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Composition-Controlled Metal–Insulator Transitions and Minimum Metallic Conductivity in the Oxide Systems $LaNi_{1-x}M_xO_3$ (M = Cr, Mn, Fe, or Co)*

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The composition-controlled metal–insulator transition in the perovskite systems $LaNi_{1-x}M_xO_3$ (M = Cr, Mn, Fe, and Co) has been investigated by transport measurements over the temperature range 12–300 K. These systems, which have critical electron densities (n_c) in the range (1–2) × 10^{20} electrons cm^{-3}, exhibit sharp metal–insulator transitions at the base temperature. The corresponding minimum metallic conductivity (σ_{min}), separating the localized and itinerant electronic regimes, is of the order of 10^2 ohm^{-1} cm^{-1}. Particular attention is paid to the idea of σ_{min} scaling with n_c, and our present results are compared with earlier studies of the metal–insulator transition in low (e.g., Ge : Sb) and high (e.g., metal–ammonia, supercritical Hg) electron-density systems. A link is established between the transport and magnetic properties of the title systems at the metal–insulator transition.

Introduction

While $LaNiO_3$ is a metal, the perovskite oxides of other transition metals ($LaMO_3$, M = Cr, Mn, Fe, and Co) are generally insulators (*1, 2*). It is of interest to investigate whether the $LaNi_{1-x}MO_3$ systems exhibit Metal–Insulator (M–I) transitions and if so, what the features of such transitions would be. In this communication we report a study of the electron-transport properties of several $LaNi_{1-x}M_xO_3$ systems over wide ranges of both composition and temperature. Besides showing composition-controlled M–I transitions, the electron transport properties of the systems also have a bearing on the question of the minimum metallic conductivity, σ_{min}, in high electron-density materials (*3, 4*). In particular, Mott (*5*) has suggested that σ_{min} scales directly with n_c, the critical electron density at the M–I transition. The title system is particularly attractive in that the critical densities of interest lie in the high electron-density regime, viz. 10^{20} electrons cm^{-3}.

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This allows a comparison of extensive experimental data with Mott's idea of the minimum metallic conductivity over several decades of n_c.

Experimental

Various members of the $LaNi_{1-x}M_xO_3$ (M = Cr, Fe, and Co) systems were prepared by the thermal decomposition (1120–1370 K) of basic carbonates coprecipitated from nitrate solutions, and the products were heated in oxygen at 1000 K for several hours. The corresponding Mn perovskites were prepared by the thermal decomposition of coprecipitated hydroxides. The method of preparation employed (coprecipitation of precursor carbonates and hydroxides) ensured the homogeneity and stoichiometry of the oxides, the latter being established by analysis. Accordingly, the active oxygen content of the oxides, determined by iodimetry, corresponded to the stated stoichiometry. Electrical resistivities (ρ) were measured on pressed pellets of near theoretical density by employing the four-probe technique, and the measurements were carried out over the tempera-

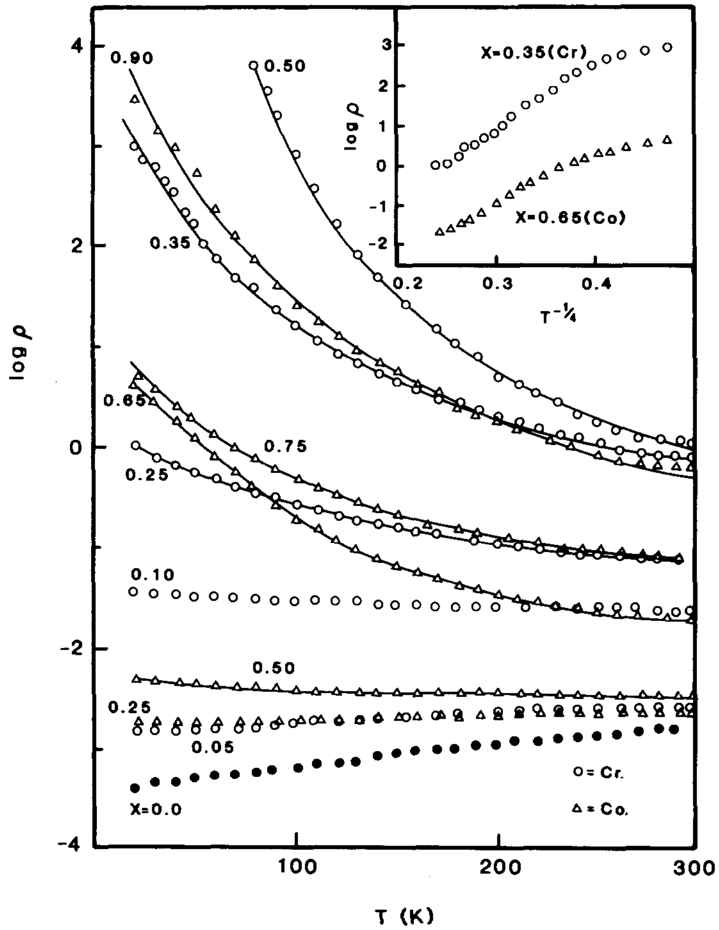

FIG. 1. A series of plots of log ρ (resistivity) versus temperature for the system $LaNi_{1-x}M_xO_3$ (M = Cr and Co). The inset shows plots of log ρ versus T. Full lines show fits to Eq. (3).

ture range 12–300 K. All the oxides possess the rhombohedral structure of $LaNiO_3$ at low values of x. The Cr and Fe systems change to an orthorhombic structure when $x > 0.35$ and $x > 0.50$, respectively. The Mn system is rhombohedral up to $x = 0.2$, but the Co system remains rhombohedral over the entire composition range.

Results and Discussion

Electrical resistivity data of the different oxides are shown in Figs. 1 and 2. We clearly see that $LaNiO_3$ ($x = 0$) shows characteristic metallic behavior in its electrical resistivity. With increase in x, the resistivity increases progressively, the precise nature of the variation depending on M (Fig. 3). Thus, when M = Cr or Mn, $\log \rho$ varies linearly with x, whereas for x = Fe or Co, the slope of the $\log \rho$ versus x plot increases when $x = 0.70$. For each system there is a characteristic critical composition (x_c) at which ($d\rho/dT$) changes sign or the activation energy for conduction becomes zero. Using the former criterion, we take x_c to be

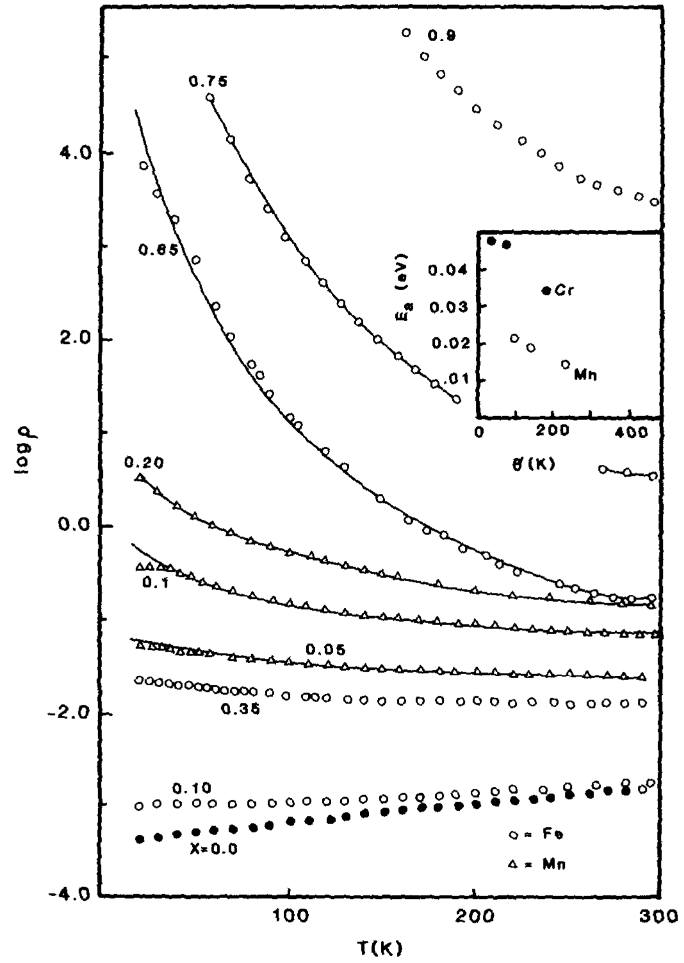

FIG. 2. A series of plots of $\log \rho$ (resistivity) versus temperature for the system $LaNi_{1-x}M_xO_3$ (M = Fe and Mn). The inset shows the plot of E_a versus θ, obtained from Eq. (3), see text.

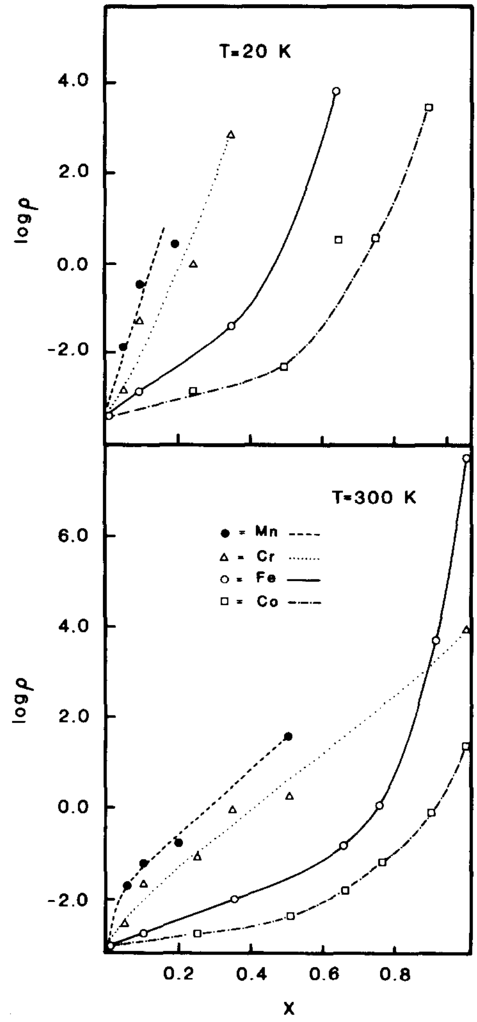

FIG. 3. A series of plots of log ρ (resistivity) versus x for $LaNi_{1-x}M_xO_3$ at 20 and 300 K.

the concentration limit at which there is a transition from metallic to nonmetallic status (*6*). The conductivity at x_c is then taken as the value of the minimum metallic conductivity, σ_{min}, separating localized and itinerant *d*-electrons in these systems (*5*). The value of σ_{min} (which is independent of M) is typically in the range $1\text{–}2 \times 10^2$ ohm^{-1} cm^{-1}. This value of σ_{min} is close to that found in $La_{1-x}Sr_xVO_3$ (*7, 8*). The values of x_c are in the range $0.03 < x_c < 0.05$ for Mn, $0.05 < x_c < 0.10$ for Cr, and $0.25 < x_c < 0.35$ for Fe and Co. It is noteworthy that at x_c, the lattice parameters are close to those of metallic $LaNiO_3$.

The existence of a minimum metallic conductivity has been questioned by several workers (*9–11*) but Mott (*5*) has pointed out the concept of σ_{min} remains valid at least at high temperatures.

Our results on the $LaNi_{1-x}M_xO_3$ system support the idea of a minimum metallic conductivity in high electron-density materials. According to Mott (*4*), the conductivity would be expected to jump discontinuously from $\sigma_{\min}$ to zero at a critical value of (V_0/Δ), where V_0 is a measure of the extent of disorder, and Δ is the one-electron bandwidth. The value of $\sigma_{\min}$ is given by (*5*)

$$\sigma_{\min} = \frac{Ce^2}{\hbar d_c} \tag{1}$$

where C is a constant and d_c is the average interelectronic spacing at the M–I transition. In addition,

$$d_c \sim n_c^{-1/3},$$

where n_c is the critical electron density, giving

$$\sigma_{\min} \simeq C\left(\frac{e^2}{\hbar}\right) n_c^{1/3} \tag{2}$$

Phosphorus-doped silicon shows an abrupt M–I transition with $\sigma_{\min} \sim 20\ \mathrm{ohm^{-1}\ cm^{-1}}$ at a critical electron density of ca. 3×10^{18} electrons $\mathrm{cm^{-3}}$, corresponding to $d_c \sim 64$ Å (*12, 13*).

Equation (2) suggests an interrelation of $\sigma_{\min}$ with the critical carrier concentration (*5, 13*). If we assume that n_c varies inversely with unit cell volume, we may obtain plots of σ against n, the electron density, for the $\mathrm{LaNi}_{1-x}M_x\mathrm{O}_3$ system.

These plots are included in Fig. 4, which shows the corresponding σ versus donor (electron) concentration behavior for a wide range of materials exhibiting a M–I transition (*14*). These range from the prototype low electron-density materials (e.g., Ge : Sb; Si : P, etc.), through to metal–ammonia solutions and supercritical (expanded) mercury at high temperatures. The latter systems are characteristic of the extreme high electron-density regime in *liquid* systems traversing the M–I transition. Also included are the conductivity data for the sodium tungsten bronzes, $\mathrm{Na}_x\mathrm{WO}_3$ (*15*). For the solid-state systems we indicate n_c and $\sigma_{\min}$ at the M–I transition. Clearly, there are intrinsic, microscopic features within each system that need to be addressed in any detailed examination of the M–I transition of individual systems; for example, the precise nature of the electronic states at concentrations far below n_c, and the effective interstate interactions in the intermediate regime (*16, 17*). Nevertheless, in terms of global, or macroscopic considerations, these *d*-electron metal oxide systems clearly correlate with other high electron-density materials such as metal–ammonia solutions, or the sodium tungsten bronzes. Note also in Fig. 4 that lower temperatures generally produce sharp M–I transitions, but this, by no means, can be considered as a universal requirement. This aspect is vividly illustrated by the data for supercritical, elemental Hg at 1823 K (*18*) (Fig. 4), which show a precipitous drop in σ for small changes in electron density. Moreover, what is clear from Fig. 4 is that there does appear to exist a fundamental interrelation between $\sigma_{\min}$, representing the experimental conductivity at which metallic conduction ($d\sigma/dT \leq 0$) transforms to thermally activated conduction ($d\sigma/dT > 0$), and n_c, the characteristic critical density at the M–I transition (*5, 6*).

The low-temperature resistivity data of the insulating (or semiconducting) compositions of the $\mathrm{LaNi}_{1-x}M_x\mathrm{O}_3$ systems obey the $T^{-1/4}$ law (*4, 5*) over a limited range of temperatures (Fig. 1). The data, on the other hand, can also be fitted to the empirical equation

$$\rho = \rho_0 \exp\{E_a/k(T + \theta)\} \tag{3}$$

over the temperature range 12–300 K; here E_a is an activation energy, T is the temperature and θ is a derived, characteristic temperature. Theoretical fits of the data to Eq. (3) are indicated by solid lines in Figs. 1 and 2. As one would expect, the value of the high-temperature limit of the electrical resistivity, ρ_0, is close to the extrapolated values of ρ at $T \to \infty$, derived from the plots of log ρ versus $1/T$. The value of σ_0 $(= 1/\rho_0)$

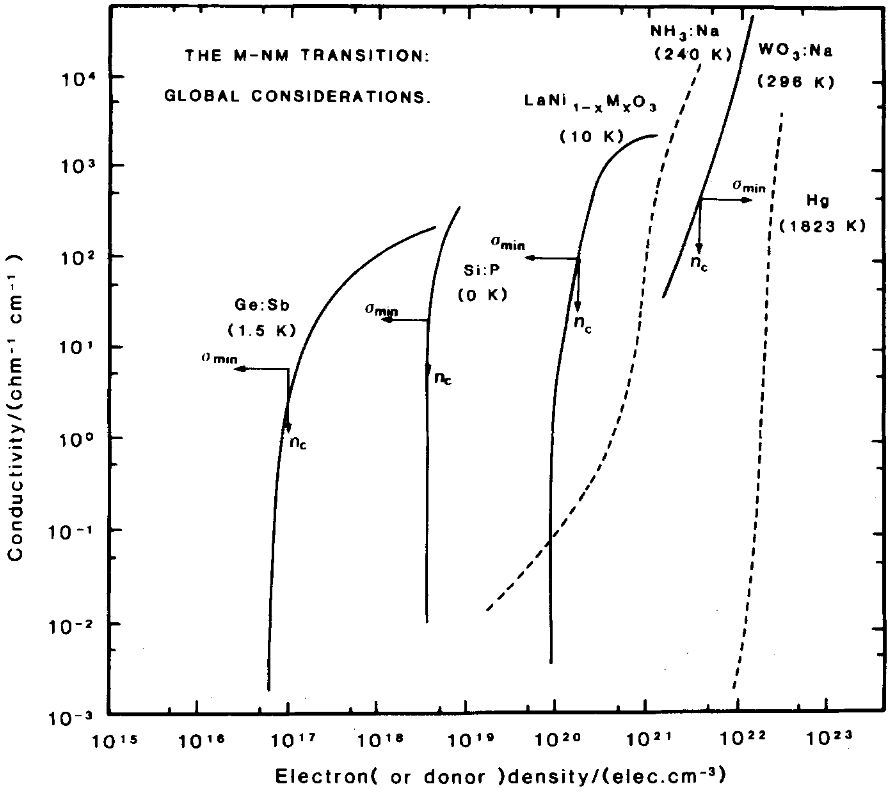

FIG. 4. The metal–insulator transition in liquid, and solid-state materials, showing the concentration dependence of the electrical conductivity for a variety of systems. The experimental data are from a variety of sources, as outlined in Ref. (*14*). The appropriate observation temperatures are given in parenthesis. The Si : P data (*12*) extend down to temperatures 1mK, and the plot shows the zero-temperature conductivity vs donor (P) density. Note the very rapid drop in σ for Si : P at 0 K, the title system at 12 K, and expanded mercury at 1823 K. For the solid state systems, both σ_{min} and n_c are indicated.

tends to σ_{min} as $E_a \to 0$. Although we do not have a clear clue as to the precise meaning of θ in the above equation, it is noteworthy that θ is typically around 550 K when E_a approaches zero (see insert of Fig. 2). This limiting value of θ is close to the Fermi temperature of $\mathrm{LaNiO_3}$ calculated from the value of the temperature-independent magnetic susceptibility (~700 × 10^{-6} emu (*19*)) assuming it to be Pauli paramagnetic. This highlights the common origin of the magnetism and electron-transport properties in these *d*-electron materials. This observation also finds support from the following considerations.

The paramagnetic Curie temperature, θ', is given by the relation

$$\theta' = \frac{2zJS(S+1)}{3k}, \tag{4}$$

and in the tight-binding approximation this reduces to

$$\theta'_{\mathrm{min}} = \frac{W_{\mathrm{min}}S(S+1)}{3k}, \tag{5}$$

where W_{min} is the electron bandwidth corresponding to σ_{min}. We find that θ'_{min} calculated from Eq. (5) is close to 600 K for an $S = \frac{1}{2}$ system taking $W_{\mathrm{min}} = 0.2$ eV. This value of θ'_{min} is not very different from the value of

θ obtained from fitting the experimental electrical conductivity data to Eq. (3). We should point out that $W_{\min}$ would be close to $(h^2/\pi^2 2m^* a_0^2)$, where m^* is the electron effective mass, and a_0 is a characteristic Bohr radius for the localized electron center.

Since

$$W_{\min} \simeq (\hbar/\tau_{\min}), \tag{6}$$

where $\tau_{\min}$ is a characteristic (resistivity) relaxation time, we obtain

$$\sigma_{\min} = \frac{2e^2}{\pi^2 \hbar a_0}. \tag{7}$$

We thus see that this derived $\sigma_{\min}$ is close to that expected from the Ioffe–Regel criterion (*5*, *13*). Since the upper limit of τ for band-like states is $\sim 10^{-14}$ sec, $W_{\min}$ would have a lower limit of 0.1 eV. If indeed we take $W_{\min} \sim 0.2$ eV, then $m^* \sim 10m_0$, where m_0 is the free-electron rest mass. This value of m^* is also similar to that obtained from the magnetic susceptibility data when we use the Brinkman–Rice formula (*19*). We notice that Eq. (3) requires ρ to be finite at $T = 0$ K; this may not be entirely correct since the present data only extend down to 12 K. In particular, the low-temperature conductivity may be susceptible to impurity contributions. Furthermore, magnetic and other effects would also complicate the situation. In the case of some members of the manganese-doped system, $LaNi_{1-x}M_xO_3$, we notice a tendency for the resistivity to flatten off at low temperatures due to magnetic interactions of the *d*-electrons. Thus, the $x = 0.05$ sample seems to form superparamagnetic clusters, while the $x = 0.10$ system shows evidence for the formation of a ferrimagnetic spin-glass (*19*).

Acknowledgments

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