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Electronic and Magnetic Properties of $LaNi_{1-x}Co_xO_3$, $LaCo_{1-x}Fe_xO_3$ and $LaNi_{1-x}Fe_xO_3$

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$LaNi_{1-x}Co_xO_3$ shows itinerant *d*-electron behavior similar to $LaNiO_3$ up to $x = 0.5$. In the range $0.5 < x < 1.0$, the cobalt spin state equilibrium is markedly affected; the localized-itinerant electron transition of $LaCoO_3$ is not seen when $x < 0.95$. In $LaCo_{1-x}Fe_xO_3$, itinerancy of *d*-electrons decreases with increase in x and the compositions with $x > 0.5$ are similar to $LaFeO_3$. If $x > 0.1$, the localized-itinerant electron transition is not seen and the cobalt spin state equilibrium is considerably altered. In $LaNi_{1-x}Fe_xO_3$, itinerancy decreases with increase in x. These observations can be satisfactorily explained in terms of Goodenough's energy band schemes.

1. Introduction

Rare earth perovskites $Ln^{3+}B^{3+}O_3$ (Ln = rare earth ion and B = transition metal ion) show localized or itinerant behavior of the *d*-electrons, depending on the spin configuration of the transition metal ion (*1–3*), the spin configuration itself being determined by the relative magnitudes of the crystal field splitting, Δ_{cf} and the exchange energy Δ_{ex}. Generally, low spins ions are associated with itinerant *d*-electrons while high spin ions are associated with localized electrons. Thus, rare earth manganites and ferrites ($LnBO_3$ with B = Mn or Fe) with high-spin transition metal ions are semiconductors with localized *d*-electrons (*4*). In rhombohedral $LaNiO_3$, Ni^{3+} has the low-spin electronic configuration, $t_{2g}^6e_g^1(S = \frac{1}{2})$. Such a low-spin configuration is expected to give rise to itinerant properties of the *d*-electrons. Accordingly, $LaNiO_3$ is metallic and Pauli-paramagnetic (*3, 5*). $LaCoO_3$ and a few other rare earth cobaltites, on the other hand, exhibit localized or itinerant *d*-electron behavior, depending on the temperature (*6–8*). $LaCoO_3$ exhibits a first-order localized-itinerant electron transition around 1210°K above which temperature, the e_g electrons form a σ^* band. Trivalent cobalt ions in $LaCoO_3$ are almost entirely in the low-spin $Co^{III}(t_{2g}^6e_g^0)$ state at low temperatures and transform to the high-spin Co^{3+} ($t_{2g}^4e_g^2$) state with increase in temperature (*6, 7*). At high temperatures, there is electron transfer from Co^{3+} to Co^{III} producing di and tetravalent cobalt states (*7*). These effects are seen nicely in terms of the magnetic susceptibility χ, and electrical resistivity ρ of $LaCoO_3$. The inverse susceptibility versus temperature curve of $LaCoO_3$ shows a plateau in the 400–650°K range due to the variation in the population of the low versus high-spin cobalt ions (establishment of short-range order) followed by a symmetry change from $R\bar{3}c$ to $R\bar{3}$ above 650°K; χT, however increases with temperature over the entire range indicating progressive formation of the paramagnetic species. Resistivity data of $LaCoO_3$ in the low-temperature region show that the resistivity is fairly high while the activation energy is low; with increase in temperature, resistivity falls markedly, accompanying the electron-transfer process and the ordering of cobalt ions referred to earlier. At temperatures above the localized-

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itinerant ($e_g \rightarrow \sigma^*$) electron transition (1210°K), $LaCoO_3$ becomes metallic. In the present study, we have examined the electrical and magnetic properties of $LaNi_{1-x}Co_xO_3$ and $LaCo_{1-x}Fe_xO_3$ over wide composition ranges to examine the interplay of localized versus collective behavior of *d*-electrons. The manner in which the electronic properties of these mixed cobaltites would be influenced by the presence of low-spin $Ni^{3+}(t_{2g}^6e_g^1)$ and high-spin $Fe^{3+}(t_{2g}^3e_g^2)$ ions is of interest.

2. Experimental

All the $LaNi_{1-x}Co_xO_3$ samples were prepared by the decomposition of the oxalate mixtures. Stoichiometric proportions of the oxalates of La, Co, and Ni (all of better than 99.9% purity) were thoroughly mixed under cyclohexane. These mixtures were then decomposed at 700°C slowly in an oxygen atmosphere. The resulting mixtures were ground again, pelletized, and heated at 900°C in pure oxygen for 48 hr. This process of grinding, pelletizing, and heating was continued till the proper compounds were obtained. $LaNi_{1-x}Co_xO_3$ compounds are reported to be stable throughout the compositions range; the crystal structures of all the compositions are rhombohedral (*9*). The $LaFe_xCo_{1-x}$ O_3 compounds were prepared by the method of Wold and Croft (*10*) starting from La and Co oxalates and Fe_2O_3, all of better than 99.9% purity.

Electrical resistivities of $LaNi_xCo_{1-x}O_3$ compounds were measured using pressed pellets sintered at 1100°K. The resistivities were measured in the range 300–1000°K with the four-probe technique (*11*). Seebeck coefficients were measured using an apparatus fabricated locally (*4*, *11*). Magnetic susceptibilities of the samples were measured by Gouy's technique over the temperature range 100–800°K.

3. Results and Discussion

$LaNi_{1-x}Co_xO_3$

Resistivity data of $LaNi_{1-x}Co_xO_3$ are shown in Fig. 1. The data clearly show that compositions up to $x = 0.50$ are metallic, just like $LaNiO_3$ itself. It appears that substitution of Co for Ni in $LaNiO_3$ gives rise to predominantly low-spin Co^{III} ions (we will examine this aspect again in connection with susceptibility data). Such low-spin ions would be associated with itinerant *d*-electrons, as evidenced by the metallic resistivity of compositions up to $x = 0.5$. The magnitude of the resistivity itself increases with x in the range 0.0–0.5, as would be expected by the introduction of scattering centres that reduce the electron mobility. When $x > 0.5$, the temperature coefficient of the resistivity of $LaNi_{1-x}Co_xO_3$ is that of a semiconductor, becoming metallic only at very high temperatures. The resistivity behavior of compositions with $x = 0.99$ and $x = 0.90$ are quite similar to that of $LaCoO_3$ (Fig. 1). The activation energies for conduction of these cobalt-rich compositions are compared with those of $LaCoO_3$ in Table I.

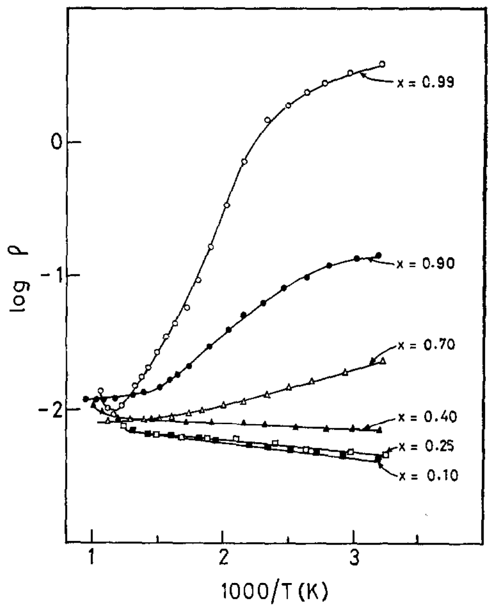

FIG. 1. Temperature variation of resistivity of $LaNi_{1-x}Co_xO_3$.

The 200–400°K region in $LaCoO_3$ occurs immediately after the high-spin Co^{3+} population reaches a maximum and electron transfer is initiated (*6–8*). In the region 400–650°K, there is short-range ordering of cobalt ions

TABLE I

ACTIVATION ENERGIES FOR CONDUCTION (IN eV) OF $LaNi_{1-x}Co_xO_3$[a]

x	200–400°K	400–650°K	650–900°K
0.70	0.06	0.06	0.0
0.90	0.06	0.18	0.05
0.99	0.09	0.50	0.19
1.00	0.20	0.54	0.19

[a] When $x = 0.5$, the system is metallic.

and resistivity decreases very sharply; electron transfer is most prominent in this region. Beyond the 400–650°K region, there is a change in symmetry from $R\bar{3}c$ to $R\bar{3}$. In the region 650–900°K, the resistivity decreases very gradually and charge-carrier saturation is attained. An examination of the activation energies in Table I indicates that for large x and low T, the Ni^{III} ions act as electron donors to the Co^{III}-ion σ^* band. At higher temperatures, creation of high-spin Co^{3+} ion seems to be suppressed by increasing Ni concentration (decreasing x). Because the donor states are tightly bound d-orbitals, the concentration of Ni atoms required for impurity-band formation is much higher than that found in conventional broad-band semiconductors. Seebeck coefficients α show that the large positive value (due to hole conduction) in $LaCoO_3$ (*7*) decreases with incorporation of Ni^{3+}, becoming very low and nearly constant if $0.5 < x < 0.7$: α becomes negative if $x < 0.5$ just as in $LaNiO_3$ (*5*).

In Fig. 2, χT values are plotted against temperature. The product χT should increase linearly with T for temperature-independent Pauli-paramagnetism (*7*, *8*, *12*). Noninteracting localized atomic moments would have a paramagnetic susceptibility described by the Curie law and the product χT would be the Curie constant. However, if the number of localized moments varies with temperature, χT does not remain constant with increasing temperature, but obeys relation (1) where n and m represent the fraction of the magnetic atom species that does or does not carry a magnetic moment (*7*, *8*, *12*):

$$\chi T = (N^2 \mu^2/3R) \qquad (n/n+m). \qquad (1)$$

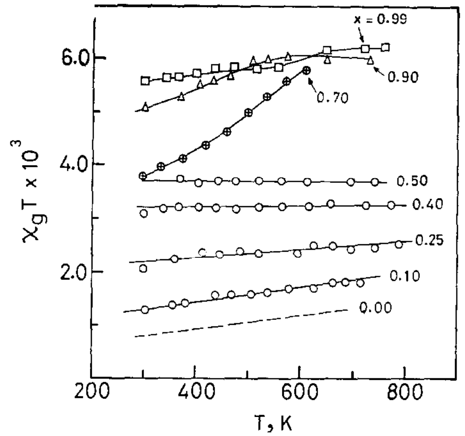

FIG. 2. Temperature variation of χT of $LaNi_{1-x}Co_xO_3$.

In the present situation, transformation is possible between diamagnetic Co^{III} and high-spin Co^{3+} ions having a $\mu = 4\mu_B$ and the variation of χT with temperature would provide direct information on the spin state transformation of cobalt in $LaNi_{1-x}Co_xO_3$. Consistent with the variation of χ with Ni concentration, we have assumed here that Ni^{3+} is always present in the low-spin $t_{2g}^6 e_g^1$ configuration.

From Fig. 2, the χT–T curve of $LaNiO_3$ is linear with a positive slope. This behavior conforms to the report (*13*) that $LaNiO_3$ has an exchange-enhanced Pauli paramagnetism that may be described by a large temperature-independent term plus a Curie-Law term having a small Curie constant. With increasing x, the decrease in slope of the χT–T curve is consistent with increased exchange enhancement among the Ni^{III}:σ^{*1} electrons due to band narrowing, the Curie-law term increasing as the temperature-independent term decreases. However, on passing from $x = 0.5$ to $x = 0.7$, there is clear evidence for the creation of high-spin Co^{3+} ions at higher temperatures. For $x = 0.7$, there ions are created above 300°K. For larger x, they are created at lower temperatures. Thus, the magnetic susceptibility data provide direct evidence for a raising of the energy difference between high-spin Co^{3+} and low-spin Co^{III} states with increasing nickel concentration, which is consistent with our inference from the resistivity data from Table I that the number of high-spin Co^{3+} ions created at a given temperature decreases with increasing nickel concentration.

The conclusions from this study are as follows. Previous qualitative energy-band schemes for $LaNiO_3$ and $LaCoO_3$ are capable of accounting for our observations. These schemes give *d*-like bands consisting of filled π^* bands (corresponding to a localized electron configuration t_{2g}^6) separated by a discrete energy gap from σ^* bands that are empty at low temperatures and contain one electron per Ni^{III} atom in $LaNi_{1-x}Co_xO_3$. Because the $Ni^{III}:3d^7$ state is more stable than a $Co^{III}:3d^6$ state, the mobile electrons occupy σ^* band states that are primarily Ni^{III} in character, these band states being transformed with increasing cobalt concentration to narrower impurity-band states and, finally, to localized donor states. A high-spin $Co^{3+}:t_{2g}^4e_g^2$ configuration is separated from the low spin Co^{III} configuration by only 0.05 eV in $LaCoO_3$, so that higher temperatures create Co^{3+} ions carrying a localized atomic moment. The high multiplicity of the high-spin state permits a large fraction of the cobalt ions to become high-spin. High temperature atomic ordering and associated charge transfer from high-spin Co^{3+} to low-spin Co^{III} ions causes a marked decrease in resistivity with increasing temperature, a first-order localized-to-itinerant $(e_g \rightarrow \sigma^*)$ electron transition occurring around 1200°K. Substitution of Ni^{III} for Co^{III} ions appears to increase the energy separation between high-spin Co^{3+} and low-spin Co^{III} states, so that high-spin Co^{3+} ions are created only at higher temperatures, if at all, as the nickel concentration increases. In $LaNi_{1-x}Co_xO_3$, significant numbers of high-spin Co^{3+} ions are created only above 300°K for $x = 0.7$; they do not appear below 800°K for $x \leqslant 0.05$. The mobility of the itinerant σ^* electrons in the narrow Ni^{III}-σ^* bands decreases with increasing cobalt concentration and for $x > 0.7$ the Co^{III}-to-Co^{3+} transitions appear to

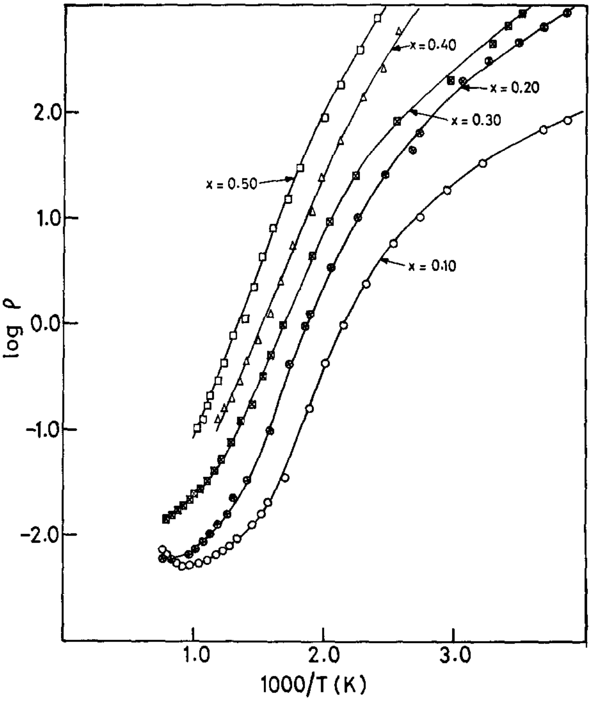

FIG. 3. Temperature variation of resistivity of $LaCo_{1-x}Fe_xO_3$.

dominate the resistivity at high temperatures. The localized-itinerant ($e_g \rightarrow \sigma^*$) electron transitions in $LaNi_{1-x}Co_xO_3$ are seen only when $x \geqslant 0.95$.

$LaFe_xCo_{1-x}O_3$

Resistivity data for $LaCo_{1-x}Fe_xO_3$ ($0.0 < x < 0.5$) are shown in Fig. 3. We see that the resistivity increases with x. The activation energy E_a in the low temperature region (77–200°K) in $LaCo_{1-x}Fe_xO_3$ is roughly the same as in $LaCoO_3$ (~0.1 eV) up to $x = 0.2$ (*7*); when $x = 0.3$, E_a appears to be slightly lower (0.08 eV). The activation energies in the regions 200–400°K and 400–650°K are summarized in Table II.

TABLE II

ACTIVATION ENERGIES FOR CONDUCTION (IN eV) OF $LaCo_{1-x}Fe_xO_3$

x	200–400°K	400–650°K
0.00	0.20	0.54
0.20	0.20	0.50
0.30	0.20	0.55
0.40	0.39	0.58
0.50	0.41	0.60

It is significant that at high values of x, the apparent E_a is considerably higher in both these regions where electron-transfer between Co^{3+} and Co^{III} is expected to occur as in $LaCoO_3$. Changes in electron transfer become particularly significant in the 400–650°K region in $LaCoO_3$ accompanied by a symmetry change (*6*, *7*). Both the charge transfer and ordering of high and low-spin ions are obviously suppressed by the presence of Fe^{3+} ions. The 650–900°K region (where the resistivity of $LaCoO_3$ reaches a minimum and there is saturation of charge carriers) is not distinctly seen in $LaCo_{1-x}Fe_xO_3$ if $x > 0.1$. The first-order, high-temperature localized-itinerant transition marked by the minimum in the log $\rho - 1/T$ curve is seen only up to $x = 0.1$ (Fig. 3). *DTA* curves also show the endothermic peak due to the transition up to $x = 0.10$.

In the iron-rich compositions, $LaCo_{1-x}Fe_xO_3$ ($x = 0.5 < x < 1.0$), the resistivity behavior is very similar to that of $LaFeO_3$.

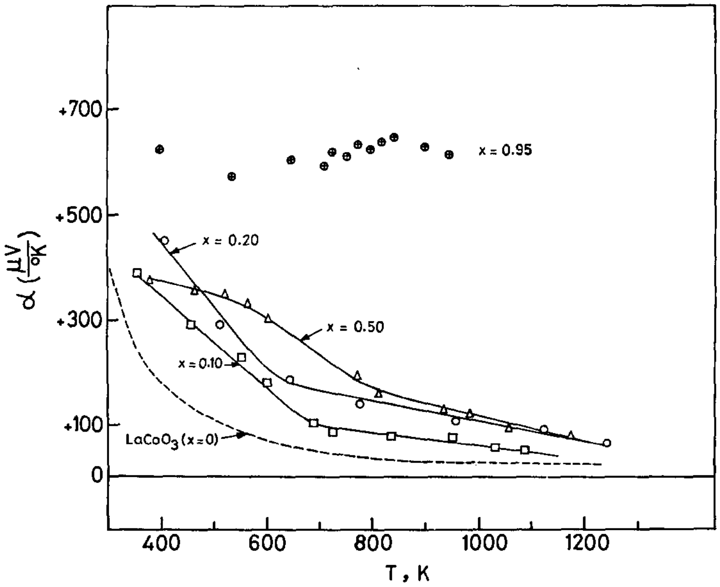

FIG. 4. Seebeck coefficient data of $LaCo_{1-x}Fe_xO_3$.

$LaFeO_3$ shows a change in E_a near the Neel temperature (750°K) (*4*). Similar changes in activation energy are seen in the iron-rich compounds ($x > 0.5$). The transition temperature is apparently not affected markedly by the presence of cobalt (*14*).

Seebeck coefficient α (Fig. 4) increase with x. Moreover, the temperature variation of α found in $LaCoO_3$ becomes less marked with increase in x. Thus, the sample with $x = 0.5$ shows a relatively weak temperature dependence (Fig. 4). Samples with $x = 0.8$ or 0.95 show a high and nearly constant α similar to $LaFeO_3$.

Magnetic susceptibility data of $LaCo_{1-x}Fe_xO_3$ are shown in Fig. 5. The plateau region found in $LaCoO_3$ disappears with increase in x. The plateau is associated with a symmetry change ($R\bar{3}c \rightarrow R\bar{3}$) in $LaCoO_3$ and has therefore been interpreted to mark a temperature region over which ordering of low-spin Co^{III} and high-spin Co^{3+} ions occurs with increasing temperature. Introduction of high-spin Fe^{3+} ions would, for low concentrations, tend to be ordered on the high-spin sublattice. The susceptibility values up to $x = 0.2$ suggest that the Fe^{3+} ions do indeed exhibit such a preference for the high-spin sublattice. This was confirmed by recording the Mössbauer spectrum of ^{57}Co-doped $LaCo_{0.8}Fe_{0.2}O_3$. At higher iron concentrations, the high-spin Co^{3+}state should be stabilized relative to the low-spin Co^{III} state, particularly as these substitutions are accompanied by an increase in the lattice parameter that changes the crystal symmetry from rhombohedral to orthorhombic. In the orthorhombic crystals, where high-spin ions are anticipated, antiferromagnetic coupling between nearest-neighbor magnetic ions can give rise to a weak ferromagnetism due to spin-canting (*15*, *16*). Susceptibility data of samples with $x \geqslant 0.3$ show the presence of weak ferromagnetism just as in $LaFeO_3$, indicating that a change from rhom-

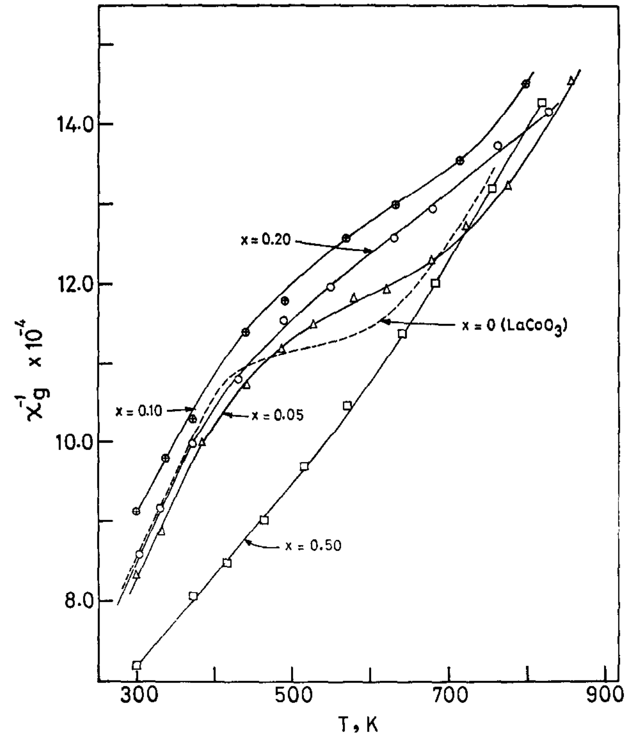

FIG. 5. Temperature variation of inverse magnetic susceptibility of $LaCo_{1-x}Fe_xO_3$.

bohedral to orthorhombic symmetry has already occurred by $x = 0.3$. Such a change in symmetry at $x = 0.5$ has been found by Wold and Croft (*10*) from X-ray studies.

$LaNi_{1-x}Fe_xO_3$

Preliminary studies on these oxides prepared by the flux method show that with increase in x the *d*-electrons become less itinerant. If $x > 0.2$, these oxides are semiconductors. Susceptibility data are consistent, with the iron being present in the high-spin Fe^{3+} ($t_{2g}^3 e_g^2$) configuration in this system. At high x(~0.5 and above), the structure becomes orthorhombic and properties akin to $LaFeO_3$ become evident. Detailed studies are, however, necessary to fully understand the properties of this system.

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