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Effect of pressure on magnetic and transport properties of $CaMn_{1-x}Ru_xO_3$ $(x=0-0.15)$: Collapse of ferromagnetic phase in $CaMn_{0.9}Ru_{0.1}O_3$

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Magnetic and transport properties of $CaMn_{1-x}Ru_xO_3$ $(x=0;0.1;0.15)$ perovskites were investigated in the temperature range 4.2–280 K, magnetic fields up to 15 kOe and hydrostatic pressure up to 12 kbar. It was found that for a substitution of $x=0.1$, an applied pressure of 12 kbar shifts up the magnetic transition temperature by ~14 K and simultaneously drastically suppresses the ferromagnetic metallic phase. For $x=0.15$, the application of pressure reduces transition temperature by about −0.28 K/kbar and suppresses the FM phase in a less pronounced manner. Observed changes in resistivity and magnetoresistance of $CaMn_{0.9}Ru_{0.1}O_3$ are described by suppression of the double-exchange interactions under pressure. They are discussed in the context of the phase separation and valency effects.

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The observation of colossal magnetoresistance (CMR) in hole-doped perovskite-type manganites $L_{1-x}A_xMnO_3$ (L = rare-earth ion; A = divalent alkaline metal) has promoted extensive studies of these compounds in the past decade.[1,2] Manganites were found to exhibit a plethora of magnetic and electronic phases, depending on the level of the doping x and the averaged A-site cation radius, $\langle r_A \rangle$. It is widely accepted that the CMR mechanism arises mainly due to the double exchange (DE) interaction mediated by hopping of spin-polarized e_g electrons, between Mn^{3+} and Mn^{4+}, thereby facilitating both the electrical conductance and the ferromagnetic (FM) coupling, in the ferromagnetic metallic (FMM) phase. On the other hand, certain electron-orbital configurations energetically favor superexchange (SE) interactions between localized electrons and may yield a formation of ferromagnetic insulating (FMI) or antiferromagnetic (AFM) phases.[3] Coexistence of FMM domains with AFM insulating regions was proved for various manganite systems.[2] External perturbations, such as magnetic and electric fields, and applied pressure may change the ratio between coexisting phases.

$CaMnO_3$, the end compound of $(La,Ca)MnO_3$ system, is a G-type antiferromagnet in its ground state with an additional weak ferromagnetic component.[4] Antiferromagnetic phase exhibits a Néel temperature of about 120 K. At this configuration each Mn magnetic moment is alternately antiparallel to its nearest Mn neighbors.[5] The nominal valence of Mn ions for stoichiometric compounds is 4+. In order to induce Mn^{3+} in the matrix, two types of substitutions are possible: at the A-site, by using a trivalent lanthanide instead Ca^{2+} or by substitution a part of Mn by a cation that exhibits a valency >4. Numerous studies performed in the first framework show, for low-substituting level, a complex state described as a canted G-type antiferromagnet or as a phase-separated state (clusters). Substituting the Mn site of $CaMnO_3$ with high-valency metal (superior to 4+) leads to CMR.[6–9] Recent studies[10,11] of Ru doping of various charge ordered (CO) AFM perovskites have proven that a very low doping is sufficient to impede the CO state and to form a FMM phase. Magnetic and resistivity measurements of Ru-doped manganites under pressure,[12] e.g., $Sm_{0.2}Ca_{0.8}Mn_{1-x}Ru_xO_3$ have shown that their magnetic and transport properties are quite sensitive to the external pressure.

We report herein on the effect of hydrostatic pressure (P) and magnetic field (H) on magnetic properties of low-doped $CaMn_{1-x}Ru_xO_3$. It is shown that a relatively modest pressure may produce an almost full collapse of the FM phase in perovskites oxides.

We performed investigation of the samples with $x=0$; 0.1; 0.15. According to magnetic, transport[6–9] and neutron diffraction[13] studies all the above doped manganites exhibit a phase separated ground state comprising G-type AFM and FM phases. The measurements were carried out on polycrystalline samples prepared by a standard ceramic route. At room temperature, all samples were found to be compatible with orthorhombic perovskite structure of *Pnma* space group.[7] The procedures of their sintering and the basic properties are described in Refs. 7 and 8. The experimental procedures of the measurements under high hydrostatic pressure are described in detail elsewhere.[12]

$CaMnO_3$: Figure 1(a) shows the results obtained for field-cooled (M_{FC}) and zero-field-cooled (M_{ZFC}) magnetization curves of $CaMnO_3$ under applied pressure. Magnetic transition temperature, i.e., critical temperature T_C, defined as the inflection point of $M(T)$ dependence implies the Néel temperature for $CaMnO_3$.[14] At ambient pressure ($P=0$), $CaMnO_3$ $(x=0)$ exhibits a transition from paramagnetic (PM) phase to G-type AFM phase at $T_C \approx 120$ K, while under pressure of $P=11.5$ kbar $T_C \approx 126$ K, see Fig. 1(a). The pressure coefficient $dT_C/dP = 0.48 \pm 0.05$ K/kbar is also shown in the inset of Fig. 1(a). This result fairly agrees with

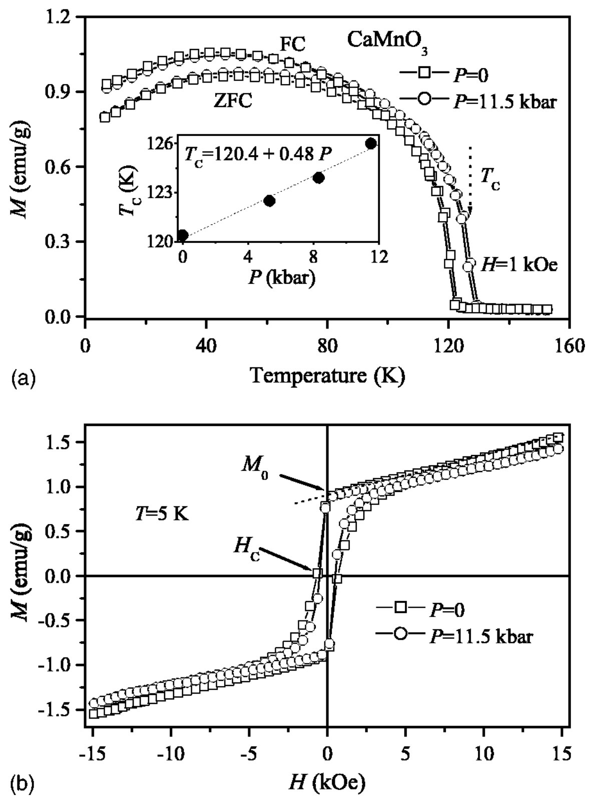

FIG. 1. (a) Temperature dependence of M_{FC} and M_{ZFC} for $CaMnO_3$ at $P=0$ and $P=11.5$ kbar in magnetic field $H=1$ kOe; Inset: pressure dependence of the Ńeel temperature; (b) Hysteresis loops of $CaMnO_3$ at $T=5$ K under ambient pressure ($P=0$) and $P=11.5$ kbar.

previous reports,[15] $dT_C/dP=0.42\pm0.02$ K/kbar, obtained for $CaMnO_3$ from the magnetization measurements. Hysteresis loops at $T=5$ K for $CaMnO_3$ at $P=0$ and at $P=11.5$ kbar are given in Fig. 1(b). The weak ferromagnetic moment M_0 observed may result from canting of the AFM moments, although recent works[14] suggest that it arises from a small defect concentration. In such a case, M_0 should be rather insensitive on applied pressure in compliance with experimental results [Fig. 1(b)]. The coercive field ($H_C \approx 0.6$ kOe) and spontaneous weak magnetization ($M_0=0.023$ μ_B/f.u. at $P=0$) obtained by a linear extrapolation of the high-field magnetization to $H=0$, were found to be nearly pressure independent. The above results are found to be in a fairly good agreement with results reported by Kafalas *et al.*[15] for other differently prepared samples.

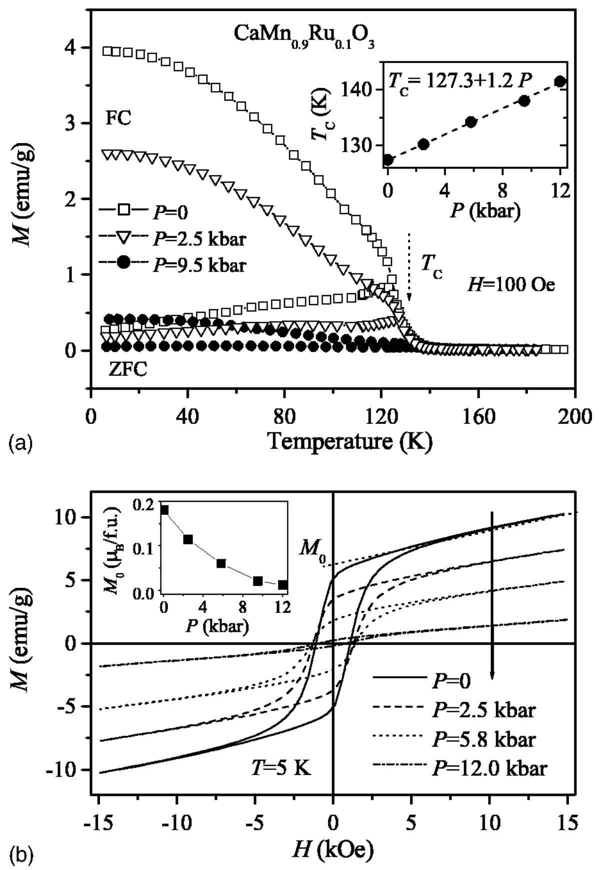

FIG. 2. (a) Temperature dependence of M_{FC} and M_{ZFC} for $CaMn_{0.9}Ru_{0.1}O_3$ under various pressures in magnetic field $H=100$ Oe. Inset: a variation of transition temperature with pressure; (b) Hysteresis loops of $CaMn_{0.9}Ru_{0.1}O_3$ at various pressures at $T=5$ K. Inset: a variation of M_0 with pressure.

$CaMn_{0.9}Ru_{0.1}O_3$: The effect of an applied pressure on low doped Ru manganite is well manifested in the case of $CaMn_{0.9}Ru_{0.1}O_3$. Temperature and magnetic field dependences of magnetization for this compound under various pressures are given in Fig. 2. The following features are clearly seen: (i) the temperature T_C—defined as noted already by the inflection point of $M(T)$ dependence—indicates now the transition to highly inhomogeneous magnetic state, with both T and H dependent ratio of AFM/FM phases,[7,9] and increases with pressure from 127 K at $P=0$ up to 141 K for $P=12$ kbar, thus exhibiting a pressure coefficient $dT_C/dP \approx 1.2$ K/kbar; (ii) the significant difference between M_{FC} and M_{ZFC} curves (at $P=0$ and under pressure) indicates magnetic frustration effects; (iii) and most interesting, the magnetization is strongly suppressed by pressure, from $M_0=0.18$ μ_B/f.u. at $P=0$ to $M_0 \approx 0.01$ μ_B/f.u. at $P=12$ kbar [see inset, Fig. 2(b)]. The low field magnetization $M(H)$ shown in Fig. 2(b) is attributed to the FM phase, whereas the AFM phase gives rise to the linear $M(H)$ dependence in high-field region. $M(H)$ dependences at $P=0$ exhibit the appearance of M_0 just below T_C (not shown). The value of M_0 increases with decreasing temperature, exhibiting behavior typical for FM phase. It appears that a relatively modest pressure $P=12$ kbar disrupts almost completely the FM phase of $CaMn_{0.9}Ru_{0.1}O_3$. At the same time the coercive field $H_C \approx 1.2$ kOe, remains practically unchanged with increasing pressure [see Fig. 2(b)].

For the sample with $x=0.1$ additional transport measurements under hydrostatic pressure were performed. The resistivity and magnetoresistance at $P=0$ and $P=9.9$ kbar are given in Fig. 3(a). It appears that the temperature dependence of both resistivity curves at $170 < T < 280$ K can be described by small polaron hopping model $\rho(T)=A\times T \times \exp(E_a W/k_B T)$, where A is a constant and E_a is an activation energy. The fit to the experimental results shows that E_a increases from the 40.4 meV for $P=0$ to 47.8 meV for P

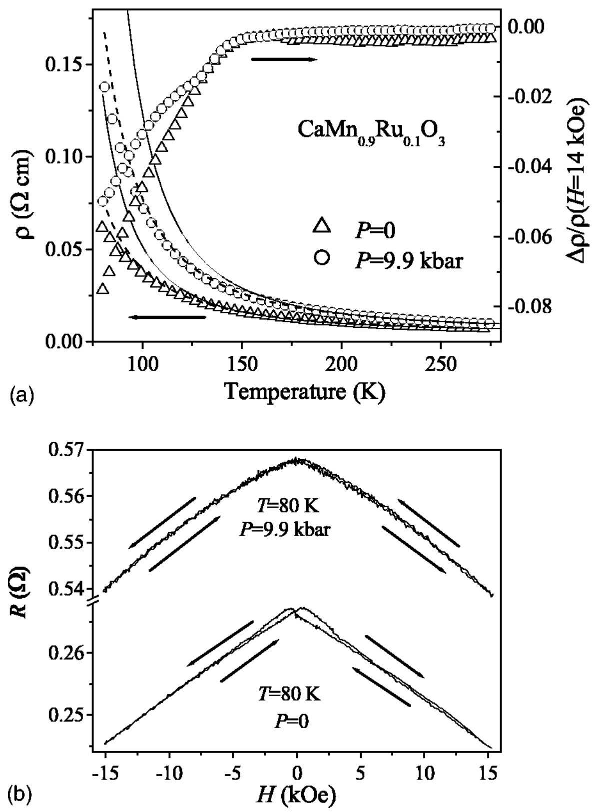

FIG. 3. (a) Temperature dependence of resistivity ($H=0$) and magnetoresistance at $H=14$ kOe for $CaMn_{0.9}Ru_{0.1}O_3$ at $P=0$ and $P=9.9$ kbar. The open symbols represent experimental data. Solid lines are fitted resistivity curves within the frame of a small polaron model and dashed lines are fitted curves for simple activated form; (b) Resistance as a function of magnetic field at 80 K under $P=0$ and under $P=9.9$ kbar.

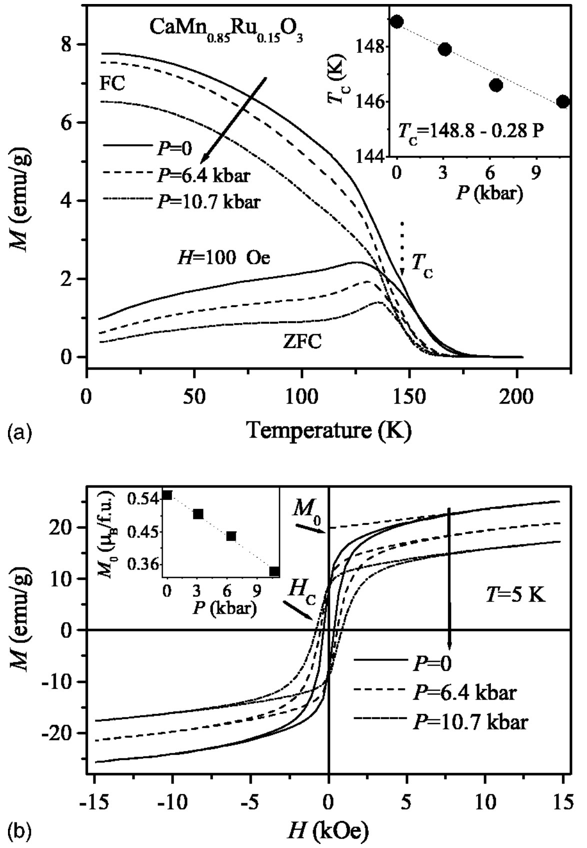

FIG. 4. (a) Temperature dependence of M_{FC} and M_{ZFC} for $CaMn_{0.85}Ru_{0.15}O_3$ at various pressures in magnetic field $H=100$ Oe. Inset: a variation of T_C with pressure; (b) Hysteresis loops of $CaMn_{0.85}Ru_{0.15}O_3$ at various pressures at $T=5$ K. Inset: a variation of M_0 with pressure.

$=9.9$ kbar, thus confirming the less conductive nature of the state induced by pressure. An attempt to fit the resistivity data of $CaMn_{1-x}Ru_xO_3$ with the model of small polaron hopping was carried out previously.[6,9] It has been found that W increases monotonically with increasing doping for $0<x<0.1$. However, it appears that the fit with a simple activation form $\rho(T)=\rho_0\times\exp(E_a/k_BT)$, where E_a stands for activation energy, exhibits an even better agreement with the experimental results, in a wider temperature range $120<T<280$ K [see Fig. 3(a)]. The fitting parameters here are $\rho_0=0.01094$ Ω cm and $E_a=23$ meV for $P=0$ and $\rho_0=0.012$ Ω cm and $E_a=28$ meV for $P=9.9$ kbar. It should be noted that the temperature range in this case is found to be too narrow to favor one model over other. However, both imply an increase in the activation energy under pressure. Magnetoresistance, which occurs only below 150 K, is strongly suppressed by pressure [see Fig. 3(a)]. The hysteretic effect of the magnetoresistance, associated with ferromagnetic hysteresis, disappears under pressure of 9.9 kbar. It is correlated well with a disappearance of the coercivity of resistivity hysteresis loop [Fig. 3(b)].

$CaMn_{0.85}Ru_{0.15}O_3$: Temperature and magnetic field dependences of magnetization for $CaMn_{0.85}Ru_{0.15}O_3$ at various pressures are shown in Fig. 4. Here also, M_{FC} and M_{ZFC} curves exhibit a great disparity below the inflection point—critical temperature T_C. It should be noted that the absence of a clear inflection point in the magnetization curves prevent a precise determination of the transition temperature to ferromagnetic state, i.e., Curie temperature, and its pressure dependence. For $CaMn_{0.85}Ru_{0.15}O_3$ an applied pressure of 10.7 kbar decreases the volume of the FM phase, by about 40% at $T=5$ K [see Fig. 4(b)]. Contrary to the M_0 behavior, H_C of the $x=0.15$ sample increases significantly with increasing pressure, from 0.33 kOe at $P=0$ to 0.81 kOe at $P=10.7$ kbar.

The effect of pressure on the magnetic and transport properties of $CaMn_{1-x}Ru_xO_3$ ($x=0;0.1;0.15$) will be discussed in conjunction with valency effect in Ru-doped manganites. It has been already pointed out[6–10] that whatever the nature of initial AFM state of undoped perovskites is, ferromagnetism and metallicity can be induced by Ru doping in a manner, leading to CMR properties. Ru in manganese sites[6–9] may exhibit two oxidation states, $Ru^{4+}(t_{2g}{}^4e_g{}^0)$ and $Ru^{5+}(t_{2g}{}^3e_g{}^0)$. It acts to increase the Mn^{3+} content in compliance with the equation for valency: $2Mn^{4+}=Ru^{5+}+Mn^{3+}$. Therefore, Ru^{5+} substitution enhances FM interactions between $Mn^{4+}(t_{2g}{}^3e_g{}^0)$ and $Mn^{3+}(t_{2g}{}^3e_g{}^1)$ ions via DE. Moreover, the Mn^{3+} can interact with both Ru^{5+} and Ru^{4+} ions through FM superexchange interaction. The FM interaction between Mn and Ru species may be also enhanced due to the hybridization of their e_g orbitals, allowing conduction paths to be created through Mn–O–Ru bridges.[7,16] Besides, inherent to pristine AFM matrix, antiferromagnetic superexchange between Mn^{4+} ions operates also in phase-separated Ru-doped manganites. At a high enough level of Ru doping the AFM superexchange between Mn^{3+} ions may also be essential. As a result of Ru doping, an inhomogeneous phase-separated magnetic state is developed, comprising both of G-type AFM and FM phases in the same *Pnma* structure.[7,9] Previous measurements of magnetization and ac-susceptibility[7,9] as well as our measurements of $M(H)$ (not shown) support a picture where at low Ru doping ($x \leqslant 0.1$) AFM and FM phases appear simultaneously with decreasing temperature. At larger Ru content ($x > 0.2$) both Curie and Néel temperatures become clearly distinguishable.[7] The evolution of both AFM and FM phases of $CaMn_{1-x}Ru_xO_3$ with progressive Ru doping resembles the phase diagram for $Sm_{0.2}Ca_{0.8}Mn_{1-x}Ru_xO_3$, where both Curie and Néel temperatures coincide near $x = 0.02$ and with increasing Ru doping they exhibit opposite temperature trend.[12]

As noted earlier, the mixed valent ionic state in low-doped $CaMn_{1-x}Ru_xO_3$ is found to be in accordance with the valency fluctuations, $Mn^{3+} + Ru^{5+} \leftrightarrow Mn^{4+} + Ru^{4+}$ occurring due to a comparable redox potential of $Mn^{3+} \leftrightarrow Mn^{4+}(1.02\ \text{eV})$ and $Ru^{5+} \leftrightarrow Ru^{4+}(1.07\ \text{eV})$.[17] The FM interactions between $Mn^{3+}-Ru^{5+}$ and $Mn^{3+}-Mn^{4+}$ are responsible for the FM clusters and compete with dominant AFM interaction between $Mn^{4+}-Mn^{4+}$ and $Ru^{5+}-Mn^{4+}$. Pi *et al.*[9] have found that the lattice parameters of some low electron-doped manganites are very sensitive to the Mn valency. For the series $CaMn_{1-x}Ru_xO_3$, $CaMn_{1-x}Mo_xO_3$, and $Sm_{1-x}Ca_xMnO_3$, a similar linear Mn valency (ν_{Mn}) dependence on the volume of the unit-cell, $dV_{cell}/d\nu_{Mn} \approx -25\text{Å}^3(V_{cell} = a \times b \times c)$ was found.[9] This feature is explained by the large difference of ionic size of $Mn^{4+}(0.52\ \text{Å})$ and $Mn^{3+}(0.65\ \text{Å})^2$ ions, suggesting that pentavalent ruthenium dominates among the Ru^{5+} and Ru^{4+} species.[9] Supposing that only Ru^{5+} ions exist in low-doped samples $CaMn^{4+}{}_{1-2x}Mn^{3+}{}_xRu^{5+}{}_xO_3$, the Mn valency may be calculated as $\nu_{Mn} = (4-5x)/(1-x)$. For $x = 0.1$ and $x = 0.15$, ν_{Mn} is estimated to be 3.9 and 3.82, respectively. Moreover, the evaluation of ν_{Mn} for $CaMn_{0.8}Ru_{0.2}O_3$ from chemical formulas ($\nu_{Mn} = 3.75$) coincides fairly well with the experimental value of the thermoelectric power $S_{300\ K} = -45\ \mu VK^{-1}$.[8] This fact also supports the validity of the assumption that Ru is pentavalent in $CaMn_{1-x}Ru_xO_3$ in a wide doping range.[8,9] According to the ionic radii of the $Mn^{3+}(0.65\ \text{Å})/Mn^{4+}(0.52\ \text{Å})$ and $Ru^{5+}(0.56\ \text{Å})/Ru^{4+}(0.62\ \text{Å})$ ions,[17,18] the valency fluctuations $Mn^{3+} + Ru^{5+} \leftrightarrow Mn^{4+} + Ru^{4+}$ are concurrent with deviation in the volume by $\Delta V = \Delta V_{Mn} + \Delta V_{Ru} = 0.3\ \text{Å}^3$ (where $\Delta V_{Mn} = V_{Mn^{3+}} - V_{Mn^{4+}}$ and $\Delta V_{Ru} = V_{Ru^{5+}} - V_{Ru^{4+}}$ and the volume of ions is calculated as a volume of a sphere). It appears, that above transformation of the alternating pairs is accompanied by an increasing or decreasing of volume. Hence, under pressure the transformation $Mn^{3+} + Ru^{5+} \rightarrow Mn^{4+} + Ru^{4+}$ is favored, inducing in fact the opposite transformation as compared to Ru doping and leading to suppression of DE ferromagnetic interaction between $Mn^{3+}-Ru^{5+}$ and $Mn^{3+}-Mn^{4+}$ pairs. It is notable that the forward conversion $Mn^{4+} + Ru^{4+} \rightarrow Mn^{3+} + Ru^{5+}$ adds carriers, whereas the reverse one ($Mn^{3+} + Ru^{5+} \rightarrow Mn^{4+} + Ru^{4+}$) reduces the number of carriers. Using typical value for the compressibility K $= -(1/V)dV/dP \approx 0.7 \times 10^{-3}(\text{kbar}^{-1})$ obtained for various manganites, in particular, for $LaMnO_3$ and $CaMnO_3$ and the experimentally derived high enough value of bulk modulus for $LaMnO_3$[19] ($B_0 = 1080 \pm 20$ kbar) in comparison with pressure used (12 kbar), one may estimate the value of pressure coefficient as: $dV_{cell}/dP = -0.147\ \text{Å}^3/\text{kbar}$ (using the volume cell of $CaMn_{0.9}Ru_{0.1}O_3$ $V_{cell} \approx 210\ \text{Å}^3$).[9] This value agrees well with such a parameter for $LaMnO_3$ in low-pressure range derived from the data of neutron diffraction measurements under pressure[20] ($dV_{cell}/dP = -0.186\ \text{Å}^3/\text{kbar}$). Then the pressure coefficient of the Mn valency in $CaMn_{1-x}Ru_xO_3$ can be calculated as $d\nu_{Mn}/dP = (dV_{cell}/dP)/)dV_{cell}/d\nu_{Mn}) \approx 6 \times 10^{-3}(\text{kbar})^{-1}$. This gives a value of $\Delta\nu_{Mn} \approx 0.1$ at pressure of about 16 kbar, hence, it is expected for $x = 0.1$ sample that the average valency of Mn increases from 3.9 to 4.0 under $P \approx 16$ kbar. The disappearance of Mn^{3+} species under a pressure predicts a suppression of the FM phase in $CaMn_{0.9}Ru_{0.1}O_3$ in very good agreement with the experimental results (see Fig. 2). The sample with $x = 0.15$ exhibits a three-times-larger volume of FM phase as compared to that of $x = 0.1$ sample (see Figs. 2 and 4). A pressure of 10 kbar causes almost the same reduction in FM moment as in the case $x = 0.1$, but it is not enough for full suppression of ferromagnetic phase (see Fig. 4). Nevertheless, the reduction in the FM volume observed is less pronounced than that in the $CaMn_{0.9}Ru_{0.1}O_3$. This observation may be attributed partly to strain effects, inherent to the AFM↔FM transition. In fact, the change in the size of the FM clusters is accompanied by a change in their volume and contributes in addition to magnetic energy, magnetoelastic and lattice strain terms. One may suppose that the total FM-AFM energy gap is lower at the cluster interface compared to that of the FM cluster bulk. Compounds with lower Ru doping level contain smaller FM clusters and higher surface/volume ratio. Therefore, it is expected that the reduction in the magnetic moment in $CaMn_{0.9}Ru_{0.1}O_3$ will be the most pronounced.

The resistivity behavior of $CaMn_{1-x}Ru_xO_3$ at low Ru doping (up to $x = 0.1$) shows that an activation energy E_a decreases for a progressive Ru doping.[6,7,9] A change in doping from $x = 0.02$ up to $x = 0.1$[7] decreases the resistivity at $T = 5$ K by 5 orders of magnitude, while the FM phase content increases and the percolation threshold is overcome for $x \approx 0.2$.[7] The simultaneous rise both of the resistivity and of the activation energy and corresponding decrease of magnetoresistance as well as the disappearance of the hysteresis of the $R(H)$ dependence in $CaMn_{0.9}Ru_{0.1}O_3$ at low temperatures under pressure is compatible with above scenario and support strongly the model of a suppression of ferromagnetic DE interactions under pressure.

Development of a highly inhomogeneous state, below the critical temperature, in Ru-doped manganites has been reported in several papers (see Refs. 6–12). In particular, magnetic susceptibility and transport measurements (Ref. 7) show a phase separation (into antiferromagnetic and ferromagnetic phases) in such systems. The enhancement as well as suppression of ferromagnetic phase under pressure has already been observed in different samples of $Sm_{0.2}Ca_{0.8}Mn_{1-x}Ru_xO_3$ with 20% of Sm and similar Ru contents (Ref. 12). Namely, for $Sm_{0.2}Ca_{0.8}Mn_{0.96}Ru_{0.04}O_3$ an applied pressure decreases both Curie and Néel temperatures, but enhances the ferromagnetic fraction. In the case of $Sm_{0.2}Ca_{0.8}Mn_{0.92}Ru_{0.08}O_3$ an applied hydrostatic pressure of 10 kbar suppresses of the ferromagnetic phase by 10% at 5 K and simultaneously increases the resistivity of the sample by about 4%. However, the observed changes are much less pronounced as compared to that of $CaMn_{0.9}Ru_{0.1}O_3$. Both $CaMn_{0.9}Ru_{0.1}O_3$ and $Sm_{0.2}Ca_{0.8}Mn_{0.92}Ru_{0.08}O_3$ have a comparable level of Ru-doping and therefore, the proposed effect of Mn valency variation with pressure should cause similar changes in the properties of both compounds. Nevertheless, satisfying description of the differences in magnetotransport properties between $CaMn_{0.9}Ru_{0.1}O_3$ and $Sm_{0.2}Ca_{0.8}Mn_{0.92}Ru_{0.08}O_3$ needs to take into account not only the doping level, but also the differences in transport and magnetic properties of their parent compounds $CaMnO_3$ and $Sm_{0.2}Ca_{0.8}MnO_3$. Additionally, $Sm_{0.2}Ca_{0.8}MnO_3$ exhibits at $T_N \approx 150$ K a magnetic transition, accompanied by a structural phase transition from pure orthorhombic structure to a $P2_1/m$ structure with strong monoclinic distortion.[10,21,22] This suggests the mechanism underlying the pressure effect in $Sm_{0.2}Ca_{0.8}Mn_{1-x}Ru_xO_3$ is likely to be different from the one proposed in the present manuscript, that is the Mn valency variation with pressure.

In summary, the FM phase of low-doped $CaMn_{1-x}Ru_xO_3$ compounds, particularly $CaMn_{0.9}Ru_{0.1}O_3$, were found to be extremely sensitive to external hydrostatic pressure. The pressure is driving a growth of the AFM phase at the expense of the FM one. While Ru doping and magnetic field promote the ferromagnetism and metallicity in a spectacular way, under pressure the valency fluctuations leading to suppression of the DE ferromagnetic interaction between Mn^{3+}, Mn^{4+}, and Ru^{5+} ions are favored. In the case of $CaMn_{0.9}Ru_{0.1}O_3$ it causes almost a full collapse of FM phase at modest pressures. The diminishing of FM interactions at relatively low pressures is quite unique among the perovskite oxides (the generic formula is AMO_3), usually exhibiting a transition from localized to itinerant electron behavior in the MO_3 array upon application of pressure.[23]

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