Magnetic anisotropy in detwinned $Tb_{0.9}Dy_{0.1}BaCo_2O_{5.5}$ single crystal

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M Baran[1,3]**, V I Gatalskaya**[1,2]**, R Szymczak**[1]**, S V Shiryaev**[2]**, S N Barilo**[2]**, G L Bychkov**[2] **and H Szymczak**[1]

[1] Institute of Physics, Polish Academy of Sciences, Aleja Lotników 32/46, PL-02 668 Warsaw, Poland
[2] Institute of Solid State and Semiconductor Physics, NAS, ulica P Brovki 17, 220072 Minsk, Belarus

E-mail: baran@ifpan.edu.pl

Abstract

Magnetic properties of detwinned Tb$_{0.9}$Dy$_{0.1}$BaCo$_2$O$_{5.5}$ single crystals have been studied. The admixture of Dy, introduced only for technological reasons, has no essential influence on the behaviour of the rare earth subsystem of this compound, which is determined by the electronic structure of the Tb^{3+} ions. It is shown that the Co^{3+} ions are Ising ions, with the easy axis along the a axis, in the temperature range 2–276 K (T_C). The Tb^{3+} ions in the AFM phase ($T < T_{N2} = 3.4$ K) are strongly anisotropic, with easy axes [101] and [10$\bar{1}$]. The magnetic field induced phase transitions have been studied, and it is shown that they are determined by anisotropic Co^{3+}–Tb^{3+} exchange interactions. It is shown that the Co^{3+} subsystem is ferrimagnetically ordered within the range $T_N < T < T_C$ ($T_N = 250$ K, $T_C = 275.5$ K) and that the ferrimagnet–antiferromagnet phase transition is of first order, whereas the ferrimagnet–paramagnet phase transition is of second order. In the region of antiferromagnetic ordering of the Co^{3+} ions, metamagnetic phase transitions have been observed for $H \parallel a$. In the temperature range 2 K $< T <$ 170 K, a small ferromagnetic component along the a axis has been observed. This could indicate partial lack of compensation of the antiferromagnetic order. The magnetic susceptibility in the vicinity of the metal–insulator transition (340 K) has been measured. It is found that this transition is accompanied by a structural phase transition responsible for the essential changes of the magnetic anisotropy of Co ions.

(Some figures in this article are in colour only in the electronic version)

[3] Author to whom any correspondence should be addressed.

1. Introduction

The unusual magnetic, resistive and structural properties of double cobaltites with general formula $LnBaCo_2O_{5+\delta}$ (Ln = Y and rare earth elements, $0 \leqslant \delta \leqslant 1$) [1–19] are connected mainly with their two-dimensional layered structure and the variety of spin states of the cobalt ions. The perovskite-like structure of $LnBaCo_2O_{5+\delta}$ can be represented as the stacking sequence of CoO_2–BaO–CoO_2–LnO_δ planes perpendicular to the c axis. The Co^{3+} ions could be in a low spin (LS, $S = 0$, $t_{2g}^6 e_g^0$), an intermediate spin (IS, $S = 1$, $t_{2g}^5 e_g^1$) or a high spin (HS, $S = 2$, $t_{2g}^4 e_g^2$) state [1, 2, 13], while the spin states of the Co^{4+} ions are LS ($S = 1/2$, $t_{2g}^5 e_g^0$), IS ($S = 3/2$, $t_{2g}^4 e_g^1$) and HS ($S = 5/2$, $t_{2g}^3 e_g^2$) [1, 2, 13, 14]. Maignan *et al* [4] have shown (i) the existence of ordering of the alternating planes containing Ba and Ln ions and (ii) a tendency of oxygen vacancies to be located in Ln planes. Moreover, by means of a thermal treatment of these compounds in a suitable atmosphere, one may vary the oxygen content [4, 10, 19], which controls the average valence state of cobalt ions (+3.5 for $\delta = 1$, +3 for $\delta = 0.5$ and +2.5 for $\delta = 0$) and their coordination environment. The geometry of the coordination environment, either pyramidal CoO_5 or octahedral CoO_6, strongly influences the spin state of cobalt ions. The oxygen deficient ($\delta = 0$) compounds with equal concentrations of Co^{2+} and Co^{3+} ions have square pyramids CoO_5 as the principal building units [20–23]. For compounds with $\delta = 0.5$ a metal–insulator transition (MI), spin state changes in the paramagnetic (PM) phase and magnetic transitions caused by competing ferromagnetic (FM) and antiferromagnetic (AFM) interactions were reported [1, 4, 11, 12, 15, 16]. In these compounds all the Co ions are trivalent and the charge ordering is irrelevant, in contrast to the case for mixed-valence manganites, whose properties depend strongly on this feature. It was also suggested [9, 18] that the ratio of LS to IS Co^{3+} ions is equal to 1 for temperatures below the MI transition, and that IS Co^{3+} ions are located in CoO_5 square pyramids with a tendency to be ferromagnetically aligned along the a axis.

The majority of studies on magnetic properties of $LnBaCo_2O_{5+\delta}$ were performed on polycrystals prepared using a standard solid-state reaction. However, the magnetic characteristics of $LnBaCo_2O_{5+\delta}$ (Ln = Gd, Tb, Eu, Nd) single crystals [9, 10, 12, 18, 24–28] were also investigated. The measurements on single crystals are of particular value in determining the magnetic properties of the system related to the anisotropy. One should note that in $LnBaCo_2O_{5.5}$ the ordering of oxygen ions in $LnO_{0.5}$ planes (into alternating filled and empty chains) leads to the transition from the tetragonal to the orthorhombic structure, usually accompanied by a heavy twinning of crystals. This effect hinders the interpretation of experimental results since the directions of the a and b orthorhombic axes become indiscernible. For the *correct* determination of the magnetic anisotropy of such crystals it is necessary to perform a detwinning process. To the best of our knowledge, only Taskin *et al* [9, 10] and Zhou *et al* [18] have implemented a detwinning operation, in their studies of $GdBaCo_2O_{5.5}$ and $EuBaCo_2O_{5.5}$ single crystals, respectively.

As a continuation of our previous study [24] on magnetic properties of $TbBaCo_2O_{5.5}$ (TBC) single crystals, we investigate herein the magnetic anisotropy of $Tb_{0.9}Dy_{0.1}BaCo_2O_{5.5}$ single crystals (TDBC) to get a deeper insight into the mechanisms crucial for the magnetism of layered cobaltites.

However, whereas the TBC single crystals were twinned (see figure 1 [24]), the TDBC single crystals of the present study were subjected to a detwinning process. The TBC crystals were too small for performing their detwinning in an attainable set-up. However, a small addition of Dy in place of Tb resulted in better crystal growth, which allowed us to obtain sufficiently large crystals. At the same time, such a small addition of Dy has no substantial effect (even at low temperatures) on the magnetic properties of the crystals under study. This is

established by comparison of the magnetization curves of TBC and TDBC single crystals for a magnetic field parallel to the c axis (i.e. for a configuration independent of twinning effects).

2. Experiment

TDBC single crystals were grown by the flux technique with a limited number of nucleation centres, on a crystal holder at substantially constant temperature and with a small positive vertical temperature gradient in the crucible. The details were described earlier [29]. As-grown single crystals were essentially oxygen deficient and had tetragonal symmetry $P4/mmm$. The crystals had the typical shape of rectangular parallelepipeds. To obtain the proper oxygen contents (with $\delta = 0.5$), the crystals were annealed at $600\,°C$ and 3 bar oxygen pressure for 20 h. The annealing was followed by isobaric cooling to room temperature at the rate of $10\,°C\,h^{-1}$. Next, in the detwinning procedure, the crystals were exposed to uniaxial pressure along the a axis with simultaneous heat treatment at $300\,°C$ for 12 h in flowing oxygen. According to the x-ray data, the TDBC single crystals after this procedure possessed orthorhombic structure, and the contribution of the disoriented regions (which characterizes the detwinning quality) determined using a polarized light optical microscope did not exceed 3–4%. The oxygen contents determined by a thermogravimetric method corresponded to $\delta = 0.5 \pm 0.02$. Measurements of the magnetization were carried out with a commercial SQUID magnetometer (Quantum Design, MPMS-5) in the temperature range 2–380 K in magnetic fields up to 50 kOe. The external magnetic field was applied along the a, b and c axes and in a particular case along the $\langle 110 \rangle$ and $\langle 101 \rangle$ directions. The thermomagnetic history of the sample used for measurements was taken into account, so the measurements were carried out in the zero-field cooling mode (ZFC) as well as in the field cooling with measurements on cooling (FCC) and field cooling with measurements on warming (FCW) modes.

3. Results of measurements

The temperature dependences of the magnetization $M(T)$ for the TDBC single crystal measured in ZFC, FCC and FCW modes in a field of 100 Oe applied along the a axis as well as in the ZFC mode for the two other crystallographic axes (b and c) are given in figure 1. One notes that making a measurement of the magnetization in the ab plane of the crystal is a good way to estimate the detwinning quality in a crystal volume. As follows from the results presented in figure 1, the anisotropy expressed as a ratio of the magnetization measured for $\boldsymbol{H} \parallel \boldsymbol{a}$ and $\boldsymbol{H} \parallel \boldsymbol{b}$, $M_a/M_b \approx 26$ in a field of 100 Oe ($T = 265$ K), characterizes well the relative volume (slightly below 4%) of the disoriented regions. As the temperature is decreased from 380 K a singularity in $M(T)$ is observed at about 340 K (see figure 2—$\chi(T)$ measured at 6 kOe for a better s/n ratio) for three magnetic field orientations ($\boldsymbol{H} \parallel \boldsymbol{a}$, $\boldsymbol{H} \parallel \boldsymbol{b}$ and $\boldsymbol{H} \parallel \boldsymbol{c}$). Furthermore, there is a sharp increase in magnetization M_a (for $\boldsymbol{H} \parallel \boldsymbol{a}$) below 300 K (figure 1) and the ferromagnetic (FM) moment arises in the cobalt sublattice with $T_C \approx 275.5$ K and with a maximum at ~265 K for ZFC and FCW modes and at ~254 K for the FCC mode. Distinctive features of this FM moment are: a narrow temperature interval in which it is observed; its relatively small value; and a strong anisotropy. In the ZFC mode the observed magnetic moments are about 0.18 μ_B/Co and 0.32 μ_B/Co in the FCC mode, which is evidence of a ferrimagnetic or weak FM ordering. With further decrease of temperature the magnetization sharply decreases, which suggests the appearance of antiferromagnetic (AFM) ordering with $T_N \sim 250$ K. The ZFC magnetization at 225 K does not exceed 0.0025 μ_B/Co.

Figure 3 shows $\chi(T) = M(T)/H_{int}$ dependences at temperatures below 50 K. In this range the contribution from rare earth ions (Ln = Tb^{3+} and Dy^{3+}) grows distinctly with
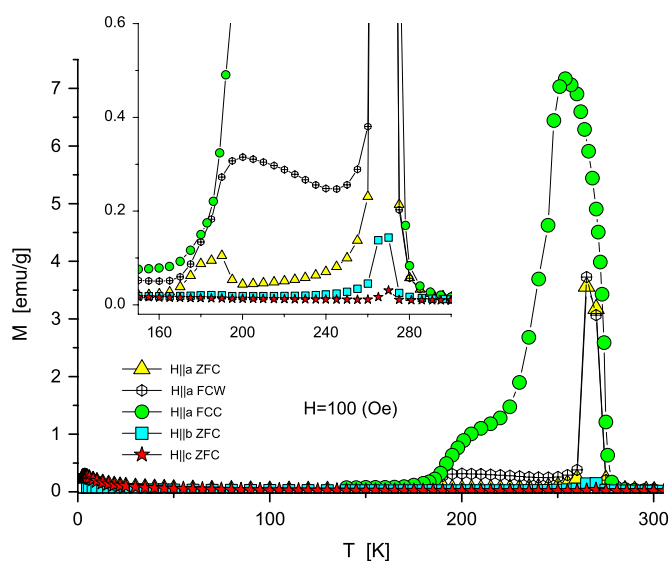
Figure 1. ZFC magnetization $M(T)$ in a field of 100 Oe applied along three crystallographic axes (a, b and c). We also show $M(T)$ for other thermomagnetic regimes (FCC and FCW) for $H \parallel a$. In the inset a part of the figure appears on an enlarged scale, to show M_b and M_c (in the same units).
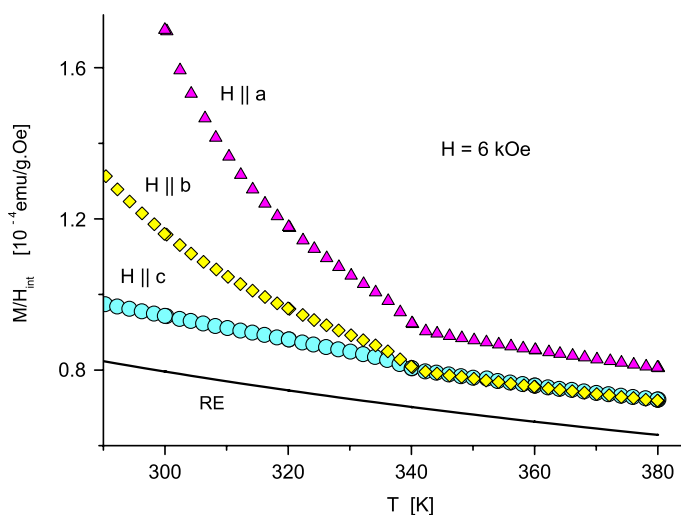

Figure 2. A high temperature part of the magnetic susceptibility ($\chi = M/H_{int}$) in the vicinity of $T_{MI} = 340$ K in $H = 6$ kOe applied along three crystallographic axes (a, b and c).

decrease of the temperature. For low fields and temperatures one must take into account the effect of demagnetizing fields, $-NM$, where $N = 0$–4π. The platelet shape of the sample precludes an exact calculation of demagnetization factors. They were roughly estimated as $N_a \approx 1$, $N_b \approx 4.5$ and $N_c \approx 7$. The susceptibility in orientations the $H \parallel a$, $H \parallel b$ and $H \parallel c$ at temperatures from about 10 to 100 K can be well described by the Curie–Weiss law. The effective magnetic moments for $H \parallel c$ and $H \parallel a$ have been determined as 10.6
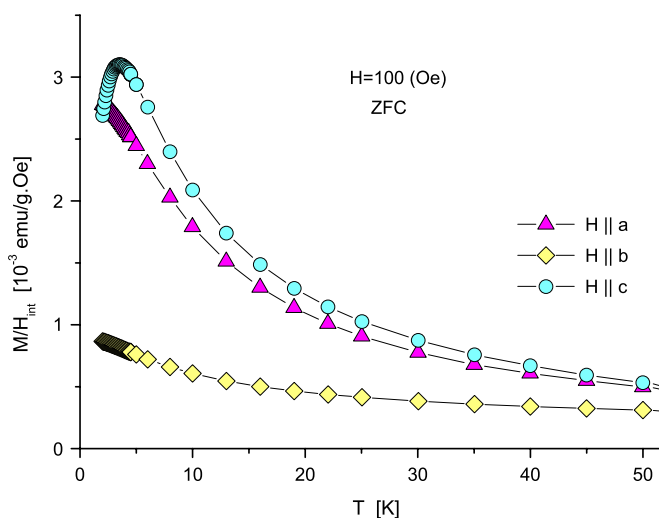
Figure 3. A low temperature part of the magnetic susceptibility ($\chi = M/H_{int}$) (for $T \leqslant 50$ K) in $H_{ext} = 100$ Oe.
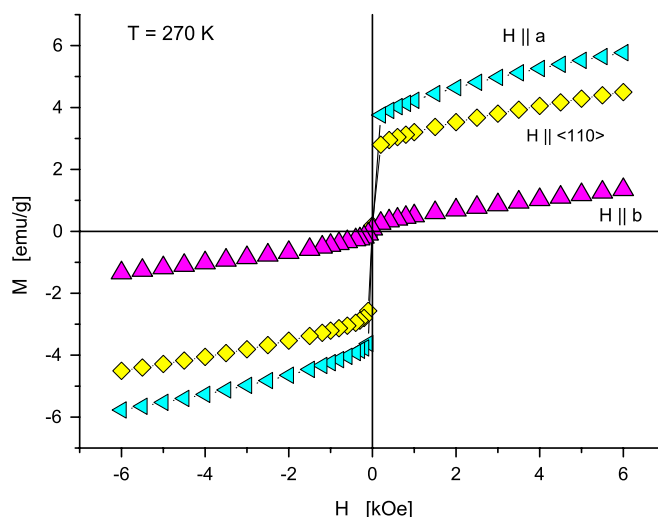

Figure 4. $M(H)$ dependences at 270 K measured for H in the ab plane.

and 9.92 μ_B/fu, respectively, which are close to the theoretical mean value of 9.8 μ_B/fu corresponding to a mixture of the two Ln ions. In the case of $H \parallel b$ the effective moment, $p_{eff} \approx 6 \mu_B$/fu, is distinctly lower, indicating Ln^{3+} ion anisotropy. Moreover, below 3.4 K, for $H \parallel c$, a decrease of susceptibility with decreasing temperature indicates an antiferromagnetic ordering of Ln ions; this effect is analogous to the one reported previously for TBC crystals [24].

Figures 4–6 display the field dependences of the magnetization. In figure 4 the $M(H)$ dependences at 270 K are presented for H in the ab plane. The paramagnetic contribution of the Ln ions (Tb^{3+} and Dy^{3+}) results in a lack of saturation and a linear contribution to the magnetization. This contribution differs for $H \parallel a$ and $H \parallel b$, which is related to the anisotropy of the paramagnetic behaviour of the Ln^{3+} ions. Figure 5 shows $M(H)$ dependences
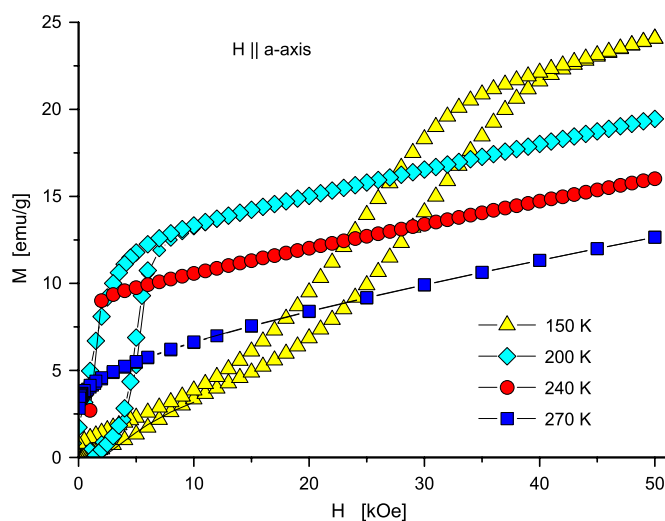
Figure 5. $M(H)$ dependences for $\boldsymbol{H} \parallel \boldsymbol{a}$ at several temperatures ($150 \leqslant T \leqslant 270$ K).
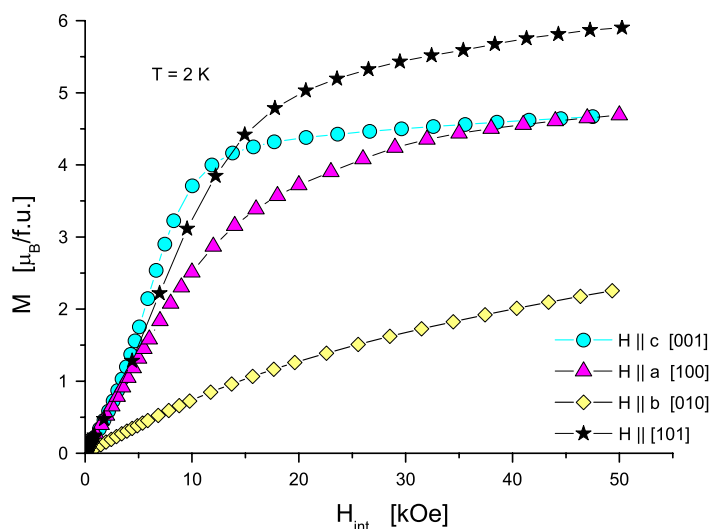
Figure 6. $M(H)$ dependences measured at 2 K for several magnetic field orientations.

for $\boldsymbol{H} \parallel \boldsymbol{a}$ at several temperatures, similar to those reported for a twinned TBC crystal [24] for $\boldsymbol{H} \parallel \boldsymbol{a}$ ($\boldsymbol{b}$). In figure 6 the $M(H_{\text{int}})$ dependences at 2 K are presented for various orientations of H in the ac plane, as well as for $\boldsymbol{H} \parallel \boldsymbol{b}$. It should be stressed that in the whole magnetic field range the $\boldsymbol{b}$ axis is the hard direction for the Ln (Tb + Dy) subsystem, and all directions lying in the ac plane are distinctly easier. In a low magnetic field region—i.e. below the metamagnetic transition (which in the case of the TDBC detwinned crystal studied was found to start at about 3.5 kOe), the anisotropy of the magnetization in the ac plane is relatively small (see figure 6). In this field range the demagnetizing fields play a distinct role in the shapes of the $M(H)$ dependences. At higher fields ($H > 3.5$ kOe), one can see that for each H_{int} value a relation $M_c > M_{\langle 101 \rangle} > M_a$ is fulfilled. Next, the picture in the ac plane changes in the
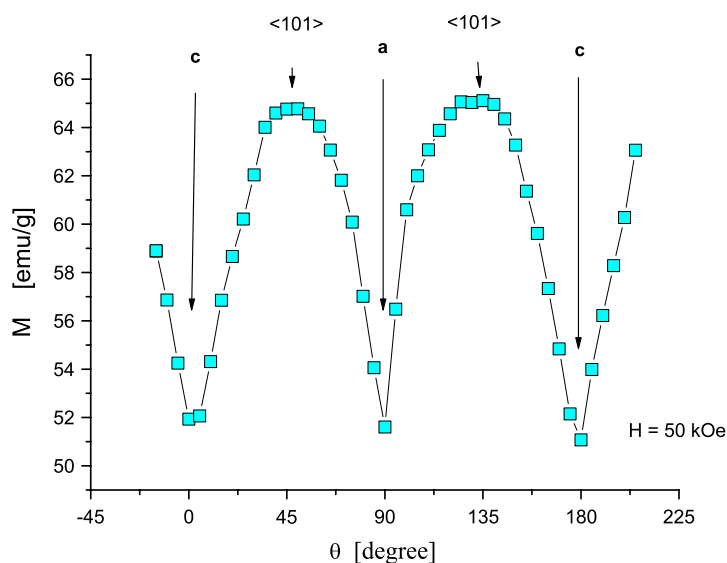
Figure 7. Angular dependence of the magnetization measured at 2 K in $H = 50$ kOe for H in the ac plane.

vicinity of 15 kOe and the $M(H)$ curves for $H \parallel c$ and $H \parallel \langle 101 \rangle$ intersect, while the roles of the c and $\langle 101 \rangle$ axes are interchanged. In a sufficiently high magnetic field ($H_{ext} > 44$ kOe) the M_a and M_c values are practically the same. As one can see, the largest moment in the highest field range was obtained in the case of $H \parallel \langle 101 \rangle$. This correlates well with the angular dependence of the magnetization at 2 K at $H = 50$ kOe in the ac plane (see figure 7). The maxima in the picture correspond to directions of the $\langle 101 \rangle$ type and the minima to the a and c axes. However, it is worth remarking that $M_c/H_{int} > M_a/H_{int}$. It is also worth mentioning that although the metamagnetic transition is most distinct for $H \parallel c$, it could also be observed for $H \parallel \langle 101 \rangle$ with practically the same value of the critical field H_{crit}.

4. Discussion of results

The results obtained for detwinned single crystals differ considerably from the results of studies on twinned crystals. The most important differences are related to the following aspects: (i) the anisotropy of the Co subsystem, especially in the FM-like region just below 276 K; (ii) the anisotropy of the Ln subsystem in the region where the Tb ions are magnetically ordered; as well as (iii) the anisotropy of the magnetic susceptibility in the paramagnetic region (above Curie temperature).

(i) One should note that the FM moment in a narrow temperature range below 276 K arises practically only for $H \parallel a$; thus the a axis can be treated as an easy axis of magnetization for the Co subsystem. The small moment observed at $H \parallel b$ seems to be connected mainly with a residual volume of disoriented regions in a crystal (and to a lesser degree with a possible disorientation of the sample). The data presented in figure 1 confirm our hypothesis of an Ising-like character of the Co subsystem in $TbBaCo_2O_{5.5}$ [24]. They also correspond to the results on other members of the $LnBaCo_2O_{5+\delta}$ family reported in the literature [9, 10]. The analysis of the magnetization dependence on the temperature in a region of FM-like ordering, particularly the difference between M_{FCC} and M_{FCW}, leads to the conclusion that there is

a coexistence of FM and AFM phases in the temperature range 170 K $< T < \sim$250 K. This means that the FM–AFM phase transition is of first order and in the above temperature range both phases are unstable, i.e. the AFM phase becomes unstable above 170 K whereas the FM phase becomes unstable below 250 K. In the range of stability of the FM phase (250 K $< T < T_C$) there exists also a magnetic domain structure, which is the reason for the differences between M_{FCC} and M_{ZFC}. With increase of the magnetic field, M_{ZFC} approaches M_{FCC}, and the upper limit of the instability range decreases. It is worth mentioning that neutron diffraction studies [30] show a structural phase transition from *Pmma* to *Pcca* in the vicinity of $T = 170$ K. The existence of an intermediate state mentioned above is confirmed by the analysis of the magnetization curves $M(H)$ (see figure 5). It is seen that for $H \parallel a$ in the range $T = 200$–270 K the $M(H)$ dependences are typical of ferromagnets or ferrimagnets (the suggestion of ferrimagnetic ordering was made by Plakhty *et al* [30] and by Taskin *et al* [9, 10]), because of the presence of magnetic domain structure. The magnetization curve at $T = 150$ K (figure 5) measured for $H \parallel a$ has a shape typical of an antiferromagnet with an easy axis parallel to the a axis and with a metamagnetic phase transition (of first order) usually observed for such an orientation of the magnetic field. Nevertheless, it is difficult to accept the very large coexistence range (about 80 K) from the point of view of phase metastability. One of the arguments in favour of such an explanation is the fact that in this region there coexist three phases (FM up, FM down and AFM). A similar situation was observed and analysed for $DyFeO_3$ near the Morin point (see [31] and references therein). The coexistence appears not only to reflect the intrinsic nature of the material but also to come from demagnetizing effects. Moreover, a similar behaviour is observed for other materials with AFM–FM first-order phase transitions, e.g. $Nd_{1/2}Sr_{1/2}MnO_3$ [32] and $Ce(Fe_{0.96}Al_{0.04})_2$ [33], which possess an even larger coexistence region. However, we cannot exclude the possibility of another interpretation of the experimental data, namely that there is an antiferromagnetic ordering that is not fully compensated along the a axis. This small ferrimagnetic moment may persist down to the lowest temperature, in agreement with the data presented in this paper.

The analysis of the magnetization curves for $H \parallel b$ confirms the Ising character of the cobalt subsystem in both AFM and FM regions. The magnetization curves in the FM region indicate the existence of a very small ferromagnetic component, considerably smaller than M_a. It may arise simply due to the presence of 3–4% of twins or a small disorientation of the sample. However, the possibility of an intrinsic nature of this component cannot be excluded, since a similar effect is observed in $GdBaCo_2O_{5.5}$ detwinned single crystals [9, 10].

(ii) Below $T_{N2} \approx 3.4$ K, Tb^{3+} ions are antiferromagnetically ordered, which accounts for the $M(H)$ dependences observed (figure 6). The behaviour presented by the Ln subsystem (see a description in the results section) indicates that its structure is relatively complex. The results given in figure 6 suggest that directions of the $\langle 101 \rangle$ type could be the easy directions (antiferromagnetic axes) and that Ln ions are highly anisotropic. With this in mind, it is possible to propose a relatively simple model to describe (at least qualitatively) a magnetic behaviour of the Ln subsystem below T_{N2}. It is assumed that the Tb^{3+} ions are ordered into four magnetic sublattices: A, [101]; B, [10$\bar{1}$]; C, [$\bar{1}$0$\bar{1}$]; and D, [$\bar{1}$01] (in each case the corresponding easy direction is given in square brackets). The magnetization processes for $H \parallel a$ and $H \parallel c$ could develop in two steps: for example for $H \parallel a$ first the sublattice C goes into B, and next D into A. These phase transitions can be of first order (as for $H \parallel c$ and $H \parallel \langle 101 \rangle$ in the form of a spin flop), as well as of second order (spin reorientation transition). Moreover, as can be seen in figure 6, these transitions are thermally broadened. The additional broadening and the lack of hysteresis are connected with the presence of demagnetizing fields and the appearance of the intermediate state in the case of first-order transitions. The system analysed is similar, from a formal point of view, to $TbFeO_3$ orthoferrite, whose properties were studied by
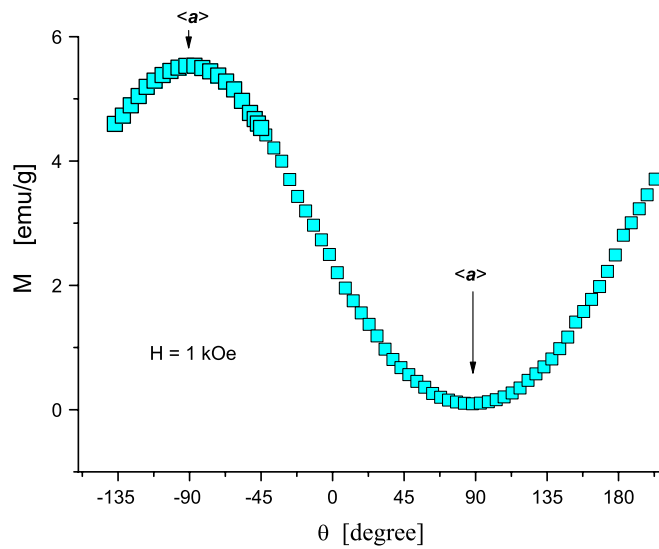
Figure 8. Angular dependence of the low field ($H = 1$ kOe) magnetization measured at 2 K for H in the ac plane.

Belov *et al* [34], Derkachenko *et al* [35] and Nikolov *et al* [36]. In contrast to the case for $TbFeO_3$ in layered cobaltites, the 3d metal ions form two AFM coupled sublattices, probably of different Co^{3+} magnetic moments, making this system very hard to analyse quantitatively. However, one can formulate some qualitative statements. On the basis of the $TbFeO_3$ properties it could be suggested that coupling of Co and Ln subsystems is realized by a molecular field from the AFM Co subsystem (described by the G vector of antiferromagnetism) acting on the Ln subsystem. Thus the magnetic field applied along the c axis (H_z) would be enhanced by an additional contribution, λG_x, where λ is a constant for the molecular field. This could result in a difference between the magnetization curves for the $H \parallel a$ and $H \parallel c$ cases for intermediate magnetic fields, giving a relation $M_c > M_{101} > M_a$. In higher fields the field induced transitions could change this relation. Perhaps the presence of the λG_x contribution influences the character of the field induced phase transition in the $H \parallel c$ configuration.

In contrast to the data shown in figure 7 (high field region), the magnetization in a low field ($H = 1$ kOe) versus the field orientation is shown in figure 8. Both measurements were performed at 2 K for H in the ac plane, but the respective dependences are quite different. This indicates:

- the existence of a ferromagnetic component of magnetization along the a axis—this may suggest a connection of this component with the cobalt subsystem, which is further confirmed by the presence of this component above T_{N2} even up to 170 K;
- the fact that the coercive field of this FM subsystem is larger than 1 kOe (the measuring field).

The magnetization curve for $H \parallel b$ (figure 6) indicates also the presence of a small ferromagnetic component. The origin of this effect cannot be related to the disorientation (a small amount of disoriented twinned region and/or an ordinary sample disorientation as was proposed for the cobalt subsystem) because of the antiferromagnetic ordering of Ln subsystem, but is rather connected with a small deformation of the crystal lattice in a low

temperature region. Recently reported NMR measurements for ^{59}Co in YBaCo$_2$O$_{5.5}$ [37] and in EuBaCo$_2$O$_{5.5}$ [38] also confirm lattice deformation in a low temperature region.

(iii) The singularity in $\chi(T)$ observed near the metal–insulator (MI) phase transition temperature $T_{MI} \approx 340$ K is expected to be directly correlated with changes of the spin state of the Co^{3+} ions [1, 3, 5, 7, 12, 15–17, 19, 39]. In the cited papers the measurements in this temperature region were performed on polycrystalline samples with the exception of those of [12], where single crystals of GdBaCo$_2$O$_{5.5}$ are studied. However, the crystals analysed in [12] were not detwinned in contrast to the TDBC crystals studied in the present work. We performed a comparison of the paramagnetic behaviours below and above the spin state transition temperature of 340 K. For two temperature ranges: 300–340 K and 340–380 K, we have performed a fitting of the Curie–Weiss law. This led to the following conclusions:

(a) Keeping in mind that the paramagnetism at these temperatures is determined by different ions (Co^{3+} and Ln^{3+}), we have calculated and analysed the changes of the effective magnetic moment, Δp_{eff}, of the paramagnetic system, between the lower and upper temperature range, in the cases of the three field orientations. The changes obtained were equal to about 4.5, 4 and 0.8 μ_B/fu for $H \parallel a$, $H \parallel b$ and $H \parallel c$, respectively. One can assume that the effective moment of the Ln^{3+} ions is not changed as the temperature goes beyond 340 K. If one relates the above changes in the magnetic moment to the spin state changes in the Co subsystem only, then it is hard to interpret them (in agreement with the point of view commonly accepted in the literature) as indicating a transition from the Co state configuration 0.5(LS) and 0.5(IS) to 0.5(HS) and 0.5(IS), which should theoretically introduce a change of 4 μ_B/fu. Such a value of Δp_{eff} is in agreement with our experimental results for $H \parallel a$ and $H \parallel b$ but not for $H \parallel c$. The relatively small value of Δp_{eff} obtained for $H \parallel c$ seems to suggest that the MI phase transition is not accompanied by a spin state transition.

(b) The changes of magnetic moment can also be estimated by subtracting the contribution of the Ln^{3+} ions (assuming that their behaviour is described by the Curie law with the mean effective moment estimated from the theory). This approach could be justified, taking into account the fact that the low temperature $\chi(T)$ behaviour for $H \parallel a$ and $H \parallel c$ is well described using the theoretical Ln^{3+} effective moment values. However, this gives values of Δp_{eff} different from those obtained in (a). The Δp_{eff} obtained were equal to about 3.3, 0 and 0 μ_B/fu for $H \parallel a$, $H \parallel b$ and $H \parallel c$, respectively. It should be underlined that the value $\Delta p_{eff} \approx 3.3$ μ_B/fu for $H \parallel a$ is quite close to the theoretically estimated $\Delta p_{eff} = 2.92$ μ_B/fu for a transition from the configuration 0.5(LS) and 0.5(IS) to 0.5(LS) and 0.5(HS). However, the conclusion in this case should be the same as in (a).

(c) The assumption of the isotropic behaviour of Ln^{3+} may be questioned when one takes into account the behaviour of the Ln^{3+} contribution at low temperature (see figure 3) as well as at 270 K (see figure 4). Hence we attempted to subtract this contribution using the Curie–Weiss parameters determined from low temperature results. With this correction one obtains $\Delta p_{eff} \approx 3.1$ μ_B/fu for $H \parallel b$, which is in good agreement with the result obtained in (b) for $H \parallel a$. However, a lack of sufficient change of p_{eff} for $H \parallel c$ prevents us from stating that the Δp_{eff} values estimated in (a) and (b) result from the changes of the spin state in the Co subsystem only.

The most acceptable scenario describing the susceptibility changes at 340 K predicts the appearance of a structural phase transition at this temperature, which changes the anisotropy of the magnetic susceptibility of the Ln^{3+} ions in such a way that they become a source of the estimated Δp_{eff}. Moreover, such a transition is not accompanied by any spin state changes in the Co subsystem. However, the relatively small temperature ranges below and above 340 K

(± 40 K) do not allow a satisfactory verification of this scenario by the fitting of the Curie–Weiss law. Thus the mechanism of this phenomenon requires further studies using other methods.

5. Conclusions

It was shown that both magnetic subsystems in $Tb_{0.9}Dy_{0.1}BaCo_2O_{5.5}$, i.e. the subsystems of rare earth and cobalt, are strongly anisotropic. Tb^{3+} ions are characterized by a strong uniaxial anisotropy with an easy axis of $\langle 101 \rangle$ type. Co^{3+} ions are of the Ising type with the easy axis along the a axis. In the lower temperature region ($T \leqslant 170$ K), usually considered for $LnBaCo_2O_{5+\delta}$ as a region of AFM ordering of Co^{3+} ions, a small ferromagnetic component with a unidirectional anisotropy was shown to exist. Besides the phase transitions induced by temperature, there were also observed transitions induced by magnetic field changes, which is typical for strongly anisotropic systems. The magnetic anisotropy and other magnetic properties of both subsystems change significantly in the vicinity of $T_{MI} = 340$ K.

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