

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 RCoO₃ compounds [1,2].

Lanthanum cobalt oxide LaCoO₃ exhibits intriguing magnetic and thermoelectric properties, also semiconducting and metallic electrical conductivity. The experimental and theoretical studies of electronic and magnetic properties of LaCoO₃ 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 LaCoO₃ compound is still missing. In the recent years numerous experimental [4–12] and theoretical [13–21] studies performed for LaCoO₃ have given contradictory results, and scenario of transition between the magnetic states of Co³⁺ ion with temperature (low-spin \Rightarrow high-spin or low-spin \Rightarrow intermediate-spin \Rightarrow high-spin) remains unclear.

To solve this problem, it is necessary to shed more light on the nature of magnetic states in LaCoO₃, 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 LaCoO₃ using experimental and theoretical tools in order to elucidate the mechanism of transitions between the magnetic states of Co³⁺ ions.

The first and apparently the only study of magnetic susceptibility under pressure in LaCoO₃ [22] has revealed a large and strongly temperature-dependent negative effect. Later the related results for LaCoO₃ 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 magneto-volume effects in this compound.

In this paper we carried out experimental studies of the influence of hydrostatic pressure on magnetic susceptibility of LaCoO₃ 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 LaCoO₃.

Experimental details and results

The LaCoO₃ 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 $T_{\max} \approx 105$ 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 $C \approx 10.4 \cdot 10^{-3}$ 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 LaCoO₃ [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 LaCoO₃ 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.

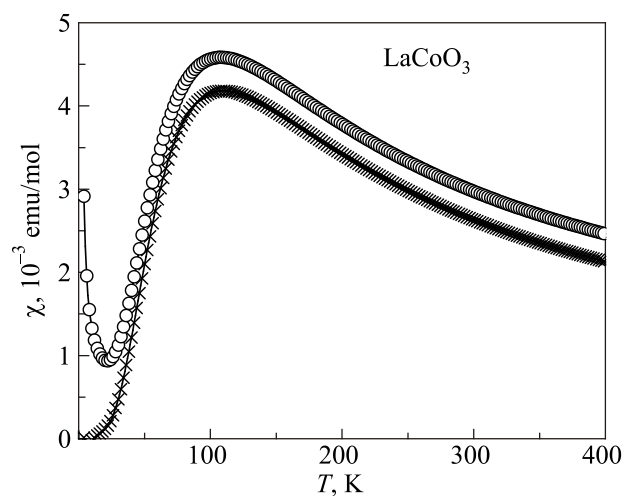


Fig. 1. Temperature dependence of magnetic susceptibility of LaCoO₃: as measured data (O), after subtracting a low temperature Curie–Weiss term (X) (see text, for details).

variation with temperature. Then dependence $\Delta(T)$, which satisfies the experiment, can be estimated from Eq. (2) as

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

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

Using the experimental data on $\chi_{\text{Co}}(T)$, 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 LaCoO_3 in Refs. 11, 12, and also x-ray magnetic circular dichroism (XMCD) measurements on 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 Co^{3+} ions, while a substantial fraction of 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 $\Delta \approx 165$ K at $T = 0$ K to $\Delta = 0$ at $T \approx 250$ 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

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

The obtained experimental data on $d\chi/dP$ are shown in Fig. 8 and appeared to be in agreement with the related data

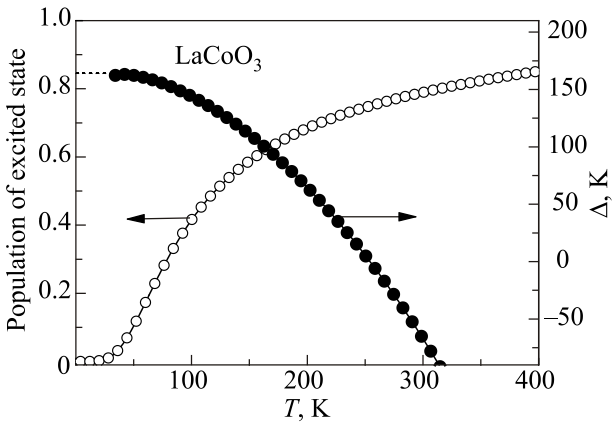


Fig. 7. Temperature dependencies of the population of excited state $w(T)$ and of the energy difference, Δ , between IS and LS states.

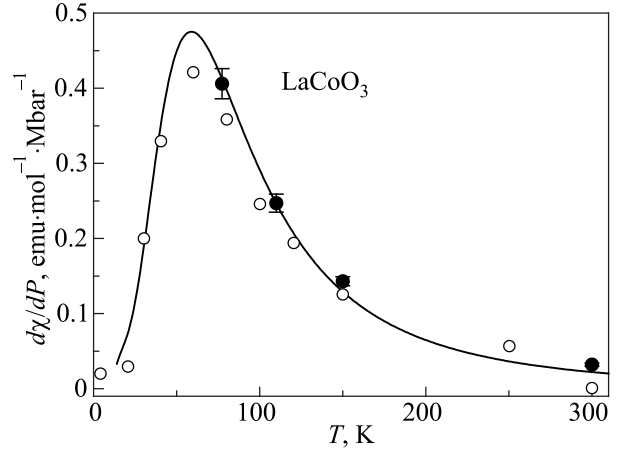


Fig. 8. Temperature dependence of the pressure derivative $d\chi/dP$ in LaCoO_3 : the experimental data of the present work (●), the indirect data resulted from volume magnetostriction study [23] (○). The solid line is the model description using Eq. (4) (see text, for details).

from measurements of volume magnetostriction in 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.

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:

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

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]), $(V(300 \text{ K}) - V(0))/V(0) \sim 0.015$ [40] and $\partial\Delta/\partial P \sim 12 \cdot 10^3$ 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 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:

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

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 $\text{La}_{1-x}\text{Pr}_x\text{CoO}_3$ system at low concentrations x [44]. In addition, the experimental results on

concentration dependencies of Co³⁺ ions contribution to χ , $\chi_{\text{Co}}(x)$, and lattice cell volume, $V(x)$, for the isostructural compounds La_{1-x}Pr_xCoO₃ ($0 \leq x \leq 0.3$) [44] allow to evaluate the chemical pressure effect on magnetic susceptibility of LaCoO₃ as:

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

Here we used the experimental data on $\chi_{\text{Co}}(T)$, the value $\partial \ln V / \partial x \approx -0.03$ 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 LaCoO₃.

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 $\Delta(0) \approx 230$ K and $d\Delta/dP \approx 22$ 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 LaCoO₃, 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 LaCoO₃ and related RCoO₃ compounds at least up to room temperature.

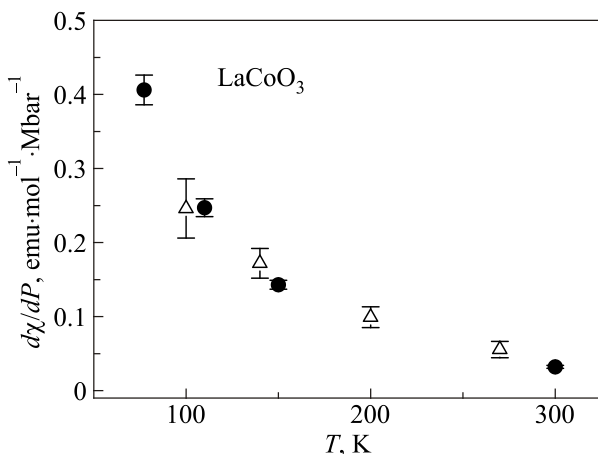


Fig. 9. Temperature dependence of the pressure derivative $d\chi/dP$ in LaCoO₃: the experimental data on the hydrostatic pressure effect of this work (●), the estimated by Eq. (7) the chemical pressure effect (Δ) (see text, for details).

Concluding remarks

In summary, the results of our study of the hydrostatic pressure effects on magnetic susceptibility of LaCoO₃, 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 Co³⁺ 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 LaCoO₃ 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 Co³⁺ ions in LaCoO₃ and related RCoO₃ 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 LaCoO₃ 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 LaCoO₃ samples. It was found that certain amount of Co³⁺ 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.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research according to the research project 17-32-50042-mol_nr. The authors acknowledge numerous discussions on the subject with V.V. Efimov.

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