On the origin of itinerant electron behaviour and long-range ferromagnetic order in $La_{1-x}Sr_xCoO_3$

On the origin of itinerant electron behaviour and long-range ferromagnetic order in La$_{1-x}$Sr$_x$CoO$_3$

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Abstract. The itinerant electron ferromagnetism in La$_{1-x}$Sr$_x$CoO$_3$ ($0.1 \leqslant x \leqslant 0.5$) has been reinvestigated. AC magnetic susceptibility studies on these systems have been carried out for the first time. The nature of the susceptibility indicates the freezing of superparamagnetic clusters at low values of x (< 0.3) and long-range ferromagnetic order at higher values of x ($\geqslant 0.3$). Electrical resistivity studies show that itinerant electron behaviour with a positive temperature coefficient of resistance at low temperatures is obtained for $x \geqslant 0.2$. Metallization and long-range ferromagnetic order thus seems to be associated with different origins. Chemical systematics obtained from the changes in lattice parameters show that the expansion of LaCoO$_3$ on the substitution of La by Sr stabilizes the paramagnetic states of Co ions which are in predominantly diamagnetic low-spin state in LaCoO$_3$. The core $S = 1$ spins of trivalant Co seems to be coupled ferromagnetically by the itinerant electron in a manner similar to the Zener double-exchange mechanism.

1. Introduction

There are relatively few perovskite oxides which have been discovered to be ferromagnetic since the early pioneering work of van Santen and Jonker (1950), Jonker and van Santen (1953), Goodenough (1958), Raccah and Goodenough (1968) and others. Among the rare-earth perovskite oxides LnMO$_3$ (Ln $\equiv$ rare-earth ion; M $\equiv$ transition-metal ion) there are those involving M $\equiv$ Mn which may be rendered ferromagnetic by substitution (Goodenough 1971, Goodenough and Longo 1970) at M sites as in La$_2$MnNiO$_6$ or La$_2$MnCoO$_6$. The others are compounds (Goodenough 1971, Goodenough and Longo 1970) such as Ln$_{1-x}$A$_x$MO$_3$ where itinerant holes are believed to be introduced into the parent LaMO$_3$ compounds by doping with divalent A ions and M $\equiv$ Co or Mn.

The conventional itinerant electron ferromagnets such as Fe, Co or Ni have charge carriers which are mainly of s character while the magnetism arises from the d electrons. In compound such as the halides or oxides the s and p electrons are usually in filled bands or shells. It is the d electrons which are in partially filled bands or orbitals. In the itinerant electron ferromagnetic oxides the d electrons have to possess simultaneously charge as well as spin character (Anderson 1991, 1992). The understanding of the origin of itinerant electron behaviour and ferromagnetism in La$_{1-x}$Sr$_x$MO$_3$ systems is therefore important in this context.

For localized electron systems such as K$_2$CuF$_4$, Rb$_2$CrCl$_4$, MnF$_3$ or oxides such as La$_2$MnNiO$_6$, it seems to be straightforward to understand the origin of ferromagnetism in terms of simple super-exchange rules (Goodenough 1955, 1962, 1963, Day 1979, Stead and Day 1982). The high electrical conductivity (10^1–10^2 S cm^{-1}) of La$_{1-x}$A$_x$MnO$_3$

compounds compared with that of other oxides known at the time led Zener (1951) to propose the double-exchange mechanism for ferromagnetism. In the mixed-valence Mn^{3+} t_{2g}^3, e_g^1–Mn^{4+} t_{2g}^3, e_g^0 systems the hopping of the e_g electron of Mn^{3+} to Mn^{4+} renders the initial Mn^{3+}–Mn^{4+} state degenerate with the final Mn^{4+}–Mn^{3+} state. Under these conditions the electron hopping would not be activated. Zener (1951) proposed that the hopping of the e_g electron with conservation of spin angular momentum leads to a ferromagnetic coupling of the t_{2g} electron because of the Hund rule coupling between the t_{2g} and e_g electrons. Such a mechanism is not applicable in a straightforward manner to $La_{1-x}Sr_xCoO_3$. The spin state of the trivalent Co ion in the parent $LaCoO_3$ is not well defined, being predominantly in the low-spin diamagnetic $Co(III)t_{2g}^6 e_g^0$ state at low temperatures. Although itinerant electron behaviour due to the mixed valence is still possible, the appearance of ferromagnetism requires the preparation of suitable paramagnetic spin states before they can participate in a cooperative magnetic ordering process. Changes in the spin-state configuration of the cobalt ions have been examined in some detail by Mössbauer spectroscopy (Bhide *et al* 1972, 1975).

Just as the definition of the spin state of the metal ion is necessary to define the ferromagnetic order parameter, one requires an operative criterion for the existence of itinerant electron behaviour and the nature of such an itinerant state. The magnitude of the resistivity may be used to define (Mott and Kaveh 1985, Lee and Ramakrishnan 1985) itinerant electron behaviour. The temperature coefficient of resistivity (TCR) in concentrated oxide systems (Rao and Ganguly 1985a, b) is found to change sign at a resistivity of about $2 \, m\Omega \, cm$. The magnitude of the resistivity of $La_{1-x}Sr_xMnO_3$ (greater than $2 \times 10^{-3} \, \Omega \, cm$ (van Santen and Jonker 1950, Jonker and van Santen 1953, Santhosh *et al* 1993) and $La_{1-x}Sr_xCoO_3$ (less than $2 \times 10^{-3} \, \Omega \, cm$ (Rao and Ganguly 1985a, b, Rao 1986)) places these two systems in different domains of metallic behaviour.

We see from the above that, although the $La_{1-x}Sr_xMO_3$ ($M \equiv Co$ or Mn) systems are magnetically similar, they are electrically different. Thus, one may expect that the establishment of long-range ferromagnetic order may be delinked from the itinerancy of the charge carried in $La_{1-x}Sr_xCoO_3$. In this paper the properties of $La_{1-x}Sr_xCoO_3$ have been reinvestigated by various techniques, some of them for the first time. We have paid attention to examining the changes in its electrical and magnetic properties in the early stages of doping. A low-field AC susceptibility study has been carried out for the first time to examine the mechanism of the onset of long-range ferromagnetic order *vis-à-vis* the formation of superparamagnetic clusters. We find evidence that the onset of itinerant electron behaviour and long-range ferromagnetic order do not appear at the same value of x.

2. Experimental details

The $La_{1-x}Sr_xCoO_3$ compounds ($x \leqslant 0.5$) were prepared by the standard ceramic technique (van Santen and Jonker 1950, Jonker and van Santen 1953, Goodenough 1958, Raccah and Goodenough 1968, Bhide *et al* 1972, 1975) using La_2O_3 (pre-fired at $1000\,°C$), cobalt oxalate, $CoC_2O_4 \cdot 2H_2O$ and $SrCo_3$ in the required stoichiometry. The starting mixture was ground thoroughly under alcohol and pre-fired at $900\,°C$ in air for 8 h. It was then reground, pelletized and fired in air at $1150\,°C$ for 24 h with several intermittent regrinding and pelletizing process. The oxygen content was determined using a standard iodimetric technique. A saturated solution of potassium iodide was used for the titrations.

The lattice parameters as well as the positional coordinates were refined using a standard powder diffration package program (Calligaris and Geremia). The computer program was provided by the International Centre for Theoretical Physics, Trieste, Italy, and was written by Professor M Calligaris and Dr S Geremia of the Department of Chemical Sciences, University of Trieste, Italy.

The electrical conductivity and AC susceptibility could be measured between 10 and 300 K. The electrical conductivity was measured using a standard four-probe technique. The AC susceptibility was measured by the standard technique (Blithe 1985) using a commercial APD Cryogenics System (P/N 2571570-C). The AC field was produced with a primary coil. The induced field in two secondary coils wound in opposite directions (for balancing) was measured. The average of two measurements with the sample in the different coils were taken to obtain an accurate estimate of the intensity as well as the phase. In reporting the results in the various figures we have calculated the so-called molar susceptibility from the induced magnetization and the amplitude h_0 of the applied AC field and the weight of the sample taken. The samples were taken in the form of a long cylinder with its axis parallel to that of the applied field. The measured AC susceptibility is expected to be accurate in the paramagnetic region at high temperatures. We find that, even at low temperatures, demagnetization effects are very strong for the measuring field (amplitude of the AC field, about 6 Oe).

3. Results

3.1. X-ray diffraction studies

The x-ray diffraction patterns of the various samples show no impurity phases when the samples were prepared by heat treatment at 1150 °C. All the samples could be indexed on the basis of a rhombohedral cell (figure 1). When heated at lower temperatures (1050 °C) there was always some small amounts of impurity phases. However, the major effect is a larger rhombohedral distortion in the samples fired at lower temperatures.

The changes in the rhombohedral unit-cell parameters (figure 2(a)) as well as the oxygen stoichiometry are given in table 1. The rhombohedral cell parameters were obtained from a refinement of the x-ray diffraction lines using a hexagonal unit cell (figure 1). The hexagonal cell parameters a_H and c_H, are also given in table 1 and figure 2(b).

Table 1. Rhombohedral, hexagonal and primitive perovskite unit-cell parameters of $La_{1-x}Sr_xCoO_{3-\delta}$.

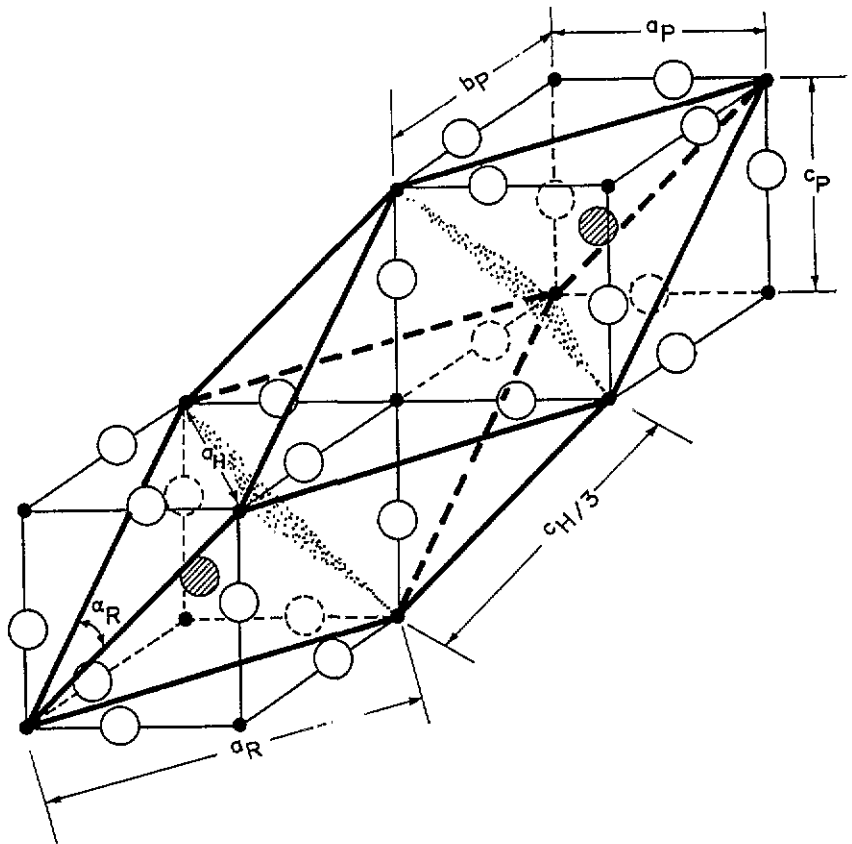|	Hexagonal		Primitive perovskite[a]		Rhombohedral		
x	a_H (Å)	c_H (Å)	a_P, b_P (Å)	c_P (Å)	c_{rhomb} (Å)	Rhombohedral angle (deg)	δ
0.50	5.419 ± 0.005	13.261 ± 0.005	3.832 ± 0.005	3.826 ± 0.005	5.416 ± 0.005	60.04	0.04±0.02
0.40	5.416	13.245	3.830	3.822	5.410	60.07	0.03
0.30	5.423	13.213	3.837	3.812	5.389	60.50	0.00
0.20	5.436	13.158	3.844	3.797	5.393	60.53	0.04
0.10	5.441	13.143	3.848	3.793	5.390	60.62	0.04
0.05	5.432	13.112	3.847	3.779	5.379	60.65	0.03

[a] $a_P = b_P = a_H/\sqrt{2}$; $c_P = c_H/2\sqrt{3}$.

Figure 1. Relationship between the rhombohedral cell and hexagonal cell parameters of $LaCoO_3$ (after Goodenough and Raccah (1967)); hatched circle, La; $\bigcirc$, oxygen; $\bullet$, Co. The primitive perovskite cell parameters a_P, b_P and c_P are shown.

The relationship between the primitive perovskite cell and the rhombohedral cell are shown in figure 1. We have assumed that $a_H \simeq \sqrt{2}a_P = \sqrt{2}b_P$ so that $c_H \simeq 2\sqrt{3}c_P$ where a_P, b_P and c_P are the primitive perovskite unit-cell parameters. It is seen that, as x increases, the unit-cell volume increases rapidly up to $x = 0.1$ after which it remains nearly independent of x. a_H and hence a_P and b_P do not change significantly with x. c_P increases with increasing x and the system becomes nearly cubic at around $x = 0.4$. For small values of x $c_P/a_P < 1$, it is seen that, as x increases, the unit-cell volume *increases* despite the creation of holes.

3.2. AC susceptibility studies

In figure 3 we show the typical results of the temperature dependence of the harmonic component of the AC (30 Hz; AC magnetic field $h_0 \simeq 6$ Oe) magnetic susceptibility χ_{AC} (full curves), normalized per formula weight of the substance as mentioned in section 2. All the samples show a maximum in the susceptibility at a temperature denoted T_{max}. The magnitude χ_{max}, of the susceptibility at the maximum, decreases with decreasing x. We find that the susceptibility behaviours of the $x = 0.3$–0.5 samples are rather similar in shape. All these samples have an asymmetry which is typical of ferromagnetic compounds

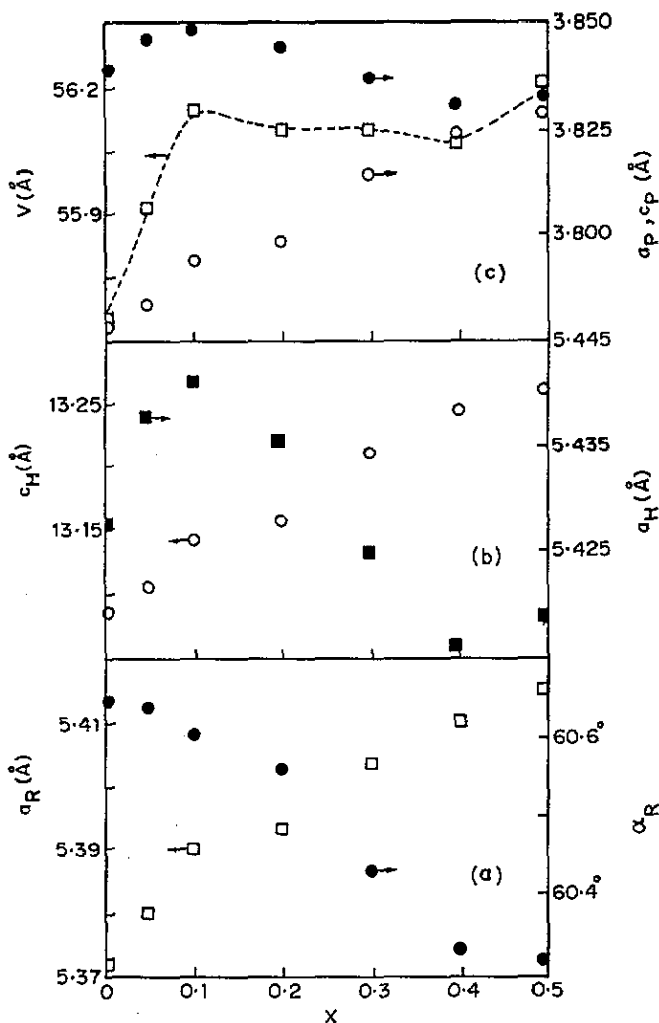**Figure 2.** Changes in lattice parameters as a function of x for $La_{1-x}Sr_xCoO_3$ for (a) a rhombohedral unit cell, (b) a hexagonal unit cell and (c) unit-cell volume and primitive perovskite cell parameters: ●, $a_P = b_P$; ○, c_P.

such as $Fe_{0.5}TiS_2$ (Negishi *et al* 1987). The sharp knee-like characteristic of intermetallic ferromagnet (Verbeek *et al* 1978) is not seen in these compounds. The $x = 0.1$ sample shows a marked decrease in the magnitude of χ_{max} as well as T_{max} (figure 3). The width $w(= T_{max} - T'$; see figure 3) of the ascending part of the susceptibility for $T > T_{max}$ is found to decrease with increasing x. The χ_{AC} versus T plots for the $x = 0.2$ and $x = 0.1$ compositions resemble that of cluster glasses (Negishi *et al* 1987).

The inverse of the AC susceptibility χ_{Sr} *per gram-atom of strontium* shows a Curie–Weiss behaviour at high temperatures (figure 4) with a positive paramagnetic Curie temperature Θ typical of ferromagnets. The temperature T_{fc} at which there is a sharp increase in the susceptibility in the χ_{AC}^{-1} versus T plots (for $T > \Theta$) may be associated with the formation of superparamagnetic clusters. T_{fc} is not very sensitive to the value of x and is within $0.8T_{max}$ of the $x = 0.5$ composition. The Curie constant C and the paramagnetic Curie temperature
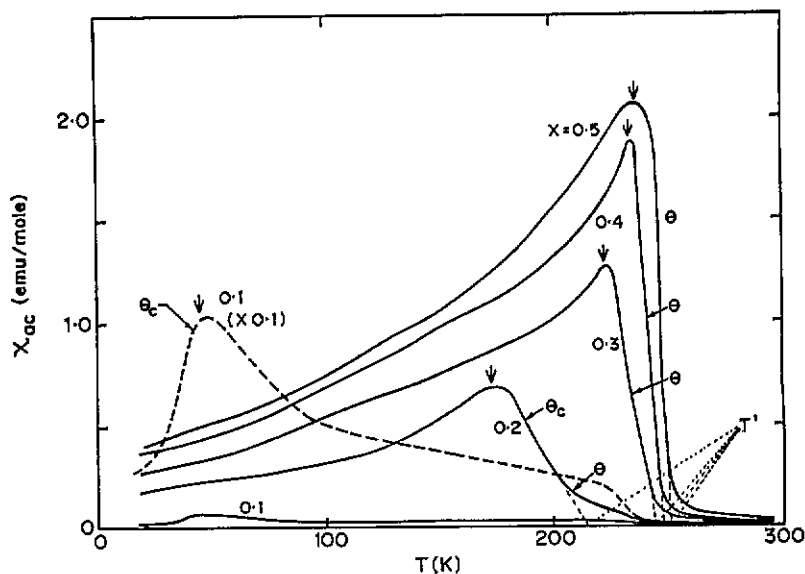
Figure 3. χ_{AC} versus T plots of the $La_{1-x}Sr_xCoO_3$ compositions; Θ and Θ_c obtained from figure 4 are indicated on the curves. The temperatures (see text) T_{max} (indicated by arrows) and T' are indicated.

Θ obtained from the high-temperature $(T > T_{fc})$ data in figure 4 are given in table 2. The Θ values thus obtained are shown in figure 3 against the corresponding curves. The Θ values are markedly higher than the temperature T_{max} at which the susceptibility reaches a maximum $\Theta \sim \frac{1}{2}(T_{max} - T')$ and is close to the temperature at which the slope $d\chi/dT$ has its maximum value. The C-values for $T > \Theta$ are nearly the same for the $x = 0.2$–0.5 compositions.

Table 2. AC susceptibility parameters for $La_{1-x}Sr_xCoO_3$. T_{max}, T' and Θ are defined in the text.

	Bulk			Cluster			
x	T_{max} (K)	Θ (K)	C^a (emu K)	C_c^b (emu K)	Θ_c (K)	T_{fc} (K)	T' (K)
0.50	238	246	1.053	—	—	—	251
0.40	234	242	0.614	—	—	—	249
0.30	228	232	0.613	—	232	244	245
0.20	174	209	0.251	15.1	186	236	215
0.10	48			20.3	40	228	85

[a] Calculated per mole of $La_{1-x}Sr_xCoO_3$.
[b] Calculated per gram-atom of Sr.

The χ_{Sr}^{-1} versus T plot (figure 4) shows a linear behaviour over a considerable temperature range for $T < T_{fc}$ for the $x = 0.1$ and 0.2 compositions. This yields another paramagnetic Curie temperature Θ_C and Curie constant C_C. The relatively large values of C_C indicate the formation of giant or superparamagnetic spins at low temperatures. Vasanthacharaya *et al* (1984) have earlier arrived at the same conclusion for the $x = 0.02$
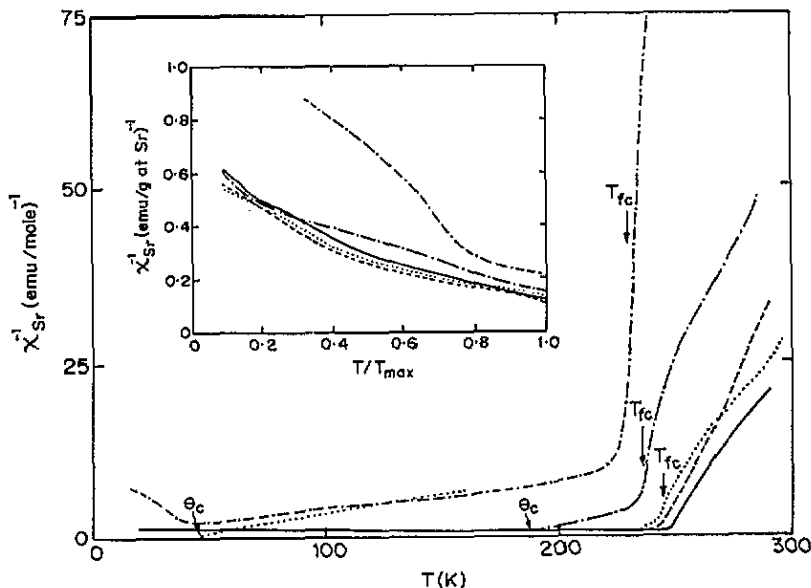
Figure 4. Plots of the inverse AC susceptibility χ_{Sr}^{-1} per gram-atom of Sr versus T for the $La_{1-x}Sr_xCoO_3$ compositions: ——, $x = 0.5$; - - - -, $x = 0.4$; · · · · · ·, $x = 0.3$; — · —, $x = 0.2$; and — · · —, $x = 0.1$. The extrapolation to obtain θ_c are shown for the $x = 0.1$ and 0.2 samples. The inset shows the plot of χ_{Sr}^{-1} versus T/T_{max}.

composition using the DC Faraday susceptibility techniques. T_{max} and Θ_C are much smaller than T_{fc} for the $x = 0.1$ composition with $T_{max} \sim \Theta_C$. In the case of the $x = 0.2$ composition, Θ_C (see table 2) instead of Θ (figure 3) is now near the midpoint of w. For the $x = 0.2$ composition the susceptibility for $T < \Theta$ is dominated by the susceptibility of the superparamagnetic clusters. The maximum in the susceptibility for $x = 0.1$ occurs at $T = \Theta_C$. This is consistent with the formation of 'giant-moment' ferromagnets (Nieuwenhuys 1975).

In the inset of figure 4 we have shown the plots of χ_{Sr}^{-1} versus T/T_{max} for $T < T_{max}$ which shows that the susceptibility below T_{max} scales well with the Sr content for $x \geqslant 0.2$. In the case of the $x = 0.1$ composition, χ_{Sr}^{-1} is a factor of 2 less than that of the other plots.

3.2.1. Nature of AC susceptibility. The total AC susceptibility consists (Fritzsche 1978) of three parts, given by terms proportional to N_f, N_c and N_b which represent the number of free spins, the number of spins in a cluster above its blocking temperature and the number of spins in a blocked cluster, respectively. In our systems we expect $N_c + N_b$ to be a constant. Above the Curie temperature, one would expect $N_b \simeq 0$. The absence of Curie-like behaviour at low temperatures suggests that $N_f \simeq 0$ in the temperature range studied.

The susceptibility of the clusters is expected to show Curie–Weiss-like behaviour for each cluster:

$$\chi_C(0) = C_C/(T - \Theta_C). \tag{1}$$

Earlier DC susceptiblity studies on the $x = 0.02$ composition showed a low-temperature enhancement of the susceptibility arising from the ferromagnetic coupling of eight nearest-neighbour Co ions for each Sr ion ($C_C \simeq 33$ emu K (g-atom Sr)$^{-1}$). It is apparent that
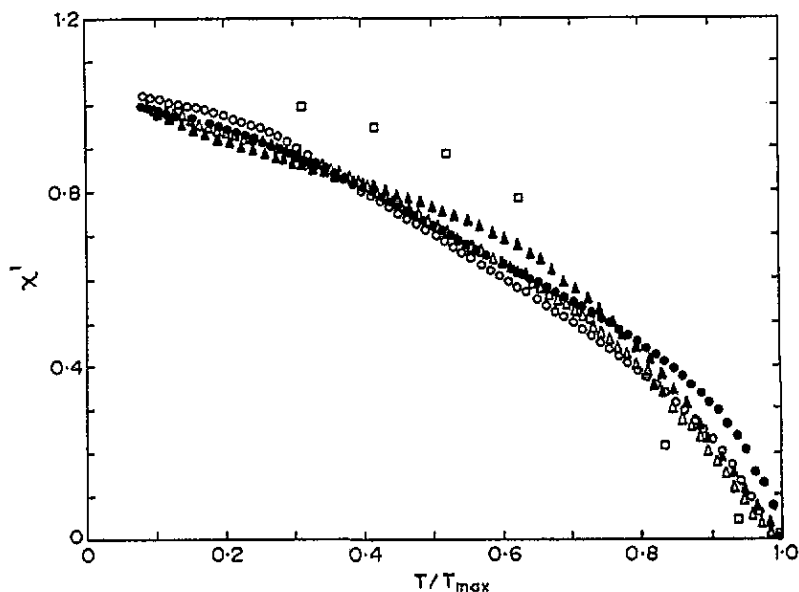
Figure 5. Normalized plots of χ versus T/T_{max} for the $La_{1-x}Sr_xCoO_3$ compositions; $\chi' = [\chi_{max} - \chi_{AC}(T)]/(\chi_{max} - \chi_b)$ for different values of x in $La_{1-x}Sr_xCoO_3$: ●, $x = 0$; □, $x = 0.2$; ○, $x = 0.3$; ▲, $x = 0.4$; △, $x = 0.5$.

when $x > 0.125$, such isolated clusters may not be present. Thus C_C is decreased to about 15 emu K (g-atom Sr)$^{-1}$ when $x = 0.2$.

An important feature of the susceptibility is that below T_{max} the plots of $[\chi_{max} - \chi(T)]/(\chi_{max} - \chi_b)$ versus T/T_{max} nearly overlap each other (figure 5) for all values of x (especially for $0.2 \leqslant x \leqslant 0.5$), where χ_b is the extrapolated value at 0 K. The decrease in the AC susceptibility is a measure of N_b, the number of blocked spins which do not follow the oscillating field. Below the freezing or blocking temperature, $N_b \neq 0$ and is expected to increase at the expense of N_c with decreasing temperature. Thus, $N_b \neq 0$ may be related to the spontaneous magnetization in ferromagnets. It has been reported that the magnetization behaviour of $La_{0.5}Sr_{0.5}CoO_3$ below T_C is not classical and does not show a saturation at low temperatures as expected from the classical Brillouin function behaviour. Goodenough has attributed the non-saturation to the itinerancy of the e_g electron in the $x = 0.5$ system. The shapes of the curves in figure 5 reflect this deviation from the Brillouin function behaviour. The scaling behaviour of the magnetic susceptibility (figure 4, inset, and figure 5) as a function of x for $0.2 \leqslant x \leqslant 0.5$ shows that the ferromagnetism in the blocked-spin state is local in character. For small concentrations of Sr, ferromagnetic clusters are formed and at larger concentrations they are connected to give long-range ferromagnetic order.

3.3. Electrical resistivity studies

The changes in the electrical resistivity of the samples as measured by us are shown in figure 6. The $x = 0.2$ samples shows a lower resistivity than the $x = 0.3$ composition in our preparations. The magnitude of the resistivity of the $x \simeq 0.2$ ($0.125 < x < 0.25$) compositions are rather sensitive to the preparation conditions. This aspect is being more thoroughly investigated. The electrical resistivity behaviour is similar to that reported earlier (Goodenough 1958, Raccah and Goodenough 1968, Rao 1986). The TCR changes sign for

the $x \geqslant 0.2$ samples which have a resistivity of less than 2 Ω cm. A positive TCR is typical of metals in which the elastic scattering length scale is less than that of the inelastic scattering length. There is a marked decrease in the resistivity at a temperature which coincides with the Θ-values mentioned above. Such a deviation from linearity below the magnetic ordering temperature has been noted earlier by Raccah and Goodenough (1968). The average slopes of the p versus T plots increase with increasing x.
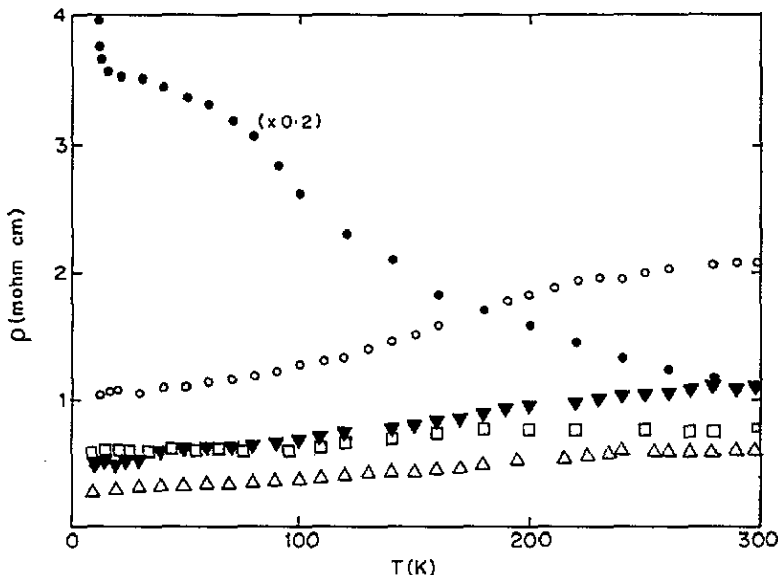

Figure 6. ρ versus T plots for $La_{1-x}Sr_xCoO_3$ samples: ●, $x = 0.1$; □, $x = 0.2$; ○, $x = 0.3$; ▼, $x = 0.4$; △, $x = 0.5$.

4. Discussion

4.1. Spin state of cobalt ions

Consideration of the spin or valence state of precursor individual species is important as it gives insight into the hybridized states in the solid. Some chemical arguments therefore become essential in understanding the properties of oxides. c_P is determined (see figure 1) by the size of both the A (La or Sr) ions. $c_P \simeq \sqrt{2}(r_A + r_X)$ while $a_P = b_P \simeq \sqrt{2}(2r_X)$. The ratio of the unit-cell volumes for two different ions A and A' is then given approximately by $(r_A + r_X)/(r_{A'} + r_X)$. Since a_P does not change much with x, the increase in the unit-cell volume in the above model is mainly due to the substitution of the La^{3+} ion ($r_{La} = 1.36$ in twelvefold coordination) by the larger Sr^{2+} ion (1.44 Å) (Shannon 1976). The ratio of the increase in the unit-cell volume on going from $LaCoO_3$ to $La_{0.5}Sr_{0.5}CoO_3$ is then expected to be 1.015 which is close to what is observed (about 1.010). The maximum at intermediate values of x is due to other electronic factors and could be crucial in understanding the details of the problem.

The activation energy for the low-spin-to-high-spin transition of trivalent cobalt ions in oxides is in general very small, being of the order of 0.02 eV. The increase in volume

due to Sr substitution for La could lead to a cooperative effect with a conversion of the diamagnetic low-spin state to paramagnetic spin states with a further increase in the volume. Trivalent cobalt ions in oxide matrices show evidence for a conversion from the low-spin $S = 0$ (Co(III) t_{2g}^6, e_g^0) state through an intermediate-spin $S = 1$ (which we shall refer to in chemical terms for convenience hereafter as Co(iii) t_{2g}^5, e_g^1) state to the high-spin $S = 2$ (Co^{3+} t_{2g}^4, e_g^2) state. The magnetic susceptibility studies are consistent with the initial formation of the Co(iii) state from the low-spin configuration. On doping with Sr one expects to obtain states derived from tetravalent cobalt ions with either low-spin Co(IV) t_{2g}^5, e_g^0 configuration or intermediate-spin Co(iv) t_{2g}^4, e_g^1.

There is also the question of the creation of holes on oxygen and the possible role of the magnetic moments on the ligands created by such doped holes in the presence or absence of orbital degeneracy. This aspect has been qualitatively examined by Ganguly *et al* (1992) in the context of the magnetic properties of systems containing trivalent Ni ions using spin conservation arguments. They suggested that, when the precursor metal oxidation states are paramagnetic (such as the $S = \frac{1}{2}$ low-spin Ni^{3+} ion), the presence of orbital degeneracy may lead to the creation of moments on the metal. In the absence of such a degeneracy the moment due to the unpaired electron may be located on the oxygen atom. The paramagnetic spin states of cobalt all have orbital degenerate states for the nearly cubic crystalline field so that the magnetic moments may be effectively located on the cobalt ions.

4.2. Magnetic susceptibility studies

For simplicity we shall consider the metallic $x = 0.5$ composition La$_{0.5}$Sr$_{0.5}$CoO$_3$ with equal amounts of trivalent and tetravalent cobalt ions. The Curie constant C_{iii-iv} for a Co(iii)–Co(iv) pair is expected to be about 1.45 emu K while for a Co(iii)–Co(IV) pair the Curie constant C_{iii-IV} is expected to be close to 0.685 emu K. The experimental (Ganguly 1986) Curie constant for the $x = 0.5$ composition as well as for the two-dimensional La$_{0.5}$Sr$_{1.5}$CoO$_4$ is close to 1.2 emu K (table 2). In the present study we obtain a value of 1.05 emu K which is characteristic of an $S = 1$ system. It would thus seem that in a lattice of $S = 1$ Co(iii) ions the doped hole is itinerant and does not contribute to a localized moment.

For low levels of doping, the eight Co ions at the corners of the cube surrounding the Sr ion are ferromagnetically coupled by the doped hole (Vasanthacharaya *et al* 1984, Madhusudan *et al* 1980, Raccah and Goodenough 1968). The spins on these eight ions form a giant magnetic moment with a Curie constant C_c for the cluster. For small values of x, C_c is the value of the Curie constant calculated *per gram-atom of Sr*. Our results are close to those of Vasanthacharaya *et al* who find that $C_c \simeq 33$ emu K (g-atom Sr)$^{-1}$ from the more accurate DC susceptibility studies for the $x = 0.02$ composition. The value expected for a cluster of eight $S = 1$ cobalt ions surrounding the doped Sr ions is about 36 emu K (g-atom Sr)$^{-1}$. We find in this study that the experimental value of C_c decreases with increasing x as expected since we are not in the dilute limit for the $x = 0.1$ and 0.2 compositions. Our results on the magnitude of the giant magnetic moments are consistent with the existence of $S = 1$ spin states with the doped hole not contributing to the temperature-dependent susceptibility in the paramagnetic state.

4.3. Electrical resistivity

In terms of the magnitude of resistivity, the $x = 0.2$–0.5 compositions which have $\rho < 2$ mΩ cm have a positive TCR and may therefore be considered to be truly metallic. The samples with a resistivity greater than 2 mΩ cm have a negative TCR. This value of

the resistivity at which TCR changes sign is found in other oxide systems (Rao and Ganguly 1985a, b) such as in $La_{1-x}Sr_xVO_3$, in which metallization (Dougier and Hagenmuller 1975) is brought about as a function of doping, as well as in $LaNi_{1-x}M_xO_3$ (M $\equiv$ Fe, Co, Cr or Mn) in which metallization is brought about (Ganguly *et al* 1984) in the $LaMO_3$ insulators simply by forming a solid solution with metallic $LaNiO_3$. The metallization processes in these two cases are very different. Ganguly and Nair (1992) have pointed out that in the layered cuprate superconductors also the *a–b* plane resistivity shows a change in sign of TCR (at low temperatures) at around 2 mΩ cm. It is outside the scope of the paper to comment on the seemingly universal nature of the magnitude (about 2 mΩ cm) of the resistivity at which the TCR changes sign. For the present we note that the magnitude of the resistivity suggests that the $La_{1-x}Sr_xCoO_3$ systems may be considered to be truly metallic for $x > 0.2$.

None of the $La_{1-x}Sr_xCoO_3$ compositions with a positive TCR shows a linear temperature dependence of the resistivity over all temperature ranges. Of particular interest is the deviation from linearity '(reported by Menyuk *et al* (1968) for the $x = 0.5$ composition)' found by us for all the compositions originating near $T = \Theta$ or T_{max} for the $x = 0.1$ composition. The ρ versus T plot shows an increased slope for $T < \Theta$, especially near $T = \Theta$. This suggests that there is an increase in the conductivity associated with ferromagnetic order. We note that even in the $x = 0.1$ composition, in which the TCR is negative as in an insulator, there is a substantial decrease in the slope of the resistivity versus temperature plot below T_{max}.

4.4. Metallization and ferromagnetism

An increase in the conductivity below the ferromagnetic ordering temperature is consistent with a Zener double-exchange mechanism. This mechanism was first applied to the $La_{1-x}Sr_xMnO_3$ system ($x = 0.5$). The itinerant e_g electron of the Mn^{3+} ion (t_{2g}^3, e_g^1) correlates ferromagnetically the spins of the core t_{2g}^3 orbitals in the Mn^{3+}–Mn^{4+} pairs. The condition for such a mechanism to operate is that there should exist a mixed-valence state such that the initial state remains degenerate with the final state after the transfer of electron from the higher-valence state to the other. An itinerant hole coupling the Co(iii) state also satisfies such a constraint.

Recent studies suggest that the doped holes are most likely to be located on the oxygen atoms just as in the cuprate superconductors. In this sense the metallization is expected to be similar to that of charge-transfer metals. The origins of itinerant electron behaviour and ferromagnetism may thus be considered to be different. This is reflected in the concentration dependences of metallization and ferromagnetism. As discussed earlier, the doped hole is itinerant on the cluster of eight Co ions each surrounding Sr ions. The clusters are expected to be connected at around $x = 0.125$. Metallic behaviour is found for $x > 0.125$. Long-range ferromagnetic order on the other hand is to be associated with a nearest-neighbour connectivity of the cobalt ions. The site percolation threshold is about 0.3 for cubic systems so that true ferromagnetic behaviour in the AC susceptibility appears for $x > 0.3$.

The model for the coexistence of coherent ferromagnetic ordering of spins on cobalt ions and itinerant electron behaviour due to holes on oxygen in $La_{1-x}Sr_xCoO_3$ is reminiscent of the behaviour of cuprate superconductors. In the latter systems the spins are on the copper atoms and the charge carriers are believed to be mainly on the oxygen atoms in the normal state. The magnitudes of the resistivity in the normal state in these two series of compounds are also similar. It has to be examined theoretically whether the seeming separation of the spin and charge components on the metal and oxygen ions is expected from the Luttinger liquid formalism that is being currently used for such metals.

Acknowledgments

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