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Magnetic phase transitions in TbBaCo₂O_{5.5} single crystals

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Abstract

Magnetization studies have been carried out on a single crystal of TbBaCo₂O_{5.5} in the temperature range 2–350 K and magnetic fields up to 50 kOe. Several spontaneous magnetic phase transitions have been observed and analysed in both Co ($T_C = 277$ K, $T_{N1} = 210$ K) and Tb ($T_{N2} = 3.44$ K) subsystems. It is shown that the spontaneous first-order phase transition at T_{N1} from an antiferromagnetic to a weak ferromagnetic state is accompanied by an intermediate state. The properties of this state are strongly determined by the thermo-magnetic history of the sample. Metamagnetic type transitions have been observed at $140 \text{ K} < T < 190 \text{ K}$ for the Co subsystem and at $T < T_{N2}$ for the Tb subsystem. The analysis of the magnetic properties of TbBaCo₂O_{5.5} points to the strongly anisotropic character of the Tb and Co subsystems. The Tb subsystem was shown to be of the Ising type. For this subsystem, the exchange interactions between nearest neighbours and next-nearest neighbours were determined. The observed properties of the Co subsystem also point to the Ising character of the Co ions. The effect of the twinning structure on magnetization processes of the weak ferromagnetic phase, especially hysteresis curves, is discussed.

1. Introduction

The oxygen-deficient layered rare earth cobaltites of the general formula LnBaCo₂O_{5+ δ} (Ln = rare earth, $0 \leq \delta \leq 1$) are of extensive interest due to their unusual structural, magnetic and transport properties. Unusual properties observed in layered LnBaCo₂O_{5+ δ} compounds are attributable to:

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- (i) a two-dimensionality due to the stacking sequence of $\text{CoO}_2\text{--BaO--CoO}_2\text{--LnO}_\delta$ planes perpendicular to the c axis,
- (ii) various spin states of cobalt ions in the cobaltites.

For example, Co^{3+} ions may exist in these compounds in low-spin (LS, $S = 0$, $t_{2g}^6 e_g^0$), in intermediate-spin (IS, $S = 1$, $t_{2g}^5 e_g^1$) or in high-spin (HS, $S = 2$, $t_{2g}^4 e_g^2$) states [1–4]. The cobalt ions are located within square base pyramids (formed by five oxygen neighbours) or in an octahedral oxygen environment. It should be mentioned that charge ordering [5, 6], metal–insulator transitions and a high value of magnetoresistance [4, 7–10] studied previously in manganites are also observed in the layered cobaltites. There are also other analogies between cobaltites and manganites. In both families of compounds the oxygen nonstoichiometry (parameter δ) has an important effect on their magnetic and transport properties because this parameter determines the valence states of both Mn and Co ions.

It was shown [3, 4, 10–14] that all members of the $\text{LnBaCo}_2\text{O}_{5+\delta}$ family undergo unusual phase transitions with increasing temperature: first-order metal–insulator and antiferromagnet (AFM) to weak ferromagnet (WFM) transitions and a second-order phase transition from WFM to the paramagnetic (PM) state. Two members of this group, $\text{EuBaCo}_2\text{O}_{5.4}$ and $\text{GdBaCo}_2\text{O}_{5.4}$, are characterized by the highest value of magnetoresistance ever observed in Co-based oxides [15]. The appearance of this effect is linked to the magnetic behaviour of the cobaltites mentioned above.

Among the various members of the $\text{LnBaCo}_2\text{O}_{5+\delta}$ family the most interesting seem to be compounds with $\delta = 0.5$. In these compounds cobalt ions are in a single valence state (3+). The crystal structure of the $\text{LnBaCo}_2\text{O}_{5.5}$ family members is orthorhombic (space group $Pmmm$) [3, 4, 7, 13, 16], corresponding roughly to the doubling of the original perovskite cell (the so-called $a_p \times 2a_p \times 2a_p$ phase, where a_p refers to the cubic perovskite cell parameters) with Co^{3+} ions equally distributed between pyramidal and octahedral sites [3, 11, 17]. The doubling along the c axis is due to the ordering of Ln and Ba into layers perpendicular to the z axis. The cell doubling in the b axis, and the transition from tetragonal to orthorhombic symmetry, is probably due to ordering of the oxide vacancies into channels perpendicular to the y axis. Two different arrangements of the spin state of Co^{3+} ions are reported in the literature for this material:

- (i) both pyramidal and octahedral Co^{3+} ions are in the IS state [3];
- (ii) octahedral Co^{3+} ions are in the LS state while square-pyramidal Co^{3+} ions are in the IS state [11, 18].

Most previous studies of the magnetic properties of $\text{LnBaCo}_2\text{O}_{5+\delta}$ compounds have been performed on polycrystalline samples. However, due to the low symmetry of the lattice of the layered cobaltites, one should expect strong dependences of magnetic phase transitions on the direction of the external magnetic field.

The main purpose of this paper is to investigate magnetic properties of single crystals $\text{TbBaCo}_2\text{O}_{5.5}$ along various crystallographic directions in order to obtain a deeper insight into the mechanisms responsible for magnetic phase transitions in the layered cobaltites. This cobaltite was chosen because of the availability of neutron diffraction data [14, 18]. Some other groups performed magnetic studies on $\text{TbBaCo}_2\text{O}_{5.5}$ [3, 14, 18, 19]. However, a full H – T phase diagram has not been clarified up to date. $\text{TbBaCo}_2\text{O}_{5.5}$ shows a metal–insulator transition at $T_{\text{MI}} = 340$ K [3]. It is suggested that the driving force for this transition is the spin-state (IS–HS) transition in which orbital degrees of freedom are responsible for a cooperative Jahn–Teller distortion. On the basis of magnetization measurements performed on $\text{GdBaCo}_2\text{O}_{5.5}$ single crystals [20, 21] one may expect that Co^{3+} ions are of the Ising type.

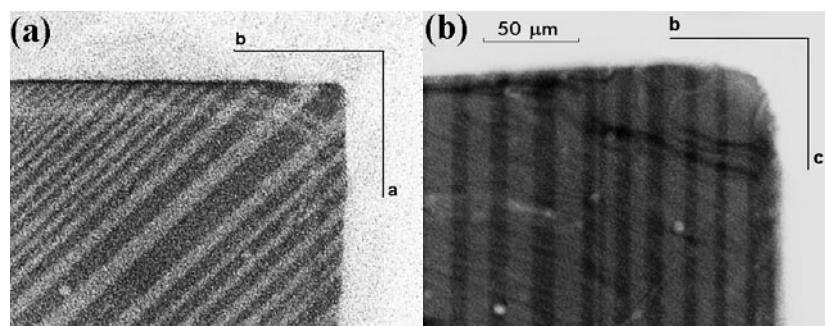


Figure 1. Pictures of crystallographic domain structures observed with a reflection-polarized-light microscope at room temperature: (a) in the (ab) plane; (b) in the (ac) or (bc) plane.

But this conclusion was not confirmed for other rare-earth-based layered cobaltites. The neutron diffraction data [18] indicate that the a axis is the easy magnetization direction for the Co subsystem. The PM to WFM transition occurs at $T_C \sim 280$ K [14, 18, 19]. The FM phase transforms into the AF one at $T_N \approx 230$ – 260 K [3, 14, 18]. An applied hydrostatic pressure of about 8 kbar increases the temperatures T_N and T_C by 2° – 3° [19]. An effect of approximately the same magnitude was observed for a sample in which ^{16}O atoms were replaced by the ^{18}O isotope [19]. This means that the main contribution to the driving force for both transitions is not related to spin–lattice coupling.

2. Experimental details

Single crystals of TbBaCo₂O_{5.5} were grown by a spontaneous crystallization method. The mixture $0.4\text{Tb}_2\text{O}_3$ – 2BaCO_3 – 3CoO was subjected to calcinations at 1100°C for 1 h and it was then melted and homogenized at 1270°C for 1 h. The system was cooled down to 1210°C at a rate of 0.5°C h^{-1} when it was quenched in air. Pieces of crystals were pulled out mechanically. They usually had a shape of rectangular parallelepipeds. The as-grown crystals are of tetragonal symmetry (space group $P4/mmm$). In the final step the crystals were annealed in oxygen under a pressure of 3 atm at 600°C for 20 h and then cooled at a rate of 10°C h^{-1} down to room temperature [22].

Room temperature powder x-ray diffraction of annealed crystals revealed orthorhombic structure (described by the $Pmmm$ space group). These data show a single phase, free of impurities. XRD of single crystals shows that they have a well-developed (ab) plane. The oxygen content was determined by the thermogravimetric method to be $\delta = 0.50(\pm 0.02)$.

The natural surfaces of these crystals were examined with an optical microscope for distinguishing polarization changes of light reflected from an anisotropic medium. Typical pictures of twinning structures observed in the (ab) plane and the (ac) plane are presented in figures 1(a) and (b), respectively. As can be seen in figure 1, the twinning boundaries intersect the (ab) plane along the $[110]$ direction and the (ac) plane or (bc) plane along the c axis. This means that the observed twinning boundary planes are of the (110) type. It is necessary to remark that in the (ab) plane there were also observed regions with boundaries perpendicular to those presented in figure 1(a). Generally, the observed twin widths are in the range 2 – $20 \mu\text{m}$.

Magnetization measurements were performed using a SQUID magnetometer (Quantum Design, MPMS-5) in the temperature range 2 – 350 K and in magnetic fields up to 50 kOe. The external magnetic field was usually applied in two perpendicular orientations: parallel and perpendicular to the c axis. In the latter case it would be parallel to the $a(b)$ axis (described as $H \parallel [100]$), to the $b(a)$ axis ($H \parallel [010]$) and to the $[110]$ direction.

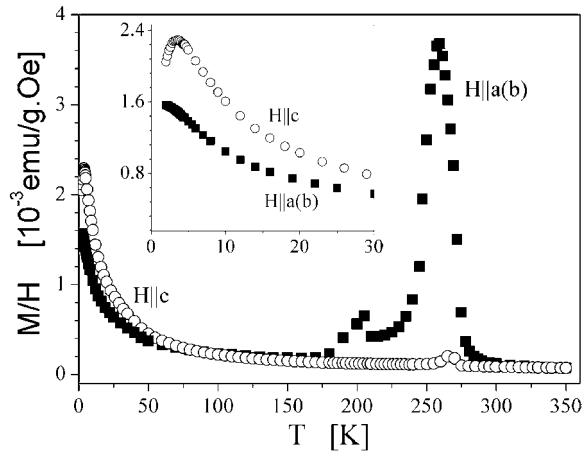


Figure 2. The dc ZFC susceptibility $\chi(T) = M(T)/H$ in $H = 1$ kOe for $H \parallel c$ (open circles) and $H \parallel a(b)$ (full squares). In the inset a low temperature region is shown at an enlarged scale.

3. Results

The temperature variation of the susceptibility $\chi = M/H$ of single-crystal $\text{TbBaCo}_2\text{O}_{5.5}$ measured under a field of 1 kOe in the zero-field-cooled (ZFC) regime is presented in figure 2. For $H \perp c$ ($H \parallel [100]$), the susceptibility, χ_{\perp} , increases rapidly with lowering temperature at $T_C \cong 277$ K, reaching a maximum near $T_{\text{max}} = 258$ K. The magnetic moment per Co ion at T_{max} is about $0.16 \mu_B$ in $H = 1$ kOe. This suggests weak ferromagnetic (WFM) ordering (or, more generally, noncollinear antiferromagnetic ordering). Further below we shall use the notation ‘WFM ordering’ to describe the magnetic structure in this temperature region. χ_{\perp} sharply decreases below T_{max} and a transition to the antiferromagnetic (AFM) state appears with $T_{N1} \cong 210$ K. At low temperatures (see the inset in figure 2) the susceptibility increases due to the paramagnetism of the Tb^{3+} ions. The behaviour of susceptibility χ_{\parallel} (for $H \parallel c$ axis), measured for the same field strength, differs considerably from that of χ_{\perp} . First of all, χ_{\parallel} is much smaller than χ_{\perp} for $T_{N1} < T < T_C$, while at low temperatures $\chi_{\parallel} > \chi_{\perp}$. Its magnitude over a broad temperature range seems to be mainly due to the paramagnetism of the Tb^{3+} ions. There can also be a small contribution from the Co ions due to some possible disorientation of the (001) plane in relation to the magnetic field direction. The $\chi_{\parallel}(T)$ dependence is described by the Curie–Weiss law with effective magnetic moment $\mu_{\text{eff}} = 9.8 \mu_B$ and paramagnetic temperature $\theta_{\parallel} = -2.3$ K. This value of the effective magnetic moment is close to the magnetic moment of free Tb^{3+} ions, $\mu_{\text{eff}}(\text{Tb}^{3+}) = 9.72 \mu_B$, which confirms their essential contribution to the magnetic susceptibility of $\text{TbBaCo}_2\text{O}_{5.5}$ crystals. The domination of this contribution for $H \parallel c$ is also clearly seen from the linear, up to $H = 50$ kOe, $M(H)$ dependences at 170 and 220 K (see figure 3), well described by the susceptibility of the free Tb^{3+} ion.

As can be clearly seen in the inset of figure 2, Tb^{3+} ions order antiferromagnetically below $T_{N2} = 3.44$ K. This characteristic behaviour of magnetic susceptibilities χ_{\perp} and χ_{\parallel} below T_{N2} suggests that the antiferromagnetic vector for the Tb^{3+} system is directed along the c axis. It should be mentioned that antiferromagnetic ordering of Tb^{3+} ions was also observed using the neutron diffraction technique [1] in polycrystalline $\text{TbBaCo}_2\text{O}_5$. It was shown [1] that at 1.5 K the Tb^{3+} magnetic moments point along the c axis and the component in this direction amounts to only about $5.6 \mu_B$, that is far below the expected free-ion value. In [1] it was suggested that a similar discrepancy observed in $\text{TbBaCo}_2\text{O}_5$ arises because even at 1.5 K the

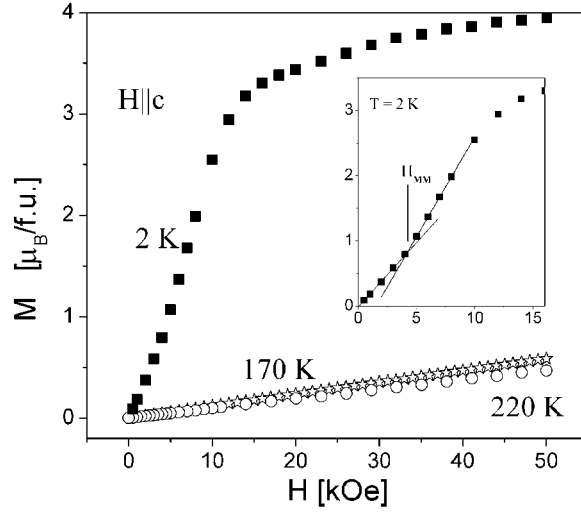


Figure 3. $M(H)$ dependences at 2, 170 and 220 K for $H \parallel c$. In the inset the region around the metamagnetic transition is shown at an enlarged scale.

long-range ordering of the Tb magnetic moments is still not completely established. Although the cobaltite investigated by Fauth *et al* [1] differs from TbBaCo₂O_{5.5} studied in this paper, nevertheless one would expect that the magnetic properties of the Tb subsystems would be similar in both compounds.

Figure 3 shows the magnetization dependence versus magnetic field $H \parallel c$ at $T = 2$ K. It is seen (inset in figure 3) that a metamagnetic type transition appears at the field $H_{MM} \approx 4.5$ kOe, which is evidence that the antiferromagnetic vector of the Tb subsystem is directed along the c axis. The magnetic moment reaches the value of $4 \mu_B/f.u.$ at $H = 50$ kOe. This is mainly due to the Tb³⁺ ions because a contribution from the Co³⁺ subsystem is expected to be low. The transition is of first order, as was confirmed by observation of a small but still observable hysteresis. The exchange interactions between the Tb³⁺ ions were roughly estimated using experimentally determined T_{N2} , θ_{\parallel} and H_{MM} . Two cases have been analysed:

- (i) uniaxial crystalline anisotropy of the Tb³⁺ subsystem smaller than the Heisenberg exchange interactions Tb³⁺-Tb³⁺, and
- (ii) uniaxial crystalline anisotropy considerably greater than Tb³⁺-Tb³⁺ exchange interactions (Ising system).

The calculations have shown that a consistent description of T_{N2} , θ_{\parallel} and H_{MM} is possible only within the framework of the Ising model. In these calculations uniaxial symmetry is assumed and Tb³⁺-Co³⁺ interactions are neglected for simplicity. On applying the molecular field approach to the Ising model one can obtain [23, 24]:

$$kT_{N2} = J_{Tb}^2(-J_1 + J_2), \quad (1)$$

$$k\Theta_{\parallel} = J_{Tb}^2(J_1 + J_2), \quad (2)$$

$$H_{MM}(T = 0) = J_1 J_{Tb} (g\mu_B)^{-1}, \quad (3)$$

where J_{Tb} is the total angular momentum of the Tb³⁺ ions ($J_{Tb} = 6$), μ_B is the Bohr magneton and g is the Landé factor ($g = 1.5$).

$$J_1 = \sum_n J_{1n}, \quad (4)$$

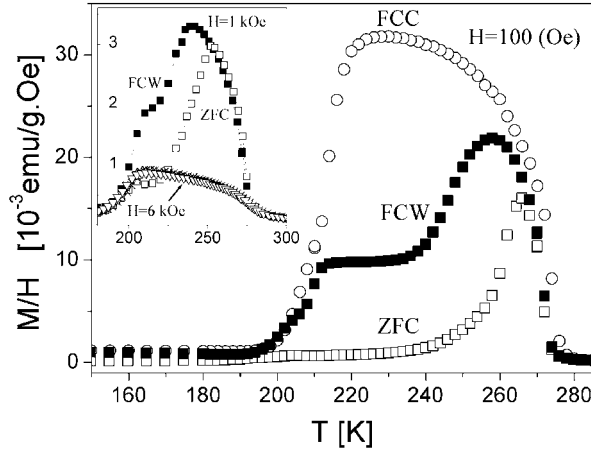


Figure 4. The dc susceptibility $\chi(T)$ in $H = 100$ Oe for $H \parallel [100]$ for three regimes: zero-field cooling (ZFC, open squares), field cooling with measurements on cooling (FCC, open circles) and on warming (FCW, full squares). In the inset similar data are shown for higher magnetic fields. For 6 kOe the data for three different cooling regimes are practically coincident.

where the sum is performed over the nearest neighbours and J_{1n} is the Tb^{3+} – Tb^{3+} exchange integral for ions belonging to different magnetic sublattices.

$$J_2 = \sum_m J_{2m}, \quad (5)$$

where the sum is performed over the next-nearest neighbours and J_{2m} is the appropriate Tb^{3+} – Tb^{3+} exchange integral. From equations (1) and (2) one can calculate $J_1 = -80$ mK, $J_2 = 16$ mK. This means that the effective exchange integral J_1 has ferromagnetic character and J_2 has antiferromagnetic character. The effective exchange integral J_1 could also be estimated from equation (3). Taking $H_{\text{MM}} \approx 4.5$ kOe one can obtain $|J_1| = 76$ mK. This highly simplified estimate of the measured parameters seems to indicate the applicability of the Ising model to the description of magnetic properties of the Tb subsystem.

The estimated value of the magnetic moment ($4 \mu_B/\text{fu}$) at $T = 2$ K for $H = 50$ kOe (figure 3) indicates that the full magnetic moment of Tb^{3+} and Co^{3+} ions is much less than that for free Tb^{3+} ions. It seems that the mechanism proposed in [1] can be responsible for the observed effect. However, an alternative explanation may also be proposed. In view of the fact that the value of $4 \mu_B/\text{fu}$ was obtained at a rather high magnetic field, the reduced magnetization value could be associated with a specific effect of the crystal field known as a level crossing effect. It is known (see, for example, [25]) that the crossing of the ground energy level of a magnetic ion in a field (magnetic and exchange) by one of the excited levels should be accompanied by a change of magnetization and of other parameters of the system. However, to justify one of the considered mechanisms further studies (especially related to the crystal field strength, which is unknown for this family of layered cobaltites) are necessary.

The results of susceptibility measurements in different cooling regimes for $H = 100$ Oe applied along the [100] direction are presented in figure 4. In addition to measurements in the ZFC regime, measurements during field cooling (FCC) and next on warming (FCW) were performed. In the vicinity of T_C the results differ only slightly one from another. However, the magnitudes of χ_{\perp} at the maximum, as well as T_{max} , depend distinctly on the cooling regime. The lowest magnitude in the χ_{\perp} maximum and the highest T_{max} value are obtained for the ZFC regime. In contrast, the highest magnitude in the χ_{\perp} maximum and the lowest T_{max} value are

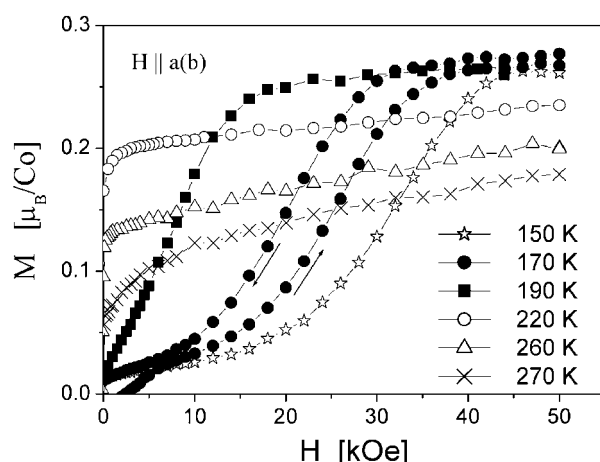


Figure 5. Isothermal magnetization curves for $H \parallel [100]$ in the range $150 \text{ K} \leq T \leq 270 \text{ K}$. As an example, the irreversibility region is shown for 170 K. For other temperatures it is omitted to make the figure more legible.

obtained for the FCC regime. The more complicated shape obtained for the FCW dependence is analysed in the discussion section (see below). One can also see (the inset in figure 4) that an increase in magnetic field strength drastically reduces the differences between susceptibility measured in various cooling regimes (ZFC, FCC and FCW), so that such differences practically vanish for $H = 6 \text{ kOe}$.

For $T > T_C$ the paramagnetic susceptibility follows the Curie–Weiss law. In order to calculate the parameters of the Curie–Weiss law related to the net contribution of cobalt ions one should extract the contribution coming from the Tb³⁺ ions, $\chi_{\text{Co}} = (\chi - \chi_{\text{Tb}})$, where χ_{Tb} is assumed to be due to the free Tb³⁺ ions. On performing this procedure for $H = 1 \text{ kOe}$ the following parameters were obtained: $\theta_2 \approx 210 \text{ K}$, $\mu_{\text{eff}} = 2.44 \mu_{\text{B}}/\text{fu}$, which corresponds to $1.22 \mu_{\text{B}}/\text{Co}^{3+}$ ion. This relatively low value suggests that in low fields about 20% of the Co³⁺ ions exist in the IS state (while the remainder are still in the LS state). For $H = 50 \text{ kOe}$ the magnetic moment per Co³⁺ ion was estimated to be about $2.8 \mu_{\text{B}}/\text{Co}$. On comparing this value with $2.83 \mu_{\text{B}}$ expected for Co³⁺ in the IS state, it is apparent that $H = 50 \text{ kOe}$ transforms practically all Co³⁺ ions from the LS state into the IS state.

In figure 5 the field dependence of magnetization for $H \parallel [100]$ is presented for the temperature range $150 \text{ K} \leq T \leq 270 \text{ K}$. A field-induced phase transition from the antiferromagnetic to weak ferromagnetic state is observed at $140 \text{ K} \leq T \leq 190 \text{ K}$. In the $M(H)$ dependence in this region, after the small hysteresis observed in low magnetic fields a hysteretic-field-induced transition appears at a transition critical field, H_{cr} . The value of H_{cr} grows with a decrease in temperature according to the relation $H_{\text{cr}} (\text{kOe}) = 134.3 - 0.69 T$. Similar observations were reported for polycrystalline [8] and single crystalline [20, 21] GdBaCo₂O_{5.5}. An example of the hysteresis related to this transition (for $T = 170 \text{ K}$) is shown in figure 5. Similar hysteresis curves were observed at various temperatures in the range $140 \text{ K} < T < 190 \text{ K}$, related to the field-induced phase transition from the AFM to the WFM state. This hysteresis is naturally not related to any domain structure but is related to the transition from the initial antiferromagnetic state to the metastable ferromagnetic state and vice versa. This transition disappears above T_{N1} , where the $M(H)$ dependence has a quite different character. As an example, the $M(H)$ dependence for 220, 260 and 270 K is shown in figure 5. The shapes (see figure 6(a) for 220 K) are typical of a WFM state

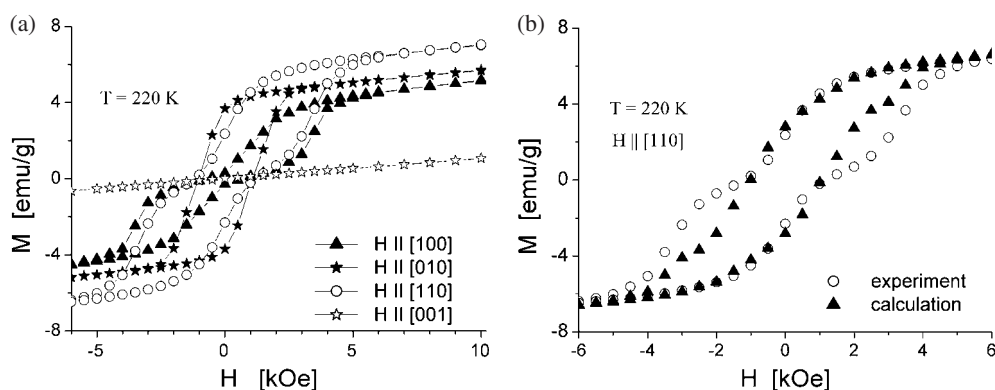


Figure 6. Hysteresis loops at 220 K: (a) for different orientations of the applied magnetic field; (b) a comparison of the calculated and experimental loops for $H \parallel [110]$.

with an irreversible low magnetic field region (strongly diminishing for $T > 250$ K) related usually to the magnetic domain structure and a reversible high magnetic field region related to the noncollinear magnetic structure. At $T = 220$ K the magnetization value of about $0.18 \mu_B/\text{Co}$ is obtained by extrapolation of $M(H)$ from $H = 10\text{--}50$ kOe to $H = 0$. This low value confirms the noncollinear magnetic order in this temperature region, in agreement with suggestions formulated earlier [4, 14, 19].

4. Discussion

The experimental data presented in this paper are generally in accordance with the results of neutron diffraction measurements [1, 3, 14, 18]. Moreover, the magnetization studies performed using single crystals of $\text{TbBaCo}_2\text{O}_{5.5}$ allow some additional conclusions to be drawn about the spin state of the Co^{3+} ions and about magnetic phase transitions induced by an external magnetic field and temperature as well as about anisotropy and magnetic interactions determining the magnetic structure existing in this material. However, these conclusions are somewhat limited because the studied crystals are twinned. A twinning structure has an important influence on magnetization processes in both antiferromagnetic and ferromagnetic phases. The twinning in our crystals (as well as in other perovskites) can be formed as a result of a structural transformation from tetragonal to orthorhombic. This leads to two kinds of crystallographic domains with different directions of the AFM vector. The directions are mutually almost perpendicular. A twinned structure in cobaltites was previously observed in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ [26] and $\text{GdBaCo}_2\text{O}_{5.5}$ [20].

In order to demonstrate the influence of the twinning structure of the investigated crystals on the results of measurements, we performed some additional measurements for H along the [010] and [110] axes. As an example, the $M(H)$ dependence obtained at 220 K for different field orientations in the (ab) plane is presented in figure 6(a). It can be concluded from figure 6(a) that saturation magnetization, M_{sat} , depends strongly on the direction of the magnetic field. This means that magnetocrystalline anisotropy due to Co^{3+} is very high. As has already been mentioned this result is in agreement with conclusions resulting from the magnetization measurements of $\text{GdBaCo}_2\text{O}_{5.5}$ single crystals [20, 21] that Co^{3+} ions are of the Ising type. Moreover, the fact that M_{sat} weakly depends on magnetic field strength up to 50 kOe means that the field does not change the volume of the crystallographic domains and

consequently is not able to shift the twin boundaries. This is in contrast with the strong effect of the magnetic field on the twin boundaries recently observed in La_{2-x}Sr_xCuO₄ [27].

At low magnetic fields (below 5 kOe) the system under study displays hysteresis loops at $T_{N1} < T < 250$ K. These loops are, in fact, a combination of various effects such as: (i) instability on magnetic field reversal typical of highly anisotropic materials [24], (ii) magnetic domain structure and (iii) crystallographic domain structure. Because of the rich twin structure and the Ising character of the Co³⁺ ions one should expect that $\text{div}M$ is not equal to zero at the twin boundaries. These surface magnetic poles should strongly affect magnetization processes. Since various effects determine these processes, it is difficult to give an explanation of the observed hysteresis loop shapes. It is, however, possible to show that the magnetization process along the [110] direction can be considered as a superposition of magnetization processes along the [100] and [010] directions, disregarding a difference in volume of both kinds of crystallographic domains (twins). On taking into account that:

- (i) according to neutron diffraction data [18] the a axis is the easy magnetization direction;
- (ii) in the crystal there are two kinds of twins with magnetization along the [100] and [010] directions;
- (iii) the development of magnetization processes in both kinds of twins is similar

it is possible to introduce the following formal relation:

$$M(H \parallel [110]) = (\sqrt{2})^{-1} \{M(H \parallel [100]) + M(H \parallel [010])\} + (1 - \sqrt{2})H\chi_{\text{Tb}}. \quad (6)$$

The hysteresis loop calculated for $H \parallel [110]$, according to relation (6), is shown in figure 6(b). The correspondence between the results of such calculations and with experimental data is relatively good, especially in high (positive and negative) magnetic fields and when the field is changed from +5 kOe to $-H_c$ and from -5 kOe to $+H_c$ (where H_c is a coercive field). It is necessary to mention that for all three hysteresis loops shown in figure 6(a), in spite of their different shapes, the coercive field has practically the same value. This could mean that the coercive field does not originate from a magnetic domain structure (in such a case H_c ($H \parallel [110]$) should be larger by $\sqrt{2}$ than (H_c) for ($H \parallel [100]$) or ($H \parallel [010]$)) and rather determines the stability region for the Ising system [24]. The differences between the calculated loop and experimental data for fields changed from $-H_c$ to negative high field and from $+H_c$ to positive high field can be interpreted as connected with the movement of magnetic domain walls. It should be noted that, on extrapolating $M(H)$ from high field to $H = 0$ for the three cases presented in figure 6(a), we obtain $\{M([100]) + M([010])\}/M([110]) = 1.418$, which is only very slightly different from the factor $\sqrt{2}$ resulting from equation (6). It should also be mentioned that the sum $M(H \parallel [100]) + M(H \parallel [010])$ describes the real magnetization of the measured single crystal.

The twin structure seems to have a distinct effect on the field-induced transitions in the temperature range $140 \text{ K} < T < 190 \text{ K}$ (figure 5). It has to be noted that the field-induced transitions are not as sharp as those observed in detwinned GdBaCo₂O_{5.5} single crystals [21], but are comparable to those observed in twinned GdBaCo₂O_{5.5} single crystals [20]. One should therefore assume that the large width of the metamagnetic phase transition in our crystals is first of all related to the presence of the twinning structure. Another factor affecting the width of the metamagnetic transition is related to the intermediate states in which the two phases coexist. Such states arise due to the demagnetizing (dipolar) fields. Usually the presence of the intermediate state makes the hysteresis very narrow or even not observable [28]. The fact that in our case we observe the relatively large hysteresis may be related to the specific nucleation processes characteristic of studied single crystals. Following [28] one could assume that in our case the magnetization curve measured for field-up is determined mainly by antiferromagnetic

wall splitting and by structural defects (mainly related to the twin structure), with the first of these factors dominant. The magnetization curve for the field-down curve is determined by a nucleation mechanism related to the defects. The properties of the intermediate state structure determine in this way the width and slope of the magnetization curves.

It is concluded from the results of the measurements performed that the paramagnetism of the studied crystals at $T > T_C$ was mainly due to Co^{3+} in various spin states. An interesting feature of the studied system is connected with the observation that a high magnetic field is able to induce the LS–IS transformation for Co^{3+} ions. Below T_C a weak ferromagnetic structure develops. On extrapolating the results from the paramagnetic to the weak ferromagnetic region one should assume that magnetic moments in this temperature region have mainly IS origin (in accordance with [14]). Both the antiferromagnetic vector and the ferromagnetic one are perpendicular to the c axis. A further decrease of temperature leads to the first-order phase transition (similar to the Morin one) from the WFM phase to the pure AFM phase at temperature T_{N1} . The $M(T)$ dependence in the temperature region between T_{N1} and T_C clearly demonstrates irreversibility, which distinctly depends on the regime of sample cooling (ZFC, FCW and FCC—see figure 4). This observation has to be related to the fact that the AFM–WFM phase transition is a first-order one in this compound. In the case of first-order magnetic phase transitions a thermodynamically stable state can be formed (due to the demagnetizing fields) in which two phases may coexist. The situation is similar to the phase coexistence near the Morin transition observed in dysprosium orthoferrite (see [29] for details and references). In the low magnetic field region the intermediate state consists of three coexisting phases: antiferromagnetic (AFM) and weak ferromagnetic with the magnetization vector directed up (WFM⁺) or down (WFM[−]). For a high enough external field the phase WFM[−] is suppressed. Figure 4 shows that the formation of the WFM phase in the ZFC regime starts at a considerably higher temperature than in the case of the FCC or FCW regimes. This suggests that the nuclei of the WFM phase are formed by the magnetic field near various defects of the crystal structure. This mechanism also explains the ‘two-step’ character of the WFM state formation. The crystals under study are twinned, so that an external field generating nuclei of the new phase in one part of the crystal (where the field is parallel to the ferromagnetic axis) is not able to generate such nuclei in other crystallographic domains (or an efficiency of this generation is considerably lower). It can be concluded from figure 4 that near $T \cong 250$ K the first step of the WFM phase formation is finished. Above this temperature two scenarios are probable:

- phase domains could develop in other crystallographic domains due to their contacts with domains of the ferromagnetic axis parallel to the applied field;
- near $T \cong 250$ K a structural phase transition could exist, making easier a formation of the WFM phase. The neutron diffraction experiments [18] indicate the possibility of such a transition. At the moment we are not able to decide which scenario describes properly the weak ferromagnetic phase formation in $\text{TbBaCo}_2\text{O}_{5.5}$ single crystals.

5. Conclusions

The magnetization measurements have been performed on twinned $\text{TbBaCo}_2\text{O}_{5.5}$ crystals. It has been found that their T – H phase diagram is very rich. Several magnetic phase transitions induced by the external magnetic field and temperature were observed and analysed. Nevertheless, many points are still not clear and require further study, especially by neutron diffraction in high magnetic fields. Such experiments should clarify the magnetic structure induced by magnetic field in both Tb and Co subsystems.

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