Itinerant electron behaviour and long-range ordering in La$_{1-x}$Sr$_x$CoO$_3$*

P GANGULY** and W H MADHUSUDAN

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012

Abstract. Electrical resistivity of La$_{1-x}$Sr$_x$CoO$_3$ is reduced significantly by the substitution of Ni^{3+} ions in place of the cobalt ions. In the La$_{1-x}$Sr$_x$Co$_{1-y}$Ni$_y$O$_3$ system, for small values of x ($x = 0.05$) superparamagnetic clusters seem to be formed at lower temperatures (< 300 K). The formation of such clusters is not affected by the presence of nickel ions. When x is large, the occurrence of long-range ordering seems to depend on the itinerancy of charge carriers.

1. Introduction

It is well established that an equilibrium between high-spin and low-spin cobalt ions exists in LaCoO$_3$ (Raccah and Goodenough, 1967; Bhide *et al* 1972). The presence of low-spin ions favour itinerant electron behaviour while the high-spin ions favour localised electron behaviour. Accordingly LaCoO$_3$ becomes metallic above 1200 K when the concentration of high-spin Co^{3+} is nearly zero. Furthermore, substitution of low-spin Ni^{3+} ions (t_{2g}^6, e_g^1) in place of the cobalt ions increases the conductivity of LaCoO$_3$, while substitution by Fe^{3+} ions decreases the conductivity (Rao *et al* 1975). Itinerancy of the charge carriers can also be brought about by the substitution of Sr^{2+} ions for La^{3+} ions in LaCoO$_3$ (Raccah and Goodenough 1968; Bhide *et al* 1975). Thus, in the oxide system La$_{1-x}$Sr$_x$CoO$_3$, the compositions corresponding to $0.30 \leqslant x \leqslant 0.50$ are metallic; at the same time compositions with $x \geqslant 0.125$ are ferromagnetic at low temperatures. The onset of ferromagnetic ordering seems to be a percolation problem and itinerant electron behaviour of the charge carrier seems to be necessary. In the present paper, we have investigated the effect of increasing the itinerant electron behaviour on the onset of ferromagnetic ordering in this oxide system. This has been carried out by substituting a part of the cobalt ions by nickel ions to form compounds of the type La$_{1-x}$Sr$_x$Co$_{1-y}$Ni$_y$O$_3$.
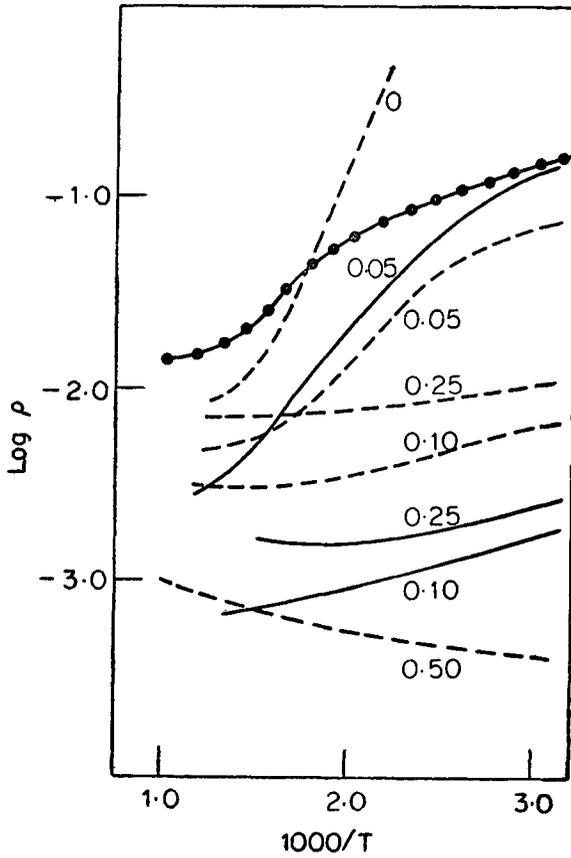
Figure 1. Log ρ *vs* T plots for La_{1-x} Sr_xCo_{1-y} Ni_yO_3 compounds. Dashed line corresponds to $y \neq 0$. Full lines correspond to $x = y$. Dotted line corresponds to $La_{0\cdot75}$ $Sr_{0\cdot25}$ $Co_{0\cdot75}$ $Al_{0\cdot25}$ O_3. The values of x are given against each curve.
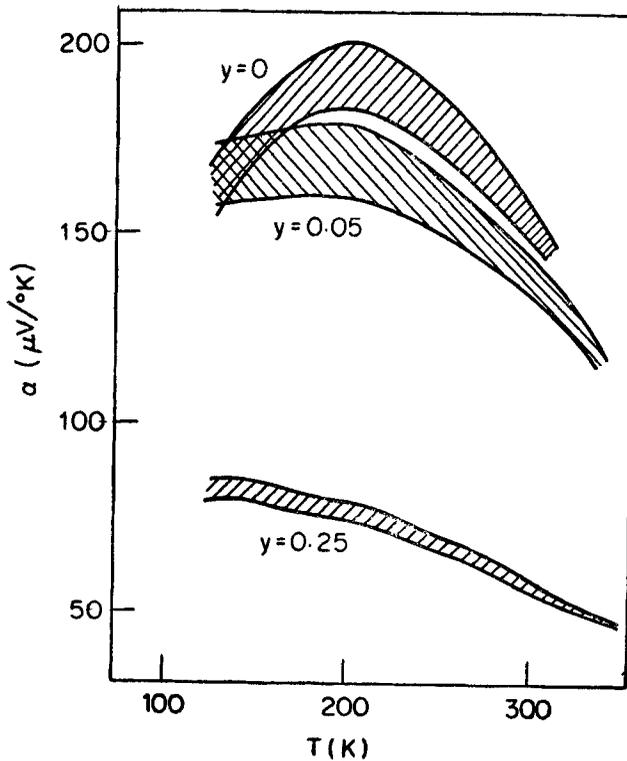
Figure 2. Seebeck coefficient, a, *vs* temperature curves for $La_{0\cdot95}Sr_{0\cdot05}$ Co_{1-y} Ni_y O_3 compounds.

2. Experimental

It was not possible to prepare $La_{1-x}Sr_xCo_{1-y}Ni_yO_3$ compounds by the mixed oxide method by heating the mixture of component oxides to 1470 K as in the case of $La_{1-x}Sr_xCoO_3$. La_2NiO_4 was always found in the nickel-substituted compounds prepared under these conditions. To circumvent these difficulties a precipitation method was used which incorporated the Na_2CO_3 flux technique as in the preparation of $LaNiO_3$ (Ganguly and Rao 1973) and at the same time ensured intimate mixing to give single-phase compounds. A 0·5 M solution of the metal nitrates was made by dissolving the corresponding oxides in the required stoichiometry in nitric acid. The metal carbonates were precipitated by adding the nitrate solution dropwise to a 2M solution of sodium carbonate under stirring. The precipitate was then filtered, dried without washing off the excess Na_2CO_3, and heated in air at 1020 K. The ignited product was repeatedly boiled with distilled water and filtered several times till the filtrate was neutral. The residue was then heated in air at 1120 K for 24 hr, pelletised and heated again in oxygen at 1120 K for 24 hr. These compounds were of single phase and had lattice parameters and stoichiometry similar to the corresponding $La_{1-x}Sr_xCoO_3$ compounds. It is not likely that significant amounts of tetravalent nickel ions are formed as not more than 5% Sr^{2+} ions can be substituted for La^{3+} ions in $LaNiO_3$ (Obayashi and Kudo 1975).

Electrical resistivity of the compounds were measured by the standard dc four-probe method. Magnetic susceptibilities of these compounds were determined by the Faraday method using a Cahn RG vacuum electrobalance.

3. Results and discussion

Typical results of the electrical resistivity measurements of the various $La_{1-x}Sr_x$ $Co_{1-y}Ni_yO_3$ compounds $(x \neq y = 0·0, 0·05, 0·10, 0·25)$ are shown in figure 1. It can be seen from figure 1 that the electrical resistivity of the nickel-substituted compositions are generally lower than the corresponding pure cobalt compounds just as in $LaCo_{1-x}Ni_xO_3$ (Rao *et al* 1975). Obviously, Ni^{3+} ions do increase the itinerancy of the charge carriers in $La_{-x}Sr_xCoO_3$ as well. Seebeck coefficient measurements on some of the $La_{0.95}Sr_{0.05}Co_{1-y}Ni_yO_3$ compounds are shown in figure 2. The Seebeck coefficient, a, is positive but decreases with increasing nickel content due to the contribution of the e_g electrons of the low-spin Ni^{3+} ions. The maximum in a around 200 K in $La_{0.95}Sr_{0.05}CoO_3$ has also been observed in the other $Ln_{1-x}Sr_xCoO_3$ compounds and has been attributed to Anderson localisation of the charge carriers (Rao and Om Parkash 1977). The changes in a around 200 K observed in the nickel substituted compounds could be attributed to similar localisation of the charge carriers associated with the cobalt ions. The Seebeck coefficient results seem to indicate that the nickel and cobalt ions contribute independently to the electrical transport properties.

The inverse magnetic susceptibility χ_M^{-1} vs T plots of the $La_{1-x}Sr_xCo_{1-y}Ni_yO_3$ compounds are shown in figures 3–5 for different values of x and y. The χ_M^{-1} vs T plots are essentially that of ferrimagnets at low temperatures.

In the $x = 0·05$ samples (figure 3), χ_M decreases with increasing nickel content above 300 K. The plateau-like feature shown by $LaCoO_3$ above 450 K is also present

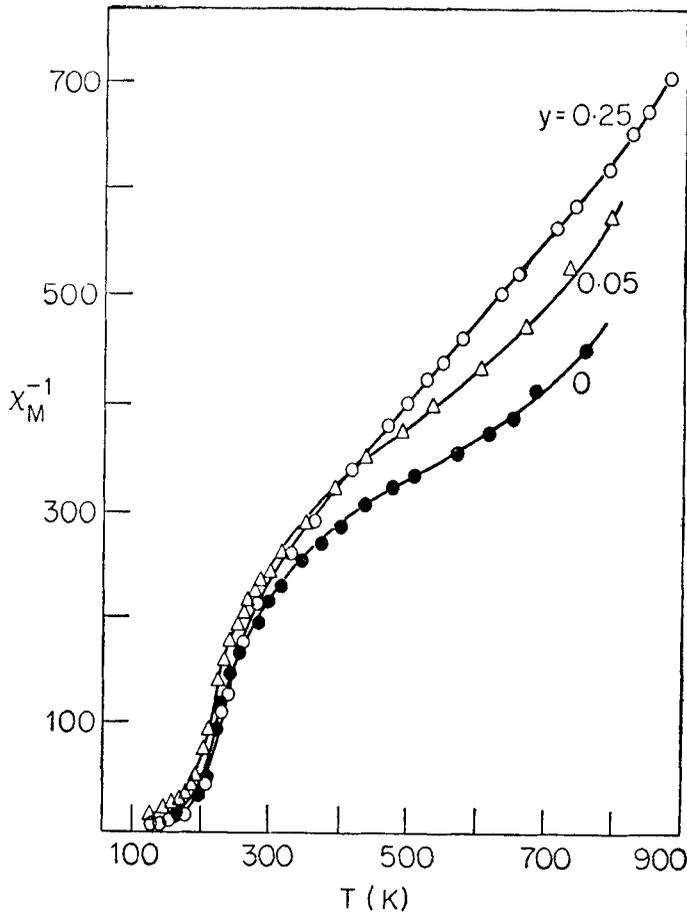**Figure 3.** χ_M^{-1} *vs.* T plots for $La_{0.95}Sr_{0.05}Co_{1-y}Ni_yO_3$ compounds.

in the $y = 0.05$ and 0.10 samples but are absent in the $y = 0.25$ sample. This is similar to the results reported earlier for $LaCo_{1-x}Ni_xO_3$ (Rao *et al* 1975). At lower temperatures, however, the $x = 0.05$ samples show a behaviour typical of ferrimagnets although the susceptibility does not diverge down to 77 K. This suggests the formation of small superparamagnetic clusters. Such a behaviour is independent of the nickel concentration even though nickel ions affect markedly the electrical properties. Thus the magnetic interactions are due to the cobalt ions alone. Recent PES studies on $LaCo_{1-x}Ni_xO_3$ solid solutions (Madhusudan *et al* 1978) reveal that the valence band of the solid solutions have features which could be associated only with the d bands of individual ionic species. The rapid increase in the susceptibility near 220 K observed in all the $x = 0.05$ samples could therefore be attributed to the formation of superparamagnetic clusters of cobalt ions in the strontium-rich regions. The ferrimagnetic behaviour could be attributed to the presence of distinguishable trivalent and tetravalent colbalt ions antiferro-magnetically coupled to each other. This implies that the motion of the charge carriers hopping between the cobalt ions of different oxidation states is frozen, and may be related to the Anderson localisation of the charge carriers mentioned earlier.
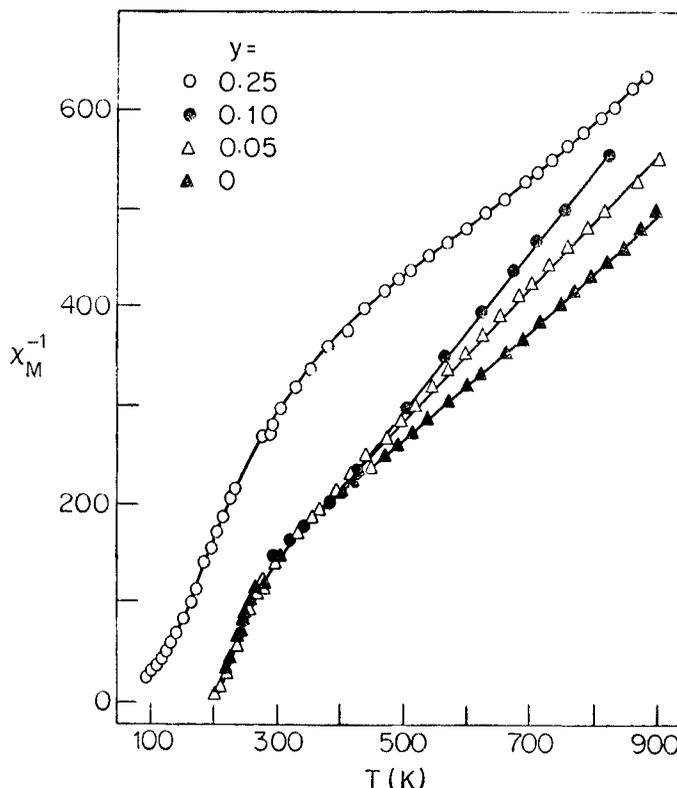
Figure 4. χ_M^{-1} *vs.* T plots for $La_{0.90}Sr_{0.10}Co_{1-y}Ni_yO_3$ compounds.

The $x = 0.10$ and $x = 0.25$ samples show magnetic behaviour similar to the $x = 0.05$ samples (figures 4 and 5) indicating once again that nickel ions do not make significant contributions to the magnetic ordering process. However, there are small effects due to nickel substitution which can be discerned in the $x = 0.25$ samples. The ordering temperature in these samples decreases with increasing nickel content (figure 5) which may be a dilution effect. Dilution can have considerable effect as seen in the magnetic susceptibility behaviour of $La_{0.75}Sr_{0.25}$ $Co_{0.75}Al_{0.25}O_3$ (figure 5) which also has a high resistivity (figure 1). The results with the aluminium substituted compounds show that even when x is high, ferrimagnetic or ferromagnetic clusters may be formed without any sign of long-range ordering. It seems that fairly mobile electrons are necessary for long-range order to percolate. Itinerant electrons could improve the magnetic correlation between the fairly large clusters. It is for this reason perhaps that $La_{0.75}Sr_{0.25}Co_{0.75}Ni_{0.25}O_3$ comes closest to the behaviour of a true ferromagnet. The anomalous behaviour of $La_{0.9}Sr_{0.1}Co_{0.75}Ni_{0.25}O_3$ (figure 4) could also be attributed to a similar reason.

Since the d bands of the cobalt ions and nickel ions are to be considered as rigid bands (Madhusudan *et al* 1978), it is unlikely that itinerant electron ferromagnetism could account for the above facts. Moreover, the itinerant electron description is not strictly valid when $x < 0.30$ in $La_{1-x}Sr_xCoO_3$. Ferromagnetic interactions could be present if a Zener double exchange mechanism between an intermediate spin Co^{iii} (t_{2g}^5, e_g^1) and low-spin Co^{iv} (t_{2g}^5, e_g^0) is assumed. Evidence for the
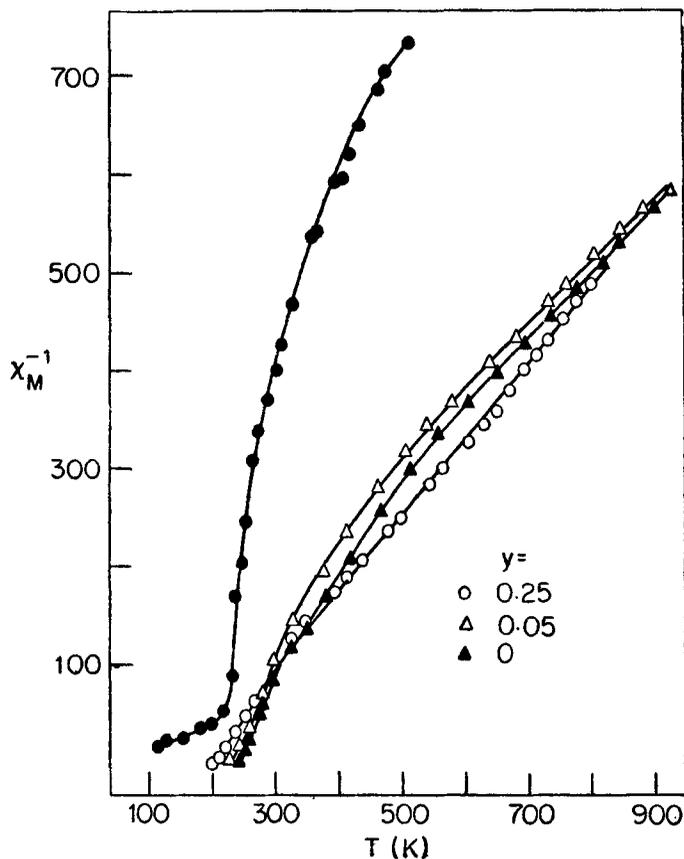
Figure 5. χ_M^{-1} vs. T plots for $La_{0.75}Sr_{0.25}Co_{1-y}Ni_yO_3$ compounds. Solid circles correspond to $La_{0.75}Sr_{0.25}Co_{0.75}Al_{0.25}O_3$.

unusual Co^{iii} intermediate spin state has been recently reported (Bahadur *et al* 1979). Presence of such spin states could favour electron hopping. Long-range ordering takes place when there is magnetic correlation between the super-paramagnetic clusters. Since large polarons could be associated with low-spin Ni^{3+} ions in metallic $LaNiO_3$, the probability of a Zener electron hopping from one cluster to another, thereby introducing magnetic correlation, is likely to increase when the intervening metal ion is nickel rather than cobalt or aluminium ions. A fairly large size of the cluster seems to be necessary for this to happen.

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