

## INFLUENCE OF HIGH PRESSURE ON THE CRYSTAL AND MAGNETIC STRUCTURE OF $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$

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*Abstract.* The crystal and magnetic structures of cobaltite  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  have been investigated by the neutron diffraction method at high pressure up to 4.6 GPa in the temperature range from 10 to 290 K. Under normal pressure, the crystal structure of this compound has a cubic symmetry with the spatial group  $Pm\bar{3}m$  which is kept throughout the investigated pressure range. Ferromagnetic ordering is observed when the temperature is reduced to  $T = T_c = 178$  K. This magnetic ordering and Curie temperature do not change at high pressure up to 4.6 GPa. It is assumed that the stability of the ferromagnetic phase for  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  is provided by preservation of the  $\text{Co}^{3+}$  ions concentration in the intermediate-spin state in the total investigated range of the pressure.

*Key words:* magnetism, neutron diffraction, high pressure.

### 1. INTRODUCTION

The studies of complex cobalt oxides have caused a wide scientific interest due to the great variety of physical properties found in these materials, including the change in the spin states of cobalt ions, insulator-metal phase transitions, the giant magnetoresistance effect, various types of orbital, charge and magnetic ordering [1–4]. In this regard, the cobaltites are considered as promising material for wide technological applications in the storage, recording the information, power supplies, permanent magnets, etc [5].

In contrast to cuprates and manganites, there is an unusual electronic configuration of cobalt magnetic ions where the energy of splitting of the ground state in a crystalline electric field  $\Delta_{\text{CF}}$  is comparable with the energy of the intra-atomic exchange interaction  $J_{\text{H}}$ . Depending on the balance of these interactions, the following states of cobalt ions  $\text{Co}^{3+}$  in cobaltites can be realized: diamagnetic low-spin state LS ( $t_{2g}^6$ ,  $S = 0$ ), magnetic intermediate spin state IS ( $t_{2g}^5 e_g^1$ ,  $S = 1$ ), and the high-spin state HS ( $t_{2g}^4 e_g^2$ ,  $S = 2$ ) [6–10].

Partial doping of rare earth element R by alkaline earth A in  $R_{1-x}A_x\text{CoO}_3$  cobaltites for  $x > 0.18$  results in stabilizing the ferromagnetic (FM) metallic ground state [11] forming in the framework of the double exchange mechanism of delocalized  $e_g$  electrons between  $\text{Co}^{3+}$  ions locating in the IS state and  $\text{Co}^{4+}$  ions locating in the LS state through oxygen ions [12–14]. It is known that the effect of high pressure results in significant changing of the magnetic and transport properties of doped cobaltites. Thus, at high pressure we have observed the decrease of the Curie temperature and magnetic moments of  $\text{Co}^{3+}$  in compounds  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  and  $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$  [8, 14]. It is assumed that these physical phenomena are caused by the change in the electronic configuration of  $\text{Co}^{3+}$  ions from the magnetic IS state to the diamagnetic LS state [15]. It should be noted that at higher levels of doping ( $x > 0.3$ ) for  $R_{1-x}A_x\text{CoO}_3$  there is stabilization of the ferromagnetic state and the Curie temperature increases with a small pressure coefficient  $dT_c/dP \approx 1 \text{ K} \times \text{GPa}^{-1}$  [9].

In the anion-deficient cobaltites the effect of giant magnetoresistance is observed and the change in the magnetic ground state from the ferromagnetic (FM) to the antiferromagnetic (AFM) with Néel temperature  $T_N \approx 150 \text{ K}$  occurs [16,17]. The difference in the magnetic properties of the oxygen-deficient and stoichiometric cobalt oxides is related to a highly competing character of magnetic superexchange interactions, determined by the geometry of the oxygen sublattice of compounds as well as by the balance of the spin states of cobalt ions. Structural phase transition at pressure  $P = 3 \text{ GPa}$  from the cubic phase with the spatial group  $Pm\bar{3}m$  to the tetragonal phase with the spatial group  $P4/mmm$  has been observed in  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.8}$  cobaltite. This transition is accompanied by the change of the antiferromagnetic (AFM) ground state of the G type to the ferromagnetic state (FM) related to the change in the electronic configuration of the cobalt  $\text{Co}^{3+}$  ions [18].

A phase transition from the cubic symmetry  $Pm\bar{3}m$  structure to the tetragonal symmetry  $P4/mmm$  structure was found in the stoichiometric cobaltite  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  at temperature  $T = 180 \text{ K}$  [19]. However, the effect of high pressure on its crystal and magnetic structure has not been studied. In this paper we present the results of such a study using the neutron diffraction at high pressures up to 4.6 GPa in the temperature range of 10–300 K.

## 2. EXPERIMENT

The ceramic  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  sample was prepared by the conventional solid – state synthesis [20] using high – purity  $\text{La}_2\text{O}_3$ ,  $\text{CoO}$ , and  $\text{BaCoO}_3$  oxides taken in the necessary proportion and carefully mixed. The synthesis was performed in air at  $1200^\circ\text{C}$  for 10 h with an intermediate annealing at  $1000^\circ\text{C}$  during 2 h and subsequent grinding. After the synthesis, the sample was slowly cooled down to the room temperature at a cooling rate of  $100^\circ\text{C}/\text{h}$ .

The neutron diffraction experiments at high pressure (up to 4.6 GPa) within the temperature range of 10–290 K were performed by means of the DN-12 spectrometer [21] installed at the IBR-2 a high-flux reactor (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia) using the high pressure cells with sapphire anvils [22]. The period of time for recording of one spectrum was equal to 12 h. The pressure in the cell was measured by means of ruby fluorescence technique. The diffraction spectra were analyzed by the Rietveld method using the FullProf program package [23].

### 3. RESULTS AND DISCUSSION

The diffraction spectra of the  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  cobaltite obtained at different pressures and temperatures are shown in Fig. 1. No evidence for the structural phase transition was found within the resolution of the high pressure experiments.

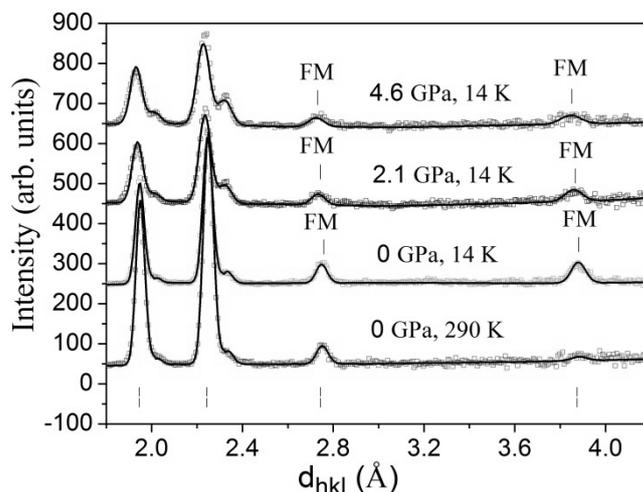


Fig. 1 – Neutron diffraction spectra of  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  obtained at 0, 1.2, and 2.7 GPa at room and low ( $T = 14$  K) temperatures processed by the Rietveld method. The nuclear peaks with the additional magnetic contribution are labeled as FM. Vertical lines indicate the calculated positions of the Bragg peaks for the cubic and ferromagnetic phases.

From processing of the neutron data, the parameters and the volume of the unit cell have been calculated. The unit cell parameter for the cubic phase at ambient conditions was found to be  $a = 3.861(1)$  Å, which agrees very well with the results obtained earlier in [19].

The temperature dependences of the unit cell parameter at various pressures are shown in Fig. 2. At Curie temperature, a sharp reduction in the unit cell parameter occurs, implying a pronounced magnetoelastic coupling in the studied compound.

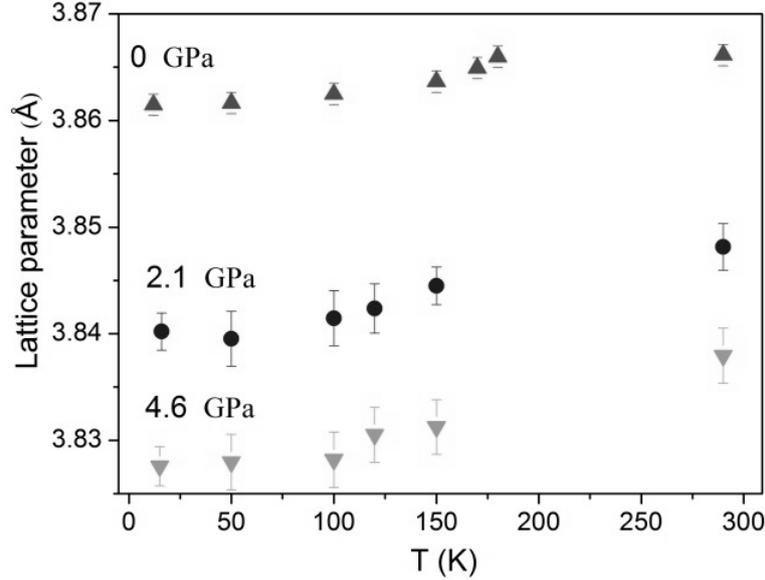


Fig. 2 – Temperature dependences of the unit cell parameter of  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  at pressures values  $P = 0, 2.1$  and  $4.6$  GPa.

The dependence of the volume of the unit cell and the interatomic distance Co–O on the pressure is presented in Fig. 3. The changes of volume and interatomic distances in  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  have nonlinear behavior that was observed in [18] for  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{2.8}$ . From the experimental data we have calculated the compressibility coefficients of the unit cell parameters and interatomic distances Co–O at 14 K as  $k_a = 3.4(1) \cdot 10^{-3} \text{ GPa}^{-1}$  and  $k_{\text{Co-O}} = 3.2(1) \cdot 10^{-3} \text{ GPa}^{-1}$ . The pressure dependence of the unit cell volume of  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  (Fig. 2) was fitted by the third order Birch-Murnaghan equation of state [24]:

$$P = 3/2B_0 (x^{-7/3} - x^{-5/3}) [1 + 3/4 (B' - 4) (x^{-2/3} - 1)], \quad (1)$$

where  $x = V/V_0$  is the relative change for the unit cell volume,  $V_0$  is the unit cell volume at  $P = 0$ , and  $B_0 = -V(dP/dV)_T$  and  $B' = (dB_0/dP)_T$  is the bulk modulus and its pressure derivative, respectively. The calculated bulk modulus for  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  cobaltite is  $B_0 = 153(8) \text{ GPa}$ . It is comparable to the corresponding values obtained for  $\text{LaCoO}_3$  (165 GPa) [7] and  $\text{La}_{0.82}\text{Sr}_{0.18}\text{CoO}_3$  ( $B_0 = 158(8) \text{ GPa}$ ) [25].

At ambient pressure and temperatures below  $T_C = 178 \text{ K}$  the increase of the structural peaks (110) and (100) located at  $d_{\text{hkl}} \sim 2.73$  and  $3.86 \text{ \AA}$ , respectively, was observed. These changes are related to the appearance of the FM phase in  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ . Similar changes are observed in the diffraction spectra at high pressures. It indicates the stability of this FM phase at high pressure.

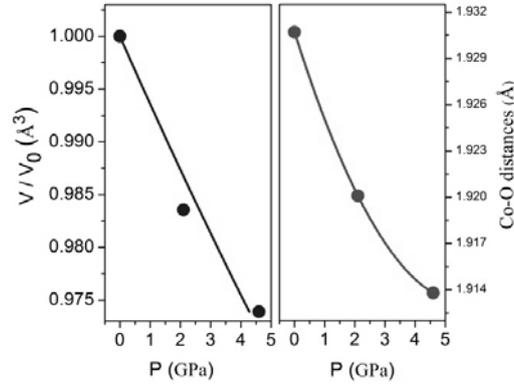


Fig. 3 – Dependences of the relative unit cell volume (left) and the interatomic distances Co-O (right) in  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  on the pressure at temperature  $T = 14$  K.

The temperature dependences of the magnetic moment of cobalt at different pressure are shown in Fig. 4. The experimental data were interpolated by the Brillouin function in the molecular-field approximation [26]:

$$\frac{\mu}{\mu_B} = B_S \cdot \left( \frac{2S}{S+1} \cdot \frac{\mu}{\mu_B} \cdot \frac{T_C}{T} \right), \quad (2)$$

where  $B_S$  – the Brillouin function,  $S$  – spin of the system ( $S = 1$ ) and  $\mu_0$  – values of magnetic moment at  $T = 0$  K. The calculated Curie temperature for cobaltite  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  in the studied pressure range was found to be nearly independent on pressure,  $T_C \approx 178$  K. This behavior is similar to cobaltite  $\text{La}_{0.5}\text{Ca}_{0.5}\text{CoO}_3$  [9] where we have observed the stabilization of the FM phase with a low baric coefficient for the Curie temperature  $dT_C/dP = 1$  K/ GPa.

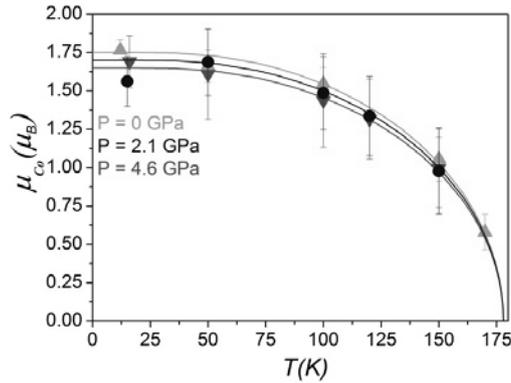


Fig. 4 – Temperature dependences of the magnetic moment of  $\text{Co}^{3+}$  ions at different pressures for the  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  compound. Interpolation of the experimental data has been carried out by using function (2).

The value of the Co magnetic moment for the FM phase is  $\mu_{\text{FM}} = 1.75(8) \mu_{\text{B}}$  at ambient pressure and  $\mu_{\text{FM}} = 1.70(8) \mu_{\text{B}}$  at pressure  $P = 4.6$  GPa and  $T = 10$  K. The stability of the magnetic moment points to preservation of the spin state of the  $\text{Co}^{3+}$  ions in the IS state at high pressure, in contrast to what we have observed in cobaltite  $\text{La}_{0.82}\text{Sr}_{0.18}\text{CoO}_{2.8}$  [25].

#### 4. CONCLUSIONS

The results of our study show that the ferromagnetic ground state and the IS spin state of  $\text{Co}^{3+}$  ions remain stable in  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  under pressure up to 4.6 GPa. No evidence of the structural phase transitions upon compression was found. The Curie temperature was found to be weakly dependent on pressure.

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