}+S_{el})}{\partial \ln T}\right]_v}, \quad (2.49)$$

$$\Gamma_{eff} = \frac{\left(\frac{\partial S_{ph}}{\partial \ln v}\right)_T + \left(\frac{\partial S_{el}}{\partial \ln v}\right)_T}{\left(\frac{\partial S_{ph}}{\partial \ln T}\right)_v + \left(\frac{\partial S_{el}}{\partial \ln T}\right)_v}. \quad (2.50)$$

Employing Eq. 2.48 into Eq. 2.50, it reads:

$$\Gamma_{eff} = \frac{\Gamma_{eff}^{ph} c_v^{ph} + \Gamma_{eff}^{el} c_v^{el}}{c_v^{ph} + c_v^{el}}, \quad (2.51)$$

where the phononic and electronic contributions are taken into account both in Γ_{eff} and in c_v . Therefore, Eq. 2.51 can be written in its final form [31]:

$$\Gamma_{eff} = \frac{\sum_i \Gamma_{eff}^i c_v^i}{\sum_i c_v^i}. \quad (2.52)$$

Equation 2.52 shows that although S is an additive quantity in a system, Γ_{eff} is not. After almost 100 years that Eduard Grüneisen (1877-1949) proposed the relation shown in Eq. 2.44, it was proposed in the literature that a singular portion of Γ_{eff} can be employed to explore the vicinities of a pressure-induced quantum critical point [8]. Equation 2.44 can be rewritten as [8]:

$$\Gamma_{eff} = \frac{\alpha_p}{c_p} \frac{c_p}{c_v} v_0 \mathcal{B}_T = \Gamma \frac{c_p}{c_v} v_0 \mathcal{B}_T, \quad (2.53)$$

where Γ is the so-called Grüneisen ratio [8]. Since α_p is more singular than c_p close to a pressure-induced quantum critical point [8], Γ is the sensitive quantity that presents a divergent-like behaviour in the vicinity of the quantum critical point. The reason α_p is more pronounced than c_p close to a QCP, or a finite- T critical end point, is that usually T is fixed and the tuning parameter is varied, making the S variation more pronounced upon varying the tuning parameter. Another way of writing Γ is employing the definition of α_p and the molar heat capacity at constant pressure $c_p = T/N(\partial S/\partial T)_p$ [28], where N is the number of particles in the system, so that:

$$\Gamma = \frac{\alpha_p}{c_p} = \frac{1}{v_0} \left(\frac{\partial v}{\partial T} \right)_p \left[\frac{1}{\frac{T}{N} \left(\frac{\partial S}{\partial T} \right)_p} \right] = \frac{1}{v_m T} \frac{\left(\frac{\partial v}{\partial T} \right)_p}{\left(\frac{\partial S}{\partial T} \right)_p}, \quad (2.54)$$

where $v_m = v/N$ is the molar volume. Employing the Maxwell relation $(\partial v/\partial T)_p = -(\partial S/\partial p)_T$ [28], Γ reads [8]:

$$\Gamma = -\frac{1}{v_m T} \frac{\left(\frac{\partial S}{\partial p} \right)_T}{\left(\frac{\partial S}{\partial T} \right)_p}. \quad (2.55)$$

Using the relation [28]:

$$\left(\frac{\partial S}{\partial T} \right)_p \left(\frac{\partial T}{\partial p} \right)_S \left(\frac{\partial p}{\partial S} \right)_T = -1, \quad (2.56)$$

$$\left(\frac{\partial T}{\partial p}\right)_S = -\frac{1}{\left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial p}{\partial S}\right)_T} = -\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p}. \quad (2.57)$$

Replacing Eq. 2.57 in Eq. 2.55, Γ can be written as:

$$\boxed{\Gamma = \frac{1}{v_m T} \left(\frac{\partial T}{\partial p}\right)_S}. \quad (2.58)$$

Equation 2.58 shows that Γ quantifies the temperature change upon adiabatically varying p , i.e., the so-called barocaloric effect. A couple of years after the proposal that Γ is the singular contribution of Γ_{eff} in the vicinities of quantum critical points [8], it was also proposed by Prof. Mariano and collaborators that Γ can be also employed to explore finite- T critical points as well [23]. The authors of Ref. [8] also proposed that Γ can be rewritten for a magnetic-field-induced quantum critical point, so that [8]:

$$\boxed{\Gamma_{mag} = -\frac{\left(\frac{\partial M}{\partial T}\right)_B}{c_B} = -\frac{1}{T} \frac{\left(\frac{\partial S}{\partial B}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_B}}, \quad (2.59)$$

where M is the modulus of the magnetization, c_B the heat capacity at constant magnetic field, Γ_{mag} the magnetic Grüneisen parameter, and B the modulus of the external magnetic field. Employing the relation [28]:

$$\left(\frac{\partial S}{\partial T}\right)_B \left(\frac{\partial T}{\partial B}\right)_S \left(\frac{\partial B}{\partial S}\right)_T = -1, \quad (2.60)$$

$$-\left(\frac{\partial T}{\partial B}\right)_S = \frac{1}{\left(\frac{\partial S}{\partial T}\right)_B \left(\frac{\partial B}{\partial S}\right)_T} = \frac{\left(\frac{\partial S}{\partial B}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_B}. \quad (2.61)$$

Replacing Eq. 2.61 in Eq. 2.59, it reads:

$$\Gamma_{mag} = -\frac{1}{T} \left[-\left(\frac{\partial T}{\partial B}\right)_S \right], \quad (2.62)$$

$$\boxed{\Gamma_{mag} = \frac{1}{T} \left(\frac{\partial T}{\partial B}\right)_S}. \quad (2.63)$$

Equation 2.63 shows that Γ_{mag} quantifies the so-called magnetocaloric effect [1], i.e., the temperature decrease due to an adiabatic removal of the external magnetic field at a starting temperature T , which is accounted by the pre-factor $1/T$. Hence, it becomes evident that Γ and Γ_{mag} are key-parameters in probing both classical and quantum criticality, as well as in the quantification of caloric effects.

2.2.2 The Brillouin-like paramagnet

Before discussing the results, for the sake of completeness, the fundamental physical aspects of the Brillouin-type paramagnet are briefly recalled, since those are connected with some of the obtained theoretical results obtained. Just to mention, the modulus of many vectorial physical quantities discussed in this Ph.D. Thesis, such as the external magnetic field, magnetization, and related quantities, are considered. The well-known from textbooks Brillouin-type paramagnet is a non-interacting model that describes the behaviour of a paramagnetic insulating system [32]. The spins are localized and the system has only two eigenstates, i.e., there is a probability that the magnetic moment is either aligned in a parallel or an anti-parallel configuration with respect to B , being hereafter defined as P_{par} and $P_{anti-par}$, respectively. Such probabilities are given by [1]:

$$P_{par}(T, B) = \frac{e^{\mu_B B / k_B T}}{2 \cosh(\mu_B B / k_B T)}, \quad (2.64)$$

$$P_{anti-par}(T, B) = \frac{e^{-\mu_B B / k_B T}}{2 \cosh(\mu_B B / k_B T)}, \quad (2.65)$$

where k_B is Boltzmann constant (1.38×10^{-23}) J/K and μ_B the Bohr magneton (9.27×10^{-24} J/T). Recalling that the entropy S can be computed employing [1]:

$$S = -k_B \sum_j P(\psi_j) \ln(P(\psi_j)), \quad (2.66)$$

where ψ_j represents the j^{th} eigenstates. Since for the case of an insulating paramagnet there is only the probabilities P_{par} and $P_{anti-par}$, it is then written:

$$S = -k_B [P_{par} \ln(P_{par}) + P_{anti-par} \ln(P_{anti-par})]. \quad (2.67)$$

Inserting Eqs. 2.64 and 2.65 into Eq. 2.67, it is straightforward to write [1]:

$$S(T, B) = -\frac{B\mu_B}{T} \tanh\left(\frac{B\mu_B}{k_B T}\right) + k_B \ln \left[2 \cosh\left(\frac{B\mu_B}{k_B T}\right) \right], \quad (2.68)$$

Upon analysing the high-temperature limit for Eq. 2.68 at a fixed B , it is obtained $S(T \rightarrow \infty, B = \text{constant}) = k_B \ln(2)$, which indicates that the two eigenstates are equally probable. In the opposite side, at a fixed B , when $T \rightarrow 0 \Rightarrow S \rightarrow 0$, as expected by the third law of Thermodynamics [1]. The latter indicates that the ground-state of a Brillouin-type paramagnet is a ferromagnetic phase. This can be analysed in terms of the two spin populations N_1 and N_2 , which refer, respectively, to the number of spins aligned in parallel or anti-parallel with respect to B . The expressions for N_1 and N_2 with respect to the total spin population $N_T = (N_1 + N_2)$ are well-known in textbooks [33], being given by:

$$\frac{N_1}{N_T} = \frac{\exp(\mu_B B / k_B T)}{\exp(\mu_B B / k_B T) + \exp(-\mu_B B / k_B T)} \quad (2.69)$$

and

$$\frac{N_2}{N_T} = \frac{\exp(-\mu_B B / k_B T)}{\exp(\mu_B B / k_B T) + \exp(-\mu_B B / k_B T)}. \quad (2.70)$$

Figure 2.1 depicts that, on one hand, when $T \rightarrow 0$ K, all magnetic moments are in a parallel alignment with respect to B . On the other hand, at high temperatures, i.e., $T \rightarrow \infty$, the populations N_1/N_T and N_2/N_T are equally probable.

Also, the heat capacity at constant magnetic field c_B can be computed employing the expression $c_B = T(\partial S / \partial T)_B$ and Eq. 2.68, so that:

$$c_B(T, B) = T \left(\frac{\partial S}{\partial T} \right)_B = \frac{B^2 \mu_B^2}{k_B T^2} \text{sech}^2 \left(\frac{\mu_B B}{k_B T} \right). \quad (2.71)$$

The maximum in c_B shown in Fig. 2.2 for various fixed values of B is associated with the famous Schottky anomaly [34, 35]. Such an anomaly is a fingerprint of two-level systems and it shows that, upon lowering T , there is a particular condition in which entropy is dramatically varied as a consequence of the ordering of the system when $T \rightarrow 0$ K. Upon approaching such a condition, it becomes energetically more favorable for the system to order in a long-range fashion and thus the population N_1/N_T is favored, which in turn dramatically affects the available eigenstates of

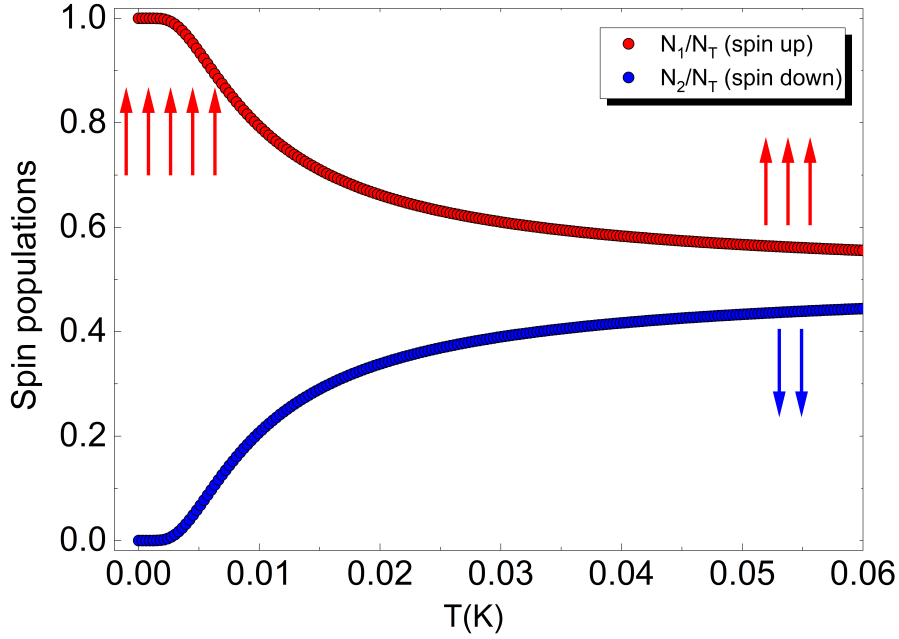


Figure 2.1: Spin populations N_1/N_T (up) and N_2/N_T (down) represented by the red and blue color data, respectively. Note that when $T \rightarrow 0$ K, $N_1/N_T \rightarrow 1$ and $N_2/N_T \rightarrow 0$, which means that the ground-state of the Brillouin-type paramagnet is a ferromagnetic phase. In the regime of high temperatures, i.e., $T \rightarrow \infty$, both N_1/N_T and N_2/N_T go to 0.5, which means that both configurations, namely spin up and down configurations are equally probable [$S = k_B \ln(2)$]. The arrows illustrate the spin populations in two distinct temperatures.

the system and, as a consequence, the entropy. As well-known from textbooks, such a maximum in c_B takes place when $(k_B T)/(\mu_B B) \simeq 0.834$ [34, 35, 36], i.e., when the thermal energy matches exactly the value of the energy between the two levels Δ . Hence, as depicted in Fig. 2.2, upon increasing the fixed value of B , the Schottky anomaly will take place at higher temperatures. This happens because when a higher B is applied, Δ is increased so that the condition for the Schottky anomaly to take place is thus reached at higher temperatures. In other words, given that $(k_B T)/(\mu_B B) \simeq 0.834$ [34, 35], if the magnetic energy increases then the thermal energy has to be increased as well in order to satisfy such a condition, which in turn makes the Schottky anomaly to be reached at higher temperatures upon increasing B . At very high temperatures, all curves shown in Fig. 2.2 converge to the same value of c_B , since S does not vary much with increasing T , namely $S \rightarrow k_B \ln(2)$. Regarding S for the Brillouin-type paramagnet, for $B = 0$ T $\Rightarrow S = k_B \ln(2)$ which is a non-temperature dependent S and thus it violates the

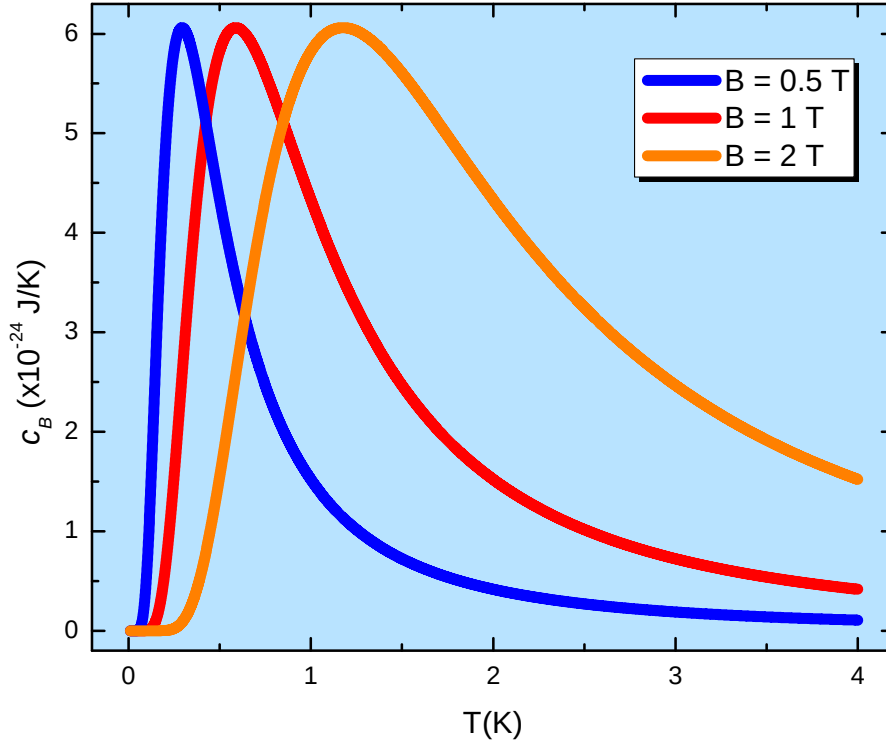


Figure 2.2: Heat capacity at constant magnetic field c_B as a function of T for $B = 0.5$ T (blue line), $B = 1$ T (red line), and $B = 2$ T (orange color line). The maximum on c_B is associated with the Schottky anomaly for two-level systems [34, 35]. More details in the main text.

third law of Thermodynamics, i.e., $S \rightarrow 0$ as $T \rightarrow 0$ [1]. Hence, to solve this issue, the mutual interactions between neighboring magnetic moments must be considered [37, 1]. At this point, the magnetic energy E associated with the dipolar interactions between adjacent spins is recalled, namely [32]:

$$E = \frac{\mu_0}{4\pi|\vec{r}|^3} \left[\vec{\mu}_1 \cdot \vec{\mu}_2 - \frac{3}{|\vec{r}|^2} (\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r}) \right], \quad (2.72)$$

where μ_0 is the vacuum permeability ($4\pi \times 10^{-7}$) T·m/A, $\vec{r}$ the distance between neighbouring spins, and $\vec{\mu}_1$ and $\vec{\mu}_2$ two arbitrary neighbouring magnetic moments. Considering no applied B , it can be written $|E| = \mu_B B_{loc}$, where B_{loc} is the modulus of the effective local magnetic field that emerges into the system as a result of the dipolar interactions between neighboring moments. Then, Eq. 2.72 becomes:

$$\mu_B B_{loc} = \frac{\mu_0}{4\pi|\vec{r}|^3} \left[\vec{\mu}_1 \cdot \vec{\mu}_2 - \frac{3}{|\vec{r}|^2} (\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r}) \right]. \quad (2.73)$$

Assuming $|\vec{\mu}_1| = |\vec{\mu}_2| = \mu_B = (9.27 \times 10^{-24})$ J/T and a typical distance between spins given by $|\vec{r}| = (5\text{\AA} = 5 \times 10^{-10})$ m, it is straightforward to notice that the

second term on the right side of the brackets does not significantly contribute to E , so that Eq. 2.73 can be approximated to:

$$B_{loc} \simeq \frac{\mu_0 \mu}{4\pi |\vec{r}|^3} \simeq \frac{(4\pi \times 10^{-7})(9.27 \times 10^{-24})}{4\pi (5 \times 10^{-10})^3} \simeq 0.01 \text{ T}. \quad (2.74)$$

Equation 2.74 enables us to conclude that $B_{loc} = 0.01 \text{ T}$ is intrinsically present in real paramagnets, since interactions between magnetic moments are always present. Therefore, since both B and B_{loc} are acting on the system, it is natural to assume that the paramagnetic system is under the influence of a resultant magnetic field, being its modulus B_r , based on the angle θ between $\vec{B}$ and $\vec{B}_{loc}$, which, employing the cosine rule, reads:

$$B_r^2 = B^2 + B_{loc}^2 - 2BB_{loc} \cos(\theta). \quad (2.75)$$

For the sake of simplicity, it is assumed that $\theta \approx 90^\circ$, so that:

$$B_r^2 = B^2 + B_{loc}^2 - \overbrace{2BB_{loc} \cos(\theta)}^{\approx 0}. \quad (2.76)$$

Hence, B_r takes the form:

$$B_r \simeq \sqrt{B^2 + B_{loc}^2}. \quad (2.77)$$

Now, replacing B for B_r in Eq. 2.68, it reads:

$$S(T, B) = -\frac{\mu_B \sqrt{B^2 + B_{loc}^2}}{T} \tanh \mu_B \left(\frac{\sqrt{B^2 + B_{loc}^2}}{k_B T} \right) + k_B \ln \left[2 \cosh \left(\frac{\mu_B \sqrt{B^2 + B_{loc}^2}}{k_B T} \right) \right]. \quad (2.78)$$

Note that, even when $B = 0 \text{ T}$, B_{loc} is still non-zero and thus S assumes a temperature-dependent mathematical form, which is now in perfect agreement with the third law of Thermodynamics [37]. Thus, although the Brillouin-type paramagnet model is non-interacting, the effective dipolar interactions between adjacent spins must be considered. It is worth mentioning that the modulus of the magnetic energy E_{mag} associated with B_{loc} is given by $E_{mag} = \mu_B B_{loc} = (9.27 \times 10^{-24})(0.01) = (9.27 \times 10^{-26}) \text{ J}$. Comparing such a result with the thermal

energy $T \simeq (9.27 \times 10^{-26})/k_B \simeq (9.27 \times 10^{-26})/(1.38 \times 10^{-23}) \simeq 6.7 \text{ mK}$. Such a result indicates that the relevance of the mutual interactions takes place on temperatures $T \leq 6.7 \text{ mK}$. In Section 2.3, the obtained results regarding the Brillouin-type paramagnet and an investigation of the role played by B_{loc} are discussed in a broader context.

2.2.3 The Friedman equations

Before discussing the results obtained in the frame of this Thesis regarding the application of both Γ and Γ_{eff} to Cosmology, a Newtonian-based derivation of the Friedman equations [38] without the cosmological constant Λ is properly given based on discussions presented in Ref. [39]. Note that Friedman has derived his equations in 1922 using Einstein field equations to describe a spatially homogeneous and isotropic expanding universe, so that a full derivation of Friedman equations including all general relativistic effects is not covered here. The latter is properly reported in Ref. [40]. Friedman has published his equations 7 years before Hubble reported what is known today as the Hubble law [41], showing that galaxies are moving away from each other and the further away they are, the faster they move away. Hubble proposed a linear relationship between the radial velocity v_R of galaxies and the distance to a particular galaxy d , so that $H = v_R d$ [41], where H is the Hubble parameter broadly discussed in Cosmology. The Hubble law is considered one of the most important relations in Cosmology [39]. Just to mention, the first experimental evidence that the universe is expanding was reported in 1912 by V. M. Slipher [42], while the observational evidence that the expansion of the universe was accelerated was only reported in 1998, cf. Ref. [43]. Back to the Newtonian-based derivation of the Friedman equations, first it is considered that the universe is a homogeneous sphere of matter with a mass M_s that does not vary in time. Such a sphere can be either contracting or expanding isotropically over time, so that its radius $R_s(t)$ is time-dependent. Considering a test mass m at the surface of the sphere, the modulus of the gravitational force F experienced by the

test mass considering Newton's law of gravity is given by [44]:

$$F = -\frac{GM_s m}{R_s^2}, \quad (2.79)$$

where G is the universal gravitational constant. Considering Newton's second law, F can be written in terms of the gravitational acceleration, which is given by:

$$F = ma = m \frac{d^2 R_s}{dt^2}, \quad (2.80)$$

which reads:

$$\mathfrak{M} \frac{d^2 R_s}{dt^2} = -\frac{GM_s \mathfrak{M}}{R_s^2}, \quad (2.81)$$

$$\frac{d^2 R_s}{dt^2} = -\frac{GM_s}{R_s^2}. \quad (2.82)$$

Multiplying both sides of Eq. 2.82 by dR_s/dt , it reads:

$$\frac{dR_s}{dt} \frac{d}{dt} \left(\frac{dR_s}{dt} \right) = -\frac{GM_s}{R_s^2} \frac{dR_s}{dt}. \quad (2.83)$$

Integrating both sides:

$$\int \left(\frac{dR_s}{dt} \right) \frac{d}{dt} \left(\frac{dR_s}{dt} \right) = \int -\frac{GM_s}{R_s^2} \left(\frac{dR_s}{dt} \right) = GM_s \int -\frac{1}{R_s^2} \left(\frac{dR_s}{dt} \right). \quad (2.84)$$

Upon analysing the term $(dR_s/dt)d/dt(dR_s/dt)$, one can notice employing the chain rule that such a term represents the time derivative of the function $1/2(dR_s/dt)^2$, i.e., $d/dt[1/2(dR_s/dt)^2] = (dR_s/dt)d/dt(dR_s/dt)$. Hence, Eq. 2.84 is rewritten as:

$$\int \frac{d}{dt} \left[\frac{1}{2} \left(\frac{dR_s}{dt} \right)^2 \right] = GM_s \int -\frac{1}{R_s^2} \left(\frac{dR_s}{dt} \right). \quad (2.85)$$

Employing basic Calculus, the integral of the derivative of a function yields in the function itself, so that:

$$\frac{1}{2} \left(\frac{dR_s}{dt} \right)^2 + c_1 = GM_s \int -\frac{1}{R_s^2} \left(\frac{dR_s}{dt} \right). \quad (2.86)$$

Now, the same analysis is employed for the term $-1/R_s^2(dR_s/dt)$, i.e., employing the chain rule one can notice that $d/dt[1/R_s] = -1/R_s^2(dR_s/dt)$, so that:

$$\frac{1}{2} \left(\frac{dR_s}{dt} \right)^2 + c_1 = GM_s \int \frac{d}{dt} \left(\frac{1}{R_s} \right), \quad (2.87)$$

$$\frac{1}{2} \left(\frac{dR_s}{dt} \right)^2 + c_1 = \frac{GM_s}{R_s} + c_2, \quad (2.88)$$

$$\frac{1}{2} \left(\frac{dR_s}{dt} \right)^2 = \frac{GM_s}{R_s} + c_3, \quad (2.89)$$

where c_1 and c_2 are integration constants and $c_3 = (c_2 - c_1)$. Given that R_s varies in time, the volume of the sphere V_s will vary as well and, as a consequence, so the matter density ρ_m , so that:

$$\rho_m = \frac{M_s}{V_s} \Rightarrow V_s = \frac{M_s}{\rho_m}. \quad (2.90)$$

Since a spherical shape is considered, Eq. 2.90 reads:

$$V_s = \frac{4}{3} \pi R_s^3 = \frac{M_s}{\rho_m}, \quad (2.91)$$

$$M_s = \frac{4}{3} \pi R_s^3 \rho_m. \quad (2.92)$$

The temporal variation of R_s can be inferred as a consequence of the change in the metric of space, as well as in so-called scale factor $a(t)$, so that:

$$R_s = a(t)r_s, \quad (2.93)$$

where r_s is the comoving radius of the sphere. Essentially, the comoving radius is a definition of measuring distances in the universe that takes into account the fact that the universe is expanding over time. It helps to keep track of how far apart objects are from each other, even as the universe expands. By making use of Eq. 2.93, the term $dR_s/dt = \dot{a}(t)r_s$. At this point, for the sake of simplicity, $a(t)$ is given solely by a . Then, together with Eq. 2.92, Eq. 2.89 reads:

$$\frac{1}{2} (\dot{a}r_s)^2 = \frac{G}{R_s} \frac{4}{3} \pi R_s^3 \rho_m + c_3, \quad (2.94)$$

$$\frac{1}{2} \dot{a}^2 r_s^2 = \frac{4\pi G}{3} R_s^2 \rho_m + c_3. \quad (2.95)$$

Employing Eq. 2.93 into Eq. 2.95:

$$\frac{1}{2} \dot{a}^2 r_s^2 = \frac{4\pi G}{3} (ar_s)^2 \rho_m + c_3, \quad (2.96)$$

$$\frac{1}{2}\dot{a}^2 r_s^2 = \frac{4\pi G}{3} a^2 r_s^2 \rho_m + c_3. \quad (2.97)$$

Dividing both sides of Eq. 2.97 by $r_s^2 a^2/2$, it yields:

$$\frac{\frac{1}{2}\dot{a}^2 r_s^2}{\frac{r_s^2 a^2}{2}} = \frac{\frac{4\pi G}{3} a^2 r_s^2 \rho_m + c_3}{\frac{r_s^2 a^2}{2}}, \quad (2.98)$$

$$\frac{\dot{a}^2}{a^2} = \frac{8\pi G}{3} \rho_m + \frac{2c_3}{r_s^2} \frac{1}{a^2}, \quad (2.99)$$

$$\left(\frac{\dot{a}}{a}\right)^2 = \frac{8\pi G}{3} \rho_m + \frac{2c_3}{r_s^2} \frac{1}{a^2}. \quad (2.100)$$

Equation 2.100 is the first Friedman equation in a Newtonian form. It connects the temporal behaviour of the scale factor with $\rho_m(t)$. However, the correct form of the first Friedman equation must take into account relativistic effects since it is derived from Einstein field equations in the frame of general relativity. Hence, the correct form of the first Friedman equation reads [38]:

$$\boxed{\left(\frac{\dot{a}}{a}\right)^2 = \frac{8\pi G}{3c^2} \rho - \frac{\kappa c^2}{r_s^2} \frac{1}{a^2}}, \quad (2.101)$$

where ρ is the energy density, κ is the space curvature constant, and c is the speed of light. Note that the relation between ρ and ρ_m is $\rho_m = \rho/c^2$ [39]. For the derivation of the second Friedman equation, the first-law of Thermodynamics is recalled:

$$dS = dU + pdV_S, \quad (2.102)$$

where dU is the infinitesimal internal energy variation. Since the expansion of the universe is adiabatic $dS = 0$, so that:

$$dU + pdV_S = 0. \quad (2.103)$$

Assuming that $V_S(t)$ and $U(t)$, Eq. 2.103 is given by:

$$\dot{U} + p\dot{V}_S = 0. \quad (2.104)$$

Recalling that $R_s(t) = ar_s$, $V_S(t)$ reads:

$$V_S(t) = \frac{4}{3}\pi R_s(t)^3 = \frac{4}{3}\pi a^3 r_s^3, \quad (2.105)$$

thus:

$$\dot{V}_S = \frac{4}{3}\pi r_s^3 (3a^2 \dot{a}) = V_S(t) \left(3 \frac{\dot{a}}{a}\right). \quad (2.106)$$

Now, $U(t)$ can be rewritten as:

$$U(t) = V_S(t)\rho, \quad (2.107)$$

then:

$$\dot{U} = V_S \dot{\rho} + \dot{V}_S \rho = V_S \left(\dot{\rho} + 3 \frac{\dot{a}}{a} \rho \right). \quad (2.108)$$

Replacing Eqs. 2.106 and 2.108 into Eq. 2.104:

$$V_S \left(\dot{\rho} + 3 \frac{\dot{a}}{a} \rho + 3 \frac{\dot{a}}{a} p \right) = 0, \quad (2.109)$$

$$\dot{\rho} + 3 \frac{\dot{a}}{a} \rho + 3 \frac{\dot{a}}{a} p = 0, \quad (2.110)$$

$$\dot{\rho} + \frac{3\dot{a}}{a}(\rho + p) = 0. \quad (2.111)$$

Equation 2.111 is the so-called fluid equation [39], connecting the energy density and pressure with the temporal evolution of the scale factor. Now, rewriting the first Friedman equation as:

$$\dot{a}^2 = \frac{8\pi G}{3c^2} \rho a^2 - \frac{\kappa c^2}{r_s^2}. \quad (2.112)$$

Taking the time derivative in both sides of Eq. 2.112, it reads:

$$2\dot{a}\ddot{a} = \frac{8\pi G}{3c^2}(\dot{\rho}a^2 + 2\rho a\dot{a}). \quad (2.113)$$

Dividing both sides by $2\dot{a}a$:

$$\frac{\ddot{a}}{a} = \frac{4\pi G}{3c^2} \left(\dot{\rho} \frac{a}{\dot{a}} + 2\rho \right). \quad (2.114)$$

Rewriting Eq. 2.111 as:

$$\dot{\rho} = -\frac{3\dot{a}}{a}(\rho + p). \quad (2.115)$$

Replacing Eq. 2.115 into Eq. 2.114:

$$\frac{\ddot{a}}{a} = \frac{4\pi G}{3c^2} \left\{ \left[-3\frac{\dot{q}}{a}(\rho + p) \right] \frac{q}{\dot{a}} + 2\rho \right\}, \quad (2.116)$$

$$\frac{\ddot{a}}{a} = \frac{4\pi G}{3c^2} (-3\rho - 3p + 2\rho) = \frac{4\pi G}{3c^2} (-\rho - 3p), \quad (2.117)$$

$$\boxed{\frac{\ddot{a}}{a} = -\frac{4\pi G}{3c^2} (\rho + 3p)}. \quad (2.118)$$

Equation 2.118 is the second Friedman equation, also known as the acceleration equation [39]. As broadly discussed in the literature, the universe is usually described by the picture of a perfect fluid, i.e., an isotropic fluid with no viscosity [45]. The equation of state (EOS) of a perfect fluid is $p = \omega\rho$ [45, 39], where ω is the so-called EOS parameter. After the Big Bang, various eras of the universe took place. First, the radiation-dominated era and, later on, the matter-dominated era was achieved. During both radiation- and matter-dominated eras, the universe expanded in a decelerated way [45, 39]. Currently, the universe is expanding in an accelerated way [43] because of the so-called dark-energy (DE). Essentially, DE is the vacuum energy and it is taken into account both in Einstein field equations and Friedman equations when the cosmological constant Λ is incorporated in such equations. The term “dark” refers to the fact that the origin of such energy is still unknown during the writing of this Thesis. Just to mention, our universe is composed nowadays of about 69% of dark energy, 7% of dark-matter, and 4% of regular matter, i.e., stars and planets, for instance [39]. The relationship between p and ρ was different for each era, given by distinct values of ω . For the radiation-dominated era $\omega = 1/3$, for the matter-dominated era $\omega \rightarrow 0$, and for the DE-dominated era $\omega = -1$. It is worth mentioning that ω is merely discussed in the literature as a numerical value, which is discussed in more details in the results section of this Thesis. Regarding the accelerated expansion, the most accepted explanation for such an acceleration is that DE is a fluid with positive ρ , but with a negative pressure [45], namely $p = -\rho$. For the expansion to be accelerated, the condition $\ddot{a} > 0$ must be fulfilled in Eq. 2.118, being the opposite also true for a decelerated expansion $\ddot{a} < 0$. Just to mention, since a represents the metric of space, $\dot{a}$ has units

of velocity while $\ddot{a}$ of acceleration [39]. By assuming that the total energy density ρ_{tot} of the universe is given by $\rho_{tot} = (\rho_{radiation} + \rho_{matter} + \rho_{DE})$ and that p is an additive physical quantity, i.e., the total pressure $p_{tot} = (p_{radiation} + p_{matter} + p_{DE})$, Eq. 2.118 can be straightforwardly rewritten:

$$\frac{\ddot{a}}{a} = -\frac{4\pi G}{3c^2}(\rho_{radiation} + \rho_{matter} + \rho_{DE} + 3p_{radiation} + 3p_{matter} + 3p_{DE}). \quad (2.119)$$

Considering the perfect fluid EOS and the value of ω for the various eras:

$$\frac{\ddot{a}}{a} = \left(\rho_{radiation} + \rho_{matter} + \rho_{DE} + 3\frac{1}{3}\rho_{radiation} + \cancel{3 \cdot 0 \cdot \rho_{matter}}^0 + 3(-1)\rho_{DE} \right), \quad (2.120)$$

$$\frac{\ddot{a}}{a} = -\frac{4\pi G}{3c^2}(2\rho_{radiation} + \rho_{matter} - 2\rho_{DE}). \quad (2.121)$$

Note that as the universe expands, a is increased. Also, based on Friedman equations, it is established in the literature that $\rho_{radiation} \propto 1/a^4$ and $\rho_{matter} \propto 1/a^3$ [46]. Also, ρ_{DE} is considered to be time-independent, which is still a topic under debate in the literature. Thus, the expansion of the universe and the increase in the scale factor makes the energy density of radiation and matter to be decreased and, in the DE-dominated era, such contributions can be considered negligible in comparison with ρ_{DE} , so that Eq. 2.121 reads:

$$\frac{\ddot{a}}{a} \simeq -\frac{4\pi G}{3c^2}(-2\rho_{DE}), \quad (2.122)$$

$$\frac{\ddot{a}}{a} \simeq \frac{8\pi G}{3c^2}\rho_{DE}. \quad (2.123)$$

The minus sign of $-2\rho_{DE}$, which comes from the consideration of a negative pressure associated with DE, makes $\ddot{a}/a$ to be positive in the DE-dominated assuming that G is always greater than zero. This implies that DE drives the accelerated expansion of the universe. This is one of the key results emerging from the Friedman equations in modern Cosmology [39]. Based on these discussions regarding the perfect fluid picture, Friedman equations, and the accelerated expansion of the universe, we have unprecedentedly connected well-established concepts of condensed matter physics, namely Γ and Γ_{eff} , to Cosmology, which is properly discussed in Section 2.3.10.

2.3 Results

2.3.1 The magnetic Grüneisen parameter for the Brillouin paramagnet

By making use of the partition function $Z = 2 \cosh\left(\frac{\mu_B B}{k_B T}\right)$ of the Brillouin-type paramagnet [1], the free energy F can be computed as:

$$F(T, B) = -k_B T \ln(Z) = -k_B T \ln\left[2 \cosh\left(\frac{\mu_B B}{k_B T}\right)\right]. \quad (2.124)$$

Hence, employing $M = -(\partial F / \partial B)_T$ [28], it reads:

$$M(T, B) = -\left(\frac{\partial F}{\partial B}\right)_T = -\frac{2\mu_B}{k_B T} \sinh\left(\frac{\mu_B B}{k_B T}\right). \quad (2.125)$$

Employing Eq. 2.125, the behaviour of M as a function of T and B can be analysed. It turns out that in the regime of both $T \rightarrow 0$ K and $B \rightarrow 0$ T, M presents a step-like behaviour, cf. Fig. 2.3.

As a step further, the analytical calculation of Γ_{mag} for the Brillouin-type

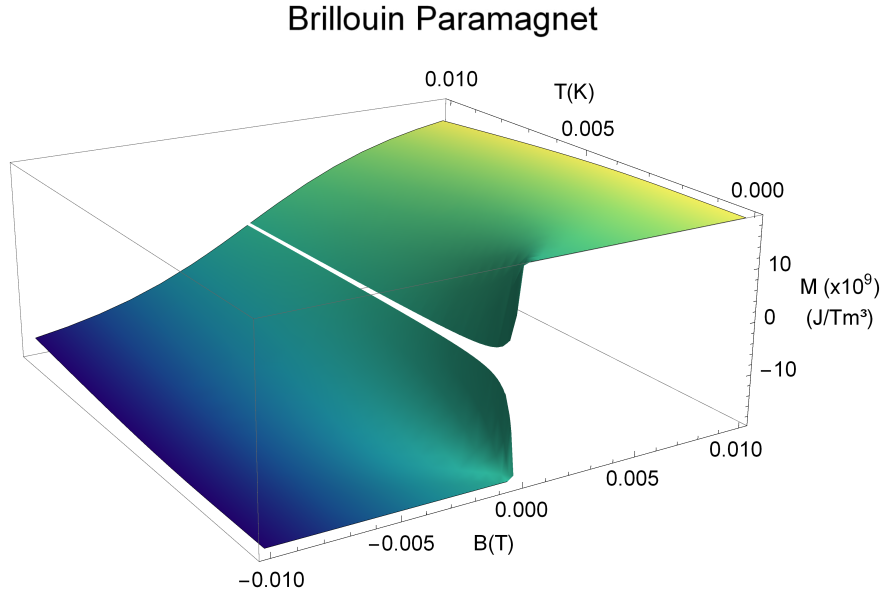


Figure 2.3: Magnetization M as a function of T and B for the Brillouin-type paramagnet. Note that in the regime of both T and B close to zero, a step-like behaviour of M is observed. Figure extracted from Ref. [47].

paramagnet, namely [47, 8]:

$$\Gamma_{mag} = -\frac{\left(\frac{\partial M}{\partial T}\right)_B}{c_B} = -\frac{1}{T} \frac{(\partial S / \partial B)_T}{(\partial S / \partial T)_B} = \frac{1}{T} \left(\frac{\partial T}{\partial B}\right)_S, \quad (2.126)$$

which quantifies the so-called magnetocaloric effect, i.e., the temperature change upon the adiabatic removal of B . For the Brillouin-type paramagnet, Γ_{mag} was already reported in the literature by us and is temperature-independent, namely $\Gamma_{mag} = 1/B$ [47, 48], showing a divergent-like behaviour and sign-change when $B \rightarrow 0$ T. Such behavior of Γ_{mag} motivated a deeper investigation of the Brillouin-type paramagnet in the frame of zero-field quantum phase transitions and the role played by the effective mutual interactions between neighboring magnetic moments in such a model. Note that, as previously discussed, the Brillouin-type paramagnet does not take into consideration the interaction between neighbouring magnetic moments and, in order to not violate the third law of Thermodynamics, the magnetic dipolar interactions must be considered. Some of the obtained theoretical results discussed in this Section were published in (Appendix 6.11):

- Gabriel O. Gomes, Lucas Squillante, A.C. Seridonio, Andreas Ney, Roberto E. Lagos, and Mariano de Souza, Magnetic Grüneisen parameter for model systems, *Physical Review B* **100**, 054446 (2019).

2.3.2 Genuine zero-field quantum phase transitions?

In this Section, the focus lies on magnetic-field driven quantum phase transitions (QPT), more specifically zero-field quantum phase transitions [25], i.e., a quantum phase transition that takes place when both $T \rightarrow 0$ K and $B \rightarrow 0$ T [10]. There are several real system reported in the literature as candidates to undergo a zero-field QPT, such as YbCo_2Ge_4 [24], $\beta\text{-YbAlB}_4$ [25], and Au-Al-Yb [26]. In this context, Γ_{mag} plays a key role in probing a genuine magnetic-field-induced QPT, being the following criteria needed to be fulfilled for such [10]:

- i) Γ_{mag} must diverge at the critical magnetic field modulus B_c , i.e., the value of B in which the QPT occurs;
- ii) concomitant with the last condition, Γ_{mag} must change sign upon crossing B_c ;
- iii) a typical scaling of the type $T/(B - B_c)^\epsilon$ must be observed, where ϵ is a scaling parameter.

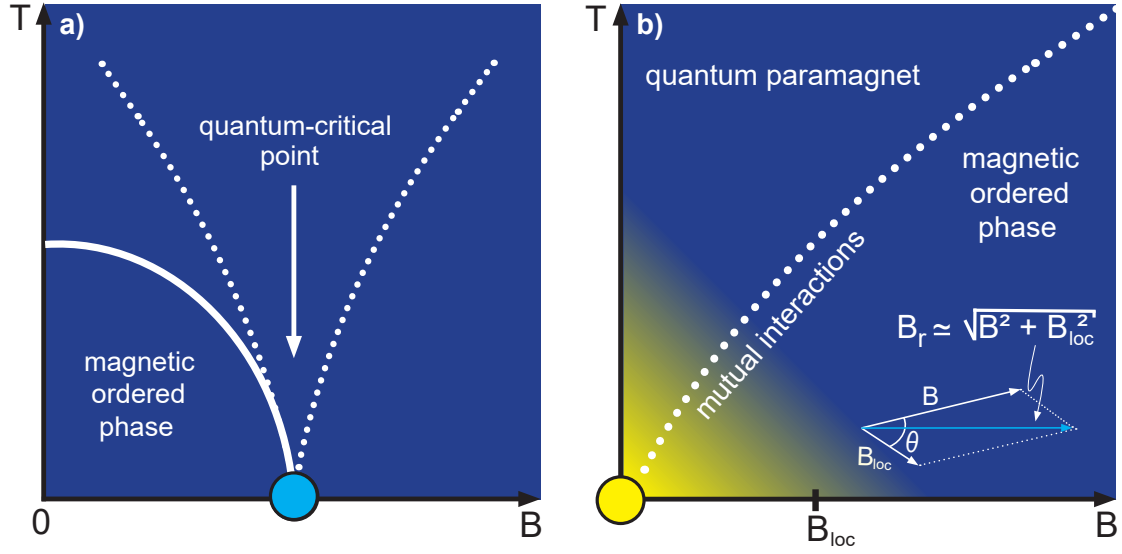


Figure 2.4: Schematic representation of T versus B for a magnetic-field-induced quantum phase transition. In panel a), the blue bullet represents a quantum critical point at finite B where a quantum phase transition, for instance, from a magnetic ordered to a quantum disordered phase takes place. The white dotted lines represent the suppression of an energy scale upon approaching the quantum critical point [8], followed by the corresponding emergence of another energy scale associated with the new phase. In panel b), the hypothetical zero-field quantum critical point is depicted (yellow bullet). The yellow gradient represents the increasing role played by the mutual interactions upon decreasing temperature. It is assumed that $B_r \simeq \sqrt{B^2 + B_{loc}^2}$, so that the angle θ between B and B_{loc} is assumed to be $\theta \simeq 90^\circ$. Figure extracted from Ref. [49].

When such three conditions are fulfilled, a genuine magnetic-field-driven QPT is probed [10], cf. Fig. 2.4.

The divergence and sign-change of Γ_{mag} was analysed in the frame of this Thesis when considering the intrinsic presence of B_{loc} in the Brillouin-type paramagnet and also in the case of the real-system β -YbAlB₄ [25], where a divergence of Γ_{mag} was reported for both B and $T \rightarrow 0$ [25]. At this point, B_{loc} is estimated for β -YbAlB₄ by making use of Eq. 2.74 in an analogous way as for the Brillouin-type paramagnet. By making use of the effective magnetic moment of the Yb atoms $\mu \simeq 1.94\mu_B$ and a typical distance between Yb atoms $r \simeq 3.5 \text{ \AA}$ [50] $\Rightarrow B_{loc} \simeq 0.04 \text{ T}$ for β -YbAlB₄. At this point, an analysis of the impact of considering the intrinsic presence of B_{loc} in both the Brillouin-type paramagnet and β -YbAlB₄ is carried out in terms of the behaviour of Γ_{mag} at ultra-low temperatures for vanishing B . It is assumed that B_r acting on the system is a sum between B and B_{loc} so that $B_r \simeq \sqrt{B^2 + B_{loc}^2}$, cf. Eq. 2.77. Hence, B is replaced by B_r in the expression for

entropy of the Brillouin-type paramagnetic (Eq. 2.78) and Γ_{mag} is computed, so that:

$$\Gamma_{mag} = \frac{B}{B^2 + B_{loc}^2}. \quad (2.127)$$

Note that for vanishing $B \Rightarrow \Gamma_{mag} \rightarrow 0$ and its divergent-like behaviour is suppressed when B_{loc} is taken into account. As a consequence, Γ_{mag} is only enhanced for vanishing B but does not diverge upon crossing $B = 0$ T. For the real-system β -YbAlB₄, Γ_{mag} can be computed via its proposed quantum critical free energy F_{QC} , given by [25]:

$$F_{QC}(T, B) = -\frac{1}{(k_B \tilde{T})^{1/2}} [(g\mu_B B)^2 + (k_B T)^2]^{3/4}, \quad (2.128)$$

where $k_B \tilde{T} \approx 6.6 \text{ eV} \approx (1.06 \times 10^{-18}) \text{ J}$, $\tilde{T}$ refers to a characteristic temperature and $g = 1.94$ is the Landé factor [51]. Note that the proposed F_{QC} refers to the valence-fluctuating character of 4f electrons in Yb atoms in β -YbAlB₄ [25]. Using Eq. 2.128, it is straightforward to calculate the quantum critical entropy, $S_{QC} = -(\partial F_{QC}/\partial T)_B$, namely:

$$S_{QC}(T, B) = \frac{3k_B^2 T}{2(k_B \tilde{T})^{1/2} (B^2 g^2 \mu_B^2 + k_B^2 T^2)^{1/4}}. \quad (2.129)$$

An analysis of the behaviour of the entropy for both the Brillouin-type paramagnet and β -YbAlB₄ considering a finite B_{loc} shows that the entropy accumulation at ultra-low temperatures, usually associated with the proximity of the quantum critical point, is suppressed since the presence of B_{loc} brings order to the system, as can be seen in the upper and lower panels of Fig. 2.5. Replacing B by B_r in Eq. 2.129 and computing Γ_{mag} by Eq. 2.126, it reads:

$$\Gamma_{mag} = \frac{B g^2 \mu_B^2}{k_B^2 T^2 + 2g^2 \mu_B^2 (B^2 + B_{loc}^2)}. \quad (2.130)$$

The behaviour of Γ_{mag} for the Brillouin-type paramagnet and for β -YbAlB₄ is depicted in Fig. 2.6, showing that a divergent-like behaviour is suppressed when B_{loc} is taken into account for both cases, being only an enhancement of Γ_{mag} observed instead of a divergent-like behaviour. For the case of β -YbAlB₄ without considering $B_{loc} \simeq 0.04 \text{ T}$, cf. orange color solid line in Fig. 2.6, Γ_{mag} does not actually diverges

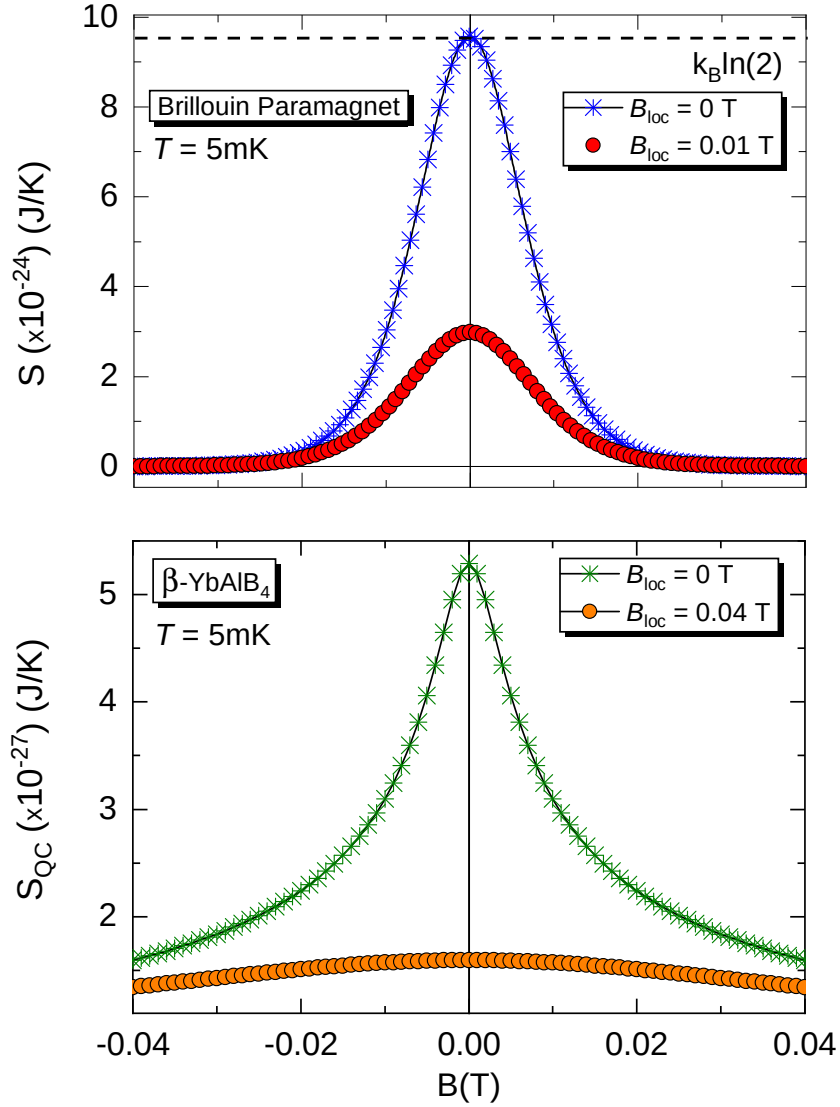


Figure 2.5: Entropy S versus B at a fixed $T = 5 \text{ mK}$ for the Brillouin-type paramagnet (upper panel) considering $B_{\text{loc}} = 0 \text{ T}$ (blue stars) and $B_{\text{loc}} = 0.01 \text{ T}$ (red circles) and for $\beta\text{-YbAlB}_4$ for $B_{\text{loc}} = 0 \text{ T}$ (green stars) and $B_{\text{loc}} = 0.04 \text{ T}$ (orange color circles). Figure extracted from Ref. [49].

for $B = 0 \text{ T}$ since a fixed $T = 5 \text{ mK}$ is considered. In the case of the Brillouin-type paramagnet, Γ_{mag} is non-temperature dependent. However, for $\beta\text{-YbAlB}_4$, Γ_{mag} depends on temperature. Upon analysing the temperature dependence of Γ_{mag} for $\beta\text{-YbAlB}_4$, one can notice that Γ_{mag} presents a divergent-like behaviour followed by a sign-change when $T \rightarrow 0 \text{ K}$ and vanishing B , cf. upper panel of Fig. 2.7. Hence, upon considering finite B_{loc} , Γ_{mag} is only enhanced and changes-sign at low- T and vanishing field but its divergent-like behaviour is suppressed, as can be seen in the lower panel of Fig. 2.7. Hence, it is shown that when finite B_{loc} is considered in

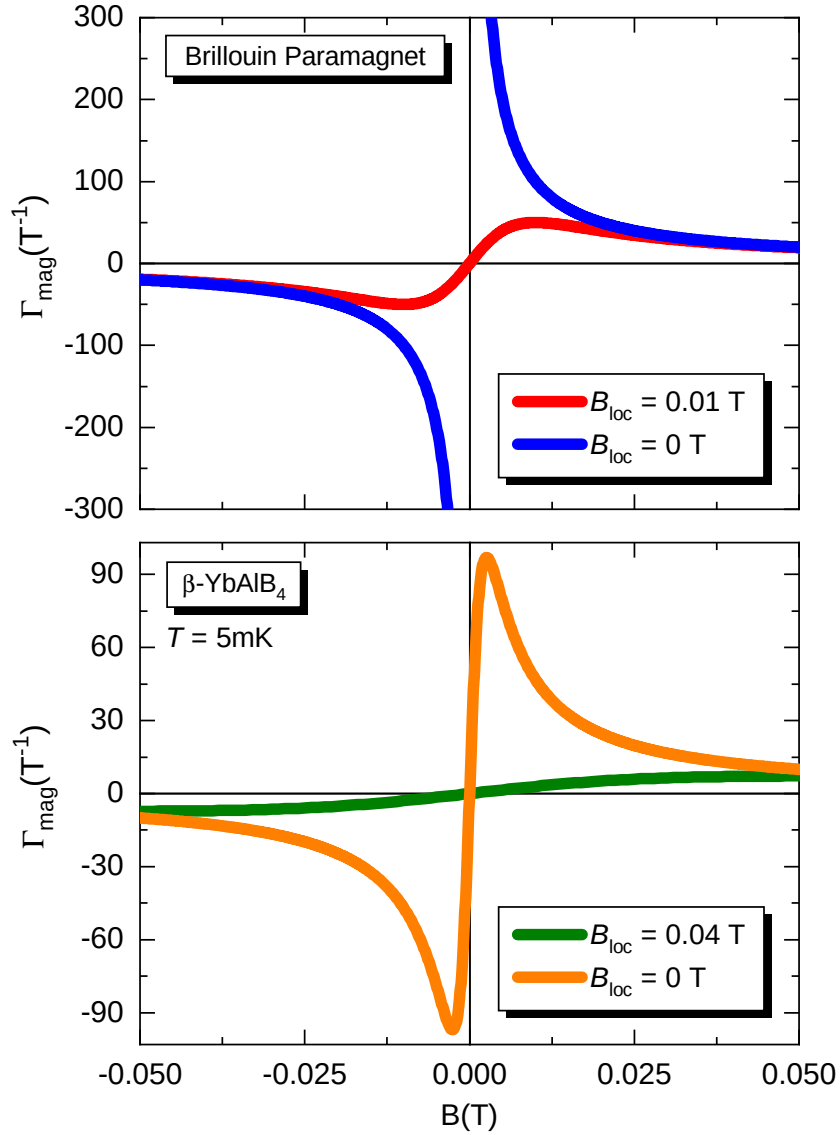


Figure 2.6: Magnetic Grüneisen parameter Γ_{mag} as a function of B for the Brillouin-type paramagnet (upper panel) considering $B_{\text{loc}} = 0 \text{ T}$ (blue line) and $B_{\text{loc}} = 0.01 \text{ T}$ (red line) and for $\beta\text{-YbAlB}_4$ at $T = 5 \text{ mK}$ for $B_{\text{loc}} = 0 \text{ T}$ (orange color line) and $B_{\text{loc}} = 0.04 \text{ T}$ (green line). Note that the divergence of Γ_{mag} is suppressed at $B = 0 \text{ T}$ when finite B_{loc} is considered. Figure extracted from Ref. [49].

real paramagnets one of the key conditions to probe a genuine zero-field quantum phase transition is not fulfilled. Such an analysis in terms of Γ_{mag} highlights the need of considering the intrinsic mutual interactions in real insulating paramagnets in the frame of zero-field quantum criticality. Next, a connection between Γ_{mag} and the canonical definition of temperature is performed.

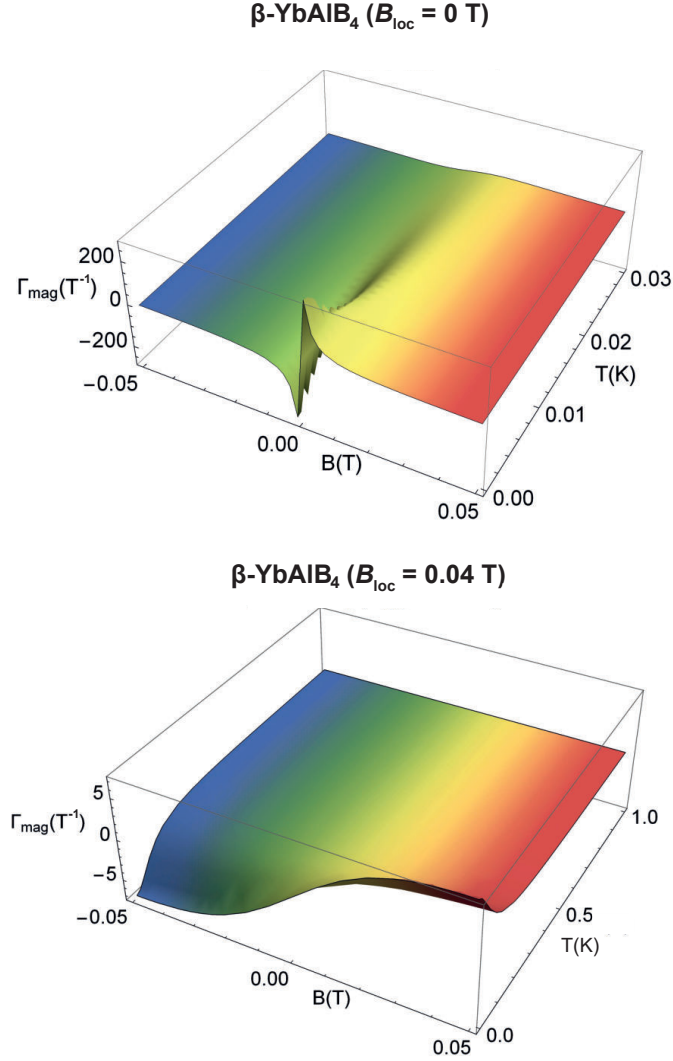


Figure 2.7: Magnetic Grüneisen parameter Γ_{mag} versus T versus B for $\beta\text{-YbAlB}_4$ considering $B_{\text{loc}} = 0$ T (upper panel) and $B_{\text{loc}} = 0.04$ T (lower panel). Figure extracted from Ref. [49].

2.3.3 Grüneisen parameter and the canonical definition of temperature

As well-known from textbooks, the concept of temperature T is universally defined as [34, 1]:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_B, \quad (2.131)$$

where E is the average magnetic energy. The upper panel of Fig. 2.8 depicts the regimes where the slope of $(\partial S / \partial E)_B$ determines the temperature. For vanishing temperatures, $(\partial S / \partial E)_B \rightarrow \infty$, while for $(\partial S / \partial E)_B \rightarrow 0$ indicates that $T \rightarrow \infty$

[1]. Note that for a positive (negative) slope of $(\partial S/\partial E)_B$, positive (negative) temperatures can be inferred, being positive and negative temperatures defined when a parallel or an anti-parallel alignment between $\vec{B}$ and $\vec{\mu}$ takes place [34, 1], respectively. Indeed, a perfect alignment between $\vec{\mu}$ and $\vec{B}$ is prevented by Quantum Mechanics, cf. Appendix 6.1. The concept of negative absolute temperatures can be a little bit indigestible at first, mainly because negative temperatures are hotter than positive ones [1]. Interestingly enough, negative temperatures were verified experimentally in the last century in the celebrated experiment of Purcell and Pound, where they used the nuclear spins of Li-7 in a LiF single-crystal that presents a long relaxation time of the order of 5 minutes under $B \simeq 0.6376$ T [52]. Essentially, the experiment consisted in applying $\vec{B}$ on the sample, so that $\vec{B}$ and the nuclear magnetic moments are in a parallel configuration (positive temperature). Then, $\vec{B}$ was reversed in a time-scale of micro-seconds so that an anti-parallel configuration between $\vec{B}$ and the nuclear magnetic moments is achieved, making the system to be at a negative temperature. In the regime where $E \rightarrow 0$ J, the value $S = k_B \ln(2)$ is nicely restored meaning that at very high temperatures, there is an equal probability for the spins to be aligned in a parallel or an anti-parallel configuration in respect to $\vec{B}$. Recalling that the average magnetic energy for the Brillouin-type paramagnet is given by [1]:

$$E(T, B) = -N\mu_B B \tanh\left(\frac{\mu_B B}{k_B T}\right), \quad (2.132)$$

it is possible to rewrite E as a function of the average magnetic moment $\langle\mu\rangle = N\mu_B \tanh(\mu_B B/k_B T)$ along $\vec{B}$, as follows:

$$E = -\langle\mu\rangle B. \quad (2.133)$$

From the expression for $\langle\mu\rangle$ given by [1]:

$$\langle\mu\rangle = N\mu_B \tanh\left(\frac{\mu_B B}{k_B T}\right), \quad (2.134)$$

it is straightforward to write B as a function of $\langle\mu\rangle$:

$$B(T, \langle\mu\rangle) = \frac{k_B T}{\mu_B} \operatorname{arctanh}\left(\frac{\langle\mu\rangle}{N\mu_B}\right). \quad (2.135)$$

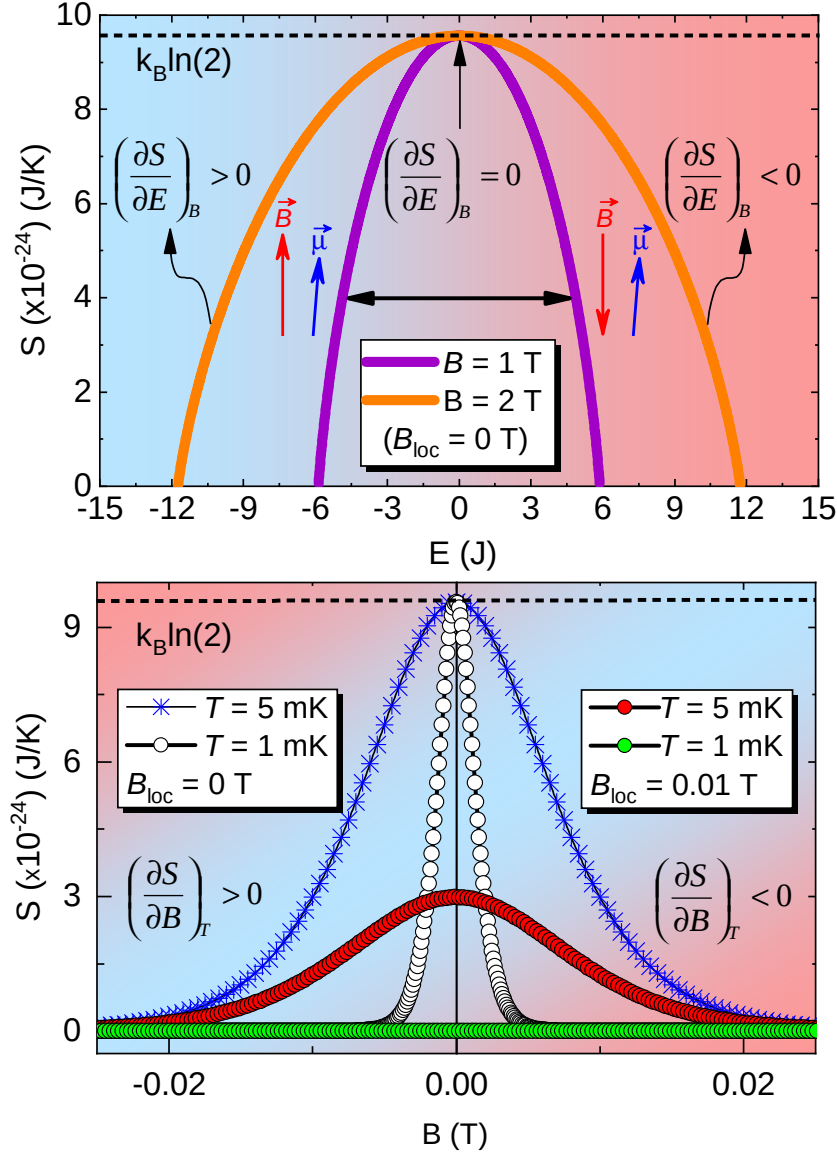


Figure 2.8: Upper panel: Magnetic entropy S as a function of the average magnetic energy E at a fixed $B = 1$ (purple line) and 2 T (orange color line). The slope of $(\partial S / \partial E)_B$ indicates positive, infinite, or negative temperatures. The definition of positive and negative temperatures are associated with a parallel or an anti-parallel configuration, respectively, between $\vec{B}$ (red arrow) and the magnetic moment $\vec{\mu}$ (blue arrow). The background colors indicate that negative temperatures are hotter than positive ones. Lower panel: Magnetic entropy S as a function of B for $B_{loc} = 0$ T at $T = 5$ mK (blue stars) and $T = 1$ mK (white circles). For $B_{loc} = 0.01$ T the red and green circles represent $T = 5$ and 1 mK, respectively. The background colors depict the insensitivity of $(\partial S / \partial B)_T$ regarding positive or negative temperatures. Figure extracted from Ref. [49].

Equation 2.135 indicates that at a certain temperature T , B is associated with a spin configuration that corresponds to a specific average magnetic moment $\langle \mu \rangle$.

Recalling that the magnetocaloric effect can be quantified by Γ_{mag} [8]:

$$\Gamma_{mag} = \frac{1}{T} \left(\frac{\partial T}{\partial B} \right)_S = \frac{1}{T} \left(\frac{\partial B}{\partial T} \right)_S^{-1}, \quad (2.136)$$

the temperature derivative of B in Eq. 2.135 can be computed and replaced it into Eq. 2.136, resulting:

$$\Gamma_{mag} = \frac{\mu_B}{T k_B \text{arctanh} \left(\frac{\langle \mu \rangle}{N \mu_B} \right)}. \quad (2.137)$$

Since $\Gamma_{mag} = 1/B$ for the Brillouin-type paramagnet [49], T as a function of B and $\langle \mu \rangle$ is given by:

$$\boxed{T(B, \langle \mu \rangle) = \frac{B \mu_B}{k_B \text{arctanh} \left(\frac{\langle \mu \rangle}{N \mu_B} \right)}}. \quad (2.138)$$

Equation 2.138 connects in an unprecedented way the Purcell and Pound experiment [53] and Γ_{mag} itself. When $\vec{B}$ and $\langle \mu \rangle$ are $\parallel$, positive temperatures are inferred. However, when $\vec{B}$ and $\langle \mu \rangle$ are anti- $\parallel$, then negative temperatures can be associated. Remarkably, the definition of temperature is encoded in Γ_{mag} and vice-versa.

2.3.4 Adiabatic magnetization in a paramagnetic insulating system

The so-called adiabatic demagnetization is well-known from textbooks [1]. In short, it refers to the cooling of a paramagnetic system upon adiabatically demagnetizing it. The basic concept behind this powerful cooling technique lies in the adiabaticity of the process, i.e., when B is adiabatically removed, the thermal energy must be reduced to maintain the entropy constant and, as a consequence, the system cools down. But what if an opposite situation sets in? What if the temperature is varied adiabatically instead of B ? Although counter-intuitive, it is indeed possible to vary the temperature adiabatically employing the application of stress [54], which is discussed in more details in the next Section. Regarding a paramagnetic insulating system without the influence of any B , B_{loc} still remains finite due to the intrinsic mutual interactions between neighboring spins, cf. previously discussed. Upon decreasing temperature until the magnetic energy associated with B_{loc} is

comparable to the thermal energy, usually below ≈ 6.7 mK, the mutual interactions become more and more relevant. In this temperature regime, the process of adiabatic magnetization can be performed, cf. shown step-by-step in Fig. 2.9.

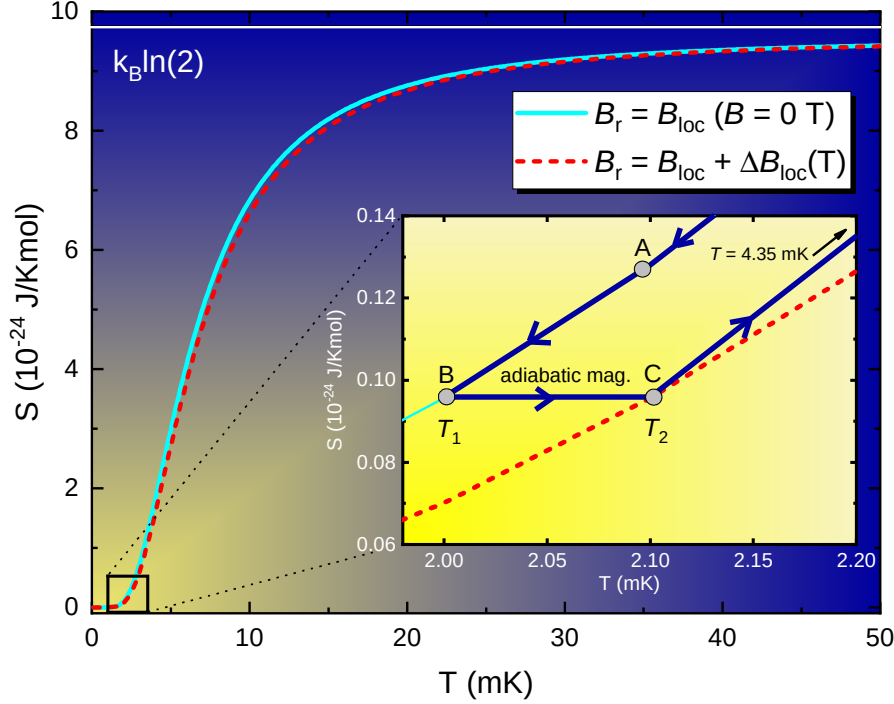


Figure 2.9: Magnetic entropy S as a function of temperature T for the Brillouin-type paramagnet considering $B_r = B_{loc}$ (cyan solid line) and $B_r = (B_{loc} + \Delta B_{loc})$ (red dashed line). The inset shows a zoom in the low- T regime describing the proposed steps for performing the adiabatic magnetization. First, the system should be cooled to a temperature where the magnetic energy associated with B_{loc} is comparable to or higher than the thermal one, which is represented by going from point A to B. Then, at an initial temperature T_1 , the temperature is adiabatically increased from T_1 to T_2 (path B to C) and, to keep the entropy constant, the mutual interactions must rearrange itself to increase the magnetic energy associated with B_{loc} to increase it by an increment ΔB_{loc} , giving rise to the proposed adiabatic magnetization. The cycle can be restarted upon increasing the temperature non-adiabatically and then cooling down the system again to point A. Figure extracted from Ref. [49].

As can be seen in Fig. 2.9, the crucial point in performing the adiabatic magnetization refers to an adiabatic temperature increase that makes the neighboring spins rearrange themselves to increase B_{loc} in order to compensate the adiabatic increase of the thermal energy. Upon increasing the temperature adiabatically from an initial temperature T_1 to a final temperature T_2 , the ratio between magnetic and thermal energies can be written as [49]:

$$\frac{\mu_B B_{loc}}{k_B T_1} = \frac{\mu_B \sqrt{B_{loc}^2 + \Delta B_{loc}^2}}{k_B T_2}, \quad (2.139)$$

where B_r after the adiabatic temperature increase is given by $B_r = \sqrt{B_{loc}^2 + \Delta B_{loc}^2}$. From Eq. 2.139, the local magnetic field increment ΔB_{loc} is given by [49]:

$$\Delta B_{loc} = B_{loc} \sqrt{\frac{T_2^2}{T_1^2} - 1}. \quad (2.140)$$

Upon assuming $T_1 = 2$ mK, $T_2 = 2.1$ mK, and $B_{loc} = 0.01$ T:

$$\Delta B_{loc} = 0.01 \sqrt{\frac{2.1^2}{2^2} - 1} \simeq 0.0032 \text{ T} \simeq 3.2 \text{ mT}. \quad (2.141)$$

Amazingly, such adiabatic magnetization can be carried out by solely manipulating the mutual interaction upon increasing the temperature adiabatically, i.e., without applying B to the paramagnetic system. As a step further, two experimental setups to perform and detect the adiabatic magnetization were proposed by us in the literature, which is discussed in the next Section. The obtained theoretical results discussed in Sections 2.3.2, 2.3.3, and 2.3.4 were published in (Appendix 6.11):

- Lucas Squillante, Isys F. Mello, Gabriel O. Gomes, A.C. Seridonio, R.E. Lagos-Monaco, H. Eugene Stanley, Mariano de Souza, Unveiling the physics of the mutual interactions in paramagnets, Scientific Reports **10**, 7981 (2020).

Also, the publication was reported by the Fapesp Agency in the following:

- “Theoretical study shows that matter tends to be ordered at low temperatures”
- Appendix 6.12.

2.3.5 Elastocaloric-induced effect adiabatic magnetization

As previously mentioned, adiabatic temperature changes can be seen, at first glance, as counter-intuitive. However, this is totally possible due to an adiabatic compression [1]. At this point, the first law of Thermodynamics is recalled, which reads [28]:

$$dQ = dU + dW, \quad (2.142)$$

where dQ is the infinitesimal heat variation and dW is the infinitesimal work performed on the system regarding its compression. As a consequence of an adiabatic compression, the temperature will change and so the internal energy, so that [28]:

$$dU = \left(\frac{\partial U}{\partial T} \right)_v dT = c_v dT. \quad (2.143)$$

The infinitesimal work performed on the system due to compression, is then given by [28]:

$$dW = -p dv. \quad (2.144)$$

The pressure under adiabatic conditions can be expressed in terms of the variation of U in response to a change of v , so that $p = -(\partial U / \partial v)_S$ [28]. Thus, Eq. 2.144 reads:

$$dW = -p dv = \left(\frac{\partial U}{\partial v} \right)_S dv = \left(\frac{\partial U}{\partial S} \right)_v \left(\frac{\partial S}{\partial v} \right)_T dv. \quad (2.145)$$

Note that the term $(\partial U / \partial S)_v = T$, following the canonical temperature definition [1]. Employing the Maxwell relation $(\partial S / \partial v)_T = (\partial p / \partial T)_v$ [28], Eq. 2.145 now reads:

$$dW = T \left(\frac{\partial p}{\partial T} \right)_v dv. \quad (2.146)$$

Upon putting Eqs. 2.143 and 2.146 into Eq. 2.142, it becomes:

$$dQ = c_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv. \quad (2.147)$$

Since $dQ = T dS$ [1, 28] and that in an adiabatic process $dS = 0$, hence $dQ = 0$ as well, so that:

$$T dS = c_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv \quad (2.148)$$

$$0 = c_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv \quad (2.149)$$

$$c_v dT = -T \left(\frac{\partial p}{\partial T} \right)_v dv. \quad (2.150)$$

Employing the Thermodynamic relation [28]:

$$\left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial T}{\partial v} \right)_p \left(\frac{\partial v}{\partial p} \right)_T = -1, \quad (2.151)$$

it can be rewritten as:

$$\left(\frac{\partial p}{\partial T} \right)_v = - \frac{1}{\left(\frac{\partial T}{\partial v} \right)_p \left(\frac{\partial v}{\partial p} \right)_T}. \quad (2.152)$$

Note that the isothermal compressibility is given by $\kappa_T = -1/v(\partial v / \partial p)_T$ [1], so that the term in Eq. 2.152 $\left(\frac{\partial v}{\partial p} \right)_T = -\kappa_T v$. Also, following the definition of the

volumetric thermal expansion $\beta = 1/v(\partial v/\partial T)_p$, the term in Eq. 2.152 $\left(\frac{\partial T}{\partial v}\right)_p = 1/\beta v$.

Employing these substitutions in Eq. 2.152, it reads:

$$\left(\frac{\partial p}{\partial T}\right)_v = -\frac{1}{\frac{1}{\beta v}[-\kappa_T v]} = \frac{\beta}{\kappa_T}. \quad (2.153)$$

Then, replacing Eq. 2.153 into Eq. 2.150:

$$c_v dT = -\frac{T\beta}{\kappa_T} dv. \quad (2.154)$$

Equation 2.154 can then be rewritten as:

$$\boxed{dT = -\frac{T\beta}{c_v \kappa_T} dv}. \quad (2.155)$$

Equation 2.155 is key in analysing the temperature variation in response to an adiabatic compression of a system. Considering that T , β , c_v , and κ_T are positive quantities, the sign of the adiabatic temperature variation is ruled solely by dv . On one hand, if $dv < 0$, the temperature of the system is adiabatically increased ($dT > 0$) in response to the decrease in its volume due to an adiabatic compression. On the other hand, if $dv > 0$, the temperature of the system is adiabatically decreased ($dT < 0$) as a consequence of an increase in the volume of the system due to an adiabatic decompression. The very same analysis can be performed now in terms of p instead of v . Considering that the entropy of the system can be varied due to p or T , so that:

$$dS(T, p) = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp. \quad (2.156)$$

Considering the definition of the heat capacity at constant pressure $c_p = T(\partial S/\partial T)_p$ [1], the term in Eq. 2.156 $(\partial S/\partial T)_p = c_p/T$ and the Maxwell relation $(\partial S/\partial p)_T = -(\partial v/\partial T)_p$ [28], Eq. 2.156 can now be rewritten as:

$$dS(T, p) = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_p dp. \quad (2.157)$$

Since an adiabatic process is considered, i.e., $dS(T, p) = 0$:

$$\frac{c_p}{T} dT = \left(\frac{\partial v}{\partial T}\right)_p dp. \quad (2.158)$$

Recalling that $\beta = 1/v(\partial v/\partial T)_p$, then $(\partial v/\partial T)_p = \beta v$ so that:

$$\boxed{dT = \frac{\beta v T}{c_p} dp.} \quad (2.159)$$

Equation 2.159 is similar to Eq. 2.155, since for an adiabatic pressurization the final p is higher than the initial one, i.e., $dp > 0$, the volume of the system is decreased and the temperature of the system is adiabatically increased ($dT > 0$), while for an adiabatic decompression the final p is lower than the initial one ($dp < 0$), the volume of the system is increased and thus the temperature is adiabatically decreased. The effect of varying the temperature upon an adiabatic pressure variation is called the barocaloric effect, which is quantified by the singular portion of Γ_{eff} , the so-called Grüneisen ratio $\Gamma = \beta/c_p = 1/Tv(\partial T/\partial p)_S$ [8, 9]. Indeed, Γ is naturally encoded in Eq. 2.159, which can be rewritten as:

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{\beta v T}{c_p}, \quad (2.160)$$

so that:

$$\frac{1}{Tv} \left(\frac{\partial T}{\partial p}\right)_S = \frac{\beta}{c_p} = \Gamma. \quad (2.161)$$

Experimentally, an adiabatic temperature change can be carried out due to the application of stress σ (Fig. 2.10), which refers to the compression or decompression of a particular direction. All the 9 stress components can be represented by a 3×3 matrix, given by [56]:

$$\sigma_{ij} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix}, \quad (2.162)$$

where σ_{ij} represents all the stress components in Voigt's abbreviated notation [56, 57], being the index i the normal plane on which the stress component is acting and j the direction of the applied stress. Hence, analogously to Eq. 2.156, it can now be written as:

$$dS(T, \sigma) = \left(\frac{\partial S}{\partial T}\right)_\sigma dT + \left(\frac{\partial S}{\partial \sigma_{ij}}\right)_{T, \sigma} d\sigma_{ij}. \quad (2.163)$$

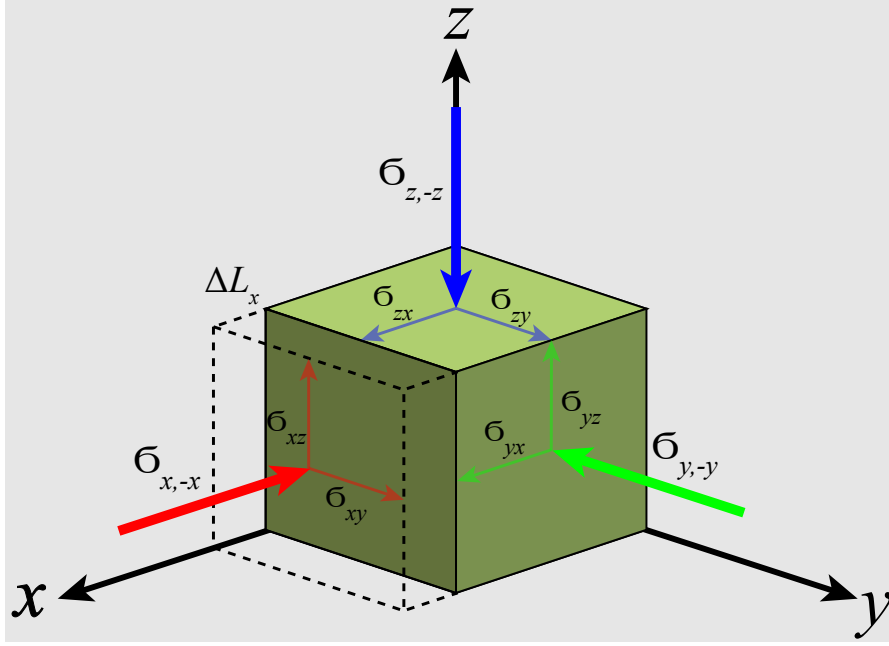


Figure 2.10: Schematic representation of both the normal ($\sigma_{x,-x}$, $\sigma_{y,-y}$, and $\sigma_{z,-z}$) and shear (σ_{xy} , σ_{xz} , σ_{yx} , σ_{yz} , σ_{zx} , and σ_{zy}) stress components in a solid. The dashed lines indicate the compression of the solid only in the x direction by the application of a uniaxial compressive stress component $\sigma_{x,-x}$, which in turn decreases the length L of the solid by a factor ΔL_x . Figure extracted from Ref. [55].

Note that the second term on the right side of Eq. 2.163, represents the entropy variation due to the application of only one stress component while the others are kept constant, being also T kept constant. In our analysis it is considered that only one of the normal components is varied, i.e., a uniaxial application of stress (Fig. 2.10), being this the reason why such an entropy variation is given at a fixed T and σ . An analogous decomposition of σ can be made in terms of the thermal expansion, so that $\alpha_{ij} = (\partial S / \partial \sigma_{ij})_{T, \sigma}$ [54]. Note that, usually, stress has units of pressure [Pa], however, in this particular case, the notation of σ_{ij} is given in terms of stress components per unit of volume, so that $\sigma_{ij} = [\text{J}]$ [56]. Also, considering that the heat capacity at constant stress $c_\sigma / T = (\partial S / \partial T)_\sigma$, Eq. 2.163 can be rewritten as:

$$dS = \frac{c_\sigma}{T} dT + \alpha_{ij} d\sigma_{ij} = 0 \quad (2.164)$$

$$\frac{c_\sigma}{T} dT = -\alpha_{ij} d\sigma_{ij}, \quad (2.165)$$

$$dT = -\frac{T}{c_\sigma} \alpha_{ij} d\sigma_{ij}. \quad (2.166)$$

It becomes clear that in Eq. 2.166, dT is the infinitesimal adiabatic temperature change, from a starting temperature T , due to the application of an adiabatic stress component σ_{ij} . Conventionally, $\sigma_{ij} < 0$ means that an uniaxial compression is carried out, while $\sigma_{ij} > 0$ is associated with an uniaxial decompression [56]. Hence, considering that c_σ , T , and α_{ij} are positive, for $d\sigma_{ij} < 0$ it implies in $dT > 0$, while for $d\sigma_{ij} > 0$, $dT < 0$. In other words, upon adiabatically compressing (decompressing) the system along a particular axis, its length is reduced (increased) and, as a consequence, its temperature is adiabatically increased (reduced) to keep the system's entropy constant. This is the so-called elastocaloric-effect, which is similar to the barocaloric effect, previously discussed. Analogously to the fact that Γ (Eq. 2.161) quantifies the barocaloric effect, Eq. 2.166 can be rewritten as [55]:

$$\left(\frac{\partial T}{\partial \sigma_{ij}} \right)_S = \frac{T \alpha_{ij}}{c_\sigma} \quad (2.167)$$

$$\boxed{\frac{1}{T} \left(\frac{\partial T}{\partial \sigma_{ij}} \right)_S = \frac{\alpha_{ij}}{c_\sigma} = \Gamma_{ec}}. \quad (2.168)$$

Equation 2.168 accounts for the definition of the elastic Grüneisen parameter Γ_{ec} , which quantifies the elastocaloric effect and was proposed in the literature in the frame of this Ph.D. Thesis, cf. Ref. [55]. Just to mention, after the proposal of Γ_{ec} it was employed by researchers of the Max Planck Institute - Dresden to investigate the phase diagram of the unconventional superconductor Sr_2RuO_4 [58]. Now, the proposed adiabatic magnetization of a paramagnetic insulating system due to an adiabatic temperature increase in terms of σ_{ij} and the magnetization M of the system are analysed, so that it is possible to write:

$$dS(T, M, \sigma_{ij}) = \left(\frac{\partial S}{\partial T} \right)_{M, \sigma} dT + \left(\frac{\partial S}{\partial M} \right)_{T, \sigma} dM + \left(\frac{\partial S}{\partial \sigma_{ij}} \right)_{T, M} d\sigma_{ij} = 0, \quad (2.169)$$

so that:

$$-\left(\frac{\partial S}{\partial M} \right)_{T, \sigma} dM = \left(\frac{\partial S}{\partial T} \right)_{M, \sigma} dT + \left(\frac{\partial S}{\partial \sigma_{ij}} \right)_{T, M} d\sigma_{ij}. \quad (2.170)$$

Employing the well-known Maxwell relation $(\partial S/\partial M)_T = -(\partial B/\partial T)_S$ [28], it is possible to write that:

$$\left(\frac{\partial B}{\partial T}\right)_S dM = \left(\frac{\partial S}{\partial T}\right)_{M,\sigma} dT + \left(\frac{\partial S}{\partial \sigma_{ij}}\right)_{T,M} d\sigma_{ij}. \quad (2.171)$$

Equation 2.171 is key in analysing the proposed adiabatic magnetization upon an adiabatic uniaxial compression. Since no B is applied to the system, it becomes evident that B in Eq. 2.171 can be recognized as B_{loc} . Essentially, Eq. 2.171 tell us that, in response to an adiabatic temperature variation due to the application of uniaxial stress in the system, there should be an increase in the magnetization of the system by a factor dM to keep the entropy constant, which in turn is originated by a variation of B_{loc} by a factor ΔB_{loc} due to the temperature increase of the system, cf. previously discussed. At this point, it is tempting to make an analogy between positive and negative temperatures in the celebrated Purcell and Pound's experiment [53] in terms of either an adiabatic expansion or contraction under application of stress. However, this is not in agreement with the well-established conditions for attaining negative temperatures [59], as discussed in Appendix 6.2. Just to mention, the proposed adiabatic magnetization resembles the celebrated Pomeranchuk effect [60], which predicts that ^3He might solidify upon heating. In the case of the adiabatic magnetization, the system is magnetized upon adiabatically heating it. Next, two proposed experimental setups are discussed to carry out the adiabatic magnetization. In the first case, the paramagnetic insulating specimen is inserted into an adiabatic chamber inside a coil with two pistons holding it, cf. Fig. 2.11. As depicted in Fig. 2.11, the sample is compressed adiabatically by the pistons decreasing its volume by a factor Δv . Hence, since it is an adiabatic compression, its temperature rises and the sample is adiabatically magnetized. The modulus of $\vec{B}_r$ is increased from $B_r = B_{loc}$ to $B_r = \sqrt{B_{loc}^2 + \Delta B_{loc}^2}$. The change in B_r in time generates a magnetic flux variation in time, which in turn gives rise to an electromotive force $\xi = -(d\Phi/dt)$ [37] opposing to such a change in flux Φ , so that an electric current flows through the coil and it can be detected by the ampere meter. Based on the electrical current measured, ΔB_{loc} can be determined. At

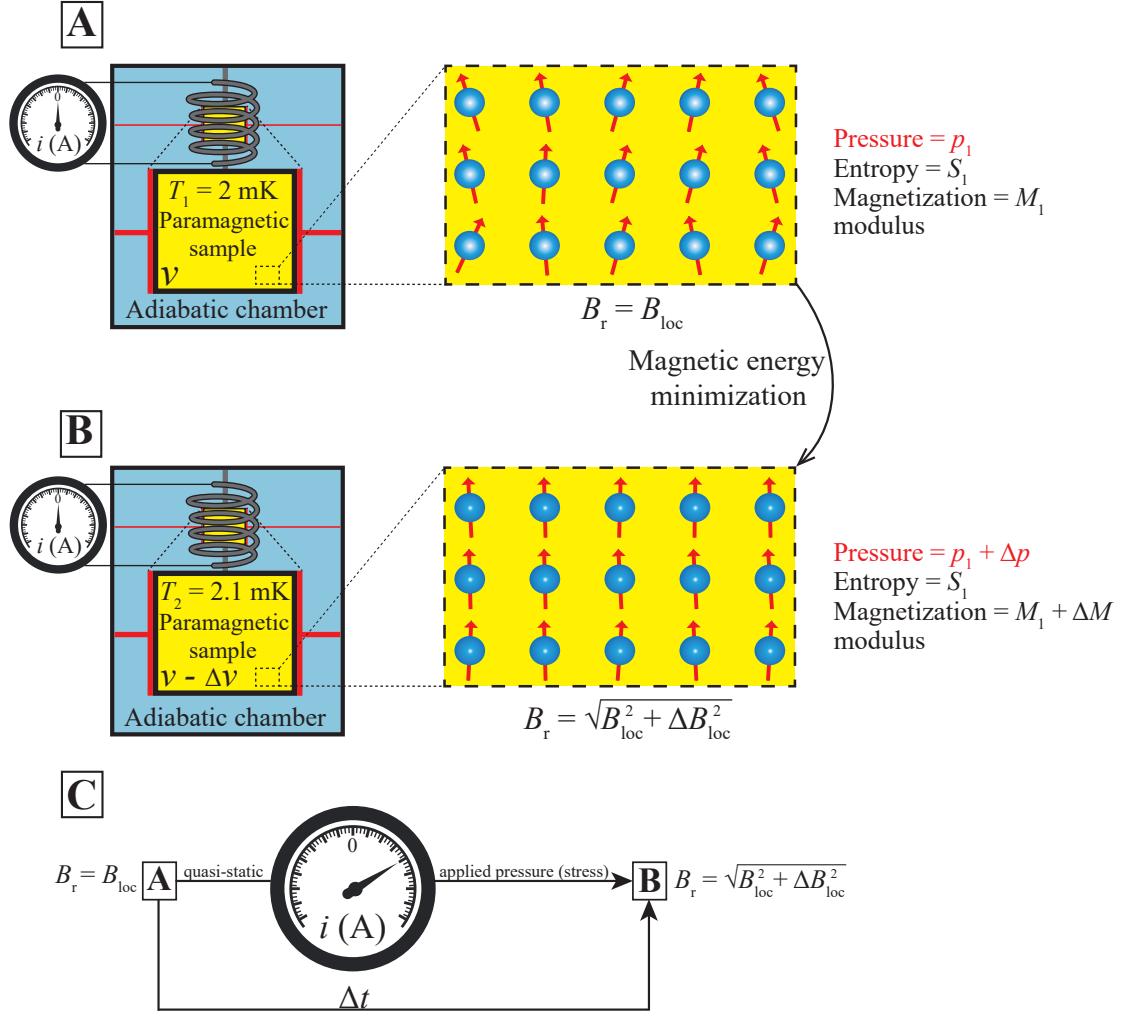


Figure 2.11: Schematic representation of the experimental setup for attaining adiabatic magnetization. In panel A, the paramagnetic insulating sample is inserted into an adiabatic chamber inside a coil connected to an ampere meter and it is supported by two lateral pistons. Essentially, an adiabatic chamber is a thermally isolated compartment designed to prevent heat exchange with the outside environment. The sample is at an initial temperature $T_1 = 2 \text{ mK}$, pressure p_1 , entropy S_1 , magnetization M_1 , and $B_r = B_{loc}$. In panel B, the two pistons compress adiabatically the sample so its volume is reduced by a factor of Δv . Hence, the final temperature is $T_2 = 2.1 \text{ mK}$, so that the entropy remains constant but the magnetization is increased in order to minimize the magnetic energy of the system so that $B_r = \sqrt{B_{loc}^2 + \Delta B_{loc}^2}$. In C, it is depicted that, upon going from A to B in a time interval Δt , the increase in B_r generates a magnetic flux variation in time, which in turn leads to an electromotive force in the coil generating thus an electric current that is measured by the ampere meter. Based on the measured electrical current, ΔB_{loc} can be determined. Figure extracted from Ref. [55].

this point, it is plausible to ask “How to apply uniaxial stress to a sample?”, and more importantly, “How to actually attain the adiabatic character that is crucial for the experimental realization of the elastocaloric effect?”. The answer to both of these questions lies in the piezoelectric device proposed in Ref. [54], cf. depicted

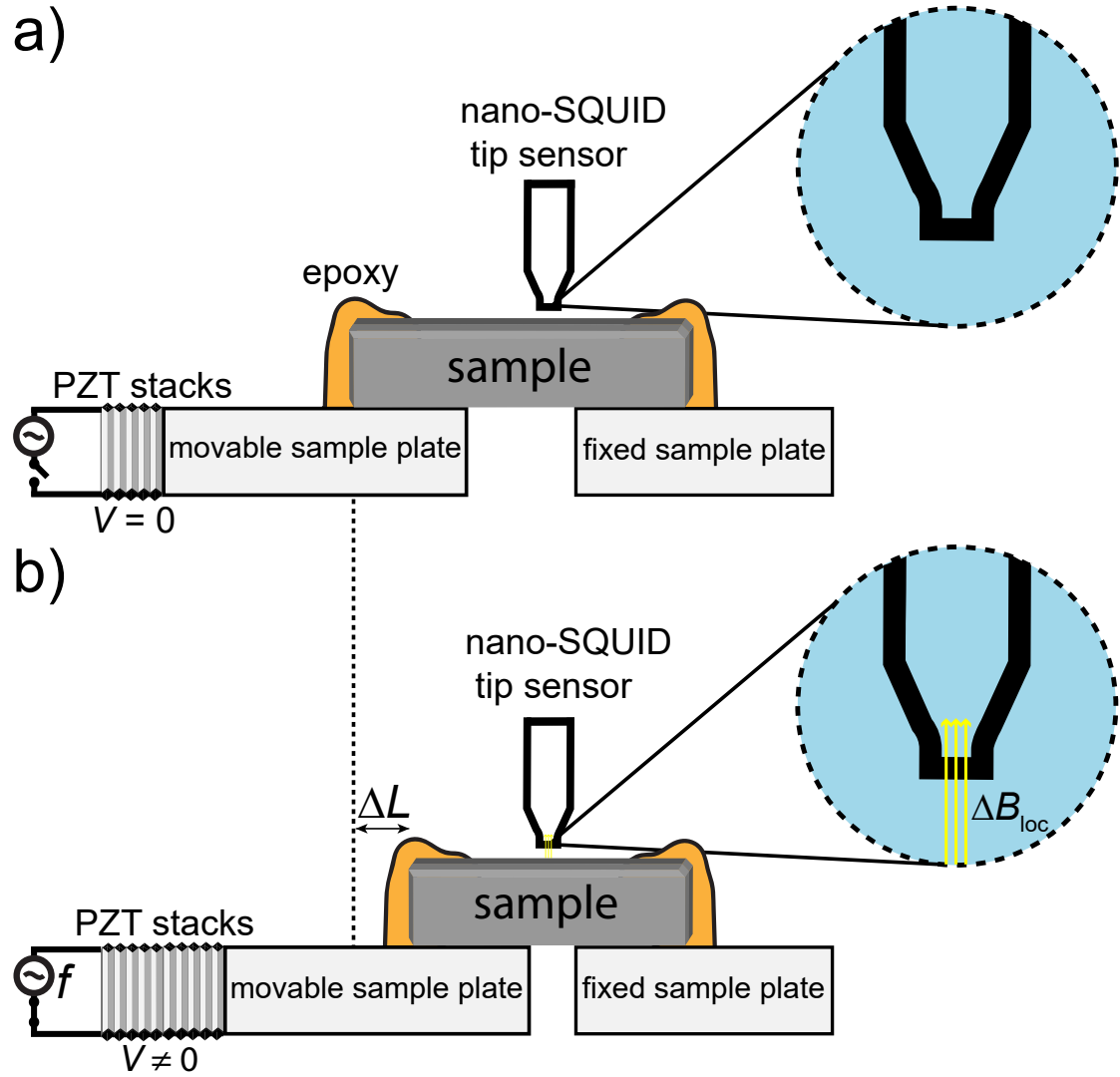


Figure 2.12: Schematic representation of the proposed experimental setup to carry out and detect the elastocaloric-induced adiabatic magnetization due to the mutual interactions. a) The sample is attached with epoxy to a movable plate, which is connected to a piezoelectric device [54, 61, 62]. b) When A.C. voltage V is applied on the piezoelectric stacks, the sample is continuously uniaxially compressed and decompressed by a factor ΔL . Due to the adiabatic compression, B_{loc} is increased by a factor ΔB_{loc} , which is detected by a nano-SQUID tip sensor [63]. Figure extracted from Ref. [55].

in Fig. 2.12. The proposed experimental setup for attaining adiabatic temperature changes is depicted in Fig. 2.12 [54, 55]. The paramagnetic insulating sample is attached with epoxy to a movable plate, which is connected to a piezoelectric (PZT) device. As soon as A.C. voltage with a chosen frequency f is applied to the PZT, the movable plate starts to oscillate back and forwards with the same frequency f of the A.C. voltage, continuously compressing and decompressing the sample.

Upon tuning f to achieve such an oscillation in a time scale higher than the one associated with thermal relaxation, the adiabatic character is attained [54]. In other words, the compression/decompression of the sample occurs faster than it can exchange heat with its surroundings. In this tiny time window of adiabaticity of about 30 ms [54], the temperature of the paramagnetic sample is continuously increased/decreased, following Eq. 2.166. Hence, considering the case of its adiabatic compression, its temperature increases and the sample is adiabatically magnetized, cf. previously discussed. To detect such ΔB_{loc} , we proposed that a nano-SQUID on a tip [63] can be employed, which is broadly used to detect magnetic fields of a few mT [63]. Just for the sake of completeness, the magnetic flux Φ through a SQUID with surface area S' is given by [37]:

$$\Phi = \int_{S'} \vec{B} \cdot d\vec{S}' = n \left(\frac{h}{2e} \right), \quad (2.172)$$

where n is an integer number, h is Planck's constant, $d\vec{S}'$ a normal vector in respect to the SQUID's junction inner area S' , and e the fundamental electron charge. The factor $(h/2e)$ is the quantum of Φ and it dictates the SQUID sensitivity to small values of Φ . Although the nano-SQUID on a tip [63] has its resolution compromised by its small S' , its spatial resolution is outstanding making it very sensitive to small magnetic moments [63], which in turn can detect $\Delta B_{loc} \simeq 3.2$ mT (Eq. 2.141). It is worth mentioning that the parameters involving the detection of ΔB_{loc} employing the nano-SQUID on a tip [63] shall depend on the physical properties of the investigated system, the temperature in which the experiment is carried out, and, of course, the characteristics of the nano-SQUID on a tip itself.

Based on the proposed adiabatic magnetization due to an adiabatic temperature increase of a paramagnetic insulating specimen, it is natural to extend the concept of an adiabatic temperature increase to investigate other interacting systems [55], such as Bose-Einstein condensates in magnetic insulators [64] and spin-ice systems [65]. In such cases, we propose that the many-body interactions between magnetic moments are rearranged as a whole when the temperature is adiabatically increased similarly to the one proposed for the paramagnetic insulating system. Hence, this

technique for adiabatically increasing temperature can be employed to explore the many-body character of the magnetic interactions in other systems. For instance, in the case of the Bose-Einstein condensate in an insulator, the Hamiltonian of the system incorporates a Zeeman term $-g\mu_B B_z S^z$, cf. Eq. 1 of Ref. [64], that governs the density of triplons in the system, being B_z the modulus of the applied external magnetic field in the z direction, and S^z the spin projection in the z direction. Considering that the resulting magnetic field B_r in the system is solely given by the effective local magnetic field generated by the mutual interactions between adjacent magnetic moments, an adiabatic temperature increase makes the magnetic moments to rearrange to compensate for the adiabatic thermal energy increase. As a consequence, the Zeeman term of the Hamiltonian is varied and so is the density of triplons. This is only one particular example regarding how the adiabatic temperature increase can be employed to investigate the many-body character of the magnetic interactions in various systems [55].

2.3.6 Grüneisen parameter and second-order phase transitions

As discussed in the last Sections, Γ quantifies caloric effects and also the entropy change upon tuning the system close to the critical point. In a step further, we have proposed that Γ can also quantify the critical temperature T_c shift in the vicinity of a second-order phase transition upon varying a tuning parameter, which can be pressure, electric or magnetic field, for instance, in an analogous way as the canonical Ehrenfest relation, which is given by [66]:

$$\frac{dT_c}{dp} = T v \left(\frac{\Delta\alpha}{\Delta c_p} \right), \quad (2.173)$$

where $\Delta\alpha$ and Δc_p refer to the jumps in the thermal expansion and the heat capacity at constant pressure due to a second-order phase transition. Equation 2.173 quantifies the shift in T_c upon applying pressure in terms of $\Delta\alpha$ and Δc_p . For the case of an adiabatic stress application, the entropy variation reads [54]:

$$dS = -\frac{c_\sigma^{cr}}{T} \left(\frac{dT_c}{d\epsilon} \right)_T d\epsilon + \frac{c_\sigma}{T} dT = 0, \quad (2.174)$$

where c_σ^{cr} is the critical contribution to the heat capacity at constant stress, $\epsilon = (L - L_0)/L_0$ refers to the strain, which is connected to σ through the Young modulus $YM = \sigma/\epsilon$ [56], L and L_0 refer to the final and initial sample lengths, respectively. The term of Eq. 2.174 $\frac{c_\sigma}{T} dT$ accounts for the entropy variation due to the elastocaloric effect, while $-\frac{c_\sigma^{cr}}{T} \left(\frac{dT_c}{d\epsilon}\right)_T$ refers to shifting T_c and thus compensating the contribution to S from the elastocaloric effect in order to keep the global entropy constant. Upon adiabatically compressing the sample, for instance, its temperature is increased contributing to the increase of the system's entropy and thus the term $\frac{c_\sigma}{T} dT$ contributes to the enhancement of S . To keep the entropy constant, the term on Eq. 2.174 $-\frac{c_\sigma^{cr}}{T} \left(\frac{dT_c}{d\epsilon}\right)_T$ must be negative, i.e., $(dT_c/d\epsilon)_T$ must be positive. In other words, upon adiabatically compressing the sample, its T_c is increased. The opposite is also true, when the sample is adiabatically decompressed, its temperature decreases and the term in Eq. 2.174 $\frac{c_\sigma}{T} dT$ contributes to decrease S . Hence, in order to keep S constant, the term in Eq. 2.174 $-\frac{c_\sigma^{cr}}{T} \left(\frac{dT_c}{d\epsilon}\right)_T$ must be positive, contributing thus to compensate the decrease in S , so that the total S variation is zero. For such a term to be positive, $(dT_c/d\epsilon)_T$ must be negative, i.e., its T_c is decreased. In summary, upon adiabatically compressing (decompressing) the system, its T_c is increased (decreased). An experimental verification of this analysis is reported in Ref. [54] for the iron-based superconductor $\text{Ba}(\text{Fe}_{0.979}\text{Co}_{0.021})_2\text{As}_2$, cf. Fig. 2.13. Rewriting Eq. 2.174:

$$\frac{c_\sigma^{cr}}{T} \left(\frac{dT_c}{d\epsilon}\right)_T d\epsilon = \frac{c_\sigma}{T} dT \quad (2.175)$$

$$\left(\frac{dT}{d\epsilon}\right)_S = \frac{c_\sigma^{cr}}{c_\sigma} \left(\frac{dT_c}{d\epsilon}\right)_T, \quad (2.176)$$

which connects the elastocaloric effect, now written in terms of ϵ instead of σ , with the T_c shift. Employing the definition of the proposed Γ_{ec} (Eq. 2.168) and multiplying both sides of Eq. 2.176 by $1/T$, it now reads:

$$\boxed{\frac{1}{T} \left(\frac{dT}{d\epsilon}\right)_S = \frac{1}{T} \frac{c_\sigma^{cr}}{c_\sigma} \left(\frac{dT_c}{d\epsilon}\right)_T = \Gamma_{ec}^{cr}}, \quad (2.177)$$

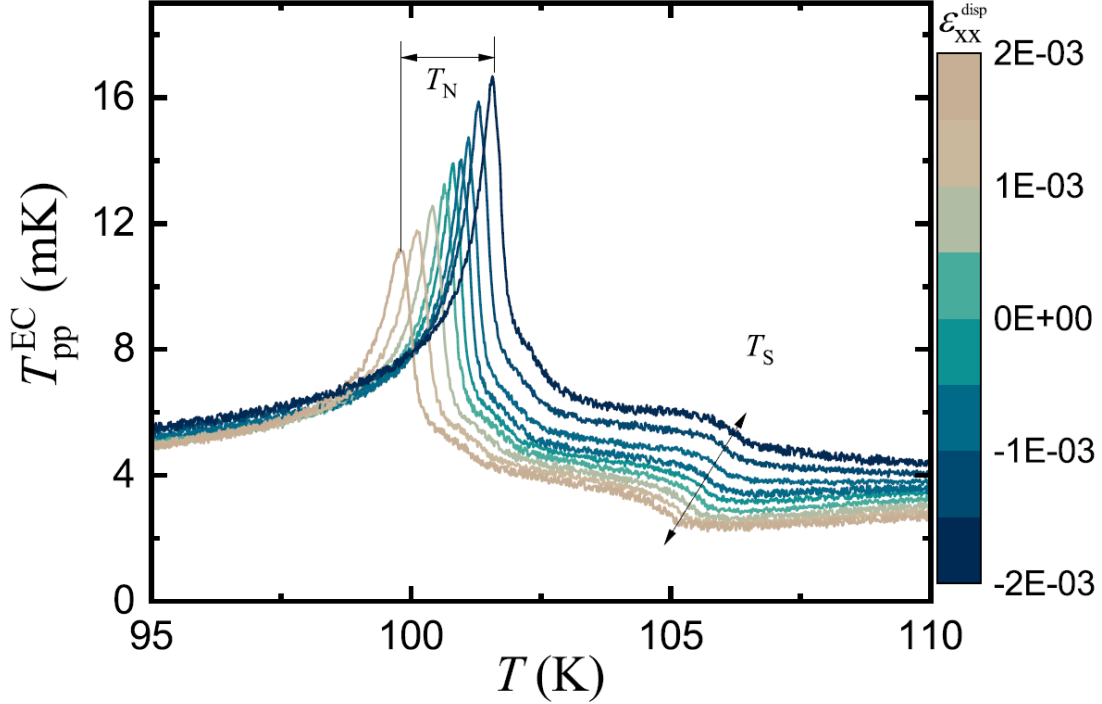


Figure 2.13: Peak to peak amplitude of the elastocaloric temperature oscillation T_{pp}^{EC} versus temperature T in which the elastocaloric effect was performed for $\text{Ba}(\text{Fe}_{0.979}\text{Co}_{0.021})_2\text{As}_2$ [54]. The uniaxial strain in the x direction ϵ_{xx}^{disp} is also indicated. It is worth mentioning that $\epsilon_{xx}^{disp} > 0$ means that the specimen length is higher than the original one (decompressed), while $\epsilon_{xx}^{disp} < 0$ implies that its length was reduced from its original size (compressed). Following discussions in the main text, note that when the sample is compressed $\epsilon_{xx}^{disp} < 0$, both the antiferromagnetic transition temperature T_N and the temperature in which a nematic/structural phase transition T_S takes place are increased, while for $\epsilon_{xx}^{disp} > 0$, T_N and T_S decreases. Figure extracted from Ref. [54].

where Γ_{ec}^{cr} quantifies the shift in T_c due to the elastocaloric effect in terms of the critical contribution of the heat capacity at constant pressure. Equation 2.177 demonstrates that, when $(dT/d\epsilon)_S > 0$, i.e., the temperature of the system is adiabatically increased as a result of a strain (adiabatic compression), $(dT_c/d\epsilon)_T$ is also positive, which means that T_c is shifted to higher temperatures. But when $(dT/d\epsilon)_S < 0$, it means that the temperature of the system is adiabatically decreased due to an adiabatic stretching of the sample, which implies on a shift in T_c to lower temperatures $[(dT_c/d\epsilon)_T < 0]$. Another important finding of this analysis is that close to a second-order phase transition, the elastocaloric effect is pronounced due to the entropy variation associated with the phase transition close to T_c [55]. Note that

close to T_c , it is possible to write an analogous relation as Eq. 2.166, so that [66, 67]:

$$dT_c = -T_c \frac{\Delta\alpha_{ij}}{\Delta c_\sigma} d\sigma_{ij} \quad (2.178)$$

$$\left(\frac{dT_c}{d\sigma_{ij}} \right)_S = -T_c \frac{\Delta\alpha_{ij}}{\Delta c_\sigma}, \quad (2.179)$$

which resembles the Ehrenfest relation, cf. Eq. 2.173 [66]. More specifically, Eq. 2.179 can be rewritten as [55]:

$$\boxed{\Gamma_{ec}^{cr} = \frac{1}{T_c} \left(\frac{dT_c}{d\sigma_{ij}} \right)_S = -\frac{\Delta\alpha_{ij}}{\Delta c_\sigma}}, \quad (2.180)$$

which quantifies the T_c shift in terms of an adiabatic stress application in analogy with the canonical Ehrenfest relation [66]. Note that $\Delta\alpha_{ij}$ and Δc_σ represent the difference between the ordinary and critical contributions of both α_{ij} and c_σ close to T_c . It is worth mentioning that Eq. 2.180 was already reported in Refs. [66, 67], but the connection to Γ_{ec} was still lacking. Furthermore, Eq. 2.180 can be extended to the magnetic and electric cases, i.e., to the magnetocaloric and electrocaloric effects [47, 49, 7], so that [55]:

$$\boxed{\Gamma_{mag}^{cr} = \frac{1}{T_c} \left(\frac{dT_c}{dB} \right)_S = -\frac{\Delta\alpha_B}{\Delta c_B}}, \quad (2.181)$$

and

$$\boxed{\Gamma_{ece}^{cr} = \frac{1}{T_c} \left(\frac{dT_c}{dE} \right)_S = -\frac{\Delta\alpha_E}{\Delta c_E}}, \quad (2.182)$$

where Γ_{mag}^{cr} and Γ_{ece}^{cr} accounts for the critical contributions of the magnetic and electric Grüneisen parameters, which quantifies the magnetocaloric and electrocaloric effects, respectively, and E is the modulus of the electric field. Hence, not only Γ quantifies caloric effects, but also it quantifies the T_c shift of a second-order phase transition upon adiabatically varying the control parameter, which can be σ_{ij} , B or E , for instance. Based on such discussions, a generalization of Γ in terms of the tuning parameter can be made, which is discussed in the next Section.

The obtained theoretical results discussed in Sections 2.3.5 and 2.3.6 were published in (Appendix 6.11):

- Lucas Squillante, Isys F. Mello, Gabriel O. Gomes, A.C. Seridonio, Mariano de Souza, Elastocaloric-effect-induced adiabatic magnetization in paramagnetic salts due to the mutual interactions, Scientific Reports **11**, 9431 (2021).

Also, the publication was reported by the Fapesp Agency in the following:

- “Researchers propose method of magnetizing a material without applying an external magnetic field” - Appendix 6.12.

2.3.7 Generalization of the Grüneisen parameter

In Section 2.2, it has become notorious that Maxwell relations are connected to the definition of Γ . In this Section, it is demonstrated that in fact Γ is naturally derived by making simple mathematical manipulations of the Maxwell relations associated with adiabatic processes. Although quite simple, to the best of our knowledge, this particular point was not properly discussed in the literature until now. Based on the well-known Maxwell relation [28]:

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial v}{\partial T}\right)_p. \quad (2.183)$$

The term $(\partial S/\partial p)_T$ can be rewritten following Eq. 2.30, so that:

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial T}{\partial p}\right)_S \left(\frac{\partial S}{\partial T}\right)_p. \quad (2.184)$$

Replacing Eq. 2.184 into Eq. 2.183, it reads:

$$\left(\frac{\partial T}{\partial p}\right)_S \left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial v}{\partial T}\right)_p, \quad (2.185)$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{\left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial T}\right)_p}. \quad (2.186)$$

Considering $c_p = T/N(\partial S/\partial T)_p$ and $\alpha_p = 1/v(\partial v/\partial T)_p$, Eq. 2.186 becomes:

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{\alpha_p v}{\frac{c_p N}{T}} = \frac{\alpha_p v T}{c_p N} = \frac{\alpha_p T v_m}{c_p}. \quad (2.187)$$

Dividing both sides of Eq. 2.187 by $1/T$, it is given by:

$$\boxed{\frac{1}{v_m T} \left(\frac{\partial T}{\partial p} \right)_S = \frac{\alpha_p}{c_p} = \Gamma}, \quad (2.188)$$

which is the definition of Γ , following Eq. 2.58. As a consequence of the thermodynamic relations, it can be seen that the definition of Γ is naturally encoded in the Maxwell relation of Eq. 2.183. A similar analysis can be made for Γ_{mag} employing the Maxwell relation [28]:

$$\left(\frac{\partial S}{\partial B} \right)_T = \left(\frac{\partial M}{\partial T} \right)_B. \quad (2.189)$$

In the case of thermodynamic relations for magnetic systems, it is widely discussed the following analogy [28]:

$$v \rightarrow -M, \quad (2.190)$$

$$p \rightarrow B. \quad (2.191)$$

The minus sign of the analogy between v and M in Eq. 2.190 is because M increases (decreases) due to the increase (decrease) of B , while v increases (decreases) due to the decrease (increase) of p [28]. In other words, M and B are directly proportional while p and v are inversely proportional. Therefore, employing such an analogy, Eq. 2.30 can be rewritten for a magnetic system by [28]:

$$\left(\frac{\partial T}{\partial B} \right)_S \left(\frac{\partial S}{\partial T} \right)_B \left(\frac{\partial B}{\partial S} \right)_T = -1, \quad (2.192)$$

$$\left(\frac{\partial S}{\partial B} \right)_T = - \left(\frac{\partial T}{\partial B} \right)_S \left(\frac{\partial S}{\partial T} \right)_B. \quad (2.193)$$

Replacing Eq. 2.193 into Eq. 2.189:

$$- \left(\frac{\partial T}{\partial B} \right)_S \left(\frac{\partial S}{\partial T} \right)_B = \left(\frac{\partial M}{\partial T} \right)_B, \quad (2.194)$$

$$\left(\frac{\partial T}{\partial B} \right)_S = - \frac{\left(\frac{\partial M}{\partial T} \right)_B}{\left(\frac{\partial S}{\partial T} \right)_B}. \quad (2.195)$$

Considering that $c_B = T(\partial S/\partial T)_B$ [28] in Eq. 2.195, it reads:

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{\left(\frac{\partial M}{\partial T}\right)_B}{\frac{c_B}{T}} = -T\frac{\left(\frac{\partial M}{\partial T}\right)_B}{c_B}. \quad (2.196)$$

Multiplying both sides of Eq. 2.196 by $1/T$:

$$\boxed{\frac{1}{T}\left(\frac{\partial T}{\partial B}\right)_S = -\frac{\left(\frac{\partial M}{\partial T}\right)_B}{c_B} = \Gamma_{mag}}. \quad (2.197)$$

Equation 2.197 is the definition of Γ_{mag} , following Eqs. 2.59 and 2.63.

Furthermore, a similar analysis can be made for the electric case where the tuning parameter is the electric field E . Given the Maxwell relation [28, 68]:

$$\left(\frac{\partial S}{\partial E}\right)_T = \left(\frac{\partial P}{\partial T}\right)_E, \quad (2.198)$$

where P is the electric polarization, the term $(\partial S/\partial B)_T$ can be rewritten following the relation [28]:

$$\left(\frac{\partial S}{\partial T}\right)_E \left(\frac{\partial T}{\partial E}\right)_S \left(\frac{\partial E}{\partial S}\right)_T = -1 \Rightarrow \left(\frac{\partial S}{\partial E}\right)_T = -\left(\frac{\partial S}{\partial T}\right)_E \left(\frac{\partial T}{\partial E}\right)_S. \quad (2.199)$$

Replacing Eq. 2.199 into Eq. 2.198:

$$-\left(\frac{\partial S}{\partial T}\right)_E \left(\frac{\partial T}{\partial E}\right)_S = \left(\frac{\partial P}{\partial T}\right)_E \Rightarrow \left(\frac{\partial T}{\partial E}\right)_S = -\frac{\left(\frac{\partial P}{\partial T}\right)_E}{\left(\frac{\partial S}{\partial T}\right)_E}. \quad (2.200)$$

Considering that the heat capacity at constant E is given by $c_E = T(\partial S/\partial T)_E$ [28], Eq. 2.200 now reads:

$$\left(\frac{\partial T}{\partial E}\right)_S = -\frac{\left(\frac{\partial P}{\partial T}\right)_E}{\frac{c_E}{T}} = -T\frac{\left(\frac{\partial P}{\partial T}\right)_E}{c_E}. \quad (2.201)$$

Multiplying both sides of Eq. 2.201 by $1/T$:

$$\boxed{\frac{1}{T}\left(\frac{\partial T}{\partial E}\right)_S = -\frac{\left(\frac{\partial P}{\partial T}\right)_E}{c_E} = \Gamma_E}, \quad (2.202)$$

which is the definition of the electric Grüneisen parameter Γ_E proposed for the first time in the literature in Ref. [69]. At this point, it is worth mentioning that,

in order to avoid confusion, note that lower case p refers to pressure, while the capital letter P is electric polarization. Last, but not least, the polar Grüneisen parameter Γ_P , proposed for the first time in the literature in Ref. [7] can be derived from the Maxwell relation [28, 68]:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial E}{\partial T}\right)_P \quad (2.203)$$

Analogously to the previously discussed cases, the term $(\partial S/\partial P)_T$ can be rewritten employing the thermodynamic relation [28]:

$$\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial S}\right)_T = -1 \Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S. \quad (2.204)$$

Replacing Eq. 2.204 into Eq. 2.203:

$$-\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial E}{\partial T}\right)_P, \quad (2.205)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\left(\frac{\partial E}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_P}. \quad (2.206)$$

Assuming that the heat capacity at constant P is $c_P = T(\partial S/\partial T)_P$ [28], Eq. 2.206 reads:

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\left(\frac{\partial E}{\partial T}\right)_P}{\frac{c_P}{T}} = T \frac{\left(\frac{\partial E}{\partial T}\right)_P}{c_P}. \quad (2.207)$$

Multiplying both sides of Eq. 2.207 by $1/T$, it reads:

$$\boxed{\frac{1}{T} \left(\frac{\partial T}{\partial P}\right)_S = \frac{\left(\frac{\partial E}{\partial T}\right)_P}{c_P} = \Gamma_P}, \quad (2.208)$$

which is the definition of Γ_P [7].

It becomes evident that the various forms of the Grüneisen parameter, namely magnetic, electric, polar, and the Grüneisen ratio, are naturally embedded in the widely employed Maxwell relations. Table 2.1 summarizes the result discussed in this regard.

Hence, a generalized form of the Grüneisen ratio Γ_g is proposed in terms of an adiabatic change of an arbitrary tuning parameter g , so that [7]:

$$\boxed{\Gamma_g = -\frac{1}{T} \frac{\left(\frac{\partial S}{\partial g}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_g} = \frac{1}{T} \left(\frac{\partial T}{\partial g}\right)_S}. \quad (2.209)$$

Maxwell-Relation	Grüneisen Parameter
$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$	$\Gamma = -\frac{1}{Tv_m} \frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p} = \frac{1}{Tv_m} \left(\frac{\partial T}{\partial p}\right)_S$ (BC)
$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$	$\Gamma_{mag} = -\frac{1}{T} \frac{\left(\frac{\partial S}{\partial B}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_B} = \frac{1}{T} \left(\frac{\partial T}{\partial B}\right)_S$ (MC)
$\left(\frac{\partial S}{\partial E}\right)_T = \left(\frac{\partial P}{\partial T}\right)_E$	$\Gamma_E = -\frac{1}{T} \frac{\left(\frac{\partial S}{\partial E}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_E} = \frac{1}{T} \left(\frac{\partial T}{\partial E}\right)_S$ (EC)
$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial E}{\partial T}\right)_P$	$\Gamma_P = -\frac{1}{T} \frac{\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P} = \frac{1}{T} \left(\frac{\partial T}{\partial P}\right)_S$ (PC)

Table 2.1: The Grüneisen ratio Γ , magnetic Γ_{mag} , electric Γ_E , and polar Γ_P Grüneisen parameters derived from the corresponding Maxwell relations, which quantify the barocaloric (BC), magnetocaloric (MC), electrocaloric (EC), and polarcaloric (PC) effects, respectively. Table extracted from Ref. [7].

Therefore, the magnitude of any caloric effect can be quantified by Γ_g depending if g is p , E , σ or B [7]. In the next Section, the maximization of caloric effects in terms of entropy arguments and the Grüneisen parameter is discussed.

2.3.8 Maximization of caloric effects

The quantification of the effectiveness of cooling devices that employ the concept of decreasing temperature due to an adiabatic change of a control parameter is key for the optimization of caloric effects. As a matter of fact, the traditional refrigerators that are vastly used in our daily lives incorporate an adiabatic compression of the refrigerant gas in order to cool its interior [2]. However, other types of cooling devices that are more efficient and eco-friendly has been widely investigated, such as devices that employ the concept of the electrocaloric effect to cool down, which refers to the temperature decrease due to an adiabatic removal of E [7]. It is worth mentioning that the search for more sustainable and eco-friendly cooling devices is in line with some of the 17 goals of the United Nations, namely: 7) industry, innovation, and infrastructure, 11) sustainable cities and communities, 12) responsible consumption and production, and 13) climate action [70]. In order to quantify the temperature change ΔT in caloric devices, it is usually employed the so-called caloric strength $CS = \Delta T / \Delta g$, where Δg is the adiabatic change of the tuning parameter and ΔT the corresponding adiabatic temperature change. Essentially, CS quantifies the amount of Δg needed to produce an adiabatic ΔT . As

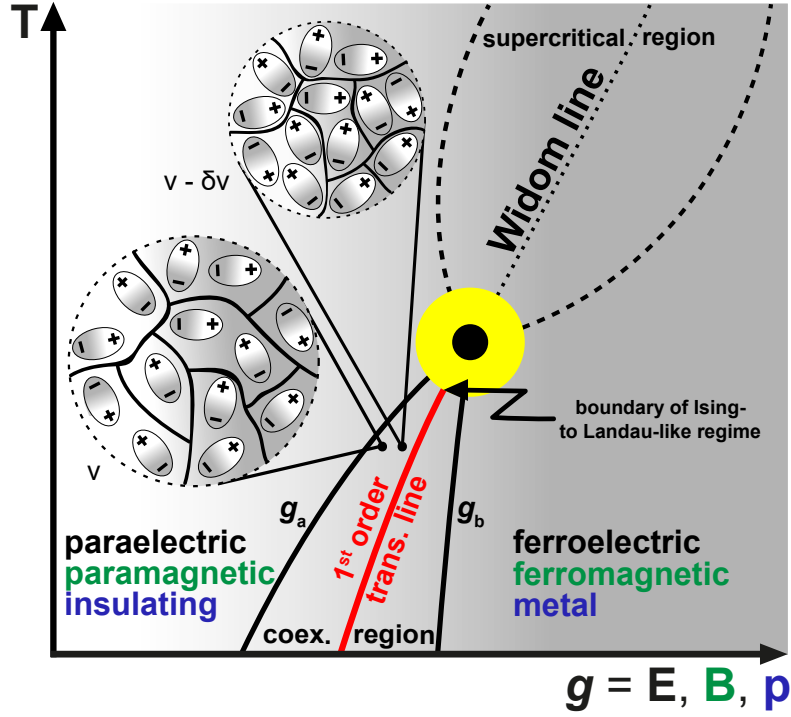


Figure 2.14: Schematic representation of a generic phase diagram temperature T versus tuning parameter g , which can be electric field E , magnetic field B , or pressure p , for instance. Above the critical point, there is a supercritical region and its corresponding Widom line. Below the critical point, black bullet, there is a coexistence region between a paraelectric and ferroelectric, paramagnetic and ferromagnetic, or insulating and metal phases. The coexistence region is delimited by the spinodal lines g_a and g_b . Within the phases coexistence region, there is a first-order transition line (red color). The yellow region around the critical point represents the boundary of the transition from Ising- to Landau-like regime [71]. The case of electric dipoles separated by domain walls in a ferroelectric phase is depicted in an initial volume v and, upon applying pressure, its volume is decreased by δv and the entropy is increased. Figure extracted from Ref. [7].

previously discussed, Γ is not solely employed to investigate phase transitions and critical phenomena, but it also quantifies caloric effects [7], cf. Table 2.1. However, when quantifying caloric effects in terms of the Grüneisen parameters, namely Γ , Γ_{mag} , and Γ_E , for instance, additional physical information can be extracted in terms of the entropy variation of the system upon tuning g . Hence, it becomes natural to investigate the optimization of caloric effects in terms of entropy arguments based on the various definitions of the Grüneisen parameter, cf. Table 2.1. The idea is that the more contributions to S are associated with a particular system, more expressive ΔT is going to be when a caloric effect is performed, i.e., when a tuning parameter is adiabatically varied. Interestingly, as widely discussed in

the literature, there is an intrinsic accumulation of S close to both classical [28] and quantum critical points [72, 73] due to the presence of competing phases in their vicinities. Hence, the high S accumulation in the proximity to a critical point alone is key to enhance the performance of caloric effects, cf. Fig. 2.14. Also, the phases coexistence region in the vicinities of the first-order transition line close to the critical point plays a crucial role on optimizing caloric effects since the mixture of phases contributes to the enhancement of S . However, there are other key ingredients in terms of material design that can be incorporated to a system in order to maximize ΔT due to the presence of several additional contributions to S , cf. Fig. 2.15. Hence, a possible generalized expression for S regarding a candidate

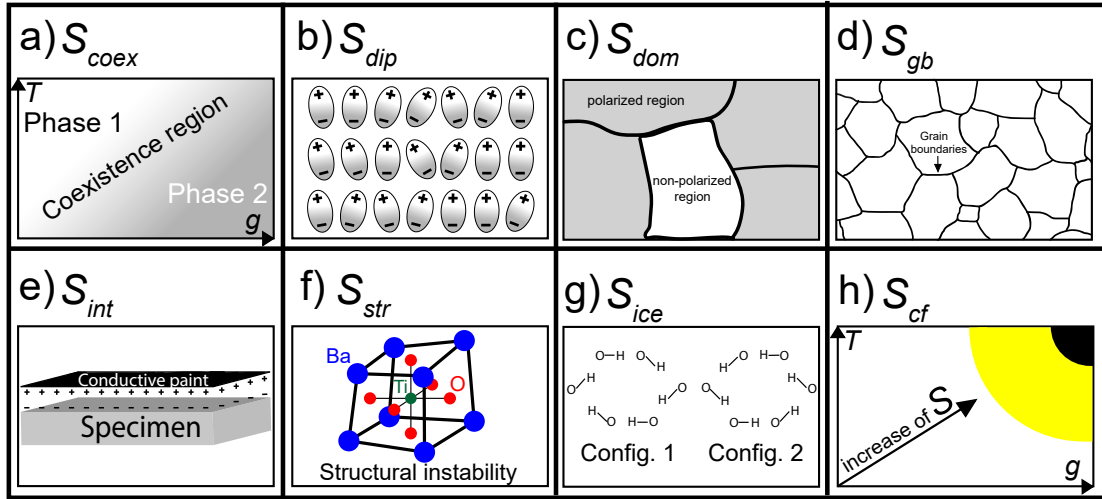


Figure 2.15: Schematic representation of several contributions to the total entropy: a) coexistence region between two arbitrary phases 1 and 2, b) distinct dipolar configurations in a ferroelectric, c) presence of domain walls in a relaxor-like ferroelectric, d) presence of grain boundaries in poly-crystalline or powdered materials, e) interface polarization due to the Maxwell-Wagner effect [74], f) structural instabilities, as it occurs, for instance, in BaTiO_3 BCC unit cell [75], g) residual entropy regarding two distinct molecular configurations [76], h) critical fluctuations associated with the proximity to the critical point. Figure extracted from Ref. [7].

system that can attain a giant caloric effect is given by [7]:

$$S_{total} = (S_{coex} + S_{dip} + S_{dom} + S_{gb} + S_{int} + S_{str} + S_{ice} + S_{cf}), \quad (2.210)$$

where S_{total} is the total entropy, S_{coex} , S_{dip} , S_{dom} , S_{gb} , S_{int} , S_{str} , S_{ice} , and S_{cf} are the contributions to S_{total} regarding, respectively, the phases coexistence region near the critical point, different dipolar configurations, the presence of domain walls, the

presence of grain boundaries in poly-crystalline or powdered materials, interface phenomena, such as Maxwell-Wagner polarization [74], structural instabilities [75], residual entropy in a solid [76], and the critical fluctuations associated with the proximity to the critical point. The various contributions to S_{total} are schematically depicted in Fig. 2.15. Such a proposal of the maximization of caloric effects in terms of entropy arguments enables the interpretation of the recently reported large electrocaloric effect at room-temperature in a multilayered capacitor [77]. Also, based on this proposal, a material can be designed to incorporate as much contributions to S as it can to attain giant caloric effects. Yet, a connection between quantum paraelectricity and enhanced caloric effects was proposed, which is discussed in the next Section.

2.3.9 Electric Grüneisen parameter and quantum paraelectricity

It is well-known from textbooks that the dielectric constant ϵ is enhanced upon approaching the Curie temperature and vanishes below it indicating a phase transition from a paraelectric to a ferroelectric phase [74]. However, some systems present a quite unusual behaviour in ϵ below the Curie temperature, such as SrTiO_3 , where ϵ enhances close to the Curie temperature, but does not vanish. Instead, ϵ stabilizes in a plateau below it [78]. This behaviour is associated with the presence of a quantum critical point in the system, the so-called quantum paraelectric behaviour [79]. In systems presenting such a quantum paraelectric behaviour, it was proposed that ϵ has the following T -dependence [81]:

$$\epsilon = A + \frac{m}{\left(\frac{T_1}{2}\right) \coth\left(\frac{T_1}{2T}\right) - T_0}, \quad (2.211)$$

where A is a non-universal constant, T_0 is a parameter related either to the ferroelectric ($T_0 > 0$) or antiferroelectric ($T_0 < 0$) effective dipolar interaction, T_1 is the temperature below which quantum fluctuations dominate, and $m = n_{ed}\mu_{ed}^2/k_B$, where n_{ed} is the electric-dipole density, and μ_{ed} refers to the local electric-dipole moment. The typical behaviour of ϵ given by Barrett's formula [81] is depicted in

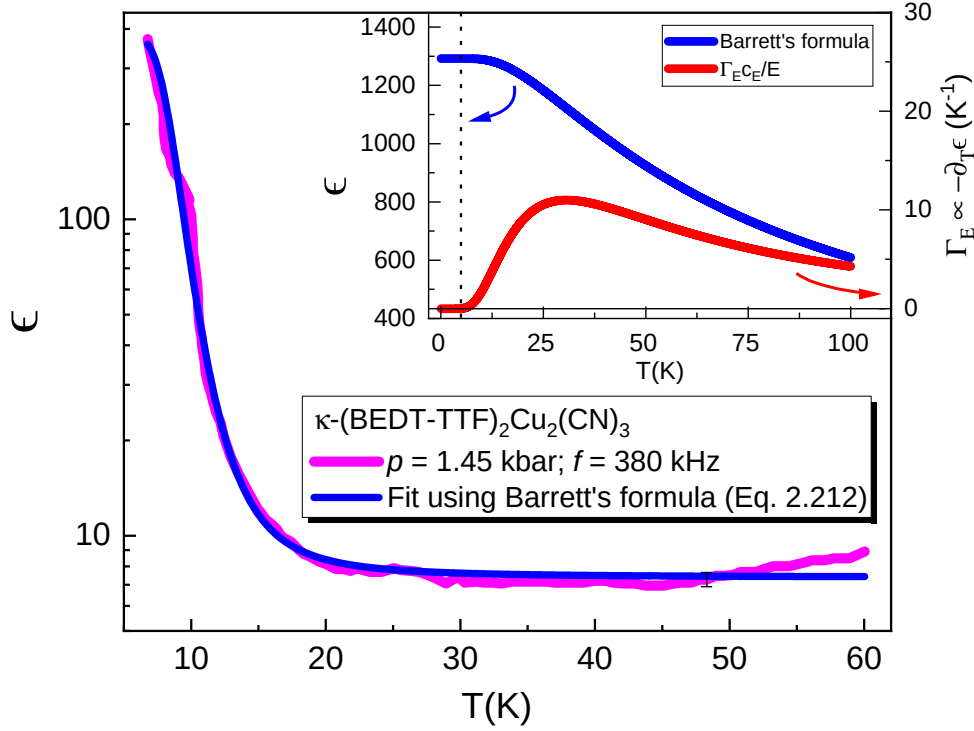


Figure 2.16: Main panel: experimental dielectric constant ϵ results as a function of temperature T for the spin-liquid candidate κ -(BEDT-TTF)₂Cu₂(CN)₃ (pink line) under a pressure of $p = 1.45$ kbar and frequency $f = 380$ kHz. Data extracted from Ref. [80]. The blue solid line represents a fitting of the experimental data employing Barrett's formula [81] (Eq. 2.211). The error bar represents a 5% error in tracing the experimental data. Inset: dielectric constant ϵ versus temperature employing the Barrett's formula (blue line) with parameters $A = 0$, $m = (8.4 \times 10^4)$ K (CGS units), $T_1 = 60$ K, and $T_0 = -35$ K [81]. The temperature derivative of electric Grüneisen parameter Γ_E multiplied by the ratio between the heat capacity at constant electric field c_E and the electric field E (red line) showing that close to the ϵ plateau, the electrocaloric effect is enhanced. Figure extracted from Ref. [7].

the inset of Fig. 2.16 (blue line). Furthermore, T_1 can be defined as the balance between thermal and the vibrational energies associated with a harmonic oscillator in an electric field by the form $T_1 = \hbar\nu/k_B$ [81], where ν is the oscillation frequency. Essentially, in this analysis the response of the electric-dipoles to an external E is treated in the harmonic approximation. The quantum critical regime is set when the energy associated with such quantum fluctuations overcomes the thermal energy. In general terms, the fingerprint of a quantum paraelectric phase is a plateau in ϵ , i.e., the quantum fluctuations affect the ferroelectric phase and instead of presenting a vanishing ϵ for $T \rightarrow 0$, as it occurs in classical ferroelectric-type transitions, ϵ remains constant. It is worth mentioning that such a plateau will be observed only when the ferroelectric transition temperature is close to T_1 , otherwise the quantum

critical fluctuations will not affect ϵ [81]. Note that the plateau in ϵ occurs because the so-called soft modes associated with the instability of the ferroelectric transition do not vanish at the Curie temperature. Instead, the soft modes survive below the Curie temperature and, as a consequence, the quantum fluctuations stabilizes the ferroelectric transition and “locks” ϵ in a finite value instead of presenting a vanishing ϵ below the Curie temperature as it is usually observed for ferroelectrics [82]. As proposed in Ref. [69], Γ_E is given by:

$$\Gamma_E = -\frac{\left(\frac{\partial P}{\partial T}\right)_E}{c_E}. \quad (2.212)$$

Assuming a linear system, i.e., a system which its electric polarization increases linearly with E so that $P = \epsilon E$, Γ_E can be rewritten as [69]:

$$\Gamma_E = -\frac{\left(\frac{\partial \epsilon E}{\partial T}\right)_E}{c_E} = -E \frac{\left(\frac{\partial \epsilon}{\partial T}\right)_E}{c_E}. \quad (2.213)$$

Employing the temperature derivative of ϵ following Barrett’s formula in Eq. 2.211, Γ_E reads [7]:

$$\Gamma_E = \frac{\epsilon_0 E}{c_E} \frac{m T_1^2}{T^2 \left[T_1 \cosh\left(\frac{T_1}{2T}\right) - 2T_0 \sinh\left(\frac{T_1}{2T}\right) \right]^2}, \quad (2.214)$$

where ϵ_0 is the vacuum permittivity. Upon analysing the behaviour of Γ_E close to the plateau of ϵ , cf. inset of Fig. 2.16 (red line), it is clear that Γ_E is maximized due to the presence of the plateau on ϵ . This indicates that systems presenting such a quantum paraelectric behaviour, there is an intrinsic enhanced electrocaloric effect in the regime where quantum fluctuations starts to play a key role since Γ_E , which quantifies the electrocaloric effect, is enhanced close to the plateau of ϵ , cf. inset of Fig. 2.16. Thus, not only Γ_E can be employed, together with ϵ measurements, to detect and probe quantum paraelectricity, but also the analysis in terms of Γ_E predicts a giant electrocaloric effect right at the onset of quantum paraelectricity.

The theoretical results discussed in Sections 2.3.7, 2.3.8 and 2.3.9 were published in (Appendix 6.11):

- Lucas Squillante, Isys F. Mello, Gabriel O. Gomes, A.C. Seridonio, Mariano de Souza, Giant caloric effects close to *any* critical end point, Materials Research Bulletin **142**, 111413 (2021).

Also, the publication was reported by the Fapesp Agency in the following:

- “Pesquisadores propõem estratégia para obter refrigeração de forma otimizada”
- Appendix 6.12.

2.3.10 Grüneisen parameter and the expansion of the universe

The accelerated expansion of the universe was originally probed via type Ia Supernova measurements in 1998 [83]. Although intensive investigations, the physical mechanism causing the accelerated expansion of the universe is still a matter of debate in the literature [84]. The Planck collaboration has provided precise measurements of cosmological parameters in recent years [85]. The so-called Λ -Cold Dark Matter (CDM) model is one of the most prominent models in the literature to account for the expansion of the universe [86, 87, 88, 89, 90, 91]. Essentially, it considers that the universe is composed by dark energy (DE), dark matter (DM), and ordinary matter. Nowadays, the universe is assumed to be dominated by vacuum energy Λ , i.e., dark energy, with a constant energy density ρ [92]. Alternative models using the approach of a dark fluid have also been proposed to unify DE and DM [93]. Various EOS have been suggested, such as the Chaplygin one [94]. However, the Chaplygin EOS conflicts with experimental observations [96], being already surpassed. Essentially, the available experimental data regarding the dimensionless coordinate distances and the X-ray gas mass fractions do not follow the EOS for the Chaplygin gas within a 99% confidence level [94]. In this context, the discrepancy between cosmological expansion models and the expansion mechanisms throughout different eras still remains. Hence, there is a need to come out with new ideas and approaches in order to bring new physical elements to such a discussion in modern Cosmology [97]. In this context, the unprecedented connection between well-established concepts of condensed matter Physics and Cosmology in

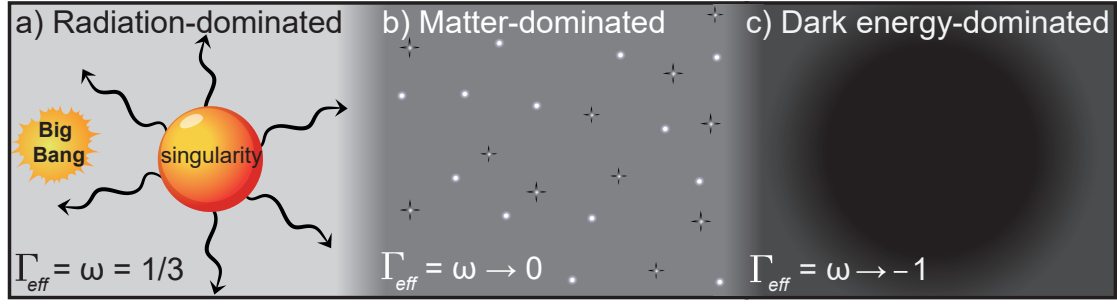


Figure 2.17: Schematic representation of the various eras of the universe, namely a) radiation-, b) matter-, and c) DE-dominated eras. The values of ω , namely Γ_{eff} , for each particular era is also shown. Figure extracted from Ref. [95].

terms of Γ_{eff} and Γ can shed light into the discrepancies regarding the description of an expanding universe. As discussed in Section 2.2.3, the universe is modeled as a perfect fluid, where the radiation, matter, and DE dominated eras are characterized by $\omega = 1/3, 0$, and -1 , respectively [91]. It has been postulated that the late stage of the universe is predominantly composed of vacuum energy ($\omega \rightarrow -1$), or DE, with $\rho \propto a(t)^{-3(1+\omega)}$, and $-1 \leq \omega < 0$ for various eras, where a is the scale factor [98]. Remarkably, the EOS for a perfect fluid $p = \omega\rho$ is similar to the well-known Mie-Grüneisen EOS, i.e. $p_a = \Gamma_{eff}E_a/v$, where p_a and E_a are the contributions of atomic vibrations to p and energy, respectively, and is widely used in the field of Condensed Matter Physics for solids and fluids [99, 100, 101]. In the case of fluids, Γ_{eff} links p and the kinetic/thermal energy of the particles, while in solids, Γ_{eff} measures the ratio of pressure to energy when v changes with a tuning parameter, such as temperature or stress. Hence, Γ_{eff} can be straightforwardly recognized as ω [95], providing an alternative interpretation to ω besides being comprised to a numerical value. This is one of the key results of this Section to be discussed into more details in the following. Now, considering Friedmann equations [38], the relationship between ρ , p , and specific entropy σ_S can be expressed as [91, 102]:

$$nT d\sigma_S = d\rho - \frac{p + \rho}{n} dn, \quad (2.215)$$

where $n = N/v$ is the number of particles N per v . Considering that $\rho = \rho(n, T)$, we write:

$$d\rho = \left(\frac{\partial \rho}{\partial T} \right)_n dT + \left(\frac{\partial \rho}{\partial n} \right)_T dn. \quad (2.216)$$

Rewriting Eq. 2.215:

$$d\sigma_S = \frac{1}{nT} \left(d\rho - \frac{\rho+p}{n} dn \right), \quad (2.217)$$

and employing Eq. 2.216, we have:

$$d\sigma_S = \frac{1}{nT} \left[\left(\frac{\partial \rho}{\partial T} \right)_n dT + \left(\frac{\partial \rho}{\partial n} \right)_T dn - \left(\frac{\rho+p}{n} \right) dn \right]. \quad (2.218)$$

Since entropy is a state function, i.e., $d\sigma_S$ must be exact. Considering a general differential function $dx = Jdy + Hdz$, if dx is exact it means that $(\partial J/\partial z)_y = (\partial H/\partial y)_z$ [1]. Therefore, from Eq. 2.218 we have:

$$\frac{\partial}{\partial T} \left\{ \frac{1}{nT} \left[\left(\frac{\partial \rho}{\partial n} \right)_T - \left(\frac{\rho+p}{n} \right) \right] \right\} = \frac{\partial}{\partial n} \left[\frac{1}{nT} \left(\frac{\partial \rho}{\partial T} \right)_n \right], \quad (2.219)$$

$$\left\{ \frac{\partial}{\partial T} \left[\frac{1}{nT} \left(\frac{\partial \rho}{\partial n} \right)_T - \frac{1}{nT} \left(\frac{\rho+p}{n} \right) \right] \right\} = -\frac{1}{n^2 T} \left(\frac{\partial \rho}{\partial T} \right)_n, \quad (2.220)$$

$$-\frac{1}{nT^2} \left(\frac{\partial \rho}{\partial n} \right)_T - \overbrace{\frac{\partial}{\partial T} \left[\frac{1}{nT} \left(\frac{\rho+p}{n} \right) \right]}^{\Upsilon} = -\frac{1}{n^2 T} \left(\frac{\partial \rho}{\partial T} \right)_n. \quad (2.221)$$

Since $\rho = \rho(T, n)$ and $p = p(T, n)$, the term Υ is given by:

$$\Upsilon = \frac{\partial}{\partial T} \left[\frac{1}{nT} \left(\frac{\rho+p}{n} \right) \right] = \frac{1}{n^2} \left[\frac{\partial}{\partial T} \left(\frac{\rho+p}{T} \right) \right] = \frac{1}{n^2} \left[\frac{\partial}{\partial T} \left(\frac{\rho}{T} + \frac{p}{T} \right) \right], \quad (2.222)$$

$$\Upsilon = \frac{1}{n^2} \left[\frac{\partial}{\partial T} \left(\frac{\rho}{T} \right) + \frac{\partial}{\partial T} \left(\frac{p}{T} \right) \right] = \frac{1}{n^2} \left[\frac{T \left(\frac{\partial \rho}{\partial T} \right)_n - \rho}{T^2} + \frac{T \left(\frac{\partial p}{\partial T} \right)_n - p}{T^2} \right], \quad (2.223)$$

which in turn can be rewritten as:

$$\Upsilon = \frac{1}{n^2 T^2} \left[T \left(\frac{\partial \rho}{\partial T} \right)_n - \rho + T \left(\frac{\partial p}{\partial T} \right)_n - p \right]. \quad (2.224)$$

Replacing Υ from Eq. 2.224 into Eq. 2.221, we have:

$$-\frac{1}{nT^2} \left(\frac{\partial \rho}{\partial n} \right)_T - \frac{1}{n^2 T} \left(\frac{\partial \rho}{\partial T} \right)_n + \frac{\rho}{n^2 T^2} - \frac{1}{n^2 T} \left(\frac{\partial p}{\partial T} \right)_n + \frac{p}{n^2 T^2} = -\frac{1}{n^2 T} \left(\frac{\partial \rho}{\partial T} \right)_n, \quad (2.225)$$

$$\frac{1}{n^2 T} \left(\frac{\partial p}{\partial T} \right)_n = \frac{\rho}{n^2 T^2} + \frac{p}{n^2 T^2} - \frac{1}{nT^2} \left(\frac{\partial \rho}{\partial n} \right)_T. \quad (2.226)$$

Multiplying both sides of Eq. 2.226 by $T^2 n^2$ we achieve the key relation:

$$T \left(\frac{\partial p}{\partial T} \right)_n = \rho + p - n \left(\frac{\partial \rho}{\partial n} \right)_T. \quad (2.227)$$

Upon analysing the temporal behaviour of ρ , the following relation can be written:

$$\dot{\rho} = \left(\frac{\partial \rho}{\partial n} \right)_T \dot{n} + \left(\frac{\partial \rho}{\partial T} \right)_n \dot{T}. \quad (2.228)$$

At this point, we recall the so-called equations of motion for an imperfect fluid in equilibrium [102]:

$$u_\mu T_{;\nu}^{\mu\nu} = \dot{\rho} + (\rho + p)\Theta + u_\mu \Delta T_{;\nu}^{\mu\nu} = 0, \quad (2.229)$$

$$N_{;\mu}^\mu = \dot{n} + n\Theta + \Delta N_{;\mu}^\mu - \Psi = 0, \quad (2.230)$$

where $N_{;\mu}^\mu$ the particle flow tensor, Ψ represents the particle source ($\Psi > 0$) or sink ($\Psi < 0$), and Θ is the fluid expansion rate. Note that the semicolon notation index is employed to represent the so-called covariant derivative. The upper index represents the 4 space coordinates. For instance, the notation of the particle flow tensor $N_{;\mu}^\mu$ represents the covariant derivative of the particle flow in the 4 space coordinates, namely, one temporal and 3 spatial ones [39]. Thus, Eq. 2.228 can be rewritten as:

$$\left(\frac{\partial \rho}{\partial T} \right)_n \dot{T} = \dot{\rho} - \left(\frac{\partial \rho}{\partial n} \right)_T \dot{n}. \quad (2.231)$$

Solving Eqs. 2.229 and 2.230 for $\dot{\rho}$ and $\dot{n}$, we have:

$$\dot{\rho} = -(\rho + p)\Theta - u_\mu \Delta T_{;\nu}^{\mu\nu}, \quad (2.232)$$

$$\dot{n} = -n\Theta - \Delta N_{;\mu}^\mu + \Psi. \quad (2.233)$$

Replacing $\dot{\rho}$ and $\dot{n}$ from Eqs. 2.232 and 2.233 into Eq. 2.231, it reads:

$$\left(\frac{\partial \rho}{\partial T} \right)_n \dot{T} = -(\rho + p)\Theta - u_\mu \Delta T_{;\nu}^{\mu\nu} - \left(\frac{\partial \rho}{\partial n} \right)_T [\Psi - n\Theta - \Delta N_{;\nu}^\nu], \quad (2.234)$$

$$\left(\frac{\partial \rho}{\partial T}\right)_n \dot{T} = \Theta \left[n \left(\frac{\partial \rho}{\partial n}\right)_T - (\rho + p) \right] - \left(\frac{\partial \rho}{\partial n}\right)_T [\Psi - \Delta N_{;\mu}^\mu] - u_\mu \Delta T_{;\nu}^{\mu\nu}. \quad (2.235)$$

Rewriting Eq. 2.227 as:

$$\left(\frac{\partial p}{\partial T}\right)_n = \frac{\rho + p - n \left(\frac{\partial \rho}{\partial n}\right)_T}{T} \Rightarrow \left(\frac{\partial \rho}{\partial n}\right)_T = \frac{-T \left(\frac{\partial p}{\partial T}\right)_n + \rho + p}{n}, \quad (2.236)$$

and inserting it into Eq. 2.235, it reads:

$$\left(\frac{\partial \rho}{\partial T}\right)_n \dot{T} = \Theta \left[-T \left(\frac{\partial p}{\partial T}\right)_n \right] - \left(\frac{\partial \rho}{\partial n}\right)_T [\Psi - \Delta N_{;\mu}^\mu] - u_\mu \Delta T_{;\nu}^{\mu\nu}. \quad (2.237)$$

Multiplying both sides of Eq. 2.237 by $(\partial \rho / \partial T)_n^{-1}$, we have:

$$\dot{T} = -T \left(\frac{\partial p}{\partial \rho}\right)_n \Theta - \left(\frac{\partial \rho}{\partial T}\right)_n^{-1} \left\{ \left(\frac{\partial \rho}{\partial n}\right)_T [\Psi - \Delta N_{;\mu}^\mu] - u_\mu \Delta T_{;\nu}^{\mu\nu} \right\}. \quad (2.238)$$

Multiplying both sides of Eq. 2.238 by $1/T$, it reads:

$$\frac{\dot{T}}{T} = - \left(\frac{\partial p}{\partial \rho}\right)_n \Theta - \frac{1}{T} \left(\frac{\partial \rho}{\partial T}\right)_n^{-1} \left\{ \left(\frac{\partial \rho}{\partial n}\right)_T [\Psi - \Delta N_{;\mu}^\mu] - u_\mu \Delta T_{;\nu}^{\mu\nu} \right\} \quad (2.239)$$

Equation 2.239 is the general law of the temperature evolution of an imperfect fluid.

For the case of a perfect fluid, there are no dissipation fluxes, so that Ψ , $\Delta T_{;\nu}^{\mu\nu}$, and $\Delta N_{;\mu}^\mu$ are zero and $\Theta = -\dot{n}/n$. Hence, Eq. 2.239 reads [102]:

$$\boxed{\frac{\dot{T}}{T} = \left(\frac{\partial p}{\partial \rho}\right)_n \frac{\dot{n}}{n}} \quad (2.240)$$

Equation 2.240 is the so-called temperature evolution law for the perfect fluid in the adiabatic regime. Considering the EOS of a perfect fluid, the term $(\partial p / \partial \rho)_n$ is recognized as ω . Since $\rho = E/v$, we have:

$$\omega = \left(\frac{\partial p}{\partial \rho}\right)_n = \left(\frac{\partial p}{\partial [E/v]}\right)_n = v \left(\frac{\partial p}{\partial E}\right)_n. \quad (2.241)$$

The definition of ω in Eq. 2.241 is exactly the same as the definition of the effective Grüneisen parameter Γ_{eff} , cf. Eq. 2.47. Also, as previously discussed, we have identified ω as Γ_{eff} in the frame of a perfect fluid picture employing the Mie-Grüneisen EOS. Now, Eq. 2.240 can be rewritten as:

$$\frac{dT}{T} = \left(\frac{\partial p}{\partial \rho} \right)_n \frac{dn}{n}. \quad (2.242)$$

Integrating both sides of Eq. 2.242 and considering that $(\partial p / \partial \rho)_n = \omega = \Gamma_{eff}$, we have:

$$\ln(T) + C_1 = \Gamma_{eff} [\ln(n) + C_2], \quad (2.243)$$

$$\ln(T) + C_1 = \ln(n^{\Gamma_{eff}}) + C_3, \quad (2.244)$$

$$\ln(T) = \ln(n^{\Gamma_{eff}}) + C_4, \quad (2.245)$$

$$\ln\left(\frac{T}{n^{\Gamma_{eff}}}\right) = C_4, \quad (2.246)$$

$$\frac{T}{n^{\Gamma_{eff}}} = C_5, \quad (2.247)$$

where C_1 and C_2 are integration constants and C_3 , C_4 , and C_5 are arbitrarily constants. Upon recalling that $n \propto 1/v$ [102], we have:

$$\frac{T}{\left(\frac{1}{v}\right)^{\Gamma_{eff}}} = C_5, \quad (2.248)$$

which in turn can be rewritten as:

$$\boxed{Tv^{\Gamma_{eff}} = constant}. \quad (2.249)$$

Equation 2.249 relates T and v during an adiabatic expansion of the universe in the context of a perfect fluid analysis. The temperature of the universe is consistently reduced as it expands during the radiation- and matter-dominated eras, which can be interpreted as a barocaloric effect [103]. The latter can be quantified using Γ (Eq. 2.58), which is the singular contribution to Γ_{eff} , as discussed in Section 2.2.1. In condensed matter Physics, the barocaloric effect is initiated by applying pressure, followed by its adiabatic removal, resulting in cooling. In the case of the universe, the

singularity before the Big Bang could be considered as the first step in performing the barocaloric effect. However, due to the inherent uncertainty in estimating precisely T and p of the expanding universe during each era [104], quantifying this (baro)caloric effect in terms of Γ is challenging. During the radiation- and matter-dominated eras, $\Gamma_{eff} > 0$, causing the temperature of the universe to decrease in response to its expansion, cf. Eq. 2.249. However, during the DE-dominated era, T increases during adiabatic expansion, with $\Gamma_{eff} < 0$, as described by Eq. 2.249. This, in turn, can be interpreted as an inverse barocaloric effect [105], which is associated to the portion of DE in the universe, which in turn can affect the temperature evolution of the universe in late stages [106]. At this point, an analysis in terms of the volume- and temperature-dependence of S across various eras is performed. Based on Eq. 2.44 and the fact that $\mathcal{B}_T = 1/\kappa_T$, $\Gamma_{eff} = v\alpha_p/\kappa_T c_v$ [9]. By employing the thermodynamic relation $\alpha_p = \kappa_T(\partial S/\partial v)_T$, it can be written:

$$v \left(\frac{\partial S}{\partial v} \right)_T = \Gamma_{eff} c_v. \quad (2.250)$$

Considering that $\Gamma_{eff} = \omega$ and $c_v = T(\partial S/\partial T)_v$, it yields:

$$v \left(\frac{\partial S}{\partial v} \right)_T = \omega T \left(\frac{\partial S}{\partial T} \right)_v. \quad (2.251)$$

For the various eras:

$$v \left(\frac{\partial S}{\partial v} \right)_T = \frac{T}{3} \left(\frac{\partial S}{\partial T} \right)_v, \quad (\text{radiation-dominated era}) \quad (2.252)$$

$$\left(\frac{\partial S}{\partial v} \right)_T \rightarrow 0, \quad (\text{matter-dominated era}) \quad (2.253)$$

$$v \left(-\frac{\partial S}{\partial v} \right)_T = T \left(\frac{\partial S}{\partial T} \right)_v. \quad (\text{DE-dominated era}) \quad (2.254)$$

Equation 2.252 highlights that during the radiation-dominated era, the isothermal entropy change caused by the universe expansion was more pronounced than the one associated with its isochoric temperature change by a factor of 3. During the matter-dominated era, S remains approximately constant, cf. Eq. 2.253. By considering $(\partial S/\partial v)_T = p/T$ [107], Eq. 2.254 can only hold true if negative pressures

are assumed. Therefore, the concept of negative pressure associated with dark energy is supported by the analysis of Eq. 2.254. According with Landau [108], a negative value of $(\partial S/\partial v)_T$ implies a metastable state. In this case, the volume portion associated with DE, spontaneously contracts and, as a result, S increases due to the potential formation of cavities [107, 108]. This contraction of the volume portion associated with dark energy can explain the accelerated expansion during the dark energy-dominated era, as proposed in Ref. [104]. The contraction of such a volume portion related to DE can be considered as the driving force associated with the accelerated expansion during the DE-dominated era, given that the so-called Hubble flow increases due to this contraction [104]. Some authors suggest that the concept of negative temperatures could be associated with the DE-dominated era [109], referred to as the phantom regime [91]. However, this assumption is questionable since the concept of negative temperatures require thermodynamic equilibrium, which is not the case of an expanding universe with a time-dependent T . This is discussed in details in Ref. [110] and is in contrast to the canonical definition of temperature based on the magnetic energy of a paramagnetic system [111], cf. discussed in the end of Appendix 6.2 of this Thesis. At this point, an analysis assuming a closed spherical universe approach [112, 104] to describe its speed of expansion in connection with Γ_{eff} is provided. Recalling the first law of Thermodynamics [1]:

$$dQ = dU + dW. \quad (2.255)$$

Given that $dQ = TdS$ and $dW = +pdv$, we have [104]:

$$TdS = dU + pdv, \quad (2.256)$$

which results in $dU = -pdv$ for an adiabatic process [104]. The Hubble parameter is defined as $H = \dot{a}/a$ [113], which represents the normalized rate of expansion. Analogously, one can determine H as the normalized rate of the universe's volume change over time [104]:

$$H = \frac{\dot{v}}{v} = \frac{\frac{dv}{dt}}{\frac{4}{3}\pi r^3}, \quad (2.257)$$

where r is the radius of the assumed spherical universe. Equation 2.257 can be rearranged as [104]:

$$H = \frac{3}{4\pi r^3} \frac{dv}{dU} \frac{dU}{dt}, \quad (2.258)$$

which, in turn, gives us:

$$\frac{dU}{dt} = \frac{4}{3} \pi r^3 H \frac{dU}{dv}. \quad (2.259)$$

Following discussions in Ref. [114], during the radiation-dominated era the universe expanded at a decelerated rate, i.e., $dU/dt < 0$. The speed of expansion reached a minimum at the matter-dominated era, i.e., $dU/dt \rightarrow 0$, and then started to increase as the universe entered in the DE-dominated era, i.e., $dU/dt > 0$, indicating that the universe is expanding in an accelerated way. Given that $dU = -p dv$ and that the volume variation of the universe is positive due to its expansion, a negative p implies that the internal energy of the universe is increasing in the DE-dominated era [104]. This allows to establish a connection between Γ_{eff} , the universe's expansion speed, and the temporal evolution of U . Given that $dU/dv = -p$ for an adiabatic expansion and $p = \omega \rho = \Gamma_{eff} \rho$ for a perfect fluid, $dU/dv = -\Gamma_{eff} \rho$. Hence, Eq. 2.259 can be rewritten as:

$$\Gamma_{eff} = \frac{3}{4\pi r^3 H \rho} \left(-\frac{dU}{dt} \right). \quad (2.260)$$

Assuming that the physical quantities r , H , and ρ are always positive, the sign of Γ_{eff} is determined solely by $-dU/dt$. Based on this, when $dU/dt < 0$, $\Gamma_{eff} > 0$; when $dU/dt \rightarrow 0$, $\Gamma_{eff} \rightarrow 0$; and when $dU/dt > 0$, $\Gamma_{eff} < 0$. The sign-change of Γ_{eff} during the transition from decelerated to an accelerated expansion is reminiscent of a phase transition near a critical end point in condensed matter physics [115]. Using Noether's theorem [116], the change in the time dependence of U during this transition can be interpreted as a symmetry breaking, which is analogous to a canonical phase transition [108]. It is worth mentioning that it is still under debate whether ω has indeed converged to -1 in the DE-dominated era or if it will vary

over time as the universe continues to expand [85]. Under the light of the proposed interpretation of ω as Γ_{eff} , it is tempting to conclude that ω , i.e., Γ_{eff} , will become time-dependent as the thermodynamic quantities embedded in Γ_{eff} , such as κ_T and c_v , change in response to the continuous temperature change and expansion of the universe. Since ω , namely Γ_{eff} , is linked to Λ through $p = \omega\rho_\Lambda = -\rho_\Lambda = -c^2\Lambda/8\pi G$ [91], where c is the speed of light and ρ_Λ is the vacuum energy density, a time-dependent ω would imply a time-dependent $\Lambda(t)$ and/or $G(t)$, as suggested in recent works [117, 118, 119]. To resolve this issue, accurate observations of ρ_Λ over time are crucial [46]. The analogy of the sign-change in Γ_{eff} between the matter- and DE-dominated eras and the proposal of a temporal behaviour of Λ under the light of Γ_{eff} are another key results in this Thesis in the frame of the application of Γ_{eff} to Cosmology. Last but not least, the connection between Γ_{eff} and Einstein field equations is made in the following. The renowned Einstein field equations, as reported in Ref. [120], link the curvature of spacetime to the distribution of energy and momentum in the universe. This set of equations is given by 2.261 [120]:

$$R_{\mu\nu} - \frac{1}{2}g_{\mu\nu}R + \Lambda g_{\mu\nu} = 8\pi GT_{\mu\nu}, \quad (2.261)$$

where $R_{\mu\nu}$ represents the Ricci curvature tensor, $g_{\mu\nu}$ is the metric tensor, and R stands for the curvature scalar. Upon considering a perfect fluid, $T_{\mu\nu}$ is related to p and ρ through the relation $T_{\mu\nu} = (p + \rho)u^\mu u^\nu + pg_{\mu\nu}$ [91, 121, 122], where u is the four-velocity vector field. Using the EOS of a perfect fluid, $T_{\mu\nu}$ can be expressed as a function of ω as $T_{\mu\nu} = (1 + \omega)\rho u^\mu u^\nu + \rho\omega g_{\mu\nu}$ [91]. Hence, Einstein field equations can be rewritten in terms of Γ_{eff} so that:

$$R_{\mu\nu} - \frac{1}{2}g_{\mu\nu}R + \Lambda g_{\mu\nu} = 8\pi G[(1 + \Gamma_{eff})\rho u^\mu u^\nu + \rho\Gamma_{eff}g_{\mu\nu}]. \quad (2.262)$$

It is then evident that Einstein field equations implicitly incorporate Γ_{eff} through $T_{\mu\nu}$. It is worth mentioning that this is the very first time in the literature that it is reported about the connection between Einstein field equations and Γ_{eff} . Note that the relationship between $T_{\mu\nu}$ and Γ_{eff} comes from the fact that $T_{\mu\nu}$ incorporates all pressure components, shear stresses, and energy density associated with the

gravitational field. The connection between Γ_{eff} and $T_{\mu\nu}$ is particularly relevant in the context of imperfect fluids, which have been suggested as a way to explain observational models that deviate from the Λ -CDM one by incorporating additional anisotropic energy fluxes and stress tensor components [123]. In such a case, $T_{\mu\nu}$ embodies a combination of perfect and imperfect fluid contributions [123]. The imperfect fluid model is consistent with recent experimental observations of an anisotropic universe expansion resulting from the formation of galaxy clusters of varying sizes during the early stages of the universe [124]. Such an anisotropic expansion has been verified through measurements of redshift space distortions [125]. Furthermore, it has been reported in the literature that the quantum vacuum in the DE-dominated era is highly inhomogeneous and anisotropic, with ∇a and $\nabla^2 a$ being expressive [126]. Inspired by the work reported in Ref. [115] on the metal-insulator coexistence region of the Mott transition, similar arguments to those reported in Ref. [115] were employed to describe the anisotropic expansion of the universe. In Ref. [115], using the Avramov/Casalini's model, different relaxation times for metallic and insulating bubbles were assumed in the coexistence region of the Mott transition. As reported in Refs. [127, 128], anisotropic effects in thermal expansion are observed upon crossing the first-order transition line within the coexistence region. An analogy to the universe by considering different rotation periods for different galaxy clusters is straightforward, where the galaxies clusters play the role of metallic/insulating bubbles. As the universe transitions from radiation-, to matter-, and DE-dominated eras, Γ_{eff} changes sign, a behaviour analogous to that observed in the pressure-induced Mott metal-to-insulator transition near a second-order critical end point [115]. Therefore, an anisotropic expansion of the universe can be inferred based on the proposal of critical points related to the universe expansion was discussed in Ref. [104]. The anisotropic expansion effects can be described through the components of the stress tensor, which, in turn, can be associated with the elastic Grüneisen parameter, $\Gamma_{ec} = 1/T(\partial T/\partial \sigma_{ij})_S$ [103] (Eq. 2.168). Since Γ_{eff} is related to Γ_{ec} , the anisotropic expansion effects can be explored through Γ_{eff} embodied in the energy-momentum tensor in Einstein field equations. If DE

continuously drives the universe towards an endless accelerated expansion, one of its possible fates is the so-called “big rip” [129, 130, 131]. Such a connection between Γ_{eff} , Γ_{ec} , and Einstein field equations offer an alternative perspective to explore such a scenario, which incorporates all stress tensor components associated with an anisotropic expansion in $T_{\mu\nu}$ and, as a consequence, in Einstein field equations. This is another key result of this Section, which provides a new avenue in the field of Cosmology for interpreting the universe’s expansion and addressing the limitations of the current standard cosmological scenario, as highlighted in Ref. [97].

The theoretical results discussed in this Section were submitted (Appendix 6.11):

- Lucas Squillante, G.O. Gomes, I.F. Mello, G. Nogueira, A.C. Seridonio, R.E. Lagos-Monaco, M. de Souza, Grüneisen meets Einstein, (submitted) (2023).

“When you want something in life you just gotta reach out and grab it.”

— Christopher McCandless, *Into The Wild*.

3

Experimental investigations on the possible multiferroic character of the Fabre salts

Contents

3.1	Strongly correlated electronic phenomena in the (TMTTF)₂X salts	74
3.2	Experimental aspects	83
3.2.1	Principle of work of the Teslatron-PT cryostat	83
3.2.2	Cleaning up of the zeolite trap	90
3.2.3	Pump and purge of the ⁴ He circulation lines	93
3.3	Experimental results	94
3.3.1	Dielectric constant	94
3.3.2	Raman spectra and fluorescence background of the TMTTF salts	96

3.1 Strongly correlated electronic phenomena in the (TMTTF)₂X salts

One of the most investigated phenomena at low temperatures is superconductivity, where the electrical resistance R_{el} of a determined system goes to zero at a critical temperature T_c . In other words, there is a current flow without energy dissipation by the well-known Joule effect ($P_d = R_{el} \cdot i^2$), where P_d is the dissipated power, and i is the electrical current. After several years since Kamerlingh Onnes first

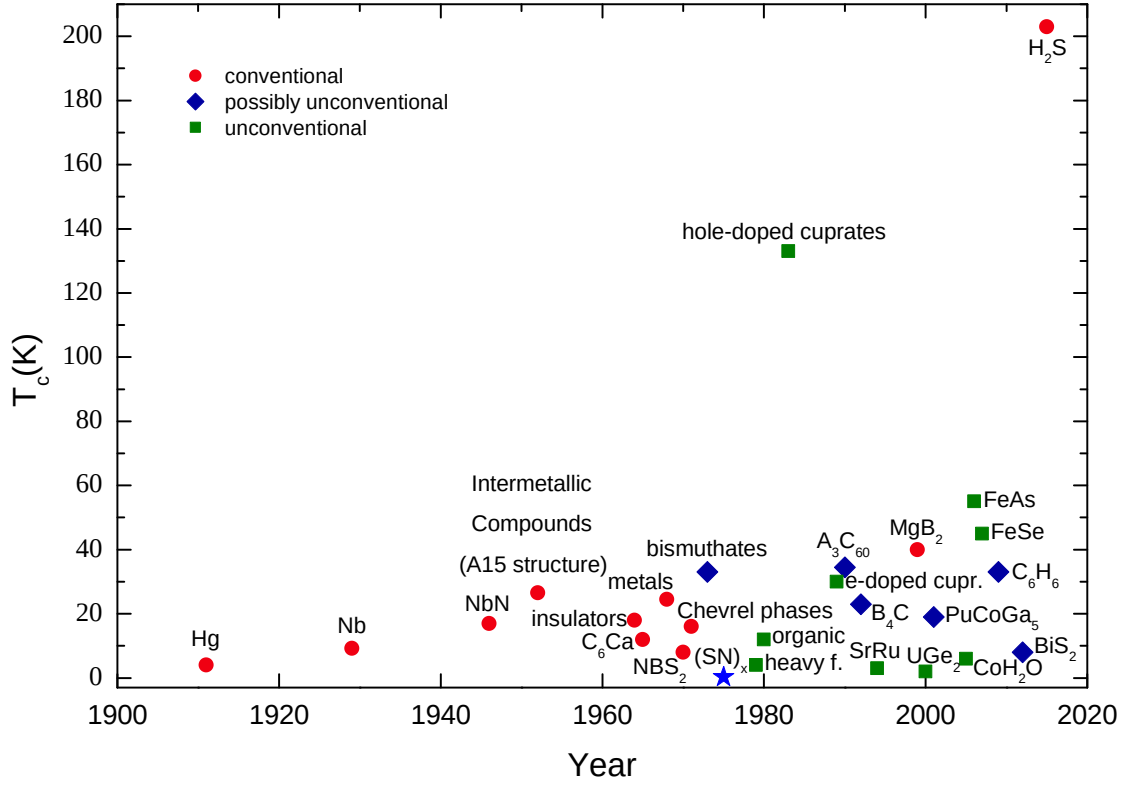


Figure 3.1: Evolution of the critical temperature T_c over the years of conventional, possibly unconventional, and unconventional superconductors. Figure adapted from Ref. [135].

observed superconductivity in a mercury (Hg) sample with $T_c \sim 4$ K [132], Meissner and Ochsenfeld [133] demonstrated experimentally what would be named afterward as the Meissner-Ochsenfeld effect, where a magnetic field $\vec{B}$ is expelled from a superconductor and a magnetic levitation occurs. Such an effect is crucial in defining superconductivity as a new state of matter. This phenomenon is so counter-intuitive that more than half-century passed since the famous BCS theory [134] was developed, which proposed an electron-electron coupling mediated by the lattice phonons in the so-called Cooper pairs [7]. There is a technological interest in synthesizing new superconducting materials with higher critical temperatures [136]. This is because of the use of superconducting materials in helping connect grids as better safety switches than conventional inductors [137], a base to develop quantum computers [138] and even in the development of Maglev trains technology [139]. Most metallic elements were discovered to superconduct below 10 K and even a group of metallic alloys have shown superconductivity [140, 32, 141]. However,

until the 80's critical temperatures above 30 K had not been observed, as shown in Fig. 3.1. In 1986, Bednorz and Müller observed for the first time superconductivity in the so-called cuprates (alloys containing copper and oxygen) above the 40 K range [142]. Also, superconductivity was discovered in the system $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) with a critical temperature of 90 K [143]. In the last decade, superconductivity was discovered in iron-based structures, the so-called iron pnictides or iron-based superconductors [144]. Such a discovery was unexpected for two main reasons: it was believed that the magnetic ions would destroy superconductivity and the fact that the non-superconducting phases of this family are metallic, totally different from the cuprate families which are Mott insulators in the underdoped regime [145, 146]. It is worth mentioning that other systems of interest also superconduct, such as the heavy fermion compound CeCu_2Si_2 [147], and the $(\text{TMTSF})_2\text{PF}_6$, where TMTSF represents a molecule of tetramethyltetraselenafulvalene, organic molecular metal [148], for instance. The BCS theory of conventional superconductors reveals how to achieve high T_c combining high-frequency phonons, strong electron-phonon coupling, and high-density of states [149]. Such conditions are satisfied for compounds dominated by hydrogen [150, 151], predicting compounds with T_c in the range of 50–235 K for numerous hydrides [152], since the hydrogen mass is low and it would increase the phonon frequency ω and thus the critical temperature T_c , as shown in the famous BCS theory relation [134, 141]:

$$k_B T_c = \frac{\hbar \omega_D}{1.45} \cdot \exp \left(-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right), \quad (3.1)$$

where $\hbar$ is the Planck's constant divided by 2π , ω_D the Debye's frequency, λ the electron-phonon coupling constant, and μ^* the Coulomb pseudopotential, which takes into account the Coulomb repulsion between electrons. In 2015 the hydrogen sulfide compound H_2S was discovered to superconduct at $T_c \sim 203$ K under 100 GPa [153]. Yet, in 2019 it was reported that a Lanthanum superhydride $\text{LaH}_{10\pm x}$ showed signatures of superconductivity at T_c above 260 K under pressures of 180-200 GPa [154, 155]. Until the writing of this Thesis, there is a report of near-ambient superconductivity in a N-doped lutetium hydride [156].

However, such results are still under high criticism and no consensus has yet been reached. In this context, it is clear that the goal to achieve high-temperature superconductivity remains a challenge. The pressurized Fabre-salt $(\text{TMTSF})_2\text{PF}_6$ show superconductivity at $T_c = 0.9 \text{ K}$ under 12 kbar [148], playing a crucial role in the frame of superconductivity to fundamentally investigate correlated phenomena, more specifically the relation between the charge-ordered and the superconducting phases that take place in these systems, aiming to discover key-factors for achieving high-temperature superconductivity. In an article published in 1964, it was predicted by W. A. Little that low-dimensional systems would be strong candidates in exhibiting superconductivity at high temperatures [157]. More specifically, the proposed model

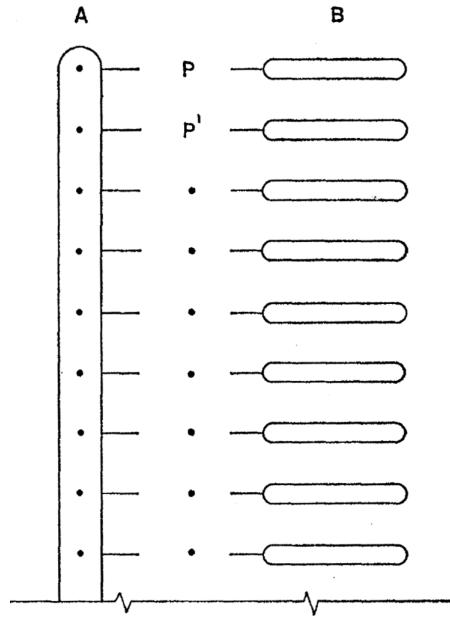


Figure 3.2: Little proposed model of a superconducting organic molecule, where the molecule A is defined as the “spine” and B are the side chains attached to the spine at points P, P’, and so on. Picture extracted from Ref. [157].

suggests that in such systems a long chain called the “spine” can be observed in which electrons fill the various states and a series of arms or side chains attached to the spine (Fig. 3.2), making the system easily polarized. In this case, the electric dipoles are formed between the structure A and B (Fig. 3.2) and, upon appropriate choosing the molecules of the side chains, it would be possible to observe an interaction between electrons in the spine due to the charge oscillations

of the side chains, and with such an attractive interaction a superconducting state can emerge. The molecular conductors discussed in this proposal present such characteristics and this is one of the main reasons that make such systems to be intensively explored by the scientific community in the last decades [11, 12]. In this context, molecular conductors have been recognized as an appropriate playground for the exploration of correlated phenomena in low-dimensions [11, 12]. Among molecular conductors, the systems of particular interest are the $(\text{TMTTF})_2X$, where TMTTF is the base molecule tetramethyltetrafulvalene and X a monovalent center-symmetric counter-anion, such as PF_6 , AsF_6 , or SbF_6 . Such systems enable the investigation of contemporary aspects in the field of correlated phenomena, like the Mott metal-insulator transition [12] and the charge-ordered phase [158]. It is possible to tune the physical properties of such systems either by employing chemical substitution of the counter-anions or by applying external hydrostatic pressure [15, 159] (Fig. 3.3). In such systems, the TMTTF molecules are organized and stacked in chains in the a -axis (Fig. 3.4) and are dimerized, resembling the model proposed by Little [157]. Theoretically, the Physics of the molecular conductors of the TMTTF family can be described by the dimerized one-dimensional extended Hubbard model [162], represented by the Hamiltonian:

$$H = t_1 \sum_{i \text{ even}, \sigma} (a_{i\sigma}^\dagger a_{i+1\sigma} + H.c.) + t_2 \sum_{i \text{ odd}, \sigma} (a_{i\sigma}^\dagger a_{i+1\sigma} + H.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_i n_i n_{i+1}, \quad (3.2)$$

where $t_1 = t(1 - \delta_d)$ and $t_2 = t(1 + \delta_d)$ are, respectively, the inter- and intra-dimer hopping terms, δ_d the dimerization degree, σ is the spin index $\uparrow$ or $\downarrow$, $a_{i\sigma}^\dagger$, $a_{i\sigma}$, and $n_{i\sigma}$ the creation, annihilator, and the number operators for one electron with spin σ at the i^{th} site, represented by $n_i = n_{i\uparrow} + n_{i\downarrow}$, U and V are the on-site and inter-site nearest-neighbor Coulomb interaction, respectively. Upon analysing the electrical resistivity *versus* temperature data of the TMTTF family salts, a metallic behaviour is observed at room temperature [163]. However, upon decreasing temperature, U increases upon lowering the temperature and splits the energy bands creating a gap. In such a temperature, a Mott-insulating phase [164] takes place, where a partially-filled energy band configuration coexists with the presence of a gap

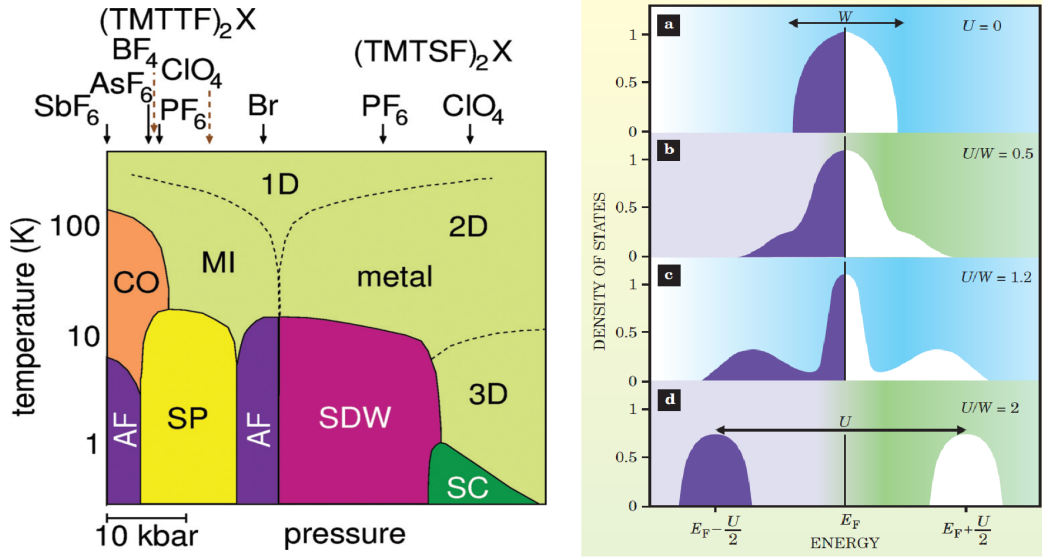


Figure 3.3: Left panel: Schematic temperature *versus* pressure phase diagram for the Fabre-Bechgaard salts. The position of the different compounds under ambient pressure is indicated above by the black arrows, such difference is directly connected with the counter-anion chemical pressure. The phases shown are Mott insulator (MI), charge-ordering (CO), antiferromagnetic (AF), spin-Peierls (SP), spin-density wave (SDW) and superconductivity (SC). The dashed lines represent cross-overs from a 1, 2, and 3D system [160]. Right panel: Density of states (DOS) as a function of the energy for several values of on-site Coulomb interaction U between electrons. Without any Coulomb repulsion taken into account ($U = 0$), the DOS has a half elliptical shape (blue = filled, white = empty) and the Fermi level E_F is located in the middle. In the case where the electron interactions are strong enough, the bands are split and thus the Mott metal-insulator transition occurs [161].

(Fig. 3.3). Such a phase only occurs due to the strong electronic correlation present in such systems. A charge-ordered phase can be achieved in the TMTTF-based molecular systems at low temperatures (typically between ~ 50 – 150 K) (Fig. 3.5), coexisting with a ferroelectric one [165], in the so-called Mott-Hubbard ferroelectric phase. Such phenomena can also be described by employing the extended Hubbard model [166]. In this case, when $U/W \approx 1$ a Mott insulator transition takes place [11], where W is the bandwidth. However, as the inter-site V term increases, a critical value of it can be found at a particular charge-ordering temperature T_{co} where the minimal energy configuration is not a homogeneous charge distribution, but a charge disproportionated one [166]. Above T_{co} , electrons are localized without the formation of electric dipoles, while below T_{co} there is a finite charge disproportionation [167] between the molecules (above a critical value of the inter-site Coulomb repulsion V_c , a charge disproportion takes place [166]), creating electric dipoles and thus

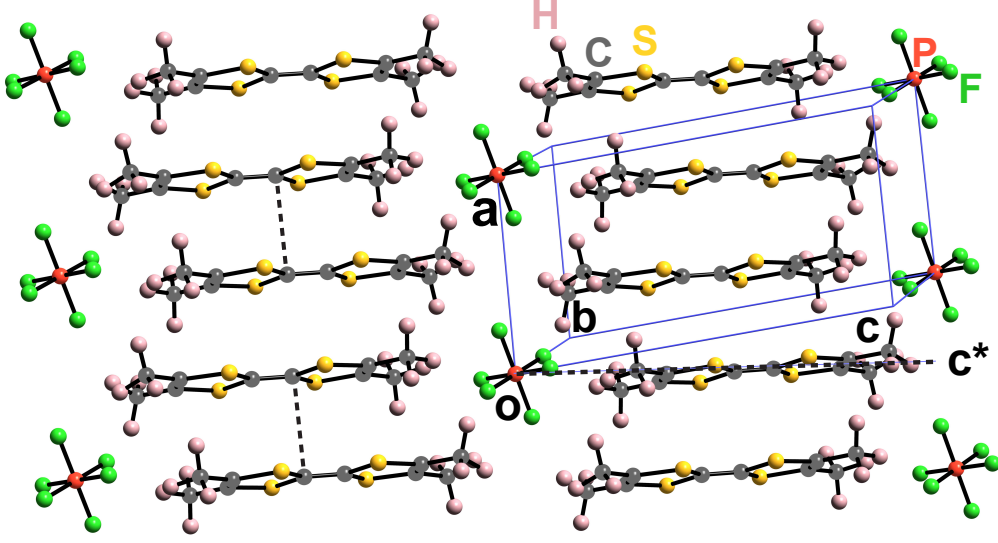


Figure 3.4: Molecular structure of the (TMTTF)₂X [16], where the counter anions X are shown and the dotted lines between two TMTTF molecules represent the dimers. The triclinic unit cell is outlined by the blue lines and a , b , c and c^* (dashed horizontal line) represent the crystallographic axes.

the emergence of a finite electrical polarization below T_{co} . From such electrical configuration, the ferroelectric phase emerges, concomitant with the charge-ordering one. Another strong evidence of ferroelectricity is an anomaly (maximum) in the dimensionless real part of the dielectric constant ϵ' measurements for such systems reported in the literature [168, 16]. Since the dielectric constant is directly associated with the polarizability of the system through the Clausius-Mossotti relation [33], such anomaly reveals a finite polarization of the system at T_{co} , where a ferroelectric phase develops. In other words, the maximum in ϵ' is associated with the free-energy variation between the two phases, namely paraelectric and ferroelectric phases, which is maximized at T_{co} vanishing above and below T_{co} . The latter can be understood upon writing the free-energy density $\hat{F}$ in terms of the order parameter, in this case the polarization P , and the relation between ϵ' and P , namely, $\hat{F} = -EP + g_0 + 1/2g_2P^2 + \dots$ [33], where the g_n are temperature-dependent coefficients, and $P = E(\epsilon' - 1)$ [33]. Hence, it becomes evident that $\hat{F}$ depends on ϵ' . Recently, we have reported on quasi-static dielectric constant measurements in the c^* -axis for the fully-hydrogenated PF₆, 97.5% deuterated PF₆, SbF₆, and AsF₆ systems, showing a systematic comparison between a normal ferroelectric

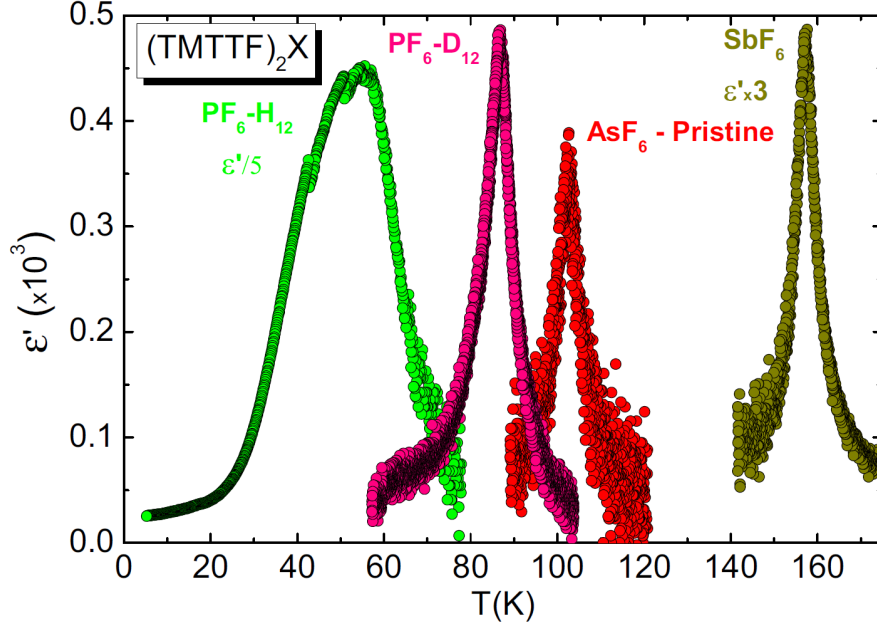


Figure 3.5: Quasi-static (fixed frequency $f = 1$ kHz) dielectric constant as a function of temperature measured in the c^* -axis for the fully-hydrogenated ($\text{PF}_6\text{-H}_{12}$) and 97.5% deuterated ($\text{PF}_6\text{-D}_{12}$) $(\text{TMTTF})_2\text{PF}_6$ systems (green and pink circles, respectively), pristine $(\text{TMTTF})_2\text{AsF}_6$ (red circles), and $(\text{TMTTF})_2\text{SbF}_6$ (dark yellow circles) systems upon cooling down the system [16]. All the experimental results in Ref. [16] were obtained in the Solid State Physics Laboratory at the São Paulo State University in Rio Claro, SP - Brazil.

behaviour of the partially deuterated PF_6 system and the relaxor-like ferroelectric behaviour of the fully-hydrogenated PF_6 one [16], as well as the transition from a normal to a relaxor ferroelectric behaviour on the AsF_6 upon increasing the X-ray irradiation exposure of the samples [16]. Currently, systems where ferromagnetism and ferroelectricity coexist (multiferroic/magnetoelectric) have been intensively explored by the scientific community [169, 170, 171], since it is a rare phenomenon and, by the fundamental point of view, very interesting to investigate the possible mechanisms that lead to a multiferroic/magnetoelectric behaviour. Furthermore, multiferroicity has been proposed to be present in the quasi-one-dimensional organic systems of the $(\text{TMTTF})_2\text{X}$ family [172]. Note that it is not yet clear whether such systems present a multiferroic or a magnetoelectric behaviour. On one hand, in a multiferroic material there is a coupling between the electric and magnetic order parameters [173], i.e., both electric magnetic phases coexist. On the other hand, a magnetoelectric system refers to the change of an electric phase under magnetic field

or vice-versa [174]. Hence, the possible multiferroic/magnetoelectric character of the TMTTF salts is one of the key points explored in this Thesis. Another extensive investigation on the Fabre-salts has been related to the vibrational modes of the TMTTF molecules. There are several representations of the vibrational character of such a molecule: b_{1u} , b_{2u} , and b_{3u} , which are infrared active and the a_g , b_{1g} , b_{2g} , and b_{3g} , which are Raman active [175], just to mention a few. It is evident that the charge distribution of the TMTTF molecule directly affects the existent vibrational modes, as can be seen in Fig. 3.6.

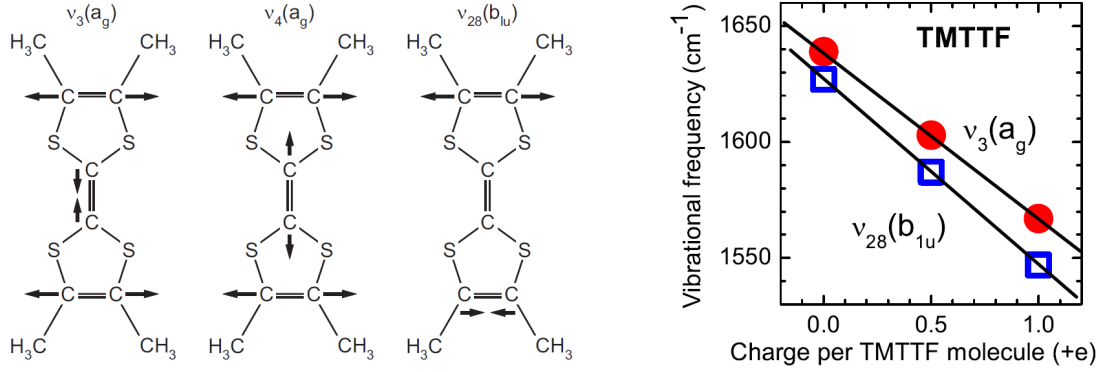


Figure 3.6: Schematic representation of the symmetric a_g modes ν_3 and ν_4 and the asymmetric b_{1u} mode ν_{28} of the TMTTF molecule (left panel). Vibrational frequency as a function of charge per TMTTF molecule (right panel) for the vibrational modes $\nu_3(a_g)$ and $\nu_{28}(b_{1u})$ [176].

Besides that, below T_{co} the charge distribution is inequivalent due to the inter-site Coulomb repulsion V [166, 177] and a splitting of the pattern of the vibrational mode is observed by infrared and Raman optical investigations (Fig. 3.7). The charge disproportionation δ observed in Fig. 3.7 is related to the difference $\Delta\nu$ between the resonant frequencies and can be computed by the following expression [175]:

$$2\delta = \frac{\Delta\nu}{80 \text{ cm}^{-1}/e}. \quad (3.3)$$

At this point, it is worth mentioning that the lock down that lasted about 2 years due to the Covid-19 pandemic severely affected the realization of the planned experiments in the frame of this Thesis. However, during the lock down period, theoretical works proposed by Prof. Dr. Mariano de Souza were developed culminating in nice publications, cf. Section 2.3. Hence, this is the reason this Thesis provides more

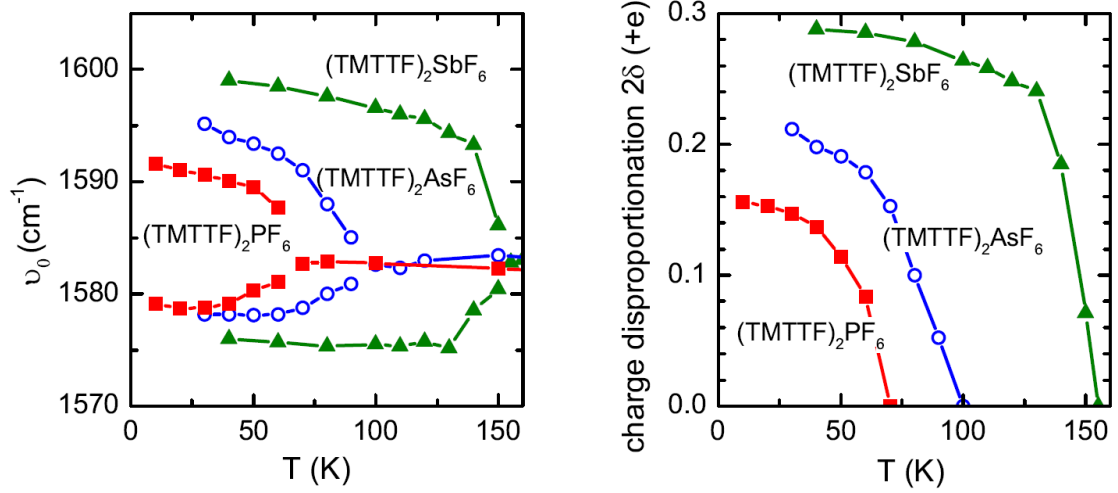


Figure 3.7: Left panel: resonance frequency ν_0 associated with the ν_{28} vibrational mode as a function of temperature T for the fully-hydrogenated $(\text{TMTTF})_2\text{X}$ ($\text{X} = \text{PF}_6$, AsF_6 , and SbF_6) systems, where a splitting of the resonance frequency is shown at T_{co} for each salt, since below this temperature a charge disproportionation takes place and the resonance frequency of the charge-rich ($\rho_0 + \delta$) and -poor ($\rho_0 - \delta$) sites differs. Right panel: charge disproportionation 2δ as a function of the temperature T . Above T_{co} there is no charge disproportionation and below it the charge disproportionation is finite [175].

theoretical results than experimental ones. The proposed target experiments will be continued in the frame of a post-doc research project.

3.2 Experimental aspects

Before discussing the obtained experimental results obtained, the basic principles of work and maintenance for an optimized and proper functioning of the Teslatron-PT cryostat are provided.

3.2.1 Principle of work of the Teslatron-PT cryostat

The Teslatron-PT cryostat relies in a ^4He closed cycle where a circulation circuit is attached to it in order to continuously cool down the interior of the cryostat. Such a cooling is achieved through a F-70 Sumitomo compressor (Fig. 3.9), which compresses and expands ^4He . In order for the ^4He to cool down, first the gas is compressed and then it does work in the so-called compression chamber in order to expand, which decreases its temperature. Such a cold ^4He is then circulated through the cryostat exchanging heat with it, returning warmer to the compressor,

and the cycle is continuously repeated. The ^4He flow/pressure is controlled by a so-called needle valve (Fig. 3.8) that uses a tapered needle to regulate the flow of ^4He . The needle is connected to a handle that enables a fine adjustment of the ^4He flow/pressure. As the needle is turned, it moves up or down within the valve body, altering the size of the opening through which the ^4He can pass. When the needle is completely closed, ^4He cannot flow through the valve and its pressure goes to zero. As the needle is gradually opened, the pressure increases. Such a needle valve is crucial to the cooling process of the cryostat, since the pressure of the ^4He flow must be precisely adjusted during the cooling steps in order to achieve base temperature, which is $T \approx 1.4\text{ K}$. Now, in order to mathematically understand the Teslatron-PT cooling process, the first-law of Thermodynamics is recalled [1]:

$$dQ = dU - dW. \quad (3.4)$$

Considering that $dW = pdv$, the first-law can be rewritten as:

$$dQ = dU - pdv. \quad (3.5)$$

Note that the sign of dW will depend if the work is being done into the system ($dW < 0$) or by the system ($dW > 0$). Such a simple analysis enables to infer that if work is done on the gas, it increases its internal energy and, as a consequence, its amount of heat, which is the case of the gas being initially compressed. On the other hand, when the gas freely expands after being compressed it performs work at expense of its internal energy and heat amount, which cools the ^4He . Such a continuous cooling process after $\sim 30\text{--}40\text{ h}$ enables the achievement of a base temperature close to 1.4 K . It is worth mentioning that the achievement of the base temperature is not a plug and play process. In order to do so, the following procedures must be followed according to Oxford Instruments operation manual listed in what follows in more details:

1) Starting of the ^4He circulation system

The ^4He circulation system lies in a room next to the Solid State Physics Laboratory to avoid excessive noise when it is in operation. Essentially, it is composed by a ^4He storage tank, the so-called zeolite trap, which works as a “strainer” to confine moisture, and the XDS 10 pump (supplied by Edwards company) that circulates the ^4He into the cryostat (Fig. 3.8). In order to initiate the cool down of the cryostat, first the ^4He circulation system must be turned on so that the ^4He is released from the storage tank and thus circulates for about 12 h before starting the compressor. Such an initial process aims to maximize the homogeneity of the ^4He circulation and, as a consequence, the corresponding efficiency of the cooling. The recommended ^4He pressure inside the storage tanks is between $\sim 0.45\text{--}0.60$ bar, cf. Fig. 3.8. In order to start the ^4He circulation system, the following steps must be carried out (see Fig. 3.8 for guidance):

- i)* Open the zeolite trap inlet valve;
- ii)* Turn on the XDS 10 circulation pump;
- iii)* Open the NW25 VTI pumping port valve to start the circulation of ^4He ;
- iv)* Evacuate the outer vacuum chamber (OVC) and leave the ^4He to circulate for about ~ 12 h. Usually, this process is performed in the afternoon of the day before the cool down starts.

2) Turning on the compressor

After step 1), the needle valve needs to be open half a turn from its fully closed position and the compressor must be started. Before doing so, it is worth mentioning that, in order to cool down the compressor due to its power dissipated when it is in operation and to avoid overheating, a chiller is attached to it operating with water at about 17°C . Hence, before turning on the compressor, the chiller must be turned on first for about 15 minutes. Afterwards, it is finally the time to switch on the compressor (Fig. 3.9) to actually initiate the cool down of the cryostat. After the compressor turned on, the OVC must be continuously pumped until the so-called pulse tube refrigerator second state (PT2) temperature sensor reads below $T = 5$ K, which takes between 30–40 h. The room where the compressor and the ^4He

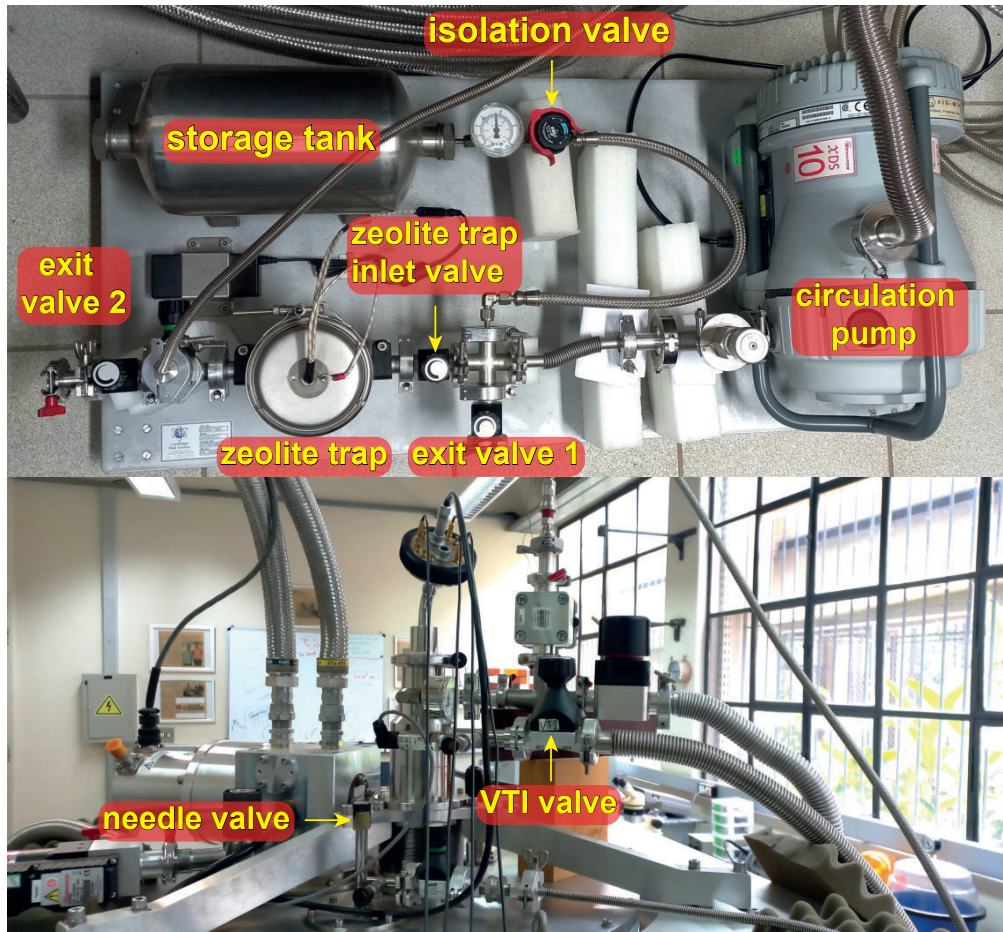


Figure 3.8: Upper panel: circulation system showing the storage tank containing ~ 0.55 bar of ^4He , the isolation valve, zeolite trap, zeolite trap inlet valve, XDS 10 circulation pump, and exit valves 1 and 2. Lower panel: top view of the Teslatron PT cryostat showing the needle valve, which controls the cooling power, and the variable temperature insert (VTI) valve.

circulation system are installed is constantly refrigerated by an air-conditioner fixed at 23°C during the whole time the system is turned on. At this point, it is worth mentioning that, in the case of a power loss during this period, the turbo pump connected to the OVC would ventilate and thus contaminate the interior of the OVC, which could lead to the freezing of moisture inside it severely compromising the vacuum and, as a consequence, the achievement of the base temperature of the cryostat. During the last several years, all the Solid State Physics group members have taken turns during this delicate period in order to always have someone at the laboratory in the eventual case of a power loss, which happens very frequently, cf. Appendix Section 6.3. However, in January/2023 it was acquired a solenoid valve that was installed between the turbo pump and the OVC pumping port (Fig. 3.10).



Figure 3.9: F-70 Sumitomo compressor showing the supply and returns ^4He lines and the water inlet and outlet lines from the chiller to cool down the compressor during its functioning.

However, only the installation of the solenoid valve is not enough to fully protect the OVC from being contaminated in the case of a power loss. It turns out that if the power supply is turned on, the solenoid valve is opened and the turbo pump is working fine. If the power goes down, the solenoid valve closes and the turbo pump ventilates in the pumping lines, which connects the turbo pump, the solenoid valve and the OVC pumping valve. Hence, if the power comes back again, the solenoid valve can be opened more quickly than the turbo pump initiates the pumping process. In such a case, the moisture from the ventilation of the turbo pump in the

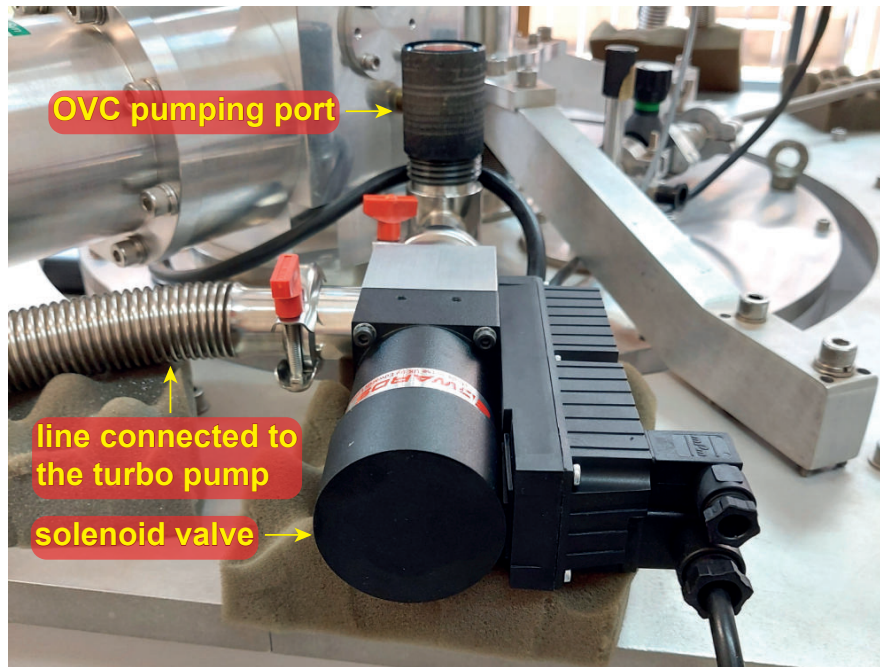


Figure 3.10: Solenoid valve installed between the turbo pump and the OVC pumping port. When a power loss occurs, it becomes de-energized and closes, protecting the OVC from the ventilation of the turbo pump. When power is re-established, it reopens and the pumping of the OVC is continued.

pumping lines can enter into the OVC, since the pumping lines will be at ambient pressure and the OVC in a lower pressure. Then, in order to prevent this to happen and to guarantee that the OVC will not be contaminated, me and Prof. Dr. Mariano de Souza developed a simple circuit to intermediate the functioning of the solenoid valve. Essentially, such an electrical circuit, cf. depicted in Fig. 3.11 is composed by a diode, a relay, and a push button. The diode is inserted into the circuit to prevent the solenoid valve to be continuously opened and closed to the instabilities in the power source. When power goes down, both the relay and push button will be de-energized and the electrical contact is opened. When power goes down, the relay is only energized if the push button is pressed. Hence, we guarantee that when power goes down, the solenoid valve is only opened when the push button is manually pressed so that the pumping lines are pumped before opening the solenoid valve again. This simple circuit guarantees that the OVC will never be contaminated by moisture in the case of a power loss followed by its subsequent returning.

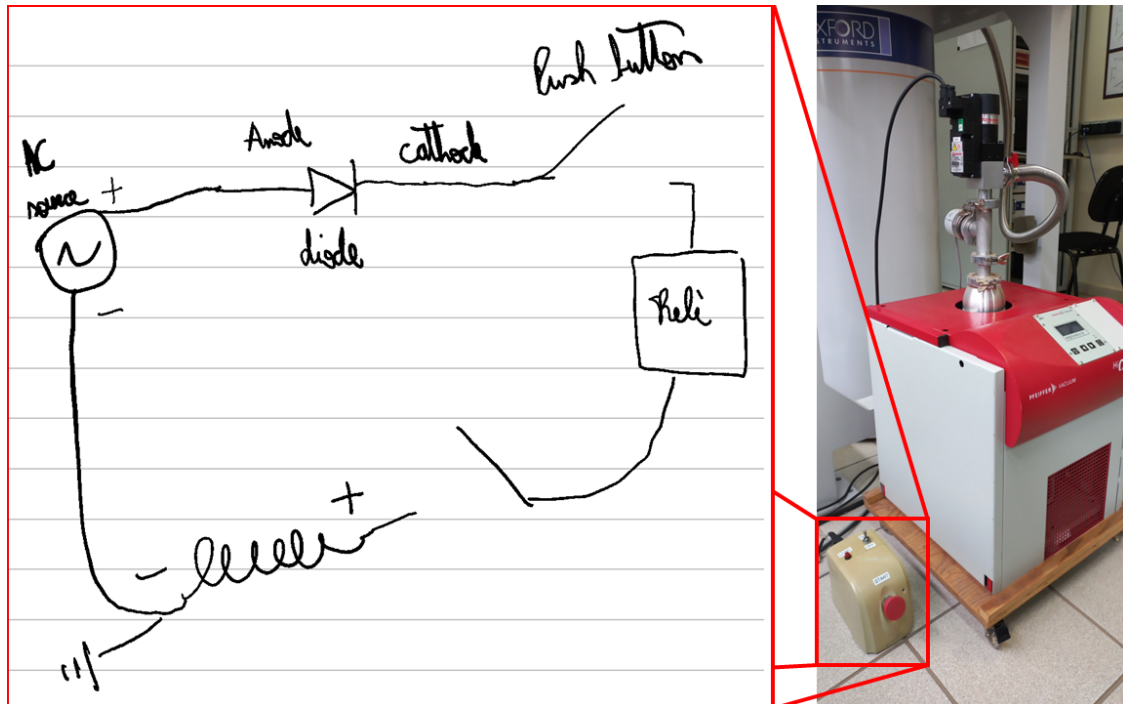


Figure 3.11: Electrical circuit drawn by us to prevent that the solenoid valve opens when power comes back on and the moisture from the ventilation of the turbo pump enters into the OVC. The circuit is composed by a diode, a push button, and a relay. In the case of power being interrupted and then normalized, the solenoid valve is only opened when the push button is manually pressed.

3) Adjusting the needle valve

Several hours after the compressor is turned on, the temperatures of the PT2, sample space, and the magnet are decreased. According to Oxford Instrument's manual, the pressure of the needle valve should be adjusted to 10 mbar when all temperatures converge and stop decreasing. Such an adjustment of the needle valve pressure must be continuously repeated until all temperatures falls below 4 K. Only at this point, the OVC can be closed and the turbo pump turned off, highlighting the importance of the solenoid valve to avoid contamination inside the vacuum chamber. Hence, the needle valve pressure should be adjusted to 5 mbar in order to achieve base-temperature ($T \simeq 1.4$ K). A typical behaviour of T as a function of time for the PT2, sample space, and the magnet is shown in Fig. 3.12.

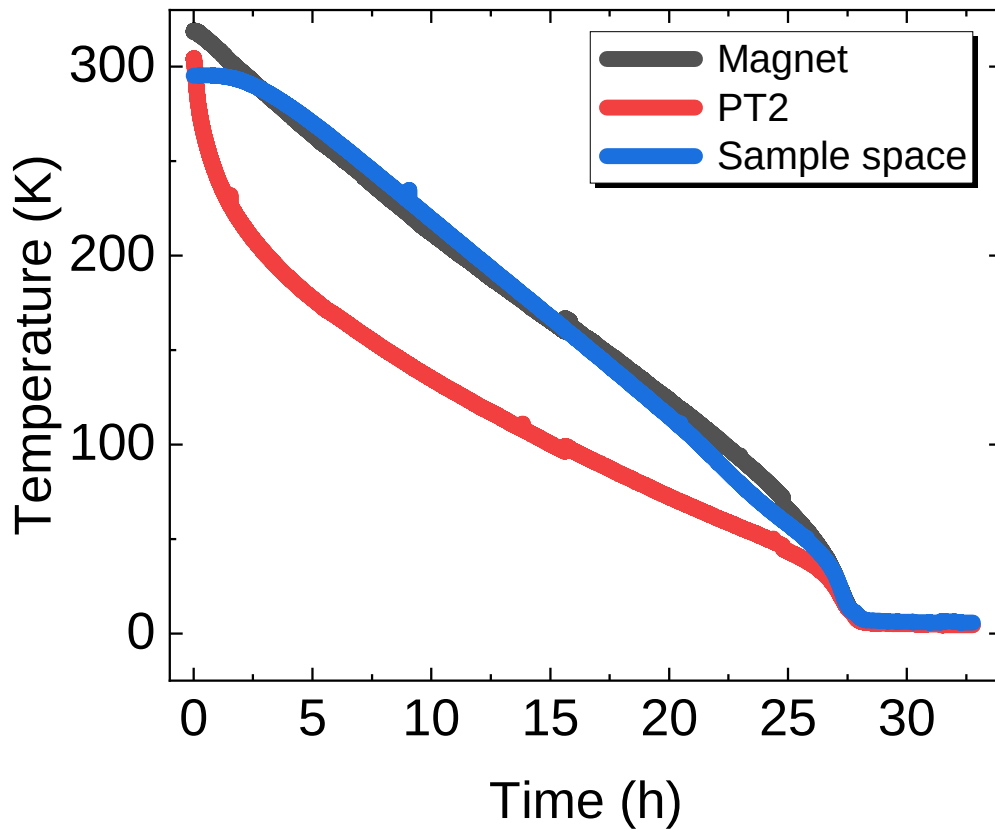


Figure 3.12: Typical behaviour of the temperature *versus* time for the magnet (gray), PT2 (red), and sample space (blue). Note that it takes about 28 h for all temperatures to reach equilibrium but the cool down is not finished. The last step (not shown) is to adjust the needle valve pressure and wait for all temperatures to further decrease until the base-temperature is achieved, which usually takes several hours.

3.2.2 Cleaning up of the zeolite trap

A zeolite trap is a device that employs the unique properties of the so-called zeolites, a family of microporous aluminosilicate minerals, to trap and remove impurities from gases [178], cf. Fig. 3.13. Such a trap works by adsorption, a process in which impurities are physically adsorbed onto the surface of the zeolite crystals. The pores of the zeolite crystals are precisely sized to selectively adsorb specific molecules, such as water vapor or hydrocarbons, while allowing the passage of other gases. The efficiency of the zeolite trap can be enhanced by heating the zeolite, which desorbs the impurities, allowing for their removal and regeneration of the trap. Zeolite traps have been extensively studied and used in a variety of industrial applications such as air-conditioning and helium circulation systems.

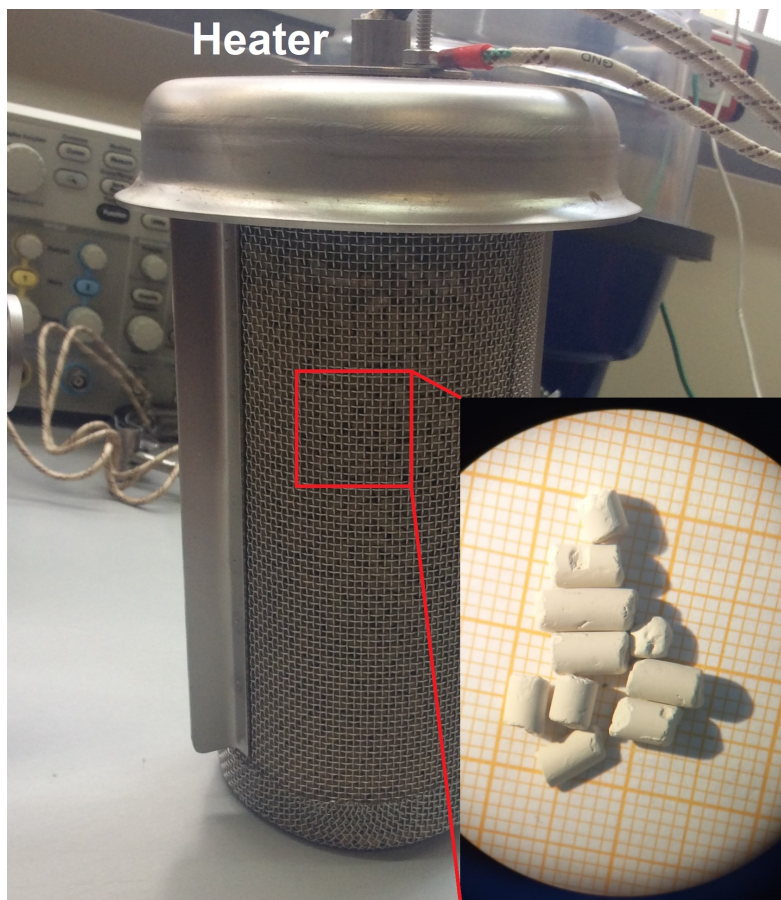


Figure 3.13: Interior of the zeolite trap and the microporous aluminosilicate minerals are shown in the inset. At the top of the zeolite trap, it is shown a heater that is used in its cleaning process.

According to Oxford Instruments' manual regarding the operation of the Teslatron PT cryostat, it is recommended that the zeolite trap (Fig. 3.8) is cleaned after each warmup of the system to room-temperature. In order to do so, the following procedure must be performed:

- Connect the turbo pump to the exit valve 2 (Fig. 3.8) but do not open it yet. Note that, at this point following the warm up procedure, the zeolite trap inlet and the VTI valves must be closed, see Fig. 3.8 for guidance;
- In the mean time, the needle valve must be connected to the power supply for at least one hour, so it heats up and the moisture is easily removed. After one hour, the exit valve, with the turbo pump already turned on, must be slowly opened so that the cleaning starts. At this point, the needle valve pressure is the key indicator to verify the achievement of an appropriate cleaning of

the zeolite trap, since, according to Oxford Instruments' manual of operation, the cleaning is completed when the needle valve reaches pressures lower than 0.5 mbar. Such a process usually takes several hours (≈ 8 h) to be completed;

- After the needle valve pressure is stabilized close to 0.5 mbar, the exit valve 2 is closed and the zeolite trap is turned off in order to cool down to room-temperature and the process is then completed.

A typical behaviour of the needle valve pressure as a function of time can be seen in Fig. 3.14. Interestingly, an exponential decay of the needle valve pressure is observed when the exit valve 2 is opened. This is not merely a coincidence. In fact, this is predicted by the so-called continuity equation regarding pumping processes, given by [179]:

$$vdp = Q_{tot}dt - S'pdt, \quad (3.6)$$

where Q_{tot} is the total amount of gas loads entering the vessel with unit of $[\text{Js}^{-1}]$ and S' is the pumping speed with unit of $[\text{m}^3\text{s}^{-1}]$. The pressure variation dp in a container of fixed volume v is dictated by Eq. 3.6, which takes into account the total amount of gas entering the vessel in a time interval dt and the quantity of gas being pumped out in the same time interval at a given pumping speed S' . Since the zeolite trap is completely sealed, i.e., there is no particle influx from the outside, Q_{tot} is equal to zero. Therefore, Equation 3.6 can be rewritten as:

$$v\frac{dp}{dt} = -S'p, \quad (3.7)$$

which in turn reads:

$$\frac{1}{p}dp = -\frac{S'}{v}dt. \quad (3.8)$$

Integrating both sides of Eq. 3.8:

$$\int_{p_0}^p \frac{1}{p}dp = \int_{t_0}^t -\frac{S'}{v}dt, \quad (3.9)$$

the following relation is achieved assuming $t_0 = 0$:

$$\ln(p) - \ln(p_0) = -\frac{S'}{v}t, \quad (3.10)$$

$$\ln p = \ln p_0 - \frac{S'}{v}t, \quad (3.11)$$

$$e^{\ln p} = e^{\ln p_0 - \frac{S'}{v}t} = e^{\ln p_0} e^{-\frac{S'}{v}t}, \quad (3.12)$$

$$p = p_0 e^{-\frac{S'}{v}t}. \quad (3.13)$$

Assuming that a characteristic time τ can be defined as $\tau = v/S'$, Eq. 3.13 reads:

$$\boxed{p = p_0 e^{-\frac{t}{\tau}}}. \quad (3.14)$$

Equation 3.14 describes the exponential decay of pressure over time due to pumping,

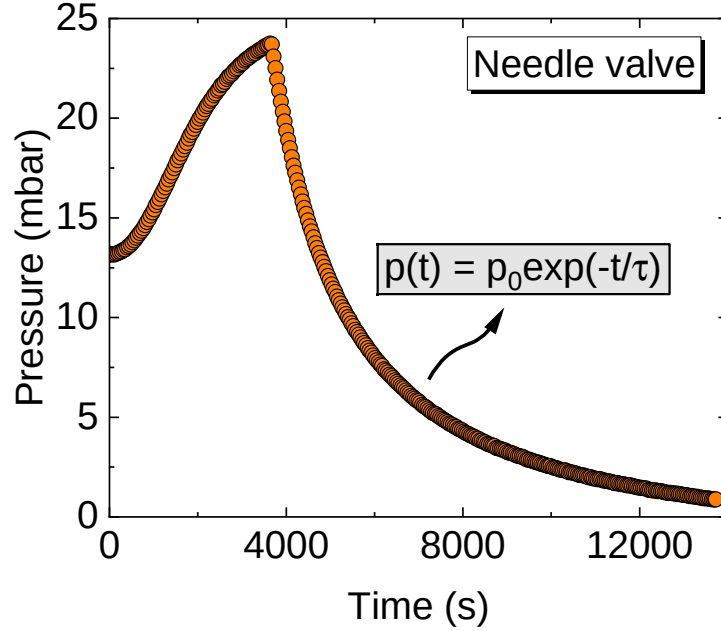


Figure 3.14: Needle valve pressure as a function of time. Note that the pressure is exponentially decreased when the exit valve 2 is opened following a mathematical relation $p(t) = p_0 \exp(-t/\tau)$, where p_0 is the pressure right before the exit valve 2 (see Fig. 3.8) is opened, t is time, and τ is the characteristic time or time constant associated with the pumping speed. The initial increase of pressure is due to the heater being turned on and, in order to optimize the cleaning of the zeolite trap, the pumping is performed with the heater still on.

which is the case of the zeolite trap cleaning shown in Fig. 3.14.

3.2.3 Pump and purge of the ^4He circulation lines

As discussed in the last Section, although a zeolite trap is inserted into the circulation lines in order to minimize the moisture in the circulating ^4He , it is strongly suggested that the ^4He circulation lines are completely cleaned periodically. Such a process is described in the following:

- First, the turbo pump is connected to the exit valve 1 (Fig. 3.8) together with the ^4He line connected to the ^4He tank. The needle and the VTI valves are completely opened, the circulation pump is turned on and the ^4He is released from the storage tank. At this point, the exit valve 1 is slowly opened so that all the ^4He is pumped out from the circulation system. The heater of the zeolite trap can be turned on to optimize this process;
- As a second step, a pump and purge of the system is carried out systematically, i.e., about 0.5 bar of ^4He is inserted and pumped out a few times in order to guarantee that all moisture is removed;
- As a final step, 0.6 bar of 5N high-purity (99.999%) ^4He is inserted and the storage tank is closed. Then, all ^4He is pumped out from the circulation lines for a few hours and the cleaning process is completed.

After following the steps above, the system is ready for the initiation of a subsequent cool down of the Teslatron-PT system.

3.3 Experimental results

3.3.1 Dielectric constant

Systematic dielectric constant measurements were carried out at both zero and under various magnetic fields values for the Fabre salts. The obtained results reproduce literature results nicely, cf. Fig. 3.15. The experiments were affected by the Covid-19 pandemic and shall be continued in the frame of future projects.

The samples were prepared upon painting the surfaces associated with the c^* axis (Fig. 3.4) with carbon paint in order to emulate a parallel plates capacitor aiming to explore the ionic contribution to the dielectric constant [16]. Next, tempered golden wires with $25\,\mu\text{m}$ diameter were attached to the surfaces painted with carbon paste. The sample was then attached to an insulating mask and the golden wires were connected to the mask employing silver paste. Then, such a mask with the contacted sample is attached to the sample holder of the cryostat that goes inside the sample

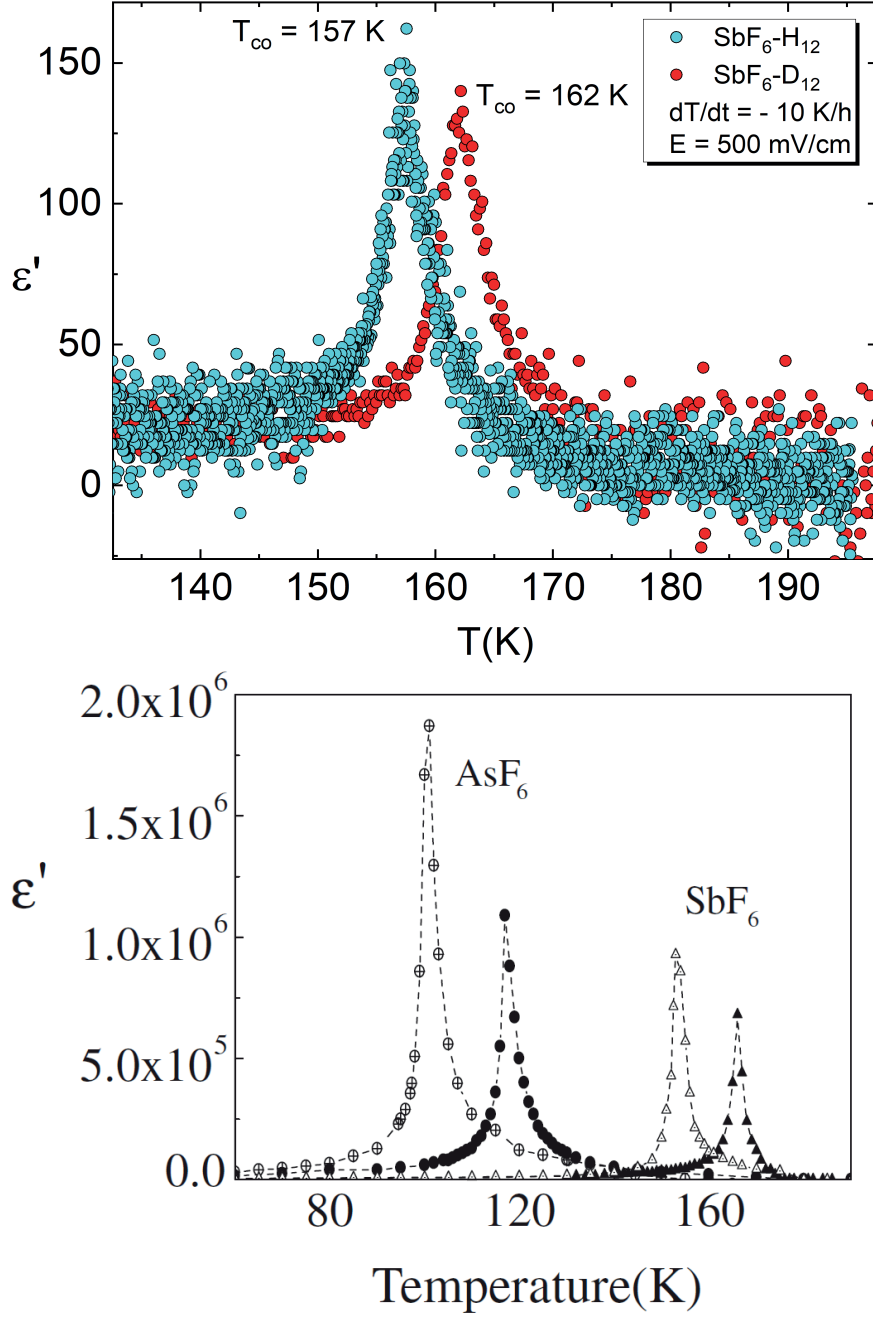


Figure 3.15: Top panel: dielectric constant ϵ' measurements as a function of temperature T for the hydrogenated (blue circles) and deuterated (red circles) variant of the $(\text{TMTTF})_2\text{SbF}_6$ systems for a fixed frequency $f = 1 \text{ kHz}$ and electric field $E = 500 \text{ mV/cm}$. Their corresponding charge-ordering temperature T_{co} are shown. Bottom panel: dielectric constant ϵ' measurements as a function of temperature T at a frequency $f = 100 \text{ kHz}$ for the hydrogenated (crossed circles) and deuterated (full circles) of $(\text{TMTTF})_2\text{AsF}_6$ and hydrogenated (white triangles) and deuterated (full triangles) of $(\text{TMTTF})_2\text{SbF}_6$. Figure extracted from Ref. [168].

chamber, which is then electrically connected to an Andeen-Hagerling capacitance bridge for the electrical capacitance measurements as a function of temperature.

3.3.2 Raman spectra and fluorescence background of the TMTTF salts

The optical investigations on the TMTTF-based salts were performed in the laboratory of Prof. Dr. Marcio Daldin Teodoro at the Federal University of São Carlos (Fapesp process number 2018/06328-1). Systematic Raman spectroscopy measurements as a function of both T and $\vec{B}$ were carried out employing the following available experimental setup:

- Solid State Diode Cobolt 08-01 Series laser with emission in $\lambda = 532$ nm (green) and high-stability with width line lower than 1 MHz and power up to 20 mW. Also, this laser has a so-called integrated optical insulator, making it immune to the destabilization by the reflections of light through the microscope.
- 3 Semrock filters attached to the experimental setup in order to achieve Raman laser lines up to 100 cm^{-1} ($\lambda = 100 \mu\text{m}$).
- Confocal attocube microscope of the attoCFM I model designed in titanium aiming to provide high mechanical and thermal stability.
- Andor Shamrock 75 cm spectrometer with Peltier cooling system, employing a diffraction grid of 1,200 lines/mm, since the intensity of the Raman signal is low. In the detection system, together with the spectrometer, a CCD silicon detector is employed, providing a resolution of about 2 cm^{-1} .
- Attocube attoDRY1000 ^4He closed-cycle cryostat, reaching the temperature range of $3.8 \text{ K} < T < 300 \text{ K}$ and external magnetic fields of $\vec{B} < 9 \text{ T}$, with mechanical vibrations in the region of the sample lower than 1 nm. In the cooling process, no liquid helium is employed and the sample is not in direct contact with ^4He that cools the confocal microscope.

In Fig. 3.16 it is shown the investigated samples attached to the sample holder. A systematic set of Raman spectra measurements were carried out as a function of temperature and, at each fixed T , the external magnetic field was then applied

ranging from 0 to 3 to 6 T, being completely removed before the temperature was varied again. Following such experimental procedure, we have measured the Raman intensity as a function of Raman shift for $T = 200, 87, 30$, and 4 K.

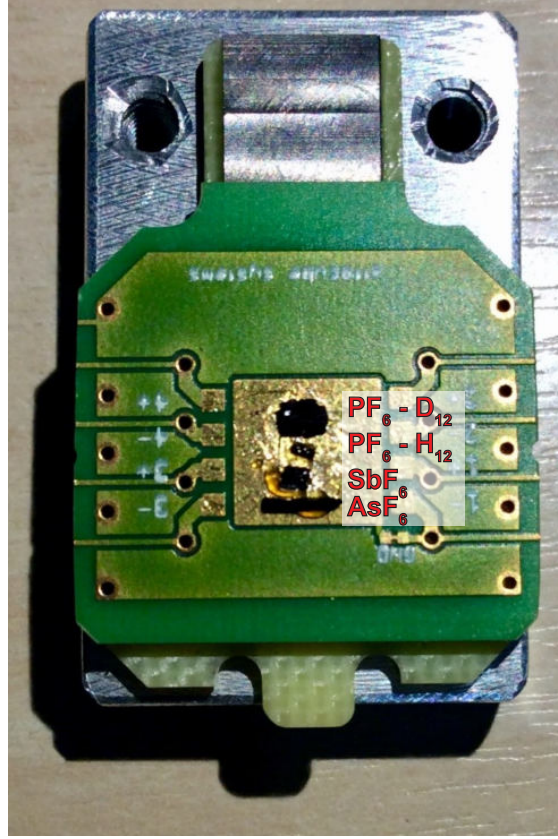


Figure 3.16: Samples attached to the sample holder. From top to bottom the samples are: deuterated variant of $(\text{TMTTF})_2\text{PF}_6$, hydrogenated variant of $(\text{TMTTF})_2\text{PF}_6$, $(\text{TMTTF})_2\text{SbF}_6$, and $(\text{TMTTF})_2\text{AsF}_6$. The area of the samples were about 2 mm^2 and their thickness of about 1 mm.

The motivation of such experiments under $\vec{B}$ was to detect evidences of multiferroicity/magnetoelectricity in the TMTTF-based systems. Hence, it was possible to check the Raman spectra results from the literature to compare our results enabling us to recover several intensity peaks associated with particular vibrational modes of the TMTTF molecule. Two key unprecedented results were extracted from such measurements. The first one is regarded to the $\vec{B}$ -dependence of the Raman intensity peak at 1476 cm^{-1} (Fig. 3.20) at $T_{co} = 87\text{ K}$ for the deuterated variant of the $(\text{TMTTF})_2\text{PF}_6$ salt, which is primordially associated with the methyl-end groups vibrational modes [181]. We have observed that, upon increasing $\vec{B}$ the

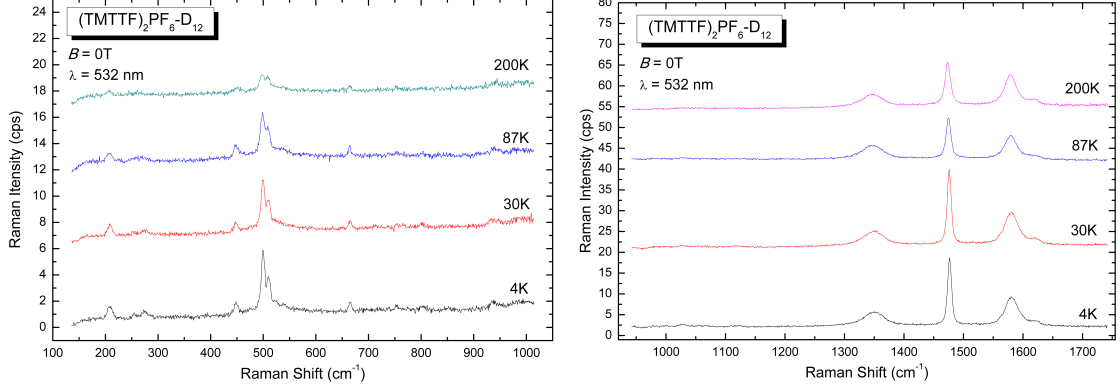


Figure 3.17: Raman intensity *versus* intensity at $\lambda = 532$ nm without external magnetic field ($B = 0$ T) for the deuterated variant of $(\text{TMTTF})_2\text{PF}_6$ at $T = 200, 87, 30$, and 4 K.

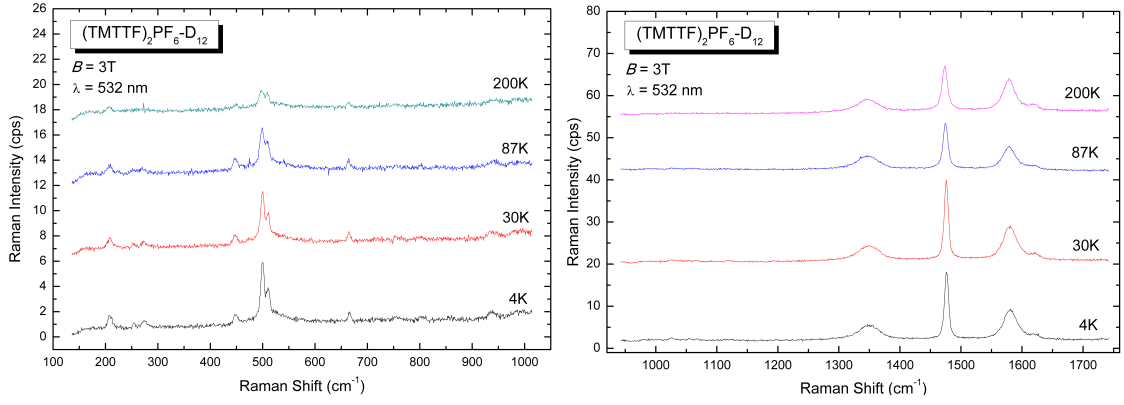


Figure 3.18: Raman intensity *versus* intensity at $\lambda = 532$ nm under $B = 3$ T for the deuterated variant of $(\text{TMTTF})_2\text{PF}_6$ at $T = 200, 87, 30$, and 4 K.

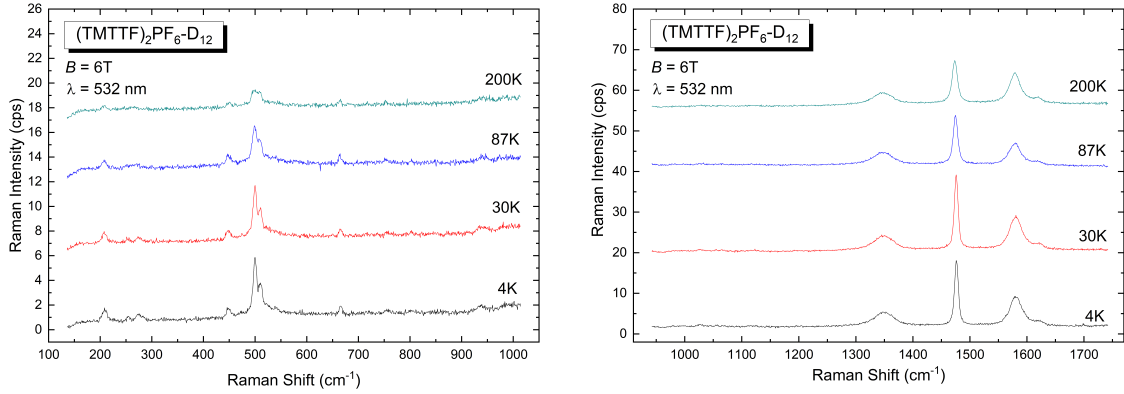


Figure 3.19: Raman intensity *versus* intensity at $\lambda = 532$ nm under $B = 6$ T for the deuterated variant of $(\text{TMTTF})_2\text{PF}_6$ at $T = 200, 87, 30$, and 4 K.

Raman intensity peak at 1476 cm^{-1} was decreased by about 27% from 0 to 6 T, which in turn can be interpreted as a magneto-optical effect similarly to that observed for layered MoS_2 (Fig. 3.21) [180]. It is worth mentioning that, until the

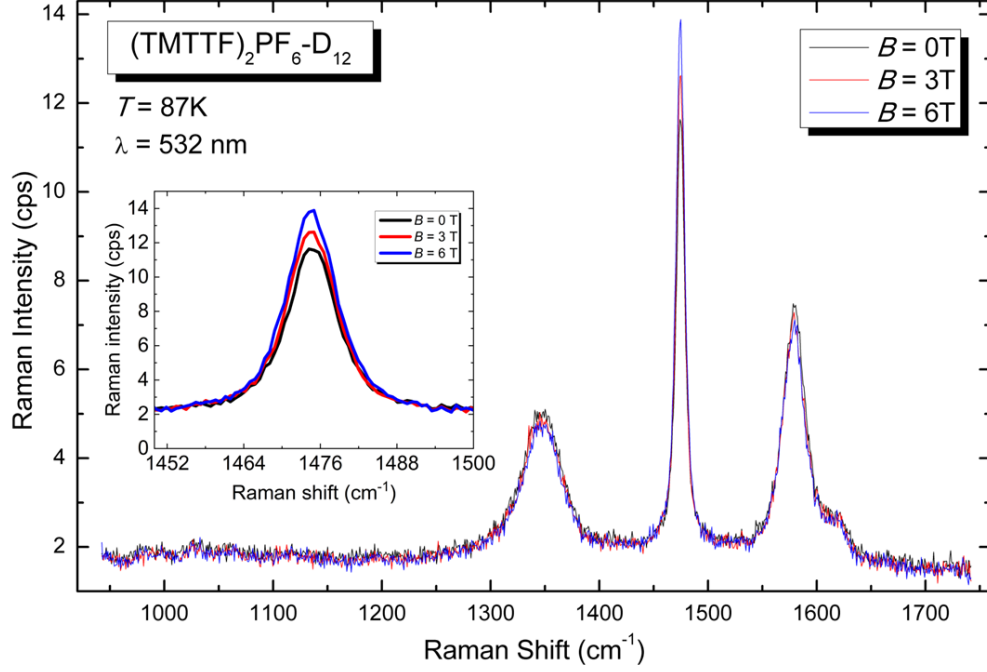


Figure 3.20: Main panel: Raman intensity as a function of Raman shift for the deuterated variant of the (TMTTF)₂PF₆ system under $B = 0\text{ T}$ (black line), $B = 3\text{ T}$ (red line), and $B = 6\text{ T}$ (blue line). Inset: zoomed region around the Raman shift 1476 cm⁻¹ to indicate that the increase of B reduces the Raman intensity.

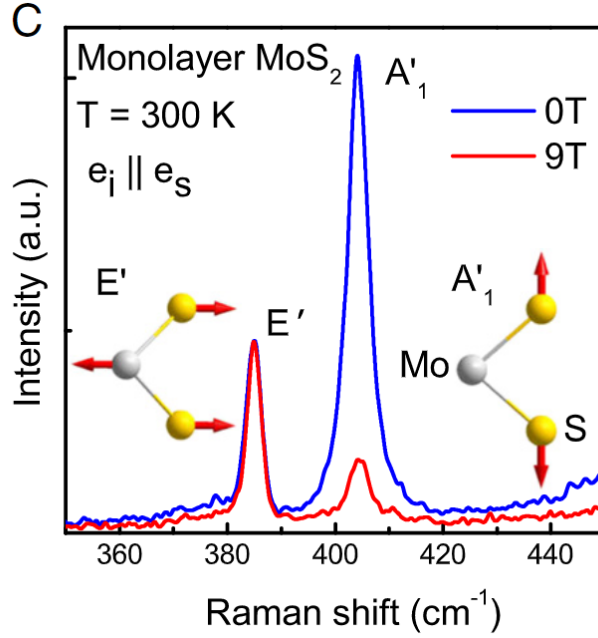


Figure 3.21: Intensity *versus* Raman shift for monolayer MoS₂ at $T = 300\text{ K}$ showing that the intensity of the Raman shift $\approx 405\text{ cm}^{-1}$ is reduced under $\vec{B} = 9\text{ T}$. The vibrational patterns of the corresponding Raman modes are also illustrated. Figure extracted from Ref. [180].

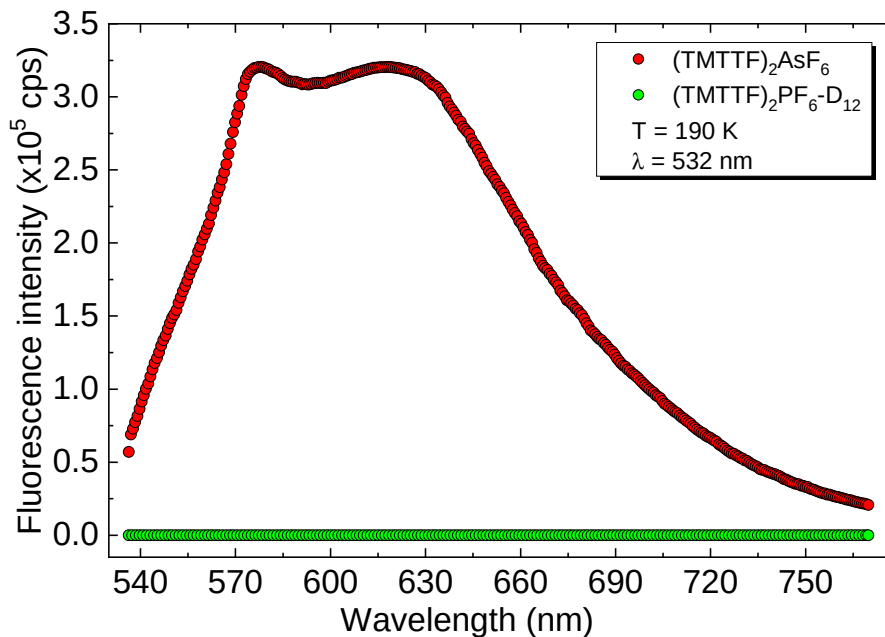


Figure 3.22: Fluorescence intensity *versus* wavelength at $T = 190$ K and $\lambda = 532$ nm for $(\text{TMTTF})_2\text{AsF}_6$ (red circles) and the deuterated variant of $(\text{TMTTF})_2\text{PF}_6$ (green circles).

writing of this Thesis, such an effect was not reported for the TMTTF-based salts yet. Another key result was related to the fluorescence background of the TMTTF-based salts, cf. Fig. 3.22. We have observed that the fluorescence background of the hydrogenated system $(\text{TMTTF})_2\text{AsF}_6$ was about five orders of magnitude higher than the one associated with the deuterated variant of the $(\text{TMTTF})_2\text{PF}_6$ system, showing that deuteration might affect the fluorescence background of the TMTTF molecules. Unfortunately, due to the dilated time of the pandemic such experiments could not be properly continued in order to check the reproducibility of the data and possible sample-to-sample dependence. However, such experimental results are unprecedented in the literature and are planned to be further explored after the finishing of my Ph.D. in the frame of a post-doc project.

“You think I know the first thing about how hard your life has been, how you feel, who you are because I read Oliver Twist? Does that encapsulate you? Personally... I don’t give a damn about all that, because you know what, I can’t learn anything from you I can’t read in some book. Unless you want to talk about you, who you are, then I’m fascinated. I’m in. But you don’t want to do that, do you sport? You’re terrified of what you might say. Your move, chief.”

— Good Will Hunting (1997)

4

Summary and conclusions

This Ph.D. Thesis represents a symbiosis between theory and experiments and it is worth mentioning that the theoretical investigated topics were only possible due to the experimental expertise of the Solid State Physics Group. The theoretical results obtained in the frame of this Thesis employing the various definitions of the Grüneisen parameter covered the fields of magnetism at ultra-low temperatures, caloric effects and critical phenomena, adiabatic magnetization in real paramagnetic systems, and the expansion of the universe, which is a central problem in modern Cosmology. The Brillouin-like paramagnet was first explored and $\Gamma_{mag} = 1/B$ was obtained, being further explored taking into account the mutual interactions between neighbouring magnetic moments. Hence, it was demonstrated that the conditions for probing a genuine zero-field quantum phase transition in terms of Γ_{mag} are not fulfilled in real paramagnetic systems when finite B_{loc} is taken into account. Also, a connection between Γ_{mag} and the canonical definition of temperature was achieved and the so-called adiabatic magnetization without external magnetic field was proposed by only manipulating the mutual interactions. Experimental setups were proposed to attain adiabatic temperature changes and to detect such a subtle effect of the adiabatic magnetization. Also, the Grüneisen ratio was employed to propose key-ingredients in terms of entropy arguments to design materials that can attain giant caloric effects and can be broadly used in technological applications, as

well as that caloric effects are enhanced close to any finite-temperature critical end point. Yet, Γ_{eff} was identified as the equation of state parameter ω in the frame of Cosmology, being recognized to be embedded in Einstein field equations enabling to describe the expansion of the universe under the light of condensed matter Physics and to propose that Γ_{ec} can be employed to investigate the anisotropic expansion of the universe. The theoretical results obtained in the frame of this Thesis significantly contributed to the advance of each field. It is remarkable that the various forms of the Grüneisen parameter are embedded in many different areas of knowledge, making one wonders which other fields of research remains unexplored until now in terms of the Grüneisen parameter.

Regarding the experimental part of this Thesis, experiments were carried out in the Solid State Physics Laboratory in Rio Claro, SP and also at the laboratory from Prof. Dr. Marcio Daldin at UFSCAR in São Carlos, SP. Among the experimental results, dielectric constant and Raman spectra measurements were carried out during the Ph.D. The goal was to probe a possible multiferroic/magnetoelectric character of the TMTTF-based salts. Unfortunately, due to the lock down of the Covid-19 pandemic that lasted 2 years, the planned experiments were severely affected and are planned to be further explored in the frame of a post-doc project. The Raman spectra measurements revealed a possible magneto-optical effect in the intensity peak 1476 cm^{-1} of the deuterated variant of the $(\text{TMTTF})_2\text{PF}_6$ system, which deserves further exploration. Also, a huge fluorescence background was observed in $(\text{TMTTF})_2\text{AsF}_6$, being 5 orders of magnitude higher than in the deuterated variant of the $(\text{TMTTF})_2\text{PF}_6$ salt. These investigations will be continued after the Ph.D. aiming to clarify the possible multiferroic/magnetoelectric and the magneto-optical behaviours in the TMTTF-based systems.

*“To know that we know, and that we do not know
what we do not know, that is true knowledge.”*

— Confucius (551 - 479 BCE)

5

Perspectives and outlook

The research topics investigated in this Ph.D. Thesis will continue to be explored after the Ph.D. The results obtained for the Grüneisen parameters, namely Γ , Γ_{eff} , Γ_E , Γ_{mag} , and Γ_{ec} , will enable to extend such analysis to other physical scenarios regarding, for instance, exotic magnetic phases and even to biological systems. Also, there are some well-established projects in this regard already ongoing that will continue to be developed after the Ph.D. Also, planned experiments for a near future are systematic dielectric constant and electric polarization measurements as a function of temperature and external magnetic field to probe the possible multiferroic/magnetoelectric character of the Fabre-salts. High-resolution thermal expansion and magnetostriction measurements are also planned for the various salts. Yet, Raman spectra measurements as a function of temperature and external magnetic field are also planned in a cooperation between Prof. Dr. Mariano de Souza, Prof. Dr. Marcio Daldin, and Orsay’s team to probe a possible magneto-optical behavior in these salts, as well as a systematic exploration of the fluorescence background of the TMTTF salts and a possible suppression of such a background upon deuterating the methyl-end groups. All these theoretical and experimental topics, among others, are planned to be continued in the frame of a post-doc research project.

Bibliography

- [1] R. Baierlein, Thermal Physics (Cambridge University Press, Cambridge, 1999).
- [2] H. B. Callen, Thermodynamics and an Introduction to Thermostatistics (John Wiley & Sons, Singapore, 1985).
- [3] S.W. Hawking, Physical Review D **13**, 191 (1976).
- [4] P. Weinberg, Philosophical Magazine **93**, 2576 (2012).
- [5] A. Klosin *et al.*, Science **367**, 464 (2020).
- [6] P. Moretti, M.A. Muñoz, Nature Communications **4**, 2521 (2013).
- [7] L. Squillante, Isys F. Mello, A.C. Seridonio, M. de Souza, Materials Research Bulletin **142**, 111413 (2021).
- [8] Lijun Zhu, Markus Garst, Achim Rosch and Qimiao Si, Physical Review Letters **91**, 066404 (2003).
- [9] M. de Souza, P. Menegasso, R. Paupitz, A. Seridonio, R.E. Lagos, Eur. J. Phys. **37**, 055105 (2016).
- [10] P. Gegenwart, Philosophical magazine **97**, 3415 (2017).
- [11] M. de Souza and J.-P. Pouget, Journal of Physics: Condensed Matter **25**, 343201 (2013).
- [12] M. de Souza and L. Bartosch, Journal of Physics: Condensed Matter **27**, 053203 (2015).

- [13] P. Monceau *et al.*, Physical Review Letters **86**, 4080 (2001).
- [14] M. de Souza *et al.*, Physical Review Letters **101**, 216403 (2008).
- [15] M. Dressel, *Naturwissenschaften* **94**, 527 (2007).
- [16] M. de Souza *et al.*, Physical Review B **97**, 045122 (2018).
- [17] G. Giovannetti *et al.*, Physical Review B **91**, 125130 (2015).
- [18] C. Putzke *et al.*, Nature Communications **5**, 5679 (2014).
- [19] C.L. Huang *et al.*, Nature Communications **6**, 8188 (2015).
- [20] K. Hasselbach, L. Taillefer, J. Flouquet, Physical Review Letters **63**, 93 (1989).
- [21] A. de Visser *et al.*, Physical Review Letters **85**, 3005 (2000).
- [22] P. Reiss, D. Graf, A.A. Haghighirad, T Vojta, A.I. Coldea, Physical Review Letters **127**, 246402 (2021).
- [23] Lorenz Bartosch, Mariano de Souza, and Michael Lang, Physical Review Letters **104**, 245701 (2010).
- [24] A. Sakai *et al.*, Physical Review B **94**, 041105 (2016).
- [25] Y. Matsumoto *et al.*, Science **331**, 316 (2011).
- [26] K. Deguchi *et al.*, Nature Materials **11**, 1013 (2012).
- [27] J.-P. Poirier, Introduction to the Physics of the Earth's interior (Cambridge University Press, Cambridge, 2000).
- [28] H.E. Stanley, Introduction to Phases Transitions and Critical Phenomena (Oxford Science Publications, New York, 1971).
- [29] E. Grüneisen, Annalen der Physik Leibniz **331**, 393 (1908).

- [30] Isys F. Mello, L. Squillante, Antonio C. Seridonio, R.E. Lagos-Monaco, M. de Souza, Grüneisen parameter, the specific heat ratio, and phases coexistence regions (2023) (submitted).
- [31] D.C. Wallace, Statistical Physics of crystals and liquids: a guide to highly accurate equations of state (World Scientific, 2002).
- [32] S. Bludell, Magnetism in Condensed Matter (Oxford University Press, Oxford, 2001).
- [33] Charles Kittel, Introduction to Solid State Physics - Eighth Edition, John Wiley & Sons (2005).
- [34] R. K. Pathria, Statistical Mechanics — Second Edition, Butterworth-Heinemann (1996).
- [35] A. Tari, The Specific Heat of Matter at Low Temperatures. (Imperial college press, London, 2003).
- [36] M. de Souza, R. Paupitz, A. Seridonio, R.E. Lagos, Brazilian Journal of Physics **46**, 206 (2016).
- [37] N. W. Ashcroft and N. David Mermin, Solid State Physics, Saunders College Publishing (1976).
- [38] A. Friedman, Z. Phys. **10**, 377-386 (1922).
- [39] B. Ryden, Introduction to Cosmology - second edition (Cambridge University Press, 2017).
- [40] J.A. Romeu, <http://hdl.handle.net/2445/59759> (2014).
- [41] E. Hubble, PNAS **15**, 168 (1929).
- [42] V.M. Slipher, Lowell Observatory Bulletin **2**, 56 (1912).
- [43] A.G. Riess *et al.*, The Astronomical Journal **116**, 1009 (1998).

- [44] M. Alonso, E.J. Finn, Fundamental University Physics volume 1 - Mechanics (Addison Wesley, 1967).
- [45] S. Weinberg, Gravitational and Cosmology: Principles and Applications of the General Theory of Relativity (John Wiley & Sons, Cambridge, 1972).
- [46] J. Prat, C. Hogan, C. Chang, J. Frieman, J. Cosmol. Astropart. Phys. **06**, 015 (2022).
- [47] G. Gomes, L. Squillante, A.C. Seridonio, A. Ney, R.E. Lagos, M. de Souza, Physical Review B **100**, 054446 (2019).
- [48] L. Squillante, M. de Souza, Investigation of molecular conductors, the magnetocaloric effect and the binary alloy FeSe_{1-x} , Master dissertation (2017) - <https://repositorio.unesp.br/handle/11449/152558>.
- [49] L. Squillante, Isys F. Mello, Gabriel O. Gomes, A.C. Seridonio, R. E. Lagos-Monaco, H. Eugene Stanley, Mariano de Souza, Scientific Reports **10**, 7981 (2020).
- [50] R.T. Macaluso *et al.*, Chemical Materials **19**, 1918 (2007).
- [51] Y. Matsumoto *et al.*, Science **331**, 316 (2011).
- [52] R. V. Pound, Physical Review **81**, 156 (1951).
- [53] E.M. Purcell and R.V. Pound, Physical Review **81**, 279 (1951).
- [54] M.S. Ikeda *et al.*, Review of Scientific Instruments **90**, 083902 (2019).
- [55] L. Squillante, Isys F. Mello, A.C. Seridonio, M. de Souza, Scientific Reports **11**, 9431 (2021).
- [56] A.M. Meyers, K.K. Chawla, Mechanical Behavior of Materials (Cambridge University Press, 2009).
- [57] T.H.K. Barron, J.G. Collins, G.K. White, Thermal expansion of solids at low temperatures **29**, 609 (1980).

- [58] Y.-S. Li *et al.*, Nature **607**, 276 (2022).
- [59] N.F. Ramsey, Physical Review **103**, 20 (1956).
- [60] I. Pomeranchuk, *Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki* **20**, 919 (1950).
- [61] C.W. Hicks, M.E. Edkins, S.D. Brodsky, D.O. Mackenzie, Review of Scientific Instruments **85**, 065003 (2014).
- [62] L. Gannon *et al.*, Review of Scientific Instruments **86**, 103904 (2015).
- [63] D. Vasyukov *et al.*, Nature Nanotechnology **8**, 639 (2013).
- [64] T. Giamarchi, C. Rüegg, O. Tchernyshyov, Nature Physics **4**, 198 (2008).
- [65] S.T. Bramwell, M. J.-P. Gingras, Science **294**, 1495 (2001).
- [66] P. Ehrenfest, Proceedings of the Academy of Science Amsterdam **36**, 153 (1933).
- [67] K. Mori, M. Hayashi, Journal of the Physical Society of Japan **33**, 1396 (1972).
- [68] J.W. Benepe, W. Reese, Physical Review B **3**, 3032 (1971).
- [69] I.F. Mello, L. Squillante, G.O. Gomes, A.C. Seridonio, M. de Souza, Journal of Applied Physics **128**, 225102 (2020).
- [70] United Nations Goals website - <https://sdgs.un.org/goals>. Accessed in January 31st 2023.
- [71] M. Zacharias, L. Bartosch, M. Garst, Physical Review Letters **109**, 176401 (2012).
- [72] J. Wu, L. Zhu, Q. Si, Journal of Physics: Conference Series **273**, 012019 (2011).

- [73] A.W. Rost, R.S. Perry, J.-F. Mercure, A.P. Mackenzie, S.A. Grigera, *Science* **325**, 1360 (2009).
- [74] J.C. Maxwell, *Electricity and Magnetism*, vol. 1 (Oxford University Press, London, 1892).
- [75] T. Trautmann, C. Falter, *Journal of Physics: Condensed Matter* **16**, 5955 (2004).
- [76] L. Pauling, *Journal of the American Chemical Society* **57**, 2680 (1935).
- [77] B. Nair *et al.*, *Nature* **575**, 468 (2019).
- [78] K.A. Muller, H. Burkard, *Physical Review B* **19**, 3593 (1979).
- [79] S.E. Rowley *et al.*, *Nature Physics* **10**, 367 (2014).
- [80] R. Rösslhuber *et al.*, *Physical Review B* **103**, 125111 (2021).
- [81] J.H. Barrett, *Physical Review* **86**, 118 (1952).
- [82] D. Shin *et al.*, *Physical Review B* **104**, L060103 (2021).
- [83] A.G. Riess, A.V. Filippenko, P. Challis, A. Clocchiatti, A. Diercks, P.M. Garnavich, R.L. Gilliland, C.J. Hogan, S. Jha, R.P. Kirshner, *Astron. J.* **116**, 1009 (1998); S. Perlmutter, G. Aldering, G. Goldhaber, R.A. Knop, P. Nugent, P.G. Castro, S. Deustua, S. Fabbro, A. Goobar, D.E. Groom, I.M. Hook, A.G. Kim, M.Y. Kim, J.C. Lee, N.J. Nunes, R. Pain, C.R. Pennypacker, R. Quimby, C. Lidman, R.S. Ellis, M. Irwin, R.G. McMahon, P. Ruiz-Lapuente, N. Walton, B. Schaefer, B.J. Boyle, A.V. Filippenko, T. Matheson, A.S. Fruchter, N. Panagia, H.J.M. Newberg, W.J. Couch, *Astrophys. J.* **517**, 565 (1999); L. Perivolaropoulos, *J. Phys.: Conf. Ser.* **68**, 012005 (2007).
- [84] V. Poulin, T. L. Smith, T. Karwal, M. Kamionkowski, *Phys. Rev. Lett.* **122**, 221301 (2019).
- [85] N. Aghanin *et al.*, *Astronomy & Astrophysics* **641**, A6 (2020).

- [86] S.A. Bonometto, L. Casarini, L.P.L. Colombo, R. Mainini, <https://arXiv:astro-ph/0612672v1> (2006).
- [87] P. Wu, H. Yu, Phys. Lett. B **644**, 16-19 (2007).
- [88] J. Grande, R. Opher, A. Pelinson, J. Solà, J. Cosmol. Astropart. Phys. **2007**, 007 (2007).
- [89] I.P. Neupane, C. Scherer, J. Cosmol. Astropart. Phys. **2008**, 1 (2008).
- [90] J.S. Bullock, M. Boylan-Kolchin, ARA&A **55**, 343 (2017).
- [91] S. Weinberg, Gravitational and Cosmology: Principles and Applications of the General Theory of Relativity (John Wiley & Sons, Cambridge, 1972).
- [92] P.J.E. Peebles, Astrophys. J. **284**, 439 (1984).
- [93] P.-H. Chavanis, Eur. Phys. J. Plus **130**, 130 (2015); P.-H. Chavanis, Phys. Lett. B **758**, 59 (2016); P.-H. Chavanis, S. Kumar, J. Cosmol. Astropart. Phys. **2017**, 1 (2017).
- [94] A. Kamenshchik, U. Moschella, V. Pasquier, Phys. Lett. B **511**, 265 (2001).
- [95] Lucas Squillante, G.O. Gomes, I.F. Mello, G. Nogueira, A.C. Seridonio, R.E. Lagos-Monaco, M. de Souza, Grüneisen meets Einstein (submitted), (2023).
- [96] Z.-H. Zhu, Astron. Astrophys. **423**, 421-426 (2004).
- [97] E. Abdalla *et al.*, J. High Energy Phys. **34**, 49 (2022).
- [98] J.A. Frieman, M.S. Turner, D. Huterer, ARA&A **48**, 385-432 (2008).
- [99] E. Grüneisen, Ann. Phys. **331**, 393-402 (1908).
- [100] S. Eliezer, A. Ghatak, H. Hora, An Introduction to Equations of State: Theory and Applications (Cambridge University Press, New York, 1986).
- [101] A.P. Chernyshev, Eur. Phys. J. B **79**, 321-325 (2011).

- [102] H.H.B. da Silva, R.S. Junior, *Setor escuro do universo: uma análise termodinâmica, Ph.D. Thesis, Federal University of Rio Grande do Norte (2014).*
- [103] L. Squillante, I. Mello, A.C. Seridonio, M. de Souza, Sci. Rep. **11**, 9431 (2021).
- [104] C.A. Melendres, J. Mod. Phys. **12**, 1527 (2021).
- [105] L. Mañosa, D. González-Alonso, A. Planes, M. Barrio, J.-L. Tamarit, I. S. Titov, M. Acet, A. Bhattacharyya, S. Majumdar, Nat. Commun. **2**, 595 (2011).
- [106] Y.-K. Chiang, R. Makiya, B. M'enard, E. Komatsu, Astrophys. J. **902**, 56 (2020).
- [107] B. Lavenda, Where Physics Went Wrong (World Scientific, Singapore, 2015).
- [108] L.D. Landau, E.M. Lifshitz, Statistical Physics - Part 1 (Pergamon Press Inc., Elmsford, 1980).
- [109] S. Braun, J.P. Ronzheimer, M. Schreiber, S.S. Hodgman, T. Rom, I. Bloch, U. Schneider, Science **339**, 52 (2013).
- [110] N.F. Ramsey, Phys. Rev. **103**, 20 (1956).
- [111] L. Squillante, I.F. Mello, G.O. Gomes, A.C. Seridonio, R.E. Lagos-Monaco, H. Eugene Stanley, Mariano de Souza, Sci. Rep. **10**, 7981 (2020).
- [112] E. Di Valentino, E. Melchiorri, J. Silk, Nat. Astron. **4**, 196 (2020).
- [113] F.-Y. Cyr-Racine, F. Ge, L. Knox, Phys. Rev. Lett. **128**, 201301 (2022).
- [114] N.G. Busca, T. Delubac, J. Rich, S. Bailey, A. Font-Ribera, D. Kirkby, J.-M. Le Goff, M.M. Pieri, A. Slosar, É. Aubourg, J.E. Bautista, D. Bizyaev, M. Blomqvist, A.S. Bolton, J. Bovy, H. Brewington, A. Borde, J. Brinkmann, B. Carithers, R.A.C. Croft, K.S. Dawson, G. Ebelke, D. J. Eisenstein, J.-C. Hamilton, S. Ho, D.W. Hogg, K. Honscheid, K.-G. Lee, B. Lundgren, E.

- Malanushenko, V. Malanushenko, D. Margala, C. Maraston, K. Mehta, J. Miralda-Escudé, A.D. Myers, R.C. Nichol, P. Noterdaeme, M.D. Olmstead, D. Oravetz, N. Palanque-Delabrouille, K. Pan, I. Pâris, W.J. Percival, P. Petitjean, N.A. Roe, E. Rollinde, N.P. Ross, G. Rossi, D.J. Schlegel, D.P. Schneider, A. Sheldon, E.S. Sheldon, A. Simmons, S. Snedden, J.L. Tinker, M. Viel, B.A. Weaver, D.H. Weinberg, M. White, C. Yèche, D.G. York, *Astron. Astrophys.* **552**, A96 (2013).
- [115] I.F. Mello, L. Squillante, G.O. Gomes, A.C. Seridonio, M. de Souza, J. *Appl. Phys.* **128**, 225102 (2020).
- [116] J. Hanc, S. Tuleja, M. Hancova, *Amer. J. Phys.* **72**, 428 (2004).
- [117] J. Socorro, M. Doleire, L.O. Pimentel, *Astrophys. Space Sci.* **360**, 20 (2015).
- [118] E.K. Hanimeli, B. Lamine, A. Blanchard, I. Tutusaus, *Phys. Rev. D* **101**, 063513 (2020).
- [119] R.K. Tiwari, A.H.A. Alfedeel, D. Sofuoglu, A. Abebe, E.I. Hassan, B.K. Shukla, *Front. Astron. Space Sci.* **9**, 965652 (2022).
- [120] A. Einstein, *Ann. Phys.* **354**, 769 (1916).
- [121] M. Dalarsson, N. Dalarsson, *Tensors, Relativity, and Cosmology* (Academic Press, San Diego, 2015).
- [122] J. Ehlers, I. Ozsv'ath, E.L. Schöcking, Y. Shang, *Phys. Rev. D* **72**, 124003 (2005).
- [123] W. Zimdahl, H.E.S. Velten, W.C. Algoner, *Universe* **5**, 68 (2019).
- [124] K. Migkas, G. Schellenberger, T.H. Reiprich, F. Pacaud, M.E. Ramos-Ceja, L. Lovisari, *A&A* **636**, A15 (2020).
- [125] P.L. Taylor, K. Markovic, A. Pourtsidou, E. Huff, *Phys. Rev. D* **105**, 084007 (2022).

- [126] Q. Wang, Z. Zhu, W.G. Unruh, Phys. Rev. D **95**, 103504 (2017).
- [127] L. Bartosch, M. de Souza, M. Lang, Phys. Rev. Lett. **104**, 245701 (2010).
- [128] M. de Souza, A. Bröhl, Ch. Strack, B. Wolf, D. Schweitzer, M. Lang, Phys. Rev. Lett. **99**, 037003 (2007).
- [129] R.R. Caldwell, M. Kamionkowski, N.N. Weinberg, Phys. Rev. Lett. **91**, 071301 (2003).
- [130] K. Mack, The end of everything (Astrophysically speaking) (Scribner Book Company, 2020).
- [131] R. Skibba, Nature **584**, 187 (2020).
- [132] H. K. Onnes, Commun. Phys. Lab. Univ. Leiden **12**, (1911).
- [133] W. Meissner and R. Ochsenfeld, *Naturwissenschaften* **21**, 787 (1933).
- [134] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Physical Review **108**, 1175 (1957).
- [135] J. E. Hirsch *et al.*, Physica C: Superconductivity and Its Applications **514**, 1 (2015).
- [136] S. R. Foltyn *et al.*, Nature Materials **6**, 631 (2007).
- [137] <http://forschung-stromnetze.info/en/projects/superconductors-protecting-the-grid/>.
- [138] T. D. Ladd *et al.*, Nature **464**, 45 (2010).
- [139] Hyung-Woo Lee, Ki-Chan Kim, and Ju Lee, IEEE Transactions on Magnetics **42**, 1917 (2006).
- [140] W. Buckel and R. Kleiner, Superconductivity, Wiley-VHC (2004).
- [141] Superconductivity, Superfluids and Condensates, James F. Annett, Oxford University Press (2003).

- [142] J. Bednorz and K. Müller, *Zeitschrift für Physik B* **64**, 189 (1986).
- [143] W. I. F. David *et al.*, *Nature* **327**, 310 (1987).
- [144] Y. Kamihara *et al.*, *Journal of the American Chemical Society* **128**, 31 (2006).
- [145] J. Paglione and R. Greene, *Nature Physics* **6**, 646 (2010).
- [146] M. R. Norman, *Science* **332**, 196 (2011).
- [147] F. Steglich *et al.*, *Physical Review Letters* **43**, 1892 (1979).
- [148] D. Jérôme, A. Mazaud, M. Ribault, K. Bechgaard, *Journal Physique Letters* **41**, L95 (1980).
- [149] V. L. Ginzburg, *Contemporary Physics* **33**, 15 (1992).
- [150] N. W. Ashcroft, *Physical Review Letters* **21**, 1748 (1968).
- [151] N. W. Ashcroft, *Physical Review Letters* **92**, 187002 (2004).
- [152] Y. Wang and Y. Ma, *The Journal of Chemical Physics* **140**, 040901 (2014).
- [153] A. P. Drozdov *et al.*, *Nature* **525**, 73 (2015).
- [154] M. Somayazulu *et al.*, *Physical Review Letters* **122**, 027001 (2019).
- [155] H. Liu *et al.*, *Proceedings of the National Academy of Sciences* **114**, 6990 (2017).
- [156] N. Dasenbrock-Gammon *et al.*, *Nature* **615**, 244 (2023).
- [157] W. A. Little, *Physical Review A* **134**, 1416 (1964).
- [158] K. Kanoda, *Hyperfine Interactions* **104**, 235 (1997).
- [159] P. Monceau, F. Ya Nad, and S. Brazovskii, *Physical Review Letters* **86**, 4080 (2001).
- [160] A. C. Jacko *et al.*, *Physical Review B* **87**, 155139 (2013).

- [161] G. Kotliar and D. Vollhardt, *Physics Today* **57**, 53 (2004).
- [162] H. Seo *et al.*, *Journal of the Physical Properties of Japan* **75**, 051009 (2006).
- [163] M. Dressel, *Naturwissenschaften* **94**, 527 (2007).
- [164] N. F. Mott, *Metal-Insulator Transitions – Second Edition*, Taylor and Francis (1990).
- [165] F. Nad and P. Monceau, *Journal of the Physical Society of Japan* **75**, 051005 (2006).
- [166] H. Seo and H. Fukuyama, *Journal of the Physical Society of Japan* **66**, 1249 (1997).
- [167] M. Dressel, M. Dumm, T. Knoblauch, and M. Masino, *Crystals* **2**, 528 (2012).
- [168] F. Nad and P. Monceau, *Journal of the Physical Society of Japan* **75**, 051005 (2006).
- [169] M. Fiebig, *Journal of Physics D: Applied Physics* **38**, 123 (2005).
- [170] S. W. Cheong and M. Mostovoy, *Nature Materials* **6**, 13 (2007).
- [171] W. Eerestein and N. D. Mathur, *Nature* **442**, 759 (2006).
- [172] Gianluca Giovanetti *et al.*, *Physical Review B* **91**, 125130 (2015).
- [173] W. Eerenstein, N.D. Mathur, J.F. Scott, *Nature* **442**, 759 (2006).
- [174] D. Khomskii, *Physics* **2**, 20 (2009).
- [175] M. Dressel, M. Dumm, T. Knoblauch, and M. Masino, *Crystals* **2**, 528 (2012).
- [176] M. Meneghetti *et al.*, *Journal of Chemical Physics* **80**, 6210 (1984).
- [177] Shunsuke Kitou *et al.*, *Physical Review Letters* **119**, 065701 (2017).
- [178] L. Yee and J. R. Anderson, *Zeolite molecular sieves: structure, chemistry, and use* (John Wiley & Sons, 2013).

- [179] I. Bello, Vacuum and ultravacuum: Physics and technology (CRC Press, 2018).
- [180] J. Ji *et al.*, PNAS **113**, 2349 (2016).
- [181] M. Dressel *et al.*, Crystals **2**, 528 (2012).
- [182] Ivan S. Oliveira, Tito J. Bonagamba, Roberto S. Sarthour, Jair C.C. Freitas, Eduardo R. de Azevedo, NMR Quantum Information Processing (Elsevier, Amsterdam, 2007).
- [183] A.P. Guimarães, Magnetism and Magnetic Resonance in Solids. (John Wiley & Sons, New York, 1998).
- [184] Landau, L.D. & Lifshitz, E.M. *Statistical Physics: Vol. 5.* (Pergamon Press, Oxford , 1959).

"Rather than love, than money, than fame, give me truth."

— Henry David Thoreau (1817 - 1862)

6

Appendices

6.1 Absence of a perfect alignment between $\vec{\mu}$ and $\vec{B}$

The magnetic moment vector $\vec{\mu}$ can be analogous to the angular momentum vector $\vec{L}$ of a spinning peon, cf. Fig. 6.1. Essentially, when a magnetic field $\vec{B}$ is applied, for instance, in the z direction, there will be a precession of $\vec{\mu}$ around the z axis, which is called Larmor precession [182]. In an analogous way, when the peon is spined, $\vec{L}$ precesses around the z axis as well due to the presence of gravity. The well-known magnetic energy E_{mag} of a magnetic moment under an applied $\vec{B}$ is given by [1]:

$$E_{mag} = -\vec{\mu} \cdot \vec{B} = -\mu B \cos(\phi), \quad (6.1)$$

where ϕ is the angle between $\vec{\mu}$ and $\vec{B}$. It turns out that the minimum energy configuration between $\vec{\mu}$ and $\vec{B}$ refers to a parallel configuration between them, i.e., $E_{min} = -\mu B$ and $\vec{\mu}$ is aligned in the direction of $\vec{B}$, while the maximum magnetic energy $E_{max} = +\mu B$ refers to an anti-parallel alignment between $\vec{\mu}$ and $\vec{B}$. It is possible to write E_{mag} in terms of the magnetic quantum number $m_j = -J, -J+1, \dots, J-1, J$ [183], which describes all the possible orientations $\vec{\mu}$ can have, being J the total angular momentum quantum number. The vector $\vec{B}$ is along the $\vec{z}$ direction and $\vec{\mu}$ and the total angular momentum vector $\vec{J}$ have the very

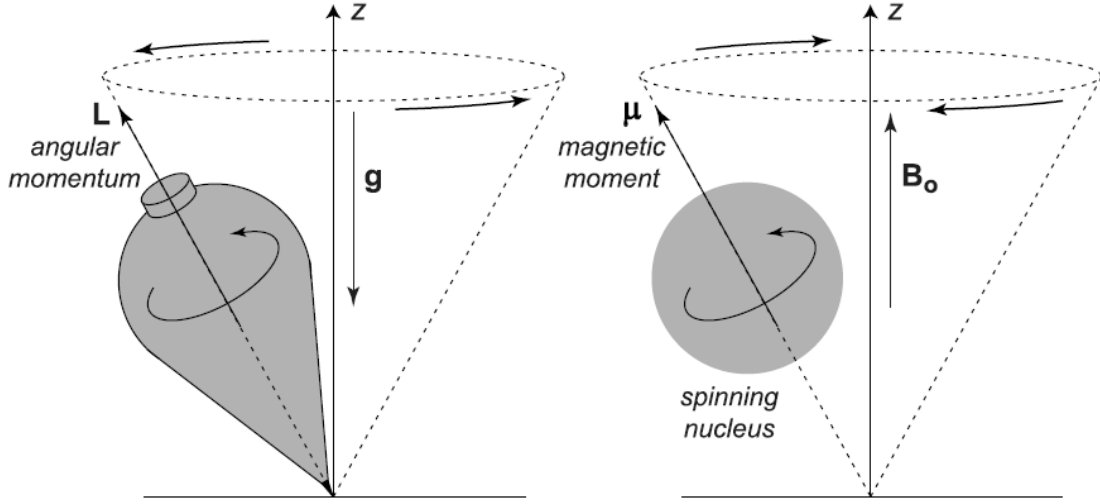


Figure 6.1: Schematic representation of the analogy between the precession of the angular momentum vector $\vec{L}$ of a peon around the $\vec{z}$ axis due to the gravitational field g and the precession of the magnetic moment vector $\vec{\mu}$ of a spinning nucleus around the $\vec{z}$ axis due to an applied magnetic field $\vec{B}$. Figure extracted from Ref. [182].

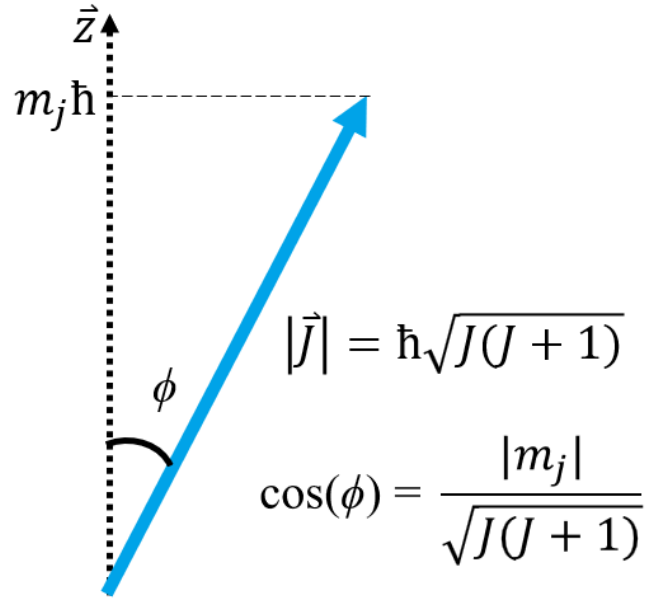


Figure 6.2: Schematic representation of the total angular momentum vector $\vec{J}$ that makes an angle ϕ in the $\vec{z}$ direction. The modulus of $|\vec{J}| = \hbar \sqrt{J(J+1)}$ [183] and its projection in the $\vec{z}$ axis is $m_j \hbar$, where m_j is the magnetic quantum number.

same direction. Upon considering the projection of $|\vec{J}| = \hbar \sqrt{J(J+1)}$ [183] in the $\vec{z}$ axis as $m_j \hbar$ [183], it is possible to rewrite $\cos(\phi)$ between $\vec{\mu}$ and $\vec{B}$ by (Fig. 6.2) [183]:

$$E_{mag} = -\mu B \cos(\phi) = -\mu B \frac{m_j \hbar}{\hbar \sqrt{J(J+1)}} = -\mu B \frac{m_j}{\sqrt{J(J+1)}}. \quad (6.2)$$

Note from Eq. 6.2 that a perfect alignment between $\vec{\mu}$ and $\vec{B}$ means that either ϕ is 0° or 180° , so that $\cos(\phi)$ is $+1$ or -1 . This means that both numerator and denominator of the fraction $m_j/\sqrt{J(J+1)}$ in Eq. 6.2 must be equal. However, upon analysing Fig. 6.2, the projection of a vector along a particular axis will never have the same length as the original vector. Hence, m_j is always lower than $\sqrt{J(J+1)}$ so that a perfect alignment, either parallel or anti-parallel, between $\vec{\mu}$ and $\vec{B}$ is prevented by Quantum Mechanics.

6.2 The impossibility of connecting adiabatic deformations and the concept of negative temperatures

As an intellectual exercise, the fundamental concepts of the Purcell and Pound's experiment [53] are recalled in order to make a connection with the concept of negative temperatures and the adiabatic stress application. Then, although such analysis looks correct at first, a discussion in terms of the requirements to attain negative temperatures is made to show that such a connection is not sustainable.

Following the canonical definition of temperature, the sign of T is ruled by either a positive or negative $(\partial S/\partial E)_B$, where E is the average magnetic energy [1]. Essentially, when a magnetic field is applied in a particular direction, the magnetic moments align in the direction of the field and then $(\partial S/\partial E) > 0$ indicating a positive temperature. However, if the magnetic field is reversed very quickly in the time-scale of micro seconds, i.e., faster than the typical spin-relaxation time, then the magnetic moments will be in an anti-parallel configuration with respect to the magnetic field and thus $(\partial S/\partial E) < 0$ leading to the concept of negative absolute temperature. Now, we present an analogy between $(\partial S/\partial E)_B$ dictating the sign of T and $(\partial S/\partial U)$ in the case of adiabatic strain with a change of temperature [184]. First, we recall the entropy associated with the deformation of a system due to a temperature change [184]:

$$S = S_0 + K\alpha_p u_{ll}, \quad (6.3)$$

where S_0 is the entropy before the deformation, K is the bulk modulus, and $u_{ll} = (v - v_0)/v_0$ refers to the relative volume change, being v_0 the initial volume of the specimen before the deformation. Since we are interested in the adiabatic case, the adiabatic bulk modulus K_{ad} must be employed and its relation with K is given by [184]:

$$\frac{1}{K_{ad}} = \frac{1}{K} - \frac{T\alpha_p^2}{c_p}, \quad (6.4)$$

which in turn can be rewritten as:

$$K = \frac{K_{ad}c_p}{(c_p + K_{ad}T\alpha_p^2)}. \quad (6.5)$$

Replacing Eq. 6.5 in Eq. 6.3, we obtain:

$$S = S_0 + \frac{\alpha_p u_{ll} K_{ad} c_p}{(c_p + K_{ad} T \alpha_p^2)}. \quad (6.6)$$

Now, we make use of the internal energy U per unit of volume associated with an adiabatic deformation [184]:

$$U = \frac{K_{ad} u_{ll}^2}{2} + \mu' \left(u_{ij} - \frac{1}{3} u_{ll} \delta_{ij} \right)^2, \quad (6.7)$$

where μ' is the shear modulus, also called modulus of rigidity, u_{ij} is the strain tensor, and δ_{ij} is the unit tensor or Kronecker delta. Solving Eq. 6.7 for K_{ad} and replacing it into Eq. 6.6, we obtain the expression for S in terms of U :

$$S = S_0 + \frac{2\alpha_p c_p \left[U - \mu' \left(u_{ij} - \frac{\delta_{ij} u_{ll}}{3} \right)^2 \right]}{u_{ll} \left\{ c_p + \frac{2\alpha_p^2 T \left[U - \mu' \left(u_{ij} - \frac{\delta_{ij} u_{ll}}{3} \right)^2 \right]}{u_{ll}^2} \right\}}. \quad (6.8)$$

Making the derivative of S in respect to U and employing the relation $T = (u_{ll} + \alpha T_0)/\alpha$ [184], where T_0 is the starting temperature, we obtain:

$$\left(\frac{\partial S}{\partial U} \right) = \frac{162\alpha_p c_p^2 u_{ll}^3}{\{2\alpha_p(\alpha_p T_0 + u_{ll}) [9U - \mu'(\delta_{ij} u_{ll} - 3u_{ik})^2] + 9c_p u_{ll}^2\}^2} = \frac{1}{T}. \quad (6.9)$$

Note that the denominator of Eq. 6.9 is always positive since it is squared. Assuming that α_p is positive and c_p is always positive, the sign change of Eq. 6.9 is ruled by

the term u_{ll}^3 . Note that the consideration that α_p is constant lies on the adiabatic character of the uniaxial stress application, since $\alpha_p = -1/v(\partial S/\partial p)_T$ [1]. Thus, if an adiabatic contraction takes place in a time-scale lower than the thermal relaxation time of the system (Fig. 2.12), u_{ll}^3 is negative since $v < v_0$ and thus $T < 0$ as well. However, in an adiabatic expansion, u_{ll}^3 is positive since $v > v_0$ and thus $T > 0$. Therefore, the sign change of T is governed by the sign of the relative volume change in an adiabatic deformation. The latter is analogous to the sign of T ruled by the direction of the magnetic moments with respect to B in the Purcell and Pound's experiment [53]. Essentially, the inversion of the voltage applied to the PZT stacks at a given frequency (Fig. 2.12), and consequently, the applied electric field, could be seen as a corresponding situation to the fast inversion of the magnetic field in the seminal experiment proposed by Purcell and Pound's.

Next, a discussion is performed about the non-validity of this approach based on the essential requirements for a thermodynamical system to be capable of negative temperatures, which reads [59]:

“(...) (1) The elements of the thermodynamical system must be in thermodynamical equilibrium among themselves in order that the system can be described by a temperature at all; (2) there must be an upper limit to the possible energy of the allowed states of the system; and (3) the system must be thermally isolated from all systems which do not satisfy both of the above conditions, i.e., the thermal equilibrium time among the elements of the system must be short compared to the time during which appreciable energy is lost to or gained from other systems. (...)”

In the experiment performed by Purcell and Pound [53], the nuclear spin system lies in thermodynamical equilibrium, which means that the temperature is kept constant during the fast inversion of the applied magnetic field, changing the regime of positive $(\partial S/\partial U)_B$ to a negative one. During the adiabatic volume change discussed in terms of a uniaxial stress application, such a deformation is always accompanied by an adiabatic temperature change to hold the entropy constant, thus violating the previously mentioned requirement (1). Also, there is no upper limit in the elastic energy associated with the adiabatic volume variation, which is

at odds with requirement (2). Following such arguments, it is straightforward to conclude that requirement (3) is also not fulfilled. Hence, the connection between adiabatic deformations and negative temperatures in connection with the Purcell and Pound's experiment is not sustainable.

6.3 Power down during experiments

During the Ph.D. period, several power losses took place, which affected our experiments since the cryostat had to be warmed up to room temperature before cooling it down again. This takes several days to finish and, by summing up the almost 40 hours to cool down the system again, significantly impacted our experiments. Some of the power loss logs can be seen in the records written in the laboratory notebook below.

$V=0$, we can use the relation:

$$\frac{R_{RB}}{R_{SG}} = \frac{R_1}{R_2}$$

$V=0$ for $R_{RB} \approx 405 \Omega$.

Since $R_1 = R_2$,

$$R_{RB} = R_{SG} \approx 405 \Omega$$

We lowered the resistance of the resistance box from $10 M\Omega$ to 405Ω until $V=0$ and concluded that we have successfully measured $R_{SG} = 405 \Omega$.

12/02/2020

Cool down initiated at 6:30 A.M. $\Rightarrow$

(sample 26/08/19)

Resistance $\rightarrow PF_6-D_{12}$ (c^* -axis) (Pins 1 and 4)

Dielectric constant $\rightarrow PF_6-D_{12}$ (c^* -axis) (Pins 6 and 11)

$$E = 100 \text{ mV/cm}, U = 0.004 \text{ V}; d = 0.4 \text{ mm}$$

14/02/2020

Warm up

Dielectric constant $\rightarrow PF_6-D_{12}$ (c^* -axis) (Pins 6 and 11)

$$E = 500 \text{ mV/cm}; U = 0.02 \text{ V}; d = 0.4 \text{ mm}$$

15/02/2020

Power down = C $\sim 9:05$ A.M.

28/02/2020

Cool down initiated at 6:30 A.M.

ϵ' $\rightarrow PF_6-D_{12}$ (c^* -axis) (Pins 1 and 4)

$$E = 500 \text{ mV/cm}; U = 0.01 \text{ V}; d = 0.2 \text{ mm}$$

R $\rightarrow PF_6-D_{12}$ (c^* -axis) (Pins 6 and 11)

until we notice that the pressure is not decreasing anymore over time due to pumping. Then, we will manually remove the offset of pressure in the iTC controller.

June 21st, 2022

ZT cleaning was restarted. Power down at 4:40 P.M.
↳ lowest pressure: pump = 3.6×10^{-4} mbar / needle valve = -1.7 mbar

June 22nd, 2022

ZT cleaning was restarted.

June 30rd, 2022

Needle valve offset pressure ≈ -1.80 mbar
OVC pumped. Final pressure at the end of the day = 2.2×10^{-4} mbar

July 4th, 2022

OVC pumped - final pressure 3.0×10^{-5} mbar

July 5th, 2022

OVC pumped - final pressure 2.5×10^{-5} mbar

July 6th, 2022

OVC pumped - final pressure 2.2×10^{-5} mbar

July 7th, 2022

OVC pumped - final pressure 1.9×10^{-5} mbar

6.4 Technical aspects

During the period of my Ph.D. I had the opportunity to spectate the fixing of a coaxial cable by soldering its tip on a R114.005.000 SMB connector, cf. Fig.6.3.

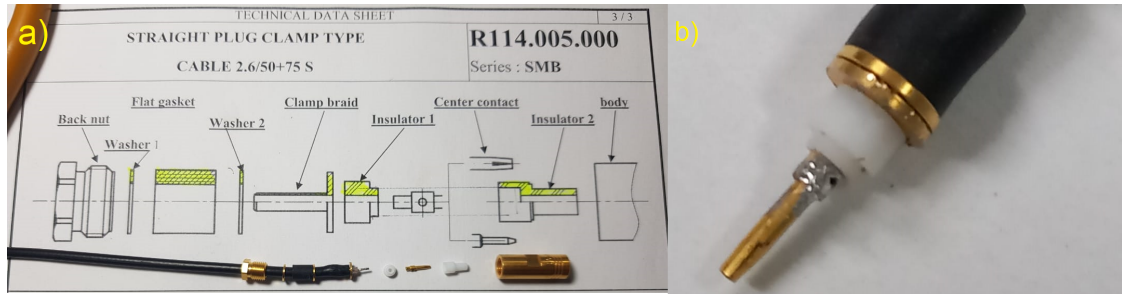


Figure 6.3: a) All the individual parts of the SMB connector together with its datasheet. b) The golden tip of the SMB connector is already soldered in the coaxial cable. Special thanks to Leandro Xavier who performed such a delicate repair.

6.5 Joint reports

During the period of my Ph.D. degree, Prof. Dr. Mariano de Souza provided me to the opportunity of acting as a co-reviewer in various manuscripts he had being requested to provide a report. The journals I have participated as a co-reviewer are the following:

- Physical Review B (12 manuscripts);
- Brazilian Journal of Physics (1 manuscript);
- AIMS Mathematics (2 manuscripts);
- Mathematical Biosciences and Engineering (2 manuscript);
- Physica A: Statistical Mechanics and Its Applications (1 manuscript);
- Physical Review Materials (2 manuscripts);
- PLOS ONE (2 manuscripts);
- Physics Letters A (1 manuscript).

Due to these great opportunities Prof. Mariano de Souza has given me, I became an active referee of Physical Review B and Physical Review Research.

6.6 Tutorships

As part of my Ph.D. degree, I acted as a tutor in the following courses ministered by Prof. Dr. Mariano de Souza:

- Physics II (First semester/2019 - volunteer);
- Solid State Physics (Second semester/2020);
- Electromagnetism (First semester/2021);
- Electromagnetism (Second semester/2021 - volunteer).

6.7 Participation in scientific events

- Autumn Meeting of the Brazilian Physical Society - Ouro Preto, MG (2023).
Poster presented: Adiabatic magnetization in paramagnetic salts without applied magnetic field.
Talk: Materials design for eco-friendly refrigeration employing entropy arguments.
- First Iberoamerican Meeting on Quantum Materials and Electronic Structures: Theory and Experiments - UFES, Vitória, ES (2023).
Poster presented: Elastocaloric-effect-induced adiabatic magnetization in paramagnetic salts due to the mutual interactions
- II Condensed Matter Theory in the Metropolis - ICTP-SAIFR/IFT-UNESP, São Paulo, SP (2022).
Poster presented: Zero-field quantum criticality and the role played by the mutual interactions in paramagnets.
Poster presented: Giant caloric effects close to *any* critical end point.

- School on disordered elastic systems - ICTP-SAIFR/IFT-UNESP, São Paulo, SP (2022);
- Autumn meeting of the Brazilian physical society - University of São Paulo (USP), São Paulo, SP (2022).

Poster presented: Giant caloric effects close to *any* critical end point.

Talk: Elastocaloric-effect-induced adiabatic magnetization in paramagnetic salts due to the mutual interactions.

- Autumn meeting of the Brazilian physical society - Online (2021).
- International conference on strongly correlated electron systems - Online (2021).

Poster presented: Zero-field quantum criticality and the role played by the mutual interactions in paramagnets.

- Autumn meeting of the Brazilian physical society - Online (2020).
- Autumn meeting of the Brazilian physical society - Aracaju, SE (2019).
- Second Brazilian synchrotron school: fundamentals and applications (2018).

Talk: Magnetic Grüneisen parameter for model systems.

Talk: Exploring the ionic dielectric constant contribution in the Mott-Hubbard phase of molecular metals.

6.8 Prizes and awards

- Honorable mention of poster entitled “Giant caloric effects close to *any* critical end point” presented at the Autumn meeting of the Brazilian physical society (2022);
- Best poster award of poster entitled “Zero-field quantum criticality and the role played by the mutual interactions in paramagnets” presented at the international conference on strongly correlated electron systems (2022);

- Best poster award of poster entitled “Elastocaloric-effect-induces adiabatic magnetization in paramagnetic salts due to the mutual interactions” presented at the First Iberoamerican Meeting on Quantum Materials and Electronic Structures: Theory and Experiments (2023).
- Honorable mention in the section “Dynamical Magnetization” of poster entitled “Adiabatic magnetization in paramagnetic salts without applied magnetic field” presented at the Autumn Meeting of the Brazilian Physical Society (2023).
- Institute of Physics (IOP) best poster award (2023) - 1st place - of poster entitled “Adiabatic magnetization in paramagnetic salts without applied magnetic field” presented at the Autumn Meeting of the Brazilian Physical Society (2023).

6.9 Graduate student representative

Based on the suggestion made by Prof. Dr. Mariano de Souza, I had the opportunity to act as the Physics graduate student representative in the Physics graduate program at Unesp, Rio Claro, SP, together with my colleague Ricardo Brandolt Júnior. During this very important period, we had the opportunity to participate and to bring the student’s vision/opinion in the graduate board meetings. We participated in numerous activities, some of which were the elaboration of normative instructions, which are the rules associated with the Physics graduate course. We also spectated the approvals of students research projects, tutorships requests, and participated in many other academic discussions that contributed a lot to our scientific careers in a broader way. In addition, we spectated 2 masters and doctoral selection processes in the Physics graduate program, which were unique experiences to learn many academic and bureaucratic aspects. Hence, it is worth mentioning that, for the first time in the history of the Physics graduate program at Unesp Rio Claro, SP, there was an active graduate student representation.

6.10 Published manuscripts as a co-author

Apart from the topics investigated in the frame of this Thesis, I had the opportunity to participate as a co-author in the following articles:

- I.F. Mello, L. Squillante, G.O. Gomes, A.C. Seridonio, Mariano de Souza, Griffiths-like phase close to the Mott transition, *Journal of Applied Physics* **128**, 225102 (2020).
- I.F. Mello, L. Squillante, G.O. Gomes, A.C. Seridonio, Mariano de Souza, Epidemics, the Ising-model and percolation theory: A comprehensive review focused on Covid-19, *Physica A: Statistical Mechanics and Its Applications* **573**, 125963 (2021).
- L. Squillante, Mariano de Souza, Review of: “High-pressure thermal conductivity and compressional velocity of NaCl in B1 and B2 phase”, Qeios ID: ZWB69H, <https://doi.org/10.32388/ZWB69H> (2021).
- Isys F. Mello, Lucas Squillante, Roberto E. Lagos-Monaco, Antonio C. Seridonio, Mariano de Souza, Grüneisen parameter, the specific heat ratio, and phases coexistence region (submitted) (2023).

6.11 Published manuscripts as first author

Apart from the articles published in the frame of this Ph.D. Thesis, there is a number of manuscripts in preparation conducted by Prof. Dr. Mariano de Souza, which I have been giving some inputs and it should be published in the near future. Next, the full articles published with me as the first author in the frame of my Ph.D. are attached.

Magnetic Grüneisen parameter for model systems

Gabriel O. Gomes,^{1,*} Lucas Squillante,¹ A. C. Seridonio,² Andreas Ney,³ Roberto E. Lagos,¹ and Mariano de Souza^{1,†}

¹*Departamento de Física, São Paulo State University (UNESP), IGCE, Rio Claro, 13506-900 São Paulo, Brazil*

²*Faculdade de Engenharia de Ilha Solteira, São Paulo State University (UNESP), Ilha Solteira, 13385-000 São Paulo, Brazil*

³*Institute of Semiconductor and Solid State Physics, Johannes Kepler University Linz, 4040 Linz, Austria*



(Received 28 February 2019; revised manuscript received 9 May 2019; published 28 August 2019)

The magnetocaloric effect (MCE), which is the refrigeration based on the variation of the magnetic entropy, is of great interest in both technological applications and fundamental research. The MCE is quantified by the magnetic Grüneisen parameter Γ_{mag} . We report on an analysis of Γ_{mag} for the classical Brillouin-like paramagnet for a modified Brillouin function taking into account a zero-field splitting originated from the spin-orbit (SO) interaction and for the one-dimensional Ising (1DI) model under a longitudinal field. For the Brillouin-like model with SO interaction and the longitudinal 1DI model, a sign-change in the MCE is observed for vanishing T and B . SO interaction leads to a narrowing of the enhancement of Γ_{mag} for T and $B \rightarrow 0$. Our findings emphasize the relevance of Γ_{mag} for exploring critical points. Also, we show that the Brillouin model with and without SO interaction can be recovered from the 1DI model in the regime of high temperatures and vanishing coupling constant J .

DOI: [10.1103/PhysRevB.100.054446](https://doi.org/10.1103/PhysRevB.100.054446)

I. INTRODUCTION

Although *classical* phase transitions are driven by thermal fluctuations [1], a genuine *quantum* phase transition (QPT) [2] takes place at $T = 0$ K. In this case, thermal fluctuations are absent, and the transition is driven by tuning a control parameter g (see Fig. 1), namely, application of external pressure, magnetic field, or changes in the chemical composition of the system of interest. Intricate manifestations of matter have been observed in the immediate vicinity of a quantum critical point (QCP) (cf. Fig. 1), i.e., the point in which the QPT takes place, such as divergence of the Grüneisen parameter computed by combining ultra-high-resolution thermal expansion and specific-heat measurements [3–5], collapse of the Fermi surface as detected via Hall-effect measurements [6], non-Fermi-liquid behavior observed by carefully analyzing the power law obeyed by the electrical resistivity, specific heat, magnetic susceptibility [7,8], and breakdown of the Wiedemann-Franz law due to an anisotropic collapse of the Fermi surface [9]. Hence, the exploration and understanding of the physical properties of interacting quantum entities on the verge of a QCP consist of topics of wide current interest, see, e.g., Ref. [10] and references therein. In this context, heavy-fermion compounds have been used as an appropriate platform to explore such exotic manifestations of matter [11]. Interestingly enough, new sorts of quantum critical behavior, having strong spin-orbit (hereafter SO) coupling and electron correlations as key ingredients, embodying an antiferromagnetic semimetal Weyl phase [15] and excitations of strongly entangled spins called spin orbitons [16], have been recently

reported in the literature. Furthermore, a QPT in graphene tuned by changing the slope of the Dirac cone has also been reported [17]. In general terms, the fingerprints of a magnetic-field-induced QPT are the divergence of the magnetic susceptibility [18] $\chi(T, B) = \mu_0(\partial M/\partial B)$ (here, M refers to the magnetization, B is an external magnetic field, and μ_0 is the vacuum permeability) for $T \rightarrow 0$ K and a sign change in the MCE near QCPs [19]. Indeed, such fingerprints have been observed experimentally in several materials. Among them are YbRh_2Si_2 [20], Cs_2CuBr_4 [21], and CeCoIn_5 [22], just to mention a few examples. Furthermore, zero-field QCPs have been also recently reported in the f -based superconductors CeCoIn_5 [23], $\beta\text{-YbAlB}_4$ [18], and quasicrystals of the series Au-Al-Yb [24]. Owing to the experimental difficulties posed by accessing a QCP under pressure and/or under an external magnetic field, zero-field QCPs are of high interest since quantum criticality is, thus, accessible simply by means of temperature sweeps. An analogous situation is encountered, for instance, in molecular conductors regarding the finite- T critical end point of the Mott metal-to-insulator transition [25–27] as well as for gases [28]. From the theoretical point of view, however, topics still under intensive debate are as follows: (i) the universality class of QPTs [11,27]; (ii) the temperature range of robustness of quantum fluctuations and the role played by them, for instance, in the mechanism behind high-temperature superconductivity [10]. Several theoretical models have been served as appropriated platforms to address these issues, being the transverse 1DI model, namely, an Ising chain under a transverse magnetic field, an appropriate playground to investigate several fundamental aspects [29,30]. Indeed, for the transverse 1DI model, exactly solved analytically, there is no spontaneous magnetization, and a phase transition occurs only at $T = 0$ K under a finite magnetic field [31], see Fig. 1. This is merely a direct consequence of the famous Mermin-Wagner theorem

*Present address: Department of Astronomy, University of São Paulo, São Paulo 05508-090, Brazil.

†mariano.souza@unesp.br

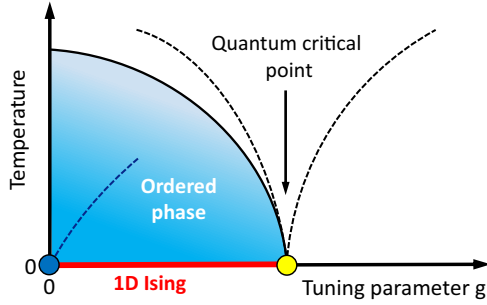


FIG. 1. Schematic phase diagram of the temperature *versus* tuning parameter g , indicating two quantum critical points. Yellow and blue bullets indicate a magnetic-field-tuned and a zero-field QCP, respectively. The red line at $T = 0$ K depicts a magnetic-field induced QPT for the transverse 1D Ising model. The dashed line for the hypothetical magnetic field-induced quantum critical point (yellow bullet) indicates the suppression of an energy scale, while the dashed line from the origin (blue bullet) represents the enhancement of the magnetic susceptibility for vanishing magnetic field [12]. In the case of a magnetic-field-induced QPT, the solid line refers to the adiabatic magnetization [13]. Figure adapted from Refs. [3,14]. Details in the main text.

[32], which forbids long-range magnetic ordering at finite temperatures in dimensions $d \leq 2$. Since the 1DI Hamiltonian considers solely nearest-neighbor interactions, computing the eigenenergy of a spin configuration is a relatively easy task [1]. As a matter of fact, in a broader context, though the Ising model, at first glance, is a *toy model* to simulate a domain in a ferromagnetic material, it still continues to attract broad interest, for instance, in the field of quantum information theory [33] and detection of Majorana edge states [34]. Motivated by the intrinsic quantum critical nature of the 1DI model under a transverse field, we explore a possible similar behavior in other exactly analytically solvable models.

The focus of the present paper lies on the report of an intrinsic diverging magnetic Grüneisen parameter for the various model systems discussed here in the limit of a vanishing magnetic field and $T \rightarrow 0$. Following the discussions in Ref. [35] in order to probe a magnetic-field-induced QCP, the criteria to be fulfilled are based on particular behavior of the magnetic Grüneisen parameter Γ_{mag} as follows: (i) a divergence of Γ_{mag} for $T \rightarrow 0$; (ii) a sign change in Γ_{mag} upon crossing the critical magnetic-field B_c , and (iii) a typical $T/(B - B_c)^\epsilon$ scaling, where ϵ is the so-called scaling exponent. Our analysis on the magnetic Grüneisen parameter, to be discussed in the following, fulfill these criteria, being the investigation of the (iii) criterium out of the scope of the present paper [12]. For *real* materials, a divergence of the magnetic Grüneisen parameter for vanishing B and $T \rightarrow 0$ might be related to the presence of residual amount of magnetic moments [35]. Hence, the divergence of the Grüneisen ratio, namely, the ratio of the thermal expansion to specific heat, is also required to probe genuine quantum criticality [35]. In the case of an *ideal* paramagnet, upon approaching zero temperature and removing the external magnetic field, one achieves the limit where mutual interactions are relevant with a typical local magnetic field of about 0.01 T for a distance between neighboring electron's spins ($S = 1/2$) of 5 Å

as discussed in Ref. [36]. It turns out that one has an intrinsic entropy change for a vanishing external magnetic field [36]. Such entropy change is related to the enhancement of Γ_{mag} for B and $T \rightarrow 0$. Surprisingly enough, the model systems to be discussed in the following incorporate such features.

This paper is organized as follows: In Sec. II, the MCE is calculated for the classical Brillouin-like paramagnet; in Sec. III, the SO interaction is taken into account to calculate the MCE for the Brillouin paramagnet for $S = 3/2$, being the results compared with those obtained in Sec. II, the 1DI model under longitudinal field is recalled, and the corresponding MCE is presented in Sec. IV.

Before starting the discussions on the MCE for the Brillouin-like paramagnet, it is worth recalling that both 1DI and the two-dimensional Ising (2DI) models provide an appropriate playground to explore critical points both theoretical and experimentally. For zero external field $B = 0$ T, the model can be exactly solved, and it is known as the famous Onsager solution [1,37,38]. The mathematical solution of both 1DI and 2DI models in the absence of an external magnetic field can be found in classical textbooks, see, e.g., Refs. [31,39,40]. A hypothetical sample with a volume of 1 mm³, the *Système International* values of $\mu_B = (9.27 \times 10^{-24})$ J T⁻¹, the Boltzmann constant $k_B = (1.38 \times 10^{-23})$ m² kg s⁻² K⁻¹, and $N = (6.022 \times 10^{23})$ atoms were employed in the calculations. For the 1DI model, we have employed a magnetic coupling constant $J = 10^{-23}$ J = 0.72 K. Also, it is worth mentioning that the MCE is quantified by Γ_{mag} .

II. THE BRILLOUIN-LIKE PARAMAGNET

In what follows, we discuss the MCE for the Brillouin paramagnet. First, we recall the Brillouin function B_J , well known from textbooks [31]:

$$B_J(J, y) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J} \coth\left(\frac{y}{2J}\right), \quad (1)$$

where $y = g_J \mu_B J B / k_B T$, g_J is the Landé gyromagnetic factor ($g_J = 2.274$), μ_B is the Bohr magneton, and J is the system's spin. The magnetization is readily written as follows:

$$M = N g_J \mu_B J B_J(J, y). \quad (2)$$

The magnetic susceptibility is computed by $\chi = (\partial M / \partial B)_{B=0}$. Figure 2 depicts the Brillouin magnetic susceptibility as a function of temperature under various magnetic fields. Remarkably, at low T for a vanishing magnetic field, χ diverges as it occurs for a magnetic field-induced QCP. It turns out that, for real systems, magnetic moments are always interacting. Such interaction is rather small when compared with the thermal energy $k_B T$, but it becomes relevant at low T and, thus, a long-range magnetic ordering takes place [41]. The calculation of the MCE for the Brillouin paramagnet is straightforward. For arbitrary values of J , it can be calculated using the expression [3],

$$\Gamma_{\text{mag}} = -\frac{1}{T} \frac{(\partial S / \partial B)_T}{(\partial S / \partial T)_B}. \quad (3)$$

We can calculate the entropy S employing the Helmholtz free-energy F per spin,

$$F = -k_B T \ln[Z_J(y)], \quad (4)$$

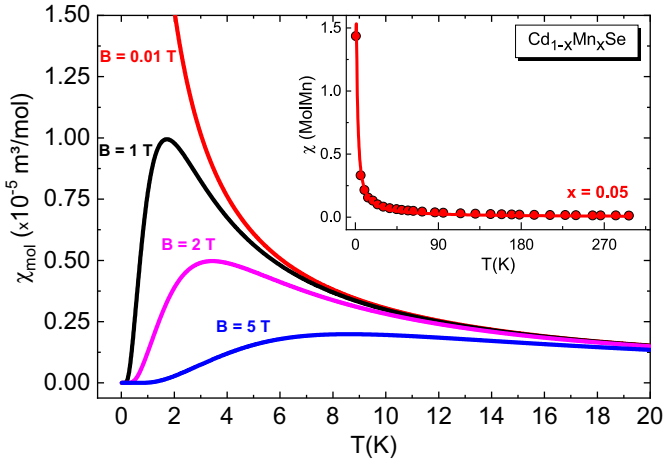


FIG. 2. Main panel: molar magnetic susceptibility $\chi_{\text{mol}} = \mu_0(dM/dB)$ as a function of T at various magnetic fields for the Brillouin paramagnet employing $J = 3/2$. The inset: experimental data of the magnetic susceptibility χ as a function of temperature for the $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ paramagnetic system with 5% concentration of Mn ($x = 0.05$) under a magnetic field of 8.5 kOe. The low- and high-temperature data were taken after zero-field cooling for increasing T ($5 \text{ K} \leq T \leq 35 \text{ K}$) and after field cooling of decreasing T , respectively. The red solid line represents a Curie-like fitting, employing the values of g and J of the $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ system. The obtained number of spins in the system is $N \sim (3 \times 10^{22})$. Data taken from Fig. 1 of Ref. [42]. Further details are discussed in the main text.

where $Z_J(y)$ is the partition function, given by

$$Z_J(y) = \frac{\sinh\left[(2J+1)\frac{y}{2J}\right]}{\sinh\left[\frac{y}{2J}\right]}. \quad (5)$$

Thus, the Helmholtz free energy is as follows:

$$F = -k_B T \ln\left(\frac{\sinh\left[\frac{(2J+1)y}{2J}\right]}{\sinh\left[\frac{y}{2J}\right]}\right). \quad (6)$$

From Eq. (6), the entropy S can be easily calculated

$$S = -\left(\frac{\partial F}{\partial T}\right)_B. \quad (7)$$

The resulting expression for the entropy reads

$$S(y) = k_B [\ln Z_J(y) - y B_J(y)]. \quad (8)$$

Regarding the entropy (S) [Eq. (8)], it is worth recalling the adiabatic demagnetization using a paramagnetic system. Upon applying a magnetic field, the spins are aligned in the direction of B reducing, thus, the entropy of the system. Then, the magnetic field is removed adiabatically, and the temperature of the system decreases. Such a well-known adiabatic demagnetization procedure is frequently employed in order to achieve low temperatures in the microkelvin range.

The calculation of the MCE is straightforward, and the resulting expression for any J regarding the Brillouin paramagnet reads

$$\Gamma_{\text{mag}} = \frac{1}{B}. \quad (9)$$

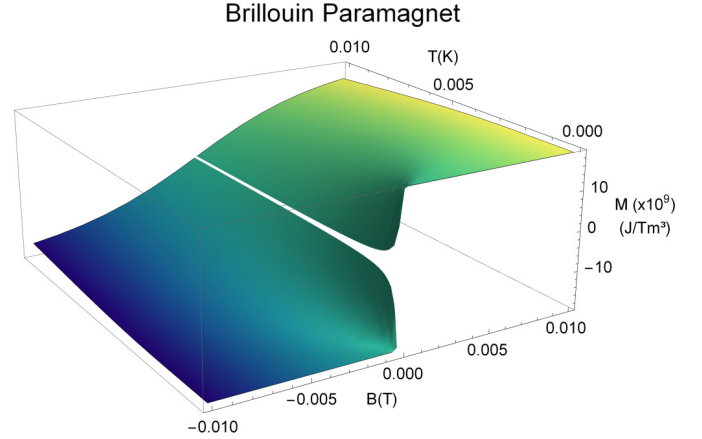


FIG. 3. Magnetization M as a function of temperature ($0 < T < 0.01 \text{ K}$) and magnetic-field ($-0.01 \text{ T} < B < 0.01 \text{ T}$) for the classical Brillouin paramagnet.

From Eq. (9), one can again directly conclude that Γ_{mag} for the Brillouin paramagnet depends only on the magnetic field, and it diverges as $B \rightarrow 0$ at any temperature (see Fig. 3).

The effect of the SO interaction on Γ_{mag} is discussed in the next section.

III. THE SPIN-ORBIT INTERACTION

The interaction between the orbital angular momentum of the nucleus and the electron spin angular momentum is the well-known SO interaction [31]. The latter leads to a splitting of the electrons' energy levels in an atom. Since the energy levels are affected by the SO interaction, it is of our interest to study the influence of the SO interaction on the Grüneisen parameter. Thus, in order to take into account the SO interaction, it is necessary to make use of the Hamiltonian, which considers such interaction. For a $S = 3/2$ system, such a Hamiltonian was already reported in Refs. [43–45], and it has the form

$$H_{\text{spin}} = \mu_B g_{pa} B_z S_z + \mu_B g_{pe} (B_x S_x + B_y S_y) + D S_z^2, \quad (10)$$

where g_{pa} , g_{pe} , and D stand for the gyromagnetic factors of the anisotropic system and the zero-field splitting constant [$D = (5.479 \times 10^{-23}) \text{ J} = 3.97 \text{ K}$], respectively. The matrices S_x , S_y , and S_z can be easily found by the usual operation rules of quantum mechanics. Thus, it is only necessary to diagonalize the resulting operator H_{spin} in order to obtain the eigenenergies. Considering that $B_y = B_z = 0$ and $B_x \neq 0$ as reported in Ref. [45], one obtains

$$H_{\text{spin}} = \begin{pmatrix} \frac{9\hbar^2 D}{4} & \frac{\sqrt{3}\hbar\mu_B g_{pe} B_x}{2} & 0 & 0 \\ \frac{\sqrt{3}\hbar\mu_B g_{pe} B_x}{2} & \frac{\hbar^2 D}{4} & \hbar\mu_B g_{pe} B_x & 0 \\ 0 & \hbar\mu_B g_{pe} B_x & \frac{\hbar^2 D}{4} & \frac{\sqrt{3}\hbar\mu_B g_{pe} B_x}{2} \\ 0 & 0 & \frac{\sqrt{3}\hbar\mu_B g_{pe} B_x}{2} & \frac{9\hbar^2 D}{4} \end{pmatrix},$$

and the diagonalization yields four values of eigenenergies given by

$$\begin{aligned}
 E_1 &= \frac{1}{2}\mu_B g_{pe} B_x + \frac{5}{4}D + \sqrt{\mu_B^2 g_{pe}^2 B_x^2 - D g_{pe} \mu_B B_x + D^2}, \\
 E_2 &= \frac{1}{2}\mu_B g_{pe} B_x + \frac{5}{4}D - \sqrt{\mu_B^2 g_{pe}^2 B_x^2 - D g_{pe} \mu_B B_x + D^2}, \\
 E_3 &= -\frac{1}{2}\mu_B g_{pe} B_x + \frac{5}{4}D + \sqrt{\mu_B^2 g_{pe}^2 B_x^2 + D g_{pe} \mu_B B_x + D^2}, \\
 E_4 &= -\frac{1}{2}\mu_B g_{pe} B_x + \frac{5}{4}D - \sqrt{\mu_B^2 g_{pe}^2 B_x^2 + D g_{pe} \mu_B B_x + D^2}.
 \end{aligned}
 \tag{11}$$

Yet, the free energy for the Brillouin-like paramagnet considering the SO interaction reads

$$\begin{aligned}
 F &= -k_B T \ln \left\{ 2 \exp \left(-\frac{2B g_J \mu_B + 5D}{4k_B T} \right) \right. \\
 &\quad \times \left[\cosh \left(\frac{\sqrt{B^2 g_J^2 \mu_B^2 - B D g_J \mu_B + D^2}}{k_B T} \right) \right. \\
 &\quad \left. + \exp \left(\frac{B g_J \mu_B}{k_B T} \right) \right. \\
 &\quad \left. \times \cosh \left(\frac{\sqrt{B^2 g_J^2 \mu_B^2 + B D g_J \mu_B + D^2}}{k_B T} \right) \right] \left. \right\}. \tag{12}
 \end{aligned}$$

Replacing $D = 0$ in Eq. (12) and simplifying the resultant expression, it is possible to obtain

$$F = -k_B T \ln \left[4 \cosh \left(\frac{y}{2J} \right) \cosh \left(\frac{y}{J} \right) \right].$$

Employing the hyperbolic trigonometric identities and again simplifying the equation,

$$F = -k_B T \ln \left(\frac{\sinh \left[\frac{2y}{J} \right]}{\sinh \left[\frac{y}{2J} \right]} \right), \tag{13}$$

which is the very same free energy of the Brillouin paramagnet in Eq. (6) employing $J = 3/2$ without considering the SO interaction. In other words, the classical Brillouin paramagnet is recovered when the zero-field splitting $D \rightarrow 0$. Since the eigenenergies were found, it is then possible to obtain the partition function and, consequently, the observable quantities, especially the magnetic Grüneisen parameter Γ_{mag} (see the Appendix). In this context, we have performed numerical calculations and made the density and three-dimensional plots of both the magnetization and the magnetic Grüneisen parameter for the Brillouin paramagnet as well as considering the SO interaction. As can be seen from Fig. 4, a comparison between the classical Brillouin system for $S = 3/2$ and SO coupling shows that the magnetization density plot is slightly altered for nonzero D . Figure 4 shows that the magnetization is much more sensitive to magnetic-field changes for any value of temperature in the case of SO interaction. The dashed white lines in the density plots of Fig. 4 were inserted aiming to compare the enhancement of Γ_{mag} for T and $B \rightarrow 0$ (magnetization cone) and its narrowing when SO interactions

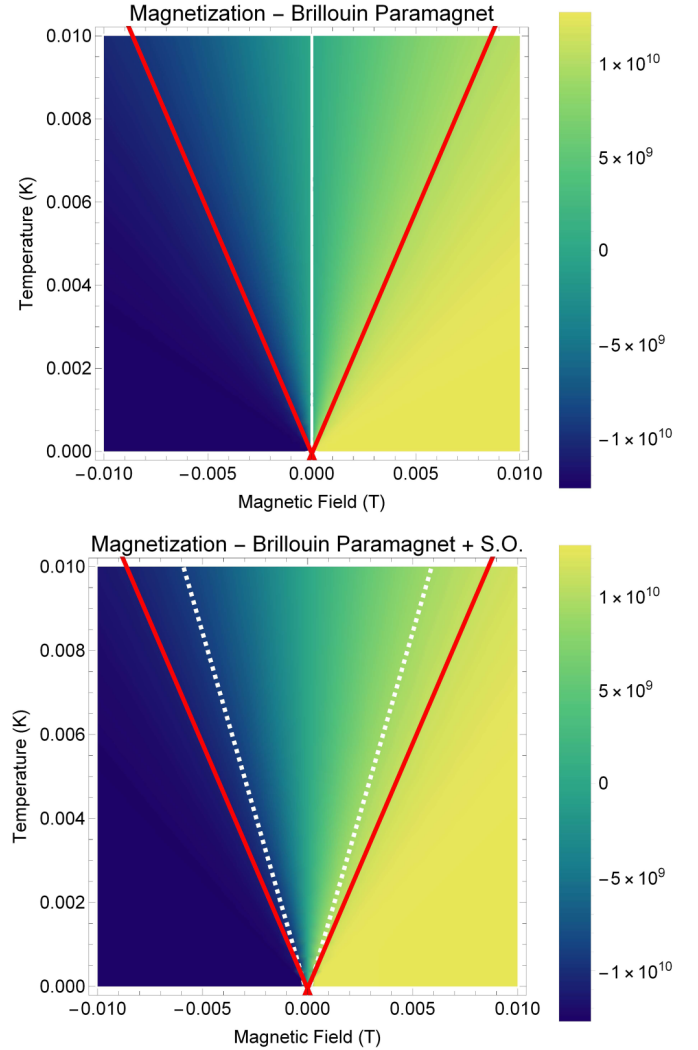


FIG. 4. Density plots of the magnetization as a function of magnetic-field ($-0.01 \text{ T} < B < 0.01 \text{ T}$) and temperature ($T < 0.01 \text{ K}$) for a Brillouin paramagnet with (lower panel) and without (upper panel) considering the SO interaction. The solid red (upper and lower panels) and dashed white (lower panel) lines are guides to the eyes. Details in the main text.

are taken into account. Note that, in the lower panel of Fig. 4, the red solid line (without SO) is plotted together with the white dashed line (considering SO) for a proper comparison. Thus, it is clear that the angular coefficient of the lines is changed when SO interaction is considered, narrowing the magnetization cone. For the case where the SO interaction is lacking, the magnetization presents a weaker dependence regarding magnetic-field changes. From the eigenenergies, we can see that, as the magnetic field approaches zero, the degree of degeneracy of the eigenenergies is two, whereas, for the case where no SO interaction is considered (analogously, for $D = 0$), we have a degree of degeneracy four (all the eigenenergies have the same value and equal zero) (see Fig. 5). The magnetic Grüneisen parameter presents a singular behavior in the vicinity of $T = 0 \text{ K}$ and $B = 0 \text{ T}$ (Fig. 6). In other words, Γ_{mag} diverges as $B \rightarrow 0 \text{ T}$, resembling a fingerprint of a quantum phase transition. At this point, it is important to recall the results reported in Ref. [3] obtained using scaling

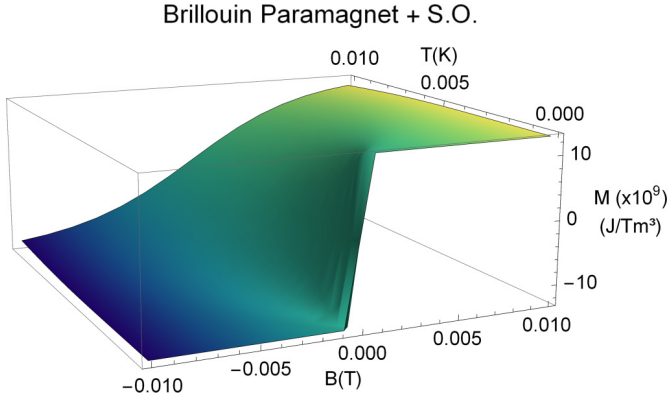


FIG. 5. Magnetization M as a function of temperature ($0 < T < 0.01$ K) and magnetic-field (-0.01 T $< B < 0.01$ T) for the Brillouin paramagnet considering SO interaction. Details in the main text.

arguments for any QCP tuned by a magnetic field,

$$\Gamma_{B,cr}(T \rightarrow 0) = -G \frac{1}{(B - B_c)}, \quad (14)$$

where cr refers to the critical contribution of Γ_B , B_c is the critical magnetic field and G is a universal prefactor. Note that Eqs. (14) and (9) are quite similar. The presence of an additional pseudoenergy scale, namely, D gives rise to a temperature-dependent magnetic Grüneisen parameter (cf. Fig. 6), and it diverges upon approaching $B = 0$ T and $T = 0$ K.

IV. THE ONE-DIMENSIONAL ISING MODEL UNDER A LONGITUDINAL FIELD

For the 1DI model, all the physical quantities discussed in this section are given per mole of particles. For the sake of completeness, we start recalling the 1DI model and its key equations [31] where the Hamiltonian for a linear chain of N

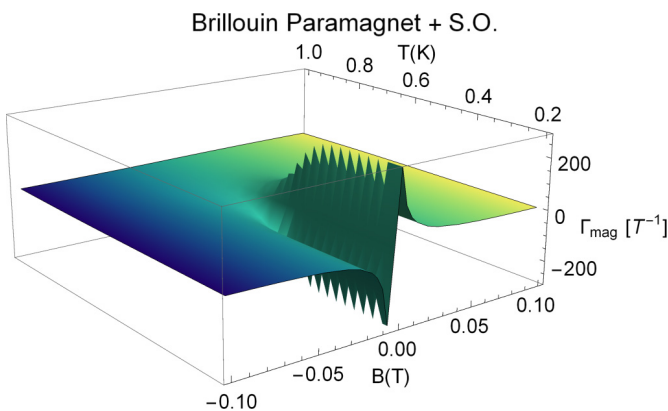


FIG. 6. Three-dimensional plot of the magnetic Grüneisen parameter Γ_{mag} as a function of magnetic field and temperature for the Brillouin paramagnet considering the SO interaction. The depicted zigzag is a consequence of the numerical calculation and, thus, not intrinsic.

spins is expressed by the form

$$H = \sum_{i=1}^N J_{i,i+1} S_i S_{i+1} - B \sum_{i=1}^N S_i, \quad (15)$$

where $J_{i,i+1}$ is the coupling constant between the i th and the $i + 1$ sites and S_i refers to the spin of the i th site. Nevertheless, the S_i terms are normalized to unity so that we can analyze the energy scales and the coupling term without adding numerical constant contributions. Also, the magnetization is given by

$$M_{1DI}(T, B) = \mu_B \frac{\sinh(\beta \mu_B B)}{[\cosh^2(\beta \mu_B B) - 2e^{2\beta J} \sinh(2\beta J)]^{1/2}}, \quad (16)$$

where $\beta = 1/k_B T$ and J is the coupling constant between two neighbor spins. From Eq. (16), one can deduce that, for the 1DI model, spontaneous magnetization is not possible, namely, $M(T \neq 0, B = 0) = 0$. It is now worth analyzing the 1DI magnetic susceptibility, which reads [31]

$$\chi_{1DI}(T, B) = \beta \mu_B^2 \frac{\cosh(\beta \mu_B B) [1 - 2e^{-2\beta J} \sinh(2\beta J)]}{[\cosh^2(\beta \mu_B B) - 2e^{-2\beta J} \sinh(2\beta J)]^{3/2}}. \quad (17)$$

For vanishing magnetic-field $\chi(T, B \rightarrow 0) = \beta \mu_B^2 e^{2\beta J}$, i.e., for $B \rightarrow 0$ and $T \rightarrow 0$, χ diverges as expected for a QCP. In other words, for the 1DI model at $T = 0$ K, a vanishing small external magnetic field suffices to produce long-range magnetic ordering. The specific heat at zero field is given by

$$C_{B=0T} = k_B \frac{\beta^2 J^2}{\cosh^2(\beta J)}. \quad (18)$$

In order to perform an analysis of the 1DI model for generic B and T , the Helmholtz free energy is calculated employing the expression [1],

$$F(B, T) = -J - k_B T \ln[\eta + \sqrt{\tau^2 + \vartheta}], \quad (19)$$

where η , τ , and ϑ stand for

$$\vartheta = \exp\left(\frac{-4J}{k_B T}\right); \quad \eta = \cosh\left(\frac{\mu_B B}{k_B T}\right); \quad \tau = \sinh\left(\frac{\mu_B B}{k_B T}\right). \quad (20)$$

Figure 7 shows the behavior of the free energy for different applied magnetic fields as a function of temperature. It can be seen that, if both J and B are held constant, an increase in the temperature causes a decrease in the free energy. We also introduce an equivalent definition of the MCE via Maxwell relations, namely, the magnetic Grüneisen parameter [19],

$$\Gamma_{mag} = -\frac{(\partial M / \partial T)_B}{C_B}, \quad (21)$$

where

$$C_B = T \left(\frac{\partial S}{\partial T} \right)_B. \quad (22)$$

Since the magnetization was already presented, the calculation of Γ_{mag} and the obtainment of the MCE for the 1DI model under a longitudinal field is also straightforward. From Eq. (16), we can see that, as $B \rightarrow 0$, also $M \rightarrow 0$, which means that there is no spontaneous magnetization at finite

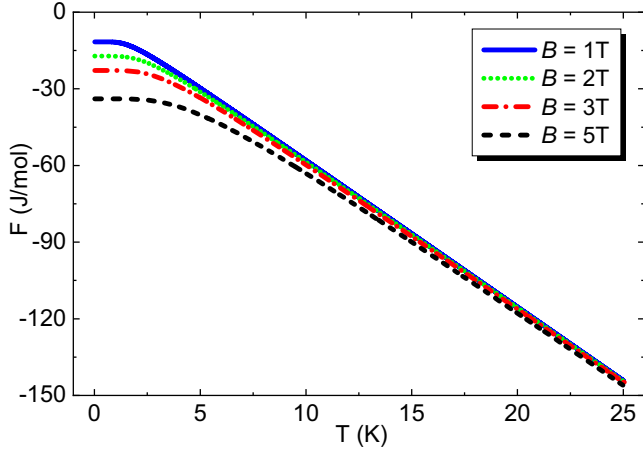


FIG. 7. The Helmholtz free-energy F [Eq. (19)] as a function of temperature for various magnetic fields, cf. label. From the data, it can be seen that, as the temperature increases, the free energy decreases. Further details in the main text.

temperature for the 1DI model as previously stated. Figures 8 and 9 show the behavior of the magnetization when T is held constant and B varies and when B is held constant and T varies, respectively. It is possible already to detect the absence of long-range magnetic order in the system. The Mermin-Wagner theorem ensures that, for the 1DI model, the spontaneous magnetization is zero for any finite temperature value. If the system would present spontaneous magnetization, in Fig. 8 it would be possible to see a discontinuity in the magnetization at $B = 0$ for a certain range of temperature values, given by $T < T_c$, which would be characteristic of a phase transition from ferromagnetic to paramagnetic behavior. However, this behavior is not present in the 1DI model. Thus, we can calculate analytically the Grüneisen parameter. The derivatives can be performed straightforwardly yielding

$$S = k_B \left[\frac{\Sigma}{k_B T (\sqrt{\vartheta} + \tau^2 + \eta)} + \ln(\sqrt{\vartheta} + \tau^2 + \eta) \right], \quad (23)$$

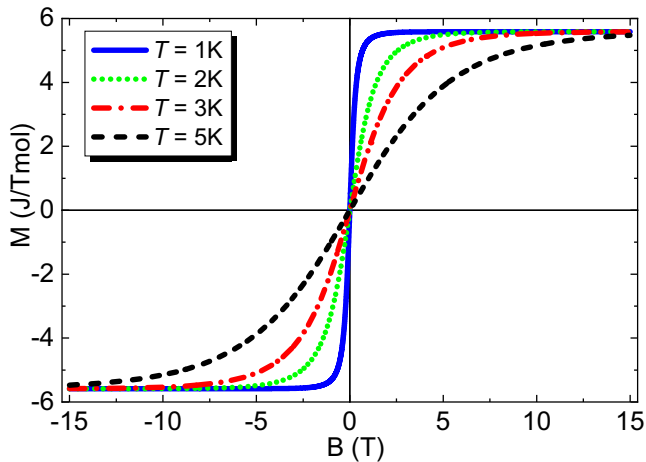


FIG. 8. Magnetization M as a function of magnetic-field B at various temperatures as indicated in the label. Further details are given in the main text.

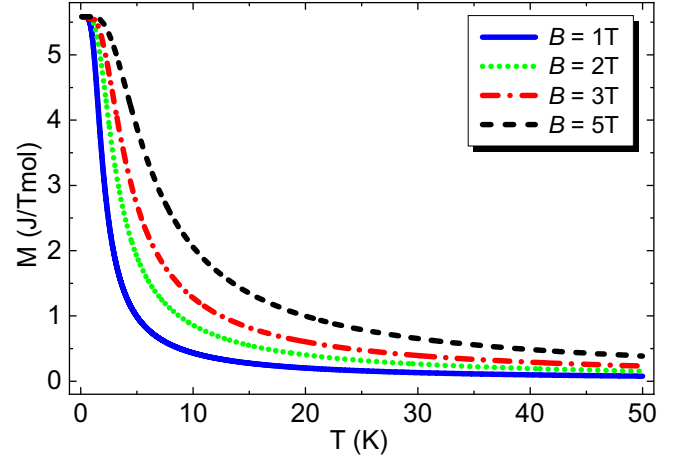


FIG. 9. Magnetization M as a function of temperature T under various values of magnetic field as indicated in the label. Further details are given in the main text.

$$\left(\frac{\partial M}{\partial T} \right)_B = - \frac{2J\tau + B\eta}{T^2 \sqrt{\vartheta} + \tau^2 (k_B \vartheta^{-1} \tau^2 + k_B)}, \quad (24)$$

$$C_B = \left[\frac{\Sigma}{T(\sqrt{\vartheta} + \tau^2 + \eta)} \right] + \frac{T\Upsilon}{\Phi\varsigma} - \frac{\Theta T \Sigma}{\varsigma^2}, \quad (25)$$

where the additional parameters Υ , Φ , Θ , ς , and Σ were introduced purely for compactness as follows:

$$\begin{aligned} \Upsilon = & 16J^2\tau^2 + 8J^2\vartheta - \frac{1}{2}D^2\vartheta^{-1}\sinh^2\left(\frac{2\mu_B B}{k_B T}\right) \\ & + D^2\vartheta^{-1}\tau \sinh\left(\frac{2\mu_B B}{k_B T}\right)\sqrt{\vartheta} + \tau^2 \\ & + 2B^2 \cosh\left(\frac{2\mu_B B}{k_B T}\right)(\vartheta^{-1}\tau^2 + 1) \\ & + 2B^2\eta\sqrt{\vartheta} + \tau^2 + 4JB \sinh\left(\frac{2\mu_B B}{k_B T}\right), \end{aligned} \quad (26)$$

$$\Phi = 2T^2\sqrt{\vartheta} + \tau^2(k_B\vartheta^{-1}\tau^2 + k_B), \quad (27)$$

$$\Theta = \frac{2\epsilon\vartheta - \frac{1}{2}B \sinh\left(\frac{2\mu_B B}{k_B T}\right)}{k_B T \sqrt{\vartheta} + \tau^2} + \sqrt{\vartheta} + \tau^2 - \frac{B\tau}{k_B T^2}, \quad (28)$$

$$\varsigma = T(\sqrt{\vartheta} + \tau^2 + \eta), \quad (29)$$

$$\Sigma = \frac{\vartheta \left[2J - \frac{1}{2}B\vartheta^{-1} \sinh\left(\frac{2\mu_B B}{k_B T}\right) \right]}{\sqrt{\vartheta} + \tau^2} - D\tau. \quad (30)$$

It can be seen that the MCE for the 1DI model is far from trivial and we study its behavior by maintaining B and J constant and varying the temperature, cf. Fig. 10. Thus, Γ_{mag} for the 1DI model is given by the expression,

$$\Gamma_{\text{mag}} = \frac{\frac{2J\tau + B\eta}{T^2 \sqrt{\vartheta} + \tau^2 (k_B \vartheta^{-1} \tau^2 + k_B)}}{\left[\frac{\Sigma}{T(\sqrt{\vartheta} + \tau^2 + \eta)} \right] + \frac{T\Upsilon}{\Phi\varsigma} - \frac{T\Theta\Sigma}{\varsigma^2}}. \quad (31)$$

It is possible to make a Taylor series expansion for Γ_{mag} for the case of the 1DI model around $B = 0$ for a fixed temperature

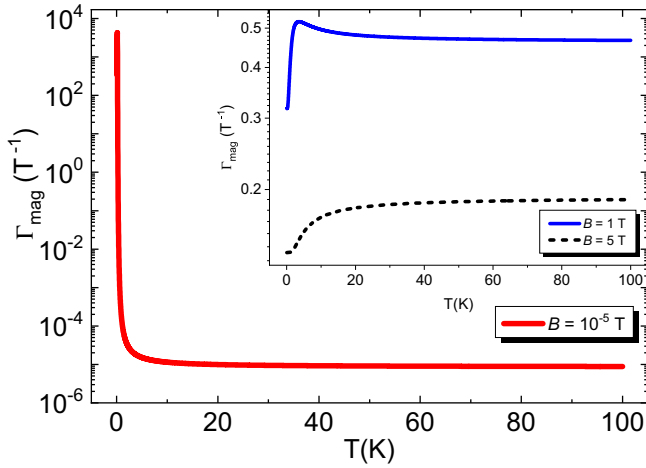


FIG. 10. Main panel: the magnetic Grüneisen parameter Γ_{mag} versus T under low-field ($B = 10^{-5}$ T). Note the logarithmic scale. As $T \rightarrow 0$ K, Γ_{mag} diverges. The absence of a classical phase transition at finite temperatures can be interpreted as a direct consequence of the Mermin-Wagner theorem. The inset: Γ_{mag} versus T for $B = 1$ and 5 T. Further details in the main text.

T (see Fig. 11). The obtained expression reads

$$\Gamma_{\text{mag}}(B, T) = \left[\frac{(e^{2J/k_B T} + 1)^2 \mu_B^2 (2J + k_B T)}{4J^2 k_B T} \right] B + O(B^3), \quad (32)$$

where $O(B^3)$ represents the higher-order terms in the expansion. For $T \rightarrow 0$ K, Γ_{mag} diverges, and a discontinuity takes place at $T = 0$ K and $B = 0$ T, cf. Fig. 12. From Eq. (32), it is shown that the mathematical function describing Γ_{mag} for the 1DI model is odd with respect to the magnetic-field

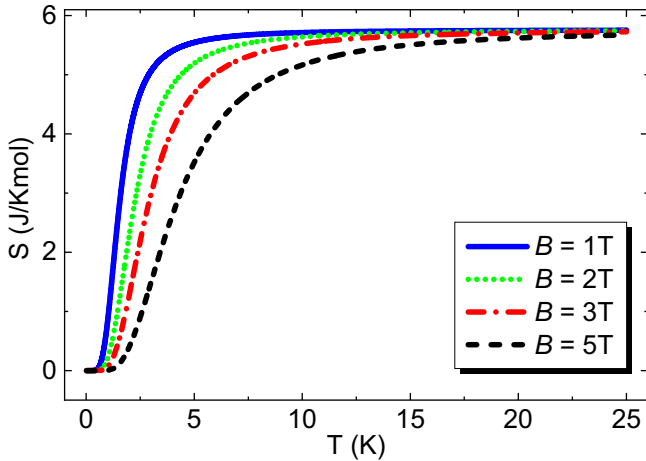


FIG. 11. Entropy S as a function of temperature T for various values of magnetic-field B , cf. indicated in the label. It can be seen that the entropy increases with temperature, which is the expected behavior of the system, i.e., the magnetic disorder is increased upon increasing the thermal energy. Another interesting aspect of the entropy function is its saturation point. When the temperature is sufficiently increased, the entropy reaches a constant value. The required temperature to the saturation increases as the magnetic coupling constant J is increased.

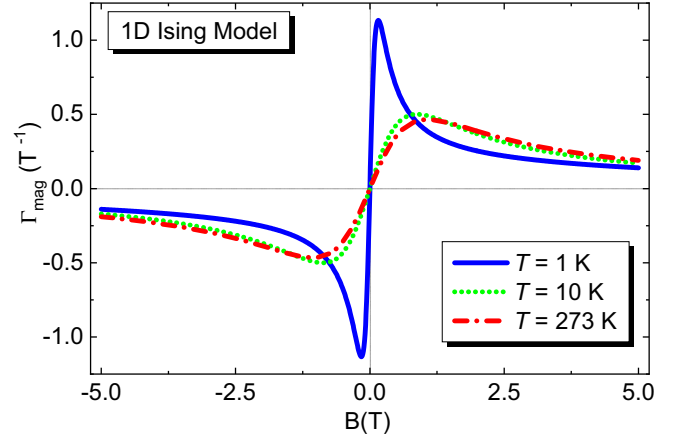


FIG. 12. The magnetic Grüneisen parameter Γ_{mag} as a function of the magnetic-field B for various temperatures (see the label) for the 1DI model under the longitudinal field. By tuning B between positive and negative values, Γ_{mag} changes sign.

B . Hence, Eq. (32) also explains the obtained symmetrical behavior of Γ_{mag} upon varying the magnetic-field B from negative to positive values, cf. Fig. 12. In order to analytically demonstrate the asymptotic equivalence of Γ_{mag} for the 1DI and the Brillouin model, it is possible to make a change in the temperature variable T to $1/T$ and make an expansion in a Taylor series around $1/T \rightarrow 0$ [46]. Thus, the expression of Γ_{mag} for the 1DI model is simplified and is expressed by

$$\Gamma_{\text{mag}}(B, T \rightarrow \infty) = \frac{\mu_B^2 B}{J^2 + \mu_B^2 B^2}. \quad (33)$$

In this context, when $J = 0$, the Γ_{mag} for the Brillouin model is elegantly recovered, namely, $1/B$ [Eq. (9)]. This means that, at high temperatures, and upon neglecting the magnetic coupling between the nearest-neighbor spins, we have shown analytically that the two magnetic models are equivalent. Similarly, it is possible to make the very same expansion for Γ_{mag} in the case of the Brillouin model upon considering the SO interaction,

$$\Gamma_{\text{mag}}(B, T \rightarrow \infty) = \frac{5g_J^2 \mu_B^2 B}{4D^2 + 5g_J^2 \mu_B^2 B^2}. \quad (34)$$

Upon comparing Eqs. (33) and (34), it is clear that both expressions have the same mathematical structure except for the constant term J^2 . Making $J = \sqrt{4/5}D/g_J$ and replacing it in Eq. (33), it can be shown that the two models are also equivalent in the asymptotic regime, namely, for $1/T \rightarrow 0$. Such mathematical similarity in the regime of high temperatures is a direct consequence of the dominant effects from thermal fluctuations, and, obviously, this does not mean that the models are physically equivalent. Yet, still considering Eq. (34), it is clear that for $D \rightarrow 0$, Eq. (9) is nicely restored. Summarizing the results obtained for the longitudinal 1DI model: (i) It does not present any classical critical behavior for any finite value of temperature as a consequence of the Mermin-Wagner theorem, and (ii) for $T \rightarrow 0$ K, it is tempting to say that the system shows intrinsic quantum critical behavior. It is important to emphasize that the Grüneisen

parameter cannot be calculated at T exactly equal to 0 K since the corresponding function is not determined at this point.

V. CONCLUDING REMARKS

Grüneisen, in 1908, realized that the volume dependence of the vibrational energy must be taken into account in order to explain thermal expansion. Slowly but steadily, the Grüneisen parameter has been incorporated as a thermodynamic coefficient, both in thermodynamical textbooks and in experimental physics; and when measured, it can provide information on other thermodynamic coefficients as shown in Refs. [28,47]. As a second step from our previous work [28], we have considered the magnetic analog of the Grüneisen parameter as a tool to further probe magnetic systems, in particular, at low temperatures when quantum phase transitions are relevant. In the Introduction, we mentioned several exotic manifestations of matter where the Grüneisen parameter could be measured. Following the Introduction, we computed this parameter for several known theoretical models, namely, the Brillouin paramagnet, yielding a temperature-independent Grüneisen parameter, proportional to the inverse of the applied magnetic field; SO interaction model yields a diverging Grüneisen parameter as the temperature goes to zero; and the longitudinal 1D Ising model, known not to exhibit any kind of phase transition at finite temperature as a consequence of the well-known Mermin-Wagner theorem. Also, we did find an equivalence at high temperatures between the 1D Ising model with a Brillouin paramagnet with vanishing coupling constant J and with or without a SO interaction included on the latter. Thus, the magnetic Grüneisen parameter can be seen as a smoking gun when we probe critical points. The relevance

of the mutual interactions for an ideal paramagnet in the limit B and $T \rightarrow 0$ was briefly discussed. Future work will consider other systems where the thermodynamic coefficients are not readily computed in a complete analytic fashion.

ACKNOWLEDGMENTS

M.d.S. acknowledges financial support from the São Paulo Research Foundation-Fapesp (Grants No. 2011/22050-4 and No. 2017/07845-7), the National Council of Technological and Scientific Development-CNPq (Grant No. 302498/2017-6), T.U.V.S.O.T.E, the Austrian Academy of Science ÖAW for the JESH Fellowship, Professor S. Sariciftci (LIOS-JKU) and Professor Reshaf Tenne (Weizmann Institute) for the hospitality. A.N. and M.d.S. gratefully acknowledge funding by the Austrian Science Fund (FWF)-Project No. P26164-N20 during the early stage of this work. M.d.S. thanks P. Gegenwart for calling our attention to Ref. [35]. A.C.S. acknowledges financial support from the National Council of Technological and Scientific Development-CNPq (Grant No. 305668/2018-8).

G.O.G. and L.S. contributed equally to this work.

APPENDIX

For the Brillouin-like paramagnet considering SO interaction, the magnetic Grüneisen parameter Γ_{mag} reads

$$\Gamma_{\text{mag}} = \frac{a(T, B)}{c(T, B)}, \quad (\text{A1})$$

where

$$\begin{aligned} a(T, B) &= -g_J \mu_B [\sinh[A] \{F(2D^2 - 3BDg_J \mu_B + 4B^2 g_J^2 \mu_B^2) \cosh[C] + 2Bg_J \mu_B (D^2 + 2B^2 g_J^2 \mu_B^2) \sinh[C]\} \\ &\quad - G \cosh[A] (2D^2 \sinh[C] + Bg_J \mu_B \{6F \cosh[C] + (3D + 4Bg_J \mu_B) \sinh[C]\}) \\ &\quad - 2FG \{2Bg_J \mu_B \cosh[(Bg_J \mu_B)/(k_B T)] + D \sinh[(Bg_J \mu_B)/(k_B T)]\}], \\ c(T, B) &= 2FG (\cosh[A] \{(2D^2 + 3B^2 g_J^2 \mu_B^2) \cosh[C] + 2BF g_J \mu_B \sinh[C]\} + 2\{(D^2 + B^2 g_J^2 \mu_B^2) \cosh[(Bg_J \mu_B)/(k_B T)] \\ &\quad - G \sinh[A] (Bg_J \mu_B \cosh[C] + F \sinh[C]) + BDg_J \mu_B \sinh[(Bg_J \mu_B)/(k_B T)]\}), \\ A &= \frac{\sqrt{B^2 g_J^2 \mu_B^2 - Bg_J \mu_B D + D^2}}{k_B T}, \\ C &= \frac{\sqrt{B^2 g_J^2 \mu_B^2 + Bg_J \mu_B D + D^2}}{k_B T}, \\ F &= \sqrt{B^2 g_J^2 \mu_B^2 + Bg_J \mu_B D + D^2}, \\ G &= \sqrt{B^2 g_J^2 \mu_B^2 - Bg_J \mu_B D + D^2}. \end{aligned}$$

- [1] K. Huang, *Statistical Mechanics* (Wiley, New York, 1987).
- [2] S. Sachdev, *Quantum Phase Transitions* (Cambridge University Press, Cambridge, U.K., 2001).
- [3] L. Zhu, M. Garst, A. Rosch, and Q. Si, Universally Diverging Grüneisen Parameter and the Magnetocaloric Effect Close to Quantum Critical Points, *Phys. Rev. Lett.* **91**, 066404 (2003).

- [4] R. Küchler, N. Oeschler, P. Gegenwart, T. Cichorek, K. Neumaier, O. Tegus, C. Geibel, J. A. Mydosh, F. Steglich, L. Zhu, and Q. Si, Divergence of the Grüneisen Ratio at Quantum Critical Points in Heavy Fermion Metals, *Phys. Rev. Lett.* **91**, 066405 (2003).
- [5] A. Steppke, R. Küchler, S. Lausberg, E. Lengyel, L. Steinke, R. Borth, T. Lhmann, C. Krellner, M. Nicklas, C. Geibel,

- F. Steglich, and M. Brando, Ferromagnetic quantum critical point in the heavy-fermion metal $\text{YbNi}_4(\text{P}_{1-x}\text{As}_x)_2$, *Science* **339**, 933 (2013).
- [6] S. Paschen, T. Luhmann, S. Wirth, P. Gegenwart, O. Trovarelli, C. Geibel, F. Steglich, P. Coleman, and Q. Si, Hall-effect evolution across a heavy-fermion quantum critical point, *Nature (London)* **432**, 881 (2004).
- [7] H. V. Löhneysen, A. Rosch, M. Vojta, and P. Wölfle, Fermi-liquid instabilities at magnetic quantum phase transitions, *Rev. Mod. Phys.* **79**, 1015 (2007).
- [8] S. Kambe, H. Sakai, Y. Tokunaga, G. Lapertot, T. D. Matsuda, G. Knebel, J. Flouquet, and R. E. Walstedt, Degenerate Fermi and non-Fermi liquids near a quantum critical phase transition, *Nat. Phys.* **10**, 840 (2011).
- [9] M. A. Tanatar, J. Paglione, C. Petrovic, and L. Taillefer, Anisotropic violation of the Wiedemann-Franz law at a quantum critical point, *Science* **316**, 1320 (2007).
- [10] M. Klanjšek, A critical test of quantum criticality, *Physics* **7**, 74 (2014).
- [11] P. Gegenwart, Q. Si, and F. Steglich, Quantum criticality in heavy-fermion metals, *Nat. Phys.* **4**, 186 (2008).
- [12] L. Squillante *et al.* (unpublished).
- [13] M. E. Zhitomirsky and A. Honecker, Magnetocaloric effect in one-dimensional antiferromagnets, *J. Stat. Mech.: Theory Exp.* (2004) P07012.
- [14] A. W. Kinross, M. Fu, T. J. Munsie, H. A. Dabkowska, G. M. Luke, Subir Sachdev, and T. Imai, Evolution of Quantum Fluctuations Near the Quantum Critical Point of the Transverse Field Ising Chain System CoNb_2O_6 , *Phys. Rev. X* **4**, 031008 (2014).
- [15] L. Savary, E.-G. Moon, and L. Balents, New Type of Quantum Criticality in the Pyrochlore Iridates, *Phys. Rev. X* **4**, 041027 (2014).
- [16] L. Mittelstädt, M. Schmidt, Z. Wang, F. Mayr, V. Tsurkan, P. Lukenheimer, D. Ish, L. Balents, J. Deisenhofer, and A. Loidl, Spin-orbition and quantum criticality in FeSc_2S_4 , *Phys. Rev. B* **91**, 125112 (2015).
- [17] F. A. Dessotti, L. S. Ricco, Y. Marques, L. H. Guessi, M. Yoshida, M. S. Figueira, M. de Souza, Pasquale Sodano, and A. C. Seridonio, Unveiling Majorana quasiparticles by a quantum phase transition: Proposal of a current switch, *Phys. Rev. B* **94**, 125426 (2016).
- [18] Y. Matsumoto, S. Nakatsuji, K. Kuga, Y. Karaki, N. Horie, Y. Shimura, T. Sakakibara, A. H. Nevidomskyy, and P. Coleman, Quantum criticality without tuning in the mixed valence compound $\beta\text{-YbAlB}_4$, *Science* **331**, 316 (2011).
- [19] M. Garst and A. Rosch, Sign change of the Grüneisen parameter and magnetocaloric effect near quantum critical points, *Phys. Rev. B* **72**, 205129 (2005).
- [20] Y. Tokiwa, T. Radu, C. Geibel, F. Steglich, and P. Gegenwart, Divergence of the Magnetic Grüneisen Ratio at the Field-Induced Quantum Critical Point in YbRh_2Si_2 , *Phys. Rev. Lett.* **102**, 066401 (2009).
- [21] N. A. Fortune, S. T. Hannahs, Y. Yoshida, T. E. Sherline, T. Ono, H. Tanaka, and Y. Takano, Cascade of Magnetic-Field-Induced Quantum Phase Transitions in a Spin- $\frac{1}{2}$ Triangular-Lattice Antiferromagnet, *Phys. Rev. Lett.* **102**, 257201 (2009).
- [22] S. Zaum, K. Grube, R. Schäfer, E. D. Bauer, J. D. Thompson, and H. v. Löhneysen, Towards the Identification of a Quantum Critical Line in the (p, b) Phase Diagram of CeCoIn_5 with Thermal-Expansion Measurements, *Phys. Rev. Lett.* **106**, 087003 (2011).
- [23] Y. Tokiwa, E. D. Bauer, and P. Gegenwart, Zero-Field Quantum Critical Point in CeCoIn_5 , *Phys. Rev. Lett.* **111**, 107003 (2013).
- [24] K. Deguchi, S. Matsukawa, N. K. Sato, T. Hattori, K. Ishida, H. Takakura, and T. Ishimasa, Quantum critical state in a magnetic quasicrystal, *Nat. Mater.* **11**, 1013 (2012).
- [25] M. de Souza, A. Brühl, C. Strack, B. Wolf, D. Schweitzer, and M. Lang, Anomalous Lattice Response at the Mott Transition in a Quasi-2D Organic Conductor, *Phys. Rev. Lett.* **99**, 037003 (2007).
- [26] L. Bartosch, M. de Souza, and M. Lang, Scaling Theory of the Mott Transition and Breakdown of the Grüneisen Scaling Near a Finite-Temperature Critical End Point, *Phys. Rev. Lett.* **104**, 245701 (2010).
- [27] M. de Souza and L. Bartosch, Probing the Mott physics in $\kappa\text{-(BEDT-TTF)}_2\text{X}$ salts via thermal expansion, *J. Phys.: Condens. Matter* **27**, 053203 (2015).
- [28] M. de Souza, P. Menegasso, R. Paupitz, A. Seridonio, and R. E. Lagos, Grüneisen parameter for gases and superfluid helium, *Eur. J. Phys.* **37**, 055105 (2016).
- [29] D. Bitko, T. F. Rosenbaum, and G. Aeppli, Quantum Critical Behavior for a Model Magnet, *Phys. Rev. Lett.* **77**, 940 (1996).
- [30] J. Steinberg, N. P. Armitage, F. Essler, and S. Sachdev, NMR relaxation in Ising spin chains, *Phys. Rev. B* **99**, 035156 (2019).
- [31] W. Nolting and A. Ramakanth, *Quantum Theory of Magnetism* (Springer, Berlin, Heidelberg, 2009).
- [32] N. D. Mermin and H. Wagner, Absence of Ferromagnetism or Antiferromagnetism in One- or Two-Dimensional Isotropic Heisenberg Models, *Phys. Rev. Lett.* **17**, 1133 (1966).
- [33] J. Zhang, F. M. Cucchietti, C. M. Chandrashekar, M. Laforest, C. A. Ryan, M. Ditty, A. Hubbard, J. K. Gamble, and R. Laamme, Direct observation of quantum criticality in Ising spin chains, *Phys. Rev. A* **79**, 012305 (2009).
- [34] F. Franchini, J. Cui, L. Amico, H. Fan, M. Gu, V. Korepin, L. C. Kwek, and V. Vedral, Local Convertibility and the Quantum Simulation of Edge States in Many-Body Systems, *Phys. Rev. X* **4**, 041028 (2014).
- [35] P. Gegenwart, Classification of materials with divergent magnetic Grüneisen parameter, *Philos. Mag.* **97**, 3415 (2017).
- [36] R. Baierlein, *Thermal Physics* (Cambridge University Press, Cambridge, U.K., 1999).
- [37] L. Onsager, Crystal statistics. I. A two-dimensional model with an order-disorder transition, *Phys. Rev.* **65**, 117 (1944).
- [38] J. Strečka, H. Čenčariková, and M. Jaščur, Exact results of the one-dimensional transverse Ising model in an external longitudinal magnetic field, *Acta Electrotechnica et Informatica* **2**, 107 (2002).
- [39] R. J. Baxter, *Exactly Solved Models in Statistical Mechanics* (Dover, Mineola, NY, 1982).
- [40] R. K. Pathria, *Statistical Mechanics*, second ed. (Butterworth-Heinemann, Oxford, 1996).
- [41] C. B. P. Finn, *Thermal Physics*, second ed., Physics and Its Applications (Taylor & Francis, Boca Raton, FL, 1993).
- [42] S. B. Oseroff, Magnetic susceptibility and EPR measurements in concentrated spin-glasses: $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ and $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$, *Phys. Rev. B* **25**, 6584 (1982).

- [43] P. Koidl, Optical absorption of Co^{2+} in ZnO, [Phys. Rev. B **15**, 2493 \(1977\)](#).
- [44] P. Sati, R. Hayn, R. Kuzian, S. Regnier, S. Schäfer, A. Stepanov, C. Morhain, C. Deparis, M. Laügt, M. Goiran, and Z. Golacki, Magnetic Anisotropy of Co^{2+} as Signature of Intrinsic Ferromagnetism in ZnO:Co, [Phys. Rev. Lett. **96**, 017203 \(2006\)](#).
- [45] A. Ney, T. Kammermeier, K. Ollefs, S. Ye, V. Ney, T. C. Kaspar, S. A. Chambers, F. Wilhelm, and A. Rogalev, Anisotropic paramagnetism of Co-doped ZnO epitaxial films, [Phys. Rev. B **81**, 054420 \(2010\)](#).
- [46] G. B. Arfken, H. J. Weber, and F. E. Harris, *Mathematical Methods for Physicists: A Comprehensive Guide*, 7th ed. (Academic, Waltham, MA, 2013).
- [47] G. O. Gomes, H. E. Stanley, and M. de Souza, Enhanced Grüneisen parameter in supercooled water, [Sci. Rep. **9**, 12006 \(2019\)](#).



OPEN

Unveiling the Physics of the Mutual Interactions in Paramagnets

Lucas Squillante¹, Isys F. Mello¹, Gabriel O. Gomes², A. C. Seridonio³, R. E. Lagos-Monaco¹, H. Eugene Stanley⁴ & Mariano de Souza¹✉

In real paramagnets, there is always a subtle many-body contribution to the system's energy, which can be regarded as a small effective local magnetic field (B_{loc}). Usually, it is neglected, since it is very small when compared with thermal fluctuations and/or external magnetic fields (B). Nevertheless, as both the temperature (T) $\rightarrow 0$ K and $B \rightarrow 0$ T, such many-body contributions become ubiquitous. Here, employing the magnetic Grüneisen parameter (Γ_{mag}) and entropy arguments, we report on the pivotal role played by the mutual interactions in the regime of ultra-low- T and vanishing B . Our key results are: *i*) absence of a genuine zero-field quantum phase transition due to the presence of B_{loc} ; *ii*) connection between the canonical definition of temperature and Γ_{mag} ; and *iii*) possibility of performing adiabatic magnetization by only manipulating the mutual interactions. Our findings unveil unprecedented aspects emerging from the mutual interactions.

Magnetic excitations in solids have been broadly investigated in the past decades, being crucial to the understanding of exotic physical phenomena such as superconductivity¹ and magnetic field induced quantum phase transitions², just to mention a few examples. It is well-known that the behavior of paramagnetic metals and insulators are nicely described, respectively, by the Pauli paramagnetism and Brillouin-like model. Such approaches are based on a spin gas scheme, i.e., interactions between magnetic moments are not taken into account and thus the system is treated as an *ideal* paramagnet. However, in *real* paramagnets the magnetic dipolar interactions between adjacent spins are always present, being usually neglected. Although the mutual interactions, also called zero-field splitting^{3,4} and *champ moléculaire*^{5,6}, have been broadly mentioned in the literature^{7–17}, a detailed discussion about their role in the magnetic properties of solids in the regime of ultra low-temperatures and vanishing external magnetic field is still lacking. Nowadays, exotic manifestations of matter, like non-Fermi-liquid behavior and unconventional superconductivity^{18–21}, emerging in the immediate vicinity of a quantum critical point (QCP), have been attracting high interest of the community. It is well-established that for a pressure-induced QCP^{22,23}, as well as for a finite temperature (T) pressure-induced critical point^{24–26}, the Grüneisen ratio, i.e., the ratio between thermal expansivity and specific heat at constant pressure, is enhanced upon approaching the critical values of the tuning parameter and it diverges right at the critical point. For a magnetic field-induced QCP²⁷ the analogous physical quantity to the Grüneisen ratio is the so-called magnetic Grüneisen parameter, hereafter Γ_{mag} ^{22,28,29}. The enhancement of both the Grüneisen ratio and Γ_{mag} in the immediate vicinity of a magnetic field-induced QCP is merely a direct consequence of the high entropy accumulation in that region^{22,23}, which in turn is related to the fluctuations of the order parameter. Also, it is well-known that Γ_{mag} quantifies the magneto-caloric effect^{30,31}, which in turn enables to change the temperature of a system upon varying adiabatically the external applied magnetic field^{22,28,29}. The fingerprints of a genuine magnetic field-induced QCP, besides the gradual suppression of an order parameter (or energy scale) at the QCP [Fig. 1a)], are: *i*) the divergence of Γ_{mag} for $T \rightarrow 0$ K at the critical magnetic field B_c ; *ii*) the sign-change of Γ_{mag} upon crossing B_c , and *iii*) its typical scaling behavior in the form $T/(B - B_c)^\epsilon$, where B is the external applied magnetic field and ϵ the scaling exponent^{23,32}. Particular attention has been paid to the so-called zero-field quantum criticality [Fig. 1b)], i.e., the system is inherently quantum critical ($B_c = 0$ T) and thus no field-sweep is required for achieving the QCP. Examples include several materials, such as YbCo_2Ge_4 ³³, $\beta\text{-YbAlB}_4$ ³⁴, and Au-Al-Yb ³⁵. In the case of $\beta\text{-YbAlB}_4$, in particular, the understanding of possible zero-field quantum criticality^{34,36,37} and the emergence of superconductivity at $T_c = 80$ mK^{38,39} remains elusive^{40,41}. Interestingly, although $\beta\text{-YbAlB}_4$ is metallic^{38,39}, its magnetic susceptibility displays a typical Curie-Weiss-like behavior³⁴ and it is thus evident that resultant local magnetic moments are still present into the system at very low

¹São Paulo State University (Unesp), IGCE - Physics Department, Rio Claro, SP, Brazil. ²Department of Astronomy, University of São Paulo, São Paulo, 05508-090, SP, Brazil. ³São Paulo State University (Unesp), Department of Physics and Chemistry, Ilha Solteira, SP, Brazil. ⁴Boston University, Department of Physics, Boston, 02215, USA. ✉e-mail: mariano.souza@unesp.br

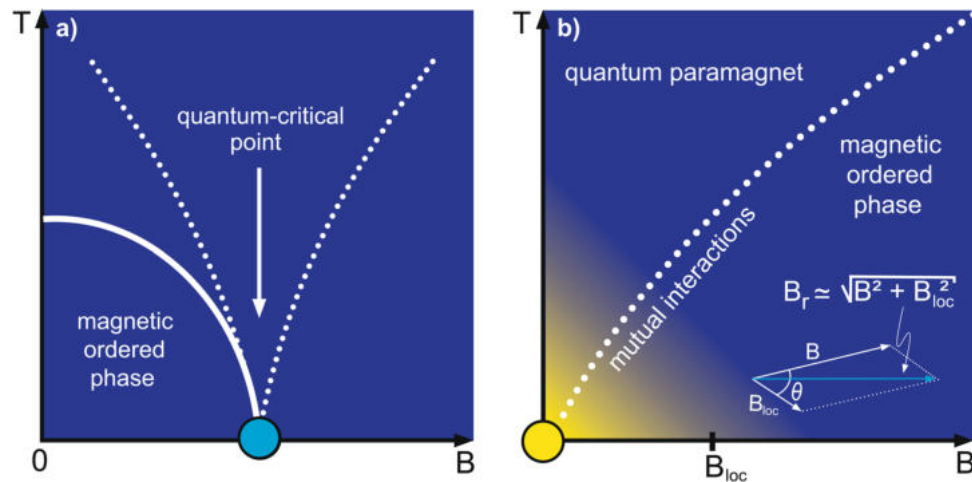


Figure 1. External magnetic field-induced quantum phase transitions. Schematic temperature T versus external magnetic field B phase diagrams. **(a)** Magnetic field-induced (cyan bullet) quantum critical point (QCP). The dotted lines depict the crossover temperatures. Figure after ref. ²². **(b)** Hypothetical zero-field quantum critical point (yellow bullet). The yellow gradient shadow represents the role played by the mutual interactions between neighboring magnetic moments, which are responsible for the emergence of an effective local magnetic field B_{loc} . We consider that B_{loc} makes an angle $\theta \simeq 90^\circ$ with B , so that the resultant magnetic field (inset) is given by $B_r \simeq \sqrt{B^2 + B_{loc}^2}$ (cyan arrow). The dotted line represents the transition from quantum paramagnet to a magnetic ordered phase. Figure created with use of Adobe Illustrator (version CC 2017)⁶². Details in the main text.

temperatures, cf. Fig. 2(A) of ref. ³⁴. Because of such exotic behavior the system is considered as a “strange metal”²³. Based on a scaling analysis of the magnetization, the authors of ref. ³⁴ argue on the crossover of β -YbAlB₄ from a non Fermi liquid to a Fermi liquid behavior. Recently, some of us reported on a surprisingly divergent behavior of Γ_{mag} for model systems, including the one-dimensional Ising model under longitudinal B and Brillouin-like paramagnets²⁹. Here, we report on the absence of zero-field quantum criticality for *any* paramagnetic insulator with non-zero effective local magnetic field (B_{loc}) and discuss the intricate role played by mutual interactions in the regime of $T \rightarrow 0$ K and $B \rightarrow 0$ T. We demonstrate the validity of our analysis for the textbook Brillouin-like paramagnet and for the proposed zero-field quantum critical system β -YbAlB₄. At some extent, our approach is reminiscent of the famous Mermin-Wagner theorem⁴², since at finite temperatures the mutual interactions give rise to long-range intrinsic magnetic fluctuations. Also, the connection between Γ_{mag} and the canonical definition of temperature is reported. Yet, we propose the possibility of carrying out adiabatic magnetization by only manipulating the mutual interactions. It is to be noted that a discussion in the literature concerning on adiabatic magnetization was reported about seventy years ago⁴³, when adiabatic magnetization was employed to produce cooling using paramagnetic salts with $(\partial S/\partial B)_T > 0$, where S is the entropy. When dealing with possible zero-field quantum criticality in paramagnets, we need to be very careful by analyzing the divergence of Γ_{mag} for $B \rightarrow 0$ T experimentally, since an enhancement of Γ_{mag} solely does not suffice to assign genuine zero-field quantum criticality²⁹. It turns out that due to the mutual interactions a spontaneous magnetically ordered phase emerges, which prevents Γ_{mag} to diverge. For the sake of completeness, it is worth recalling that paramagnetic systems have been used to achieve low-temperatures in the range of μ K (electronic spins) and nK (nuclear spins) employing the adiabatic demagnetization method¹¹. Nevertheless, the achievement of exactly 0 K using this process is limited by the increase of the mutual interactions’ relevance upon approaching the ground-state [Fig. 1(b)]. In quantitative terms, considering that in an ideal paramagnet neighboring magnetic moments $\vec{\mu}$ are separated by a distance r ⁴⁴, the magnetic dipolar energy is roughly given by $U_{dip} \simeq (\mu_0 \mu^2)/(4\pi r^3)$ ¹², where $\mu_0 = (4\pi \times 10^{-7})$ T·m/A is the vacuum magnetic permeability. Since classically the magnetic energy is given by $U_{mag} = -\mu B_{loc} \cos\phi$, being ϕ the angle between $\vec{\mu}$ and $\vec{B}_{loc}$, the local dipolar magnetic field is roughly given by $B_{loc} \simeq \mu_0 \mu / 4\pi r^3$. Hence, for $r = 5$ Å, a typical distance between neighboring spins in a paramagnet, and considering $\mu = \mu_B = (9.27 \times 10^{-24})$ J/T, an intrinsic effective local magnetic field $B_{loc} \simeq 0.01$ T can be estimated¹¹. It is worth emphasizing that although we have considered that B_{loc} emerges purely from the magnetic dipolar interactions between neighboring magnetic moments, it is clear that the electrostatic energy is also present into the system. Nevertheless, the electrostatic energy overcomes the magnetic energy only in the regime of relatively high temperatures⁴⁵. Considering that we are interested in the physical properties of paramagnets in the ultra-low T ($\ll 1$ K) regime our analysis of B_{loc} for real systems remains appropriate, when only the magnetic dipolar interactions are considered. If we consider the Hydrogen atom, for instance, we must take into account the interaction between electronic and nuclear spins, i.e., the hyperfine coupling, so that when the distance between electron and nucleus is the Bohr radius, the electron perceives a local magnetic field from the nuclear spin $B_{loc} \simeq 0.0063$ T. The latter is roughly one order of magnitude lower than typical values of B_{loc} in real paramagnets as expected, since the nuclear magnetic moment is roughly 1000 times lower than the electronic one. In the frame of Quantum Mechanics, the Eigenenergies of the Hydrogen for the Zeeman splitting are obtained through the following Hamiltonian¹⁵:

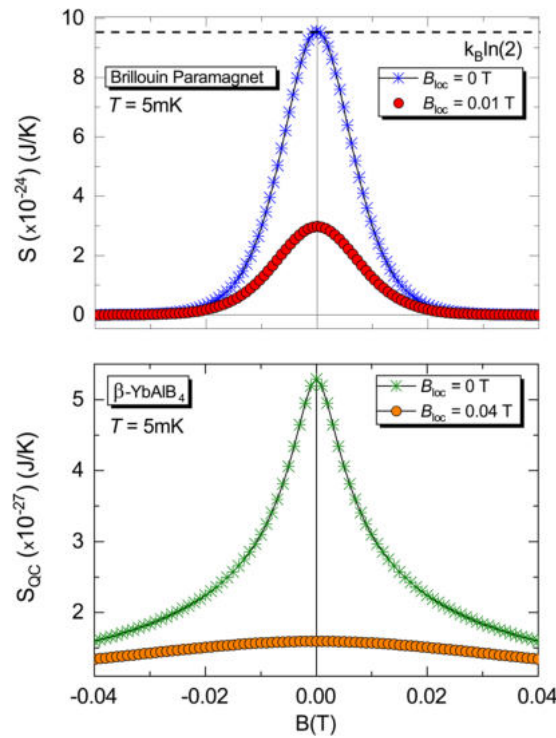


Figure 2. External magnetic field dependence of the entropy. Entropy S versus external magnetic field B for an arbitrarily fixed temperature of $T = 5$ mK. Upper panel: Brillouin paramagnet employing both $B_{loc} = 0$ (blue asterisks) and 0.01 T (red circles), considering neighboring magnetic moments separated by a distance $r = 5$ Å. Lower panel: S_{QC} versus B for β -YbAlB₄ employing $B_{loc} = 0$ (green asterisks) and 0.04 T (orange circles). Figure created with use of OriginPro (version 2020)⁶³ and Wolfram Mathematica (version 11)⁶⁴. Details in the main text.

$$\hat{H} = A(\sigma^e \cdot \sigma^p) - \mu_e \sigma^e \cdot \mathbf{B} - \mu_p \sigma^p \cdot \mathbf{B}, \quad (1)$$

where the indexes e and p refers to electron and proton, respectively; σ is the spin operator and A is a constant related to the magnetic interaction between electron and proton¹⁵. The first term of this simple Hamiltonian (Eq. 1) is independent of the external magnetic field and, therefore, it is connected to the zero-field splitting. Indeed, the Zeeman splitting starts at $U_{mag} = 0$ J and the magnetic energy difference between the energy levels enhances as the external magnetic field is increased. It turns out that the Eigenenergies of the Hamiltonian (Eq. 1) show a quite similar behavior, being that in this case for $B = 0$ T the magnetic energy is $U_{mag} = A$. Analogously, if we consider two neighboring magnetic moments, we can treat the mutual interactions between them employing the Hamiltonian (Eq. 1), being necessary only to associate them to the indexes e and p . As we have mentioned before, given its relatively low strength, B_{loc} is relevant only for vanishing external applied magnetic fields and in the regime of ultra low-temperatures. In other words, B_{loc} begins to be important only when the thermal and magnetic energies are comparable, recalling that $U_{mag} = -\vec{\mu} \cdot \vec{B}_{loc}$ and $U_{mag} = +\vec{\mu} \cdot \vec{B}_{loc}$ represent, respectively, the minimum and maximum magnetic energies. The magnetic energy can also be expressed in terms of the total angular momentum quantum number J , as well as in terms of the magnetic quantum number m_j , which represents the number of allowed orientations of $\vec{\mu}$. The modulus of the total angular momentum vector $\vec{J}$ is given in terms of J , namely $|\vec{J}| = \hbar \sqrt{J(J+1)}$, where $\hbar$ is Planck's constant divided by 2π . Each value of $m_j = -J, -J+1, \dots, J-1, J$ describes a particular orientation of the magnetic moment and its respective magnetic energy, since $\mu = g\mu_B m_j$, where g is the gyromagnetic factor⁴⁶. Here it is worth emphasizing that in our analysis we consider $\vec{\mu}$ oriented along the $\vec{z}$ direction. In the frame of Quantum Mechanics, the magnetic energy is written as $U_{mag} = -[m_j / \sqrt{J(J+1)}] \mu B_{loc}$ ⁴⁶. At this point, we stress that in our analysis B_{loc} is the effective magnetic field generated by the magnetic dipolar interaction between neighboring magnetic moments. Since $\sqrt{J(J+1)}$ is always greater than $|m_j|$, the magnetic energy is not exactly $\pm \mu B_{loc}$ as expected classically, and thus we can infer that ϕ will never be exactly zero or π ⁴⁶. In fact, the absence of a perfect alignment between $\vec{\mu}$ and $\vec{B}_{loc}$ can be observed in the results shown in Fig. 2 for the Brillouin paramagnet (upper panel) and β -YbAlB₄ (lower panel). Note that the entropy is lowered upon increasing B , but it will never be exactly zero for any finite value of B . Yet, in quantitative terms, in the case of β -YbAlB₄³⁴, using the effective Yb magnetic moment $\mu \simeq 1.94 \mu_B$ and the Yb-Yb separation of $r \simeq 3.5$ Å⁴⁷, results in $B_{loc} \simeq 0.04$ T. Even considering the fact that the system undergoes a superconducting transition at $T_c = 80$ mK^{38,39}, intrinsic magnetic moments survive in β -YbAlB₄ at very low- T ³⁴, so that the

Yb valence fluctuations⁴⁸ do not affect our analysis. We consider that such resultant magnetic moment is responsible for the emergence of B_{loc} and thus, even into the superconducting dome, B_{loc} is relevant and prevents that zero-field quantum criticality takes place. Interestingly enough, in the case of α -YbAlB₄⁴⁹ the magnetic moments are fully screened and thus it is not possible to infer resultant magnetic dipolar interactions. After this Introduction, we present and discuss our findings.

Results and Discussion

Absence of a genuine zero-field quantum phase transition due to the presence of B_{loc} . We start our analysis based on entropy arguments. In the case of an ideal paramagnet described by the textbook Brillouin-like model¹¹, the entropy can be derived from the probabilities of the spins (we consider $J = 1/2$) to align parallel or anti-parallel to B and it is given by:

$$S(B, T) = -\frac{B\mu_B}{T} \tanh\left(\frac{B\mu_B}{k_B T}\right) + k_B \ln\left[2 \cosh\left(\frac{B\mu_B}{k_B T}\right)\right], \quad (2)$$

where k_B is the Boltzmann constant (1.38×10^{-23} J/K). The entropy S (Eq. 2) as a function of B at $T = 5$ mK (chosen arbitrarily), assuming $B_{loc} = 0$ (blue asterisks) and $B_{loc} = 0.01$ T (red circles), is plotted in the upper panel of Fig. 2. Now, we recall the proposed quantum critical free-energy F_{QC} for β -YbAlB₄³⁴:

$$F_{QC}(B, T) = -\frac{1}{(k_B \tilde{T})^{1/2}} [(g\mu_B B)^2 + (k_B T)^2]^{3/4}, \quad (3)$$

where $k_B \tilde{T} \approx 6.6$ eV $\approx (1.06 \times 10^{-18})$ J, $\tilde{T}$ refers to a characteristic temperature and $g = 1.94$ ³⁴. Using Eq. 3, it is straightforward to calculate the quantum critical entropy, $S_{QC} = -(\partial F_{QC}/\partial T)_B$, namely:

$$S_{QC}(B, T) = \frac{3k_B^2 T}{2(k_B \tilde{T})^{1/2} (B^2 g^2 \mu_B^2 + k_B^2 T^2)^{1/4}}. \quad (4)$$

Considering that B_{loc} makes an angle $\theta \simeq 90^\circ$ with B , we can write the resultant magnetic field $B_r \simeq \sqrt{B^2 + B_{loc}^2}$ ¹¹, as depicted in the inset of Fig. 1b). It turns out that when using B_r directly in the partition function for the Brillouin paramagnet⁴⁵ instead of B , the derived physical quantities will naturally have B replaced by B_r in their respective mathematical expressions. Thus, a key point of our analysis is that we have replaced B by B_r in the expression of the entropy for the Brillouin paramagnet following the latter approach.

The obtained entropy S_{QC} (Eq. 4) as a function of B for β -YbAlB₄ considering arbitrarily chosen $T = 5$ mK, $B_{loc} = 0$ (green asterisks) and $B_{loc} = 0.04$ T (orange circles), is plotted in the lower panel of Fig. 2. Essentially, in our analysis of the entropy we have used $B_r = B$ ($B_{loc} = 0$ T) and $B_r = \sqrt{B^2 + B_{loc}^2}$ in Eqs. 2 and 4. As depicted in Fig. 2, for both the Brillouin-like paramagnet (upper panel) and β -YbAlB₄ (lower panel) the entropy is expressively lowered at zero external magnetic field when B_{loc} is taken into account, since B_{loc} favours long-range magnetic order¹¹. Hence, the magnetic entropy is released and the third law of Thermodynamics is obeyed¹⁴. These results suggest that, upon considering B_{loc} , the entropy accumulation when $B \rightarrow 0$ T is lowered and as a consequence Γ_{mag} is only enhanced, but it does not diverge.

We focus now on the analysis of Γ_{mag} , which can be calculated employing the well-known relation²²:

$$\Gamma_{mag} = -\frac{1}{T} \left(\frac{\partial S}{\partial B} \right)_T, \quad (5)$$

taking into account B_{loc} . Hence, in the following we consider in addition to the external magnetic field (B) the effects of B_{loc} on Γ_{mag} . We thus replace B by B_r in Eqs. 2 and 4, so that:

$$\Gamma_{mag} = \frac{B}{B^2 + B_{loc}^2}, \quad (6)$$

for the Brillouin paramagnet²⁹, while for β -YbAlB₄, Γ_{mag} reads:

$$\Gamma_{mag} = \frac{Bg^2 \mu_B^2}{k_B^2 T^2 + 2g^2 \mu_B^2 (B^2 + B_{loc}^2)}. \quad (7)$$

The results of Γ_{mag} for the Brillouin paramagnet and β -YbAlB₄ (Eqs. 6 and 7, respectively) are shown in Figs. 3 and 4. A careful analysis of Γ_{mag} for the Brillouin paramagnet (upper panel of Fig. 3) enables us to relate our findings with the seminal experiment proposed by Purcell and Pound⁵⁰ regarding the achievement of negative temperatures in laboratory¹¹, as well as with the well-known impossibility of achieving absolute zero temperature for $B_{loc} \neq 0$ T, to be discussed in the next subsection. In the case of β -YbAlB₄, $\Gamma_{mag} \rightarrow \infty$ for $T \rightarrow 0$ K and $B \rightarrow 0$ T when $B_{loc} = 0$ T (upper panel of Fig. 4), but it does not do so for $B_{loc} \neq 0$ T (lower panel of Fig. 4). Hence, the consequence of taking $B_{loc} \neq 0$ T into account is that Γ_{mag} will never diverge for $T \rightarrow 0$ K and $B \rightarrow 0$ T, since B_r will never be zero and thus we cannot infer a genuine zero-field quantum critical point. This is one of the main results

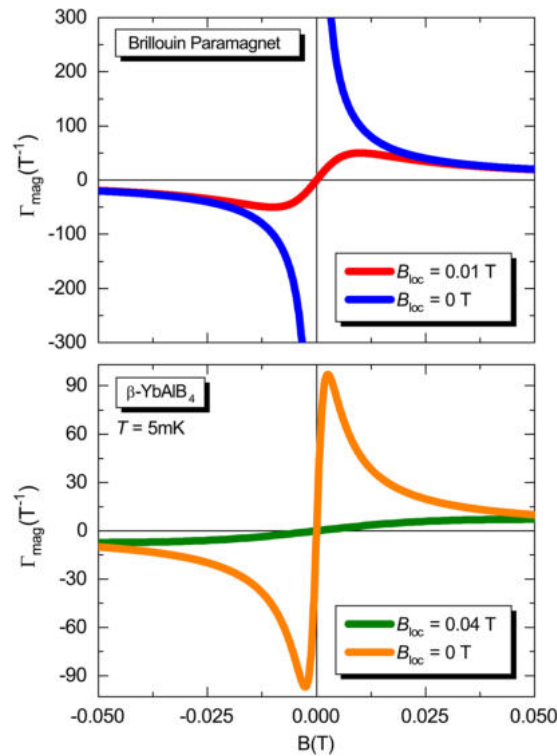


Figure 3. External magnetic field dependence of the magnetic Grüneisen parameter. Upper panel: Magnetic Grüneisen parameter Γ_{mag} versus external magnetic field B for the Brillouin paramagnet considering $B_{loc} = 0.01$ T (red line) and 0 T (blue line), cf. labels. Lower panel: Γ_{mag} versus B for β -YbAlB₄ considering $B_{loc} = 0.04$ T (orange line) and 0 T (green line) and $T = 5$ mK. Figure created with use of Wolfram Mathematica (version 11)⁶⁴. Details in the main text.

of our work. We stress that we are not dealing with a simple shift in the position of the maximum value of Γ_{mag} , cf. Eq. 6. The situation is quite different, for instance, for the one-dimensional Ising model under transverse magnetic field⁵¹, where the critical field for the divergence of Γ_{mag} is shifted when the ratio of the critical field to coupling constant between nearest neighbor is changed⁵¹. When analyzing Eqs. 6 and 7, respectively, for the Brillouin paramagnet and β -YbAlB₄, considering $\Gamma_{mag} \neq 0$ T, we observe that the maximum of Γ_{mag} is centered at $B = B_{loc}$ for the Brillouin paramagnet, while for β -YbAlB₄ it is centered at $B = [B_{loc}^2 (k_B^2 T^2) / (2g^2 \mu_B^2)]^{1/2}$, i.e., when $T = 0$ K the maximum is located at $B = B_{loc}$, cf. Fig. 3. The maxima were obtained by the simple optimization of the Γ_{mag} functions (Eqs. 6 and 7), i.e., making $(\partial \Gamma_{mag} / \partial B)_T = 0$ in both cases. Yet, it is worth mentioning that the position of the maximum value of Γ_{mag} is related to the well-known Schottky anomaly^{12,14}, to be discussed into more details in the following. For β -YbAlB₄, under the condition $k_B T = \mu_B B_{loc}$, considering $B_{loc} = 0.04$ T, we obtain $T = \mu_B B_{loc} / k_B \simeq 24$ mK. The latter indicates the temperature onset of B_{loc} relevance for this system. It is worth mentioning that the lowest temperature of the experiments reported in Fig. 2(A) of ref. 34 for β -YbAlB₄ was $T \simeq 10$ mK and the lowest external magnetic field was 0.31 mT. In terms of Maxwell-relations, namely $(\frac{\partial M}{\partial T})_B = (\frac{\partial S}{\partial B})_T$, being M the magnetization, it is tempting to say that the results of Fig. 2(A) of ref. 34 are at odds with a diverging Γ_{mag} . Yet, considering β -YbAlB₄, our analysis is corroborated by the results presented in Fig. S2 of ref. 34, namely Γ_{mag} versus external magnetic field for various temperatures. There, a clear decrease of Γ_{mag} was observed experimentally upon decreasing B . However, in the frame of zero-field quantum criticality, we would expect an enhancement of Γ_{mag} for $T \rightarrow 0$ K and $B \rightarrow 0$ T²³. In ref. 52, the authors discuss that the free energy scaling for the systems CeCu_{6-x}Au_x and Au-Al-Yb, approximant and quasicrystal, respectively, follow the same scaling behavior as β -YbAlB₄. These systems are also considered to be zero-field quantum critical. Then, our analysis can be extended to *all* systems that follow the same scaling behavior of the free energy reported in ref. 34, see Eq. 3. The main result of this subsection is that zero-field quantum criticality will not hold in *any* system where resultant magnetic moments are non-negligible. A corresponding situation is also observed for the one-dimensional (1D) Ising model under longitudinal magnetic field^{29,53}, where the magnetic coupling constant J' (we make use of J' to avoid confusion with the momentum quantum number J) plays the role analogously to B_{loc} , i.e., Γ_{mag} only diverges for $J' \rightarrow 0$. In fact, the 1D Ising model under longitudinal field²⁹ is equivalent to the Brillouin paramagnet in two distinct cases, namely: *i*) at the ferromagnetic ground state where J' can be associated with a local magnetic field, which in turn acts as B_{loc} and; *ii*) in the limit $T \rightarrow \infty$ for finite B , where due to the increase of the thermal energy the ferromagnetic ordering is suppressed giving rise to a paramagnetic phase²⁹. Hence, considering the similar role played by J' and B_{loc} , it becomes evident that Γ_{mag} only diverges for vanishing

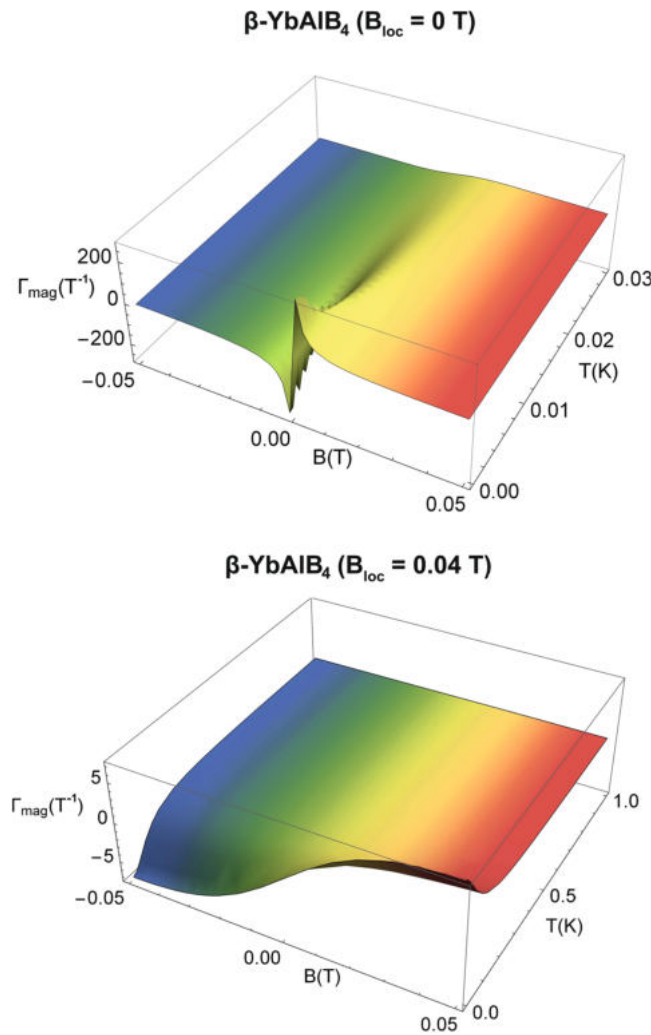


Figure 4. External magnetic field and temperature dependence of the magnetic Grüneisen parameter. Magnetic Grüneisen parameter Γ_{mag} versus external magnetic field B versus temperature T for β -YbAlB₄ using $B_{loc}=0$ (upper panel) and $B_{loc}=0.04$ T (lower panel). Note that Γ_{mag} does not diverge in the limit of $T \rightarrow 0$ K and $B \rightarrow 0$ T when $B_{loc} \neq 0$ T. For clarity, two distinct temperature ranges were employed in the plots. Figure created with use of OriginPro (version 2020)⁶³ and Wolfram Mathematica (version 11)⁶⁴. Further details in the main text.

values of J' , analogously to the case for the Brillouin paramagnet when $B_{loc}=0$ T, as discussed previously. In general terms, *any* system with finite mutual interactions will not show a diverging Γ_{mag} and thus zero field quantum criticality cannot take place. This analysis reinforces the universal character of the mutual interactions and their role in the field of quantum criticality. In the frame of the original work reported by Weiss⁵, the molecular field is associated with the mutual interactions, which in turn leads to the ordering of the magnetic moments within the regime of relevance of such interactions³. Hence, in the same way as the Curie temperature¹² represents the critical temperature for ferromagnets, analogously for the mutual interactions we can infer a *pseudo critical temperature* T_c , which defines their regime of relevance.

Connection between the canonical definition of temperature and Γ_{mag} . Considering the definition of temperature $1/T=(\partial S/\partial E)_B$ ^{11,14}, absolute zero temperature can be inferred when $(\partial S/\partial E)_B \rightarrow \infty$ (upper panel of Fig. 5), where E refers to the average magnetic energy, being $E = k_B T^2 \frac{\partial \ln Z}{\partial T} = -\mu_B B N \tanh\left(\frac{\mu_B B}{k_B T}\right)$, with $Z = 2 \cosh\left(\frac{\mu_B B}{k_B T}\right)$ the partition function for the Brillouin paramagnet¹¹ and N refers to the number of particles. Upon analyzing the behavior of the entropy S as a function of the external magnetic field at various temperatures for the Brillouin paramagnet, depicted in the lower panel of Fig. 5, we observe that there is an intrinsic entropy accumulation when $B \rightarrow 0$ T. This is naturally expected, since for $B = 0$ T the entropy achieves its maximum value, namely $S = k_B \ln(2)$. From the expression for the average magnetic energy, we can easily write $T(E, B)$ as:

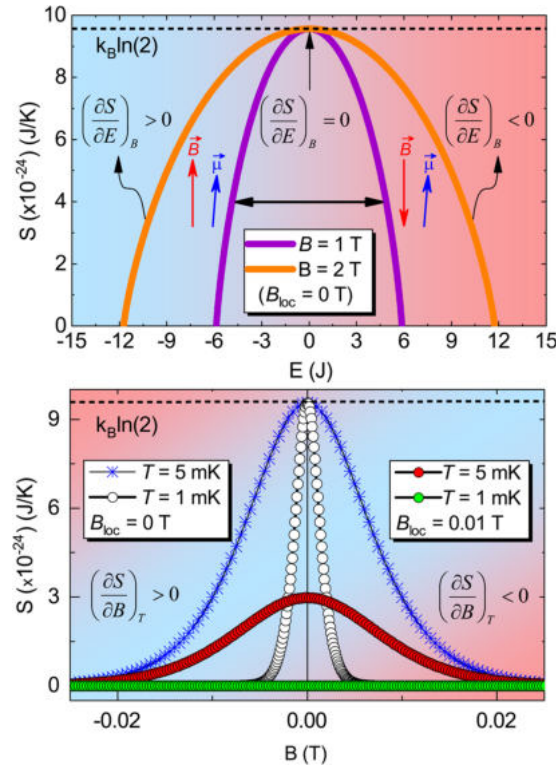


Figure 5. Average magnetic energy and external magnetic field dependence of the entropy. Upper panel: Entropy S as a function of the average magnetic energy E for $B = 1, 2$ T; $B_{loc} = 0$ T and $N = (6.022 \times 10^{23})$. The horizontal black arrow indicates the possibility of changing the sign of the magnetic energy when the direction of the external magnetic field (red arrow) is varied in the time scale of μs resulting predominantly in an anti-parallel configuration of the magnetic moment in respect to $\vec{\mu}$ (blue arrow), as proposed in the Purcell and Pound's experiment⁵⁰. The colorful background indicates that negative (red) temperatures are hotter than positive (blue) ones. Lower panel: Entropy S as a function of the external magnetic field B for the Brillouin model at $T = 5$ and 1 mK considering $B_{loc} = 0$ T and $B_{loc} = 0.01$ T, cf. label. The dashed lines in both panels represent the entropy saturation $S = k_B \ln(2)$, i.e., the entropy value for $(\mu_B B / k_B T) \rightarrow 0$. The colorful background depicts the insensitivity of $(\partial S / \partial B)_T$ regarding positive or negative temperatures, cf. discussed in the main text. Figure created with use of OriginPro (version 2020)⁶³ and Wolfram Mathematica (version 11)⁶⁴.

$$T(E, B) = \frac{\mu_B B}{k_B \operatorname{arctanh}\left(-\frac{E}{\mu_B B N}\right)}, \quad (8)$$

and then plug it in the expression for the entropy (Eq. 2) obtaining thus $S(E, B)$:

$$S(E, B) = -\frac{Ek_B \operatorname{arctanh}\left(\frac{E}{\mu_B B N}\right)}{B\mu_B N} + k_B \ln \frac{2}{\sqrt{1 - \frac{E^2}{B^2 \mu_B^2 N^2}}}. \quad (9)$$

Note that when $E = 0$ J in Eq. 9, $S = k_B \ln(2)$ is nicely recovered, cf. upper panel of Fig. 5. Then, employing Eq. 9, we compute separately the magnetic field and energy derivatives of S , namely $\left(\frac{\partial S}{\partial B}\right)_T$ and $\left(\frac{\partial S}{\partial E}\right)_B$, respectively. It turns out that both derivatives are related to each other by the simple form:

$$\left(\frac{\partial S}{\partial B}\right)_T = \frac{E}{B} \left(\frac{\partial S}{\partial E}\right)_B. \quad (10)$$

Based on Eq. 10 we discuss in the next the connection between $(\partial S / \partial E)_B$ and $(\partial S / \partial B)_T$. Employing the expression for the average magnetic energy, discussed previously, and upon analyzing Fig. 5 (upper panel), it is clear that negative values of E correspond to positive values of T , since the employed values of $B = 1$ and 2 T in our calculations are positive and constant making thus T the quantity that rules the sign of E . Hence, upon analyzing the results shown in the lower panel of Fig. 5, we can infer directly neither negative, infinite nor absolute zero

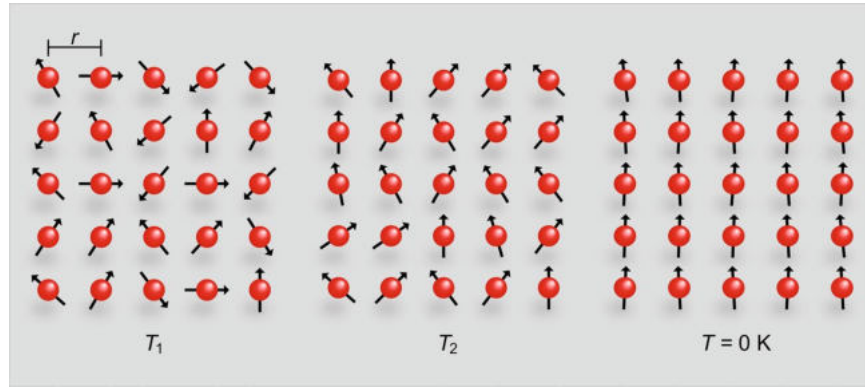


Figure 6. The ground-state of a paramagnet. Schematic representation of the intrinsic magnetic moments (black arrows) of the electrons (red spheres), separated by a distance r , for the Brillouin paramagnet. Upon lowering the temperature $T_1 > T_2 > T = 0$ K in the absence of external magnetic field, all magnetic moments are naturally aligned along the same direction and a magnetically ordered phase takes place, since an effective local magnetic field B_{loc} is intrinsically present due to the mutual interactions between adjacent magnetic moments^{3,4,11}. Note the lack of perfect alignment of the magnetic moments in respect to B_{loc} , cf. discussion in the main text. Figure created with use of Adobe Illustrator (version CC 2017)⁶².

temperature in the same way as upon analyzing the upper panel of Fig. 5, since a fixed positive value of T was employed. However, for finite values of B when the limit $T \rightarrow \infty$ is considered in the lower panel of Fig. 5, the entropy saturates ($S = k_B \ln 2$) and thus $(\partial S / \partial B)_T \rightarrow 0$. In the same way, when $T \rightarrow 0$ K, $(\partial S / \partial B)_T \rightarrow \infty$. This is in agreement with both a diverging (zero temperature) and vanishing (infinite temperature) of $(\partial S / \partial E)_B$. However, strictly speaking $(\partial S / \partial E)_B$ will never diverge since $\vec{\mu}$ and $\vec{B}$ cannot be perfectly aligned, as discussed previously, and thus the achievement of absolute zero temperature is prevented. Yet, when the local magnetic field $B_{loc} = 0$ T (blue asterisks and open circles in the lower panel of Fig. 5), upon approaching $T = 0$ K, $(\partial S / \partial B)_T \rightarrow \infty$ and thus absolute zero temperature can be indirectly inferred. However, when $B_{loc} \neq 0$ T (red and green circles in the lower panel of Fig. 5), for vanishing T and B , such an entropy accumulation [$(\partial S / \partial B)_T \rightarrow \infty$] is suppressed and, as a consequence, the achievement of absolute zero temperature is also prevented. Evidently, such a divergence of the entropy for vanishing T and B would violate the third law of Thermodynamics⁴, strengthening thus our argument that a genuine zero-field QCP cannot take place, cf. discussions in the previous subsection. Thus, we have demonstrated in two different ways that the achievement of absolute zero temperature is not possible when considering finite B_{loc} . Also, in the lower panel of Fig. 5, when $B_{loc} = 0$ T, the entropy for $B = 0$ T is exactly the same for both data set (blue asterisks and open circles), since for $B = 0$ T the resultant entropy $S = k_B \ln(2)$ is nicely recovered for any $T \neq 0$ K⁴. This is not the case when B_{loc} is taken into account, being that for $B = 0$ T the entropy depends on T^4 , as depicted in the lower panel of Fig. 5.

The entropy as a function of the average energy (upper panel of Fig. 5) can be easily obtained through Eq. 9 employing the arbitrarily fixed values of $B = 1$ and 2 T. Figure 6 depicts schematically the relevance of B_{loc} for $T \rightarrow 0$ K and $B \rightarrow 0$ T, since a ferromagnetic ground state only emerges due to the presence of finite mutual interactions in the system. Recalling that the absence of long-range magnetic ordering in low-dimensional systems at finite temperature is a direct consequence of the Mermin-Wagner theorem⁴². Interestingly enough, when considering the equilibrium spin populations in a two-level system, well known from classical textbooks^{3,4,11}, namely:

$$\frac{N_1}{N_T} = \frac{\exp(\mu B / k_B T)}{\exp(\mu B / k_B T) + \exp(-\mu B / k_B T)} \quad (11)$$

and

$$\frac{N_2}{N_T} = \frac{\exp(-\mu B / k_B T)}{\exp(\mu B / k_B T) + \exp(-\mu B / k_B T)}, \quad (12)$$

being N_1 and N_2 the spin populations regarding the lower and upper energy levels, respectively, and N_T the total number of spins. It turns out that for vanishing T and positive values of B , the ratio $\frac{N_1}{N_T}$ becomes 1 and $\frac{N_2}{N_T}$ is zero, which means that all spins point roughly along the same direction, i.e., a ferromagnetic ordering takes place, as schematically shown in Fig. 6 for $T = 0$ K. In the following we make a link between Γ_{mag} , the definition of temperature and the Purcell and Pound's experiment⁵⁰. Before starting the discussions, we stress that we are not proposing a new definition of temperature. Recalling that the average magnetic energy is given by¹¹:

$$E = -N\mu_B B \tanh\left(\frac{\mu_B B}{k_B T}\right), \quad (13)$$

it is possible to rewrite E as a function of the average magnetic moment $\langle \mu \rangle = N\mu_B \tanh(\mu_B B/k_B T)$ along the external magnetic field, as follows:

$$E = -\langle \mu \rangle B. \quad (14)$$

From the expression for $\langle \mu \rangle$ it is possible to write the external magnetic field in respect to $\langle \mu \rangle$:

$$B \left(T, \left\langle \mu \right\rangle \right) = \frac{k_B T}{\mu_B} \operatorname{arctanh} \left(\frac{\langle \mu \rangle}{N\mu_B} \right). \quad (15)$$

Equation 15 indicates that at a certain temperature T , the value of an external magnetic field B is associated with a spin configuration that corresponds to a specific average magnetic moment $\langle \mu \rangle$. Recalling that the magneto-caloric effect can be quantified by Γ_{mag} ²²:

$$\Gamma_{mag} = \frac{1}{T} \left(\frac{\partial T}{\partial B} \right), \quad (16)$$

we can compute the temperature derivative of B in Eq. 15 and replace it into Eq. 16, resulting:

$$\Gamma_{mag} = \frac{\mu_B}{T k_B \operatorname{arctanh} \left(\frac{\langle \mu \rangle}{N\mu_B} \right)}. \quad (17)$$

Since $\Gamma_{mag} = 1/B$ for the Brillouin paramagnet²⁹, we write T as a function of B and $\langle \mu \rangle$:

$$T = \frac{B\mu_B}{k_B \operatorname{arctanh} \left(\frac{\langle \mu \rangle}{N\mu_B} \right)}. \quad (18)$$

Equation 18 connects in an unprecedented way the Purcell and Pound experiment⁵⁰ and Γ_{mag} itself. When B and $\langle \mu \rangle$ are $\parallel$, positive temperatures are inferred. However, when B and $\langle \mu \rangle$ are anti- $\parallel$, then negative temperatures can be associated. It is remarkable that the definition of temperature is encoded in Γ_{mag} and vice-versa. Next, we focus on the scaling analysis of the magnetization. When investigating the behavior of Γ_{mag} , an important consideration is its scaling behavior, see, e.g. ref. ²³ and references cited therein. Upon analyzing the scaling behavior for the Brillouin paramagnet, shown in Fig. 7, we observe that all data collapse in the same line only for external magnetic field values close to B_{loc} . By considering much higher or lower values of external magnetic field when compared with B_{loc} , a breakdown of the scaling behavior of the magnetization is observed. As a matter of fact, the scaling analysis reflects the behavior of Γ_{mag} as a function of T , so that the maxima depicted in Fig. 7 are associated with the Schottky anomaly, which in turn is only observed in the presence of mutual interactions. In other words, due to the intrinsic mutual interactions present into the system, the validity of the scaling in the Brillouin paramagnet is limited only to external magnetic field values close to B_{loc} . Thus, our scaling analysis also demonstrates the relevance of B_{loc} in the limit of both $B \rightarrow 0$ T and $T \rightarrow 0$ K. In Fig. S3 of ref. ³⁴ the authors show a scaling behavior of β -YbAlB₄ upon analyzing the critical contribution of the magnetization M_c . Interestingly enough, there is a breakdown of the scaling behavior for applied magnetic fields higher than 0.5 T, which resembles the scaling behavior of the Brillouin paramagnet discussed here, and the scaling is only valid for low values of B for β -YbAlB₄. At this point, it is worth recalling that Γ_{mag} can also be written as follows²²:

$$\Gamma_{mag} = -\frac{(dM/dT)_B}{c_B}, \quad (19)$$

where c_B is the specific heat at constant external magnetic field. Upon employing Eq. 19, it can be directly inferred that when $(-dM/dT)_B \rightarrow \infty \Rightarrow \Gamma_{mag} \rightarrow \infty$ if c_B is non-singular. Thus, we make use of Eq. 19 in order to infer the divergence of Γ_{mag} for the scaling analysis of the Brillouin paramagnet, as shown in Fig. 7. It is worth mentioning that since Γ_{mag} for the Brillouin paramagnet is temperature independent²⁹, we thus make use of the magnetization scaling in our analysis. Interestingly, also for the one-dimensional Ising model under transverse magnetic field Γ_{mag} also depends on T ⁵¹. We observe from Fig. 7 that when $B_{loc} = 0$ T, for arbitrarily chosen $B = 0.001$ T, the scaling consists in a straight line. Since a logarithm scale was used in both axes of Fig. 7, the straight line indicates a divergence of Γ_{mag} for $B \rightarrow 0$ T and $T \rightarrow 0$ K. However, when $B_{loc} = 0.01$ T the divergence of Γ_{mag} is suppressed and such linear behavior is no longer observed, opening the way for the appearance of a Schottky-like maximum. Hence, the scaling plots depicted in Fig. 7 demonstrate in another way the non-divergence of Γ_{mag} when $B_{loc} \neq 0$ T for the Brillouin paramagnet. Also, the maximum in Γ_{mag} shown in both panels of Fig. 3 when $B_{loc} \neq 0$ T is due to the Schottky anomaly^{12,14}, as previously mentioned. As well-known from textbooks, such maximum takes place when $(k_B T)/(\mu_B B) \simeq 0.834$ ^{12,13}. Upon continuously decreasing the temperature of the system, the spins occupy preferably the lower energy level and, as a consequence, all spins will occupy the same energy level in the ground state. This can be visualized in the spins scheme depicted in Fig. 6, and it is in line with our analysis for the spin populations, cf. Eqs. 11 and 12. The Schottky anomaly can also be captured in the scaling analysis for the Brillouin model (Fig. 7) where a maximum takes place at $T/B_r \approx 0.5602$. Now, we use again the definition of the magneto-caloric effect (Eq. 16)²². Knowing that $\Gamma_{mag} = 1/B$ for the Brillouin paramagnet²⁹, it is straightforward to

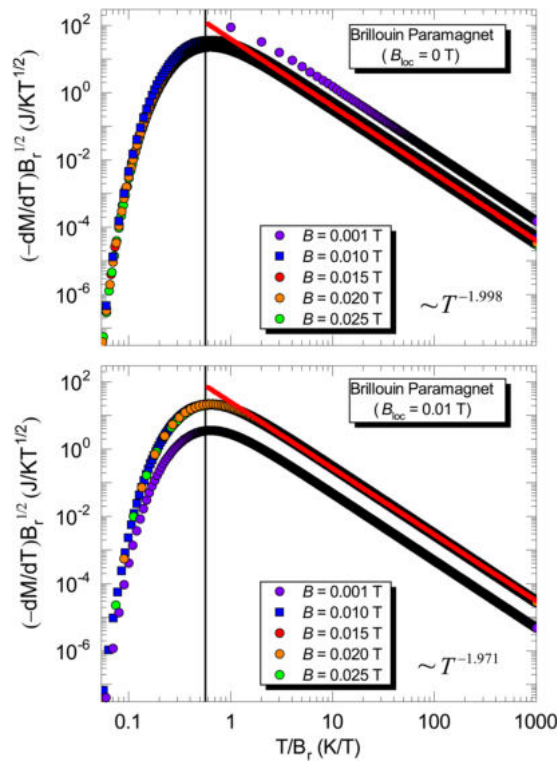


Figure 7. Scaling analysis for the Brillouin paramagnet. Scaling behavior of the magnetization for the Brillouin paramagnet for fixed values of external magnetic field considering $B_{loc} = 0$ T (upper panel) and $B_{loc} = 0.01$ T (lower panel). The solid vertical lines in both panels indicate the position of the Schottky maximum, while the red solid line indicates the overlap (scaling) of all data set in the regime of high temperatures. The scaling exponent is $\epsilon = 1$, the same one of β -YbAlB₄, and dM/dT scales with temperature as $\sim T^{-1.998}$ (upper panel) and as $\sim T^{-1.971}$ (lower panel). Figure created with use of OriginPro (version 2020)⁶³ and Wolfram Mathematica (version 11)⁶⁴. Details in the main text.

write $\frac{T}{B} = \left(\frac{\partial T}{\partial B}\right)_S$. Hence, this simple analysis indicates that temperature and magnetic field are interconnected. Indeed, in the adiabatic demagnetization the temperature is decreased upon removing the external applied magnetic field, in order to keep the ratio $(\mu_B B_r)/(k_B T)$ constant.

Possibility of performing adiabatic magnetization by only manipulating the mutual interactions. Our proposal is distinct from the adiabatic demagnetization method itself, since no external magnetic field is required. As pointed out in ref.¹¹, although counter-intuitive it is possible to increase the temperature adiabatically. The idea behind is based on the connection between the uncertainty principle and the entropy. The entropy of the system can be written as follows¹¹:

$$S = -k_B \sum_j P(\Psi_j) \ln P(\Psi_j), \quad (20)$$

where $P(\Psi_j)$ is the probability of the system to be at the energy Eigenstate Ψ_j and j is the label of the corresponding Eigenstate. It is clear that the entropy increases with the uncertainty associated with the particle according with Eq. 20 and thus, in order to hold the entropy constant, the uncertainty must also be held constant. In an adiabatic expansion, the increase of the volume causes an enhancement in the spatial uncertainty¹¹. However, in this process, the gas particles that do work will lose energy and then they will have a decrease in their linear momentum, i.e., the momentum uncertainty is lowered as well. Thus, there is a compensation of such uncertainties and, as a consequence, the entropy remains constant during this process¹¹. Following similar arguments, adiabatic magnetization of the mutual interactions can be achieved. As depicted in Fig. 8, upon increasing the temperature adiabatically, a spontaneous magnetization takes place as a direct consequence of the constrain of holding the entropy constant. Since there is no external applied magnetic field we have $B_r = B_{loc}$ and, in order to hold S (Eq. 2) constant, the magnetic energy should also be changed in this process, so that adiabatic magnetization is achieved. This can also be easily understood in terms of the uncertainty principle. It is straightforward to calculate the uncertainty $\Delta E = U_{mag} - E$ of the magnetic energy, which reads:

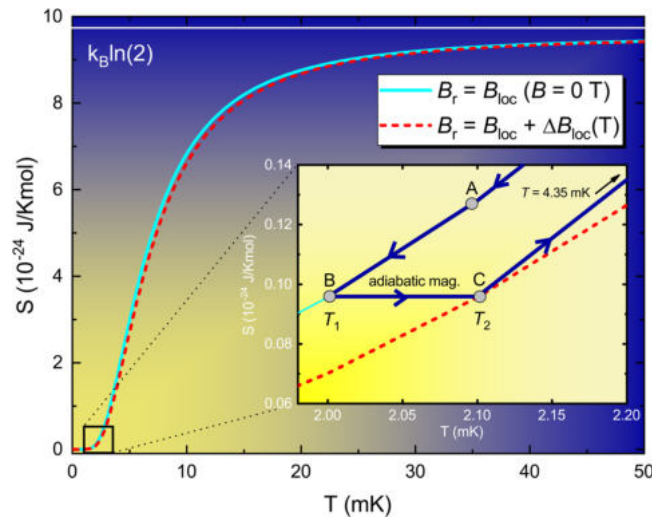


Figure 8. Adiabatic demagnetization of the mutual interactions. Main panel: entropy as a function of temperature for $B = 0$ T (solid cyan curve) and for $\Delta B_{loc} = 0.0032$ T (red dashed line). The yellow gradient indicates the region of relevance of B_{loc} in the regime of ultra-low temperatures. Inset: schematic representation of the adiabatic magnetization employing the mutual interactions. The steps are as follows: i) the system is cooled down to a sufficiently low temperature where the magnetic energy associated with B_{loc} overcomes the thermal fluctuations (path A to B); ii) the temperature is adiabatically increased from B (T_1) to C (T_2) and, in order to hold the entropy constant, the system is magnetized adiabatically, i.e., a finite value of ΔB_{loc} emerges into the system and thus, the entropy changes from the solid cyan to the *fictitious* red dashed line, which emulates S versus T for the corresponding value of $(B_{loc} + \Delta B_{loc})$; iii) upon increasing the temperature from C, the entropy will vary and, as a consequence, the system will be demagnetized at $T = 4.35$ mK (indicated by the solid black arrow), going back to its original configuration of $\Delta B_{loc} = 0$ T. Such process can be restarted by cooling the system again from $T = 4.35$ mK to point A. Figure created with use of OriginPro (version 2020)⁶³ and Wolfram Mathematica (version 11)⁶⁴.

$$\Delta E = \mu_B B_{loc} \left[N \tanh \left(\frac{\mu_B B_{loc}}{k_B T} \right) - \cos \phi \right]. \quad (21)$$

Strictly speaking, the treatment of the mutual interactions would require a many body approach. In fact, in a many-body picture the mutual interactions can be described by the Hamiltonian^{54,55}:

$$H = -J' \sum_{(ij)} \vec{S}_i \cdot \vec{S}_j + D r_{nm}^3 \sum_{i>j} \frac{\vec{S}_i \cdot \vec{S}_j}{|\vec{r}_{ij}|^3} - \frac{3 \left(\vec{S}_i \cdot \vec{r}_{ij} \right) \left(\vec{S}_j \cdot \vec{r}_{ij} \right)}{|\vec{r}_{ij}|^5}, \quad (22)$$

where $\vec{S}$ is the spin vector oriented along the local z_i Ising (111) axis, i and j refer to the two sites of the lattice, $\vec{r}$ is the position vector, $D = (\mu_0 \mu^2) / (4\pi r_{nm}^3)$, and r_{nm} is the distance between nearest-neighbor spins. The second term of the Hamiltonian (Eq. 22) embodies the magnetic energy associated with the interaction between a single magnetic moment and its nearest neighbors, since the dipolar interaction is short range. Hence, in our analysis of Eq. 21 we consider that the local magnetic field perceived by a certain magnetic moment is associated with the resultant magnetic field generated by the various neighboring magnetic moments in its immediate surrounding, cf. Hamiltonian 22. Upon analyzing Eq. 21, it is clear that ΔE is minimized when $\cos \phi \rightarrow 1$. Such a condition would indicate a maximum alignment of the magnetic moments because of the local magnetic field. Thus, in order to increase the temperature of the system adiabatically, a quasi-static process is required, i.e., the temporal uncertainty Δt should be maximized while ΔE is minimized. However, still considering Eq. 21, for $B_{loc} = 0 \Rightarrow \Delta E = 0$, indicating that in the absence of mutual interactions the uncertainty principle would be violated. In the same way, the absence of the mutual interactions would imply in the violation of the third law of Thermodynamics, as pointed out previously⁴. The only way to reduce the magnetic energy adiabatically is, however, varying the total angular momentum projection. Such a behavior is naturally expected in the adiabatic magnetization, since $\cos \phi$ is increased. At this point, we recall the magnetic energy, namely $U_{mag} = -\frac{m_J}{\sqrt{J(J+1)}} \mu_B B_{loc}$. In the adiabatic magnet-

ization process, the projection of $\vec{J}$ on the z -axis is increased, while its projections on the x and y -axes are reduced and, as a consequence, the magnetic energy decreases, being thus the magnetization of the system increased, since $m_J = -J, -J+1, \dots, J-1, J$. This is the principle of work behind the adiabatic magnetization of the mutual interactions here proposed. The magnetic field increment ΔB_{loc} of the mutual interaction that emerges in the adiabatic magnetization is associated with the increased projection of $\vec{J}$ along the z -axis. In general terms, in the adiabatic

magnetization process (Fig. 8) of the mutual interactions, the temperature is adiabatically increased from T_1 to T_2 and, in order to do so, the magnetic energy needs to compensate the temperature variation in order to hold the entropy constant. Thus, we can write:

$$\frac{\mu_B B_{loc}}{k_B T_1} = \frac{\mu_B \sqrt{B_{loc}^2 + \Delta B_{loc}^2}}{k_B T_2}, \quad (23)$$

where ΔB_{loc} is the magnetic field increment that will emerge into the system to compensate the adiabatic increase of temperature. It is clear that such ΔB_{loc} refers to the adiabatic magnetization employing only the mutual interactions of the system. Then, ΔB_{loc} can be easily determined by:

$$\Delta B_{loc} = B_{loc} \sqrt{\frac{T_2^2}{T_1^2} - 1}. \quad (24)$$

It is worth emphasizing that such adiabatic magnetization process can only be performed in the temperature range where the magnetic energy associated with the mutual interactions are not overcome by the thermal fluctuations. In the case of real paramagnets ($B_{loc} \simeq 0.01$ T), as discussed previously, the typical temperature onset of the mutual interactions relevance is $T \leq 6$ mK. After magnetizing the system adiabatically, if the temperature is further increased such magnetization will be released when the thermal energy equals the corresponding magnetic energy associated with ΔB_{loc} . Thus, the entropy is recovered to its original configuration, i.e., $\Delta B_{loc} = 0$ T, making this process a single shot closed-cycle, which can be restarted. Although we have provided a particular numerical example in Fig. 8, namely T_1 (T_2) = 2.0 (2.1) mK, such process can be carried out between any T_1 and T_2 within the temperature range of relevance of B_{loc} . The fascinating aspect behind this process is that no external magnetic field is required in order to perform the adiabatic magnetization, being only the mutual interactions of the system employed.

On the role of the mutual interactions in other physical systems. An analogous situation to the mutual interactions in paramagnets can also be found for the Bose-Einstein condensation (BEC). Strictly speaking, BEC should occur at $T = 0$ K, but due to the presence of finite interactions between particles BEC takes place at $T \neq 0$ K⁵⁶, being the energy of the system equivalent to the chemical potential itself and all particles occupy the same energy level. The fact that interactions between particles prevent an ideal BEC corresponds to a similar physical situation of how the mutual interactions in insulating paramagnets prevent the existence of ideal paramagnets. Also, in the frame of BEC in magnetic insulators^{57,58}, where dimers formed by pairs of spin $S = 1/2$ with a ground state $S = 0$ (spin-singlet) and $S = 1$ (triplet) bosonic excitations, the interdimer interaction plays the role analogous to the mutual interaction in insulating paramagnets. Indeed, the interdimer interaction is the key ingredient for the stabilization of a long-range magnetic ordering⁵⁶. Yet, in dipolar spin-ice systems⁵⁵ the dipole-dipole interactions are relevant, so that we consider an “effective nearest-neighbor energy scale” composed by two distinct contributions, namely nearest-neighbor exchange energy between $\langle 111 \rangle$ Ising magnetic moments and a nearest neighbor dipolar energy scale⁵⁵. The “spin-spin” interactions in such systems can be nicely tuned via doping, which in turn enables to change the distance between magnetic moments⁵⁹. For spins arranged in a pyrochlore structure of corner-sharing tetrahedra spin-ice, we have a residual entropy originating from the degeneracy of the “disordered” ground-state.

Conclusions

Our findings suggest the absence of zero-field quantum criticality in the presence of mutual interactions. Interactions will eventually, as $T \rightarrow 0$ K and $B \rightarrow 0$ T, break down the spin gas scheme, so spontaneous magnetization will emerge at some very low-temperature with $B = 0$ T. We have shown that the magnetic Grüneisen parameter for *any* paramagnet with mutual interactions will never diverge as $T \rightarrow 0$ K and $B \rightarrow 0$ T. As a consequence, zero-field quantum criticality cannot be inferred. As a matter of fact, we are faced to a many body interactions problem, cf. Hamiltonian 22. Our analysis, based on the magnetic Grüneisen parameter and entropy arguments, although validated by the results obtained for the textbook Brillouin-paramagnet and for the proposed zero-field quantum critical paramagnet β -YbAlB₄, is universal and can be applied to *any* system with mutual interactions. Also, we have discussed the impossibility of achieving absolute zero temperature due to the presence of finite mutual interactions in real paramagnets regarding the connection between Γ_{mag} and the canonical definition of temperature. Given the recent advances in the investigation of model systems employing cold atoms⁶⁰, our findings suggest that the mutual interactions can be mimicked by tuning the Hubbard on-site Coulomb repulsion U , as reported in ref. ⁶¹. Yet, we have proposed the concept of adiabatic magnetization employing solely the mutual interactions. We anticipate that the proof of concept regarding adiabatic magnetization of the mutual interactions can be achieved, with some technical efforts, in any laboratory where temperatures of a few mK are attainable precisely. The role of the mutual interactions in other physical systems like Bose-Einstein condensates, Bose-Einstein condensation of magnons and spin-ice were also discussed.

Methods

Softwares. All the calculations presented in this work were performed employing the software Wolfram Mathematica Version 11. Figures 1 and 6 were created from scratch using the software Adobe Illustrator Version CC 2017. Figures 2, 3, 5, 7 and 8 were plotted using the software OriginPro Version 2020 based on data set generated employing the software Wolfram Mathematica Version 11. Figure 4 was plotted using the 3D plot function

of the software Wolfram Mathematica Version 11. In Figs. 2, 3 (lower panel) and 5, $T = 5$ mK was chosen arbitrarily due to the numerical impossibility of computing S and Γ_{mag} exactly at $T = 0$ K. The same holds true for $T = 1$ mK in Fig. 5.

Derivation of the observables considering B_{loc} in the Brillouin paramagnet. The partition function Z for the Brillouin paramagnet¹² reads:

$$Z(B, T) = \sum_{m_j=-J}^J \exp\left(\frac{\mu_B g m_j B}{k_B T}\right), \quad (25)$$

converging to the expression:

$$Z(B, T) = \frac{\sinh\left[\left(1 + \frac{1}{2J}\right) \frac{\mu_B g B}{k_B T}\right]}{\sinh\left(\frac{\mu_B g B}{k_B T}\right)}. \quad (26)$$

Considering $J = 1/2$ and $g = 2$ we have:

$$Z(B, T) = \frac{\sinh\left(2 \frac{\mu_B B}{k_B T}\right)}{\sinh\left(\frac{\mu_B B}{k_B T}\right)}, \quad (27)$$

which in turn is simplified as:

$$Z(B, T) = 2 \cosh\left(\frac{\mu_B B}{k_B T}\right). \quad (28)$$

Considering the existence of a local magnetic field B_{loc} which can vectorially be added to the external magnetic field B , the resultant magnetic field is $B_r = \sqrt{B^2 + B_{loc}^2}$, cf. previous discussions. Replacing B by B_r in Eq. 25, the partition function is now given by:

$$Z(B, T) = 2 \cosh\left(\frac{\mu_B \sqrt{B^2 + B_{loc}^2}}{k_B T}\right). \quad (29)$$

Thus, the corresponding Helmholtz free energy reads:

$$F(B, T) = -k_B T \ln \left[2 \cosh\left(\frac{\mu_B \sqrt{B^2 + B_{loc}^2}}{k_B T}\right) \right]. \quad (30)$$

From Eq. 30, the entropy $S = -(\partial F / \partial T)_B$ is:

$$S(B, T) = -\frac{\sqrt{B^2 + B_{loc}^2} \mu_B}{T} \tanh\left(\frac{\sqrt{B^2 + B_{loc}^2} \mu_B}{k_B T}\right) + k_B \ln \left[2 \cosh\left(\frac{\sqrt{B^2 + B_{loc}^2} \mu_B}{k_B T}\right) \right]. \quad (31)$$

Equation 31 is exactly the same as Eq. 2 when B is replaced by B_r . We thus have shown that only replacing B as B_r in the expressions for the Brillouin paramagnet is consistent, since computing the observables from the partition function considering B_r instead of B provides the same results. It is worth mentioning that we have performed all the magnetic field derivatives of the entropy with respect to B instead of B_r , since B_{loc} was considered constant in our analysis. If we compute the magnetic field derivatives of S with respect to B_r instead of B , there would be a difference between such expressions by a factor of $B / \sqrt{B^2 + B_{loc}^2}$, which is 1 when $B_{loc} = 0$. Interestingly enough, the calculation of Γ_{mag} is affected by this aspect. Considering $(\partial S / \partial B)_T$ in Eq. 5, Γ_{mag} reads:

$$\Gamma_{mag} = \frac{B}{(B^2 + B_{loc}^2)}, \quad (32)$$

which becomes $\Gamma_{mag} = 1/B$ when $B_{loc} = 0$. Yet, when $(\partial S / \partial B_r)_T$ is considered in Eq. 5, Γ_{mag} is given by:

$$\Gamma_{mag} = \frac{1}{\sqrt{B^2 + B_{loc}^2}}, \quad (33)$$

which is also $\Gamma_{mag} = 1/B$ when $B_{loc} = 0$ ²⁹. The very same argument can be used when dealing with the calculations of Γ_{mag} for β -YbAlB₄³⁴ taking B_{loc} into account.

Received: 13 February 2020; Accepted: 20 April 2020;

Published online: 14 May 2020

References

- Mathur, N. D. *et al.* Magnetically mediated superconductivity in heavy fermion compounds. *Nature* **394**, 39–43 (1998).
- Gegenwart, P. *et al.* Magnetic-Field Induced Quantum Critical Point in YbRh₂Si₂. *Phys. Rev. Lett.* **89**, 056402 (2002).
- Kittel, C. *Introduction to Solid State Physics 8th ed.* (John Wiley & Sons, Hoboken, 2005).
- Ashcroft, N. W. & Mermin, N. D. *Solid State Physics*. (Saunders College Publishing, Orlando, 1976).
- Weiss, P. L. 'hypothèse du champ moléculaire et la propriété ferromagnétique. *J. Phys. Theor. Appl* **6**, 661–690 (1907).
- Pauling, L. A theory of ferromagnetism. *Proc. Nat. Acad. Sci. USA* **39**, 551–560 (1953).
- Mendelssohn, K. *Cryophysics*. (Interscience Publishers, London, 1960).
- Mendelssohn, K. *The Quest for Absolute Zero*. (World University Library, London, 1966).
- Madelung, O. *Introduction to Solid-State Theory*. (Springer-Verlag Berlin Heidelberg, New York, 1978).
- van Vleck, J. H. Nobel Lecture. NobelPrize.org. Nobel Media AB 2019, <https://www.nobelprize.org/prizes/physics/1977/vleck/lecture/> (Fri. 27 Sep 2019).
- Baierlein, R. *Thermal Physics*. (Cambridge University Press, Cambridge, 1999).
- Blundell, S. *Magnetism in Condensed Matter*. (Oxford University Press, Oxford, 2001).
- Tari, A. *The Specific Heat of Matter at Low Temperatures*. (Imperial college press, London, 2003).
- Pathria, R. K. *Statistical Mechanics 2nd ed.* (Butterworth-Heinemann, Oxford, 1996).
- Feynmann, R., Leighton, R. B. & Mathew, S. *Lecture on Physics Vol. II and III*. (Addison-Wesley, Palo Alto, 1964).
- Pobell, F. *Matter and Methods at Low Temperatures*. (Springer-Verlag Berlin Heidelberg, New York, 2007).
- Fazekas, P. *Lecture Notes on Electron Correlation and Magnetism*. (World scientific publishing, Singapore, 1999).
- Putzke, C. *et al.* Anomalous critical fields in quantum critical superconductors. *Nat. Commun.* **5**, 5679 (2014).
- Huang, C. L. *et al.* Anomalous quantum criticality in an itinerant ferromagnet. *Nat. Commun.* **6**, 8188 (2015).
- Isono, T. *et al.* Quantum criticality in an organic spin-liquid insulator κ -(BEDT-TTF)₂Cu₂(CN)₃. *Nat. Commun.* **7**, 13494 (2016).
- Michon, B. *et al.* Thermodynamic signatures of quantum criticality in cuprate superconductors. *Nature* **567**, 218–222 (2019).
- Zhu, L., Garst, M., Rosch, A. & Si, Q. Universally diverging Grüneisen parameter and the magnetocaloric effect close to quantum critical points. *Phys. Rev. Lett.* **91**, 066404 (2003).
- Gegenwart, P. Classification of materials with divergent magnetic Grüneisen parameter. *Philos. Mag.* **97**, 3415–3427 (2017).
- Bartosch, L., de Souza, M. & Lang, M. Scaling theory of the Mott transition and breakdown of the Grüneisen scaling near a finite-temperature critical end point. *Phys. Rev. Lett.* **104**, 245701 (2010).
- de Souza, M. *et al.* Grüneisen parameter for gases and superfluid helium. *Europ. J. of Phys* **37**, 055105 (2016).
- Gomes, G., Stanley, H. E. & de Souza, M. Enhanced Grüneisen parameter in supercooled water. *Sci. Rep* **9**, 12006 (2019).
- Dasa, D., Gnidaa, D., Wiśniewska, P. & Kaczorowski, D. Magnetic field-driven quantum criticality in antiferromagnetic CePtIn₄. Proceedings of the National Academy of Sciences, <https://doi.org/10.1073/pnas.1910293116> (2019).
- Garst, M. & Rosch, A. Sign change of the Grüneisen parameter and magnetocaloric effect near quantum critical points. *Phys. Rev. B* **72**, 205129 (2005).
- Gomes, G. *et al.* Magnetic Grüneisen parameter for model systems. *Phys. Rev. B* **100**, 054446 (2019).
- Smith, A. Who discovered the magnetocaloric effect? Warburg, Weiss, and the connection between magnetism and heat. *Eur. Phys. J. H* **38**, 507–517 (2013).
- Moya, X., Kar-Narayan, S. & Marthur, N. D. Caloric materials near ferroic phase transitions. *Nat. Mat* **13**, 439–450 (2014).
- Gegenwart, P., Si, Q. & Steglich, F. Quantum criticality in heavy-fermion metals. *Nature Phys* **4**, 186–197 (2008).
- Sakai, A. *et al.* T/B scaling without quasiparticle mass divergence: YbCo₂Ge₄. *Phys. Rev. B* **94**, 041106 (2016).
- Matsumoto, Y. *et al.* Quantum criticality without tuning in the mixed valence compound β -YbAlB₄. *Science* **331**, 316–319 (2011).
- Deguchi, K. *et al.* Quantum critical state in a magnetic quasicrystal. *Nature Mater* **11**, 1013–1016 (2012).
- Ramires, A. *et al.* β -YbAlB₄: A critical nodal metal. *Phys. Rev. Lett.* **109**, 176404 (2012).
- Tomita, T. *et al.* Strange metal without magnetic criticality. *Science* **349**, 506–509 (2015).
- Kuga, K. *et al.* Superconducting properties of the non-Fermi-liquid system β -YbAlB₄. *Phys. Rev. Lett.* **101**, 137004 (2008).
- Nakatsuji, S. *et al.* Superconductivity and quantum criticality in the heavy-fermion system β -YbAlB₄. *Nature Phys* **4**, 603–607 (2008).
- Coleman, P. Theory perspective: SCES 2016. *Philos. Mag.* **97**, 3527–3543 (2017).
- Tomita, T. *et al.* Unconventional quantum criticality in β -YbAlB₄ detached from its magnetically ordered phase. *Phys. Proc* **75**, 482–487 (2015).
- Mermin, N. D. & Wagner, H. Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic Heisenberg models. *Phys. Rev. Lett.* **17**, 1113 (1966).
- Wolf, W. P. Cooling by adiabatic magnetization. *Phys. Rev* **115**, 1196 (1959).
- Odom, B. *et al.* New measurement of the electron magnetic moment using a one-electron quantum cyclotron. *Phys. Rev. Lett.* **97**, 030801 (2006).
- Reif, F. *Fundamentals of Statistical and Thermal Physics*. (Waveland Press, Long Grove, 1965).
- Guimarães, A. P. *Magnetism and Magnetic Resonance in Solids*. (John Wiley & Sons, New York, 1998).
- Macaluso, R. T. *et al.* Crystal structure and physical properties of polymorphs of LnAlB₄ (Ln = Yb, Lu). *Chem. Mater.* **19**, 1918–1922 (2007).
- Matsumoto, Y. *et al.* T/B scaling of magnetization in the mixed valent compound β -YbAlB₄. *J. Phys.: Conf. Ser.* **391**, 012041 (2012).
- Kuga, K. *et al.* Quantum valence criticality in a correlated metal. *Science Adv.* **4**, eaao3547 (2018).
- Purcell, E. M. & Pound, R. V. A nuclear spin system at negative temperature. *Phys. Rev* **81**, 279 (1951).
- Wu, J., Zhu, L. & Si, Q. Entropy accumulation near quantum critical points: effects beyond hyperscaling. *J. Phys. Conf. Ser.* **273**, 012019 (2011).
- Matsukawa, S. *et al.* Pressure-driven quantum criticality and T/H scaling in the icosahedral Au–Al–Yb approximant. *J. Phys. Soc. Japan* **85**, 063706 (2016).
- Squillante, L. & de Souza, M. unpublished results.
- Feynman, R. P. *Statistical Mechanics*. (Addison-Wesley, Massachusetts, 1998).
- Bramwell, S. T. & Gingras, M. J.-P. Spin ice state in frustrated magnetic pyrochlore materials. *Science* **294**, 1495–1501 (2001).
- Görlitz, A. *et al.* Realization of Bose-Einstein condensates in lower dimensions. *Phys. Rev. Lett.* **87**, 130402 (2001).

57. Sachdev, S. Quantum magnetism and criticality. *Nat. Phys* **4**, 173–185 (2008).
58. Giamarchi, T. & Rüegg, C. & Tchernyshyov, Bose-Einstein condensation in magnetic insulators. *Nat. Phys* **4**, 198–204 (2008).
59. Lau, G. C. *et al.* Zero-point entropy in stuffed spin-ice. *Nat. Phys* **2**, 249–253 (2006).
60. Braun, S. *et al.* Negative absolute temperature for motional degrees of freedom. *Science* **339**, 52–55 (2013).
61. Rapp, A., Mandt, S. & Rosch, A. Equilibration rates and negative absolute temperatures for ultracold atoms in optical lattices. *Phys. Rev. Lett.* **105**, 220405 (2010).
62. Adobe Illustrator CC (Adobe, United States, <https://www.adobe.com/products/illustrator.html>) (2017).
63. OriginPro (OriginLab Corporation, United States, <https://www.originlab.com/>) (2020).
64. Wolfram Mathematica 11 (Wolfram, United States, <https://www.wolfram.com/mathematica/>).

Acknowledgements

M. de S. acknowledges financial support from the São Paulo Research Foundation – Fapesp (Grants Nos. 2011/22050-4 and 2017/07845-7), National Council of Technological and Scientific Development – CNPq (Grants No. 302498/2017-6), and TUVSOTE. ACS acknowledges CNPq (Grant No. 305668/2018-8). This work was partially granted by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil (Capes) - Finance Code 001 (Ph.D. fellowship of L.S. and I.F.M.). The Boston University Center for Polymer Studies is supported by NSF Grants PHY-1505000, CMMI-1125290, and CHE-1213217, and by DTRA Grant HDTRA1-14-1-0017. A.C.S. acknowledges financial support from the National Council of Technological and Scientific Development – CNPq (Grant No. 305668/2018-8).

Author contributions

L.S., G.O.G. and I.F.M. carried out the calculations and generated the figures. L.S. and M.de.S. wrote the paper with contributions from A.C.S., R.E.L., G.O.G., I.F.M. and H.E.S. All authors revised the manuscript. M.de.S. conceived and supervised the project.

Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to M.d.S.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2020



OPEN

Elastocaloric-effect-induced adiabatic magnetization in paramagnetic salts due to the mutual interactions

Lucas Squillante¹, Isys F. Mello¹, Antonio C. Seridonio² & Mariano de Souza¹✉

The temperature change under adiabatic stress, i.e., the elastocaloric effect, is a well-understood phenomenon and of particular interest due to its potential application in alternative ways for refrigeration. Here, we demonstrate that in the regime of low-temperatures (a few mK) real paramagnets can be magnetized when compressed adiabatically without applied magnetic field. Such adiabatic magnetization is a genuine many-body problem, stemming from the inherent dipolar mutual interactions between adjacent magnetic moments. We showcase experimental setups to carry out adiabatic magnetization and thus to access such a subtle effect. Perspectives of further investigations by controlling the mutual interactions in Bose–Einstein condensates in magnetic insulators and dipolar spin-ice systems via the adiabatic increase of temperature are also presented. Yet, we discuss the connection between the elastic Grüneisen parameter and the shift on the critical temperature of second-order phase transitions under adiabatic stress, as well as its connection with the Ehrenfest relation.

The understanding of the behavior of magnetic excitations in solids continues to be a topic of broad interest. Indeed, the interplay between magnetism and superconductivity^{1,2}, a proper description and the search for materials aiming to maximize the magnetocaloric effect^{3,4}, magnetic-field-induced quantum phase transitions^{5–7}, and exotic excitations like magnetic skyrmions^{8,9} are currently fertile fields of research. It has been almost a century since paramagnetic salts have been employed for cooling in the adiabatic demagnetization process¹⁰. It is well-known that the intrinsic mutual interactions between adjacent magnetic moments are the limiting factor in the attainment of lower temperatures, typically a few mK, using this process^{7,10}. Essentially, such mutual interactions generate an effective local magnetic field B_{loc} that prevents further demagnetization for magnetic fields lower than B_{loc} and, as a consequence, the system cannot be cooled below such a temperature. The many-body effects emerging from the mutual interactions show up when both the thermal and the magnetic dipolar energy^{10,11} become comparable. Recently, we have reported on the influence of such many-body effects in preventing the realization of a genuine zero-field quantum phase transition in real paramagnets⁷. Also, we have reported on the possibility of performing adiabatic magnetization⁷ by only manipulating the mutual interactions between spins. At this point, it is worth mentioning that the adiabatic magnetization here discussed is achieved without an external magnetic field and thus it differs from the known adiabatic magnetization usually reported in the literature concerning the so-called inverse magnetocaloric effect^{12,13}. Essentially, the idea consists in increasing the temperature adiabatically^{10,14}, so that the system is magnetized in order to maintain the entropy constant⁷. This is particularly true based on the fact that in an adiabatic process the total entropy should be held constant, while the entropy associated with the various excitations involved can be either decreased or increased¹⁵. Also, considering the reversibility of an adiabatic process, the adiabatic magnetization can be restarted as long as the system lies in a temperature range, in which the magnetic excitations associated with the mutual interactions are relevant. Here, we discuss the basic concepts of Thermodynamics associated with the adiabatic temperature increase, as well as experimental setups for the realization of elastocaloric-effect-induced adiabatic magnetization in paramagnetic salts. Yet, we discuss the possibility of exploring many-body effects in other magnetic systems via the adiabatic increase of temperature.

¹IGCE - Physics Department, São Paulo State University (Unesp), Rio Claro, SP 13506-900, Brazil. ²Department of Physics and Chemistry, São Paulo State University (Unesp), Ilha Solteira, SP 15385-000, Brazil. ✉email: mariano.souza@unesp.br

Temperature change due to an adiabatic compression

Based on concepts of Thermodynamics, the temperature of a system can be increased, without heat exchange with the surroundings, via adiabatic compression^{10,16}. In such a case, upon applying pressure the volume v varies quasi-statically. Next, we derive the expression for temperature change due to an adiabatic pressurization. We start recalling the first law of Thermodynamics^{16,17}:

$$dQ = dU + dW, \quad (1)$$

where dQ is the infinitesimal heat variation, dU the infinitesimal internal energy variation, and dW the infinitesimal work performed on the system upon applying external pressure. In a quasi-static process, the internal energy variation dU can be written as¹⁷:

$$dU = \left(\frac{\partial U}{\partial T} \right)_v dT, \quad (2)$$

where T is the temperature. The term $\left(\frac{\partial U}{\partial T} \right)_v$ in Eq. (2) can be recognized as the heat capacity at constant volume c_v ¹⁷ and thus:

$$dU = c_v dT. \quad (3)$$

The infinitesimal work dW performed on the system is given by $dW = -pdv$ ^{10,16,17}, where p is the applied pressure. Employing the relation for an adiabatic process $p = -\left(\frac{\partial U}{\partial v} \right)_S$ ¹⁷, where S is the entropy, the infinitesimal work dW can be written as follows:

$$dW = -pdv = \left(\frac{\partial U}{\partial v} \right)_S dv = \left(\frac{\partial U}{\partial S} \right)_v \left(\frac{\partial S}{\partial v} \right)_T dv. \quad (4)$$

The term $\left(\frac{\partial U}{\partial S} \right)_v = T$ in Eq. (4) is the canonical definition of temperature¹⁰. Also, employing the Maxwell-relation $\left(\frac{\partial S}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v$ ¹⁷, Eq. (4) becomes:

$$dW = T \left(\frac{\partial p}{\partial T} \right)_v dv. \quad (5)$$

Replacing Eqs. (3) and (5) into Eq. (1):

$$dQ = c_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv. \quad (6)$$

Recalling that $dQ = TdS$ ^{10,16,17} we write^{17,18}:

$$TdS = c_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv, \quad (7)$$

Since $dQ = TdS$ an adiabatic compression at a fixed T means that $dQ = 0$ and thus implying that S must remain constant ($dS = 0$) during this process. Therefore, Eq. (7) becomes:

$$c_v dT = -T \left(\frac{\partial p}{\partial T} \right)_v dv. \quad (8)$$

Employing the relation¹⁷:

$$\left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial T}{\partial v} \right)_p \left(\frac{\partial v}{\partial p} \right)_T = -1 \Rightarrow \left(\frac{\partial p}{\partial T} \right)_v = -\frac{1}{\left(\frac{\partial T}{\partial v} \right)_p \left(\frac{\partial v}{\partial p} \right)_T} \quad (9)$$

and using the Thermodynamic relations for the isothermal compressibility $\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T$ ¹⁷ and the volumetric thermal expansion $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p$ ¹⁷, Eq. (9) becomes:

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{\beta}{\kappa_T}. \quad (10)$$

Thus, replacing Eq. (10) into (8) we have:

$$c_v dT = -\frac{T\beta}{\kappa_T} dv.$$

Resulting thus in the key expression:

$$dT_S = -\frac{T\beta}{c_v \kappa_T} dv, \quad (11)$$

where dT_S refers to the infinitesimal temperature variation in an adiabatic compression. Equation 11 indicates that upon adiabatically compressing a solid, its volume is reduced ($dv < 0$) and thus the temperature is increased adiabatically ($dT_S > 0$) starting in a certain T . The temperature increase due to an adiabatic volume change here discussed is isentropic and thus a reversible adiabatic process. The very same mathematical analysis as in Eq. (11) can be performed upon analysing the increase of temperature due to an adiabatic increase of pressure. Now, we make use of the following thermodynamic relation¹⁴:

$$dS(T, p) = \left(\frac{\partial S}{\partial T} \right)_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp. \quad (12)$$

The derivative on the first term of the right side of Eq. (12) is $(\partial S/\partial T)_p = c_p/T$, where c_p is the heat capacity at constant pressure. Also, employing the Maxwell-relation $(\partial S/\partial p)_T = -(\partial v/\partial T)_p$ ¹⁷ Eq. (12) becomes:

$$dS = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T} \right)_p dp. \quad (13)$$

Considering a reversible adiabatic process [$dS(T, p) = 0$], Eq. (13) reads:

$$\frac{c_p}{T} dT_S = \left(\frac{\partial v}{\partial T} \right)_p dp_S, \quad (14)$$

where dp_S is the adiabatic pressure change. Thus, we achieve:

$$dT_S = \frac{\beta v T}{c_p} dp_S. \quad (15)$$

Essentially, Eq. (15) is similar to Eq. (11). Both Eqs. (11) and (15) can be employed to either describe an adiabatic compression ($dv < 0$, $dp > 0$) or expansion ($dv > 0$, $dp < 0$). However, in this work we have focused on the case of an adiabatic increase of temperature ($dT_S > 0$), i.e., an adiabatic compression. Note that in Eq. (15) the adiabatic temperature increase is written in terms of an infinitesimal adiabatic pressure change dp_S . Thus, in the light of Eq. (15) the temperature is increased due to an adiabatic application of pressure. At this point, we recall that the cooling of a system using pressure as the tuning parameter is the so-called barocaloric effect. The physical parameter that quantifies the barocaloric effect is the Grüneisen parameter $\Gamma_p = 1/T(\partial T/\partial p)_S$ ¹⁹. Interestingly enough, by manipulating Eq. (15) we obtain:

$$\left(\frac{\partial T}{\partial p} \right)_S = \frac{\beta v T}{c_p}. \quad (16)$$

Multiplying both sides of Eq. (16) by $1/T$, gives us:

$$\frac{\beta v}{c_p} = \frac{1}{T} \left(\frac{\partial T}{\partial p} \right)_S = \Gamma_p. \quad (17)$$

Note that Eq. (17) embodies naturally the definition of Γ_p ¹⁹. Experimentally, one of the ways of increasing the temperature adiabatically upon pressurization is by employing an adiabatic application of stress, which is discussed in the next Section.

Uniaxial stress application

Another way of promoting an adiabatic increase of temperature lies in the application of an uniaxial stress under adiabatic conditions¹⁸. The entropy variation in an adiabatic process with respect to the temperature and applied stress σ is given by¹⁸:

$$dS = \left(\frac{\partial S}{\partial T} \right)_\sigma dT + \left(\frac{\partial S}{\partial \sigma_{ij}} \right)_{T, \sigma} d\sigma_{ij} = 0, \quad (18)$$

where σ_{ij} represents the Voigt's abbreviated notation²⁰ for the stress components, the index i corresponds to the plane normal on which the stress is applied and j the direction of the applied stress²¹. Experimentally, the application of uniaxial stress on the specimen may be accompanied by an undesired strain gradient due to the bending of the sample²². Thus, in order to avoid such a strain gradient, a symmetric mounting of the stress application setup is required, as discussed in Ref.²². Essentially, the symmetric mounting lies in attaching a rigid cap foil on top of the sample's edges, to ensure that both lower and upper surfaces of the sample's edges are firmly secured and thus a homogeneous stress application is attainable^{18,22}, cf. Fig. 1. In our analysis, we consider that all stress components are kept constant except for one of the normal stresses since we are interested in the case of an uniaxial applied stress, cf. Fig. 1. Thus, considering that $(\partial S/\partial \sigma_{ij})_{T, \sigma} = \alpha_{ij}$, where α_{ij} is the thermal expansion coefficient in the Voigt's abbreviation, and $(\partial S/\partial T)_\sigma = c_\sigma/T$, where c_σ is the heat capacity at constant stress. Thus, rewriting Eq. (18) we achieve:

$$dT_S = -\frac{T}{c_\sigma} \alpha_{ij} d\sigma_{ij}. \quad (19)$$

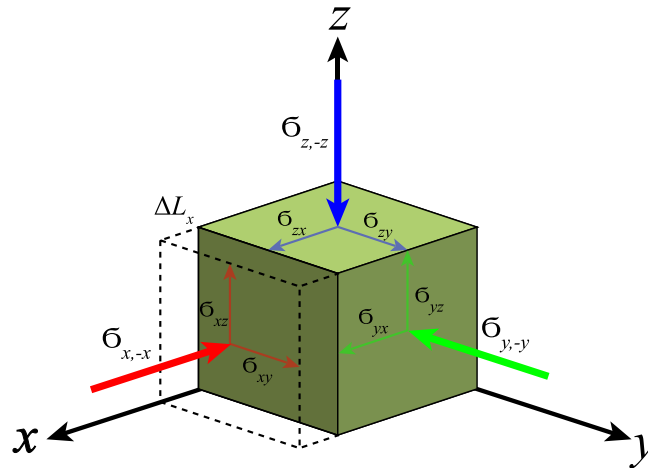


Figure 1. Uniaxial stress application in a solid. Schematic representation of the 9 stress components: 3 normal stresses ($\sigma_{x,-x}$, $\sigma_{y,-y}$, and $\sigma_{z,-z}$) and 6 shear stresses (σ_{xy} , σ_{yx} , σ_{yz} , σ_{zy} , σ_{zx} , and σ_{xz}). All the stress components can be represented in the Voigt's abbreviated notation σ_{ij} ²⁰, as discussed in more details in the main text. The dashed lines indicate the length variation ΔL_x when an uniaxial compressive stress $\sigma_{x,-x}$ is applied. Figure based on Ref.²¹. The application of uniaxial stress can be used for the adiabatic magnetization of a paramagnetic salt, cf. depicted in Fig. 2 and discussed in the main text.

Since we focus on the case of an adiabatic compression, $d\sigma_{ij}$ is recognized as the compressive stress, which is conventionally negative²¹. Thus, dT_S in Eq. (19) is positive meaning an adiabatic increase in temperature under an adiabatic uniaxial compressible stress. Thus, Eq. (19) can be rewritten as follows:

$$\frac{1}{T} \left(\frac{\partial T}{\partial \sigma_{ij}} \right)_S = \frac{\alpha_{ij}}{c_\sigma} = \Gamma_{ec}. \quad (20)$$

Following discussions in our previous work¹⁹, we define Γ_{ec} as the elastic Grüneisen parameter, which quantifies the temperature change due to an adiabatic uniaxial strain application. A key aspect regarding Eq. (19) refers to the experimental difficulties posed in achieving adiabatic conditions. In this regard, the oscillating strain technique can be employed, cf. depicted in Fig. 3. Using this technique, the strain frequency should be tuned in a time-scale lower than the thermal relaxation time of the system¹⁸. Thus, the system is strained more quickly than it exchanges heat with its surroundings and thus an adiabatic strain on the specimen can be attained. At this point, we consider that the entropy variation dS also depends on the magnetization change dM and thus we write:

$$dS(T, M, \sigma) = \left(\frac{\partial S}{\partial T} \right)_{M, \sigma} dT + \left(\frac{\partial S}{\partial M} \right)_{T, \sigma} dM + \left(\frac{\partial S}{\partial \sigma_{ij}} \right)_{T, M} d\sigma_{ij}. \quad (21)$$

Because of a reversible adiabatic process $dS(T, M, \sigma) = 0$ and thus:

$$-\left(\frac{\partial S}{\partial M} \right)_{T, \sigma} dM = \left(\frac{\partial S}{\partial T} \right)_{M, \sigma} dT + \left(\frac{\partial S}{\partial \sigma_{ij}} \right)_{T, M} d\sigma_{ij}. \quad (22)$$

Employing the Maxwell relation $\left(\frac{\partial S}{\partial M} \right)_T = -\left(\frac{\partial B}{\partial T} \right)_S$ ¹⁷, Eq. (22) becomes:

$$\left(\frac{\partial B}{\partial T} \right)_S dM = \left(\frac{\partial S}{\partial T} \right)_{M, \sigma_{ij}} dT + \left(\frac{\partial S}{\partial \sigma} \right)_{T, M} d\sigma_{ij}. \quad (23)$$

Equation 23 embodies the principle of the adiabatic magnetization under the application of uniaxial stress. In order to hold the entropy constant when the temperature is increased adiabatically, there has to be a variation of the magnetization dM to compensate the entropy change associated with both dT_S and $d\sigma_{ij}$, as well as a change of the magnetic field B in respect to the adiabatic temperature variation. It is clear that B should be recognized as B_{loc} , since there is no external magnetic field acting on the system. Essentially, an adiabatic application of σ_{ij} in a paramagnetic system implies in an adiabatic temperature increase and to hold S constant, the system is spontaneously magnetized adiabatically by dM . Note that we have considered that a paramagnetic insulator presents a finite magnetization in the absence of an external magnetic field when $T \rightarrow 0$ K due to the intrinsic presence of B_{loc} , being thus its ground-state a ferromagnetic phase, cf. discussions presented in Ref.⁷. Therefore, the infinitesimal magnetization dM in Eq. (23) is due to the magnetic energy increase associated with the mutual interactions in order to keep the entropy constant as a response to an adiabatic increase of temperature. Based on such discussions, it is tempting to infer the concept of positive and negative temperatures^{10,23,24} in terms of adiabatic deformations. However, the requirements for such are not fulfilled²⁴.

The Grüneisen parameter and strain-dependent second-order phase transitions

As discussed by us in Ref.¹⁹, the Grüneisen parameter is enhanced close to any critical point due to the intrinsic entropy accumulation near it and, as previously discussed, the elastic Grüneisen parameter quantifies the elastocaloric effect. As discussed in the next, the elastic Grüneisen parameter incorporates the shift in the critical temperature T_c of a second-order phase transition due to the application of stress. Under adiabatic conditions, such a shift in T_c occurs because the temperature variation of the specimen due to the elastocaloric effect has to compensate the entropy change associated with the strain¹⁸. We make use of the expression for the entropy variation of an infinitesimal strain $d\varepsilon$ under adiabatic conditions ($dS = 0$) close to a second-order phase transition¹⁸:

$$dS = -\frac{c_\sigma^{(cr)}}{T} \left(\frac{dT_c}{d\varepsilon} \right)_T d\varepsilon + \frac{c_\sigma}{T} dT = 0, \quad (24)$$

where $c_\sigma^{(cr)}$ is the critical contribution to the heat capacity at constant stress. The first term on the right side of Eq. (24) associates the entropy change due to $(dT_c/d\varepsilon)_T$ and the second term accounts for the entropy variation due to the elastocaloric effect of the specimen¹⁸. Rearranging Eq. (24), we have¹⁸:

$$\left(\frac{dT}{d\varepsilon} \right)_S = \frac{c_\sigma^{(cr)}}{c_\sigma} \left(\frac{dT_c}{d\varepsilon} \right)_T. \quad (25)$$

Equation 25 relates the elastocaloric effect to the corresponding shift in T_c ¹⁸. Note that Γ_{ec} can be determined in terms of $d\varepsilon$ upon multiplying both sides of Eq. (25) by $1/T$. Since Eq. (25) accounts for the critical contribution to the heat capacity near T_c , it is associated with the critical contribution to the elastic Grüneisen parameter Γ_{ec}^{cr} , namely:

$$\Gamma_{ec}^{cr} = \frac{1}{T} \left(\frac{dT}{d\varepsilon} \right)_S = \frac{1}{T} \frac{c_\sigma^{(cr)}}{c_\sigma} \left(\frac{dT_c}{d\varepsilon} \right)_T. \quad (26)$$

Interestingly, Γ_{ec}^{cr} quantifies the shift in T_c in the vicinity of a second-order phase transition due to an adiabatic strain. If $(dT/d\varepsilon)_S > 0$ in Eq. (26) implies that the temperature of the system is adiabatically increased in response to the strain, which is the case of an adiabatic compressible stress ($\sigma_{ij} < 0$), cf. Eq. (19). Thus, $(dT_c/d\varepsilon)_T$ is also positive, i.e., T_c is shifted to higher temperatures in response to the adiabatic strain. Based on similar arguments, if $(dT/d\varepsilon)_S < 0$ in Eq. (26), T_c is shifted to lower temperatures. It is well-known that $c_\sigma^{(cr)}$ is enhanced close to T_c and thus, based on Eq. (26), Γ_{ec}^{cr} is enhanced as well. Hence, a pronounced elastocaloric effect is expected close to a second-order phase transition. This is in perfect agreement with our recent work about giant caloric effects close to critical points, cf. discussed in Ref.¹⁹. Next, we discuss the connection between the Grüneisen parameter in the vicinity of T_c and the celebrated Ehrenfest relation²⁵. Note that close to T_c , Eq. (19) can be easily rewritten in terms of the thermal expansion and heat capacity jumps, $\Delta\alpha_{ij}$ and Δc_σ , which correspond to the difference between critical and ordinary contributions to the thermal expansion coefficient and heat capacity, respectively. Hence, we have:

$$dT_c = -T_c \frac{\Delta\alpha_{ij}}{\Delta c_\sigma} d\sigma_{ij}. \quad (27)$$

Rearranging Eq. (27), we achieve^{26,27}:

$$\left(\frac{dT_c}{d\sigma_{ij}} \right)_S = -T_c \frac{\Delta\alpha_{ij}}{\Delta c_\sigma}, \quad (28)$$

which has some resemblance with the Ehrenfest relation²⁵. Equation 28 indicates the T_c variation under adiabatic stress. More specifically, Eq. (28) takes into account the critical contribution to the elastic Grüneisen parameter Γ_{ec}^{cr} , which reads:

$$\Gamma_{ec}^{cr} = \frac{1}{T_c} \left(\frac{dT_c}{d\sigma_{ij}} \right)_S = -\frac{\Delta\alpha_{ij}}{\Delta c_\sigma}. \quad (29)$$

In this case, Γ_{ec}^{cr} quantifies the shift in T_c under the application of an adiabatic stress analogously to the shift in T_c under application of pressure in the well-known Ehrenfest relation. Although Eq. (29) has already been reported in Refs.^{26,27}, its connection with the Grüneisen parameter is still lacking. It is worth mentioning that such an analysis can be extended to other cases, such as the magneto-caloric and the electro-caloric effects, namely^{6,7,19}:

$$\Gamma_{mag}^{cr} = \frac{1}{T_c} \left(\frac{dT_c}{dB} \right)_S = -\frac{\Delta\alpha_B}{\Delta c_B}, \quad (30)$$

and

$$\Gamma_{ece}^{cr} = \frac{1}{T_c} \left(\frac{dT_c}{dE} \right)_S = -\frac{\Delta\alpha_E}{\Delta c_E}, \quad (31)$$

where Γ_{mag}^{cr} and Γ_{ece}^{cr} are the critical contributions to the magneto-caloric and electro-caloric Grüneisen parameters, and E is the electric field. Thus, in an analogy with the canonical Ehrenfest relation, Eqs. (29), (30), and

(31) quantify the T_c shift of a second-order phase transition under the adiabatic application of stress, magnetic field, or electric field, respectively.

Adiabatic magnetization by only manipulating the mutual interactions between spins

The magnetic interactions between adjacent magnetic moments in a real paramagnet lead to a finite effective local magnetic field B_{loc} , which is usually about 0.01 T considering an average distance between magnetic moments of $5\text{\AA}$ ⁷. By cooling the paramagnetic system down to temperatures, in the range in which the energy associated with the magnetic interactions are relevant (usually $T < 6\text{ mK}$)⁷, many-body effects set in. In such a temperature range it is possible to increase the temperature adiabatically, cf. previous discussions. Essentially, in order to keep the entropy constant there has to be an increase of the local field to compensate such temperature increase⁷, i.e., the system is magnetized. For the sake of completeness, we recall some relevant results reported by us in Ref.⁷. The microscopic treatment of the mutual interactions requires a many-body approach, which can be described by the Hamiltonian^{7,28,29}:

$$H = -J' \sum_{\langle ij \rangle} \vec{S}_i^{z_i} \cdot \vec{S}_j^{z_j} + D r_{nn}^3 \sum_{i>j} \frac{\vec{S}_i^{z_i} \cdot \vec{S}_j^{z_j}}{|\vec{r}_{ij}|^3} - \frac{3(\vec{S}_i^{z_i} \cdot \vec{r}_{ij})(\vec{S}_j^{z_j} \cdot \vec{r}_{ij})}{|\vec{r}_{ij}|^5}, \quad (32)$$

where J' is the magnetic coupling constant, $\vec{S}$ is the spin vector oriented along the local z_i Ising $\langle 111 \rangle$ axis, i and j refer to the two sites of the lattice, $\vec{r}$ is the position vector, $D = (\mu_0 \mu^2)/(4\pi r_{nn}^3)$, μ_0 is the vacuum permeability, μ the magnetic moment, and r_{nn} is the distance between nearest-neighbor spins. The second term of the Hamiltonian (Eq. 32) embodies the magnetic energy associated with the interaction between a single magnetic moment and its nearest neighbors. The Hamiltonian of Eq. (32) is key in understanding the adiabatic magnetization here discussed, since it takes into account the microscopic character of the mutual interactions responsible to give rise to B_{loc} . It turns out that when the temperature is increased adiabatically, the mutual interactions are altered in order to increase the magnetic energy and to keep the entropy constant. In our analysis, we employ a simple mean-field-type (molecular-field) approach to treat the mutual interactions, which is discussed in the next. At this point, the understanding of the adiabatic magnetization requires a treatment in terms of the uncertainty principle. In order to keep the entropy constant during the adiabatic magnetization process, the magnetic energy U_{mag} of the paramagnetic system has to be changed, which is given by³⁰:

$$U_{mag} = -\frac{m_J}{\sqrt{J(J+1)}} \mu B_{loc} = -\mu B_{loc} \cos \phi, \quad (33)$$

where m_J is the magnetic quantum number, J the total angular momentum quantum number, and ϕ is the angle between μ and B_{loc} . Employing U_{mag} , the energy uncertainty ΔE can be calculated by the expression¹⁰:

$$\Delta E = U_{mag} - E, \quad (34)$$

where E is the average magnetic energy. Plugging Eq. (33) into Eq. (34) and $E = \mu_B B_{loc} N \tanh\left(\frac{\mu_B B_{loc}}{k_B T}\right)$ ¹⁰, where N is the number of particles, we have⁷:

$$\Delta E = \mu_B B_{loc} \left[N \tanh\left(\frac{\mu_B B_{loc}}{k_B T}\right) - \cos \phi \right]. \quad (35)$$

In Eq. (35), ΔE is minimized when $\cos \phi \rightarrow 1$ ⁷. Since the adiabatic magnetization is performed during a quasi-static process, this means that the uncertainty in time Δt should be maximized, while ΔE is minimized. The condition for ΔE to be minimized lies in varying the total angular momentum projection⁷. This is attainable by increasing only the z -axis projection of the total angular momentum vector $\vec{J}$. The consequence of the enhancement of the $\vec{J}$ projection in the z -axis is that the magnetic energy is decreased and thus the system is magnetized⁷, meaning that the angle ϕ between μ and B_{loc} is lowered. In summary, the genesis of the increment ΔB_{loc} in the adiabatic magnetization process is given by the increase of the $\vec{J}$ projection in the z -direction. This is one of the key results reported in Ref.⁷. In general terms, in the adiabatic magnetization process (Fig. 2) of the mutual interactions, the temperature is adiabatically increased from T_1 to T_2 and thus we can write⁷:

$$T_2 = T_1 \frac{\sqrt{B_{loc}^2 + \Delta B_{loc}^2}}{B_{loc}}, \quad (36)$$

where μ_B is the Bohr magneton, k_B is the Boltzmann constant, and ΔB_{loc} is the magnetic field increment that will emerge into the system to compensate the adiabatic increase of temperature. The term ΔB_{loc} refers to the adiabatic magnetization by only manipulating the mutual interactions of the system upon adiabatically increasing its temperature. Then, ΔB_{loc} can be determined by the simple expression⁷:

$$\Delta B_{loc} = B_{loc} \sqrt{\frac{T_2^2}{T_1^2} - 1}. \quad (37)$$

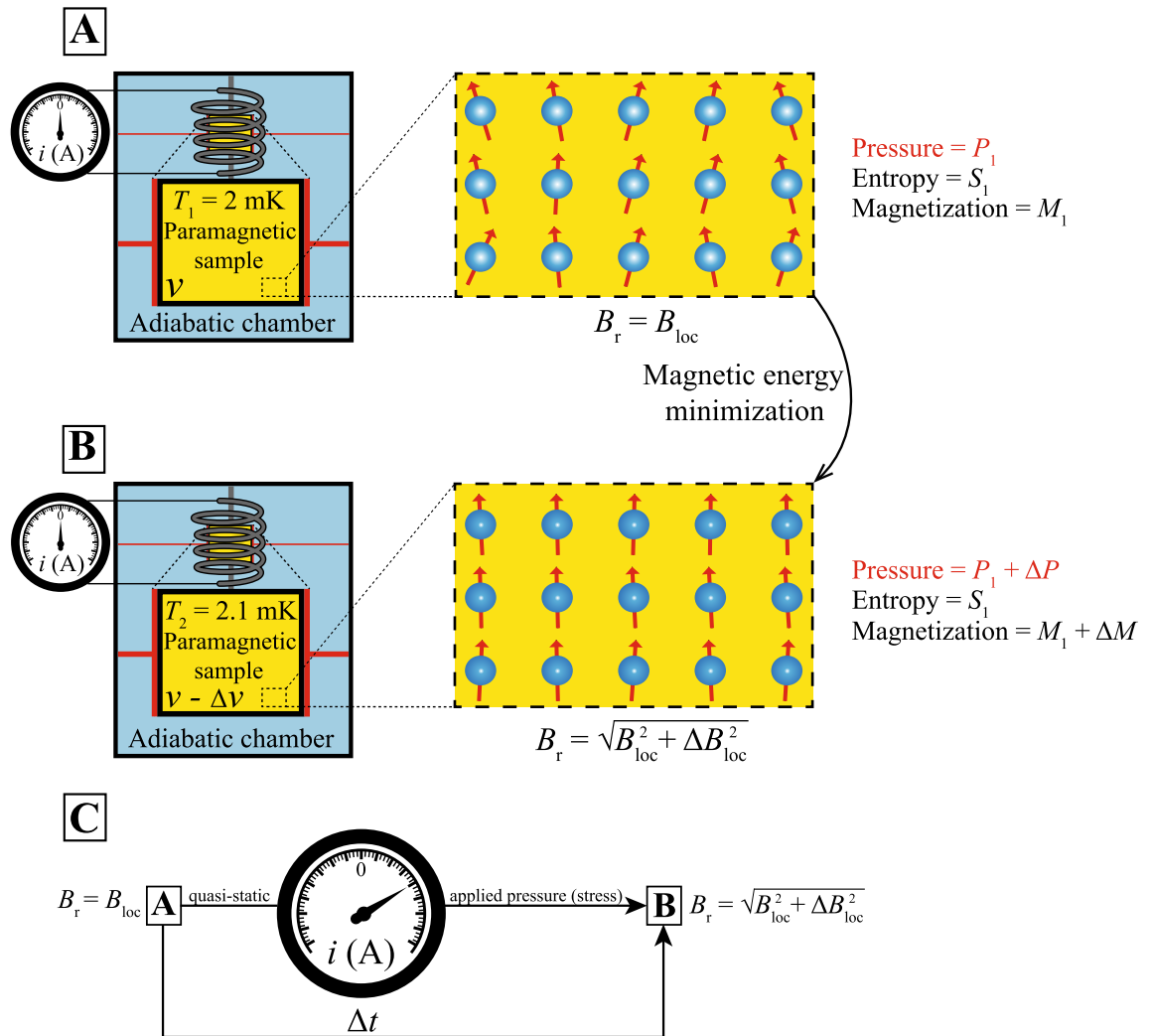


Figure 2. Schematic representation of the steps for performing the adiabatic magnetization of a paramagnetic specimen⁷. (A) A sample with volume v is inserted inside a coil, which is attached to an ampere meter, into an adiabatic chamber and the temperature is decreased to $T_1 = 2 \text{ mK}$, being the sample under pressure p_1 , with entropy S_1 , and magnetization M_1 . External magnetic fields are absent and thus the resulting magnetic field $B_r = B_{loc}$ due to the intrinsic mutual interactions between adjacent magnetic moments (represented by the red arrows). The dashed lines represent a zoom of the paramagnetic sample inside the coil and the spins inside the sample. (B) A quasi-static pressure, more specifically the stress as depicted in Fig. 3, is applied so that the volume is reduced by a factor Δv , leading thus to an adiabatic increase of the sample temperature to $T_2 = 2.1 \text{ mK}$. The sample is now under a pressure ($p_1 + \Delta p$) and it is magnetized by a factor ΔM in order to hold the entropy S_1 constant. Since the magnetization of the sample is increased (minimization of the energy, cf. discussions in the main text), the spins are slightly vertically aligned since now the resulting field is $B_r \simeq \sqrt{B_{loc}^2 + \Delta B_{loc}^2}$. (C) During the time interval Δt from process A to B (quasi-static applied pressure, i.e., stress cf. Fig. 3), the magnetic field is increased from B_{loc} to $\sqrt{B_{loc}^2 + \Delta B_{loc}^2}$ and thus the magnetic flux is changed over Δt inducing an electromotive force, which in turn is associated with a finite electrical current, which can be measured by the ampere meter. Some parts of this figure were created employing templates available in Ref.³¹.

Experimental realization of the adiabatic magnetization

In order to carry out the adiabatic magnetization of a paramagnetic system, it must be isolated from the surrounding in a low-temperature condition ($T < 6 \text{ mK}$) and pressure, which experimentally can be the stress, cf. illustrated in Fig. 3, must be quasi-statically applied to increase its temperature adiabatically. Upon increasing the stress as shown in Fig. 3, in such a quasi-static process, the temperature will be increased adiabatically and then the paramagnetic system will be magnetized by a term ΔB_{loc} , as previously discussed, in order to keep the entropy constant⁷.

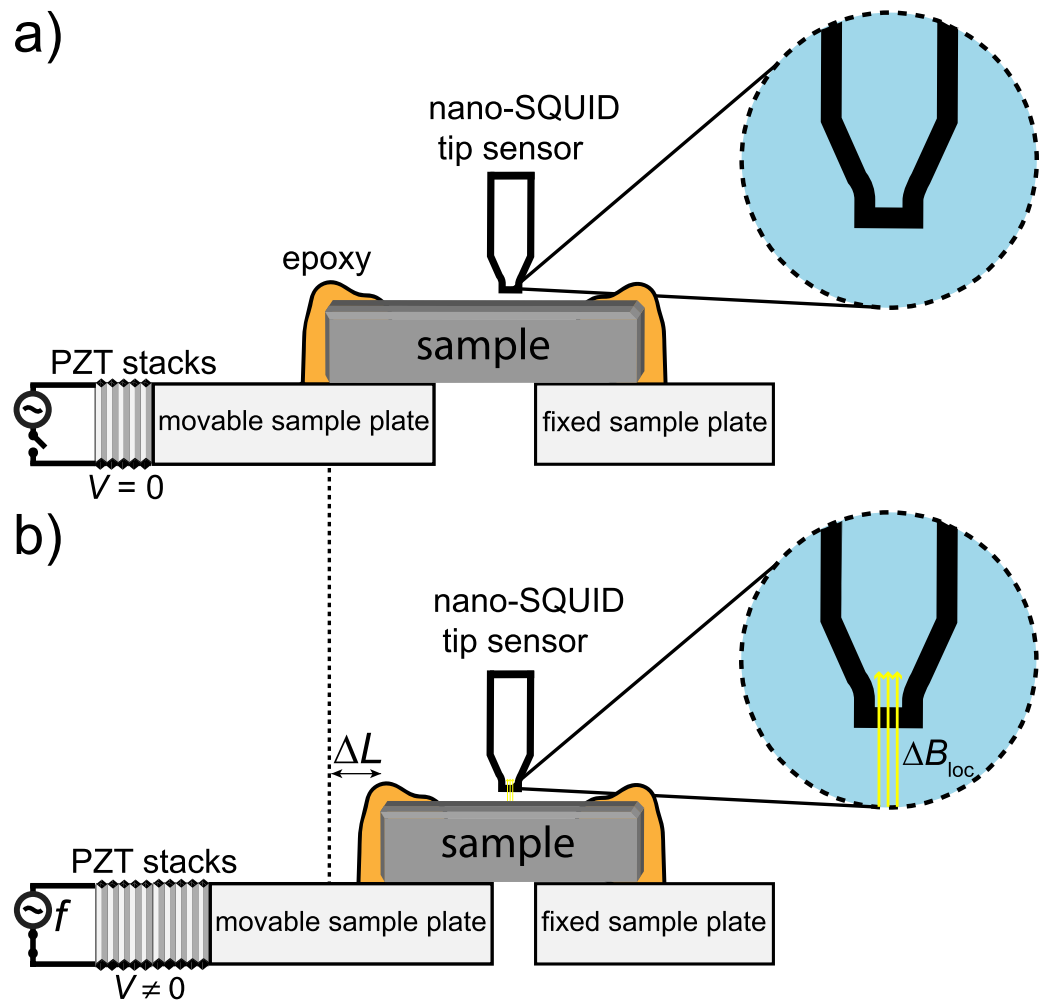


Figure 3. Schematic representation of the adiabatic magnetization process in a paramagnetic salt employing an experimental setup for the application of uniaxial stress. The sample is attached to both movable and fixed plates by using epoxy. A nano-SQUID tip sensor is placed close to the sample. Lead zirconate titanate (PZT) piezoelectric stacks are attached to the movable plate. In (a) there is no applied A.C. voltage $V = 0$ and thus no deformation of the PZT stacks takes place. In (b) an A.C. voltage $V \neq 0$ is applied to the PZT stacks at a given frequency f making the PZT stacks to deform. Hence, the sample is uniaxially compressed leading to a variation of its length L by ΔL . The adiabatic regime can be achieved upon tuning f . The employed frequency should be higher than the inverse relaxation time τ^{-1} of the system, since τ represents the time scale of the heat exchange between the sample and its surroundings, cf. Ref.¹⁸. In this process, the temperature of the system is adiabatically increased and thus an adiabatic magnetization of the sample takes place, which is detected by the attached nano-SQUID tip sensor. Figure prepared based on Refs.^{18,22,37}. More details in the main text.

SQUID

Another possible way of measuring ΔB_{loc} would be employing a nano-SQUID on a tip³², which presents outstanding sensitivity to measure the magnetic field generated by a single magnetic moment. In the present case, we are interested in measuring the local field during the adiabatic magnetization process. Essentially, the presence of a magnetic flux Φ through the SQUID affects its corresponding superconducting electrical current. Such magnetic flux depends on the magnetic field acting on the SQUID and the surface area S' of the superconducting loop. The magnetic flux Φ through the SQUID is given by³³:

$$\Phi = \int_{S'} \vec{B} \cdot d\vec{S}' = n \left(\frac{h}{2e} \right), \quad (38)$$

where n is an integer number, h is Planck's constant, and e the fundamental electron charge. The factor $(h/2e)$ is the quantum of magnetic flux Φ_0 and it dictates the SQUID's sensitivity. Considering the conditions of the adiabatic temperature increase from T_1 to T_2 (cf. Fig. 2) for the realization of the adiabatic magnetization, we estimate $\Delta B_{loc} \approx 3.2 \text{ mT}$ ⁷. In the particular case of a nano-SQUID on a tip³², given the fact that Φ depends on S' , the sensitivity for detecting magnetic fields is compromised by the nanometer size of such a device. However, the

spatial resolution of the device is improved and its sensitivity to magnetic dipoles increased, i.e., the nano-SQUID on a tip is extremely sensitive to small magnetic moments³², enabling thus the detection of ΔB_{loc} generated from the adiabatic magnetization process in a paramagnetic system. Given the high-sensitivity of the SQUID's critical current to both temperature and magnetic field, the nano-SQUID on a tip is also a very accurate scanning cryogenic thermal sensor^{34–36}. Thus, employing such a device, a very sensitive thermal imaging of energy dissipation of nanoscale processes can be carried out^{34–36}. Hence, the thermal mapping of the adiabatic heating during the adiabatic magnetization can be carried out employing the oscillating strain experimental setup proposed in Ref.¹⁸ with an attached nano-SQUID on tip³², cf. depicted in Fig. 3. The relevant parameters involving the use of a nano-SQUID on a tip for measuring the adiabatic magnetization here discussed, such as the width of the measured signal for a particular frequency of the PZT stacks A.C. voltage, shall depend on the particular physical properties of the investigated system.

Adiabatic increase of temperature in interacting systems

The adiabatic increase of temperature upon applying pressure (stress, as depicted in Fig. 3) can lead to other investigations in the frame of many-body systems. There is a subtle difference between applying pressure/stress (Fig. 3) to a system and then sweeping its temperature non-adiabatically with the case of increasing its temperature adiabatically upon applying external pressure/stress (Fig. 3). When adiabatic pressurization takes place in an interacting system, it will rearrange itself as a whole due to the many-body effects in order to hold the entropy constant, which obviously is not the case for non-adiabatic conditions. Thus, employing adiabatic temperature changes, the many-body character of various interacting systems can be explored in an unprecedented way. This is particular true for Bose–Einstein condensates (BEC) in magnetic insulators³⁸ and dipolar spin-ice²⁹ systems, just to mention a few examples. In the specific case of the BEC in a magnetic insulator reported in Ref.³⁸, the adiabatic increase of temperature in such a system will change the energy ε of a triplon (Eq. 2 of Ref.³⁸) and, as a consequence, the density of triplons will be altered due to the so-called Zeeman term $-g\mu_B B S^z$ in the triplon energy, where g is the gyromagnetic ratio, S^z is the spin projection in the z direction, and z is the direction of the external magnetic field. Considering that the resulting magnetic field of the system depends on both the external applied magnetic field and B_{loc} inherent to this particular system, the adiabatic increase of temperature will change B_{loc} , which in turn will change the density of triplons as well. Note that in this particular case, both an external magnetic field and B_{loc} are considered⁷, which is not the case for the adiabatic magnetization due to the mutual interactions discussed previously. Hence, the adiabatic increase of temperature can be seen as an alternative way for investigating the system's interactions and its phase diagram. This is a simple example of an investigation of the many-body character in interacting systems that can be carried out by employing an adiabatic increase of temperature. Yet, we point out that a similar case of the adiabatic magnetization for the Brillouin-like paramagnet, performed in the temperature range below which is associated with the relevance of the magnetic dipolar mutual interactions, can be carried out for the case of electric dipoles. More specifically, when considering the temperature regime where the interactions between electric dipoles are relevant, the Langevin equation³⁹ can be employed following the approach reported in Ref.⁷ to demonstrate that when the temperature is adiabatically increased, a spontaneous adiabatic electric polarization of the system takes place, analogously to the adiabatic magnetization.

Conclusions

We have revisited the basic concepts associated with the increase of temperature under adiabatic application of hydrostatic pressure and uniaxial stress. Experimentally, the attainable mechanism to increase the temperature adiabatically is the application of stress. Following our previous work⁷, we have proposed experimental setups for detecting the magnetic response under adiabatic conditions. Furthermore, we have proposed an alternative way for exploring various exotic phases of matter, like BEC in magnetic insulators and spin-ice, upon changing the temperature adiabatically. Yet, we have discussed that the elastic Grüneisen parameter quantifies the shift in the critical temperature T_c of a second-order phase transition under an adiabatic strain, as well as its connection with the Ehrenfest relation.

Methods

All the figures presented in this work were created employing the software Adobe Illustrator Version CC 2017 and a few templates available in Ref.³¹ were used in the creation of the figures.

Received: 27 October 2020; Accepted: 16 April 2021

Published online: 03 May 2021

References

- Mathur, N. D. *et al.* Magnetically mediated superconductivity in heavy fermion compounds. *Nature* **394**, 39–43 (1998).
- Bert, J. A. *et al.* Direct imaging of the coexistence of ferromagnetism and superconductivity at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface. *Nat. Phys.* **7**, 767–771 (2011).
- Pecharsky, V. K. & Gschneidner, K. A. Jr. Magnetocaloric effect and magnetic refrigeration. *J. Magn. Magn. Mater.* **200**, 44–56 (1999).
- Tishin, A. M. & Spichkin, Y. I. *The Magnetocaloric Effect and its Applications* (CRC Press, 2003).
- Sachdev, S. *Quantum Phase Transitions* (Cambridge University Press, 2011).
- Gomes, G. O. *et al.* Magnetic Grüneisen parameter for model systems. *Phys. Rev. B* **100**, 054446 (2019).
- Squillante, L. *et al.* Unveiling the physics of the mutual interactions in paramagnets. *Sci. Rep.* **10**, 7981 (2020).
- Fert, A., Reyren, N. & Cros, V. Magnetic skyrmions: advances in physics and potential applications. *Nat. Rev. Mater.* **2**, 17031 (2017).

9. Peng, L. *et al.* Controlled transformation of skyrmions and antiskyrmions in a non-centrosymmetric magnet. *Nat. Nanotechnol.* **15**, 181–186 (2020).
10. Baierlein, R. *Thermal Physics* (Cambridge University Press, 1999).
11. Blundell, S. *Magnetism in Condensed Matter* (Oxford University Press, 2001).
12. Krenke, T. *et al.* Inverse magnetocaloric effect in ferromagnetic Ni–Mn–Sn alloys. *Nature* **4**, 405–454 (2005).
13. Moya, X. *et al.* Cooling and heating by adiabatic magnetization in the $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ magnetic shape-memory alloy. *Phys. Rev. B* **75**, 184412 (2007).
14. Sonntag, S. E., Borgnakke, C. & Wylen, G. J. V. *Fundamentals of Thermodynamics* (Wiley, 2003).
15. Landau, L. D. & Lifshitz, E. M. *Statistical Physics* Vol. 5 (Pergamon Press, 1959).
16. Callen, H. B. *Thermodynamics* (Wiley, 1960).
17. Stanley, H. E. *Introduction to Phase Transitions and Critical Phenomena* (Oxford Science Publications, 1971).
18. Ikeda, M. S. *et al.* AC elastocaloric effect as a probe for thermodynamic signatures of continuous phase transitions. *Rev. Sci. Instrum.* **90**, 083902 (2019).
19. Squillante, L., Mello, I. F., Seridonio, A. C. & de Souza, M. Giant caloric effects close to any critical end point. Preprint at [arXiv:2003.13060](https://arxiv.org/abs/2003.13060) (2020).
20. Barron, T. H. K., Collins, J. G. & White, G. K. Thermal expansion of solids at low temperatures. *Adv. Phys.* **29**, 609–730 (1980).
21. Meyers, M. A. & Chawla, K. K. *Mechanical Behavior of Materials* (Cambridge University Press, 2009).
22. Hicks, C. W., Barber, M. E., Edkins, S. D., Brodsky, D. O. & Mackenzie, A. P. Piezoelectric-based apparatus for strain tuning. *Rev. Sci. Instrum.* **85**, 065003 (2014).
23. Purcell, E. M. & Pound, R. V. A nuclear spin system at negative temperature. *Phys. Rev.* **81**, 279 (1951).
24. Ramsey, N. F. Thermodynamics and statistical mechanics at negative absolute temperatures. *Phys. Rev.* **103**, 20 (1956).
25. Ehrenfest, P. Phasenumwandlungen im üblichen und erweiterten Sinn, klassifiziert nach den entsprechenden Singularitäten des thermodynamischen Potentials. *Proc. Acad. Sci. Amst.* **36**, 153–157 (1933).
26. Mori, K. & Hayashi, M. Effect of a two-dimensional pressure on the Curie points of triglycine sulphate and Rochelle salt. *J. Phys. Soc. Jpn.* **33**, 1396–1400 (1972).
27. Moin, P. B. Ehrenfest equations for second-order phase transition under hydrostatic and uniaxial stresses. *Ph. Transit.* **89**, 1074–1077 (2016).
28. Feynman, R. P. *Statistical Mechanics* (Addison-Wesley, 1998).
29. Bramwell, S. T. & Gingras, M. J.-P. Spin ice state in frustrated magnetic pyrochlore materials. *Science* **294**, 1495–1501 (2001).
30. Guimarães, A. P. *Magnetism and Magnetic Resonance in Solids* (Wiley, 1998).
31. Vectorized images available at <https://www.vecteezy.com>.
32. Vasyukov, D. *et al.* A scanning superconducting quantum interference device with single electron spin sensitivity. *Nat. Nanotechnol.* **8**, 639–644 (2013).
33. Ashcroft, N. W. & Mermin, N. D. *Solid State Physics* (Saunders College Publishing, 1976).
34. Halbertal, D. *et al.* Nanoscale thermal imaging of dissipation in quantum systems. *Nature* **539**, 407–410 (2016).
35. Halbertal, D. *et al.* Imaging resonant dissipation from individual atomic defects in graphene. *Science* **358**, 1303–1306 (2017).
36. Marguerite, A. *et al.* Imaging work and dissipation in the quantum Hall state in graphene. *Nature* **575**, 628–633 (2019).
37. Gannon, L. *et al.* A device for the application of uniaxial strain to single crystal samples for use in synchrotron radiation experiments. *Rev. Sci. Instrum.* **86**, 103904 (2015).
38. Giamarchi, T., Rüegg, C. & Tchernyshyov, O. Bose–Einstein condensation in magnetic insulators. *Nat. Phys.* **4**, 198–204 (2008).
39. Kittel, C. *Introduction to Solid State Physics* 8th edn. (Wiley, 2005).

Acknowledgements

M. de S. acknowledges financial support from the São Paulo Research Foundation – Fapesp (Grants Nos. 2011/22050-4, 2017/07845-7, and 2019/24696-0), National Council of Technological and Scientific Development – CNPq (Grants No. 302498/2017-6 and 302887/2020-2), and TUVSOTE. A.C.S. acknowledges financial support from the National Council of Technological and Scientific Development – CNPq (Grant No. 305668/2018-8). This work was partially granted by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil (Capes) - Finance Code 001 (Ph.D. fellowship of L.S. and I.F.M.).

Author contributions

L.S. and I.F.M. carried out the calculations and L.S. generated the figures. L.S. and M.deS. wrote the paper with contributions from A.C.S. and I.F.M. All authors revised the manuscript. M.deS. conceived and supervised the Project.

Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to M.S.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2021



Giant caloric effects close to *any* critical end point

Lucas Squillante^a, Isys F. Mello^a, A.C. Seridonio^b, Mariano de Souza^{a,*}

^a São Paulo State University (Unesp), IGCE – Physics Department, Rio Claro, SP, Brazil

^b São Paulo State University (Unesp), Department of Physics and Chemistry, Ilha Solteira, SP, Brazil

ARTICLE INFO

Keywords:

Multilayers
Electronic materials
Crystal structure
Dielectric properties
Ferroelectricity

ABSTRACT

The electrocaloric (EC) effect, i.e., the reversible temperature change due to adiabatic variations of the electric field, is of great interest due to its potential technological applications in refrigeration. Based on entropy arguments, we present a new framework to attain giant EC effects. Our findings are fourfold: (i) we employ the recently-proposed electric Grüneisen parameter Γ_E to quantify the EC effect and discuss its advantages over the existing so-called electrocaloric strength; (ii) prediction of giant caloric effects *close to any* critical end point; (iii) proposal of potential key-ingredients to enhance the EC effect; (iv) demonstration of Γ_E as a proper parameter to probe quantum ferroelectricity in connection with the celebrated Barrett's formula. Our findings enable us to interpret the recently-reported large EC effect at room-temperature in oxide multilayer capacitors [5], paving thus the way for new venues in the field.

1. Introduction

Nowadays, there is an increasing scientific interest regarding new cooling devices that can be both efficient and more environmentally friendly, see, e.g., Refs. [1–3] and references cited therein. Much efforts have been made to develop such devices employing, for instance, both magnetocaloric (MC) [4] and electrocaloric (EC) effects [5], i.e., the cooling as a consequence of the adiabatic removal of magnetic and electric field, respectively, being such effects different from each other in terms of the adiabatic variation of distinct tuning parameters. When dealing with magnetocaloric devices, one of the limitations is the requirement, in many cases, to have a superconducting refrigerated permanent magnet, reducing thus the cost-benefit of employing such devices in technological applications. The main advantage of electrocaloric devices in turn is highlighted by the fact that only an adiabatic electric field sweep is needed for cooling the system. Furthermore, caloric effects in multiferroic materials have been currently investigated [6,7]. Our approach is also valid for such systems. More recently, the EC effect became even a more attractive topic because of the discovery of large electrocaloric effect in oxide multilayer capacitors [5].

Considering the EC effect in real systems, it is natural to look for its optimization aiming to increase the benefits in potential practical applications, as well as aiming to lower the cost. However, the mechanism for attaining maximized EC effects, as well as the appropriated conditions for such, remains elusive. Here, based on entropy arguments, we

propose potential key-ingredients to achieve giant EC effects. Fig. 1 depicts a schematic phase diagram, namely temperature as a function of the tuning parameter, highlighting the merge of the coexistence region into the second-order critical end point. The latter is key in understanding the enhancement of the EC effect in the vicinity of a critical end point, as we discuss into more details in the following. It is clear that in order to have a more pronounced EC effect, the entropy of the system must be enhanced. Since the entropy is an extensive physical quantity, by summing up all contributions to the total entropy, we can achieve higher entropy values and thus a more expressive EC effect [9]. In order to estimate the EC effect, the so-called EC strength, namely $\Delta T/\Delta E$, is usually employed, where T is the temperature and E the electric field. In this framework, systems that present a high temperature variation with relatively low E adiabatic sweeps are considered good candidates for large EC effects. Nonetheless, by employing solely the EC strength it is not straightforward to perform a systematic investigation as a function, for instance, of T and E for different systems aiming to maximize the EC effect. This is particularly true specially because the EC strength does not take into account the starting temperature of the adiabatic process, preventing thus a proper comparison between the EC effect for different systems. We use the electric Grüneisen parameter Γ_E , proposed in Ref. [10], to estimate the EC effect taking the entropy variations in respect to T and E into account, as well as the starting temperature. Note that Γ_E naturally embodies the non-linear effects of the EC effect since the adiabatic T derivative of E is taken into account, being thus distinct

* Corresponding author.

E-mail address: mariano.souza@unesp.br (M. de Souza).

<https://doi.org/10.1016/j.matresbull.2021.111413>

Received 23 November 2020; Received in revised form 3 May 2021; Accepted 12 May 2021

Available online 19 May 2021

0025-5408/© 2021 Elsevier Ltd. All rights reserved.

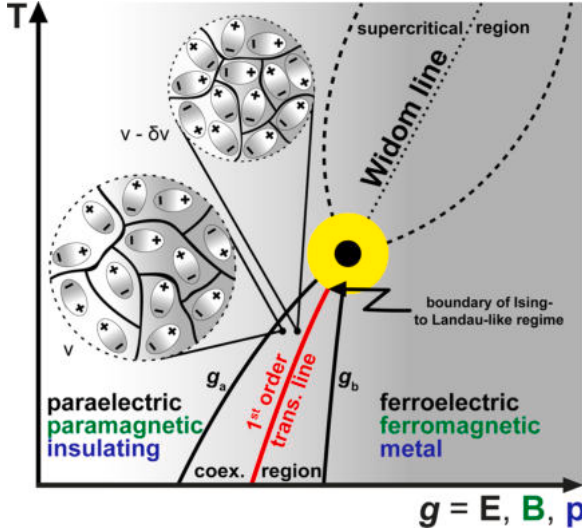


Fig. 1. The phases coexistence region, the first-order transition line and the finite-temperature critical end point. Schematic phase diagram temperature T versus tuning parameter g showing the coexistence region, the first-order transition line, the spinodal lines g_a and g_b , the Widom line embedded in the supercritical region, and the finite- T critical end point (black bullet). The various phases with their corresponding tuning parameters, namely electric field E , magnetic field B , and pressure p , are also shown. Within the coexistence region, two distinct electric-dipoles configurations are schematically shown, corresponding to two distinct volumes, namely v and $v - \delta v$. Upon increasing p , the electric dipolar interaction is enhanced and the entropy is also increased as a direct consequence of approaching the first-order transition line and the critical end point. The region between the electric-dipoles represents the non-polarized state. The yellow region indicates the Landau-like regime [8], being the border of the change from Ising- to Landau-like regime also indicated. More details in the main text. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

from the case of the usually employed $\Delta T/\Delta E$ in the EC strength approach [11]. We show that Γ_E is not only more appropriate, when compared with the usual EC strength, to analyze the entropy sources for the EC effect, but also it can be considered as a *smoking-gun* for predicting maximized EC effects in real systems. This is one of the key results of this work. We also discuss electrostriction effects and demonstrate their relation with the structural instability entropy contribution, which in turn is associated with one of the contributions responsible for the enhancement of the EC effect. Furthermore, we generalize the Grüneisen parameter for the various existent caloric effects and discuss Γ_E in connection with Barrett's [12] formula for ferroelectric quantum critical systems.

2. Results

2.1. The electric Grüneisen parameter and the electrocaloric effect

The well-known magnetocaloric effect can be quantified by the so-called magnetic Grüneisen parameter [13]. Analogously, Γ_E quantifies the EC effect [10]:

$$\Gamma_E = \frac{-\left(\frac{\partial P}{\partial T}\right)_E}{c_E} = -\frac{1}{T} \frac{\left(\frac{\partial S}{\partial E}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_E} = \frac{1}{T} \left(\frac{\partial T}{\partial E}\right)_S. \quad (1)$$

where c_E , P , and S refer, respectively, to the specific heat at constant E , the electric polarization and the entropy. It turns out that Γ_E is also connected with the material dielectric constant ϵ by the relation $\Gamma_E =$

$\frac{E}{c_E} \left(-\frac{\partial \epsilon}{\partial T} \right)_E$ [10]. In relaxor-type ferroelectrics, upon tuning the system close to the critical end point by applying external pressure [14], the dielectric response can be dramatically altered since the Coulomb repulsion between charges is enhanced and so does the entropy and E required to polarize the system, cf. Fig. 1. Recently, we have proposed that the relaxation time is entropy-dependent for *any* system close to the critical end point [10]. We have shown that close to the first order transition line of *any* phases coexistence region the relaxation time is significantly enhanced and we are faced with a Griffiths-like phase. As a consequence, we infer here that *any* caloric effect will be enhanced close to the first order transition line and critical end point. This is one of the main results of this work.

2.2. Giant caloric effects close to any critical end point

Upon approaching a critical end point (Fig. 1), an intrinsic entropy accumulation takes place due to the phases coexistence and presence of the critical fluctuations [15–19]. Considering the Maxwell-relation $\left(\frac{\partial P}{\partial T}\right)_E = \left(\frac{\partial S}{\partial E}\right)_T$ [20,21], an enhancement of $\left(\frac{\partial S}{\partial E}\right)_T$ near the critical point is also reflected in an increase of $\left(\frac{\partial P}{\partial T}\right)_E$. Hence, it is straightforward to infer that a giant EC effect takes place near the E -induced finite- T critical point [22], since such effect is quantified by Γ_E , which also depends on $\left(\frac{\partial P}{\partial T}\right)_E$, cf. Eq. (1). Interestingly, in Ref. [23] the authors report on ϵ measurements for the spin-liquid candidate κ -(BEDT-TTF)₂Cu₂(CN)₃, being $\epsilon = \epsilon/\epsilon_0$ and ϵ_0 the vacuum permittivity. There, a significant increase of ϵ close to the critical end point is observed. By carefully analyzing such ϵ experimental results [23], an estimate of Γ_E taking into account the temperature derivative of the electric polarization (or dielectric constant) shows that Γ_E can reach giant values. Indeed, for $p = 1.45$ kbar, using a frequency of 7.5 kHz, at $T \approx 10$ K, i.e., upon approaching the critical point, $\Gamma_E \approx 10^{-5}$ m/V. For PbSc_{0.5}Ta_{0.5}O₃, a large EC effect near the critical point around room- T was recently reported [5]. Making use of the data reported in Ref. [5] regarding the driving E and the effective T change ΔT , we estimate the EC effect to be $\Gamma_E \approx 10^{-9}$ m/V. The value of Γ_E calculated for PbSc_{0.5}Ta_{0.5}O₃ is associated with a temperature variation $\Delta T \approx 5.5$ K [5], which is considered as a large EC effect in the literature. Thus, although the numerical value of Γ_E itself for this system is relatively low, it is indeed associated with a large EC effect at room-temperature. The estimated value of Γ_E for κ -(BEDT-TTF)₂Cu₂(CN)₃ under the optimal conditions of frequency and pressure is much larger than that estimated for PbSc_{0.5}Ta_{0.5}O₃. Such a result is suggestive that the EC effect in κ -(BEDT-TTF)₂Cu₂(CN)₃ should be more pronounced. The relatively high compressibility inherent to molecular conductors together with their layered structure [16,19] can be considered as possible key factors for such a large EC effect. The Γ_E values for both systems here considered were computed under the conditions corresponding to points in their phase diagrams, which are close to the first-order transition line and critical point. These are real examples that illustrate the main result of this work regarding a giant EC effect near the critical end point employing Γ_E . Now, we generalize the Grüneisen parameter for *any* external parameter tuned adiabatically. Following Eq. (1), we write a generalized expression for the Grüneisen parameter considering any external tuning parameter $g = B, E, p$, being B the external magnetic field and p the pressure (Fig. 1):

$$\Gamma_g = \frac{1}{T_s} \left(\frac{\partial T}{\partial g}\right)_s, \quad (2)$$

where T_s is the starting temperature of the adiabatic process. Hence, following Eq. (2), our analysis can be extended to *any* other physical scenarios with distinct tuning parameters. Table 1 summarizes the various caloric effects here discussed.

Table 1

The thermodynamic (Γ), magnetic (Γ_{mag}), electric (Γ_E), and polar (Γ_P) Grüneisen parameters with their corresponding Maxwell-relations. BC, MC, EC, and PC refer, respectively, to the barocaloric, magnetocaloric, electrocaloric, and polarcularic [24] effects; v_m is the molar volume and M the magnetization. Details in the main text.

Maxwell-Relation	Grüneisen Parameter
$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$	$\Gamma = \frac{1}{Tv_m} \left(\frac{\partial S}{\partial p}\right)_T = \frac{1}{Tv_m} \left(\frac{\partial T}{\partial p}\right)_S$ (BC)
$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$	$\Gamma_{mag} = \frac{1}{T} \left(\frac{\partial S}{\partial B}\right)_T = \frac{1}{T} \left(\frac{\partial T}{\partial B}\right)_S$ (MC)
$\left(\frac{\partial S}{\partial E}\right)_T = \left(\frac{\partial P}{\partial T}\right)_E$	$\Gamma_E = \frac{1}{T} \left(\frac{\partial S}{\partial E}\right)_T = \frac{1}{T} \left(\frac{\partial T}{\partial E}\right)_S$ (EC)
$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial E}{\partial T}\right)_P$	$\Gamma_P = \frac{1}{T} \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T} \left(\frac{\partial T}{\partial P}\right)_S$ (PC)

Interestingly enough, to the best of our knowledge, although hitherto not properly discussed in the literature, the origin of the Grüneisen parameter lies on Maxwell-relations when considering adiabatic processes [25,26]. This is universal and can be extended to all forms of writing the Grüneisen parameters reported in the literature [18,27–29, 13], cf. Table 1. Since an entropy accumulation inherently takes place near any critical point, the adiabatic variation of the corresponding tuning parameter towards its critical value will enhance its respective caloric effect. This is another key result of this work. For instance, if pressure is removed adiabatically, the barocaloric effect will be pronounced near the critical pressure. This can also be extended for both the magnetocaloric and electrocaloric (polarcaloric) effects. Of course, such an entropy accumulation near the critical point depends on the properties of the system of interest, being the shape of the first-order transition line (Fig. 1) also crucial. Regarding relaxor-type ferroelectric systems [22], upon applying external pressure the system can be tuned to approach its critical point [14]. In a simple picture, the entropy can be associated with the degree of disorder into the system, i.e., the number of possible configurations, and thus it is natural to consider that the disorder intrinsic to relaxor-type ferroelectrics is significantly enhanced near the critical point, which in turn is associated with the previously-mentioned entropy accumulation. Our analysis suggests that there are some key-ingredients to maximize the EC effect. This is discussed in the following. A possible generalized expression for the various contributions to the entropy of a system candidate to giant EC effects reads:

$$S = S_{coex} + S_{dip} + S_{dom} + S_{gb} + S_{int} + S_{str} + S_{ice} + S_{cf}, \quad (3)$$

where S_{coex} refers to the entropy associated with the coexistence region near a critical point; S_{dip} is the entropy contribution originating from distinct dipolar configurations; S_{dom} is associated with the presence of domains in relaxor-type ferroelectrics; S_{gb} is the grain-boundaries entropy contribution inherent to poly-crystalline materials; S_{int} represents the entropy contribution due to interface-effects, e.g., Maxwell-Wagner polarization [30–33]; S_{str} corresponds to the contribution associated with structural instabilities as it occurs, for instance, in BaTiO₃ [34]; S_{ice} is associated with the residual entropy of the possible configurations of the molecules in a solid [35], and S_{cf} takes into account the entropy contribution from the critical fluctuations in the Ising-regime, cf. Fig. 1. Note that at some extent the enhancement of the EC effect is directly associated with the coexistence of both polarized and non-polarized regions. This highlights the relevance of the coexistence region near finite- T critical points [22,36,37]. The various contributions to the total entropy (Eq. (3)) are schematically illustrated in Fig. 2. Hence, in order

to maximize the EC effect a system should incorporate more contributions to the total entropy as possible, which is another important result of the present work. Regarding the interface effect, the authors of Ref. [38] discuss its role on giant ϵ based on Maxwell-Wagner polarization [30–32]. Furthermore, in Ref. [39] the role played by the thickness of the interface d in the dielectric constant $\epsilon^* = (\epsilon' - i\epsilon'')$ is given by $L/\epsilon_m^* = [2d/\epsilon_i^* + (L - 2d)/\epsilon_b^*]$, where L is the specimen length, ϵ_m^* is the measured dielectric constant, ϵ_i^* and ϵ_b^* refer to the interface and bulk dielectric constant, respectively. Note that when $2d \rightarrow L$, ϵ_m^* will mostly be due to the interface effects contribution. In other words, when the length of the specimen is comparable to $2d$, the interface contribution will dominate. Considering that Γ_E depends on the T derivative of ϵ , higher values of ϵ due to interface effects can also contribute to the enhancement of the EC effect, since S_{int} will be enhanced as well. Yet, the EC effect is enhanced with the increase of the latent heat of a first-order transition upon approaching the critical point and, as a consequence, with the corresponding associated S variation. Hence, following such arguments, the high entropy accumulation near critical points, due to the critical fluctuations and/or the proximity to the first-order transition line, can give rise to an even more pronounced EC effect. In Ref. [5] the authors were able to drive the ferroelectric transition to the supercritical regime and thus to access 1.5 times the entropy associated with the latent heat of such a transition, increasing thus the EC effect. In general terms, following previous discussions, our findings suggest that the maximization of the EC effect is essentially fourfold: (i) the EC effect will be enhanced in the coexistence regime of the phase diagram of any system, being not maximum in the critical end point itself, but near it due to the proposed change from Ising- to Landau-like (mean-field) regime near the critical point [8]. More specifically, the EC effect will be maximized upon approaching the first-order transition line in the region, in which the system changes from Ising- to Landau-regime, cf. Fig. 1; (ii) the relaxor-like character of ferroelectrics is also important due to the intrinsic enhancement of S inherent to the presence of ferroelectric domains; (iii) multilayered systems present interface effects, such as the Maxwell-Wagner polarization, being associated with another entropy contribution that can enhance the EC effect; (iv) the structural instabilities contribute to the enhancement of the total entropy and thus to the increase of the EC effect. In an ideal situation, the EC effect will be maximized when all contributions to the total entropy, described in Eq. (3), are taken into account. It would be challenging to design a material in this framework. Yet, a similar discussion as the one here proposed for the maximization of the EC effect can also be performed for the magnetocaloric effect [40,41]. In this regard, the recently reported relatively large magnetocaloric effect in Gd₃Ni/Gd₆₅Ni₃₅ composite microwires constitutes a meaningful example [42]. The coexistence of magnetic phases of both nanocrystalline Gd₃Ni and amorphous Gd₆₅Ni₃₅, together with the structural disorder introduced by the amorphous phase, lead to an enhancement of the magnetic entropy change of the system and thus to a large magnetocaloric effect.

2.3. Electrostriction effects

Following previous discussions, we define the electrostriction coefficient. Using Maxwell-relations [15], the magnetostriction coefficient can be related with the pressure derivative of the magnetization M , as follows [43]:

$$\left(\frac{\partial M}{\partial p}\right)_T = -\frac{1}{\nu\mu_0} \left(\frac{\partial \nu}{\partial H}\right)_T, \quad (4)$$

where μ_0 is the vacuum magnetic permeability, ν is the volume of the specimen, and H the magnetic field strength. Note that the M variation upon applying pressure is directly associated with the volume change upon applying external magnetic field. Thus, analogously, for the electric case, we define:

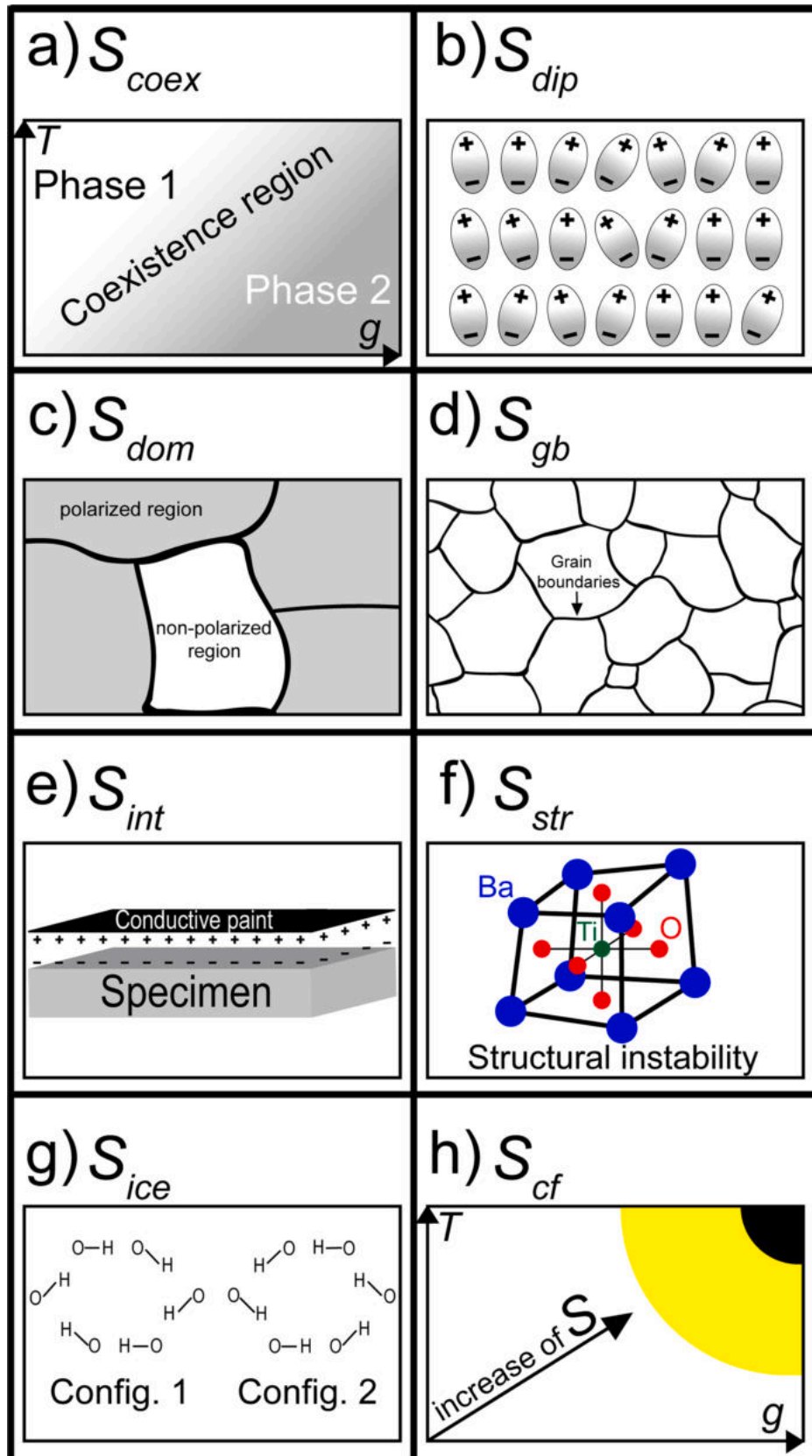


Fig. 2. The various entropy contributions to the total entropy. Schematic representation of the various contributions to the total entropy. (a) Coexistence of two generic phases 1 and 2; (b) distinct electric dipolar configurations in a ferroelectric material; (c) ferroelectric domains and the coexistence of polarized and non-polarized regions; (d) presence of grain-boundaries, usually inherently present in poly-crystalline materials; (e) a finite electric polarization existent between the conductive paint and the specimen, which is responsible for the so-called Maxwell-Wagner polarization; (f) cartoon of a distorted $BaTiO_3$ BCC unit cell, illustrating the S_{str} contribution to the total entropy; (g) residual entropy contribution S_{ice} associated with two distinct molecular configurations, cf. proposed by Pauling [35], and (h) enhancement of the total entropy due to critical fluctuations upon approaching the finite- T critical end point (Fig. 1). Details in the main text.

$$\left(\frac{\partial P}{\partial p}\right)_T = -\frac{\epsilon_0}{v} \left(\frac{\partial v}{\partial D}\right)_T, \quad (5)$$

where D is the modulus of the electric displacement vector. Note that the electrostriction effect, namely the volume variation upon applying an electric field, is associated with the p -dependence of P . At this point, it is worth recalling that the electromechanical strain is given by $x = QP^2$, where Q is the electrostriction coefficient [44,45]. Thus, since $P^2 \propto E^2$, being $P = \epsilon_0 \chi E$, we can infer that $x \propto E^2$ and $\Delta T = \frac{1}{2} \frac{\beta T}{\alpha} P^2$, being χ the electric susceptibility and β a phenomenological parameter, and consequently $x \propto \Delta T$ [46]. Considering the Gibbs free energy obtained from Landau's theory, we can compute the entropy variation as a function of Q [46], namely:

$$\Delta S = -\frac{1}{2} \beta P^2 + QP^2 \frac{\partial \sigma}{\partial T} + s \sigma \frac{\partial \sigma}{\partial T} + \alpha \left(\sigma + T \frac{\partial \sigma}{\partial T} \right), \quad (6)$$

where s refers to the elastic compliance coefficient, σ refers to the stress, and α is the thermal expansion coefficient. Eq. (6) describes the variation of S associated with structural changes in a system, being thus related with the contribution S_{str} to the total entropy in Eq. (3).

2.4. The electric Grüneisen parameter and quantum ferroelectricity

In a classical paraelectric-to-ferroelectric transition, it is well-known that ϵ as a function of T is maximized at the ferroelectric transition temperature, indicating that the system becomes more polarizable. A handful of investigations have been carried out focussing on the behavior of ϵ upon applying pressure, aiming to unveil the effect of p on the ferroelectric phase. Several systems reported in the literature present a quantum-phase transition from ferroelectric to a quantum ferroelectric upon pressurization [47–50]. In such cases, the T -dependence of ϵ follows Barrett's formula [12]:

$$\epsilon = A + \frac{m}{\left(\frac{T_1}{2}\right) \coth\left(\frac{T_1}{2T}\right) - T_0}, \quad (7)$$

where A is a non-universal constant, T_0 is a parameter related either to the ferroelectric ($T_0 > 0$) or antiferroelectric ($T_0 < 0$) effective dipolar interaction, T_1 is the temperature below which the quantum fluctuations dominate, and $m = n\mu^2/k_B$, where n is the electric-dipole density, μ refers to the local electric-dipole moment, and k_B is Boltzmann constant. Furthermore, T_1 can be defined as the balance between thermal and the vibrational energies associated with a harmonic oscillator in an electric field by the form $T_1 = \hbar\nu/k_B$ [12], where $\hbar$ is Planck's constant and ν is the oscillation frequency. Essentially, in this analysis the response of the electric-dipoles to an external E is treated in the harmonic approximation. The quantum critical regime is set when the energy associated with such oscillation overcomes the thermal energy. In general terms, the fingerprint of a quantum paraelectric phase is a plateau in ϵ , i.e., the quantum fluctuations affect the ferroelectric phase and instead of presenting a vanishing ϵ for $T \rightarrow 0$, as it occurs in classical ferroelectric-type transitions [51], ϵ remains constant [47]. It is worth mentioning that such a plateau will be observed only when the ferroelectric transition temperature is close to T_1 , otherwise the quantum critical fluctuations will not affect ϵ [12]. Since Γ_E is related with the temperature derivative of ϵ , we can write it in terms of Barrett's formula:

$$\Gamma_E = \frac{\epsilon_0 E}{c_E} \frac{m T_1^2}{T^2 \left[T_1 \cosh\left(\frac{T_1}{2T}\right) - 2T_0 \sinh\left(\frac{T_1}{2T}\right) \right]^2}. \quad (8)$$

Upon analyzing the behavior of Γ_E using Barrett's formula (Eq. (8)), the enhancement of Γ_E (left flank) in warming up marks the temperature in which quantum fluctuations dominate the ferroelectric phase, cf. inset of Fig. 3, which is associated with the maximization of the EC effect at

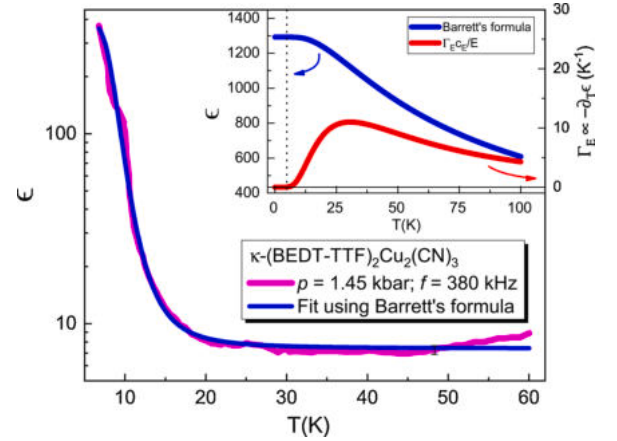


Fig. 3. The dielectric constant of the spin-liquid candidate κ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$ and Barrett's formula. Main panel: dielectric constant ϵ as a function of temperature T (magenta solid line) for the spin-liquid candidate κ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$ under pressure $p = 1.45$ kbar, frequency $f = 380$ kHz, and fitting of the data set employing Barrett's formula (blue solid line). Experimental data set taken from Ref. [23]. The vertical error bar refers to a 5% error in the data tracing. Inset: Temperature dependence of the dielectric constant ϵ using Barrett's formula [12] (blue solid line) and $\Gamma_E \propto -\partial_T \epsilon$ in terms of Barrett's formula (Eq. (8)) (red solid line). The parameters are $A = 0$, $m = (8.4 \times 10^4)$ K (using CGS units), $T_1 = 60$ K, and $T_0 = -35$ K [12]. The vertical dashed line represents the temperature in which ϵ is constant and thus $-\partial_T \epsilon = 0$. Details in the main text. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$T \sim 27$ K. Thus, we propose that a pronounced EC effect is expected in quantum ferroelectrics close to the temperature in which the quantum fluctuations dominate the system. Note that Γ_E can be considered not only as an indicator to quantify the EC effect using entropy arguments, but also it can be seen as an appropriate physical parameter to demonstrate, or even predict, a quantum ferroelectric behavior. Note that the EC effect close to a quantum critical point can be even more pronounced when the electric-dipole density $n = N/v$, where N is the number of electric-dipoles, is enhanced upon pressurization. As pressure is increased, v decreases and thus n increases, making thus the EC effect more pronounced, cf. Eq. (8). Thus, employing Barrett's formula and Γ_E , we predict that systems presenting a quantum critical ferroelectric ground-state should also show a pronounced EC effect, which is another key result of this work. Right on the critical end point we have $\partial_S S = 0$ and, as a consequence $\Gamma_E = 0$. Yet, it is worth mentioning that the flattening of ϵ inherently to Barrett's formula at low- T is merely a consequence of the effective electric dipolar interaction and quantified by T_0 , being an analogous situation also found for magnetic systems [52]. As previously discussed [10], the relaxation time is entropy-dependent upon approaching the critical point. As a consequence, the dielectric response of the system at a particular frequency is dramatically affected under pressurization close to the critical region. This particular behavior prevents the analysis of such data set using the Barrett's formula for various p values. Hence, we stick our analysis to ϵ measurements reported in Ref. [23] for the spin-liquid candidate κ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$ under $p = 1.45$ kbar and $f = 380$ kHz, cf. Fig. 3, i.e., the system is located on the verge of the Mott second-order critical end point. Also, it is worth mentioning that we have limited our analysis until 60 K in order to rule out possible electrical contacts contribution to ϵ [23]. Note that Barrett's formula fits the experimental data set quite well, being $T_1 \approx 86$ K obtained in this fitting. Amazingly, the obtained value of T_1 in this analysis is in line with the proposal of a finite- T quantum critical behavior of the Mott transition, reported in Refs. [53, 54]. The obtained value of T_1 from the fitting indicates that quantum fluctuations associated with the proposed *strange quantum-critical fluid*

[53,54] set in around such a temperature under the conditions of p and f shown in Fig. 3. A deeper understanding of this peculiar behavior deserves further investigations.

3. Conclusions

Using the Grüneisen parameter and entropy arguments, we have demonstrated an intrinsic enhancement of caloric effects near *any* finite- T critical end point. The present work embodies an extension of the discussions presented in Ref. [22] not only to the EC effect, but also to *any* caloric effect. Furthermore, we have generalized the Grüneisen parameter for any tuning parameter g strengthening our argument that any caloric effect is more pronounced in the vicinity of a critical end point. We have proposed that Γ_E is an appropriate parameter to quantify the EC effect in various systems when compared with the usually employed EC strength, since the starting temperature and the entropy contributions to the EC effect are taken into account when Γ_E is used. Also, using entropy arguments we have proposed potential key-ingredients to enhance the EC effect. Yet, we have shown that Γ_E is key in analyzing a ferroelectric quantum-critical behavior in connection with Barrett's formula. Last but not least, it would be challenging to measure caloric effects close to triple points [37,55].

4. Methods

All the calculations present in this work are exactly solvable. The software Wolfram Mathematica® Version 11 was employed to process data. Figs. 1 and 2 were generated using Adobe Illustrator®; the data set depicted in Fig. 3 was generated employing the software OriginPro® Version 2018. The data set shown in the inset of Fig. 2 was generated in Wolfram Mathematica® Version 11 and plotted with OriginPro® Version 2018.

Author contributions

MdeS and LS wrote the paper with contributions from ACS and IFM. LS carried out the calculations and generated the figures. All authors revised the manuscript. MdeS conceived and supervised the project.

Lucas Squillante: Formal analysis, Writing – Original Draft, Writing – Review & Editing, Visualization

Isys F. Mello: Writing – Review & Editing

A.C. Seridonio: Writing – Review & Editing

Mariano de Souza: Conceptualization, Writing – Original Draft, Writing – Review & Editing, Supervision, Project administration, Funding acquisition, Formal analysis

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgements

MdeS acknowledges financial support from the São Paulo Research Foundation – FAPESP (Grants No. 2011/22050-4, 2017/07845-7, and 2019/24696-0), National Council of Technological and Scientific Development – CNPq (Grants No. 302887/2020-2), CJR; and TUVSOTE. ACS acknowledges CNPq (Grants No. 305668/2018-8). This work was partially granted by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brazil (CAPES) – Finance Code 001 (Ph.D. fellowship of LS and IFM).

References

- [1] X. Moya, S. Kar-Narayan, N.D. Mathur, Caloric materials near ferroic phase transitions, *Nat. Mater.* 13 (2014) 439–450, <https://doi.org/10.1038/nmat3951>.
- [2] J.F. Scott, Electrocaloric materials, *Annu. Rev. Mater. Res.* 41 (2011) 229–240, <https://doi.org/10.1146/annurev-matsci-062910-100341>.

- [3] M. Romanini, et al., Giant and reversible barocaloric effect in trinuclear spin-crossover complex $\text{Fe}_3(\text{bntz})_6(\text{tcnset})_6$, *Adv. Mater.* (2021) 2008076, <https://doi.org/10.1002/adma.202008076>.
- [4] J. Liu, T. Gottschall, J.F. Skokov, J.D. Moore, O. Gutfleisch, Giant magnetocaloric effect driven by structural transitions, *Nat. Mater.* 11 (2012) 620–626, <https://doi.org/10.1038/nmat3334>.
- [5] B. Nair, et al., Large electrocaloric effects in oxide multilayers capacitors over a wide temperature range, *Nature* 575 (2019) 468–472, <https://doi.org/10.1038/s41586-019-1634-0>.
- [6] H. Ursic, et al., A multicaloric material as a link between electrocaloric and magnetocaloric refrigeration, *Sci. Rep.* 6 (2016) 26629, <https://doi.org/10.1038/srep26629>.
- [7] Z. Jiang, et al., Electrocaloric Effects in Multiferroics, 2021. arxiv:2102.13526v1.
- [8] M. Zacharias, L. Bartosch, M. Garst, Mott metal-insulator transition in compressible lattices, *Phys. Rev. Lett.* 109 (2012) 176401, <https://doi.org/10.1103/PhysRevLett.109.176401>.
- [9] Z.K. Liu, X. Li, Q.M. Zhang, Maximizing the number of coexisting phases near invariant critical points for giant electrocaloric and electromechanical responses in ferroelectrics, *Appl. Phys. Lett.* 101 (2012) 082904, <https://doi.org/10.1063/1.4747275>.
- [10] I.F. Mello, L. Squillante, G.O. Gomes, A.C. Seridonio, M. de Souza, Griffiths-like phase close to the Mott transition, *J. Appl. Phys.* 128 (2020) 225102, <https://doi.org/10.1063/5.0018604>.
- [11] G.G. Guzmán-Verri, P.B. Littlewood, Why is the electrocaloric effect so small in ferroelectrics? *APL Mater.* 4 (2016) 064106, <https://doi.org/10.1063/1.4950788>.
- [12] J.H. Barrett, Dielectric constant in perovskite type crystals, *Phys. Rev.* 86 (1952) 118, <https://doi.org/10.1103/PhysRev.86.118>.
- [13] G.O. Gomes, L. Squillante, A.C. Seridonio, A. Ney, R.E. Lagos, M. de Souza, Magnetic Grüneisen parameter for model systems, *Phys. Rev. B* 100 (2019) 054446, <https://doi.org/10.1103/PhysRevB.100.054446>.
- [14] K. Gesi, Effect of hydrostatic pressure on ferroelectric and related phase transitions, *Phase Transit.* 40 (1992) 187–215, <https://doi.org/10.1080/01411599208207747>.
- [15] H.E. Stanley, *Introduction to Phases Transitions and Critical Phenomena*, Oxford Science Publications, New York, 1971.
- [16] L. Bartosch, M. de Souza, M. Lang, Scaling theory of the Mott transition and breakdown of the Grüneisen scaling near a finite-temperature critical end point, *Phys. Rev. Lett.* 104 (2010) 245701, <https://doi.org/10.1103/PhysRevLett.104.245701>.
- [17] M. de Souza, L. Bartosch, Probing the Mott physics in κ -(BEDT-TTF) $_2$ X salts via thermal expansion, *J. Phys.: Condens. Matter* 27 (2015) 053203, <https://doi.org/10.1088/0953-8984/27/5/053203>.
- [18] M. de Souza, P. Menegasso, R. Paupitz, A. Seridonio, R.E. Lagos, Grüneisen parameter for gases and superfluid helium, *Eur. J. Phys.* 37 (2016) 055105, <https://doi.org/10.1088/0143-0807/37/5/055105>.
- [19] M. de Souza, et al., Anomalous lattice response at the Mott transition in a quasi-2D organic conductor, *Phys. Rev. Lett.* 99 (2007) 037003, <https://doi.org/10.1103/PhysRevLett.99.037003>.
- [20] C. Ye, J.B. Wang, B. Li, X.L. Zhong, Giant electrocaloric effect in a wide temperature range in PbTiO_3 nanoparticle with a double-vortex domain structure, *Sci. Rep.* 8 (2018) 293, <https://doi.org/10.1038/s41598-017-18275-0>.
- [21] R. Pirc, et al., Electrocaloric effect and dipolar entropy change in ferroelectric polymers, *Ferroelectrics* 426 (2012) 38–44, <https://doi.org/10.1080/00150193.2012.671101>.
- [22] B. Rožič, et al., Influence of the critical point on the electrocaloric response of relaxor ferroelectrics, *J. Appl. Phys.* 110 (2011) 064118, <https://doi.org/10.1063/1.3641975>.
- [23] R. Rösslhuber, et al., Phase Coexistence at the First-Order Mott-Transition Revealed by Pressure-Dependent Dielectric Spectroscopy κ -(BEDT-TTF) $_2\text{Cu}_2(\text{CN})_3$, 2019. arxiv: 1911.12273.
- [24] J.W. Benerpe, W. Reese, Electronic studies of KH_2PO_4 , *Phys. Rev. B* 3 (1971) 3032, <https://calhoun.nps.edu/handle/10945/47574>.
- [25] A. Grünebohm, T. Nishimatsu, Influence of defects on ferroelectric and electrocaloric properties of BaTiO_3 , *Phys. Rev. B* 93 (2016) 134101, <https://doi.org/10.1103/PhysRevB.93.134101>.
- [26] X. Moya, E. Defay, V. Heine, N.D. Mathur, Too cool to work, *Nat. Phys.* 11 (2015) 202–205, <https://doi.org/10.1038/nphys3271>.
- [27] L. Zhu, M. Garst, A. Rosch, Q. Si, Universally diverging Grüneisen parameter and the magnetocaloric effect close to quantum critical points, *Phys. Rev. Lett.* 91 (2003) 066404, <https://doi.org/10.1103/PhysRevLett.91.066404>.
- [28] R. Küchler, et al., Divergence of the Grüneisen ratio at quantum critical points in heavy fermion metals, *Phys. Rev. Lett.* 91 (2003) 066405, <https://doi.org/10.1103/PhysRevLett.91.066405>.
- [29] G. Gomes, H.E. Stanley, M. de Souza, Enhanced Grüneisen parameter in supercooled water, *Sci. Rep.* 9 (2019) 12006, <https://doi.org/10.1038/s41598-019-48353-4>.
- [30] J.C. Maxwell, *Electricity and Magnetism*, vol. 1, Oxford University Press, London, 1892.
- [31] K.W. Wagner, Erklärung der dielektrischen Nachwirkungsvorgänge auf Grund Maxwellscher Vorstellungen, *Arch. J. Elektrotech.* 2 (1914) 371, <https://doi.org/10.1007/BF01657322>.
- [32] R.W. Sillars, The properties of a dielectric containing semiconducting particles of various shapes, *J. Inst. Electr. Eng.* 80 (1937) 378–394, <https://doi.org/10.1049/pws.1937.0015>.

- [33] P. Lunkenheimer, et al., Multiferroicity in an organic charge-transfer salt that is suggestive of electric-dipole-driven magnetism, *Nat. Mater.* 11 (2012) 755, <https://doi.org/10.1038/nmat3400>.
- [34] T. Trautmann, C. Falter, Lattice dynamics, dielectric properties and structural instabilities of SrTiO_3 and BaTiO_3 , *J. Phys. Condens. Matter* 16 (2004) 5955, <https://doi.org/10.1088/0953-8984/16/32/028>.
- [35] L. Pauling, The structure and entropy of ice and of other crystals with some randomness of atomic arrangement, *J. Am. Chem. Soc.* 57 (1935) 2680–2684, <https://doi.org/10.1021/ja01315a102>.
- [36] S.F. Banani, H.O. Lee, A.A. Hyman, M.K. Rosen, Biomolecular condensates: organizers of cellular biochemistry, *Nat. Rev. Mol. Cell Biol.* 18 (2017) 285–298, <https://doi.org/10.1038/nrm.2017.7>.
- [37] P.G. Debenedetti, *Metastable Liquids: Concepts and Principles*, Princeton University Press, Princeton, 1996.
- [38] P. Lunkenheimer, et al., Origin of apparent colossal dielectric constants, *Phys. Rev. B* 66 (2002) 052105, <https://doi.org/10.1103/PhysRevB.66.052105>.
- [39] A. Serghei, M. Tress, J.R. Sangoro, F. Kremer, Electrode polarization and charge transport at solid interfaces, *Phys. Rev. B* 80 (2009) 184301, <https://doi.org/10.1103/PhysRevB.80.184301>.
- [40] N.M. Bruno, S. Yuce, On the instability of the giant direct magnetocaloric effect in $\text{CoMn}_{0.915}\text{Fe}_{0.085}\text{Ge}$ at. % metamagnetic compounds, *Sci. Rep.* 10 (2020) 14211, <https://doi.org/10.1038/s41598-020-71149-w>.
- [41] N.A. Zarkevich, V.I. Zverev, Viable materials with a giant magnetocaloric effect, *Crystals* 10 (2020) 815, <https://doi.org/10.3390/cryst10090815>.
- [42] Y.F. Wang, et al., The Large Magnetocaloric Effect and Refrigerant Capacity in Nanocrystalline/Amorphous $\text{Gd}_3\text{Ni}/\text{Gd}_{65}\text{Ni}_{35}$ Composite Microwires, 2020. arxiv: 2007.10428.
- [43] H.U. Häfner, Volume magnetostriction of intermediate valence systems, *J. Magn. Magn. Mater.* 47 (1985) 299–301, [https://doi.org/10.1016/0304-8853\(85\)90422-6](https://doi.org/10.1016/0304-8853(85)90422-6).
- [44] V. Sundar, R.E. Newnham, Electrostriction and polarization, *Ferroelectrics* 135 (1992) 431–446, <https://doi.org/10.1080/00150199208230043>.
- [45] A.J. Bell, F. Chu, M. Daglish, DiC7: an orientational glass model of electrostriction in relaxor dielectrics, *Ferroelectrics* 133 (1992) 115, <https://doi.org/10.1080/00150199208217985>.
- [46] S.-G. Lu, B. Rozic, Q.M. Zhang, Z. Kutnjak, R. Pirc, Electrocaloric effect in ferroelectric polymers, *Appl. Phys. A* 107 (2012) 559, <https://doi.org/10.1007/s00339-012-6830-9>.
- [47] S.E. Rowley, et al., Ferroelectric quantum criticality, *Nat. Phys.* 10 (2014) 367–372, <https://doi.org/10.1038/nphys2924>.
- [48] K.A. Müller, H. Burkard, SrTiO_3 : an intrinsic quantum paraelectric below 4 K, *Phys. Rev. B* 19 (1979) 3593, <https://doi.org/10.1103/PhysRevB.19.3593>.
- [49] G.A. Samara, Vanishing of the ferroelectric and antiferroelectric states in KH_2PO_4 -type crystals at high pressure, *Phys. Rev. Lett.* 27 (1971) 103, <https://doi.org/10.1103/PhysRevLett.27.103>.
- [50] S. Horiuchi, Y. Okimoto, R. Kumai, Y. Tokura, Quantum phase transition in organic charge-transfer complexes, *Science* 299 (2003) 229–232, <https://doi.org/10.1126/science.1076129>.
- [51] M. de Souza, et al., Probing the ionic dielectric constant contribution in the ferroelectric phase of Fabre salts, *Phys. Rev. B* 97 (2018) 045122, <https://doi.org/10.1103/PhysRevB.97.045122>.
- [52] L. Squillante, I.F. Mello, G.O. Gomes, A.C. Seridonio, R.E. Lagos-Monaco, H. E. Stanley, M. de Souza, Unveiling the physics of the mutual interactions in paramagnets, *Sci. Rep.* 10 (2020) 7981, <https://doi.org/10.1038/s41598-020-64632-x>.
- [53] T. Furukawa, K. Kobashi, Y. Kurosaki, K. Miyagawa, K. Kanoda, Quasi-continuous transition from a Fermi liquid to a spin liquid in $\kappa\text{-(ET)}_2\text{Cu}_2(\text{CN})_2$, *Nat. Commun.* 9 (2018) 307, <https://doi.org/10.1038/s41467-017-02679-7>.
- [54] T. Furukawa, K. Miyagawa, H. Taniguchi, R. Kato, K. Kanoda, Quantum criticality of Mott transition in organics materials, *Nat. Phys.* 11 (2015) 221–224, <https://doi.org/10.1038/nphys3235>.
- [55] V.M. Ishchuk, V.L. Sobolev, Investigation of two-phase nucleation in paraelectric phase of ferroelectrics with ferroelectric-antiferroelectric-paraelectric triple point, *J. Appl. Phys.* 92 (2002) 2086, <https://doi.org/10.1063/1.1493661>.

Grüneisen meets Einstein

Lucas Squillante¹, Gabriel O. Gomes², Isys F. Mello¹, Guilherme Nogueira¹, Antonio C. Seridonio³, Roberto E. Lagos-Monaco,¹ and Mariano de Souza^{1*}

¹São Paulo State University (Unesp), IGCE - Physics Department, Rio Claro - SP, Brazil.

²University of São Paulo, Department of Astronomy, São Paulo, Brazil.

³São Paulo State University (Unesp), Department of Physics and Chemistry, Ilha Solteira - SP, Brazil.

*Corresponding author(s). E-mail(s): mariano.souza@unesp.br;

Abstract

For a perfect fluid, pressure p and energy density ρ are related via the equation of state (EOS) $\omega = p/\rho$, where ω is the EOS parameter, being its interpretation usually constrained to a numerical value for each universe era. Here, based on the Mie-Grüneisen EOS, we show that ω is recognized as the effective Grüneisen parameter Γ_{eff} , whose singular contribution, the so-called Grüneisen ratio Γ , quantifies the barocaloric effect. Our analysis suggests that the negative p associated with dark-energy implies a metastable state and that in the dark-energy-dominated era ω is time-dependent, which reinforces recent proposals of a time-dependent cosmological constant. Furthermore, we demonstrate that Γ_{eff} is embodied in the energy-momentum stress tensor in the Einstein field equations, enabling us to analyse, in the frame of an imperfect fluid picture, anisotropic effects of the universe expansion. We propose that upon going from decelerated- to accelerated-expansion, a phase transition-like behavior can be inferred. Yet, our analysis in terms of entropy, Γ , and a by us adapted version of Avramov/Casalini's model to Cosmology unveil hidden aspects related to the expansion of the universe. Our findings pave the way to interpret cosmological phenomena in connection with concepts of condensed matter Physics via Γ_{eff} .

Keywords: universe expansion, perfect and imperfect fluids, Grüneisen parameter, Einstein field equations, energy-momentum stress tensor

1 Introduction

The observational evidence supporting the hypothesis that the universe is currently undergoing an accelerated expansion process is astonishing, see Fig. 1 a-c) [1]. The physical mechanism governing the dynamics of such accelerated expansion, as well as its physical origin remain under debate [1]. Type Ia Supernova apparent magnitude measurements as a function of the redshift indicate accelerated cosmological expansion [2]. The obtaining of experimentally reliable cosmological parameters is of crucial importance to probe the validity of the various proposed theoretical models aiming to correctly predict the observed behavior of galaxy motions and apparent magnitude measurements. In the last few years, the Planck collaboration [3] has provided precise measurements regarding cosmological parameters. Among the proposed models [4–7] to describe the expansion of the universe, the so-called Λ -Cold Dark Matter (CDM) model plays an important role, being CDM the only type of dark matter considered in such a model [8], which assumes the existence of a cosmological constant Λ . It has been discussed that Λ governs the accelerated expansion process that counterbalances the gravitational attraction caused by ordinary matter [9]. Essentially, the three contributions involved in the dynamics of the late-time universe expansion are: *i*) CDM; *ii*) dark energy (DE), which is implicitly taken into account by considering the existence of Λ ; and *iii*) ordinary matter. The current universe is assumed to be dominated by Λ

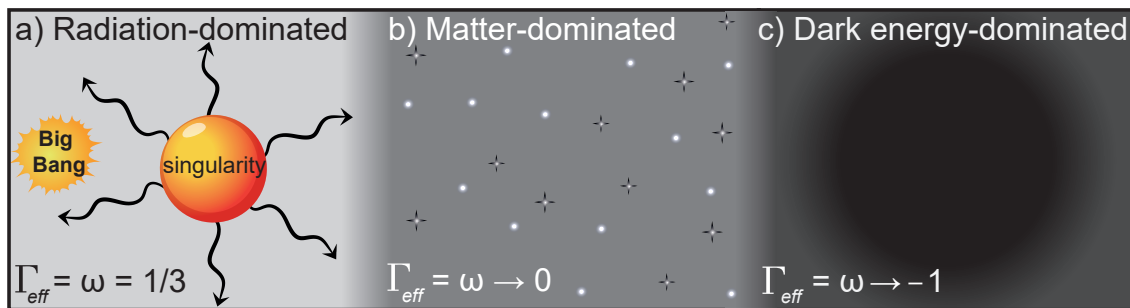


Fig. 1 Schematic representation of the various eras of the universe. In panel a), the radiation-dominated era ($\Gamma_{eff} = \omega = 1/3$), right after the Big Bang, is depicted. In b), the matter-dominated era is depicted ($\Gamma_{eff} = \omega \rightarrow 0$). In c), the dark-energy-dominated era is sketched, $\Gamma_{eff} = \omega \rightarrow -1$. The colour gradient represents the proposed role of the dark-energy in the accelerated expansion of the universe. Upon going from a) to c), the sign-change of Γ_{eff} is reminiscent of a phase transition-like behaviour within a phases coexistence region close to a critical point, as it occurs in condensed matter Physics [10].

with a time-independent energy density ρ associated with DE [11]. Although the Λ -CDM model has been extensively explored throughout the last decades, alternative models using the concept of a Dark Fluid (DF) have been proposed with the goal of unifying DE and dark matter (DM) [12]. In this context, a number of EOS have been proposed. For instance, in Ref. [13], the authors proposed a model for a DF based on the so-called Chaplygin EOS. In this approach, the early stages of the universe are modeled by a pressureless fluid, i.e., a scenario in which DM governs the universe dynamics. The late stages of

the cosmological expansion process are, following discussions in [13], governed by a fluid of constant ρ , being hence responsible for the current accelerated expansion of the universe. However, for the timespan between these two limiting cases, the predictions of the DF model based on the Chaplygin gas are in odd with experimental observations [14], since the current available experimental data regarding the dimensionless coordinate distances and the X-ray gas mass fractions do not follow the EOS for the Chaplygin gas within a 99% confidence level [14]. Furthermore, sophisticated DF models have been employed to properly reconcile experimental data with the theoretical description of the cosmological expansion [15], such as the generalized and modified Chaplygin gas models [16, 17]. In short, there is a discrepancy between the models employed to describe cosmological expansion and the mechanisms governing the expansion throughout different eras. Here, we explore the Thermodynamics of an evolving universe with focus on the so-called effective Grüneisen parameter [10, 18–21], hereafter Γ_{eff} . We demonstrate that the so-called EOS parameter ω is recognized as Γ_{eff} via Mie-Grüneisen EOS [22], which enables us to infer that Γ_{eff} is embodied in the energy-momentum stress tensor $T_{\mu\nu}$ in Einstein field equations. We discuss the behaviour of Γ_{eff} throughout the various eras employing the EOS of a perfect fluid and the modified Chaplygin gas. In our analysis we consider a flat universe scenario, i.e, $k = 0$ in the Friedmann–Lemaître–Robertson–Walker (FLRW) metric of the Einstein field equations, except for the discussion regarding a phase-transition-like behaviour from decelerated- to accelerated-expansion in the frame of a closed spherical model for the universe.

1.1 Thermodynamics of an expanding universe under the light of a perfect fluid approach

There is a long-standing debate in the literature about the applicability of equilibrium Thermodynamics to describe the expansion of the universe. While some authors claim that such treatment is erroneous, arguing that its continuous expansion is a non-equilibrium phenomenon [23], others argue that the time-scale associated with the cosmic expansion is much higher than the one associated with experimental observations, so that a thermodynamic equilibrium scenario can be inferred [24]. Under this perspective, we discuss in the following the Thermodynamics associated with the perfect fluid picture using Γ_{eff} . A general parametrization of the kind $p = p(\rho)$, where p is pressure and ρ the energy density, is usually employed to describe a homogeneous and isotropic universe, as well as to analyse the EOS for distinct periods of the universe inflation. For a perfect fluid, p and ρ are linked via ω , the so-called EOS parameter, by the simple form $p = \omega\rho$ [9]. For the radiation, matter, and DE dominated eras, $\omega = 1/3, 0$, and -1 , respectively [9]. It has been discussed that the late stage of the universe is composed predominantly by vacuum energy ($\omega \rightarrow -1$), i.e., DE, where $\rho \propto a(t)^{-3(1+\omega)}$, and $-1 \leq \omega < 0$ [25] for the various eras, being a the scale factor. Considering Friedmann equations [26], the

relation between ρ , p , and the specific entropy σ reads [9]:

$$nT d\sigma = d\rho - \frac{p + \rho}{n} dn, \quad (1)$$

where n is the number of particles per volume and T temperature. From Eq. 1, the temporal evolution of the temperature for a perfect fluid is given by [27] (see supplementary material):

$$\frac{\dot{T}}{T} = \left(\frac{\partial p}{\partial \rho} \right)_n \frac{\dot{n}}{n}. \quad (2)$$

Interestingly enough, the EOS for a perfect fluid is reminiscent of the well-known Mie-Grüneisen EOS, namely $p_a = \Gamma_{eff} E_a / V$, where p_a and E_a refer, respectively, to the contributions of the atomic vibrations to p and energy, which is broadly employed in condensed matter Physics for solids and fluids [22, 28, 29]. Evidently, in the case of fluids, Γ_{eff} links p and the kinetic/thermal energy of the particles. For solids, Γ_{eff} weights the ratio between pressure and energy when V is changed upon varying a tuning parameter, e.g., T or stress. Unambiguously, based on the above discussions, it becomes evident that ω plays the role of Γ_{eff} in the EOS of a perfect fluid in the description of the universe expansion. Thus, under the light of a perfect fluid-based approach, Γ_{eff} dictates how p and ρ are affected in terms of the temporal evolution of the scale factor for each era, which in turn governs the expansion of the universe. One of the key-results of the present work refers to the perspective that ω is not simply an EOS parameter, i.e., it is not merely a proportionality factor linking p and ρ , as it will become clear in the following. Integrating Eq. 2 we achieve the well-known expression (see supplementary material):

$$TV^{\Gamma_{eff}} = constant, \quad (3)$$

which relates T and V with Γ_{eff} during an adiabatic expansion of the universe in the frame of a perfect fluid analysis [30, 31]. Thus, it is clear that its temperature is continuously reduced as it expands, which in turn can be interpreted as a barocaloric effect [32]. The latter is quantified upon employing the singular contribution to Γ_{eff} , the so-called Grüneisen ratio Γ , namely [19, 33]:

$$\Gamma = \frac{1}{V_m T} \left(\frac{\partial T}{\partial p} \right)_S, \quad (4)$$

where V_m and S refer to the molar volume and the entropy, respectively. In condensed matter Physics, the first step for the realization of a barocaloric effect is the application of pressure, followed by its adiabatic removal, so that cooling is achieved. In the case of the universe, the singularity before the Big Bang could be considered as the first step for the realization of a barocaloric effect. Considering the inherent uncertainty in the estimation of T and p of the

expanding universe at each era [34], a quantification of such a (baro)caloric effect in terms of Γ is precluded. In the radiation- and matter-dominated eras, $\Gamma_{eff} > 0$ and, as a consequence, the temperature of the universe decreases to compensate its expansion, so that the adiabatic character is obeyed. However, counterintuitively, during the DE-dominated era, T increases during the adiabatic expansion, i.e., $\Gamma_{eff} < 0$, cf. Eq. 3, which is the principle of an inverse barocaloric effect [35]. This holds true only for the portion associated with the proposed DE, which, in turn, can dictate the temperature evolution of the universe in its late stages [36]. At this point, we recall the relation between Γ_{eff} and Γ [33]:

$$\Gamma_{eff} = \Gamma \frac{c_p}{c_v} \frac{V}{\kappa_T}. \quad (5)$$

Given that $c_p/c_v = \kappa_S/\kappa_T$ [37], where κ_S and κ_T are, respectively, the adiabatic and isothermal compressibilities, Γ_{eff} reads:

$$\Gamma_{eff} = \frac{\Gamma \kappa_S V}{\kappa_T^2} \Rightarrow \Gamma = \frac{\Gamma_{eff} \kappa_T^2}{\kappa_S V}. \quad (6)$$

Employing the canonical definition of κ_S and κ_T [37], the fact that $\Gamma_{eff} = \omega$, and $(\partial V/\partial p)_S = -V/\omega p$ from the perfect fluid EOS, we achieve a relation between Γ and ω , namely Γ_{eff} , for the matter- and radiation-dominated eras in the frame of a perfect fluid:

$$\Gamma = \frac{\omega}{pV}. \quad (7)$$

Hence, since $\omega = \Gamma_{eff} = 1/3$ and $0 \Rightarrow \Gamma = 1/3pV$ and 0 for the radiation- and matter-dominated eras, respectively. Given that the temperature evolution of the universe can be interpreted as a barocaloric effect, which in turn is quantified by Γ , our analysis enables us to infer that the adiabatic temperature variation of the universe was continuously diminished upon approaching the matter-dominated era. For the DE-dominated era, the peculiarity of $p < 0$ is crucial and must be taken into account, so that for $\omega = \Gamma_{eff} = -1 \Rightarrow \Gamma = -(pV)^{-1}$, which is consistent with an inverse barocaloric effect associated with the DE-dominated era, as well as with our analysis for the adiabatic expansion considering $\omega = \Gamma_{eff} = -1$, cf. Eq. 3.

Now, we make an analysis in terms of the volume- and temperature-dependence of S for the various eras. At this point, we recall that we are dealing with an adiabatic expansion, so that $dS = 0$. Using $\Gamma_{eff} = v\alpha_p/\kappa_T c_v$ [19] and the thermodynamic relation $\alpha_p = \kappa_T(\partial S/\partial V)_T$, it is straightforward to obtain:

$$V \left(\frac{\partial S}{\partial V} \right)_T = \Gamma_{eff} c_v. \quad (8)$$

Since $\Gamma_{eff} = \omega$ and employing $c_v = T(\partial S/\partial T)_V$, we have:

$$V \left(\frac{\partial S}{\partial V} \right)_T = \omega T \left(\frac{\partial S}{\partial T} \right)_V. \quad (9)$$

Thus, for the various eras:

$$V \left(\frac{\partial S}{\partial V} \right)_T = \frac{T}{3} \left(\frac{\partial S}{\partial T} \right)_V, \quad (\text{radiation-dominated era}) \quad (10)$$

$$\left(\frac{\partial S}{\partial V} \right)_T \rightarrow 0, \quad (\text{matter-dominated era}) \quad (11)$$

$$V \left(-\frac{\partial S}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial T} \right)_V. \quad (\text{DE-dominated era}) \quad (12)$$

A simple analysis of Eq. 10 enables us to infer that in the radiation-dominated era, the isothermal entropy variation due to the universe expansion was more pronounced than the one associated with its isochoric temperature-dependent variation by a factor 3. On the verge of the regimes change from decelerated- to accelerated-expansion, S remains approximately constant, cf. Eq. 11, which is in perfect agreement with our analysis of Eq. 7 for the matter-dominated era. Considering that $(\partial S/\partial V)_T = p/T$ [23], Eq. 12 only holds true upon assuming negative pressures. Hence, the assumption of a negative pressure associated with DE is recovered upon analysing Eq. 12. Yet, it is straightforward to infer that there is a balance between the volume and the temperature dependence of S . At this point, it is worth exploring the consequences of the consideration of a negative p associated with DE. As a matter of fact, the concept of negative p and its link with a metastable state was nicely discussed by Landau [38]. Thus, based on Ref. [38], $(\partial S/\partial V)_T < 0$ implies in a metastable state, where a spontaneous contraction of the system, in this case the volume portion associated with DE, takes place and, as a consequence, S is increased due to the possible formation of cavities [23, 38]. Following discussions in Ref. [34], the contraction of the volume portion associated with DE can explain the accelerated expansion in the DE-dominated era, since the so-called Hubble flow is increased due to such a contraction. Although there are some approaches considering the possibility of associating the concept of negative temperatures to the DE-dominated era [39–41], in some cases called phantom regime, this is questionable since, as nicely discussed in Ref. [42], negative temperatures require thermodynamic equilibrium as it is found, for instance, in the canonical definition of temperature based on the magnetic energy of a paramagnetic system [43]. At this point, given our recognition of ω as Γ_{eff} , we discuss the various contributions to ω . In condensed matter Physics, the various contributions to Γ_{eff} , namely, magnetic, phononic, and electronic, must

be taken into account, so that [19]:

$$\Gamma_{eff} = \frac{\sum_i \Gamma_{eff,i} c_{v_i}}{\sum_i c_{v_i}}, \quad (13)$$

where c_v is the specific heat at constant volume. The index i represents the i^{th} contribution to Γ_{eff} and c_v . Going beyond the simple picture of a perfect fluid, i.e., in the frame of a multicomponent universe [9], we propose that ω , namely Γ_{eff} , can also be expressed as the sum of its various distinct contributions, namely:

$$\omega = \frac{\sum_i \omega_i \rho_i}{\sum_i \rho_i}, \quad (14)$$

where ω_i and ρ_i refer to the contributions coming from the radiation-, matter-, and DE-dominated eras. Note that, following Eq. 14, the ultimate value of ω depends on the dominance of a particular component of ρ for each era. Just for the sake of completeness, it is worth mentioning that considering an universe composed by an ideal gas, $\omega = \Gamma_{eff} = 2/3$ [19, 44]. Now, we make use of the approach of a closed spherical universe [34, 45] aiming to analyse its speed of expansion in connection with Γ_{eff} . Assuming that the universe is an isolated system and that its expansion is adiabatic, we recall the first-law of Thermodynamics:

$$dQ = dU + dW, \quad (15)$$

where dQ , dU , and dW are the infinitesimal heat, internal energy, and work increments. Since $dQ = TdS$ and $dW = +pdV$, i.e., the universe is performing work on the hypothetical spherical wall of the “container” at the expense of its internal energy in order to expand, we have [34]:

$$TdS = dU + pdV, \quad (16)$$

which for an adiabatic process leads to $dU = -pdV$ [34]. In a Newtonian-like approach, considering that the Hubble parameter $H = \dot{a}/a$ [46] is the normalized rate of expansion, H can be analogously determined in terms of the normalized rate of the temporal evolution of the universe’s volume, namely [34]:

$$H = \frac{\dot{V}}{V} = \frac{\frac{dV}{dt}}{\frac{4}{3}\pi r^3}, \quad (17)$$

where r is the radius of the hypothetical spherical universe discussed at this point. Equation 17 can thus be rewritten as [34]:

$$H = \frac{3}{4\pi r^3} \frac{dV}{dU} \frac{dU}{dt}, \quad (18)$$

so that [34, 47]:

$$\frac{dU}{dt} = \frac{4}{3}\pi r^3 H \frac{dU}{dV}. \quad (19)$$

Following discussions in Ref. [47], during the radiation-dominated era $dU/dt < 0$, i.e., the universe is expanding in a decelerated way. Upon reaching the matter-dominated era, the speed of expansion reaches a minimum, i.e., $dU/dt \rightarrow 0$, and then, as it enters in the DE-dominated era, $dU/dt > 0$ indicating that the universe is expanding in an accelerated way. Since $dU = -pdV$ and the volume variation is positive due to the universe expansion, negative p implies that the internal energy of the universe is increasing in the DE-dominated era [34]. Hence, a connection between Γ_{eff} , the speed of expansion of the universe, and the temporal evolution of U can be made. As previously discussed, for an adiabatic expansion $dU/dV = -p$ and since for the perfect fluid $p = \omega\rho = \Gamma_{eff}\rho \Rightarrow dU/dV = -\Gamma_{eff}\rho$. Hence, Eq. 19 can be rewritten as:

$$\Gamma_{eff} = \frac{3}{4\pi r^3 H \rho} \left(-\frac{dU}{dt} \right). \quad (20)$$

Assuming that r , H , and ρ are always positive, the sign of Γ_{eff} is governed solely by $-dU/dt$. Thus, in the regimes $dU/dt < 0 \Rightarrow \Gamma_{eff} > 0$; $dU/dt \rightarrow 0 \Rightarrow \Gamma_{eff} \rightarrow 0$, and for $dU/dt > 0 \Rightarrow \Gamma_{eff} < 0$. Such a simple analysis enables us to recover the behaviour of Γ_{eff} throughout the various eras, cf. Fig. 1. The sign-change of Γ_{eff} upon going from decelerated- to an accelerated-expansion emulates the case of a phase transition close to a critical endpoint in condensed matter Physics [21]. Based on Noether's theorem [48], the change in the time dependence of U upon going from the decelerated to accelerated periods can be interpreted as a symmetry breaking, which is analogous to the case of a canonical phase transition [38]. Also, it is worth mentioning that it is under debate in the literature whether ω has indeed converged to -1 in the DE-dominated era or if it would change over time as the universe keeps expanding [3]. Under the light of the here-proposed recognition of ω as Γ_{eff} , it is tempting to infer that eventually there would be a time-dependence of ω , namely Γ_{eff} , since the thermodynamic quantities embedded in Γ_{eff} , such as, κ_T and c_v , will vary as a consequence of the continuous temperature change and expansion of the universe. Hence, since ω , namely, Γ_{eff} , in the perfect fluid approach is linked with Λ via $p = \omega\rho_\Lambda = -\rho_\Lambda = -c^2\Lambda/8\pi G$ [9], where c is the speed of light, ρ_Λ the vacuum energy density, and G the gravitational constant, the result of a time-dependent ω extracted from our analysis implies in a $\Lambda(t)$ or $G(t)$ (or both), as proposed in some recent works [49–51]. To clarify such an issue, accurate experimental observations of ρ_Λ over time are highly desirable [52]. In the following, we employ the modified Chaplygin gas EOS as a working horse to demonstrate that the identification of $\omega = \Gamma_{eff}$ is not restricted to the perfect fluid EOS.

1.2 The modified Chaplygin gas

The EOS of the modified Chaplygin gas reads [17]:

$$p = B\rho - \frac{A}{\rho^\alpha}, \quad (21)$$

where A , B , and α are non-universal constants, being $0 < \alpha \leq 1$ [17]. In the limit of the early stage of the universe, $\rho \rightarrow \infty$ and thus, Eq. 21 becomes simply $p \simeq B\rho$, which recovers the EOS for a perfect fluid with B playing the role of ω . As the universe expands, ρ is continuously reduced and thus both terms of the right side of Eq. 21 contribute to p . Using the relation $(dU/dV)_S = -p$ and the corresponding expression for the internal energy, please refer to Eq. 5 of Ref. [17], ρ and p reads:

$$\rho = \left(\frac{A}{B+1} \right)^{1/(\alpha+1)} \left[1 + \left(\frac{\delta}{V} \right)^{R^*} \right]^{1/(\alpha+1)}, \quad (22)$$

$$p = - \left(\frac{A}{B+1} \right)^{1/(\alpha+1)} \frac{(B+1)}{[1 + (\delta/V)^{R^*}]^{\alpha/(\alpha+1)}} \left\{ 1 - \frac{B}{B+1} \left[1 + \left(\frac{\delta}{V} \right)^{R^*} \right] \right\}, \quad (23)$$

where $\delta = [b^*(B+1)/A]^{1/R^*}$, b^* is an integration constant, and $R^* = (B+1)(\alpha+1)$ [17]. A characteristic volume is defined as $V^* = \delta B^{1/R^*}$ [17], where $V < V^*$ accounts for positive pressures and $V > V^*$ negative ones [23]. Essentially, $V < V^*$ mimics the radiation-dominated era while $V = V^*$ the matter-dominated era, and $V > V^*$ the DE dominated one. For the early stages of the universe, i.e., $V \ll \delta$, ρ and p reads [17]:

$$\rho \approx \left(\frac{A}{B+1} \right)^{1/(\alpha+1)} \left(\frac{\delta}{V} \right)^{(B+1)}, \quad (24)$$

$$p \approx B \left(\frac{A}{B+1} \right)^{1/(\alpha+1)} \left(\frac{\delta}{V} \right)^{(B+1)}. \quad (25)$$

Rewriting p in terms of ρ and based on the fact that $\omega = \Gamma_{eff}$, we have then for $V \ll \delta$, $\Gamma_{eff} \approx B$, which restores the result for the perfect fluid when $B = 1/3$. Thus, for the early stage of the universe, the modified Chaplygin gas recovers nicely Γ_{eff} for the perfect fluid. Also, for $V = V^*$, $p = 0$ and thus $\Gamma_{eff} = 0$ as well, which is in perfect agreement with the result for the matter-dominated era employing the EOS of a perfect fluid. For late times, i.e., $V \gg \delta$, so that ρ and p reads [17]:

$$\rho \approx \left(\frac{A}{B+1} \right)^{1/(\alpha+1)} \left[1 + \frac{1}{\alpha+1} \left(\frac{\delta}{V} \right)^{R^*} \right], \quad (26)$$

$$p \approx - \left(\frac{A}{B+1} \right)^{1/(\alpha+1)}. \quad (27)$$

In such a regime, ρ behaves as a mixing of two fluids [17]. Employing $\rho(p)$, Γ_{eff} can be computed:

$$\Gamma_{eff} = - \frac{(\alpha+1)V^{R^*}}{[(\alpha+1)V^{R^*} + \delta^{R^*}]}. \quad (28)$$

Since we are dealing with the case of $V \gg \delta$, $\Gamma_{eff} \rightarrow -1$, which is in line with the result for the DE dominated era employing the EOS for a perfect fluid. Note that δ introduces the mixture character between the EOS of a perfect fluid and the Chaplygin gas. Interestingly, Eq. 28 has some reminiscence with the results obtained by some of us for the van der Waals EOS, namely $\Gamma_{eff} = (2/3)V/(V - Nb)$ [19], where N is the number of particles and b the volume associated with them. Note that for $V \gg Nb \Rightarrow \Gamma_{eff} \rightarrow 2/3$, which recovers Γ_{eff} for the ideal gas [19]. In the present case, δ^{R^*} plays a role analogous to Nb , since when $V \gg \delta^{R^*} \Rightarrow \Gamma_{eff} \rightarrow -1$, so that the result for the DE-dominated era in the frame of the perfect fluid picture is nicely restored. Indeed, the analogy between the ideal gas and perfect fluid holds true since both have the same $T_{\mu\nu}$ [53]. Our analysis of the universe expansion in the frame of the modified Chaplygin gas considering a finite δ in terms of Γ_{eff} is in line with the proposal of a “cosmological” mixture composed by DE and DM. In other words, the mixture of the two contributions to p embedded in the modified Chaplygin gas EOS, cf. Eq. 21, is captured in the analysis of Γ_{eff} (Eq. 28) in terms of the parameter δ^{R^*} . Furthermore, the consideration of a finite value of δ^{R^*} is crucial since ω , namely Γ_{eff} , will never be exactly -1 , as expected for the DE-dominated era in the frame of a perfect fluid. Making an analogy with the van der Waals gas, cf. previous discussion, and, considering that the universe is expanding adiabatically, it is natural to expect that the value of δ^{R^*} will become smaller and smaller than V , making, eventually, $\Gamma_{eff} \rightarrow -1$.

1.3 Grüneisen parameter and the Einstein field equations: anisotropic expansion effects

It is well-known that the celebrated Einstein field equations relate the curvature of spacetime in terms of a generalized distribution of energy and momentum. This set of equations is given by [54]:

$$R_{\mu\nu} - \frac{1}{2}g_{\mu\nu}R + \Lambda g_{\mu\nu} = 8\pi G T_{\mu\nu}, \quad (29)$$

where $R_{\mu\nu}$ is the Ricci curvature tensor, $g_{\mu\nu}$ the metric tensor, R the curvature scalar. For a perfect fluid, the term $T_{\mu\nu}$ is related with p and ρ by $T_{\mu\nu} = (p + \rho)u^\mu u^\nu + p g_{\mu\nu}$ [9, 55, 56], where u is the four-velocity vector field. Thus, using the EOS of a perfect fluid it is straightforward to write $T_{\mu\nu}$ as a function of ω

as $T_{\mu\nu} = (1+\omega)\rho u^\mu u^\nu + \rho\omega g_{\mu\nu}$ [9]. Since $\omega = \Gamma_{eff}$, we rewrite unprecedentedly the Einstein field equations in terms of Γ_{eff} employing the EOS of a perfect fluid, namely:

$$R_{\mu\nu} - \frac{1}{2}g_{\mu\nu}R + \Lambda g_{\mu\nu} = 8\pi G[(1 + \Gamma_{eff})\rho u^\mu u^\nu + \rho\Gamma_{eff}g_{\mu\nu}]. \quad (30)$$

Hence, it becomes clear that the Einstein field equations naturally embody Γ_{eff} through $T_{\mu\nu}$. To the best of our knowledge, up to date, there is no discussion in the literature about the Einstein field equations in connection with the Grüneisen parameter. Note that the link between $T_{\mu\nu}$ and Γ_{eff} is given by the fact that $T_{\mu\nu}$ embodies pressure components, shear stresses and the energy density associated with the gravitational field. Such terms/components dictate the relation between p and ρ via the EOS. In other words, the consideration of particular terms in $T_{\mu\nu}$ establishes the form of the EOS. Our analysis regarding the connection between Γ_{eff} and $T_{\mu\nu}$ is of particular interest considering an imperfect fluid, which represents one of the possible scenarios to explain current observational models that deviate from the Λ -CDM model by considering additional anisotropic energy fluxes and the stress tensor components [57]. In this picture, the effective stress energy-momentum tensor is $T_{\mu\nu} = [T_{(per)\mu\nu} + T_{(imp)\mu\nu}]$ [57], where the indexes (*per*) and (*imp*) refer to the contributions from perfect and imperfect fluids, respectively. The analysis in terms of an imperfect fluid model is in line with recent experimental observations regarding an anisotropic expansion of the universe, which in turn can be seen as a direct consequence of the formation of galaxy clusters with different sizes in the early stages [58]. For the sake of completeness, it is worth mentioning that the anisotropic expansion has been probed via measurements of the redshift space distortions [59]. Also, for the DE-dominated era, it was reported in the literature that quantum vacuum is very inhomogeneous and anisotropic, being ∇a and $\nabla^2 a$ expressive [60]. At this point, we employ similar arguments than those reported in Ref. [21] by some of us regarding the metal-insulating coexistence region of the Mott transition aiming to describe the anisotropic expansion of the universe. It turns out that the dynamics of particles in inner galaxy clusters depends on particular aspects of a specific considered galaxy cluster [61]. In Ref. [21], using Avramov/Casalini's model as a working horse, we assumed different relaxation times for metallic and insulating bubbles embedded in the coexistence region of the Mott metal-to-insulator transition. As reported in Refs. [10, 62], upon crossing the first-order transition line within the coexistence region of the Mott transition, anisotropic effects in the thermal expansion are observed. An analogous situation can be considered for the universe assuming different periods of rotation for distinct galaxy clusters. In this analogy, the galaxies clusters play the role of the metallic/insulating bubbles. Upon going from radiation-, passing by matter-, to DE-dominated era, Γ_{eff} changes sign, a behavior analogous to that observed in the pressure-induced Mott metal-to-insulator transition close to a second-order critical endpoint, cf. Ref. [21]. Thus, based on the fact that

the scale factor varies over time, an anisotropic expansion of the universe can be inferred as well. As a matter of fact, the proposal of the presence of critical points related to the universe expansion was discussed in Ref. [34]. It is clear that anisotropic expansion effects can be described in terms of stress tensor components, which in turn can be associated with the elastic Grüneisen parameter recently proposed by some of us [32], namely $\Gamma_{ec} = 1/T(\partial T/\partial \sigma_{ij})_S$, where σ_{ij} represents the stress tensor components. Note that Γ_{ec} equals Γ (Eq. 4) when p is rewritten in terms of σ_{ij} . Hence, since Γ_{eff} is related to Γ , cf. Eq. 6, anisotropic expansion effects can be explored in terms of Γ_{ec} embedded in Γ_{eff} , which in turn is incorporated in $T_{\mu\nu}$ in Einstein field equations. Considering that DE drives accelerated expansion without “reins”, one of the ultimate fates of the universe would be the proposed “big rip”, a topic still under debate in the literature, see, e.g., Refs. [63–65]. Such a scenario can be treated in terms of Γ_{ec} , which incorporates all stress tensor components and is embodied in $T_{\mu\nu}$ in the Einstein field equations. Hence, we propose an alternative path to describe the possible scenario of a “big rip” of the universe under the light of Condensed Matter Physics. Now, we make an analysis of the various eras using the approach proposed by Casalini using Avramov’s model for glasses [66–68] adapted by us to Cosmology. We start recalling the expression for the relaxation time τ [21, 69]:

$$\tau = \tau_0 \exp \left(\frac{C}{TV^{\Gamma_{eff}}} \right), \quad (31)$$

where C is a non-universal constant and τ_0 a reference relaxation time. Note that Γ_{eff} , namely ω , dictates the behavior of τ . Here, we propose a characteristic expansion time to each cluster of galaxies, which we assume, in turn, to be related to the frequency f distribution of their rotating masses [70]. We recall that a cluster of galaxies can be formed by a few thousands of galaxies [70, 71]. In other words, our assumption is, following Avramov’s model for glasses, that there is a distribution of f inherent to the existence of distinct rotating galaxies clusters masses. Hence, the ratio $\tau/\tau_0 \propto f_0/f$, where f_0 is a characteristic frequency of such distribution of cluster masses. It is evident that f is linked to a corresponding period of rotation, so that τ emulates the behaviour of such a rotation period. Thus, under such assumptions, employing Eq. 31 considering Γ_{eff} for the various eras, we have:

$$\frac{\tau}{\tau_0} = \exp \left(\frac{C}{TV^{1/3}} \right), \quad (\text{radiation-dominated era}) \quad (32)$$

$$\frac{\tau}{\tau_0} = \exp \left(\frac{C}{T} \right), \quad (\text{matter-dominated era}) \quad (33)$$

$$\frac{\tau}{\tau_0} = \exp \left(\frac{CV}{T} \right). \quad (\text{DE-dominated era}) \quad (34)$$

In terms of rotation period, our analysis reveals that, in the radiation-dominated era, the period of the rotating galaxies clusters was reduced as the universe expands, cf. Eq. 32, while in the matter-dominated era such a period was V -independent, cf. Eq. 33. In the DE-dominated era, in turn, the period of the rotating galaxies clusters is exponentially increased as the universe expands, cf. Eq. 34. Our analysis suggests an expressive slowing-down of the dynamics of the rotating galaxies clusters in the DE-dominated era, being, astonishingly, a similar situation found on the verge of the Mott metal-insulator transition [21]. Hence, it is clear that ω , here recognized as Γ_{eff} , plays a key role in the dynamics of rotating galaxies clusters throughout the eras.

2 Conclusion

We have identified the EOS parameter ω as Γ_{eff} via Mie-Grüneisen EOS and analysed it for the perfect and imperfect fluids, as well as for the modified Chaplygin gas. Our analysis suggests that in the DE-dominated era ω is time-dependent, which implies that Λ varies over time. We have proposed that the barocaloric effect associated with the adiabatic universe expansion, as well as the anomalous behaviour of DE regarding an inverse barocaloric effect, can be quantified by the Grüneisen ratio. We have shown that Γ_{eff} changes sign upon going from decelerated- to accelerated-expansion, indicating a phase transition-like behaviour. Our findings suggest that the temperature of the universe was diminished adiabatically upon approaching the matter-dominated era, while for the DE-dominated era our analysis points to an inverse barocaloric effect associated with DE. We propose that negative pressures associated with DE necessarily imply in a metastable state and that negative temperatures usually associated with the phantom phase may be erroneous due to the lack of a thermal equilibrium associated with the universe continuous expansion. Employing an adapted version of Avramov/Casalini's model to Cosmology, the dynamics of rotating galaxies clusters was analysed in terms of Γ_{eff} for the various eras. We have shown that Γ_{eff} is naturally embedded in $T_{\mu\nu}$ in the Einstein field equations. In this regard, our analysis provides an alternative path to describe anisotropic effects associated with the expansion of the universe under the light of Γ_{eff} , which is connected with the possibility of a “big rip”. We suggest that our analysis in terms of Γ_{eff} can be extended to other metrics, e.g., the Kerr metric, corresponding to a rotating uncharged axially-symmetric black hole [72]. It is challenging to revisit the Thermodynamics of black holes and related topics of Cosmology using Γ_{eff} . Our findings open a new avenue in the field of Cosmology to interpret the expansion of the universe, aiming to contribute to the current necessity of new approaches and interpretations to account for the limitations of the current standard cosmological scenario, cf. highlighted in Ref. [73].

Acknowledgments. MdeS acknowledges financial support from the São Paulo Research Foundation – Fapesp (Grants number 2011/22050-4,

2017/07845-7, and 2019/24696-0), National Council of Technological and Scientific Development – CNPq (Grants number 302887/2020-2). ACS acknowledges National Council of Technological and Scientific Development – (Grants No. 308695/2021-6). This work was partially granted by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil (Capes) - Finance Code 001 (Ph.D. fellowship of L.S. and I.F.M.).

Author contributions. LS carried out the calculations and generated the figure. IFM carried out an analysis of the gravitational waves in terms of Γ_{eff} (not shown). MdeS and LS wrote the paper with contributions from ACS, RELM, GOG, GN, and IFM. GN participated only in the early stage of this project. ACS, RELM, GOG, and IFM revised the manuscript. MdeS conceived and supervised the whole project.

Additional information. Correspondence and requests for materials should be addressed to MdeS.

Competing interests. The authors declare no competing financial interests.

Data availability. All data generated or analysed during this study are included in this published article [and its supplementary information files].

References

- [1] V. Poulin, T. L. Smith, T. Karwal, M. Kamionkowski, Early dark energy can resolve the Hubble tension. *Phys. Rev. Lett.* **122**, 221301 (2019).
- [2] A.G. Riess, A.V. Filippenko, P. Challis, A. Clocchiatti, A. Diercks, P.M. Garnavich, R.L. Gilliland, C.J. Hogan, S. Jha, R.P. Kirshner, Observational evidence from supernovae for an accelerating universe and a cosmological constant. *Astron. J.* **116**, 1009 (1998); S. Perlmutter, G. Aldering, G. Goldhaber, R.A. Knop, P. Nugent, P.G. Castro, S. Deustua, S. Fabbro, A. Goobar, D.E. Groom, I.M. Hook, A.G. Kim, M.Y. Kim, J.C. Lee, N.J. Nunes, R. Pain, C.R. Pennypacker, R. Quimby, C. Lidman, R.S. Ellis, M. Irwin, R.G. McMahon, P. Ruiz-Lapuente, N. Walton, B. Schaefer, B.J. Boyle, A.V. Filippenko, T. Matheson, A.S. Fruchter, N. Panagia, H.J.M. Newberg, W.J. Couch, The Supernova Cosmology Project, Measurements of Ω and Λ from 42 high-redshift supernovae. *Astrophys. J.* **517**, 565 (1999); L. Perivolaropoulos, Accelerating universe and scalar-tensor theories. *J. Phys.: Conf. Ser.* **68**, 012005 (2007).
- [3] N. Aghanin *et al.*, Planck 2018 results. VI. Cosmological parameters. *Astronomy & Astrophysics* **641**, A6 (2020).
- [4] S.A. Bonometto, L. Casarini, L.P.L. Colombo, R. Mainini, Cosmologies with dynamical and coupled dark energy vs. CMB data, <https://arXiv:astro-ph/0612672v1> (2006).

- [5] P. Wu, H. Yu, Generalized Chaplygin gas model: constraints from Hubble parameter versus redshift data. *Phys. Lett. B* **644**, 16-19 (2007).
- [6] J. Grande, R. Opher, A. Pelinson, J. Solà, Effective growth of matter density fluctuations in the running Λ CDM and Λ XCDM models. *J. Cosmol. Astropart. Phys.* **2007**, 007 (2007).
- [7] I.P. Neupane, C. Scherer, Inflation and quintessence: theoretical approach of cosmological reconstruction. *J. Cosmol. Astropart. Phys.* **2008**, 1 (2008).
- [8] J.S. Bullock, M. Boylan-Kolchin, Small-scale challenges to the Λ CDM paradigm. *ARA&A* **55**, 343 (2017).
- [9] S. Weinberg, *Gravitational and Cosmology: Principles and Applications of the General Theory of Relativity* (John Wiley & Sons, Cambridge, 1972).
- [10] L. Bartosch, M. de Souza, M. Lang, Scaling theory of the Mott transition and breakdown of the Grüneisen scaling near a finite-temperature critical end point. *Phys. Rev. Lett.* **104**, 245701 (2010).
- [11] P.J.E. Peebles, Tests of cosmological models constrained by inflation. *Astrophys. J.* **284**, 439 (1984).
- [12] P.-H. Chavanis, Is the universe logotropic? *Eur. Phys. J. Plus* **130**, 130 (2015); P.-H. Chavanis, The logotropic dark fluid as a unification of dark matter and dark energy. *Phys. Lett. B* **758**, 59 (2016); P.-H. Chavanis, S. Kumar, Comparison between the logotropic and Λ CDM models at the cosmological scale. *J. Cosmol. Astropart. Phys.* **2017**, 1 (2017).
- [13] A. Kamenshchik, U. Moschella, V. Pasquier, An alternative to quintessence. *Phys. Lett. B* **511**, 265 (2001).
- [14] Z.-H. Zhu, Generalized Chaplygin gas as a unified scenario of dark matter/energy: observational constraints. *Astron. Astrophys.* **423**, 421-426 (2004).
- [15] K. Boshkayev, R. D'Agostino, O. Luongo, Extended logotropic fluids as unified dark energy models. *Eur. Phys. J. C* **79**, 332 (2019).
- [16] F.C. Santos, M.L. Bedran, V. Soares, On the thermodynamic stability of the generalized Chaplygin gas. *Phys. Lett. B* **636**, 86-90 (2006).
- [17] F. C. Santos, M. L. Bedran, V. Soares, On the thermodynamic stability of the modified Chaplygin gas. *Phys. Lett. B* **646**, 215 (2007).
- [18] M. de Souza, L. Bartosch, Probing the Mott physics in κ -(BEDT-TTF)₂X salts via thermal expansion. *J. Phys.: Condens. Matter* **27**, 053203 (2015).

- [19] M. de Souza, P. Menegasso, R. Paupitz, A. Seridonio, R.E. Lagos, Grüneisen parameter for gases and superfluid helium. *Eur. J. Phys.* **37**, 055105 (2016).
- [20] G. Gomes, H.E. Stanley, M. de Souza, Enhanced Grüneisen parameter in supercooled water. *Sci. Rep.* **9**, 12006 (2019).
- [21] I.F. Mello, L. Squillante, G.O. Gomes, A.C. Seridonio, M. de Souza, Griffiths-like phase close to the Mott transition. *J. Appl. Phys.* **128**, 225102 (2020).
- [22] S. Eliezer, A. Ghatak, H. Hora, *An Introduction to Equations of State: Theory and Applications* (Cambridge University Press, New York, 1986).
- [23] B. Lavenda, *Where Physics Went Wrong* (World Scientific, Singapore, 2015).
- [24] R.D. Astumian, The unreasonable effectiveness of equilibrium theory for interpreting nonequilibrium experiments. *Am. J. Phys.* **74**, 683 (2006).
- [25] J.A. Frieman, M.S. Turner, D. Huterer, Dark energy and the accelerating universe. *ARA&A* **48**, 385-432 (2008).
- [26] A. Friedman, Über die Krümmung des Raumes. *Z. Phys.* **10**, 377-386 (1922).
- [27] R. Silva, J.A.S. Lima, M.O. Calvão, Temperature evolution law of imperfect relativistic fluids. *Gen. Relativ. Gravit.* **34**, 865-875 (2002).
- [28] E. Grüneisen, Zusammenhang zwischen Kompressibilität, Thermischer Ausdehnung, Atomvolumen und Atomwärme der Metalle. *Ann. Phys.* **331**, 393-402 (1908).
- [29] A.P. Chernyshev, The Mie-Grüneisen equation of state for metal nanoparticles. *Eur. Phys. J. B* **79**, 321-325 (2011).
- [30] A. Dalgarno, Molecular processes in the early universe. *J. Phys.: Conf. Ser.* **4**, 10-16 (2005).
- [31] K. Huang, S. Weinberg, Ultimate temperature and the early universe. *Phys. Rev. Lett.* **25**, 895 (1970).
- [32] L. Squillante, I. Mello, A.C. Seridonio, M. de Souza, Elastocaloric-effect-induced adiabatic magnetization in paramagnetic salts due to the mutual interactions. *Sci. Rep.* **11**, 9431 (2021).
- [33] L. Zhu, M. Garst, A. Rosch, Q. Si, Universally diverging Grüneisen parameter and the magnetocaloric effect close to quantum critical points. *Phys.*

- Rev. Lett.* **91**, 066404 (2003).
- [34] C.A. Melendres, Thermodynamics in the evolution of the dark universe. *J. Mod. Phys.* **12**, 1527 (2021).
 - [35] L. Mañosa, D. González-Alonso, A. Planes, M. Barrio, J.-L. Tamarit, I. S. Titov, M. Acet, A. Bhattacharyya, S. Majumdar, Inverse barocaloric effect in the giant magnetocaloric La–Fe–Si–Co compound. *Nat. Commun.* **2**, 595 (2011).
 - [36] Y.-K. Chiang, R. Makiya, B. Ménard, E. Komatsu, The cosmic thermal history probed by Sunyaev–Zeldovich effect tomography. *Astrophys. J.* **902**, 56 (2020).
 - [37] J.-P. Poirier, *Introduction to the Physics of the Earth's Interior* (Cambridge University Press, 2000).
 - [38] L.D. Landau, E.M. Lifshitz, *Statistical Physics - Part 1* (Pergamon Press Inc., Elmsford, 1980).
 - [39] P.F. González-Díaz, C.L. Sigënza, Phantom thermodynamics. *Nucl. Phys. B* **697**, 363 (2004).
 - [40] Y. Soo Myung, On phantom thermodynamics with negative temperature. *Phys. Lett. B* **671**, 216 (2009).
 - [41] E.N. Saridakis, P.F. González-Díaz, C.L. Sigüenza, Unified dark energy thermodynamics: varying ω and the -1-crossing. *Class. Quantum Grav.* **26**, 165003 (2009).
 - [42] N.F. Ramsey, Thermodynamics and statistical mechanics at negative absolute temperatures. *Phys. Rev.* **103**, 20 (1956).
 - [43] L. Squillante, I.F. Mello, G.O. Gomes, A.C. Seridonio, R.E. Lagos-Monaco, H. Eugene Stanley, Mariano de Souza, Unveiling the physics of the mutual interactions in paramagnets. *Sci. Rep.* **10**, 7981 (2020).
 - [44] S.H. Pereira, On the Sackur-Tetrode equation in an expanding universe. *Rev. Mex. Fis.* **57**, 11 (2011).
 - [45] E. Di Valentino, E. Melchiorri, J. Silk, Planck evidence for a closed Universe and a possible crisis for cosmology. *Nat. Astron.* **4**, 196 (2020).
 - [46] F.-Y. Cyr-Racine, F. Ge, L. Knox, Symmetry of cosmological observables, a mirror world dark sector, and the Hubble constant. *Phys. Rev. Lett.* **128**, 201301 (2022).

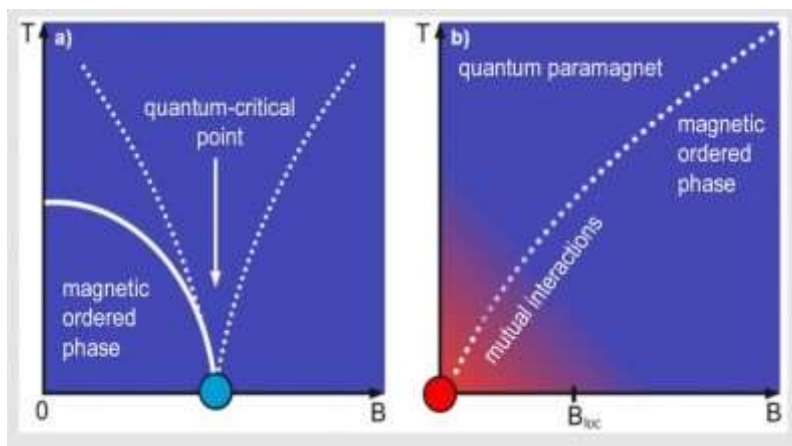
- [47] N.G. Busca, T. Delubac, J. Rich, S. Bailey, A. Font-Ribera, D. Kirkby, J.-M. Le Goff, M.M. Pieri, A. Slosar, É. Aubourg, J.E. Bautista, D. Bizyaev, M. Blomqvist, A.S. Bolton, J. Bovy, H. Brewington, A. Borde, J. Brinkmann, B. Carithers, R.A.C. Croft, K.S. Dawson, G. Ebelke, D. J. Eisenstein, J.-C. Hamilton, S. Ho, D.W. Hogg, K. Honscheid, K.-G. Lee, B. Lundgren, E. Malanushenko, V. Malanushenko, D. Margala, C. Maraston, K. Mehta, J. Miralda-Escudé, A.D. Myers, R.C. Nichol, P. Noterdaeme, M.D. Olmstead, D. Oravetz, N. Palanque-Delabrouille, K. Pan, I. Pâris, W.J. Percival, P. Petitjean, N.A. Roe, E. Rollinde, N.P. Ross, G. Rossi, D.J. Schlegel, D.P. Schneider, A. Shelden, E.S. Sheldon, A. Simmons, S. Snedden, J.L. Tinker, M. Viel, B.A. Weaver, D.H. Weinberg, M. White, C. Yèche, D.G. York, Baryon acoustic oscillations in the Ly α forest of BOSS quasars. *Astron. Astrophys.* **552**, A96 (2013).
- [48] J. Hanc, S. Tuleja, M. Hancova, Symmetries and conservation laws: consequences of Noether's theorem. *Amer. J. Phys.* **72**, 428 (2004).
- [49] J. Socorro, M. Doleire, L.O. Pimentel, Variable cosmological term $\Lambda(t)$. *Astrophys. Space Sci.* **360**, 20 (2015).
- [50] E.K. Hanimeli, B. Lamine, A. Blanchard, I. Tutusaus, Time-dependent G in Einstein's equations as an alternative to the cosmological constant. *Phys. Rev. D* **101**, 063513 (2020).
- [51] R.K. Tiwari, A.H.A. Alfedeel, D. Sofuoglu, A. Abebe, E.I. Hassan, B.K. Shukla, A cosmological model with time dependent Λ , G and viscous fluid in general relativity. *Front. Astron. Space Sci.* **9**, 965652 (2022).
- [52] J. Prat, C. Hogan, C. Chang, J. Frieman, Vacuum energy density measured from cosmological data. *J. Cosmol. Astropart. Phys.* **06**, 015 (2022).
- [53] J.L. Anderson, *Principles of Relativity Physics* (Academic Press Inc., New York, 1967).
- [54] A. Einstein, Die Grundlage der allgemeinen Relativitätstheorie. *Ann. Phys.* **354**, 769 (1916).
- [55] M. Dalarsson, N. Dalarsson, *Tensors, Relativity, and Cosmology* (Academic Press, San Diego, 2015).
- [56] J. Ehlers, I. Ozsváth, E.L. Schücking, Y. Shang, Pressure as a source of gravity. *Phys. Rev. D* **72**, 124003 (2005).
- [57] W. Zimdahl, H.E.S. Velten, W.C. Algoner, Matter growth in imperfect fluid cosmology. *Universe* **5**, 68 (2019).

- [58] K. Migkas, G. Schellenberger, T.H. Reiprich, F. Pacaud, M.E. Ramos-Ceja, L. Lovisari, Probing cosmic isotropy with a new X-ray galaxy cluster sample through the L_X – T scaling relation. *A&A* **636**, A15 (2020).
- [59] P.L. Taylor, K. Markovič, A. Pourtsidou, E. Huff. Redshift space distortions: unmixing radial scales in projection. *Phys. Rev. D* **105**, 084007 (2022).
- [60] Q. Wang, Z. Zhu, W.G. Unruh, How the huge energy of quantum vacuum gravitates to drive the slow accelerating expansion of the Universe. *Phys. Rev. D* **95**, 103504 (2017).
- [61] A.D. Erlykin, A.W. Wolfendale, Cosmic rays in the inner galaxy and the diffusion properties of the interstellar medium. *Astrop. Phys.* **42**, 70 (2013).
- [62] M. de Souza, A. Brühl, Ch. Strack, B. Wolf, D. Schweitzer, M. Lang, *Phys. Rev. Lett.* **99**, 037003 (2007).
- [63] R.R. Caldwell, M. Kamionkowski, N.N. Weinberg, Phantom energy: dark energy with $\omega < 1$ causes a cosmic doomsday. *Phys. Rev. Lett.* **91**, 071301 (2003).
- [64] K. Mack, *The end of everything (Astrophysically speaking)*, (Scribner Book Company, 2020).
- [65] R. Skibba, Crunch, rip, freeze or decay — how will it all end? *Nature* **584**, 187 (2020).
- [66] R. Casalini, C.M. Roland, *Phys. Rev. E* **69**, 062501 (2004).
- [67] M. Paluch and C.M. Roland, *J. Non-Cryst. Solids* **316**, 413 (2003).
- [68] I. Avramov, A. Milchev, *J. Non-Cryst. Solids* **104**, 253 (1988).
- [69] R. Casalini, U. Mohanty, C.M. Roland, *J. Chem. Phys.* **125**, 014505 (2006).
- [70] M. Manolopoulou, M. Plionis, Galaxy cluster’s rotation. *MNRAS* **465**, 2616 (2017).
- [71] M. Plonis, O. López-Cruz, D. Hughes, A pan-chromatic view of clusters of galaxies and the large-scale structure (Springer, 2008).
- [72] R.P. Kerr, Gravitational field of a spinning mass as an example of algebraically special metrics. *Phys. Rev. Lett.* **11**, 237 (1963).

- [73] E. Abdalla *et al.*, Cosmology intertwined: A review of the particle physics, astrophysics, and cosmology associated with the cosmological tensions and anomalies. *J. High Energy Phys.* **34**, 49 (2022).

6.12 Fapesp agency divulgation articles

In this Section, the news published in the Fapesp agency regarding some of the articles I have participated as the first author are included.



Theoretical study shows that matter tends to be ordered at low temperatures

August 05, 2020

By José Tadeu Arantes | Agência FAPESP – Classical phase transitions

are governed by temperature. One of

the most familiar examples is the phase transitions of water from solid to liquid to gas. However, other parameters govern phase transitions when temperatures approach absolute zero, including pressure, the magnetic field, and doping, which introduce disorder into the molecular structure of a material.

This topic is treated from the theoretical standpoint in the article “[Unveiling the physics of the mutual interactions in paramagnets](#)”, published in *Scientific Reports*, an online journal owned by Springer Nature.

The paper resulted from discussions held in the laboratory in the context of the doctoral research of the two main authors, Lucas Squillante and Isys Mello, supervised by the last author, [Mariano de Souza](#), a professor in the Physics Department of São Paulo State University’s Institute of Geosciences and Exact Sciences (IGCE-UNESP) in Rio Claro, Brazil.

The other coauthors are [Roberto Eugenio Lagos Mônaco](#) and [Antonio Carlos Seridonio](#), also professors at UNESP, and [Harry Eugene Stanley](#), a professor at Boston University (USA).

The study was supported by FAPESP via a grant awarded to the project “[Exploring thermodynamic and transport properties of strongly correlated electron systems](#)”, for which Souza was the principal investigator.

“In paramagnetic materials, there’s always a subtle many-body contribution to the system’s energy. This contribution can be considered a small effective local magnetic field. It’s usually overlooked, given the very small amount of energy associated with it compared to the energy associated with thermal fluctuations or external magnetic fields. Nevertheless, when the temperature and external

magnetic field approach zero, such many-body contributions become significant,” Souza told **Agência FAPESP**.

The study showed that matter always tends to be ordered at low temperatures owing to many-body interactions. The noninteracting spin gas model therefore does not occur in the real world because a many-body interaction between the spins in the system would impose order.

“We found that in actual materials, there’s no such thing as a critical point at which a quantum phase transition occurs in a genuine zero field because of the persistence of the residual magnetic field created by the many-body interaction. In a broader context, ideal Bose-Einstein condensation can’t be obtained because of this interaction,” Souza said.

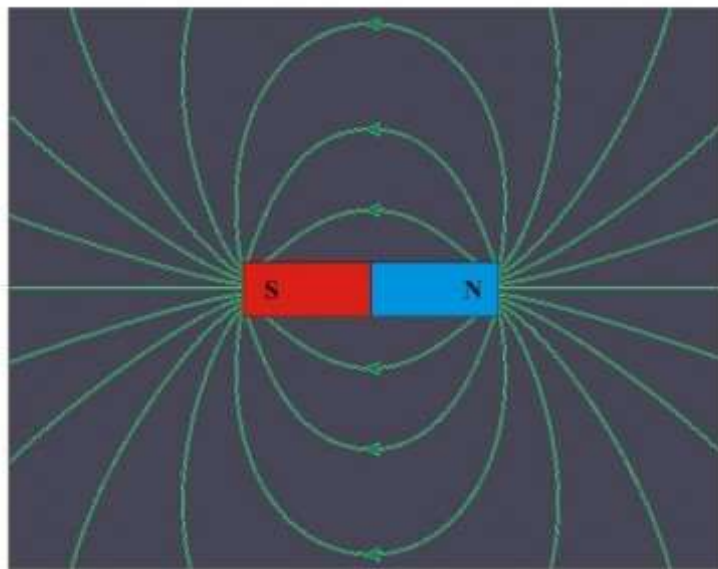
A Bose-Einstein condensate, often referred to as the “fifth state of matter” (the others being solid, liquid, gas and plasma), is a group of atoms cooled to within a hair of absolute zero. When they reach that temperature, the atoms have no free energy to move relative to each other and fall into the same quantum states, behaving as a single particle.

Bose-Einstein condensates were first predicted and calculated theoretically by Satyendra Nath Bose (1894-1974) and Albert Einstein (1879-1955) in 1924, but it was not until 1995 that Eric A. Cornell, Carl E. Wieman and Wolfgang Ketterle managed to make one using ultracold rubidium gas, for which all three were awarded the 2001 Nobel Prize in Physics.

“What our study showed was that although a nonideal Bose-Einstein condensate can be obtained experimentally, the ideal condition for condensation can’t be achieved because it presupposes that particles don’t perceive or interact with each other, whereas residual interaction always occurs, even in the vicinity of absolute zero,” Souza said.

“Another discovery was that matter can be magnetized adiabatically [*without heat loss or gain*] via these mutual interactions alone.”

The article “Unveiling the physics of the mutual interactions in paramagnets” can be read at: www.nature.com/articles/s41598-020-64632-x.



Researchers propose a method of magnetizing a material without applying an external magnetic field

July 28, 2021

By José Tadeu Arantes | Agência FAPESP – Magnetizing a material without applying an external magnetic field is proposed by researchers at São Paulo State University (UNESP), Brazil,

in an article [published](#) in the journal *Scientific Reports*, where they detail the experimental approach used to achieve this goal.

The study was part of the PhD research pursued by Lucas Squillante under the supervision of [Mariano de Souza](#), a professor at UNESP's Department of Physics in Rio Claro. Contributions were also made by Isys Mello, another PhD candidate supervised by Souza, and [Antonio Seridonio](#), a professor at UNESP's Department of Physics and Chemistry in Ilha Solteira. The group was [supported by FAPESP](#).

“Very briefly put, magnetization occurs when a salt is compressed adiabatically, without exchanging heat with the external environment,” Souza told **Agência FAPESP**. “Compression raises the temperature of the salt and at the same time rearranges its particles’ spins. As a result, the total entropy of the system remains constant and the system remains magnetized at the end of the process.”

To help understand the phenomenon, it is worth recalling the basics of spin and entropy.

Spin is a quantum property that makes elementary particles (quarks, electrons, photons, etc.), compound particles (protons, neutrons, mesons, etc.) and even atoms and molecules behave like tiny magnets, pointing north or south – up spin and down spin – when submitted to a magnetic field.

“Paramagnetic materials like aluminum, which is a metal, are magnetized only when an external magnetic field is applied. Ferromagnetic materials, including iron, may display finite magnetization

even in the absence of an applied magnetic field because they have magnetic domains,” Souza explained.

Entropy is basically a measure of accessible configurations or states of the system. The greater the number of accessible states, the greater the entropy. Austrian physicist Ludwig Boltzmann (1844-1906), using a statistical approach, associated the entropy of a system, which is a macroscopic magnitude, with the number of possible microscopic configurations that constitute its macrostate. “In the case of a paramagnetic material, entropy embodies a distribution of probabilities that describes the number of up spins or down spins in the particles it contains,” Souza said.

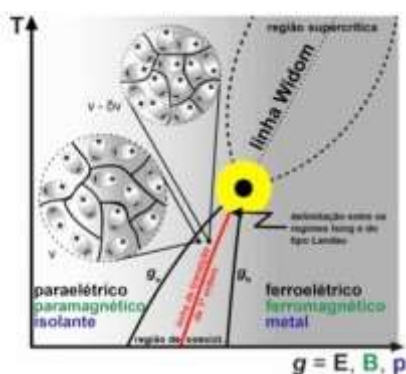
In the recently published study, a paramagnetic salt was compressed in a single direction.

“Application of uniaxial stress reduces the volume of the salt. Because the process is conducted without any exchange of heat with the environment, compression produces an adiabatic rise in the temperature of the material. A rise in temperature means a rise in entropy. To keep total entropy in the system constant, there must be a component of local reduction in entropy that offsets the rise in temperature. As a result, the spins tend to align, leading to magnetization of the system,” Souza said.

The total entropy of the system remains constant, and adiabatic compression results in magnetization. “Experimentally, adiabatic compression is achieved when the sample is compressed for less time than is required for thermal relaxation – the typical time taken by the system to exchange heat with the environment,” Souza said.

The researchers also propose that the adiabatic rise in temperature could be used to investigate other interacting systems, such as Bose-Einstein condensates in magnetic insulators, and dipolar spin-ice systems.

The article “Elastocaloric-effect-induced adiabatic magnetization in paramagnetic salts due to the mutual interactions” is at: www.nature.com/articles/s41598-021-88778-4.



Pesquisadores propõem estratégia para obter refrigeração de forma otimizada

05 de novembro de 2021

Agência FAPESP – Em artigo

[publicado](#) *Materials Research Bulletin*,

pesquisadores brasileiros demonstraram que, nas vizinhanças de pontos críticos, o chamado efeito calórico (resfriamento magnético ou elétrico, por exemplo) é gigante.

A pesquisa foi conduzida pelo grupo Solid State Physics, liderado pelo professor [Mariano de Souza](#), do Departamento de Física da Universidade Estadual Paulista (Unesp) em Rio Claro, em parceria com o grupo de [Antonio Seridonio](#), do Departamento de Física e Química da Unesp em Ilha Solteira. E contou com [apoio](#) da FAPESP.

“Os referidos efeitos calóricos permitem um resfriamento do sistema em ‘resposta’ à variação de um parâmetro externo de controle, como, por exemplo, pressão, campo magnético ou campo elétrico. Para tal, é necessário que não ocorram trocas de calor entre o sistema e seus arredores. Tal condição define o chamado ‘caráter adiabático’, o qual é imprescindível para a realização do efeito calórico em questão”, diz Souza.

A ideia central desse processo de resfriamento é que, para manter a entropia do sistema constante, sua temperatura varia espontaneamente.

“Em termos práticos: inicialmente o sistema deve ser fixado em uma dada temperatura e, em seguida, o parâmetro de controle é aumentado até um determinado valor. Na sequência, o sistema é isolado da sua vizinhança, ou seja, não existem trocas de calor envolvidas no processo. Nessa condição, o parâmetro de controle é então removido. Como consequência natural da condição adiabática, é necessário que ocorra uma variação da temperatura como ‘resposta’ natural à variação do parâmetro controle”, explica Souza.

Em outras palavras, a energia térmica é variada para compensar a variação de energia do sistema associada à remoção adiabática do parâmetro de controle. Os pesquisadores demonstraram que efeitos calóricos são maximizados nos arredores de pontos críticos.

“De forma simplificada, um ponto crítico em um dado diagrama de fases pode ser entendido como aquele associado aos valores críticos de temperatura e parâmetro de controle [ponto na cor preta na figura], como os campos elétrico e magnético ou pressão, os quais governam as mudanças de fase de uma determinada substância. Ocorre que, próximo do ponto crítico, existem flutuações expressivas do chamado parâmetro de ordem, que é a grandeza física associada às fases envolvidas [por exemplo, no caso magnético, o parâmetro de ordem é a magnetização], fazendo com que a resposta termodinâmica manifestada, por exemplo, na expansão térmica e na compressibilidade do sistema, apresente um comportamento singular”, afirma Souza.

O trabalho em pauta propõe o aproveitamento das flutuações inerentes do parâmetro de ordem nas proximidades do ponto crítico para a maximização dos efeitos calóricos. “Utilizando argumentos físicos baseados no conceito de entropia, a qual pode ser entendida em termos simples como uma medida do grau de desordem do sistema, demonstramos que é possível a realização de efeitos calóricos gigantes quando a matéria é colocada em condições extremas”, relata Souza.

Para que o efeito calórico seja otimizado, os pesquisadores demonstraram que a maximização da entropia constitui o “ingrediente” mais importante. Ademais, propuseram que outros “ingredientes físicos”, como, por exemplo, a presença de paredes de domínio e a instabilidade estrutural contribuem para o aumento dos efeitos calóricos.

“É sabido que uma maneira de aumentar a entropia associada a um dado sistema físico é diminuir seu volume. Ocorre que, para reduzir o volume, é necessária a aplicação de pressão. Dessa forma, fica evidente a importância da aplicação de pressão no contexto dos efeitos calóricos – neste caso denominado efeito barocalórico. Com base no fato de que nas vizinhanças de um ponto crítico a entropia é aumentada expressivamente devido à competição entre fases [conforme a figura], é natural esperar que, em tal região do diagrama de fases, a realização dos efeitos calóricos seja maximizada. Isso é uma mera consequência do fato de que quanto maior a entropia acumulada no sistema mais expressiva será a variação de temperatura no efeito calórico”, ensina Souza.

Os resultados obtidos pelo grupo têm impacto e relevância tecnológica com base na possibilidade de otimizar efeitos calóricos. O artigo científico, intitulado *Giant caloric effects close to any critical end point*, constitui parte da tese de doutorado de Lucas Squillante, orientando de Souza. Seridonio e a doutoranda Isys Mello (Unesp em Rio Claro) também assinam o texto, que pode ser lido em:

www.sciencedirect.com/science/article/abs/pii/S0025540821002105?via%3Dihub.