Studies on the spin-state equilibria of cobalt ions in the system La$_{1-x}$Na$_x$Co$_{1-x}$Nb$_x$O$_3$ ($x \leqslant 0 \cdot 40$)

OM PARKASH*, N CHATURVEDI, M TIWARI[1] and
DEVENDRA KUMAR[2]

School of Materials Science and Technology, [1]Department of Electrical Engineering,
[2]Department of Ceramic Engineering, Institute of Technology, Banaras Hindu University,
Varanasi 221 005, India

Abstract. The spin-state equilibria of cobalt ions in the system La$_{1-x}$Na$_x$Co$_{1-x}$Nb$_x$O$_3$ ($x \leqslant 0 \cdot 40$) has been studied by measuring its magnetic susceptibility as a function of temperature in the range 300–600 K. It is found that the behaviour of the samples with $x \leqslant 0 \cdot 10$ is similar to that of LaCoO$_3$, while compositions with $x \geqslant 0 \cdot 20$ behave quite differently, exhibiting simple paramagnetic behaviour.

Keywords. Lanthanum sodium cobalt niobium oxide; spin-state equilibria; magnetic susceptibility.

1. Introduction

Lanthanum cobaltate (LaCoO$_3$) exhibits interesting electrical and magnetic properties due to the coexistence of low-spin as well as high-spin cobalt ions in it (Raccah and Goodenough 1967; Bhide *et al* 1972). The spin-state and valence state equilibria of the cobalt ions have been studied using Mössbauer spectroscopy and magnetic susceptibility measurements (Bhide *et al* 1972). At low temperatures cobalt ions are present in the low-spin state, Co^{III}, having the electronic configuration $t_{2g}^6 e_g^0$ with $s = 0$. On heating, low-spin cobalt ions, Co^{III} transform to high-spin cobalt ions, Co^{3+} having the electronic configuration, $t_{2g}^4 e_g^2$ ($s = 2$). This continues up to 200 K where the population of high-spin ions attains a maximum value. Beyond 200 K, electron transfer starts from Co^{III} to Co^{3+} giving rise to Co^{2+}, Co^{IV} etc. Ordering of low- and high-spin ions occurs within the temperature range 400–650 K. This is reflected by a plateau in the inverse susceptibility vs. temperature plot. The population of high spin ions decreases with increasing temperature and finally vanishes at 1210 K where it undergoes a localized to collective behaviour of d-electrons.

Recently, we studied the possibility of the formation of a solid solution between LaCoO$_3$ and NaNbO$_3$ in order to study the electrical behaviour of the resulting materials. It is found that a solid solution is formed over the entire range of composition in the system La$_{1-x}$Na$_x$Co$_{1-x}$Nb$_x$O$_3$ (Parkash *et al* 1988a). The structure and electrical conduction in this system have been reported (Parkash *et al* 1988b). It was considered worthwhile to study the magnetic susceptibility behaviour of these samples to see how the spin-state equilibria of cobalt ions is affected by simultaneous substitution of sodium at the lanthanum site and niobium at the cobalt site in LaCoO$_3$. In the resulting system, the electrical charge neutrality is

---

*For correspondence.

maintained internally without creating vacancies in any sublattice or change of oxidation state of any other ion. In this paper we report the results of our studies on the magnetic susceptibility measurements of compositions with $x \leqslant 0.40$. This study of spin-state equilibria is important as the properties of transition metal oxides are largely determined by the spin-state of the transition metal ions (Rao and Subbarao 1970).

2. Experimental

Compositions with $x = 0.01$, 0.05, 0.10, 0.20, 0.30 and 0.40 were prepared by the ceramic method using sodium carbonate, lanthanum oxalate, niobium pentoxide and titanium dioxide, all of purity greater than 99.5%. The details of the method of preparation have been reported earlier (Parkash *et al* 1988a). All the samples were found to be single phase solid solutions as indicated by X-ray diffraction patterns which did not contain any lines characteristic of the constituent oxides. The crystal structure and lattice parameters of these compositions have been reported earlier (Parkash *et al* 1988a). The magnetic susceptibility was measured as a function of temperature using a Gouy balance.

3. Results and discussion

Magnetic susceptibility was measured at various field strengths in the range 0.5–4.0 kG and the average was taken. The susceptibility was found to be independent of field strength indicating the absence of any magnetic ordering in these materials at and above 300 K. Plots of inverse susceptibility, χ^{-1} vs. T for all the samples are shown in figure 1. Compositions with $x = 0.01$, 0.05 and 0.10 show two regions within the temperature range 300–600 K. At low temperatures χ^{-1} vs. T plots are linear and a plateau is observed beyond 480 K for samples with $x = 0.01$, 0.05 and
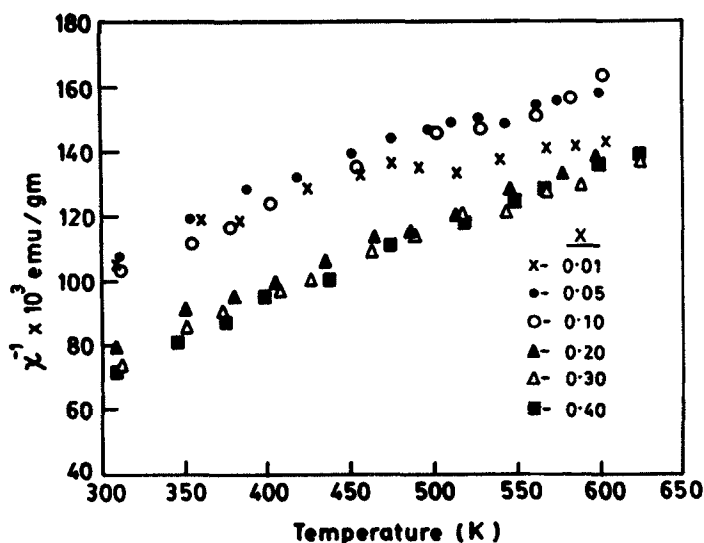

Figure 1. χ^{-1} vs. T plots for various samples in the system $La_{1-x}Na_xCo_{1-x}Nb_xO_3$.

0·10. The plateau in the χ^{-1} vs. T plot of $LaCoO_3$ signifies the ordering of low-spin and high-spin cobalt ions. It follows that the behaviour of compositions with $x = 0.01$, 0·05 and 0·10 is essentially similar to $LaCoO_3$. There is slight shift of the temperature where the ordering starts. This may be due to slight changes in the values of crystal field splitting, Δ_{cf} and exchange energies, Δ_{ex} which determine the energy difference between the low-spin state, Co^{III} and the high-spin state, Co^{3+}. It is worth mentioning that the temperature where the plateau starts is quite close to the temperature where the conductivity attains its saturation value (Parkash *et al* 1988b).

No plateau is observed in the χ^{-1} vs. T plots of compositions with $x \geqslant 0.20$. Their χ^{-1} vs. T plots are linear within the temperature range 300–600 K. This shows that the spin-state and valence state equilibria of cobalt ions is significantly affected in these compositions compared to that in $LaCoO_3$. The electrical conduction behaviour of these compositions is also different from that in compositions with $x = 0.01$ and 0·05.

In order to study the variation of population of high-spin and low-spin ions, we have plotted χT as a function of temperature, T, for all the samples in figure 2. χT should remain constant for a simple paramagnetic material obeying the Curie law while it should vary with T if the relative population of the two spin-states change as a function of temperature. The ratio of high spin to low-spin ions, m/n for such a case is given by

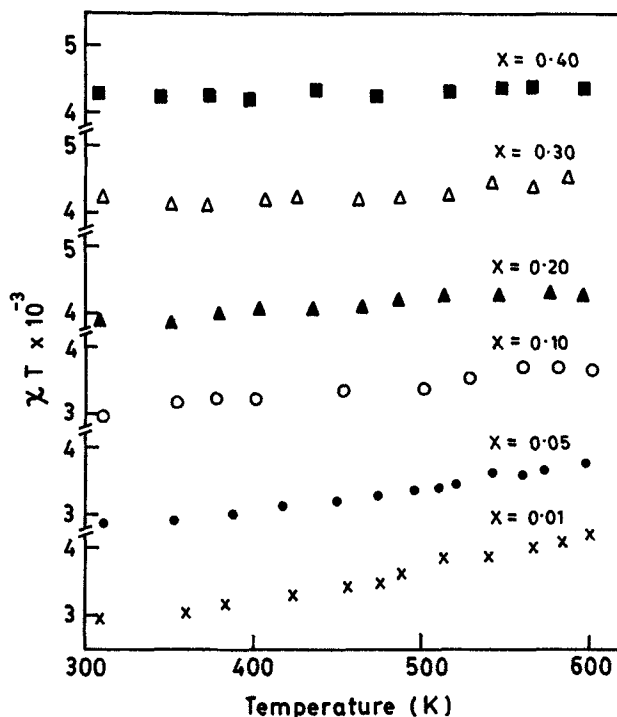$$\frac{n}{m} = \frac{Co^{III}}{Co^{3+}} = \frac{1}{[(N^2\mu^2/3RT)-1]}. \tag{1}$$

Figure 2. χT vs. T plots for various samples in the system $La_{1-x}Na_xCo_{1-x}Nb_xO_3$.

Table 1. Magnetic susceptibility χ and effective magnetic moment/cobalt ion for various samples in the system $La_{1-x}Na_xCo_{1-x}Nb_xO_3$.

x	χ at 300 K (emu/g) ($\times 10^{-6}$)	μ_{eff}/cobalt ion
0·01	9·8	3·3
0·05	9·3	3·2
0·10	10·3	3·2
0·20	13·0	3·7
0·30	20·0	4·7
0·40	20·0	5·4

It is observed from figure 2 that χT keeps increasing with T for samples with $x = 0·01$, 0·05 and 0·10. The increase in χT with T decreases with increasing x and the compositions with $x = 0·30$ and 0·40 show almost flat χT vs. T plots characteristic of simple paramagnetic behaviour. This is in conformity with our earlier conclusions drawn from χ^{-1} vs. T plots discussed above.

Values of effective magnetic moment/cobalt ion, μ_{eff}, for various samples at 300 K are given in table 1. It is noted that χ increases with increasing x while μ_{eff}/cobalt ion remains almost constant for the compositions with $x \leqslant 0·10$ beyond which it increases rapidly with x. In the system $La_{1-x}Na_xCo_{1-x}Nb_xO_3$, Nb^{5+} is in a d^0 configuration and magnetically insensitive. With increasing x, Co^{3+} ions become magnetically isolated and the high-spin state of trivalent cobalt ions are most likely. In the high-spin state Co^{3+} is in $t_{2g}^4 e_g^2$ configuration with 4 unpaired electrons which give the spin only value of $\mu_{eff} \sim (24)^{\frac{1}{2}} = 4·90$. Slight variation may be due to orbital contributions.

Acknowledgements

References

Bhide V G, Rajoria D S, Rao G R and Rao C N R 1972 *Phys. Rev.* **B6** 1021
Parkash O, Kumar R, Kumar D and Bahadur D 1988a *J. Mater. Sci. Lett.* **7** 383
Parkash O, Kumar D and Kumar R 1988b *Bull. Mater. Sci.* **10** 245
Raccah P M and Goodenough J B 1967 *Phys. Rev.* **155** 932
Rao C N R and Subbarao G V 1970 *Phys. Status Solidi.* (a), **1** 597