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Combined strain and high pressure oxygen treatment effects and phase separation in $La_{067}Ca_{0.33}MnO_3$ thin films

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An evidence for phase separation in high-pressure oxygen treated $La_{0.67}Ca_{0.33}MnO_3$/(100)MgO thin films is presented. This phase separated state is not observed for the $x = 0.33$ classical doping level neither for bulk material, nor for as prepared thin films. It originates from the combined influence of two factors: large strains due to the film-substrate lattice mismatch and high pressure (100 bar) annealing in oxygen. These factors weaken double exchange, drastically enhance low-field magnetoresistance, and lead to hysteresis phenomena. The experimental results are interpreted in terms of phase separation of the film volume into the ferromagnetic conductive matrix with inclusions of spin-glass-like clusters.

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Hole doped perovskite manganites of general formula $A_{1-x}B_xMnO_3$, where A is a trivalent rare-earth ion, and B is a divalent alkaline-earth ion, belong to the family of strongly correlated systems with complex interplay between the spin, charge, lattice, and orbital degrees of freedom. Among numerous interesting physical effects observed in doped manganites (the metal-insulator transition, interplay between ferro- and antiferromagnetism, charge ordering, etc.) the most fascinating one is the "colossal" magnetoresistance (CMR) effect that had attracted enormous interest during several last years [1]. Extremely high CMR values, exceeding 10^6% at 60 K and in a magnetic field of 80 kOe, were reported [2]. This CMR phenomenon is common to the class of doped oxide magnetic semiconductors in which similar, or even greater (exceeding eleven orders of magnitude), CMR values were observed [3] at low temperatures. It was demonstrated that introduction of carriers in the parent antiferromagnetic insulating $LaMnO_3$ compound either by divalent cation doping [4], or by creation of vacancies in one of sublattices [5], leads to ferromagnetism, conductivity, and CMR. Owing to suppression of spin fluctuations by the magnetic field maximum magnetoresistance is observed in the vicinity of a ferromagnetic ordering temperature (T_C) and is accompanied by metal-semiconductor transition. Basic physics of doped manganites is described within the framework of "double exchange" model [6] assuming domination of ferromagnetic exchange over the antiferromagnetic superexchange, and conductivity *via* carrier hopping with spin memory between the localized states with strong on-site Hund's rule coupling. For a long time the $A_{1-x}B_xMnO_3$ compounds with the "classical" $x \approx 0.33$ doping level and large ionic radius of doping cation were considered as model ones for investigations of physics of "double exchange". Recently the electronic phase separation model [7] (ferromagnetic conductive droplets in antiferromagnetic insulating matrix) was proposed as an alternative for explanation of CMR phenomena in doped manganites. Due to reduced dimensionality the physical properties of thin film manganites differ substantially from that of the bulk. For example, an evidence for coexistence of ferromagnetic metallic and chargeordered insulating phases (with matrix being insulating antiferromagnetic) in strained $La_{0.67}Ca_{0.33}MnO_3$ thin films at low temperatures was recently presented [8].

In this letter we experimentally show that by the combined influence of two factors: large film-substrate lattice mismatch and high pressure oxygen treatment, it is possible to transfer the homogeneous thin film of the classical ferromagnetic conductive $La_{0.67}Ca_{0.33}MnO_3$ composition into the new phase separated state.

Epitaxial 2500 Å thin films of $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) were prepared on (100)MgO substrates by pulsed laser deposition. The target was made using a traditional ceramic technology by mixing high-purity binary oxides and repeated cycles of grinding and sintering. Deposition was carried out at the substrate temperature 700 °C under 300 mTorr partial O_2 pressure. After deposition the oxygen pressure in the chamber was increased up to 1 atm and the films were slowly cooled to the ambient temperature. The first anneal was per-

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formed in the flowing oxygen at 850 °C for 2 hours. The second anneal was carried out in an autoclave under the 100 bar oxygen pressure at the same temperature and for the same duration. Resistivity was measured by conventional four-probe *dc* or *ac* techniques at frequencies lower 80 Hz in a superconducting solenoid with the electric current parallel to the magnetic field. Magnetic properties were measures in the $5 \leq T \leq 300$ K temperature range using the vibrating sample magnetometer. Chemical composition of the deposited films was found to be identical to that of the target as was confirmed by the scanning electron microprobe microanalysis and Rutherford backscattering. The results of X-ray diffraction investigations show that under the above-mentioned conditions manganite films with lattice parameter $a \approx 3.9$ Å grow epitaxially in "cube-on-cube" mode on the surface of (100)MgO substrate (lattice parameter $a \approx 4.213$ Å). Due to the large film-substrate lattice mismatch anisotropic strains exist in the film.

The temperature dependence of zero field resistivity $\rho(0,T)$ and magnetoresistance $MR_H(H,T)$ for as-deposited, annealed thin films, and the target are compared in Fig.1. Magnetoresistance defined here as

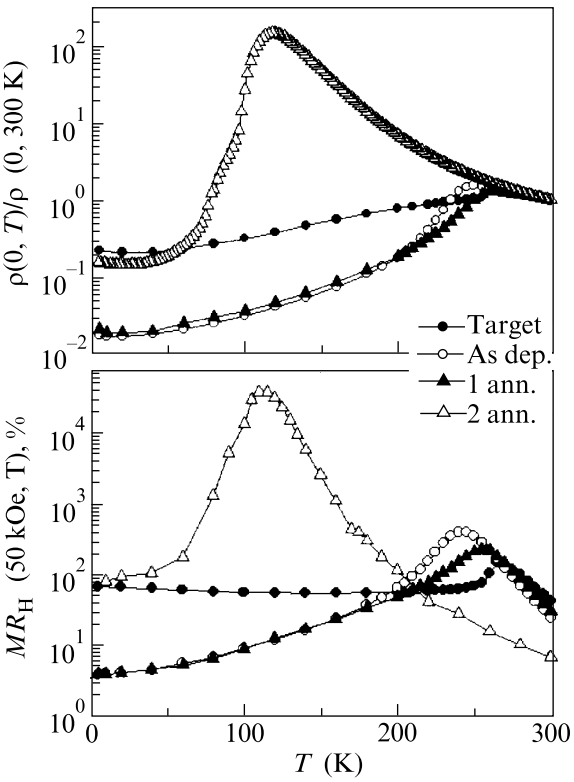

Fig.1. Temperature dependences of normalized zero field resistivity $\rho(0,T)/\rho(0,300\,\mathrm{K})$ (top panel) and magnetoresistance $MR_H(50\,\mathrm{kOe}, T)$ (bottom panel) for $La_{0.67}Ca_{0.33}MnO_3$ thin films and the target

$MR_H(H,T) = (\rho(H,T)-\rho(0,T))/\rho(H,T)\cdot 100\%$, where $\rho(H,T)$ and $\rho(0,T)$ are resistivity values under the applied magnetic field H and in zero field, respectively, at temperature T. For the convenience of comparison the $\rho(0,T)$ curves are normalized to the corresponding resistivity values at 300 K. Note the logarithmic scale in the graphs. In the vicinity of the ferromagnetic ordering temperature variations of resistivity and magnetoresistance for as-deposited film and the film annealed in flowing oxygen are similar to that of the target. Substantial magnetoresistance, observed for the target at low (< 100 K) temperatures, is due to the tunneling of spin-polarized carriers through the grain boundaries of polycrystalline material. Small $MR_H(50\,\mathrm{kOe}, T)$ values at low temperatures observed for all thin films indirectly confirm their high crystalline quality. Drastic increase in both resistivity and magnetoresistance are observed for the film subjected to high pressure treatment. The peak in both curves is shifted at 130 K to lower temperatures as compared to as-prepared films. This is accompanied by hysteresis phenomena observed both in $\rho(0,T)$ and $MR_H(H,T)$ curves (Fig.2). Each curve presented in the bottom panel of Fig.2, as well as magnetization data for this film, were recorded after zero field warming the film to 300 K and its subsequent cooling to the temperature of measurement. Maximum drop in resistivity under application of the magnetic field was observed in small (≤ 2 kOe) fields for the temperature range close to that where the peak in $\rho(0,T)$ curve is observed (compare Fig.1 and the lower panel of Fig.2). No hysteresis phenomena were observed for as-prepared film as well as for the film annealed in flowing oxygen. The results of low temperature magnetic measurements are presented in Fig.3. Upon application of a magnetic field typically ferromagnetic hysteresis loops were obtained for all films. Slowly varying background from the substrate was subtracted from all curves shown in the upper panel of Fig.3. The coercive force increased from $H_C = 310$ Oe for as prepared film to 413 Oe for the film annealed under high oxygen pressure. Hysteresis phenomena observed for this film are illustrated in the bottom panel of Fig.3. Large differences between the zero-field cooled and field cooled curves are observed below 150 K. These results can be understood in terms of phase separation. Under the combined influence of film-substrate strains and high pressure oxygen treatment the volume of the film is separated into two phases: the conductive ferromagnetic matrix, giving the dominant contribution into the magnetic properties and conductivity at low temperatures, see the upper panels of Figs.2 and 3, and probably antiferromagnetically ordered spin-glass regions, which are responsible for hysteresis phenomena

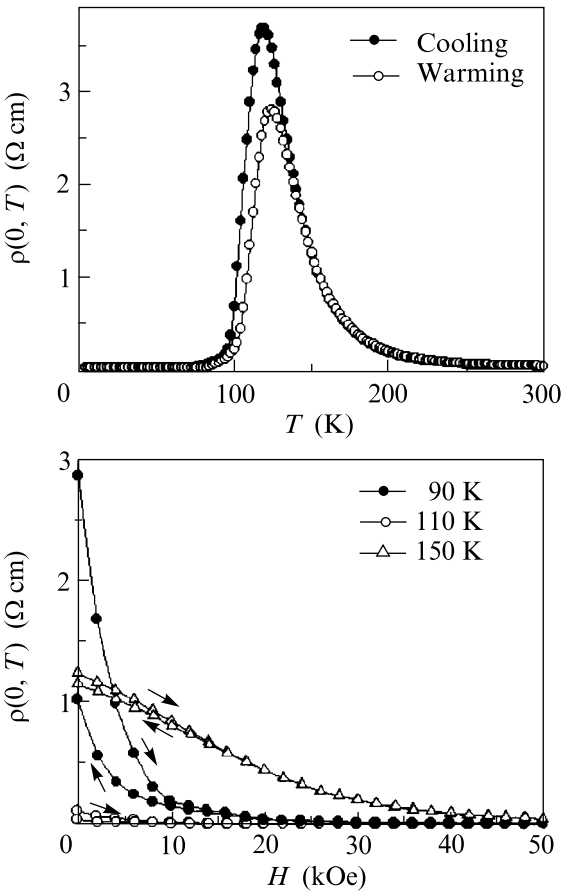

Fig.2. Temperature variation of resistivity (top panel) and magnetoresistance (bottom panel) for $La_{0.67}Ca_{0.33}MnO_3$ thin film annealed under the 100 bar oxygen pressure

(see the upper panel of Fig.2 and the lower panel of Fig.3) and sharp drop of resistivity under application of relatively weak magnetic field (see the lower panel of Fig.2). From the data of Fig.3 we can estimate the volume of the ferromagnetic phase in the sample annealed under high oxygen pressure being ≈ 0.56 relative to that in the as-prepared film. The most important fact reported here is the absolutely different nature of the phase-separated state observed. According to the known pictures of phase separation in manganites proposed theoretically [7] and observed in thin films [8] the matrix must consist of the antiferromagnetically ordered insulating phase with small ferromagnetic conductive regions. The phase separated state observed in our films differs also from the spin-glass state observed in the bulk $Y_{0.7}Ca_{0.33}MnO_3$ material [9] where it is caused by strain effects associated with the Mn-O-Mn bond angle reduction and variations in one-electron bandwidth (W) of the e_g band owing to the small size of doping cation. The bulk $Y_{0.7}Ca_{0.33}MnO_3$ material is insulating in the whole temperature range. As it is clearly seen from the upper panels of Figs.2 and 3 in our case the major part of the film volume is occupied by the *conductive ferromagnetic* phase.

Theoretical description of phase diagram of doped manganites is usually carried out using the following parameters: the nearest neighbor hopping amplitude t for e_g electrons, Hund's coupling J_H, antiferromagnetic coupling between the localized t_{2g} spins J_{AF}, and on-site Coulomb interaction U [10–14]. In the conventional "double exchange" models J_H is often considered as infinite and U is neglected. The results of calculations within the ferromagnetic Kondo lattice [11,12], mean field [13], and random-field Ising [14] models with an account for the antiferromagnetic coupling show the possibility of phase separation for some values of J_{AF}/t parameter. Coexistence of large size clusters of ferromagnetic conductive and antiferromagnetic insulating phases

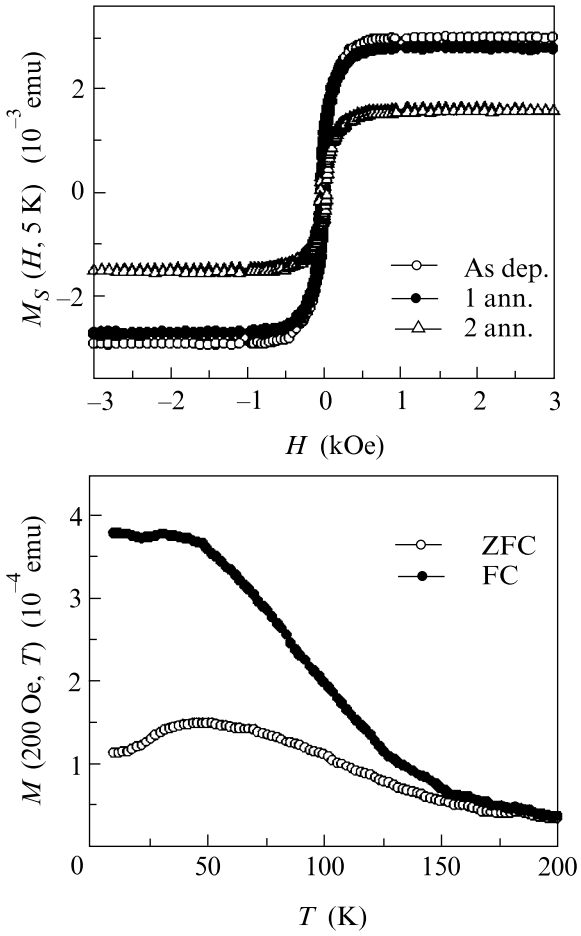

Fig.3. Magnetization curves for thin films at 5 K (top panel); zero field cooled (ZFC) and field cooled (FC) magnetization recorded in a field of 200 Oe for $La_{0.67}Ca_{0.33}MnO_3$ thin film annealed under high oxygen pressure

in manganese oxides was found to be possible [14] in the case when strong coupling interactions (t and J_{AF}), which are necessary to produce the ordered phases, are modified by the quenched disorder caused by chemical substitution, or high pressure oxygen treatment as in our case, due to the buckling of MnO_6 octahedra and reduction of the Mn-O-Mn bond angle.

In summary, for pulsed laser deposited $La_{0.67}Ca_{0.33}MnO_3/(100)MgO$ thin films we had experimentally demonstrated the instability of the classical "double exchange" ferromagnetic conductive state towards combined influence of two perturbations: high pressure oxygen treatment and large film-substrate strain effects. The resulting new phase separated state consists of two phases: ferromagnetic matrix with spin-glass-like inclusions.

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1. J. Coey, M. Viret, and S. von Molnar, Adv. Phys. **48**, 167 (1999).
2. G. Xiong, Q. Li, H. Ju, S. Mao et al., Appl. Phys. Lett. **66**, 1427 (1995).
3. Y. Shapira, S. Foner, and T. Reed, Phys. Rev. **B8**, 2299 (1973).
4. E. Wollan and W. Koehler, Phys. Rev. **100**, 545 (1955).
5. A. Arulraj, R. Mahesh, G. Subbana et al., J. Solid State Chem. **127**, 87 (1996).
6. C. Zener, Phys. Rev. **B 82**, 403 (1951).
7. E. L. Nagaev, Usp. Fiz. Nauk **166**, 833 (1996).
8. A. Biswas, M. Rajeswari, R. C. Srivastava et al., Phys. Rev. **B63**, 184424 (2001).
9. X. L. Wang, J. Horvat, H. K. Liu et al., J. Magn. Magn. Mater. **182**, L1 (1998).
10. Yu. A. Izyumov and Yu. N. Skryabin, Usp. Fiz. Nauk **171**, 121 (2001).
11. S. Yunoki and A. Moreo, Phys. Rev. **B58**, 6403 (1998).
12. E. Dagotto, S. Yunoki, A. L. Malvezzi et al., Phys. Rev. **B58**, 6414 (1998).
13. D. I. Golosov, M. R. Norman, and K. Levin, cond-mat/9712094.
14. A. Moreo, M. Mayr, A. Feiguin et al., Phys. Rev. Lett. **84**, 5568, (2000).