A Magnetic Susceptibility Study of Spin-state Transitions in Rare-earth Trioxocobaltates(III)

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Rare-earth trioxocobaltates(III), $Ln[CoO_3]$, with Ln = Pr, Nd, Tb, Dy, and Yb exhibit low-spin to high-spin transitions of cobalt characterised by a maximum in the $\Delta\chi^{-1}$ against temperature plots where $\Delta\chi$ is the cobalt contribution to the magnetic susceptibility. The susceptibility behaviour is distinct from that of $La[CoO_3]$ which shows a plateau in the χ^{-1}–T curve accompanied by a structural transition. The temperature at which the $\Delta\chi^{-1}$–T curve shows a maximum increases with the decrease in the size of the rare-earth ion. The susceptibility behaviour of solid solutions of $La_{1-x}Nd_xCoO_3$ has been investigated to see how the behaviour characteristic of $Nd[CoO_3]$ changes to that of $La[CoO_3]$.

TRANSITIONS from the low-spin to the high-spin state of d^6 transition-metal ions are known to occur in transition-metal complexes as well as oxides.[1,2] These transitions can be abrupt or gradual and are sometimes accompanied by structural changes. Spin-state transitions have been extensively investigated by magnetic susceptibility and Mössbauer experiments in the case of iron(II) complexes. Among the transition-metal oxides the rare-earth trioxocobaltates(III) of formula $Ln[CoO_3]$ (Ln = La or rare earth) are so far the only solids known to exhibit such transitions.[2-4] Magnetic susceptibility and Mössbauer studies of $La[CoO_3]$ have shown that the cobalt ions in $La[CoO_3]$ are almost entirely in the low-spin state at low temperatures and transform to the high-spin state with increase in temperature.[5,6] In the 400—650 K region $La[CoO_3]$ exhibits a plateau in the χ^{-1} against T plot due to short-range ordering of the low- and high-spin ions. After the plateau region, there is long-range ordering of the two spin states accompanied by a change in the crystal symmetry. The exact shapes of the χ^{-1} against T plots have not been worked out in the case of the rare-earth cobaltates where both the rare-earth and cobalt ions have magnetic moments. A recent study [2] of the models for spin-state transitions in solids has shown that the nature of the χ^{-1} against T plots varies with the mechanism of the transition, but unfortunately with the exception of $La[CoO_3]$, no other experimental data are available for verifying these models. We, therefore, considered it important to investigate the temperature variation of the contribution to the magnetic susceptibility of cobalt ions in a few rare-earth trioxocobaltates(III), $Ln[CoO_3]$ (Ln = rare earth), in order to characterise the spin-state transitions in these systems. For this purpose, we measured the susceptibilities of $Ln[CoO_3]$ compounds (Ln = Pr, Nd, Gd, Tb, Dy, Ho, and Yb) in the range 100—1 000 K along with the corresponding aluminates, $Ln[AlO_3]$. From the difference in the susceptibilities of the corresponding cobaltates and aluminates, we have obtained the contribution of the cobalt ions to the susceptibility at different temperatures.

EXPERIMENTAL

All the materials were prepared using starting materials of better than 99.9% purity. Rare-earth trioxocobaltates(III) were prepared by the thermal decomposition of the corresponding cobalticyanides.[7] This procedure gives essentially stoicheiomtric cobaltates as the only solid products. The rare-earth aluminates were prepared from a stoicheiometric mixture of the rare-earth and aluminium nitrates, precipitated as hydroxides using ammonia (except in the case of $Pr[AlO_3]$). These were decomposed at 1 370 K in air with intermittent grinding. The compound $Pr[AlO_3]$ was prepared by heating a stoicheiometric mixture of Pr_2O_3 and Al_2O_3 in a vacuum. Solid solutions of $La_{1-x}Nd_xCoO_3$ were prepared by taking a stoicheiometric mixture of $La[CoO_3]$ and $Nd[CoO_3]$, converting them into nitrates, and decomposing at 1 070 K. The product was repeatedly ground and sintered at 1 120 K. X-Ray diffraction patterns of $La_{1-x}Nd_xCoO_3$ were recorded to ensure that the products were not mixtures, but true solid solutions. The crystal structure of the solid solution is identical to that of rhombohedral $La[CoO_3]$ when $x \leqslant 0.3$ and similar to that of tetragonal $Nd[CoO_3]$ when $x \geqslant 0.6$.

Magnetic susceptibility measurements were carried out in the 100—1 000 K range by the Faraday method employing a Cahn RG electrobalance. The susceptibilities were independent of field strength and all measurements were made at 3 000 G(1 G = 10^{-4} T). The instrument was calibrated with $HgCo(SCN)_4$. The values of χ_M are in c.g.s. units and the uncertainty in susceptibility measurements is *ca.* 0.1%. X-Ray diffraction patterns were recorded with a Philips X-ray diffractometer.

RESULTS AND DISCUSSION

The values of μ_{eff} and θ of $Ln[CoO_3]$ and $Ln[AlO_3]$ compounds obtained from our susceptibility data are listed in Table 1. The $\mu_{eff.}$ values of $Ln[AlO_3]$ at low temperatures are close to those expected for the Ln^{3+} ions; deviations are, however, seen at high temperatures. In view of this we have obtained the contribution of Co^{3+} ions to the susceptibility, $\Delta\chi$, by point to point subtraction of the susceptibility of $Ln[AlO_3]$ from that of $Ln[CoO_3]$. We have plotted the inverse of this difference between the magnetic susceptibilities of Pr, Nd, Tb, Dy, and Yb cobaltates and the respective aluminates, $\Delta\chi_M^{-1}$, against temperature in Figure 1. In principle, this difference should directly give the contribution to susceptibility from the cobalt ions, although such a subtraction procedure would involve greater uncertainties when the rare-earth ions have high magnetic moments as in $Gd[CoO_3]$ or $Ho[CoO_3]$. The shapes

of the $\Delta\chi^{-1}$–T plots of Pr, Nd, Tb, and Dy cobaltates are distinctly different from the χ^{-1}–T plot of La[CoO_3]. Unlike La[CoO_3] which shows a plateau in the χ^{-1}–T curve (in the 450—600 K region), the former cobaltates show promiment maxima in the $\Delta\chi^{-1}$–T curves. In Figure 2 we have plotted the $\mu_{eff.}$(Co) values of these cobaltates against temperature, the $\mu_{eff.}$ values being calculated from the $\Delta\chi$ values assuming that the Curie law holds. We see that $\mu_{eff.}$ (Co) of the cobaltates is essentially constant at low temperatures and shows a marked increase around a temperature corresponding to the maximum in the $\Delta\chi^{-1}$–T curve (Figure 1).

Magnetic susceptibilities of Gd[CoO_3] and Ho[CoO_3] are very close (within 0.5%) to those of the corresponding aluminates, Gd[AlO_3] and Ho[AlO_3], up to relatively high temperatures suggesting that most of the cobalt ions are in the diamagnetic low-spin state in these two cobaltates up to these temperatures (Figure 3). Deviation from the Curie–Weiss law found at low temperatures (*ca.* 500 K) in these compounds seem to be entirely ascribable to the rare-earth ion. The interpretation of the suceptibility of Gd[CoO_3] below 500 K by Casalot *et al.*[8] in terms of high-spin Co^{3+} ions appears to be in doubt since both Gd[CoO_3] and Gd[AlO_3] show identical susceptibility behaviour.

TABLE 1

Magnetic moments, $\mu_{eff.}$, and θ values of Ln[CoO_3] and Ln[AlO_3] [a]

Compound	Temperature range/K	$\mu_{eff.}$ [b] (Ln[BO_3])	θ/K (Ln[BO_3])	$\mu_{eff.}$ (Ln^{3+}) [c] theoretical
Pr[CoO_3]	<190	3.73	35	
	>700	6.36	524	
Pr[AlO_3]	<325	3.58	53	3.58
	>325	3.75	90	
Nd[CoO_3]	<250	3.71	51	
Nd[AlO_3]	<325	3.58	67	3.62
	325—550	3.87	132	
	>550	4.14	237	
Gd[CoO_3]	<370	7.80	3	
	370—500	8.56	70	
Gd[AlO_3]	<370	7.78	4	7.94
	370—500	8.52	62	
Tb[CoO_3]	<350	10.38	2	
	350—675	11.03	48	
	>675	12.52	245	
Tb[AlO_3]	<350	10.20	2	9.72
	350—625	10.76	40	
	>625	11.10	82	
Dy[CoO_3]	<365	10.41	3	
	365—625	11.02	47	
	>645	12.53	245	
Dy[AlO_3]	<310	10.18	1	10.63
	310—603	10.76	40	
	>625	11.08	79	
Ho[CoO_3]	<325	10.58	4	
	350—650	11.25	45	
	>650	12.33	176	
Ho[AlO_3]	<325	10.57	4	10.6
	350—650	11.26	44	
	>650	11.75	109	
Yb[CoO_3]	<375	5.38	77	
	375—850	5.67	107	
Yb[AlO_3]	<700	4.69	99	4.54
	>700	4.50	37	

[a] $\mu_{eff.}$ (Ln[BO_3]), where B = Co or Al, and θ (Ln[BO_3]) were obtained from least-squares fit of the susceptibility data to a Curie–Weiss law. [b] Units are Bohr magneton, $\mu_B = 0.927 \times 10^{-23}$ A m^2. [c] Calculated from the equation $\mu_{eff.} = g\sqrt{J(J+1)}\mu_B$.

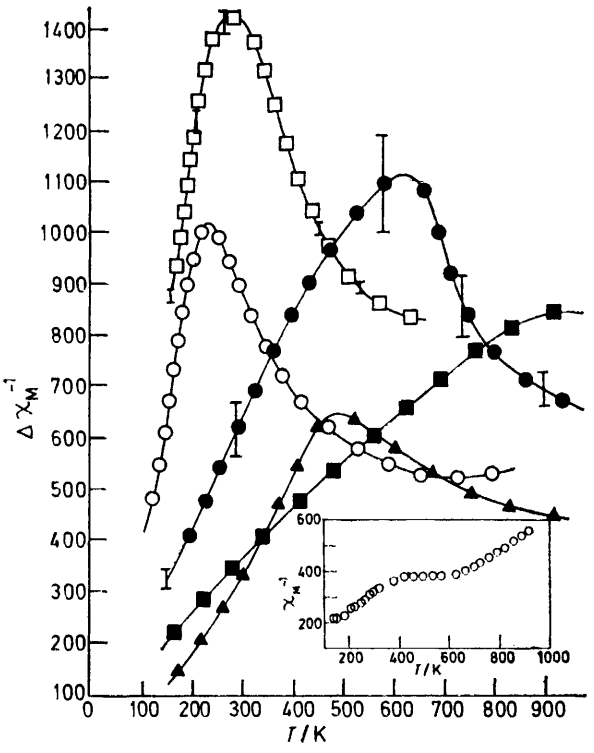

FIGURE 1 Plots of cobalt contribution to the inverse susceptibility against temperature in Pr(○), Nd(□), Tb (▲), Dy (●), and Yb (■) trioxocobaltates. $\Delta\chi$ values are in c.g.s. units. Error bars on a few points are shown to indicate experimental uncertainties. The χ^{-1}–T curve of La[CoO_3] is shown in the inset for comparison

From Figure 1 we see that the temperature corresponding to the maximum in the $\Delta\chi^{-1}$–T curves, T_{ms}, increases as the size of the rare-earth ion decreases. The same trend is seen in the temperature, $T\mu$, at which $\mu_{eff.}$ starts increasing significantly in the $\mu_{eff.}$(Co)–T plots of Figure 2. The values of T_{ms} and $T\mu$ are quite close to each other and both are listed in Table 2. We can consider these temperatures to reflect the spin-state equilibria in the rare-earth cobaltates. We shall refer to these temperatures as spin-state transition temperatures (following Demazeau *et al.*[9]). In the case of Gd and Ho cobaltates where we could not obtain clear maxima in the $\Delta\chi^{-1}$–T plots, we can take the tempera-

TABLE 2

Spin-state transition temperature (K) of Ln[CoO_3] compounds

Ln	T_{ms} from $\Delta\chi^{-1}$–T plots	$T\mu$ from μ_{eff}(Co)–T plots [a]
La	100 [b]	
Pr	220	200
Nd	285	240
Gd	500 [c]	
Tb	490	430
Dy	590	590
Ho	650 [c]	
Yb	860	830

[a] Temperature around which $\mu_{eff.}$(Co) shows a marked increase from the nearly constant value in Figure 2. [b] From ref. 4. [c] Temperature at which Ln[CoO_3] shows deviation in susceptibility from that of Ln[AlO_3].

tures at which χ^{-1} of the cobaltate differs from that of the aluminates (Figure 3) to be close to the spin-state transition temperatures; these temperatures do indeed fit in nicely with the other data (Table 2). The trend in spin-state transition temperatures found here also finds support from the susceptibility measurements of Demazeau *et al.*[9] on $Y[CoO_3]$ and $Lu[CoO_3]$ (prepared under high oxygen pressures) and of Kappatsch *et al.*[10] on

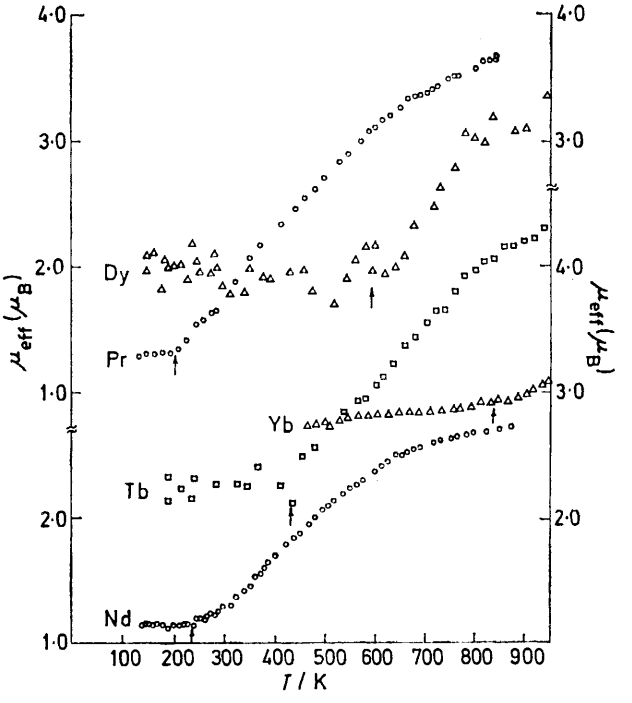

FIGURE 2 Plot of $\mu_{eff}(Co^{3+})$ in $Ln[CoO_3]$ against temperature. Arrows indicate $T\mu$ values

$Y[CoO_3]$. The χ^{-1}–T curves of these workers are similar to those of the $\Delta\chi^{-1}$–T plots shown in Figure 1. The transition temperatures of Demazeau *et al.*[9] vary in the order Gd < Y < Lu. The actual values of the transition temperatures found by us are generally higher, possibly due to the presence of slight non-stoicheiometry in the samples.

It has been pointed out that the low-spin–high-spin equilibria in rare-earth cobaltates is governed by the relative magnitudes of exchange energy and crystal-field splitting, Δ_{cf}. It is possible that the polarization of the ligand orbitals (in the CoO_6 octahedra) by the rare-earth ions may significantly affect Δ_{cf}. The increasing trend in the spin-state transition temperatures with the decreasing size of the rare-earth ion would suggest an increase in Δ_{cf} as we go down the rare-earth series. This would be consistent with the known decrease in the unit-cell volume of the cobaltates with the decreasing size of the rare-earth ion.[10] It can also be argued that Δ_{cf} should increase as we go down the rare-earth series because the π^* orbital gets significantly stabilised as we go from La to Lu as suggested by Demazeau *et al.*[9] It is possible that other factors may also contribute to the observed trend in the spin-state transition temperatures.

In the dynamic model of Ramasesha *et al.*[2] the difference in the low-spin and high-spin population is determined by a coupling constant which determines the strength of coupling of an ion *vs.* cage mode to the spin states; during such a vibration the symmetry of the crystal field changes and the two spin states mix. It is possible that as we go down the rare-earth series, the value of the coupling constant changes. We must point out that the shapes of the $\Delta\chi^{-1}$–T plots in the case of Pr, Nd, Tb, and Dy cobaltates in Figure 1 suggest that the mechanism of the spin-state transitions is likely to be different from that in $La[CoO_3]$ which shows a plateau in the χ^{-1}–T curve accompanied by a structural transition.[5,6] The shapes of the curves can be explained on the basis of the dynamic model of Ramasesha *et al.*[2] referred to earlier.

We have found another example of spin-state transition in a cobalt oxide system where the above model seems to be applicable. This is the oxide $La_2Co_{0.5}Li_{0.5}O_4$ which was described some time ago by Blasse.[11] This oxide is essentially diamagnetic up to *ca.* 300 K; above this temperature, the population of the high-spin state increases progressively. The χ^{-1}–T plot of this oxide shows a maximum around 275 K. The only difficulty with this system seems to be that there is

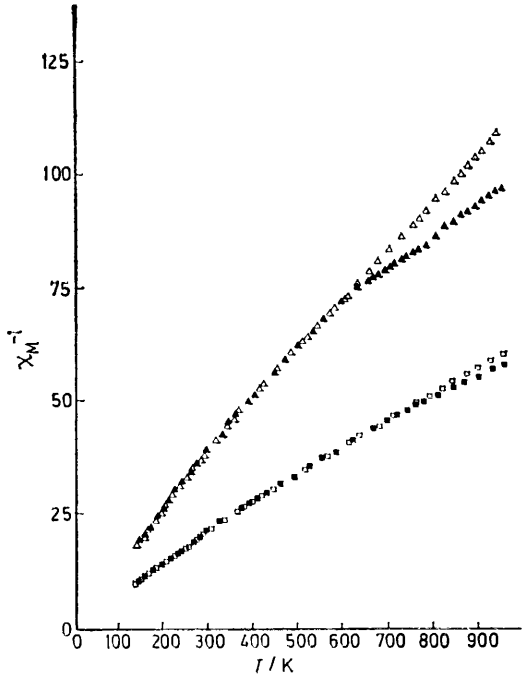

FIGURE 3 Inverse susceptibility against temperature plots for Gd and Ho trioxocobaltates and aluminates: $Gd[AlO_3]$ (△), $Gd[CoO_3]$ (▲), $Ho[AlO_3]$ (□), $Ho[CoO_3]$ (■)

always a small poroportion of Co^{2+} which may also contribute to the observed shape of the χ^{-1}–T plot.

A comment on the nature of cobalt states in $Ln[CoO_3]$ compounds at temperature well beyond the maxima in the $\Delta\chi^{-1}$–T curves would be pertinent. There is evidence to show that in this temperature range there may be charge transfer between high- and low-spin Co^{3+} producing Co^{2+} and Co^{4+} charge-transfer states.[3-5]

Such charge-transfer states are of importance in explaining the electron transport properties of the rare-earth cobaltates.

In order to find out whether there is a gradual vari-

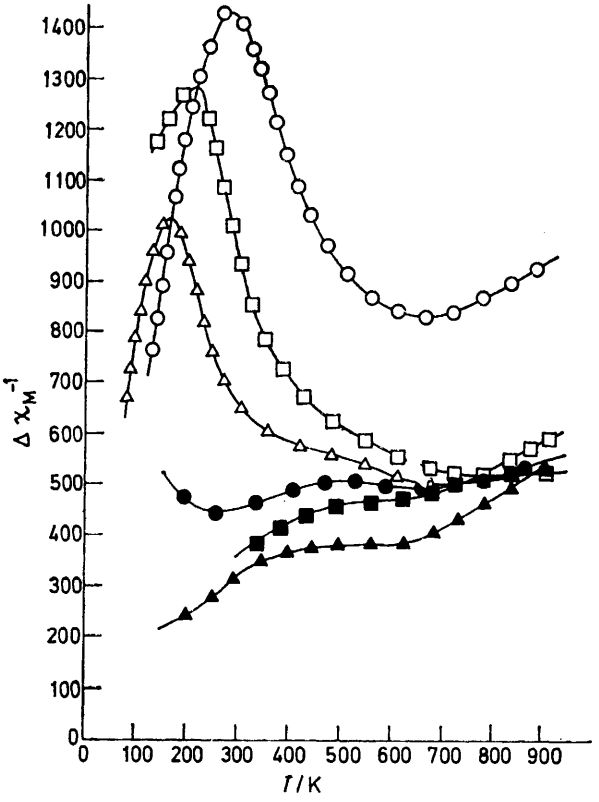

FIGURE 4 Temperature variation of the cobalt contribution to the inverse susceptibility of $La_{1-x}Nd_xCoO_3$: $x = 1$ (○), $x = 0.8$ (□), $x = 0.6$ (△), $x = 0.3$ (●), $x = 0.1$ (■), $x = 0$ (▲)

ation in the spin-state transition temperature in a solid solution of two rare-earth cobaltates, we have investigated the susceptibility behaviour of the $La_{1-x}Nd_xCoO_3$ system. In Figure 4 the contribution from the Co^{3+} ion to the magnetic susceptibility of the solid solutions is plotted against temperature. Figure 4 shows that the maximum in $\Delta\chi^{-1}$–T plot (shown by $Nd[CoO_3]$) is seen in $La_{1-x}Nd_xCoO_3$ solid solutions with $x \geqslant 0.6$. The temperature at which the maximum is seen progressively decreases with decrease in x, indicating that Δ_{cf} probably increases with increase in x as expected. Solid solutions with $x \leqslant 0.3$ do not appear to show such maxima; the susceptibility behaviour of the composition with $x = 0.1$ is in fact similar to that of $La[CoO_3]$ with a slight shift of the plateau region. It may be noted that compositions with $x \leqslant 0.3$ possess the rhombohedral structure of $La[CoO_3]$ while those with large x ($\geqslant 0.6$) possess the $Nd[CoO_3]$ structure.

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