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Phase separation in transition metal oxides $Ln_{2/3}A_{1/3}MO_3$, Ln =La, Pr; A = Ca, Sr and M = Mn, Co

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The low temperature properties of the polycrystalline perovskite systems $Ln_{2/3}A_{1/3}MO_3$ with Ln = La, Pr; A = Ca, Sr and M = Mn, Co including electrical resistance, magnetization, ac susceptibility were studied. The compounds behave as “cluster glass” systems, showing both spin-glass-like and ferromagnetic behavior. The electrical conduction shows negative magnetoresitance.

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1. Introduction

The manganese and cobalt perovskites display remarkable magnetic and transport properties of interest for technical applications. In these materials, a complex interplay between the charge, spin, lattice, and orbital degrees of freedom has challenged our understanding of transition-metal oxides. The coupling of these competing interactions has recently been shown to commonly result in the occurrence of spontaneous phase separation between different electronic and magnetic states, at low temperatures [1-3]. This phase-separated state is a common characteristic of many transition metal oxides and from magnetic point of view it often results in mictomagnetic behavior. Several studies have also reported unusual relaxation dynamics and frequency-dependent phenomena. In the manganites $La_{1-x}Ca_xMnO_3$, the resistivity is lowest (at 80 K) for $x = 1/3$ composition corresponding to nearly ferromagnetic behaviors, while high resistivities correspond to compositions in which the antiferromagnetic interactions are dominant. For a broad range of doping, these materials have a paramagnetic-to-ferromagnetic (FM) transition upon cooling, which is accompanied by a sharp drop in the resistivity. The transition temperature (T_c) is raised in a magnetic field, and thus the system can be tuned between the low and high conductivity phases by applying a magnetic field. This results in a “colossal” magnetoresistance (CMR) near T_c (as much as 100 000% in thin films) [4]. $Pr_{1-x}Ca_xMnO_3$ perovskites are insulating for any Ca doping in zero magnetic field, although the energy difference between the insulating state and a metallic phase, for $x = 0.25$– 0.50, is expected to be unusually small. This low-bandwidth compound is insulating at zero magnetic field, and has a charge ordering transition around 220 K followed by antiferromagnetic and ferromagnetic transitions at 130 and 110 K, respectively, [5,6].

The substitution of divalent alkaline-earth (A = Ca, Sr, Pb) elements for Ln in $LnMnO_3$ where Ln is a lanthanide, leads to the conversion of Mn^{3+} ($t^3_{2g}e^1_g$ state) into Mn^{4+} ($t^3_{2g}e^0_g$ state) ions. Their spin states do not depend on temperature because the Hund energy is higher than the crystal field energy. For example $LaMnO_3$, the parent compound of rare earth manganites is an AFM insulator. The lattice structure of manganites is perovskite-like and nearly cubic. Rhombohedral, orthorhombic or other lattice distortions result from the tilting and stretching of oxygen octahedra around Mn ions. These distortions appear for structural (mismatch of ionic radii) and electronic (Jahn-Teller effect of Mn^{3+}) reasons [1-3].

Since the discovery of “colossal” magnetoresistance (MR) effect in manganites, search for other MR materials has been widely conducted in various transition-metal oxides. Among them, cobaltites with the perovskite structure are of potential interest [7,8]. In these oxides, cobalt is susceptible to accommodate various oxidation states (Co^{2+}, Co^{3+}, and Co^{4+}) and various kinds of magnetic states are competing with a subtle balance due to the variety of spin states and spin interactions of cobalt ions. Therefore, a dramatic modification in the magnetic state and thereby the magnetoresistive property can be expected, by tuning the chemical composition. In cobalt perovskites there are various spin states for trivalent (low-spin LS: $t^6_{2g}e^0_g$; intermediate-spin IS: $t^5_{2g}e^1_g$; high-spin HS: $t^4_{2g}e^2_g$) and tetravalent cobalt ions (LS: $t^5_{2g}e^0_g$; IS: $t^4_{2g}e^1_g$; HS: $t^3_{2g}e^2_g$). $LaCoO_3$ is a diamagnetic insulator at low temperatures with a low spin state (LS) of Co^{3+} ($S = 0$). With increasing temperature some of Co ions are progressively converted to IS or to HS state due to the small difference between Hund and crystal field energies that allows the thermal excitation of t_{2g} electrons on e_g levels. Upon doping A^{2+} ions into $LaCoO_3$, some of trivalent Co ions become tetravalent that also contain a mixture of low and high spin sates [9,12]. Both double and superexchange interactions are present in these compounds. Most researchers have subscribed to the opinion that the magnetic behavior in cobaltites has the same origin as in the case of manganites [7-11]. The coexistence of ferromagnetic and antiferromagnetic tendencies in manganites and cobaltites suggests that there should be glassy behavior associated with the frustration of the different interactions. The present work is an investigation of the low temperature magnetic properties of the $Ln_{2/3}A_{1/3}MO_3$ compounds, where Ln =La, Pr; A = Ca, Sr and M = Mn or Co.

2. Experimental

The $La_{2/3}Ca_{1/3}CoO_3$, $La_{2/3}Sr_{1/3}CoO_3$, $Pr_{2/3}Ca_{1/3}CoO_3$ and $Pr_{2/3}Ca_{1/3}MnO_3$ compounds were prepared by conventional solid state reactions at high temperatures [13]. The powder x-ray diffraction patterns were recorded by using a Bruker D8 Advance AXS diffractometer with Cu Ka radiation. An Oxford Instruments MagLab System 2000 was used for magnetization and ac susceptibility measurements in the temperature range 4 - 300 K. We used a Faraday-type balance to determine the dc susceptibility in the temperature range from 300 to 1000 K. The resistivities were measured in a cryogen free magnet cryostat CFM-7 T (Cryogenic Ltd.) by the four-probe technique, in the temperature range from 5 to 300 K and magnetic fields up to 7 T.

3. Results and discussion

The X-ray diffraction patterns for all the studied samples showed the presence of a single phase. The samples have perovskite structure with orthorhombic ($Pr_{2/3}Ca_{1/3}MnO_3$, $Pr_{2/3}Ca_{1/3}CoO_3$) or rhombohedral ($La_{2/3}Sr_{1/3}CoO_3$, $La_{2/3}Ca_{1/3}CoO_3$) symmetry. In Fig. 1 is described the temperature dependence of the FC and ZFC magnetization for the $Pr_{2/3}Ca_{1/3}MnO_3$ compound. The magnetization has a history dependence with a bifurcation between zero field cooling (ZFC) and field cooling (FC) data at an irreversibility temperature T_{irr}. Fig. 2 shows the *M(H)* curves for $La_{2/3}Ca_{1/3}CoO_3$ and $La_{2/3}Sr_{1/3}CoO_3$ samples. The magnetization measurements do not show saturation indicating the absence of the true long-range magnetic order in the system. As can be seen, the hysteresis loop is much narrower for the sample with A = Sr and the magnetization is higher at 15 K, indicating that beside antiferromagnetic clusters some ferromagnetic ones can coexist. The ac susceptibility is frequency dependent in the vicinity of the freezing temperature. The frequency dependence of the real part of the complex susceptibility $\chi'(T)$ is depicted in Fig. 3 for the sample $Pr_{2/3}Ca_{1/3}MnO_3$, in the range from 100 to 2500 Hz at an excitation field H_{ac} = 1 Oe. Similar behaviors were found for all the investigated samples. The temperatures corresponding to the maximum of $\chi'(T)$ curves are 106 K for $Pr_{2/3}Ca_{1/3}MnO_3$, 148 K for $La_{2/3}Ca_{1/3}CoO_3$, 181 K for $La_{2/3}Sr_{1/3}CoO_3$ and 16 K for $Pr_{2/3}Ca_{1/3}CoO_3$ and these were identified with Curie temperatures.

The magnetic measurements showed typical features of the presence of magnetic clusters in the systems. The presence of FM clusters in the systems is also suggested by a downward curvature in the temperature dependence of the reciprocal susceptibility $1/\chi$ (not shown) at lower temperatures, but closer to T_c points. In the high temperature range, 300 – 900 K, $1/\chi(T)$ has almost a linear behavior. The paramagnetic Curie temperatures, Θ, Curie constants *C* and the effective magnetic moments μ_{eff} respectively were determined.

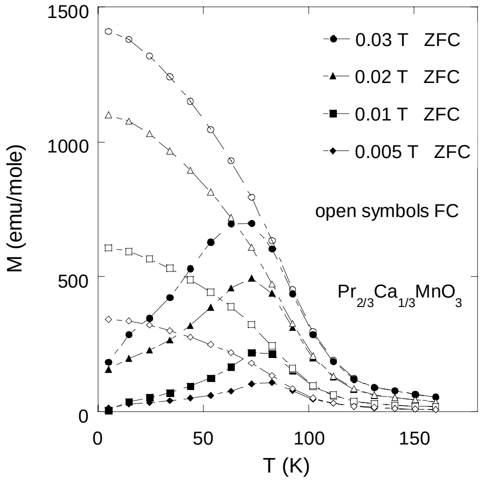

Fig. 1. Field cooled (open symbols) and zero field cooled (closed symbols) magnetizations of $Pr_{2/3}Ca_{1/3}MnO_3$ as a function of temperature.

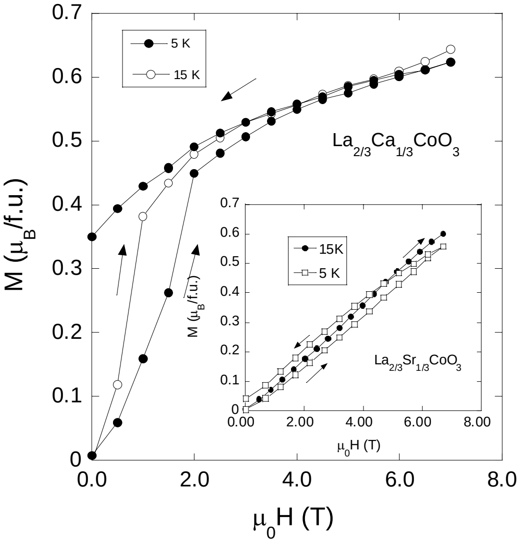

Fig. 2. 5 K and 15 K M(H) curves for the sample $La_{2/3}Ca_{1/3}CoO_3$ and $La_{2/3}Sr_{1/3}CoO_3$ (in inset).

For $Pr_{2/3}Ca_{1/3}MnO_3$ we found Θ =96 K and μ_{eff} ~ 4.8 μ_B. In the case o cobalt perovskites the data indicate the presence of Co^{3+} in all the three states LS, IS and HS. For $La_{2/3}A_{1/3}CoO_3$ when A = Ca, we have Θ =-75 K and an effective magnetic moment μ_{eff} ~ 3.7 μ_B while for A = Sr, Θ = -50 K and μ_{eff} ~ 3.9 μ_B. In the case of $Pr_{2/3}Ca_{1/3}CoO_3$, Θ =-25 K and μ_{eff} ~ 3.6 μ_B.

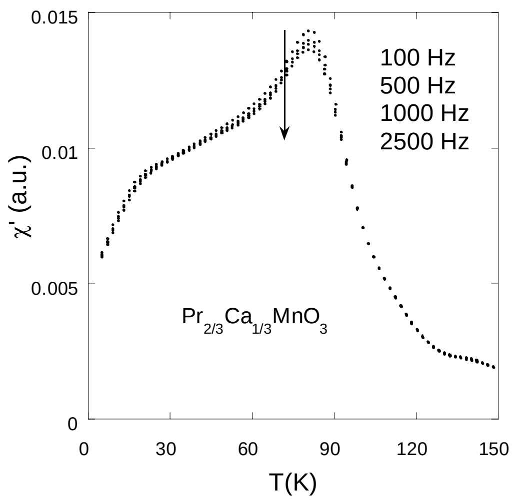

Fig. 3. Frequency dependence of $\chi'(T)$ for the sample $Pr_{2/3}Ca_{1/3}MnO_3$.

Both the real $\chi'(T)$ and imaginary $\chi''(T)$ components of ac susceptibility, of $Pr_{2/3}Ca_{1/3}MnO_3$ sample have peaks at $T \sim 16$ K, as shown in Fig. 4, in spite of the fact that no features were seen in $M(T)$ and $\rho(T)$ curves. This behavior can be correlated with the presence of magnetic clusters in the system, i.e. holes-rich and holes-poor regions due to the spin state transition (SST) of Co^{3+} from LS to IS states.

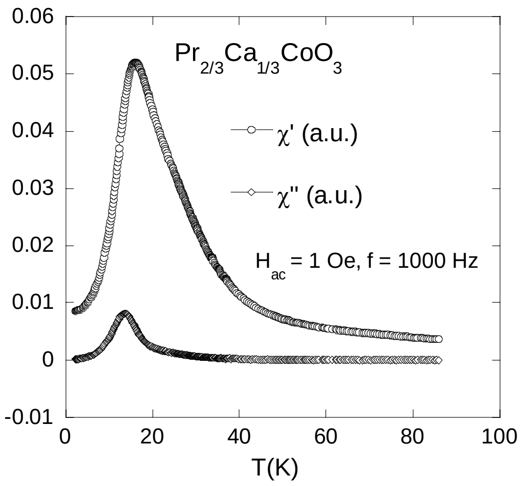

Fig. 4. Real (χ') and imaginary (χ'') components of the ac susceptibility of $Pr_{2/3}Ca_{1/3}CoO_3$ measured in zero applied static magnetic field. H_{ac} = 1 Oe and f = 1000 Hz.

The cobaltite samples have semiconducting behavior in the whole temperature range while $Pr_{2/3}Ca_{1/3}MnO_3$ is insulating in low magnetic fields (below 4 T). Temperature dependences of electrical resistivity $\rho(T)$ in zero field and 7 T, and the magnetoresistance (in insets) are shown in Fig. 5 and 6 for the $La_{2/3}Sr_{1/3}CoO_3$ and $Pr_{2/3}Ca_{1/3}CoO_3$ samples.

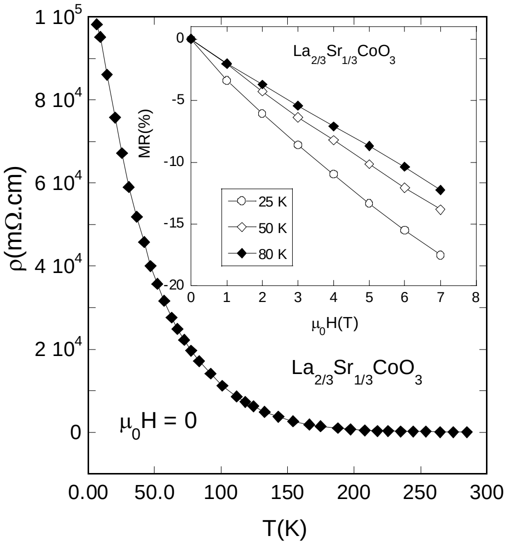

Fig. 5. $\rho(T)$ curve for the sample $La_{2/3}Sr_{1/3}CoO_3$ in 0 T. In inset: magnetoresistance, MR, at 25, 50 and 80 K.

The magnetotransport properties for cobaltites do not seem to be linked to the occurrence of magnetic transition from paramagnetic state to the cluster glass state, as ac susceptibility measurements indicated. This behavior can be correlated with the grain-boundary effects that could mask the change of conductivity expected due to magnetic transitions. A negative magnetoresistance $MR = [\rho(H)-\rho(0)]/\rho(0)$ of about 24% (at 100 K) was found for the sample $La_{2/3}Ca_{1/3}CoO_3$, 18 % (at 25 K) for $La_{2/3}Sr_{1/3}CoO_3$ while for the sample $Pr_{2/3}Ca_{1/3}CoO_3$ the MR is only a few percents in a magnetic field of 7 T (at temperatures between 7 and 20 K).

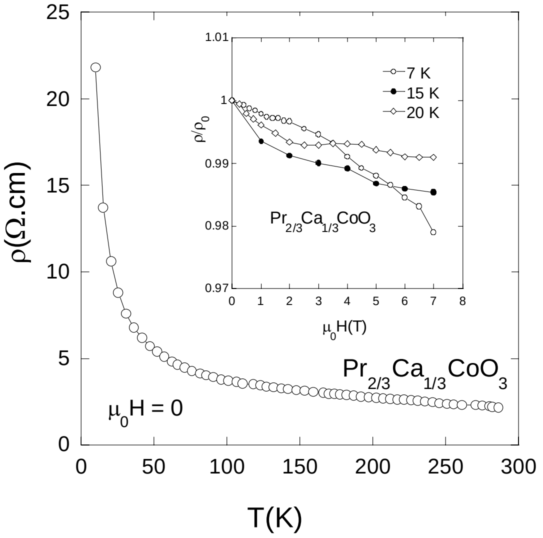

Fig. 6. $\rho(T)$ curve for the sample $Pr_{2/3}Ca_{1/3}CoO_3$ in 0 T. In inset: $\rho(H)/\rho(0)$, at 7, 15 and 20 K.

Conduction in cobaltites is based on the hybridized IS Co^{3+}/LS Co^{4+} configurations in the presence of itinerant e_g electrons[11,12], while in manganites the e_g electrons are scattered by the Mn ions. In both systems, the substitution of Ca^{2+} and Sr^{2+} for Ln leads to segregation in holes-rich (ferromagnetic clusters) embedded in a non-ferromagnetic (AFM or PM) matrix.

The above mentioned magnetic behaviors and the negative magnetoresistance are typical features of the electronic phase separation in transition metal oxides. At low temperatures the FM clusters extend and interact each other and the cluster glass state occurs.

4. Conclusions

The solid solutions $Ln_{2/3}A_{1/3}MO_3$ where Ln = La, Pr; A = Ca, Sr and M = Mn or Co form perovskite structures with orthorhombic or rhombohedral symmetry.

The samples behaves as “cluster glass” showing both spin-glass-like and ferromagnetic behavior. The presence of correlated magnetic clusters, at low temperatures, was confirmed by magnetization measurements, the frequency dependence of the ac susceptibility and from non-linear ac susceptibility. The data suggest that the FM clusters (hole rich regions) are embedded in some AFM (or PM) regions.

The electrical behavior of the studied samples has the main features of conduction in a phase separated system: it shows negative magnetoresistance and it is controlled by grain-boundary effects.

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