AIP | Journal of Applied Physics

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Citation: J. Appl. Phys. **109**, 07E115 (2011); doi: 10.1063/1.3549615
View online: http://dx.doi.org/10.1063/1.3549615
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v109/i7
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JOURNAL OF APPLIED PHYSICS **109**, 07E115 (2011)

Metal-insulator transition in $Nd_{1-x}Eu_xNiO_3$ probed by specific heat and anelastic measurements

V. B. Barbeta,[1,a)] R. F. Jardim,[2] M. S. Torikachvili,[3] M. T. Escote,[4] F. Cordero,[5]
F. M. Pontes,[6] and F. Trequattrini[7]
[1]*Departamento de Física, Centro Universitário da FEI, São Bernardo do Campo, 09850-901, Brazil*
[2]*Instituto de Física, Universidade de São Paulo, CP 66318, São Paulo, 05315-970, Brazil*
[3]*Department of Physics, San Diego State University, San Diego, California 92182-1233, USA*
[4]*Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas, Universidade Federal do ABC, Santo André, 09210-170, Brazil*
[5]*CNR-ISC, Istituto dei Sistemi Complessi, Via del Fosso del Cavaliere 100, 00133, Rome, Italy*
[6]*Departamento de Química, Universidade Estadual Paulista, Bauru, 17033-360, Brazil*
[7]*Physics Department, University of Roma "La Sapienza", P.le A. Moro 5, 00185, Rome, Italy*

(Presented 17 November 2010; received 1 October 2010; accepted 15 November 2010; published online 24 March 2011)

Oxides RNiO$_3$ (R = rare-earth, $R \neq$ La) exhibit a metal-insulator (MI) transition at a temperature T_{MI} and an antiferromagnetic (AF) transition at T_N. Specific heat (C_P) and anelastic spectroscopy measurements were performed in samples of $Nd_{1-x}Eu_xNiO_3$, $0 \leq x \leq 0.35$. For $x = 0$, a peak in C_P is observed upon cooling and warming at essentially the same temperature $T_{MI} = T_N \sim 195$ K, although the cooling peak is much smaller. For $x \geq 0.25$, differences between the cooling and warming curves are negligible, and two well defined peaks are clearly observed: one at lower temperatures that define T_N, and the other one at T_{MI}. An external magnetic field of 9 T had no significant effect on these results. The elastic compliance (s) and the reciprocal of the mechanical quality factor (Q^{-1}) of NdNiO$_3$, measured upon warming, showed a very sharp peak at essentially the same temperature obtained from C_P, and no peak is observed upon cooling. The elastic modulus hardens below T_{MI} much more sharply upon warming, while the cooling and warming curves are reproducible above T_{MI}. Conversely, for the sample with $x = 0.35$, s and Q^{-1} curves are very similar upon warming and cooling. The results presented here give credence to the proposition that the MI phase transition changes from first to second order with increasing Eu doping. © *2011 American Institute of Physics*. [doi:10.1063/1.3549615]

A number of RNiO$_3$ compounds (R = rare-earth, $R \neq$ La) are metallic at high temperatures and display a metal-insulator (MI) transition at a temperature T_{MI}, which depends upon the R ion-size of the rare-earth. They also exhibit an antiferromagnetic (AF) transition at T_N, due to the spin ordering of the Ni sublattice. For R = Nd and Pr $T_{MI} \approx T_N$, while for the other rare-earths T_{MI} is higher than T_N, with T_N increasing slightly and T_{MI} decreasing as a function of the R ionic radius.[1]

The magnetic order of NdNiO$_3$ was studied by powder neutron diffraction (PND), revealing the presence of a wave propagation vector $k = (1/2,0,1/2)$, and an unusual up-up-down-down stacking of ferromagnetically ordered planes along the simple cubic (111) direction was proposed.[2] Conversely, soft x-ray resonant scattering experiments showed that the (1/2,0,1/2) reflection is of magnetic origin, without orbital ordering. Besides, the results were not consistent with the spin arrangement proposed by PND, and indicated a non-collinear antiferromagnetic ordering scheme.[3]

Recently, high resolution PND experiments in NdNiO$_3$ unambiguously established the occurrence of two different NiO$_6$ octahedra at low temperatures, as well as the corresponding change from orthorhombic (*Pbnm*) to monoclinic ($P2_1/n$) symmetry.[4] This being the case, a charge ordered state is observed at low temperatures and the twofold e_g orbital degeneracy is lifted, opening an energy gap. Therefore, the low temperature phase may not be classified as a charge transfer insulator as originally suggested, but could be better described as a band insulator.[4]

Although much research has addressed the general physical properties of these systems there are still many open questions regarding the role played by the correlation between magnetic and electronic properties. Within this context, here we present and discuss measurements of specific heat (C_p) and anelastic spectroscopy near the MI phase transformation.

Polycrystalline samples of $Nd_{1-x}Eu_xNiO_3$, $0 \leq x \leq 0.35$, were prepared from sol-gel precursors, sintered at temperatures ~1000 °C, under oxygen pressures up to 80 bar. Details of the sintering process for preparing these samples are described elsewhere.[5] All samples were characterized by x-ray powder diffraction in a Brucker D8 Advance diffractometer. The x-ray diffraction patterns showed no extra reflections due to impurity phases, and indicated that all samples have a high degree of crystallinity.

Specific heat (C_p) measurements in the temperature range from 2–310 K upon cooling and warming were performed in a physical property measurement system from Quantum Design equipped with a superconducting 9 T magnet.

[a)] Author to whom correspondence should be addressed. Electronic mail: vbarbeta@fei.edu.br.

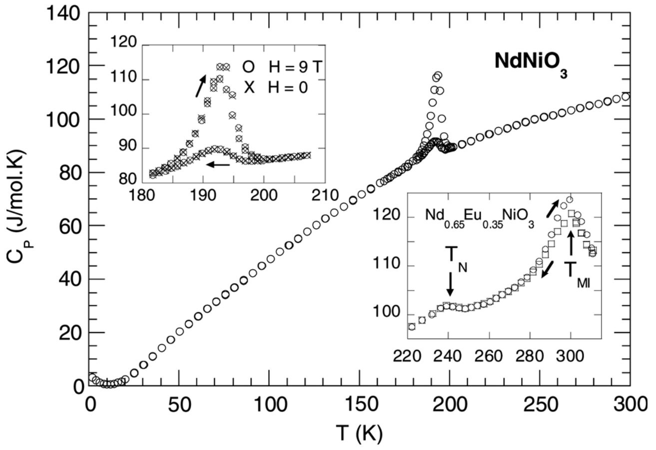

FIG. 1. Temperature dependence of C_p for $NdNiO_3$ upon cooling and warming. The upper inset displays the transition region with $H = 0$ and $H = 9$ T. The lower inset shows the $C_p(T)$ data for the $Nd_{0.65}$ $Eu_{0.35}$ NiO_3 sample upon cooling (squares) and warming (circles).

Complex Young's modulus measurements $E(\omega, T) = E' + iE''$ were performed as a function of temperature, by electrostatically exciting the fundamental flexural modes of the samples, and detecting the vibrational amplitude.[6] The energy dissipation or reciprocal of the mechanical quality factor $Q^{-1}(\omega, T) = E''/E'$ was determined from the decay of the free oscillations or from the width of the resonance peak. Due to the porosity of the sintered materials the values of elastic compliance $s = E^{-1}$ were not absolute, and therefore were normalized to the s_0 value, obtained at the fundamental frequency $f_0 = f(T = 0)$.

The $C_\mathbf{p}$ results for $NdNiO_3$ are displayed in Fig. 1 for both the warming and the cooling cycles. The sharp peak observed upon warming at $T_{MI} = T_N \sim 195$ K defines the MI and AF transitions. The peak in $C_p(T)$ at T_{MI} upon cooling is much reduced. The difference in $C_p(T)$ near T_{MI} upon cooling and warming suggests a complex interaction between the crystalline and magnetic structures and perhaps that the phase transition at T_{MI} has a first order character. The difficulties in extracting accurate values of $C_p(T)$ near first order transitions using relaxation calorimetry are well known.[7] However, the large difference between the cooling and warming cycles in this case is compelling enough to suggest intrinsic behavior.

When Nd is partially replaced by Eu, both T_{MI} and T_N are shifted to higher temperatures. For the $x = 0.35$ sample (the lower inset of Fig. 1), the electronic and magnetic transitions are separated in temperature, and two peaks in $C_p(T)$ are clearly identified. In this case, there is no significant difference between the cooling and the warming curves. The application of an external magnetic field as high as 9 T resulted in no appreciable change in $C_p(T)$ data, as displayed in the upper inset of Fig. 1 for the $NdNiO_3$ sample. Similar field independent behavior was also observed in the $Nd_{0.65}$ $Eu_{0.35}$ NiO_3 sample (not shown).

A background contribution to $C_p(T)$ was subtracted from the curves and the resulting specific heat ($C_R(T)$) is displayed in Fig. 2. Such a subtraction was performed by excluding the region close to the phase transition in the warming cycle, and fitting the resulting curve to a smooth base-line. The resulting curve for the $x = 0$ sample displays a very sharp peak at $T_{MI} = T_N \sim 195$ K. However, the partial substitution of Nd with Eu results in a separation of the two transitions. This is clearly seen in the $x = 0.25$ sample which exhibits two peaks: one at $T \sim 240$ K related to the AF transition, and the other one at $T \sim 270$ K due to the MI transition. The separation in temperature of the two transitions is even more evident in the $x = 0.35$ sample where the two peaks are completely resolved in spite of some smearing in comparison with the $x = 0$ sample. The values of T_{MI} from these curves are in agreement with those previously obtained through resistivity measurements.[8]

Photoemission spectra (PES) measurements performed across the MI phase transition in systems with $T_{MI} = T_N$ ($NdNiO_3$ and $PrNiO_3$), revealed a temperature-dependent loss of spectral weight near the chemical potential, extending well below the transition temperature. Alternatively, samples with $T_{MI} > T_N$ ($SmNiO_3$ and $EuNiO_3$) showed a quite different behavior. These results were interpreted as an indication that there is a qualitative difference between these two systems, and that there is an interplay between magnetic and electronic properties in samples with $T_{MI} = T_N$.[9]

Similar results were obtained through PES measurements performed in the metallic phase in samples of $Nd_{1-x}Sm_xNiO_3$.[10] It was observed that for $x > 0.4$ ($T_{MI} > T_N$) the spectra above T_{MI} shows a pseudogap, different from the behavior of the spectra obtained for $x \leq 0.4$ ($T_{MI} = T_N$), which is typical of a metal. This difference in the nature of the metallic state was assumed to be caused by changes in the strength of the electronic correlation between the two regions. Another result indicating a crossover in the nature of the MI phase transition was obtained through magnetic susceptibility data. Measurements performed in samples of $NdNiO_3$ and $Nd_{0.5}Sm_{0.5}NiO_3$ after the subtraction of the magnetic rare-earth contribution, indicated a change from Pauli to Curie-Weiss paramagnetism with increasing Sm doping in the $NdNiO_3$ sample.[11] It was also observed that below T_N the magnetic susceptibility increases with decreasing temperature, with no difference between the field-cooled and zero-field-cooled cycles, a situation that is not characteristic of a system with localized spin. Finally, based on electrical resistivity measurements, it was suggested that the MI

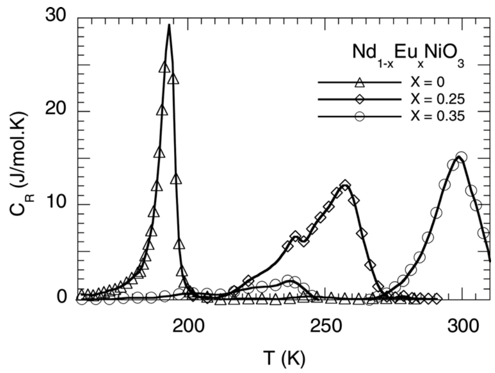

FIG. 2. Temperature dependence of the specific heat (C_R) of Nd_{1-x} Eu_x NiO_3 for three selected samples, obtained after subtracting the background contribution (see the text). Lines are just a guide to the eye.

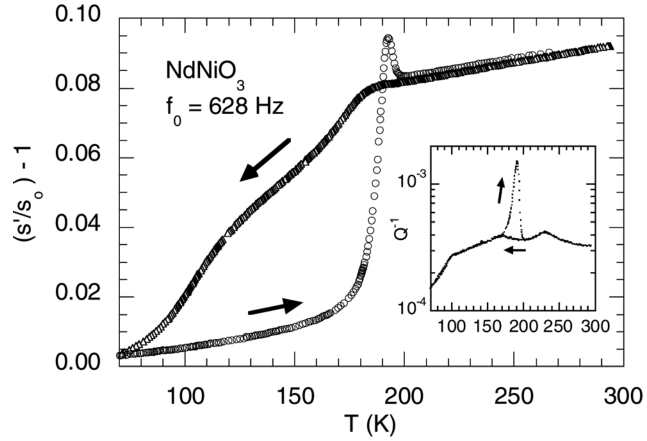

FIG. 3. Elastic compliance $(s/s_0)-1$ for $x=0$. The inset shows the corresponding graph of Q^{-1}.

phase transition is first order only when $T_{MI}=T_N$, and second order for $T_{MI}>T_N$.[11]

The elastic compliance curves $(s/s_0)-1$ obtained for the $x=0$ sample showed essentially the same behavior above $T_{MI}\sim 195$ K upon cooling and warming, as shown in Fig. 3. Below T_{MI}, the hardening is very gradual upon cooling, extending over more than 100 K. Conversely, the softening upon warming is abrupt, resulting in a very strong hysteresis between both curves. The energy dissipation (inset of Fig. 3) has a marked peak upon warming at $T\sim 191$ K, due to the MI phase transition. It was also expected that such a peak would be found in the cooling curve marking the phase transition, but the presence of this peak is not evident or completely absent.

The cooling behavior of $(s/s_0)-1$ below T_{MI} is possibly caused by the coexistence of the metallic and insulating phases; a typical situation of a first-order phase transition. The coexistence of both phases below T_{MI} has been previously reported from electrical resistivity measurements.[12] Different from transport measurements, which mainly reflect the percolation of the conducting phase, the observed variation of the elastic compliance below T_{MI} is related to the volumetric fraction of the transformed phase and indicates that even at 70 K (the lowest temperature of these measurements), some residual metallic phase still remains within the sample.

Alternatively, for the specimen with $x=0.35$, the elastic compliance (s) and the reciprocal of the mechanical quality factor (Q^{-1}) showed no significant hysteresis upon cooling and warming (not shown in Fig. 3). Previous electrical resistivity measurements also showed a negligible hysteresis for samples with $x\geq 0.25$,[8] indicating that the phase transition above this concentration is possibly of second order.

In conclusion, we have found that it is possible to distinguish two different regimes in the MI phase boundary in $Nd_{1-x}Eu_xNiO_3$: (i) for $x=0$, $T_{MI}=T_N$, there is a strong thermal cycle hysteresis in the $C_p(T)$, and the transition has a first order character; (ii) for $x\geq 0.25$, $T_{MI}>T_N$, the thermal hysteresis is negligible, and the MI transition has a second order character. These propositions are consistent with the features observed in elastic modulus measurements, which also showed a strong hysteresis upon cooling and warming for the $x=0$ sample, a feature that has been found to be insignificant in the $x=0.35$ sample. Previous magnetic susceptibility and electrical resistivity measurements in a series of $Nd_{1-x}Eu_xNiO_3$ samples are consistent with this picture.[8]

This work was supported by the Brazilian agency Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) under Grant No. 2005/53241-9. Three of us (R.F.J., M.T.E., and F.M.P.) acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for fellowships. M.S.T. gratefully acknowledges support of the National Science Foundation under Grant No. DMR-0805335

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