

Solid State Communications 110 (1999) 179-183

solid state communications

Strong ferro-antiferromagnetic competition and charge ordering in $Pr_{0.67}Ca_{0.33}MnO_3$

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Received 13 October 1998; accepted 21 November 1998 by F. Yndurain

Abstract

In this article we present d.c. resistivity, a.c. impedance, magnetization and dielectric permittivity measurements in $Pr_{0.67}Ca_{0.33}MnO_3$. A rise in the imaginary part of impedance was detected at the charge ordering transition temperature (T = 225 K). This indicates an intrinsic capacitive behavior of the sample in the charge ordering state. The a.c. impedance is presented here as a valid and easy tool to characterize the charge ordering transition. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: A. Magnetically ordered materials; D. Dielectric response; D. Electronic transport

1. Introduction

The extremely high values of colossal magnetoresistance (CMR) reported in recent years for mixed valence manganites, particularly in Ln_{0.67}A_{0.33}MnO_{3±δ} (Ln = trivalent rare earth, A = Ca, Sr), justify the great theoretical and experimental efforts made in this field [1–3]. This intrinsic magnetoresistance is associated with the occurrence of a ferromagnetic– paramagnetic (FM–PM) transition at the same temperature at which a metal–insulator (M–I) transition takes place ($T_c = T_{MI}$). Within the framework of the double exchange interaction (DE) [4], the presence of mobile e_g electrons hopping from Mn³⁺

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to Mn^{4+} ions, conserving their spin (Hund's coupling), is responsible for the close relationship of both ferromagnetism and metallic conductivity in these compounds. Complete ferromagnetic order of the t_{2g} spins minimizes magnetic scattering and hence resistivity. It is the so called double exchange ferromagnetism (DE-FM). However, antiferromagnetic superexchange (AF-SE) interaction between the localized t_{2g} (S = 3/2) spin core is also present at the same time [5], and several works have shown how the relative strength of these FM–AF interactions can be tuned changing the radius of the rare-earth [6,7].

 $Pr_{1-x}Ca_xMnO_3$ provides one of the best examples to understand some of the issues involved in FM-AF interactions in CMR materials [8]. In the example, $Pr_{0.7}Ca_{0.3}MnO_3$ does not suffer the typical M–I transition associated with the intrinsic CMR, and some

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nominal stoichiometry. Numbers in parenthesis are the standard deviations. (The ionic radius were taken from Ref. [18])					
Atom	Site (Pbnm)	X	у	ζ	
Mn	4a	0	0	0	
Pr/Ca	4c	-0.0317(1)	0.0053(4)	0.25	
O _(I)	4c	0.009(1)	0.562(1)	0.25	
O _(II)	8d	-0.282(1)	-0.062(1)	0.275(1)	
t = 0.931		$d_{\rm Mn-O_1} = 1.945(1)$	a = 5.4239(2)		
$\langle \theta \rangle = 157^{\circ}$		$d_{\rm Mn-O_{II}} = 1.992(5)$	b = 5.4508(1)		
		$d_{\rm Mn-O_{II}} = 1.936(5)$	c = 7.6629(1)		
$\chi^2 = 2.31$			$c/\sqrt{2} = 5.4185(1)$		
$R_{\rm b} = 6.86$					
$R_{wp} = 9.21$					

Room temperature structural parameters refined for $Pr_{0.67}Ca_{0.33}MnO_{3\pm\delta}$. The site occupancies were kept at fixed values consistent with the nominal stoichiometry. Numbers in parenthesis are the standard deviations. (The ionic radius were taken from Ref. [18])

authors [9,10] have reported a complex magnetically frustrated state and the appearance of charge ordering (CO) below a certain temperature for this compound. However, the origin of this magnetic frustration is not clear now, and the mechanism for the CO developing has not been satisfactorily explained.

We have observed an insulating state in the whole temperature range, with a CO transition at ≈ 225 K. This transition has also been evidenced by means of a.c. impedance and dielectric permittivity measurements at several frequencies. To the best of our knowledge this constitutes the first measurement of this kind carried out in CO manganites.

2. Experimental

Polycrystalline samples of $Pr_{0.67}Ca_{0.33}MnO_{3\pm\delta}$ were prepared using the solid state reaction method. A stoichiometric mixture of oxides (Pr_6O_{11} , CaO, MnO and MnO₂, at least 99.995% in purity) was heated in air at different temperatures (1100°C, 70 h; 1200°C, 30 h), with intermediate grinding steps and pressed into disks. The temperature was ramped at 5°C min⁻¹, and cooled down to room temperature at 2°C min⁻¹. In the final sintering process the pellets were annealed at 1300°C for 100 h, with an intermediate grinding at 30 h. The oxygen content was found to be $3 \pm \delta =$ 2.983(2), as determined by iodometric analysis. X-ray powder patterns were collected at room temperature with a Phillips PW1710 diffractometer, working with Cu K_α ($\lambda = 1.5481$ Å). Structural information was derived using the program LS1, based on the Rietveld method, and fitting profiles to pseudo-Voigt functions [11]. Electrical resistivity was measured using the four-probe method at a constant current. For impedance measurements, a General Digital Bridge 1689 was used. An arrangement of parallel plates, with an area, A, and separated by a distance, d, was applied to read the impedance values $Z(\omega)$ with the Genrad Bridge, assuming

$$\frac{1}{Z} = \frac{1}{R}(1 + \mathrm{i}\omega RC). \tag{1}$$

The dielectric permittivity, ε , was estimated from the capacitance measurements according to $\varepsilon = Cd/A$. Also the relaxation of V(t) was measured between the plates, after the application of a current step at t = 0. FC–ZFC curves were measured between $4 \text{ K} \le T \le 300 \text{ K}$ with a Quantum Design SQUID magnetometer in a field of 100 Oe.

3. Results and discussion

X-ray analysis of the samples confirms the formation of the perovskite, and only a small amount (<1.5% w/w) of ferrimagnetic Mn₃O₄ has been detected as an impurity [12]. However, as this compound is not magnetically ordered above $T_C =$ 42 K does not influence the main conclusions of this article. The room temperature lattice and positional parameters refined for Pr_{0.67}Ca_{0.33}MnO_{3±δ} are given in Table 1. The values correspond well with those

Table 1



Fig. 1. (a) The d.c. resistivity vs. temperature. The rise at 225 K denotes the appeareance of CO. (b) d ln $\rho/d(1/kT)$ vs. *T*, two peaks can be observed coinciding with the $T_{\rm CO}$ and $T_{\rm N2}$ transitions. An unusually large energy gap is observed at $T_{\rm CO}$.

determined from neutron diffraction experiments for similar compositions [8]. As can be seen in Table 1, one of the Mn–O bonds is much larger than the other two. This produces the internal distortion of the MnO₆ octahedra without changing the symmetry (Pbnm) but modifying the crystal structure in such a way that $(c/\sqrt{2}) < a < b$ (O'-Pbnm) [5]. The low Mn–O–Mn angle is also noticeable. The small value of this angle reduces the electronic bandwidth and is the responsible for many interesting features of the magnetotransport properties in this compound.

As illustrated by the d.c. resistivity curve in Fig. 1(a), $Pr_{0.67}Ca_{0.33}MnO_{3\pm\delta}$ remains insulating in the measured range because of the decrease in the influence of the DE-FM interaction. The increase in the resistivity curve at ≈ 225 K suggests the appearance



Fig. 2. (a) Imaginary part of impedance measured at several frequencies. (b) Temperature dependence of dielectric permittivity $\varepsilon(\omega)$. The sharp increase at 225 K denotes capacitive behavior of the sample below this temperature. Open circles represent data obtained from capacitive measurements. Below ≈ 160 K complex relaxation behavior produces the observed frequency splitting.

of a CO transition at this temperature. This transition is also observable as a peak in the d ln $\rho/d(1/kT)$ vs. T plot (Fig. 1(b)) [13]. In a traditional semiconductor material a constant value (associated to the activation energy, E_a) is expected in this plot. However, an unusually large gap of 350 meV appears just at the CO transition which indicates a very large energy associated to the CO process.

Above the CO transition temperature, i.e. in the charge-localized-paramagnetic state, several authors have reported a small polaron conduction mechanism in the adiabatic limit [14]. The values of $E_a \approx 160 \text{ meV}$ obtained by us at $T \ge 225 \text{ K}$ agrees with this conduction mechanism above the charge ordering state. Similar values (around 100 meV) near $\approx 125 \text{ K}$



Fig. 3. Magnetization (FC–ZFC) of the sample. A clear irreversibility between the FC and ZFC curves is observable below $T_{CO} \approx 225$ K, probably due to some kind of magnetic frustration.

could also indicate the presence of a hopping conduction mechanism below $T_{\rm CO}$.

At low temperatures, 77 K $\leq T \leq 130$ K, voltage measurements of the dielectric relaxation were made in order to confirm the earlier presumption. Fitting the V(t) isotherms to a stretched exponential behavior $(\exp - (t/\tau)^{\beta})$ the relaxation times (τ) and $\beta \approx 0.7$ were obtained. The temperature dependence of τ can be described by an Arrhenius law with $E_a \approx 100$ meV. This is the same value as that obtained from the resistivity data in the same temperature range.

The course of the imaginary part of the a.c. electrical impedance is shown in Fig. 2(a). The main features of this curve are the rapid rise and the frequency splitting at the CO transition temperature $(T_{\rm CO})$. These two effects reflect capacitive behavior of the sample, probably associated to electric dipole formation below $T_{\rm CO}$. To explore in more detail the existence of such intrinsic capacitive behavior, the temperature dependence of the dielectric permittivity, $\varepsilon(T)$, (Fig. 2(b)) has been studied at several frequencies. To ensure accuracy in the values of $\varepsilon(\omega)$ near $T_{\rm CO}$, we have derived the data close to zero from capacitive measurements. The extremely large values of $\varepsilon(\omega)$ below 225 K suggest the existence of a very effective charge localizing effect, confirming the hypothesis of an intrinsic capacitive behavior in $Pr_{0.7}Ca_{0.3}MnO_3$ at $T \le T_{CO}$. Below 160 K, a frequency splitting in $\varepsilon(\omega)$ associated to a complex dielectric relaxation behavior is observed (Fig. 2(b)), presumably due to some kind of magnetic frustration in the system.

However, neutron diffraction experiments [9] revealed the existence of three different phase transitions for $Pr_{0.7}Ca_{0.3}MnO_3$: A CO at $T_{CO} = 200$ K; an AF ordering at $T_{\rm N} = 140$ K; and a CAF structure below $T_{CAF} = 110$ K. Although the resistivity (Fig. 1(a)) and the FC-ZFC curves (Fig. 3) confirm the transitions deduced from neutron diffraction experiments, some important differences become evident. All the transitions observed anticipate to some degree (≈ 20 K) those determined by neutron diffraction (our analysis gave a result of %Mn = 29.6 \pm 0.02, practically identical to the samples examined in neutron diffraction experiments by Yoshizawa et al. [9]). The existence of a long-range magnetic order is a requirement to obtain a magnetic reflection in neutron diffraction patterns. Probably, the transition temperatures determined here point to the beginning of a short-range magnetic arrangement. Similar disagreement with the magnetic transition temperatures determined by neutron diffraction has been reported for x = 0.5 by Maignan et al. [10] and Damay et al. [15] based on a.c. susceptibility measurements.

Moreover, magnetic measurements revealed an additional paramagnetic insulating to the antiferromagnetic insulating (PMI–AFI) transition at $T_{\text{NI}} \approx T_{\text{CO}} \approx 225$ K. Also Lees et al. [16] recently reported that CO appears at $T \ge 250$ K for $x \ge 0.3$, but our data show this transition at 225 K for x = 0.33.

The close coupling between the CO and AF transition temperatures ($T_{\rm CO} \approx T_{\rm Nl}$) must be emphasized. The AF order developed below T_{N1} maximizes magnetic scattering and hence minimizes polaron hopping between different Mn sites creating electric dipoles. Moreover, we have observed a clear irreversibility of the FC-ZFC magnetization curves below $T_{\rm CO}$. In such a narrow band system, the hysteresis in the FC-ZFC curves below 225 K reflects the competition between AF coupled t_{2g} and incipient FM coupled eg states. The existence of this magnetically frustrated state has been explained in terms of the existence of FM clusters in a PM matrix by Cox et al. [17]. These clusters would be parallel aligned at $T_{\rm c} = 130$ K, giving rise to the spontaneous magnetization observed below this temperature.

In summary, we have studied the magnetic and

electric properties of the charge ordering state in $Pr_{0.7}Ca_{0.3}MnO_3$. Both direct measurements of ωRC and $\varepsilon(\omega)$ vs. *T* indicate an intrinsic capacitance below $T_{CO} = 225$ K. These capacitive effects are accompanied with a splitting in the FC–ZFC magnetization curves suggesting the existence of a strong FM–AFM competition. Complex dielectric relaxation processes have also been observed below 160 K. Finally, the values of E_a points to a polaron hopping conduction mechanism in the whole temperature range in this material.

Acknowledgements

The authors acknowledge support from Ministerio de Educación y Ciencia (M.E.C.) of Spain (Project Ref. MAT-98-0416). F.R. also acknowledges an F.P.U. fellowship from M.E.C. and U.S.C.

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