Pressure effects on oxygen-deficient Ba-substituted cobaltites

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Neutron diffraction studies of the $La_{0.5}Ba_{0.5}CoO_{2.8}$ at the different temperatures has been performed. This solid solution crystallizes in the cubic structure (Pm3m space group) and exhibits below T_N ~ 250K G-type antifferomagnetic ordering. Applied pressure suppresses magnetic ordering. Anomalous changes of the lattice parameters under pressure have been found.

Key words: high pressure; cobaltites; Rietveld analyses; neutron diffraction

I. INTRODUCTION

Complex cobalt oxides $LnCoO_3$ with perovskite structure are of great interest due to unusual magnetic and electronic properties. Cobalt ions can be three- or four-valent and in octahedral symmetry can be in low spin LS (t_{2g}^6, S=0 for Co^{3+}; t_{2g}^5, S=1/2 for Co^{4+}), intermediate spin IS ($e_g^1t_{2g}^5$, S=1 for Co^{3+}; $e_g^1t_{2g}^4$, S=3/2 for Co^{4+}) or high spin HS ($e_g^2t_{2g}^4$, S=2 for Co^{3+}; $e_g^2t_{2g}^3$, S=5/2 for Co^{4+}) configurations. Crystal field splitting of the Co 3d state is comparable with the Hund's exchange energy, therefore transitions between different spin states are possible in dependence of different environment.

Among the doped cobaltites, the system $La_{1-x}Sr_xCoO_3$ is the most extensively investigated. The spin glass behavior has been reported for $0.01<x<0.18$ as well as a ferromagnetic long-range ordering that coincides with an insulator-to-metal transition vs concentration for $x>0.18$ (Wu and Leighton, 2003). However, in contrast to manganites there is no metal-insulator transition in the vicinity of the Curie point. A similar metallic ferromagnetic state was observed in barium doped cobaltites above barium content x = 0.2 (Troyanchuk *et al.*, 2012). The nature of the

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ferromagnetic state in hole-doped cobaltites has been under intense debate (Goodenough and Senaris-Rodriguez, 1995).

The structural studies performed on the cubic oxygen stoichiometric perovskite $La_{0.5}Ba_{0.5}CoO_3$ have revealed the onset of a long range tetragonal phase accompanying a para-ferromagnetic transition occurring at T_C = 180 K (Fauth *et al*., 2001). The tetragonal distortion has been discussed in terms of a cooperative and static Jahn-Teller (JT) distortion of the CoO_6 octahedron. It was assumed that the JT effect is favored by the intermediate spin-state (IS) configuration of the Co^{3+}(d6) and Co^{4+}(d5) species derived from the measured ferromagnetic moment -1.9 μ_B per cobalt ion. However, the Sr-doped ferromagnetic cobaltites have approximately the same magnetic moment value and don't show structural transition at the Curie point (Sikolenko *et al.*, 2004; Sikolenko *et al.*, 2009). Moreover, the EXAFS and neutron diffraction studies have not found an appreciable local JT distortion in $La_{1-x}Sr_xCoO_3$ (Sundaran *et al*., 2009). So the reasons for the observed structural transition in $La_{0.5}Ba_{0.5}CoO_3$ may have another nature taking into account the pronounced metallic state below the onset of the structural transition [4]. Relatively small decrease of the oxygen content in $La_{0.5}Ba_{0.5}CoO_{3-d}$ leads to unique low temperature structural phase separation into antiferromagnetic and ferromagnetic phases.

In a case of oxygen-deficient samples $La_{0.5}Ba_{0.5}CoO_{3-\delta}$ when δ changes from 3 to 2.5 the oxidation level of the Co ions changes from 3.5 to 2. Our previous study (Troyanchuk *et al.*, 2011) shows that in a case of δ=2.87 a phase separation occurs at T < 150K. Two cubic phase (space group Pm3m) with a slightly different lattice and different oxygen content were observed. The major phase has δ = 2.92 and exhibits ferromagnetic ordering, oxygen content of the minor phase was 2.75 and antiferromagnetic ordering was observed. Below we present the magnetic and crystal structure dependence vs temperature and external pressure for the δ=2.8 sample.

II. EXPERIMENTAL

$La_{0.5}Ba_{0.5}CoO_{2.8}$ sample was prepared by a solid-state phase reaction method using high-purity $BaCO_3$, La_2O_3 and CoO taken in stoichiometric ration and thoroughly mixed with a planetary ball mill (RETSCH PM-100). The synthesis was performed at 1200 ºC for 10 hours in air, followed by cooling at rate of 100 ºC h down to 300 ºC. After synthesis the sample have been annealed at 550 C in air for 24h and quenched.

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The neutron powder diffraction experiment at ambient pressure was performed using high resolution diffractometer E9 operated at the BER-II reactor in Helmholtz Center Berlin in the temperature range 2 – 300K using the OS orange cryostat. High pressure experiment was performed using D1B diffractometer of Institute Laue Langevin, equipped with Paris-Edinburg high pressure cell and cryostat.

The neutron diffraction data were analyzed by the Rietveld method using the FullProf software package (Rodrigues-Carvajal, 1993).

III. RESULTS

At ambient pressure the diffraction data were collected at the temperatures 2; 50, 100; 150; 200 and 300K. The crystal structure at all temperatures can be described in the frame of cubic a_p x a_p x a_p cell with Pm-3m space group. La(Ba), Co and O ions occupy the 1b, 1a and 3d Wyckoff positions, respectively. Both La and Ba ions as well as oxygen vacancies are statistically distributed over lattice. No phase separation was observed. Figure 1 presents a typical diffraction pattern at 2K and the result of Rietveld analysis of the crystal and magnetic structure. Below T_N ~ 250K additional reflections appear, they can be indexed in $2a_p$ x $2a_p$ x $2a_p$ supercell. This means that the magnetic structure is G-type antiferromagnetic. Figure 2 presents the temperature dependence of the calculated magnetic moment. The lattice parameter a= 3.898 Å remains practically constant at all temperatures.

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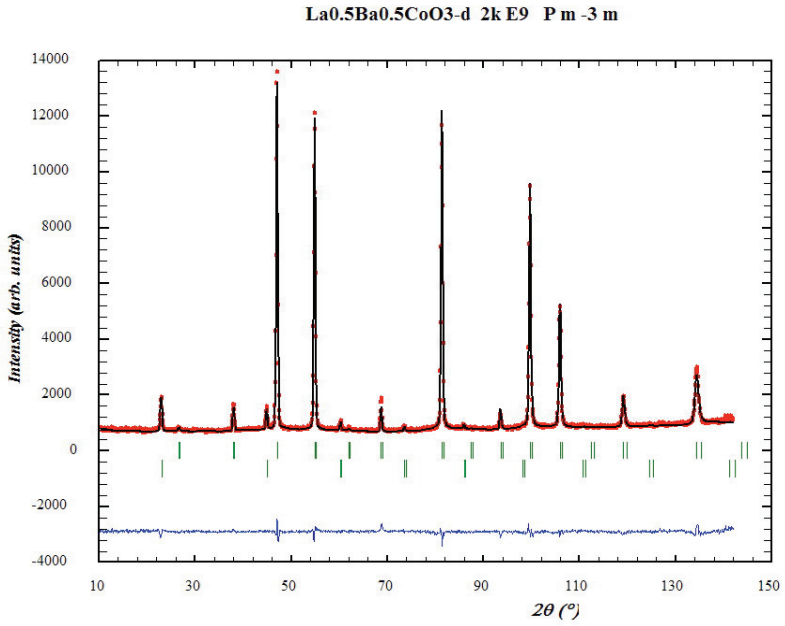


Figure 1. Neutron diffraction pattern of $La_{0.5}Ba_{0.5}CoO_{2.8}$, collected at T = 2K at the E9 diffractometer. Experimental points, calculated curves for crystal and magnetic (AF G-type) structures and difference are shown. The tick marks indicate the calculated positions of the Bragg peaks

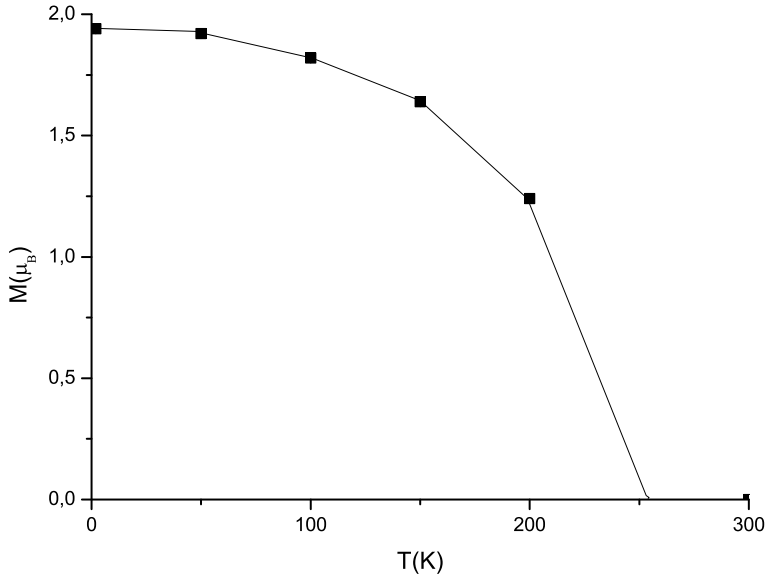


Figure 2. Magnetic moment temperature dependence. Values, obtained from Rietveld refinement of neutron powder diffraction data from the E9 instrument.

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The high pressure experiment was performed at 1, 3, and at 4.3 GPa at the temperatures 100 and 150K and at 4.3 GPA at the 50K. Suppression of the antiferromagnetic satellites (011) and (111) with the increase of pressure has been observed. The lattice parameter decreases with pressure until 2 GPa, but further pressure increase does not influence its value of lattice parameter. Figure 3 presents the diffraction pattern at the 100 K and 2 GPa as well as pressure dependence of the (200) reflection.

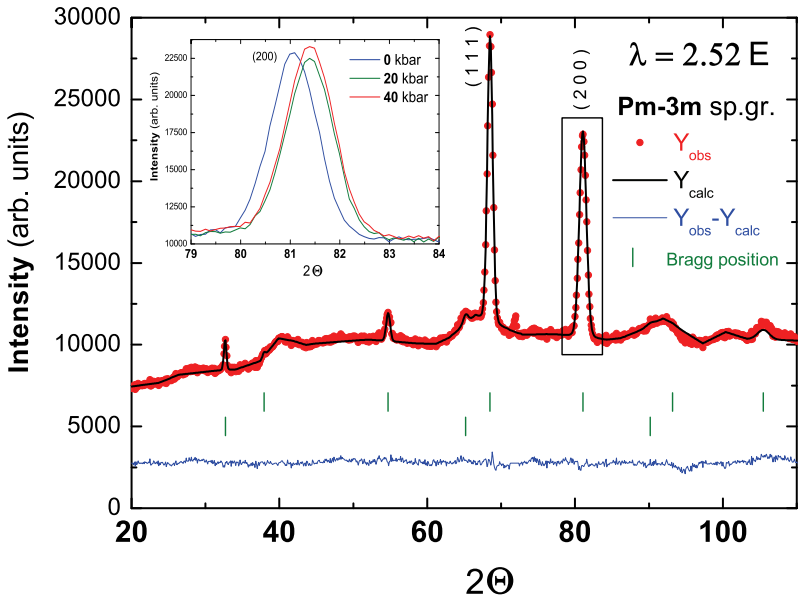


Figure 3. Neutron powder diffraction pattern for $La_{0.5}Ba_{0.5}CoO_{2.8}$ at the 100 K: experimental curve (open circles), refined curve (solid line) and residual curve (solid line at the bottom). The tick marks indicate the calculated positions of the Bragg peaks. The inset shows the temperature behavior of (200) peak at different pressure. Data from D1B diffractometer.

IV. DISCUSSION

The average oxidation state of cobalt in $La_{0.5}Ba_{0.5}CoO_{2.8}$ is almost 3. Due to oxygen deficiency half of the Co ions are found in CoO_5 pyramids with Co predominately in high spin state, and half of Co ions are found in CoO_6 octahedra, and are preferentially in low spin state (Soda *et al.*, 2004). Superexchange between Co ions in pyramids specify antiferromagnetic interaction. The calculated magnetic moment (see figure 2) seems to agree with this suggestion. For Co^{3+} (HS) ion the expected magnetic moment values is between 3 and 4 μ_B (Troyanchuk *et al.*, 2011; Troyanchuk *et al.*, 2008), whereas the observed one is 1.95 μ_B, thus suggesting smaller magnetic moment in octahedra.

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Cobaltites are very sensitive to the external pressure since the crystal-field splitting energy Δ_{cf} strongly depends on variation in the Co-O bond length d_{Co-O}. Applied pressure leads to the ferromagnetic intermediate or insulating nonmagnetic LS state because these spin states have smaller ionic radii than high spin one.. Therefore we have observed a suppression of antiferromagnetic ordering in $La_{0.5}Ba_{0.5}CoO_{2.8.}$ We did not find any indication for phase separation or additional contribution to the Bragg peaks which could be associated with the ferromagnetic ordering.

V. CONCLUSION

We have studied a temperature dependence of crystal and magnetic structure of the oxygen deficient $La_{0.5}Ba_{0.5}CoO_{2.8}$. This solid solution crystallizes in cubic structure and exhibit a G-type antiferromagnetic ordering below 250 K. Applied external pressure leads to suppress of antiferromagnetic ordering.

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