Journal of Physics: Condensed Matter

PAPER

Non-linear conduction due to depinning of charge order domains in $Fe_3O_2BO_3$

To cite this article: E C dos Santos *et al* 2017 *J. Phys.: Condens. Matter* **29** 205401

View the article online for updates and enhancements.

Related content

- Magnetic structure of Cu2MnBO5 ludwigite: thermodynamic, magnetic properties and neutron diffraction study
Evgeniya Moshkina, Clemens Ritter, Evgeniy Eremin et al.

- Unusual ground states in ${R_5T_4X_{10}}$ (R = rare earth; T = Rh, Ir; and X = Si, Ge, Sn): a review
S Ramakrishnan and Sander van Smaalen

- Crystal structure and magnetism of Fe2(OH)[B2O4(OH)]
Yotaro Kurayoshi, Shigeo Hara, Hirohiko Sato et al.

IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

This content was downloaded from IP address 186.217.236.60 on 29/05/2019 at 17:59

J. Phys.: Condens. Matter **29** (2017) 205401 (5pp) https://doi.org/10.1088/1361-648X/aa6960

Non-linear conduction due to depinning of charge order domains in $Fe_3O_2BO_3$

E C dos Santos[1], E F da Silva[1], J C Fernandes[2], L Ghivelder[3], D C Freitas[2,4], M A Continentino[4] and L Walmsley[1]

[1] Departamento de Física, IGCE—Universidade Estadual Paulista UNESP—C.P. 178, 13500-970, Rio Claro—SP, Brazil
[2] Instituto de Física, Universidade Federal Fluminense, Campus da Praia Vermelha, 24210-346, Niterói, RJ, Brazil
[3] Instituto de Física, Universidade Federal do Rio de Janeiro, Caixa Postal 68528, 21945-970, Rio de Janeiro, RJ, Brazil
[4] Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud, 150—Urca, 22290-180, Rio de Janeiro, RJ, Brazil

E-mail: everton.santos@ntnu.no, everlinferreira@hotmail.com, joaoraia40@gmail.com, luisghiv@if.ufrj.br, daniele@cbpf.br, mucio@cbpf.br and walmsley@rc.unesp.br

Received 15 February 2017, revised 24 March 2017
Accepted for publication 27 March 2017
Published 10 April 2017

Abstract

The oxyborate $Fe_3O_2BO_3$ presents a charge density wave (CDW) transition close to room temperature. As we show here, this is associated with a well defined anomaly in the specific heat. Below this transition, when applying in a single crystal of $Fe_3O_2BO_3$ a DC voltage above a temperature dependent threshold, a high current is liberated in this material. We study the conduction in single crystals of $Fe_3O_2BO_3$ with voltage applied parallel and perpendicular to the crystallographic *c* axis direction. The observed currents are attributed to the depinning of charge ordered domains above a threshold voltage V_{T2} that gives rise to a collective conduction due to coherent domains. Compliance limited DC data shows that above a lower threshold voltage depinning is smooth and follows a power law scaling. Similar depinning with power law scaling is also revealed in the AC conductivity.

Keywords: charge density wave, structural phase transition, non-linear conductance, charge ordering, oxyborates, transition metal oxides

(Some figures may appear in colour only in the online journal)

1. Introduction

The problem of one-dimensional electronic systems of free electrons interacting with lattice distortions has been much studied [1–4]. Under certain conditions these linear chain compounds develop a charge density wave modulation below the *Peierls transition* associated with the formation of an electron-phonon condensate. The observation of a contribution to the total conductivity due to this condensate below the transition puts in evidence the pinning mechanisms responsible for avoiding this phenomenon. In order to overcome the pinning potential, a threshold electric field needs to be applied for depinning the CDW and to allow the contribution of the condensate to conduction. A summary of the experimental work, dealing with the application of DC and AC signals in CDW systems can be found in Grüner's review [3]. A more recent review of the field is found in [4].

$Fe_3O_2BO_3$ has the ludwigite $M_2M'O_2BO_3$ chemical formula, M and M′ being transition metal ions (see figure 1). The ludwigites belong to the family of oxyborates and are characterized by the presence of low dimensional units in the form of three legged ladders (3LL) along the *c*-axis of their crystalline structure [5, 6]. $Fe_3O_2BO_3$ presents a unique structural transition concomitant with the charge ordering (CO) of an itinerant electron in the rungs of the ladders [6–8]. This transition, associated with the formation of a *transverse* CDW, i.e. with the atomic displacements transverse to the direction of the ladders (figure 1), was identified by the first time around 283 K by x-ray diffraction [6]. Subsequently, the doubling of the *c*-axis lattice parameter could already be observed, by the

 © 2017 IOP Publishing Ltd Printed in the UK

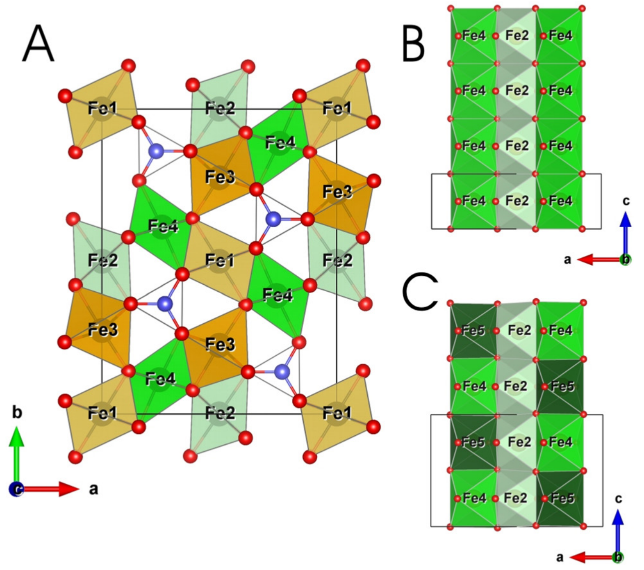

Figure 1. (A) The schematic structure of $Fe_3O_2BO_3$ ludwigites projected along the *c* axis together with the oxygen polyhedra centered on the Fe ions. The two subunits in the form of three legged ladders are shown. The numbers indicate the crystallographic sites and the lines the unit cell. The boron ions have trigonal coordination. The $4-2-4$ ladder before (B) and after (C) the dimerization transition are also shown. This figure was generated by Vesta software [9].

same technique, at 290 K [7]. Mössbauer spectroscopy has seen the charge-order transition around 300 K [10].

In a recent article [11], some of us have proposed that the negative differential resistance (NDR) phenomenon observed by applying DC current in single crystals of $Fe_3O_2BO_3$ is a consequence of the depinning of charge ordered domains.

In this work, specific heat results in $Fe_3O_2BO_3$ in the room temperature range are presented providing the first thermodynamic evidence for the CDW transition in this material. Conductance measurements with application of DC and AC voltage are also shown. The effects of application of DC voltage are much more dramatic than those seen by the application of current [11]. In a single crystal of $Fe_3O_2BO_3$ when voltage is applied, above a certain temperature dependent threshold, a high current is liberated, sufficient to melt the contacts and obliging to restart the measurements with another sample. We use different approaches to circumvent this problem and study the conduction in single crystals of $Fe_3O_2BO_3$ with voltage applied parallel and perpendicular to the crystallographic *c*-axis direction.

2. Experimental

Single crystals of $Fe_3O_2BO_3$ were grown, and confirmed as single phase, by x-ray spectra as described in [12]. They grow as needles having the longest size parallel to the *c* axis with typical dimensions (0.5 mm × 0.2 mm × 0.2 mm). For the transport studies, they were mounted inside a Janis CCS-150 closed cycle cryostat, after being carefully assembled on a sheet of mica attached to an aluminum sample holder. For the electrical contacts in the opposite sides of the samples, gold wires (0.025 mm) were used, connected to the sample with silver

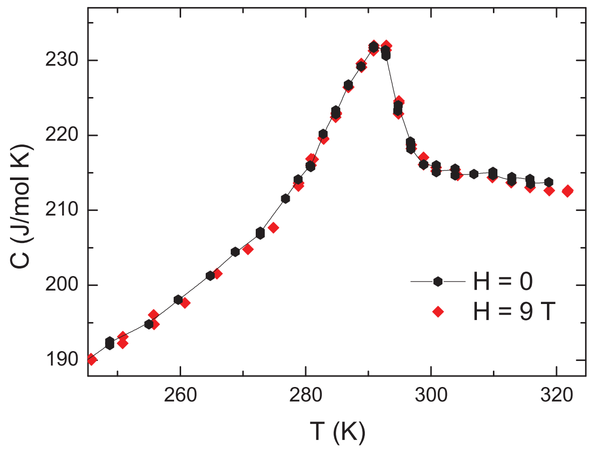

Figure 2. Specific heat as a function of temperature of $Fe_3O_2BO_3$ in zero magnetic field and for an applied magnetic field of 9 *T*. The maximum at 292 K is associated with the CO transition.

conductive paint. Due to the very small size of the samples, a two contacts measurement was done, but as the minimal resistance was around 10^2 Ω and contacts resistance below 1 Ω, this was not a real problem. For the same reason it was only possible to measure along the crystallographic *c*-axis and perpendicular to it. DC voltage was applied and current measured using a Keithley 2430 source-meter. Impedance measurements were performed using a Solartron 1260 A Impedance Analyser, applying AC voltage (*rms*) from 0.5 V to 3 V, the limit *rms* voltage of the equipment. Specific heat measurements as a function of temperature and magnetic field were performed in a Quantum Design PPMS employing nine crystalline needles put together in the puck with a total mass of 2.6 mg.

3. Results and discussion

3.1. Specific heat results

Figure 2 shows specific heat results as a function of temperature near the CDW or CO transition in zero magnetic field and for an applied magnetic field of 9 *T*. Notice that the peak and its temperature, $T_{CO} = 292$ K, are insensitive to the applied magnetic field confirming the charge ordering or structural character of this transition. The temperature of the peak is close but does not coincide with those obtained by other techniques [6, 7, 10]. This is a characteristic feature of critical phenomena in low dimensional systems, in which a substantial amount of short range order is built in the system in the vicinity of the phase transition. In [11], resistivity measurements along the *c*-axis direction show an anomaly at around 304 K, when a very low current is applied.

3.2. Transport measurements

In order to avoid melting the contacts, as mentioned above, we show in figure 3 the resistance of our Fe ludwigite sample as a function of an applied DC voltage, *with the current limited by adding a resistor in series with the sample*. As can be seen, when the resistor is very large and strongly limits the current in the sample, the resistance is independent of the applied

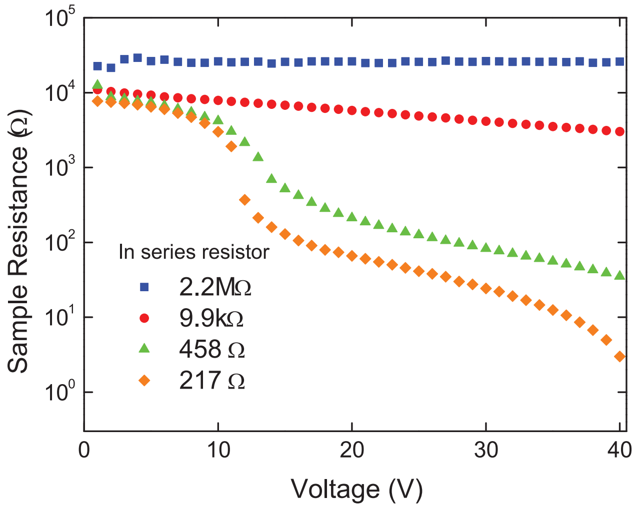

Figure 3. Sample resistance versus DC voltage applied at 295 K for the series combination of the single crystal of $Fe_3O_2BO_3$ (in *c* axis) and a resistor of: 2.2 MΩ, 9.9 kΩ, 458 Ω and 217 Ω.

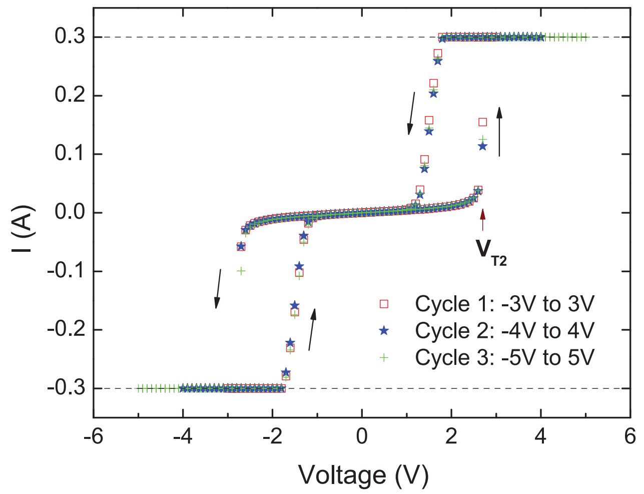

Figure 4. Current limited by a compliance of ±0.3 A (dashed lines) for a DC voltage applied perpendicular to the *c*-axis of $Fe_3O_2BO_3$ single crystal at 295 K. First, from −3 V to 3 V (open red squares), second, from −4 V to 4 V (blue stars) and third, from −5 V to 5 V (green crosses). The sharp increase in the current that defines V_{T2} is also indicated.

voltage. When a smaller resistor (9.9 kΩ) is used, there is a linear decrease in the sample resistance with voltage. For much smaller resistors, the nonlinear behavior with voltage shows up and the resistance of the sample drops to very low values as the voltage increases.

In figure 4, DC voltage is applied to a $Fe_3O_2BO_3$ single crystal perpendicular to its *c*-axis at 295 K. A current compliance limits the current to 0.3 A. A sharp increase in the current occurs around $V_{T2} = 2.6$ V (see figure 4) and the compliance current set in the equipment is attained (dotted lines). Decreasing the current, the transition to a low current state takes place around 1.7 V. The same data is seen cycling the voltage two more times. Similar behavior is found when the cycles are delayed for 30 s (not shown). The hysteretic behavior of the I × V curve suggests some kind of discontinuous or first-order-like transition at V_{T2}.

Measurements performed perpendicular to the *c*-axis in a second sample, applying DC voltage in smaller steps, have identified two distinct voltage thresholds. The first one (V_{T1}) shows the change from linear to nonlinear behavior. The second (V_{T2}) is related to the sharp increase in current described in figure 4. In figure 5, V_{T1} and V_{T2} values are given respectively in panel a and b for temperatures between 200 K and 300 K. In figure 6 the first threshold, V_{T1}, is shown at 300 K (a) and 260 K (b). For comparison, we notice that two threshold voltages have also been observed below 40 K in the CDW system $K_{0.30}MoO_3$ [13]. The first threshold also marked the change from linear to nonlinear behavior of the V-I curve. The second, in that case much less temperature dependent, marks a sharp increase in current by several orders of magnitude observed for an applied voltage around 5 V.

In figure 7(a), we show I × $(V\text{-}V_{T1})/V_{T1}$ for $V_{T1} \leqslant V \leqslant 0.9V_{T2}$ and temperatures in the range 300 K to 260 K. The data satisfy the equation [16],

$$I(V) = C\left(\frac{V - V_{T1}}{V_{T1}}\right)^{\eta} + I_0 \quad (1)$$

showing scaling behavior. This implies a cooperative nature of the depinning process, as in a dynamical critical phenomenon involving many degrees of freedom. Here I_0 is the ohmic current and the first term is due to the CDW current, which for a rigid displacement of the CDW(CO) is proportional to the velocity v [3] of the condensate. The smooth rise of the current I with the difference $V - V_{T1}$ indicates a continuous transition characterized by a critical exponent η different from the discontinuous behavior near V_{T2}. The best fitting for the 300 K data yields $\eta = 1.56$ (full line in figure 7(a)). In figure 7(b), a similar plot has been done for the data taken at 295 K with a delay of 30 s between cycles. The excellent reproducibility of data can be observed. The solid line is the best fit (first cycle) with equation 1 yielding $\eta = 1.65$.

For conventional CDW systems, Fisher [15] estimated the velocity v of the condensate using a mean field approach and predicted that $v \propto (V - V_{T1})^{\eta}$ with the exponent $\eta = 3/2$. Notice that we consider that the transition in $Fe_3O_2BO_3$ close to 292 K can be classified indistinctly as CO or CDW[5]. In fact CO and CDW are in some way similar phenomena, CDW having the amplitude of modulation weak, and CO having it relatively large and commensurate with the lattice [16]. Then, from the theoretical point of view we expect that in analyzing the depinning, theories formulated for CDW can be applied to our system. This is also the case of the behavior close to the second threshold V_{T2} shown in figure 4, which is in qualitative agreement with the model of depinning with stress overshoot [17]. For a value of stress overshoot higher than a critical one, depinning occurs by a finite jump in the average velocity $\bar{v}$ and is accompanied by hysteresis, both features characteristic of first-order like phase transitions, as we observe. It is important to remark that for several cycles, as shown in figure 4, the behavior is reproducible.

[5] It is shown in [8] that a 3LL with (1/3) band filling is unstable to a staggered CDW as a half-filled linear chain is to a conventional CDW.

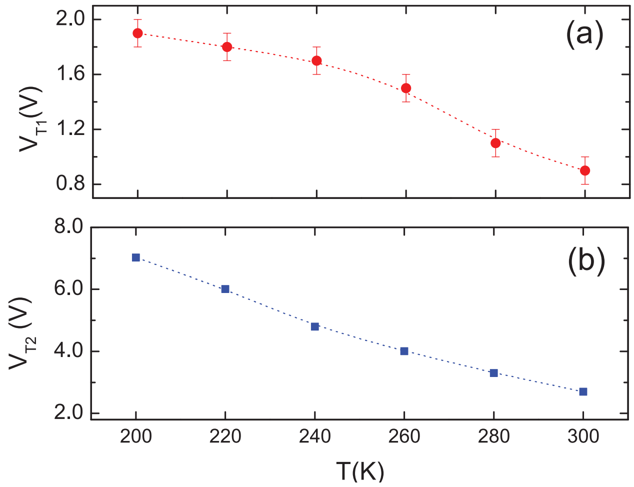

Figure 5. Voltage thresholds versus temperature observed for a DC voltage applied perpendicular to the *c*-axis of $Fe_3O_2BO_3$ single crystal. (a) V_{T1} marks the change from linear to nonlinear behavior; (b) V_{T2} marks the sudden increase in current shown in figure 4.

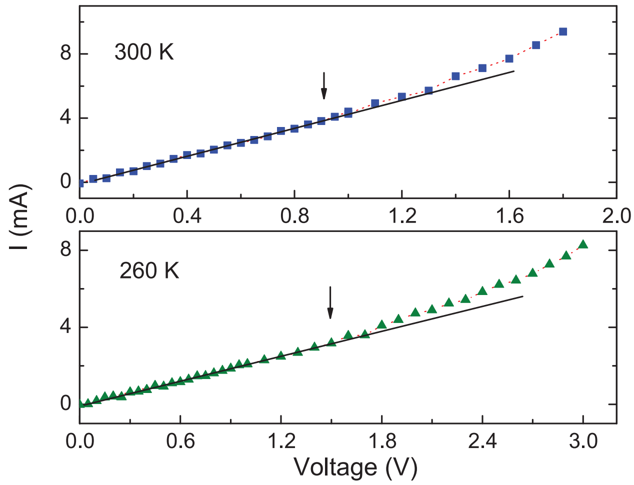

Figure 6. The *I* versus *V* data showing the first threshold V_{T1} at (a) 300 K; (b) 260 K. Arrows indicate V_{T1}.

The depinning of the CO domains was also studied by applying AC signals in the direction parallel to the crystallographic *c*-axis. In this direction the resistivity is lower, and a more extended range could be accessed, within the limited range of the Solartron Analyzer. In figure 8 the real part of resistivity is shown as a function of frequency (log scale) for several applied *rms* signals, at fixed temperatures of 295 K and 255 K. Both, the resistivity and its frequency dependence decrease with the increase of the AC signal, pointing towards a more conductive state. Besides, when the DC conductivity (σ_{DC}) is subtracted from the data, for the higher values of *rms* voltage, a clear characteristic frequency is observed, ranging in a nonlinear way from 5.4×10^4 Hz at 295 K to 1.6×10^4 Hz at 255 K. Above this frequency, the behavior of the AC conductivity (σ) changes inflection and shows power law scaling. We assume that this frequency plays the same role as the threshold voltage V_{T1} in the DC data of figure 7 and associate it with a *pinning frequency* ω_P. In the inset of figure 9 we have plotted $\log(\sigma(\omega) - \sigma_{\mathrm{DC}})$ versus $\log(\omega/\omega_P)$, for temperatures in the range 295 K to 270 K. A power law scaling is clearly observed

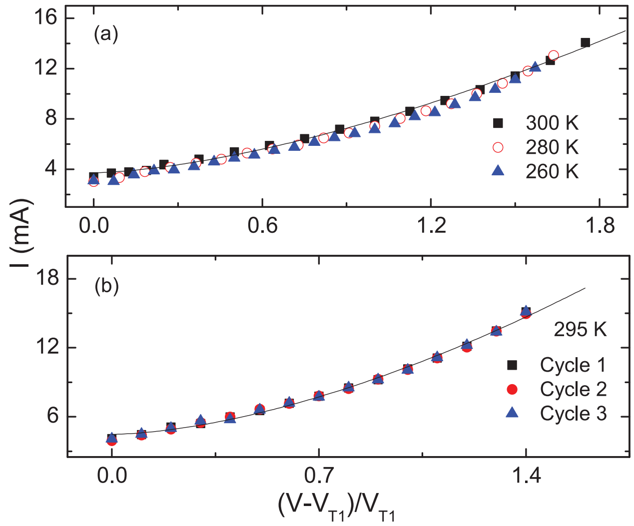

Figure 7. (a) *I* versus (*V*- V_{T1})/ V_{T1} for $V_{T1} \leqslant V \leqslant 0.9V_{T2}$ at 300 K, 280 K and 260 K. The solid line is the fitting of equation 1 at 300 K with $\eta = 1.56$ and $I_0 = 3.72$ mA. (b) At 295 K for three different cycles with a delay of 30 s (not shown in figure 4). The solid line is the best fitting with $\eta = 1.65$ and $I_0 = 4.47$ mA.

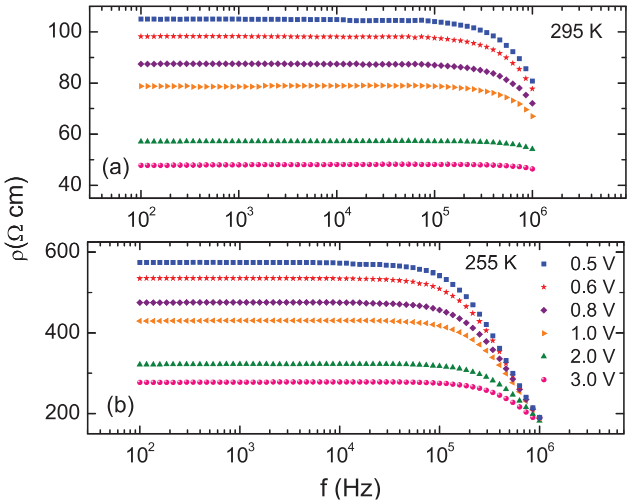

Figure 8. Real part of AC resistivity as a function of frequency (log scale) for several applied *rms* signals as the temperature is decreased at (a) 295 K and (b) 255 K.

above the pinning frequency. In figure 9, the data is plotted for $(\omega/\omega_P) \geqslant 1$. The full line shows the best fit to the data at 270 K using a power law with $\eta = 1.63$. It is interesting to note the similarity of the η values in the data of figures 7 and 9. In [14], in a combination of a DC plus AC techniques applied at 125 K in a very small and high purity sample of $NbSe_3$, an archetypical CDW material, a value of $\eta = 1.23 \pm 0.07$ has been found, in a plot of I_{CDW} versus $(V - V_T)/V_T$. The important fact seen in the AC conductivity is that the scaling is associated with (ω/ω_P), with the pinning frequency appearing very naturally as a scaling frequency in the log $\times$ log plot. Both, DC and AC scaling behavior are observed only between 300 K and approximately 255 K. As this range of temperatures is close to the charge order transition temperature, there is a complete screening of the density fluctuations involved in transport by normal carriers.

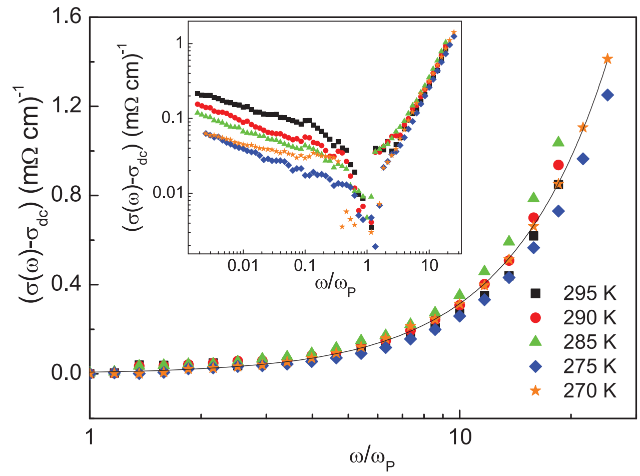

Figure 9. $(\sigma(\omega) - \sigma_{DC})$ versus ω/ω_P (log scale) for the 3 V *rms* voltage and $\omega/\omega_P \geqslant 1$ at several temperatures. The full line is the best fitting by $\sigma(\omega) - \sigma_{DC} = C(\omega/\omega_P)^\eta$ with $\eta = 1.63$ at 270 K. Inset: Full range shown in log x log scale.

4. Conclusions

In this work we presented specific heat results on the ludwigite $Fe_3O_2BO_3$, near room temperature. They provide the first thermodynamic evidence for the CDW transition in this system. We also carried out a systematic study of the transport properties of this ludwigite near this transition showing unambiguous evidence of a CDW contribution to its electric conduction. Different methods were used to obtain the transport properties by the application of DC voltage in single crystals of $Fe_3O_2BO_3$. In this system current must be limited if voltage is applied above a certain temperature dependent threshold, to avoid a huge current that melts the contacts and sometimes burns the sample. By setting a current compliance of 0.3 A, we could identify in the data with voltage applied perpendicular to the *c* axis two threshold voltages. In the range $V_{T1} \leqslant V \leqslant 0.9V_{T2}$ depinning is smooth and characterized by a power law scaling behavior, with the critical exponent $\eta \approx 3/2$. At the upper threshold V_{T2}, the current *jumps* discontinuously to the value set by the compliance. It presents hysteresis in the $I \times V$ curve, as in a first order transition. The behavior of our system close to V_{T1} and V_{T2} is not unique and has been observed in conventional CDW systems. Theoretically, they can be described by pinning of domains by impurities and stress overshoot depinning, respectively. The stress overshoot depinning theory [17] is non dissipative, and the similarity of the $I \times V$ curve with it, reinforces our conviction that the huge current liberated without current compliance is due to the strongly coupled electron plus lattice distortion system, i.e. to conduction by depinned charge ordered domains. In the present case, the application of voltage above V_{T2} leads to large currents without compliance, and to stress overshoot like behavior with compliance. In the current controlled situation seen in [11] this limit is not reached and the dynamics is still dissipative as also seen here for $V_{T1} \leqslant V \leqslant 0.9V_{T2}$.

Finally, for *rms* AC voltage applied in the *c*-axis direction, we observed depinning with power law scaling in ω/ω_P. When the DC component is subtracted from the AC conductivity this is described by an exponent very similar to that obtained for the DC data. The characteristic depinning frequencies in the temperature range investigated are weakly temperature dependent and of order 10^4 Hz.

Acknowledgments

We would like to thank Manuel Nunez–Regueiro for useful discussions. This work was partially supported by Brazilian agencies FAPESP, FAPERJ, CAPES and CNPq.

References

[1] Fröhlich H 1954 *Proc. R. Soc. A* 223 296–305
[2] Lee P A, Rice T M and Anderson P W 1974 *Solid State Commun.* **14** 703–9
[3] Grüner G 1988 *Rev. Mod. Phys.* **60** 1129–81
[4] Monceau P 2012 *Adv. Phys.* **61** 325
[5] Freitas D C, Continentino M A, Guimarães R B, Fernandes J C, Ellena J and Ghivelder L 2008 *Phys. Rev.* B **77** 184422
Medrano C P C, Freitas D C, Sanchez D R, Pinheiro C B, Eslava G G, Ghivelder L and Continentino M A 2015 *Phys. Rev.* B **91** 054402
[6] Mir M, Guimarães J B, Fernandes J C, Continentino M A, Doriguetto A C, Mascarenhas Y P, Ellena J, Castelhano E E, Freitas R S and Ghivelder L 2001 *Phys. Rev. Lett.* **87** 147201
[7] Bordet P and Suard E 2009 *Phys. Rev.* B **79** 144408
[8] Latgé A and Continentino M A 2002 *Phys. Rev.* B **66** 094113
[9] Momma K and Izumi F 2011 *J. Appl. Crystallogr.* **44** 1272
[10] Larrea J J, Sánchez D R, Litterst F J, Baggio-Saitovitch E M, Fernandes J C, Guimarães R B and Continentino M A 2004 *Phys. Rev.* B **70** 174452
[11] dos Santos E C, Freitas D C, Fier I, Fernandes J C, Continentino M A, de Oliveira A J A and Walmsley L 2016 *J. Phys. Chem. Solids* **90** 65
[12] Guimarães R B, Mir M, Fernandes J C, Continentino M A, Borges H A, Cernicchiaro G, Fontes M B, Candela D R S and Baggio-Saitovitch E 1999 *Phys. Rev.* B **60** 6617
[13] Martin S, Fleming R M and Schneemeyer L F 1988 *Phys. Rev.* B **38** 5733
[14] Bhattacharya S, Higgens M J and Stokes J P 1989 *Phys. Rev. Lett.* **63** 1503
[15] Fisher D S 1983 *Phys. Rev. Lett.* **50** 1486
[16] Khomskii D I 2014 *Transition Metal Compounds* (Cambridge: Cambridge University Press) p 254
[17] Schwartz J M and Fisher D S 2001 *Phys. Rev. Lett.* **87** 096107