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MAGNETISM
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Hysteresis of Magnetoresistance in Granular $La_{0.7}Ca_{0.3}MnO_3$ at Low Temperatures

K. A. Shaykhutdinov[a], S. V. Semenov[a, b], D. A. Balaev[a], M. I. Petrov[a], and N. V. Volkov[a, b]

[a] *Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*
e-mail: dir@iph.krasn.ru
[b] *Siberian Federal University, Svobodnyĭ pr. 79, Krasnoyarsk, 660041 Russia*

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Abstract—The magnetoresistance of granular $La_{0.7}Ca_{0.3}MnO_3$ is studied experimentally over wide ranges of temperatures and magnetic fields. The emphasis is on anomalously large hysteresis of magnetoresistance at low temperatures ($T = 4.2$ K). The observed $\rho(H)$ dependence can be qualitatively explained by spin-dependent tunneling of electrons through the dielectric boundaries of conducting granules characterized by a wide spread in the magnetic-moment magnitudes.

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It is a matter of a common knowledge that lanthanide manganites $R_{1-x}A_xMnO_3$ compounds (R are trivalent rare-earth ions, e.g., La^{3+} and Pr^{3+}, and A are divalent ions Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}) in the form of single crystals, thin films, and polycrystals exhibit colossal magnetoresistance (MR), which makes them promising materials for study and practical applications. In optimally doped $La_{0.7}Ca_{0.3}MnO_3$ single crystals, the MR reaches a maximum near the Curie temperature T_C coinciding with the temperature T_p of the metal–insulator transition. The MR is a maximum in magnetic fields of several teslas. In polycrystalline $R_{1-x}A_xMnO_3$ samples, the maximum MR can be reached below the temperature of a magnetic phase transition and is dependent on many factors, such as the granule size, the presence of impurities, and preparation technology [1].

Moreover, due to the granular structure of the materials, a important and sometimes dominant mechanism determining the magnetotransport properties of polycrystalline $R_{1-x}A_xMnO_3$ compounds is the tunneling of spin-polarized electrons through intergranular dielectric boundaries. In this case, MR is high in fields on the order of 1 T or lower below T_C [2, 3].

The main objective of this work is to study the spin-polarized transport under conditions of tunneling of charge carriers through intergranular boundaries in $La_{0.7}Ca_{0.3}MnO_3$ and its correlation with transport properties of granular $La_{0.7}Ca_{0.3}MnO_3$ at low temperatures.

Polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ was prepared from highly pure reagents $La_2(CO_3)_3$, $CaCO_3$, and MnO_2 by a standard solid-phase synthesis method. The final synthesis was performed at 800°C for 24 h. X-ray diffraction studies show that samples exhibit a perovskite-like structure; foreign inclusions were not detected. Figure 1 shows the results of studying the microstructure of samples on a scanning electron microscope (SEM) (Figs. 1a, 1c) and a transmission electron microscope (TEM) (Fig. 1b). It turned out that $La_{0.7}Ca_{0.3}MnO_3$ granules are almost spherical in shape, with the average granule size being ~200 nm. The size-distribution function of granules in $La_{0.7}Ca_{0.3}MnO_3$ is presented in Fig. 1c. High-resolution transmission electron microscopy of a single granule shows that the inner portion of a granule is single-crystal $La_{0.7}Ca_{0.3}MnO_3$, and that the outer ~5-nm-thick shell is amorphous (Fig. 1b). This shell is insulating and nonmagnetic or slightly antiferromagnetic [3, 4] and acts as a potential barrier between neighboring granules. Thus, the microstructural and X-ray diffraction studies of polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ indicate that, at temperatures below T_C, a sample contains a developed network of tunneling contacts consisting of the conducting cores and nonconducting shells of granules. Therefore, one can expect that the transport properties of such a network will be determined by tunneling of spin-polarized electrons through the potential barriers.

The magnetotransport properties of $La_{0.7}Ca_{0.3}MnO_3$ were measured by the standard four-probe method in fields up to 60 kOe. The temperature dependence of the magnetization $M(T)$ was measured by a vibrating-coil magnetometer on warming of the sample.

Figure 1d presents the temperature dependences of the electrical resistivity $\rho(T)$ of $La_{0.7}Ca_{0.3}MnO_3$ measured in fields $H = 0$, 20, 60 kOe. The temperature dependence of the magnetization $M(T)$ is shown in the inset to Fig. 1d. It is well known that the magnetic and transport properties of single-crystal and polycrystalline samples of manganites can differ substantially, as

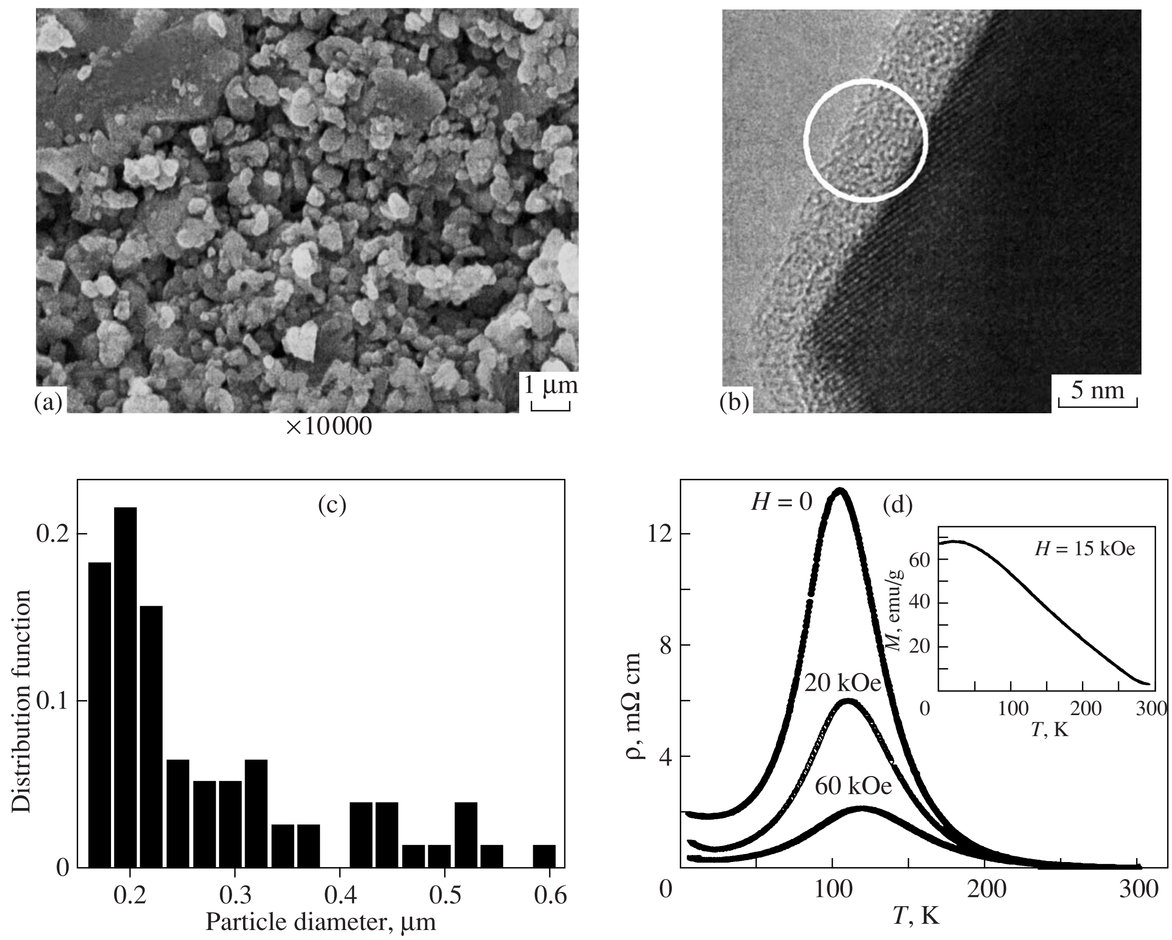

Fig. 1. (a) SEM image of polycrystalline $La_{0.7}Ca_{0.3}MnO_3$, (b) TEM image of a single granule, (c) the size distribution of granules obtained from analyzing the SEM images, and (d) the $\rho(T)$ dependence for $La_{0.7}Ca_{0.3}MnO_3$ measured at various values of an external magnetic field H. The inset shows the $M(T)$ dependence for $La_{0.7}Ca_{0.3}MnO_3$.

was observed in our case. It is seen that the Curie temperature T_C differs significantly from the metal–insulator transition temperature T_p ($\approx$110 K at $H = 0$), which practically coincide in single crystals. At low temperatures, the $\rho(T)$ dependence exhibits a clearly pronounced minimum, after which the resistivity increases as the temperature decreases. The temperature dependence of MR is shown in Fig. 2 for different values of the magnetic field H. It is seen that, at low temperatures, the quantity $\Delta\rho/\rho(H = 0)$ is comparable in value to that observed near the metal–insulator transition. The smooth $M(T)$ dependence up to the Curie temperature is likely due to the difference of the crystallite sizes, which leads to a T_C distribution in the sample. The maximum in the $M(T)$ curve at $T_N \approx 25$ K is indicative of the possible existence of an antiferromagnetic phase corresponding to the material of the outer granule shell depleted in oxygen [4], which causes a change in the charge states of manganese ions.

Figure 3 shows the $\rho(H)$ dependence of a sample measured at $T = 4.2$ K, and the inset to Fig. 3 presents the $M(H)$ dependence measured at this temperature. It

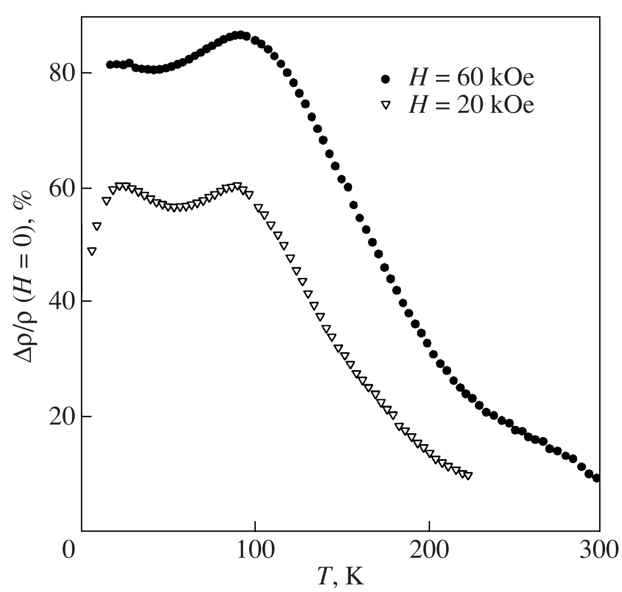

Fig. 2. Temperature dependence of the magnetoresistance $\Delta\rho/\rho(H = 0)$ of $La_{0.7}Ca_{0.3}MnO_3$.

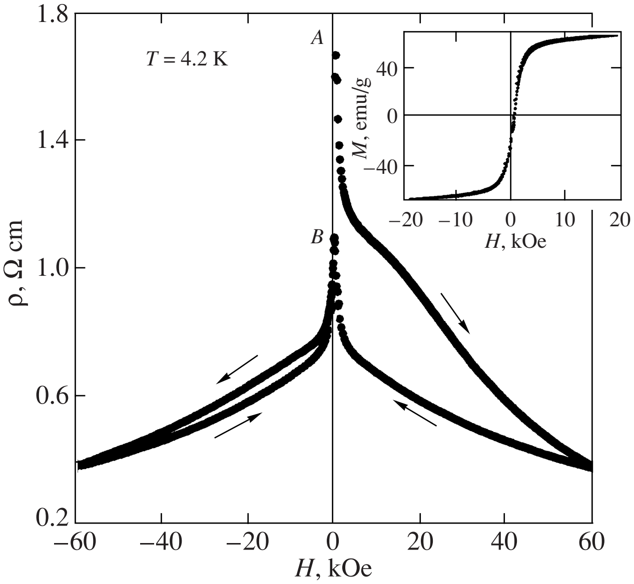

Fig. 3. $\rho(T)$ dependence for $La_{0.7}Ca_{0.3}MnO_3$ measured at $T = 4.2$ K. The inset shows the $M(H)$ dependence for $La_{0.7}Ca_{0.3}MnO_3$ measured at $T = 4.2$ K.

is seen that the $\rho(H)$ dependence exhibits hysteresis; the arrows show the sweep direction of the magnetic field. The initial run of the $\rho(H)$ varying from the nonmagnetic state (point A, $\rho(H\uparrow = 0)$ is characterized by significant MR in weak magnetic fields; Indeed, in a field of ~3 kOe, the MR is ≈40% of that in a field of 60 kOe. In strong fields, the resistivity decreases smoothly. As the magnetic field decreases from 60 kOe to 0, the $\rho(H)$ dependence exhibits significant hysteresis; in this case, $\rho(H\downarrow = 0)$ at point B is substantially smaller than the initial value $\rho(H\uparrow = 0)$. On further cycling of magnetic field, the $\rho(H)$ dependence exhibits insignificant hysteresis. The maximum resistivity $\rho(H\uparrow = 0)$ is achieved only after warming of the sample. Note that hysteresis of the magnetization $M(H)$ is insignificant (inset to Fig. 3), which is typical of polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ samples.

Such hysteretic behavior of the $\rho(H)$ can be qualitatively explained in terms of spin-dependent tunneling of electrons through intergranular boundaries in $La_{0.7}Ca_{0.3}MnO_3$. Indeed, according to the electron microscopy study, the average granule size is ~200 nm and the size distribution is Gaussian. On the other hand, the thickness of the insulating shell (~5 nm) surrounding each granule is determined by the preparation technology and is most likely the same for all granules. Therefore, with such a thickness of the insulating barrier, a sample contains ferromagnetic granules differing in size and coercive force [1]. Since the insulating-barrier thicknesses and the conducting properties of granule cores in a sample are the same, a transport current flowing through the network of tunneling junctions passes with equal probability through granules with different sizes. In this case, the hysteresis of $\rho(H)$ can be qualitatively explained as follows. In the unmagnetized state, the magnetic moments of individual granules are randomly oriented, which determines the maximum total electrical resistance of the network of tunneling contacts. When a weak external magnetic field (up to ~3 kOe) is applied, the large granules make the main contribution to the magnetization (inset to Fig. 3) and magnetoresistance. Then, the magnetic moments of smaller granules are oriented along the field, which corresponds to the segment with a smooth decrease in the resistivity. As the external magnetic field H is decreased to zero, the quantity $\rho(H\downarrow = 0)$ is lower than $\rho(H\uparrow = 0)$, since the magnetic moments of coarse granules remain codirected. Further insignificant hysteresis is due to magnetization reversal in smaller granules.

Thus, the observed specific hysteresis of $\rho(H)$ in $La_{0.7}Ca_{0.3}MnO_3$ is due to spin-dependent tunneling of carriers through the insulating boundaries of conducting granules exhibiting a spread in the magnetic-moment magnitudes.

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