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LETTER TO THE EDITOR

Evidence for Jahn–Teller polaron formation and spin-cluster-assisted variable-range-hopping conduction in $La_{0.7}Ca_{0.3}MnO_3$

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Abstract. Resistivity (15–710 K), magnetization (80–723 K), and calorimetric (200–623 K) measurements on $La_{0.7}Ca_{0.3}MnO_3$ have shown evidence for the formation of Jahn–Teller (JT) polarons below ∼545 K. Above 560 K, activated conduction with $E_a = 0.05$ eV is observed and $\chi^{-1}(T)$ shows Curie–Weiss behaviour. Over the temperature range 270–340 K, the conductivity follows Mott's VRH model and $\chi^{-1}(T)$ provides evidence of the formation of spin clusters. Calorimetric study shows phase transitions at T_c (=245 K), 345 K and 545 K. The role of the JT polaron in determining the electronic and magnetic properties above T_c is discussed.

The recent discovery [1] of colossal magnetoresistance (CMR) in thin films of $La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba etc) has led to subsequent detailed investigation of the structural, electrical, and magnetic properties of these ferromagnetic mixed-valence manganites. Substitution of Ca^{2+} for La^{3+} in the antiferromagnetic insulator $LaMnO_3$ gives rise to an equivalent amount of Mn^{4+} which induces ferromagnetism in $La_{1-x}Ca_xMnO_3$. The maximum Curie temperature ($T_c = 272$ K) as well as the minimum resistivity is observed for $x \approx 0.3$, and the maximum charge-ordering temperature ($T_{CO} = 265$ K) is observed for $x = 5/8$ [2, 3]. Both ferromagnetism and the electrical conductivity are explained in terms of the double-exchange (DE) interaction arising from strong on-site Hund's rule coupling between Mn^{3+} and Mn^{4+} ions [4]. Hopping of the e_g electron of Mn^{3+} between these manganese ions in the lattice gives rise to metallic conductivity in the ferromagnetic region.

Above T_c the electrical conduction in $La_{0.7}Ca_{0.3}MnO_3$ is shown to follow the activated hopping conduction law [5] $\rho \propto \exp(E/kT)$, with the activation energy $E \sim 0.1$ eV, as well as Mott's variable-range-hopping (VRH) conduction rule [6–8], $\rho \propto \exp(T_0/T)^{1/4}$, where $kT_0 = 18\alpha^3/N(E)$, which gave an unrealistically small value of the localization length, $\xi = 1/\alpha$. Viret *et al* [6] have shown that a modified function $kT_0 \propto \alpha^3 J_H v$ gives a hopping distance comparable to the lattice spacings. It has been proposed that a polaronic conduction mechanism can enhance the resistivity in the paramagnetic region, and that the Jahn–Teller (JT) distortion of Mn^{3+} may assist polaron formation [9–11].

In order to examine the validity of the proposed conduction mechanisms above RT, we have investigated the resistivity and magnetic susceptibility behaviour of $La_{0.7}Ca_{0.3}MnO_3$

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below 723 K and found strong evidence for the formation of JT polarons. In this report we show that this JT polaron determines the electronic and magnetic properties above T_c.

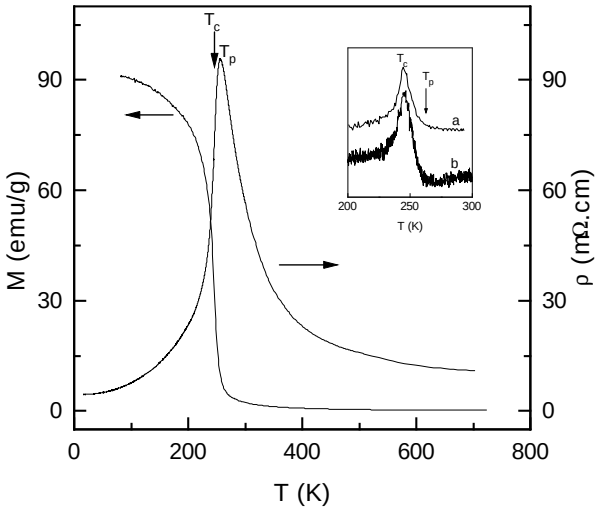

Figure 1. The temperature variation of the resistivity and magnetization (measured at 0.5 T) of $La_{0.7}Ca_{0.3}MnO_3$. Inset: (a) dM/dT, and (b) $d\rho/dT$.

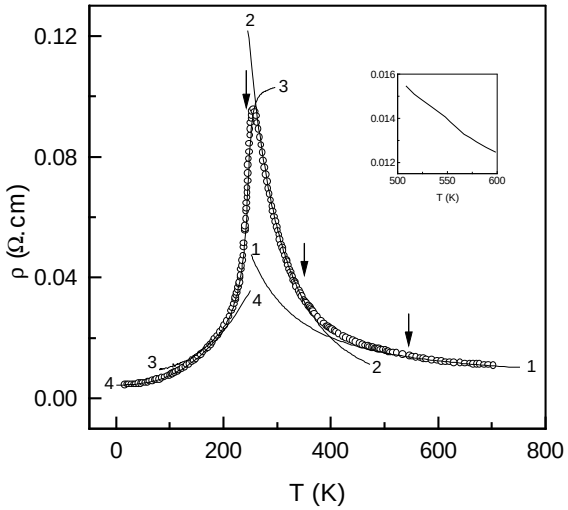

Figure 2. The experimental (circles) and the calculated (solid lines) $\rho(T)$ curves; the numbers correspond to the respective equations given in the text from which the resistivity curves are calculated using the least-squares-fitted parameters. The arrows indicate the temperatures at which the DSC curve shows phase transitions. The inset shows the drop in resistivity at 540 K.

Polycrystalline $La_{0.7}Ca_{0.3}MnO_{3\pm0.01}$ was synthesized by the ceramic method and heated at a sufficiently high temperature (1300 °C) to ensure maximum compositional homogeneity [12]. Figure 1 shows the resistivity and the magnetization (measured at 0.5 T) curves of $La_{0.7}Ca_{0.3}MnO_3$. The resistivity curve shows a maximum at $T_p \approx 260$ K and a sharp drop at T_c which coincides with the sharp increase in the magnetization curve.

$T_c \approx 245$ K, obtained from the derivative curves of both magnetization and resistivity (shown in the inset). The shape of the $d\rho/dT$ curve is similar to the magnetic specific heat data reported by Park *et al* [13], and both the $d\rho/dT$ and dM/dT curves rise above the background at $\sim T_p$. Thus, the resistivity behaviour close to T_c seems to be affected by the short-range ordering which becomes predominant below T_p.

The resistivity curve shows a slope change above 540 K (inset, figure 2), and the resistivity above 560 K follows the thermally activated conduction law

$$\rho(T) = \rho_1 \exp(E_a/kT) \tag{1}$$

with the activation energy $E_a = 0.05$ eV and $\rho_1 = 4.75 \times 10^{-3}$ Ω cm. Figure 2 shows that the resistivity of the sample below 560 K is higher than that expected from the resistivity curve calculated using the above equation (curve 1). The high-temperature differential scanning calorimetry (DSC) curve of $La_{0.7}Ca_{0.3}MnO_3$ shown in figure 3 indicates that a structural transition ($\Delta H \approx 0.7$ J g^{-1}) takes place at 545 K. This weak transition may be assigned to that due to the JT distortion of the MnO_6 octahedra as observed for $LaMnO_3$ for which the cubic–tetragonal transition due to the JT distortion is observed at ~700 K (for $La_{0.7}Ca_{0.3}MnO_3$ the proportion of JT ions, Mn^{3+}, is reduced to 70%, so a decrease in the transition temperature can be expected) [14]. This JT distortion gives rise to a local lattice distortion around the conduction electron, and the composite consisting of the electron and the surrounding lattice distortion (the JT polaron) [15] can move through the lattice as a whole. Thus, below 545 K, JT polarons are formed and the electrons are trapped by the lattice distortion which enhances the resistivity (figure 2). A second-order phase transition at ~345 K with a heat capacity change of ~240 mJ K^{-1} g^{-1} is also observed in the DSC curve (figure 3). This weak transition with the characteristic base-line shift is like a transition from rigid structure at low temperature to a flexible structure [16].

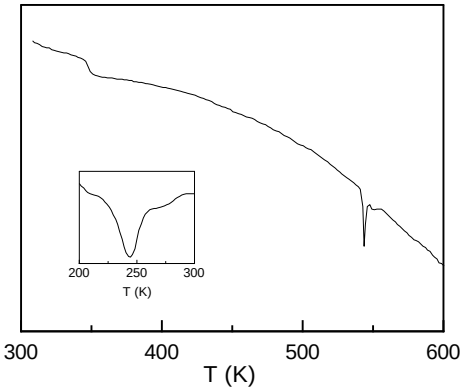

Figure 3. The DSC curve of $La_{0.7}Ca_{0.3}MnO_3$, above room temperature (heating rate: 5 K min^{-1}). Inset: the DSC curve below RT showing a transition at T_c.

Between the two transition temperatures (345–545 K), the resistivity of the compound is continuously increased as the temperature is decreased, and the activated conduction mechanism gave an extremely poor fit to the data. However, in the temperature range 265–340 K the resistivity follows Mott's VRH expression (curve 2 in figure 2):

$$\rho(T) = \rho_\infty \exp(T_0/T)^{1/4} \tag{2}$$

with $T_0 = 15 \times 10^6$ K, and $\rho_\infty = 18 \times 10^{-9}$ Ω cm. Since there are reports showing that, above T_c up to 300 K, the resistivity follows the activated hopping conduction law [5],

we have tested the validity of this mechanism in the same temperature region. It was found that this nearest-neighbour hopping mechanism gave a least-squares fit only between 275 and 303 K. The deviation of the VRH behaviour above 340 K is associated with the second-order phase transition for $La_{0.7}Ca_{0.3}MnO_3$. Since polarons are formed below 545 K, and polaronic conduction is expected to follow the relation $\rho/T^s \propto \exp(E/kT)$, where $s = 1$ in the adiabatic limit and $s = 3/2$ in the non-adiabatic limit [17], we have tried to fit the resistivity curve between 345 and 545 K in both of the limits. Neither of these two approximations were found to be valid in this temperature region. However, a perfect least-squares fit over the entire temperature region (345–545 K) is obtained when $s = 5/2$. At present we are not able to comment on the theoretical implications of such a high value of s.

The above results are in accordance with the theoretical predictions of Millis *et al* [9, 18], who showed earlier that the DE model alone cannot explain the resistivity behaviour of the manganites at $T > T_c$. Röder *et al* [10] later showed that with the inclusion of finite JT coupling along with the DE, the desired effect proposed by Millis *et al* [9] can be obtained. Photoemission studies [19] suggested that strong small-polaron effects are responsible for the insulating behaviour of the manganites above T_c, and the optical [20] data are consistent with the models which include both DE and JT effects. Since the JT polarons affect the spins of their neighbours, they function like magnetic polarons as proposed by Kusters *et al* [11]. De Teresa *et al* [8, 21] have shown that small magnetic polarons are responsible for the enhanced magnetoresistance near T_c in the manganites.

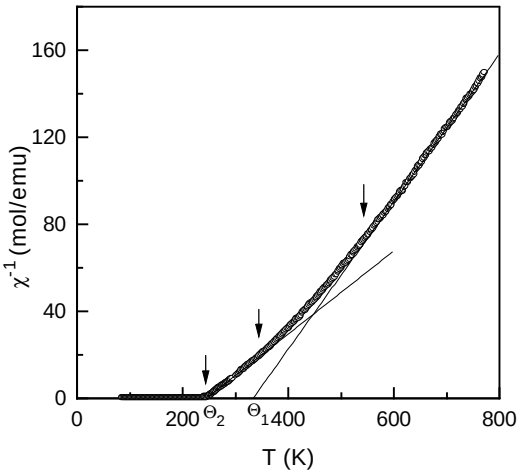

Figure 4. The $\chi^{-1}(T)$ curve (circles) showing the least-squares fit to the Curie–Weiss expression below 340 K and above 560 K (see the text for details). The arrows indicate the temperatures at which the DSC curve shows phase transitions.

In figure 4, the inverse of the magnetic susceptibility is shown. From a high-temperature fit using the Curie–Weiss equation, $\chi = C/(T - \Theta)$, the paramagnetic Curie temperature Θ (Θ_1) is obtained as 333 K and the Curie constant $C = 2.9$ emu K mol^{-1} (C_1) whereas immediately above T_c, a similar fit gave $\Theta = 246$ K (Θ_2) and $C = 5.3$ emu K mol^{-1} (C_2). The Curie constant obtained from the high-temperature region is larger than that expected for $La_{0.7}Ca_{0.3}MnO_3$ ($C = 2.64$ for $0.7Mn^{3+}$, $S = 2$ and $0.3Mn^{4+}$, $S = 3/2$). Some other important features of both the low- and high-temperature fits to $\chi^{-1}(T)$ are (a) $\Theta_2 \approx T_c$, (b) the fit in the low-temperature region deviates above ∼345 K, (c) the high-temperature

fitted curve deviates below ∼560 K, and (d) the ratio $C_2/C_1 = 1.8$. The $\chi^{-1}(T)$ curve over the temperature range 345–560 K can be fitted to Curie–Weiss behaviour for small segments whose C-values continuously increase from 2.9 to 5.3 as the temperature is decreased. One such fit of χ^{-1} versus T/T_c below 540 K deviates at $\sim 1.8T_c$ with $\Theta \approx 1.25T_c$ as observed by De Teresa *et al* [21] However, over the entire temperature range 345–560 K the $\chi^{-1}(T)$ curve is non-linear and found to show a T^2-dependence. The Curie–Weiss behaviour with a large value of C below 345 K implies that spin clusters are present which behave like paramagnetic species above T_c. Since the Curie constant in this temperature region is almost twice the value expected for $La_{0.7}Ca_{0.3}MnO_3$, it seems that the Mn ions are existing as dimers. ESR linewidth studies above T_c for the manganites suggested the possibility of the formation of Mn^{3+}–Mn^{4+} *spin clusters* in the paramagnetic state and a decrease in the thermal broadening rate above $T \approx 560$ K [22]. These dimers are then of the form Mn^{3+}–O–Mn^{4+}, the Zener pairs, which are responsible for ferromagnetism in the manganites [4].

For $SrRuO_3$, a well known ferromagnetic oxide with the same perovskite structure as the manganites, with Ru^{4+} having a d^4 electronic configuration but with negligible JT distortion when compared to Mn^{3+}, $\chi^{-1}(T)$ above the Curie temperature shows Curie–Weiss behaviour with a Curie constant comparable to that expected for a low-spin d^4 (t_{2g}^4) system [14, 23]. The much lower value of T_c for $La_{0.7}Ca_{0.3}MnO_3$ when compared to the paramagnetic Curie temperature Θ_1 then indicates that the JT distortion is responsible for the decrease in the magnetic transition temperature. Thus it appears that T_c for $La_{0.7}Ca_{0.3}MnO_3$ would have been close to 333 K (Θ_1) if there was no JT distortion at 545 K. However, a second-order phase transition is observed at this anticipated temperature (figure 3). The effect of the oxygen isotope on T_c for the above two systems also suggested the formation of JT polarons in the manganites [24]. Since the Curie temperature $T_c \propto W_{eff}$, the bandwidth of polarons, a lower T_c-value can be expected for polarons with extremely small bandwidth, and the maximum value of T_c depends on the strength of the JT coupling.

Both the VRH behaviour and the low-temperature Curie–Weiss behaviour deviate above ∼340 K where a second-order phase transition is observed. Similarly, the deviation of the high-temperature inverse susceptibility from the Curie–Weiss law and the high-temperature resistivity curve from the activated conduction behaviour are almost in the same temperature region (∼560 K) below which a structural transition due to Jahn–Teller distortion is observed. This implies that magnetization induced by the trapped electron is localized within the JT ion Mn^{3+} and its immediate Mn^{4+} neighbours, which causes a reduction in the magnetization. The direct correlation between the behaviour of the high-temperature ($T > T_c$) resistivity and magnetic susceptibility data indicates that the anomalies at different temperatures can be linked to the existence of magnetic polarons.

As both $\chi^{-1}(T)$ and $\rho(T)$ below 560 K continuously vary from the high-temperature fitted curves as the temperature is reduced, this could be due to the continuous growth of the magnetic polarons until another characteristic temperature ∼345 K is reached. At this temperature the polaron becomes indistinguishable [25] between the Mn^{3+} and Mn^{4+} ions due to DE, so magnetic clusters are formed with a Curie constant that is double the expected value. The resistivity below this temperature follows the VRH behaviour. The second-order transition at ∼345 K may be thought of as another cooperative distortion due to the strong coupling of the JT ion Mn^{3+} with its neighbouring Mn^{4+}, forming the cluster. From small-angle neutron diffraction results it has been shown that the magnetic clusters above T_c are ∼12 Å in size, and below $\sim 1.8T_c$ the volume thermal expansion of $La_{2/3}Ca_{1/3}MnO_3$ deviates from the calculated anharmonic Grüneisen-like phonon contribution [21]. This change in the volume thermal expansion is a consequence of the JT distortion at the structural transition temperature.

Below T_p the resistivity falls drastically; this coincides with the sharp increase in the magnetization, and the similarity of the $d\rho/dT$ and dM/dT curves indicates that the sharp drop in resistivity below T_p (figure 1) is associated with ferromagnetic ordering. The resistivities of the manganites below T_c were shown to follow $\rho \propto 1-(M/M_s)^2$ as well as $\ln(\rho) \propto (-M/M_s)$ dependences [6, 26]. However, in the present case, the resistivity below T_p could be scaled with the magnetization curve (curve 3 in figure 2), using

$$\rho(T) = a + b(1 - M(T)/M_s) \tag{3}$$

where M_s is the saturation magnetization, and a and b are constants used for scaling. This shows that in the temperature region 200–256 K the electrical conduction is predominantly influenced by the magnetic ordering due to the reduced scattering of the electrons in the magnetically ordered state. The localized charge carriers are released because of long-range ordering [25] when cooled below T_p, and an abrupt decrease in resistivity is observed. Below 180 K ($0.75T_c$) the relation

$$\rho(T) = \rho_0 + \rho_1 T^{2.5} \tag{4}$$

with $\rho_0 = 4.47 \times 10^{-3}$ Ω cm is found to give a good fit to the resistivity data (curve 4 in figure 2). This shows that the resistivity in this temperature region is a combined effect of the electron–electron, electron–phonon, and electron–magnon scattering [27]. It is interesting to note that in the asymptotic limit, the resistivity values (ρ_1 in equation (1) and ρ_0 in equation (4)) are almost identical, whereas the value of ρ_∞ obtained from the VRH law in equation (2) is many orders of magnitude less than ρ_1.

The present results give evidence for the formation of JT polarons in the manganites. For $La_{0.7}Ca_{0.3}MnO_3$ the magnetic polarons formed by the JT distortion are responsible for the observed anomalous behaviour in the electrical and magnetic properties. The Curie–Weiss behaviour of the magnetic susceptibility and activated conduction breaks down below ∼560 K due to the formation of JT polarons. These polarons behave like magnetic polarons, and the size of the polarons increases as the temperature is decreased, which is reflected by the continuous increase of the Curie constant, and condense to form spin clusters. The onset of this cluster formation is shown as a weak second-order phase transformation at 345 K, and below this temperature there is no further growth of their size until the long-range-ordered state is reached. These results provide more support for the proposal that there is *spin-cluster* formation [22]. Between the ferromagnetic ordering and the cluster condensation temperatures, the resistivity follows Mott's variable-range-hopping conduction law.

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