Complex low-temperature transport behaviour of RNiO$_3$-type compounds

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Abstract. The temperature-dependent electrical resistance behaviour of PrNiO$_3$, NdNiO$_3$, Nd$_{0.99}$Sr$_{0.01}$NiO$_3$ and Sm$_{0.55}$Nd$_{0.45}$NiO$_3$ in zero field as well as in the presence of a magnetic field (H) is reported. The application of H up to 70 kOe does not influence the *so-called* metal–insulator transition in any of these compounds significantly. Interestingly, the magnitude of the magnetoresistance, $\Delta\rho/\rho = \{\rho(H) - \rho(0)\}/\rho(0)$, in the vicinity of 35 K is significantly larger than that noted below 10 K. It appears that there are sign crossovers in the magnetoresistance as the temperature is varied below the transition temperature in most of these compounds. The present results suggest that the physics below the transition temperature is quite complex.

The subject of metal–insulator (MI) transitions [1] gained considerable attention following the discovery of high-temperature superconductivity and giant magnetoresistive (GMR) effects in perovskite-related systems. The compounds of the type RNiO$_3$ (R = rare earth), crystallizing in the GdFeO$_3$-type orthorhombic structure are of considerable current interest [2] in this regard. These compounds are currently believed to belong to a family of so-called 'charge-transfer-gap compounds' [3, 4] and these are the only known transition metal oxides located at the boundary that separates 'low-charge-transfer-gap metals' from 'charge-transfer insulators' in the framework developed by Zaanen, Sawatzky and Allen [4]. Very little work was done on their properties before 1991, presumably because of the difficulties of their preparation, since elevated temperatures and high oxygen pressures are required to stabilize the Ni^{3+} state. Only recently have these compounds attracted some attention (see, for instance, references [2, 5–19]). The transition seems to occur without any noticeable changes in the lattice symmetry for R. While LaNiO$_3$, with a less-distorted rhombohedral $R\bar{3}c$ structure, is known to be metallic down to 1.5 K, the MI transition temperature (T_{MI}) increases with decreasing ionic size of R depending upon the degree of distortion of the perovskite structure [17, 18]. Thus the T_{MI}-values for R = Pr, Nd, Sm and Eu are 130, 200, 400 and 460 K, respectively. The application of external pressure drastically reduces T_{MI} [15, 16] in contrast to the lanthanide contraction effects, and this is believed to arise from the straightening of the O–Ni–O bond. It has been proposed [5, 6] that, in some of these nickelates, metallic and non-metallic phases coexist over a wide temperature range below T_{MI} (above about 60 K).

In these interesting systems, the origin of the metal–insulator transition, the nature of the state below T_{MI} and the magnetism are far from being completely understood [2]. It is therefore of interest to subject these to further studies. We present here the results of

electrical resistance (ρ) measurements in zero magnetic field (H) as well as in the presence of H on the following compounds: $PrNiO_3$, $NdNiO_3$, $Nd_{0.99}Sr_{0.01}NiO_3$ and $Sm_{0.55}Nd_{0.45}NiO_3$. It is surprising to note that a small degree of hole doping by means of Sr substitution (5%) in $NdNiO_3$ is sufficient to take T_{MI} to 1.5 K [12]. The value of T_{MI} has been reported to vary smoothly through the series $Sm_{1-x}Nd_xNiO_3$ (reference [7]) and the transition for $x = 0.45$ seems to be near 300 K. Thus, these systems, whose transport properties are sensitive to pressure and hole doping, are also worth investigating by means of the application of H to see whether H modifies these features—the more so since the presence of H is known to have very large effects on the electrical transport in some oxides [1]. While aiming to contribute to the understanding of the behaviour of these appealing systems by means of the application of H, we also raise new questions on the basis of our electrical resistance data.
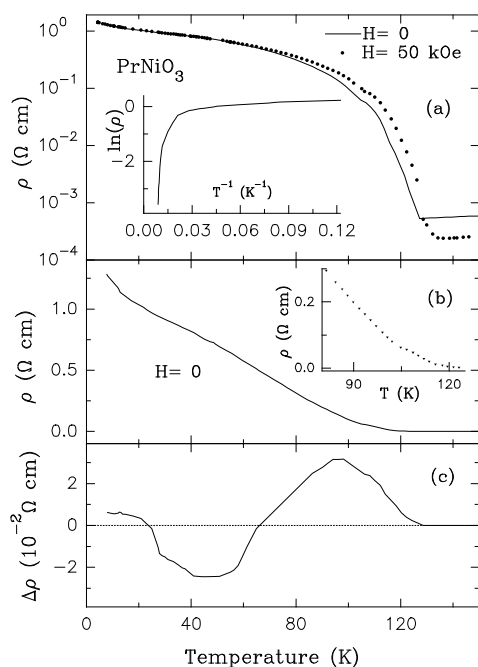
Figure 1. The electrical resistance as a function of temperature for $PrNiO_3$ in zero field and in the presence of a magnetic field ($H = 50$ kOe) plotted both on logarithmic (a) and linear (b) scales. Panel (c) shows the field-induced shift in resistivity ($\Delta\rho = \rho(50$ kOe$) - \rho(0$ kOe$)$) as a function of temperature. In the inset of (a), the data below the transition temperature are plotted as $\ln\rho$ versus inverse temperature to show the absence of a single activated energy over the entire low-temperature range. The data on the linear scale in the vicinity of T_{MI} are shown in the inset of (b) to highlight a step near 102 K.

Polycrystalline samples were prepared by a soft-chemistry route. Stoichiometric amounts of the metal nitrates (purity 99.99%) were dissolved in citric acid. The citrate solution was evaporated and the resulting resin was decomposed in air at 600 °C. The organic materials were completely eliminated in a subsequent heat treatment in air at 800 °C for 2 h. The black precursor powders were reacted at 1000 °C under 200 bar of O_2 pressure for 12 h and subsequent sintering of the pellets was carried out under the same conditions. X-ray diffraction patterns confirm the single-phase nature of the samples. The electrical resistivity (ρ) measurements were performed in the temperature interval 4.2–300 K by a
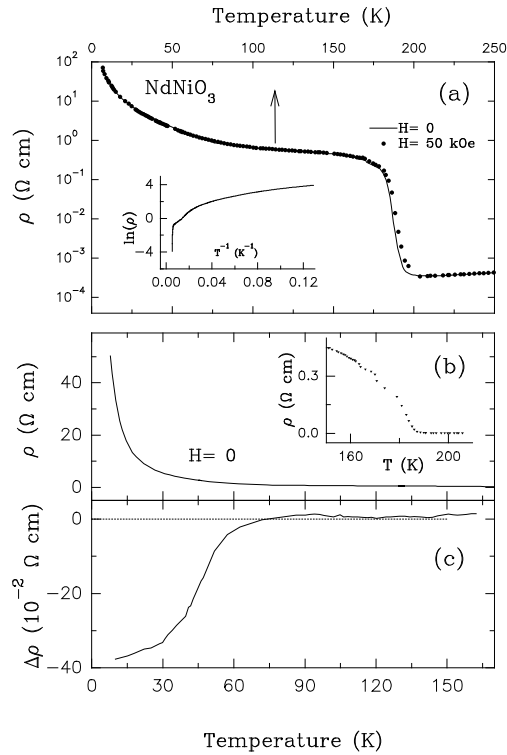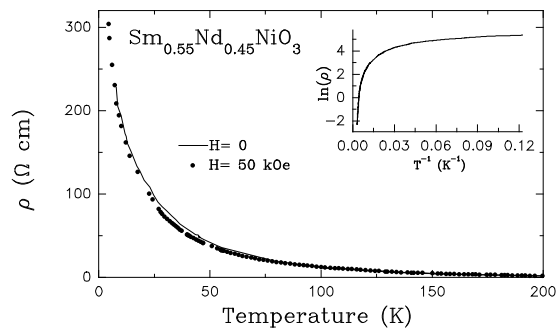
Figure 2. The electrical resistance as a function of temperature for NdNiO$_3$ in zero field and in the presence of a magnetic field ($H = 50$ kOe), plotted both on logarithmic (a) and linear (b) scales. Panel (c) shows the field-induced shift in resistivity ($\Delta\rho = \rho(50 \text{ kOe}) - \rho(0 \text{ kOe})$) as a function of temperature. In the inset of (a), the data below the transition point are plotted as $\ln\rho$ versus inverse temperature to show the absence of activated behaviour. The data on the linear scale on the vicinity of T_{MI} are shown in the inset of (b) to highlight a step near 170 K.

conventional four-probe method in zero field and as well as in the presence of $H = 50$ kOe; a conducting silver paint was used for making electrical contacts. In addition, the data were obtained as a function of H up to 70 kOe at selected temperatures (5, 10 and 35 K). The direction of $\boldsymbol{H}$ is the same as that of the excitation current. A Keithley nanovoltmeter was employed to measure the voltages across the electrical leads, and the error in the values of the magnetoresistance, $\Delta\rho/\rho = \{\rho(H) - \rho(0)\}/\rho(0)$, is less than 0.1%.

The temperature- (T-) dependent ρ-behaviours in the absence and in the presence of a field ($H = 50$ kOe), while warming, are shown in figures 1–4 for all of the samples in different ways. As known from the literature, ρ shows a sharp upturn with decreasing T at 130, 190 and 150 K for PrNiO$_3$, NdNiO$_3$ and Nd$_{0.99}$Sr$_{0.01}$NiO$_3$ respectively. However, for Sm$_{0.55}$Nd$_{0.45}$NiO$_3$, we do not see any such sharp ρ-variation below 300 K, in contrast to that observed by Frand *et al* [7]; presumably, T_{MI} for our sample may be slightly greater than 300 K. It is interesting to note that 1 at.% of Sr substitution for Nd is sufficient to depress T_{MI} from 190 K to 150 K. A finding of considerable interest is that the application of magnetic field causes only a negligible shift in T_{MI}; if there is any shift at all, it is a marginal upward one of the temperature at which there is a sharp upturn in ρ, e.g., by a few degrees for PrNiO$_3$, in contrast to the large changes produced by chemical and external pressures. Thus, this study may suggest that even in *low*-charge-gap systems, excitations
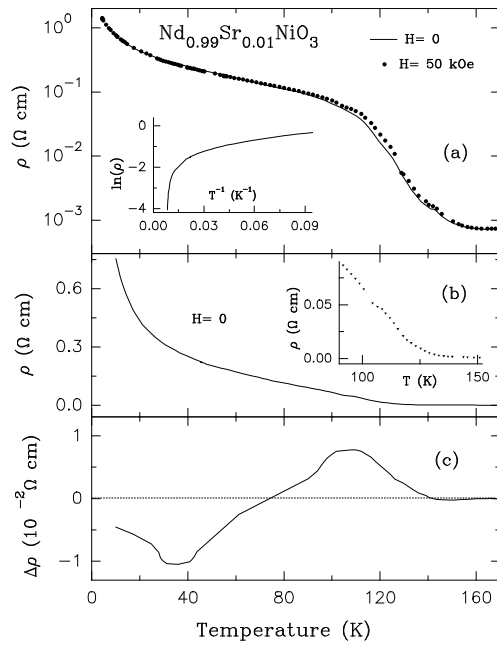
Figure 3. The electrical resistance as a function of temperature for $Nd_{0.99}Sr_{0.01}NiO_3$ in zero field and in the presence of a magnetic field ($H = 50$ kOe), plotted both on logarithmic (a) and linear (b) scales. Panel (c) shows the field-induced shift in resistivity ($\Delta\rho = \rho(50$ kOe$) - \rho(0$ kOe$)$) as a function of temperature. In the inset of (a), the data below the transition point are plotted as $\ln\rho$ versus inverse temperature to show the absence of activated behaviour. The data on the linear scale in the vicinity of T_{MI} are shown in the inset of (b) to highlight a step near 105 K.

Figure 4. The electrical resistance as a function of temperature for $Sm_{0.55}Nd_{0.45}NiO_3$ in zero field and in the presence of a magnetic field ($H = 50$ kOe). In the inset, the data below the transition point are plotted as $\ln\rho$ versus inverse temperature to show the absence of activated behaviour.

caused by H do not modify the MI transition significantly. It is to be remarked that, in the RMnO$_3$-derived systems, the application of external pressure induces the same effect on the temperature-dependent electrical resistance as that of external field [20, 21]. The field-induced effects noted for these manganites are thus of a special kind (e.g., related to a double-exchange mechanism), as proposed in the literature.

As regards the T-dependence of ρ in the presence of H, the values are higher or
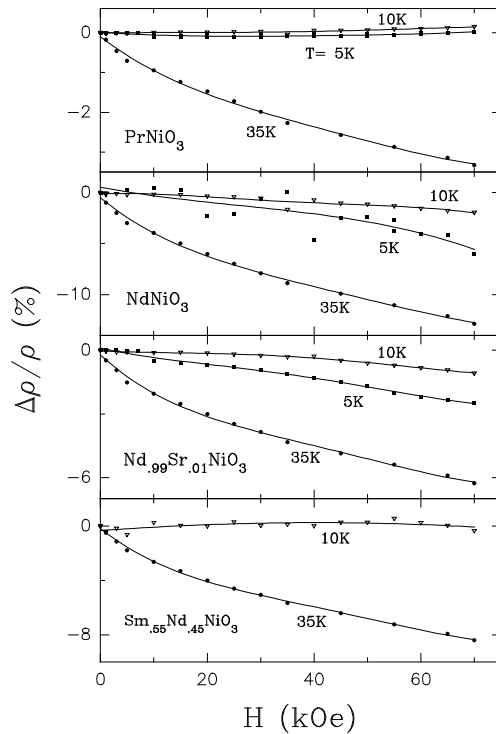
Figure 5. The magnetoresistance for PrNiO$_3$, NdNiO$_3$, Nd$_{0.99}$Sr$_{0.01}$NiO$_3$ and Sm$_{0.55}$Nd$_{0.45}$NiO$_3$ as a function of magnetic field at 5, 10 and 35 K. For the last sample, the data at 5 K are practically the same as those at 10 K.

lower, relative to the respective zero-field values, according to the temperature range considered. In other words, there is a distinct crossover of the sign of $\Delta\rho$ for most of the compounds (except Sm$_{0.55}$Nd$_{0.45}$NiO$_3$), interestingly resulting in significantly negative values for a certain low-temperature range below the MI transition temperature (see the lower parts of figures 1–3 for the qualitative variation with T), clearly below about 65 K. The resistance above T_{MI} is so small that we cannot track the sign of the magnetoresistance with confidence and, therefore, the following discussion is restricted to temperatures below T_{MI}. For a fixed value of the (charge-transfer) gap, one would naively expect the magnitude of (negative) $\Delta\rho/\rho$ to increase with decreasing temperature, in contrast to the experimental observation. $\Delta\rho/\rho$ becomes positive in the range 65–130 K, which is very prominent for PrNiO$_3$; in the same T-range the coexistence of metallic and non-metallic phases has been proposed [5, 6]; it appears that the positive contribution from the metallic phase dominates the magnetoresistance in this range; the magnitude however is large at, for instance, 100 K (about 25%) for PrNiO$_3$ compared to simple metals. Below about 65 K, the sign of $\Delta\rho/\rho$ becomes negative, indicative of weakening of this metallic-like contribution. There is in fact a sudden change in the slope of the plot of ρ versus T at 102 K (as a result of which there is a step-like feature in the logarithmic plot as well at 102 K); at the same temperature the magnitude of the positive magnetoresistance is also at its maximum and we believe that the weakening of the metallic contribution actually sets in at this temperature. The sign changes in $\Delta\rho/\rho$ and a sudden change in the slope of the plot of ρ versus T about 10–20 K below T_{MI} are noted for NdNiO$_3$ as well as for Sr-substituted samples,

though the positive $\Delta\rho/\rho$ is less prominent in terms of magnitude. For $Sm_{0.55}Nd_{0.45}NiO_3$, $\Delta\rho/\rho$ remains negative over a wider temperature range well above 10 K. The negative magnetoresistance of significant magnitude in an intermediate-T range below 65 K can in fact be seen more reliably when we make measurements as a function of H, as shown in figure 5. The magnitude of $\Delta\rho/\rho$ is rather small at 5 K and 10 K (see figure 5) and the sign is either positive (for $PrNiO_3$) or negative depending upon the sample. However, for instance, for $NdNiO_3$, at 35 K, the value is large and negative—say, about -12% in a field of 70 kOe. On the basis of such sign reversals, we propose that there are subtle effects operative at low temperatures in these Ni compounds. For instance, the magnitude of the gap itself may be a function of temperature which may also be responsible for the absence of activated behaviour with a single activation energy over the entire temperature range below T_{MI} (*vide infra*). Alternatively, the temperature dependence of complex magnetic structure at very low temperature [2, 19] coupled with possible interference from the magnetism from R ions with that of Ni and consequent temperature-dependent superzone boundary effects [22] may be responsible for these anomalies. It is believed [19] that there are equal numbers of antiferromagnetic and ferromagnetic interactions among Ni ions, which can also respond differently to magnetic field at different temperatures.
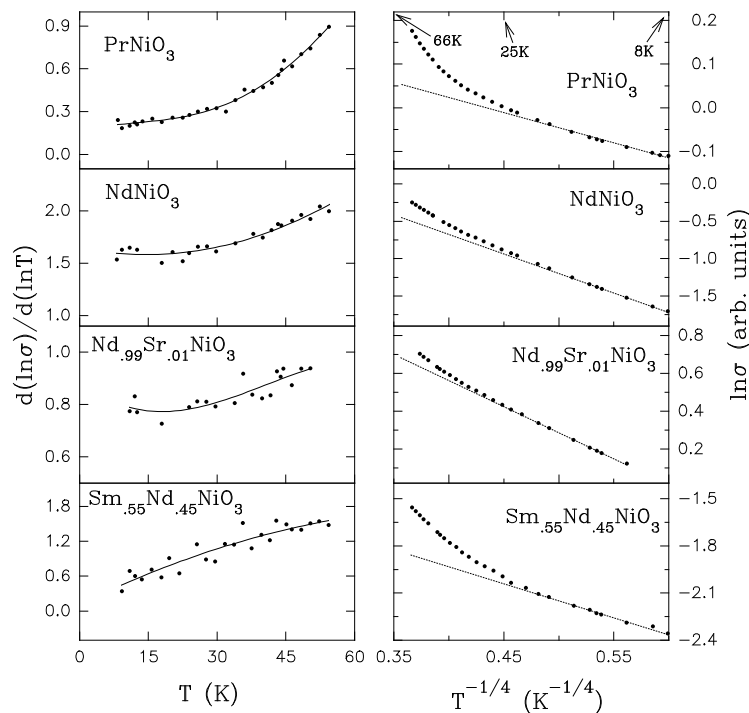
Figure 6. A plot of $d(\ln\sigma)/d(\ln T)$ showing that the compounds can be described rather as metals at low temperatures as the plots do not diverge (left); a smooth line is drawn through the points. In the panels on the right-hand side, the logarithm of conductivity is plotted versus $T^{-1/4}$ and a dotted straight line through the data points (below about 30 K) is drawn to show the possible role of variable-range hopping at very low temperatures.

From the plots of $\ln\rho$ versus $1/T$ (for the range 5 K to T_{MI}) shown in the insets of figures 1–4, it is apparent that ρ does not exhibit activated behaviour, though, in a limited temperature range below T_{MI}, the activated behaviour has been found [5, 6]. In

some oxides, a different conduction mechanism, namely variable-range hopping (VRH) (see Raychaudhuri [1], Chainani *et al* [23]) has been shown to take over at low temperatures. In systems like LaNi$_{1-x}$Fe$_x$O$_3$ (reference [23]) ($x > 0.2$), it has been noted that disorder-related VRH dominates. In order to address this issue for the present class of compounds, we plot conductivity (σ) on a logarithmic scale as a function of $T^{-0.25}$ in figure 6 (below 60 K). It is apparent that the plots are not linear for any of these compounds over the entire temperature range below T_{MI}, compelling us to conclude that a VRH mechanism, if present, is restricted to low temperatures (below about 30 K). Attempts to fit the data to the $T^{-0.5}$-dependence arising from the possible existence of a gap due to Coulomb repulsion between carriers are also found to be unsatisfactory [1]. Mobius [24] has recently suggested that a negative temperature coefficient of resistivity (TCR) does not necessarily mean that the compound under investigation is a semiconductor; $d\ln(\sigma)/d\ln(T)$ should diverge at low temperatures for the negative TCR to be attributed to semiconducting behaviour. We find that, in our compounds (figure 6), there is no such divergence as T tends to zero. This seems to suggest that these Ni compounds can be described in fact as some kind of metal at very low temperatures T_{MI}. (We have however continued to use the term 'T_{MI}' throughout this article for historical reasons.) It may be remarked that the plot of thermopower versus T for NdNiO$_3$ (reference [6]) has been shown to exhibit an upturn to smaller magnitudes (at about 100 K) well below the transition, which might signal entering a phase different from the one in the range 100 K to T_{MI}. If the low-temperature phase is truly metallic, there is an urgent need to explore the mechanism responsible for this metallicity. The double-exchange mechanism, proposed for the by now well-known manganites (GMR systems) as giving rise to the semiconductor–metal transition, cannot be invoked, as Ni does not exist in a mixed-valence state in these compounds. At this juncture, it is worthwhile to recall recent findings on Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ (reference [25]), in which non-activated behaviour for some intermediate temperature in the charge-ordered state has been noted; the authors propose that the antiferromagnetic magnetic structure contains both antiferromagnetic and ferromagnetic couplings; carrier exchange is hindered between sites with antiparallel interaction, while it is allowed for the parallel coupling; as a result the carriers remain delocalized on zigzag-like paths (parallel coupling) along a definite axis of the Wigner crystal, and strongly localized in the perpendicular in-plane direction. Possibly, similar effects may be operative in the present perovskites, as the magnetic structures are believed to show zigzag parallel-coupling paths at low temperatures.

In conclusion, the present data appear to reveal subtle differences in the physics of some of these nickelates (at least) in three temperature ranges (say, $T < 25$ K, 25 K $< T < 65$ K and 65 K $< T < T_{MI}$). It appears that, like the MI transition, the low-temperature state below T_{MI} is interesting in itself. On the basis of the present ρ-data alone, one is led to propose that the low-temperature state in some of these compounds is ultimately metallic-like, though in the intermediate-temperature range (below T_{MI}) features due to semiconducting behaviour have been noted in the literature. Further studies will be required to gain a deeper understanding of the low-temperature physics of these compounds.

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