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Pressure effect on magnetic and structural properties of $La_{1-x}Sr_xCoO_{3-\delta}$

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Pressure-induced changes in ferromagnetic transition temperature (T_C), saturation magnetization (M_S), remanent magnetization (M_R), and coercive field (H_C) as well as the changes in the lattice parameters were investigated for both stoichiometric and oxygen-deficient $La_{1-x}Sr_xCoO_{3-\delta}$ compounds in the wide range of substitutions, $0.3<x<1$ and charge doping $3.18<v_{Co}=3+x-2\delta<3.76$. Comparison of our results with previous data for lightly substituted and stoichiometric oxygen compounds shows that dT_C/dP depends mostly on x, changing the sign from negative to positive in the range of $0.2<x<0.3$ and remaining near 1.5 K/kbar for $0.5<x<1$. Decrease in saturation magnetization with pressure was observed for compounds with full oxygen content. In contrast, M_S increases linearly with increasing pressure for compounds with the same level of charge doping but with varying oxygen contents. The ^{59}Co nuclear-magnetic-resonance study has shown that the ferromagnetic state of oxygen-deficient $SrCoO_{2.88}$ is partly due to double-exchange interactions between cobalt ions: Co^{4+} with intermediate-spin (IS) ($S=3/2$) state and Co^{3+} with the spin state switching between low-spin ($S=0$) and IS ($S=1$). Presence of localized IS Co^{4+} indicates that ferromagnetism of $SrCoO_{2.88}$ is due to rather complex exchange interactions that include superexchange. For $La_{0.33}Sr_{0.67}CoO_{2.85}$, no localized state of Co has been observed and all Co ions are in the mixed-valence state in agreement with the double-exchange-driven ferromagnetic metallic state observed for this composition. The value of bulk modulus for $La_{0.33}Sr_{0.67}CoO_{2.85}$ [$K_0=1540(25)$ kbar] was found to be much higher than that for $SrCoO_{2.88}$ [790(15) kbar].

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I. INTRODUCTION

$La_{1-x}Sr_xCoO_{3-\delta}$ solid solution oxides crystallize in perovskite-type ABO_3 structure with a lanthanide ion (e.g., La^{3+}) and an alkaline earth ion (e.g., Sr^{2+}) at the A site and a cobalt ion at the B site. These oxides with $0<x<0.5$ and fully stoichiometric oxygen content have been the subject of intensive research due to their interesting magnetic and transport properties, in particular, the possibility to change a spin state of Co ion.[1,2] The parent compound $LaCoO_3$ is a nonmagnetic insulator with Co^{3+} present in low-spin (LS) state $t_{2g}^6e_g^0$; $S=0$ at low temperatures. These ions can be thermally excited from LS state into intermediate-spin (IS) state $t_{2g}^5e_g^1$; $S=1$ at $T\approx 100$ K.[1,2] At higher temperature, near 500 K, the system undergoes the insulator-to-metal transition that is frequently associated with a transition to high-spin (HS) state $t_{2g}^4e_g^2$; $S=2$ (Ref. 3). The substitution of Sr ion for La in $LaCoO_3$, resulting in mixed valency of Co ion, leads to a development of ferromagnetic (FM) double-exchange (DE) interactions between Co^{3+} and Co^{4+} ions. Because of the presence of various possible spin states of Co^{3+} and Co^{4+} ions with increasing doping, the ferromagnetism in $La_{1-x}Sr_xCoO_3$ arises as a result of competition between the DE and superexchange (SE) interactions. At low temperatures, the phase separation takes place into hole-rich clusters with FM ordering and hole-poor matrix with antiferromagnetic superexchange interactions between Co^{3+} ions. For $x=0.18$, the clusters coalescence and with x increasing to 0.5 the FM-DE interactions are dominating with Curie temperature increasing from 160 to 250 K (Refs. 4–6). At the same time, the electrical conductivity increases with increasing x and for $x\approx 0.2$ the system undergoes a transition to a metallic state.[5] Hence, for values of $x\approx 0.18-0.20$ the percolation threshold (PT) of FM clusters is reached and a transition from localized to itinerant electron behavior is observed. Thus, the physical properties of this system depend on Co^{3+}/Co^{4+} ratio. The formal oxidation state of Co ion is affected by both the Sr substitution at the A site and by the deviation from oxygen stoichiometry $3-\delta$ and is defined as $v_{Co}=3+x-2\delta$. It has been reported that the oxygen content has profound influence on the magnetic and transport properties of $La_{1-x}Sr_xCoO_{3-\delta}$ similar to other nonstoichiometric transition-metal perovskites.[7–9] In $Sr_xCoO_{3-\delta}$ system, the Curie temperature decreases with decreasing oxygen content from 280 ($\delta=0$) to 220 K for $\delta=0.2$ (Ref. 7). Raveau *et al.* found that the $Sr_{1-x}Ln_xCoO_{3-\delta}$ (Ln=La-Ho) compounds become metallic ferromagnets for v_{Co} larger than +3.43.[10] According to that study, the attainable oxygen content and consequently v_{Co} are strongly affected by the size of the A site cation. The cobaltites with the same v_{Co} are expected to have similar magnetic properties because of the same Co^{3+}/Co^{4+} ratio. An additional feature that merits study of properties of these materials as a function of oxygen content is their high electronic and ionic conductivities above room temperature.[11]

Magnetic properties of $La_{1-x}Sr_xCoO_{3-\delta}$ have been usually studied as a function of temperature and magnitude of magnetic field. Another parameter, which enables the control of physical properties, is the external pressure. It was shown that pressures up to 18.2 kbar increase the spin-state transition of $LaCoO_3$ from 100 to about 190 K (Ref. 12). Masuda *et al.* found resistivity anomaly in $Pr_{0.7}Ca_{0.3}CoO_3$ at low temperature under pressure which indicates the existence of the phase transition.[13] Fujita *et al.*[14] found that external pressure causes a phase transition from a nearly metallic to an insulating state for $Pr_{0.8}Ca_{0.2}CoO_3$. For metallic ferromagnetic single crystal of $La_{0.82}Sr_{0.18}CoO_3$, a pressure-induced increase in electrical resistivity with simultaneous decrease in the Curie temperature have been observed by Lengdsdorf *et al.*[15] Fita *et al.*[16] found strong dependence of the pressure coefficient (dT_C/dP) on doping level for both $La_{1-x}Ca_xCoO_3$ and $La_{1-x}Sr_xCoO_3$ systems. It was shown that while in Ca-substituted crystals, the applied pressure strongly suppressed the ferromagnetism; for Sr-substituted crystals, the dT_C/dP increased with doping, changing sign from negative at $x=0.2$ to positive at $x=0.3$ and $x=0.5$. The intricate behavior was attributed to a competition of two different ferromagnetic mechanisms with expanding the lattice of $La_{1-x}Sr_xCoO_3$ caused by the substitution with a larger Sr ion. The structural changes under pressure have been studied only for compounds with fully stoichiometric oxygen content $La_{0.82}Sr_{0.18}CoO_3$ (Ref. 15) and $LaCoO_3$ (Refs. 17 and 18).

In order to investigate a dependence of magnetic properties of cobaltites on v_{Co} and to clarify the influence of pressure on these properties, we have performed studies of highly Sr-substituted $La_{1-x}Sr_xCoO_{3-\delta}$ ($x \geq 0.33$) polycrystalline samples with varying oxygen content, with v_{Co} in the vicinity and far above the FM percolation threshold at $v_{Co} \approx 3.2$. We have chosen five samples from the region above PT, namely, two stoichiometric samples $La_{0.5}Sr_{0.5}CoO_3$ and $La_{0.33}Sr_{0.67}CoO_3$, their oxygen-deficient compositions $La_{0.5}Sr_{0.5}CoO_{2.89}$ and $La_{0.33}Sr_{0.67}CoO_{2.85}$, and the "end" parent compound $SrCoO_{2.88}$. We have studied also one sample from the region below PT $La_{0.67}Sr_{0.33}CoO_{2.925}$. Hence, the investigated compounds have v_{Co} varying from 3.18 to 3.76. Comparison of our results with those obtained previously for lightly substituted and stoichiometric $La_{1-x}Sr_xCoO_3$ compounds[15,16] shows that dT_C/dP depends mostly on x increasing rapidly in the range of $0.2 < x < 0.5$ and remains almost constant for $0.5 < x < 1$. Pressure dependence of lattice parameters for oxygen-deficient samples shows that $SrCoO_{2.88}$ is more compressible than $La_{0.33}Sr_{0.67}CoO_{2.85}$.

II. SYNTHESIS AND EXPERIMENTAL TECHNIQUES

The conventional solid-state reaction was used to prepare single-phase polycrystalline cobaltites. Appropriate molar ratios of La_2O_3, $SrCoO_3$, and Co_3O_4 were mixed and repetitively finely grounded and fired in air at temperatures between 800 °C and 1000 °C. The samples were then pressed into pellets and fired at 1100 °C–1120 °C. Obtaining single-phase sample of $SrCoO_x$ required quenching from the high temperatures on copper plate. Samples with various oxygen contents were obtained by additional annealing either in high-pressure oxygen (sample of $SrCoO_{2.88}$) or in air followed by quenching in liquid nitrogen. Oxygen content of these samples was checked by thermogravimetric measurements with an accuracy of 0.01.

The magnetic measurements were performed in the temperature range 4.2–290 K with magnetic field up to 16 kOe and under pressure up to 11 kbar using a Princeton Applied Research 4500 vibrating sample magnetometer. At this temperature range, the oxygen content of the samples is fixed. Temperature dependence of magnetization $M(T)$ was measured using zero-field-cooling (ZFC) and field-cooling (FC) procedure, whereas $M(H)$ dependence was measured after FC in maximum applied field. For these measurements, a miniature container of CuBe with an inside diameter of 1.42 mm was employed as a pressure cell.[19] A mixture of mineral oil and kerosene as well as silicone oil were used as pressure-transmitting media. The pressure at low temperature was determined by the pressure dependence of the superconducting transition temperature of pure tin placed near the sample. The pressure coefficients for transition temperature dT_C/dP, saturation magnetization dM_S/dP, coercive field dH_C/dP, and remanent magnetization dM_R/dP were determined from the experimental data within linear approximation. Additionally, the measurements of ac susceptibility at ambient pressure for various frequencies were performed with the ac susceptibility and dc magnetization option of the physical property measurement system of Quantum Design.

The spin-echo nuclear-magnetic-resonance (NMR) experiment has been performed at 4.2 K using an automated broadband phase-sensitive spin-echo spectrometer. The NMR spectra were recorded by measuring integrated spin-echo intensity every 2 MHz in the frequency range of 20–400 MHz at zero external magnetic field and at constant excitation radio frequency field level. Multiple data acquisition and averaging have been executed in order to increase the signal-to-noise ratio. The spectra were corrected for the usual ω^2 dependence of spectrum intensity.

Structural analysis was performed at ambient pressure using Philips X'Pert PRO MPD powder diffractometer with an angle-dispersive x-ray diffraction mode (ADXRD). The x-ray diffraction patterns were refined using Rietveld method. High-pressure studies were carried out at F2.1 beamline (Hasylab/DESY) using a cubic anvil x-ray diffraction press MAX80. Measurements were done using the energy dispersive x-ray diffraction (EDXRD) mode. The diffraction angle was fixed at 4.508°. NaCl was used as pressure transmitting medium (NaCl-to-sample volume ratio was 5:1) and position of its 002 line served for pressure calibration. The diffraction measurements were carried out in the pressure interval of 0–43.2 kbar at $30(\pm 2)$ °C. The bulk moduli (K_0) were determined by fitting the second-order Birch-Murnaghan equation of state (EOS), with K' fixed at four, to the experimental data, using the EOS program.[20]

III. MAGNETIC PROPERTIES AT AMBIENT PRESSURE

A. dc magnetization

Temperature and field dependences of magnetization show marked divergence of zero-field-cooling and field-cooling magnetization M_{ZFC} and M_{FC} at low temperatures

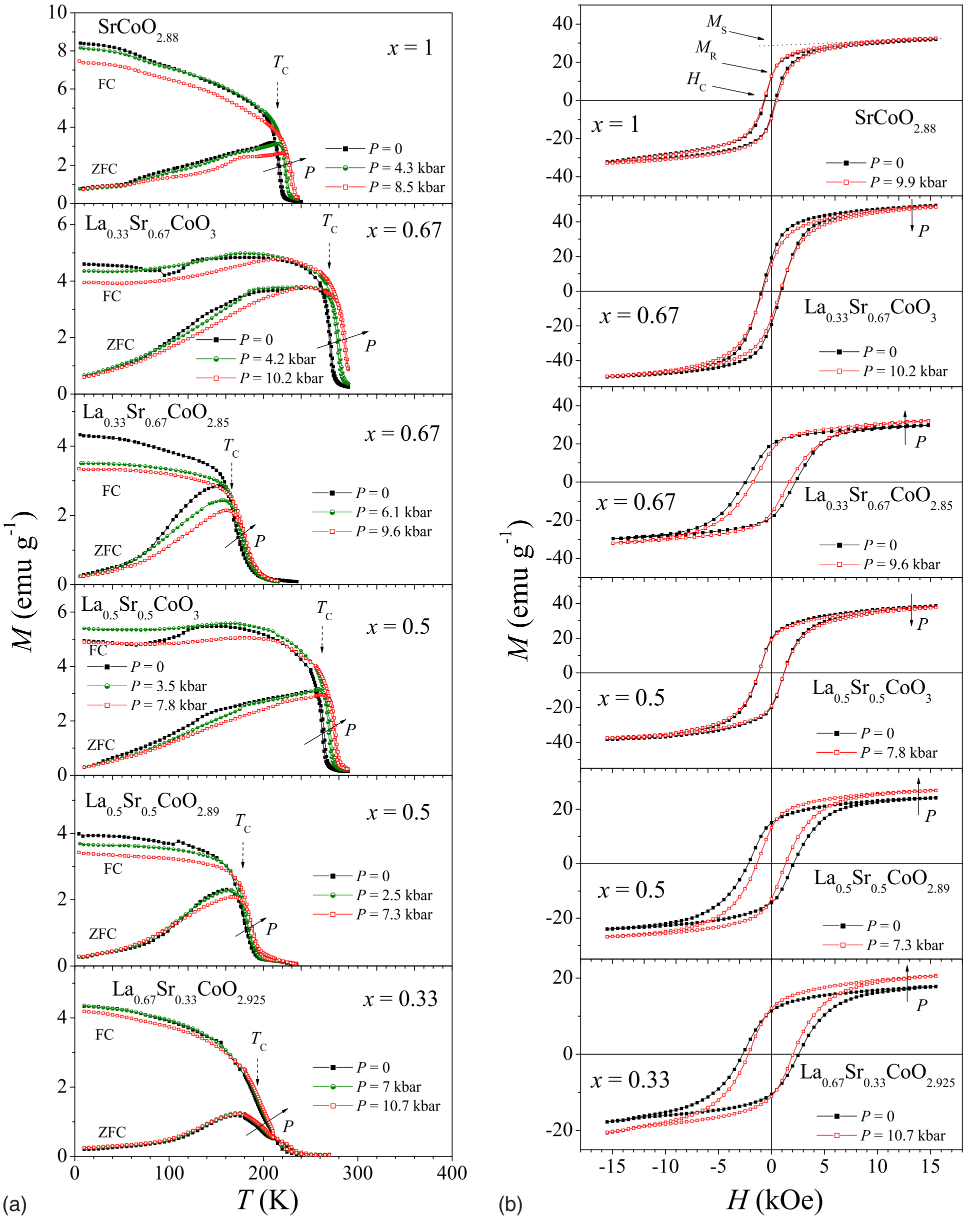

FIG. 1. (Color online) (a) Temperature and pressure dependences of magnetization measured in dc field of 100 Oe and (b) magnetic field and pressure dependences of magnetization at 10 K.

and saturation magnetization M_S [Figs. 1(a) and 1(b), respectively] for all investigated compounds. From the $M(H)$ dependence, we can conclude that all investigated compounds are typical ferromagnets. The Curie temperature was determined from the magnetization $M(T)$ curve as the temperature of the maximum slope. Table I summarizes the magnetic properties of investigated cobaltites at ambient pressure. The oxygen stoichiometric compounds are characterized by the higher values of T_C and M_S. Lowering of T_C in the case of oxygen-vacant compounds may be explained by the breaking of Co^{3+}-O^{2-}-Co^{4+} bonds which are responsible for the FM-DE interaction, in addition to concomitant lowering of v_{Co}, as proposed in Ref. 9. The data shown in Table I support that observation; samples with progressively increasing oxygen vacancy content exhibit lower T_C's despite their higher v_{Co} that normally would result in increased T_C (Refs. 4–6).

Our results differ somewhat from those obtained by Raveau *et al.*[10] These authors have inferred that $Sr_{1-x}Ln_xCoO_{3-\delta}$ (Ln=La-Ho) compounds become strong ferromagnets above a specific v_{Co} value of +3.43. In our case two compounds, namely, $La_{0.5}Sr_{0.5}CoO_{2.89}$ and $La_{0.33}Sr_{0.67}CoO_{2.85}$ with v_{Co} below +3.43 show clear ferromagnetic behavior. In Ref. 10, it was shown that the oxygen

TABLE I. The magnetic properties of investigated cobaltites at ambient pressure.

	T_C (K)	M_S $\left(\frac{\text{emu}}{\text{g}}\right)$	H_C (kOe)	M_R $\left(\frac{\text{emu}}{\text{g}}\right)$
$SrCoO_{2.88}$	215.5	27.57	0.51	10.30
$La_{0.33}Sr_{0.67}CoO_3$	270.0	43.37	0.93	19.12
$La_{0.33}Sr_{0.67}CoO_{2.85}$	166.2	25.30	2.45	19.58
$La_{0.5}Sr_{0.5}CoO_3$	262.0	33.11	1.20	19.98
$La_{0.5}Sr_{0.5}CoO_{2.89}$	174.9	22.85	2.19	15.01
$La_{0.67}Sr_{0.33}CoO_{2.925}$	194.0	15.06	2.72	11.40

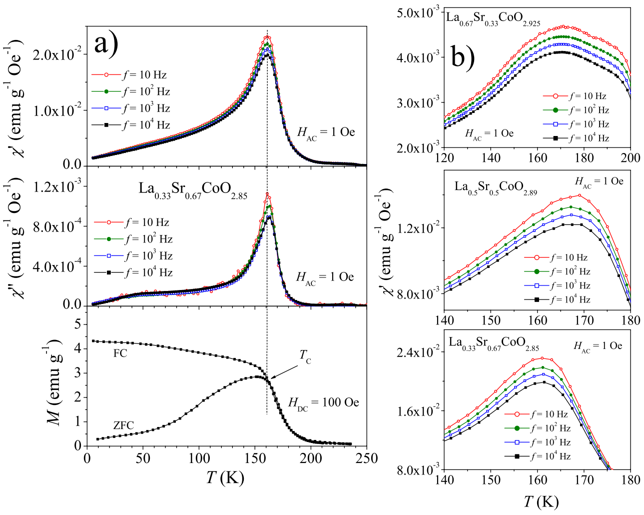

FIG. 2. (Color online) (a) Temperature dependences of real and imaginary parts of magnetic susceptibility for $La_{0.33}Sr_{0.67}CoO_{2.85}$ measured at ac magnetic field amplitude of 1 Oe and of magnetization measured at dc field of 100 Oe. (b) Temperature dependence of the real part of magnetic susceptibility for $La_{0.67}Sr_{0.33}CoO_{2.925}$, $La_{0.5}Sr_{0.5}CoO_{2.89}$, and $La_{0.33}Sr_{0.67}CoO_{2.85}$ in the vicinity of its maximum.

content and, consequently, v_{Co} depend strongly on the size of A site cation. The size of A site cation affects also the magnitude of the structural distortions from cubic symmetry as measured by the Co-O-Co bond angle, which defines the strength of FM-DE coupling. In our study, we focused on Sr substitutions for the largest Ln=La, i.e., compounds with the cubic symmetry and the highest T_C's.

B. ac susceptibility

The temperature dependence of both real and imaginary components of ac susceptibility was measured at four frequencies: 10, 10^2, 10^3, and 10^4 Hz; a probing ac magnetic field of 1 Oe was applied. In Fig. 2(a), an example of the temperature dependences of the real part χ' and imaginary part χ'' of the ac susceptibility is shown for $La_{0.33}Sr_{0.67}CoO_{2.85}$. The common features for all of the studied samples are the following: (i) maximum of both curves $\chi'(T)$ and $\chi''(T)$ occurs at the temperature which is very close to T_C determined from dc magnetic measurements; (ii) maximum of both curves $\chi'(T)$ and $\chi''(T)$ does not depend on the frequency [see Fig. 2(b) for $\chi'(T)$]. Both features indicate the presence of FM interactions. It should be stressed that for all of the studied samples, no trace of spin-glass behavior was noticed.

C. Nuclear magnetic resonance

Resonance frequency f_{res} of ^{59}Co NMR is determined by the value of a local magnetic field B_{Co} experienced by ^{59}Co nucleus $f_{res}=\gamma B_{Co}$, where γ is the nuclear gyromagnetic ratio and $\gamma/2\pi=10.103$ MHz T^{-1} for ^{59}Co. In magnetically ordered materials, B_{Co} mostly arises from the hyperfine interaction which couples spin of ^{59}Co nucleus to the Co electronic moment, i.e., $f_{res}=\gamma B_{Co}^{iso}=\gamma g\mu_B A\langle S\rangle$, where A is the local hyperfine coupling constant and $\langle S\rangle$ is the temperature averaged on-site electron spin of Co ions. This relation shows that the local magnetic field and NMR frequency depend on the Co on-site electron spin. It is known that in the case of magnetically ordered materials, the hyperfine coupling constant A of $3d$ transition metal ions is approximately equal to $A=10$ T/μ_B.[21] In the case of cobaltites with localized spin states of Co, the above relation predicts an increase in f_{res} by 100 MHz with the increase in local Co spin by the single electron spin of $S=1/2$.

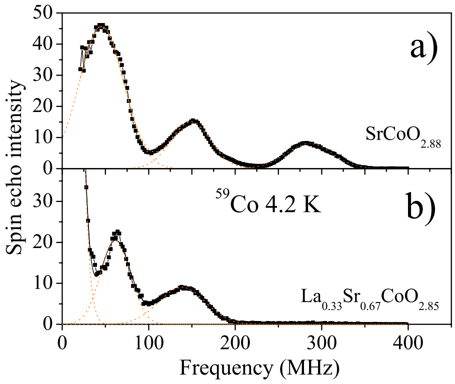

FIG. 3. (Color online) ^{59}Co NMR spectra for (a) $SrCoO_{2.88}$ and for (b) $La_{0.33}Sr_{0.67}CoO_{2.85}$.

There have been only very few NMR works on cobaltites which can be used as an experimental verification of the ^{59}Co NMR frequency dependence on Co valence and spin state. In the case of $LaCoO_3$, the in-field ^{59}Co NMR measurements at low temperatures have confirmed that Co^{3+} ions are in the LS state (S=0) and no contribution from the hyperfine field was observed.[22] Moreover, this state was also observed for the $La_{1-x}Sr_xCoO_3$ system in the doping range of $0<x<0.5$. It coexists with the two other phases: the FM metallic phase with dominating DE interactions giving rise to a broad ^{59}Co NMR spectra in the range of 100–200 MHz and the spin cluster phase characterized by a small nonzero local field at ^{59}Co nuclei indicating the formation of local Co magnetic moments. This phase coexistence was interpreted as being due to the phase-separation phenomenon observed for manganites and cobaltites and resulting primarily from two competing tendencies: delocalization due to DE interaction and localization related to the Jahn-Teller effect. ^{59}Co NMR results obtained for the $La_{1-x}Sr_xCoO_3$ system in low-doping range ($0<x<0.5$) show that the FM metallic state originates from DE interactions involving charge transfer between mixed-valence Co ions.[22,23] However, the spin state of mixed-valence Co ions has not been specified until now.

^{59}Co NMR spectra obtained for $SrCoO_{2.88}$ and $La_{0.33}Sr_{0.67}CoO_{2.85}$ samples are shown in Figs. 3(a) and 3(b), respectively. Both spectra show rather rich structure consisting of several broad lines located in the frequency range of 20–300 MHz indicating complex valence and spin state of ferromagnetic Co ions for each of the studied samples.

For the composition $La_{0.33}Sr_{0.67}CoO_{2.85}$ (v_{Co}=+3.37), well inside the ferromagnetic region, the ^{59}Co NMR spectrum shows clearly two distinct resonance lines centered around 140 and 60 MHz. In addition, the low-frequency part of the spectrum indicates considerable intensity present below the available frequency range of our experimental equipment. This intensity can be tentatively assigned to the ^{139}La resonance, which has been observed in the spectra in the frequency range of 0–50 MHz in the previous study of $La_{1-x}Sr_xCoO_3$.[23] The broad ^{59}Co line centered around 140 MHz can be assigned to the Co ions in the mixed-valence state Co^{3+}/Co^{4+} for the ferromagnetic metallic phase of the sample in agreement with the results of the earlier NMR works.[22,23] In addition, our experiment allows identifying spin state S of the Co^{3+}/Co^{4+} mixed-valence state. This frequency corresponds to a very fast jump of the e_g electron between Co^{4+} and Co^{3+} with the e_g spin states of the first ion occupied by one electron and the empty e_g states for the second Co. Taking formally the rules linking NMR frequency with ionic spin, the possible Co states giving rise to the mixed-valence state $Co^{3+/4+}$ corresponding to this frequency are pairs of the Co ions, Co^{4+} with the IS state ($S=3/2$) and Co^{3+} with the LS state ($S=0$). The mixed-valence state of $Co^{3+/4+}$ originating from such a pair of Co ions will have the frequency value in between the frequencies corresponding to LS Co^{3+} (which is zero)[22] and the frequency of IS Co^{4+} which has not been identified for cobalites until now. As will be shown below for $SrCoO_{2.88}$, the Co^{4+} IS state is characterized by the frequency value close to 300 MHz expected for Co ion with $S=3/2$. Therefore, the representation of Co^{3+} ions in LS state ($S=0$) and Co^{4+} in IS ($S=3/2$) state giving rise to $Co^{3+/4+}$ mixed valence is fully justified by the present results. The second line in the spectrum located at around 60 MHz has not been reported before in the ^{59}Co NMR spectra recorded for $La_{1-x}Sr_xCoO_3$ system. Its frequency and the corresponding local field establish this line as due to Co ions with the spin state between $S=0$ and $S=1/2$ or $S=1$. We suggest to assign it to the Co^{3+} ions with some "intermediate" spin state between LS with $S=0$ and IS state with $S=1$. Jump of e_g electron between Co ions in these two states can be moderated by the presence of Co^{4+} with a DE-type active mechanism, giving rise to a cluster-glass state consisting of Co^{3+} and Co^{4+} ions with the concentration below percolation threshold enabling the formation of the ferromagnetic state.

^{59}Co spectrum obtained for the oxygen-deficient $SrCoO_{2.88}$ sample presented in Fig. 3(b) consists of three well-separated lines. Two of them located at around 150 and 50 MHz have almost the same frequencies as observed in the spectrum for $La_{0.33}Sr_{0.67}CoO_{2.85}$ and, consequently, can be interpreted in a similar way as discussed previously. The third line not present in the spectrum for $La_{0.33}Sr_{0.67}CoO_{2.85}$ is located around 290 MHz, and, using the relation between frequency and spin, this line can be assigned to the Co ions with the spin state $S=3/2$. In stoichiometric $SrCoO_3$, the charge neutrality requires that Co ions are in the Co^{4+} state. Combining these two results, we can assign the 290 MHz line to the Co^{4+} ions with IS state ($S=3/2$). This interpretation indicates that the ferromagnetic state of oxygen-deficient $SrCoO_{2.88}$ is partly due to the double-exchange interactions between cobalt ions: Co^{4+} with IS ($S=3/2$) state and Co^{3+} with the spin state switching between LS ($S=0$) and IS ($S=1$).

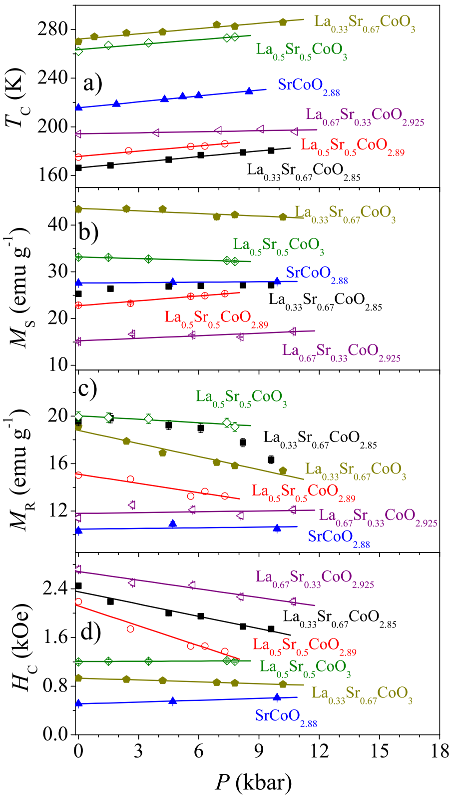

FIG. 4. (Color online) Pressure dependences of the (a) Curie temperature, (b) the saturation magnetization, (c) remanent magnetization, and (d) coercive field for all of the investigated compounds.

IV. DEPENDENCE OF MAGNETIC PROPERTIES ON EXTERNAL PRESSURE

A. T_C vs P

Curie temperature increases with increasing pressure [Fig. 4(a)] for all investigated compounds with charge doping $3.18 < v_{Co} < 3.76$. This indicates strengthening of the FM interactions. The smallest increase is observed for the $La_{0.67}Sr_{0.33}CoO_{2.925}$ sample located slightly below PT. The pressure coefficients of T_C for the compounds from the region above the PT with nonstoichiometric oxygen content, namely, $La_{0.5}Sr_{0.5}CoO_{2.89}$ and $La_{0.33}Sr_{0.67}CoO_{2.85}$, are slightly higher than those for the fully stoichiometric ones ($La_{0.5}Sr_{0.5}CoO_3$, $La_{0.33}Sr_{0.67}CoO_3$). The pressure coefficient is the highest for $SrCoO_{2.88}$. Values of the pressure coefficients are listed in Table II.

Our results agree very well with the previously published results when described in terms of substitution level x (Refs. 15 and 16). Linear increase in dT_C/dP can be noticed in the substitution range from 0.2 to 0.5, with the sign change from the negative to positive (see Fig. 5). This strong dependence is due to the competition of two effects discussed in Ref. 16. One of them is related to the pressure-induced increase in the energy gap between t_{2g} and e_g levels, leading to the suppression of the magnetic IS state and, consequently, to the suppression of the ferromagnetism.[15] The second effect corresponds to the increase in Co-O-Co bond angle and to the

TABLE II. The pressure dependence of magnetic properties of investigated cobaltites.

	$\frac{dT_C}{dP}$ $\left(\frac{\mathrm{K}}{\mathrm{kbar}}\right)$	$\frac{dM_S}{dP}$ $\left(\frac{\mathrm{emu}}{\mathrm{g\ kbar}}\right)$	$\frac{dH_C}{dP}$ $\left(\frac{\mathrm{kOe}}{\mathrm{kbar}}\right)$	$\frac{dM_R}{dP}$ $\left(\frac{\mathrm{emu}}{\mathrm{g\ kbar}}\right)$
$SrCoO_{2.88}$	1.62	≈0	0.01	≈0
$La_{0.33}Sr_{0.67}CoO_3$	1.33	−0.20	−0.01	−0.37
$La_{0.33}Sr_{0.67}CoO_{2.85}$	1.55	nonlin[a]	−0.07	nonlin[a]
$La_{0.5}Sr_{0.5}CoO_3$	1.18	−0.11	≈0	−0.10
$La_{0.5}Sr_{0.5}CoO_{2.89}$	1.45	0.36	−0.11	−0.26
$La_{0.67}Sr_{0.33}CoO_{2.925}$	0.29	0.18	−0.05	≈0

[a]Nonlinear pressure dependence.

reduction in Co-O bond length, which is known to favor DE interactions in magnetic perovskites. For a low level of Sr substitution, the first effect dominates; hence $dT_C/dP < 0$ for $x = 0.18$ (Ref. 15) and $x = 0.2$ (Ref. 16). For higher-doping level, the energy gap between e_g and t_{2g} levels is suppressed by the hole-doping effect and expansion of the Co-O bond length, both caused by the substitution with larger Sr ion. Therefore, the latter mechanism dominates, providing $dT_C/dP > 0$. In the higher-substitution range $0.5 < x < 1$, the pressure coefficient dT_C/dP only slightly depends on x (Fig. 5). The increase in T_C with pressure in this doping range cannot be explained simply by the strengthening of DE interactions. The number of the Co^{3+}-O^{2-}-Co^{4+} pairs decreases and completely disappears for $x = 1$; moreover, for stoichiometric samples, T_C at ambient pressure does not fall but conversely increases from 262 ($x = 0.5$) to 280 K ($x = 1$). In this case, SE-FM interactions are important along with DE ones. It is worth to note that the FM order below 280 K reported for $SrCoO_3$ is mediated by the SE interactions between IS Co^{4+} ions.[24] The positive value of dT_C/dP in the range of $0.5 < x < 1$ may be explained mainly by the pressure-induced contraction of Co-O bond length since the Co-O-Co bond angle is very close to 180° and does not vary significantly with pressure. Additionally, the energy gap between t_{2g} and e_g levels is small enough (due to the lattice expansion caused by the substitution with a larger Sr ion) and, therefore, stabilizes the IS Co^{4+} state which appears to be not so sensitive to pressure.

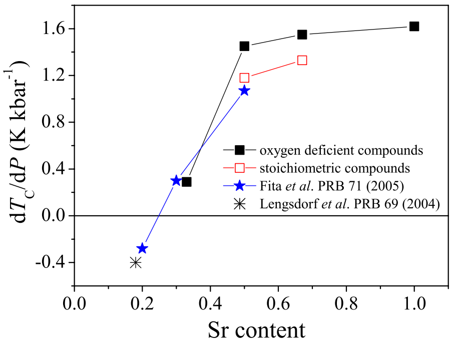

FIG. 5. (Color online) Dependence of pressure coefficient dT_C/dP on Sr substitution; the current results are compared with results of Fita *et al.* (Ref. 16) and Lengsdorf *et al.* (Ref. 15).

It is important to notice that while the T_C depends in general on the charge doping v_{Co} (Ref. 25), the dT_C/dP appears to depend mostly on the Sr substitution level x, indicating that the subtle effects related to the crystal lattice compressibility and the dependence of the Co-O bond lengths and the Co-O-Co bond angles on pressure offset the charge doping induced by oxygen vacancies.

B. Pressure dependence of spontaneous magnetization, remanent magnetization, and coercive field

For $La_{0.5}Sr_{0.5}CoO_{2.89}$, we observed linear $M_S(P)$ dependence up to 7.3 kbar [Fig. 4(b)], whereas for the sample with larger amount of strontium ($La_{0.33}Sr_{0.67}CoO_{2.85}$), a pronounced linear increase in M_S with increasing pressure was noticed only up to 3 kbar. Above 3 kbar, M_S practically does not change (within experimental error) up to 9.6 kbar. For $SrCoO_{2.88}$, the $M_S(P)$ dependence is virtually constant. Small decrease in M_S with increasing pressure is observed for compounds with full oxygen stoichiometry ($La_{0.5}Sr_{0.5}CoO_3, La_{0.33}Sr_{0.67}CoO_3$). This implies that the FM phase volume fraction decreases gradually with pressure. It may be explained by the reduction in the average spin of Co ion due to the pressure-induced IS to LS state transition. In contrast, for samples with the same level of substitution but with nonstoichiometric oxygen content, namely, $La_{0.5}Sr_{0.5}CoO_{2.89}$ and $La_{0.33}Sr_{0.67}CoO_{2.85}$, M_S increases linearly with increasing pressure. These differences seem to be correlated with a formal valence of Co ion—a decrease in saturation magnetization under pressure is observed for compounds with higher values of v_{Co}, despite an exception in $SrCoO_{2.88}$ with $dM_S/dP \approx 0$.

The values of the remanent magnetization and coercive field were determined by the interpolation from upper branch of $M(H)$. Comparison of $M_S(P)$ and $M_R(P)$ dependences for the substituted compounds with oxygen vacancies ($La_{0.5}Sr_{0.5}CoO_{2.89}$ and $La_{0.33}Sr_{0.67}CoO_{2.85}$) indicates mirror image effect, namely, increase in M_0 with increasing P [Fig. 4(b)] corresponds to the decrease in M_R with increasing P [Fig. 4(c)]. The value of the pressure coefficient dM_R/dP for $La_{0.5}Sr_{0.5}CoO_{2.89}$ is comparable with that of dM_S/dP but with an opposite sign. The $La_{0.5}Sr_{0.5}CoO_3$ and $La_{0.33}Sr_{0.67}CoO_3$ compounds do not show this effect; both M_S and M_R decrease linearly with increasing pressure. In the case of $SrCoO_{2.88}$, M_R does not change with increasing pressure, similar to M_S. The sensitiveness of the remanent magnetization to external pressure is comparable for most of the investigated compounds, except for $SrCoO_{2.88}$ (with the highest value of v_{Co}). For the substituted compounds with oxygen vacancies ($La_{0.5}Sr_{0.5}CoO_{2.89}$ and $La_{0.33}Sr_{0.67}CoO_{2.85}$), a linear decrease in H_C with increasing pressure was found [Fig. 4(d)]. In the case of remaining compounds, the H_C changes marginally with increasing pressure ($La_{0.33}Sr_{0.67}CoO_3, SrCoO_{2.88}$) or does not change definitely ($La_{0.5}Sr_{0.5}CoO_3$). Similar to the behavior of M_S, coercive field is less sensitive to pressure for the compounds with higher Co^{4+} ion concentrations.

The discrepancy between the dT_C/dP values of the nonstoichiometric sample with $\upsilon_{\text{Co}}=+3.28$ and the stoichiometric sample with $\upsilon_{\text{Co}}=+3.3$ together with the complex variation in $M_S(P)$ and $M_R(P)$ on pressure, and the influence of the A site cation on magnetotransport properties[10] suggests that the strength of FM-DE interactions can be affected by many factors such as valence state of the Co ion, the level and kind of substitution at the A site, and the oxygen content. The possible short-range or long-range ordering as well as cobalt spin state may be equally important. Further studies of magnetic properties are required for systems with different level of substituting ion and with fixed oxygen vacancy content to elucidate the role of these factors.

V. STRUCTURAL PROPERTIES

$La_{1-x}Sr_xCoO_{3-\delta}$ crystallizes at room temperature in rhombohedrally distorted perovskite structure with $R\bar{3}c$ space group for $x \leq 0.5$ and in simple cubic $Pm\bar{3}m$ for $x > 0.5$.[7,9,26–28] Van Doorn and Burggraaf proposed a tetragonal $a_p \times a_p \times 2a_p$ superstructure with distinct microdomains for $La_{0.3}Sr_{0.7}CoO_{2.82}$.[28] The same tetragonal superstructure was detected by James *et al.*[29] in $La_{0.1}Sr_{0.9}CoO_{3-\delta}$. In a most recent work, it has been shown that for highly Sr-substituted $La_{0.33}Sr_{0.67}CoO_{3-\delta}$ with oxygen vacancies $(0 < \delta < 0.5)$, three structure types are observed depending on the δ value.[25]

The Rietveld refinement of XRD patterns performed at ambient pressure indicated a simple cubic perovskite cell $(Pm\bar{3}m)$ for $La_{0.33}Sr_{0.67}CoO_{2.85}$ with the lattice parameter $a=3.841\,7(2)$ Å. For $SrCoO_{2.88}$, a tetragonal $(I4/mmm)$ distortion was observed with $a=10.873\,3(8)$ Å and $c=7.668\,1(6)$ Å. High-pressure x-ray diffraction spectra [shown for eight selected pressures in Figs. 6(a) and 6(b)] do not indicate any structural phase transition in the studied pressure range. However, the possibility of such a transition cannot be excluded because the resolution of EDXRD method may not be sufficient for the observation of small distortions due to relatively high value of full width at half maximum of the sample peak. In that case, only the pseudocubic lattice parameter for $SrCoO_{2.88}$ could be determined. Position of 111 diffraction peak was applied for the determination of the lattice parameter, as the other ones overlap with NaCl peaks for the highest pressures. The lattice parameter a for $La_{0.33}Sr_{0.67}CoO_{2.85}$ decreases from 3.844 Å at ambient pressure to 3.813 Å at 37.7 kbar. For $SrCoO_{2.88}$, the pseudocubic lattice parameter decreased from 3.843 Å at $P=0$ to 3.807 Å at 23.3 kbar. Our values of lattice parameters calculated from both ADXRD and EDXRD methods agree quite well with those reported in Ref. 7 (pseudocubic $a \approx 3.84$ Å) and Ref. 26 $(a \approx 3.839$ Å), for $SrCoO_{2.88}$ and for $La_{0.33}Sr_{0.67}CoO_{2.85}$, respectively.

The relative unit cell volumes as a function of pressure determined from diffraction data are presented in Fig. 7. The Birch-Murnaghan equation of state was fitted to the experimental points in the range of 0–23 kbar for $SrCoO_{2.88}$ and of 0–38 kbar for $La_{0.33}Sr_{0.67}CoO_{2.85}$. Some deviations from the model predictions observed above 23 kbar for $SrCoO_{2.88}$ and near 5–7 kbar for $La_{0.33}Sr_{0.67}CoO_{2.85}$ may arise due to nonfully hydrostatic conditions inside the press. Other reasons such as some structural changes under pressure cannot be fully excluded. The discrepancies observed for the highest pressures studied may also be influenced by inaccuracies in deconvoluting of the 111 perovskite peak and 100 peak of hexagonal boron nitride, the sample-container material.

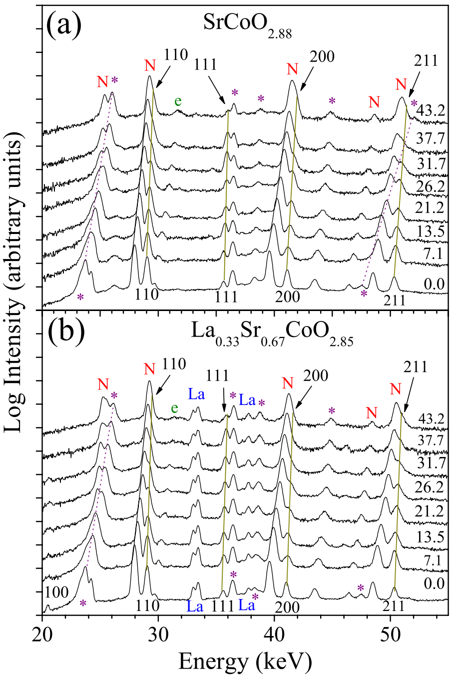

FIG. 6. (Color online) X-ray diffraction patterns under pressure for (a) $SrCoO_{2.88}$ and (b) $La_{0.33}Sr_{0.67}CoO_{2.85}$. The Bragg diffraction peaks associated with the perovskite phase are indexed and connected (as guide for the eyes) by solid lines. Peaks belonging to hexagonal boron nitride (BN) (sample container) and to NaCl are marked " *" and "N," respectively. Fast changing with pressure 002 and 004 peaks of hexagonal BN are connected by dotted lines. The numbers on the right refer to the pressure values (in kbar units). "La" indicates the La fluorescence lines.

The fitting results show that $La_{0.33}Sr_{0.67}CoO_{2.85}$ is much less compressible than $SrCoO_{2.88}$ [$K_0=1540(25)$ and 790(15) kbar, respectively; Fig. 7]. This finding correlates with the results of magnetic measurements showing that the phase-transition temperature T_C varies faster with pressure for

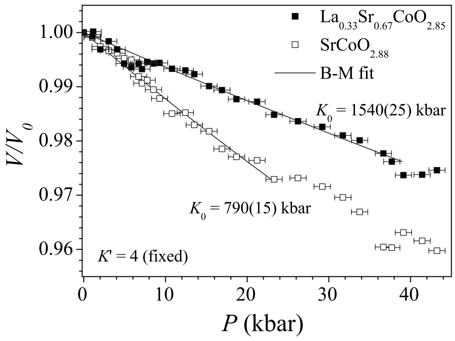

FIG. 7. Variation in the relative unit-cell volume with pressure for both studied compounds. The solid lines refer to the fitted Birch-Murnaghan equation of state.

$SrCoO_{2.88}$ (i.e., the value of dT_C/dP is higher). Comparison with literature data for a partial or full substitution of Sr by La for stoichiometric samples indicates different trends for nonstoichiometric samples. The bulk modulus for $La_{0.33}Sr_{0.67}CoO_{2.85}$ sample is virtually identical to that of rhombohedral samples $La_{0.82}Sr_{0.18}CoO_3$ and $LaCoO_3$ [$K_0=1580(80)$ kbar (Ref. 15) and 1500(20) kbar (Ref. 17), respectively] determined by other groups using the diamond-anvil cell technique. However, the most recent experiments (performed with a different pressure marker) yield a lower K_0 value of 1220(30) kbar for $LaCoO_3$ (Ref. 18). The correlation between bulk modulus and spin state of Co ion, with lower spin state of Co ion corresponding to higher K_0, was suggested in Refs. 17 and 18. Our NMR and compressibility studies show that a large difference in K_0 values cannot be explained by the spin state of Co alone. In the case of $La_{0.33}Sr_{0.67}CoO_{2.85}$, there are Co^{4+} ions with IS and Co^{3+} ions in LS. For $SrCoO_{2.88}$, there are Co^{4+} ions with IS ($S=3/2$) and Co^{3+} ions with spin switching between LS ($S=0$) and IS ($S=1$). Hence, for the Co^{3+} ions, there is only some admixture of LS. Higher compressibility of $SrCoO_{2.88}$ ($K_0=790$ kbar) in comparison with $La_{0.33}Sr_{0.67}CoO_{2.85}$ ($K_0=1540$ kbar) may also be due to the smaller Co ion radius of the higher-valence state ($v_{Co}=+3.76$) in this compound. However, the scarcity and scatter of experimental data on the influence of composition on bulk modulus in this system require further studies.

VI. CONCLUSIONS

The influence of pressure on magnetic and structural properties was investigated for highly Sr-substituted $La_{1-x}Sr_xCoO_{3-\delta}$ materials with stoichiometric and oxygen-deficient compositions. We have observed an increase in T_C with increasing pressure for all investigated compounds with charge doping $3.18<v_{Co}<3.76$. Our results agree very well with the previously published[15,16] results when described in terms of substitution level x and confirm strong dependence of dT_C/dP on x in the range $0.2<x<0.5$. This was attributed to the competition of two effects: the first one related to the pressure-induced suppression of IS state and, consequently, ferromagnetism and the second one favoring the FM interactions by both (i) increasing the Co-O-Co bond angle and (ii) contracting the Co-O bond length. For substitution range $0.5<x<1$, it was found that dT_C/dP only slightly varies with Sr content and reaches the largest values of about 1.6 K/kbar. The increase in FM phase volume fraction under pressure evidenced by positive dM_S/dP was observed only for oxygen-deficient compounds with v_{Co} smaller than +3.4. The influence of pressure on saturation magnetization and coercive field was also attenuating with an increase in the formal oxidation state of Co ion. In the case of the remanent magnetization, we have rather observed a decrease in M_R with increasing pressure (except for $SrCoO_{2.88}$ and $La_{0.67}Sr_{0.33}CoO_{2.925}$). The value of bulk modulus (K_0) for $La_{0.33}Sr_{0.67}CoO_{2.85}$ was found to be much higher than that for $SrCoO_{2.88}$. The ^{59}Co NMR study has shown that the ferromagnetic state of oxygen-deficient $SrCoO_{2.88}$ is partly due to the double-exchange mechanism between cobalt ions: Co^{4+} with IS ($S=3/2$) state and Co^{3+} with the spin state switching between LS ($S=0$) and IS ($S=1$). However, the presence of localized Co^{4+} with IS ($S=3/2$) indicates that the ferromagnetic state of this composition is due to complex exchange interactions also including superexchange. In the case of $La_{0.33}Sr_{0.67}CoO_{2.85}$, NMR indicates that all Co give rise to the mixed-valent state of Co similar to that observed in the case of the oxygen-deficient $SrCoO_{2.88}$ and no localized state of Co has been observed in agreement with the double-exchange-driven ferromagnetic metallic state observed for this composition. The achievable valence state of Co ion can be controlled by several factors such as the kind and amount of the lanthanide ion and the oxygen content. Strength of the ferromagnetic interactions between both mixed-valent and isovalent Co ions can be affected by many factors such as the valence state of the Co ion, structural distortions, oxygen defect concentration, as well as cobalt spin state. The observed increase in T_C with pressure for oxygen-deficient samples indicates that new compositions can be designed with improved FM properties by the manipulation of oxygen content and vacancy order.

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