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Effect of cobalt deficiency on physical properties of the $GdBaCo_{2-x}O_{5+\delta}$ single crystal

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Abstract. The effect of cobalt deficiency in a single crystal of double layered cobaltite $GdBaCo_{1.86}O_{5.32}$ on the magnetic properties was investigated. We have found that in the region 210 - 400 K the sample has the ferrimagnetic state with the Neel temperature (T_N ~ 400 K) which is above the Curie temperature (T_C ~ 262 K). In the paramagnetic region T = 410 - 650 K the effective magnetic moment is μ_{eff} = 8.78 μ_B, that points out the intermediate spin state (IS) of Co^{3+} ions.

Introduction

Layered double perovskites based on cobalt $LnBaCo_2O_{5.5 \pm \delta}$ show a number of unusual physical properties and possess a rich phase diagram due to the complex relationship between charge, spin and orbital degrees of freedom. These compounds show colossal magnetoresistance and display several phase transitions: antiferromagnetic (AF) - ferromagnetic (FM), ferromagnetic - paramagnetic (PM) and insulator - metal (I/M) [1, 2].

The magnetic properties of these compounds are related to the spin state of the Co ions. The spin state and the nature of phase transitions are fundamental aspects of the study of cobaltites. The competition between crystal field, Coulomb correlations, and the intra-atomic exchange energies leads to the existence of three possible spin states of Co^{3+} ions: high (HS), intermediate (IS) and low (LS) states. In the literature there are almost no data about magnetic susceptibility at high temperatures (T > 400 K), although they can give information on the spin state of Co ions.

Experiment

A single crystal of layered double cobaltite was grown by zone melting in the installation URN - 2 -3P. Crystal growth was carried out under ambient condition. Elemental analysis of the single crystal is made by the atomic absorption spectrometer Solaar M6 (AAS). The oxygen concentration is determined by direct reduction of the sample in a stream of hydrogen in a thermogravimetric installation. The error in determining of the elemental composition is less than 2%. The distribution of elements in the sample was studied by scanning electron microscope Inspect F (FEI) with energy dispersive spectrometer EDAX. The phase composition and unit cell parameters of the samples are monitored by x-ray powder diffractometry $Cu_{K\alpha}$ radiation in x-ray diffractometer DRON 3.0 in the temperature range 300 - 900 K [3]. Measurements of magnetic susceptibility (χ_{dc}) were carried out using Faraday balance in the temperature range 200 <T < 650 K. Temperatures of phase transitions were investigated by method of differential scanning calorimetry on thermoanalizatore Netzsch STA 409 PC Luxx in air flow in the temperature range 300 - 1400 K at a heating rate and cooling 5 K / min.

Results and discussions

The length and the diameter of the sample were near 52 mm and 5 mm, respectively. The crystal consisted of two major longitudinal monocrystalline blocks. Laue x-ray from the cleavage of one of these units was obtained and shown on Fig.1. Laue reflections are clear, any defects associated with twinning were not observed. The direction of crystal growth is parallel to the axis [120] in orthorhombic representation. The sample is spitted easily along the (001) plane. Direction [001] is perpendicular to the growth axis.

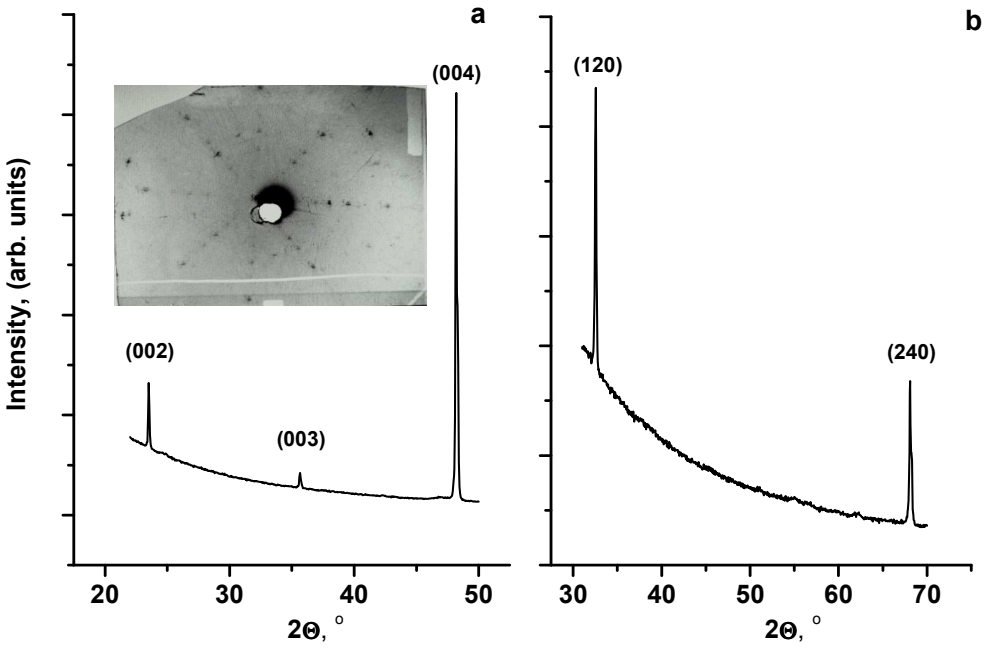

Fig. 1. XRD patterns of the single crystal $GdBaCo_{1.86}O_{5.32}$ parallel (a) and perpendicular (b) to the growth direction. Inset shows Laue pattern of facet parallel to the growth direction.

During the study of the elements distribution in the crystal by the electron microscope it was found that crystal surface up to a depth near 200 microns is multiphase. In the process of melting and crystallization of the growing the crystal surface was partially decomposed to Gd_2O_3 and complex oxide Ba_xCoO_y. The inner part is single phase and homogeneous. For further studies the inner part was used exclusively. Its composition corresponds to the formula $GdBaCo_{1.86}O_{5.32}$. In our sample 97% of the cobalt ions have state Co^{3+} and 3% - Co^{4+} state. X-ray analysis confirmed that the interior of the crystal is a single phase. The unit cell parameters of the initial polycrystalline sample, our single crystal and polycrystalline sample with a similar ratio of Co^{3+}/Co^{4+} ions [4] are given in Table 1.

Table 1. The unit cell parameters of $GdBaCo_{1.86}O_{5.32}$ and $GdBaCo_2O_{5.53}$ at 298 K. The absolute error in the determination of the unit cell parameters is ± 0.001 Å.

Sample	a, Å	b, Å	c, Å	V, Å^3
Polycrystalline sample	3.890	7.805	7.524	228.45
Single crystal	3.901	7.836	7.507	229.49
Polycrystalline sample $GdBaCo_2O_{5.53}$ [4]	3.875	7.822	7.533	228.33

The introduction of vacancies in the cobalt sublattice in a polycrystalline sample weakly changes the volume of the unit cell, but significantly distorts the structure of the double perovskite comparing with $GdBaCo_2O_{5.53}$ [4]. The single crystal had been quickly cooled that strongly influenced on the oxygen content. The crystal did not have time to oxidize during the cooling process, whereby it has a larger unit cell volume.

As a result of high temperature X-ray analysis of the single crystal there was established two phase transitions in the temperature range from 300 K to 860 K. In the heating process from 300 K to 400 K significant increasing of the parameter *c* and slight decreasing of the parameter *b* are observed. Upon further heating in the temperature range 700 - 850 K unit cell changes from orthorhombic symmetry *Pmmm* to the tetragonal one *P4/mmm*. Parameters *a* and *b* become equal to each other. Thus, the structure transitions are located within the ranges 300 - 400 K and 700 - 850 K. According to [4] in $GdBaCo_2O_{5.53}$, these are the metal - insulator and *Pmmm* → *P4/mmm* transitions.

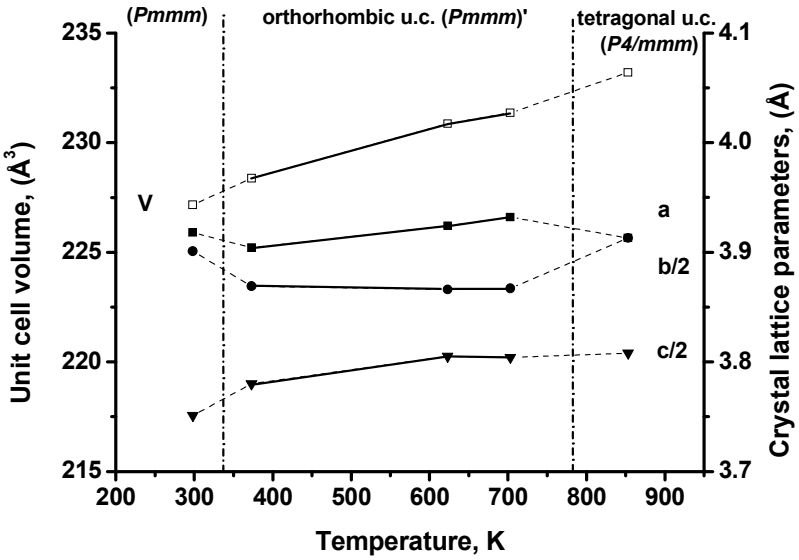

Fig. 2. The temperature dependence of the parameters and volume of the unit cell for $GdBaCo_{1.86}O_{5.32}$ crystal.

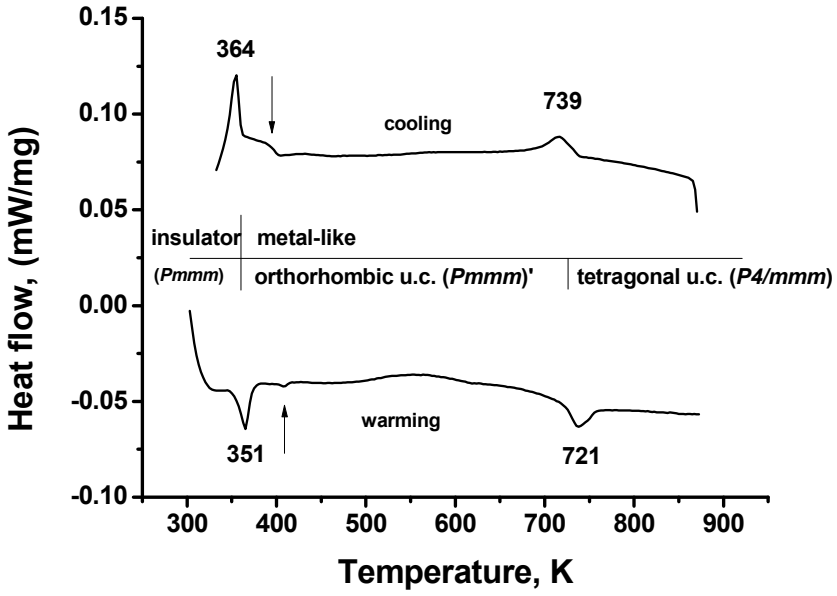

Fig. 3. Calorimetric measurements of the crystal $GdBaCo_{1.86}O_{5.32}$. The cooling curve - at the top, the heating curve - at the bottom. The arrows marked complementary thermal effects.

Calorimetric measurements (see Fig. 3) confirm the presence of both phase transitions in the crystal $GdBaCo_{1.86}O_{5.32}$. Hysteresis phenomena point to the phase transitions of the first kind.

Curves of cooling and heating of the crystal $GdBaCo_{1.86}O_{5.32}$ at ~ 400 K have an unusual effect marked by arrows. In the literature it was mentioned that at this temperature there were no anomalies. In the crystal $GdBaCo_{1.86}O_{5.32}$ with cobalt deficiency the significant shift of the phase transition to lower temperatures (compared with $GdBaCo_2O_{5.53}$ [4]) are observed. This can be associated with the change of the space group *Pmmm* → *P4/mmm*.

Magnetic properties of $LnBaCo_2O_{5.5}$ depend on the spin state of Co ions and the exchange interactions between them. In the perovskite structure Co^{3+} ions can be in different spin states: HS ($t_{2g}^4 e_g^2, S = 2$), IS ($t_{2g}^5 e_g^1, S = 1$) and LS ($t_{2g}^6 e_g^0, S = 0$). Co^{4+} ions can have HS ($t_{2g}^3 e_g^2, S = 5/2$) and LS ($t_{2g}^5 e_g^0, S = 1/2$) states. Co^{2+} ions can be in the HS state ($t_{2g}^5 e_g^2, S = 3/2$) only. The magnetic phase transition from the antiferromagnetic to ferromagnetic state and the metal - insulator transition are observed at T = 250 K and at T ~ 360 K, respectively, according to the phase diagram for compositions with the oxygen content near δ = 5.5 [1]. In our sample the ratio Co^{3+}/Co^{4+} is close to one for $GdBaCo_2O_{5.53}$. The temperature measurements of the magnetization and magnetic susceptibility can provide information about the type of magnetic ordering and spin state of the magnetic ions. Fig. 4 presents the temperature dependence of magnetization in a field 440 Oe for the single crystal $GdBaCo_{1.86}O_{5.32}$.

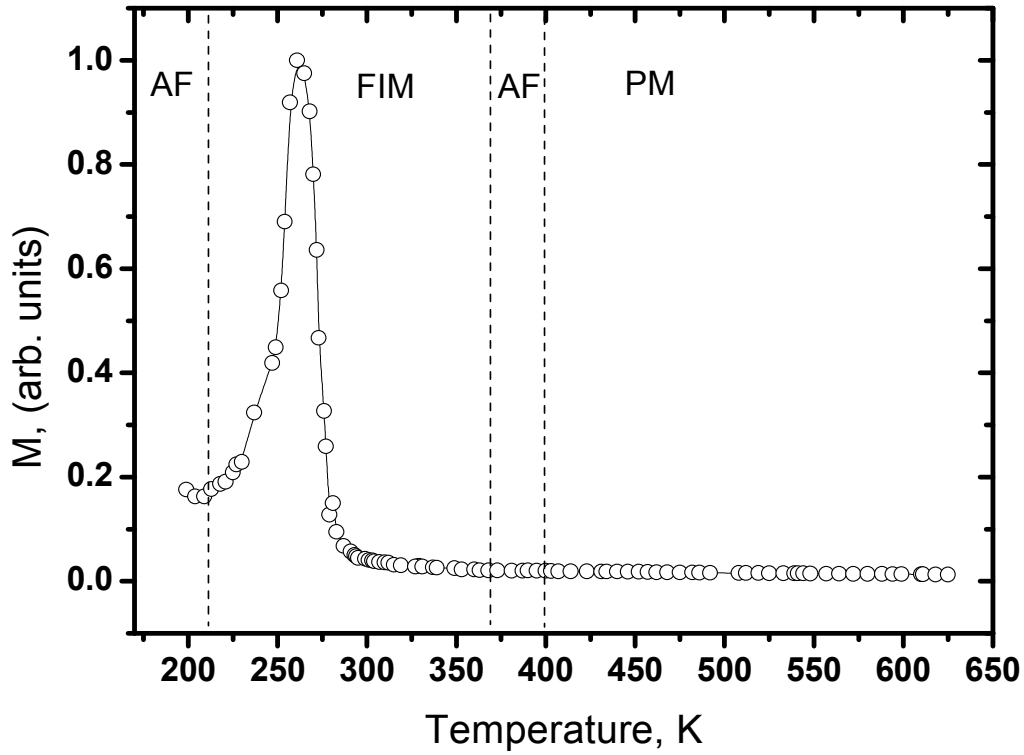

Fig. 4. The temperature dependence of magnetization in a field 440 Oe for the single crystal $GdBaCo_{1.86}O_{5.32}$.

At T = 210 - 280 K the maximum of the magnetization appears which is similar to the maximum of the magnetization M(T) for $GdBaCo_2O_{5.5}$ [1]. Features of the reciprocal magnetic susceptibility behavior above 300 K are shown in Fig. 5. Small anomaly in behavior of $1/\chi$ (T) is visible near 400 K. This corresponds to complementary thermal effects on DSC (see Fig. 3).

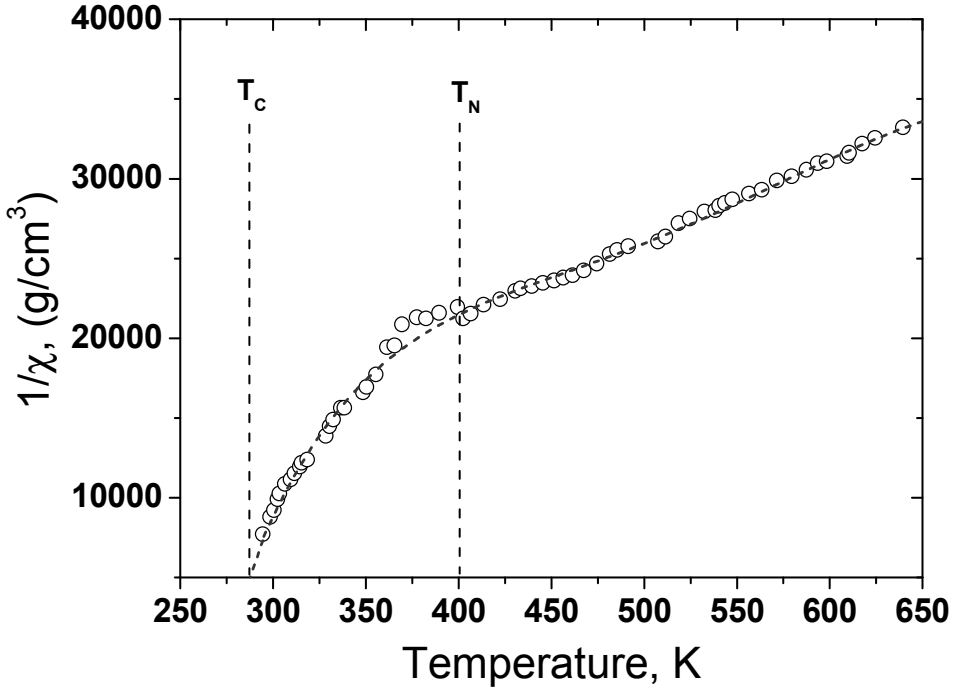

Fig. 5. The temperature dependence of the reciprocal magnetic susceptibility in the magnetic field H=2.65 kOe for the single crystal $GdBaCo_{1.86}O_{5.32}$.

The temperature dependence of the reciprocal magnetic susceptibility $1/\chi$ (T) has a form specific for ferrimagnets with the value of T_N above T_C [5]. Such behavior of $1/\chi$ (T) is observed for $Y(Ba_{0.9}Ca_{0.1})Co_2O_{5.5}$ where disorder is introduced by changing the cation radius [6]. The negative value of the paramagnetic Curie temperature θ = - 16 K and hyperbolic dependence of $1/\chi$ (T) indicate the competition of AF and FM interactions and ferrimagnetic (FIM) ordering in the presence of three or more magnetic sublattices. This is possible because the cobalt ions have two types of environment (octahedral and pyramids) and Co^{3+} ions can have the spin values S = 2, 1, 0. Based on of the magnetic measurements (Fig. 4 and 5) we can present a diagram of the magnetic transitions. The transition from AF to FIM state is observed near 210 K. FIM state remains until 370 K due to neighbouring FM order. At T = 370 - 400 K the magnetic ions are ordering antiferromagnetically. At higher temperatures the sample transforms to the paramagnetic state. The law of the Curie - Weiss holds above T > 450 K with an effective magnetic moment μ_{eff} = 8.78 μ_B which is significantly less than the calculated value μ_{eff} = 10.40 μ_B for HS state of Co^{3+} and Co^{4+} ions. A similar value μ_{eff} = 8.99 μ_B was observed in the temperature range 360 - 400 K in $GdBaCo_2O_{5.43}$ [7]. Low value μ_{eff} indicates that part of the cobalt ions has either IS or LS states. At present two types of spin ordering below temperature of I/M transition are proposed: a) all the cobalt ions are in IS state; b) the cobalt ions in pyramids are present in IS state and in octahedron - in LS and HS states with ratio 1:1. Above temperature of the insulator -metal transition Co^{3+} ions can transformed to HS state.

Considering the different combinations of spin states of Co^{3+} ions in $GdBaCo_{1.86}O_{5.32}$, we calculated the effective magnetic moment μ_{eff} in the paramagnetic region. In the Table 2 the values of μ_{eff} for the different states of Co^{3+} ions in octahedral and pyramidal positions are shown. As we do not know in which position vacancies of cobalt ions are formed, the calculations of μ_{eff} were carried out with the assumption that all vacancies are formed either in the octahedral sites or in the pyramid, only. It is seen that the experimental value μ_{eff} is closest to estimated value μ_{eff} for IS state of Co^{3+} ions in all positions. Above T > 650 K part of the cobalt ions can transform in HS state. In this case the slope of $1/\chi$ (T) must decrease. Obviously, I/M transition is connected with anomalous lattice distortions and the transition of Co ions from the orbital ordering IS state to a disordered IS state [8].

Table 2. The experimental effective magnetic moment of the single crystal $GdBaCo_{1.86}O_{5.32}$ and theoretical models for the different cases of the Co^{3+} spin states excluding the magnetic moment of Co^{4+} ion. Co_o – octahedral position, Co_p - pyramidal position.

The spin state of the Co^{3+} ions	Effective magnetic moment, μ_B
Single crystal, exp.	8.78
Co_o^{3+}(HS)+Co_p^{3+}(HS)	10.37
Co_o^{3+}(IS)+Co_p^{3+}(IS)	8.82
[0.5*Co_o^{3+}(LS) + 0.5*Co_o^{3+}(HS)] + Co_p^{3+}(IS)	9.02 - 9.05
Co_o^{3+}(LS) + Co_p^{3+}(HS)	9.13 - 9.33
Co_o^{3+}(LS) + Co_p^{3+}(IS)	8.36 - 8.43

Conclusions

The magnetic phase diagram for single crystal $GdBaCo_{1.86}O_{5.32}$ with cobalt deficiency was obtained in the temperature range 200 - 650 K It differs from magnetic diagram for cobalt stoichiometric $GdBaCo_2O_{5.5}$. It is shown that in the region 200 - 370 K, the sample has the ferrimagnetic state with the Neel temperature (370 K) above the Curie temperature (262 K). The vacancies in the cobalt sublattices lead to increase antiferromagnetic interactions and do not affect much on ferromagnetic interactions. Both the Curie temperature and the temperature of metal-insulator transition remain the same in comparing with values for $GdBaCo_2O_{5.5}$. All Co^{3+} ions have the intermediate state with an effective magnetic moment $\mu_{eff} = 8.78\ \mu_B$ in the paramagnetic region from 450 to 650 K.

Acknowledgements

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