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Pressure effects on the charge-ordering state in $Sm_{0.2}Ca_{0.8}Mn_{1-x}Ru_xO_3$ $(x=0,0.04)$

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Transport properties of $Sm_{0.2}Ca_{0.8}Mn_{1-x}Ru_xO_3$ $(x=0,0.04)$ have been investigated in the temperature range 15–300 K in external magnetic fields up to 1.5 T and hydrostatic pressure up to 1 GPa. The 4% Ru doping in Mn site converts the low-temperature robust orbital ordered phase observed in the undoped compound to a two-phase (ferromagnetic and charge ordered) ground state. As a result of such doping (phase-separated ground state), colossal magnetoresistance, slow relaxation of resistivity with logarithmic time dependence, and prehistory effects that are enhanced by pressure are observed in $Sm_{0.2}Ca_{0.8}Mn_{0.96}Ru_{0.04}O_3$. In contrast, the above effects are absent in $Sm_{0.2}Ca_{0.8}MnO_3$.

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I. INTRODUCTION

Hole-doped perovskite-type manganites of the type $R_{1-x}A_xMnO_3$ (A is a divalent cation, such as Sr^{2+}, Ca^{2+}, Ba^{2+}, or Pb^{2+}, and R is a trivalent rare-earth ion such as La^{3+}, Pr^{3+}, Sm^{3+}, or Nd^{3+}) are attracting a lot of attention due to the existence of a metal-insulator transition and the appearance of colossal magnetoresistance (CMR) in these compunds.[1] Mn^{4+} ions and mobile holes in the e_g band of manganese are created either by replacing R^{3+} ions by A^{2+} or by introducing a lanthanide deficiency in an appropriate heat treatment. Properties of the CMR manganites have been interpreted using the double-exchange model between Mn^{3+} and Mn^{4+} ions[1–3] and the dynamic Jahn-Teller effect.[4] For example, the end compounds of the most popular CMR system $La_{1-x}Ca_xMnO_3$ with $x=0$ and $x=1$ are antiferromagnetic (AF) insulators, while the compounds with an intermediate doping level $(0.2<x<0.5)$ are ferromagnetic (FM) and metallic at temperatures below the Curie temperature T_C.[1]

It should be noted that the number of literature reports on electron-doped manganites is relatively small, in particular when compared to the rich variety of publications concerning the hole-doped materials. The essential difference between the hole-doped $(x<0.5)$ and electron-doped $(x>0.5)$ manganites consists in the fact that at low temperatures FM ordering is observed in the hole-doped systems, while an AF and insulating state appears in the electron-doped ones.[1] AF ordering in the electron-doped compounds is frequently accompanied by a transition to a charge-ordered (CO) state.[5] The most investigated CO manganites are those with the doping level close to the commensurate value of $x=0.5$.[6–8]

The insulating CO and AF ground state of electron-doped manganites is characterized by the presence of stripe phase consisting of extremely stable pairs of distorted $Mn^{3+}O_6$ stripes, which are separated periodically by stripes of a nondistorted $Mn^{4+}O_6$ octahedron.[9] The length of the stripes was found[9] to be in the range of a few hundreds of angstroms. Such paired stripes were observed, for example, in $(BiCa)MnO_3$,[9] $(PrCa)MnO_3$,[9] and $(SmCa)MnO_3$.[10,11]

It has been demonstrated in the literature that in some electron-doped $R_{1-x}Ca_xMnO_3$ compounds [$R=$Pr, La (Ref. 12), Eu (Ref. 13), Sm (Ref. 14)], the CMR effect is observed only within a narrow doping range close to a critical level $x_c\cong 0.80-0.90$. This fact has been attributed to the existence of extremely stable CO and AF insulating states for $0.5\leqslant x<x_c$ and the appearance of FM or cluster-glass-like ordering accompanied by charge delocalization for $x>x_c$, which responsible for the CMR effect in applied magnetic fields.[12,15]

The $Sm_{1-x}Ca_xMnO_3$ system at $0.5<x<0.9$ constitutes a typical electron-doped manganite.[15] CO is observed within the doping range $0.5<x<0.8$, and CMR appears for $0.8<x<0.9$.[15] The long-range CO disappears at doping levels $0.75<x<0.85$, and only one-dimensional (1D) orbital ordering (OO) of the d_x^2 orbitals in the C-type AF monoclinic phase persists below the critical temperature T_N.[11] In particular, the doping level of $Sm_{0.2}Ca_{0.8}MnO_3$ is close to the CMR range, but nevertheless, no CMR effect appears in this compound. Remarkably, the disappearance of twin-domain structures, accompanied by a structural phase transition from the $P2_1/m$ structure with strong monoclinic distortions to a pure orthorhombic structure, has been observed in this compound when the temperature increased above the Néel temperature $T_N\sim 150$ K.[10,11] Substitution of Mn by Ru in this compound induces the appearance of short-range FM ordering and CMR.[16] It was suggested in Ref. 16 that the origin of the ordering is the FM superexchange between Ru^{4+}, Ru^{5+}, and Mn^{3+} ions.

In this paper we report on our investigations of the effect of hydrostatic pressure (P) and magnetic field (H) on transport properties of electron-doped $Sm_{0.2}Ca_{0.8}MnO_3$ (SCMO) and $Sm_{0.2}Ca_{0.8}Mn_{0.96}Ru_{0.04}O_3$ (SCMRO) compounds. This study is motivated by appearance of a magnetically phase-separated (PS) ground state of inhomogeneous OO and FM ordering in SCMRO.[16] The enhanced effect of external P and H, when compared to the parent SCMO system, may be expected at the temperature range of the phase separation. Moreover, the effect of the applied pressure on CO manganites has been investigated until now only for hole-doped $La_{0.9}Sr_{0.1}MnO_3$,[17] $Pr_{0.7}Ca_{0.3}MnO_3$,[18] and for the commensu-

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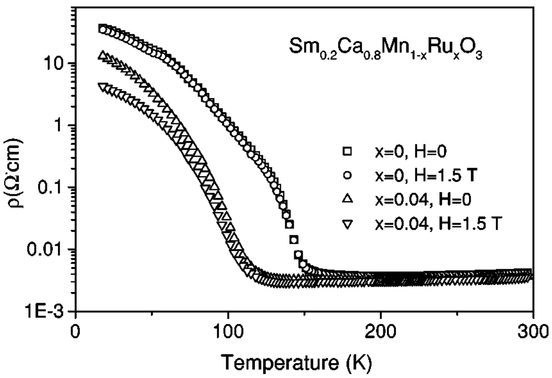

FIG. 1. Temperature dependences of the resistivity of $Sm_{0.2}Ca_{0.8}MnO_3$ and $Sm_{0.2}Ca_{0.8}Mn_{0.96}Ru_{0.04}O_3$.

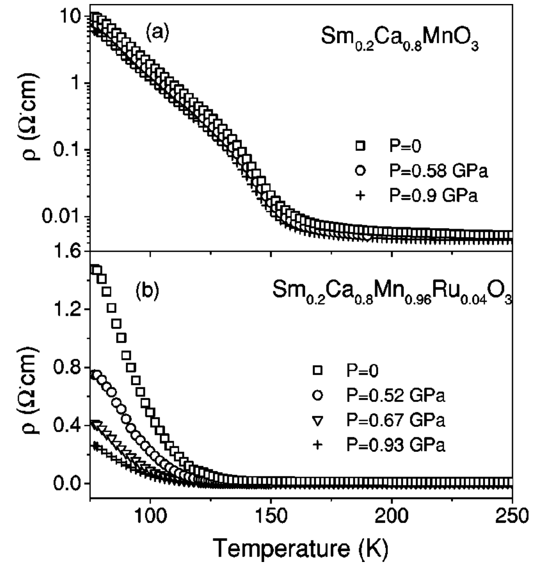

FIG. 2. Temperature dependences of the resistivity of (a) $Sm_{0.2}Ca_{0.8}MnO_3$ and (b) $Sm_{0.2}Ca_{0.8}Mn_{0.96}Ru_{0.04}O_3$ at various applied pressures.

rate doping level $(NdLa)_{0.5}Sr_{0.5}MnO_3$, $Pr_{0.5}Sr_{0.5}MnO_3$,[18] and $(NdSm)_{0.5}Sr_{0.5}MnO_3$ manganites.[19] At the same time, to the best of our knowledge, no studies of electron-doped CMR manganites have ever been reported.

II. EXPERIMENTAL RESULTS

The results presented in this work were obtained on polycrystalline samples of $Sm_{0.2}Ca_{0.8}MnO_3$ and $Sm_{0.2}Ca_{0.8}Mn_{0.96}Ru_{0.04}O_3$ prepared by a standard ceramic route. The procedures of sintering and preliminary characterization of the samples [x-ray diffraction (XRD), energy dispersive spectroscopy (EDS), and scanning electron microscopy (SEM)] are described in Ref. 16.

The dc resistivity ρ was measured using a four-probe method. The investigations were performed at ambient pressure in the temperature range $15<T<300$ K and under hydrostatic pressure up to $P=1$ GPa in the range $77<T<300$ K. The methodology of measurements performed under external pressure is described in detail elsewhere.[20] The magnetoresistance (MR), defined as $\mathrm{MR}=[\rho(T,H)-\rho(T,0)]/\rho(T,H)$, where $\rho(T,H)$ and $\rho(T,0)$ are the values of resistivity under nonzero and zero magnetic field, respectively, was measured at applied magnetic fields up to 1.5 T oriented perpendicular to the direction of the measuring current flow.

Figure 1 shows the dependences of the resistivity ρ of SCMO and SCMRO compounds as a function of temperature (recorded under cooling), with and without applied magnetic field. At zero applied field, for both compounds, the conductivity changes from the semimetallic one in the paramagnetic (PM) region to an insulatorlike one in the vicinity of T_N.[10,16] The resistivity change of SCMO in the vicinity of T_N due to the application of $H=1.5$ T is insignificant, while a noticeable MR, up to almost 200% at lowest temperatures, is observed for SCMRO below T_N, consistently with the results published Refs. 10 and 16.

Figure 2 shows the temperature evolution of the zero-field resistivity of both compounds for various applied pressures. SCMO [Fig. 2(a)] demonstrates a very weak decrease of T_N with pressure below the ambient pressure value of 150 K.[16] The absolute value of the coefficient dT_N/dP does not exceed 2–3 K/GPa. The magnetic field weakly influences the resistivity of SCMO in the investigated pressure and temperature range (see Fig. 1), excluding a narrow temperature interval near T_N. In marked contrast, the T_N of SCMRO strongly decreases with pressure, as illustrated in Fig. 2(b). The coefficient dT_N/dP for this compound was found to be about 12 K/GPa, see Fig. 3. The effect of the applied magnetic field is also more pronounced on SCMRO, as can be seen in Fig. 1. Moreover, the effect of the applied field is strongly influenced by the pressure, as shown in Fig. 4.

It follows from the data shown in Fig. 4 that a significant MR of about -20% is observed in SCMRO at $P=0$ in the vicinity of T_N. Applied pressure enhances the magnitude of the MR to about -45% at $P=0.93$ GPa. Moreover, with increasing pressure the temperature of the MR minimum decreases and the interval in which a negative MR effect exists broadens: see Fig. 4. However, the change of the MR minimum temperature with pressure increasing from zero to about 1 GPa (about 26 K) and corresponding T_N change (about 11 K) are markedly different as shown in Figs. 3 and 4. Observe that an initial, relatively small, pressure increase dramatically changes the temperature of the resistivity mini-

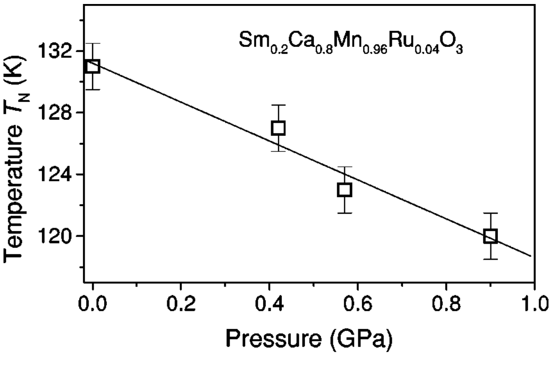

FIG. 3. Pressure dependence of the Néel temperature of $Sm_{0.2}Ca_{0.8}Mn_{0.96}Ru_{0.04}O_3$.

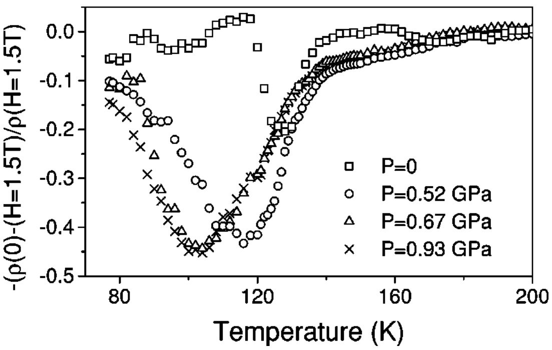

FIG. 4. Magnetoresistance of $Sm_{0.2}Ca_{0.8}Mn_{0.96}Ru_{0.04}O_3$ at $H = 1.5\,T$ as a function of temperature under various pressures.

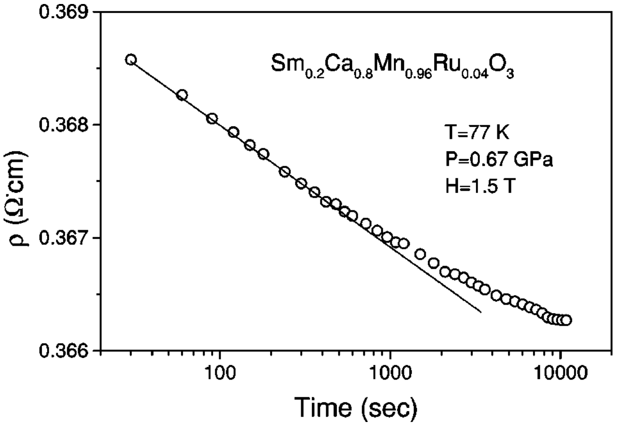

FIG. 6. Time dependence of the resistivity of $Sm_{0.2}Ca_{0.8}Mn_{0.96}Ru_{0.04}O_3$ under pressure $P = 0.67$ GPa after application of $H = 1.5\,T$.

mum and the magnitude of the MR effect, while a further increase of P induces only small variations of these parameters: see Fig. 4.

The influence of pressure on the MR effect in SCMRO is further illustrated in Fig. 5, in which the MR vs H dependence (the magnetoresistance loops), recorded under various pressures at $T = 77\,K$, is presented. One can see that the MR effect clearly increases with increasing pressure. At the same time, the MR loops do not close and show remarkable hysteresis, which is also enhanced by the applied pressure. The hysteretic behavior shown in Fig. 5 may reflect the existence of pressure and field-dependent metastable states as the ramping of H during the recording of MR loops may induce a continuous transition between distinct metastable states. The prominent feature of the discussed metastable states is the time dependence and relaxation of the measured resistivity, as shown for the case of the resistivity of SCMRO at $P = 0.67$ GPa, $T = 77\,K$, and $H = 1.5\,T$ in Fig. 6. The time decay of ρ in Fig. 6 obeys a well-pronounced logarithmic law characteristic also for relaxation of magnetization (magnetic viscosity or aftereffect) (Ref. 21) as well as other parameters[22,23] of magnetically ordered compounds. In contrast to the data presented in Figs. 5 and 6, the MR loops of a parent SCMO compound at 77 K are closed: the absolute values of the MR effect are very small (about 1% at $H = 1.5\,T$) and practically independent of P. The absence of time-dependent effects in the SCMO resistivity is also remarkable.

The inhomogeneous magnetic ground state of SCMRO manifests itself also in the magnetic prehistory effect at $T < T_N$: see Fig. 7. Here the $\rho(T)$ curves were measured in zero-field-cooled (ZFC) and field-cooled (FC) conditions during a warm-up cycle at $H = 1.5\,T$ with $P = 0$ [Fig. 7(a)] and $P = 0.93$ GPa [Fig. 7(b)]. Notice that the relative difference between the $\rho(T)$ curves recorded in different magnetic regimes, the prehistory effect, becomes enhanced by the ap-

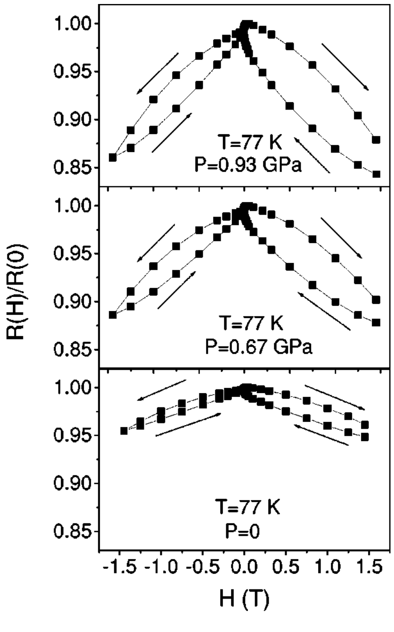

FIG. 5. Magnetoresistance loops of $Sm_{0.2}Ca_{0.8}Mn_{0.96}Ru_{0.04}O_3$ at various pressures.

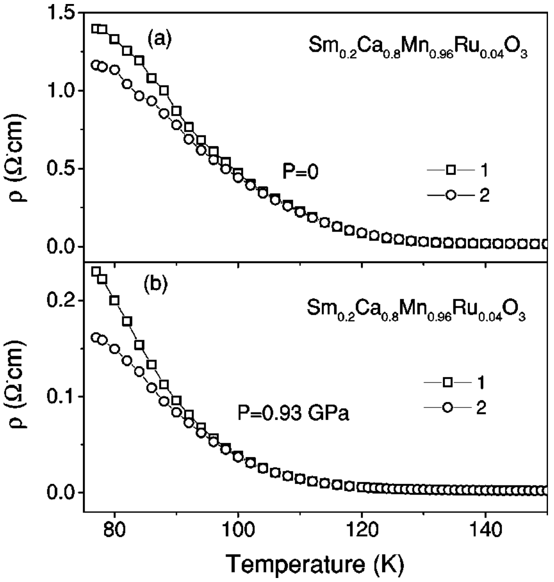

FIG. 7. Temperature dependences of the resistivity of $Sm_{0.2}Ca_{0.8}Mn_{0.96}Ru_{0.04}O_3$ (warming run) under $H = 1.5\,T$ for $P = 0$ (a) and $P = 0.93$ GPa (b) after (curve 1) ZFC and subsequent application of $H = 1.5\,T$ at $T = 77\,K$ and (curve 2) FC at $H = 1.5\,T$.

plied pressure, but disappears at temperatures approaching T_N; see Fig. 7.

III. DISCUSSION AND CONCLUDING REMARKS

An abrupt change at $T = T_N$ of the character of the SCMO resistivity dependence on temperature, from a semimetal- to an insulatorlike one, is accompanied by structural and magnetic transitions. Namely, at $T = T_N$ strong monoclinic distortions of *Pnma* structure occur and structural twinning domains are formed.[10,24,25] Simultaneously, a magnetic transition from the PM to C-type AF state with 1D OO takes place.[10,11] The AF state of SCMO is extremely robust, and a magnetic field stronger than 25 T is required to flip the antiparallel spins at $T < 100$ K.[25] This is the reason for the observed weak pressure and magnetic field dependence of T_N and low-temperature ($T < T_N$) resistivity of SCMO: Figs. 1 and 2.

The doping of the SCMO system with Ru^{4+} (or Ru^{5+}) in the Mn site destroys the OO state and promotes the ferromagnetic interaction either by increasing the Mn^{3+} concentration and, correspondingly, Mn^{3+}-Mn^{4+} FM double exchange or by developing FM superexchange interactions with the surrounding Mn^{3+} species.[16,25] At the doping level of about 10%, a percolation network of growing FM clusters develops, resulting in the establishment of a FM metalliclike state in SCMRO.[16] A metallic percolation network is clearly absent in SCMRO compound doped only with 4% of Ru. Therefore, an insulatorlike $\rho(T)$ dependence is observed at low temperatures: see Fig. 1. Notice that an abrupt decrease of the resistivity observed at temperature increasing above 130 K coincides with the structural transition between monoclinic $P2_1/m$ and orthorhombic *Pnma* structures and with the magnetic transition from the C-type AF phase to the short-ordered FM state. Simultaneously, the phase-separated magnetic state appears, as confirmed by the observation of two maxima in the ac susceptibility of SCMRO.[16,26] The resulting strong competition between FM and AF interactions, as expected within the phase-separation scenario,[24,25] may enhance the sensitivity of SCMRO to external perturbations such as field, pressure, etc. It is well known[18,27] that an increase in the hydrostatic pressure results in effects similar to those of increasing the hole-doping level. Namely, the temperature range of existence of the FM phase increases, while the resistivity and percolation threshold decreases. It is worth noting that for SCMRO the applied pressure restrains the temperature range of the AF phase, similar to the effects of the Ru doping reported in Ref. 24.

Doping with Ru results in a coexistence of AF (OO) and FM domains at $T < T_N$. The coexistence of AF and FM domains is responsible for the relaxation of the resistivity in SCMRO. Measurements of the time dependence of ρ indicate that the relaxation obeys a logarithmic law. This provides a strong argument in favor of the existence of a wide distribution of energy barriers that are separating the metastable and stable resistivity states.[21] A similar situation is observed for other internal parameters, e.g., the thermal expansion coefficient[22,23] when measured in the vicinity of the magnetic first-order phase transition. A large thermal hysteresis, ΔT about 80 K, appearing between the rising and falling branches of the $\rho(T)$ characteristic[16] in SCMRO strongly supports speculation that the magnetic transition to the AF (OO) state is of first order. The volume of FM metalliclike domains increases with time, as reflected by the decrease of ρ with time in Fig. 6, through overcoming energy barriers between FM and AF regions. In spite of very recent observations of some minute FM ordering in SCMO at $T < T_N$ by electron magnetic resonance,[28] time-dependent phenomena, as well as the enhanced effect of external P and H, are absent in this compound. This is an additional argument supporting the idea that Ru doping is responsible for the above-discussed effects. A recent thermodynamic analysis of the behavior of manganites with two subsequent PM-FM and FM-AF (CO) magnetic transitions[29] is consistent with our results. Namely, the low-temperature transition is claimed to be of first order and the relaxation phenomena were observed in the temperature range of the coexistence of two phases in accordance with Refs. 17 and 29. The presence of a magnetic field during the cooling of a SCMRO sample through the orbital ordering temperature T_{OO} enhances the FM volume on the expanse of the OO phase, Fig. 7. This result agrees with model presented in Ref. 29. Moreover, it can be directly seen in Fig. 7 that the resistivity of field-cooled SCMRO is noticeably smaller than that after ZFC. One may argue that an applied field aligns magnetic moments in the FM domains at the magnetic ordering temperature and thus eliminates spin-disorder scattering contributions to the resistivity. It is important to note that such prehistory effects are also absent in the parent, undoped SCMO compound.

In conclusion, the influence of hydrostatic pressure and magnetic field on the transport properties of electron-doped $Sm_{0.2}Ca_{0.8}MnO_3$ and $Sm_{0.2}Ca_{0.8}Mn_{0.96}Ru_{0.04}O_3$ ceramics was investigated. Doping of SCMO by 4% of Ru in the Mn site converts the low-temperature robust orbital ordered phase into a two-phase (ferromagnetic+antiferromagnetic) ground state. As a result, the investigated compounds behave markedly different under the influence of applied pressure and magnetic field. At ambient pressure, $Sm_{0.2}Ca_{0.8}Mn_{0.96}Ru_{0.04}O_3$ is characterized by (i) colossal magnetoresistance in the vicinity of the magnetic ordering temperature about 130 K and at lowest temperatures $T < 77$ K, (ii) slow relaxation of the resistivity, and (iii) prehistory effects (the difference in the values of resistivity obtained after ZFC and FC through $T = 130$ K). The above effects are enhanced, in a nonlinear way, by the external hydrostatic pressure. In marked contrast, all of the above effects are absent in $Sm_{0.2}Ca_{0.8}MnO_3$.

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