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Pressure effect on magnetic susceptibility of $LaCoO_3$

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The effect of pressure on magnetic properties of $LaCoO_3$ is studied experimentally and theoretically. The pressure dependence of magnetic susceptibility χ of $LaCoO_3$ is obtained by precise measurements of χ as a function of the hydrostatic pressure P up to 2 kbar in the temperature range from 78 K to 300 K. A pronounced magnitude of the pressure effect is found to be negative in sign and strongly temperature dependent. The obtained experimental data are analysed by using a two-level model and DFT+U calculations of the electronic structure of $LaCoO_3$. In particular, the fixed spin moment method was employed to obtain a volume dependence of the total energy difference Δ between the low spin and the intermediate spin states of $LaCoO_3$. Analysis of the obtained experimental $\chi(P)$ dependence within the two-level model, as well as our DFT+U calculations, have revealed the anomalous large decrease in the energy difference Δ with increasing of the unit cell volume. This effect, taking into account a thermal expansion, can be responsible for the temperatures dependence of Δ, predicting its vanishing near room temperature.

PACS: 71.20.Eh Rare earth metals and alloys;
75.30.Mb Valence fluctuation, Kondo lattice, and heavy-fermion phenomena;
75.80.+q Magnetomechanical effects, magnetostriction.

Keywords: $LaCoO_3$ compound, magnetic susceptibility, pressure effect, DFT+U calculations, spin states crossover.

The cobalt oxides are of growing interest since the discovery in them of a giant magnetoresistance, a large thermoelectric effect, a large value of the Hall effect, and anomalous magnetic properties. Their peculiar physical properties partially originate from a rich variety of the valence and spin states of Co ions. The Co^{3+} ions in the $LaCoO_3$ compound and in the rare-earth $RCoO_3$ cobaltites have an electronic $3d^6$ configuration, and these ions can be in low-spin (LS, $S = 0$), intermediate spin (IS, $S = 1$) and high-spin (HS, $S = 2$) states. The energy gap between these states can be quite small and the spin state can vary with temperature. This leads to a significant change in electric, magnetic, and transport properties of $RCoO_3$ compounds [1,2].

Lanthanum cobalt oxide $LaCoO_3$ exhibits intriguing magnetic and thermoelectric properties, also semiconducting and metallic electrical conductivity. The experimental and theoretical studies of electronic and magnetic properties of $LaCoO_3$ have been carried out by many groups (see e.g. Refs. 1–3 and references therein). However, a detailed understanding of the magnetic properties observed in the $LaCoO_3$ compound is still missing. In the recent years numerous experimental [4–12] and theoretical [13–21] studies performed for $LaCoO_3$ have given contradictory results, and scenario of transition between the magnetic states of Co^{3+} ion with temperature (low-spin ⇒ high-spin or low-spin ⇒ intermediate-spin ⇒ high-spin) remains unclear.

To solve this problem, it is necessary to shed more light on the nature of magnetic states in $LaCoO_3$, which appear to be very sensitive, in particular, to the volume changes. Therefore, one can expect, that the spin state transitions can be influenced by varying the pressure. Actually, the most direct indicator of the spin state of cobalt ions is the magnetic susceptibility behavior. This gives us a direction to investigate the pressure effect on magnetic properties of $LaCoO_3$ using experimental and theoretical tools in order to elucidate the mechanism of transitions between the magnetic states of Co^{3+} ions.

The first and apparently the only study of magnetic susceptibility under pressure in $LaCoO_3$ [22] has revealed a large and strongly temperature-dependent negative effect. Later the related results for $LaCoO_3$ were obtained from measurements of the volume magnetostriction [23]. However, the comparison of the magnetostriction data [23] with the results of direct measurements of magnetic susceptibility under pressure [22] shows their significant quantitative discrepancy, which motivates further study of magnetovolume effects in this compound.

In this paper we carried out experimental studies of the influence of hydrostatic pressure on magnetic susceptibility of $LaCoO_3$ at temperatures from $T = 78$ to 300 K. The obtained experimental data are analyzed by using a two-level model [4,24] and DFT+U calculations. In particular, the fixed spin moment method [25] was employed to obtain a volume dependence of the total energy difference between the LS, IS and HS states of $LaCoO_3$.

Experimental details and results

The $LaCoO_3$ single crystal was grown by the floating zone method [26] and its single phase and the rhombohedrally distorted perovskite type structure were confirmed by structural analysis. For additional characterization of the sample, the temperature dependence of its magnetic susceptibility $\chi(T)$ was measured in the temperature range of 2–400 K and a magnetic field of 1 T, using a Quantum Design SQUID magnetometer. The obtained temperature dependence (Fig. 1) shows a pronounced maximum at $T_{max} \simeq 105$ K and appears to be in agreement with the results of previous studies [24,26–28]. At low temperature, the Curie–Weiss-like contribution was observed, $\chi_{CW} = C/T + \chi_0$, with $C \simeq 10.4 \cdot 10^{-3}$ K·emu/mole and $\chi_0 \sim 0.3 \cdot 10^{-3}$ emu/mole. Here C/T term implies a number of paramagnetic impurities and χ_0 is the temperature-independent host contribution. In addition, it should be noted that because of a negligible magnetic anisotropy in $LaCoO_3$ [26], the magnetic field direction can be arbitrarily chosen relative to the crystallographic axes.

The measurements of the uniform pressure effect on magnetic susceptibility of $LaCoO_3$ were carried out under helium gas pressure P up to 2 kbar, using a pendulum type magnetometer [29]. The sample was cut in the shape of parallelepiped with dimensions of $3 \times 3 \times 2$ mm and a mass of 0.125 g. It was placed inside a small compensating coil located at the lower end of the pendulum rod. Under switching on magnetic field, the value of current through the coil, at which the magnetometer comes back to its initial position, is the measure of the sample magnetic moment. To measure the pressure effects, the pendulum magnetometer was inserted into a cylindrical non-magnetic pressure cell, which was placed inside a cryostat. In order to eliminate the effect on susceptibility of the temperature changes during applying or removing pressure, the measurements were performed at fixed temperatures in the range between 78 and 300 K. The relative errors of measurements of χ under pressure did not exceed 0.1% for employed magnetic field $H = 1.7$ T.

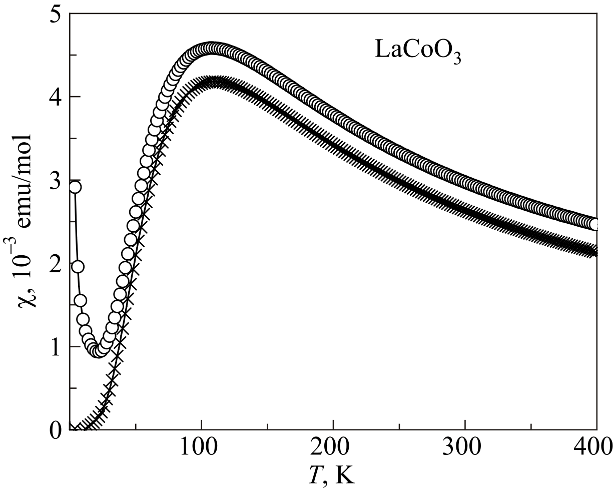

Fig. 1. Temperature dependence of magnetic susceptibility of $LaCoO_3$: as measured data (○), after subtracting a low temperature Curie–Weiss term (×) (see text, for details).

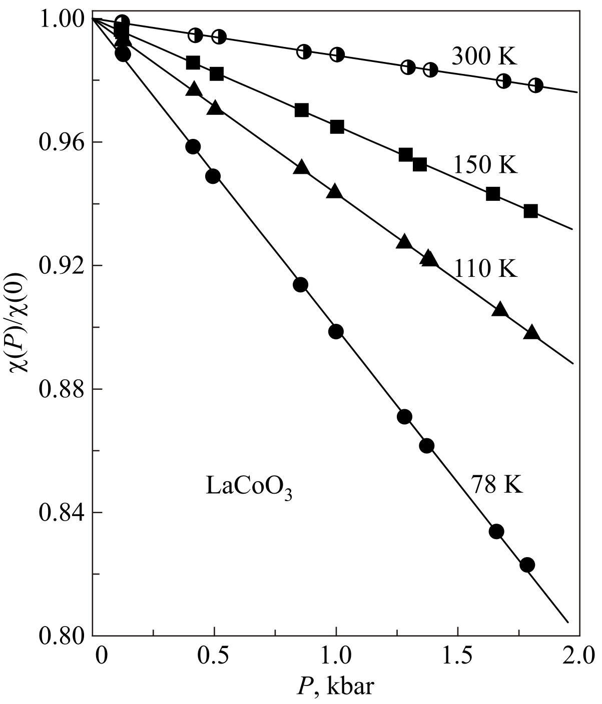

Fig. 2. Pressure dependence of magnetic susceptibility of LaCoO$_3$, normalized to its value at $P = 0$, at different temperatures.

The experimental $\chi(P)$ dependencies, normalized to the value of χ at zero pressure, are presented in Fig. 2. As seen in Fig. 2, there is a pronounced decrease of χ under pressure, which is linear within experimental errors. The corresponding values of the pressure derivative $d\ln\chi/dP$ are listed in Table 1 together with the values of χ at $P = 0$.

Table 1. Magnetic susceptibility χ of LaCoO$_3$ at $P = 0$ and its pressure derivative $d\ln\chi/dP$ at different temperatures

T, K	χ, 10^{-3} emu/mol	$d\ln\chi/dP$, Mbar^{-1}
78	4.06	–100±5
110	4.36	–56.7±3
150	4.12	–34.7±1.5
300	2.87	–12±0.5

Computational details and results

It has been established, that DFT–LSDA approximation predicts an incorrect ground state of LaCoO$_3$ [30–32]. To go beyond the DFT–LSDA, the DFT+U method has been employed and basically provided the semiconducting ground state of LaCoO$_3$ at ambient conditions (see e.g. [13–16,21]).

The present calculations of volume-dependent electronic structure for LaCoO$_3$ were performed using the linearized augmented plane wave method with a full potential (FP–LAPW, Elk implementation [33]). We also compared the FP–LAPW results on many occasions with the calculations performed by using the Quantum-Espresso code [34,35]. We have used the projector-augmented wave (PAW) potentials [36,37], which are for direct use with the Quantum-Espresso code.

The DFT+U approach was employed within the generalized gradient approximation (GGA) for the exchange-correlation functional [38]. The effective Coulomb repulsion energy $U_{\text{eff}} = U - J = 2.75$ eV was adopted for Co^{3+} ions according to Refs. 16, 21, where such value of $U \equiv U_{\text{eff}}$ has provided the correct ground-state.

The calculated density of electronic states (DOS) for the ground state of LaCoO$_3$ is shown in Fig. 3. Our DFT+U calculations have provided the paramagnetic ground state with a band gap about 0.5 eV, which is close to the experimental value [39]. For this low-spin state of Co^{3+}, the valence band is composed by the Co t_{2g} states and $2p$ orbitals of oxygen, whereas the conduction band is formed by the e_g states of Co. For the low-spin configuration the basic features of calculated here electronic structure of LaCoO$_3$ are in agreement with results of previous calculations [15,16,21]. We have also calculated the volume dependence of the total energy $E(V)$, and obtained the theoretical equilibrium volume $V_{\text{th}} \cong 56$ Å^3 per formula unit of LaCoO$_3$. This theoretical volume appeared to be slightly larger (about 1.5%) than the experimental volume at $T = 5$ K (see Ref. 40), presumably due to the employed GGA+U approach.

In order to shed light on magnetic properties of LaCoO$_3$ we have employed the fixed spin moment (FSM) method [25]. It was demonstrated (see e.g. Ref. 41), that FSM method can provide valuable information about metastable magnetic phases. By this way we calculated the total energy of LaCoO$_3$ as a function of the magnetic moment per formula unit. The results of these fixed spin moment calculations are shown in Fig. 4.

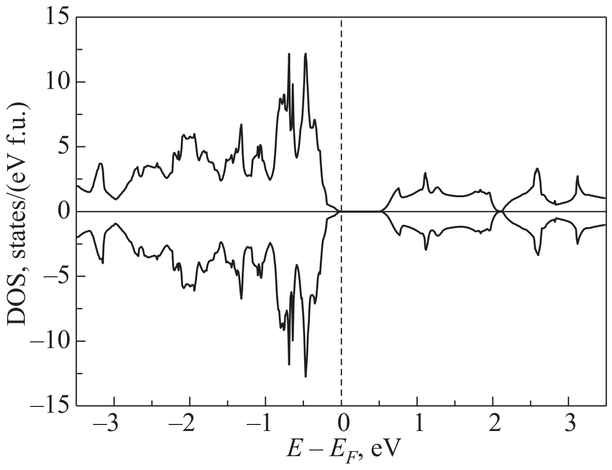

Fig. 3. Spin resolved density of electronic states for LS configuration of LaCoO$_3$. The Fermi level is indicated by a vertical dashed line.

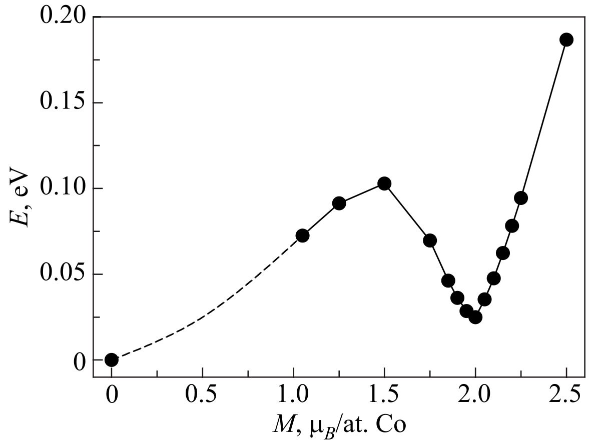

Fig. 4. Fixed moment calculation of the total energy for $LaCoO_3$ at the theoretical equilibrium volume. The energies are given relative to the LS state.

One can see clear minimum in the E vs M curve with magnetic moment of $2\mu_B$, presumably corresponding to the intermediate-spin state of Co^{3+} ion in $LaCoO_3$. According to our FSM calculations, the high-spin state of $LaCoO_3$ ($S = 2$ of Co^{3+} ion) appeared to be about 1 eV higher in energy than the LS state. These results prove that the transition from nonmagnetic to magnetic state in $LaCoO_3$ actually takes place between LS and IS states. It is remarkable that the minimum in Fig. 4 is situated energetically only 25 meV above the LS state. For this IS state of $LaCoO_3$ the spin subbands are split and partly overlapped, as can be seen in Fig. 5. Therefore our calculated ferromagnetic IS state appeared to be half metallic, though the value of DOS at E_F is rather small, and the conduction and valence bands in fact touch each other.

We have also calculated the volume dependence of the total energy difference between IS and LS states of $LaCoO_3$, $\Delta = E_{\mathrm{IS}} - E_{\mathrm{LS}}$, which is presented in Fig. 6. This volume dependence corresponds to substantial increase of Δ under pressure, and also indicates a possibility of the spin states crossover under thermal expansion.

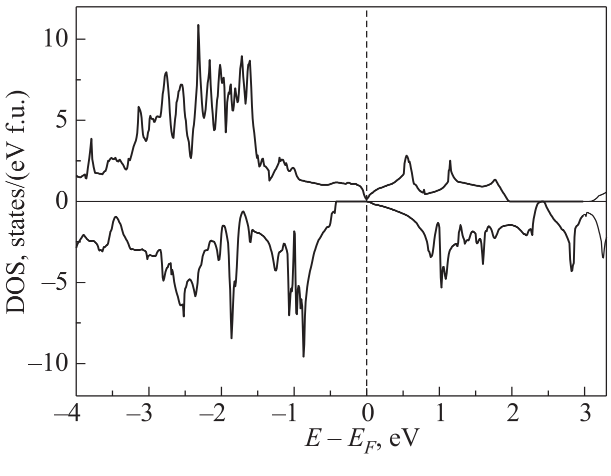

Fig. 5. Spin resolved density of electronic states for IS configuration of $LaCoO_3$. The Fermi level is indicated by a vertical dashed line.

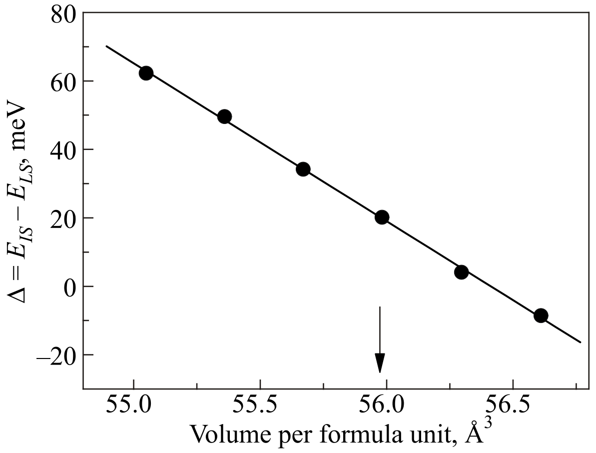

Fig. 6. Calculated volume dependence of the total energy difference between the IS and the LS states of $LaCoO_3$. The arrow indicates the theoretical volume.

Discussion

The unusual temperature dependence of magnetic susceptibility $\chi(T)$ in $LaCoO_3$ is commonly assumed to be caused by a temperature driven transition of the Co^{3+} ions from the non-magnetic low spin state LS to a magnetic state: either intermediate spin, IS, or high spin, HS, state. As was shown in Ref. 24, the Co ions contribution to susceptibility, $\chi_{\mathrm{Co}}(T)$, at least up to 300 K, can be successfully described within LS→IS scenario by the expression for the two-level system [4,24] with the energy difference Δ for these two states:

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

Here the multiplier C/T describes the Curie susceptibility of the excited state supposing a negligible interaction between the Co^{3+} moments; 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 multiplier $w(T)$ is the population of the excited state expressed by

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

where $2S+1$ and ν are the spin and orbital degeneracy of the excited state, respectively, and the energy difference between the excited and ground states, Δ, is in units of temperature T.

Note that according to the approach used, the behavior of $\chi_{\mathrm{Co}}(T)$ is determined by the single parameter Δ and its variation with temperature. Then dependence $\Delta(T)$, which satisfies the experiment, can be estimated from Eq. (2) as

$$\Delta(T) = T\ln\left[\nu(2S+1)\frac{1-w(T)}{w(T)}\right]. \qquad (3)$$

To analyze the experimental data on $\chi_{\rm Co}(T)$, we used the appropriate values of the model parameters: $g = 2$, $S = 1$ and $\nu = 1$ (the latter supposes that orbital degeneracy of IS state is lifted due to local distortions of the crystal lattice).

Using the experimental data on $\chi_{\rm Co}(T)$, we have evaluated within Eqs. (1) and (3) temperature dependencies of the excited state population, $w(T)$, and of the energy difference $\Delta(T)$, which are presented in Fig. 7.

It should be noted, that the obtained temperature dependence of the population of excited state, $w(T)$, appeared to be in a qualitative agreement with the results of combined analysis of x-ray powder diffraction (XPD) and high-resolution extended x-ray absorption fine structure (EXAFS) for $\rm LaCoO_3$ in Refs. 11, 12, and also x-ray magnetic circular dichroism (XMCD) measurements on $\rm LaCoO_3$ single crystal [9]. Specifically, in the temperature range from ~ 50 to 300 K the thermally induced spin-state transition was reported with a gradual growth of the IS state fraction of $\rm Co^{3+}$ ions, while a substantial fraction of $\rm Co^{3+}$ ions remains in the LS state up to temperatures about 150 K.

As one can see, there is a noticeable decrease in $\Delta(T)$ with increasing temperature from $\Delta \simeq 165$ K at $T = 0$ K to $\Delta = 0$ at $T \simeq 250$ K. The obtained data on temperature dependence of Δ are close to that reported in Ref. 15.

To analyze the pressure effect data within Eqs. (1) and (2), we can estimate a pressure derivative of the magnetic susceptibility, $d\chi/dP$, which is given by

$$\frac{d\chi(T)}{dP} \simeq \frac{d\chi_{\rm Co}(T)}{dP} = -\chi_{\rm Co}(T)\left[\frac{1}{T}-\frac{\chi_{\rm Co}(T)}{C}\right]\frac{d\Delta}{dP}. \qquad (4)$$

The obtained experimental data on $d\chi/dP$ are shown in Fig. 8 and appeared to be in agreement with the related data from measurements of volume magnetostriction in $\rm LaCoO_3$ [23]. This set of data can be fairly described by Eq. (4) (solid line in Fig. 8) using the fitting value $d\Delta/dP = +12$ K/kbar.

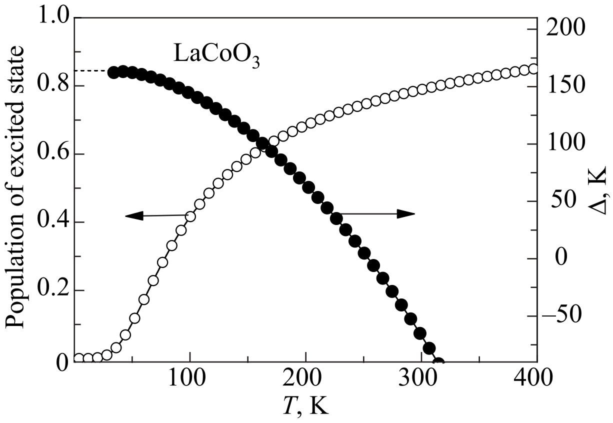

Fig. 7. Temperature dependencies of the population of excited state $w(T)$ and of the energy difference, Δ, between IS and LS states.

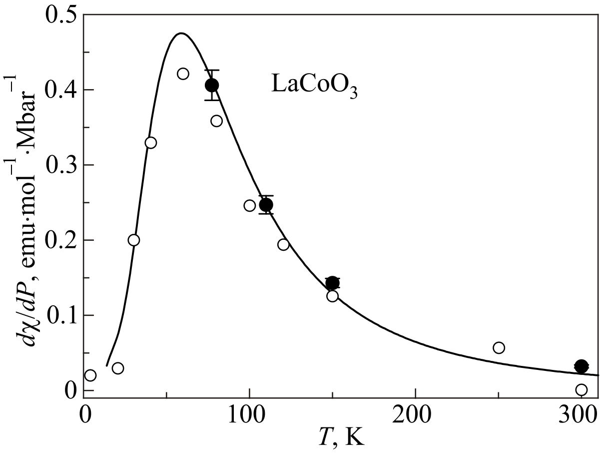

Fig. 8. Temperature dependence of the pressure derivative $d\chi/dP$ in $\rm LaCoO_3$: the experimental data of the present work (●), the indirect data resulted from volume magnetostriction study [23] (○). The solid line is the model description using Eq. (4) (see text, for details).

Note that the strong increase of Δ under pressure implies a substantial temperature dependence of this parameter due the change in volume via thermal expansion. The corresponding effect in Δ can be approximately estimated as:

$$\delta\Delta = \Delta(T)-\Delta(0) \approx \frac{\partial\Delta}{\partial\ln V}\times\frac{V(T)-V(0)}{V(0)}, \qquad (5)$$

where $\partial\Delta/\partial\ln V = -B\times\partial\Delta/\partial P$, B is the bulk modulus. Using the values $B \sim 1.35$ Mbar (average value of $B \sim 1.22$ Mbar [43] and 1.5 Mbar [43]), $(V(300\,{\rm K})-V(0))/V(0) \sim 0.015$ [40] and $\partial\Delta/\partial P \sim 12\cdot10^3$ K/Mbar (this work), we obtain a rough estimate of $\delta\Delta$ at $T = 300$ K to be about –240 K, which is in a reasonable agreement with $\Delta(T)$ dependence in Fig. 7.

It should be noted that some improvement of the model description can be obtained by taking into account i) a temperature dependence of elastic properties [45], ii) a possible manifestation of the interaction between $\rm Co^{3+}$ moments in the excited IS state and iii) a contribution of HS state at higher temperatures range, which are not considered in the present analysis. Nevertheless, we presume that improvements of the model will not lead to noticeable changes in the obtained parameters:

$$\Delta \simeq 165\,{\rm K}\ \text{at}\ T = 0\,{\rm K},\quad d\Delta/dP \simeq 12\ {\rm K/kbar}. \qquad (6)$$

We note that our estimate of $d\Delta/dP$ appeared to be close to the reported value of the chemical pressure effect on Δ, $d\Delta/dP \sim 10$ K/kbar, resulted from analysis of the magnetic properties of $\rm La_{1-\it x}Pr_{\it x}CoO_3$ system at low concentrations x [44]. In addition, the experimental results on concentration dependencies of Co^{3+} ions contribution to χ, $\chi_{\text{Co}}(x)$, and lattice cell volume, $V(x)$, for the isostructural compounds $La_{1-x}Pr_xCoO_3$ $(0 \le x \le 0.3)$ [44] allow to evaluate the chemical pressure effect on magnetic susceptibility of $LaCoO_3$ as:

$$\frac{d\chi(T)}{dP} \simeq \frac{d\chi_{\text{Co}}(T)}{dP} = \frac{\partial\chi_{\text{Co}}(T)}{\partial x}\left(-B\frac{\partial \ln V}{\partial x}\right)^{-1}. \qquad (7)$$

Here we used the experimental data on $\chi_{\text{Co}}(T)$, the value $\partial \ln V/\partial x \simeq -0.03$ of Ref. 44 and the bulk modulus value $B = 1.35 \pm 0.15$ Mbar. The resulting estimates of the derivative of magnetic susceptibility with respect to the chemical pressure for arbitrarily chosen temperatures in the range 78–300 K are shown in Fig. 9. As is seen, these estimates reasonably agree with the experimental data on the hydrostatic pressure effects in $LaCoO_3$.

Finally it should be noted, that theoretical studies of the volume dependence of Δ also show a positive pressure effect. However, the estimated from data of Ref. 13 values of both $d\Delta/dP$ and Δ itself appear to be an order of magnitude higher than the experimental results of the present work. On the other hand, our DFT+U calculations have provided the values $\Delta(0) \simeq 230$ K and $d\Delta/dP \simeq 22$ K/kbar, which appeared to be in much better agreement with that obtained from the present experiments.

As it has been demonstrated, the experimental data on the pressure effect in magnetic susceptibility of $LaCoO_3$, as well as its $\chi(T)$ dependence at ambient pressure, are satisfactorily described at low and moderate temperatures within LS→IS scenario by the two-level system model with energy splitting Δ. This gives an evidence of the applicability of the approach used to describe magnetic properties of $LaCoO_3$ and related $RCoO_3$ compounds at least up to room temperature.

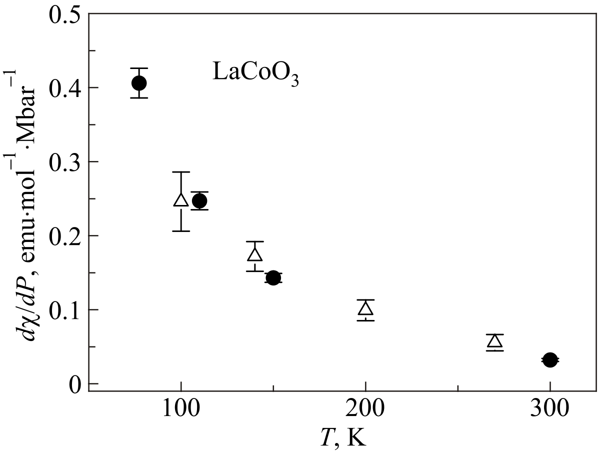

Fig. 9. Temperature dependence of the pressure derivative $d\chi/dP$ in $LaCoO_3$: the experimental data on the hydrostatic pressure effect of this work (●), the estimated by Eq. (7) the chemical pressure effect (△) (see text, for details).

Concluding remarks

In summary, the results of our study of the hydrostatic pressure effects on magnetic susceptibility of $LaCoO_3$, combined with the related literature data on volume magnetostriction [23], have been consistently described within the approach of a thermal population of the IS state of the Co^{3+} ions. We analyzed our data using a simple two-level model [4,24] and revealed the anomalous large increase in the energy difference Δ between LS and IS states with increasing pressure.

The estimated magnitude of this effect is in a reasonable agreement with the results of present DFT+U calculations of the volume dependence of Δ. Our results are also consistent with the literature data on manifestation of the pressure-induced continuous depopulation of the IS state in the behavior of the physical properties of $LaCoO_3$ under high pressures (see Refs. 43,46).

In addition, the established similarity of the effects of physical and chemical pressures on Δ and χ allows to conclude that the spin state of Co^{3+} ions in $LaCoO_3$ and related $RCoO_3$ cobaltites is predominantly governed by the interatomic spacing variations.

Finally, it should be noted that in recent works (see e.g. [5,7,8,10,18,19]) there were attempts to revive the LS–HS scenario, and the problem of the true spin state transitions in $LaCoO_3$ is still a subject of debate. In this connection, however, one should take into consideration the results of recent XPD and EXAFS diffraction studies [11,12] on polycrystalline $LaCoO_3$ samples. It was found that certain amount of Co^{3+} ions in the HS state are located predominantly within the surface layer of the crystallines, and this effect can be explained by influence of structural defects due to oxygen vacancies and distorted chemical bonds at the boundary of powder grains.

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