



## Spontaneous and field-induced magnetic transitions in YBaCo<sub>2</sub>O<sub>5.5</sub>

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### ABSTRACT

A detailed study of magnetic properties of cobaltite YBaCo<sub>2</sub>O<sub>5.5</sub> has been performed in high (up to 35 T) magnetic fields and under hydrostatic pressure up to 0.8 GPa. The temperatures of paramagnet–ferromagnet (PM–FM) and ferromagnet–antiferromagnet (FM–AF) phase transitions and their pressure derivatives have been determined. It has been revealed that in the compound with yttrium, in contrast to those with magnetic rare earth atoms, the AF–FM field-induced magnetic phase transition is accompanied by a considerable field hysteresis below 240 K, and the magnetic field of 35 T is not sufficient to complete this transition at low temperatures. The hysteresis value depends on the magnetic field sweep rate, which considered as an evidence of magnetic viscosity that is especially strong in the region of coexistence of the FM and AF phases. High values of susceptibility for the field-induced FM phase show that Co spin state in these compounds changes in strong magnetic field.

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### 1. Introduction

The Co-based perovskites with chemical formulae RBaCo<sub>2</sub>O<sub>5+x</sub> (R is a rare earth or Y; 0 ≤ x ≤ 1) possess a unique combination of different physical properties. They demonstrate magnetic phase transitions and giant magnetoresistance [1,2], metal-insulator transition (MIT) [3], and also effects of charge and orbital ordering [4]. Since the difference between the energy of crystal field splitting for Co d-electrons and the energy of the interatomic exchange interaction is very small, the Co<sup>3+</sup>-ions can easily switch between the low-spin (LS) state ( $t_{2g}^5 e_g^0, S = 0$ ) the intermediate-spin (IS) state ( $t_{2g}^4 e_g^1, S = 1$ ), and high-spin (HS) state ( $t_{2g}^4 e_g^2, S = 2$ ) [5]. In other words, there exists an additional spin-state degree of freedom in cobaltites, which is absent in cuprates and manganites.

From structural point of view the compounds RBaCo<sub>2</sub>O<sub>5+x</sub> can be considered as layered perovskites. Their crystal structure consists of sandwiches CoO<sub>2</sub>–BaO–CoO<sub>2</sub>–RO<sub>x</sub> stacked along the c-axis of the orthorhombic lattice. Unusual properties of these systems are attributed to the events arising within CoO<sub>2</sub>-planes divided by intermediate RO<sub>x</sub> layers, which play the role of donors

of charge carriers (electrons or holes). One can control the charge carriers by varying oxygen concentration in doping RO<sub>x</sub> layers. Here the nominal valence of the Co ions can be changed within rather wide interval from 2.5+ (50% Co<sup>2+</sup> and 50% Co<sup>3+</sup>) at x = 0 up to 3.5+ (50% Co<sup>3+</sup> and 50% Co<sup>4+</sup>) at x = 1.

A tendency towards ordering of oxygen in doping layers is worth special notice. Specific types of ordering were observed at concentrations x = 0, 0.44, 0.5, 0.75, 1.0. [6,7]. At low temperature near oxygen concentration x = 0.5 the uniform distribution of the charge carriers becomes unstable and the phase separation appears either to two dielectric phases under electron doping (R = Y, 0.44 < x < 0.5) [8], or to metallic and dielectric phases under hole doping (R = Gd, 0.5 < x < 0.7) [6]. The formal valence 3+ for all Co-ions corresponds to oxygen content x = 0.5. The structure with concentration x = 0.5 plays a special role. At first it was assumed to be a completely ordered system of two types of Co positions with half of them having pyramidal oxygen environment CoO<sub>5</sub>, and the rest an octahedral one [9]. Pyramids and octahedrons alternate along the crystallographic b-axis. However, further studies showed that this system has a more complex structure. It was revealed [8] that the compound YBaCo<sub>2</sub>O<sub>5.5</sub> is characterized by phase instability so it is necessary to use multi-phase models for describing its physical properties.

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The orthorhombic structure of  $\text{RBaCo}_2\text{O}_{5.5}$  compounds with unit cell  $a_p \times 2a_p \times 2a_p$  (where  $a_p$  is the parameter of a pseudo-cubic perovskite cell) was described at first within the space group Pmmm [10,11]. Further neutron studies [12] showed that the magnetic structure of  $\text{NdBaCo}_2\text{O}_{5.5}$  in temperature range 230–275 K should be characterized by the wave vector  $k = [\frac{1}{2}, 0, 0]$ . At the same time, magnetic measurements indicate the presence of a spontaneous magnetic moment that is possible only for  $k = 0$ . To overcome this contradiction the crystal structure should be doubled along the  $a$ -direction (unit cell  $2a_p \times 2a_p \times 2a_p$ ). Detailed studies of X-ray diffraction in single crystal  $\text{GdBaCo}_2\text{O}_{5.5}$  [13] revealed the existence of superstructural reflections corresponding to doubling of the cell parameter  $a$ . The reflections were indexed within the space group Pmma where the cobalt ions occupy four independent positions in the unit cell  $2a_p \times 2a_p \times 2a_p$ . Besides, synchrotron studies showed the first-order structural transition Pmmm–Pmma in compounds  $\text{RBaCo}_2\text{O}_{5.5}$  ( $R = \text{Nd, Tb}$ ) coinciding with the metal-insulator transition [14]. Symmetry lowering at transition is due to the Co-ions ordering in different spin-states [13,15]. NMR studies of  $\text{YBaCo}_2\text{O}_{5.5}$  [16] and also magnetic measurements of untwinned single crystal of  $\text{GdBaCo}_2\text{O}_{5.5}$  [17] showed that at low temperature a part of the Co-atoms (admittedly in pyramidal environment) was in a state with IS, while the rest of Co (in octahedral environment) were in a LS state.

In spite of numerous studies, details of magnetic structure for both the antiferromagnetic phase and the phase with spontaneous magnetic moment remain unclear. Taking into account strong anisotropy of magnetic properties of single crystals  $\text{GdBaCo}_2\text{O}_{5.5}$ , a model of magnetic structure was proposed in Refs. [6,17], for which the  $\text{Co}^{3+}$  ions with spin  $S = 1$  form pairs of ferromagnetic chains along the crystallographic  $a$ -axis, the moment being also oriented along the  $a$ -axis. Pairs of the chains in  $ac$  planes form a ferromagnetic structure with relatively strong interaction within the plane. At the same time, along the  $b$ -axis these planes are separated one from other with the layers containing cobalt in LS-state, hence the exchange interaction between the magnetic layers is weakened. Magnetic phase transitions between low-temperature AF and high-temperature FM phases and also giant magnetoresistance appear due to change of the relative orientation of magnetization vectors of the weakly connected FM layers, variation of temperature or magnetic field application influencing this ordering easily.

It should be noted that the magnetic structure obtained on the basis of the Pmma symmetry [7,18] differs substantially from the one proposed earlier [6]. Here the spontaneous magnetic moment arises as a result of non-equivalence of the Co magnetic moments either in two pyramidal positions [18] or in octahedral position [7]. But in all the models the moments are lined up into chains along the  $a$ -axis.

Measurements of the magnetization and magnetoresistance in compounds  $\text{RBaCo}_2\text{O}_{5.5}$  in strong magnetic fields were carried out only for single crystals with  $R = \text{Gd}$  and  $\text{Eu}$  [19,20] and polycrystals with  $R = \text{Gd}$  and  $\text{Tb}$  [2,10]. Below the temperature  $T_i \sim 250$  K of transition into AF state, the field-induced magnetic phase transition was observed, which was most pronounced for compounds with  $R = \text{Gd}$  and  $\text{Tb}$ . In the  $\text{GdBaCo}_2\text{O}_{5.5}$  single crystal such a transition was observed only when magnetic field was applied along the  $a$ -axis [19]. For all the compounds the critical field of the transition increases linearly with temperature lowering at least down to 100 K. With further temperature decrease the compounds with Gd and Eu show different behavior. In the Gd system the average transition field achieves maximum value of 16 T at 75 K and then goes down to 13 T at 4.2 K [10]. At the same time, in the compound with Eu the critical field of transition continues to increase linearly with decreasing temperature and achieves 25 T at 4.2 K [20]. Up to now it is not clear whether it is

due to the difference of the lattice parameters or to the influence of rare earth ions on the exchange interactions in the cobalt subsystem. It can be cleared up by studying the compounds with the non-magnetic R-ions, such as Y, La or Lu. Unfortunately, growing of single crystals with these elements is extremely difficult problem [6].

From the measurements of magnetic and transport properties of polycrystalline samples of  $\text{YBaCo}_2\text{O}_{5.5}$  it was established [8] that this compound undergoes a metal-insulator transition at 297 K and also a cascade of magnetic phase transitions  $\text{PM} \rightarrow \text{FM} \rightarrow \text{AF}$  with characteristic temperatures of  $T_C = 290$  K,  $T_i = 270$  K which is typical behavior for such compounds. For the sample with oxygen concentration  $x = 0.52 \pm 0.02$  an additional anomaly of the susceptibility at  $T_L = 180$  K [7] was found, which was attributed to the structural transition into two-phase state with different types of the spin-state superstructure [21].

In the work presented here we studied magnetic properties of a high-quality polycrystalline sample  $\text{YBaCo}_2\text{O}_{5.5}$  in both static and high-pulsed magnetic fields. For evaluation of the lattice volume influence upon magnetic properties, we also performed measurements of magnetization under hydrostatic pressure. Due to phase instability of the compound with  $x = 5.5$ , phase decomposition seems to be inevitable. In spite of the study of this system having been already carried out under the conditions of light hole doping, it was supposed to be rather interesting to look at the magnetic behavior of the system from the other side of watershed, namely under light electron doping, i.e. when  $x \rightarrow 5.5 - 0$ . Our preliminary magnetic measurements showed that magnetic behavior of such samples differs significantly from that described earlier [7]. We measured both the temperatures of magnetic phase transitions paramagnet–ferromagnet (PM–FM) and ferromagnet–antiferromagnet (FM–AF), and also their pressure derivatives. It was found that in the yttrium compound, as distinct from the compounds with magnetic R-atoms at temperatures below 240 K the field-induced AF–FM magnetic phase transition is accompanied by a considerable field hysteresis and magnetic viscosity effects.

## 2. Experimental details

The sample of  $\text{YBaCo}_2\text{O}_{5.5}$  was synthesized by a solid state reaction using  $\text{Y}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$  and  $\text{BaCO}_3$  of a minimum purity of 99.99%. The respective amounts of starting reagents were mixed and calcinated at temperatures 1000–1200 °C during at least 100 h in air, with several intermediate grindings. The final annealing was performed in oxygen flow at 600 °C (for several hours) with subsequent slow cooling. Phase purity of the compound was checked with conventional X-ray diffractometer (SIEMENS D500). Oxygen content was determined by iodometric titration and thermogravimetric hydrogen reduction [22] to be  $5.49 \pm 0.01$ .

X-ray diffraction studies were carried out with Dron-4 diffractometer (Cu  $K\alpha$  radiation,  $2\theta$  angle range 5–113°, step 0.02°) at room temperature. A pyrographite monochromator and the Soller collimator were used for resolution enhancement. For crystal structure refinement “FullProf” package [23] was used.

Magnetization was measured using Quantum Design MPMS SQUID-magnetometer in magnetic fields up to 5 T. For magnetization measurements under pressure, we used a miniature pressure cell made of a non-magnetic Cu–Ti-alloy [24]. Before the measurements, the pressure cell was calibrated at low temperatures by a pressure-induced shift of superconducting transition temperature in Pb.

Measurements of high-field magnetization curves of random powder samples were performed using an induction technique in pulsed magnetic fields up to 35 T with the pulse duration time

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