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LETTER TO THE EDITOR

Metal–insulator transition in the spin-glass system $La_{0.85}Sr_{0.15}CoO_3$

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Abstract. Electrical resistivity measurements (20–300 K) show a metal–insulator transition in low-temperature-sintered samples of the spin-glass insulating composition $La_{0.85}Sr_{0.15}CoO_3$. Insulating behaviour is observed only for samples sintered at high temperatures. The results can explain the widely differing electrical resistivity behaviour reported for different compositions in the $La_{1-x}Sr_xCoO_3$ system.

Extensive studies on electronic and magnetic properties of strontium-substituted lanthanum cobaltate, $La_{1-x}Sr_xCoO_3$, have provided many interesting results during the past four or five decades. Jonker and Van Santen (1953) first reported that substitution of Sr^{2+} for La^{3+} in the diamagnetic insulator $LaCoO_3$ gives rise to ferromagnetic properties for $x > 0.10$, and that the compositions with $x \geqslant 0.25$ become metallic below room temperature. Itoh *et al* (1994) have shown that there exist spin-glass ($0 < x \leqslant 0.18$) and cluster-glass ($0.18 \leqslant x \leqslant 0.50$) regions in the $La_{1-x}Sr_xCoO_3$ system and that there is no ferromagnetic long-range order taking place, as reported previously. Anil Kumar *et al* (1998a) have concluded that the cluster-glass-like magnetic properties of $La_{0.5}Sr_{0.5}CoO_3$ originate from its magnetocrystalline anisotropy and that the compound is a long-range ordered ferromagnet. Caciuffo *et al* (1999) have very recently reported that long-range ferromagnetic order between clusters is realized even for Sr doping as low as $x = 0.10$ and the transition to a spin-glass state is observed only for $x < 0.1$. They have observed identical T_c for all compositions in the range $0.10 \leqslant x \leqslant 0.30$, contrary to previous reports (Jonker and Van Santen 1953, Itoh *et al* 1994, Golovanov *et al* 1996) that T_c varies with x in $La_{1-x}Sr_xCoO_3$.

Senaris-Rodriguez and Goodenough (1995) have reported re-entrant semiconductive behaviour for $0.20 \leqslant x \leqslant 0.25$ and metallic ferromagnetic behaviour for $0.30 \leqslant x \leqslant 0.50$ whereas Golovanov *et al* (1996) have observed that the $x = 0.18$ composition shows signs of a metal–insulator (MI) transition and that the $x = 0.20$ composition shows metallic behaviour. There are also other reports in the literature which indicate the metallic (Chainani *et al* 1992, Yamaguchi *et al* 1995) as well as insulating (Mineshige *et al* 1996, Mahendiran and Raychaudhuri 1996) behaviour of the $x = 0.20$ composition in the $La_{1-x}Sr_xCoO_3$ system. These widely differing results on the electrical and magnetic properties indicate that the phase diagram of $La_{1-x}Sr_xCoO_3$ is not yet understood properly for low doping levels $x \leqslant 0.25$.

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Different magnetic phase diagrams are obtained (Itoh *et al* 1994, Senaris-Rodriguez and Goodenough 1995) for $La_{1-x}Sr_xCoO_3$ ($0 \leqslant x \leqslant 0.50$) when the compounds are processed through different routes. It has been shown that, at lower values of x, the material segregates into hole-rich ferromagnetic regions and hole-poor semiconducting matrix (Senaris-Rodriguez and Goodenough 1995, Caciuffo *et al* 1999). Asai *et al* (1994) have earlier observed the presence of a magnetic impurity phase in their single crystal sample of the spin-glass composition $La_{0.92}Sr_{0.08}CoO_3$. Our recent studies have revealed that sample processing is very critical in determining the true magnetic behaviour of different compositions in the $La_{1-x}Sr_xCoO_3$ system (Anil Kumar *et al* 1998b, Anil Kumar *et al* 1998c). In this letter, we report the electrical resistivity behaviour of $La_{0.85}Sr_{0.15}CoO_3$ samples sintered at different temperatures. The x = 0.15 composition, which is expected to be insulating, shows a metal–insulator transition or insulating behaviour depending on the temperature at which the sample is sintered.

The $La_{0.85}Sr_{0.15}CoO_{3-\delta}$ samples were prepared by the ceramic method as reported previously (Anil Kumar *et al* 1998b). The sample, initially heated at 1000 °C for 72 h, was sintered in air at 1000 °C/12 h, 1100 °C/12 h, 1100 °C/24 h, 1200 °C/12 h and 1250 °C/12 h. These sintered samples are denoted as S1, S2, S3, S4, and S5, respectively. Oxygen stoichiometry measurements indicated that the samples sintered above 1000 °C are nearly stoichiometric: $3–\delta$ (in $La_{0.85}Sr_{0.15}CoO_{3-\delta}$) = 2.96±0.02, 2.99±0.02, 3.00±0.02, 3.00±0.02, and 2.99±0.02 for S1, S2, S3, S4, and S5, respectively. $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ was also synthesized and sintered (δ = 0.05 for the sample sintered at 1000 °C) under identical conditions (Anil Kumar *et al* 1998c). The ac susceptibility at 10 Oe/27 Hz was measured using the mutual inductance method. Resistivity measurements in the temperature range 20–300 K were made on the sintered pellets by the conventional four probe method.

Figure 1 shows the temperature variation of the resistivities of two samples, S1 and S2. The sample S1 shows positive temperature coefficient of resistance below ∼250 K and a broad resistivity maximum at ∼265 K indicating a MI transition at this temperature. For the sample S2, the maximum in the resistivity curve is shifted to ∼235 K, showing negative temperature coefficient of resistance above this temperature. A minimum is observed in the resistivity curve at ∼140 K and the resistivity increases below this temperature as the temperature is

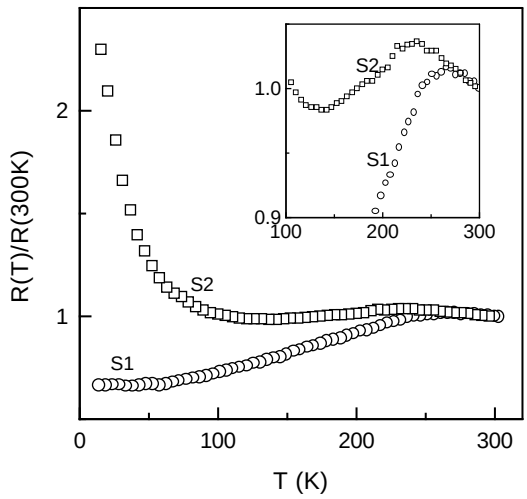

Figure 1. The temperature dependence of the normalized resistivities of the samples S1 (circles) and S2 (squares). Inset: the expanded curves showing the MI transitions.

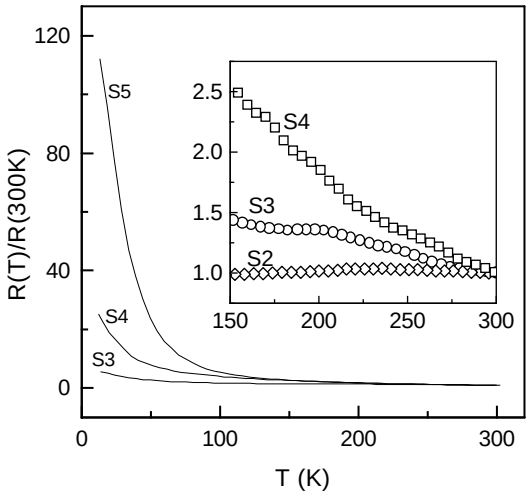

Figure 2. The temperature dependence of the normalized resistivities of the samples S3, S4, and S5. Inset: the expanded curves of S2 (diamonds), S3 (circles), and S4 (squares).

decreased. These features can be seen very clearly in the inset of figure 1, which shows the expanded resistivity curves around the metal–insulator transition temperature. Figure 2 shows the resistivity curves of the sample sintered at higher temperatures. The samples S4 and S5, which are sintered at higher temperatures ($\geqslant$1200 °C), show insulating behaviour below room temperature. The resistivity at low temperatures increases with increasing sintering temperature.

The resistivity curve of S2 is similar to that reported by Senaris-Rodriguez and Goodenough (1995) for their $x = 0.20$ and 0.25 samples sintered at 1000 °C, where the maximum and the minimum in the resistivity curves are indicated as metal–insulator transitions. Mahendiran and Raychaudhuri (1996) have observed a resistivity behaviour similar to that of S2 for their $x = 0.20$ sample sintered at 1100 °C and a minimum in the resistivity below 100 K for samples with $0.25 \leqslant x \leqslant 0.40$. Ibarra *et al* (1998) have also reported a minimum in the resistivity below 100 K for $x = 0.30$ sample sintered at 1000 °C, compared to the positive temperature coefficient of resistivity at low temperatures reported by Yamaguchi *et al* (1995) for a high-quality crystalline sample of the same composition. Widely differing resistivity behaviours are observed for a given composition when sintered at different temperatures.

The ac susceptibility curves of the samples sintered at different temperatures are compared in figure 3. For the sample S1, which shows an almost constant resistivity above 270 K and metallic-type resistivity behaviour below ∼250 K, a sharp magnetic transition is observed at ∼250 K. The magnetic transition temperature decreases with increasing sintering temperature. Caciuffo *et al* (1999) have attributed a magnetic transition at ∼250 K for all compositions in the range $0.05 \leqslant x \leqslant 0.30$ of $La_{1-x}Sr_xCoO_3$, for their samples annealed at 1000 °C, to the freezing of ferromagnetic clusters whose fraction in the samples increases with increasing x. The ferromagnetic Curie temperature of single phase $La_{0.5}Sr_{0.5}CoO_3$ is ∼250 K (Anil Kumar *et al* 1998c), which is the maximum T_c observed in the $La_{1-x}Sr_xCoO_3$ system. The normalized ac susceptibility and resistivity curves of $La_{0.5}Sr_{0.5}CoO_3$ and $La_{0.85}Sr_{0.15}CoO_3$ samples, sintered at 1000 °C, are compared in figure 4. The susceptibility curves of both the compositions sintered at this temperature are almost identical, showing a sharp magnetic transition at the same temperature. Similarly, the resistivity curves show a T_c anomaly in the same temperature region.

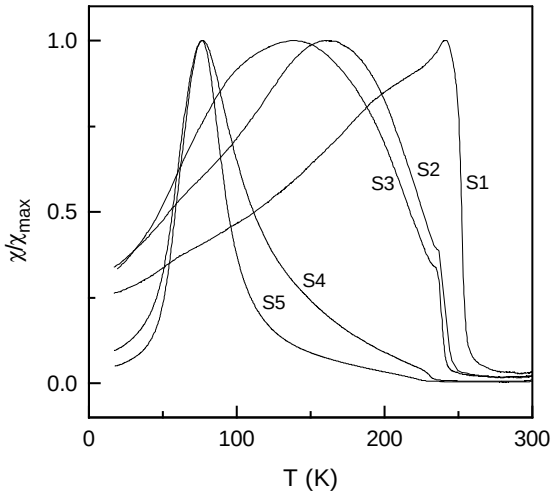

Figure 3. Normalized ac susceptibility curves of the samples S1, S2, S3, S4, and S5.

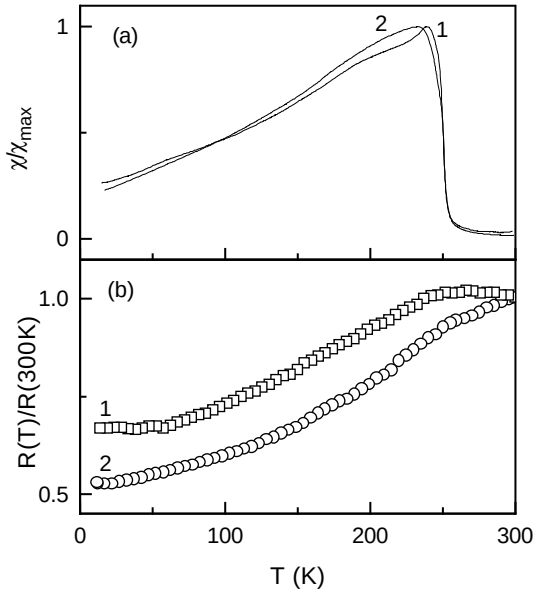

Figure 4. Comparison of (a) ac susceptibility and (b) resistivity curves of the samples sintered at 1000 °C: 1, $La_{0.85}Sr_{0.15}CoO_3$; 2, $La_{0.5}Sr_{0.5}CoO_3$.

The identical susceptibility and resistivity behaviours of the $x = 0.15$ and 0.50 compositions (of which the former is expected as an insulating spin-glass and the latter as ferromagnetic and metallic) in the $La_{1-x}Sr_xCoO_3$ system, sintered at a relatively lower temperature, can be attributed to the inhomogeneity of the samples (Senaris-Rodriguez and Goodenough 1995, Anil Kumar *et al* 1998b, Anil Kumar *et al* 1998c). Chainani *et al* (1992) have reported that XPS valence band spectra of different compositions in the $La_{1-x}Sr_xCoO_3$ system ($0.10 \leqslant x \leqslant 0.40$), processed and sintered at 950 °C, did not show a clear emergence of a Fermi cutoff in the metallic cases as distinct from the insulating ones. Saitoh *et al* (1997),

on the other hand, have observed systematic changes in the valence band spectra which reflects the semiconductor–to–metal transition, on hole doping, for samples sintered at 1300 °C. The present results indicate that it is difficult to distinguish metallic and insulating compositions if the samples are processed and sintered at low temperatures.

The metal–insulator transition observed in $La_{0.85}Sr_{0.15}CoO_3$, sintered at low temperatures, is due to the inhomogeneity of the samples as concluded from magnetic measurements (Anil Kumar *et al* 1998b). The widely differing resistivity behaviours, reported in the literature, for different compositions ($x < 0.30$) of $La_{1-x}Sr_xCoO_3$, processed and sintered at different temperatures, may also be due to the inhomogeneity of those samples sintered at relatively low temperatures. A detailed evaluation of the electrical and magnetic properties of single phase compositions is required to construct an accurate phase diagram of strontium-substituted lanthanum cobaltates.

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