JOURNAL OF SOLID STATE CHEMISTRY 53, 140–143 (1984)

Magnetic Interactions in the Oxide Systems $LaNi_{1-x}M_xO_3$ (M = Cr, Fe, or Co)*

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Received September 27, 1983; in revised form December 30, 1983

Magnetic susceptibilities of several members of the series of oxides of the general formula $LaNi_{1-x}M_xO_3$ (M = Cr, Fe, or Co) are reported. The oxides show evidence for interesting ferrimagnetic (Cr and Co) and antiferromagnetic (Fe) interactions.

Introduction

Our recent studies of the $LaNi_{1-x}Mn_xO_3$ ($0.0 < x \leq 0.50$) system have revealed a variety of magnetic properties ranging from Stoner-enhanced Pauli paramagnetism to ferromagnetism with increasing x; the $x = 0.10$ sample showed ferrimagnetic spin-glass behavior below 40 K (1). We have now investigated the magnetic properties of other $LaNi_{1-x}M_xO_3$ systems where M = Cr, Fe, or Co. These systems are of interest since $LaNiO_3$ ($x = 0.0$) is metallic and Pauli paramagnetic while the other transition metal perovskite oxides are generally insulators; $LaCrO_3$ and $LaFeO_3$ show antiferromagnetic ordering while $LaCoO_3$ is essentially diamagnetic at low temperatures (2–5). Electron transport and magnetic properties due to the host as well as the guest metal ions in the $LaNi_{1-x}M_xO_3$ systems arise from $3d$ electrons. In this brief communication, we report the magnetic properties of $LaNi_{1-x}M_xO_3$ (M = Cr, Fe, and Co) systems over the range 12–300 K, having prepared the oxides by a low-temperature method which ensured greater homogeneity and a wider composition range. Measurements on the Fe system have been carried out in the range 12–1000 K, since the magnetic ordering temperatures are high at large x. The chromium compounds examined by us have been prepared for the first time.

Experimental

$LaNi_{1-x}M_xO_3$ systems were prepared by the thermal decomposition (1120–1370 K) of the basic carbonates precipitated from a solution of nitrates (6). The active oxygen content, determined by iodimetric titration, was generally found to correspond to the expected stoichiometry. Wherever there was oxygen deficiency, the samples were heated in oxygen at 1000 K for several hours to obtain the required stoichiometry.

* Contribution No. 234 for Solid State and Structural Chemistry Unit.

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0022-4596/84 $3.00

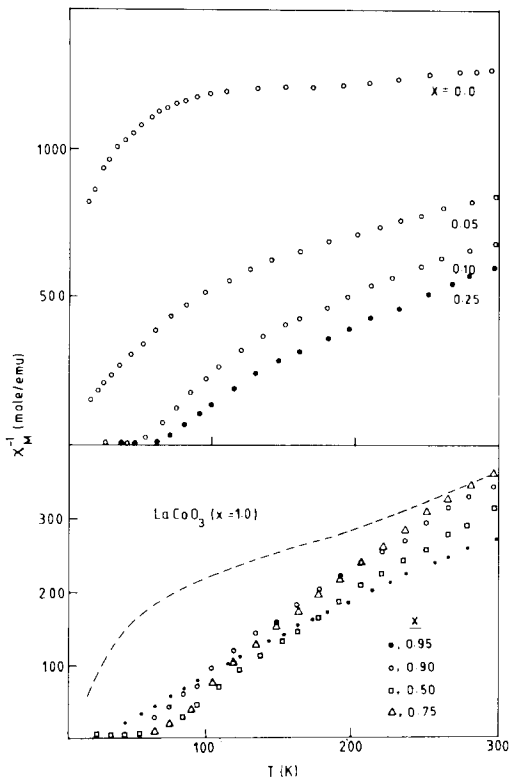

FIG. 1. Inverse susceptibility–temperature plots of $LaNi_{1-x}Co_xO_3$.

The nonstoichiometry in the oxides, $LaNi_{1-x}M_xO_{3+\delta}$, was within $\delta = \pm 0.01$. All the compounds possess the rhombohedral structure of $LaNiO_3$ at low values of x. The Cr and Fe systems become orthorhombic when $x > 0.35$ and 0.50, respectively. The Co system is rhombohedral over the entire composition range. Magnetic susceptibility measurements were carried out by the Faraday method using a Cahn RG vacuum electrobalance. An Air Products Displex CS201 closed-cycle refrigeration unit was used for attaining temperatures in the range 12–300 K.

Results and Discussion

$LaNi_{1-x}Co_xO_3$. Plots of the inverse molar magnetic susceptibility, χ_M^{-1}, against temperature of these oxides are shown in Fig. 1. With the exception of the $x = 0.05$ sample, all the other compositions show high susceptibilities at low temperatures. The curves in the low-temperature region are suggestive of ferrimagnetic behavior. The Curie temperature, θ, obtained from the plots (below 150 K) shows a maximum around $x = 0.5$ and is not sensitive to x in the region 0.25–0.75 (Fig. 2). It is interesting that even the smallest amounts of Ni or Co ($x = 0.10$ or 0.95) completely change the magnetic behavior. We have found no cusp in the low-field dc susceptibility curves and are therefore unable to subscribe to the presence of spin-glass-like states (*7*). The low value of spontaneous magnetization (0.5 μ_B/Co ion) reported by Asai *et al.* (*7*) in the composition range $0.00 < x \leq 0.50$ may not be due to ferromagnetic ordering. The insensitivity of θ to x in the region 0.50 ± 0.25 may be taken to reflect the importance of near-neighbor interactions (due to the random distribution of Co^{3+} and Ni^{3+} ions) as well as of chemical inhomogeneities. Mössbauer and neutron diffraction studies would be helpful in fully understanding the magnetic behavior of these solids.

$LaNi_{1-x}Fe_xO_3$. In Fig. 3 we show the χ_M^{-1}–T plots of these oxides. In the composition range $0.25 \leq x \leq 0.90$, we see a mini-

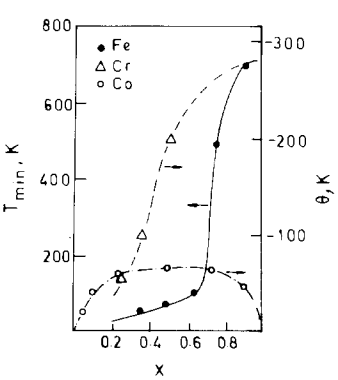

FIG. 2. Plots of the Curie temperatures, θ, of $LaNi_{1-x}Co_xO_3$ and $LaNi_{1-x}Cr_xO_3$ and T_{min} of $LaNi_{1-x}Fe_xO_3$ against their compositions.

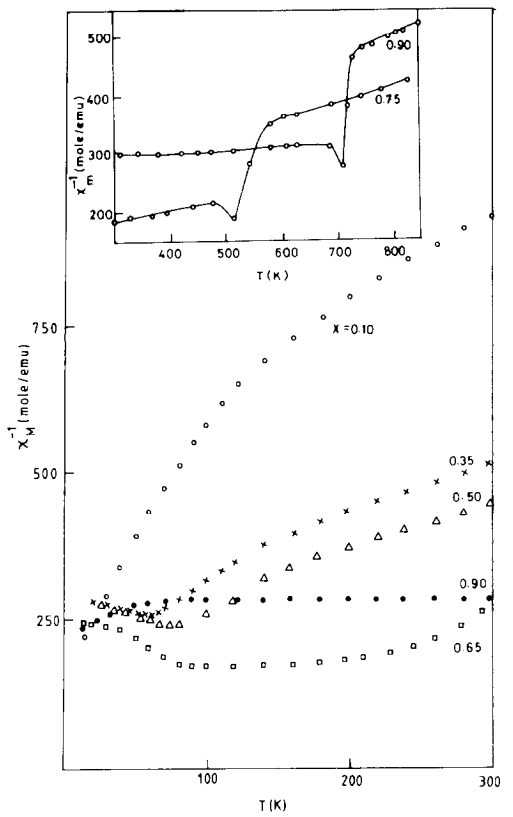

FIG. 3. Inverse susceptibility–temperature plots of $LaNi_{1-x}Fe_xO_3$ ($T < 300$ K). In the inset, data on the $x = 0.75$ and 0.90 samples are shown at temperatures above 300 K; there is considerable thermal hysteresis and field-dependence of the susceptibility in this region.

mum in these plots, with the temperature T_{min} increasing with x (Fig. 2). The minimum becomes more pronounced with increasing x and there is a sharp rise in the value of T_{min} at $x = 0.75$. Samples with $x \geq 0.75$ also show evidence for magnetic ordering. The ordering temperatures of the $x = 0.75$ and 0.90 samples are 515 and 710 K, respectively, compared to 750 K found in $LaFeO_3$ ($x = 0.0$). Asai and Sekizawa (*8*) have found a $LaFeO_3$-like impurity phase in all their samples with $x > 0.2$, contrary to our present findings. Based on their magnetization and Mössbauer data, they suggested spin-glass-like behavior to be present in samples with $0.0 < x \leq 0.2$ at low temperatures. We have, however, found no cusp in our low-field susceptibility measurements.

Based on the Goodenough–Kanamori superexchange rules (*9*), the following electron transfer reaction is likely to occur:

$$Fe^{3+}(t_{2g}^3 e_g^2) + Ni^{3+}(t_{2g}^6 e_g^1) \rightarrow Fe^{4+}(t_{2g}^3 e_g^1) + Ni^{2+}(t_{2g}^6 e_g^2)$$

This would favor a ferromagnetic ground state. Introduction of small amounts of Ni^{3+} in $LaFeO_3$ would therefore reduce the strength of the antiferromagnetic interaction in $LaFeO_3$. When the concentration of Ni^{3+} is large (small x in $LaNi_{1-x}Fe_xO_3$), however, we would have to consider the nature and strength of Ni–O–Ni interactions. If the Ni–O–Ni interaction is antiferromagnetic, we would expect long-range ordering. Only if it is ferromagnetic, would we expect spin-glass behavior; an antiferromagnetic ordering would be favored if the

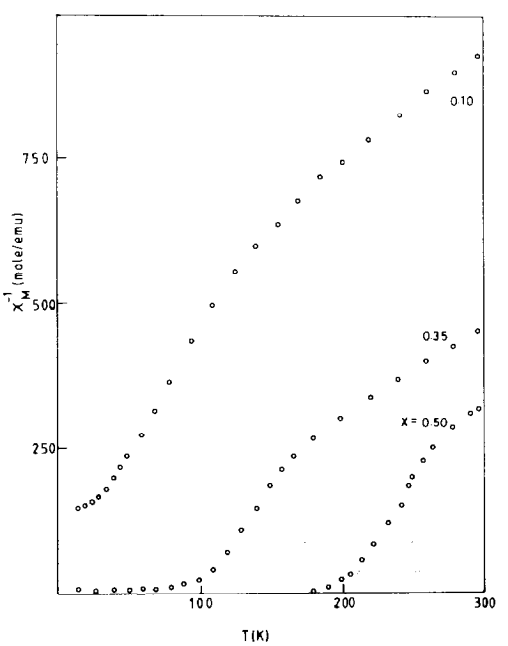

FIG. 4. Inverse susceptibility–temperature plots of $LaNi_{1-x}Cr_xO_3$.

degeneracy of the e_g levels is lifted. The susceptibility behavior of $LaNi_{1-x}Fe_xO_3$ when $x \leq 0.5$ does not altogether eliminate the possibility of a distribution of antiferromagnetic clusters of different sizes.

$LaNi_{1-x}Cr_xO_3$. The χ_M^{-1}–T plots of these oxides are shown in Fig. 4. With the exception of the $x = 0.10$ sample, the other samples show a divergent susceptibility at low temperatures; the data are suggestive of ferrimagnetic behavior. The $x = 0.5$ sample is ferrimagnetic at low temperatures ($\theta = -200$ K), but obeys the Curie–Weiss law at high temperatures, with a θ indicative of antiferromagnetic interactions (*6*); the μ_{eff} value corresponds to the presence of localized moments at Cr^{3+} and low-spin Ni^{3+} ions. The ordering temperature of the $0.25 \leq x \leq 0.50$ samples increases with x. It is rather difficult to understand the nature of the magnetic interactions in this system. The Goodenough–Kanamori rules (*9*) predict a ferromagnetic ground state between Cr^{3+} and Ni^{3+} (low-spin), if the e_g orbitals of the latter are degenerate. Only if the e_g orbitals of Ni^{3+} are nondegenerate would we expect antiferromagnetic interactions.

Acknowledgment

The authors thank the Department of Science and Technology, Government of India, for support of this research.

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