

Effect of Coulomb blockade on the low- and high-temperature resistance of $\text{La}_{1-x}\text{M}_x\text{MnO}_3$ ($M=\text{Sr}, \text{Ca}$) films

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The nature of low- and high-temperature anomalies in electrical properties of $\text{LaSr}(\text{Ca})\text{MnO}$ films with clusterized structure is investigated. Results concern the cluster sizes $D=100\text{--}150 \text{ \AA}$, in which charge quantization is of importance but quantum confinement does not yet have an appreciable effect on the electrical properties of the samples. The electrical properties of the samples are determined by spin-dependent tunneling. It is shown that minima on resistance versus temperature curves may be explained by taking into account the Coulomb interaction of charge carriers with “metallic” clusters and tunneling between the clusters. We have found that transition from spin-dependent tunneling to percolation mechanism of conductivity in monocrystalline $\text{LaCa}(\text{Sr})\text{MnO}$ films containing “metallic” clusters is not only accompanied by a sharp increase in the efficiency of interaction between atomic, magnetic, and electronic subsystems, but also promotes the appearance of the effect similar to a window in the Coulomb blockade in the absence of a minimum on $R(T)$ curves. The experimental results suggest that the character of a maximum on $R(T)$ curves is determined by competitive interaction of the effects resulting from magnetic ordering with Coulomb blockade.

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I. INTRODUCTION

The perovskite manganites $R_{1-x}A_x\text{MnO}_3$, where R is a trivalent rare-earth ion and $A=\text{Sr}, \text{Ca}, \text{Ba}$ is a divalent alkaline-earth ion, showing the colossal magnetoresistive effect, continue to attract the steadfast attention of researchers due to many interesting properties caused by the interaction of their electronic and magnetic subsystems. The temperature dependence of the sample resistance is one of the characteristics of such interaction, and generally looks like the curves presented in Fig. 1.

There is no doubt that a significant part of the samples described in the literature, with positive temperature coefficient of resistance $dR/dT > 0$, at temperatures lower than the Curie temperature (T_C), remains in the insulator state at all temperatures of measurements¹⁻⁴ with conductivity essentially below the minimum of metallic conductivity,

$$\sigma_{\min} = \frac{\pi e^2}{4z\hbar a} \left[\frac{B}{V_0} \right]_{\text{crit}}^2, \quad (1)$$

where z is the coordination number, a is the distance between doping centers, V_0 is the amplitude of the random potential, and B is the width of the band.⁵ Thus, we can suggest only a formal similarity between the $R(T)$ curves for manganites and metals. According to Mott’s idea about the minimum metallic conductivity,⁵ the metallic behavior is observed if the inequality $\sigma > \sigma_{\min}$ holds. Mott’s calculations have shown that for materials with the coordination number $z=6$, the value of $\sigma_{\min}=300 \text{ \Omega}^{-1} \text{ cm}^{-1}$ is a good approximation.⁵ However, the reported results show that the presence of a maximum on the temperature dependences of resistance $R(T)$ and the subsequent decrease in resistance values at cooling the samples, caused by a fall of disorder in magnetic subsystem at $T < T_C$, are not, as a rule, related to the onset of metallic conductivity.³

When the sample is not in a state with metallic conductivity, its conductivity is limited by some varieties of tunnel mechanism. According to Refs. 1, 3, and 4, at $\sigma < \sigma_{\min}$, the conductivity of samples is determined by spin-dependent tunneling of charge carriers between clusters with metallic conductivity. In this case, the temperature dependences of resistance can be described with the help of a simple model that assumes the increase in the cluster size with lowering temperature due to sequential delocalization of the electronic states in peripheral areas of clusters during magnetic ordering. Typical $R(T)$ curves with a maximum, a minimum, followed by an increase in the resistance at low temperatures are presented in Fig. 1. Different sensitivity of electrical properties of the samples to the change of their magnetic state, which is determined by the position of $R(T)$ maxima

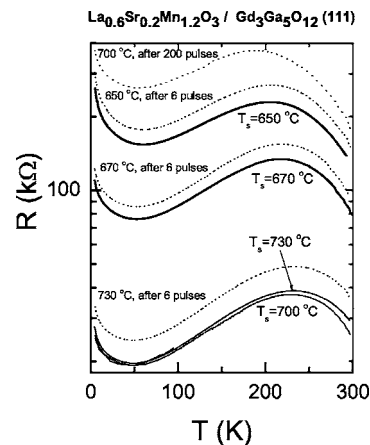


FIG. 1. Typical temperature dependences of resistance for LaSrMnO films deposited on $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ substrates at various temperatures: initial state (solid lines) and after laser irradiation (dash curves).

relative to magnetization curves $M(T)$, is caused by differences in the cluster structure.^{3,4}

It has been shown³ that the calculated $R(T)$ dependences describe well the experimental curves as being at low ($C_m^0 < 0.15$) and high ($C_m^0 \geq 0.2$) concentrations of metallic phase (C_m^0). However, the proposed model did not predict an increase in the resistance in the low-temperature range.

The nature of a minimum on $R(T)$ curves has not been explained yet and the unambiguous interpretation of the results is still lacking. It is known only that the $R(T)$ minimum is observed on the $R(T)$ curve of the samples with sufficiently large resistivity values and is absent in the low-resistance samples.

Various mechanisms can be responsible for the appearance of a minimum on $R(T)$ curves. In samples with strongly nonuniform structure and with properties caused by the presence of clusters with metallic conductivity, the most attractive explanation is in terms of the capture of free charge carriers by localized states in peripheral areas of clusters. However, the character of the temperature dependences of resistance $R(T)$ at $T < T_{\min}$ does not correspond to the dependence with a fixed activation energy caused by the presence of the characteristic group of localized states. Furthermore, this process should depend, to a great extent, on the mean size of clusters. At a concentration of free holes $p \cong 3 \times 10^{21} \text{ cm}^{-3}$, the thickness of the space-charge layer depleted of holes

$$h = \left(\frac{2\epsilon\epsilon_0 V_D}{ep} \right)^{1/2}, \quad (2)$$

where V_D is the barrier height,⁶ is $\sim 10 \text{ \AA}$, which is a large value for small clusters. The attempt to relate the observed effect to the h/D ratio (where D is a cluster size) has not given a reasonable result.

Earlier, according to the data of Refs. 7–9, a rather plausible explanation of the appearance of minima on $R(T)$ curves in terms of charge ordering was presented. However, this approach was unable to explain the differences in the experimental results for samples with different doping by strontium or calcium.

In this paper, we analyze the influence of Coulomb interactions on $R(T)$ curves of LaSr(Ca)MnO films with monocrystalline structure at tunneling of the charge carriers between nanosize clusters. The relationship between various parameters characterizing the samples is studied and it is shown that taking into account a Coulomb blockade, without any quantum confinement effects, a satisfactory description of the temperature dependences of resistance in a low-temperature range may be obtained, both at small and high concentration of metallic phase (C_m^0). Furthermore, this model explains the presence of a minimum and subsequent increase in resistance at small C_m^0 corresponding to the values lower than a percolation threshold. We also come to the conclusion that a maximum on $R(T)$ curves at all C_m^0 values originates from a competition of Coulomb blockade with the mechanisms of magnetic and atomic ordering in peripheral areas of clusters at cooling the samples to a temperature below T_C .

II. SAMPLE PREPARATION AND EXPERIMENT

The investigated films were grown by pulsed laser deposition^{10,11} using an excimer KrF laser with pulse duration $\tau = 25 \text{ ns}$ and fluence $\Phi = 1.5\text{--}3.0 \text{ J/cm}^2$, at 300 mTorr O_2 from $\text{La}_{0.6}\text{Sr}_{0.2}\text{Mn}_{1.2}\text{O}_3$ and $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ targets. Films were grown on single-crystalline substrates SrLaGaO_4 , $\text{Nd}_3\text{Ga}_5\text{O}_{12}$, $\text{Gd}_3\text{Ga}_5\text{O}_{12}$, SiO_2/Si , $(\text{LaAlO}_3)_{0.3} \cdot (\text{Sr}_2\text{AlTaO}_6)_{0.7}$ [denoted in the text as SAT-30], and $(\text{LaAlO}_3)_{0.22} \cdot (\text{Sr}_2\text{AlTaO}_6)_{0.78}$ [SAT-22] at deposition temperatures T_s varying between 650 and 730 °C. Deviations from stoichiometry did not show a fundamental influence on the cluster structure and properties of the samples, which to a greater degree depend on growth conditions and elastic stress at the film-substrate boundary specified by substrate type, rather than by stoichiometry.^{3,4} Indeed, by representing the stoichiometric $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ as a solid solution of two compounds described by a general chemical formula $M_2\text{O}_3$ ($M = \text{La}, \text{Mn}, \text{Sr}$), i.e., writing $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3 = (\text{LaMnO}_3)_{1-x}(\text{SrMnO}_3)_x$, it can be seen that the excess manganese forms structural groups with similar chemical composition in the solid solution of three compounds: $\text{La}_{0.6}\text{Sr}_{0.2}\text{Mn}_{1.2}\text{O}_3 = \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 = (\text{LaMnO}_3)_{1-2x}(\text{SrMnO}_3)_x(\text{Mn}_2\text{O}_3)_x$, where $x = 0.2$. The excess manganese is spread more or less uniformly in the sample volume. The changes in chemical composition of the samples affect only relative intensities of the diffraction lines, but not their positions.¹ However, we consider that deviations from stoichiometry in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ result in an increase of local pressures, promoting phase separation and provoking formation of the clusters. The presented results refer to the films with monocrystalline structure.^{1,3,4}

Transport measurements, using the conventional four-probe technique, were performed over the 4.2–300 K temperature range. Measurements of film magnetization, using a commercial SQUID magnetometer, were carried out in a similar temperature range (5–300 K). Generally, according to detailed x-ray investigations, the orthorhombic phase prevailed in the investigated samples.^{1,3,4,12}

III. EXPERIMENTAL RESULTS

A. Cluster structure and conductivity mechanism of the films

In the systems with a disordered structure, the clusters are formed under the influence of chemical bond forces and the temperature. The clusters represent the order fluctuations in the disordered medium.^{10,13,14} Typical representatives of such systems are amorphous or glassy materials. For investigated monocrystalline films of manganites, on the contrary, clusters are the most defective structural formations in the medium with the perfect long-range atomic order and in this sense they are comparable to the clusters in high-temperature superconductors (HTSC's), which are also typical representatives of metal oxides.¹¹

As has been already mentioned and according to,^{1,3,4} at $\sigma < \sigma_{\min}$ the conductivity of samples is defined by spin-dependent tunneling of charge carriers between clusters with a metallic conductivity. In layers with monocrystalline structure, clusters representing fluctuations of disorder in the or-

dered medium start to be formed due to the electronic mechanisms of phase separation^{15,16} acting during growth of the films. Because of the diverse length of Mn-O bonds, the manganese ions with different charge states are the sources of local internal stress, which finally play a significant role resulting in the change in local microstructure in the areas of hole (or electronic) “drops” with the formation of clusters. The formation of clusters is a result of relaxation of elastic stresses caused by redistribution of charge states of manganese: Mn^{2+} , Mn^{3+} , Mn^{4+} . Mn^{3+} ions are mainly presented at a matrix, and there are Mn^{3+} and Mn^{4+} ions in the clusters. Even though the chemical compositions of the films allow the metallic behavior, due to the capture of free holes by localized states in peripheral areas of flat clusters, at lateral cluster size $D=100$ Å, cluster thickness $D/3 \approx 30$ Å, and the thickness of the space-charge layer depleted of holes $h \approx 10$ Å,^{1,3,4} about 1/3 of the cluster volumes only can participate in conductivity. The reason for the low conductivity value is a complex phase composition of cluster structure and the presence of dielectric clusters. Therefore, for most films, $\sigma < \sigma_{min}$. The sizes of interface zones, which are the basic sources of the localized states, with a smooth transition from the order to the disorder, are comparable to the sizes of small clusters ($D < 30$ Å).

Planes containing Mn-O bonds appear to be substantially fragmented, but nevertheless remain coherently embedded into a monocrystalline structure of LaCa(Sr)MnO films. The length of Mn-O bonds decreases from $Mn^{2+}-O$ to $Mn^{3+}-O$, and further to $Mn^{4+}-O$.^{4,17,18} The concentration ratio for manganese ions of different valency can be estimated from the x-ray analysis.³ Taking into consideration the capture of free holes by localized states in peripheral areas of clusters, we conclude that under optimum growth conditions of the samples, the value of $C_m^0 = 15-20\%$ (at $T=300$ K) is close to expected C_m^0 values, provided that all holes, formed at doping of the films by strontium (calcium), participate in the formation of the hole drops. This confirms the assumption that the electronic mechanisms of phase separation are the original causes of clusterization in the manganites. Real shapes of clusters, formed on the basis of the hole drops, are determined by anisotropy of the atomic order in the crystal.

Clusterized fragments of Mn-O planes alternate with non-clusterized planes such as (112),^{1,3} containing La, Sr (Ca), O, with fixed lengths of bonds keeping the long-range order and supporting orientation and continuity of fragments of Mn-O planes, coherently incorporated in monocrystalline structure of LaCa(Sr)MnO films.^{3,4} It is actually the basic obstacle for the formation of polycrystalline structure. Continuity of Mn-O planes due to the presence of hard planes containing no manganese, with fixed lengths of bonds, is the important condition facilitating the processes of atomic and magnetic ordering in peripheral areas of clusters^{1,3,4} providing the low activation energies for these processes.

Schematically, the cross section of monocrystalline film with clusters is presented in Fig. 2. Fragments of Mn-O planes belonging to the clusters are shown by bold lines. And though in this model all Mn-O planes appear fragmented, not all of them participate in the formation of clusters. As was already noted, the electronic mechanisms of phase separation play the main role in this process. In the presence of a large

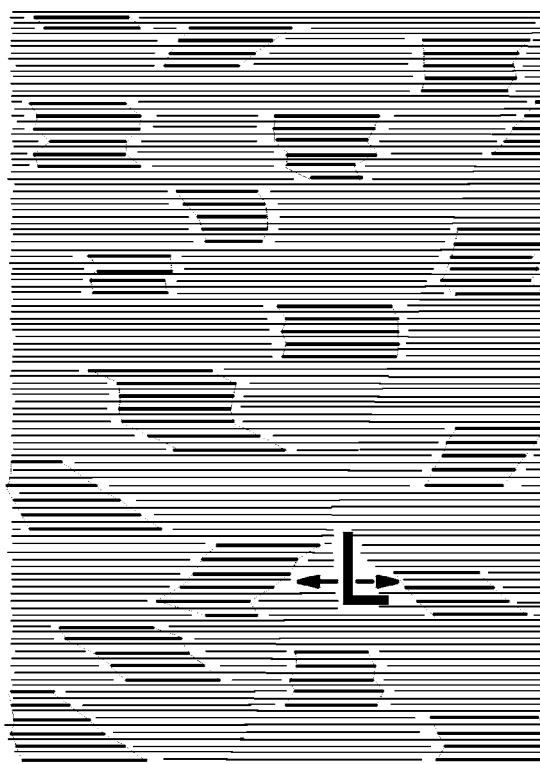


FIG. 2. Model of cross section of the film with cluster structure.

quantity of defects, the continuity of Mn-O planes allows quick reconstruction of the cluster structure when the temperature or magnetic field is changed.

The flexible structure of cluster peripheral areas, capable of being reconstructed under external effects such as temperature, magnetic field, and pressure, results in convertible changes of the cluster structure configuration and causes the features of electrical and magnetic properties of the films, including the effect of colossal magnetoresistance. The phase composition of the clusters determines the interaction efficiency of the electronic and magnetic subsystems. The local microstructure of clusters is formed by two primary factors: the growth temperature and the type of a substrate.^{3,12}

If the tunneling of electrons between “metallic” clusters were the unique mechanism of conductivity of the films, their resistivity would grow exponentially with an increase of average distance (L) between clusters,^{1,3}

$$\rho = \rho_0 \exp\left(\frac{L}{L_0}\right), \quad (3)$$

where L_0 is a constant, ρ_0 includes a factor of the order of $\exp(\Phi^{1/2})$, and Φ is the effective barrier height that is assumed to be constant. At distances between clusters (L) measured in angstroms, $L_0 = 12.5$ Å for LaSrMnO films and $L_0 = 16.25$ Å for LaCaMnO films. The main parameters of this process can be determined from experiments, considering a model of quasi-two-dimensional clusters in the form of plates parallel to the film surface. Let the plates be of a lateral size D and, in accordance with the x-ray data, thickness $D/3$. When such clusters form a regular lattice, there are

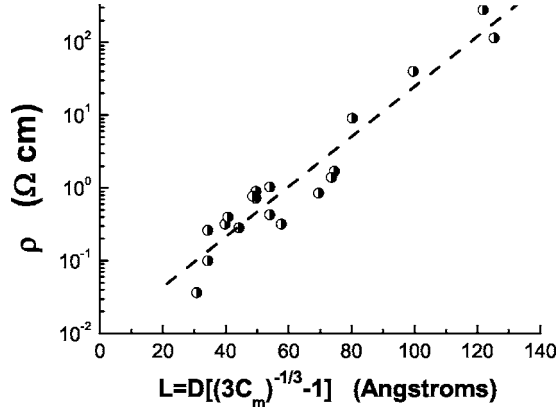


FIG. 3. Resistivity of LaSrMnO films vs average distance $L=D[(3C_m)^{-1/3}-1]$ between clusters with metallic conductivity.

$1/(L+D)^3$ clusters per unit volume and the metallic phase concentration is

$$C_m = \frac{1}{3}D^3 \frac{1}{(L+D)^3},$$

which yields

$$L = D[(3C_m)^{-1/3} - 1]$$

and

$$\rho = \rho_0 \exp\left\{\frac{D}{L_0}[(3C_m)^{-1/3} - 1]\right\}. \quad (4)$$

The C_m values were determined using the optical absorption data^{10,11,13,19-21} and taking into account the mechanisms of optical transitions²²⁻²⁶ and the results of x-ray diffraction measurements.^{3,4,12} In some of the films, $C_m \approx 15-18\%$, however it is lower than a percolation threshold, and metallic conductivity was not observed in the vicinity of T_{\max} . A shift in the percolation threshold to $C_m^{\text{crit}}=0.5-0.6$ is peculiar to thin-film objects.^{27,28} Metallic conductivity is present at low temperatures. It is characteristic for LaCaMnO films on SAT-30 and on SAT-22 substrates. Figure 3 shows the $\rho = f(L)$ dependence calculated according to Eq. (3). A high value of the preexponential factor $\rho_0=0.0081 \Omega \text{ cm}$ is related to a reduced concentration of holes (p) in the samples owing to their localization in peripheral areas of the clusters. We believe that some scattering of the points in Fig. 3 is related to the fact that we did not take into account individual parameters of the cluster structure for the films, considering that in all cases the average size of clusters is identical and does not depend on the type of substrate and growth temperature of the films, i.e., $D=100 \text{ \AA}$.

In our previous papers,^{3,4} it was shown that at temperatures below T_C as a result of an active interaction of the atomic, electronic, and magnetic subsystems, the amplitude of random potential decreases, while the metallic phase concentration increases and the sample resistance drops. For the tunneling mechanism of electrical conductivity, two alternatives have been considered. (i) At small concentration of a metallic phase ($C_m < 0.15$), the relations between various pa-

rameters of the films can be described assuming that C_m increases linearly with the $T_{\max}-T$ interval during cooling the samples,^{1,3}

$$C_m(T) = C_m^0 + B(T_{\max} - T), \quad (5)$$

where C_m^0 is the metallic phase concentration at $T=T_{\max}$. (ii) At small C_m , far away from the insulator-metal transition, for tunneling of electrons between clusters, the temperature dependence of resistivity $\rho(T)$ at $T < T_{\max}$ is given by the following relation:³

$$\rho = \rho_0 \exp\left\{\frac{D^0}{L_0} \left[[C_m^0 + B(T_{\max} - T)] - C_m^{\text{crit}} \right]^{-\nu} \times [3^{-1/3} [C_m^0 + B(T_{\max} - T)]^{-1/3} - 1] \right\}. \quad (6)$$

Due to the presence of small clusters, smaller than the double thickness of the hole depleted layer h (2) which do not contribute to C_m ($D < 2h$), the temperature dependence of D has to be found separately from that of the metallic phase concentration C_m . It was reasonable to take advantage of the percolation theory results, assuming that changes in $D(T)$ are similar to a change in the correlation radius, $L^*(C_m) \approx |C_m - C_m^{\text{crit}}|^{-\nu}$, where $\nu=0.85$ is a critical index,²⁷

$$D(T) \approx D^0 \left[[C_m^0 + B(T_{\max} - T)] - C_m^{\text{crit}} \right]^{-\nu}. \quad (7)$$

The increase of small cluster size up to $D_{\text{crit}} \approx 2h$ with decreasing temperature is equivalent to the generation of new clusters with metallic conductivity. Equation (6) holds in the region where the metallic phase concentration is below the percolation threshold, i.e., $C_m < C_m^{\text{crit}}=0.5$. Under these conditions, the samples belong to the class of systems with variable potential relief.

Equation (6) provides a satisfactory fit of the experimental $R(T)$ curve for LaSrMnO sample, with the exception of the low-temperature region.³ A pure tunneling mechanism leads to slow changes of resistance with temperature. The (negative) magnetoresistance (MR) reaches a maximum at 4.2 K and decreases monotonously with increasing temperature, presenting one of the most striking features of spin-dependent tunnelling.^{1,29-31} The maximum change of MR occurs also in low magnetic fields.¹

To fit the $\rho(T)$ data obtained for the samples with C_m closer to the insulator-metal transition, displaying steep $R(T)$ curves, we need to introduce the nonlinear $C_m(T)$ dependence given by

$$C_m = C_m^0 + G(T_{\max} - T)^t, \quad (8)$$

where $t=1.75$ is the critical index usually characterizing the conductivity of a highly nonuniform medium close to the percolation threshold²⁷ and G is a constant. On the insulator side of the transition, the exponential dependence of resistivity on the average distance between clusters, characteristic for the tunneling mechanism, gives

$$\rho(T) = \rho_0 \exp \left\{ \frac{D^0}{L_0} [C_m^0 + G(T_{\max} - T)^t] - C_m^{\text{crit}} \right\}^{-\nu} \times [3^{-1/3} [C_m^0 + G(T_{\max} - T)^t]^{-1/3} - 1] \quad (9)$$

instead of Eq. (6). The results of our calculations based on Eq. (9) for the LaCaMnO film on SAT-30 with $C_m^0=0.2$ are in good agreement with the experiment.³

B. Cluster structure and correlation between low- and high-temperature resistances of the films

Detailed analysis of relations between various parameters of the samples has shown that the sizes of clusters and their concentration determine the resistance values at room temperature, as seen in Fig. 3. This resistance is caused by the tunnel mechanism of conductivity.^{1,3,4} If the drop in resistance R at $T < T_{\max}$ during the reconstruction of cluster structure at cooling were limited by the effects of Coulomb blockade, then the correlation between the resistance of the samples at room temperature and $R(T)$ behavior at low temperatures should be observed, including the formation of a minimum and the subsequent increase in resistance as the temperature is decreased further. It is very important that the $T=290$ K point is higher than the values of Curie temperature or temperatures of a maximum when magnetic ordering is still not present and the interplay between electronic and magnetic subsystems is absent. Thus these effects do not influence the values of resistivity at $T=290$ K. At the same time, it is obvious that at high temperatures ($T > T_{\max}$), when small clusters participate in tunneling, the Coulomb blockade should be the main effect determining the temperature dependence of resistance.

According to recent results,^{1,3,4} the ρ_{290} value as well as the rapidity of decrease in resistance at cooling the samples below T_{\max} are determined by the parameters of cluster structures, mainly by the concentration of metallic phase (C_m). Therefore, supposing that the presence of a minimum on $R(T)$ curves and the subsequent increase in resistance are related to the Coulomb interaction of charge carriers during tunneling between clusters with metallic conductivity, then using the resistivity value at room temperature ρ_{290} , it is possible to predict the $R(T)$ curve shape at low temperatures and the position of the particular point T_{\min} on the temperature scale. This possibility is connected with the fact that the effects of Coulomb blockade are unambiguously related to the basic parameters of the cluster structure, namely the sizes of clusters and the distance between them. It can be observed qualitatively already in Fig. 1, where eight $R(T)$ curves for LaSrMnO films deposited on $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ substrates are presented: $R(T)$ dependences for four samples differing in growth temperature ($T_s=650$ °C; $T_s=670$ °C; $T_s=700$ °C; and $T_s=730$ °C) are added to four curves for the same samples irradiated by UV laser (KrF; $\hbar\omega=5.01$ eV; $\tau=25$ ns) at an energy density of $\Phi=0.12$ J/cm² at the sample surface. The data in Fig. 1 clearly show that the maximum on $R(T)$ curves is displaced toward low temperatures, and a minimum, on the contrary, toward high temperatures with an

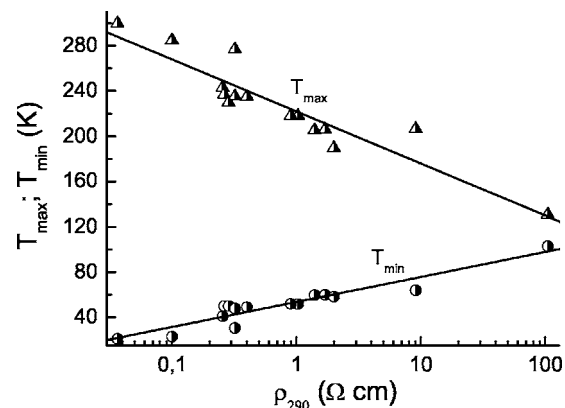


FIG. 4. Positions of critical points (T_{\max} and T_{\min}) on temperature axis for $R(T)$ dependences vs resistivity at room temperature.

increase in resistivity at room temperature (ρ_{290}). The general picture is well seen in Fig. 4, where the data for films of the same structure deposited on the substrates of three types are presented. There is a linear relationship between positions of a maximum (T_{\max}) and a minimum (T_{\min}): $T_{\min} = \alpha T_{\max} + \gamma$, where $\alpha=-0.46$ and $\gamma=154.3$.¹

It is also seen from data in Fig. 1 that the increase of the ρ_{290} values results not only in the displacement of the critical points positions on the temperature axis, but also in the rise of resistance in the low-temperature range. The relation between ρ_{290} and the low-temperature resistance appears to be nonlinear. For example, for relatively low-resistance samples, presented by the bottom curves in Fig. 1, the resistance at T_{\min} is approximately 1.5–1.6 times lower than the values at $T=290$ K, and on the contrary, for high-resistance samples (see the top curves in Fig. 1), the resistivity at T_{\min} is 1.1–1.3 times higher than ρ_{290} values. The resistivity at a minimum (ρ_{\min}) rises with an increase in ρ_{290} values (Fig. 5) stronger than the resistivity at the maximum (ρ_{\max}). This is in agreement with the observation that the effects of Coulomb blockade should exhibit themselves more pronouncedly in the high-resistance samples and operate most effectively at low temperatures. Power-mode dependences observed in both cases are characteristic for the description of relations

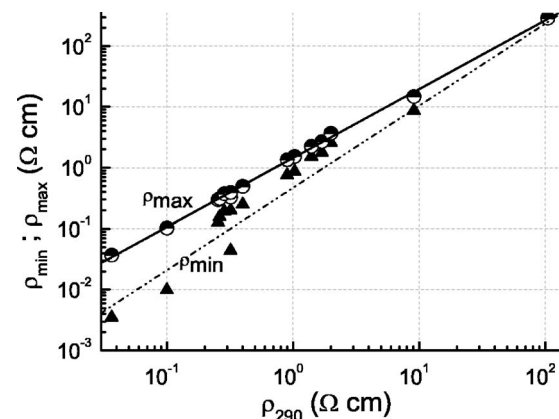


FIG. 5. Growth of resistivity in extreme points of $R(T)$ curves (ρ_{\max} and ρ_{\min} at T_{\max} and T_{\min}) vs increase in resistance at room temperature (ρ_{290}).

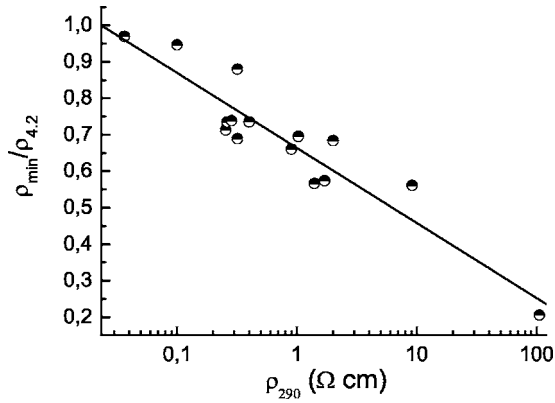


FIG. 6. Ratio between resistivities of LaSrMnO films at T_{\min} and $T=4.2$ K ($\rho_{\min}/\rho_{4.2}$) vs resistivity at room temperature (ρ_{290}).

between parameters of the samples under consideration.^{1,3} A distinct dependence (of logarithmic type) of resistivities at $T=4.2$ K and at T_{\min} ratio ($\rho_{\min}/\rho_{4.2}$) on ρ_{290} values is observed: $\rho_{\min}/\rho_{4.2} \sim \log(1/\rho_{290})$ (Fig. 6). Also, the decrease of $\rho_{\min}/\rho_{4.2}$ ratio values with the increase of ρ_{290} values is a good illustration of the statement that the efficiency of the Coulomb blockade becomes stronger with decreasing temperature and with the increase in resistivity of the films at room temperature.

Optical and x-ray investigations, used to estimate the parameters of cluster structures, are carried out at room temperature.^{1,3} The reported results can serve as a good illustration showing the influence of the cluster structure on properties of the films not only at high but also at low temperatures.

The described regularities are observed in a wide interval of the resistivity changes: $\rho_{290}=0.03\text{--}110$ Ω cm. At room temperature, the top border of the ρ values is close to 100 Ω cm, which corresponds to $\sim 3\%$ of the metallic phase concentration (C_m). In the 60–180 K temperature interval, the $R(T)$ curve of such a sample has a range where the resistance practically does not depend on temperature [Fig. 7(a)]. It is possible to see a maximum ($T_{\max}=131$ K) and a minimum ($T_{\min}=103$ K) on $R(T)$ dependence only at a very large magnification, studying a corresponding area of the curve [Fig. 7(a)] in detail. The temperature interval between a maximum and a minimum on $R(T)$ curve is narrow: $\Delta T = T_{\max} - T_{\min} = 28$ K.

The curves in Fig. 7(b) represent the typical temperature dependences of resistance, $R(T)$, and magnetization, $M(T)$, with the distinctly marked maximum and minimum on the $R(T)$ curve. The maximum in resistance corresponds to the ratio $M(T_{\max})/M(5\text{ K})=0.23$ value. We studied predominantly the nature of such $R(T)$ curves, which are characteristic for the samples having resistivity at room temperature (ρ_{290}) in the limits of 0.1–10 Ω cm.

In contrast to Fig. 7(a), Fig. 7(c) represents other extreme case in which the minimum on the $R(T)$ curve practically disappears and can be seen only in a more detailed scale (see the right-hand side of the y axis), and the increase in resistance at $T < T_{\min}$ appears very weak. The efficiency of interaction of the electronic and magnetic subsystems is already high enough. Similar $R(T)$ curves are observed for the

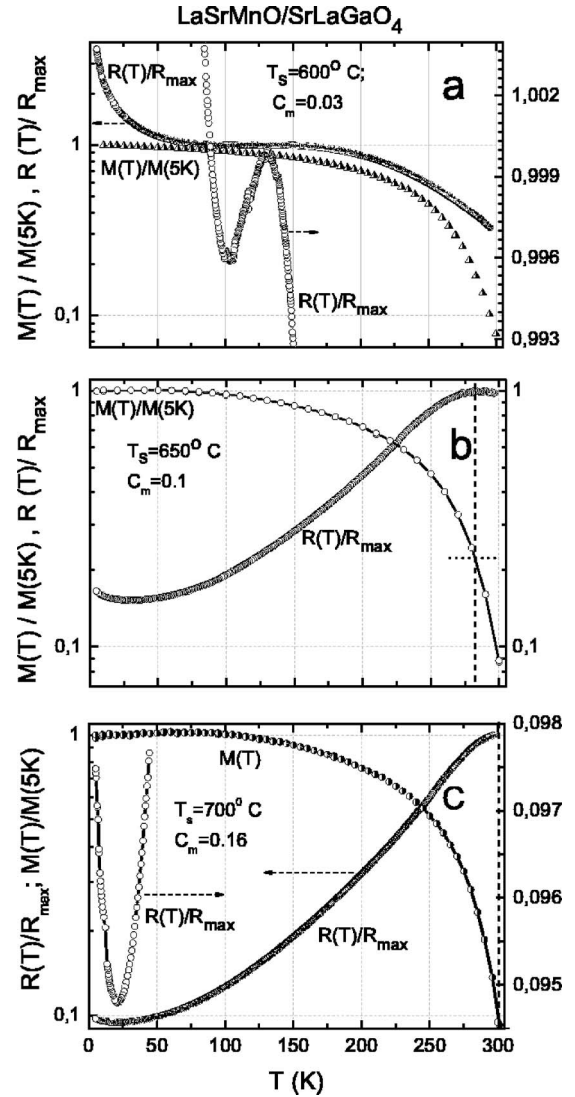


FIG. 7. Examples of $R(T)$ curves for LaSrMnO films. $M(T)$ is the temperature dependence of magnetization.

samples in the vicinity of the metal-insulator transition. For the sample with the $R(T)$ curve presented in Fig. 7(c), the resistivity at a minimum is 3.45×10^{-3} Ω cm. Corresponding to this ρ value, the magnitude of conductivity $\sigma \approx 290$ Ω^{-1} cm^{-1} is very close to the minimum of metallic conductivity value ($\sigma \approx 300$ Ω^{-1} cm^{-1}) calculated by Mott for the coordination number equal to 6.⁵

C. Influence of Coulomb blockade on $R(T)$ curves

According to the model under consideration,^{1,3,4} the decrease in resistance of the samples at cooling below T_C is realized due to magnetic ordering in peripheral areas of clusters and delocalization of the electronic states with the further increase in the concentration of free holes and due to expansion of the volume of the central part of the clusters with metallic conductivity. Due to conservation of monocrystalline structure, a high mobility of defects with low activation energy for reorganization of the local defect structure is realized.

Without taking into account the Coulomb interaction of the charge carriers with the clusters at tunneling between them, this model does not give a minimum on $R(T)$ curves and the subsequent increase in resistance below this minimum. At the same time, the efficiency of the Coulomb blockade determined by the dimensions of clusters is high just at low temperatures.^{32,33}

The character of the temperature dependence of resistance determined by Coulomb interaction of charge carriers at tunneling between clusters with metallic conductivity³² is given by the equation

$$\rho(T) = \rho_0 \exp\left(\frac{W_D}{kT}\right), \quad (10)$$

where k_B is the Boltzmann constant and W_D is the charging energy dependent on the cluster size (D),

$$W_D \approx \frac{e^2}{\varepsilon D} \left[1 - \left(\frac{C_m}{C_m^{\text{crit}}} \right)^{1/3} \right], \quad (11)$$

e is the electronic charge, ε is a permittivity, and C_m^{crit} corresponds to a percolation threshold, where the equation $(L_c/D)^3 = C_m^{\text{crit}}/C_m$ (L_c is the correlation radius) is true. For $W_D \gg kT$, the contribution of Coulomb interactions of electrons with clusters in resistance of the samples, according to formulas (10) and (11), strongly grows. In this case, the sharp decrease in the probability of tunneling allows us to speak about the rise of Coulomb blockade for tunnel transitions of electrons between clusters.

Taking into account the occurrence of Coulomb interaction of charge carriers with the clusters requires for a tunnel mechanism the addition in Eqs. (6) and (9) of factors dependent on the charging energy W_D given by Eq. (11).³³ In conformity with two considered approximations, these factors look like

$$Q_1(T) = \exp \left\{ \frac{e^2}{\varepsilon} \frac{1}{k} \frac{1}{D^0} \frac{1}{T} [C_m^0 + B(T_{\text{max}} - T)] - C_m^{\text{crit}|p} \left[1 - \left(\frac{C_m^0 + B(T_{\text{max}} - T)}{C_m^{\text{crit}}} \right)^{1/3} \right] \right\}, \quad (12)$$

$$Q_2(T) = \exp \left\{ \frac{e^2}{\varepsilon} \frac{1}{k} \frac{1}{D^0} \frac{1}{T} [C_m^0 + G(T_{\text{max}} - T)^f] - C_m^{\text{crit}|p} \left[1 - \left(\frac{C_m^0 + G(T_{\text{max}} - T)^f}{C_m^{\text{crit}}} \right)^{1/3} \right] \right\}. \quad (13)$$

At these assumptions [see formulas (5) and (8)], functions Q_1 and Q_2 vary slowly with temperature. However, their account in Eqs. (6) and (9) makes the calculated curves closer to experimental ones. The account of the Q_1 factor in formula (6) for the temperature dependence of resistance results in the appearance of a minimum on the calculated $R(T)$ curve at low temperatures that is concerned with the presence of a factor proportional to $1/T$ in the exponent of Eq. (12). At the same time, the fitting procedure of a calculated curve to an experimental one has shown that the linear approximation (5) for the description of relation be-

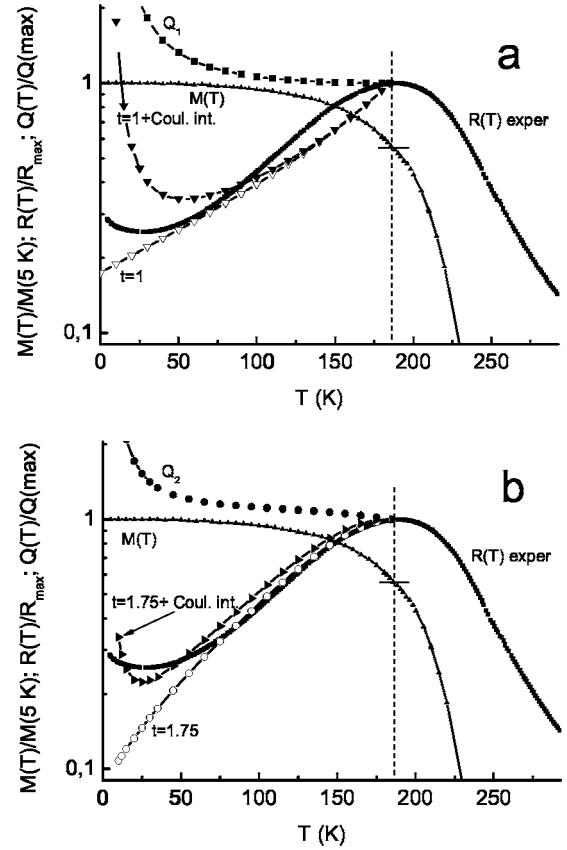


FIG. 8. Experimental $[R(T)_{\text{exper}}]$ and calculated $R(T)$ curves for LaCaMnO film at $C_m^0=0.125$. (a) Calculations with use of linear dependence (5) for C_m on T and Eqs. (6) and (12). $t=1$ is the calculated temperature dependence of relative resistance $[R(T)/R_{\text{max}}]$ according to Eq. (6), where $T_{\text{max}}=185$ K, $D^0=44.2$ Å, $L_0=16.25$ Å, $B=8 \times 10^{-4}$ K $^{-1}$, $C_m^{\text{crit}}=0.5$. $t=1 + \text{Coul. int.}$ is the calculated temperature dependence of relative resistance $[R(T)/R_{\text{max}}]$ taking into account the Coulomb interaction given by Eq. (12). Q_1 is a function Eq. (12). (b) Calculations with use of nonlinear dependence (8) for C_m on T and Eqs. (9) and (13). $t=1.75$ is the calculated temperature dependence of relative resistance $[R(T)/R_{\text{max}}]$ according to Eq. (9), where $T_{\text{max}}=185$ K, $D^0=44.2$ Å, $L_0=16.25$ Å, $G=2.3 \times 10^{-5}$ K $^{-1}$, $t=1.75$, $C_m^{\text{crit}}=0.5$. $t=1.75 + \text{Coul. int.}$ is the calculated temperature dependence of relative resistance $[R(T)/R_{\text{max}}]$ taking into account the Coulomb interaction given by Eq. (13). Q_2 is a function Eq. (13) for $G=2.3 \times 10^{-5}$ K $^{-1}$. $M(T)$ is the temperature dependence of relative magnetization $[M(T)/M(5 \text{ K})]$.

tween C_m and T does not provide good correspondence of calculation with the experiment. At high temperatures, in the $2T_{\text{min}} < T < T_{\text{max}}$ temperature interval, the resistance values for the calculated $R(T)$ curve decrease too quickly in comparison with the experimental points. At low temperatures, the increase in resistance appears too fast [Fig. 8(a)]. As a result, we were obliged to pay attention to the formulas (8) and (9) supposed nonlinear dependence of concentration of a metallic phase on temperature. In that case, as can be seen in Fig. 8(b), it is possible to describe correctly the character of the temperature dependence of the resistance not only at high but also at low temperatures, and to point correctly to the position of a minimum (T_{min}) on the temperature axes for $R(T)$ dependence. Comparison of the results in Figs. 8(a) and

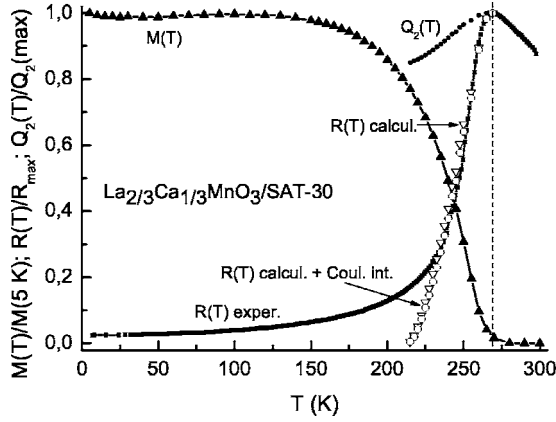


FIG. 9. Experimental $[R(T)_{\text{exper}}]$ and calculated $R(T)$ curves for LaCaMnO film at $C_m^0=0.2$. Calculations with use of nonlinear dependence (8) for C_m on T and Eqs. (9) and (13). $R(T)_{\text{calcul.}}$ is calculated temperature dependence of relative resistance $[R(T)/R_{\text{max}}]$ according to Eq. (9), where $T_{\text{max}}=270$ K, $D^0=44.2$ Å, $L_0=16.25$ Å, $G=2.3 \times 10^{-4}$ K $^{-1}$, $t=1.75$, $C_m^{\text{crit}}=0.5$. $R(T)_{\text{calcul.}} + \text{Coul. int.}$ is the calculated temperature dependence of relative resistance $[R(T)/R_{\text{max}}]$ taking into account the Coulomb interaction given by Eq. (13). $Q_2(T)$ is function (13) for $G=2.3 \times 10^{-4}$ K $^{-1}$. $M(T)$ is the temperature dependence of relative magnetization $[M(T)/M(5$ K)].

8(b) shows once again the utility of the use of the percolation theory elements for the description of conductivity of strongly nonuniform media in the vicinity of the insulator-metal transition.

For films with $C_m \geq 0.2$, the $R(T)$ curves exhibit no low-temperature minimum, while the maximum of $R(T)$ coincides with the onset of increase in magnetization $M(T)$. At temperatures $T < T_{\text{max}}$, the fast decrease in resistance is observed in a narrow temperature interval (Fig. 9). The relative variation rate, $(dR/dT)/R$, reaches 7%/K (which is five to six times the maximum value in the previous group), characterizing a high sensitivity of electrical properties to the state of a magnetic subsystem. The relative derivative $(dR/dT)/R$ for LaSr(Ca)MnO films can achieve 25–30%/K.³⁴ As was already noted, for such samples, described by a fast decrease in resistance at $T < T_{\text{max}}$, $R(T)$ curves are well described by the formula (9). According to estimations of σ_{min} values, for such samples (predominantly on SAT-30 or on SAT-22 substrates), the percolation insulator-metal transition is realized in the 200–210 K temperature interval, where the C_m value increases up to $C_m^{\text{crit}}=0.5$ (Fig. 9). Really, according to Eq. (8), at $T=210$ K we have $C_m=0.45 < C_m^{\text{crit}}=0.5$, and at $T=200$ K we get $C_m=0.52 > C_m^{\text{crit}}=0.5$. At $T < 100$ K, the conductivity of this film $\sigma > 10^3$ Ω $^{-1}$ cm $^{-1}$, which is essentially higher than $\sigma_{\text{min}} \approx 300$ Ω $^{-1}$ cm $^{-1}$. In the region of metallic conductivity, at $T < 180$ K, the LaCaMnO films on SAT-22 and SAT-30 substrates exhibited a nearly quadratic temperature dependence of resistivity: $\rho(T)=\rho_0+AT^{2.27}$ (Fig. 10), where $\rho_0=5.37 \times 10^{-4}$ Ω cm and $A=1.1 \times 10^{-8}$ Ω cm K $^{-2.27}$ values are in agreement with the data reported for manganites.³⁵ At low temperatures, the $\rho(T)$ curve can be approximated by a linear dependence, $\rho=\rho_0(1+\alpha T)$, with the temperature coefficients of resistance $\alpha=7.1 \times 10^{-3}$ K $^{-1}$ (LaCaMnO films on

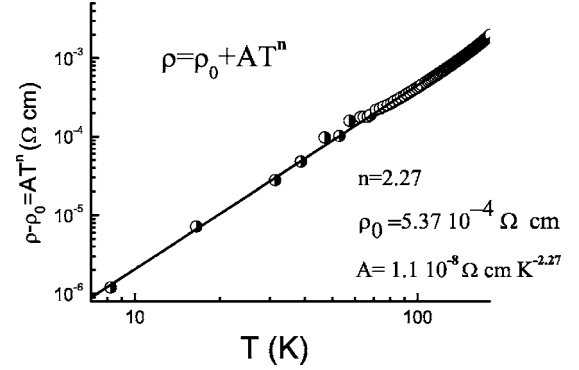


FIG. 10. Temperature dependence of the film resistivity after insulator-metal transition.

SAT-22) and 3.7×10^{-3} K $^{-1}$ (LaCaMnO films on SAT-30), which are close to the values of these coefficients for pure metals (Co, Al).

Using a factor (13) for the description of the $R(T)$ curve, the account of the Coulomb interaction of electrons with the clusters influences a little the view of this dependence, but nevertheless makes it closer to the experimental $R(T)$ curve. It is easy to see with a comparison of the points in Fig. 9. However, the C_m value varies so quickly that, as a result, the $Q_2(T)$ function decreases with the lowering temperature and, consequently, for the same temperatures, the points calculated with the account of Coulomb interaction are situated lower in comparison with the curve calculated without taking into account the Coulomb blockade. In that case, the fast increase in the concentration of the metallic phase results in a strong increase in the probability of tunneling, a sharp decrease in resistance of the samples, and, in that way, creates the visibility of an occurrence of a window in the Coulomb blockade.

IV. DISCUSSION

It was demonstrated that the presence of a maximum on $R(T)$ curves and the subsequent decrease in resistance at cooling the manganites are not necessarily related to the realization of metallic conductivity. It is generally known that the nature of a maximum on $R(T)$ curves is caused by the decrease of the disorder in a magnetic subsystem at $T < T_C$, and this conclusion is beyond any doubt. If the transition to a metallic state is not realized, a minimum on $R(T)$ curves appears at low temperatures. The insulator-metal transition with lowering temperature is possible at the concentration of metallic phase $C_m^0 \geq 0.2$ only. After such transition, a monotonous decrease in resistance is observed at cooling, with the temperature coefficients of resistance close to the values typical for pure metals.

Because of the presence of space-charge layers depleted of holes in peripheral areas of clusters [see formula (2)], the concentration of a metallic phase (C_m) and a ferromagnetic phase (x^F) cannot coincide. As a first approximation, for existing cluster sizes $D=100$ – 150 Å, it is possible to believe that $x^F \approx 2C_m$.³ Magnetic properties of the films are determined by the cluster structure and by the interaction of

clusters.^{3,4} As a result of tunneling between clusters, the exponential dependence of conductivity on magnetization is observed,³

$$\sigma \cong \sigma_{01} \exp \left\{ \left[\frac{M}{\xi} \right]^{1/\nu} \right\}, \quad (14)$$

where σ_{01} and ξ are constants, and $\nu=0.85$ is a critical index in the percolation theory. The dependence of σ on M described by Eq. (14) is true in the vicinity of percolation threshold. For samples with $C_m^0 \geq 0.2$, the exponential dependence of σ on M is observed in the wide temperature interval corresponding to the interval of magnetization change: $0.05 < M(T)/M(5 \text{ K}) < 0.85$.³ At the same time, for samples with smaller C_m^0 values that have a minimum on $R(T)$ curves, the interrelation between σ and M values can be approximated by the formula (14) in the low-temperature region only. It is one more confirmation that even for a ferromagnetic state, the samples with a minimum on $R(T)$ curves get to the vicinity of the percolation threshold at low temperatures only, while remaining in the insulator state in the whole temperature interval under consideration.

It is necessary to distinguish two topologically different processes of increase in the magnetic order under the convertible changes of cluster structure due to change of temperature or a magnetic field: (i) directly in the clusters and (ii) between the clusters. In the first case, the question is about the increase in sizes of ferromagnetic clusters by arranging the atomic groups in the peripheral areas of clusters. Here, the local atomic order and distribution of concentration of the free charge carriers in the peripheral areas of clusters play the basic role. In the second case, the form, relative orientation of clusters, and the average distance between them, determining the threshold value of magnetization, are of decisive importance. An increase in the concentration of a metallic phase and a decrease in the resistance at $T < T_{\max} \cong T_C$ occurs as a consequence of delocalization of holes in the peripheral areas of “metallic” clusters, which increase in the volume of their central part with metallic conductivity.

Electrical properties of the samples have different sensitivity to the change of their magnetic state. Different positions of $R(T)$ maxima relative to $M(T)$ curves prove it. These positions determine the threshold values of magnetization and indicate the beginning of an active influence of magnetic ordering on the conductivity (Figs. 7–9). At $T < T_{\max}$, the derivative dR/dT decreases with an increase in the threshold $M(T)$ value.³ Formation of a minimum on $R(T)$ curves and the subsequent growth of resistance at cooling occur if the threshold $M(T)$ values are in an interval $0.1 < M(T)/M(5 \text{ K}) < 0.9$. If the threshold values of magnetization $M(T)/M(5 \text{ K}) < 0.1$, the insulator-metal transition is realized and the occurrence of a minimum on $R(T)$ curves is impossible.

It is established that a minimum on the calculated $R(T)$ curves and the subsequent growth of resistance with lowering temperature appear due to Coulomb interactions of the charge carriers with the clusters at tunneling between them. In this respect, the results of electrical measurements are

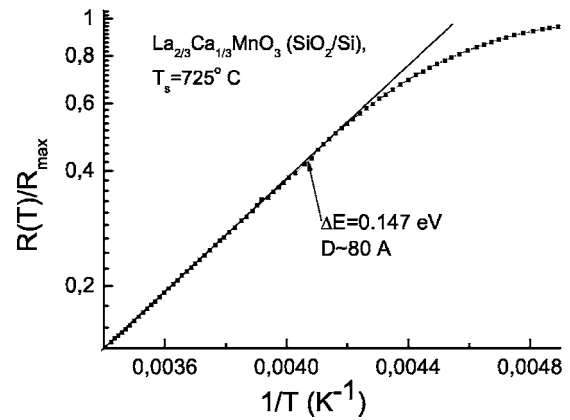


FIG. 11. Illustration of the Coulomb blockade action at $T > T_{\max}$: $R(T)$ curve at high temperatures in the $\log [R(T)/R_{\max}] - 1/T$ view.

very important at high temperatures exceeding the Curie temperature, T_C , and the temperature of a maximum, T_{\max} , when magnetic ordering does not yet influence the cluster structure. The correlation between the resistivity values at room temperature and parameters of samples at low temperatures (see Figs. 4–6) is an important qualitative illustration of the treatment of the low-temperature anomalies nature in electrical properties in favor of the Coulomb blockade. The action of the other reasons for a possible correlation between electrical properties of the films in the different temperature regions, caused by an influence of the magnetic order, is actually blocked, as at $T=290 \text{ K} (T < T_C)$, for the predominant majority of the films, the magnetic ordering did not begin yet. However, the Coulomb blockade acts well in this temperature region also. For this reason, it is evident that the $R(T)$ maximum forms as a result of the dramatic opposition of magnetic ordering and Coulomb blockade. We can demonstrate this phenomenon by the example of the sample with the $R(T)$ curve shown in Fig. 8.

For not too large C_m^0 and T_{\max} values, the temperature dependences of resistance at $T < T_{\max}$ have very extended sections straightened in the coordinates $\log R - 1/T$ (Fig. 11). According to the formula (11), for activation energy $W_D = 0.147 \text{ eV}$, the size of the spherical cluster (D_{sphere}) is about 80 \AA . Taking into account that the form of clusters is not spherical, the linear sizes of clusters having a not spherical form but of the same volume value are coordinated well to x-ray data giving the linear sizes of real clusters in the limits of $100\text{--}150 \text{ \AA}$.^{1,3,4,12,21}

It is necessary to note that the presented estimation of the cluster sizes is coordinated to the magnetization results of Gittleman *et al.*³⁶ obtained with the Kerr technique, and with the calculations of the sizes of the hole “drops” under the action of electronic mechanisms of phase separation in the samples.^{20,37}

The formation of a minimum on $R(T)$ curves, as well as a slow decrease in the resistance at $T < T_{\max}$, are related to the high values of resistivity (ρ) for the present doping level of the films with strontium (calcium). It is observed if unsuitable substrates are used, or if the conditions of the film growth are not optimal. In particular, there is an influence of the deviation from the optimal deposition temperature. At a

fixed chemical composition of the samples, a change of conditions of the film deposition allows us to modify their electrical properties over a wide range.

The increase in ρ values is related only to a minor degree to the reduced concentration of free holes because of small sizes of clusters. This reason, caused by the capture of free holes on localized states in peripheral areas of clusters, is quite obvious. However, in accordance with the x-ray investigations,^{1,3,4,12} the average size of clusters depends a little on the type of substrate or conditions of the film deposition. The principal reason for the inconsistency between concentration of the metallic phase in the films with a level of doping by Sr or Ca is caused by the change in the phase composition of clusterized structure.^{3,4,12} Examining the influence of phase composition of the cluster structure on conductivity of the films, it is necessary to take into account that because of an incorrect choice of a substrate or due to deviation of technology from the optimal one, there are crystallographic distortions of the rhombohedral type, followed by the appearance of a gap $E_{g1} \approx 0.25$ eV (Ref. 21) in the density of e_g states responsible for hole conductivity of manganites. The gap is formed upon removal of the orbital degeneracy as a result of Jahn-Teller distortions.^{18,21,22} Transition of all clusters into a state with the gap $E_{g1} \approx 0.25$ eV can be accompanied by the increase in ρ values by ten orders of magnitude.²¹

At the high concentration of dielectric clusters, preventing the reorganization of cluster structure into the infinite cluster (for example, in LaCaMnO films on SiO₂/Si substrates, Fig. 8), the realization of the percolation mechanism of conductivity is complicated, the dR/dT values are low, the metallic conductivity is not realized, and the basic mechanism of conductivity is spin-dependent tunneling between “metallic” clusters. In this case, the slow decreases in the resistance during the lowering temperature are observed at $T < T_{\max}$, and the minimum on $R(T)$ curves is realized at low temperatures. We have shown that the most probable reason for its occurrence is the increase in resistance due to the action of Coulomb blockade. The submitted results and the analysis of interrelation between the various parameters of samples prove it (Figs. 4–9 and 11). The general parameters determining the interrelation between the data in Figs. 4–6 are the key parameters of the cluster structure—the phase composition, concentration of a metallic phase, and the size of clusters—which determine the average distances between clusters with metallic conductivity. The Coulomb interaction of this type is possible before the insulator-metal transition only. Therefore, it is not accidental that a minimum on $R(T)$ curves and the subsequent growth of resistance at cooling are observed only in the samples remaining in an insulator state throughout the examined temperature interval and are absent if the metallic conductivity is realized. Except for the mechanism related to the Coulomb blockade, all other possible mechanisms of formation of a minimum on $R(T)$ curves do not exclude its occurrence after the transition into a state with the metallic conductivity.

Qualitative agreement of our results is confirmed by quantitative calculations. Examining the formulas (5)–(13) attentively, one can see that, on the one hand, resistance of the samples decreases at cooling due to the increase in concen-

tration of the metallic phase (C_m) and the corresponding decrease in the intercluster distances (L) as a result of the magnetic ordering in the peripheral areas of clusters according to the formula $L = D[(3C_m)^{-1/3} - 1]$. On the other hand, a term proportional to $1/T$ and sharply growing at low temperatures is presented in the indices of the exponents (12) and (13). As a consequence of these confronting processes, at slow growth of C_m values, the influence of the contribution caused by the Coulomb interaction on the resistance behavior starts prevailing, and the resistance of samples increases with the lowering temperature after reaching a minimum.

Changes in the magnetic order, induced by cooling below T_C or by an external magnetic field, initiate rearrangement of the cluster structure, and C_m increases at the expense of peripheral regions of the clusters. If the resulting concentration of the metallic phase comes near to $C_m^{\text{crit}} = 50\%$, the system exhibits an insulator-metal transition of the percolation type. The metallic phase content above the percolation threshold is reached only in the structures characterized by minimum stresses, in which orthorhombic clusters are predominantly formed. This process is facilitated in the films grown on SAT-22 or SAT-30 substrates, where the maximum of $R(T)$ coincides with the onset of the magnetization growth (Fig. 9), at a high rate of the resistance variation in the region of $T < T_{\max} \approx T_C$. It is observed for the structures where orthorhombic clusters prevail that the lattice distortions are small, the splitting between x^2-y^2 and z^2 states is not observed, and the additional gap in the e_g states is not formed. A small quantity of the rhombohedral clusters does not prevent the magnetic ordering³ and the confluence of the orthorhombic clusters with metallic conductivity into an “infinite” cluster, at the fast growth of concentration of a metallic phase (C_m) and at the high rate of change in the resistance dR/dT (Fig. 9). The insulator \rightarrow metal transition is realized in the high-temperature region where the Coulomb blockade negligibly influences the conductivity, i.e., the term proportional to $1/T$ in the exponent (13) varies insignificantly in comparison with the C_m values. Moreover, the increase in the sizes of “metallic” clusters is realized so quickly that the term proportional to $1/T$ in the formula (13) for the factor $Q_2(T)$ grows more slowly in comparison with the decrease in a value of the term proportional to $1/D$, and, as a result, the decrease in Q_2 values with lowering temperature is observed. In the case of a fast C_m growth at cooling the samples below T_{\max} , it looks similar, to some extent, to the occurrence of a window in the Coulomb blockade.

If the rhombohedral clusters (hindering the structure rearrangement into the infinite percolation cluster) predominate, the dR/dT values are low, the state of metallic conductivity is not attained, and the conductivity mostly proceeds via the mechanism of spin-dependent tunneling with the participation of metallic clusters. Starting from the reported results,^{1,3,4,21} it is necessary to believe that the rhombohedral clusters possess antiferromagnetic properties and “shield” the interactions between ferromagnetic clusters, putting obstacles in the way of the formation of the long-range ferromagnetic order in the samples and reducing the rate of the decrease in resistance of the samples at cooling below T_{\max} .

However, irrespective of the changing rate of resistance at cooling the samples below T_{\max} , the presence of a maximum

on $R(T)$ curves, as well as the occurrence of any extremum on every curve, is caused by a competition of two possible mechanisms: (i) the mechanism of decrease in the resistance caused by increase in the concentration of a metallic phase due to magnetic ordering in peripheral areas of the clusters, and (ii) the mechanism of increase in the resistance caused by the Coulomb blockade action. For the same chemical composition of the samples, the position of a maximum, as one can see in Figs. 8 and 9, can be changed, to a great extent, by the changes in the phase composition of the clusters,^{3,4,12} determining the rate of magnetic ordering of the cluster structure with decreasing temperature.

The increase in the concentration of rhombohedral clusters with dielectric properties for LaCaMnO films on SiO₂/Si substrates in comparison with the films on SAT-30 substrates^{3,4} shifts a maximum on the $R(T)$ curve over 80 K to low temperatures (see Figs. 8 and 9). At the same time, the resistance behavior for these two samples in the high-temperature region, caused by the Coulomb blockade, differs only a little.

According to the stated results, it is necessary to relate the LaSr(Ca)MnO films to the structures with the rearranged potential relief.³⁸ Furthermore, it is necessary to note that the interpretation of experimental results appears possibly due to the formation of clusters of a large, $\sim 100\text{--}150$ Å, size,^{1,3,4,12,21} at which the very effective influence of the charge quantization, resulting in the Coulomb blockade, is observed. However, the quantum-confinement effects still do not show an appreciable influence on sample properties. For such clusters, the inequality $\delta E \ll k_B T$ is still true, where δE is the separation energy between the quantum-confinement levels, and

$$\delta E = [D^3 N(E_F)]^{-1} \cong [D^3 p/E_F]^{-1}, \quad (15)$$

where E_F is the Fermi energy, p is the concentration of holes, and D is the linear cluster size.^{20,39,40} At the sizes of clusters $D\text{--}100\text{--}150$ Å they still display a quasicontinuous spectrum and metallic conductivity, however the presence of separation energies between the quantum-confinement levels should affect their conductivity value. In particular, along with the capture of holes by localized states in the peripheral areas of clusters, this peculiarity can be a reason for the increased $\rho_o = 0.0081 \Omega \text{ cm}$ value, appreciated according to the formula (3) and data in Fig. 3. For manganites, the critical size of clusters at which they transform into the system of tunneling-coupled quantum dots is near 40–60 Å.^{14,20,39} The quantum-dot system enables the electron to perform the acts of elastic tunneling between clusters at which $\rho(T)$ dependences may be caused by the final width of the energy levels. Tunneling coupling between quantum dots creates really a window in the Coulomb blockade with $R(T) = \text{const}$ regions.^{14,20,39,40} However, for the investigated films, the charge quantization effects and the quantum-confinement phenomena result only in an increased resistivity of the clusters, still preserving the metallic conductivity, and in the occurrence of features such as a maximum and a minimum on $R(T)$ curves. For manganites, these features modify a fundamental effect, concerned with the decrease in resistance of the samples at cooling, which is accompanied by colossal

magnetoresistance at the presence of an external field. At the same time, they play the major role in the formation of a significant variety of electrical, optical, and magnetic properties of these remarkable materials.

V. CONCLUSIONS

We have studied an opportunity to use the cluster structure concept for the description of electrical properties of manganites, assuming that the clusters with metallic conductivity are formed on the basis of the phase-separation mechanisms. It is shown that the formation of a cluster system in LaSr(Ca)MnO films and changes in their configuration at cooling the samples with consecutive delocalization of the electronic states in the peripheral areas of ferromagnetic clusters with metallic conductivity predetermine a behavior of the films over the whole examined temperature range.

A good correlation between electrical properties of LaSr(Ca)MnO films is established at high and low temperatures, caused by action of the Coulomb interactions of charge carriers with the clusters during tunneling. Action of the Coulomb blockade results in the occurrence of two anomalies on $R(T)$ curves: a maximum in the high-temperature region and a minimum at low temperatures.

For films with low concentration of the metallic phase ($C_m^0 < 0.15$), quantitative calculations with the use of elements of the percolation theory describe correctly the temperature dependence of resistance of samples and allow us to predict the position of a minimum on $R(T)$ curves in the low-temperature region. In such a way, formation of a minimum on $R(T)$ curves is possible if the samples remain in an insulator state in the whole investigated temperature interval, and such a conclusion corresponds to the experiment.

In the samples possessing a high concentration of “metallic” clusters ($C_m^0 \geq 0.2$), i.e., closer to the percolation threshold, the fast increase in the concentration of the metallic phase with lowering temperature results in a change of $R(T)$ curves, possible under creation of a window in the Coulomb blockade.

The interpretation of the nature of anomalies on $R(T)$ curves of manganites with the attraction of representations about cluster structure of these materials is a good illustration of the relevance and validity of the use of the tunnel model for the description of electrical properties of the samples. At the same time, the necessity of applying a tunneling model together with elements of percolation theory for the best conformity of calculations with experiment characterizes a proximity of the investigated samples to the insulator-metal transition.

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