



Experimental study of charge ordering transition in $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$

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Abstract

Charge ordering and antiferromagnetic transitions in $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ have been studied by resistivity, thermo-power, magnetic susceptibility and capacitance measurements. Strong magnetic competition arising from the distorted perovskite structure leads to a complex behavior. The appearance of the charge ordering coincides with antiferromagnetism at ≈ 225 K, leading to a large capacitive response of the material. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Colossal magnetoresistance; Charge ordering

The study of manganese oxides with mixed valence (as $\text{A}_{1-x}\text{B}_x\text{MnO}_3$; where $\text{A} = \text{La}^{3+}$, Pr^{3+} , etc. and $\text{B} = \text{Ca}^{2+}$, Sr^{2+} , etc.) has greatly advanced in the last few years [1]. These doped systems are characterized by a strong competition between two different ground states: a charge-ordered (CO) insulating state, where the electric charges are localized and a charge-delocalized (CD) state, having metallic-like conductivity [2,3]. The magnetic properties of these two states are also quite different: the CO state is antiferromagnetic (AF) while the CD state is ferromagnetic. The ferromagnetic properties of these compounds were qualitatively explained by the double-exchange (DE) model developed by de Gennes [4], but the superexchange (SE) interaction is also superimposed in this scenario. Above a characteristic temperature both states transform into a charge-localized state (CL), characterized by being paramagnetic and with a semiconducting behavior of electrical resistivity. The CD–CL transition is very sensitive to an applied mag-

netic field, giving rise to the colossal magnetoresistance (CMR) effect [5].

The energetic balance between the CO, CD, and CL states can be tuned by several methods. For example, the CO or CL states are stabilized by an increase in the structural distortion from the ideal perovskite lattice. The system $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ is ideal to study this effect, due to the perfect matching of the A-site ionic radii. Because of this fact, this compound has been the subject of several studies [6–9].

Polycrystalline samples of $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ were prepared using the solid-state reaction method with a final sintering treatment at 1300°C for 100 h. Oxygen content was determined by iodometric analysis. X-ray powder diffraction analysis confirms the formation of the perovskite and only a small amount of Mn_3O_4 (<1.5% w/w) has been detected as an impurity. Electrical resistivity was measured by the standard four-probe method. Parallel plate arrangements were applied to read impedance values $Z(\omega)$ on a Genrad 1690 digital bridge, assuming

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$$\frac{1}{Z} = \frac{1}{R} + j\omega C.$$

Thermopower was measured on bare pellets using gold-plated electrodes, at temperatures $T \pm \Delta T/2$, $\Delta T = 1$.

As illustrated by the resistivity curve presented in Fig. 1, $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ remains insulating in the temperature range studied, and at $T = 225$ K we observe the appearance of CO state by a sudden rise in the curve. The low value of the mean angle Mn–O–Mn, caused by small $\langle \text{Pr, Ca} \rangle$ size is responsible for the break in the DE interaction. Thermopower measurements (Fig. 1) show the CO state and also the development of an AF order below 160 K, as we shall discuss later. The noncoincidence of the activation energies for conduction and thermopower is a proof of small polaron conduction in the CD state [10]. Magnetic susceptibility measurements show a peak corresponding to an AF transition at the same temperature as when CO appeared (Fig. 2). The close relation between these two effects is caused by the importance of the magnetic interactions relative strength

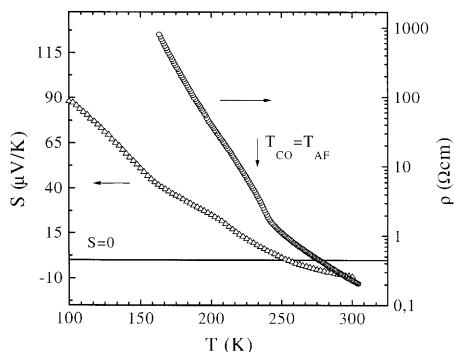


Fig. 1. Resistivity and thermopower (circles and triangles, respectively) versus temperature. The rise in the resistivity and thermopower curves at 225 K denotes the appearance of CO.

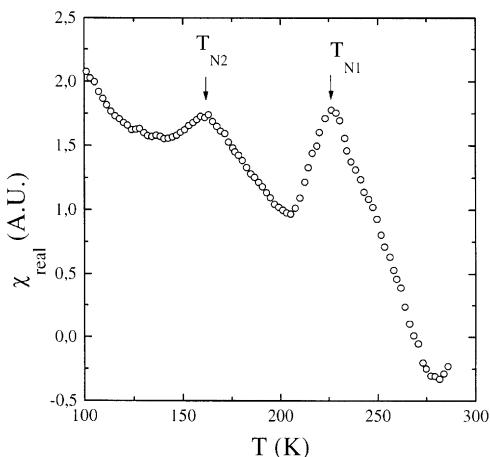


Fig. 2. Magnetic susceptibility (real part) versus T . The magnetic transitions (T_{N1} and T_{N2}) are indicated. T_{N1} coincides with the CO temperature.

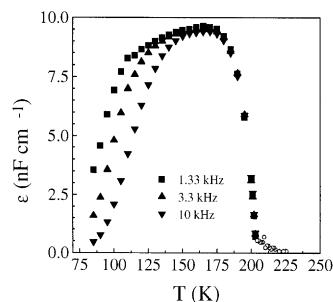


Fig. 3. Dielectric constant versus T below 225 K at different frequencies. Note the high capacitive effect present in this region. Complex relaxation processes are present below 160 K.

in the transport properties. A second AF transition at ≈ 160 K is also detected. Both are consequences of the strong magnetic competition in temperature.

As a consequence of AF order in the CO state, polaron hopping between neighboring Mn sites is minimized. This allows the formation of electric dipoles which cause the capacitive response below 225 K (Fig. 3). At temperatures below the second antiferromagnetic transition at 160 K, strong relaxation phenomena are present in the sample. Capacitive measurement should be a direct proof of charge ordering states.

In summary, we observe how magnetic interactions in $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ lead to a CO state coincident with the appearance of an AF order at 225 K. This charge ordering induces a strong capacitive response that we can measure directly. Below this temperature several complex magnetic transitions are present in the sample.

This work has been financially supported by the Spanish DGICYT (PB94-1528).

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