Magnetic phase transition and electronic transport in single-crystalline $La_{0.7}Ca_{0.3}MnO_3$

N. G. Bebenin,* R. I. Zainullina, N. S. Bannikova, and V. V. Ustinov
Institute of Metal Physics, Ural Division of RAS, Kovalevskaya Street 18, Ekaterinburg 620041, Russia

Ya. M. Mukovskii
Moscow State Steel and Alloys Institute, Leninskii Prospekt 4, Moscow 119049, Russia
(Received 4 April 2008; revised manuscript received 15 July 2008; published 15 August 2008)

The results of measurements of temperature and magnetic-field dependences of magnetization, resistivity, thermopower, and Hall effect in $La_{0.7}Ca_{0.3}MnO_3$ single crystal are reported. It is shown that below 220 K, the holes of low mobility dominate conductivity, so that the crystal behaves as a "bad" metal, which is at the threshold of localization at $T=220$ K. Above 250 K, $La_{0.7}Ca_{0.3}MnO_3$ is in the paramagnetic semiconductor state with the nearest-neighbor hopping conductivity. The ferromagnetic-to-paramagnetic phase transition is first order; the transition heat is about 0.04 kJ/mol. Application of a magnetic field results in the shift of T_C toward higher temperatures with the rate $dT_C/dH \approx 0.8$ K/kOe. The shift in T_C is the driving force for the colossal magnetoresistance (CMR) effect observed in $La_{0.7}Ca_{0.3}MnO_3$.

DOI: 10.1103/PhysRevB.78.064415 PACS number(s): 75.47.Lx

I. INTRODUCTION

The lanthanum manganites $La_{1-x}D_xMnO_3$, where D=Ca, Sr, or Ba, are ferromagnets in the range of $0.1<x<0.5$ (see Refs. 1–3). Near the Curie temperature T_C, they exhibit colossal magnetoresistance (CMR), which is the reason why these complex oxides attract attention. It has been established that well below T_C, the manganites are semiconductors at $x<x_c$ and metals at $x>x_c$, where x_c is the critical concentration for metal-semiconductor transition. In the metallic state, resistivity ρ obeys the relation $\rho(T)=\rho(0)+AT^2$. As the temperature approaches the Curie temperature, the resistivity rapidly increases and reaches a maximum somewhat above T_C. In the paramagnetic state, as a rule, ρ gradually decreases with increasing T except in La-Sr single crystals with $x \geq 0.25$, where resistivity slowly increases with T even above T_C.

If the divalent element is Ba or Sr, whose ionic radii are greater than that of La, the residual resistivity $\rho(0)$ decreases with increasing x more or less gradually even near x_c.[3,4] On the contrary, if D=Ca, whose radius is less than that of La, the compositional metal-semiconductor transition is extremely sharp.[5] Likewise, the La-Ca crystals with $x>x_c$ show a very steep increase in resistivity near T_C and the value of magnetoresistance is much greater in $La_{1-x}Ca_xMnO_3$ than in $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Ba_xMnO_3$ with the same x. Whereas in La-Sr and La-Ba crystals the ferromagnetic-to-paramagnetic phase transition is second order, in $La_{1-x}Ca_xMnO_3$ with calcium content of around 0.33, the transition is most likely to be first order,[6–13] although some authors believed that it is second order at arbitrary x and reported the critical exponents for $La_{0.7}Ca_{0.3}MnO_3$. These facts indicate that the mechanism of the CMR effect in La-Ca crystals may differ from that in other lanthanum manganites. Unfortunately the available data on the kinetic properties of $La_{1-x}Ca_xMnO_3$ crystals remain insufficient to make a certain conclusion. In particular, Hall-effect data were involved in the analysis of conductivity in the paramagnetic state only.[14]

To fill the gap in part, we have performed a study of magnetic properties and electronic transport in $La_{0.7}Ca_{0.3}MnO_3$ single crystal. The results of measurements of temperature and magnetic-field dependence of magnetization, resistivity, thermopower, and Hall effect are reported. The analysis of the data obtained allows us to reveal the type of charge carriers and the mechanism of conductivity below and above the Curie temperature. It is found that the magnetic transition is certainly first order, which explains why the CMR effect is so large in the La-Ca manganites.

II. EXPERIMENTAL DETAILS

The single crystal of nominal composition $La_{0.7}Ca_{0.3}MnO_3$ was grown by the floating-zone method. The as-grown crystal has the shape of a cylinder of about 40 mm in length and ≈ 4 mm in diameter with the rod axis close to the cubic [110] direction. The La-Ca rods produced by the floating-zone technique are always inhomogeneous because of the low value of Ca distribution coefficient.[15] In view of this, the element distribution along the rod was measured with an electron-probe microanalyzer and then the region was found where the Ca content is equal to 0.30 ± 0.01. The sample in the form of a plate of size $7.2 \times 2.4 \times 0.73$ mm^3 was cut for resistivity, thermopower, and Hall-effect experiments. The magnetization measurements were performed using a vibrating sample magnetometer on a similar plate of smaller size cut from the neighboring part of the rod. The resistivity was measured by a four-probe technique. The Hall-effect measurements were carried out in two opposite directions of the magnetic field and the electric current. In all experiments, a magnetic field H was applied perpendicular to the plane of a sample. Indium contacts were made with an ultrasonic soldering iron.

III. RESULTS OF MEASUREMENTS

Figure 1 shows magnetization curves $M(H)$. If $T \leq 220$ K, the shape of the curves is typical of a ferromagnet. At $T>220$ K, the increase in T results in a rapid decrease in M and an essential change in the shape of the curves, so that

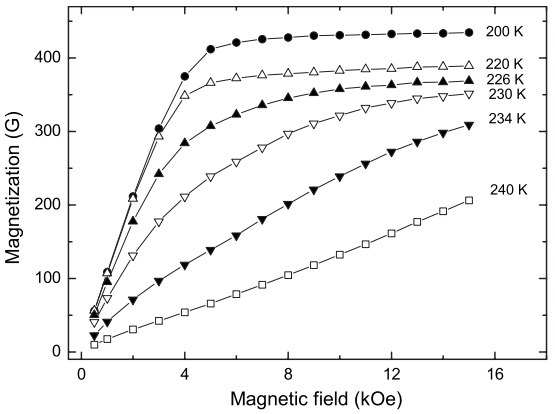

FIG. 1. Magnetization curves for $La_{0.7}Ca_{0.3}MnO_3$ single crystal.

the $T=234$ and 240 K curves show no tendency to saturation.

The temperature dependence of magnetization taken on heating in various magnetic fields is shown in Fig. 2. Below 220 K, this dependence is weak, but in the range of 220–250 K, there is a rapid fall in M. Near $T_S=227$ K (see inset of Fig. 2) there is a weak peculiarity, whose position is independent of H. The inflection point, which we identify as the Curie temperature T_C, is shifted to higher temperatures by a magnetic field. Figure 3 shows that T_C is approximately a linear function of H: $T_C=(227+B_MH)$ K, where $B_M \approx 0.8$ K/kOe. Our value of dT_C/dH coincides with that obtained by Mira *et al.*[6] in thermal-expansion measurements.

Figure 4 shows the temperature dependence of resistivity taken at $H=0$ and $H=10$ kOe. In the ferromagnetic state, below roughly 150 K, the experimental data can be fitted to $\rho(T)=\rho(0)+AT^2$, with $\rho(0)=1.3\times10^{-4}$ Ω cm and $A=2.3\times10^{-8}$ Ω cm K^{-2}, which is consistent with the results reported by Okuda *et al.*[5] Above 150 K the dependence of ρ on T is stronger. In the range of 220–250 K, we see rapid increase in resistivity from 1.87×10^{-3} Ω cm at $T=220$ K up to 61.2×10^{-3} Ω cm at $T=250$ K. Inset (a) of Fig. 4 shows

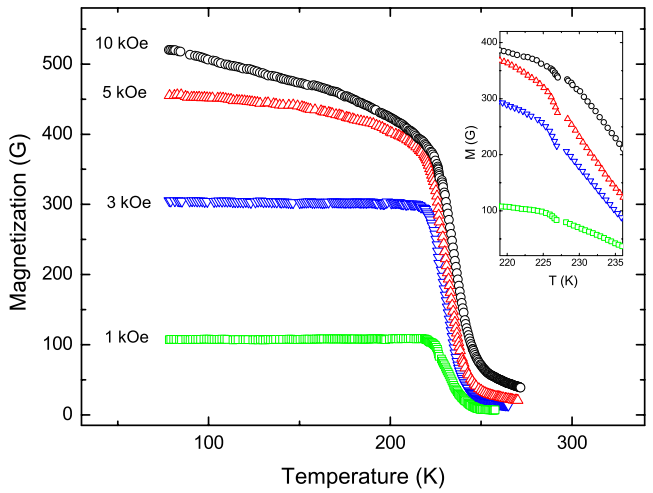

FIG. 2. (Color online) Temperature dependence of magnetization measured on heating in various fields. The inset shows that there is a field independent peculiarity at $T_S=227$ K.

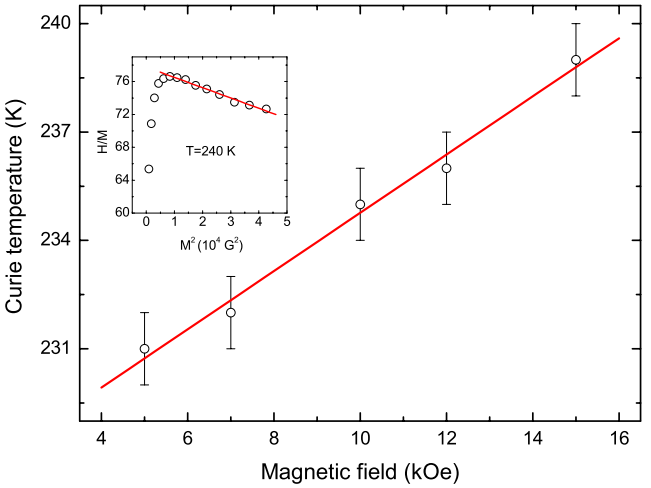

FIG. 3. (Color online) Magnetic-field dependence of the Curie temperature in $La_{0.7}Ca_{0.3}MnO_3$. Inset: Arrott-Belov curve for $T=240$ K.

the thermal hysteresis, which is detectable in the range of 224–230 K. Above 250 K, we observe the activated-type behavior of resistivity with activation energy $E^{\rho}=905$ K $=78$ meV; see inset (b) of Fig. 4.

The application of a magnetic field results in a decrease in resistivity and a shift of the ρ-T curve toward higher temperatures. The shape of the curve remains practically unchanged if ρ is not too high (say, less than 0.03 Ω cm); see inset of Fig. 5. To characterize this shift quantitatively, we define T_ρ as a temperature at which $\rho=0.02$ Ω cm and we display T_ρ as a function of H in Fig. 5. One can see that above 4 kOe, the experimental points fall into the straight line and $dT_\rho/dH=B_\rho \approx 0.8$ K/kOe.

Figure 6 shows temperature dependence of magnetoresistance, which is defined as $\Delta\rho/\rho=[(\rho(H)-\rho(0))]/\rho(0)$, measured in the field of 10 kOe. One can see a narrow peak with

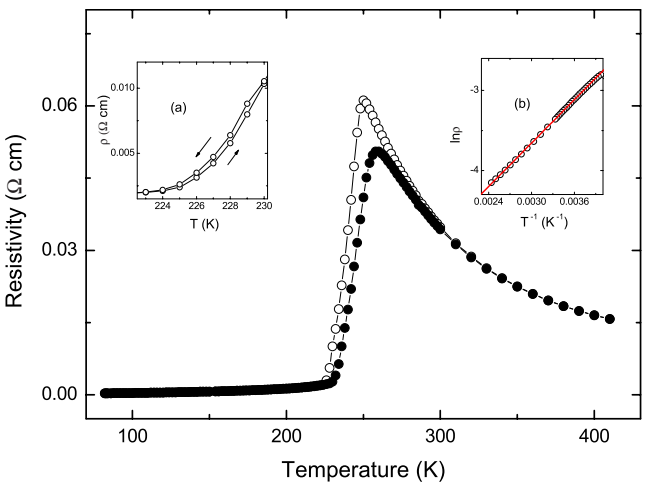

FIG. 4. (Color online) Temperature dependence of the resistivity of $La_{0.7}Ca_{0.3}MnO_3$ single crystal measured at $H=0$ (open circles) and $H=10$ kOe (solid circles) in the heating run. Inset (a): Temperature hysteresis in the vicinity of $T_S=227$ K. Inset (b): ln ρ versus inverse temperature in the paramagnetic state.

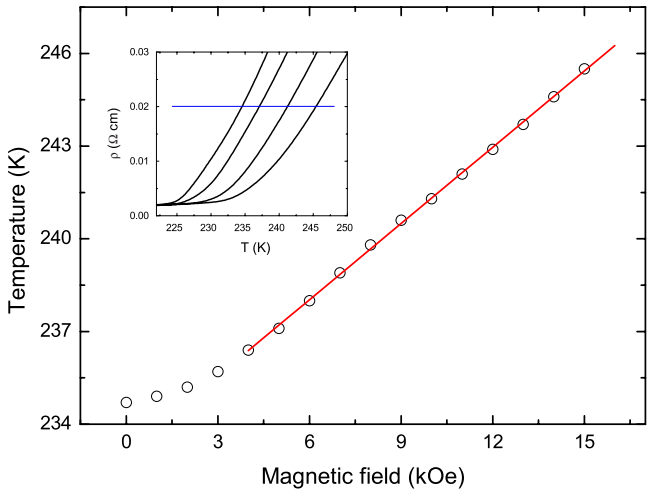

FIG. 5. (Color online) Magnetic-field dependence of T_ρ, defined as the temperature at which $\rho=0.02$ Ω cm. The inset shows the ρ-T curves taken (from left to right) at $H=0$, 5, 10, and 15 kOe.

a maximum at $T=230$ K, the value of $|\Delta\rho/\rho|$ being about 0.73, which is much greater than in $La_{0.7}Sr_{0.3}MnO_3$ or $La_{0.72}Ba_{0.28}MnO_3$; see Refs. 3 and 4.

The magnetic-field dependence of $\Delta\rho/\rho$ is displayed in Fig. 7. If $T\leq 220$ K, the magnetoresistance is small. The magnetoresistance measured at $T=226$ and 230 K saturates at the field of about 5 and 10 kOe, respectively. The $T=234$ K curve also demonstrates the tendency to saturation, although the magnetic fields used in our experiments seem to be too weak to reach the saturation. At $T\geq 258$ K, the magnetoresistance shows the H^2 behavior typical for the paramagnetic phase.

Now let us turn to the Hall-effect data. Figure 8 shows the magnetic-field dependence of Hall resistivity ρ_H for some temperatures. When magnetic fields are high enough for domain-wall displacement as well as for the magnetization vector rotation to be completed, the ρ_H-H curves are close to straight lines.

The normal, R_0, and anomalous (spontaneous), R_s, Hall coefficients are defined by the relation

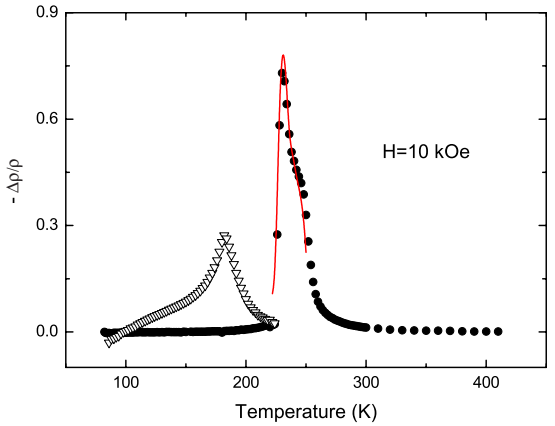

FIG. 6. (Color online) Temperature dependences of the magnetoresistances of $La_{0.82}Ca_{0.18}MnO_3$ (open triangles) and $La_{0.7}Ca_{0.3}MnO_3$ (solid circles) single crystals. The solid line is the result of calculations in accordance with Eq. (4).

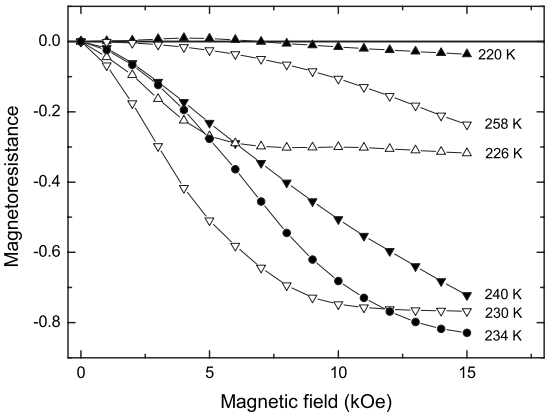

FIG. 7. Magnetic-field dependence of magnetoresistance at various temperatures.

$$\rho_H = R_0 B + R_s M, \tag{1}$$

where B stands for the magnetic-field induction inside the sample. In our case (the sample in the form of a rather thin plate), the magnetic induction may be taken to be equal to the field H. After measuring the Hall resistivity and magnetization, we plot ρ_H/H versus M/H, determining thereby R_0 and R_s. The results are shown in Fig. 9. The normal Hall coefficient is positive and depends on temperature weakly. The spontaneous Hall coefficient is negative as in other La manganites and its absolute value increases with temperature, at $T=220$ K, the value of R_s being larger than R_0 by 2 orders of magnitude.

In the paramagnetic state, $M=\chi H$, where χ is magnetic susceptibility, so that Eq. (1) gives $\rho_H=(R_0+\chi R_s)H$. As we can obtain the effective Hall coefficient $R_{\text{eff}}=R_0+\chi R_s$ only, to separate the normal and anomalous Hall effects is difficult. In the present work we do not try to do this.

The temperature dependence of thermopower S for $H=0$ and $H=10$ kOe is displayed in Fig. 10. The thermopower is small in value. It is negative below 94 K, positive from 94 to 198 K, and then again changes its sign. Above 216 K, the thermopower increases, reaches a maximum at 246 K, and gradually decreases with increasing T at higher temperatures, changing its sign at $T\approx 300$ K. One can see a weak pecu-

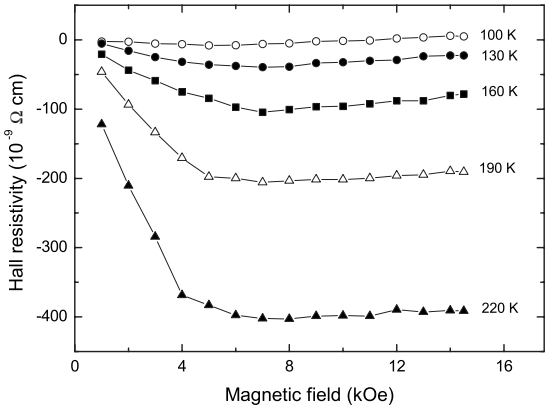

FIG. 8. Hall resistivity versus magnetic field.

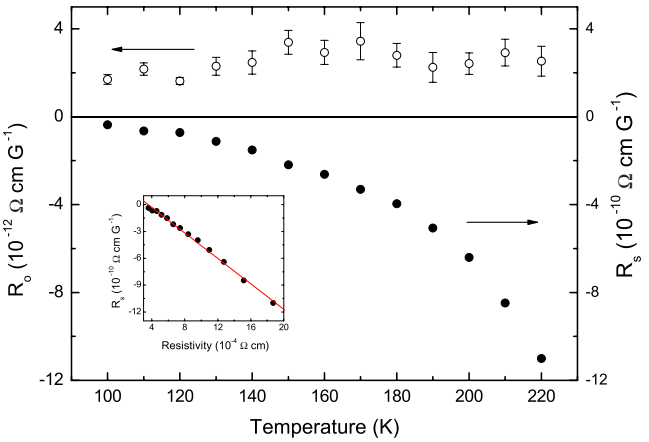

FIG. 9. (Color online) Temperature dependences of normal, R_0, and spontaneous, R_s, Hall coefficients for $La_{0.7}Ca_{0.3}MnO_3$ single crystals. Inset: The spontaneous Hall coefficient against the resistivity.

liarity near 227 K, i.e., at the temperature at which the peculiarity on M-T curves is seen. The effect of a magnetic field on the thermopower is similar to the effect of the field on the resistivity.

IV. DISCUSSION

It is reasonable to divide the whole temperature region into three parts, below 220 K (low temperatures), above 250 K (high temperatures), and the range from 220 to 250 K (transition region), and to discuss the properties of the manganite studied in these regions separately.

A. Low-temperature region

Below 220 K, the magnetization depends on temperature weakly. The value 527 G of the magnetization measured at

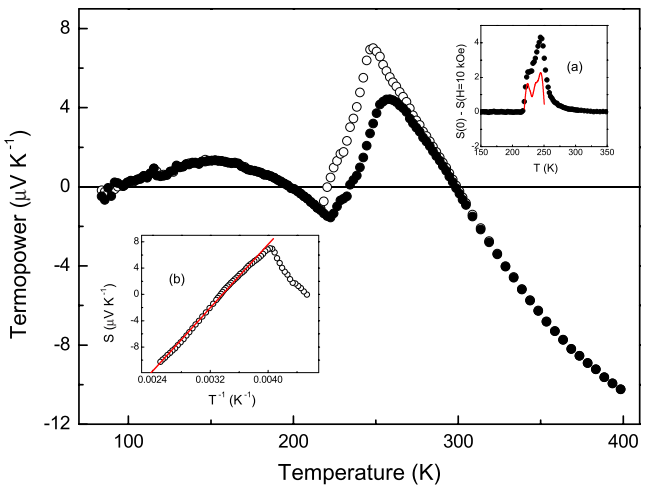

FIG. 10. (Color online) Temperature dependence of thermopower of $La_{0.7}Ca_{0.3}MnO_3$ single crystal measured at $H=0$ (open circles) and $H=10$ kOe (solid circles) in the heating run. Inset (a): Experimental (solid circles) and calculated (line) $S(0)-S(H=10$ kOe). Inset (b): Thermopower at $H=$O versus inverse temperature in the paramagnetic state.

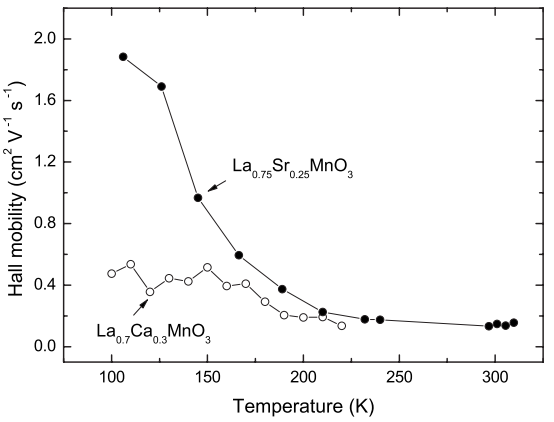

FIG. 11. Hall mobilities for $La_{0.7}Ca_{0.3}MnO_3$ (open circles) and $La_{0.75}Sr_{0.25}MnO_3$ (solid circles) single crystals.

$T=78$ K, $H=15$ kOe corresponds to a magnetic moment of $3.34\mu_B$/Mn site, which is close to the value reported by Tomioka *et al.*[16]

The normal Hall coefficient is positive; therefore holes dominate conductivity. The negative sign of the thermopower below 94 K indicates, however, that there are charge carriers of electron type that play the role of minority carriers. The increase in S with T observed up to $T \approx 160$ K points to the reduction in the electron contribution into S. Above 160 K, however, the increase in the temperature results in the increase in the electron contribution. The value of the thermopower is small, which points to metallic type of conductivity.

In Fig. 11 we display the temperature dependence of Hall mobility μ_H, defined as $\mu_H=R_0/\rho(H=0)$. The data for $La_{0.75}Sr_{0.25}MnO_3$ ($T_C=341$ K) published in Ref. 17 are given for comparison. One can see that in $La_{0.7}Ca_{0.3}MnO_3$, the mobility is small in value and less than in $La_{0.75}Sr_{0.25}MnO_3$; at $T>160$ K μ_H gradually decreases with rising temperature. In the La-Sr crystal, μ_H decreases with increasing T only at $T<230$ K but it is practically independent of temperature over the interval of 230–310 K, signaling the absence of a true metallic conductivity. The mobility values in the both crystals are close to each other near and somewhat lower 220 K. Taking into consideration that the resistivity of our $La_{0.7}Ca_{0.3}MnO_3$ is 1.87×10^{-3} Ω cm at $T=220$ K and that estimates made for CMR manganites[1] suggest that the minimum metallic conductivity σ_m is on the order of 10^3 $(\Omega\ \mathrm{cm})^{-1}$, we may infer that in the low-temperature region, the single crystal under study behaves as a "bad" metal, which is at the threshold of localization at $T=220$ K.

This conclusion agrees with the fact that spontaneous Hall coefficient is proportional to ρ as evident from the inset of Fig. 9. It follows that R_s is dominated by skew scattering, which is typical of metals.

B. High-temperature region

Above 250 K, the crystal is in the paramagnetic state. The resistivity measured at $H=0$ can be well fitted to $\rho(T)=\rho_0\exp(E^\rho/k_BT)$, with $\rho_0=1.7\times10^{-3}$ Ω cm and E^ρ

=78 meV. Similar to the La-Sr and La-Ba manganites,[3,17] in the paramagnetic state, the magnetoresistance can be explained by a reduction in the activation energy with increasing magnetization.

It is mentioned above that to determine R_0 and R_s in the paramagnetic state is difficult because the experiment can give $R_{\rm eff}=R_0+\chi R_s$ only; for example, $R_{\rm eff}\approx -2.8\times 10^{-11}$ Ω cm G^{-1} at $T=300$ K. To obtain a rough estimate of μ_H, let us assume $|R_0|$ to be much greater than $|\chi R_s|$ and hence $R_0\approx -2.8\times 10^{-11}$ Ω cm G^{-1}. The resistivity $\rho(T=300\ {\rm K})=0.0348$ Ω cm; therefore under this assumption $|\mu_H|\approx 0.08$ cm^2 V^{-1} s^{-1}. Obviously, it is the upper bound for $|\mu_H|$ because if $|\chi R_s|$ cannot be neglected, the values of $|R_0|$ and $|\mu_H|$ are less. It is well known that a so small Hall mobility points to hopping conductivity.[18] Since our CMR manganite is a double-exchange material, the spin of the hopping electron, which is parallel to the spins of the core electrons of the ion on which it resides, must be parallel to the net spin of the core electrons of the ion, into which the electron wants to hop. In the paramagnetic state, the localized spins are parallel only if the distance between them is less than the spin correlation length. As the transition is first order, the correlation length is finite even in the vicinity of T_C, being on the order of a few lattice constants above T_C. Therefore the hopping distance cannot be arbitrarily large and hopping between nearest neighbors must take place. This conclusion agrees with the fact that in zero magnetic field, the activation energy E^ρ is independent of temperature.

Let us turn to the thermopower. It is seen from inset (b) of Fig. 10 that above 250 K, the experimental $S(T)$ can be more or less successfully fitted to

$$S=\frac{k_B}{e}\left(\frac{E^S}{k_BT}+A^S\right), \tag{2}$$

where the thermopower activation energy E^S is about 12 meV and $A^S\approx -0.47$. The scanning tunneling spectroscopy experiments reported by Fäth *et al.*[19] indicated that the Fermi level E_F lies in the energy gap. As the thermopower activation energy E^S is very small (even less than k_BT), the conductivity is likely to be dominated by charge carriers of effective energy layer around E_F because in this case E^S is determined by an asymmetrical (with respect to E_F) part of the density of states. Therefore E^S can indeed be significantly less than E^ρ, which is determined mainly by a symmetrical part.[20]

C. Magnetic phase transition and colossal magnetoresistance

Figure 2 clearly demonstrates that in the range of 220–250 K, there are two peculiarities in the M-T curves: The first one is at about 227 K and does not depend on magnetic field, while the second is the inflection point, which is identified as the Curie temperature $T_C(H)$. Remembering that the thermal hysteresis is observed around 227 K [inset (a) of Fig. 4] and taking into consideration the results published by Radaelli *et al.*[21] and Huang *et al.*,[22] we may suppose that at $T_S=227$ K, the manganite studied undergoes the structural transition between two orthorhombic *Pnma* phases. In the $La_{0.74}Ca_{0.26}MnO_3$ single crystal studied earlier, T_S was found to be ≈ 233 K[11]. Thus we see that if Ca content is around 0.3, the structural transition temperature depends on x weakly, which agrees with the results in Refs. 21 and 22.

The rapid decrease in the magnetization indicates that the magnetic transition is first order. This is confirmed by the inset of Fig. 3, where we plot H/M against M^2 for $T=240$ K: The sign of the slope of the isotherm is negative, which according to the Banerjee criterion,[23] is evidence that the transition is first order. Since we know how the Curie temperature depends on magnetic field, we can estimate the latent heat q for the magnetic transition by making use of the Clapeyron equation:

$$\frac{dT_C}{dH}=-\frac{T_C\Delta M}{q}. \tag{3}$$

ΔM stands for difference between the magnetizations of the high-temperature and low-temperature phases. Taking $T_C\approx 230$ K, $\Delta M\approx -M(T=220\ {\rm K}, H=10\ {\rm kOe})\approx -400$ G, $dT_C/dH=0.8$ K/kOe, we obtain very small latent heat, $q\approx 0.04$ kJ/mol.

Let us turn now to the magnetoresistance. In Fig. 6 we display the $\Delta\rho/\rho-T$ curves for $La_{0.7}Ca_{0.3}MnO_3$ and for the $La_{0.82}Ca_{0.18}MnO_3$ ($T_C=180$ K) single crystal studied earlier.[24] It is known that in the CMR manganites, $|\Delta\rho/\rho|$ typically decreases as the Curie temperature goes up. The opposite holds in our case: the magnetoresistance of $La_{0.7}Ca_{0.3}MnO_3$ is much higher than that of $La_{0.82}Ca_{0.18}MnO_3$. This suggests that the origin of the CMR effect in the $x=0.18$ crystal differs from that in the $x=0.3$ manganite.

In $La_{0.82}Ca_{0.18}MnO_3$, the magnetic transition is second order and the reduction in the resistivity in a magnetic field results from the suppression of the magnetic fluctuation in the vicinity of the Curie temperature. This manganite is in the semiconductor state at any temperature and the magnetic field is not usually strong enough for a metallic state to appear.

The situation in $La_{0.7}Ca_{0.3}MnO_3$ is opposite in the sense that the magnetic transition is first order. The equality $B_M=B_\rho$ indicates that in $La_{0.7}Ca_{0.3}MnO_3$, the magnetoresistance results mainly from the shift of the magnetic transition point in a magnetic field. To make this statement more obvious, let us consider a ferromagnet in which the Curie temperature is a random function $T_C(\mathbf{r})$ of coordinate. Suppose that the first-order magnetic transition occurs in a temperature region whose width δ_c is much less than the average transition temperature T_C. Obviously, the resistivity is determined by T and $T_C(\mathbf{r})$. In the transition region, $T_C(\mathbf{r})$ enters as $T-T_C(\mathbf{r})$; a weak noncritical dependence of ρ on T is of minor importance. In a magnetic field, the resistivity depends on H, first, explicitly (due to change in the scattering probability, charge-carrier concentration, etc.) and, second, because of the shift in the transition temperature. Therefore, the resistivity is a functional of $T-T_C(\mathbf{r})$: $\rho(T)=F_{T,H}\{T-T_C(\mathbf{r})\}$, where the subscripts denote the noncritical dependence on T and H. If the shift in the transition temperature is much less than T_C, we can consider the shift as being independent of $\mathbf{r}$ because the variation in ΔT_C caused by the variation in $\mathbf{r}$ should be a quantity on the next order of smallness. Finally, let us as-

sume that the noncritical dependence of the functional on T and H is negligible: $\rho(T,H)=F_{T=T_C,H=0}\{T-T_C(\mathbf{r},H=0)-\Delta T_C(H)\}=\rho(T-\Delta T_C(H),H=0)$, then for the magnetoresistance we obtain the simple formula

$$\frac{\Delta\rho(T,H)}{\rho}=\frac{\rho[T-\Delta T_C(H)]-\rho(T)}{\rho(T)}, \tag{4}$$

where $\rho(T)=\rho(T,H=0)$. Using relation (4) and the data presented in Figs. 4 and 5, we have calculated the magnetoresistance of our $La_{0.7}Ca_{0.3}MnO_3$ crystal. The result of the calculations is shown in Fig. 6 as the solid line. One can see that the calculated curve agrees well with the experimental one. Therefore in the transition region, the shape of the $(\Delta\rho/\rho)$-T curve for a given H is determined by the temperature dependence of resistivity at $H=0$ and the shift in the Curie temperature induced by the magnetic field.

It has to be pointed out that our approach is entirely phenomenological. In the phase-separation scenario,[2] near T_C there is a mixture of the metallic or, better say, the low-resistivity phase and the semiconductor one. Moreover the application of a magnetic field increases the volume of the low-resistivity phase. The approximations made by us correspond to neglecting the temperature and the magnetic-field dependence of the resistivity of the low-resistivity and semiconductor phases, so that the decrease in the resistivity of the sample results solely from the increase in the volume of the low-resistivity phase. One can see from the inset of Fig. 5 that at $H=0$, the rapid increase in the resistivity starts at $T_{pt}=224$ K. It is reasonable to assume that at this temperature, the infinite cluster of the low-resistivity phase disappears i.e., the percolation transition occurs. This transition results in the essential difference in the shape of the $(\Delta\rho/\rho)$-H curves at $T\leq 220$ K and at $T\geq 226$ K; see Fig. 7. The saturation of the magnetoresistance, which occurs at $H\approx 5$ kOe if $T=226$ K and at $H\approx 10$ kOe when $T=230$ K, implies that the infinite low-resistivity cluster is absent in weak magnetic fields but it is restored in the fields indicated. In other words, $T_{pt}(H=5\text{ kOe})\approx 226$ K and $T_{pt}(H=10\text{ kOe})\approx 230$ K. It follows that $dT_{pt}/dH=0.8$ K/kOe $=dT_C/dH$. Therefore the driving force for the increase in the low-resistivity phase volume is the shift in T_C in a magnetic field.

The temperature dependence of magnetothermopower can be analyzed in similar way. The solid line in inset (a) of Fig. 10 shows $S(T-\Delta T_C(H))-S(T)$ versus temperature for $H=10$ kOe. One can see that the calculated curve satisfactorily reproduces the positions of peculiarities but the calculated values of ΔS are less than the experimental ones. It is likely that the magnetic field reduces the thermopower of the phases more effectively than their resistivity. The analysis of the thermopower in terms of phase separation can be found, e.g., in Ref. 1.

V. CONCLUSION

The study of magnetic properties and electronic transport in $La_{0.7}Ca_{0.3}MnO_3$ single crystal has shown that below 220 K, the manganite is in the ferromagnetic low-resistivity state. The transport properties are dominated by holes of very low mobility. Overall, the $La_{0.7}Ca_{0.3}MnO_3$ crystal behaves as a very bad metal, which is at the threshold of localization at $T=220$ K.

Above 250 K, $La_{0.7}Ca_{0.3}MnO_3$ is in the paramagnetic semiconductor state with the nearest-neighbor hopping conductivity. The thermopower is likely to be determined by asymmetry of the density of states near the Fermi level.

The ferromagnetic-to-paramagnetic phase transition is first order. The application of a magnetic field results in the shift of T_C toward higher temperatures at the rate $dT_C/dH\approx 0.8$ K/kOe. The transition heat is about 0.04 kJ/mol. The temperature dependence of magnetoresistance at a given H is determined by the temperature dependence of resistivity at $H=0$ and the magnetic-field-induced shift in the Curie temperature. This shift results in the increase in the volume of the low-resistivity phase and is therefore the driving force for the CMR effect observed in the $La_{0.7}Ca_{0.3}MnO_3$ single crystal.

ACKNOWLEDGMENTS

This work was supported by RFBR Grants No. 06-02-16085 and No. NSh-3257.2008.2.

*Corresponding author; bebenin@imp.uran.ru

[1] M. B. Salamon and M. Jaime, Rev. Mod. Phys. **73**, 583 (2001).
[2] E. Dagotto, *Nanoscale Phase Separation and Colossal Magnetoresistance: The Physics of Manganites and Related Compounds* (Springer-Verlag, Berlin, 2002).
[3] N. G. Bebenin, R. I. Zainullina, N. S. Chusheva, V. V. Ustinov, and Ya. M. Mukovskii, J. Magn. Magn. Mater. **300**, e111 (2006).
[4] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, Phys. Rev. B **51**, 14103 (1995).
[5] T. Okuda, Y. Tomioka, A. Asamitsu, and Y. Tokura, Phys. Rev. B **61**, 8009 (2000).
[6] J. Mira, J. Rivas, L. E. Hueso, F. Rivadulla, M. A. López Quintela, M. A. Señarís Rodríguez, and C. A. Ramos, Phys. Rev. B **65**, 024418 (2001).
[7] D. Kim, B. Revaz, B. L. Zink, F. Hellman, J. J. Rhyne, and J. F. Mitchell, Phys. Rev. Lett. **89**, 227202 (2002).
[8] V. S. Amaral, J. P. Araújo, Yu. G. Pogorelov, J. B. Sousa, P. B. Tavares, J. M. Vieira, P. A. Algarabel, and M. R. Ibarra, J. Appl. Phys. **93**, 7646 (2003).
[9] F. Rivadulla, J. Rivas, and J. B. Goodenough, Phys. Rev. B **70**, 172410 (2004).
[10] C. P. Adams, J. W. Lynn, V. N. Smolyaninova, A. Biswas, R. L. Greene, W. Ratcliff, S. W. Cheong, Y. M. Mukovskii, and D. A. Shulyatev, Phys. Rev. B **70**, 134414 (2004).
[11] R. I. Zainullina, N. G. Bebenin, V. V. Ustinov, Ya. M. Muk-

ovskii, and D. A. Shulyatev, Phys. Rev. B **76**, 014408 (2007).
[12] M. H. Phan, S. Ch. Yu, N. H. Hur, and Y. H. Jeong, J. Appl. Phys. **96**, 1154 (2004).
[13] H. S. Shin, J. E. Lee, Y. S. Nam, H. L. Ju, and C. W. Park, Solid State Commun. **118**, 377 (2001).
[14] S. H. Chun, M. B. Salamon, Y. Tomioka, and Y. Tokura, Phys. Rev. B **61**, R9225 (2000).
[15] D. Shulyatev, S. Karabashev, A. Arsenov, Ya. Mukovskii, and S. Zverkov, J. Cryst. Growth **237-239**, 810 (2002).
[16] Y. Tomioka, A. Asamitsu, and Y. Tokura, Phys. Rev. B **63**, 024421 (2000).
[17] N. G. Bebenin, R. I. Zainullina, V. V. Mashkautsan, V. V. Ustinov, and Ya. M. Mukovskii, Phys. Rev. B **69**, 104434 (2004).
[18] N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Solids*, 2nd ed. (Clarendon, Oxford, 1979).
[19] M. Fäth, S. Freisem, A. A. Menovsky, Y. Tomioka, J. Aarts, and J. A. Mydosh, Science **285**, 1540 (1999).
[20] I. P. Zvyagin, in *Hopping Transport by Solids*, edited by M. Pollak and B. Shklovskii (Elsevier, Amsterdam, 1991), p. 143.
[21] P. G. Radaelli, G. Iannone, M. Marezio, H. Y. Hwang, S.-W. Cheong, J. D. Jorgensen, and D. N. Argyriou, Phys. Rev. B **56**, 8265 (1997).
[22] Q. Huang, A. Santoro, J. W. Lynn, R. W. Erwin, J. A. Borchers, J. L. Peng, K. Ghosh, and R. L. Greene, Phys. Rev. B **58**, 2684 (1998).
[23] S. K. Banerjee, Phys. Lett. **12**, 16 (1964); S. V. Vonsovskii, *Magnetism* (Wiley, New York, 1974), Vol. 2, Chap. 25.
[24] N. G. Bebenin, R. I. Zainullina, N. S. Bannikova, V. V. Ustinov, and Ya. M. Mukovskii, Phys. Solid State **50**, 691 (2008).