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Antiferromagnet-ferromagnet transitions in $La_{1-x}Ba_xCoO_{3-\delta}$ induced by pressure and magnetic field

Keywords: cobaltites, phase transition, crystal structure, neutron diffraction

1. Introduction

Rare earth cobaltites $LaCoO_3$ with a perovskite structure and hole-doped $Ln_{1-x}A_xCoO_3$ (Ln – lantahanide, A – alkaline earth metal: Ca, Sr or Ba) attract much interests as they exhibit many unusual magnetic and transport phenomena [1]. The Co ions in an octahedral symmetry may have either high (HS), intermediate (IS) or low spin state (LS) as the energies of the crystal-field splitting of both the Co *3d* states (E_{cf}) and the Hund's rule exchange energy (E_{ex}) are comparable.

Cobaltites are very sensitive to external pressure as the energy of the crystal-field splitting of the Co 3*d* states (E_{cf}) strongly depends on the variation of bond length Co-O and Co-O-Co angle. Applied pressure should stabilize non-magnetic state LS as result of increasing interval between t_{2g} and e_g levels by decreasing bond length Co-O causing a depopulation of magnetic state e_g. This effect has been observed in $Pr_{1-x}Ca_xCoO_3$ system [2]. Pressure effect on temperature of ferromagnetic transition T_C was found to be very different for different compounds [3, 4]. High negative dT_C/dP value was found in low doped compositions LaCaCoO and LaSrCoO. This value changes sign by Sr doping level [3]. Positive sign of dT_C/dP was found for $La_{1-x}Ba_xCoO_3$ system in the whole doping interval. For $x = 0.5$ compound this coefficient is 1.8 K/kbar being maximal value for cobaltites [4]. A possible explanation of pressure effect was proposed in [4]. According to [4] the population of IS state is determined not only by competition between E_{cf} and intra-atomic exchange interaction J_{ex} but also depends on bandwidth W resulting from σ-bonding Co-O-Co interactions. The broadening of W stabilizes the higher spin state therefore the population of higher spin states does not decrease under pressure despite increasing E_{cf}.

In this paper, we report that both the external pressure and external magnetic field induce ferromagnetic-antiferromagnetic transition in the anion-deficient cobaltites.

2. Experimental procedures

Ceramic samples of the $La_{1-x}Ba_xCoO_{3-\delta}$ ($x \geq 0.5$) system were obtained by a solid-state reaction technique using the high purity oxides La_2O_3, CoO and carbonate $BaCO_3$ taken in a stoichiometric ratio and thoroughly mixed in a planetary mill (Retsch PM100, 300 rpm, 30 min). Synthesis was carried out in air at 1200°C for 10 h in air using a two-step procedure with an interim annealing at 1000°C for 2 h followed by a thorough grinding. Samples were cooled from 1200°C with a rate of 100°C/h down to 300°C. Strong oxygen reduction ($\delta = 0.2$) was performed by annealing in vacuum sealed quartz ampoule with metallic tantalum as an oxygen getter. The amount of tantalum is calculated from the desired oxygen deficit value. The value of oxygen deficit was estimated by the weight loss after sample decomposition into La_2O_3 and BaO simple oxides and metallic cobalt as well as by an analysis of neutron diffraction data (accuracy of 0.03). Ceramic samples were subjected to the study of structure by scanning electron microscopy (SEM) and X-ray diffraction (XRD). For SEM images the LEO 1455VP microscope was used. X-ray diffraction analysis was carried out at room temperature on the DRON-3M diffractometer in K_α-radiation of Cu. The neutron diffraction data at ambient pressure were collected using the FIREPOD fine-resolution powder diffractometer (E9) (wavelength 1.791 Å.) [5] at the Hahn-Meitner Institute (Berlin, Germany). The neutron diffraction measurements under pressure were performed at the D20 diffractometer [6] in the Institute Laue Langevin (Grenoble, France) using Paris-Edinburg cell, equipped with cryostat. The pressure region was from ambient pressure (1 bar) till 65 kbar and temperature region from 50 K to 300 K. Diffraction patterns were collected at scattering angles 10–120 degrees with neutron wavelength 1.3 Å. The sample was mixed with NaCl for better pressure control. Experimental data were analyzed by Rietveld method using FullProf software package [7]. Magnetic properties of the samples were investigated with PPMS set-up in magnetic fields up to 14 T and temperature range 5–320 K (Cryogenic Ltd).

3. Experimental results

Structural study using scanning electron microscopy method has shown the samples to consist of crystallites with clearly defined cutting and high density (Fig. 1). Crystallite size is in the range from 0.5 up to 5 μm. Note the presence of layered structure with the layers thickness in nanometric diapason. That is characteristic of crystalline structure containing cobalt ions. Investigation of composition of synthesized samples by registration of element distribution along any given line on the surface has shown a good accordance with prescribed parameters. There is insignificant variation observed of La, Ba and Co content in different crystallites so one can regard the sample as practically homogeneous on the composition.

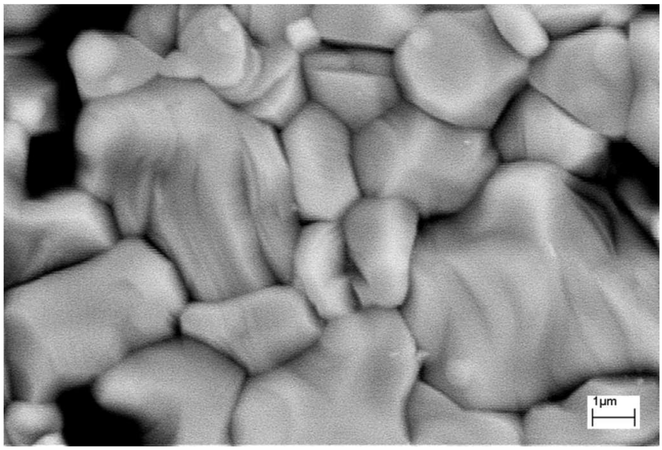

Fig. 1. SEM image of the surface structure of $La_{0.5}Ba_{0.5}CoO_{2.8}$

The temperature dependence of the magnetization measured upon cooling for the anion deficient composition $La_{0.5}Ba_{0.5}CoO_{2.8}$ is presented in Fig. 2a. Under normal pressure this compound was found to be antiferromagnet with ordering temperature T_N about 250 K. The dependence below 150 K exhibits an anomalous behavior as the magnetization drops with decreasing temperature. The isotherms of the magnetization *vs.* magnetic field are presented in Fig. 2b. One can see that the magnetic field induces a magnetic hysteresis in the temperature range 5–50 K. Furthermore, the magnetic susceptibility slightly increases with increasing magnetic field. This type of behavior can be associated with a metamagnetic phase transition. The magnetic hysteresis disappears above 50 K and the magnetization *vs.* field dependence becomes similar to that of superparamagnetism. The value of the magnetic moment is in the whole studied temperature range much lower than expected for a ferromagnetic state. One can conclude that the weak ferromagnetic component is associated with clusters embedded in an antiferromagnetic or paramagnetic matrix.

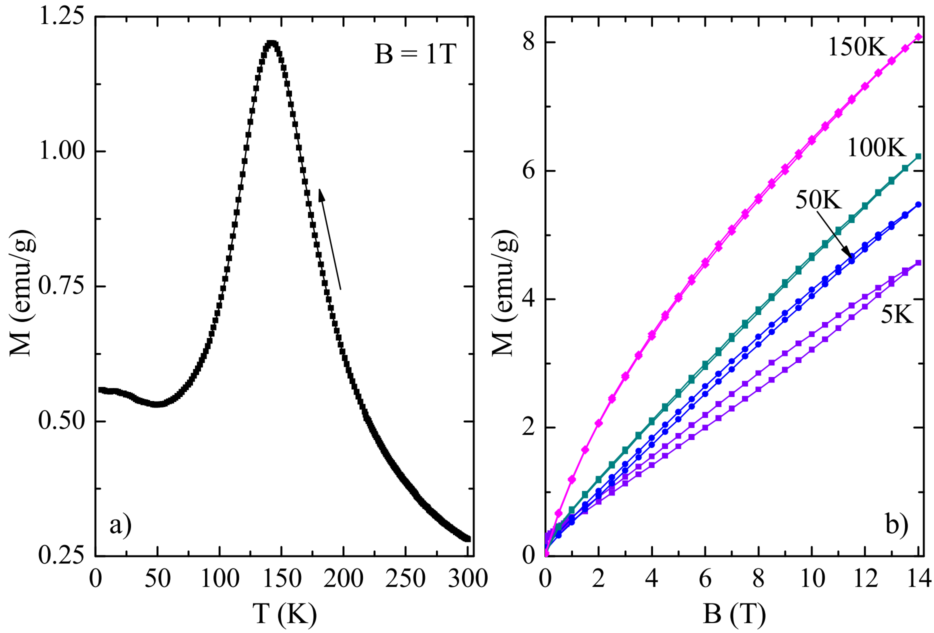

Fig. 2. Magnetization vs. temperature (*a*) and magnetization vs. field isotherms (*b*) for the $La_{0.5}Ba_{0.5}CoO_{2.8}$ sample

Phase transition antiferromagnet-ferromagnet can be induced also by external magnetic field. In Fig. 3a there are isotherms of field magnetization dependences shown for $La_{0.45}Ba_{0.55}CoO_{3-\delta}$ compositions which evidence this hypothesis. Indeed the large magnetic hysteresis observed in the (1–14) T range of the fields can be associated with field induced transition from antiferromagnetic into ferromagnetic state in some clusters. This hypothesis is supported by magnetoresistance data (Fig. 3b). One can see that magnetoresistance well correlates with magnetization data. So one can conclude that antiferromagnetic phase has much larger resistivity than ferromagnetic one. It is can be related to larger anion deficiency of the antiferromagnetic phase.

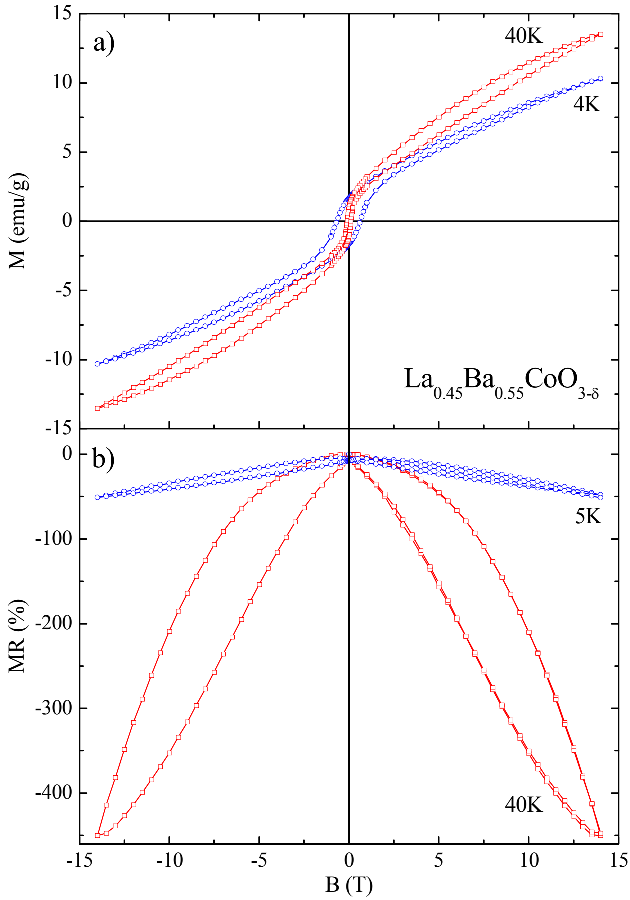

Fig. 3. Magnetization vs. field isotherms (a) and magnetoresistance *vs*. field (b) for the $La_{0.45}Ba_{0.55}CoO_{3-\delta}$ sample

Neutron powder diffraction (NPD) of anion-deficient $La_{0.5}Ba_{0.5}CoO_{2.8}$ data at ambient pressure have been collected in the range 2–300 K. Rietveld refinement carried out on the NPD patterns (Fig. 4) assumes cubic symmetry of the lattice (space group $Pm\bar{3}m$). We did not observe significant changes of the nuclear structure upon cooling down to 2 K.

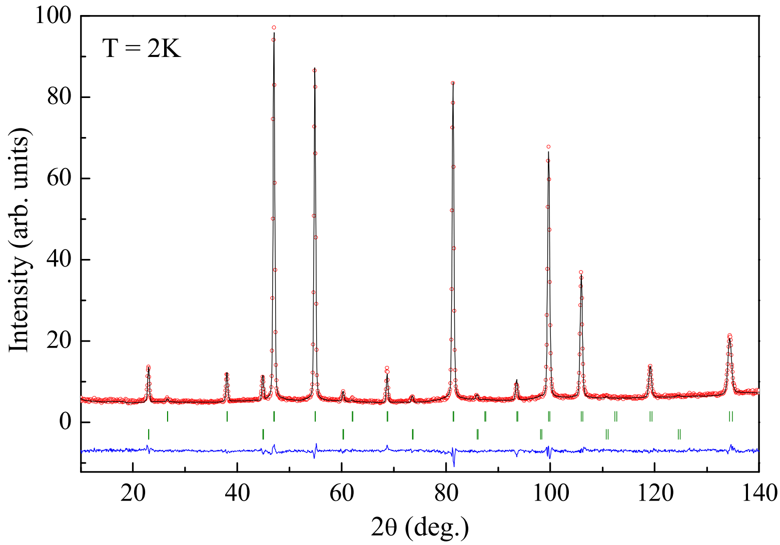

Fig. 4. Observed pattern, calculated profile, and difference curve of the Rietveld refinement done on the NPD data for the sample $La_{0.5}Ba_{0.5}CoO_{2.8}$ obtained at 2 K. Tick marks below the graph indicate the calculated positions of the Bragg peaks for nuclear and magnetic diffraction

The NPD data under pressure have been collected at 50, 100 and 300 K. We did not observe significant changes of the nuclear structure upon cooling up to the highest pressure 65 kbar used in the experiment. Half-width of reflexes increases slightly under pressure. However, unit cell parameter decreases from 3.90 down 3.83 Å by increasing pressure up to 65 kbar at 50 K (Fig. 5). The pressure was found to result in gradual decrease of antiferromagnetic reflexes intensity disappearing practically at 65 kbar and 50 K. Beginning from 40 kbar the intensities of (100) and (110) reflexes strongly increase by occurring ferromagnetic component. This indicates co-existence of antiferromagnetic and ferromagnetic components at pressure about 40 kbar. Ferromagnetic moment value is 1.9 μ_B/Co at 65 kbar (Fig. 5). This value is very close to ferromagnetic moment of stoichiometric $La_{0.5}Ba_{0.5}CoO_3$ [8, 9] with unit cell parameter (a = 3.88 Å, near the Curie point T_C = 190 K) much higher than that of $La_{0.5}Ba_{0.5}CoO_{2.8}$ at 65 kbar and 50 K.

We suggest that the pressure effect on the magnetic ground state in cobaltites can be considered in terms of cobalt spin state crossover. In the simplest scheme the magnetic ground state is determined by the spin state of cobalt ions which strongly depends on the unit cell volume, doping level and 3d(Co)-2p(O) hybridization. Pressure is expected to favor the population of the LS state since the ionic radius of LS Co^{3+} (0.685 Å) is smaller than that of IS Co^{3+} (0.717 Å) [10] and the difference in ionic radii leads to a lattice-volume expansion observed at the LS into IS transition [11]. However, the ionic radius of HS Co^{3+} (0.750 Å) is larger than that of IS Co^{3+}. The IS state in cobaltites is realized via large $3d$(Co)-$2p$(O) hybridization [12]. This hybridization should enhance under pressure. Hence, high pressure can induce the HS into IS transition at appropriate conditions.

As evidenced from the present work the pressure induced antiferromagnet-ferromagnet transition is not accompanied by a perceptible distortion of the lattice (Fig. 5). Apparently the IS state is stabilized by the increase of the $3d$(Co)-$2p$(O) hybridization resulting from the large volume contraction (Fig. 5). This is in agreement with the theoretical consideration [12]. The observed magnetic moment value (1.9μ_B/Co) indicates that cobalt ions located in both pyramids CoO_5 and octahedrons CoO_6 adopt the IS state.

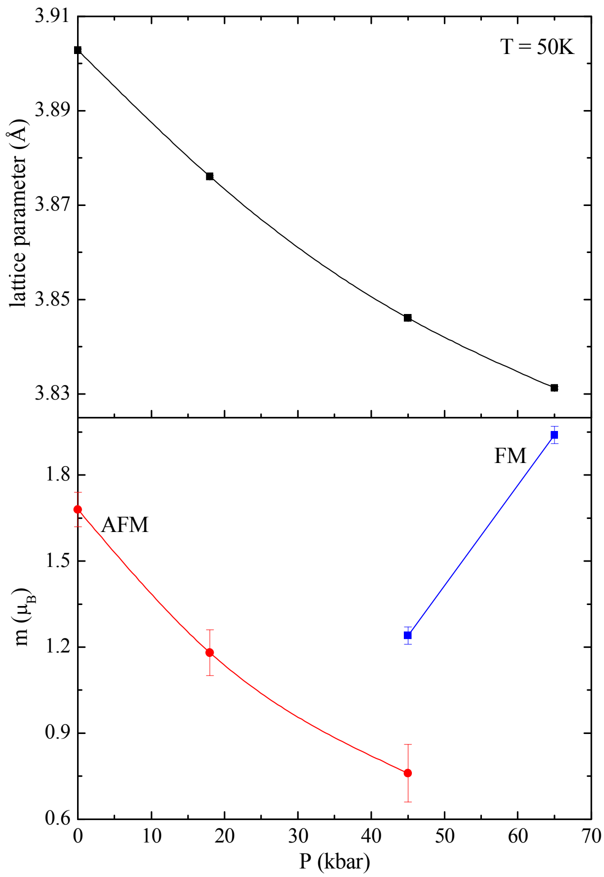

Fig. 5. Lattice parameter vs. pressure (upper panel) and antiferromagnetic/ferromagnetic moment *vs.* pressure (lower panel) for the $La_{0.5}Ba_{0.5}CoO_{2.8}$ at $T = 50$K

4. Summary

The effect of pressure on the antiferromagnetic ground state in anion deficient samples $La_{1-x}Ba_xCoO_{3-\delta}$ was investigated. It was found that both applied pressure and external magnetic field induces a transition from the antiferromagnetic to the ferromagnetic state. The observed magnetic moment for $La_{0.5}Ba_{0.5}CoO_{2.8}$ at 65 kbar is 1.9μ_B/Co. Our results are in accordance with a model in which the driving force of the antiferromagnet-ferromagnet transition should be a spin state crossover from HS to LS induced by pressure or magnetic field. Magnetic interactions between Co ions in HS state are antiferromagnetic while in IS one they are ferromagnetic. Both the types of magnetic interactions are associated obviously with superexchange via oxygen.

Acknowledgments

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Abstract

Magnetic properties of the anion deficient cobaltites $La_{1-x}Ba_xCoO_{3-\delta}$ ($x \geq 0.5$) have been studied. Magnetic field induces very large changes in resistivity accompanied by large magnetic hysteresis. It is found that an applied pressure transforms antiferromagnetic state into ferromagnetic one. It is assumed that a ground magnetic state strongly depends on unit cell volume and transition is associated with the cobalt ions spin state crossover. It is suggested that the antiferromagnetic state corresponds to high spin state of cobalt ions whereas ferromagnetic one is due to intermediate spin state of cobalt ions.

Streszczenie

Zbadano wpływ naprężenia na podstawowy antyferromagnetyczny stan w anion-zubożonym $La_{1-x}Ba_xCoO_{3-\delta}$

Ustalono że tak oddziaływanie ciśnienia jak zewnętrznego pola magnetycznego indukuje przejście ze stanu antyferromagnetycznego w stan ferromagnetyczny.

Obserwowana wartość momenty magnetycznego dla $La_{0.5}Ba_{0.5}CoO_{2.8}$ przy 65 kbar jest równa $1.9\mu_B$/Co.

Otrzymane wyniki są zgodne z modelem, w którym siła dynamiczna antiferromagnetyczno-ferromagnetycznego przejścia ze stanu HS w stan LS jest spowodowany przez ciśnienie lub pole magnetyczne. Oddziaływanie magnetyczne pomiędzy jonami Co w stanie HS jest ferromagnetyczne, a w stanie IS – antyferromagnetyczne. Oba typy oddziaływań mogą być związane z superoddziaływaniem z atomami tlenu.

Słowa kluczowe: cobaltites, przejścia fazowe, struktura kryształów, dyfrakcja neutronów neutron