Low-temperature electrical conductivity of $LaNi_{1-x}Fe_xO_3$

LETTER TO THE EDITOR

Low-temperature electrical conductivity of $LaNi_{1-x}Fe_xO_3$

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Abstract. We report the electrical conductivity between 2 and 300 K for $LaNi_{1-x}Fe_xO_3$ across the composition-controlled metal–insulator (m–i) transition. Using a method first suggested by Möbius, we identify the critical concentration x_c to be 0.3 for the m–i transition. The negative temperature coefficient of resistivity observed at low temperatures in the metallic phase follows a temperature dependence characteristic of disorder effects. The semiconducting compositions ($x \geqslant 0.3$) do not show a simple activation energy but exhibit variable-range hopping at high temperatures confirming that the m–i transition in this system is driven by increasing disorder effects.

The electronic properties of transition metal compounds continue to be a fascinating field of research nearly fifty years after the inadequacies of the one-electron picture were pointed out by Mott in explaining the insulating ground state of NiO [1]. Over the last ten years, intense activity in the study of metal–insulator transitions in general, and in the high-T_c cuprates in particular, has led to various novel concepts in the understanding of the electronic properties of solids (see, for example, reference [2] for a recent review on metal–insulator transitions in a variety of systems). Systematic studies on the origin of metal–insulator transitions in transition metal compounds have led to a general classification scheme based on the work of Zaanen, Sawatzky and Allen (see [3]). Specifically, the energy position of the ligand p-derived energy levels vis-à-vis the transition metal d-derived states results in determining the lowest-energy excitation for transition metal compounds. Thus, we have (i) the Mott–Hubbard insulator with the d–d metal, (ii) the charge-transfer insulator with the p–d metal, and (iii) the covalent insulator, as different possible ground states depending on the values of the charge-transfer energy (Δ), the on-site Coulomb correlation energy (U) and the p–d hopping integral (t). In this picture, a tuning of U/t or Δ/t can result in metal–insulator transitions and such situations are indeed realized in transition metal compounds [4–7].

However, there exists a class of transition metal compounds exhibiting metal–insulator transitions derived from substitutions but which cannot be described by a change in U, Δ or t. The series of compounds $LaNi_{1-x}M_xO_3$, where M = Mn, Fe and Co, exhibit composition-controlled transitions and belong to this class. In this series, $LaNiO_3$ is a correlated p–d metal, and its structural, electrical and magnetic properties have been extensively studied [8–13]. In recent work, it has been shown that electron–electron interactions play an important role in determining the transport and magnetic properties, with the charge carriers

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exhibiting an effective mass of about 10 times the free-electron value [12]. Further, the high carrier concentration, the rather low electron diffusivity and the observation of $k_F l \sim 1$ (the Ioffe–Regel limit where k_F is the Fermi wave-vector and l is the mean free path of the electron) indicated that $LaNiO_3$ is close to a metal–insulator transition. The large Pauli-like susceptibility has been independently interpreted [13] in terms of an enhanced susceptibility as in the Brinkman–Rice model of a correlated-electron system.
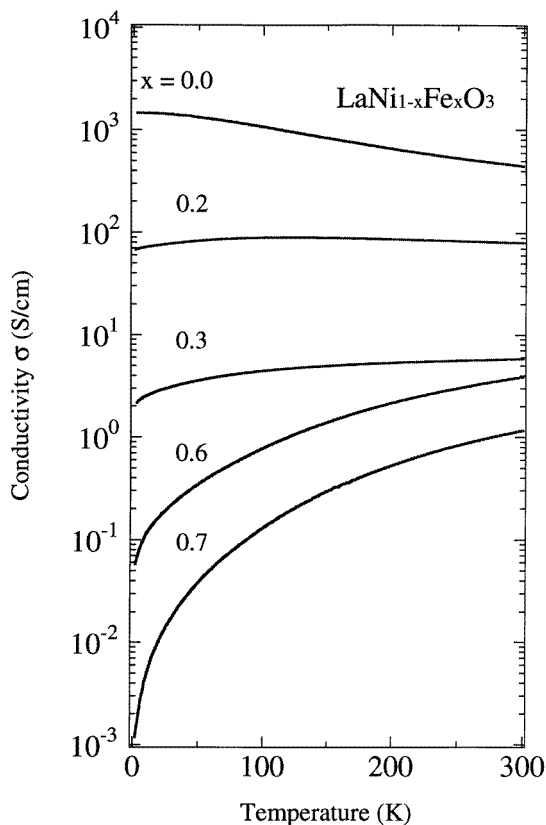

Figure 1. The electrical conductivity of $LaNi_{1-x}Fe_xO_3$ for $x = 0.0, 0.2, 0.3, 0.6$ and 0.7 obtained using the four-probe method between 2 and 300 K.

Homovalent substitution for the Ni^{3+} ion with M^{3+} in $LaNi_{1-x}M_xO_3$, where M = Mn, Fe and Co, leads to metal–insulator transitions as has been reported earlier in the literature [10]. An important observation to note in these substitutions is that the critical concentration x_c required for the m–i transition depends on the substituent ion, i.e. for M = Mn, $x_c = 0.2$, for M = Fe, $x_c = 0.3$ and for M = Co, $x_c = 0.65$ [10]. This observation rules out the possibility of the transitions being caused by percolation since in that case one would expect transitions to occur at the same values of x_c for any substituent. From a careful low-temperature study of the electrical conductivity and tunnelling of the series $LaNi_{1-x}Co_xO_3$, it was shown that the transition originates from increasing disorder effects in a system with long-range Coulomb interactions [12, 14]. Beyond x_c, a Coulomb gap is formed and a systematic change in the electrical conductivity and tunnelling has been reported across the m–i transition.

In this work, we study the electrical conductivity between 2 and 300 K in $LaNi_{1-x}Fe_xO_3$ across the metal–insulator transition as a function of x. The electrical conductivity decreases systematically for increasing values of x over the entire measured temperature range. Using a method first suggested by Möbius as the most reliable way to identify a m–i transition [15] we show that the m–i transition results in a qualitative change in the conductivity across the critical concentration, $x_c = 0.3$. The negative temperature coefficient of resistivity (TCR) observed at low temperatures in the metallic phase follows a temperature dependence that is expected from a disordered metal. The semiconducting compositions exhibit variable-range hopping (VRH) at high temperatures confirming that the m–i transition in this system too is driven by increasing disorder effects.

We now describe the experimental procedure. The $LaNi_{1-x}Fe_xO_3$ samples were prepared by the usual nitrate route starting with predried metal oxalates in the required proportions, and details of the sample preparation and characterization have been described elsewhere [16]. All of the samples form in the rhombohedral perovskite structure as was confirmed by x-ray diffraction measurements. The samples were in the form of well-sintered polycrystalline pellets obtained by heating for several days at 800 °C and had a density of more than 80% of the theoretical density calculated using the known volume of the unit cell from x-ray diffraction data. The electrical conductivity measurements were carried out using the conventional dc four-probe method in a pumped He cryostat.
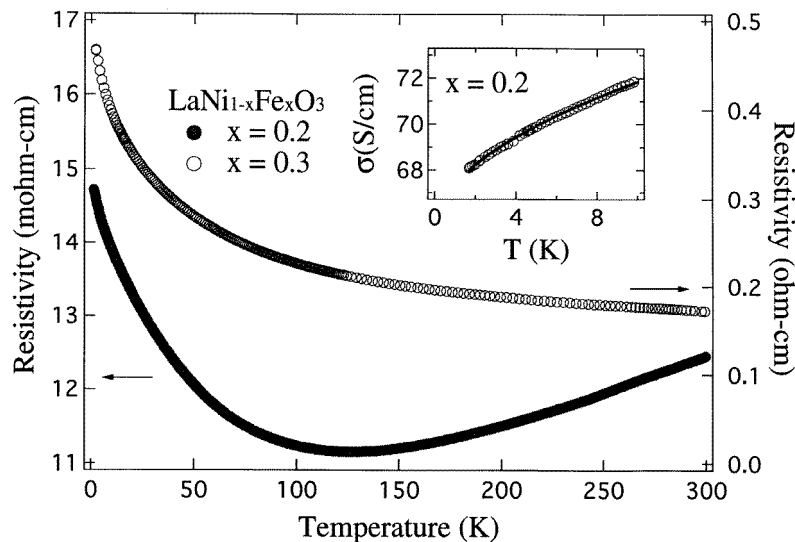

Figure 2. The electrical resistivity of $LaNi_{1-x}Fe_xO_3$ for $x = 0.2$ and $x = 0.3$ showing a gradual change from a positive to a negative TCR for the $x = 0.2$ sample while the $x = 0.3$ sample has a negative TCR at all temperatures. The inset shows the fit to the equation $\sigma(T) = \sigma(0) + \beta T^{0.5}$, indicative of a disordered metal.

We now give the results and discuss them. In figure 1 we plot the electrical conductivity between 2 and 300 K for $LaNi_{1-x}Fe_xO_3$ ($x = 0.0, 0.2, 0.3, 0.6, 0.7$). The conductivity of metallic $LaNiO_3$ is very similar to that reported in the literature [9, 10, 12, 13]. As a function of composition, a systematic decrease in the absolute conductivity is observed for increasing Fe substitution over the entire range of measurements. An important point to note is that even for the lowest level of substitution studied here ($x = 0.2$), a change in

the TCR is obtained at low temperatures. In order to see this more clearly, we plot the resistivity as a function of temperature for $x = 0.2$ and 0.3 in figure 2 on an expanded scale. While the $x = 0.3$ data show a negative TCR over the measured temperature range like that of a semiconductor, the $x = 0.2$ composition shows a positive TCR at temperatures above 125 K which changes gradually to a negative TCR below 125 K. This could be interpreted as a gradual temperature-dependent metal–insulator transition. While the data at low T do not follow an activated behaviour, a behaviour at variance with activated behaviour is not enough to prove metallicity. However, as we shall show below, the $x = 0.2$ compound is definitely metallic and only for $x \geqslant 0.3$ do we obtain a semiconducting ground state.
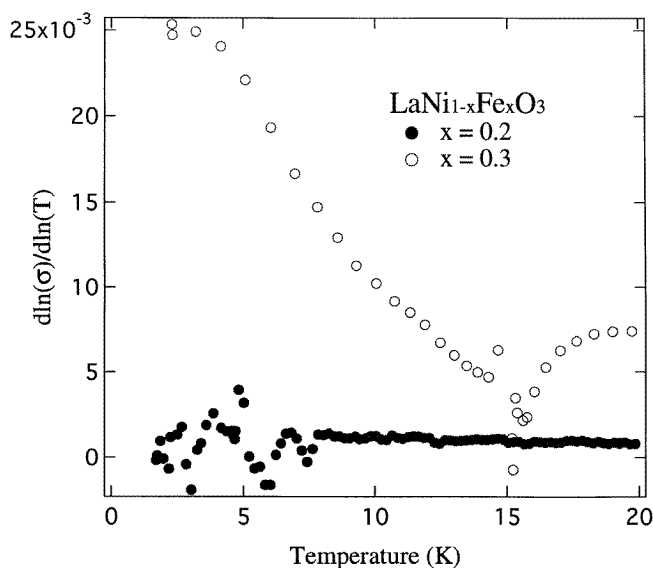

Figure 3. The plot of $d(\ln \sigma)/d(\ln T)$ for the $x = 0.2$ and 0.3 compositions showing that the $x = 0.2$ compound is definitely metallic for $T \to 0$.

Möbius has recently suggested a reliable method for investigating the metallic or semiconducting behaviour by evaluating the derivative $d(\ln \sigma)/d(\ln T)$ [15]. If σ tends to a finite non-zero value as $T \to 0$, i.e. for a metallic system, $d(\ln \sigma)/d(\ln T)$ should tend to 0 as $T \to 0$. In contrast, if σ follows an exponential dependence (e.g. VRH), $d(\ln \sigma)/d(\ln T) \to$ infinity, as $T \to 0$. However, it has been pointed out that on the insulating side, the derivative $d(\ln \sigma)/d(\ln T)$ need not always diverge. For example, there exists a theoretical prediction [17] for cascade processes in an insulator which can result in $\sigma(T)$ being proportional to T^p with $p \gg 1$, resulting in the derivative $d(\ln \sigma)/d(\ln T) \to p$ as $T \to 0$. In figure 3 we have plotted $d(\ln \sigma)/d(\ln T)$ for $x = 0.2$ and 0.3. A qualitative difference is observed between the two cases. Note that the plot of $d(\ln \sigma)/d(\ln T)$ versus T has a lot of scatter at low T associated with intrinsic difficulties of calculating the derivative of a discrete set of data with statistical errors without taking recourse to any prior smoothing of the experimental results. However, we find a clear trend for the $x = 0.2$ case, suggestive of an approach to 0 as $T \to 0$. In contrast, $d(\ln \sigma)/d(\ln T)$ for $x = 0.3$ is clearly an increasing function tending to a finite value as $T \to 0$. This establishes that the $x = 0.2$ composition is metallic at the lowest temperatures while the $x = 0.3$ compound is semiconducting. While the $x = 0.2$ composition is metallic, the negative TCR obtained at low temperatures has been observed in many metallic systems and its origin was addressed earlier. For example, in $LaNi_{1-x}Co_xO_3$, the negative TCR at low temperatures has been identified as originating from increasing disorder effects upon substitution in a metallic

system with long-range Coulomb interactions. The disorder increases as a function of x and eventually results in the formation of a Coulomb gap at the critical concentration [12, 14]. Similar behaviour has also been observed in Si:P, granular Al and Nb:Si systems where disorder leads to a negative TCR at low temperatures resulting in a $\sigma(T) \propto T^{0.5}$ when the systems are well into the metallic phase [18]. In the present case too, as is shown in the inset to figure 2, the low-temperature conductivity ($T < 10$ K) fits an equation of the form $\sigma(T) = \sigma(0) + \beta T^{0.5}$ for $x = 0.2$, indicative of the role of disorder arising from the random substitution for Ni ions with Fe ions.
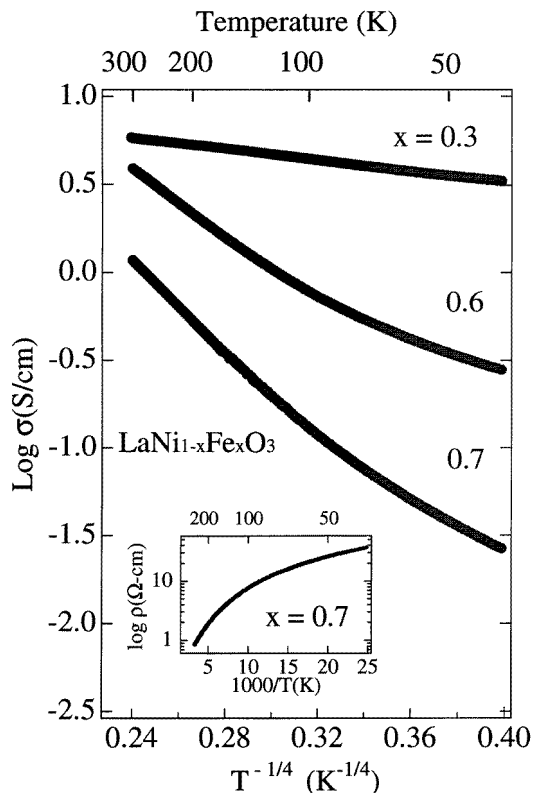

Figure 4. The high-temperature data for $LaNi_{1-x}Fe_xO_3$ plotted as $\log(\sigma)$ versus $T^{-1/4}$ indicating VRH for the semiconducting compositions with $x \geqslant 0.3$. The inset shows a plot of $\log(\rho)$ versus T^{-1} for $x = 0.7$, indicating that even for the most semiconducting composition we do not obtain any range of temperatures from which we can estimate a simple activation energy.

For the semiconducting case, it is known that if the gap is induced by disorder in the presence of long-range Coulomb interactions, the plot of $\log(\sigma)$ as a function of $T^{-1/2}$ should be linear and the gap is called a soft Coulomb gap or the Efros–Shklovskii gap [19]. We have made a careful check of the temperature dependence of the conductivity at low temperatures to investigate this behaviour and do not find the same. It appears that extensive measurements at much lower temperatures will be required to understand the true ground-state nature of these compounds. The conductivity of the semiconducting compositions does not follow a simple activation energy as in a typical semiconductor. In the inset to figure 4, we show $\log(\rho)$ versus $1/T$ for the most semiconducting compound

($x = 0.7$) and we find that there is no range of temperatures from which we can estimate a simple activation energy. Similar results are obtained for $x = 0.3$ and 0.6. However, we find evidence for Mott's variable-range hopping [20] by plotting $\log(\sigma)$ as a function of $T^{-1/4}$ for the semiconducting compositions ($x > 0.3$), as is shown in figure 4. While the low-temperature data show some deviation from linearity, the high-temperature data are fairly linear from room temperature till about 50 K for the $x = 0.3$ composition and till about 100 K for the $x = 0.6$ and 0.7 compositions, confirming that three-dimensional disorder effects dominate the conductivity of the semiconducting phase.

In conclusion, the low-temperature electrical conductivity in $LaNi_{1-x}Fe_xO_3$ shows a clear qualitative change across the m–i transition. The negative TCR at low T in the metallic composition is due to disorder effects arising from the random substitution for Ni with Fe ions. The high-temperature conductivity follows VRH and confirms the role of three-dimensional disorder in causing the m–i transition in these homovalent substituted systems

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