Magnetoresistance in the paramagnetic insulating state of Pr$_{0.50}$Ca$_{0.50}$CoO$_3$.

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Abstract. We have studied the magnetic and magnetotransport properties of Pr$_{0.50}$Ca$_{0.50}$CoO$_3$ (prepared using high pressure routes). We find that below the metal-insulator and spin state transition (MIT), the system can be described as a paramagnetic insulator. In this regime, it presents a considerable negative magnetoresistance (20%-40%), while above MIT the magnetoresistance is negligible or even slightly positive. These results seem in contradiction with the spin state picture usually drawn for this system.

1. Introduction

Cobalt oxides are attracting a growing interest due to their interesting properties for different applications as mixed conductors, solid oxides fuel cells, thermopower generators, room temperature ferromagnets or magnetodielectric materials [1-4]. Also, their complex behaviour makes them very interesting from a fundamental point of view: magnetoresistance (MR), intriguing metal-insulator transitions (MIT), superconductivity, spin state (SS) transitions, etc [5-11]. The ability of cobalt ions in perovskite-type structures to present different SS as a function of temperature, applied field, pressure, chemical tuning, etc., plays a major role in this richness.

The changes of the spin state of cobalt can take place by means of two differentiated ways. They can occur smoothly with temperature, signalling that the transition between low spin (LS with $S=0$ and $t_{2g}^6$) and higher SS (intermediate spin, IS, with $S=1$, $t_{2g}^5 e_g^1$; and high spin, HS, with $S=2$, $t_{2g}^4 e_g^2$), in the case of Co$^{3+}$, takes place by thermal activation, as in LaCoO$_3$ [9,10]. Alternatively, SS changes can take place suddenly, like in RBaCo$_2$O$_{5.50}$ family ($R$=rare earth, Y) presenting a change in spin state at a well defined temperature that is linked to a metal (higher spin) to insulator (lower spin) transition [11].

Pr$_{0.50}$Ca$_{0.50}$CoO$_3$ is another system where a sudden spin state transition has been reported [12-20]. This compound displays a sudden enhancement of the resistivity (on cooling), described as a MIT, that is accompanied by an abrupt change of the cell volume and an anisotropic variation of cell parameters. The explanation widely accepted consists on the formation, on cooling, of a mixed localized Co$^{3+}$ ($S=0$, $t_{2g}^6$) and Co$^{4+}$ ($S=\frac{1}{2}$, $t_{2g}^5$) LS states; whereas above T$_{MI}$ a delocalized homogeneous $t_{2g}^5(\sigma^*)^{0.5}$ state would be responsible for carrier conduction (as reported earlier for Pr$_{0.50}$Sr$_{0.50}$CoO$_3$).

It is worth to recall that Pr$_{0.50}$Sr$_{0.50}$CoO$_3$ is ferromagnetic (T$_C$= 225 K) and metallic up to well above T$_C$ [21]. Double exchange is thought to contribute to the ferromagnetic interaction leading to a peak in the MR at T$_C$. R$_{0.50}$Sr$_{0.50}$CoO$_3$ ($R$= La, Nd, Sm, and Eu) display a similar behaviour [22-24].

In this paper we present the results of a magnetic and magnetotransport study of Pr$_{0.50}$Ca$_{0.50}$CoO$_3$ that makes us to put some question marks on the picture described above.
2. Experimental

Polycrystalline samples have been prepared by solid state reaction using high purity (>99.99%) Pr$_6$O$_{11}$, Co$_3$O$_4$ and CaCO$_3$ precursors. Final firing has been done at 1160°C under O$_2$ atmosphere. To reach optimal oxygen content, sample was heat treated under high oxygen pressure (900°C with $P_{O_2}$=200 bar during 14 hours; and 475°C with $P_{O_2}$=150 bar during 6 hours). Final sample has been examined by x-ray powder diffraction using a Siemens D-5000 diffractometer and found to be single phased and free from impurities. Resistivity, magnetotransport and magnetization measurements have been done with a PPMS and a SQUID system respectively (Quantum Design) using DC fields.

![Graph](image)

FIG. 1 (Color online): (a) Variation under temperature of the resistivity of Pr$_{0.50}$Ca$_{0.50}$CoO$_3$ at zero field and under 9T. Measurements have been done following a cooling-heating cycle. The inset draws the plot of ln($\rho$) vs. 1/T showing a linear behaviour above $T_{MI}$. (b) MR obtained as the difference between the resistivity measured at zero field and at 9T.

3. Results and discussion

DC resistivity measured at zero field and under 9T of applied field in cooling-heating cycles is plotted in Fig. 1(a). $\rho(T)$ shows a sudden drop (on heating) at $T_{MI} \approx 80$ K, as found in Refs. [12,14,15]. Above $T_{MI}$ $\rho$ is around 1 m$\Omega$cm, quite low for a polycrystalline oxide. This value is comparable in magnitude with that found for $R_{0.50}Sr_{0.50}$CoO$_3$ and different RBaCo$_2$O$_{5-\delta}$ compounds [21-24]. Inset in Fig. 1(a) shows that, in this temperature region ($T>T_{MI}$), $\rho(T)$ is thermally activated (with rather low activation energy, 3.8 meV). Consequently, it displays a semiconducting-like, rather than a metallic, behaviour. The activation energy is smaller than the thermal $k_BT$ energy, and an extrinsic origin of this behaviour cannot be ruled out. Below $T_{MI}$, resistivity shows a markedly insulating character. This transition presents a thermal hysteresis of about 4K. 9T of applied field does not significantly alter the behaviour of $\rho(T)$. This field shifts down $T_{MI}$ by 5 K and a peak in the MR appears very near the MIT transition [Fig.1(b)]. Below $T_{MI}$ there is a considerable negative MR (20%-40%) but above $T_{MI}$ MR is near zero and its sign depends on temperature: it becomes positive [$\rho(\mu_0H=9T) > \rho(\mu_0H=0)$] above $T \approx 100$ K.

It has been interpreted, as a widely accepted picture of the electronic changes taking place at the transition, that above $T_{MI}$ the electronic configuration of Co is $t_{2g}^5\sigma^{0.5}$ while below this temperature, Co presents a mixture of Co$^{3+}$ and Co$^{4+}$ (both in low spin state) [12-17]. Besides, our measurements show that above 100 K, an applied field of 9T barely affects the resistivity and, in fact, $\rho$ slightly enlarges with the field. This demonstrates that the mobility of itinerant electrons does not depend on the magnetic arrangement of the core spins ($t_{2g}^5$). A first consequence of this observation is that the ferromagnetic interactions observed above $T_{MI}$ ($\theta_c = +65$ K) cannot be attributed to double-exchange as main mechanism. Moreover, this observation puts a question mark on the conduction mechanism widely accepted above $T_{MI}$. Hund’s rule exchange coupling of the electron in the $e_g$ state to the core localized spins in the $t_{2g}$ levels is expected to be weaker than for instance in magnetoresistive manganites. But from the electronic configuration $t_{2g}^5\sigma^{-0.5}$, a term $\propto \cos \theta/2$ ($\theta$ being the angle between
neighboring core spins) in the hopping probability must be present. Looking at the experimental data shown in Fig. 1 we remark that a very strong field (9T) does not drive to any reduction of the resistivity above $T_{MI}$. This contrasts with the behavior of metallic $\text{Pr}_{0.50}\text{Sr}_{0.50}\text{CoO}_3$ that shows a measurable magnetoresistance [21] above $T_C$. Concerning the insulating phase of $\text{Pr}_{0.50}\text{Ca}_{0.50}\text{CoO}_3$, Co ions are supposed to be in a LS state. Thus, the conduction would take place by hopping of $t_{2g}$ electrons from nonmagnetic $\text{Co}^{3+}$ ($S=0$) to $\text{Co}^{4+}$ ($S=\frac{1}{2}$). In that case (as the departing ion is nonmagnetic) the hopping probability could be (in first approximation) independent of the orientation of the moment of the arrival ion. In spite of this, magnetoresistance below $T_{MI}$ takes values ranging between 20% and 40%.

Figure 2(a) shows the DC magnetization (M) and the inverse susceptibility ($\chi^{-1}$) measured under 0.1 T of applied field on heating after zero field cool (ZFC) and field cool (FC) processes. Above the MIT, a paramagnetic regime is clearly evidenced by $\chi^{-1}(T)$ that follows a linear behaviour rendering $\theta_C= 60$ K. Very near this temperature $M(T)$ displays a local maximum and below this temperature it decreases for a short temperature interval. On further cooling, $M(T)$ (FC measurement) increases down to 5 K, although the value of the magnetization at low T is rather small (~0.3 $\mu_B$/f.u.). Besides, the ZFC branch displays a strange behaviour, with another maximum at around 25K. Thus, ZFC and FC branches present important differences below this temperature. In the paramagnetic region, an effective paramagnetic moment $\mu_{eff}= 4.43(2)\mu_B$/f.u. is found. Assuming a paramagnetic contribution from $\text{Pr}^{3+}$ ions of 3.58$\mu_B$/Pr, the estimated moment from Co ions is 3.64(3)$\mu_B$/Co. This value is in agreement with previous works [12] and indicates that Co ions could take higher spin states ($3.39\mu_B$/Co for $\text{Co}^{3+}$-IS, $\text{Co}^{4+}$-IS and 3.67$\mu_B$/Co for $\text{Co}^{3+}$-HS, $\text{Co}^{4+}$-LS).

![Graph showing magnetization and inverse susceptibility](image)

FIG 2. (a) Temperature dependence of the magnetization measured under 0.1T on heating after zero filed cooling and field cooling (left axis). Inverse of DC susceptibility (right axis). (b) M-H cycles collected at low temperatures (2K and 10K). The insets show in detail the low field region at the two temperatures (for the sake of comparison, scales in both insets are identical).

We have further investigated the low temperature magnetic behaviour through the M(H) isothermal-hysteresis cycles at 10K and at 2K that are plotted in Figure 2(b). The hysteresis loops displayed would indicate a ferromagnetic order at these temperatures. However, it is worth to mention that there is a strong change in the hysteresis loop between these two temperatures. The remanence and the coercivity are much larger at 2K (0.27 $\mu_B$/f.u and 1070 Oe) than at 10K (0.03 $\mu_B$/f.u and 60 Oe). According to these values, FM is rather weak at 10 K. More importantly, the first magnetization curve measured at 10K, as can be appreciated in the corresponding inset in Fig. 2(b), is out of the hysteresis cycle. This strongly indicates that, at this temperature, the weak ferromagnetism is induced by the applied field rather than being spontaneous. At 2K first magnetization curve is inside the cycle,
although the slope near zero field is very similar to that at 10K. This denotes that the opening of the cycle could be attributed to a freezing of the spin dynamics rather to a change in the magnetic order. The fact that FM signal is induced by the field rather than spontaneous, helps to understand the large difference between ZFC and FC branches of M(T). Also to be mentioned is the fact that magnetization does not saturate with an applied field of 5T. We interpret this as a consequence of the paramagnetic contribution of Pr ions.

4. Summary and conclusions

In summary, by means of resistivity, magnetotransport, magnetic measurements we have investigated the metal insulator transition in Pr$_{0.50}$Ca$_{0.50}$CoO$_3$ (with $\gamma \approx 0$). We have tried to examine our results in the framework of the picture drawn in previous works, that attribute the origin of this MIT to a change from LS states of Co$^{3+}$(t$_{2g}^6$) and Co$^{4+}$(t$_{2g}^5$) below T$_{MI}$, to t$_{2g}^5$(\sigma*)$^{0.5}$ state above T$_{MI}$. We have found that the behaviour of the magnetoresistance is in contradiction with this simple picture. Besides the paramagnetic contribution from Pr ions, magnetization measurements show important changes below T$_{MI}$, but no evidences of spontaneous ferromagnetic order are found down to 2K. Below T$_{MI}$ (as seen at 10K) it is very likely that the small ferromagnetic signal is induced by the applied magnetic field. Our results also point towards this possibility at the lowest temperature investigated (2K).

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