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Pressure-tuned spin state and ferromagnetism in $La_{1-x}M_xCoO_3$ $(M=Ca,Sr)$

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Pressure effect on magnetic order and anisotropy of low-doped $La_{1-x}Ca_xCoO_3$ $(0.1 \leqslant x \leqslant 0.2)$ and $La_{1-x}Sr_xCoO_3$ $(0.1 \leqslant x \leqslant 0.3)$ single crystals and ceramics was studied by magnetization measurements. It was found that applied hydrostatic pressure leads to a quite different effect on ferromagnetic (FM) interactions in materials doped with ions of different size. For $La_{1-x}Ca_xCoO_3$, a remarkable suppression of FM interactions leading to a contraction of FM phase fraction was observed under pressure, in good agreement with reduction of effective paramagnetic moment μ_{eff} and already reported pressure-induced increase of electrical resistivity. The behavior may be explained by recently proposed mechanism of pressure-induced suppression of double exchange FM interactions in cobaltites, due to an increase of the energy of the crystal-field splitting $(t_{2g}-e_g)$, leading to a suppression of e_g-electron hopping. In strong contrast, an opposite pressure effect on ferromagnetism was found in $La_{1-x}Sr_xCoO_3$. It appears that pressure enhances visibly the FM interactions in the spin- or cluster-glass state as well as in the long-range FM state for $x=0.3$ but surprisingly the pressure coefficient dT_C/dP changes sign at the percolation threshold. The intricate behavior indicates on a competition of at least two different mechanisms on overall pressure effect in $La_{1-x}Sr_xCoO_3$ with an expanded unit cell caused by doping with a large size ion. In addition, in Sr-doped single crystals with developed long-range FM order, a drastic changes in magnetic anisotropy with pressure were observed at around 9 kbar, leading in the case of $La_{0.7}Sr_{0.3}CoO_3$ to nearly isotropic magnetization within the *ac* plane at $P>9$ kbar. The radical changes in the magnetic anisotropy suggest some kind of pressure-induced phase transition.

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I. INTRODUCTION

Doped cobaltite perovskites $La_{1-x}M_xCoO_3$ $(M=Ca,Sr,Ba)$, exhibiting such intriguing properties as large magnetoresistance[1,2] and enormous Hall effect,[3] have recently attracted much attention due to their unique feature to change the spin-state of the Co^{3+} ion.[4–13] The additional spin-state degree of freedom provides new physical effects, leading to unusual magnetic and transport properties as compared with those found in manganites. The spin-state of undoped $LaCoO_3$ exhibits a gradual crossover with increasing temperature from the low-spin (LS) state $(t^6_{2g}e^0_g;S=0)$ to the intermediate-spin (IS) state $(t^5_{2g}e^1_g;S=1)$ at around 100 K.[14,15] This results from the competition between comparable in magnitude the crystal-field with energy Δ_{CF} ($t_{2g}-e_g$ splitting) and the intraatomic (Hund) exchange with energy J_{ex}, leading to redistribution of electrons between t_{2g} and e_g levels. Since Δ_{CF} is found to be very sensitive to the variation in the Co-O bond length ($d_{Co—O}$), the subtle balance between Δ_{CF} and J_{ex} may be easy disrupted by different kind of effects such as hole-doping and chemical or external pressure.[16,17] Both, chemical pressure on CoO_6 octahedra, generated usually by decreasing the average La-site ionic radius $\langle r\rangle$, and external pressure lead to the insulating nonmagnetic LS state because Δ_{CF} strongly increases with decreasing the CoO_6 volume, causing depopulation of the magnetic e_g level. Pressure is expected to favor the population of the LS state since the ionic radius of LS Co^{3+} (0.685 Å) is smaller than that of IS Co^{3+} (0.717 Å) (Ref. 18) and the difference in ionic radius leads to lattice-volume expansion observed at the LS→IS transition.[16]

It is generally accepted that the ferromagnetism in hole-doped $La_{1-x}M_xCoO_3$ arises as a result of the double-exchange (DE) interaction between Co^{3+} and Co^{4+}, facilitating also the electrical conductance in the ferromagnetic metallic (FMM) phase. Similarly to the case of doped manganites, the ferromagnetic (FM) state evolves as a result of increasing doping level at low *x*, in the paramagnetic matrix of $LaCoO_3$ with dominant antiferromagnetic (AFM) superexchange interactions between Co^{3+} through a spin- or cluster-glass-state region.[19,20] The competition of different kinds of interactions leads to a highly inhomogeneous ground state exhibiting the coexistence of FM regions, spin-glass regions, and hole-poor LS regions.[21,22] However, the hole-doping effect on the transport and magnetic properties is more intricate in cobaltites as compared with that one in manganites because the DE mechanism involves the $t_{2g}-e_g$ energy, which is dependent on lattice parameters and crystal symmetry. Partly for this reason, orthorhombic $R_{0.5}Ca_{0.5}CoO_3$ $(R=La,Pr,Nd)$ with Δ_{CF} weakly dependent on the doping level, doped by smaller *M* ions do not achieve the metallic state and their ferromagnetic moment remains small, while the rhombohedral Sr- and Ba-doped compounds with larger unit cell and smaller Δ_{CF} become metallic with rather large FM moment.[5,9]

Due to strong dependence of Δ_{CF} on Co-O bond length, the pressure appears to be a unique tool for tuning the ferromagnetism in doped cobaltites by modifying the $t_{2g}-e_g$ energy splitting. Another important parameter, controlling the strength of DE interaction, is the Co-O-Co bond angle (θ), which is directly related to electronic transfer energy between Co atoms. While it is general feature of manganites that external pressure increases θ driving system to FMM state,[23] it is known that the value of the angle θ increases under pressure for rhombohedral $LaCoO_3$ (Ref. 18) but remains nearly constant for orthorhombic $P_{0.7}Ca_{0.3}CoO_3$.[24] It means that the structural response for the external pressure is less obvious in cobaltites. The pressure effect on transport and magnetic properties of cobaltites consists of two main competing effects of different origin. The already discussed mechanism related to increase of the $t_{2g}-e_g$ splitting strongly suppresses the electron hopping and consequently the ferromagnetic interactions and conductance. The latter is expected to favor ferromagnetism with increasing θ. Combining chemical and external pressure one can separate different physical mechanisms responsible for ferromagnetism in $La_{1-x}M_xCoO_3$ and clarify if the DE interactions play an essential role on it. Although this issue is of significant interest there are only few pressure studies on transport and magnetic properties performed until now in $R_{1-x}Ca_xCoO_3$ (R=La,Pr,Nd) (Refs. 5,24) and in $La_{0.82}Sr_{0.18}CoO_3$.[17] The electrical resistivity was found to increase under pressure for all of the studied samples. For $La_{0.82}Sr_{0.18}CoO_3$, the reduction of Co magnetic moment and of T_C was observed simultaneously with the tendency to develop of an insulating state. This unusual behavior, which is opposite to that observed for manganites, reveals that the effect driven by increasing Δ_{CF}, leading to suppression of the electron hopping and ferromagnetic interactions, clearly dominates over the opposite effect caused by increasing the bond angle θ. Moreover, the correlation between Co magnetic moment and T_C, found for $La_{0.82}Sr_{0.18}CoO_3$ strongly suggests that the FM interactions depend on the crystal-field splitting Δ_{CF}, in compliance with specific DE mechanism.[17]

In order to clarify the intriguing origin of pressure effect and of interplay between the Co^{3+} spin-state degree of freedom and ferromagnetism, we report, in this paper, the results of magnetization measurements under pressure performed for $La_{1-x}Ca_xCoO_3$ and $La_{1-x}Sr_xCoO_3$ single crystals and ceramics with different doping level. While for Ca-doped materials, we observed the remarkable suppression of both magnetic moment in the FM state and T_C, in good agreement with the tendency to develop insulating state with increasing pressure,[5] more intricate pressure effect was found surprisingly in Sr-doped compounds. Namely, the enhancement of FM cluster phase at low doping and a drastic change in the anisotropy of long-range FM order, indicating a some kind of pressure-induced phase transition at higher doping level, were observed.

II. EXPERIMENTAL DETAILS

Single crystals of $La_{1-x}Ca_xCoO_3$ ($x=0.1;0.15$) and $La_{1-x}Sr_xCoO_3$ ($x=0.1;0.2;0.3$) were grown by a floating zone method using radiative heating under oxygen pressure of 1 bar with a typical growth rate of 1 mm/h. Crystals were found to be single phase (pseudocubic with slight rhombohedral distortions, space group $R\overline{3}c$), as confirmed by powder x-ray diffraction. The point Laue patterns indicated some twinning, usually observed for pseudocubic perovskites. Additionally, the polycrystalline samples of $La_{0.8}Ca_{0.2}CoO_3$ and of $La_{0.85}Sr_{0.15}CoO_3$ were prepared by a standard ceramic route. The polycrystal of $La_{0.8}Ca_{0.2}CoO_3$ was employed to extend the range of the investigation of Ca substituted samples since we were not able to grow single crystals of $La_{1-x}Ca_xCoO_3$ with well-fixed Ca-content for x as high as 0.2. Please note that, similar difficulties in the growth of single crystals with higher Ca-doping level were reported in Ref. 6. The polycrystal of $La_{0.85}Sr_{0.15}CoO_3$ was employed to verify if the measurements performed on polycrystalline materials provide an reliable data. The details of growing condition and sintering procedure including x-ray and neutron-diffraction data are presented elsewhere.[25–27]

Cylinder-shape samples with typical size of 1 mm in diameter and 4 mm in height were used for measurements of magnetization (M) under hydrostatic pressure (P) up to 12 kbar. All the magnetic measurements were performed in the temperature range 5–240 K at magnetic field up to 15 kOe using a PAR model 4500 Vibrating Sample Magnetometer. For these measurements a miniature container of CuBe with inside diameter of 1.42 mm was employed as a pressure cell[28] and a mixture of mineral oil and kerosene was used as a pressure-transmitting medium. The pressure at low temperatures was determined by the pressure dependence of the superconducting transition temperature of pure tin placed near the sample.

Temperature and field dependences of magnetization $M(T)$ and $M(H)$ at ambient pressure and various values of P were measured for each of the studied samples. For single crystalline samples, the angular dependences of magnetization in the *ac* plane at low temperatures were determined for each fixed value of P. Later on the $M(T)$ and $M(H)$ measurements were performed for the direction of easy axis of magnetization in the *ac* plane. In this way, magnetic-field orientation was fixed in the measurements of $M(T)$ and of $M(H)$ dependences with various pressures, what was important for correct interpretation of magnetization changes in cobaltites with rather strong magnetic anisotropy.

III. RESULTS AND DISCUSSION

$La_{1-x}Ca_xCoO_3$. Figures 1 and 2 present the pressure effect on magnetic order in low doped single crystals ($x=0.1$ and $x=0.15$) by zero-field-cooled (ZFC) and field-cooled (FC) magnetization vs temperature measured at $H=100$ Oe and by FC hysteresis loops of magnetization at low temperatures. All of the $M(T)$ and $M(H)$ curves presented are taken at the direction of easy axis of magnetization, determined previously from the angular dependence of magnetization in the *ac* plane (not shown). Both compounds exhibit an inhomogeneous magnetic ground state (FM clusters embedded into a paramagnetic matrix), which manifests itself at low temperatures by a pronounced divergence of ZFC and FC $M(T)$ curves. In addition, the $M(H)$ curves show the spontaneous

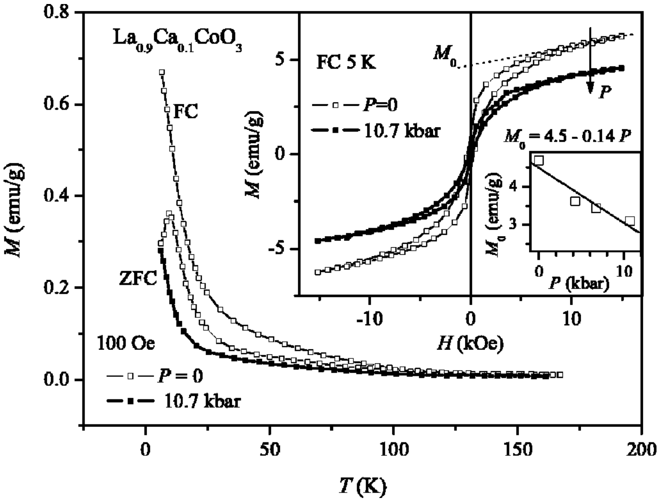

FIG. 1. Temperature dependence of M_{ZFC} and M_{FC} for $La_{0.9}Ca_{0.1}CoO_3$ single crystal measured at 100 Oe in the *ac* plane at ambient pressure and under 10.7 kbar (under pressure M_{FC} only is presented). Insets show the hysteresis loops of magnetization at $T=5$ K at ambient pressure and at 10.7 kbar and a variation of M_0 with pressure.

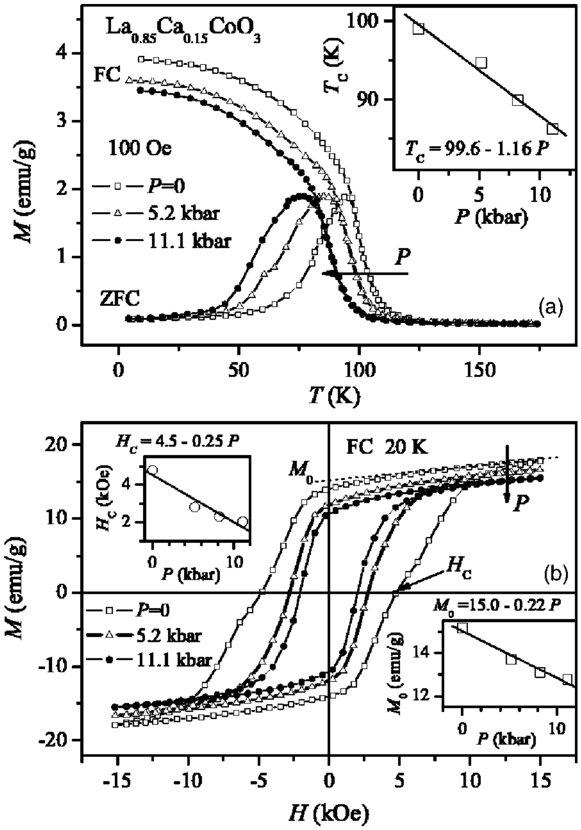

FIG. 2. (a) The temperature dependence of M_{ZFC} and M_{FC} for $La_{0.85}Ca_{0.15}CoO_3$ single crystal measured at 100 Oe in the *ac* plane under various pressures. Inset shows a pressure dependence of the Curie temperature. (b) Hysteresis loops of the magnetization of $La_{0.85}Ca_{0.15}CoO_3$ at $T=20$ K under various pressures. Insets show a variation of the spontaneous moment M_0 and coercive field H_C with pressure.

FM moment (M_0) extracted by a linear extrapolation of $M(H)$ from high-field region to $H=0$. The ZFC-FC irreversibility below 100 K and the peak in ZFC magnetization both observed at ambient pressure in $La_{0.9}Ca_{0.1}CoO_3$ (see Fig. 1) have been attributed to the formation of a cluster-glass state.[25] The FM hole-rich clusters of small size with mobile phase boundaries are assumed to appear around the Ca ions as a result of the phase separation. It is shown in Fig. 1 that an applied pressure suppresses strongly this FM cluster phase, leading to the disappearance of the peak in M_{ZFC} and reduction in the spontaneous FM moment by 30% at 10.7 kbar. This behavior is opposite to that one typical for low doped manganites, where the FM cluster phase fraction enlarges with increasing pressure.

In addition to the appearance of FM cluster phase, the further doped $La_{0.85}Ca_{0.15}CoO_3$ demonstrates a sharp increase in M_{FC}, indicating ferromagnetism at temperatures below $T_C \approx 100$ K, see Fig. 2(a). The long-range FM phase has been recently identified by neutron diffraction[7] in $La_{1-x}Ca_xCoO_3$ and found to spread over significant fraction of the samples for $x > 0.1$. It is shown in Fig. 2 that an applied pressure decreases both the Curie temperature and spontaneous FM moment at 20 K for $La_{0.85}Ca_{0.15}CoO_3$ and the observed changes of T_C and of M_0 can be approximated by linear pressure dependence with the coefficients of $dT_C/dP = -1.16$ K/kbar and of $dM_0/dP = -0.22$ emu/g kbar for T_C and for M_0, respectively. This implies that the ferromagnetic interactions weaken and the FM phase volume fraction contracts gradually with increasing pressure.

The very similar negative value of pressure coefficient $dT_C/dP = -0.92$ K/kbar, was found for polycrystalline $La_{0.8}Ca_{0.2}CoO_3$ from $M(T)$ data presented for several pressures in Fig. 3(a). In addition to the ferromagnetic behavior similar to that observed for the $x=0.15$ sample, the $x=0.2$ composition exhibits additional transition below T_C, evidenced at 90 K by a pronounced hysteresis of low field $M_{FC}(T)$ taken upon cooling and warming, see ambient pressure data presented in Fig. 3(b). Most likely, this hysteretic behavior is associated with a first-order structural transition from rhombohedral $R\bar{3}c$ phase to orthorhombic *Pnma* phase, discovered very recently for $La_{0.8}Ca_{0.2}CoO_3$ in the neutron powder-diffraction measurements by Burley *et al.*[7] The temperature of $R\bar{3}c \rightarrow Pnma$ transition was found to increase dramatically from 0 to 300 K for Ca content of around $x=0.2$ when x increases by 0.03 only. Probably, due to a small deviation from stoichiometry our sample indicates the lower values of both T_C and structural transition temperature, as compared with those reported in Ref. 7.

We found that the hysteresis in $M_{FC}(T)$ shifts rapidly to low temperatures with increasing pressure and disappears above 5 kbar. This unequivocally implies that the orthorhombic phase collapses under pressure. The behavior is in agreement with the expectation that an external pressure acts in favor of the $R\bar{3}c$ phase with the unit-cell volume smaller at low temperatures as compared to that of the *Pnma* phase.[7] The latter unique feature of $La_{1-x}Ca_xCoO_3$ unit cell is directly related to the changes in the average Co^{3+} spin-state, as discussed in Ref. 7.

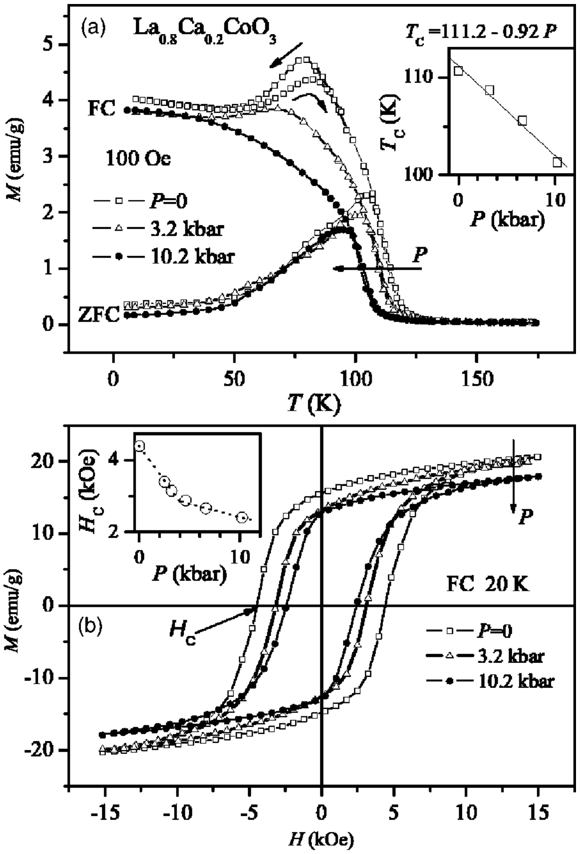

FIG. 3. (a) Temperature dependence of M_{ZFC} and M_{FC} for $La_{0.8}Ca_{0.2}CoO_3$ polycrystal measured at 100 Oe under various pressures. Arrows indicate both cooling and warming regimes for M_{FC} at ambient pressure. Inset shows a pressure dependence of the Curie temperature. (b) Hysteresis loops of the magnetization of $La_{0.8}Ca_{0.2}CoO_3$ at $T=20$ K under various pressures. Inset shows a variation of the coercive field H_C with pressure.

Additional evidences for the pressure-induced transition at low temperatures follow from the high-field magnetization data. The hysteresis loops $M(H)$ at 20 K, presented in Fig. 3(b), exhibit two features: (i) the high-field magnetization decreases with increasing pressure as expected but clearly in nonlinear way, in the contrast to behavior observed for $La_{0.85}Ca_{0.15}CoO_3$ single crystals; (ii) the coercive field H_C diminishes by about twice in the value under pressure of 10 kbar, and the $H_C(P)$ dependence demonstrates a distinct change in the slope around 5 kbar (see the inset), in contrast to the almost linear $H_C(P)$ dependence observed for $La_{0.85}Ca_{0.15}CoO_3$ [see the inset of Fig. 2(b)]. The former feature was examined more comprehensively by additional measurements of $M(T)$ in $H=15$ kOe, presented for various pressures in Fig. 4. It is seen that the magnetization decreases smoothly with increasing pressure, at temperatures above 80 K, and clearly indicates discontinuity at low temperatures. The pressure dependence $M(P)$ taken at 20 K demonstrates a gradual initial decrease and an abrupt drop in M by ≈10% at around 5 kbar (see the inset of Fig. 4). This jump in M at low temperature is a signature of the pressure-induced phase transition in $La_{0.8}Ca_{0.2}CoO_3$. We suggest that the sharp fall in M originates from a sudden change in the average Co^{3+} spin-state (by increase of the LS fraction in the sample) due to the contraction of unit-cell at the *Pnma* $\rightarrow R\bar{3}c$ transition.

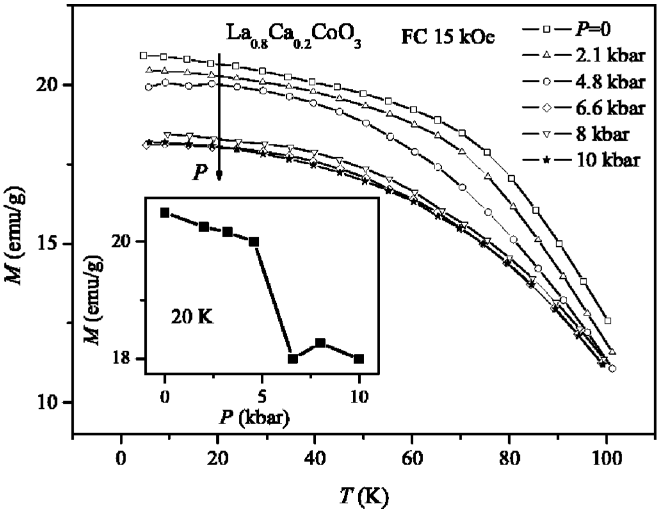

FIG. 4. Temperature dependence of M_{FC} for $La_{0.8}Ca_{0.2}CoO_3$ polycrystal measured at 15 kOe under various pressures. Inset shows a discontinuous change in M_{FC} with pressure at low temperature.

Further evidence for the origin of negative pressure effect on ferromagnetism in $La_{1-x}Ca_xCoO_3$ was obtained from investigation of the magnetic susceptibility in paramagnetic state. The $M(T)$ curves measured for single crystals with $x=0.1$ and $x=0.15$ at the temperatures above 100 K at $H=10$ kOe under various pressures are represented in Fig. 5(a) by the plots H/M vs temperature. The straight lines approximate a Curie-Weiss dependence $M/H=C/(T-\theta_W)$ with two independent parameters. The slope provides the value of Co effective paramagnetic moment μ_{eff} while the intercept yields the paramagnetic Curie temperature θ_W. For both crystals, an applied pressure shifts θ_W to low temperatures and increases the slope of $H/M(T)$. The latter corresponds to a reduction of μ_{eff} under pressure. The θ_W and μ_{eff} values determined, as described above, for several pressures are compared in Fig. 5(b) and Fig. 5(c) with the data obtained for Sr-doped compounds (see the second part of the chapter). It should be noted that at ambient pressure both θ_W and μ_{eff} values for $La_{0.85}Ca_{0.15}CoO_3$ agree within 10% with those reported for polycrystalline samples[7,4] while in the case of $La_{0.9}Ca_{0.1}CoO_3$ these parameters are distinctly lower, most likely because of the overestimation of Ca content in our crystal.

The negative value of pressure coefficient $d\theta_W/dP$ observed for both Ca-doped samples, comparable in the order of magnitude with that of dT_C/dP, confirms conclusion of the pressure-induced origin of the suppression of ferromagnetic interactions in $La_{1-x}Ca_xCoO_3$. With an assumption of DE ferromagnetic interactions, this behavior is in agreement with observed pressure-induced suppression of conductivity (i.e., electron hopping) in $La_{0.5}Ca_{0.5}CoO_3$.[5] The pressure dependence of $\mu_{eff}(P)$ with negative coefficient $d\mu_{eff}/dP<0$ [see Fig. 5(c)] gains insight into a nature of suppression of ferromagnetism in $La_{1-x}Ca_xCoO_3$. Observed remarkable re-

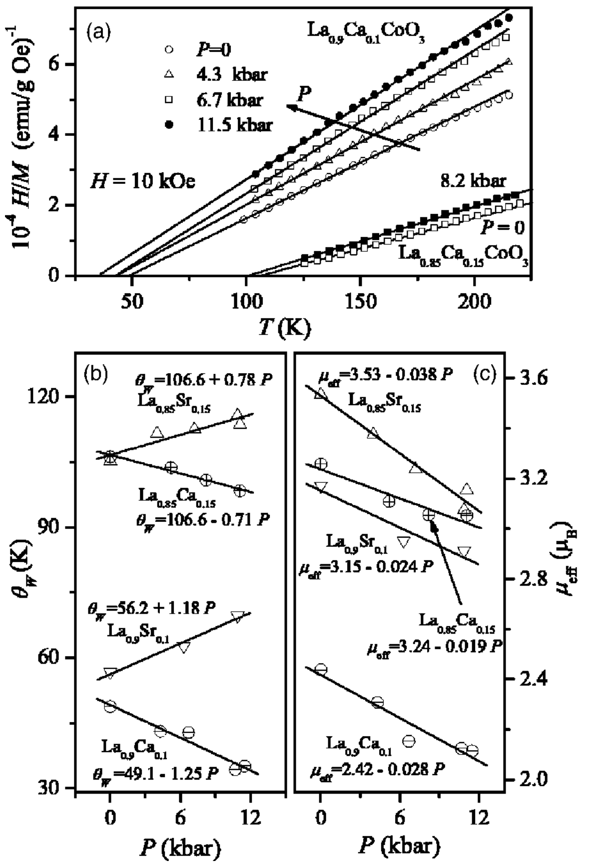

FIG. 5. (a) H/M vs temperature curves for $La_{0.9}Ca_{0.1}CoO_3$ and $La_{0.85}Ca_{0.15}CoO_3$ single crystals measured at 10 kOe under various pressures. Solid lines are a Curie-Weiss fit with two independent parameters θ_W and μ_{eff}. (b) Pressure dependences of paramagnetic Curie temperature θ_W for $La_{1-x}Ca_xCoO_3$ and $La_{1-x}Sr_xCoO_3$ with $x=0.1$; 0.15. (c) Pressure dependences of Co effective paramagnetic moment μ_{eff} for $La_{1-x}Ca_xCoO_3$ and $La_{1-x}Sr_xCoO_3$ with $x=0.1$; 0.15.

duction in the Co effective paramagnetic moment, $\mu_{eff}=g[S(S+1)]^{1/2}\mu_B$, suggests, within a simple spin-only picture ($g=2$), a considerable diminishing the effective spin S under pressure. This effect is attributed to an increase of the energy of the crystal-field splitting Δ_{CF} in accordance with global feature of cobaltites. As it was proposed in Ref. 17, such a pressure-induced increase of Δ_{CF} leads to a suppression of electron hopping of an e_g electrons and, consequently, to a decrease of DE FM interactions. This mechanism is dominant in $La_{1-x}Ca_xCoO_3$ as it is evidenced by good correlation between the $d\mu_{eff}/dP$ and dT_C/dP and/or $d\theta_W/dP$ data. The contribution to the pressure effect caused by variation of the Co-O-Co bond angle θ seems to be much smaller in Ca-doped cobaltites. In fact, a very insignificant change in θ under pressure of 20 kbar has been found in $P_{0.7}Ca_{0.3}CoO_3$ (Ref. 24) in contrast to the large increase of the Co-O-Co bond angle (by ≈10° at 40 kbar) in $LaCoO_3$.[18]

$La_{1-x}Sr_xCoO_3$. Figures 6 and 7 present the temperature and field dependences of magnetization measured under various pressures for $La_{0.9}Sr_{0.1}CoO_3$ single crystals and $La_{0.85}Sr_{0.15}CoO_3$ ceramics. For single-crystal sample the magnetization is taken along the easy axis in the *ac* plane of the crystal. Both low-doped samples are placed on the phase diagram carrier content-transition temperature far below the appearance of long-range FM phase and exhibit a mixed glassy and FM cluster state, evidenced at low temperatures by a marked divergence of ZFC and FC $M(T)$ curves and by an existence of a spontaneous FM moment. The common feature, which is evident from magnetization data, is that an applied pressure enhances the FM moment in both samples. The effect is more pronounced for the $x=0.1$ sample where both FC magnetization and FM moment at 20 K increase by about twice under pressure of 10 kbar. This behavior is strongly contrasted with discussed already the negative pressure effect on ferromagnetism in $La_{1-x}Ca_xCoO_3$. In order to verify the increase of FM moment with pressure, we have

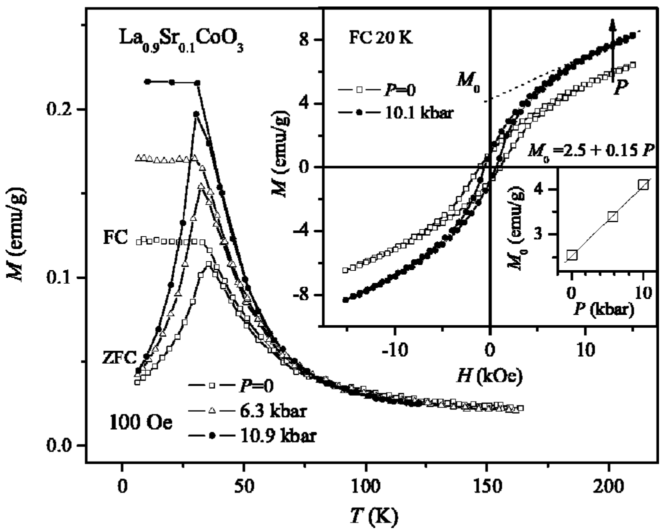

FIG. 6. Temperature dependence of M_{ZFC} and M_{FC} for $La_{0.9}Sr_{0.1}CoO_3$ single crystal measured at 100 Oe in the *ac* plane under various pressures. Insets show the hysteresis loops of magnetization at $T=20$ K at ambient pressure and at 10.1 kbar and a variation of M_0 with pressure.

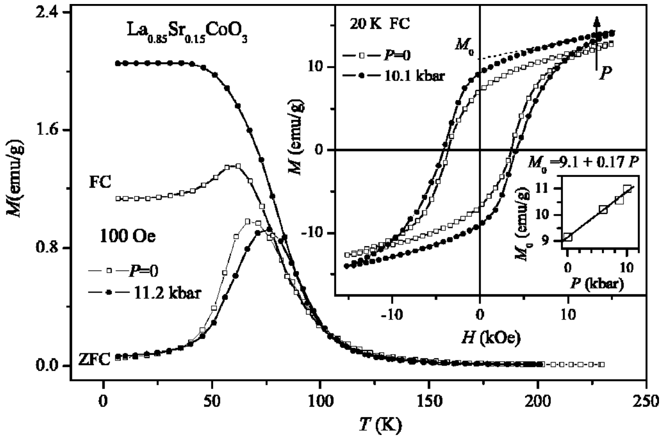

FIG. 7. Temperature dependence of M_{ZFC} and M_{FC} for $La_{0.85}Sr_{0.15}CoO_3$ polycrystal measured at 100 Oe at ambient pressure and under 11.2 kbar. Insets show the hysteresis loops of magnetization at $T=20$ K at ambient pressure and under 10.1 kbar and a variation of M_0 with pressure.

analyzed the paramagnetic phase properties for both $La_{0.9}Sr_{0.1}CoO_3$ and $La_{0.85}Sr_{0.15}CoO_3$. Results of fitting the Curie-Weiss parameters for $M(T)$ curves measured at 10 kOe under various pressures (not shown) were presented in Fig. 5(b) and Fig. 5(c). It appears that the paramagnetic Curie temperature θ_W increases noticeably with increasing pressure, suggesting an increase of ferromagnetic interactions. This is in good agreement with low-temperature magnetization data indicating the pressure-enhanced FM moment in low doped $La_{1-x}Sr_xCoO_3$. The $\theta_W(P)$ dependences presented in Fig. 5(b) directly demonstrate the opposite pressure effect on FM interactions in Ca- and Sr-doped cobaltites, suggesting different structural response for compounds doped with ions of different ionic radius. On the other hand, the pressure dependences of Co paramagnetic moment $\mu_{\text{eff}}(P)$ appear to be quite similar for compounds doped by Ca or Sr atoms with the values of pressure coefficient $d\mu_{\text{eff}}/dP < 0$ comparable in the magnitude, see Fig. 5(c). The latter quantity can be served as a rough measure of the rate of the increase of crystal-field splitting energy Δ_{CF} (or the rate of increase in the population of LS state) with increasing pressure in accordance with universal feature of cobaltites.

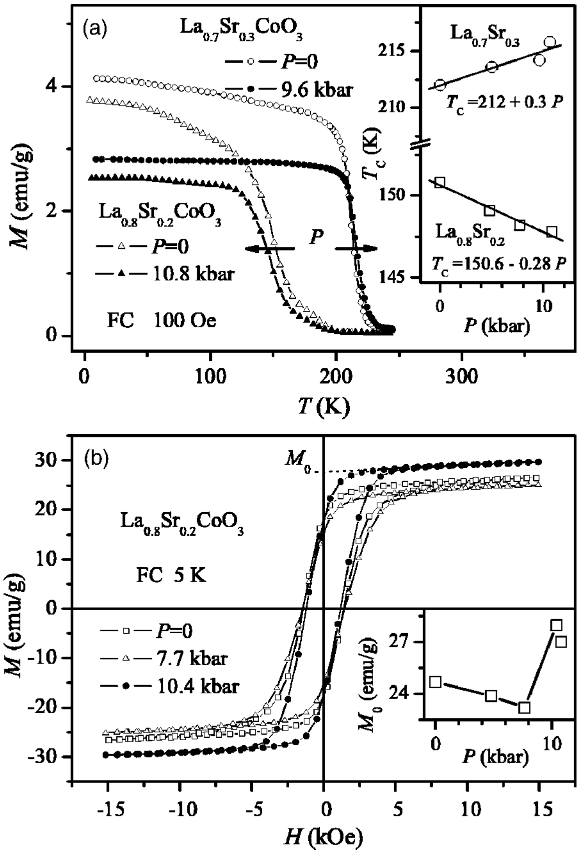

FIG. 8. (a) Temperature dependence of M_{ZFC} and M_{FC} for $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.7}Sr_{0.3}CoO_3$ single crystals measured in the *ac* plane at 100 Oe at ambient pressure and under 10.8 kbar and 9.6 kbar for the first and second crystal, respectively. Inset shows pressure dependences of the Curie temperature. (b) Hysteresis loops of the magnetization of $La_{0.8}Sr_{0.2}CoO_3$ at $T=5$ K under various pressures. Inset shows a nonmonotonic variation of M_0 with pressure.

The pressure-enhanced ferromagnetism in Sr-doped cobaltites appears to be in contradiction with recent observation of the pressure-induced suppression of ferromagnetism in $La_{0.82}Sr_{0.18}CoO_3$ single crystals.[17] In order to illuminate this confusion we have investigated additionally two higher-doped samples of $La_{1-x}Sr_xCoO_3$ single-crystals with expected long-range FM order. Figure 8(a) shows the temperature dependences of low-field FC magnetization measured along the easy axis of magnetization in the *ac* plane under ambient pressure ($P=0$) and under high pressure for both $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.7}Sr_{0.3}CoO_3$ single crystals. The $M(T)$ curves reveal a sharp rise in magnetization at T_C indicating on ferromagnetism. At $P=0$, T_C values determined by a maximal slope in $M(T)$ are in agreement with the data of phase diagram carrier concentration-transition temperature for $La_{1-x}Sr_xCoO_3$ (Ref. 6) and $T_C \approx 151$ K found by us for the $x=0.2$ sample is very close to that reported for $La_{0.82}Sr_{0.18}CoO_3$ single crystals in Ref. 17. It appears that T_C varies with pressure in different manner strikingly depending on doping level. The inset of Fig. 8(a) shows the linear dependences $T_C(P)$ obtained for $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.7}Sr_{0.3}CoO_3$ single crystals with pressure coefficients of opposite sign, $dT_C/dP \approx -0.28$ K/kbar and $dT_C/dP \approx +0.3$ K/kbar for the first and second crystal, respectively. It is notable that the value of dT_C/dP for our $x=0.2$ sample is close in the magnitude to that previously observed in the sample with $x=0.18$ (≈ -0.4 K/kbar), located near the transition to FM metallic state.[17] Hence, our results together with those of Ref. 17 suggest that an applied pressure suppresses ferromagnetism in the limited region of the phase diagram only, namely, at the percolation threshold, whereas the pressure generally enhances FM interactions in $La_{1-x}Sr_xCoO_3$ for both cluster-glass and long-range FM states. In addition, we found very recently the coefficient $dT_C/dP = +1.07$ K/kbar for $La_{0.5}Sr_{0.5}CoO_3$ (Ref. 29) exhibiting the essentially metallic FM state. Such complex dependence of pressure effect on doping level may originates from the competition of two different mechanisms discussed above. The change of the sign of pressure coefficient dT_C/dP may be a signature of first-order transition from localized to itinerant electron behavior, with discontinuous decrease in Co—O distance, occurring due to the bondlength fluctuations as proposed by Goodenough *et al.*[30] In fact, a discontinuous contraction of the Co-O distance was observed in $La_{1-x}Sr_xCoO_3$ at $x \approx 0.25$ by Mineshige *et al.*[11] Furthermore, an unusual compressibity of Co—O bond length is expected to appear at the localized-itinerant crossover due to the bond-length fluctuations and such effect leads to change of the sign of pressure coefficient of tolerance factor in perovskites.[30] We suggest that this is crucial factor, responsible for the negative pressure effect on ferromagnetic interactions in $La_{1-x}Sr_xCoO_3$ around $x \approx 0.2$, where the percolation threshold of FM clusters is reached and the insulator-metal transition occurs.

The sharp increase in dT_C/dP detected for $La_{1-x}Sr_xCoO_3$ in the vicinity of the insulator-metal transition is quite similar to that one observed recently in $La_{1-x}Ca_xMnO_3$ (Ref. 31) and in $Pr_{1-x}Sr_xMnO_3$ (Ref. 32) single crystals. The behavior was attributed to the different nature of magnetic interactions below and above the transition, namely, the DE interactions dominate in the metallic state being more sensitive to pressure than superexchange interactions dominating the magnetic and transport properties below the transition. We suggest that the above feature is inherent to doped perovskites exhibiting the insulator-metal transition.

In contrast to doping with larger Sr ion, doping with smaller Ca^{2+} ion increases the global structural distortion driving the system from rhombohedral to orthorhombic phase,[6,7] and accordingly the crystal-field splitting Δ_{CF} does not decrease significantly with doping. Therefore, the number of the e_g electrons does not increase substantially, the number of holes introduced into the t_{2g} orbitals increase only, and the insulator-metal transition is not accomplished in $La_{1-x}Ca_xCoO_3$ (even $La_{0.5}Ca_{0.5}CoO_3$ remains nearly metallic only).[5,6] For these reasons the DE mechanism does not work well in $La_{1-x}Ca_xCoO_3$ and the alternative mechanism of pressure-induced increase of the crystal-field splitting Δ_{CF} is dominant leading to a remarkable suppression of FM interactions under pressure over whole range of doping.

Figure 8(b) presents the hysteresis loops $M(H)$ of $La_{0.8}Sr_{0.2}CoO_3$ single crystals measured at 5 K along the easy axis in the *ac* plane under various pressures. $M(H)$ curves demonstrate a clearly nonmonotonic change of spontaneous FM moment M_0 with increasing pressure in the region of 11 kbar. In the inset of Fig. 8(b), it is shown that M_0 decreases gradually with increasing pressure up to pressure of 8 kbar and then sharply rises by about 20% in the magnitude around pressure of 9 kbar. Such an anomalous behavior in M_0 strongly suggests a pressure-induced phase transition in $La_{0.8}Sr_{0.2}CoO_3$. Studies of magnetic anisotropy in the *ac* plane as a function of applied pressure provide an additional insight into this subject. The pressure effect on the magnetic anisotropy of $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.7}Sr_{0.3}CoO_3$ single crystals is evidenced by angular dependences of magnetization $M(\varphi)$ measured in the *ac* plane at 5 K and at $H=15$ kOe under various pressures, as shown in Fig. 9. The $M(\varphi)$ curves reveal a twofold symmetry [i.e., two maxima of M occur in the full angular range $(0<\theta<360°)$] suggesting an easy-axis anisotropy in the *ac* plane. In addition, a minor anisotropy in magnetization was found in the *ab* plane signifying that the FM moment is directed along the *c* axis. A similar uniaxial anisotropy has been observed for several low doped manganites.[31,33] A picture of twofold symmetry is extensively distorted in the case of $La_{0.8}Sr_{0.2}CoO_3$ exhibiting the double-maxima most likely resulting from twinning effect [see Fig. 9(a)]. The main feature that demonstrates the evolution of $M(\varphi)$ with pressure is a strong suppression of magnetic anisotropy with increasing applied pressure for both crystals (see Fig. 9). These changes with pressure are clearly discontinuous: the anisotropy decreases slightly only up to pressure of 8 kbar and then suddenly drop down significantly. This behavior is exposed in the insets of Fig. 9 where the maximal M_{max} and minimal M_{min} values of magnetization at 15 kOe taken in orthogonal directions of the *ac* plane are shown as function of pressure. The pressure effect is more pronounced for $La_{0.7}Sr_{0.3}CoO_3$ with developed long-range FM order, where the magnetic anisotropy dramatically decreases in a very restricted region of pressure, leading to nearly isotropic magnetization within the *ac* plane at $P>9$ kbar. These radical changes in magnetic anisotropy around pressure of 9 kbar together with an anomalous behavior in spontaneous FM moment M_0 strongly suggest that some kind of a pressure-induced phase transition occurs in both $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.7}Sr_{0.3}CoO_3$ single crystals. However, no indication of the structural phase transition was found in $La_{0.82}Sr_{0.18}CoO_3$ single crystal with pressure varying up to 140 kbar despite the dramatic pressure-induced increase of electrical resistivity occurred.[17] Hence, the origin of the above-discussed pressure-induced changes in magnetization remains puzzling and further studies including various kinds of high-pressure measurements have to be carried out to clarify this unusual behavior.

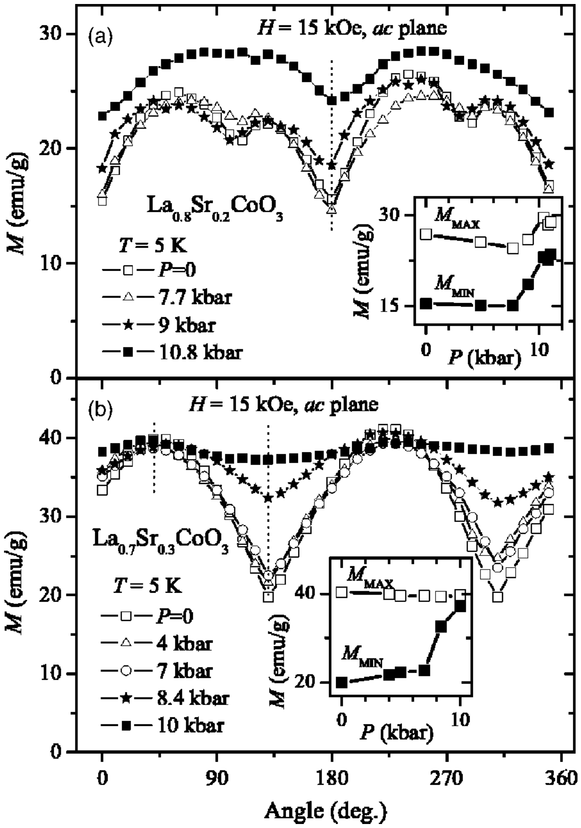

FIG. 9. Angular dependence of the magnetization $M(\varphi)$ of $La_{0.8}Sr_{0.2}CoO_3$ (a) and $La_{0.7}Sr_{0.3}CoO_3$ (b) single crystals in the *ac* plane at applied magnetic field of 15 kOe under various pressures. Insets show a variation of the maximal M_{max} and minimal M_{min} values of magnetization with pressure.

In summary, we have investigated the pressure effect on magnetic order in low-doped $La_{1-x}Ca_xCoO_3$ and $La_{1-x}Sr_xCoO_3$ single crystals and polycrystals. It was found that applied hydrostatic pressure suppresses strongly the FM interactions in Ca-doped materials leading to a remarkable suppression of the FM phase. Simultaneously observed the decrease of an effective spin S with pressure supports explanation that, a dominant mechanism of pressure-induced suppression of DE FM interactions in $La_{1-x}Ca_xCoO_3$ is attributed to an increase of the energy of the crystal-field splitting Δ_{CF}, leading to a depopulation of the LS state and suppression of e_g-electron hopping. In contrast, a very complex pressure effect critically depending on doping level was found in

$La_{1-x}Sr_xCoO_3$. It appears that pressure clearly enhances the FM interactions in the spin- or cluster-glass state as well as in the long-range FM state at $x=0.3$ but surprisingly the pressure coefficient dT_C/dP changes sign at the percolation threshold around $x\sim 0.2$. This intricate behavior indicates on a competition of at least two different mechanisms responsible for pressure effect in $La_{1-x}Sr_xCoO_3$ with an expanded unit cell caused by doping with a large size ion.

For both $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.7}Sr_{0.3}CoO_3$ single crystals with well developed long-range FM order, a drastic changes in magnetic anisotropy in the *ac* plane were observed under applied pressure of about 9 kbar, leading in the case of $La_{0.7}Sr_{0.3}CoO_3$ to nearly isotropic magnetization within the *ac* plane at $P>9$ kbar. The radical changes in magnetic anisotropy suggest that some kind of a pressure-induced phase transition occurs in both crystals.

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[1] G. Briceno, H. Chang, X. Sun, P. G. Schultz, and X. D. Xiang, Science **270**, 273 (1995).

[2] I. Troyanchuk, D. D. Khalyavin, T. K. Soloukh, H. Szymczak, Q. Huang, and J. W. Lynn, J. Phys.: Condens. Matter **12**, 2485 (2000).

[3] A. V. Samoilov, G. Beach, C. C. Fu, N.-C. Yeh, and R. P. Vasquez, Phys. Rev. B **57**, R14 032 (1998).

[4] K. Muta, Y. Kobayashi, and K. Asai, J. Phys. Soc. Jpn. **71**, 2784 (2002).

[5] H. Masuda, T. Fujita, T. Miyashita, M. Soda, Y. Yasui, Y. Kobayashi, and M. Sato, J. Phys. Soc. Jpn. **72**, 873 (2003).

[6] M. Kriener, C. Zobel, A. Reichl, J. Baier, M. Cwik, K. Berggold, H. Kierspel, O. Zabara, A. Freimuth, and T. Lorenz, Phys. Rev. B **69**, 094417 (2004).

[7] J. C. Burley, J. F. Mitchell, and S. Short, Phys. Rev. B **69**, 054401 (2004).

[8] F. Fauth, E. Suard, and V. Caignaert, Phys. Rev. B **65**, 060401(R) (2001).

[9] M. Paraskevopoulos, J. Hemberger, A. Krimmel, and A. Loidl, Phys. Rev. B **63**, 224416 (2001).

[10] D. Louca, J. L. Sarrao, J. D. Thompson, H. Röder, and G. H. Kwei, Phys. Rev. B **60**, 10 378 (1999); D. Louca and J. L. Sarrao, Phys. Rev. Lett. **91**, 155501 (2003).

[11] A. Mineshige, M. Kobune, S. Fudjii, Z. Ogumi, M. Inaba, T. Yao, and K. Kikuchi, J. Solid State Chem. **142**, 374 (1999).

[12] K. Tsutsui, J. Inoue, and S. Maekawa, Phys. Rev. B **59**, 4549 (1999).

[13] P. Ravindran, H. Fjellvåg, A. Kjekshus, P. Blaha, K. Schwarz, and J. Luitz, J. Appl. Phys. **91**, 291 (2002).

[14] M. A. Señarís Rodríguez and J. B. Goodenough, J. Solid State Chem. **116**, 224 (1995).

[15] M. A. Korotin, S. Yu. Ezhov, I. V. Solovyev, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. B **54**, 5309 (1996).

[16] K. Asai, O. Yokokura, M. Suzuki, T. Naka, T. Matsumoto, H. Takahashi, N. Mori, and K. Kohn, J. Phys. Soc. Jpn. **66**, 967 (1997); K. Asai, A. Yoneda, O. Yokokura, J. M. Tranquada, G. Shirane, and K. Kohn, *ibid.* **67**, 290 (1998).

[17] R. Lengsdorf, M. Ait-Tahar, S. S. Saxena, M. Ellerby, D. I. Khomskii, H. Micklitz, T. Lorenz, and M. M. Abd-Elmeguid, Phys. Rev. B **69**, 140403(R) (2004).

[18] T. Vogt, J. A. Hriljac, N. C. Hyatt, and P. Woodward, Phys. Rev. B **67**, 140401(R) (2003).

[19] J. Wu and C. Leighton, Phys. Rev. B **67**, 174408 (2003).

[20] D. N. H. Nam, K. Jonason, P. Nordblad, N. V. Khiem, and N. X. Phuc, Phys. Rev. B **59**, 4189 (1999).

[21] P. L. Kuhns, M. J. R. Hoch, W. G. Moulton, A. P. Reyes, J. Wu, and C. Leighton, Phys. Rev. Lett. **91**, 127202 (2003); M. J. R. Hoch, P. L. Kuhns, W. G. Moulton, A. P. Reyes, J. Lu, J. Wu, and C. Leighton, Phys. Rev. B **70**, 174443 (2004).

[22] J. Mira, J. Rivas, G. Baio, G. Barucca, R. Caciuffo, D. Rinaldi, D. Fiorani, and M. A. Señarís-Rodríguez, J. Appl. Phys. **89**, 5506 (2001).

[23] H. Y. Hwang, T. T. M. Palstra, S.-W. Cheong, and B. Batlogg, Phys. Rev. B **52**, 15 046 (1995).

[24] T. Fujita, T. Miyashita, Y. Yasui, Y. Kobayashi, M. Sato, E. Nishibori, M. Sakata, Y. Shimojo, N. Igawa, Y. Ishii, K. Kakurai, T. Adachi, Y. Ohishi, and M. Takata, J. Phys. Soc. Jpn. **73**, 1987 (2004).

[25] H. Szymczak, M. Baran, G.-J. Babonas, R. Diduszko, J. Fink-Finowicki, and R. Szymczak, J. Magn. Magn. Mater. **285**, 386 (2005).

[26] D. Shulyatev, S. Karabashev, A. Arsenov, and Ya. Mukovskii, J. Cryst. Growth **198–199**, 511 (1999).

[27] V. V. Sikolenko, A. P. Sazonov, I. O. Troyanchuk, D. Többens, U. Zimmermann, E. V. Pomjakushina, and H. Szymczak, J. Phys.: Condens. Matter **16**, 7313 (2004).

[28] M. Baran, V. Dyakonov, L. Gladczuk, G. Levchenko, S. Piechota, and H. Szymczak, Physica C **241**, 383 (1995).

[29] The pressure data for $La_{0.5}Sr_{0.5}CoO_3$ ceramics were obtained by us when the manuscript has been already reviewed.

[30] J. B. Goodenough, *Rare Earth-Manganese Perovskites*, Vol. 33 of *Handbook on the Physics and Chemistry of Rare Earth*, edited by K. A. Gschneidner, Jr., J.-C. G. Bünzli, and V. K. Pecharsky (Elsevier Science, Amsterdam, 2003).

[31] V. Markovich, I. Fita, R. Puzniak, M. I. Tsindlekht, A. Wisniewski, and G. Gorodetsky, Phys. Rev. B **66**, 094409 (2002).

[32] V. Markovich, I. Fita, R. Puzniak, A. Wisniewski, K. Suzuki, J. W. Cochrane, Y. Yuzhelevskii, Ya. M. Mukovskii, and G. Gorodetsky, Phys. Rev. B **71**, 134427 (2005).

[33] I. M. Fita, R. Szymczak, M. Baran, V. Markovich, R. Puzniak, A. Wisniewski, S. V. Shiryaev, V. N. Varyukhin, and H. Szymczak Phys. Rev. B **68** 014436 (2003).