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Effects of Temperature and Pressure on the Magnetic Properties of $La_{1-x}Pr_xCoO_3$

Anatoliy S. Panfilov, Anastasiya A. Lyogenkaya,* Gennadiy E. Grechnev, Volodymyr A. Pashchenko, Leonid O. Vasylechko, Vasyl M. Hreb, and Andrei V. Kovalevsky

For $La_{1-x}Pr_xCoO_3$ cobaltites with $x = 0$, 0.1, 0.2, and 0.3, the temperature dependence of magnetic susceptibility $\chi(T)$ is studied in the temperature range from 5 to 400 K. Also, the crystal structure of these cobaltites is investigated, and the effect of hydrostatic pressure up to 2 kbar on their susceptibility is measured at fixed temperatures $T = 78$, 150, and 300 K. The specific dependencies $\chi(T)$ and the large negative pressure effect observed in $La_{1-x}Pr_xCoO_3$ are assumed to arise from Co^{3+} ions, which contribution to the total susceptibility is evaluated using $La_{1-x}Pr_xAlO_3$ as a reference system. The obtained experimental data on temperature and pressure effects in magnetism are analyzed in the framework of a two-level model with energy gap Δ between the ground state of the system with zero spin of Co^{3+} ions and the excited higher-spin state. In this model, magnetism of Co^{3+} ions is determined by the temperature-induced population of the excited state, and the magnitude of the pressure effect is governed by the volume dependence of Δ. The results of the analysis, supplemented by the theoretical calculations of the electronic structures of $LaCoO_3$ and $PrCoO_3$, indicate a significant increase in Δ with a decrease in the unit cell volume both under hydrostatic pressure and by substituting La with Pr having a smaller ionic radius. The estimated effects of the physical and chemical pressures on Δ and χ are similar in magnitude, indicating a strong correlation of the spin state of Co^{3+} ions with the lattice volume.

1. Introduction

In $RCoO_3$ cobaltites, which have perovskite-like crystal structures, the Co^{3+} ions can exist in three different spin states, corresponding to the low (LS, $S = 0$), intermediate (IS, $S = 1$) and high (HS, $S = 2$) spin values. The energy difference between these states, determined by the competition between the splitting of the ionic energy levels by the crystal field in t_{2g} and e_g states and Hund's intra-atomic exchange interaction, is rather small. As a result, the relative positions of these spin states appear to be very sensitive to external factors such as temperature, pressure, and magnetic field. This situation generates different spin crossovers and provides the observed peculiar behavior and variety of physical properties of the $RCoO_3$ systems (see the studies by Raveau and Seikh and Takami[1–3] and references therein).

The large number of investigations of physical properties of $RCoO_3$ cobaltites were conducted to reveal the scenario of transition between spin states of Co^{3+} ions with increasing temperature. In a number of experimental and theoretical papers,[4–10] the authors proposed the LS → HS-type scenario to explain the physical properties of $RCoO_3$. In contrast, many works have given evidence in favor of the LS → IS scenario.[11–17] Therefore, the nature of different spin states of Co^{3+} ions in $RCoO_3$ and their transformation under external and chemical pressures are still the subjects of active experimental and theoretical studies.

The transitions between the spin states of Co^{3+} with increasing temperature is most clearly manifested in the magnetic properties of $LaCoO_3$ compound, where La has no magnetic moment and the contribution of cobalt ions to the total susceptibility χ appears to be predominant. At low temperatures, $LaCoO_3$ is in the ground LS state ($S = 0$), being a nonmagnetic semiconductor. With increasing temperature, the states of a higher spin, IS and/or HS, begin to be populated, leading to a rapid increase in magnetic susceptibility and a pronounced maximum in $\chi(T)$ at $T \approx 100$ K, followed by a decrease in susceptibility close to the Curie–Weiss law.[13,14,18] Results of a detailed analysis of the temperature dependence of magnetic susceptibility in

Dr. A. S. Panfilov, Dr. A. A. Lyogenkaya, Prof. G. E. Grechnev, Dr. V. A. Pashchenko
B. Verkin Institute for Low Temperature Physics and Engineering
National Academy of Sciences of Ukraine
61101 Kharkov, Ukraine
E-mail: lyogenkaya@ilt.kharkov.ua

Prof. L. O. Vasylechko, V. M. Hreb
Lviv Polytechnic National University
79013 Lviv, Ukraine

Prof. A. V. Kovalevsky
Department of Materials and Ceramic Engineering
CICECO – Aveiro Institute of Materials
University of Aveiro
3810-193 Aveiro, Portugal

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/pssb.202000085.

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$LaCoO_3$[13,14] convincingly argue in favor of the LS→IS scenario of the spin crossover, which is valid at least for the range of low and moderate temperatures. In addition, an important result of this analysis is the evaluated temperature dependence of the energy difference between IS and LS states, which decreases with increase in temperature and vanishes at about room temperature.

One of the efficient ways to further investigate the phenomenon of spin crossover is to study the effect of high pressure on the magnetic properties of cobaltites. Such investigations for $LaCoO_3$[19-22] and for a number of $RCoO_3$ compounds (R = Pr, Nd, Sm, and Eu)[21] have revealed a strong decrease under pressure of the Co ions' contribution to the total susceptibility and a shift of the characteristic maximum on $\chi(T)$ dependence to higher temperatures.

A number of investigations were based on the studies of the Co^{3+} spin state in $La_{1-x}R_xCoO_3$ compounds. In these compounds, the substitution of La with rare-earth elements has provided a decrease in the cell volume due to a decrease in the ionic radius along the R^{3+} series. The corresponding effects of chemical pressure on magnetic susceptibility of $La_{1-x}Pr_xCoO_3$,[23] $La_{1-x}Nd_xCoO_3$,[24] $La_{1-x}Sm_xCoO_3$,[25] and $La_{1-x}Eu_xCoO_3$[14,26] revealed some similarity in the behavior of magnetism of Co^{3+} ions in these compounds with the relevant effects of physical pressure in $LaCoO_3$. However, it should be noted that a quantitative analysis of the spin state of Co^{3+} ions in such systems, based on their magnetic properties, requires proper account of the rare-earth background magnetism.

In this article, we provide the results of extensive studies of structural and magnetic properties of $La_{1-x}Pr_xCoO_3$ compounds. The main goal of this work is to explore the dependence of the spin state of cobalt ions in these compounds on temperature, as well as on the lattice volume changes, both under hydrostatic pressure and by substituting La with Pr, which has a smaller ionic radius. For this purpose, we have investigated the magnetic susceptibility of the isostructural $La_{1-x}Pr_xCoO_3$ cobaltites ($0 \le x \le 0.3$) in the temperature range $5 - 400$ K, and also under applied hydrostatic pressure up to 2 kbar at fixed temperatures $T = 78$, 150, and 300 K. The experimental data on the excitation energies Δ and their pressure derivatives were analyzed using the corresponding theoretical estimates for $LaCoO_3$ and $PrCoO_3$ obtained by the ab initio calculations based on the fixed spin moment method.[27]

2. Experimental Section

2.1. Preparing and Crystal Structure Study of $La_{1-x}Pr_xCoO_3$ Compounds

The powder samples of $La_{1-x}Pr_xCoO_3$ ($x = 0$, 0.1, 0.2 and 0.3) were prepared by conventional solid-state method using high-purity La_2O_3 (Sigma Aldrich, ≥99.9%), Pr_6O_{11} (Sigma Aldrich, 99.9%), and Co_3O_4 (Sigma Aldrich, 99.5%). Before weighing, lanthanum oxide was calcined at 973 K for 2 h in air to remove moisture. Praseodymium oxide was annealed at 1273 K for 2 h with 3 °C min^{-1} cooling and heating rates to remove absorbed species and attain the equilibrium composition of Pr_6O_{11}, confirmed by XRD. The precursor powders were mixed in stoichiometric proportion and calcined consecutively at 1173, 1273, and 1323 K for 10 h at each temperature, with intermediate regrindings. Resulting powders were uniaxially compacted as disk-shaped samples and sintered at 1373 K for 24 h.

Phase and structural characterizations of the samples were carried out using Rigaku D/Max-B and modernized DRON-3M powder diffractometers (Cu Kα radiation, $\lambda = 1.54185$ Å). Crystal structure parameters including unit cell dimensions, coordinate, and isotropic displacement parameters of atoms were derived from the diffraction data collected in 2Θ range of 20°–125° by full profile Rietveld refinement applying WinCSD program package.[28]

Examination of XRD patterns of the $La_{1-x}Pr_xCoO_3$ materials had revealed pure rhombohedral perovskite structure for the samples with $x = 0.1$ and 0.2 (**Figure 1**). The main features of XRD pattern of $La_{0.7}Pr_{0.3}CoO_3$ material were similar to the aforementioned specimens. Nevertheless, the careful examination of the pattern allowed to detect extra features, which cannot be described in a single $R\bar{3}c$ structural model (Figure 1). This observation pointed to the coexistence of rhombohedral and orthorhombic perovskites in the sample with nominal composition $La_{0.7}Pr_{0.3}CoO_3$. This coexistence was in excellent agreement with the data of thorough X-ray synchrotron powder diffraction investigation of $RCoO_3$-$R'CoO_3$ (R, R′ = La, Pr, Nd, Sm) systems,[29] according to which the phase-separation region occured in $La_{1-x}Pr_xCoO_3$ perovskite materials at $0.25 \le x \le 0.4$.

Phase composition and crystal structure of the materials studied were fully confirmed by full-profile Rietveld refinement. For the $La_{1-x}Pr_xCoO_3$ samples with $x = 0.1$ and 0.2, an excellent

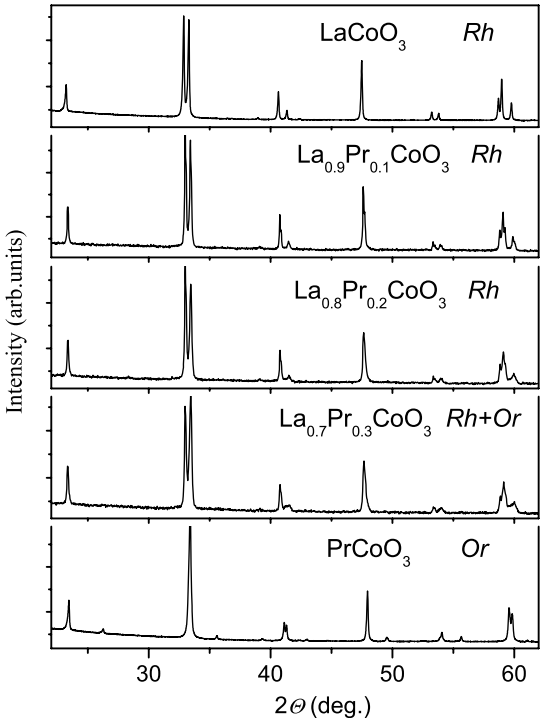

Figure 1. XRD patterns of $La_{1-x}Pr_xCoO_3$ materials (Cu Kα radiation) in comparison with the parent $LaCoO_3$ and $PrCoO_3$ compounds with rhombohedral (Rh) and orthorhombic (Or) perovskite structures.

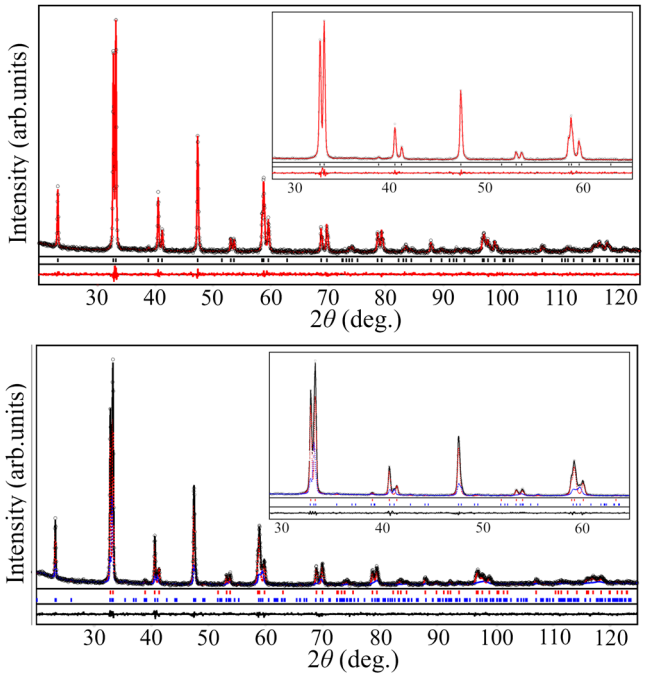

Figure 2. Top panel: graphical results of full-profile Rietveld refinement of $La_{0.9}Pr_{0.1}CoO_3$ structure in the single-phase $R\bar{3}c$ rhombohedral model. Bottom panel: Simultaneous two-phase Rietveld refinement showing the presence of 71 wt% of $R\bar{3}c$ and 29 wt% of *Pbnm* perovskite phases (blue and red curves, respectively) in the $La_{0.7}Pr_{0.3}CoO_3$ sample. Experimental XRD patterns (black circles) are shown in comparison with the calculated patterns (blue and red lines). The difference between measured and calculated profiles is shown as a curve below the diagrams. Short vertical bars indicate the positions of diffraction maxima in $R\bar{3}c$ (red) and *Pbnm* (blue) structures.

Table 1. Lattice parameters, positional, and displacement parameters of atoms in $La_{1-x}Pr_xCoO_3$ structures.

Atoms	Parameters	$x = 0$	$x = 0.1$	$x = 0.2$	$x = 0.3$	
Sites	Residuals	$R\bar{3}c$	$R\bar{3}c$	$R\bar{3}c$	$R\bar{3}c$	*Pbnm*
					(71 wt.%)	(29 wt.%)
	a, Å	5.4419(2)	5.4393(3)	5.4359(4)	5.4341(3)	5.4407(9)
	b, Å	–	–	–	–	5.3565(8)
	c, Å	13.0885(5)	13.0797(9)	13.069(1)	13.0504(9)	7.594(1)
La/Pr,	*x*	0	0	0	0	−0.0152(13)
6*a* in $R\bar{3}c$	*y*	0	0	0	0	0.0289(9)
c in *Pbnm*	*z*	1/4	1/4	1/4	1/4	1/4
	B_{iso}, Å^2	0.76(9)	0.79(6)	0.62(5)	0.56(5)	0.60(12)
Co,	*x*	0	0	0	0	0
6*b* in $R\bar{3}c$	*y*	0	0	0	0	1/2
b in *Pbnm*	*z*	0	0	0	0	0
	B_{iso}, Å^2	0.9(2)	0.79(12)	0.89(10)	1.13(11)	0.9(3)
O1,	*x*	0.553(5)	0.546(3)	0.546(3)	0.551(3)	0.032(12)
e in $R\bar{3}c$	*y*	0	0	0	0	0.505(8)
c in *Pbnm*	*z*	1/4	1/4	1/4	1/4	1/4
	B_{iso}, Å^2	1.6(6)	1.2(4)	0.9(3)	0.7(3)	1.0(18)
O2,	*x*	–	–	–	–	−0.308(5)
d in *Pbnm*	*y*	–	–	–	–	0.258(12)
	z	–	–	–	–	0.041(5)
	B_{iso}, Å^2	–	–	–	–	1.0(11)
	R_I	0.038	0.039	0.033	0.043	0.093
	R_P	0.094	0.120	0.122	0.151	0.151

fit between calculated and experimental profiles was achieved in the space group $R\bar{3}c$ (**Figure 2**, top panel).

In contrast, only including the additional *Pbnm* phase into the full profile Rietveld refinement procedure well-described all the diffraction features of the $La_{0.7}Pr_{0.3}CoO_3$ material, which cannot be satisfactorily fitted in the single-phase perovskite model (Figure 2, bottom panel). Refined structural parameters of the materials studied are shown in **Table 1**. In the refinement procedure, the unit cell dimensions, atomic coordinates, and displacement parameters of atoms were refined together with profile parameters and corrections for the adsorption and instrumental sample shift.

The obtained structural parameters of $La_{1-x}Pr_xCoO_3$ perovskite materials studied in this work agreed well with the structural data for the parent $LaCoO_3$ and $PrCoO_3$ compounds and the mixed lanthanum–praseodymium cobaltites,[29,30] proving the existence of two kinds of solid solutions in $LaCoO_3$–$PrCoO_3$ pseudobinary system.

2.2. Magnetic Properties

For the synthesized samples of $La_{1-x}Pr_xCoO_3$, the temperature dependence of their magnetic susceptibility was measured in the range from 5 to 400 K in a magnetic field of 1 T, using a Quantum Design SQUID magnetometer. Similar measurements were also carried out for $La_{1-x}Pr_xAlO_3$ compounds, which were prepared by a combination of solid-state synthesis at 1373 K following by arc-melting in Ar atmosphere.[31] Comparing data for both systems made it possible to derive properly the contribution of cobalt ions to magnetic susceptibility of $La_{1-x}Pr_xCoO_3$. The obtained experimental data for $La_{1-x}Pr_xCoO_3$ and $La_{1-x}Pr_xAlO_3$ are shown in **Figure 3** and **4**, respectively, and in general, are in agreement with the relevant data in the study by Kobayashi et al.[23]

The appreciable Curie-like rise of the susceptibility of $La_{1-x}Pr_xCoO_3$ was observed at low temperatures which obeys a relation

$$\chi(T) \simeq C_{\text{imp}}/T + \chi_0 \quad (1)$$

where C_{imp}/T term is assumed to originate from a small amount of the paramagnetic impurities and χ_0 is the host susceptibility. The corresponding values of parameters in Equation (1), estimated from $\chi(T)$ versus $1/T$ dependence, are shown in **Table 2**. The estimates of Pr ions magnetism at $T \to 0$ K are also shown in Table 2. This magnetism of the Pr ions mainly contributes to χ_0 value of $La_{1-x}Pr_xCoO_3$ compounds with increasing Pr content.

For $LaCoO_3$, our value of $\chi_0 \simeq 1.0 \times 10^{-3}$ emu mol^{-1} (hereinafter referred to as $\chi_{0(LaCoO_3)}$) coincides in order of magnitude

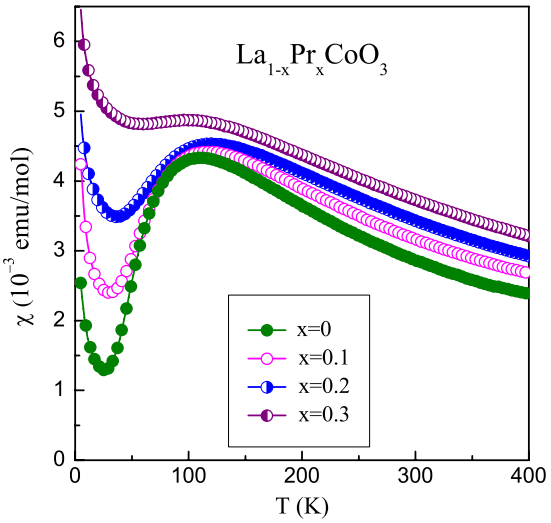

Figure 3. Temperature dependencies of magnetic susceptibility of $La_{1-x}Pr_xCoO_3$ compounds.

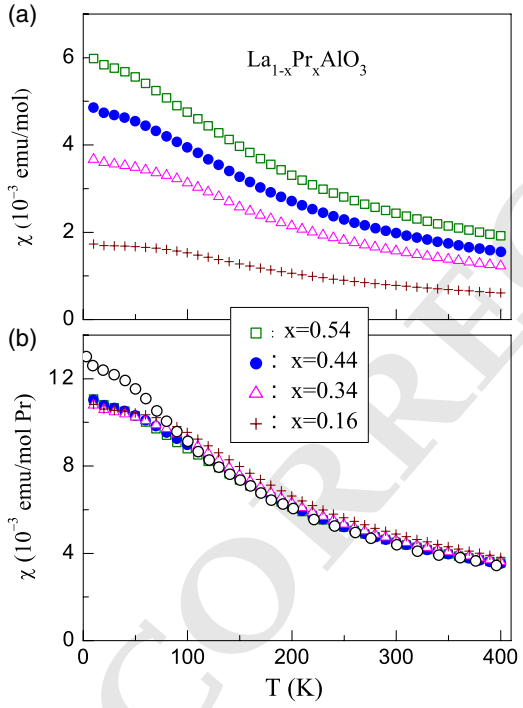

Figure 4. a) Temperature dependencies of the molar magnetic susceptibility of $La_{1-x}Pr_xAlO_3$ compounds and b) their values normalized per mole of Pr. (∘)—data for x=1 from the study by Kobayashi et al.[23] (some deviation from the general regularity below 100 K is apparently due to manifestation of the structural phase transition in $PrAlO_3$).[31]

with the corresponding literature data, e.g., 0.65,[13] 0.50,[32] and 0.16,[14] in units of 10^{-3} emu mol^{-1}. We assume that noticeable difference in the reported values of χ_0 may be due to manifestation of a small and different amount of the magnetically ordered clusters, which were usually observed in the real crystals of

Table 2. Estimated from Equation (1), the Curie constant of the paramagnetic impurities C_{imp} (in units of 10^{-3} K emu mol^{-1}) and host susceptibility χ_0 in the low-temperatures region for $La_{1-x}Pr_xCoO_3$ compounds together with contribution of the Pr ions χ_{Pr} at $T \to 0$ K (both in units of 10^{-3} emu mol^{-1}). For details of the χ_{Pr} estimates, see Section 4.

x	C_{imp}	χ_0	$\chi_{Pr}(T \to 0K)$
0.0	8.4	1.0	–
0.1	11.4	2.1	1.06
0.2	8.6	3.4	2.12
0.3	8.5	4.85	3.18

$LaCoO_3$.[33–37] For all our samples of $La_{1-x}Pr_xCoO_3$, the presence of these foreign phases was apparently confirmed by a sharp divergence of the $\chi(T)$ dependencies at $T \approx 85$ K measured in $H = 0.01$ T with cooling in a field (FC) and with heating in a field after cooling in zero field (ZFC). This typical low field manifestation of the foreign magnetic phases in cobaltites[33–37] was not detected in our FC and ZFC data for $H = 1$ T.

In comparison with $La_{1-x}Pr_xCoO_3$, in $La_{1-x}Pr_xAlO_3$ compounds, the impurity Curie-like effect was noticeably smaller and it can be omitted in the subsequent discussion. In addition, as shown in Figure 4b, the values of χ per mole of Pr for $La_{1-x}Pr_xAlO_3$, estimated from data for different concentrations of Pr, coincide well with each other, that indicates an approximate additivity of the Pr contribution in this system. This additivity also simplified the account of the Pr magnetism when extracting the temperature-induced spin contribution of the Co^{3+} ions from the total susceptibility of $La_{1-x}Pr_xCoO_3$.

The uniform pressure effect on the magnetic susceptibility of $La_{1-x}Pr_xCoO_3$ was studied under helium gas pressure P up to 2 kbar, using a pendulum-type magnetometer.[38] To eliminate the effect on susceptibility of the temperature changes when pressure was applied, the measurements were carried out at fixed temperatures 78, 150, and 300 K. The relative experimental errors did not exceed 0.1% for the used magnetic field $H = 1.7$ T.

The experimental dependencies of $\chi(P)$ for the studied $La_{1-x}Pr_xCoO_3$ compounds are shown in **Figure 5**, **6**, and **7**, being close to linear within the experimental errors and the used interval of pressures. As shown from Figure 5, a huge decrease in the susceptibility with increasing pressure was found at $T = 78$ K, which amounts to about 10% per kbar for $LaCoO_3$. With increasing temperature, the pressure effect value decreased markedly, and it was an order of magnitude smaller at room temperature. For different temperatures, the obtained pressure derivatives of magnetic susceptibility, $d\ln\chi/dP \equiv (\Delta\chi/\chi)/\Delta P$ at $P \to 0$, for the studied compounds are shown in **Table 3** together with the values of χ at $P = 0$.

3. Details and Results of Electronic Structure Calculations for $PrCoO_3$

To shed light on the magnetic properties of $La_{1-x}Pr_xCoO_3$ system, we have carried out the calculations of electronic structure for $LaCoO_3$ and $PrCoO_3$ compounds. The details of

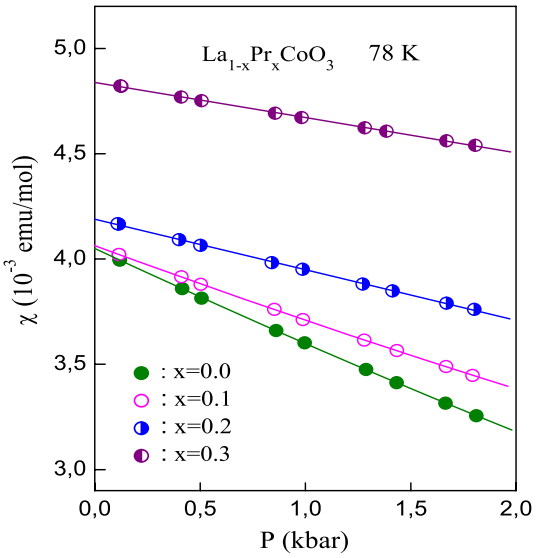

Figure 5. Pressure dependence of magnetic susceptibility for $La_{1-x}Pr_xCoO_3$ compounds at temperature 78 K (the magnitude of the error is less than the size of the symbols).

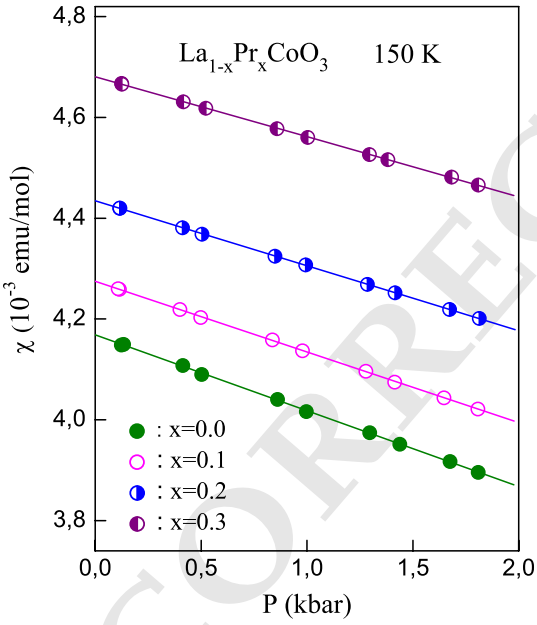

Figure 6. Pressure dependence of magnetic susceptibility for $La_{1-x}Pr_xCoO_3$ compounds at temperature 150 K (the magnitude of the error is less than the size of the symbols).

corresponding calculations for $LaCoO_3$ are given in the studies by Panfilov et al.[20,21] In contrast to rhombohedral $LaCoO_3$, $PrCoO_3$ is orthorhombic. As was shown in the studies by Pandey et al. and Topsakal et al.,[39,40] the DFT-LSDA approximation predicts an incorrect metallic ground state of $PrCoO_3$. Actually, its ground state is a paramagnetic insulator with the low-spin state of Co^{3+} ion.[41] There is the singlet ground state of Pr^{3+} ions, and only Van Vleck-type magnetization remains

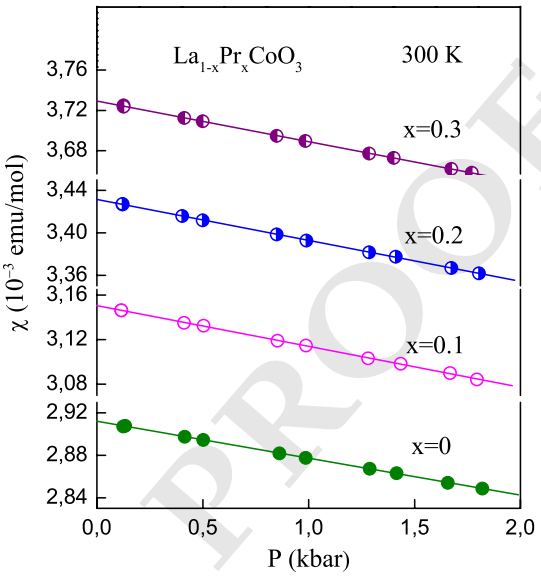

Figure 7. Pressure dependence of magnetic susceptibility for $La_{1-x}Pr_xCoO_3$ compounds at temperature 300 K (the magnitude of the error is less than the size of the symbols).

Table 3. Magnetic susceptibility χ at $P = 0$ and its pressure derivative d $\ln\chi/dP$ for $La_{1-x}Pr_xCoO_3$ compounds at $T = 78$, 150, and 300 K.

x	χ[10^{-3}emu mol^{-1}]			$-$d $\ln\chi/dP$ [Mbar^{-1}]		
	78 K	150 K	300 K	78 K	150 K	300 K
0.0	4.05	4.17	2.91	115 ± 5	36 ± 1	12.0 ± 0.4
0.1	4.06	4.27	3.15	90 ± 4	33 ± 1	11.6 ± 0.4
0.2	4.19	4.43	3.43	57 ± 3	29 ± 1	11.3 ± 0.4
0.3	4.84	4.68	3.73	35 ± 2	26 ± 1	10.8 ± 0.4

at low temperatures.[41,42] To obtain the semiconducting ground state of $PrCoO_3$, it is necessary to use the DFT+U formalism.[39,40]

The present calculations of electronic structure for orthorhombic $PrCoO_3$ were carried out using a linearized augmented plane wave method with full potential (FP-LAPW, Elk implementation).[43] The results of the FP-LAPW method were compared with the corresponding calculations carried out using the Quantum-Espresso code.[44,45] We have used the projector-augmented wave (PAW) potentials,[46,47] which are directly applicable for the Quantum Espresso code. The DFT+U approach was used within the generalized gradient approximation (GGA) for the exchange-correlation functional.[48] The on-site Coulomb interaction, U, and exchange interaction, J, parameters were adopted according to the study by Pandey et al.[39] ($U = 3.5$ eV, $J = 1.0$ eV, for Co 3d, and U = 3.5 eV, $J = 0.7$ eV, for Pr 4f electrons, respectively).

Our calculations have provided a dielectric ground state for the LS configuration of $PrCoO_3$ with the energy gap about 1 eV, which is close to the experimental value.[39,40] For this LS state of Co^{3+}, the valence band is formed by t_{2g} states of cobalt and 2p oxygen orbital, whereas the conduction band is formed by

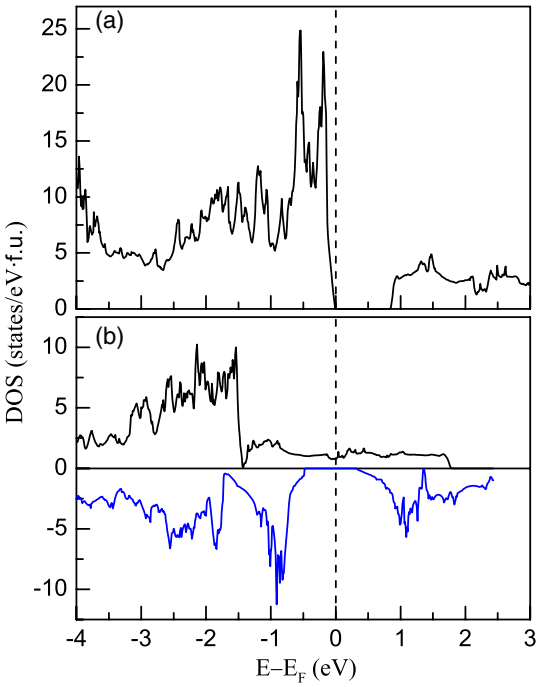

Figure 8. a) Density of electronic states for the LS configuration of cobalt ions in $PrCoO_3$; b) DOS for the IS configuration for different spin directions. The Fermi level is marked by a dashed vertical line.

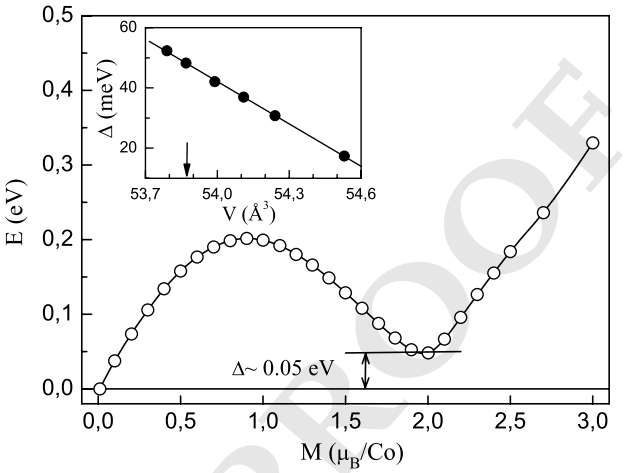

Figure 9. Dependence of the total energy on magnetic moment of Co^{3+} ion for $PrCoO_3$ calculated by the fixed spin moment method at the theoretical equilibrium volume. The energies are given for the formula unit relative to the ground-state LS ($M = 0$). In the inset: the volume dependence of the energy difference between the IS and LS states, Δ; the arrow indicates the value of the theoretical equilibrium volume.

e_g states of cobalt. The calculated density of electronic states (DOS) for the ground state of $PrCoO_3$ is shown in **Figure 8**a. The main features of the calculated electronic structure for the LS state of $PrCoO_3$ appeared to be in agreement with the results of previous calculations.[39,40]

We have also calculated the volume dependence of the total energy $E(V)$ and obtained the value of equilibrium volume $V_{th} \cong 53.9$ Å^3 for the formula unit of orthorhombic $PrCoO_3$. This theoretical value of the volume is appeared to be close to the experimental value at $T = 12$ K (53.99 Å^3).[49]

To study the magnetic properties of $PrCoO_3$ we have used the fixed spin moment (FSM) method.[27,50] The results of FSM calculations for the total energy E of $PrCoO_3$ are shown in **Figure 9** as a function of magnetic moment of Co^{3+} ion. A pronounced minimum in the $E(M)$ dependence was revealed at $M \simeq 2\mu_B$, indicating the presence of the intermediate spin state of Co^{3+} ion in $PrCoO_3$ ($S = 1$). Its energy is slightly higher ($\simeq 0.05$ eV) than the energy of the ground LS state of Co^{3+} ions ($S = 0$), whereas the HS state ($S = 2$), according to our calculations, has a much higher energy (≈ 0.6 eV).

We have also calculated the volume dependence of the total energy difference between the IS and LS states in $PrCoO_3$, $\Delta = E_{IS} - E_{LS}$, for isotropic volume changes, which is shown in the inset in Figure 9 and described by the derivative $d\Delta/d\ln V \simeq -2.5$ eV. It corresponds to a significant increase in Δ under pressure. In contrast, when the lattice of $PrCoO_3$ is expanding, the IS state approaches LS. Basically, this indicates the possibility of the LS–IS spin states crossover when the volume increases due to thermal expansion. In this connection, it should be noted, that shown in Figure 9b spin-polarized DOS of IS state was calculated with the FSM method for $T = 0$ K. The band structure calculation at high temperatures is extremely complicated problem, not solved satisfactory within the density functional theory. Therefore, one cannot extrapolate this "ferromagnetic" half-metal IS state to the region of high temperatures. Actually, the experimental data of Tachibana et al.[51] definitely indicate, that $PrCoO_3$ is nonmagnetic insulator up to temperatures of about 600 K.

4. Discussion

It is commonly assumed that the unusual temperature dependence of $\chi(T)$ in $LaCoO_3$ is caused by the temperature-induced gradual transition of the Co^{3+} ions from the nonmagnetic LS state ($S = 0$) to a magnetic state with an IS ($S = 1$) and/or to the high spin state HS ($S = 2$).

For $La_{1-x}Pr_xCoO_3$, the $\chi(T)$ dependence, considering paramagnetic impurities, is given by

$$\chi(T) = \chi_{Co}(T) + \chi_{0(LaCoO_3)} + C_{imp}/T + \chi_{Pr}(T) \quad (2)$$

Here $\chi_{Co}(T)$ is the temperature-induced contribution of the Co^{3+} ions; $\chi_{0(LaCoO_3)}$, the temperature-independent host susceptibility which is presumably determined by the dominant Van Vleck paramagnetism of the Co^{3+} ions,[13,16] C_{imp} the impurity Curie constant, $\chi_{Pr}(T)$ the contribution of the Pr ions. To study the evolution of the spin state of cobalt ions in $La_{1-x}Pr_xCoO_3$, it is necessary to extract properly their contribution, χ_{Co}, from the total magnetic susceptibility of the compounds. Some problems arise in this way already in the reference $LaCoO_3$ compound. According to the literature data, the real crystals of this material contain a certain number of magnetically ordered clusters formed by crystal defects,[33] nanostructures,[34,35] surface magnetism of the Co ions,[36] or by foreign Co_3O_4 phase,[37] which

substantially distort the temperature dependence of the intrinsic magnetic susceptibility in the temperature range below 85 K. This makes it difficult to quantify the low-temperature data and, in particular, probably explains the considerable scatter of literature data for $LaCoO_3$ on the magnitude of χ_0. In view of the foregoing, further analysis of the experimental data was carried out for a temperature region above 85 K, where manifestation of the foreign magnetic phases is assumed to be substantially suppressed.

To extract the contribution of the Co^{3+} ions, χ_{Co}, from the total magnetic susceptibility of $La_{1-x}Pr_xCoO_3$ compounds with Pr content x, we used the expression

$$\chi_{Co}(T) = \chi(T) - \chi_{0(LaCoO_3)} - C_{imp}/T - x \cdot \chi_{PrAlO_3}(T) \quad (3)$$

It follows from Equation (2), assuming $\chi_{Pr}(T) = x \cdot \chi_{PrAlO_3}(T)$. Here we have accepted that for all compounds the value $\chi_{0(LaCoO_3)} \simeq 0.2 \times 10^{-3}$ emu mol^{-1}, which is equal to the theoretical estimate of the Van Vleck paramagnetism of the Co^{3+} ions[52] and fairly close to the observed χ_0 value in the most perfect crystals of $LaCoO_3$.[14,20] The individual values of the impurity Curie constant, C_{imp}, were taken from Table 2. To estimate the contribution to $\chi(T)$ of the Pr ions, $x \cdot \chi_{PrAlO_3}(T)$, we have taken the temperature dependence of molar susceptibility of $PrAlO_3$, $\chi_{PrAlO_3}(T)$, averaged over our data in Figure 4b. The latter is characterized by the value $\chi_{PrAlO_3}(0) \simeq 10.6 \times 10^{-3}$ emu mol^{-1}, which was used to estimate the values of low temperature contribution of the Pr ions, $x \cdot \chi_{PrAlO_3}(0)$, shown in Table 2. For $T \geq 150$ K, the $\chi_{PrAlO_3}(T)$ dependence obeys the Curie–Weiss law with reasonable values of the Curie constant $C \simeq 1.7$ K emu mol^{-1} and the paramagnetic Curie temperature $\Theta \simeq -75$ K.

The resulted dependencies of $\chi_{Co}(T,x)$ are shown in **Figure 10**. They demonstrate that with increasing Pr content, there is a noticeable shift of the $\chi_{Co}(T)$ maximum to higher temperatures with a simultaneous decrease in its height. This effect is very similar to the behavior of the $\chi(T)$ isobars in $LaCoO_3$ with increasing pressure,[19] and it can be considered as manifestation

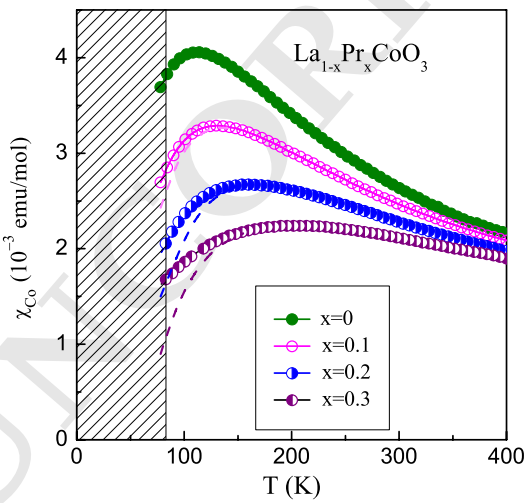

Figure 10. Temperature-induced contribution of the Co^{3+} ions, $\chi_{Co}(T)$, to magnetic susceptibility of $La_{1-x}Pr_xCoO_3$ for different Pr content x together with the proposed refinements at low temperatures (dashed lines, see text for details).

of the chemical pressure effects in $La_{1-x}Pr_xCoO_3$ due to the lattice volume decrease with increase in the Pr content.

As was shown, for example, in the studies by Zobel et al. and Baier et al.[13,14] for $LaCoO_3$, at low and moderate temperatures, the $\chi_{Co}(T)$ term in Equation (2) can be properly described with the LS→IS transition scenario by an expression for the two-level system[13–15] with the energy difference Δ for these levels

$$\chi_{Co}(T) = \frac{N_A g^2 \mu_B^2 S(S+1)}{3k_B T} w(T) \equiv \frac{C}{T} w(T) \quad (4)$$

Here, the factor C/T describes the Curie-type susceptibility of the excited state, N_A is the Avogadro number, μ_B the Bohr magneton, k_B the Boltzmann constant, g the Lande factor, and S the spin number. The factor $w(T)$ determines the population of the excited state with temperature

$$w(T) = \frac{\nu(2S+1)e^{-\Delta/T}}{1+\nu(2S+1)e^{-\Delta/T}} \quad (5)$$

where $2S+1$ and ν are the spin and orbital degeneracies of excited state, Δ is the difference between the energies of excited and ground states, expressed in units of temperature T. In addition, in the framework of this approach, the parameter Δ also depends on temperature by the relation resulted from Equation (5)[16]

$$\Delta(T) = T\ln\left[\nu(2S+1)\frac{1-w(T)}{w(T)}\right] \quad (6)$$

In the following examination of the experimental data within the aforementioned approach, we used the set of model parameters from the studies by ZObel et al., Baier et al., and Knížek et al.:[13,14,16] $g=2$, $S=1$, $\nu=1$ (it is assumed, that the orbital degeneracy of IS state is lifted due to local distortions of the crystal lattice).

Using the experimental dependence $\chi_{Co}(T,x)$ (Figure 10) and Equation (4) and (6), we have estimated the temperature dependence of the excited-state energy, $\Delta(T)$, in $La_{1-x}Pr_xCoO_3$ compounds for different Pr content x, which is shown in **Figure 11**. As shown, there is a noticeable decrease in $\Delta(T)$ with increasing temperature. In particular, for $x=0$, the value of $\Delta \simeq 155$ K at $T \simeq 80$ K falls down to $\Delta \simeq 0$ at $T \simeq 250$ K, being close in magnitude and temperature dependence to the available literature data for $LaCoO_3$.[16] Another feature of the $\Delta(T,x)$ behavior is the strong growth of Δ at fixed temperature with increasing x. According to Figure 11, the rate of Δ change with x is about $\partial\Delta/\partial x \approx 520, 650$, and 770 K at $T \simeq 150, 200$, and 300 K, respectively, giving the averaged value $\partial\Delta/\partial x = 650 \pm 120$ K. One can presume that this effect to be due to a decrease in the cell volume with increasing Pr concentration x. Therefore, we have estimated the chemical pressure effect on Δ

$$\frac{\partial\Delta}{\partial P} = -\frac{\partial\Delta}{\partial x}\left(B\frac{\partial \ln V}{\partial x}\right)^{-1} = 14 \pm 4 \text{K kbar}^{-1} \quad (7)$$

using our room temperature experimental data on the volume change with x, $\partial \ln V/\partial x \simeq -0.03$, and the bulk modulus value $B \simeq 1.5$ Mbar.[53] It should be noted that to specify properly the magnitude of the chemical pressure effect at different

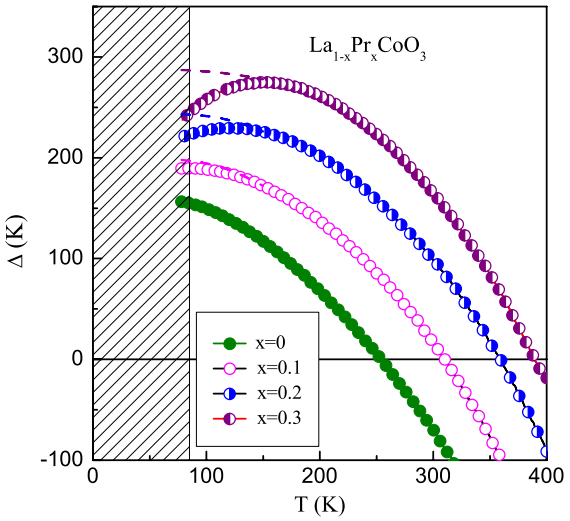

Figure 11. Temperature dependence of the excited state energy Δ in $La_{1-x}Pr_xCoO_3$ compounds for different Pr contents. The dashed lines at low temperatures are corrections for an anticipated manifestation of the foreign magnetic phases (see text for details).

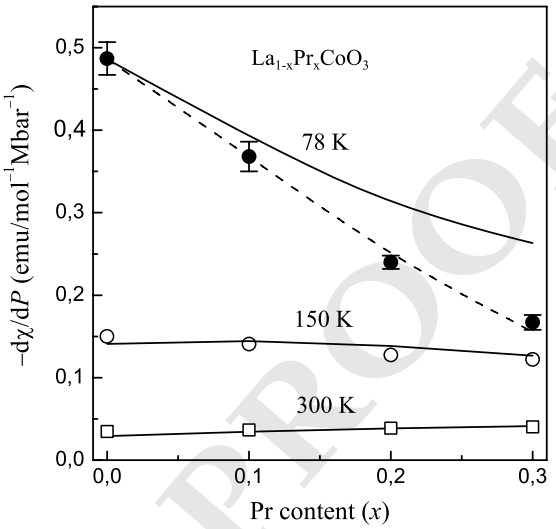

Figure 12. Experimental data on the pressure derivative of magnetic susceptibility, $d\chi/dP$, for $La_{1-x}Pr_xCoO_3$ compounds versus Pr content at different temperatures (points, for $T = 150$ and 300 K, the experimental errors do not exceed the size of the symbols) and their model description by Equation (8) (the solid lines). The dashed line is an improved model description of the data for $T = 78$ K, considering an anticipated manifestation of the foreign magnetic phases in $\chi(T)$ (see text for details).

temperatures, it is necessary to consider the temperature dependencies of the bulk modulus $B(T)$ and, especially, the $\partial \ln V(T)/\partial x$ value, originated from difference in the thermal expansion of the compounds due to the peculiarities of manifestation of the spin crossover.[13,14,54,55]

To analyze our experimental data on the hydrostatic pressure effect in magnetic susceptibility, we assumed that its magnitude is predominantly determined by the contribution of $\chi_{Co}(T)$, i.e., $d\chi(T)_{/d}P \simeq d\chi_{Co}(T)/dP$. According to Equation (4) and (6), the derivative $d\chi_{Co}(T)/dP$ can be expressed as follows

$$\frac{d\chi_{Co}(T)}{dP} = -\frac{\chi_{Co}(T)}{T}\left[1 - T\frac{\chi_{Co}(T)}{C}\right]\frac{d\Delta}{dP}. \quad (8)$$

Here, the only fitting parameter is the derivative $d\Delta/dP$, whose value is chosen according to the best agreement of the expression (8) with experiment.

The obtained for $La_{1-x}Pr_xCoO_3$ experimental values of $d\chi/dP(\equiv \chi d \ln \chi/dP$, see Table 3), are shown in **Figure 12,** as a function of Pr content at T = 78, 150, and 300 K. Here, the solid lines correspond to the model description, according to Equation (8), using the values of χ_{Co} in Figure 10, the Curie constant $C = 1$ K emu mol^{-1} and the values of $d\Delta/dP = 14$, 13, and 16 K kbar^{-1} at $T = 78$, 150, and 300 K, respectively. As shown, there is a reasonable agreement of the model (8) with the experimental data at $T = 150$ and 300 K, whereas at $T = 78$ K, the agreement is somewhat worse. We believe that this is due to using in Equation (8), the overestimated values of χ_{Co}, arising from the manifestation of foreign impurity phases, which probably takes place at lower temperatures. In Figure 10, the proposed dependencies $\chi_{Co}(T)$ in $La_{1-x}Pr_xCoO_3$ are shown by dashed lines for different x in the range 78 − 150 K. This correction provides agreement between the model and the experimental data at $T = 78$ K (dashed line in Figure 12), and, in turn, improves the shape of the $\Delta(T)$ dependence (dashed lines in Figure 11). It should be noted that the aforementioned improvements in the model description of the low temperature experimental data provide convincing evidence in favor of the proposed refinement of the $\chi_{Co}(T)$ dependencies in Figure 10.

Let us now discuss the hydrostatic pressure effect on the excited state energy Δ. As was estimated by fitting the model parameter $d\Delta/dP$ in Equation (8) to obtain the best agreement with experimental data, the value of $d\Delta/dP$ falls in the range of 13–16 K kbar^{-1} at different temperatures, being the lowest in magnitude at $T = 150$ K. The non-monotonic temperature dependence of this parameter is presumably related to the fact, that the physical meaning value is the derivative of Δ with respect to volume, and not to pressure. Then assuming the parameter $d\Delta/d \ln V$ to be a constant for the studied compounds and using the relation

$$d\Delta/dP = -B^{-1}d\Delta/d \ln V \quad (9)$$

we expect that the dependence of $d\Delta/dP$ on temperature can arise from a temperature dependence of the bulk modulus, $B(T)$. In the absence of direct data on the $B(T)$ behavior for $La_{1-x}Pr_xCoO_3$ compounds, it should be noted that essential temperature dependence of some elastic constants was observed in $LaCoO_3$.[56,57] This dependence, along with the generally accepted tendency for B to decrease with increasing temperature, shows a maximum between 150 and 200 K. Such behavior should lead to a minimum of $d\Delta/dP$ value in this temperature range, which is in a qualitative agreement with our experimental data.

Summing up the results of analysis of the pressure effects on magnetic susceptibility in $La_{1-x}Pr_xCoO_3$ compounds, we have obtained the temperature averaged value of the pressure derivative for energy of the excited state to be

$$d\Delta/dP = 14.3 \pm 1.5\,\mathrm{K\,kbar} - 1 \quad (10)$$

Substituting this value in Equation (9) and using the room temperature value $B \simeq 1.5$ Mbar,[53] we estimate the volume derivative of Δ equal to

$$d\Delta/d\ln V \simeq -21.5 \times 10^3\,\mathrm{K} \simeq -1.9\,\mathrm{eV} \quad (11)$$

The large and negative volume effect on Δ is also supported by theoretical studies for $LaCoO_3$ and $PrCoO_3$. The detailed calculations of the excited state energy Δ and its volume dependence for $LaCoO_3$ have given the values $\Delta(0) \simeq 230$ K and $d\Delta/d\ln V \simeq 29 \times 10^3\,\mathrm{K} \simeq -2.5$ eV.[20,21] For $PrCoO_3$ compound, the present DFT+U calculations have provided the corresponding values $\Delta(0) \simeq 570$ K and $d\Delta/d\ln V \simeq 29 \times 10^3\,\mathrm{K} \simeq -2.5$ eV. Therefore, for boundary compounds $LaCoO_3$ and $PrCoO_3$, the theoretical Δ were found substantially different, and in a qualitative agreement with the behavior of Δ in $La_{1-x}Pr_xCoO_3$ compounds for increasing concentration of Pr (Figure 11). In contrast, the volume derivative of Δ appeared to be almost the same in $LaCoO_3$ and $PrCoO_3$, $d\Delta/d\ln V \simeq -2.5$ eV, in a reasonable agreement with the experimental estimations for $La_{1-x}Pr_xCoO_3$ compounds, based on the analysis of pressure effects in magnetic susceptibility (Equation (11)). It should be noted that some difference between the experimental and calculated values of $d\Delta/d\ln V$ may be due to uncertainty in experimental bulk moduli, according to Equation (9).

We believe that the estimated strong volume dependence of the excited state energy Δ determines the main mechanism of its temperature dependence originated from the change in volume via thermal expansion. Namely, for $LaCoO_3$, a volume growth of about 1.6%[54] under heating from 0 to 300 K should result in a decrease in Δ by about 330 K, which is reasonably consistent with the behavior of $\Delta(T)$ in Figure 11.

Note that, some refinement of the analysis results and improvements of the used model should consider few factors, which were not considered here. One of them is a possible manifestation in magnetism of the HS states at higher-temperature region. Further, magnetic interactions between the Co^{3+} moments could play some role in the excited states. In addition, to convert experimentally measured pressure derivatives of susceptibility into volume derivatives, one need data on elastic properties of the systems under consideration and their temperature dependence, which are absent at the moment. Nevertheless, we expect that these possible improvements in the model analysis will not lead to noticeable refinements of the obtained parameters, which, in particular, for $LaCoO_3$ are

$$\Delta \simeq 155\,\mathrm{K\ at}\ T = 78\,\mathrm{K}, d\Delta/dP \simeq 14\,\mathrm{K\,kbar^{-1}}. \quad (12)$$

These estimates are closely consistent with analogous data obtained in the study by Panfilov et al.[20] from the magnetovolume effect study in single-crystalline $LaCoO_3$.

5. Conclusions

In summary, we have studied the effects of temperature and hydrostatic pressure on magnetic susceptibility of $La_{1-x}Pr_xCoO_3$ compounds ($x = 0$, 0.1, 0.2, and 0.3), supplemented by the investigation of their crystal structure. The entire set of the obtained experimental data on temperature and pressure effects in the magnetism of this family of compounds has been consistently described within the LS–IS scenario in terms of changes in the population of the excited IS state of Co^{3+} ions with variations in temperature and lattice volume under hydrostatic and chemical pressure.

One of the main results of this work is a quantitative estimation of the anomalously large volume dependence of the excited state energy Δ, which is presumably a primary source of the temperature dependence of this parameter due to the effect of thermal expansion. The revealed large and negative volume effect on Δ is consistent with the results of ab initio calculations for the boundary compounds, $LaCoO_3$ and $PrCoO_3$, which also supports the LS–IS scenario.

In addition, as shown from Equation (7) and (10), the observed for $La_{1-x}Pr_xCoO_3$ similarity between effects of physical and chemical pressure indicates a strong correlation of the Co^{3+} spin state with the lattice volume.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

electronic structure calculations, high-pressure effects, magnetic measurements, $RCoO_3$ compounds, spin crossovers

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