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CURRENT-DEPENDENT POSITIVE MAGNETORESISTANCE IN Ga-DOPED $La_{0.5}Ca_{0.5}MnO_3^*$

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The magnetic and transport properties of the Ga-doped charge-ordering state $La_{0.5}Ca_{0.5}MnO_3$ have been studied. A current-dependent large positive magnetoresistance (1080%) at 5 K was observed. These observations are interpreted in terms of the spin-dependent tunnelling process between ferromagnetic clusters embedded in an antiferromagnetic matrix.

Keywords: manganese oxide, magnetoresistance, spin-dependent tunnelling
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The manganese oxide $La_{0.5}Ca_{0.5}MnO_3$ (LCMO) has attracted considerable attention for its remarkable magnetic and transport properties related to the charge-ordering state.[1−4] Unlike an analogous sample with a larger average radius of A site ions ($\langle r_A \rangle$), such as: $Nd_{0.5}Sr_{0.5}MnO_3$[5] (0.12365nm), which displays a charge-ordering state with fair conductive ability, LCMO has a small $\langle r_A \rangle$ (0.1198nm), i.e. a narrow e_g bandwidth (W) of one electron and shows an insulating state. On cooling, LCMO first undergoes a phase transition from the paramagnetic (PM) state to the ferromagnetic (FM) state at $T_C = 220$ K, then another from the FM state to the antiferromagnetic (AFM) charge-ordering state at $T_N = 170$ K. At low temperatures, the insulating charge-ordering state can be melted by an external magnetic field, which gives rise to metallic behaviour and leads to a resistivity drop of several orders of magnitude, and a very large negative magnetoresistance (MR) ensues.

Substitution is an effective way to study this kind of strong-correlated system. Especially, the substitution on the Mn site[6,7] is attractive because it destroys the perfection of the Mn–O plane and the original magnetic exchange interaction, which should be very useful for understanding the mechanism of the magnetic and transport properties. As is known, charge-ordering is very sensitive to the commensurate ratio of Mn^{3+}/Mn^{4+}, and new exchange coupling will be introduced in the Mn–O plane if magnetic ions are used as a substitute for Mn ions. In this work, for simplicity, we prepared a Ga ion doped sample with the composition of $La_{0.505}Ca_{0.495}Mn_{0.99}Ga_{0.01}O_3$, in which the ratio of Mn^{3+}/Mn^{4+} was deliberately kept as 1:1. The magnetic and transport properties of this compound are studied. Very interestingly, a current-dependent positive magnetoresistance (PMR) has been observed at low temperatures.

The polycrystalline sample was prepared by the standard solid-state reaction technique. The X-ray diffraction patterns of the sample indicate that the sample is single phase without detectable secondary phase or impurity. In addition, since the radius of the Ga ion is close to that of the Mn ion and the doping level of Ga is low, no evident change in the structure compared with LCMO is found. The magnetization was measured as a function of temperature and magnetic field using a SQUID magnetometer. The transport properties were determined by the standard four-probe method with the applied magnetic field parallel to the measuring current.

Fig.1 shows the temperature dependence of the magnetization at 1 T on warming and cooling. In the warming process, similar to LCMO, the doped sample transforms from an AFM state to a FM state rapidly,

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then subsequently to a PM state. The discrepancy of AFM transition temperature in these two processes suggests the first-order nature of the AFM charge-ordering phase transition.[2] A weak FM state below 120 K is observed and can be attributed to FM clusters. At low temperatures, the alternating Mn^{3+} and Mn^{4+} ions are coupled ferromagnetically forming the "zigzag chains" in LCMO, while the interchain coupling is AFM.[1] When some of the Mn ions are replaced, the charge-ordering is partly destroyed due to the absence of charge transfer between the Ga and Mn ions, and FM clusters in the AFM matrix will be introduced by the vacancies of the magnetic ions, similar to that occurring in the case of oxygen vacancies.[8] The magnetization in the cooling process also implies the magnetic frustration in the interface between FM clusters and the AFM matrix, agreeing with our analysis. The low level of doping and the constant Mn^{3+}/Mn^{4+} ratio cause the AFM state to be the ground state in the doped sample.

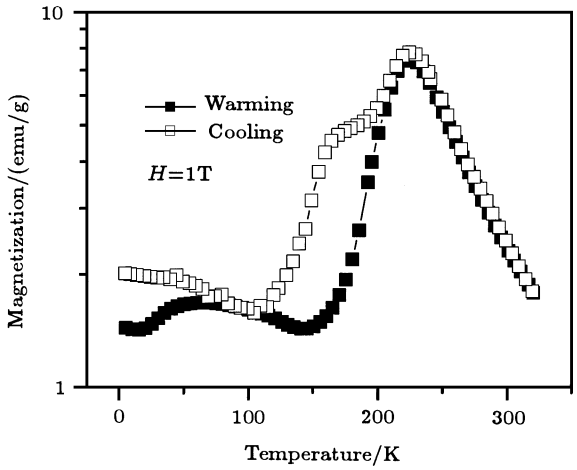


Fig.1. The temperature dependence of the magnetization on warming and cooling (measured at a magnetic field of 1T).

The magnetic field dependence of magnetization at 5 K is shown in Fig.2. The initial magnetization curve of the doped sample displays an obvious difference from LCMO, which exhibits a linear behaviour, because of the AFM charge-ordering state.[9] For the doped sample, the magnetization increases sharply for $H < 0.5$ T, then rises gently until the magnetic field is large enough, where another slope-up occurs. The first slope-up should be attributed to the FM clusters due to the doped Ga ions, and the second slope-up corresponds to the melting of the charge-ordering state. The H_{CO} (charge-ordering critical melting field) of LCMO is very high at low temperatures. The crippling of the magnetic interaction induced by Ga ions causes the melting process to occur at a lower field in the doped sample.[9] The magnetic hysteresis indicates the irreversibility of the melting of the charge-ordering state. We also noticed that the magnetization is still far from a fully FM saturation even at 6 T, which confirms that the ground state is also the AFM charge-ordering.

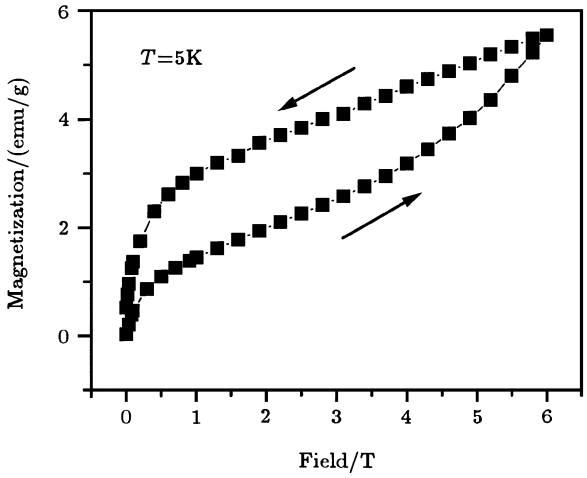


Fig.2. The initial magnetization and demagnetization curves of the sample at 5K.

The resistivity at 5 K was measured as a function of the magnetic field with different measurement currents in the field-increasing and the field-decreasing procedures, which are shown in Figs.3(a) and 3(b), respectively. We find that the difference of resistivity is hardly distinguishable when the current is smaller than 1.5×10^{-5} A. With the increase of the field, the resistivity first has an obvious drop in the low magnetic field region, then goes through a slower decrease until the magnetic field is larger than the H_{CO}, where a sharp drop of resistivity recurs. The first two drops of resistivity are identified with the magnetization change in Fig.2. However, a fancy transport feature occurs when a larger current is applied. When the current is larger than 4.6×10^{-5} A, the PMR feature appears. For example, the resistivity is 9.1 Ω·cm at zero magnetic field under a 1.0×10^{-3} A current, which is one order smaller than 326 Ω·cm with a 1.0×10^{-6} A current. Following the increase of the magnetic field, the resistivity increases slowly at first, then begins to slope-up rapidly, and reaches a peak of 108 Ω·cm at 4.6 T. Thus, a much larger PMR, 1080%, has been observed. Here, the MR is defined as $(\rho_H - \rho_0)/\rho_0$, where ρ_H and ρ_0 denote the resistivity in an external

field and in zero field, respectively. After a critical applied field (H_P), the resistivity begins to decrease along a curve independent of applied current. The resident resistivity ρ_0 has an obvious decrease with the current. This means that the sample has a non-ohmic nature. The inset to Fig.3 shows the current dependence of H_P and the PMR at H_P. Since no peak is found from the $\rho-H$ curve when the current is smaller than 4.6×10^{-5} A, the H_P is assumed to be zero. With the increase of the current, the H_P increases rapidly at first, then tends

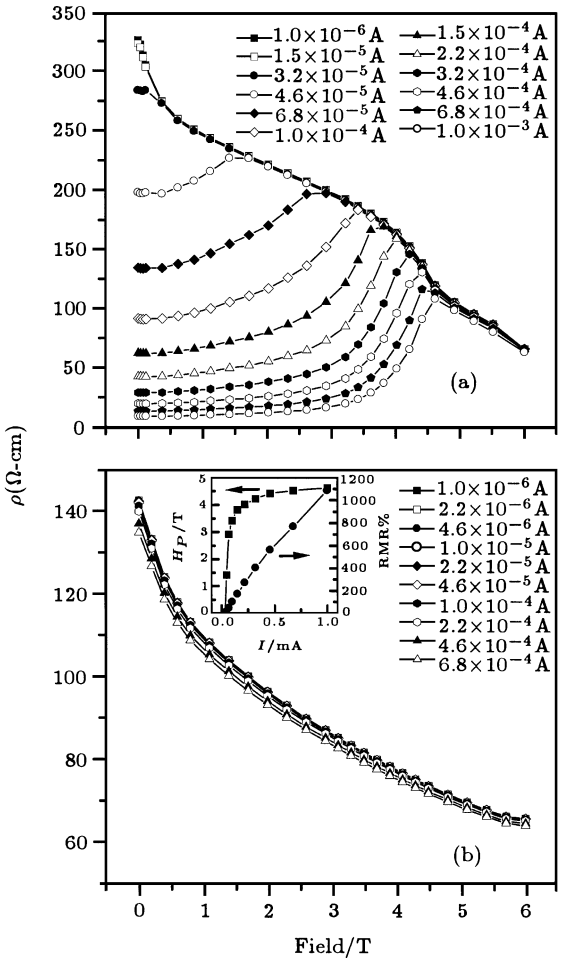


Fig.3. The resistivity as a function of the magnetic field with different measurement currents at 5K in the magnetic field-increasing (a) and the magnetic field-decreasing (b) processes. The inset shows the current dependence of the H_P and the PMR at H_P.

to a saturated value, which is the same as the H_{CO}. The PMR at H_P continues a linear growth with the current.

In the field-decreasing process (Fig.3(b)), the variation of resistivity is completely different from the field-increasing process. The resistivity shows a gentle rise with the decrease of the field and has a clear slope-up at a low field region. The difference of resistivity between these two processes is in accordance with the magnetic irreversibility. No PMR was found even when the magnetic field was increased again, unless the sample has been warmed to room temperature and cooled down in zero magnetic field. To check whether the PMR feature is related to the heating of the current, the voltage and temperature under a large fixed current have been inspected continuously for a long time, and no obvious variation has been observed for either of them. Thus, the heat-effect can be excluded.

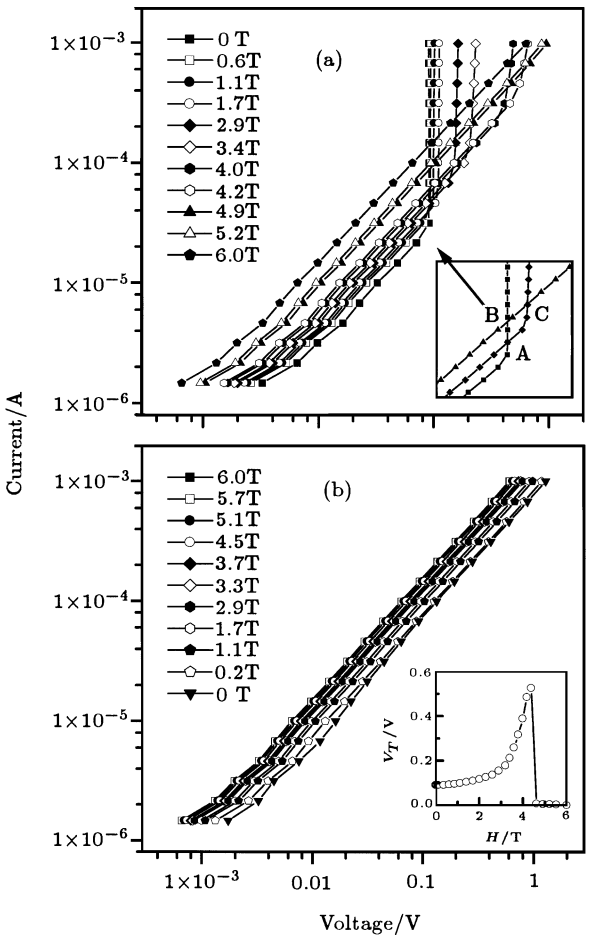


Fig.4. The current–voltage curve in the magnetic field-increasing (a) and the magnetic field-decreasing (b) processes at 5K. The inset to Fig.4(a) is the zooming-out figure of the I–V curve at 0, 2.9 and 4.9T near V_T. The inset to Fig.4(b) shows the magnetic field dependence of V_T.

For a better understanding of the PMR feature, the current–voltage curves at 5 K under different magnetic fields have been measured and are shown in Fig.4. In the field-increasing process (Fig.4(a)), the I–V curve of zero magnetic field, as expected, is nonlinear and has an abrupt turn. Below the turning

voltage (V_T), the sample shows typical ohmic conductive behaviour. The current has a rapid increase when the voltage is larger than V_T. It seems that the transport property displays clear variety at V_T, and we noticed that this variety is a reversible process. The inset to Fig.4(a) is a close view of the I–V curve near V_T. From this figure, some characters of the I–V curve in the field-increasing process can be found. Firstly, the V_T increases with the field. Secondly, the resistivity decreases with the field under the small current condition. Thirdly, the I–V curve is linear in a large enough field. The unusual transport behaviour leads the cross point (such as point A in the inset of Fig.4(a)) of the I–V curves at different field strengths. When the voltage is smaller than V_A, the higher the field, the lower the resistivity. However, when the voltage is larger than V_A, the feature reverses, which is the PMR effect. The inset to Fig.4(b) shows the V_T as a function of the field. The V_T exhibits an exponential growth with the field until a collapse at 4.6 T. This field is equal to the critical melting field H_{CO} and the saturated value of H_P. The agreement of the three values suggests that the AFM charge-ordering state has a close relationship with the PMR. Since the I–V curves in the field-decreasing process (Fig.4(b)) are linear, there is no cross point for the different I–V curves, so the sample does not show the PMR feature in this process, as described in Fig.3(b).

Although the PMR feature has been reported in bulks and superlattices,[10−12] the current-dependent PMR in rare-earth manganese oxide has not been reported previously. As is known, LCMO behaves as an insulator with a very high resistivity at low temperatures. Why do the transport properties have such remarkable changes after a small replacement of Mn by Ga? The contribution of the Ga ions is the key to understanding this singular feature. Although the AFM charge-ordering is still the ground state, the embedded FM clusters wreck the insulating state of LCMO, and strengthen the metallic conductivity, which makes the resistivity far below the resistivity of LCMO under the same conditions. The nonlinear I–V curves imply that the strange transport features can be considered as the results of some kind of tunnelling process. We suggest that it should stem from the tunnelling process existing between the FM clusters. The simple model can be assumed as a number of conductive FM clusters separated and surrounded by the AFM charge-ordering insulating matrix. There are some spin-dependent tunnelling-type nanostructures, such as the granular metals system with a non-magnetic insulating matrix,[13,14] a polycrystalline magnetic system with insulating grain boundaries,[15,16] and a layer-type junction with semiconductor or non-magnetic insulator barriers.[17,18] The difference of this model and these nanostructures is that, for the former, the spin tunnelling process exists inside the grains with an AFM matrix as the barrier.

In a typical FM/I/FM tunnelling structure, the effective barrier height (Δ_{eff}) will decrease under a magnetic field. However, V_T, being proportional to Δ_{eff}, shows an exponential growth with the field. The increase of V_T may reflect a variation of the barrier. We assume that the Fermi level of the barrier rises correspondingly under the magnetic field, which leads Δ_{eff} to rise. Also, the barrier is an AFM matrix, so the pinning effect will block the parallelism of the FM cluster under the external magnetic field, elevating the Δ_{eff}. Then we can observe V_T slowly growing with the increase of the magnetic field. When the magnetic field is high enough to melt the AFM charge-ordering state, the barrier will break down and V_T will drop to zero, then the I–V curve is displayed as a line. The effect of the AFM barrier in this model is similar to the blocking of the charge transport path by AFM in another model about the PMR feature in $(NdSr)MnO_3$.[12] But considering the polycrystalline feature of the sample, we suggest that this model is more suitable here, and further research is still needed on the mechanism about the exponential growth of the Δ_{eff}. Another effect of the magnetic field is that it can align the core spin of the Mn ions, reducing the spin scattering of the itinerant electrons. As a result, the conductive ability will be strengthened by the increase of the magnetic field. When the current is small enough, while the corresponding voltage is smaller than V_T, the enhancement of conductive ability should be the chief mechanism, which causes the negative MR.

In conclusion, we have successfully prepared and studied the Ga-doped charge-ordering state $La_{0.5}Ca_{0.5}MnO_3$ sample. The nonlinear I–V curve and the PMR feature have been observed. These curious features could be explained on the basis of the tunnelling between the FM clusters, which is induced by the non-magnetic Ga ions.

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