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Ferromagnetic state of $La_{1-x}Ba_xCoO_3$ under applied pressure: Factors controlling the sign reversal of pressure effect in cobaltites

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Pressure effect on magnetic properties of polycrystalline $La_{1-x}Ba_xCoO_3$ ($0.1 \leqslant x \leqslant 0.5$) was studied by magnetization measurements in the temperature range 5–240 K, magnetic field up to 16 kOe, and under hydrostatic pressure up to 10.5 kbar. For low-doped cobaltites ($x = 0.1,0.15$), it was found that applied pressure enhances the ferromagnetic (FM) cluster phase, resulting in an increase of both spontaneous FM moment and transition temperature of clusters T_C^{cl}, while the freezing temperature T_f lowers under pressure appreciably ($dT_f/dP \approx -1.4$ K/kbar), suggesting the weakening of interaction between clusters. For higher-doped $La_{1-x}Ba_xCoO_3$ ($0.2 \leqslant x \leqslant 0.5$), having developed long-range FM order, the systematic increase of T_C under pressure was observed with coefficient dT_C/dP linearly increasing with doping up to 1.8 K/kbar at $x = 0.5$, the highest value reported for cobaltites. The positive value of the dT_C/dP coefficient found for the Ba compound in a whole range of studied doping is in strong contrast to that found in Ca and Sr cobaltites, where the dT_C/dP was found to change a sign from a negative to a positive one with increasing doping. It is shown that the sign reversal of the dT_C/dP coefficient for $La_{1-x}M_xCoO_3$ ($M =$ Ca,Sr,Ba) cobaltites can be caused by the hole doping and also, independently, by the lattice expansion only induced by an increase of the dopant ion size. The complex pressure effect on ferromagnetic transition T_C in cobaltites is well described in terms of competing e_g-electron bandwidth W and crystal-field splitting energy, basing on the known pressure variations of the steric factors. For $La_{1-x}Ba_xCoO_3$ with $x = 0.3,0.5$, having a high enough concentration of intermediate spin Co states, we observed a Jahn-Teller-like magnetic transition signified by a distinct hysteresis in field-cooled magnetization below T_C. This transition was found to disappear under moderate applied pressure, evidenced for $La_{0.7}Ba_{0.3}CoO_3$ by abrupt changes in the spontaneous magnetization and coercive field at 5 K.

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I. INTRODUCTION

Ferromagnetic perovskite cobaltites $La_{1-x}M_xCoO_3$ ($M =$ Ca,Sr,Ba) have recently attracted much attention because of their unusual magnetic and transport properties that are primarily due to the unique feature of the Co ion to change its spin state.[1–6] Due to the strong competition between the crystal-field splitting energy Δ_{cf} and the intra-atomic (Hund) exchange interaction J_{ex}, a Co^{3+} ion exhibits three alternative spin configurations: the nonmagnetic low-spin (LS) ($t_{2g}^6 e_g^0$; $S = 0$), intermediate-spin (IS) ($t_{2g}^5 e_g^1$; $S = 1$), and high-spin (HS) ($t_{2g}^4 e_g^2$; $S = 2$) states.[7] Different Co^{3+} species may coexist in crystals and switching between them depends strongly on doping, temperature, and changes in crystal structure. This notable feature makes cobaltites extremely sensitive to external effects such as pressure,[8–10] strain,[11] or electric field.[12]

Hole-doped cobaltites exhibit ferromagnetism likely arising from the exchange interaction between Co^{3+} and Co^{4+} ions, and the ferromagnetic (FM) state develops with increasing doping similarly to the case of that in manganites. In cobaltites, the hole-doping effect on the transport and magnetic properties is more intricate because the ferromagnetic interactions are dependent on variable Co spin state, and therefore on lattice parameters and crystal symmetry. Conversely, the population of the magnetic IS state depends also on the bandwidth W which results from the σ-bonding Co-O-Co interactions, namely, an increase of W stabilizes a higher spin state.[9] Moreover, any change in the Co spin state brings upon changes in the lattice parameters. This interplay between the variable spin state and the lattice is an additional source of phase separation in cobaltites, exhibiting generally a highly inhomogeneous ground state with coexisting hole-rich FM regions, spin-glass regions, and hole-poor LS regions.[13,14] The coexistence of ferromagnetic and glassy states has been observed in $La_{1-x}Sr_xCoO_3$ for different doping levels up to $x = 0.5$.[15,16]

The IS state with a partially filled e_g level, which therefore is a Jahn-Teller (JT) active state, plays a crucial role in the ferromagnetic state of cobaltites. It has been found that the concentration of JT IS states increases with lattice expansion of $La_{1-x}M_xCoO_3$, caused by the larger M dopant ion size (Ref. 6). This leads to the formation of the JT magnetopolarons in the lattice when the average radius at the A site exceeds the critical value of $\langle r_A \rangle_C = 1.22$ Å (Ref. 17). It appears that the JT magnetopolaron formation is most preferable for Ba-doped cobaltites, where the percentage of JT sites reaches a value of 80% at $x = 0.5$ (Ref. 17). This finding correlates well with the observation of the unique long-range tetragonal phase in $La_{0.5}Ba_{0.5}CoO_3$, compatible only with static JT distortion of CoO_6 octathedra.[5] In addition, the inhomogeneous magnetic state of $La_{1-x}M_xCoO_3$ was recently found to develop toward the coexistence of competing ferromagnetic and antiferromagnetic orders with an increase of the dopant ion size from 1.18 Å (Ca^{2+}) to 1.47 Å (Ba^{2+}).[18]

Cobaltites are very sensitive to the external pressure since the crystal-field splitting energy $\Delta_{\mathrm{cf}} \sim (d_{\text{Co-O}})^{-5}$ strongly depends on the variation in the Co-O bond length $d_{\text{Co-O}}$. An applied pressure leads to the insulating nonmagnetic LS state[8] because the gap between t_{2g} and e_g levels increases with contraction $d_{\text{Co-O}}$, causing depopulation of the magnetic e_g state. The behavior is compatible with fact that the ionic radius of LS Co^{3+} (0.545 Å) is smaller than that of IS Co^{3+} (0.56 Å).[2] The same mechanism is responsible for the pressure-induced suppression of magnetization observed, in general, in ferromagnetic cobaltites, while the pressure effect on ferromagnetic transition temperature T_C was found to be very different for various $\mathrm{La}_{1-x}M_x\mathrm{CoO}_3$ compositions. Namely, while the large negative values of coefficient dT_C/dP were observed for both low-doped ($x \sim 0.2$) Ca and Sr compounds,[10,19] the change of sign of the dT_C/dP coefficient from negative to positive with a further increase in Sr doping, between $x = 0.2$ and $x = 0.3$, was found.[10] At high Sr doping for $x > 0.5$, the dT_C/dP achieves values of ~1.5 K/kbar.[20] The intricate behavior was attributed to a competition of two antagonistic effects. The first one is related to the pressure-induced suppression of the magnetic IS state and the second one, known for magnetic perovskites, enhances the FM interactions by increasing the Co-O-Co bond angle and contracting the bond length $d_{\text{Co-O}}$ (Ref. 10). Surprisingly, the small positive value of dT_C/dP was reported for half-doped $\mathrm{La}_{0.5}\mathrm{Ca}_{0.5}\mathrm{CoO}_3$ only very recently.[21] Therefore, we may suggest that the analogous sign reversal in dT_C/dP occurs also in Ca-doped cobaltites at a higher doping level ($x \sim 0.5$). In summary, $\mathrm{La}_{1-x}M_x\mathrm{CoO}_3$ (M = Ca,Sr) cobaltites demonstrate a complex dependence of pressure coefficient dT_C/dP both on the doping level and on the size of the dopant ion. In order to clarify the intriguing origin of the pressure effect on T_C, we report the results of magnetization measurements under pressure performed for $\mathrm{La}_{1-x}\mathrm{Ba}_x\mathrm{CoO}_3$. We found that the coefficient dT_C/dP is essentially positive in the full range of studied Ba doping ($0.15 < x < 0.5$) and it increases linearly with hole doping similarly to that observed in the Ca- and Sr-doped cobaltites. Comparing all the data obtained up to now for $\mathrm{La}_{1-x}M_x\mathrm{CoO}_3$ (M = Ca,Sr,Ba), we demonstrate that the sign reversal of dT_C/dP can be caused by the hole doping and also, independently, by the lattice expansion only, realized by the increasing size of the dopant ion at a constant hole-doping level. It is shown also that the complex pressure effect on ferromagnetic transition T_C in cobaltites can be successfully described in terms of the competing e_g-electron bandwidth W and crystal-field splitting energy Δ_{cf}, taking into account the pressure-dependent steric factors.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of $\mathrm{La}_{1-x}\mathrm{Ba}_x\mathrm{CoO}_3$ (x = 0.1, 0.15,0.2,0.3,0.5) were prepared by the standard solid-state reaction method. The proper quantities of $\mathrm{La_2O_3}$, $\mathrm{Co_3O_4}$, and $\mathrm{BaCO_3}$ were ground and calcined in air for 3 h at 950 °C. Powders obtained were pressed into pellets and further sintered in air for 12 h at different temperatures, depending on composition. The synthesis temperature was decreased gradually from 1260 °C for the $x = 0.1$ compound down to 1180 °C for the $x = 0.5$ samples. The samples were then slowly cooled at a rate of 30 K/h down to room temperature to achieve the high oxidation state. The oxygen content was estimated by thermogravimetric analysis to be close to the stoichiometric value of 3.0 in all samples except for the $x = 0.5$ sample, where it was less by about 0.03. Polycrystalline $\mathrm{La}_{1-x}\mathrm{Ba}_x\mathrm{CoO}_3$ cobaltites were found to be single phase and no impurities were present as confirmed by powder x-ray diffraction. For samples with $0.1 \leqslant x \leqslant 0.3$, the rhombohedral $R\bar{3}c$ structure was found, while for the $x = 0.5$ sample, the cubic $Pm\bar{3}m$ space group was identified. Due to the large ionic radius of Ba^{2+}, the $\mathrm{La}_{1-x}\mathrm{Ba}_x\mathrm{CoO}_3$ lattice expands significantly with increasing x and the crystal symmetry becomes cubic at $x > 0.35$ in agreement with earlier reports.[22]

Cylinder-shape samples having a diameter of 1 mm and a height of 4 mm were used for measurements of magnetization (M) under hydrostatic pressure (P) up to 10.5 kbar. All the magnetic measurements were performed in the temperature range 5–240 K in magnetic fields up to 16 kOe using a Princeton Applied Research (Model 4500) vibrating sample magnetometer. For these measurements, a miniature container of CuBe with an inside diameter of 1.4 mm was employed as a pressure cell, and a mixture of mineral oil and kerosene was used as a pressure-transmitting medium.[23] 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.

III. RESULTS AND DISCUSSION

A. Pressure effect on ferromagnetic cluster glass state (x = 0.1,0.15)

Figure 1 presents a pressure effect on the magnetization of low-doped $\mathrm{La}_{0.85}\mathrm{Ba}_{0.15}\mathrm{CoO}_3$. At this doping level $\mathrm{La}_{1-x}\mathrm{Ba}_x\mathrm{CoO}_3$ shows no long-range FM order, but rather a magnetic glassy behavior in accordance with the phase diagram demonstrating magnetic percolation at $x \sim 0.2$ as reported in Ref. 22. The temperature at which irreversibility between zero-field-cooled (ZFC) and field-cooled (FC) magnetization occurs indicates the appearance of ferromagnetic hole-rich clusters below $T_C^{\mathrm{cl}} \sim 185$ K. The magnetic moments become blocked below freezing temperature $T_f \sim 125$ K corresponding to the ZFC magnetization peak [see Fig. 1(a)]. Between T_C^{cl} and T_f the cluster moments behave just as atomic spins in paramagnets and the coercivity is zero due to thermal fluctuations (superparamagnetic behavior), while below T_f the magnetic moments are blocked and the coercivity appears.[1] On the other hand, this highly inhomogeneous system (FM clusters embedded in a paramagnetic matrix) has been suggested[22] to form a spin- or cluster-glass state below T_f. It is shown in Fig. 1 that an applied pressure strongly enhances the FM cluster phase resulting in (i) an increase in the spontaneous FM magnetization M_0 and high-field paramagnetic susceptibility χ_{hf} by 90% and 50%, respectively, under 10 kbar at 40 K [M_0 is extracted by a linear extrapolation of the $M(H)$ curve from the high-field region to $H = 0$ and $\chi_{\mathrm{hf}} = dM/dH$ is a slope of the $M(H)$ between 5 and 16 kOe]; (ii) an increase

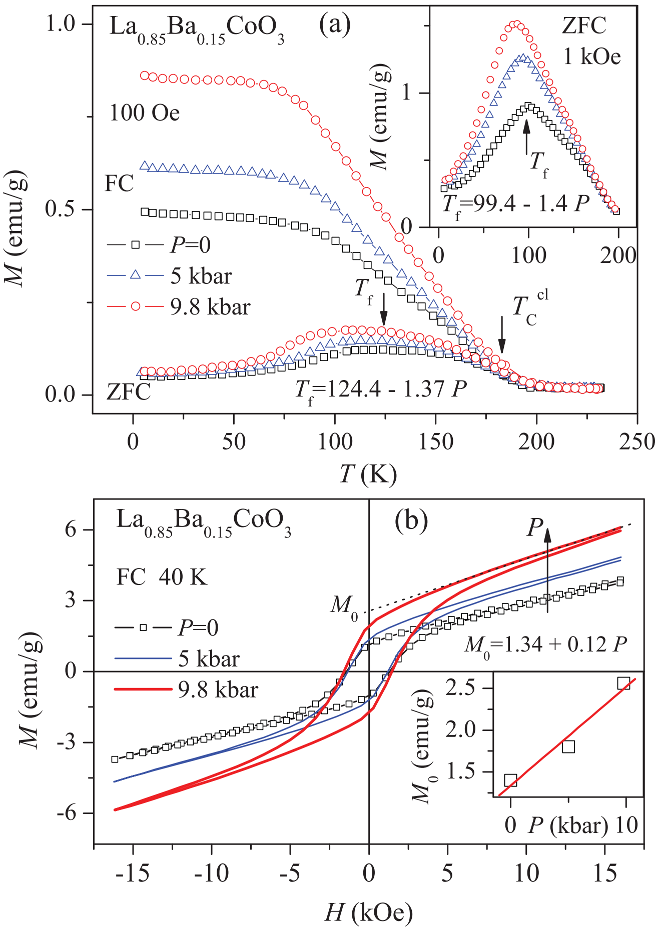

FIG. 1. (Color online) (a) Temperature dependence of ZFC and FC magnetization for $\mathrm{La_{0.85}Ba_{0.15}CoO_3}$ measured at 100 Oe at ambient, 5, and 9.8 kbar pressure. The inset shows a shift of ZFC magnetization peak temperature T_f with pressure, determined in 1 kOe. (b) Hysteresis loops of the FC magnetization of $\mathrm{La_{0.85}Ba_{0.15}CoO_3}$ measured at 40 K under the same values of pressure. The inset shows the increase of the spontaneous magnetization M_0 with pressure.

in T_C^{cl} with coefficient $dT_C^{\mathrm{cl}}/dP = 0.5$ K/kbar; and (iii) an almost twofold increase in the gap between ZFC and FC curves under 10 kbar. Another noticeable feature, clearly visible in the field of 100 Oe, is the suppression of freezing temperature T_f under the pressure shown by a shift of maximum in the ZFC magnetization to lower temperatures. Additionally, this shift was also noticed at a higher field of 1 kOe at which the freezing temperature is visibly reduced due to the field effect (see the inset in Fig. 1). In both cases, T_f linearly decreases with pressure with the coefficient $dT_f/dP \approx -1.4$ K/kbar. A similar behavior has been observed in low-doped Ca ($x = 0.15$) and Sr ($x = 0.1$) cobaltites;[10] furthermore, the same pressure coefficient $d\ln T_f/dP \approx -0.013$ kbar^{-1} was estimated for $\mathrm{La_{1-x}}M_x\mathrm{CoO_3}$ cobaltites with a dominated cluster-glass state. On the contrary, the perovskite manganites show, in general, the pressure-induced increase of the freezing temperature and the conversion of the spin-glass phase into a FM phase,[24] that is in compliance with the well-known pressure enhancement of the ferromagnetic double exchange interactions in manganites. An opposite effect observed in cobaltites is due to the specific pressure impact on the Co spin state. Namely, an applied pressure increases a population of nonmagnetic LS states in the hole-poor paramagnetic matrix that should break the superexchange intercluster interactions,[25] therefore the FM clusters become less interacting under pressure. This mechanism may explain the pressure-induced suppression of freezing temperature T_f and an extension of the temperature region of superparamagnetic state in $\mathrm{La_{0.85}Ba_{0.15}CoO_3}$. Notice that the simultaneous growth of the FM cluster phase volume and an increase of the ferromagnetic temperature T_C^{cl} of the clusters under pressure are not in contradiction with the enhancement of superparamagnetism observed. In addition, in low-doped $\mathrm{La_{0.9}Ba_{0.1}CoO_3}$, exhibiting a six times lower spontaneous magnetization M_0 as compared to that of $x = 0.15$ composition, we also found a positive coefficient dT_C^{cl}/dP and a 50% increase at 10 kbar in M_0 at 40 K (not shown). The origin of the positive pressure effect on ferromagnetic transition T_C in $\mathrm{La_{1-x}Ba_xCoO_3}$ will be discussed later on.

B. Pressure effect on ferromagnetic state (x = 0.2,0.25,0.3,0.5)

At doping level x between 0.2 and 0.5, $\mathrm{La_{1-x}Ba_xCoO_3}$ shows long-range FM order;[3,22] nevertheless, additional spin-glass and paramagnetic phases also coexist with dominant FM phase due to the strong tendency of cobaltites with variable Co spin states to phase separation. Figure 2 presents a pressure effect on magnetic characteristics of two compositions, $x = 0.2$ and $x = 0.25$. Both samples show at low temperatures a large difference between ZFC and FC magnetization at 100 Oe, which only slightly increases under pressure. A sharp increase in FC magnetization indicates an appearance of ferromagnetism below $T_C = 189$ K ($x = 0.2$) and 196 K ($x = 0.25$) [see Fig. 2(a)]. One can notice that T_C determined as a temperature of minimum in derivative dM/dT increases with applied pressure linearly, with the coefficient $dT_C/dP = 0.43$ K/kbar ($x = 0.2$) and 0.64 K/kbar ($x = 0.25$) [see the inset in Fig. 2(a)]. This behavior is quite surprising, since the essentially negative pressure coefficient dT_C/dP has been found earlier at such a doping level for Ca and Sr cobaltites.[10,19] The strong effect of the dopant ion size on dT_C/dP in $\mathrm{La_{1-x}}M_x\mathrm{CoO_3}$ will be explained later on.

The pressure effect on the ferromagnetic moment at 5 K for $x = 0.2$ and $x = 0.25$ compounds is presented in Fig. 2(b) by the FC magnetization hysteresis loops for the field range of ±16 kOe. Both spontaneous magnetization M_0 and high-field magnetization decrease considerably under pressure indicating contraction of the FM phase volume, despite the increase in T_C (a measure of effective ferromagnetic interactions). For $x = 0.25$ composition, M_0 diminishes by about 30% at 10 kbar. A very similar suppression of the FM moment has been observed in Ca- and Sr-doped cobaltites as well.[10,20] Most likely this effect is related to the universal feature of cobaltites to diminish Co spin under applied pressure. We notice additionally that the coercive field H_C for the $x = 0.25$ compound decreases slightly under pressure, while for lower doping $x = 0.2$ it is insensitive to the pressure.

Figure 3 shows the temperature and field dependences of magnetization measured at several applied pressures for the sample with optimal Ba doping $x = 0.3$ at which T_C reaches

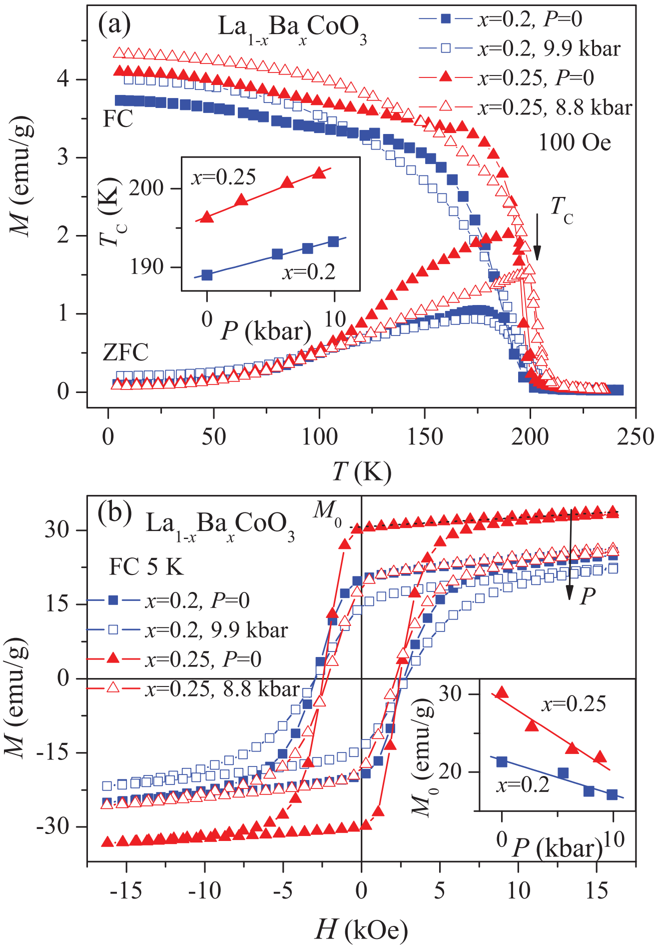

FIG. 2. (Color online) (a) The temperature dependences of ZFC and FC magnetization at 100 Oe for $La_{0.8}Ba_{0.2}CoO_3$ and $La_{0.75}Ba_{0.25}CoO_3$ cobaltites at ambient pressure and under hydrostatic pressure. The inset shows a pressure dependence of the Curie temperature T_C for both compositions. (b) Hysteresis loops of the FC magnetization of two compositions at 5 K at ambient pressure and under hydrostatic pressure. The inset shows a variation in spontaneous magnetization M_0 with pressure.

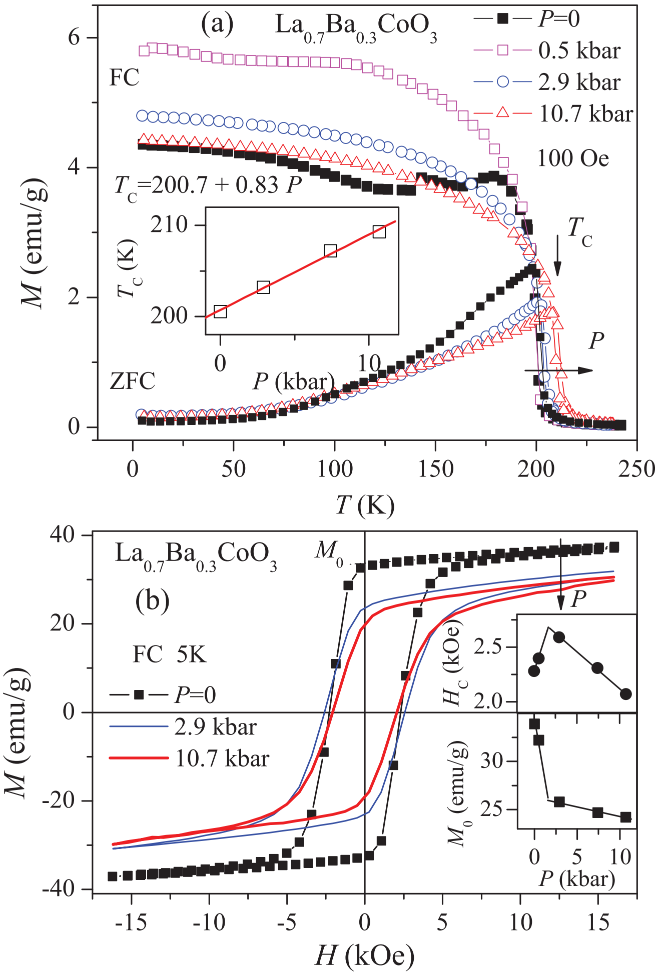

FIG. 3. (Color online) (a) Temperature dependence of ZFC and FC magnetization at 100 Oe for $La_{0.7}Ba_{0.3}CoO_3$ under various pressures. The inset shows the linear increase of Curie temperature T_C with pressure. (b) Hysteresis loops of the FC magnetization taken for $La_{0.7}Ba_{0.3}CoO_3$ at 5 K under various pressures. The insets show spectacular changes in pressure dependences of the spontaneous magnetization M_0 and coercive field H_C around 2.5 kbar.

the maximal value of ≈ 200 K (Ref. 22) and the spontaneous magnetization $M_0 = 37.3$ emu/g ($\approx 1.6\ \mu_B$/Co) at 5 K is the largest. This sample reveals an increase of T_C under pressure with a large value of $dT_C/dP = 0.83$ K/kbar [see the inset in Fig. 3(a)]. At ambient pressure, the low-field FC magnetization of $La_{0.7}Ba_{0.3}CoO_3$, measured at cooling, exhibits a puzzling nonmonotonic change below T_C [Fig. 3(a)], while it shows a quite usual monotonous decrease with temperature when measured in a warming regime (see Fig. 4). A clear hysteresis in FC magnetization $M(T)$ taken at cooling and at warming indicates some type of phase transition which appears to pass in two steps, evidenced by two sharp jumps in derivative dM/dT at 170 and 140 K (see the inset in Fig. 4). This hysteresis was also reproducible at a higher measured field of 1 kOe but it was not detectable at 5 kOe. Notice that the slight traces of nonmonotonic behavior in FC magnetization at 100 Oe are also visible in the less-doped samples with $x = 0.2$ and $x = 0.25$ [see Fig. 2(a)]. Certainly, it develops in $La_{1-x}Ba_xCoO_3$ with increasing Ba content. Interestingly, this anomalous behavior of FC magnetization is suppressed rapidly by applied pressure, so that, just at 0.5 kbar, it can be visible at much lower temperatures, while at 2.9 kbar pressure the FC $M(T)$ curves show no hysteresis [see Fig. 3(a)]. After pressure release, the hysteresis in FC magnetization was reestablished again at approximately the same temperatures as presented in Fig. 4. Evidence of the pressure-induced phase transition in $La_{0.7}Ba_{0.3}CoO_3$ at moderate pressure is obtained also from high-field magnetization data at 5 K. It is seen in the lower inset of Fig. 3(b) that the spontaneous magnetization M_0 reduces with pressure in a very nonuniform way. M_0 decreases rapidly with coefficient $dM_0/dP \approx -2.8$ emu/g kbar in the range 0–2.9 kbar and it decreases very slowly with $dM_0/dP \approx -0.2$ emu/g kbar between 2.9 and 10.7 kbar. A very similar pressure dependence also exhibits the magnetization at 10 kOe and at 5 K (not shown). It was also found that the coercive field H_C changes with pressure nonmonotonously: it increases at low pressure but decreases linearly between 2.9 and 10.7 kbar [see the upper inset of Fig. 3(b)]. Both

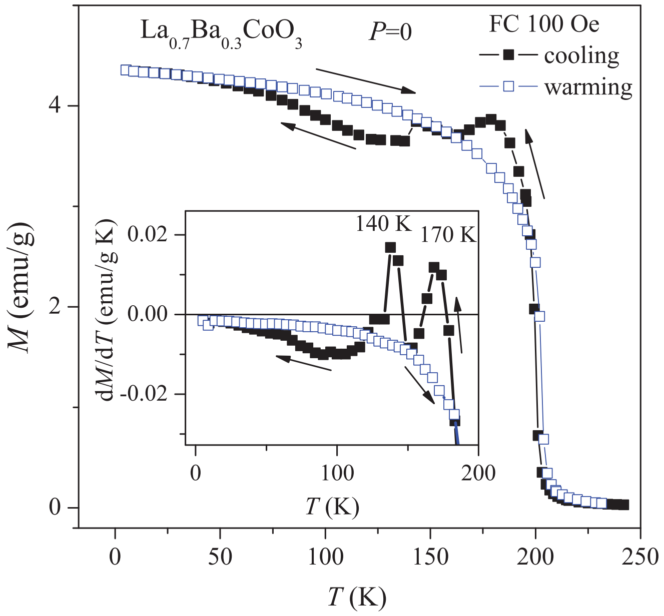

FIG. 4. (Color online) Temperature dependences of FC magnetization at 100 Oe for $La_{0.7}Ba_{0.3}CoO_3$ measured at ambient pressure in both cooling and warming regimes indicated by arrows. The inset shows two sharp jumps in the derivative dM/dT at 170 K and 140 K, an indication of a two step magnetic transition under cooling.

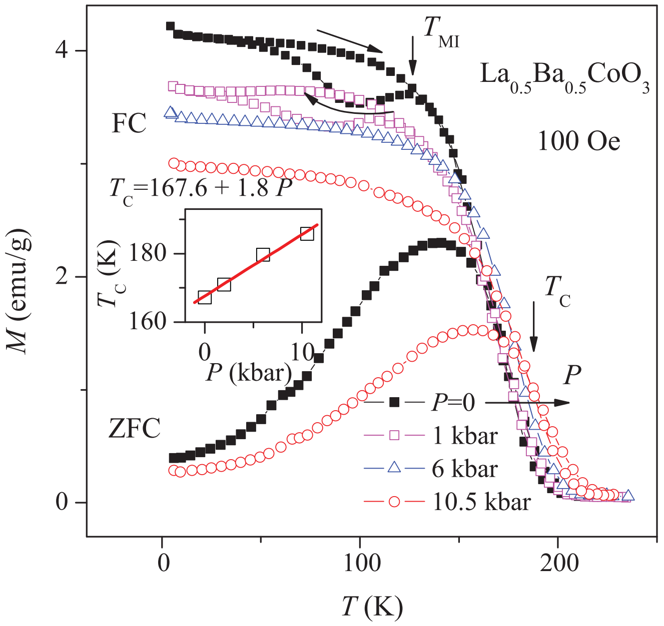

FIG. 5. (Color online) Temperature dependence of ZFC and FC magnetization at 100 Oe for half-doped $La_{0.5}Ba_{0.5}CoO_3$ under various pressures. Hysteresis in FC magnetization, taken for cooling and warming, appears at ambient pressure at temperature T_{MI} = 120 K assigned to the metal-insulator-like transition in Ref. 5. No hysteresis was found in FC magnetization at 6 and 10.5 kbar [both cooling and warming FC $M(T)$ branches coincide]. The inset shows the linear increase of Curie temperature T_C with pressure.

$M_0(P)$ and $H_C(P)$ dependences presented together with the observation of a disappearance of hysteresis in the FC $M(T$, 100 Oe) curves unambiguously indicate the qualitative change in magnetic state of $La_{0.7}Ba_{0.3}CoO_3$ at a modest pressure of approximately 2.5 kbar. Additionally, this feature becomes apparent in the sudden increase in the slope of the $M(H)$ curve at 10 kOe and at 5 K between 0.5 and 2.9 kbar pressure (not shown).

Figure 5 presents the temperature dependences of FC and ZFC magnetization at 100 Oe measured at several applied pressures for half-doped $La_{0.5}Ba_{0.5}CoO_3$. At ambient pressure, the apparent discrepancy between the FC $M(T)$ curves taken in cooling and warming regimes appears at temperature ~120 K, below the ferromagnetic transition temperature $T_C = 168$ K. Similarly to the $La_{0.7}Ba_{0.3}CoO_3$ case, an applied pressure easily suppresses this hysteretic behavior: at 1 kbar it emerges at temperatures 20 K lower than at ambient pressure, while at 6 kbar pressure no hysteresis occurs [both FC $M(T)$ branches obtained at cooling and at warming coincide]. Interestingly, the temperature of hysteresis onset in FC magnetization coincides with the temperature $T_{MI} \sim 120$ K of metal-insulator-like transition which is accompanied by an upturn of the magnetoresistive ratio, reported for $La_{0.5}Ba_{0.5}CoO_3$ in Ref. 5. This transition was suggested to be of JT origin in compliance with the theoretical prediction that in the system of JT IS Co ions two different orbitally ordered states may exist: one of the states corresponds to a gapless semiconductor and the other to a metal.[7] This agrees well with the observation of the unique long-range tetragonal structure, compatible only with the cooperative static JT distortion of CoO_6 octahedra, in $La_{0.5}Ba_{0.5}CoO_3$.[5] It is worth pointing out that the largely expanded $La_{0.5}Ba_{0.5}CoO_3$ lattice is characterized by the highest concentration of JT active states among doped cobaltites.[6] These findings provide insight into the nature of the pressure-induced transition in $La_{1-x}Ba_xCoO_3$ at $x = 0.3$ and $x = 0.5$. An applied pressure favors the population of the LS state and leads to a decrease of the concentration of JT IS states in the system. Therefore, it is possible to destroy a weakly orbitally ordered configuration of IS Co ions by relatively moderate pressure. This mechanism was suggested to be responsible for the recently observed pressure-induced total disappearance of ferromagnetism, originating from the JT orbital ordering of Co^{3+} ions, in $LaCoO_3$ nanoparticles.[26] In summary, we may conclude that $La_{1-x}Ba_xCoO_3$ with $x = 0.3, 0.5$, having larger lattice parameters (in comparison with Ca- and Sr-doped cobaltites) and therefore higher concentrations of JT IS Co states,[6] exhibit below T_C a JT magnetic transition signified by a distinct hysteresis in low-field FC magnetization. An applied moderate pressure is capable of suppressing the JT transition, leading to qualitative variation of the magnetic ground state evidenced for $La_{0.7}Ba_{0.3}CoO_3$ by abrupt changes in the spontaneous magnetization M_0 and coercive field H_C at 5 K.

Figure 5 demonstrates another notable feature of $La_{0.5}Ba_{0.5}CoO_3$. From the FC $M(T)$ curves, a strong pressure-induced increase in T_C is deduced with the largest value of $dT_C/dP = 1.8$ K/kbar reported for cobaltites. One can notice that the pressure effect on T_C is essentially positive for $La_{1-x}Ba_xCoO_3$, in strong contrast to that observed for Ca- and Sr-doped cobaltites. Obtained dT_C/dP values are presented

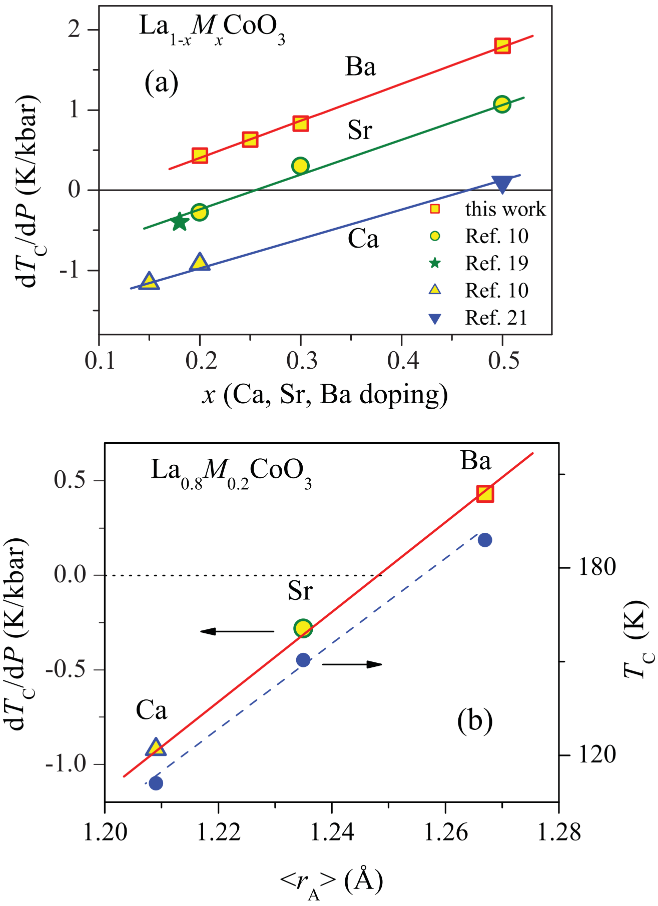

FIG. 6. (Color online) (a) Linear dependence of pressure coefficient dT_C/dP on doping for La$_{1-x}M_x$CoO$_3$ (M = Ca,Sr,Ba) cobaltites. Size dopant-ion effect is evidenced by the parallel shift of the $dT_C/dP(x)$ line to larger values with increasing ion size. (b) Linear increase in both dT_C/dP and T_C with increasing average ionic radius $\langle r_A \rangle$ at constant hole doping $x = 0.2$. dT_C/dP changes sign from negative to positive at $\langle r_A \rangle = 1.25$ Å.

in Fig. 6(a) together with those reported for cobaltites earlier. Remarkably, with increasing divalent metal M doping the coefficient dT_C/dP of La$_{1-x}M_x$CoO$_3$ always increases linearly, changing its sign in the cases of Ca and Sr, while for Ba doping it remains positive for the entire doping range. Figure 6(a) clearly demonstrates ion size effect: the dT_C/dP systematically increases with the increasing size of the doped ion for each doping level between 0.2 and 0.5. It appears that the straight lines approximating the $dT_C/dP(x)$ dependence for Ca, Sr, and Ba are moved parallel toward positive values as the atomic number of the ion increases. We explain further that this remarkable size effect in cobaltites is directly related to the variable spin state of the Co ion. Notice that it is in contrary to the situation in isostructural perovskite manganites with the invariable Mn spin state showing the essentially positive pressure effect on T_C.

C. Inverse pressure effect on ferromagnetic transition in cobaltites

We discuss a possible origin of the complex dependence of pressure coefficient dT_C/dP on the level of doping and the size of the dopant ion, presented in Fig. 6(a). Cobaltites exhibit a strong interplay between the Co spin state and the ferromagnetic interaction among IS Co^{3+} and LS Co^{4+} ions (Ref. 19). An effective hopping of an e_g electron from Co^{3+}(t_{2g}^5 e_g^1) to Co^{4+}(t_{2g}^5 e_g^0), which provides a powerful FM interaction and conducting state, takes place in cobaltites when the IS state is largely populated. Conversely, an ineffective electron hopping and minor ferromagnetic interaction take place in compounds with strongly depopulated magnetic IS state due to the dominating influence of crystal-field splitting energy Δ_{cf}. On the other hand, the population of the IS state is determined not only by the competing Δ_{cf} and intra-atomic (Hund) exchange interaction J_{ex} but it also depends on the bandwidth W resulting from the σ-bonding Co-O-Co interactions.[9] The impact of bandwidth W acts in line with the Hund energy, i.e., the broadening of W stabilizes the higher spin state. In this scenario, the FM transition temperature T_C is simply proportional to the effective energy $(W/2 - \Delta_{\text{cf}} + J_{\text{ex}})$ [see Fig. 4(a) in Ref. 9]. While the J_{ex} does not depend on pressure, the $\Delta_{\text{cf}} \sim (d_{\text{Co-O}})^{-5}$ and bandwidth $W \sim \cos\omega\ (d_{\text{Co-O}})^{-3.5}$[5] are strongly dependent on pressure, namely, both parameters increase with pressure due to contraction of the Co-O bond length $d_{\text{Co-O}}$ and the bending angle $\omega = (180^\circ - \langle\text{Co-O-Co}\rangle)/2$. Here, the Co-O-Co bond angle varies from 180° to $(180^\circ - 2\omega)$. Therefore,

$$dT_c/dP \sim d(W/2 - \Delta_{\text{cf}})/dP$$
$$= (W/2)[-\tan(\omega)\omega\kappa(\omega) - 3.5\kappa(d_{\text{Co-O}})] + 5\Delta_{\text{cf}}\kappa(d_{\text{Co-O}}), \qquad (1)$$

where $\kappa(d_{\text{Co-O}})$ and $\kappa(\omega)$ are the bond length and bond angle compressibility, respectively. Note that for hole-doped manganites, where the impact of Δ_{cf} may be neglected, always the positive value of dT_C/dP, indicating the stabilization of the FM metallic state under pressure, may be estimated from the changes in structural parameters, $d_{\text{Mn-O}}$ and ω (Refs. 27 and 28). In fact, the $dT_C/dP > 0$ has been observed for various manganites, except for only one exotic case of Ru-doped manganites.[29] In strong contrast, in cobaltites the coefficient dT_C/dP may change sign due to a competition between bandwidth W and crystal-field splitting Δ_{cf} (Ref. 10). It follows from expression (1) that the sign reversal of the pressure coefficient of T_C is determined by the Δ_{cf}/W ratio. Namely, $dT_C/dP = 0$ when

$$\Delta_{\text{cf}}/W = 0.35 + 0.1\tan(\omega)\omega\kappa(\omega)/\kappa(d_{\text{Co-O}}). \qquad (2)$$

Using the values of the bond compressibilities $\kappa(\omega) \approx -0.02$ kbar^{-1} and $\kappa(d_{\text{Co-O}}) \approx -4.8 \times 10^{-4}$ kbar^{-1} (obtained for LaCoO$_3$ in Ref. 8) and the average value $\omega \approx 5^\circ$ reported for Sr- and Ba-doped cobaltites,[30] we have evaluated that dT_C/dP changes sign at $\Delta_{\text{cf}}/W \approx 0.38$. That is to say, dT_C/dP >0 when the bandwidth W is large enough as compared to the $e_g - t_{2g}$ energy so that the t_{2g} level lies within the bandwidth of the e_g electrons; therefore the population of the higher spin state does not decrease under pressure despite increasing Δ_{cf}.

Thus, a qualitative understanding of the observed in $\mathrm{La}_{1-x}M_x\mathrm{CoO}_3$ ($M=$Ca,Sr,Ba) cobaltites inversion of pressure effect on ferromagnetic transition T_C, shown in Fig. 6(a), can be obtained in terms of the competing bandwidth W and crystal-field splitting energy Δ_{cf} taking into account the pressure variations of the steric factors. For further comprehension, we show in Fig. 6(b) the dependence of dT_C/dP on average ionic radius $\langle r_A\rangle$ for $\mathrm{La}_{1-x}M_x\mathrm{CoO}_3$ at constant hole doping $x = 0.2$. Here, $\langle r_A\rangle$ is calculated using values of ionic radii in ninefold oxygen coordination.[31] With lattice expansion due to an increase in the substituted ion size from 1.18 Å (Ca^{2+}) to 1.47 Å (Ba^{2+}), the dT_C/dP linearly increases and changes its sign around $\langle r_A\rangle = 1.25$ Å. In this process, with a fixed level of hole doping, the effective energy ($W/2 - \Delta_{\mathrm{cf}} + J_{\mathrm{ex}}$) enlarges because of lattice expansion only, mainly due to a decrease of Δ_{cf}. This is evidenced by the linear increase of T_C with increasing $\langle r_A\rangle$ at constant doping $x = 0.2$, presented in Fig. 6(b). Hence, the $dT_C/dP(\langle r_A\rangle)$ dependence shown in Fig. 6(b) demonstrates well the lattice-expansion origin of inversion in pressure effect on the FM transition in cobaltites. It can be evaluated from the data presented in Fig. 6(a) that at higher doping level $x = 0.3$ the expansion-induced sign reversal in dT_C/dP occurs at significantly lower $\langle r_A\rangle \approx 1.22$ Å, due to the larger contribution from the bandwidth W in this case.

At the high level of doping for $x = 0.5$, the bandwidth W for the Ca compound is already large enough to overcome the Δ_{cf} and hence to cause a small positive value of dT_C/dP as reported in Ref. 21. The further increase in the effective bandwidth at constant hole doping $x = 0.5$, by account of the lattice expansion, induced by the substitution of the Ca ion by larger ions (Sr and Ba), leads to an increase in dT_C/dP from 0.1 to 1.8 K/kbar [see Fig. 6(a)]. We argue that the sign reversal of coefficient dT_C/dP observed in $\mathrm{La}_{1-x}M_x\mathrm{CoO}_3$ ($M =$ Ca,Sr,Ba) cobaltites is attributed to the competition of two factors: the bandwidth W of e_g electrons and the energy distance between t_{2g} and e_g orbital levels. The coefficient dT_C/dP may change sign, from negative to positive, at the doping process when W broadens mainly because of increasing hole doping and also it occurs at constant hole doping when effective bandwidth ($W/2 - \Delta_{\mathrm{cf}} + J_{\mathrm{ex}}$) broadens because of lattice expansion only. The dT_C/dP coefficient becomes positive when the bandwidth W is large enough and the t_{2g} level lies within the e_g bandwidth, preventing in this case the depopulation of a higher spin state under pressure.

In addition, basing on the above results, we may explain the puzzling, negligibly small, pressure effect on T_C reported recently for $\mathrm{Nd}_{0.78}\mathrm{Ba}_{0.22}\mathrm{CoO}_3$ cobaltite.[32] Indeed, this composition, characterized by the average ionic radius $\langle r_A\rangle = 1.23$ Å and the hole-doping level $x = 0.22$, appears to be close to fulfillment of the condition for $dT_C/dP = 0$ (see Fig. 6). Notice that at a higher doping level for $x > 0.2$, the sign reversal in dT_C/dP must be expected at an $\langle r_A\rangle$ value lower than 1.25 Å, due to the larger, in this case, contribution from the bandwidth W. In order to examine this issue experimentally, we measured the low-field (100 Oe) temperature dependences of magnetization for two compositions of polycrystalline $\mathrm{Nd}_{1-x}\mathrm{Ba}_x\mathrm{CoO}_3$, $x = 0.22$ and $x = 0.24$, at ambient and ∼10 kbar pressure (not shown). From these data, we calculated for the lower doped $x = 0.22$ sample ($\langle r_A\rangle = 1.231$ Å) the negative coefficient $dT_C/dP \approx -0.24$ K/kbar, while for the $x = 0.24$ sample ($\langle r_A\rangle = 1.237$ Å) the positive $dT_C/dP \approx 0.1$ K/kbar was revealed. Consequently, we argue that for $\mathrm{Nd}_{1-x}\mathrm{Ba}_x\mathrm{CoO}_3$ cobaltites the pressure coefficient dT_C/dP increases with increasing doping and changes its sign around $x = 0.23$, very similar to the behavior of $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{CoO}_3$ presented in Fig. 6(a).

IV. CONCLUSIONS

In summary, the effect of pressure on the ferromagnetic cluster-glass state ($x = 0.1,0.15$) and long-range ferromagnetic state ($x = 0.2,0.25,0.3,0.5$) in polycrystalline $\mathrm{La}_{1-x}\mathrm{Ba}_x\mathrm{CoO}_3$ was investigated. It was found that applied pressure enhances the FM cluster phase in $\mathrm{La}_{0.85}\mathrm{Ba}_{0.15}\mathrm{CoO}_3$ resulting in an increase of both spontaneous FM magnetization and T_C^{cl} of clusters, while the freezing temperature T_f lowers under pressure appreciably ($dT_f/dP \approx -1.4$ K/kbar) suggesting the reduction of interaction between clusters. This behavior appears to be common for low-doped cobaltites and is opposite to that observed for manganites, where, in general, pressure converts the spin-glass state into a FM state. For higher-doped $\mathrm{La}_{1-x}\mathrm{Ba}_x\mathrm{CoO}_3$ ($0.2 \leqslant x \leqslant 0.5$), exhibiting developed long-range FM order, a systematic increase of T_C under pressure was observed with coefficient dT_C/dP linearly increasing with doping up to 1.8 K/kbar at $x = 0.5$. For highest Ba-doped ($x = 0.3,0.5$) cobaltites, with excessive concentration of JT IS Co states, we observed a JT-like magnetic transition, signified by a distinct hysteresis in FC magnetization below T_C, which dramatically disappears under moderate applied pressure.

An essentially positive dT_C/dP coefficient found for the Ba compound is in strong contrast to that found for Ca and Sr cobaltites, where the dT_C/dP changes sign from negative to positive with increasing doping. Comparing all the data for $\mathrm{La}_{1-x}M_x\mathrm{CoO}_3$ ($M =$ Ca,Sr,Ba) cobaltites, we have shown that the sign reversal of dT_C/dP can be induced in various ways: (i) by the hole doping, and alternatively, (ii) by the lattice expansion induced by the increasing size of the dopant ion. The size effect is clearly evidenced by a linear increase in coefficient dT_C/dP with an increasing average ionic radius $\langle r_A\rangle$ at constant hole doping $x = 0.2$. In this case, the dT_C/dP coefficient changes sign from negative to positive at $\langle r_A\rangle = 1.25$ Å because of lattice expansion only. It is shown that the complex pressure effect on ferromagnetic transition T_C in cobaltites can be successfully described in terms of the competition of e_g-electron bandwidth W and crystal-field splitting energy Δ_{cf}, taking into account the pressure variations of the steric factors. It appears that the sign reversal of dT_C/dP occurs when the ratio $\Delta_{\mathrm{cf}}/W \approx 0.38$ and $dT_C/dP > 0$ holds at large enough bandwidth W.

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

[2] P. G. Radaelli and S.-W. Cheong, Phys. Rev. B **66**, 094408 (2002).

[3] 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).

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

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

[6] D. Phelan, Despina Louca, K. Kamazawa, M. F. Hundley, and K. Yamada, Phys. Rev. B **76**, 104111 (2007).

[7] 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).

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

[9] J.-S. Zhou, J.-Q. Yan, and J. B. Goodenough, Phys. Rev. B **71**, 220103(R) (2005).

[10] I. Fita, R. Szymczak, R. Puzniak, I. O. Troyanchuk, J. Fink-Finowicki, Ya. M. Mukovskii, V. N. Varyukhin, and H. Szymczak, Phys. Rev. B **71**, 214404 (2005).

[11] D. Fuchs, C. Pinta, T. Schwarz, P. Schweiss, P. Nagel, S. Schuppler, R. Schneider, M. Merz, G. Roth, and H. v. Löhneysen, Phys. Rev. B **75**, 144402 (2007).

[12] A. Herklotz, A. D. Rata, L. Schultz, and K. Dörr, Phys. Rev. B **79**, 092409 (2009).

[13] P. L. Kuhns, M. J. R. Hoch, W. G. Moulton, A. P. Reyes, J. Wu, and C. Leighton, Phys. Rev. Lett. **91**, 127202 (2003).

[14] 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).

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

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

[17] D. Phelan, J. Yu, and Despina Louca, Phys. Rev. B **78**, 094108 (2008).

[18] J. Yu, Despina Louca, D. Phelan, K. Tomiyasu, K. Horigane, and K. Yamada, Phys. Rev. B **80**, 052402 (2009).

[19] 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).

[20] J. Pietosa, A. Wisniewski, R. Puzniak, I. Fita, M. Wojcik, W. Paszkowicz, R. Minikayev, J. Nowak, Ch. Lathe, S. Kolesnik, and B. Dabrowski, Phys. Rev. B **79**, 214418 (2009).

[21] N. O. Golosova, D. P. Kozlenko, E. V. Lukin, and B. N. Savenko, JETP Lett. **92**, 110 (2010).

[22] P. Mandal, P. Choudhury, S. K. Biswas, and B. Ghosh, Phys. Rev. B **70**, 104407 (2004).

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

[24] S. V. Trukhanov, I. O. Troyanchuk, A. V. Trukhanov, I. M. Fita, A. N. Vasil'ev, A. Maignan, and H. Szymczak, JETP Lett. **83**, 33 (2006).

[25] R. Caciuffo, D. Rinaldi, G. Barucca, J. Mira, J. Rivas, M. A. Señarís-Rodríguez, P. G. Radaelli, D. Fiorani, and J. B. Goodenough, Phys. Rev. B **59**, 1068 (1999).

[26] I. Fita, V. Markovich, D. Mogilyansky, R. Puzniak, A. Wisniewski, L. Titelman, L. Vradman, M. Herskowitz, V. N. Varyukhin, and G. Gorodetsky, Phys. Rev. B **77**, 224421 (2008).

[27] V. Laukhin, J. Fontcuberta, J. L. García-Muñoz, and X. Obradors, Phys. Rev. B **56**, 10009(R) (1997).

[28] G. Garbarino, C. Acha, D. Vega, G. Leyva, G. Polla, C. Martin, A. Maignan, and B. Raveau, Phys. Rev. B **70**, 014414 (2004).

[29] V. Markovich, I. Fita, R. Puzniak, E. Rozenberg, C. Martin, A. Wisniewski, A. Maignan, B. Raveau, Y. Yuzhelevskii, and G. Gorodetsky, Phys. Rev. B **70**, 024403 (2004).

[30] E. Efimova, V. Efimov, D. Karpinsky, A. Kuzmin, J. Purans, V. Sikolenko, S. Tiutiunnikov, I. Troyanchuk, E. Welter, D. Zajac, V. Simkin, and A. Sazonov, J. Phys. Chem. Solids **69**, 2187 (2008).

[31] R. D. Shannon, Acta Crystallogr. Sect. A: Cryst. Phys. Diffr. Theor. Gen. Crystallogr. **32**, 751 (1976).

[32] N. O. Golosova, D. P. Kozlenko, V. V. Sikolenko, A. P. Sazonov, I. O. Troyanchuk, B. N. Savenko, and V. P. Glazkov, JETP Lett. **84**, 16 (2006).