Magnetic phase diagram and structural separation of $La_{0.7}(Ca_{1-v}Sr_v)_{0.3}MnO_3$ thin films

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The structural, magnetic, and transport properties of $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ films, deposited on a LaAlO₃ (001) single crystalline substrate by rf-magnetron sputtering using "soft" (or powder) targets, have been investigated. It was found that at $0.3 \le y \le 0.5$ both the rhombohedral (R3c) and the orthorhombic (*Pnma*) crystal phases in the form of nanoscale clusters are coexistent at room temperature. The observed structural clustering is accompanied by two-stage magnetic and electronic transitions, and governed by a nonuniform distribution of the lattice strain through the film. It was shown that for the films with $0 \le y \le 0.5$ the nonlinear (almost parabolic) MR(*H*) dependence is typical while, for $0.65 \le y \le 1.0$, the linear MR(*H*) behavior is observed at room temperature. The magnetotransport properties of films are explained within the framework of field-dependent activation-energy model. The magnetic phase diagram for $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ thin-film system is also presented. © 2007 American Institute of Physics.

I. INTRODUCTION

The discovery of a huge negative magnetoresistive effect in doped manganite perovskites with the general formula $R_{1-r}A_r$ MnO₃ where R is a rare-earth cation and A is alkali or alkaline earth cation,¹ called "colossal magnetoresistance (CMR)," induced interests in these compounds.^{2–5} The transport and the magnetic properties of doped manganites can be understood within the framework of "double-exchange (DE)" model which considers the magnetic coupling between Mn³⁺ and Mn⁴⁺, resulting from the motion of an itinerant electron between two partially-filled d shells with a strong on-site Hund's coupling,⁶⁻⁸ and taking into account the Jahn-Teller spin- and charge-lattice interactions.^{9,10} At the same time, since the hole-doped perovskite manganites belong to the strongly correlated systems, they manifest a tendency toward phase separation, typically involving the ferromagnetic (FM) metallic and the charge-ordered insulating domains.¹¹ Such a phase-separated state usually occurs in a temperature range below the Curie point $(T_{\rm C})$. The nanoscale structural correlation, on the other hand, was observed recently in a La_{0.75}(Ca_{0.45}Sr_{0.55})_{0.35}MnO₃ single crystal at a temperature above $T_{\rm C}$.¹² The main reason for this effect is that $La_{0.7}(Ca_{1-v}Sr_v)_{0.3}MnO_3$ tends to experience a structural transition from the rhombohedral (R3c) to the orthorhombic (Pnma) crystal lattice with a decreasing temperature near y $\simeq 0.5$.¹³⁻¹⁶ Moreover, this transition is controlled by an external magnetic field, indicating a small difference between the ground state energies for these crystal symmetries.¹⁵ Therefore, it is reasonable to suggest that any external perturbation of the crystal lattice (such as lattice strain, for example) leads to a structural modification in this compound.

In this paper we report on the magnetotransport properties of as-deposited $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ films at a fixed Mn^{3+}/Mn^{4+} ratio but with various sizes of the dopant atoms. The films at $0.3 \le y \le 0.5$ show a multiple microstructure at room temperature, which contains nanoscale clusters of both the orthorhombic and the rhombohedral crystal lattices. The films with $0 \le y \le 0.5$ demonstrate a nonlinear (nearly parabolic) behavior of magnetoresistance (MR) versus applied magnetic field while, for $0.65 \le y \le 1.0$, the linear MR(*H*) is observed at room temperature. Based on the experimental data, the magnetic phase diagram is constructed for the $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ thin-film system.

II. EXPERIMENTAL TECHNIQUES

The films were prepared by on-axis rf-magnetron sputtering using the so-called "soft" (or powder) target.¹⁷ The substrate was a LaAlO₃ (LAO) single crystal with an out-ofplane lattice parameter $c \approx 0.379$ nm for the pseudocubic symmetry. The total pressure in chamber was 4×10^{-2} Torr with a gas mixture of Ar and O₂(2:1). The deposition rate was about 6 nm/min. The substrate temperature during deposition was 750 °C. After deposition the substrate heater was turned off and the films were cooled, inside the chamber, with a temperature rate of about -10 K/min. The atomic

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FIG. 1. XRD patterns in the vicinity of (004) Bragg peak for $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ films.

force microscopy analysis (not shown) reveals that the surface roughness (the peak-to-valley distance) of the films does not exceed 5 nm. La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO₃ films were prepared with y=1.0, 0.9, 0.8, 0.65, 0.5, 0.3, and 0. The thickness of all the films was $d \approx 100$ nm. The θ -2 θ x-ray diffraction (XRD) patterns were obtained using a Rigaku diffractometer with Cu $K\alpha$ radiation. The high-resolution electron-microscopy (HREM) studies were carried out using a Philips CM300UT-FEG microscope with a field emission gun operated at 300 kV. The point resolution of the microscope was in the order of 0.12 nm. The cross-sectional specimens were made by the standard technique using mechanical polishing followed by ion-beam milling at a grazing incidence. All the microstructural analyses were performed at room temperature. The resistance was measured by using the four-probe method in a temperature range of 4.2-300 K and at a magnetic field up to 5 T. The in-plane field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves in a field up to 100 Oe and the magnetization hysteresis loops at 10 K were taken with a Quantum Design SQUID magnetometer.

III. MICROSTRUCTURES

The analysis of θ -2 θ XRD scans (not shown) manifests that the deposition results in highly *c*-oriented films without trace of the parasitic phases. Figure 1 shows, in detail, the (004) Bragg peaks for all the La_{0.7}(Ca_{1-y}Sr_y)_{0.3} MnO₃ films. The substitution of Ca with Sr shifts the Bragg peak to the high-angle side while, for $y \ge 0.8$, the opposite tendency is observed. Therefore, the out-of-plane lattice parameter of films depends nonmonotonically on *y*, in contrast to the bulk. The reduction in Sr concentration naturally leads to a decrease in the lattice parameter because of a smaller Ca-ion radius than that for Sr. The observed nonmonotonic behavior of *c* can be explained by a more accumulation of the lattice strain and a more tetragonal crystal-lattice distortion, during the epitaxial growth of La_{0.7}Ca_{0.3}MnO₃ than those in La_{0.7}Sr_{0.3}MnO₃.

For a further illustration, Fig. 2 exhibits the highmagnification cross-sectional HREM images of the $La_{0.7}Sr_{0.3}MnO_3$ [Fig. 2(a)] and the $La_{0.7}Ca_{0.3}MnO_3$ [Fig. 2(b)] films, including the respective interface between film



FIG. 2. High-magnification cross-sectional HREM images for (a) $La_{0.7}Sr_{0.3}MnO_3$ and (b) $La_{0.7}Ca_{0.3}MnO_3$ films. Dashed lines indicate the film-substrate interface. Insets A and B are the corresponding FFT and moiré patterns, respectively.

and substrate (denoted by white dashed lines). Inset A is the corresponding fast Fourier transform (FFT) of HREM images. The FFT pattern of La_{0.7}Sr_{0.3}MnO₃/LAO interface reveals elongated and slightly split spots in both c (normal to the interface) and a (along the interface) directions (indicated by white triangles). This is an evidence for a semicoherent (or weakly coherent) lattice coupling between film and substrate. On the contrary, the FFT for La_{0.7}Ca_{0.3}MnO₃/LAO interface produces a rectangular pattern with well-defined spot splitting only in the out-of-plane direction, manifesting a nearly coherent interface between film and substrate. These are confirmed by the moiré pattern (or the inverse Fourier transforms²¹) [inset B of Figs. 2(a) and 2(b)]. It is seen that the edge misfit dislocation occurs in the La_{0.7}Sr_{0.3} MnO₃ film. The measurement of various interspot spacings on the high-magnification HREM image allows us to obtain the average values of lattice parameters. The analysis reveals that both films are in a tetragonal distortion of the crystal lattice with $c/a \approx 1.01$ and 1.02 for $La_{0.7}Sr_{0.3}MnO_3$ and $La_{0.7}Ca_{0.3}MnO_3$, respectively, where *a* is the in-plane lattice parameter.

Figure 3 shows the high-magnification cross-sectional HREM images of $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ for y=0.5 [Fig. 3(a)] and 0.65 [Fig 3(b)], respectively. The y=0.5 film contains areas with more or less different crystal structure, the



FIG. 3. (a) and (b) Cross-sectional HREM images for the $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ films with y=0.5 and 0.65, respectively. Insets are the corresponding FFTs. Dashed lines in (a) indicate regions in different crystal structures. (c) and (d) Fourier filtration of the original HREM images in (a) and (b), respectively.

boundaries of which are marked by white dashed lines. It is coincident with the FFT pattern which exhibits that the main spots are elongated in the out-of-plane direction, confirming a variety of the lattice parameters. Moreover, the additional slight spots (corresponding to the doubled lattice parameter) are distinguishable on FFT pattern (denoted by the white arrow) in zones with a violent atomic ordering. Similar zone in the real space is indicated by the white arrow in Fig. 3(a). Figure 3(c) shows the Fourier filtration of the original HREM image, which allows us to distinguish the areas with different atomic ordering more accurately. These areas, corresponding to black and white regions in Fig. 3(c), have size from a few nm to ten nm. The measurement of a large number of interdot spacings and angles between dot rows allow us to obtain the average lattice parameters for both crystalline phases. Upon the analysis, one can conclude that the more ordered zones manifest a rhombohedral crystal structure with $a_R \simeq 0.5484$ nm and $\alpha_R \simeq 60.35^\circ$ while the more disordered ones have an orthorhombic crystal lattice with a tetragonal ratio of $c/a \approx 1.02$ and $a \approx 0.3812$ nm. Therefore, the La_{0.7}(Ca_{1-v}Sr_v)_{0.3}MnO₃ film at y=0.5 can be treated as a composite object which involves two kinds of the nanoscale clusters with a different crystal lattice. The observed contradiction with the XRD data, which manifest only a single nonsplitted Bragg peak, can be explained by the similarity of the lattice parameters (for a pseudocubic symmetry) for both crystal structures and the detection limit of the x-ray diffraction with Cu $K\alpha$ radiation. For comparison, Fig. 3(b) shows that the film at y=0.65 manifests almost a uniform crystal lattice. The inset in Fig. 3(b) displays that FFT produces a rectangular pattern of circular and nonelongated spots. In Fig. 3(d) the contrast of the Fourier filtration represents more monotonous than that observed for y=0.5. The analysis reveals that this film has mainly a rhombohedral crystal structure with $a_R \simeq 0.5524$ nm and $\alpha_R \simeq 60.46^\circ$, which are coincident with the bulk.¹⁵

The observed structural separation on the orthorhombic and rhombohedral clusters in the y=0.5 film probably was triggered by a nonuniform distribution of the lattice strain



FIG. 4. Temperature dependence of the FC (solid symbols) and the ZFC (open symbols) magnetizations for $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ films. Arrows indicate the Curie points for magnetic phase-separated films.

and a ferroelastic phase transition in the LAO substrate. It is reasonable that, owing to a significant lattice mismatch between the substrate and the film, the lattice strains are accumulated in the film during deposition. As reported recently, under a compressive biaxial strain the film grows in the island mode and the strains are distributed nonuniformally through the sample.^{22,23} The edge of an island is the region of high strain, while the top of the island is with the low strained region of the film should be transformed to an orthorhombic phase, while the transition in the high-strained region is blocked by an accumulated elastic energy. On the other hand, the observed structural clustering might be from a chemical nature, which was provided by a nonuniformity of the Sr concentration during sputtering.

IV. MAGNETIC AND TRANSPORT PROPERTIES

Figure 4 shows the in-plane FC (solid symbols) and ZFC (open symbols) temperature-dependent magnetization curves, M(T), for y=1.0, 0.8, 0.65, 0.5, 0.3, and 0. The applied magnetic field was H=100 Oe. It is seen that the substitution of Sr for Ca leads to a gradual increase of $T_{\rm C}$, except y=0.5 and 0.3 films. For these films M(T) manifests a behavior, which is typical for the two-phase magnetic system. The first transition occurs at $T_{C1} \simeq 260$ K and the second one at $T_{C2} \leq 130$ K, as a slight change in the slope of the FC curve. It worth noting, that the similar two-step M(T) behavior recently was observed in a single crystal at y=0.45 and explained by an occurrence of the structural transition at a temperature below $T_{\rm C}$.¹⁶ The microstructural analysis for y =0.5 of a composite film, however, involves two kinds of the nanoscale clusters with a different crystal lattice. It is reasonable to suggest that the two-stage M(T) dependence should be a simple superposition of two separated FM transitions in clusters with the rhombohedral and orthorhombic structure. At the same time, the y=0.3 film also demonstrates the two-



FIG. 5. Temperature dependence of the resistivity for $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ films without (solid symbols) and with (open symbols) an applied magnetic field of 5 T. Arrows indicate the two-stage MI transition in the films with y=0.5 and 0.3.

step M(T) behavior and can be treated as a crystal-phaseseparated system, though the FM response at T_{C1} is significantly suppressed with respect to y=0.5.

Figure 5 is the temperature-dependent resistivity, $\rho(T)$, for the same films without (solid symbols) and with (open symbols) an applied magnetic field of 5 T. The magnetic field was parallel to the film surface and perpendicular to the transport current. It is seen that the y=0 film demonstrates a typical CMR $\rho(T)$ behavior with the well-defined metalinsulator (MI) transition at $T_{\rm P} \simeq 200$ K while y=1.0 manifests only a change of the slope on the $\rho(T)$ dependence at $T \simeq 300$ K. It is known that the La_{0.7}Sr_{0.3}MnO₃ compound, due to a large one-electron bandwidth, does not undergo the real MI transition near the Curie point and keeps a metal-like state in the paramagnetic phase up to high temperatures.^{5,15} The y=0.3 and 0.5 films, on the other hand, demonstrate a two-peak behavior of $\rho(T)$, which can be treated as two MI transitions at $T_{P1} \leq 210$ K and $T_{P2} \leq 130$ K (indicated by arrows), which are governed by the appearance of the FM ordering in the rhombohedral and orthorhombic clusters, respectively. It is confirmed by the similar two-peak temperature behavior of MR for y=0.5, which is shown in the inset. Moreover, these peaks occur at the temperatures close to $T_{\rm P1}$ and T_{P2} on the $\rho(T)$ curve. Here the MR value is defined by $100\% \times [\rho(0) - \rho(H)]/\rho(0)$, where $\rho(0)$ and $\rho(H)$ are the resistivities with and without a magnetic field of 5 T, respectively.

Figure 6 displays the magnetic-field dependence of MR at room temperature for the y=0.3, 0.5, 0.8, and 0.9 films. In this case the MR value is defined by $100\% \times [\rho(H) - \rho(0)]/\rho(0)$. It is seen that a magnetoresistive effect at room



FIG. 6. Magnetic-field dependence of the MR ratio for $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ films, measured at room temperature. Inset displays the experimental (solid lines) and the theoretical (dashed lines) MR(*H*) dependence for the films with y=0.3 and 0.9.

temperature is enhanced with the increasing of Sr doping and the MR(*H*) dependence changes from almost parabolic (*y* = 0.3 and 0.5) to close to linear (*y*=0.8 and 0.9). The similar variation of the MR(*H*) behavior at $T \ge T_{\rm C}$ have already been observed in these lanthanides and explained by a transition from the insulating to metal-like state with the increasing of Sr concentration.^{24–27}

V. DISCUSSION

Figure 7 exhibits the magnetic phase diagram for La_{0.7}(Ca_{1-y}Sr_y)_{0.3} MnO₃ films deposited on the LAO substrate. The triangular symbols display $T_{\rm P}$, the MI transition temperature. It is seen that a decreased Sr doping, in general, leads to a reduced $T_{\rm C}$, which is coincident with the published results for the bulk¹⁵ and the thin films deposited on NdGaO₃.²⁷ Since the FM ordering is governed by the transfer interaction of the e_g -orbital carrier between the neighboring Mn sites, which should be determined mainly by the Mn-O bond length and the Mn-O-Mn angle,²⁴ $T_{\rm C} \sim W$ $\sim \cos \varphi/d_{\rm Mn-O}^{3.5}$, where W is the bandwidth, φ is the tilt angle on the bonding plane, and $d_{\rm Mn-O}$ is the Mn-O bond length.^{28,29} Consequently, the change of the crystal lattice from rhombohedral to orthorhombic, due to the substitution



FIG. 7. Magnetic phase diagram for the $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}MnO_3$ thin-film system. Solid squares and open triangles correspond to the Curie points and the MI transition temperatures, respectively. The concentration range for structural phase-separated state is crosshatched.

of Ca for Sr, which is usually accompanied by a decreased tilt angle, must lead to a narrowed W and a reduced $T_{\rm C}$. It is known that the parent La_{0.7}Sr_{0.3}MnO₃ compound is in the rhombohedral crystal structure with $\varphi \approx 165^{\circ}$ while La_{0.7}Ca_{0.3}MnO₃ is orthorhombic with $\varphi \approx 155^{\circ}$. However, in contrast to the bulk which shows the structural R3c $\rightarrow Pnma$ transition at a certain y concentration,¹⁵ the prepared films manifest a sufficiently broad concentration range $(0.3 \le y \le 0.5)$, where both crystalline phases coexist. It was already suggested that the observed multiple clustering in these films is probably governed by a nonuniform distribution of the lattice strain and triggered off by a ferroelastic phase transition in the LAO substrate, which occurs at T=544 °C.³⁰ Consequently, for the films with $0.3 \le y \le 0.5$, it is reasonable that, with decreasing temperature, the FM phase appears at first in the rhombohedral clusters and then in the orthorhombic regions of film, providing the two-stage M(T) behavior. The slight rise of magnetization at T_{C1} for the film with y = 0.3 (curve labeled with 0.3 in Fig. 4) can be explained by a decreased amount of clusters in the orthorhombic structure. The analyses on Figs. 4 and 5 present the magnetic and electronic transition temperatures $(T_{C2} \simeq T_{P2})$ \simeq 130 K) are almost coincident for the orthorhombic regions in the films with y = 0.3 and 0.5, confirming the typical MI transition resulted from the DE mechanism.⁵ At the same time, a significant discrepancy between the FM and the MI transition temperatures is observed for the rhombohedral clusters: $T_{C1} \simeq 260$ K against $T_{P1} \simeq 180$ and 210 K for y =0.3 and 0.5, respectively. This can be supported with the percolating mechanism of the MI transition, which is frequently observed in the inhomogeneous manganites, independent of the physical nature of inhomogeneity.¹¹

Let us consider the field-dependent magnetoresistance of films at room temperature. According to the phase diagram, the films with a significant Sr doping ($y \ge 0.65$) manifest the onset of FM transition at $T \ge 300$ K. Therefore, the MR(H) obeys the DE mechanism of charge transport, which predicts a square dependence on the magnetization: MR(H) $=C(M/M_s)^{2.31}$ Here M is the magnetization, M_s is the saturation magnetization, and C is a constant, nearly independent of field and temperature. The films with a large Cacontent $(y \le 0.5)$, on the other hand, have a Curie point below room temperature, and at $T > T_{\rm C}$ demonstrate the thermally activated polaronic transport of carriers (see Fig. 5), expressed by $R(T,H) = R_0 T \exp(E_A/k_B T)$. R_0 is a constant, which is inversely proportional to the polaron hopping frequency, E_A is the activation energy, and $k_{\rm B}$ is the Boltzmann constant. Consequently, the films with $y \le 0.5$ can be treated as the paramagnetic insulators at room temperature. The MR(H) behavior of such materials is explained, as a rule, by two approaches. The first approach, based on an idea that the hopping probability of the insulator with a short-range magnetic ordering should be modified with a multiplicative term $(1+M^2/M_s^2)/2$.³² In this case the negative magnetoresistance ratio also has a square dependence upon the magnetization, with C=1, and expressed by MR(H)= $(M/M_s)^2$. The second approach assumes that the trapping of charge (treated as ferromagnetic polaron) can be minimized by the transition of the paramagnetic neighborhood from random disorder to spin alignment due to an applied magnetic field.^{26,33} In this case the activation energy has to be changed in the presence of the magnetic field, $E_A = E_A^0(1 - \langle \cos \theta_{ij} \rangle)$, where E_A^0 is the field-independent activation energy and θ_{ij} is the angle between the *i* and the *j* ion spins. Taking into account that, for the uncorrelated spins, $\langle \cos \theta_{ij} \rangle = \langle \cos \theta_i \rangle^2 = (M/M_s)^2$, $MR(H) = \exp[-\alpha(M/M_s)^2]$ where $\alpha = E_A^0/k_BT$.

First of all, let us analyze the field-dependent MR of low Sr-doped films. Since it is assumed that these films turn out to be in the paramagnetic state, the magnetization can be expressed by the Brillouin function $B_S(g\mu_BSH/k_BT)$, where g = 2 is the Landé factor and μ_B is the Bohr magneton. The average spin for this composition is $S = \sqrt{0.3S_1(S_1+1)} + 0.7S_2(S_2+1) = 2.3076$, where $S_1 = 3/2$ and $S_2=2$ are the spin values of Mn⁴⁺ and Mn³⁺ ions, respectively. The previous analysis on the $\rho(T)$ dependence for y = 0 at $T \ge T_{\rm C}, T_{\rm P}$ allows us to estimate the fieldindependent activation energy as $E_A^0 = 1500$ K, and therefore, α =5 at T=300 K. Inset in Fig. 6 displays both experimental (solid line) and theoretical (dashed lines) MR(H) curves for y=0.3. For a better agreement between theory and experiment $S_{\text{eff}} = NS$ was employed as the fitting parameter. Here, $S_{\rm eff}$ is treated as the effective polaron spin which consists of N single ions.²⁶ It is seen that both approaches describe the MR(H) behavior for y=0.3 with the same degree of accuracy. Moreover, the fitting parameters are close to each other, N=3.5 and 2.35 in Appel³² and for the field-dependent activation-energy model,^{26,33} respectively.

Unfortunately the MR(H) dependence for the film with y=0.9 is not adequately described in the framework of the DE model, since a parabolic MR(H) dependence was predicted, instead of a nearly linear one in the experiment.³¹ The main reason for this is probably the inhomogeneous (phaseseparated) magnetic state of high Sr-doped ($y \ge 0.65$) films at room temperature. It is confirmed by the anhysteretic MR(H)behavior in the low-field range, which contradicts with the results for the similar films in the completely FM state.³⁴ The hysteresis becomes apparent in the form of two split peaks near the coercive field, which are provided by the hysteretic behavior of the magnetization loop for the ferromagnet.³⁵ Therefore, it is concluded that the films with $y \ge 0.65$ at room temperature represent the magnetic phase-separated system, containing the FM and the paramagnetic (PM) clusters. As discussed previously, the formation of the multiphase magnetic state can also be affected by a nonuniform distribution of the lattice strain. The description of magnetoresistance for such a magnetic phase-separated system can be understood in the framework of Wagner et al.³⁶ According to this phenomenological model, the activation barrier (they considered the Mott hopping mechanism of conductivity,³ but it is not a principal point in our case) includes two main field-affected terms. The first is similar to that considered above for the PM state, revealing $E_A \sim B_S^2(g\mu_B H/k_B T)$, while the second one (the so-called Weiss magnetization contribution) becomes dominant in the FM state and manifests a linear magnetic-field dependence of the activation energy $E_A \sim B_S(g\mu_B H/k_B)$. The experimental MR(H) dependence for y=0.9 (see inset in Fig. 6) was fitted with the expression $MR(H) = \exp[-\alpha(M/M_s)]$ with the number of single ion

Therefore, the magnetotransport properties of the $La_{0.7}(Ca_{1-y}Sr_y)_{0.3}$ MnO₃ films at room temperature can be excellently described within the framework of field-affected activation-energy approximation, taking into account a competition between the spin-dependent trapping of charges in the PM state and the Weiss-magnetization contribution to the FM state.

VI. CONCLUSIONS

We have studied the magnetic and the transport properties of $La_{0.7}(Ca_{1-v}Sr_v)_{0.3}MnO_3$ films on $LaAlO_3$ (001) single crystal substrate. The microstructural analysis reveals that the films with $0.3 \le y \le 0.5$ are phase-separated at room temperature in nanoscale clusters with the orthorhombic and the rhombohedral crystal structures. The observed clustering is accompanied by the two-stage magnetic and electronic transitions. It is suggested that the main reason for structural phase separation is the accumulation of nonuniformally distributed lattice strains during the epitaxial growth of film and the ferroelastic transition of substrate. It was shown that, for the films with $0 \le y \le 0.5$, a nonlinear (nearly parabolic) MR(*H*) dependence is typical while, for $0.65 \le y \le 1.0$, the linear MR(H) behavior is observed at 300 K. The magnetotransport properties of $La_{0.7}(Ca_{1-\nu}Sr_{\nu})_{0.3}MnO_3$ films at room temperature can be explained on the basis of fielddependent activation-energy model, considering simultaneously the spin-dependent trapping of charges in the PM state and the Weiss-magnetization contribution to the FM ordering. From the experimental data, the magnetic phase diagram is constructed for the $La_{0,7}(Ca_{1-\nu}Sr_{\nu})_{0,3}MnO_3$ thinfilm system.

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- ¹J. Volger, Physica (Utrecht) **20**, 49 (1954).
- ²S. Chahara, T. Ohno, K. Kasai, and Y. Kozono, Appl. Phys. Lett. **63**, 1990 (1993).
- ³R. von Helmolt, J. Wecker, B. Holzapfer, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).
- ⁴S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L.

- H. Chen, Science 264, 413 (1994).
- ⁵For a review, see *Collosal Magnetoresistance Oxides*, edited by Y. Tokura (Gordon and Breach, London, 1999).
- ⁶C. Zener, Phys. Rev. 82, 403 (1951).
- ⁷P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).
- ⁸P.-G. de Gennes, Phys. Rev. **118**, 141 (1960).
- ⁹A. J. Millis, Phys. Rev. B 53, 8434 (1996); A. J. Millis, R. Mueller, and B.
 I. Shraiman, *ibid.* 54, 5389 (1996); 54, 5405 (1996); A. J. Millis, B. I.
 Shraiman, and R. Mueller, Phys. Rev. Lett. 77, 175 (1996).
- ¹⁰J. Zang, A. R. Bishop, and H. Röder, Phys. Rev. B **53**, R8840 (1996).
- ¹¹E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. **344**, 1 (2001).
- ¹²V. Kiryukhin, T. Y. Koo, H. Ishibashi, J. P. Hill, and S.-W. Cheong, Phys. Rev. B **67**, 064421 (2003).
- ¹³P. G. Radaelli, M. Morezio, H. Y. Hwang, S.-W. Cheong, and B. Batlogg, Phys. Rev. B 54, 8992 (1996).
- ¹⁴P. G. Radaelli, M. Morezio, H. Y. Hwang, and S.-W. Cheong, J. Solid State Chem. **122**, 444 (1996).
- ¹⁵Y. Tomioka, A. Asamitsu, and Y. Tokura, Phys. Rev. B 63, 024421 (2000).
- ¹⁶A. N. Ulyanov, S. C. Yu, N. Yu Starostyuk, N. E. Pismenova, Y. M. Moon, and K. W. Lee, J. Appl. Phys. **91**, 8900 (2002).
- ¹⁷V. G. Prokhorov, G. G. Kaminsky, V. A. Komashko, J. S. Park, and Y. P. Lee, J. Appl. Phys. **90**, 1055 (2001).
- ¹⁸M. Schefzik, R. Scheuermann, L. Schimmele, A. Seeger, D. Herlach, O. Kormann, J. Major, and A. Rock, Philos. Mag. A **79**, 1561 (1999).
- ¹⁹O. I. Lebedev, G. Van Tendeloo, S. Amelinckx, H. L. Ju, and K. M. Krishnan, Philos. Mag. A 80, 673 (2000).
- ²⁰T. K. Nath, R. A. Rao, D. Lavric, C. B. Eom, L. Wu, and F. Tsui, Appl. Phys. Lett. **74**, 1615 (1999).
- ²¹E. Snoeck, B. Warot, H. Ardhuin, A. Rocher, M. J. Casanove, R. Kilaas, and M. J. Hytch, Thin Solid Films **319**, 157 (1998).
- ²²A. Biswas, M. Rajeswari, R. C. Srivastava, T. Venkatesan, R. L. Green, Q. Lu, A. L. de Lozanne, and A. J. Millis, Phys. Rev. B 63, 184424 (2001).
- ²³V. G. Prokhorov, G. G. Kaminsky, V. A. Komashko, Y. P. Lee, J. S. Park, and H. C. Ri, Appl. Phys. Lett. **80**, 2707 (2002).
- ²⁴H. Y. Hwang, S. W. Cheong, N. P. Ong, and B. Batlogg, Phys. Rev. Lett. **77**, 2041 (1996).
- ²⁵Y. Lyanda-Geller, S. H. Chun, M. B. Salamon, P. M. Goldbart, P. D. Han, Y. Tomioka, A. Asamitsu, and Y. Tokura, Phys. Rev. B 63, 184426 (2001).
- ²⁶G. Jakob, W. Westerburg, F. Martin, and H. Adrian, Phys. Rev. B 58, 14966 (1998).
- ²⁷P. R. Broussard, S. B. Qadri, V. M. Browning, and V. C. Cestone, J. Appl. Phys. **85**, 6563 (1999).
- ²⁸C. M. Varma, Phys. Rev. B **54**, 7328 (1996).
- ²⁹M. Medarde, M. Mesot, P. Lacorre, S. Rosenkranz, P. Fisher, and K. Grobcht, Phys. Rev. B 52, 9248 (1995).
- ³⁰S. Bueble, K. Knorr, E. Brecht, and W. W. Schmahl, Surf. Sci. **400**, 345 (1998).
- ³¹N. Furukawa, J. Phys. Soc. Jpn. **64**, 2734 (1995).
- ³²J. Appel, Phys. Rev. **141**, 506 (1966).
- ³³M. Viret, L. Ranno, and J. M. D. Coey, Phys. Rev. B **55**, 8067 (1997).
- ³⁴A. de Andés, S. Taboada, J. M. Colino, R. Ramirez, M. Garsia-Hernándes, and J. L. Martinez, Appl. Phys. Lett. 81, 319 (2002).
- ³⁵G. J. Snyder, M. R. Beasley, T. H. Geballe, R. Hiskes, and S. DiCarolis, Appl. Phys. Lett. **69**, 4254 (1996).
- ³⁶P. Wagner, I. Gordon, L. Trappeniers, J. Vanacken, F. Herlach, V. V. Moshchalkov, and Y. Bruynseraede, Phys. Rev. Lett. **81**, 3980 (1998).