

## Evolution of ferromagnetic order in $\text{LaMnO}_{3.05}$ single crystals: Common origin of both pressure and self-doping effects

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The pressure effect on magnetic order and anisotropy of low-doped  $\text{LaMnO}_{3.05}$  single crystals with two competing ferromagnetic and antiferromagnetic insulating phases was studied by magnetization measurements. It was found that applied hydrostatic pressure leads to an increase of both Curie and Néel temperatures, with different rates:  $dT_C/dP=0.8$  K/kbar and  $dT_N/dP=0.16$  K/kbar. External pressure strongly suppresses the magnetic anisotropy, resulting in a decrease of the coercive field  $H_C$  with  $dH_C/dP=-0.1$  kOe/kbar. The results obtained indicate that the applied pressure both enhances ferromagnetic interactions and enlarges the volume fraction of the ferromagnetic phase. The evolution of the ferromagnetic phase was explained taking into account the reduction of the Jahn-Teller distortion with increasing pressure. Changes in ferromagnetic characteristics  $T_C$ ,  $H_C$ , and spontaneous magnetization  $M_0$  result mainly from the shortening of the long Mn-O distance in the  $\text{MnO}_6$  octahedron. Moreover, we found a similarity in dependences of those parameters on the degree of the  $\text{MnO}_6$  distortion for two different effects: hydrostatic pressure and the level of self-doping  $\delta$ . Such a similarity strongly suggests that pressure-induced suppression of the Jahn-Teller distortion is responsible for the observed enhancement of ferromagnetism in the  $\text{LaMnO}_{3.05}$  crystals.

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### I. INTRODUCTION

Lanthanum-based manganite perovskites exhibiting colossal magnetoresistance (CMR) have attracted great attention in recent years.<sup>1,2</sup> Since in manganites the ferromagnetism (FM) is correlated with the metallic properties and CMR effect, the origin of FM and the possibility to control it are of profound interest. The FM and metal-like behavior occurring in hole-doped manganites results usually from a substitution of La sites, by divalent ions such as  $\text{Ca}^{2+}$  or  $\text{Sr}^{2+}$ , in the undoped parent compound  $\text{LaMnO}_3$  being an antiferromagnetic (AFM) insulator.

It is commonly accepted that double-exchange<sup>3</sup> interactions between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions are responsible for ferromagnetism in the metallic phase of highly doped manganites. For low-doped compositions, the superexchange interaction between the  $\text{Mn}^{3+}$  ions is responsible for the appearance of FM and/or AFM insulating phases. For the latter, the Jahn-Teller (JT) coupling plays an important role leading to the orbital ordering of  $\text{Mn}^{3+}$  ions and determining also the sign of exchange coupling in accordance with degree of static deformation of the  $\text{MnO}_6$  octahedra.<sup>4</sup> The magnetic phase separation occurs with increasing doping, as a result of competition between different kinds of interactions in the system, leading to a mixed AFM-FM ground state.

The scenario above describes also the behavior of so-called self-doped  $\text{La}_{1-x}\text{Mn}_{1-x}\text{O}_3$  compounds in which the hole concentration is controlled by the nonstoichiometry of La and Mn ions.<sup>5,6</sup> In the conventional nomenclature the formula  $\text{LaMnO}_{3+\delta}$  with  $\delta\sim 3x$  replaces the formula  $\text{La}_{1-x}\text{Mn}_{1-x}\text{O}_3$  and is commonly used, although that one

indicating a cation deficiency is more accurate.<sup>7</sup> With increasing oxygen excess (in reality, it corresponds rather to an increase of the cation deficiency in the sample), the FM insulating phase appears in  $\text{LaMnO}_{3+\delta}$  followed by evolution to the dominant FM metallic phase. These changes give evidence of direct correlation between magnetic and structural properties; namely, the magnetic behavior of the system evolves from AFM to FM with a reduction of JT distortion in the  $\text{MnO}_4$  plane when structure symmetry changes from the orthorhombic to the rhombohedral.<sup>8-11</sup>

The cooperative JT distortion can be suppressed in  $\text{LaMnO}_3$  in several ways: (1) by substitution of the  $\text{La}^{3+}$  by divalent ion, (2) providing the above-described self-doping, and (3) applying a hydrostatic pressure. Recently, it was observed using synchrotron x-ray diffraction that the JT distortion is continuously reduced with increasing pressure leading to complete suppression of the orbital order above 180 kbar.<sup>12</sup> This effect originates from strongly anisotropic compressibility of the lattice, allowing transformation of the distorted  $\text{MnO}_6$  octahedron to a regular one at the pressure of about 180 kbar. For comparison, in low-doped  $\text{La}_{0.78}\text{Ca}_{0.22}\text{MnO}_3$  crystals, in which the JT distortion is already significantly reduced by doping, the orbital ordering is entirely suppressed above 14 kbar.<sup>13</sup>

Since both pressure and doping effects tend to reduce the distortion of the  $\text{MnO}_6$  octahedra, it is expected that the pressure will enhance the ferromagnetic exchange interactions in the same manner as it takes place for doping process. The present high-pressure study was performed with the goal to probe the mechanism of the evolution of ferromagnetic insulating state in  $\text{LaMnO}_{3+\delta}$  suggested in Refs. 8–10. The com-

position of the investigated sample is close to that for which the first-order transition between the distorted orthorhombic phase  $O'$  ( $c/\sqrt{2} < a < b$ ) and pseudocubic phase  $O$  ( $c/\sqrt{2} \sim a \sim b$ ) occurs with a jump in the unit-cell volume.<sup>14</sup> For this region of phase diagram, the magnetic ground state depends strongly on oxygen content because of the change of interplane exchange constant  $J_c$  from a negative to positive value, leading to the transition from the AFM to FM state.<sup>10</sup>

Until now, no systematic magnetic studies have been carried out on self-doped manganites under pressure. An earlier investigation of a pressure effect on transport properties of self-doped manganites has been performed only for highly doped  $\text{La}_{0.94}\text{Mn}_{0.98}\text{O}_3$  crystals ( $T_C \approx 220$  K) located in the carrier concentration–temperature phase diagram near the percolation threshold of the FM metallic phase, for which the double-exchange interactions play an essential role.<sup>15</sup> In the present paper, we report the pressure effects on magnetic order and anisotropy of low-doped  $\text{LaMnO}_{3.05}$  crystals ( $T_C \approx 120$  K) for which the superexchange mechanism is dominant. We focus our attention on the relation between the pressure-induced changes in ferromagnetic characteristics and deformation of the  $\text{MnO}_6$  octahedron in order to clarify the origin of the pressure effect in  $\text{LaMnO}_{3.05}$ .

## II. EXPERIMENT

Single crystals of  $\text{LaMnO}_{3+\delta}$  were grown using an improved electrochemical deposition method proposed by McCarroll, Ramanujachary, and Greenblatt.<sup>16</sup> A modification of the original method allowed us to obtain high-quality crystals with controlled oxygen nonstoichiometry in a wide range of content.<sup>17</sup> For the series of samples obtained, the structure symmetry changes, with increasing oxygen content, from highly distorted orthorhombic  $Pbnm$  symmetry to the rhombohedral  $R3c$  symmetry. The composition with lattice parameters  $a = 5.529$  Å,  $b = 5.572$  Å, and  $c = 7.756$  Å, located at the boundary between the distorted orthorhombic phase  $O'$  and pseudocubic phase  $O$ , was chosen for the high-pressure magnetic study. The sample studied had near-cubic shape of about 1.2 mm in size. The oxygen content in the sample was estimated to be close to the value of 3.05. This estimation is based on known dependences of both lattice parameters and  $T_C$  on oxygen excess  $\delta$ , given for the  $\text{LaMnO}_{3+\delta}$  system in Refs. 10 and 11.

The dc magnetization was measured using both the vibrating sample magnetometer (PAR 4500) and superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS5). Both field and temperature dependences of magnetization for the direction of magnetic field applied along principal crystallographic axes, as well as the angular dependences of magnetization in main crystallographic planes at several temperatures below  $T_C$ , were measured.

Measurements under hydrostatic pressure up to 12 kbar were performed in the temperature range 4.2–160 K at the magnetic field up to 16 kOe using the vibrating sample magnetometer. For these measurements a miniature container of CuBe with an inner diameter of 1.42 mm was used as a pressure cell and a mixture of mineral oil and kerosene was

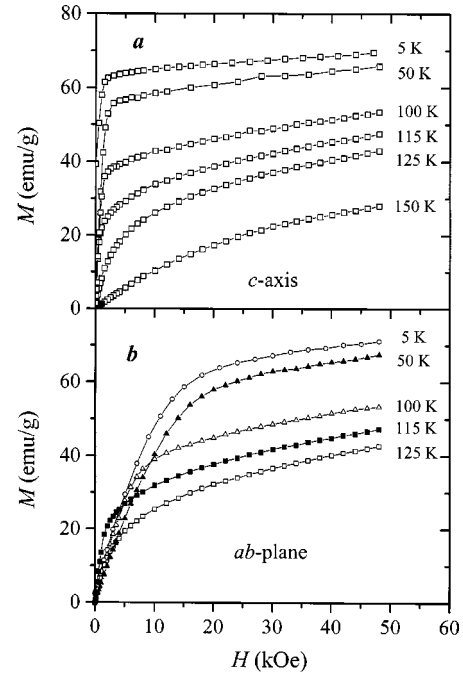


FIG. 1. The field dependence of magnetization of  $\text{LaMnO}_{3.05}$  crystals at various temperatures (a) along the  $c$  axis and (b) in the  $ab$  plane. Measurements were performed at decreasing magnetic field.

used as a pressure-transmitting medium.<sup>18</sup> The pressure at low temperatures was determined using the pressure dependence of the superconducting transition temperature of the pure Sn probe placed near the sample.

## III. RESULTS AND DISCUSSION

The field dependence of the magnetization measured at various temperatures along the  $c$  axis and in the  $ab$  plane is presented in Fig. 1. The magnetization curves obtained demonstrate the appearance of the ferromagnetic moment at temperatures below 125 K. It was found that the  $c$  axis is an easy magnetization axis. The magnetization in the  $ab$  plane (hard plane) was found to be almost independent of the field direction.  $M(H)$  does not saturate up to 50 kOe and  $M$  is by 30% less in magnitude than the theoretical spin-only value of  $3.8\mu_B/\text{Mn}$  site. The results obtained suggest the existence of a substantial amount of the AFM phase coexisting along with the dominant FM phase in the  $\text{LaMnO}_{3.05}$  sample. Another indication of the existence of the AFM phase is a nonmonotonic change in initial slope of  $M(H)$  with temperature seen in Fig. 1(b). The AFM feature is clearly evident by a shift of the maximum in the  $M(T)$  dependence in the  $ab$  plane, to lower temperatures, with increasing  $H$ , whereas the  $M(T)$  measured along the  $c$  axis is monotonic (see Fig. 2). A maximum in  $M(T)$  attributed to the AFM structure is masked at low temperatures by another anomaly in magnetization, i.e., the pronounced change in the  $M(T)$  slope around 60 K, which is better labeled at higher fields (see inset in Fig. 2). The latter probably originates from a cluster-glass or superparamagnetic like behavior usually observed for mixed

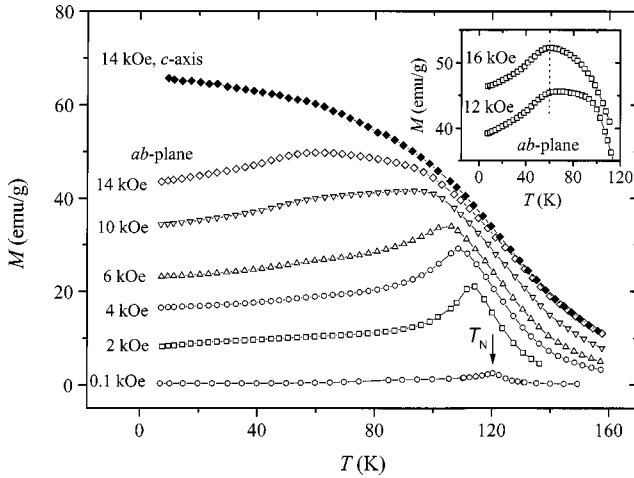


FIG. 2. The temperature dependence of zero-field-cooled magnetization of  $\text{LaMnO}_{3.05}$  at various magnetic fields applied in the  $ab$  plane (open symbols) and along the  $c$  axis (solid symbols). Inset demonstrates anomaly in the magnetization around 60 K.

AFM-FM low-doped manganites.<sup>19</sup> This phase-separated state manifests itself at low temperatures by a marked difference between zero-field-cooled and field-cooled magnetization (see Fig. 3).

The above-mentioned AFM and FM features are clearly exhibited for  $\text{LaMnO}_{3.05}$  in the temperature dependence of low-field magnetization, both zero-field-cooled ( $M_{ZFC}$ ) and field-cooled ( $M_{FC}$ ), measured at ambient pressure and under pressure of 9.8 kbar, presented in Fig. 3. The  $M(T)$  curves reveal a two-step magnetic ordering: the first step corresponds to the ferromagnetic transition at  $T_C$  determined by a maximal slope in  $M(T)$ , and the second one corresponds to

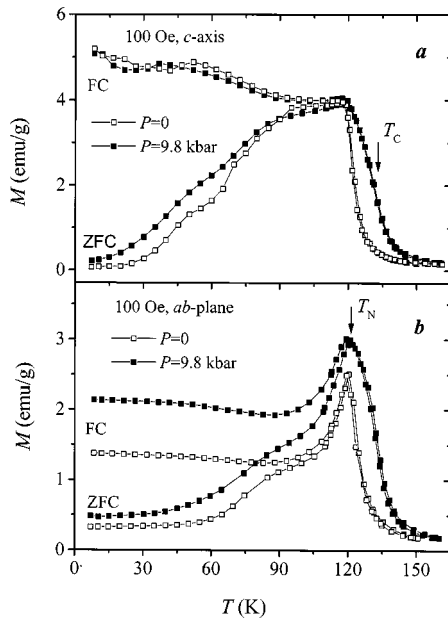


FIG. 3. Zero-field-cooled and field-cooled magnetization ( $M_{ZFC}$ ,  $M_{FC}$ ) of  $\text{LaMnO}_{3.05}$  single crystals measured at 100 Oe applied (a) along the  $c$  axis and (b) in the  $ab$  plane at ambient pressure (open symbols) and at 9.8 kbar pressure (solid symbols).

AFM ordering at slightly lower temperature  $T_N$  assigned by a sharp peak in magnetization measured in the  $ab$  plane (see lower panel of Fig. 3). The latter is in accordance with the fact that AFM ordering in the parent compound  $\text{LaMnO}_3$  occurs along the  $b$  axis.<sup>20</sup> Measurements performed at several pressures show that both Curie and Néel temperatures increase linearly with applied pressure with quite different pressure coefficients:  $dT_C/dP=0.8$  K/kbar and  $dT_N/dP=0.16$  K/kbar. As a result, at higher pressure the two-step character of magnetic ordering becomes more pronounced and at 9.8 kbar,  $T_C$  and  $T_N$  are distinctly separated by 10 K as shown in Fig. 3. Magnetization measurements allow us to distinguish two transition temperatures because of the sufficiently large fraction of the AFM phase in the sample. Our results are in good agreement with data of De Renzi *et al.*,<sup>21</sup> who detected in muon-spin-rotation experiments the phase separation in self-doped  $\text{LaMnO}_{3.05}$ , in the temperature range between a higher transition temperature  $T_C$  and a lower one  $T_N$ .

The main feature of pressure effect in  $\text{LaMnO}_{3.05}$  is an enhancement of ferromagnetic interactions while the AFM phase characteristics only slightly depends on pressure. The value of  $dT_C/dP=0.8$  K/kbar obtained is between values of 0.3 and  $\sim 1.5$  K/kbar observed recently for insulating ferromagnetic crystals  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $x=0.18, 0.2, 0.22$ ), respectively, with the level of doping close to the percolation threshold.<sup>22,23</sup> The nature of the pressure dependence  $T_C(P)$  will be discussed later. However, at first, we would like to comment why  $T_N$  is quite insensitive to applied pressure. For the parent compound  $\text{LaMnO}_3$  the value of the pressure coefficient  $dT_N/dP=0.72$  K/kbar was reported by Zhou and Goodenough.<sup>24</sup> A monotonic decrease of the pressure coefficient  $dT_N/dP$  for cation-deficient  $\text{La}_{1-x}\text{MnO}_3$  single crystals, with increasing self-doping, from 0.68 K/kbar for  $x=0.01$  to 0.33 K/kbar for  $x=0.13$  was observed by us very recently.<sup>25</sup> This decrease was explained within a framework of the model of the two coexisting AFM and FM phases coupled through superexchange at their interface, proposed by Muroi and Street.<sup>11</sup> The FM cluster cants the surrounding spins in the AFM matrix because of an interface superexchange interactions, leading to a weakening of the AFM interactions in the hole-free phase. A weakening of the AFM interactions with increasing doping in  $\text{LaMnO}_{3+\delta}$  was observed experimentally using neutron diffraction by Ritter *et al.*<sup>8</sup> The mechanism above becomes more important with increasing volume fraction of the FM phase, resulting in a decrease of  $dT_N/dP$  value with increasing self-doping. Our present value of  $dT_N/dP=0.16$  K/kbar, obtained for  $\text{LaMnO}_{3.05}$  crystals with a higher level of self-doping in comparison with  $\text{La}_{1-x}\text{MnO}_3$  crystals<sup>25</sup> having a predominant AFM phase, agrees well with the observed trend in  $dT_N/dP$  versus doping.<sup>25</sup>

It is shown in Fig. 3(b) that  $M_{FC}$  measured in the  $ab$  plane increases under pressure, indicating a reduction in magnetic anisotropy. Additionally, the magnetic anisotropy was studied by measurements of angular dependences of magnetization  $M(\theta)$  in the  $ac$  plane at several temperatures below  $T_C$  at a magnetic field of 10 kOe, presented in Fig. 4(a). All

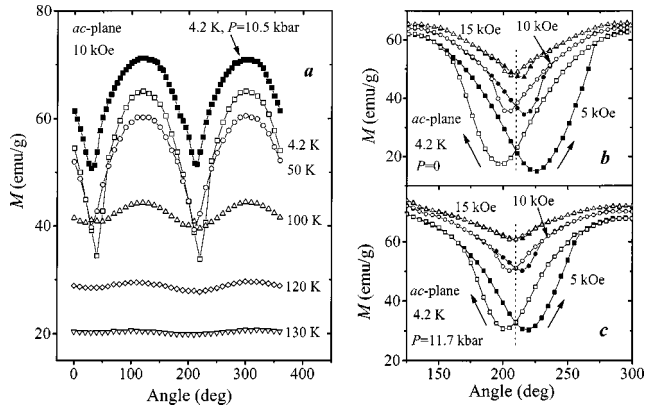


FIG. 4. The angular dependence of the magnetization  $M(\theta)$  of  $\text{LaMnO}_{3.05}$  single crystal in the  $ac$  plane: (a) at an applied magnetic field of 10 kOe and at ambient pressure (open symbols) and at 10.5 kbar (solid symbols), (b) irreversibility in  $M(\theta)$  observed at reversing directions of angle variation (indicated by arrows) around the hard magnetization direction at various applied magnetic fields and at ambient pressure, and (c) the same at 11.7 kbar pressure.

$M(\theta)$  curves show a twofold symmetry (i.e., two maxima of magnetization occur in the range  $0^\circ < \theta < 360^\circ$ ), suggesting a uniaxial anisotropy of the form  $K \sin 2\theta$ , where  $K$  is an anisotropy constant and  $\theta$  is the angle between the magnetic field  $H$  and the easy magnetization axis. A similar uniaxial anisotropy has been observed recently for several FM crystals  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  with  $x=0.18, 0.2, 0.22$  (Refs. 22 and 23) as well as for heavily doped  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (Ref. 26) single crystals. Therefore we suppose that it is a common behavior for doped manganites. It is commonly accepted that the single-ion anisotropy resulting from both the spin-orbit coupling and splitting of the ground state of  $\text{Mn}^{3+}$  in a crystal field is the most important contribution to the magnetocrystalline anisotropy in  $\text{LaMnO}_3$ .<sup>8,20,27</sup> As proposed by Matsumoto,<sup>20</sup> the single-ion anisotropy constant  $D$  changes sign and becomes negative when the distortion of  $\text{MnO}_6$  octahedra is sufficiently reduced with increasing doping. The negative value of  $D$  is responsible for the easy-axis anisotropy. This is the only one reasonable explanation of the observed type of anisotropy in doped manganites.

In Fig. 4(a) we show that the magnetic anisotropy decreases significantly with increasing pressure, by about 30% under pressure of 10.5 kbar as compared to ambient pressure values. A reduction of anisotropy could be attributed mainly to the following two factors: (i) the JT distortion of  $\text{MnO}_6$  octahedra is suppressed by pressure,<sup>12</sup> and (ii) the applied pressure enlarges the volume fraction of the more isotropic FM phase at the expense of the strongly anisotropic AFM phase.

Figure 4(b) shows a remarkable hysteresis of the magnetization when the magnetic field direction is changed from the easy axis to the hard magnetization direction. It appears that the magnetization is outstripped by the direction of magnetic field, resulting in a metastable state in a limited region around the hard direction where the magnetization is thermodynamically unstable. The increase of both the magnetic field and the applied pressure suppress gradually hysteresis

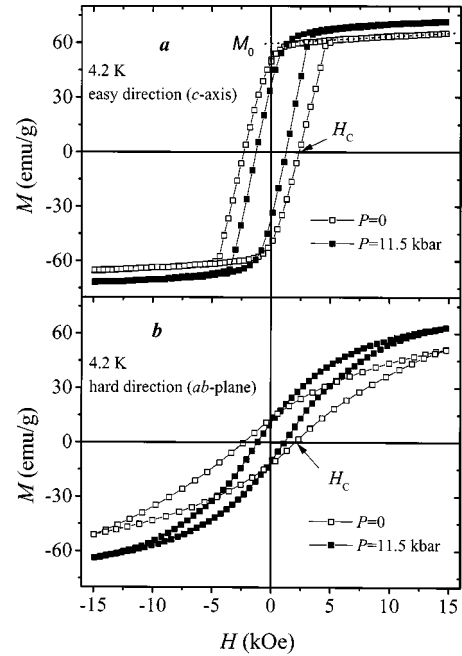


FIG. 5. Hysteresis loops of the magnetization of  $\text{LaMnO}_{3.05}$  single crystals at 4.2 K for both (a) easy and (b) hard magnetization directions at ambient pressure (open symbols) and at 11.5 kbar (solid symbols).

in  $M(\theta)$  [see Figs. 4(b) and 4(c)]. This behavior reflects a competition between magnetic field and coercivity in the sample. The coercivity, originating from the phase separation and determined essentially by the crystalline anisotropy of the AFM clusters as proposed by Muroi and Street,<sup>11</sup> is believed to be responsible for the hysteretic phenomena. The phase-separation model is able to explain our results, i.e., the decrease of coercivity with pressure due to the reduction of anisotropy and increase of the FM phase volume fraction. Diminishing of the coercivity under pressure is clearly demonstrated by hysteresis loops of the magnetization  $M(H)$  taken at 4.2 K for both easy and hard directions at ambient pressure and at 11.5 kbar pressure, shown in Fig. 5. The spontaneous magnetization  $M_0$  was determined by a linear extrapolation of the high-field magnetization for the easy direction to  $H=0$  (see upper panel) and the coercive field  $H_C$  was taken at zero magnetization as indicated by arrows.

The low-temperature hysteresis loop exhibits several features of the pressure effect on  $\text{LaMnO}_{3.05}$ : (i) the magnetic anisotropy decreases markedly under pressure being reflected in significant changes in magnetization loop for hard direction (lower panel); (ii) the spontaneous magnetization increases linearly with  $dM_0/dP=0.022\mu_B/\text{kbar}$ , indicating the increase of the FM phase volume fraction; (iii) the coercive field  $H_C$  decreases linearly with  $dH_C/dP=-0.1\text{ kOe/kbar}$ . The obtained pressure dependences  $H_C(P)$  and  $M_0(P)$  together with  $T_C(P)$  and  $T_N(P)$  data are collected in Fig. 6. The main conclusion following from Fig. 6 is that the ferromagnetism is enhanced in  $\text{LaMnO}_{3.05}$  with contraction of the unit cell under pressure. Qualitatively, a similar enhancement of FM is observed in the series

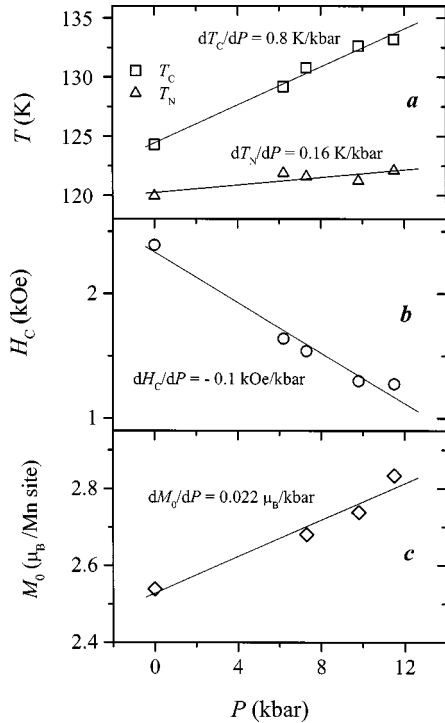


FIG. 6. Pressure dependences of (a) the Curie and Néel temperatures,  $T_C$  and  $T_N$ , (b) coercive field  $H_C$ , and (c) spontaneous magnetization  $M_0$  for  $\text{LaMnO}_{3.05}$  crystals. The lines present the linear fit.

of  $\text{LaMnO}_{3+\delta}$  when the unit cell contracts with increasing  $\delta$ .<sup>10,11</sup>

Comparing two effects of applied pressure and of progressive doping, we emphasize beforehand that similarity in magnetic behavior does not correlate with changes in the unit-cell volume, but it appears as a consequence of the crystallographic anisotropy of the  $\text{LaMnO}_3$  lattice. In the following we will show that both applied pressure and progressive doping and self-doping promote the FM enhancement in a similar way, through reduction of the distortion of the  $\text{MnO}_6$  octahedra. We focus on the mechanism that can explain the pressure effect on  $\text{LaMnO}_{3.05}$  presented in Fig. 6 and correlate our data with structural and magnetic data obtained for  $\text{LaMnO}_{3+\delta}$  series by several authors.

Solovyev *et al.*<sup>4</sup> have shown, by using the local-spin-density approximation (LSDA), that the cooperative JT distortion strongly affects magnetocrystalline anisotropy and superexchange interactions in the  $\text{LaMnO}_3$ . The polarization of  $d$  orbitals in the  $ab$  plane, induced by the JT distortion, suppresses strongly the ferromagnetic contribution to the interplane exchange coupling  $J_c$  and has an insignificant effect on the intraplane coupling  $J_{ab}$ .<sup>4</sup> As a consequence,  $J_c$  changes its sign while  $J_{ab}$  remains positive with increasing local tetragonal distortion of the lattice when the parameter  $R=l/s$  varies from 1 to 1.13 (here,  $l$  and  $s$  are the long and the short Mn-O bond lengths in the  $\text{MnO}_6$  octahedron). It should be mentioned that the parameter  $R$  can be used as a rough measure of the strength of JT distortion, with the value of 1.13 corresponding to undoped  $\text{LaMnO}_3$  being large enough to stabilize the  $A$ -type AFM ordering.<sup>4</sup> This scenario

was reproduced experimentally by Prado *et al.*<sup>10</sup> for  $\text{LaMnO}_{3+\delta}$ : with decreasing tetragonal distortion caused by the increase of oxygen content,  $J_c$  changes its sign for  $R=1.07$ , leading to a transition from the AFM to FM ground state. The transition is extended over the range  $1.03 < R < 1.07$ , where a highly frustrated or mixed AFM-FM state occurs.

For the sample studied, Mn-O bond lengths in the  $ab$  plane,  $l=2.016$  Å and  $s=1.927$  Å, are calculated from the lattice parameter data according to relationships between Mn-O distances and lattice parameters presented in Ref. 10. The value of  $R=1.046$  is in the range where the transition from AFM to FM state is expected to evolve. In this range the magnetic properties are the most sensitive to  $R$  variation in accordance with above-discussed mechanism of interplay between the superexchange and JT distortion.<sup>4</sup>

Now, we discuss how the parameter  $R$  varies with applied pressure and, on the other hand, with increasing self-doping in the  $\text{LaMnO}_{3+\delta}$  system. Detailed information about the pressure dependences of the lattice parameters and all three Mn-O distances of the distorted  $\text{MnO}_6$  octahedra was obtained for  $\text{LaMnO}_3$  in a recent x-ray diffraction study by Loa *et al.*<sup>12</sup> Owing to strongly anisotropic compressibility with the soft direction along the longest axis in the  $ab$  plane, the long Mn-O bond contracts with pressure much more than the short bond:  $dl/dP = -1.5 \times 10^{-3}$  Å kbar<sup>-1</sup> and  $ds/dP = -10^{-4}$  Å kbar<sup>-1</sup> (the values are derived from the data presented in Fig. 2 of Ref. 12). This suggests a linear decrease of the JT distortion with pressure,  $dR/dP = -7.25 \times 10^{-4}$  kbar<sup>-1</sup>. Therefore, the  $\text{MnO}_6$  octahedra are expected to be regular in pure  $\text{LaMnO}_3$  at 180 kbar and in doped  $\text{LaMnO}_{3.05}$  crystals at a much lower pressure of about 60 kbar due to the smaller initial value of  $R=1.046$ .

Information about the deformation of  $\text{MnO}_6$  octahedra with increasing oxygen excess in  $\text{LaMnO}_{3+\delta}$  can be derived from structural data presented in Ref. 10 (see Fig. 2 therein). The linear fit of Mn-O distances versus  $\delta$  within the range  $3.05 < \delta < 3.09$  related to the pseudocubic phase gives the following coefficients:  $dl/d\delta = -1.946$  Å,  $ds/d\delta = +0.76$  Å, and  $dR/d\delta = -1.43$ .

Assuming that the JT distortion plays a crucial role in the formation of the magnetic ground state of  $\text{LaMnO}_{3+\delta}$ , let us compare the change of  $T_C$  associated with the same change of  $R$  caused by different effects. For the pressure data, the slope of  $T_C$  vs  $R$  can be calculated using the value of  $dT_C/dP = 0.8$  K/kbar obtained for  $\text{LaMnO}_{3.05}$  [see Fig. 6(a)] and the value of  $dR/dP = -7.25 \times 10^{-4}$  kbar<sup>-1</sup> estimated above, so  $dT_C/dR = (dT_C/dP)/(dR/dP) = -1100$  K. On the other hand, this quantity can be calculated from the data obtained for the  $\text{LaMnO}_{3+\delta}$  system with variations of  $\delta$ , taking into account the estimation  $dT_C/d\delta = 1300$  K in the range  $3.05 < \delta < 3.09$  (Ref. 10):  $dT_C/dR = (dT_C/d\delta)/(dR/d\delta) = -910$  K. The values of  $dT_C/dR$  calculated from different independent data coincide within 20%, suggesting a universal dependence of  $T_C$  on the distortion parameter  $R$ :  $T_C$  increases with a reduction of  $R$  at the same rate irrespective of the way of diminishing  $\text{MnO}_6$  octahedra distortion. Therefore, we can regard  $R$  as a parameter

controlling the magnetic state of the  $\text{LaMnO}_{3+\delta}$  system around  $\delta \sim 0.05$ .

In contrast, the change in  $T_C$  normalized to the change in the unit-cell volume  $V$  appears to be much larger in the doping process as compared with those induced by pressure. Similar calculations with regard to the compressibility  $dV/dP = -5.2 \times 10^{-2} \text{ \AA}^3 \text{ kbar}^{-1}$  (Ref. 12) and the linear dependence between  $V$  vs  $\delta$  with  $dV/d\delta = -13.7 \text{ \AA}^3$  (Ref. 10) show that  $dT_C/dV$  differs by a factor of about 6 for both effects. Such a large difference agrees with more anisotropic contraction of the unit cell in the case of oxygen doping, with a consequent  $\sim 8$  times larger value of  $dR/dV$  compared with an estimation from pressure data. These facts again support a concept of the common mechanism responsible for the enhanced ferromagnetism in both effects that involve the reduction of the  $\text{MnO}_6$  distortion.

Further insight into the nature of pressure-enhanced ferromagnetism in  $\text{LaMnO}_{3.05}$  is gained from comparison of both coercive field  $H_C$  and spontaneous magnetization  $M_0$  data under pressure and at variation of  $\delta$ . The analysis shows that values of  $dH_C/dR$  calculated as  $(dH_C/dP)/(dR/dP)$  and as  $(dH_C/d\delta)/(dR/d\delta)$ , are 140 and 120 kOe, respectively. Also,  $dM_0/dR$  (calculated in a similar way from both pressure data and data obtained with a variation of  $\delta$ ) is equal to  $-30\mu_B$  and  $-37\mu_B$ , respectively. For these estimates, slopes  $dH_C/dP = -0.1 \text{ kOe/kbar}$  and  $dM_0/dP = 0.022\mu_B/\text{kbar}$  obtained for  $\text{LaMnO}_{3.05}$  (see Fig. 6) along with  $dH_C/d\delta = -171 \text{ kOe}$  and  $dM_0/d\delta = -53\mu_B$  derived from data presented in Ref. 11 are used. We stress again that while both  $dH_C/dR$  and  $dM_0/dR$  estimated for two various effects differ in magnitude by less than 20%, the corresponding values of  $dH_C/dV$  and  $dM_0/dV$  differ by a factor of 6–9. This similarity in magnetic behavior strongly suggests that the JT distortion is the most essential feature determining the magnetic ground state in  $\text{LaMnO}_{3.05}$ .

In addition, the effect of pressure on magnetic properties of  $\text{LaMnO}_{3.05}$  can be predicted quite well based on the data obtained at variation of  $\delta$  with regard to pressure-dependent structural data. Hence, the following pressure coefficients were calculated:  $(dT_C/dP)_{\text{calc}} = (dT_C/d\delta)/(dR/d\delta)/(dR/dP)$  equal to 0.66 K/kbar,  $(dH_C/dP)_{\text{calc}} = (dH_C/d\delta)/(dR/d\delta)/(dR/dP)$  equal to  $-0.087 \text{ kOe/kbar}$ , and  $(dM_0/dP)_{\text{calc}} = (dM_0/d\delta)/(dR/d\delta)/(dR/dP)$  equal to  $0.027\mu_B/\text{kbar}$ . All calculated values coincide within 20% of the experimental values presented in Fig. 6. The result above demonstrates remarkable agreement between various structural and magnetic data for the  $\text{LaMnO}_{3+\delta}$  series obtained by several authors.

Thus, we found that the changes in  $T_C$ ,  $H_C$ , and  $M_0$  normalized to the variation in the distortion of the  $\text{MnO}_6$  octahedra, i.e., to changes of the parameter  $R = l/s$ , are al-

most the same for both pressure and oxygen-doping effects. In contrast, changes of the same parameters normalized to the contraction of the unit-cell volume differ more than by a factor of 6. This gives compelling evidence that the evolution of the FM observed in  $\text{LaMnO}_{3.05}$  with increasing pressure is driven by a reduction of the  $\text{MnO}_6$  distortion.

It is worth noting that a very similar model of the suppression of JT distortions in the Ru-O octahedra under pressure leading to pressure-induced transition from the AFM insulating phase to FM metallic one was proposed recently by Snow *et al.* for ruthenates  $\text{Ca}_2\text{RuO}_4$  and  $\text{Ca}_3\text{Ru}_2\text{O}_7$ .<sup>28</sup> These octahedral distortions were found to stabilize an AFM insulating phase in ruthenates<sup>29</sup> in exactly the same manner as for  $\text{LaMnO}_3$  considered in Ref. 4.

#### IV. CONCLUSIONS

In summary, we have studied the effect of pressure on the magnetic order and the anisotropy of self-doped  $\text{LaMnO}_{3.05}$  crystals, which are located in the carrier concentration–temperature phase diagram at the boundary between the distorted orthorhombic phase and pseudocubic phase and exhibit two competing FM and AFM phases. It was found that applied hydrostatic pressure leads to an increase of both Curie and Néel temperatures and strongly suppresses magnetic anisotropy. The magnetic anisotropy in  $\text{LaMnO}_{3.05}$  was found to be of twofold symmetry with an easy magnetization axis aligned with the  $c$  axis.

Our results clearly indicate that applied pressure enhances ferromagnetism in  $\text{LaMnO}_{3.05}$ : the ferromagnetic interactions increase and the volume fraction of the FM phase increases at the expense of the AFM phase. Analysis involving comparison of our data with the effect of self-doping on magnetic and structural properties of  $\text{LaMnO}_{3+\delta}$  and based on pressure-dependent structural data reveals that the FM phase evolves with pressure due to a reduction of the JT distortion of the  $\text{MnO}_6$  octahedra. The changes in the FM characteristics such as  $T_C$ ,  $H_C$ , and  $M_0$  follow closely the contraction of the principal long Mn-O bond length. Moreover, almost the same dependence of those parameters on the degree of the  $\text{MnO}_6$  distortion holds for the  $\text{LaMnO}_{3+\delta}$  series with a  $\delta$  variation. This similarity strongly suggests that the pressure-induced suppression of the JT distortion is responsible for pressure-enhanced ferromagnetism in  $\text{LaMnO}_{3.05}$ .

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