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Near-neighbour impurity effect on the spin-state transitions in $LaCoO_3$ at low temperature ($12 < T < 300$ K)

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Abstract. The low-temperature magnetic susceptibility behaviour of $LaCoO_3$ prepared under different conditions as well as substituted samples such as $LaCo_{0.95}M_{0.05}O_3$ (M = Al, Ga, Cr, Fe, Mn, Ni) and $La_{0.98}Sr_{0.02}CoO_3$ have been investigated in the temperature range 12–300 K. Earlier interpretations of the magnetic susceptibility have been reexamined. In the case of $LaCoO_3$ samples containing Al, Ga, Cr and Fe impurities spin-state transitions involving a temperature independent activation energy (~ 0.01 eV) are observed at $T < 200$ K. Analysis of the data indicates that either the excited state has an intermediate-spin ($t_{2g}^5 e_g^1$) configuration or only half the Co ions are involved in the activated transition to the high-spin ($t_{2g}^4 e_g^2$) configuration. Al^{3+}, and Cr^{3+} increases the activation energy considerably. Substitution of $L \neq 0$ ions such as Mn^{3+} and Ni^{3+} or Co^{4+} (low-spin) seems to introduce ferromagnetic interactions and stabilizes the paramagnetic state. $LaCoO_3$, when Co is substituted by Mn (5%) or La is substituted by Sr (2%) show giant magnetic moments. When Co is substituted by Ni (5%) a ferromagnetic ground state is observed.

Keywords. Near-neighbour impurity; lanthanum cobaltate; spin-state transitions

1. Introduction

$LaCoO_3$ has many unusual properties the most investigated of which is the so-called low-spin Co^{III} ($t_{2g}^6 e_g^0$, $^1A_1$ state) to high-spin Co^{3+} ($t_{2g}^4 e_g^2$ $^5T_2$ state) transition (Jonker and van Santen 1953; Heikes *et al* 1964; Jonker 1966; Goodenough 1958; Naiman *et al* 1965; Menyuk *et al* 1967; Bhide *et al* 1972). At low temperatures ($T < 80$ K) the inverse magnetic susceptibility (χ_m^{-1}) *vs* temperature plot was initially reported to show a minimum followed by a maximum at lower temperatures (Jonker and van Santen 1953; Heikes *et al* 1964). However single crystal studies (Naiman *et al* 1965) as well as ceramic samples prepared by repeated heating and grinding (Menyuk *et al* 1967) did not show these features. Naiman *et al* (1965) pointed out that the susceptibility behaviour below 300 K of single crystals oriented perpendicular to the (110) axis could be explained by including spin-orbit effects and an activated process in which the activation energy changes linearly with temperature over the entire range. Mössbauer studies (Bhide *et al* 1972) have shown that the Co^{3+}/Co^{III} ratio is a maximum around 200 K so that a continuous increase in the population of the $^5T_2$ state from 0 to 300 K is unlikely to be correct. Madhusudan *et al* (1980) studied the influence of small amounts of various M ions in the series $LaCo_{1-x}M_xO_3$ ($x \leqslant 0.1$, M = Al, Cr, Fe, Ga, Mn) for $T > 80$ K and have observed that the susceptibility at low-temperatures could be described by an activated process with the activation energy being independent of temperature. The activation energy was ~ 0.01 eV. For such low activation energies the influence of

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magnetic exchange interactions in stabilizing the paramagnetic spin state could be considerable. It was of interest to investigate the low-temperature region ($T < 80$ K) in which this behaviour could manifest itself. In this paper we report the results of our studies in which we have reinvestigated the magnetic susceptibility behaviour of $LaCoO_3$ prepared by different methods as well as the influence of various neighbouring ions with special reference to the low-temperature behaviour. The results show some surprising features, the most important of which are the possibility of an intermediate spin-state involved in the transitions, the presence of giant magnetic moments in the presence of small amounts of Mn or Sr^{2+} as well as the stabilization of a ferromagnetic ground state in the presence of small amounts of Ni^{3+}.

2. Experimental

The preparation of the $LaCo_{0.95}M_{0.05}O_3$ samples (M = Al, Ga, Cr, Fe, Mn, Ni) and $La_{0.98}Sr_{0.02}CoO_3$ have been described earlier (Madhusudan *et al* 1980; Vasanthacharya *et al* 1983). The $LaCoO_3$ samples were prepared both by the decomposition of coprecipitated basic carbonates and $LaCo(CN)_6$ in air at 1170 K. These samples will be referred to as 900 AA and 900 CNA, respectively. The 900 AA had a slight oxygen deficiency ($\sim 1\%$). The sample was further heated in oxygen at 1170 K for 5 days to give a nearly stoichiometric sample (900 BO) which was then heated in air at 1273 K for 24 hr (1000 CA) and finally heated in oxygen at 1273 K for 24 hr (1000 DO). The Co^{3+} content in the last three samples as determined by iodimetric titrations was the same and close to the required stoichiometry.

The magnetic susceptibility was measured using the Faraday technique and employing a Cahn-RG micro-balance and an Air-products closed cycle Displex CS201 refrigeration unit. An electromagnet with specially shaped pole pieces and a maximum magnetic field of 4500 G was used. $HgCo(CNS)_4$ was used as the calibrant for susceptibility studies.

3. Results and discussion

3.1 *$LaCoO_3$*

The χ_M^{-1} *vs* T plots of the $LaCoO_3$ samples prepared under various conditions are shown in figure 1. There does not seem to be any systematics in the behaviour which is dependent on the method of preparation. Samples 900 AA, 900 BO and 900 CNA show a weak field-dependent susceptibility below 80, 50 and 65 K respectively, which could be attributed to the presence of a ferromagnetic impurity. The others do not show the field-dependence at low temperatures.

Naiman *et al* (1965) used the formula

$$(\mu_{\text{eff}})^2 = \frac{3(24{\cdot}5 + 54/x) + [5(13{\cdot}5 - 10/x)\exp(-x/2) + 7(12 - 16/x)\exp(-5x/4)]}{\exp(E/kT) + [(3 + 5\exp(-x/2) + 7\exp(-5x/4))]} \tag{1}$$

where $x = \lambda/kT$ is the spin-orbit coupling parameter and E is the energy separating the diamagnetic $^1A_1$ ground state and the lower paramagnetic doublet arising out of the distortion of the $^5T_2$ excited state. Assuming $\lambda = 400\ \text{cm}^{-1}$ and using the experimental

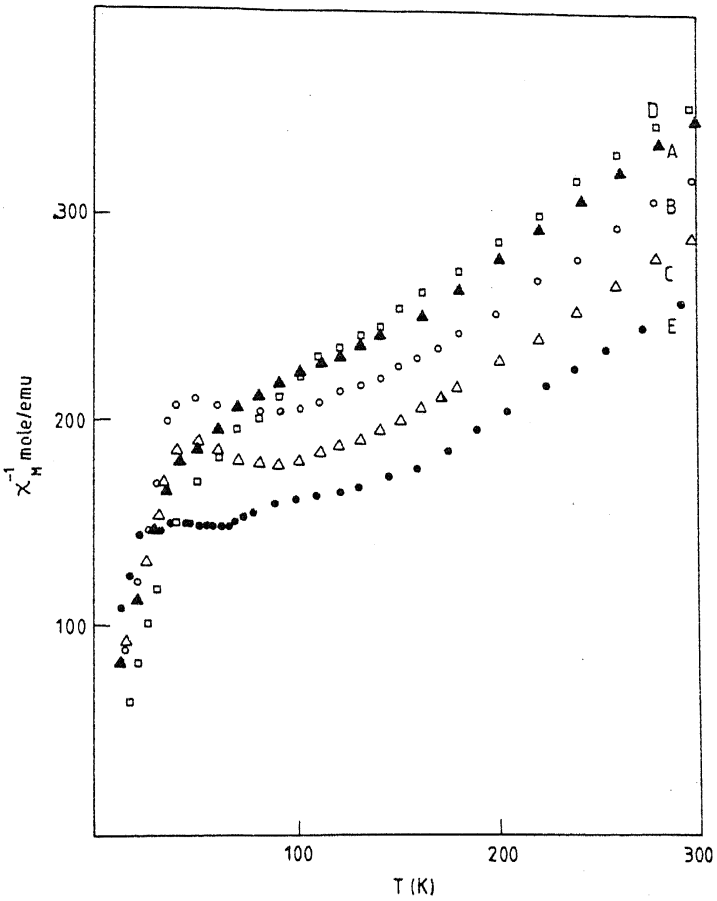

Figure 1. $\chi_M^{-1} - T$ plots for $LaCoO_3$ prepared under various conditions. A = 900 AA, B = 900 BO, C = 1000 CA, D = 1000 DO and E = 900 CNA.

value of $(\mu_{\text{eff}})^2$, E can be evaluated, as a function of temperature. Naiman *et al* (1965) observed that E increased linearly with temperature. We indeed find such a nearly linear behaviour although there is a slight curvature as can be seen from figure 2 for the sample 1000 DO and 1000 CA. Although (1) seems to be obeyed some comments are in order!

(i) The above formula can only be used when the crystal distortions are small relative to kT (Griffith 1958). Since there is a substantial distortion of the CoO_6 octahedra at the lowest temperatures (Naiman *et al* 1965; Wold *et al* 1957; Raccah and Goodenough 1967) the validity of (1) is doubtful.

(ii) Results of Mössbauer studies (Bhide *et al* 1972) are not consistent with such an interpretation since the distribution of spin states shows a marked anomaly above 200 K, so that the applicability of (1) above this temperature is subject to doubt.

We believe that the proportionality of E with T observed from (1) is fortuitous. For small values of kT or very large values of $x(kT \ll \lambda)$, the terms in the square bracket in both the numerator and the denominator becomes negligibly small. Equation (1) therefore simplifies to

$$(\mu_{\text{eff}})^2 = \frac{3[49/2 + 54T/\lambda]}{\exp(E/kT)}, \tag{2}$$

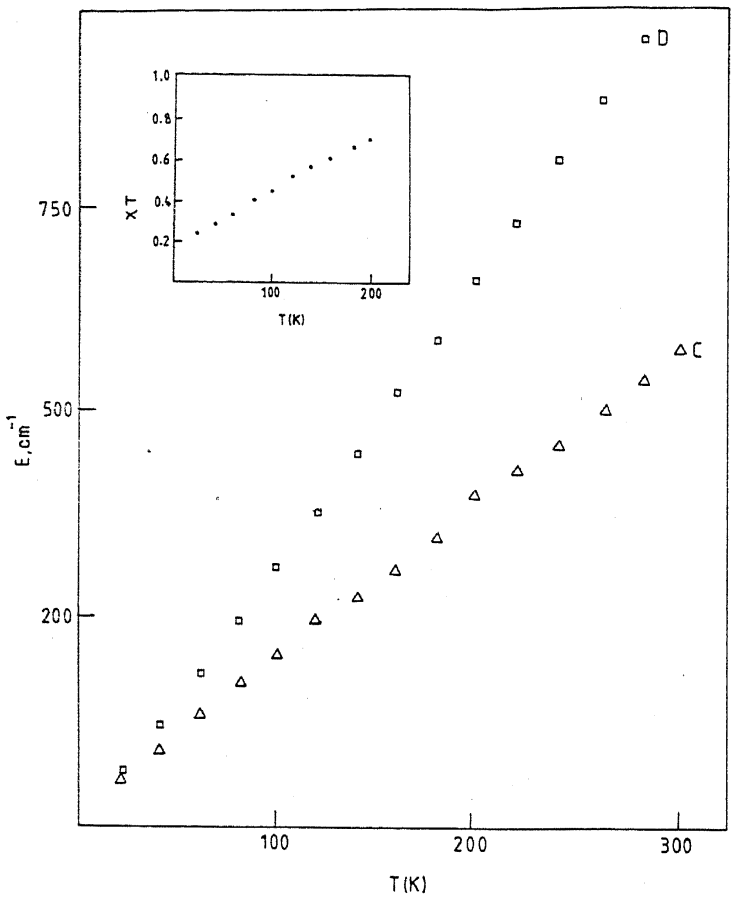

Figure 2. E_a *vs* T plots for sample 1000 CA and 1000 DO calculated from figure 1. Inset shows χ_{T-T} for sample D.

when $E\alpha T$ and since $\chi T\alpha(\mu_{\text{eff}})^2$ we obtain

$$\chi = C'/T + B. \tag{3}$$

Plots of χT *vs* T are indeed nearly linear when $T < 200$ K. We note from figure (1) that all the samples show a Curie-like behaviour at low temperatures. The C'/T term in (3) could be attributed to this behaviour which in turn could be associated with the presence of a paramagnetic species. The term B in (3) could be associated with either a temperature-independent susceptibility or a term χ_{act} arising from an activated process involving a transition from the $^1A_1$ ground state to a paramagnetic state.

If figure 3 the variation of χ_{act} has been plotted as a function of temperature for some $LaCoO_3$ samples. These show a maximum at a temperature (T_{max}) indicated by arrows. The plots of $\log(\chi_{\text{act}}T)$ *vs* $1/T$ (figure 4) are linear in the temperature range 50–200 K indicating the activated nature of the process since $\chi_{\text{act}}T$ is a measure of the number of paramagnetic ions assuming that they obey a Curie law. The activation energy E_a obtained from the slopes is nearly equal to kT_{max} (table 1) so that relation $\chi_{\text{act}} = A/T\exp(-E_a/kT)$ could be valid since $d\chi_{\text{act}}/dT = 0$ when $E_a = kT$. E_a is nearly the same for all the samples except 900 AA. For an activated process the susceptibility χ_{act} may be obtained from the Boltzmann distribution. χ_{act} may be written as

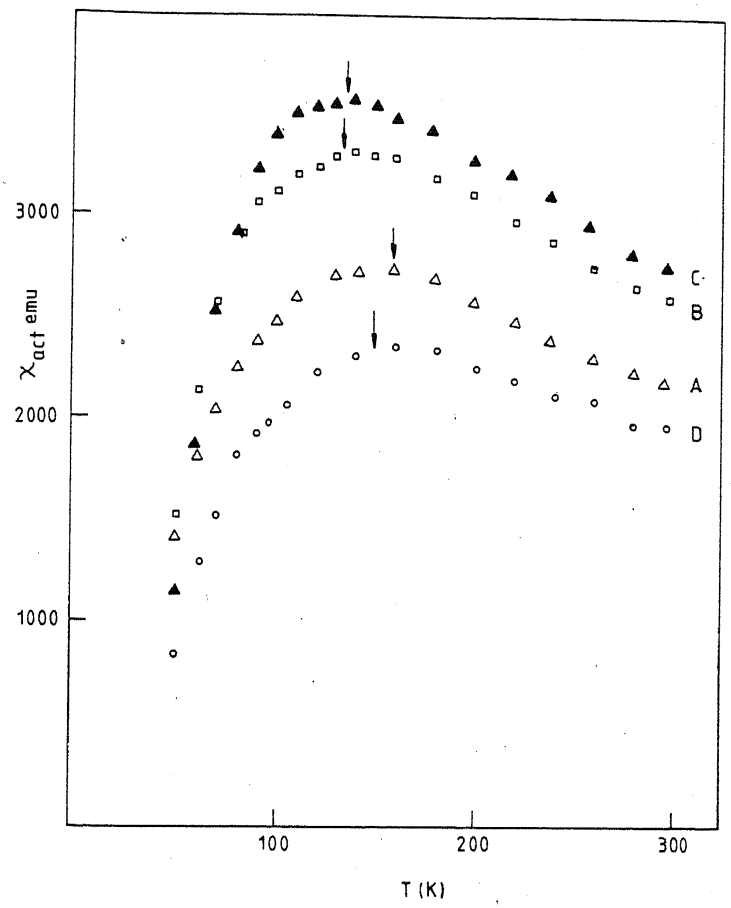

Figure 3. $\chi_{act}-T$ plots for various $LaCoO_3$ sample. A, B, C and D are same as in figure 1.

(Demazeau *et al* 1980)

$$\chi_{act} = \frac{1}{T} \times \frac{gC\exp(-E_a/kT)}{1+g\exp(-E_a/kT)}, \tag{4}$$

where g is the degeneracy and C is the Curie constant of the paramagnetic state. When $T \to \infty$ or $1/T \to 0$ we obtain

$$(\chi_{act}T)_{T\to\infty} = gC/1+g. \tag{5}$$

The plots of log $(\chi_{act}T)$ *vs* $1/T$ (figure 4) yield a value $(\chi_{act}T)_{T\to\infty}$ in the range 1 to 1·3. If the paramagnetic state is the high spin $^5T_2$ state the expected value is 2·8 since $g = 15$ and $C = 3$ (spin only value). The discrepancy between observed and expected values may be resolved if we assume that only half the Co ions undergo a spin-state transition. This agrees with the earlier models (Goodenough 1958; Raccah and Goodenough 1967) and implies that there are two different Co sites which would be inconsistent with $R\bar{3}c$ symmetry (Menyuk *et al* 1967; Wold *et al* 1957; Raccah *et al* 1967). We also note that if the paramagnetic state is an intermediate spin state such as a $^3A_{2g}$ state with the configuration $d_{xz}^2 d_{yz}^2 d_{xy}' d_{z^2}^1 d_{x^2-y^2}^0$ the expected value of χ_{act} $(T \to \infty)$ is 1 when $C = 1{\cdot}35$ as is observed for $Sr_2Co_2O_5$ (Grenier *et al* 1979). The $^3A_{2g}$ state is expected only for strongly distorted octahedra (Demazeau *et al* 1980). When the e_g electron is itinerant we may expect a stabilization of the $^3A_{2g}$ state also. However the presence of an

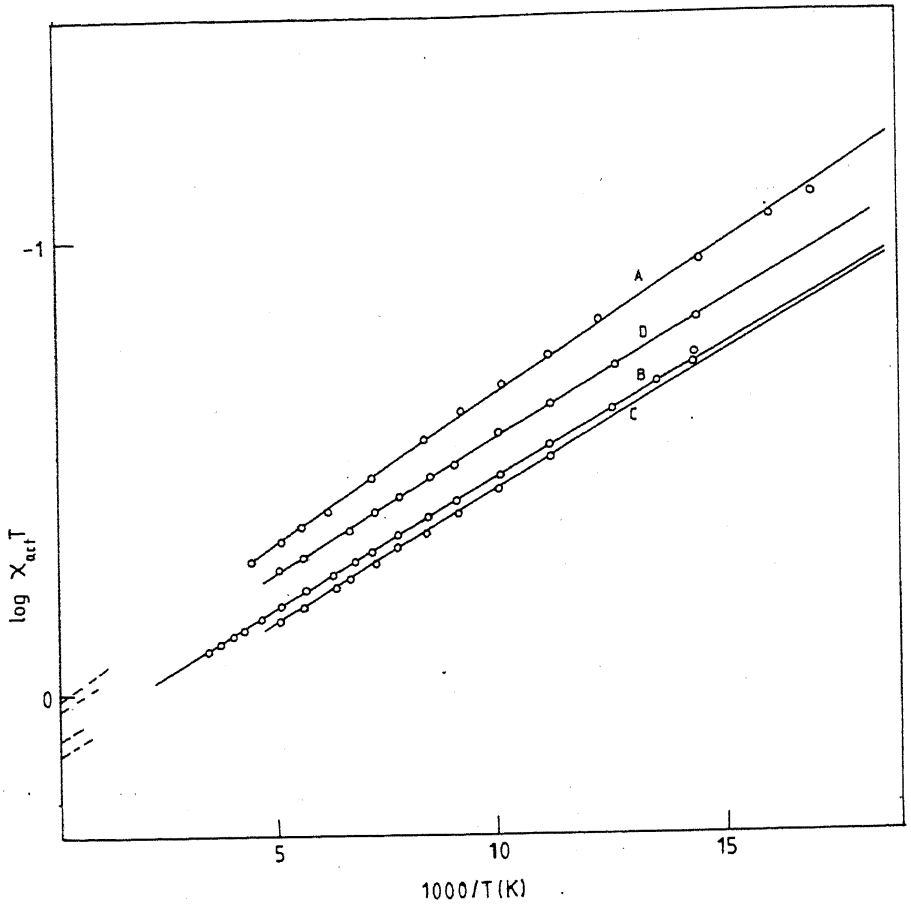

Figure 4. Log $\chi_{act}T-1/T$ plots for various $LaCoO_3$ samples.

Table 1. Magnetic susceptibility parameters for various compounds

Compound	$C^{(a)}$	E_a (eV)$^{(b)}$	T_{max} (K)$^{(c)}$	kT_{max} (eV)	$\chi_{act}T(T\rightarrow\alpha)^{(d)}$
900 AA	0·197	0·0132	150	0·0129	0·95
900 BO	0·159	0·0114	132	0·0113	1·20
1000 CA	0·207	0·0118	136	0·0117	1·29
1000 DO	0·253	0·0118	145	0·0124	1·02
$LaCo_{1-x}M_xO_3$					
M = Al	0·08	0·0140	162	0·0139	1·20
Fe	0·27	0·0114	145	0·0124	0.933
Ga	0·064	0·0108	132	0·0113	1·20
Cr	0·235	0·013	150	0·0129	1·20

(a) Obtained from low-temperature Curie-like behaviour
(b) Obtained from plots of log ($\chi_{act}T$) *vs* $1/T$
(c) Temperature at which χ_{act} *vs* T plots show a maximum
(d) Obtained from the intercept of log($\chi_{act}T$) *vs* $1/T$ plots at $1/T=0$

intermediate spin state at low temperature would require a reinterpretation of Mössbauer results which seem clearly to show the evidence for the presence of the high spin $^5T_2$ state.

3.2 $LaCo_{0.95}M_{0.05}O_3$, $M = Al, Ga, Fe, Cr$

The χ_M^{-1} *vs* T plots of the $LaCo_{0.95}M_{0.05}O_3$ (M = Al, Ga, Fe, Cr) are shown in figure 5. While the Al and Ga samples show a pronounced minimum the Fe and Cr samples show a continuous decrease in the χ_M^{-1} *vs* T plots. However, by subtracting the contributions from the Curie-like behaviour at low-temperatures to obtain χ_{act}, we find that the plots of log χ_{act} *vs* $1/T$ are straight lines and the results are similar to those obtained with $LaCoO_3$ samples. The T_{max} and E_a values are given in table 1. Only when M = Al or Cr is E_a significantly higher. This is consistent with the significantly smaller size of the Al ion which could increase the crystal field splitting energy Δ_{cf} and the pronounced octahedral crystal field stabilization energy associated with Cr^{3+} ion.

We have observed that the Curie constant C (table 1) obtained from the low temperature Curie-like behaviour when M = Fe and Cr is very close to that expected from the spin-only values of these ions (0·295 and 0·194 respectively). There is therefore probably no contribution to the low temperature behaviour from paramagnetic species associated with Co^{3+} ions. We note that C' for the $LaCoO_3$ samples is in the range of 0·16 to 0·22 which corresponds roughly to 5 or 7 % of high-spin Co^{3+} $(t_{2g}^4 e_g^2)$ $^5T_2$ states.

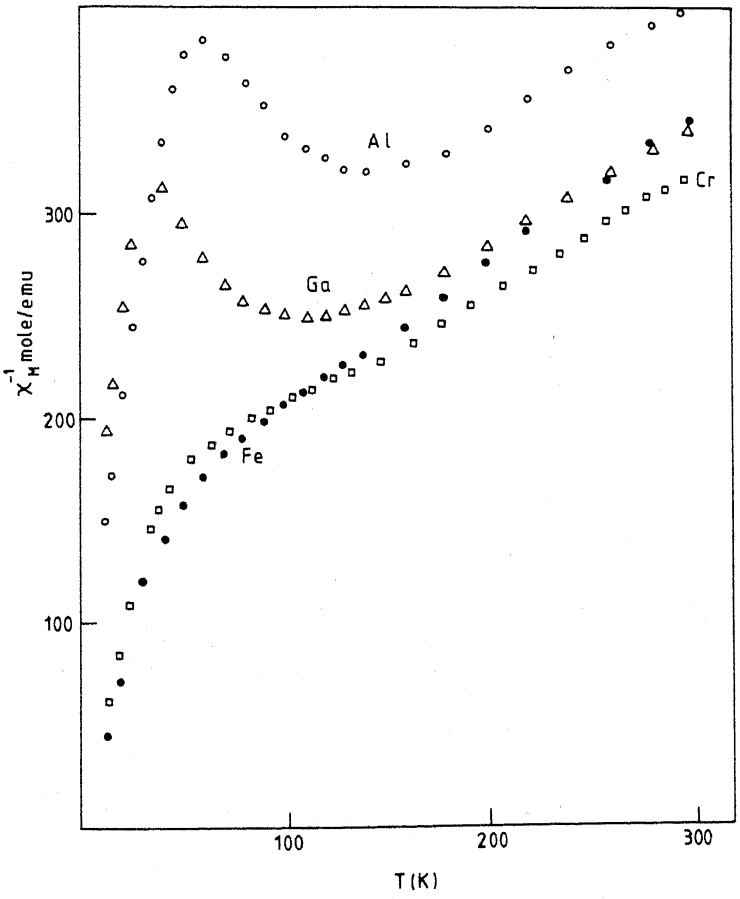

Figure 5. $\chi_M^{-1} - T$ plots for some $LaCo_{0.95}M_{0.05}O_3$ samples (M = Al, Cr, Fe and Ga).

The significance of these results is not clear to us. It has been pointed out by Ramasesha *et al* (1979) that mixing of spin states could lead to a finite population of the high-spin ion even at 0 K.

3.3 $LaCo_{0.95}M_{0.05}O_3$ ($M = Mn, Ni$) and $La_{0.98}Sr_{0.02}CoO_3$

The magnetic susceptibility of the $LaCo_{0.95}Mn_{0.05}O_3$ $LaCo_{0.95}Ni_{0.05}O_3$ and $La_{0.98}Sr_{0.02}CoO_3$ samples is shown in figure 6. Although the high-temperature susceptibility of all the samples is similar to that of $LaCoO_3$ (Madhusudan *et al* 1980) the low temperature susceptibilities are entirely different. $LaCo_{0.95}Mn_{0.05}O_3$ and $La_{0.98}Sr_{0.02}CoO_3$ show a Curie-like behaviour at low temperatures with C of 0·6 and 0·66 emu K/mol respectively, which is much too high to be associated with 5% of Mn^{3+} ions or 2% of Co^{4+} ions. These results have been interpreted (Vasanthacharya *et al* 1983) as evidence for existence of giant magnetic moments. For 5% Mn a C value of 0·5 would indicate the presence of giant moment with $S = 5$ while for 2% Sr a C value of 0·66 would indicate an $S = 16$. The exact model in which these moments are formed is difficult to predict at this stage, but the results indicate that in the case of Mn ions only the nearest neighbours are involved while in the case of Sr^{2+} ions a large molecular cluster is involved probably involving the Co ions adjacent to Sr^{2+} ions.

The surprising feature is the ferromagnetic behaviour at low temperatures of the Ni substituted compound. The Curie constant evaluated from the slope of the χ_M^{-1} *vs* T plot

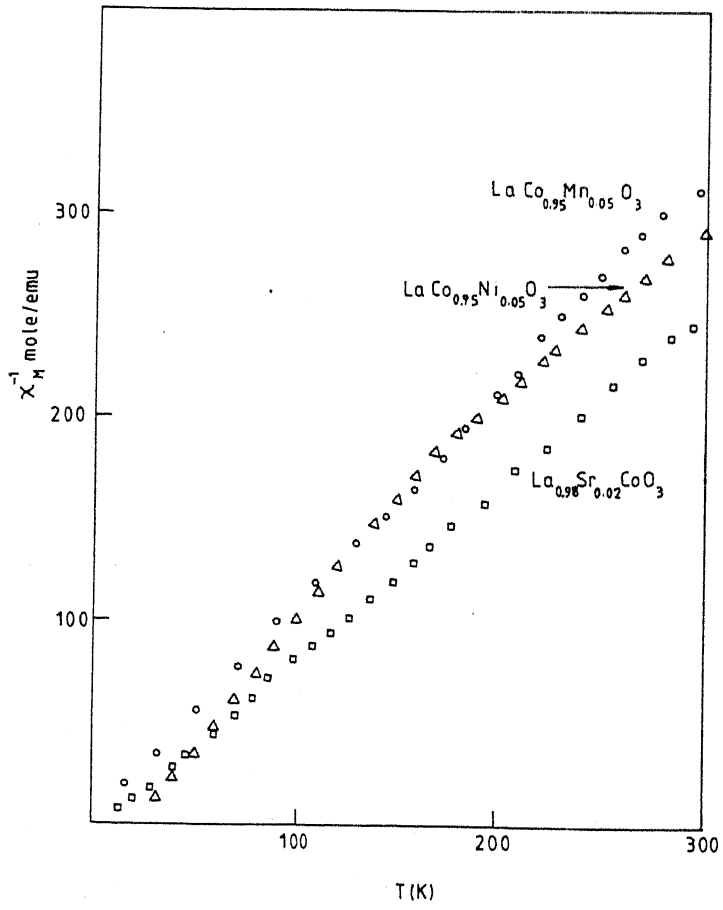

Figure 6. $\chi_M^{-1} - T$ plots for $LaCo_{0.95}Mn_{0.05}O_3$, $LaCo_{0.95}Ni_{0.05}O_3$ and $La_{0.98}Sr_{0.02}O_3$.

below 190 K is 0·8 while above 190 K is 1·18. These values are closer to the spin only value for an intermediate spin $S = 1$ Co species than for $S = 2$ species.

The above results could be important to understand the influence of magnetic exchange interaction in stabilizing the spin configurations. We note that an E_a of 0·01 eV correspond to nearly 120 K so that ordinary magnetic exchange interactions could stabilize a paramagnetic state. It seems that only ferromagnetic interactions affect the spin state. Ions such as Fe^{3+} or Cr^{3+} which are $L = 0$ ions would be involved in antiferromagnetic exchange interactions. We also note that ions such as Mn^{3+}, Ni^{3+} or Co^{4+} (low spin) are $L \neq 0$ ions and these ions could introduce locally a distortion of its octahedra. The intramolecular distortion due to the Jahn–Teller effect at the Mn^{3+}, Ni^{3+} or Co^{4+} sites may introduce a lattice strain near the site which favour the high-spin $^5T_2$ state (Madhusudan *et al* 1980; Kambara 1981). Once the paramagnetic spin state is stabilized long range magnetic exchange interactions become favoured.

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