Metal-insulator transition in Nd$_{1-x}$Eu$_x$NiO$_3$ probed by specific heat and anelastic measurements

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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$_x$NiO$_3$, 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 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 $T_{MI}$. On the other hand, 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.

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 of 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 $R = \text{Nd}$ 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.

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 (FM) ordered planes along the simple cubic (111) direction was proposed. On the other hand, 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.

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. 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.

Although much work have 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$_x$NiO$_3$, 0 $\leq$ x $\leq$ 0.35, were prepared from sol-gel precursors, sintered at temperatures $\sim$ 1000°C, under oxygen pressures up to 80 bar. Details of sintering process for preparing these samples are described elsewhere. 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 to 310 K, upon cooling and warming, were performed in a Physical Property Measurement System.

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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 vibration amplitude. 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. In light of 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 $C_P$ results for NdNiO$_3$ are displayed in Figure 1 for both the warming and 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. Difficulties in extracting accurate values of $C_P(T)$ near first order transitions using relaxation calorimetry are known. However, the large difference between the cooling and warming cycles in this case is compelling enough to suggest intrinsic behavior.

![Figure 1](image1.png)

**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.

When Nd is partially replaced by Eu, both $T_{MI}$ and $T_N$ are shifted to higher temperatures. For the $x = 0.35$ sample (lower inset of Figure 1), 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 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 Figure 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).

![Figure 2](image2.png)

**FIG. 2.** Temperature dependence of the specific heat ($C_P$) of Nd$_{1-x}$Eu$_x$NiO$_3$, for three selected samples, obtained after subtracting the background contribution (see text). Lines are just a guide to the eye.

A background contribution to $C_P(T)$ was subtracted from the curves and the resulting specific heat ($C_R(T)$) is displayed in Figure 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.

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. On the other hand, 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 $T_{MI} = T_N$.

Similar results were obtained through PES measurements performed in the metallic phase, in samples of Nd$_{1-x}$Sm$_x$NiO$_3$. It was observed that for $x > 0.4$ ($T_{MI} > T_N$) the spectra above $T_{MI}$ shows a pseudogap, different from the spectra behavior 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
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 magnetic rare-earth contribution, indicated a change from 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 phase transition is first order only when $T_{MI} = T_N$, and second order for $T_{MI} > T_N$.

The energy dissipation (inset of Figure 3) has a marked increasing temperature, with no difference between the $T_{MI}$ phase transition. The coexistence of both phases 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.

The cooling behavior of $(s/s_0) - 1$ below $T_{MI}$ is possibly caused by the coexistence of the metallic and insulating phases, typical situation of a first-order phase transition. The coexistence of both phases below $T_{MI}$ has been reported previously, from electrical resistivity measurements. Differently 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.

On the other hand, 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). Previous electrical resistivity measurements also showed a negligible hysteresis for samples with $x \geq 0.25$, 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$_x$NiO$_3$: (i) for $x < 0.25$, $T_{MI} = T_N$, 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 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$_x$NiO$_3$ samples are consistent with this picture.

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