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Electron Transport and Magnetic Properties of $La_{1-x}Sr_xCo_{1-y}Ti_yO_3$ ($x = 0^a$ or $x = y^b$)

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The two systems (a) and (b) for different values of x were synthesized. Their electron transport and magnetic properties show a change in behavior above a critical value of x. Unlike the system $La_{1-x}Sr_x CoO_3$, itinerant electron ferromagnetism is not observed. This is explained on the basis of the absence of an itinerant band of Co^{4+} whose generation is restricted on account of substitution of Ti^{4+}. Electron transport in these two systems is compared with that of $LaCoO_3$ or $La_{1-x}Sr_xCoO_3$ and is discussed in view of the presence of different valence states of cobalt and change in crystal field splitting. Spin-state equilibria in these two systems are similar to that in $LaCoO_3$.

Introduction

The system $Ln^{3+}_{1-x}M^{2+}_x CoO_3$ (Ln = rare earth ions, $M = Ca^{2+}$, Sr^{2+}, or Ba^{2+}) has been studied extensively because of its novel electronic and magnetic properties (*1–8*). In $La_{1-x}Sr_xCoO_3$, which has been investigated more than others (*1–6*), for $x > 0.125$, the induction of sufficient Co^{4+} ions (which forms the itinerant band) is responsible for ferromagnetic as well as metallic behavior. Here, the same transition metal ion is in two valence states. Similarly, the systems $LaMM'O_3$ (where M,M' = Fe, Co, and Ni) have also been found to have interesting electrical and magnetic properties (*9, 10*). We considered it worthwhile to replace one of the transition metal ions by a diamagnetic ion of the transition series. Hence we synthesized and characterized the following two systems: (a) $LaCo_{1-x}Ti_xO_3$ and (b) $La_{1-x}Sr_xCo_{1-x}Ti_xO_3$. In (a), Co^{2+} ions would be generated as more and more Ti^{4+} ions are substituted, and on the other hand, in (b) cobalt is expected to be in only the Co^{3+} state. This system is analogous to $La_{1-x}Sr_x CoO_3$, where Co^{4+} is intentionally replaced by Ti^{4+}. It is expected that this interplay of different valence states of cobalt in these systems would effect the electron transport as well as magnetic properties considerably.

Experimental

All the samples of the systems $LaCo_{1-x}Ti_xO_3$ and $La_{1-x}Sr_xCo_{1-x}Ti_xO_3$ were prepared by decomposition of appropriate

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mixtures of oxalates or oxides of high purity of the constituent elements. The resulting solids were repeatedly ground, in a ball mill, pressed as pellets, and fired at 1475K for several hours. X-Ray diffraction patterns were taken at each stage to monitor the completion of the reaction. The standard errors in a_R and α_R are ±0.005 Å and 0.05°, respectively. The dc electrical resistivity measurements were made in the temperature range 300–1000K by the usual two-probe and four-probe techniques for high- and low-resistivity samples in locally fabricated cells. Frequency dependence of resistivity was measured at 77 and 293K up to 10 kHz frequency using the same cell. Seebeck coefficients were measured relative to platinum in the temperature range 400–1000K. DTA was done using MOM-505 Derivatograph (Hungarian). Magnetic susceptibility measurements were carried out with a PAR vibrating sample magnetometer (Model 150) between 300 and 700K. Chemical analysis shows that in the $LaCo_{1-x}Ti_xO_3$ system, for $x = 0.05$, the sample is nearly stoichiometric. However, the amount of Co^{3+} is found to be more than what is expected for charge neutrality for $x = 0.15$, 0.3, and 0.5. The δ values for these are +0.006, +0.016, and +0.168, respectively. A similar observation has been reported earlier (*11*, *12*). In view of this, the system $LaCo_{1-x}Ti_xO_3$ will be designated as $LaCo_{1-x}Ti_xO_{3+\delta}$ in the text. However, in the system $La_{1-x}Sr_xCo_{1-x}Ti_xO_3$, cobalt ions exist in the 3+ state only.

TABLE I

LATTICE PARAMETERS OF $LaCo_{1-x}Ti_xO_{3+\delta}$ AND $La_{1-x}Sr_xCo_{1-x}Ti_xO_3$

System	x	a (Å)	$\alpha_{R'}$ (°)
$LaCo_{1-x}Ti_xO_{3+\delta}$[a]	0.00	5.380	60.87
	0.05	5.388	60.78
	0.15	5.420	60.49
$La_{1-x}Sr_xCo_{1-x}Ti_xO_3$[b]	0.00	5.380	60.87
	0.05	5.381	60.71
	0.30	5.420	60.48

[a] Compositions with $x = 0.3$ and $x = 0.5$ are cubic with lattice constants of 5.50 and 5.56 Å, respectively.

[b] Composition with $x = 0.5$ is cubic with a lattice constant of 5.46 Å.

Results and Discussion

$LaCoO_3$ is a perovskite with rhombohedral distortion ($a_R = 5.386$ Å, $\alpha_R = 60.87°$). Substitution of Sr^{2+} for La^{3+} reduces the lattice distortion and the sample with $x = 0.5$ becomes cubic (*3*). A similar trend is noticed in the present two series. The lattice constants of the two series are tabulated in Table I. For the system $LaCo_{1-x}Ti_xO_{3+\delta}$, as we substitute Ti^{4+} (ionic radius ~0.64 Å), some Co^{2+} ions (ionic radius ~0.82 Å) are generated for charge neutrality. The larger size of Co^{2+} ions results in an increase in the lattice constant and a decrease in the lattice distortion. Samples with $x = 0.3$ and 0.5 are cubic. No splitting of X-ray lines was observed, as was observed by Ramdass *et al.* (*12*). This could be due to a difference in heat treatment schedule. Similarly, in the system $La_{1-x}Sr_xCo_{1-x}Ti_xO_3$, the lattice constant increases and the distortion decreases slowly with x; the sample with $x = 0.5$ is again cubic. Log of resistivity, ρ, for the system $LaCo_{1-x}Ti_xO_{3+\delta}$ is plotted against the inverse of temperature in Fig. 1. We have also given the resistivity data for $LaCoO_3$ for comparison (*13*). The resistivity behavior of the sample with $x = 0.05$ is similar to that of $LaCoO_3$ over the temperature range studied. Samples with $x = 0.15$, 0.3, and 0.50 show behavior different from that of $LaCoO_3$. In general, the trend is similar to that observed by Ramdass *et al.* (*12*). The activation energies for different regions are tabulated in Table II. It is noteworthy that there is a considerable change in the trend around the composition $x = 0.15$.

The Seebeck coefficient, α, for $LaCo_{1-x}$

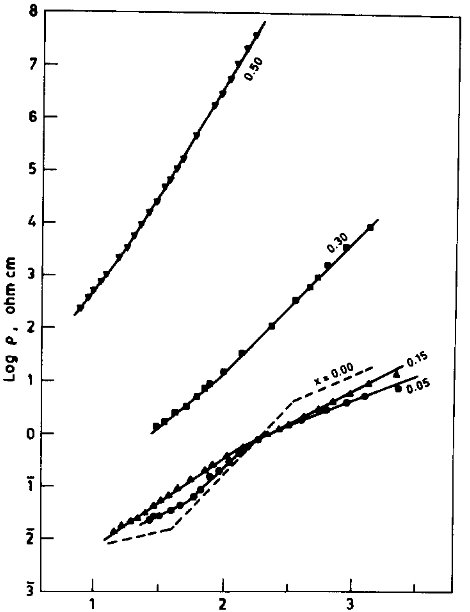

FIG. 1. Plot of log ρ_{dc} versus 1000/T for the system $LaCo_{1-x}Ti_xO_{3+\delta}$.

$Ti_xO_{3+\delta}$, is plotted against inverse of temperature in Fig. 2. This is negative for x = 0.05 up to 500K and thereafter it becomes positive and remains constant. For x = 0.15 it is positive but small and is essentially independent of temperature. For x = 0.3 and 0.5, α is positive and large and shows pronounced variation with temperature. Also, it appears to increase with x above a critical concentration. A similar trend is noticed by Ramdass *et al.* (*12*).

TABLE II

DIFFERENT REGIONS AND ENERGY OF ACTIVATION, E_a, in $LaCo_{1-x}Ti_xO_{3+\delta}$

x	Region (°K) I	Region (°K) II	Energy of activation, E_a (eV) Region I	Energy of activation, E_a (eV) Region II
0.00[a]	200–400	400–650	0.20	0.54
0.05[b]	300–450	450–575	0.24	0.49
0.15	300–475	475–900	0.26	0.35
0.30	300–500	500–700	0.48	0.40
0.50	450–775	775–1050	0.84	0.66

[a] For x = 0.05, region III extends from 575 to 700K with an activation energy of 0.25 eV.

[b] For x = 0.00, region III extends from 600 to 900K with an activation energy of 0.19 eV.

We also measured the frequency dependence of the conductivity for all the samples of the series $LaCo_{1-x}Ti_xO_{3+\delta}$ at 77 and 293K (RT); a few typical results are shown in Fig. 3. It is observed that all the samples showed a frequency dependence at 77K. However, at room temperature, only the samples with $x > 0.15$ showed a frequency dependence but the slope is much less at room temperature.

These electron transport properties can be understood in terms of the band picture of $LaCoO_3$ given by Bhide *et al.* (*13*). LaCoO_3 is a p-type semiconductor in which low-spin Co(III) ($t_{2g}^6\, e_g^0$) is separated from high-spin Co^{3+} ($t_{2g}^4\, e_g^2$) ions by approximately 0.02 eV. The electrical conduction up to 400K gives an activation energy of 0.2 eV (see Table II and Fig. 1). This value corresponds to the gap between filled t_{2g} orbitals and empty σ* bands having e_g symmetry. As we increase x, the activation energy in the first region increases slowly up to x = 0.15. The drop in resistivity and the high activation energy above 400K in LaCoO_3 are attributed to the small difference in energy between high- and low-spin states and to the entropy associated with random spin directions (*6*). Now, when we substi-

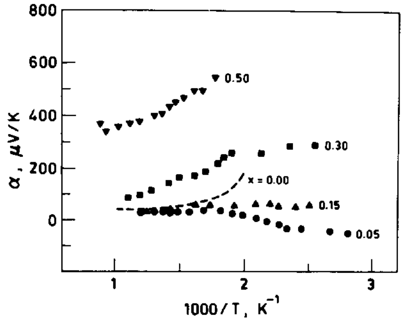

FIG. 2. Plot of α versus 1000/T for the system La$Co_{1-x}Ti_xO_{3+\delta}$.

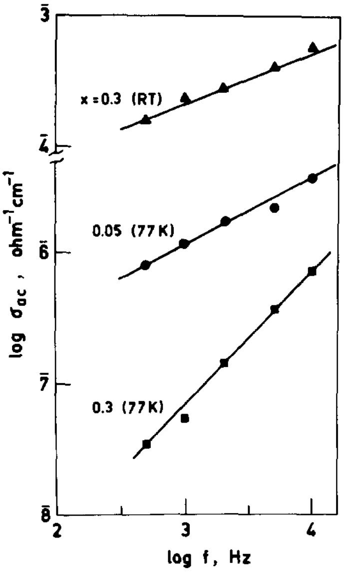

FIG. 3. Plot of log σ_{ac} versus log f for the system $LaCo_{1-x}Ti_xO_{3+\delta}$.

tute Ti^{4+}, Co^{2+} ($t_{2g}^5\, e_g^2$) high-spin ions are generated from high-spin Co^{3+} ions ($t_{2g}^4\, e_g^2$). These Co^{2+} ions act as donor centers. This makes electrons majority carriers, which is reflected in a negative Seebeck coefficient for the sample with $x = 0.05$ at room temperature and up to about 500K. This behavior is similar to that found in $LaMn_{1-x}Co_xO_3$ for a low value of x (*14*). However, when the temperature is raised above 500K, these donor states probably get exhausted. Hence, above 500K, this gives an ordinary intrinsic behavior similar to $LaCoO_3$. It may be mentioned that E_a for conduction also changes around the same temperature. The positive Seebeck coefficient for $x = 0.15$ indicates that holes are majority charge carriers in these samples. Normally, as more and more Ti^{4+} are substituted, n-type semiconductivity should result. However, the observed trend is rather the reverse. This is probably caused by a decrease in the electron mobility resulting from the trapping of electrons in Ti^{4+}–Co^{2+} clusters. These clusters become significant in number in samples with $x > 0.15$. The trapped electrons need additional activation energies for hopping. This may be the reason for a sharp increase in activation energy in samples with $x > 0.15$. The decrease of Seebeck coefficient at high temperature could be due to release of trapped electrons. The E_a for conduction in the second region is complicated by the fact that high- and low-spin states differ little in energy, Co^{2+} and Co^{4+} states are formed due to electron transfer, and high E_a is attributed to the driving force due to entropy associated with random spin directions (*6*). It is also evident from the frequency dependence of the conductivity data at room temperature that conduction is partly by hopping of charge carriers for samples with $x > 0.15$. In samples with $x \leq 0.15$, it is possible that at low temperatures (77K) conduction may be due to hopping between localized sites. This behavior is very similar to that found in the case of $La_{1-x}Sr_xVO_3$ (*15*). For $x \leq 0.15$, the frequency dependence $\sigma \sim \omega^s$ has a value of $S < 0.5$ and a pronounced temperature dependence. We also observe a similar behavior. Paths containing different numbers of single site distances contribute to the ac conductivity and hence the frequency dependence of conductivity is weakened and the temperature variation is enhanced (*15, 16*). Cluster formation in this system may also lead to a similar type of behavior (*17*).

To gain further insight into these similarities of the system with $LaCoO_3$ or $La_{1-x}Sr_x$ CoO_3, we plotted the inverse of the susceptibility against temperature for the system $LaCo_{1-x}Ti_xO_{3+\delta}$ in Fig. 4. All the samples exhibit a plateau in the range 350–550K as found in $LaCoO_3$, which indicates short-range ordering of spin states. This ordering of spin states is also indicated in the DTA plot by small peaks. Above and below the plateau region, χ^{-1} versus T plots are linear for all these samples. Below room temperature, also, these samples have been reported to show linear behavior and ab-

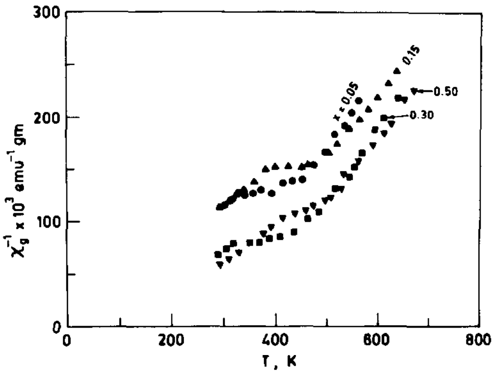

FIG. 4. Plot of inverse of susceptibility against temperature for $LaCo_{1-x}Ti_xO_{3+\delta}$.

sence of magnetic ordering is indicated (*12*). The susceptibility values of Ramdass *et al.* (*12*) differ from ours but the trend is similar. The susceptibility values could differ on account of different δ values. It is interesting to note that in this system ($0 < x < 0.5$), the susceptibility behavior is essentially similar to that of $LaCoO_3$. This could be due to the presence of significant amounts of trivalent cobalt ions in the system in all the samples as found by chemical analysis. In addition, ferromagnetic interaction is not feasible in the absence of a sufficient concentration of Co^{4+} ions, which form the itinerant band and are responsible for ferromagnetic as well as metallic behavior in the system $La_{1-x}Sr_xCoO_3$ (*2*, *3*).

Preliminary studies on the system $La_{1-x}Sr_xCo_{1-x}Ti_xO_3$ have been carried out and have been compared with the previous system and with $La_{1-x}Sr_xCoO_3$.

Log of resistivity and Seebeck coefficient are plotted against inverse of temperature in Fig. 5. The behavior of the sample with $x = 0.05$ is similar to that of $LaCoO_3$. All the regions observed in the resistivity plot of $LaCoO_3$ are distinctly seen in the plot of this sample. The Seebeck coefficient is positive and decreases with temperature up to about 700K in a fashion similar to $LaCoO_3$, after which it remains practically constant, indicating saturation of charge carriers. A positive Seebeck coefficient indicates that holes are the majority charge carriers. Thus it is observed that the mechanism of conduction in this material ($x = 0.05$) at and above room temperature is similar to that of $LaCoO_3$. On the other hand, the behavior of the samples with $x = 0.30$ and $x = 0.50$ is different from that of $LaCoO_3$. For these, the activation energy of conduction changes continuously with temperature and the Seebeck coefficient is independent of temperature. The observed trend in resistivity and thermoelectric power behavior in the samples with $x = 0.3$ and 0.5 may be due to thermally activated hopping of small polarons which may occur between Co(III) sites through intermediate Co^{3+} sites involving two activation energies. Our explanation is based on the model suggested by Austin and Mott (*18*), where two types of centers A and B are present and are separated by a constant energy ΔU. For this model to operate, $\Delta U \gg kT$. In our case, the two types of centers are low-spin Co(III) and high-spin Co^{3+}. As we increase

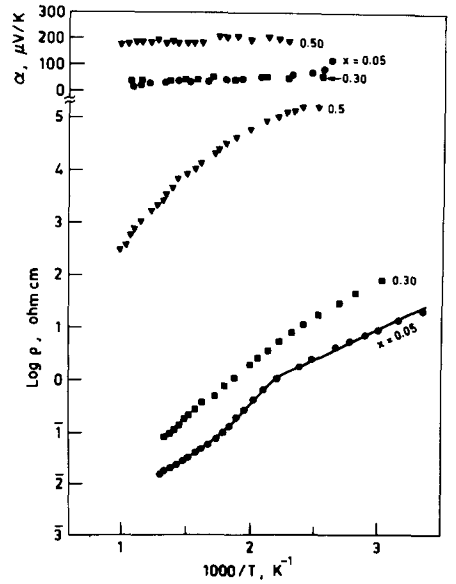

FIG. 5. Plot of log ρ_{dc} and α versus inverse of temperature for the system $La_{1-x}Sr_xCo_{1-x}Ti_xO_3$.

x, the crystal field splitting decreases and for $x = 0.3$ and 0.5, probably $\Delta U \gg kT$ and this model is operative. If the hopping energy is divided equally between the two sites, the Seebeck coefficient should be independent of temperature and is indeed so in our case. A similar observation has been made in the case of $La_{1-x}Sr_xCrO_3$ and is explained in terms of small polaron hopping (*19*).

To gain further insight into the mode of conduction, we measured the ac conductivity for all the samples of the series $La_{1-x}Sr_xCo_{1-x}Ti_xO_3$ at 77 and 293K. A few typical plots of log σ_{ac} versus log f are shown in Fig. 6. It was observed that the sample with $x = 0.05$ showed a frequency-independent conductivity at room temperature while frequency dependence was observed at 77K. On the other hand, the samples with $x = 0.3$ and 0.5 showed frequency dependence at both temperatures. However, the slopes are less than what is expected for single site hopping and have a pronounced temperature dependence. This trend is similar to that observed in $LaCo_{1-x}Ti_xO_{3+\delta}$. It is possible that at low concentration ($x = 0.05$) and at low temperatures, there is localization of charge carriers due to disorder exhibiting frequency-dependent conductivity. At higher temperatures (RT and above), however, the conductivity is again frequency independent. For higher concentrations ($x = 0.3$, 0.5), small polaron hopping between Co(III) sites through Co^{3+} is in accord with the observed frequency dependence in these materials. Furthermore, Co(III) and Co^{3+} sites seem to be randomly distributed in these materials, which leads to multiple hopping. Multiple hopping is more pronounced at higher temperatures and this leads to a reduced frequency dependence of σ_{ac} (*16*). This type of hopping between equivalent sites through intermediate sites gives rise to weak frequency dependence (*20*).

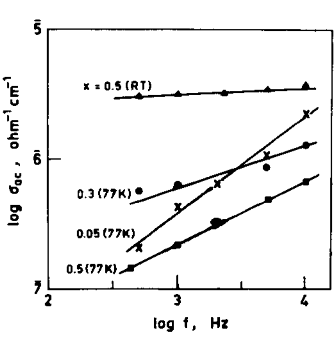

FIG. 6. Plot of log σ_{ac} versus log f for the system $La_{1-x}Sr_xCo_{1-x}Ti_xO_3$.

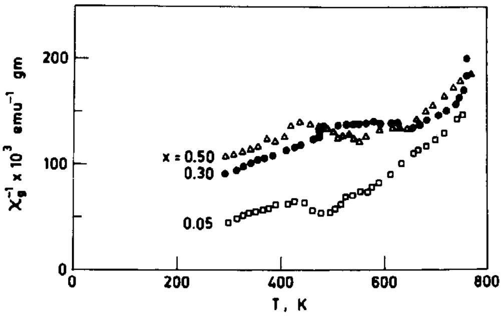

FIG. 7. Plot of inverse susceptibility against temperature for the system $La_{1-x}Sr_xCo_{1-x}Ti_xO_3$.

We plotted the inverse of the susceptibility versus temperature in Fig. 7 for this system. Though these plots are similar to that for the previous system, the plateau region in this case lies between 450 and 650K. This indicates that the energy difference between high- and low-spin states increases compared to $LaCoO_3$ as the crystal field splitting decreases. This also supports our earlier assumption of $\Delta U \gg kT$. The susceptibility behavior of this system could also perhaps be explained assuming the existence of La-rich and Sr-rich regions as in the case of $La_{1-x}Sr_xCoO_3$ (*3*). The magnitude of the susceptibility in the two systems we have presently investigated is also comparable. All these observations suggest that spin-state equilibria in these two systems are essentially similar. In fact, the system $La_{1-x}Sr_xCo_{1-x}Ti_xO_3$ should in principle show magnetic behavior similar to $LaCoO_3$, the reason being that the only magnetic ion common to the two systems is Co^{3+}. It would be interesting to compare the three systems (a) $LaCo_{1-x}Ti_xO_{3+\delta}$, (b) $La_{1-x}Sr_xCo_{1-x}Ti_xO_3$, and (c) $La_{1-x}Sr_xCoO_3$, where there is considerable change in the valence states of cobalt. In these systems cobalt ions exist in (a) divalent and trivalent states, (b) in trivalent state only, and (c) in trivalent and tetravalent states, respectively. In $La_{1-x}Sr_xCoO_3$, the Co^{4+} forms the itinerant band which is mainly responsible for itinerant electron ferromagnetism. In the present two systems because of the substitution of Ti^{4+}, the formation of Co^{4+} is restricted. This, in fact, is the reason for the localized behavior and the absence of ferromagnetic exchange interaction.

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