Spin structure and magnetic phase transitions in TbBaCo$_2$O$_{5.5}$

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Spin ordering in TbBaCo$_2$O$_{5.5}$ and its temperature transformation reproducible for two differently synthesized samples are studied. One of the ceramic samples, in addition to the main phase $a_p \times 2a_p \times 2a_p$, $Pmmm$ ($Z = 2$), where $a_p$ is parameter of perovskite cell, contains about 32% of the phase $a_p \times a_p \times 2a_p$, $Pmmm$ ($Z = 1$) with statistical distribution of oxygen over the apical sites. The other sample is a single phase $a_p \times 2a_p \times 2a_p$, $Pmmm$ ($Z = 2$) with well defined octahedral and pyramidal sublattices. Treatment of neutron diffraction patterns of the double-phase sample gives a sophisticated spin structure. Knowing the spin structure of the single-phase sample, one can choose only proper magnetic lines, which give exactly the same results for both samples. The spin structure at $T = 265 \text{ K}$ unambiguously indicates the phase $2a_p \times 2a_p \times 2a_p$, $Pnma$ ($Z = 4$). At $T_N = 290 \text{ K}$, the spins order with the wave vector $k_{19} = 0$ (phase 1). At $T_a = 255 \text{ K}$, a magnetic transition takes place to the phase 2 with $k_{12} = b_2 / 2$. The extinction law of magnetic reflections below $T_a = 170 \text{ K}$ evidences that the crystal structure changes to $2a_p \times 2a_p \times 4a_p$, $Pcca$ ($Z = 8$). The wave vector of the spin structure becomes again $k_{19} = 0$ (phase 3). The basis functions of irreducible representations of the group $G_k$ have been found. Using results of this analysis, the magnetic structure in all phases is determined. The spins are always parallel to the $x$ axis, and the difference is in the values and the mutual orientation of the moments in the ordered nonequivalent pyramidal or octahedral positions. Spontaneous moment $M_0 = 0.3(5) \mu_B / \text{Co}$ at $T = 260 \text{ K}$ is due to ferrimagnetic ordering of the moments $M_{P_{y1}} = 0.46(9) \mu_B$ and $M_{P_{y2}} = -1.65(9) \mu_B$ in pyramidal sites (Dzyaloshinskii-Moriya canting is forbidden by symmetry). The moments in the nonequivalent octahedral sites are: $M_{O_{y1}} = -0.36(9) \mu_B$, $M_{O_{y2}} = 0.39(9) \mu_B$. At $T = 230 \text{ K}$, $M_{P_{y1}} = 0.28(8) \mu_B$, $M_{P_{y2}} = 1.22(8) \mu_B$, $M_{O_{y1}} = 1.39(8) \mu_B$, $M_{O_{y2}} = -1.52(8) \mu_B$. At $T = 100 \text{ K}$, $M_{P_{y1}} = 1.76(6) \mu_B$, $M_{P_{y2}} = 1.76 \mu_B$, $M_{O_{y1}} = 3.41(8) \mu_B$, $M_{O_{y2}} = -1.47(8) \mu_B$. The moment values together with the ligand displacements are used to analyze the spin-state/orbital ordering in the low-temperature phase.

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I. INTRODUCTION

The giant magnetoresistive cobaltites $RBaCo_2O_{4+\delta}$ ($R = Y$, or rare earth) demonstrate spin ordering, apparently, coupled with the orbital ordering on the background of Co$^{3+}$ spin-state transitions. As a result of competition between the intraatomic exchange and the crystal field, Co$^{3+}$ ions can exist in the low-spin state (LS, $\tau_{2g}^{2} \epsilon_{g}^{0}$, $S = 0$), intermediate-spin state (IS, $\tau_{2g}^{5} \epsilon_{g}^{1}$, $S = 1$), and the high-spin state (HS, $\tau_{2g}^{7} \epsilon_{g}^{2}$, $S = 2$). Due to rather small energy gaps of about 30–100 meV between these states,2–3 the LS evolves to the IS and then to the HS as the temperature increases. These temperature-dependent spin-state transformations may be accompanied by both the spin structure and the spin-state ordering transitions, which were investigated using neutron diffraction4–6 and magnetization measurements.7

The crystal structure shown in Fig. 1(a) is found now for all of the series members.8–11 It is usually described by the space group $D_{2h}^{2} Pmmm$, and the unit cell parameters are expressed through parameter $a_p$ of the pseudocubic perovskite cell as $a_1 = a_p$, $a_2 = 2a_p$, $a_3 = 2a_p$. The structure motif is given by the oxygen octahedra and square pyramids, which coordinate the Co$^{3+}$ ions and alternate along the $y$ axis. Apical oxygen sites shown by the open circles can be partially occupied. This means that even at the ideal average oxygen content of 5.5 some disorder can appear due to the oxygen redistribution among these sites. The regular study12 of the crystal lattice dependence on the oxygen content from 5.00 to 5.52 in YBaCo$_2$O$_{4+\delta}$, had discovered, in addition to $a_p \times 2a_p \times 2a_p$, a superstructure with tetragonal unit cell $3a_p \times 3a_p \times 2a_p$, at 0.25 $\leq \chi \leq 0.44$. At low oxygen content, $\chi \approx 0.19$, nearly tetragonal unit cell $a_p \times a_p \times 2a_p$ shown in Fig. 1(b) was found. Similar structure was observed at $\chi = 0.4$ for a fast-cooled sample.4 A variety of different crystal phases12 inevitably leads to controversies of the magnetic structures determined up to now.

The first neutron diffraction study of magnetic ordering4 was carried out on the fast cooled ceramic of TBBaCo$_2$O$_{4.5}$ with the crystal structure described in Fig. 1(b). The magnetic unit cell at $T = 150 \text{ K}$ was determined as a chemical one doubled in all three directions. Six nearest neighbors of any spin had an opposite direction. Magnetic moments had two components, $M_r = 1.33(3) \mu_B$ and $M_z = 0.70(5) \mu_B$. This sample had no phase with spontaneous moment at about 270 K. Unfortunately, no neutron diffraction data were presented for a slowly cooled sample, which might be expected to have the crystal structure of interest described in Fig. 1(a).

Neutron diffraction studies4 that have been performed on a powder sample of NdBaCo$_2$O$_{5.47}$ show two phase transitions, to the antiferromagnetic phase at $T_N \approx 275 \text{ K}$ and to the spin-state ordered (SSO) phase at $T_{SSO} \approx 230 \text{ K}$. The
spin-state ordering is discovered in octahedra with the moments of 2.6(2)\(\mu_B\) and 0.1(1)\(\mu_B\) at 85 K, which are interpreted as IS and LS, respectively. The cobalt ions of the same spin state are arranged in the rows along [0,0,1], which alternate along [1,0,0]. Some widening of magnetic reflections, in comparison with the nuclear ones, is explained by a finite correlation length \(\xi \sim 350\) Å of the SSO. Nothing special has been detected in the temperature range of the spontaneous moment, and there is no explanation of its nature. It is mentioned that the same behavior has been observed in TbBaCo\(_2\)O\(_{5.46}\) \((T_N \sim 295\) K, \(T_{SSO} \sim 250\) K). On the other hand no SSO has been found in NdBaCo\(_2\)O\(_{5.38}\), which indicates that this state exists in a narrow range of the oxygen content near \(x=0.5\).

The third and, to our knowledge, the last neutron-diffraction work\(^6\) has been made on a single crystal of TbBaCo\(_2\)O\(_{5.52(2)}\) grown by a floating zone method. As-grown crystal was annealed in flowing oxygen. A number of superlattice reflections have been detected with the wave vectors \(k_s=b_1/3\) (or \(k_s=2b_1/3\)), \(k_f=b_1/6\) (or \(k_s=b_2/3\)) \(k_5=b_3/4\) in addition to \(k_{32}=b_3/2\). Hereafter the wave vectors \(k_s\) are given in Kovalev’s notation,\(^13\) and \(b_1, b_2, b_3\) are the reciprocal lattice vectors, corresponding to \(a_1, a_2, a_3\), which are shown in Fig. 1(a). Huge intensity change, up to two times, of the basic reflection \((0,2,0)\) has been also observed in the magnetically ordered state. At 270 K, where a spontaneous moment of 0.2 \(\mu_B\) along \(a_1\) has been measured, the Co\(^{3+}\) ions in octahedral sites are discovered to be in the LS state, and only the spins in pyramidal sites are ordered. The ordering is described by two wave vectors, \(k_{22}=b_1/2\) and \(k_{19}=0\). The former gives the antiferromagnetic spin component along \(a_1\), while the latter is for the ferromagnetic component along \(a_1\).

At \(T=270\) K, the moment value is found to be \(M_{Py}=0.71(2)\mu_B\), with the spontaneous magnetization being equal to 0.18 \(\mu_B/\text{Co}\).

Taskin et al.\(^7\) have concluded on the basis of magnetic measurements performed with a detwinned single crystal of GdBaCo\(_2\)O\(_{5.50}\) that the moments in one plane with pyramidal sites are ordered ferromagnetically along [1,0,0]. The moments in the second pyramidal plane are ferromagnetically ordered in the opposite direction. Taking into account the structural data,\(^10\) the moment in the octahedral sites in between these two planes is assumed to be zero.

This short and not comprehensive review of controversial publications clearly demonstrates that the Co\(^{3+}\) spin ordering in these materials, which one could expect to be independent on the rare earth, at least in the high-temperature range, is still unknown. Usually the data obtained from single crystals are more reliable than those from polycrystalline samples synthesized by a ceramic technology. However, the single crystal grown using very promising floating zone method and then thermally treated in the flowing oxygen to a proper oxygen content shows all superlattice reflections,\(^6\) which have been observed for very different oxygen contents.\(^12\) This gives an indication that the results are very sensitive to the oxygen distribution over possible crystallographic sites and to the sample homogeneity at some average oxygen content. It seems that the conclusions made on the basis of investigation of one sample are valid but for this sample. We believe that as a criterion of correct solution of the spin structure should be the same result obtained with different samples of the same material.

We present in this paper the results of neutron diffraction studies of the TbBaCo\(_2\)O\(_{5+x}\) magnetic structure performed on two polycrystalline samples synthesized at different conditions. One sample (I) contains two ordered phases. The phase of interest \(a_p\times2a_p\times2a_p\) has the oxygen content 5.49(2). The second phase has the unit cell \(a_p\times2a_p\times2a_p\) with statistically occupied position of the apical oxygen and the average oxygen content with 5.42(2). In addition, there is a phase with short-range ordering and a periodicity of \(3a_p\). The other sample (II) has a single phase \(a_p\times2a_p\times2a_p\) with the oxygen content 5.53(1). Historically the sample I was the first studied, but we solved magnetic structure of its main phase only after a single-phase sample II. Two structures were found to be identical. Essentially the same results obtained for \(x=0.49(2)\) and \(x=0.53(1)\) indicate that the spin structure and its temperature transformation are found for TbBaCo\(_2\)O\(_{5.5}\). We shall give the actual value of \(x\), when necessary.

The magnetic structure is different of those reported before. Below the Néel temperature \(T_N=290\) K, the magnetic unit cell is \(2a_p\times2a_p\times2a_p\). The refinement of all allowed by symmetry magnetic structure models that give a spontaneous moment in the frame of commonly used space group \(Pnmm\) results in very bad agreement with experiment \((\chi^2=92)\). Assuming that the unit cell doubling is due to a structural phase transition to the highest subgroup \(D_{3d}-Pmma\), the fit goodness has been improved to \(\chi^2=1.7\), which gives a confidence of correct solution. At \(T=260\) K, the moments \(M_{Py1}=0.46(9)\mu_B\) and \(M_{Py2}=1.65(9)\mu_B\) in two nonequivalent pyramidal sites are ordered ferrimagnetically, resulting in a spontaneous moment \(M_{0}\approx 0.30(3)\mu_B\) per one Co\(^{3+}\) ion. The moments in two nonequivalent octahedral sites are also opposite, but of equal value, \(M_{Oc1}=-0.36(9)\mu_B\), \(M_{Oc2}=-0.39(9)\mu_B\). When taking into account the very vicinity of \(T_N\), we may assume that one of the Co\(^{3+}\) ions in the pyramidal sublattice is in the HS state. The other one, as well as the ions in an octahedral sublattice, have an admixture of the LS state with one of the excited states. Instead of SSO into the composite, but of equal value, \(M_{0}\approx 0.30(3)\mu_B\) per one Co\(^{3+}\) ion. The moments in two nonequivalent octahedral sites are also opposite, but of equal value, \(M_{Oc1}=-0.36(9)\mu_B\), \(M_{Oc2}=-0.39(9)\mu_B\). When taking into account the very vicinity of \(T_N\), we may assume that one of the Co\(^{3+}\) ions in the pyramidal sublattice is in the HS state. The other one, as well as the ions in an octahedral sublattice, have an admixture of the LS state with one of the excited states. Instead of SSO into the
The general conclusions are made in Sec. V. Possible spin-state/orbital ordering in phase 3 is analyzed. In the process of the spin structure determination, the symmetry analysis is always used. In Sec. IV, the spin order and its temperature transformations are discussed in terms of the energy gaps between three spin states of Co\textsuperscript{3+}, as well as possible spin-state/orbital ordering in phase 3 is analyzed. The general conclusions are made in Sec. V.

II. EXPERIMENT

A. Synthesis of the samples and their attestation

The TbBaCo\textsubscript{3}O\textsubscript{4+s} sample I was synthesized from a mixture of high-purity oxides and carbonates Tb\textsubscript{3}O\textsubscript{11}, BaCO\textsubscript{3}, and Co\textsubscript{2}O\textsubscript{4} in the stoichiometric proportion. After preliminary annealing at 900 °C, the pellets were thoroughly ground in an agate mortar. The synthesis was carried out in air at 1180 °C during 6 h with following cooling down to room temperature at a rate of 100 K/h. The sample has been checked using x-ray diffraction. The neutron diffraction experiment itself has given the final answer on the sample quality. Two different perovskitelike phases of nearly the same oxygen content, which have not been observed with x-rays because of poor resolution are found (see Sec. III).

An initial sample II of TbBaCo\textsubscript{3}O\textsubscript{4+s} was synthesized by the standard solid-state reaction using Tb\textsubscript{3}O\textsubscript{7}, BaCO\textsubscript{3}, and Co\textsubscript{2}O\textsubscript{4} of a minimum purity of 99.99%. The powders were mixed and calcinated at temperatures 1000–1200 °C during at least 100 h in air with several intermediate regrindings. Then the sample was oxidized under oxygen pressure of about 60 bar at 800 °C. The sample with the desired oxygen content (x\approx0.5) was prepared from the oxidized sample by annealing in oxygen flow during 20 h and cooling down slowly with the rate of 1 K/min to room temperature. Oxygen content was determined by iodometric titration as 5.52(1). Averaging with the neutron diffraction result 5.54(2) at T=308 K presented in Sec. III (Table III), we take for the oxygen content 5.53(1). As was observed during the treatment of the neutron diffraction patterns, the sample contained some impurities that gave weak unrecognized reflections. When calculating the integrated intensities of magnetic reflections, a comparison of differential diffraction patterns with those for the sample I was useful to get rid of the spurious effects due to admixture of erroneous phases.

B. Magnetic measurements

The dc magnetization has been measured on a Quantum Design PPMS system in the temperature range from 5 K to 350 K. The magnetization field dependence for both samples (inset to Fig. 2 and curve 2 in Fig. 4) shows clear evidence of the spontaneous magnetic moment in the narrow temperature range of about 250–290 K. The second weak maximum in Fig. 3 indicates a phase transition that occurs in sample II at T\approx180 K, with field dependence of magnetization (Fig. 4) being different below this maximum (curves 4, 5) and in between two maxima (curve 3).

C. Neutron diffraction experiments

Neutron diffraction experiments have been carried out on Swiss Spallation Neutron Source SINQ (Ref. 15) at Paul Scherrer Institute, Switzerland. Neutron diffraction patterns show clear evidence of the spontaneous magnetic moment in the narrow temperature range of about 250–290 K. The second weak maximum in Fig. 3 indicates a phase transition that occurs in sample II at T\approx180 K, with field dependence of magnetization (Fig. 4) being different below this maximum (curves 4, 5) and in between two maxima (curve 3).

FIG. 2. Temperature dependence of magnetization measured in the field 1 T for the sample I. Thin line shows contamination of Tb\textsuperscript{3+}. Field dependence in the maximum of magnetization is shown in the inset.

FIG. 3. Temperature dependence of magnetization measured in the field 0.1 T for sample II. In addition to the main maximum at 260 K, the second weak maximum can be noticed at 180 K.
Scherrer Institute. Two powder diffractometers have been used, HRPT,\textsuperscript{16} and DMC. The former is a powder diffractometer with the monochromator take-off angle of 120°, which provides very high resolution down to Δd/d ~ 10\textsuperscript{−3}. This instrument with the wavelength λ = 1.886 Å or λ = 1.494 Å has been used for the crystal structure refinement. The cold neutron powder diffractometer DMC with the wave length λ = 4.200 Å is very efficient in the magnetic structure investigations of TbBaCo\textsubscript{2}O\textsubscript{5.5}.

Our strategy was the following. First, the crystal structure was refined in the paramagnetic phase by the profile analysis\textsuperscript{17,18} on the basis of data from the HRPT diffractometer. Second, with this crystal structure the spin order was determined from the DMC data. Well resolved magnetic reflections on the differential diffraction patterns allowed finding the wave vector of magnetic structure. Using the procedure given in Ref. 19, the basis functions have been constructed for irreducible representations of the wave-vector group. Different models of magnetic structure obtained with these basis functions were checked using the integrated intensities of magnetic reflections. The data from two samples were combined, if it was desirable to improve statistics or to get rid of spurious reflections, which were different for each sample. Then the crystal structure has been refined again by means of the profile analysis of the HRPT data, with the magnetic parameters being fixed. Finally, the magnetic structure parameters have been refined once more with corrected atomic positions. This procedure of alternating refinement of crystal structure and magnetic ordering has occurred to be very efficient. In this way it has been discovered that the spin ordering at the Néel point is not consistent with the space group \textit{Pmmm}.

III. CRYSTAL AND MAGNETIC STRUCTURE

A. Crystal structure in the paramagnetic phase

The first attempt to fit the HRPT diffraction pattern from sample I measured in the paramagnetic phase (T = 302 K) has failed. The commonly used structure with the unit cell a\textsubscript{p} × 2a\textsubscript{p} × 2a\textsubscript{p}, described by the space group \textit{Pmmm} results in very poor values of the least squares residual χ\textsuperscript{2} = 155 and the profile reliability factor \(R_{wp} = 8.1\). The origin of this discrepancy becomes clear from a simple intensity comparison of two reflections, (0,1,0) and (0,0,1), which are well resolved when measured on the DMC diffractometer (Fig. 5). Expected intensities of these reflections for the phase \(a_p \times 2a_p \times 2a_p\) of TbBaCo\textsubscript{2}O\textsubscript{5.5} are shown by the grey bars. The experimental intensity of (0,1,0), which is about two times weaker, gives an idea that there is an essential admixture of a phase with the unit cell \(a_p \times a_p \times 2a_p\), since it has no reflection in this position. A superstructure diffuse peak at the \((1/3,0,0)\) angle indicates a partially disordered phase, probably, found in Ref. 12. This peak is well fitted by a Lorentzian with the width corresponding to the correlation length \(\xi = 62(6)\) Å, as shown in the inset of Fig. 5.

In spite of some traces of unrecognized erroneous phases [reflections marked as ‘??’], when using the FULLPROF program,\textsuperscript{17,18} we have made quite successfully a two-phase profile analysis of the diffraction pattern displayed in Fig. 6. The χ\textsuperscript{2} has been improved to χ\textsuperscript{2} = 14, and the profile reliability factor to \(R_{wp} = 2.4\%), which are reasonable values for the sample of this homogeneity. Two phases have the unit cells \(a_p \times 2a_p \times 2a_p\) and \(a_p \times a_p \times 2a_p\), shown in Figs. 1(a) and 1(b), respectively, with the space group \textit{Pmmm}. Corresponding to these phases, Bragg positions are indicated by the upper and the lower series of ticks below the profile. The difference between observed and calculated profiles is shown at the bottom. The phase fractions are found to be 68(1)% and 32(1)% respectively. The structure parameters are collected in Tables I and II.

FIG. 4. Isotherms of magnetization measured at some characteristic temperatures for sample II.

FIG. 5. Diffraction pattern from sample I measured on the DMC diffractometer at the same temperature as that in Fig. 6 below. Positions of the Bragg reflections \((h,k,l)\) for the phase \(a_p \times 2a_p \times 2a_p\), unrecognized reflections (???) and a superstructure peak \((1/3,0,0)\) are indicated by arrows. A fit of the \((1/3,0,0)\) peak by a Lorentzian is shown in the inset.

FIG. 6. Diffraction pattern from sample I above \(T_N\). The best fit by two phases, \(2a_p \times 2a_p \times 2a_p\) (\textit{Pmmm}) and \(a_p \times a_p \times 2a_p\) (\textit{Pmmm}).
Although occupancies of the apical oxygen sites show that the oxygen content of the phase $a_p \times a_p \times 2a_p$ is only 0.07 smaller than of the main phase $a_p \times 2a_p \times 2a_p$, the vacancies and the oxygen atoms in the former are not ordered along the $y$ axis, which would result in the alternating rows of octahedra and pyramids as in the latter. Similar structure was reported for a fast-cooled sample of TbBaCo$_2$O$_{5.4}$. The ions Tb$^{3+}$ and Ba$^{2+}$ were found to be partially ordered, with transition $T = 308$ K and $T = 302$ K from the two-phase neutron powder profile analysis in the frame of space group $Pmmm$ ($Z=2$) $[a_1 = 3.8698(1) \text{Å}, a_2 = 7.8167(1) \text{Å}, a_3 = 7.5179(1) \text{Å}]$. The phase fraction is 68(1)%.

### Table I

| Atom  | Position | $x/a_1$ | $y/a_2$ | $z/a_3$ | $B$  | $n$   |
|-------|----------|---------|---------|---------|------|------|
| Tb    | $2p$     | 0.5     | 0.2744(3)| 0.5     | 1.15(7)| 1    |
| Ba    | $2o$     | 0.5     | 0.2493(5)| 0       | 0.74(9)| 1    |
| CoPy  | $2q$     | 0       | 0       | 0.2590(9)| 0.12(5)| 1    |
| CoOc  | $2r$     | 0       | 0.5     | 0.2622(9)| 0.12(5)| 1    |
| O1    | $1a$     | 0       | 0       | 0       | 0.8(1)  | 0.97(1) |
| O1'   | $1c$     | 0       | 0       | 0.5     | 0      | 0.02(1) |
| O2    | $1e$     | 0       | 0.5     | 0       | 1.34(8) | 1.00(1) |
| O3    | $1g$     | 0       | 0.5     | 0.5     | 1.34(8) | 0.98(2) |
| O4    | $2s$     | 0.5     | 0       | 0.3100(5)| 1.45(5) | 1    |
| O5    | $2t$     | 0.5     | 0.5     | 0.2660(6)| 1.45(5) | 1    |
| O62   | $4u$     | 0       | 0.248(1)| 0.2960(3)| 1.31(5) | 1    |

### Table II

| Atom  | Position | $x/a_1$ | $y/a_2$ | $z/a_3$ | $B$  | $n$   |
|-------|----------|---------|---------|---------|------|------|
| Tb    | [Ba]     | 0.5     | 0.5     | 0.5     | 0.2(1) | 0.82(2)[0.18(2)] |
| Ba    | [Tb]     | 0.5     | 0.5     | 0       | 0.5(1) | 0.82(2)[0.18(2)] |
| Co    | $2q$     | 0       | 0       | 0.244(1)| 1.0(1)(2)| 1    |
| O1    | $1a$     | 0       | 0       | 0.6(1)  | 1.00(2)| 1    |
| O2    | $1c$     | 0       | 0       | 0.5     | 0.6(1) | 0.42(2)|
| O3    | $2r$     | 0       | 0.5     | 0.2935(8)| 0.6(1) | 1    |
| O4    | $2s$     | 0.5     | 0       | 0.3029(8)| 0.6(1) | 1    |

$^a_x = 14; R_{wp} = 2.4; R_{Bragg1} = 3.3; R_{Bragg2} = 2.9. [\text{Bragg1} \rightarrow (a_p \times a_p \times 2a_p); \text{Bragg2} \rightarrow (a_p \times a_p \times 2a_p)].$
Reflections Data for the magnetic and crystal structure refinement in this comes equal to 4\(k\) wave vector corresponding to this doubling is decreases to zero, and simultaneously reflections doubling of the magnetic unit cell along the 3, but the latter should vanish at this 2 due to a structural phase tran-

The lattice parameters, \(x\), and criteria of the refinement quality are: \(T=380\) K, \(a_1=3.8556(1)\) Å, \(a_2=7.8279(3)\) Å, \(a_3=7.5391(3)\) Å, \(x=0.54(2)\), \(\chi^2=11\); \(R_{wp}=5.2\); \(R_{Bragg}=7.4\); \(T=400\) K, \(a_1=3.8529(1)\) Å, \(a_2=7.8458(2)\) Å, \(a_3=7.5563(2)\) Å, \(x=0.54(2)\), \(\chi^2=4.3\); \(R_{wp}=4.0\); \(R_{Bragg}=6.6\).

| Atom   | Position | \(x/a_1\) | \(y/a_2\) | \(z/a_3\) | B  | n  | \(x/a_1\) | \(y/a_2\) | \(z/a_3\) | B  | n  |
|--------|----------|---------|---------|---------|----|----|---------|---------|---------|----|----|
| Tb     | 2\(p\)   | 0.5     | 0.2666(6) | 0.5     | 0.51(6) | 1  | 0.5     | 0.2678(4) | 0.5     | 0.82(4) | 1  |
| Ba     | 2\(o\)   | 0.5     | 0.2473(7) | 0       | 0.09(7) | 1  | 0.5     | 0.2480(5) | 0       | 0.24(5) | 1  |
| CoPy   | 2\(q\)   | 0       | 0       | 0.253(2) | 0.69(7) | 1  | 0       | 0       | 0.253(1) | 0.35(9) | 1  |
| CoOc   | 2\(r\)   | 0       | 0.5     | 0.254(2) | 0.69(7) | 1  | 0       | 0.5     | 0.255(1) | 1.4(1)  | 1  |
| O1     | 1\(a\)   | 0       | 0       | 0       | 1.2(1)  | 1.00(2) | 0       | 0.5     | 0       | 1.0(1) | 1.00(2) |
| O1’    | 1\(c\)   | 0       | 0       | 0.5     | 0       | 1.00(2) | 0.5     | 0       | 0       | 1.0(1) | 0.14(2) |
| O2     | 1\(e\)   | 0.5     | 0       | 0       | 0.8(1)  | 1.00(2) | 0.5     | 0       | 0       | 1.0(1) | 1.00(2) |
| O3     | 1\(g\)   | 0       | 0.5     | 0.5     | 3.2(2)  | 1.00(2) | 0.5     | 0       | 0.5     | 1.0(1) | 0.94(2) |
| O4     | 2\(s\)   | 0.5     | 0       | 0.3071(8) | 1.02(8) | 1  | 0.5     | 0       | 0.3092(6) | 1.50(4) | 1  |
| O5     | 2\(t\)   | 0.5     | 0.2679(8) | 1.45(9) | 1  | 0.5     | 0.2694(6) | 1.50(4) | 1  |
| O6     | 4\(u\)   | 0       | 0.2403(6) | 0.2965(5) | 1.02(6) | 1  | 0       | 0.2414(5) | 0.2960(3) | 1.29(5) | 1  |

At \(T_1=255\) K, intensity of the (1,1,2) reflection abruptly decreases to zero, and simultaneously reflections (0,0,1), (1,1,1) arise. This indicates an additional antiferromagnetic doubling of the magnetic unit cell along the \(a_1\) axis. The wave vector corresponding to this doubling is \(k_{2z}=b_1/2\). Data for the magnetic and crystal structure refinement in this phase, which we call as phase 2, have been obtained at 230 K.

A second transition to phase 3 occurs at \(T_2=170\) K, close to the weak peak of magnetization at \(T=180\) K (Fig. 3). Reflections (0,0,1) and (1,1,1) exhibit no visible change at this temperature, while reflection (1,1,2) appears again. Former two reflections exist if a spin direction reverses when being translated by \(a_1\), but the latter should vanish at this antitranslation. The discrepancy is removed, if the unit cell edge \(a_3\) of the crystallographic unit cell with \(a_3=2a_p\) becomes equal to \(4a_p\) below \(T_2\) due to a structural phase tran-

![FIG. 7. Diffraction patterns from sample II collected on DMC diffractometer with a temperature step of 10 K. Indices are given for the unit cell \(2a_p\times2a_p\times4a_p\).](image)

At \(T_2=170\) K, intensity of the (1,1,2) reflection abruptly decreases to zero, and simultaneously reflections (0,0,1), (1,1,1) arise. This indicates an additional antiferromagnetic doubling of the magnetic unit cell along the \(a_1\) axis. The wave vector corresponding to this doubling is \(k_{2z}=b_1/2\). Then the wave vector that describes magnetic order in the new phase is \(k_{1\alpha}=0\), and reflection (1,1,2) is allowed. Experimental data for this phase have been collected at \(T=100\) K.

### 1. Phase 1

Since the high-temperature phase 1 is of the main interest for understanding the nature of ferromagnetic moment, and its structure is important for deriving the magnetic order in two other phases, we pay more attention to the experimental data obtained at the magnetization maximum 260–265 K. First of all, knowing the wave vector \(k_{2\alpha}=b_1/2\) of magnetic ordering from the paramagnetic phase \((a_p\times2a_p\times2a_p)\) with the assumed space group \(G=D_{2h}\) of the wave vector \(k_{2\alpha}\). This means that one has to find the basis functions \(S^{G}_{hN}\) of irreducible representations of the group \(G_k\), where \(i,\nu,\lambda,\mu\) numerate atom, representation,
and element of the representation matrix, respectively. This procedure is described in detail in Ref. 19.

Two Co\(^{3+}\) ions in pyramidal coordination (Py1, Py2) occupy crystallographic position 2\(q:\{1-(0,0,0); 2-(0,0,-z)\}\), while the other couple in octahedral coordination (Oc1, Oc2) is situated in the position 2\(r:\{1-(0,1/2,0); 2-(0,1/2,-z)\}\).\(^{20}\) The coordinate \(z\) for every pair is indicated in Tables I and III as determined for samples I and II at \(T=302\) K and \(T=308\) K, respectively. The small group of the wave vector \(k_{20}=b_1/2\),

\[
G_k \in g_1, g_2, g_3, g_4, g_5, g_6, g_7, g_8.
\]

includes the symmetry elements \(g_1=\{h|\tau_0\}\), where \(h\) and \(\tau_0\) are, respectively, a rotational element at the unit cell origin and an accompanying translation. The numbering of \(g\) corresponds to handbook 13, which contains the matrices of \(h\). The rotational part of \(G_k\) is the same for all three phases. The magnetic representation for every pair of equivalent Co ions, a matrix \(D_{M}^{\tau}\) of dimensionality \(6 \times 6\), can be reduced by means of Eqs. (8.21) and (8.22) of Ref. 19 to 1D \((\lambda=\mu =1)\) irreducible representations \(\tau_v\) given in Table 32 (Ref. 13) as

\[
D_{M}^{\tau_v} = \tau_2 + \tau_3 + \tau_4 + \tau_5 + \tau_7 + \tau_8.
\]

Expression of \(D_{M}^{\tau_v}\) through \(\tau_v\) is the same for both pyramidal and octahedral sublattices as well as the basis functions, which are obtained by means of Eq. (9.15) (Ref. 19) and collected in Table IV as projections of the unit vectors \(S_i\) on the crystal axes. We shall call these modes

\[
f = \frac{1}{\sqrt{2}}(S_1 + S_2) \quad \text{and} \quad a = \frac{1}{\sqrt{2}}(S_1 - S_2).
\]

A very important conclusion should be made: The wave vector \(k_{20}=b_1/2\) means a pure antiferromagnetism along \(x, y,\) or \(z\), i.e., \(f_a,f_b,-f_a,\) or \(a_a,-a_a\), where \(a=x,y,z\). To obtain a spontaneous moment one should add a ferromagnetic spin component with \(k_{20}=0\). If this component is orthogonal to the antiferromagnetic one, it should be due to Dzyaloshinskii-Moriya spin canting, which is normally too weak (~10\(^{-2}\) at \(T=0\)) to explain \(M_0 \sim 10^{-1}\) in the very vicinity to \(T_N\).

The differential patterns \(I(T)-I(T>T_N)\) are presented in Fig. 9. When comparing the patterns (a) and (b) for the samples I and II, respectively, one may see a series of additional reflections in the former, probably from the phase \(2a_x \times 2a_x \times 2a_x\). Nevertheless, common for both samples magnetic reflections, when normalized, have equal intensities in the limits of a standard deviation. Therefore, we have combined them to obtain better statistics, since magnetic reflections are very weak just below the Néel point. In particular, very important are reflections (0,1,0), (0,0,2) and (0,2,0), (2,0,0) with \(k_{20}=0\) shown in Figs. 9(c) and 9(d), respectively. They allow us to obtain the ferromagnetic component \(M_0\), and, moreover, reflection (0,1,0) indicates that \(M_0\) arises in the part \(2a_x \times 2a_x \times 2a_x\) of the unit cell. To decrease the influence of the lattice spacing temperature change the intensity difference is taken for very close temperatures, both sides of \(T=255\) K. Even though the temperature shift is clearly seen for the reflection (0,0,2) because of a strong nuclear contamination. Approximately equal values of the negative and positive wings suggest that its intensity change is close to zero. On the contrary, a change of the (0,1,0) intensity is obvious. The nuclear contamination is small, and therefore the effect of temperature shift is negligible. The antiferromagnetic reflection (1,0,0) close to (0,1,0), is very weak to influence (0,1,0) intensity. [For the sake of easier comparison and discussion, the spin structures for all magnetic phases with calculated and experimental intensities are shown in Figs. 10(a)–10(c), 10(aa), 10(bb), and 10(cc), and the moment values are collected in Table VIII at the end of analysis for all

![FIG. 9. Differential diffraction patterns: (a) \(I(265\) K)–\(I(300\) K) sample I; (b) \(I(260\) K)–\(I(308\) K) sample II; (c), (d) \(I(250\) K)–\(I(265\) K) sample I. Miller indices are given for the unit cell \(2a_x \times 2a_x \times 2a_x\). The curve is a guide to the eye for (a), (b) and the best fit for (c), (d).](214407-7)
three phases.] The other statistically significant ferromagnetic reflection is (0,2,0), and we make a conclusion that a spontaneous moment contribution in diffraction pattern is directly observed.

With the basis functions of irreducible representations for the symmetry group of the wave vector $k_{320}=b_1/2$ collected in Table IV the integrated intensities of 13 magnetic reflections with the indices given in Figs. 9(b)–9(d) have been calculated for the unit cell $2a_p \times 2a_p \times 4a_p$ as

$$I(Q) \propto |F(Q)|^2 - |eF(Q)|^2$$

and averaged over the orthorhombic twins. Here $F(Q)$ is the magnetic structure amplitude, $Q$ is the neutron transferred momentum, and $e=Q/Q$. The experimental data from the differential patterns measured on the DMC diffractometer have been used for the spin structure refinement. The integrated intensities have been obtained by the fit of a definite angular range by the sum of Gaussians. Due to the temperature change of the lattice parameters, a differential peak, like angular range by the sum of Gaussians. Due to the temperature change of the lattice parameters, a differential peak, like angular range by the sum of Gaussians.

The best result of all possible combinations including at least one $f_{\alpha}$ function is found for the collinear models containing $f_{\alpha}$ either in pyramids or in octahedra with a reasonable spontaneous moment $M_\alpha=0.3(2) \mu_B$/Co, but with very bad fit goodness of $\chi^2=92$. The best fit with $\chi^2=19$ has been achieved with a combination of the antiferromagnetic modes $M_{py}\delta \alpha, M_{py3}\delta \alpha, M_{Oc5}\delta \alpha, M_{Oc7}\delta \alpha, (M_{py1}=M_{py3}, M_{Oc5}$

![FIG. 10. Ordering of the Co$^{3+}$ moments $M_\alpha$ in three phases of TbBaCo$_2$O$_{5.53}$: (a) ferrimagnetic phase 1 at $T=260$ K; (b) antiferromagnetic phase 2 at $T=230$ K; (c) antiferromagnetic phase 3 at $T=100$ K. The circles shadowing and the arrows lengths reflect the different moment value. The vectors $a_1, a_2, a_3$ define the chemical unit cell for each phase. Calculated (grey bars) and experimental intensities (aa), (bb), (cc) correspond to the structures (a), (b), (c). For experimental values the following symbols are used: (aa) $\bigcirc-2n+1, \bullet-2n; (bb) \triangle -h=2n+1, \square -h=2n; (cc) \bigcirc-2n+1, l=2n, \triangle -h=2n+1, l=2n+1, \square -h=2n, l=2n+1$. Indexing is always in the unit cell (c) $-a_3=4a_p$.](image-url)
TABLE V. Atomic coordinates \( x/a_1, y/a_2, z/a_3 \), isotropic temperature factors \( B \), and position occupancies \( n \) determined for TbBaCoO\(_{4.4} \) (sample II) at \( T=260 \) K from the neutron powder profile analysis, using orthorhombic space group \( Pmma \) (\( Z=4 \)). The lattice parameters, \( x \), and criteria of the refinement quality are:

\[
\begin{align*}
a_1 &= 7.7382(2) \text{ Å}, \\
a_2 &= 7.8024(2) \text{ Å}, \\
a_3 &= 7.5247(2) \text{ Å}; \\
x &= 0.53(2); \\
\chi^2 &= 3.8; \\
R_{wp} &= 3.7; \\
R_{Bragg} &= 4.8.
\end{align*}
\]

| Atom     | Position | \( x/a_1 \) | \( y/a_2 \) | \( z/a_3 \) | \( B \) | \( n \) |
|----------|----------|-------------|-------------|-------------|-------|--------|
| Tb       | 4h       | 0           | 0.2739(3)   | 0.5         | 0.63(4) | 1      |
| Ba       | 4g       | 0           | 0.2478(5)   | 0           | −0.17(5) | 1      |
| CoPy1    | 2e       | 0.25        | 0           | 0.247(3)    | 0.3(1)   | 1      |
| CoPy2    | 2e       | 0.25        | 0           | 0.736(3)    | 0.3(1)   | 1      |
| CoOc1    | 2f       | 0.25        | 0.5         | 0.252(5)    | 1.1(1)   | 1      |
| CoOc2    | 2f       | 0.25        | 0.5         | 0.746(5)    | 1.1(1)   | 1      |
| O1       | 2e       | 0.25        | 0           | 0.001(3)    | 0.5(1)   | 0.94(2) |
| O1'      | 2e       | 0.25        | 0           | 0.5         | 0       | 0.13(2) |
| O2       | 2f       | 0.25        | 0.5         | −0.003(3)   | 1.74(8)  | 1.02(2) |
| O3       | 2f       | 0.25        | 0.5         | 0.496(3)    | 1.74(8)  | 0.97(2) |
| O5       | 4f       | 0.003(2)    | 0           | 0.3026(7)   | 1.39(5)  | 1      |
| O61      | 4k       | 0.25        | 0.2526(6)   | 0.2887(9)   | 0.83(6)  | 1      |
| O62      | 4k       | 0.25        | 0.2314(6)   | 0.6943(9)   | 0.83(6)  | 1      |

\( =M_{Oc}(\gamma) \). Certainly, the ferromagnetic reflections (0,1,0) and (0,2,0) have zero intensities in this case, and \( M_{Oc}=0 \).

The results obtained in the frame of the space group \( G=D_{2h}^5-Pmmm \) with both unit cells, \( a_p \times 2a_p \times 2a_p \) \( (k_{20} = b_1/2) \) and \( 2a_p \times 2a_p \times 2a_p \) \( (k_{19}=0) \), are not consistent with the experiment. The only thing that we know exactly is that the \( a_1 \) doubling should be due to a structural phase transition that would provide two pairs of nonequivalent positions in both pyramidal and octahedral sublattices. Since refinement for the doubled unit cell in the frame of the space group \( Pmmm \) has failed, we chose the highest subgroup of the space group \( Pmmm \) that fits a structural transition with \( k_{20} \) and with small distortions of the \( Pmmm \) phase, which is \( D_{2h}^5-Pmma \).\(^{21}\) The difference with the \( Pmmm \) group is in location of equivalent pairs of Co ions in the unit cell \( 2a_p \times 2a_p \times 2a_p \). The ions with coordinates \( z \) and \( −z \) are not located any more one above the other, but are shifted by \( x =1/2 \). Four Co ions in pyramidal sublattice are distributed among \( 2e \) positions \([1−(1/4,0,z);4−(3/4,0,−z)]\) and \([2−(1/4,0,z);3−(1/4,0,−z)]\), where \( z_{2,3}=−z_{1,4} \). Octahedral Co ions occupy, respectively, positions \( 2f[5−(1/4,1/2,z);8−(3/4,1/2,−z)] \) and \([6−(1/4,1/2,z);7−(3/4,1/2,−z)]\), where \( z_{6,7}=−z_{5,8} \). (The origin is shifted by \( x=−1/4 \) from that for the \( Pmmm \) setting.\(^{20}\)) Visually the difference in ordering of equivalent Co positions in a (0,1,0) plane among either pyramidal or octahedral sites is the following: they are ordered chessboard like, but are not built into the alternating rows along [0,0,1] as in the group \( Pmmm \).

For the space group \( G=D_{2h}^5-Pmma \), the magnetic representation \( D_{2h}^{19} \) of the group \( G_{k_{19}} \) includes irreducible representations indicated by Eq. (2), and the basis functions given in Table IV correspond now to the pairs of equivalent Co ions 1–4, 2–3 in pyramids and 5–8, 6–7 in octahedra [Fig. 10(a)]. Again a spontaneous moment cannot be provided without \( f_a \) modes, and the best fit is obtained with the \( f_x \) basis function for all 4 couples of equivalent atoms in both pyramidal and octahedral sites. The value of \( \chi^2=1.7 \) gives confidence that our hypothesis reflects the reality. Spin structure is described in Fig. 10(a), with the results of intensity calculations being shown in Fig. 10(aa). The moment values for all 16 Co\(^{3+} \) ions in the unit cell \( 2a_p \times 2a_p \times 2a_p \) are collected in Table VIII. The spin structure refinement has shown that crystallographic space group in the high temperature magnetic phase 1 is \( Pmma \), instead of commonly used \( Pmmm \). Actually the results of the spin structure refinement have been obtained in two stages. First, we have determined the spin structure in the frame of \( Pmma \) with coordinates \( z \) of Co ions at \( T=308 \) K for the space group \( Pmmm \) from Table III. Second, the spin structure parameters thus obtained have been used to fit in the frame of unit cell \( 2a_p \times 2a_p \times 2a_p \) and space group \( Pmma \) the diffraction patterns from both samples measured on the HRPT diffractometer at \( T=260 \) K. Then new coordinates \( z \) have been used in the spin structure refinement.

The crystal structure parameters for sample II are collected in Table V. When comparing atomic coordinates with those from Table III one can see that the difference is not essential for Co\(^{3+} \) ions in both coordinations, while there are noticeable changes for oxygen positions. Although the fit goodness for the space group \( Pmma \) \( (\chi^2=3.8; \ R_{wp}=3.7) \) is better than for \( Pmmm \) \( (\chi^2=11; \ R_{wp}=5.2) \), it is obvious that a refinement of the crystal structure itself would not allow distinguishing two models, while for the spin structure the difference of the refinement quality is crucial. It is worthwhile to remind that a transition from \( Pmmm \) to \( Pmma \) symmetry was observed directly by appearance of superstructure reflections in x-ray diffraction\(^{14} \) for GdBaCoO\(_{5.5} \) and DyBaCoO\(_{5.5} \), the neighbors of TbBaCoO\(_{5.5} \) in a series of isomorphic rare-earth materials.
2. Phase 2

This phase appears due to a change of the wave vector to \( \mathbf{k}_{22} = \mathbf{b}_3 / 2 = (2 \pi / a_3) [0, 0, 1/2] \) in the frame of the same space group \( Pmna \). This means that the direction of each spin is reversed when being translated by \( a_3 \). \( D_{19} \) is expressed through \( \tau_n \) by (2), and the basis functions are given in Table IV. The spin structure [Fig. 10(b)] and the moment values given in Table VIII have been obtained using these functions and experimental data collected at \( T = 230 \) K.

3. Phase 3

As mentioned above, magnetic reflections with \( l = 2n + 1 \), like \((0,0,1)\) and \((1,1,1)\), arise due to the antitranslation \( a_3 \), which prohibits reflections with \( l = 2n \), like \((1,1,2)\). For removing this discrepancy the phase transition at \( T_3 \) should be a structural one with the wave vector \( \mathbf{k}_{22} = \mathbf{b}_3 / 2 \). The highest subgroup that fits the structural transition with \( \mathbf{k}_{22} \) and with small distortions of the \( Pmna \) phase is \( D_{19}^{b} \)-\( Pcca \).23 The magnetic wave vector for the new chemical unit cell \( 2a_{p} \times 2a_{p} \times 4a_{p} \) is \( \mathbf{k}_{19} = 0 \). Cobalt ions occupy two nonequivalent fourfold sites (Py1 and Py2) \((4d: 1-(1/4,0, z); 2-(3/4,0, -z); 3-(1/4,0,1/2+z); 4-(3/4,0,1/2-z) \) in pyramidal coordination as well as two nonequivalent fourfold sites (Oc1 and Oc2) \(4e: 1-(1/4,1/2,z); 2-(3/4,1/2,-z); 3-(1/4,1/2,1/2 +z); 4-(3/4,1/2,1/2-z) \) in octahedral coordination. The correspondence between these numbers and those indicated in Fig. 10 is given in Table VI. Eight 1D irreducible representations \( \tau_n \) enter the magnetic representation of dimensionality \( 12 \times 12 \) as

\[
D_{19}^{m} = \tau_1 + 2\tau_2 + \tau_3 + 2\tau_4 + 2\tau_5 + \tau_6 + 2\tau_7 + \tau_8.
\]

The basis functions are collected in Table VI. Usually four combinations of \( S_i \) are called as

\[
F = \frac{1}{\sqrt{2}}(S_1 + S_2 + S_3 + S_4),
\]

\[
G = \frac{1}{\sqrt{2}}(S_1 - S_2 + S_3 - S_4),
\]

\[
A = \frac{1}{\sqrt{2}}(S_1 - S_2 - S_3 + S_4),
\]

\[
C = \frac{1}{\sqrt{2}}(S_1 + S_2 - S_3 - S_4).
\]

The refinement was made again in two steps, like for the phase 1. At the beginning, the unit cell \( 2a_{p} \times 2a_{p} \times 4a_{p} \) was built of two cells \( 2a_{p} \times 2a_{p} \times 2a_{p} \) using the \( Pmna \) space group and the structural parameters from Table V for each one. The spin structure was found from the combinations of basis functions \( M_{Py1} F_s - M_{Py2} F_s \) and \( M_{Oc1} A_3 - M_{Oc2} A_3 \). With this spin order, the structural parameters have been obtained by the profile refinement on the HRPT data collected at \( T = 100 \) K. The results are given in Table VII. The difference with original atomic coordinates is not sufficient to make a conclusion on the phase transition without the arguments on magnetic structure. This structure is described in Fig. 10(c), the final fit is shown in Fig. 10(cc), and the moment values are given in Table VIII.

| \( \nu \) | \( m \to \) | 1 | 2 |
|---|---|---|---|
| 1 | 2 | 4 | 1 2 3 4 |
| Py1 | 1 | 12 | 4 | 1 12 9 4 |
| Py2 | 2 | 11 | 10 | 3 2 11 10 3 |
| Oc1 | 5 | 16 | 13 | 8 5 16 13 8 |
| Oc2 | 6 | 15 | 14 | 7 6 15 14 7 |

Table VI. Basis functions \( S_{19}^{m} \) of irreducible representations \( \tau_{19} \) for the pyramidal and octahedral sublattices of the phase 3.

IV. DISCUSSION

Spin structures for all magnetic phases are described in Fig. 10 together with the results of intensity calculations. The experimental (symbols) and the calculated (grey bars) intensities corresponding to the best fit are shown in Figs. 10(aa), 10(bb), and 10(cc) below each model. A number of other reasonable models composed of the basis functions of irreducible representations of the groups \( G_{19} \in Pmna \) (phase 1), \( G_{22} \in Pmna \) (phase 2), and \( G_{19} \in Pcca \) (phase 3) have been tested, but with the residual squares \( \chi^2 \) > 10, which means that these models are improbable in comparison with those described in Fig. 10. The models of spin order suggested before have been also checked with the following
TABLE VII. Atomic coordinates \(x/a_1, y/a_2, z/a_3\), isotropic temperature factors \(B\), and occupancies \(n\) of crystallographic positions determined for TbBaCo\(_2\)O\(_5\) (sample II) at \(T=100\) K from the neutron powder profile analysis. Orthorhombic space group is \(Pcc\) (\(Z=8\)), and the lattice parameters are \(a_1=7.7359(2)\) Å, \(a_2=7.7900(2)\) Å, \(a_3=15.0263(5)\) Å. The refinement quality is characterized by \(\chi^2=5.6; R_{wp}=4.1; R_{Bragg}=6.7\).

| Atom   | Position | \(x/a_1\) | \(y/a_2\) | \(z/a_3\) | \(B\) | \(n\) |
|--------|----------|-------|--------|--------|------|------|
| Tb1    | 4c       | 0     | 0.271(1) | 0.25   | 0.70(5) | 1    |
| Tb2    | 4c       | 0     | 0.723(1) | 0.25   | 0.70(5) | 1    |
| Ba     | 8f       | 0.005(3) | 0.2502(6) | -0.0032(6) | -0.33(8) | 1    |
| CoPy1  | 4d       | 0.25  | 0       | 0.135(1) | 0.01(1) | 1    |
| CoPy2  | 4d       | 0.25  | 0       | 0.376(2) | 0.01(1) | 1    |
| CoOc1  | 4e       | 0.25  | 0.5     | 0.125(2) | 1.4(2) | 1    |
| CoOc2  | 4e       | 0.25  | 0.5     | 0.376(3) | 1.4(2) | 1    |
| O1     | 4d       | 0.25  | 0       | 0.000(1) | 0.16(8) | 0.94 |
| O1'    | 4d       | 0.25  | 0       | 0.2500   | 0       | 0.13 |
| O2     | 4e       | 0.25  | 0.5     | 0.001(2) | 1.9(1) | 1.02 |
| O3     | 4e       | 0.25  | 0.5     | 0.252(2) | 1.9(1) | 0.97 |
| O4     | 8f       | -0.003(2) | 0.009(2) | 0.1498(4) | 1.06(7) | 1    |
| O5     | 8f       | 0.004(2) | 0.486(1) | 0.1338(4) | 1.06(7) | 1    |
| O61    | 8f       | 0.256(3) | 0.2319(8) | 0.1552(5) | 0.74(7) | 1    |
| O62    | 8f       | 0.252(2) | 0.2538(8) | 0.8555(5) | 0.74(7) | 1    |

results, which unambiguously evidence that they do not fit the crystal structure shown in Fig. 1(a): Fauth et al.\(^3\) - \(\chi^2=20\); Soda et al.\( ^5\) - \(\chi^2=89\). Taskin et al.\( ^7\) - No reflections due to suggested unit cell doubling along the \(y\) axis have been observed.

The first objective of this work was to study the spin order independently on a sample. Two samples prepared by different technologies exhibit magnetic diffraction patterns, which can be interpreted using completely different magnetic structures. It is shown that sample I consists of two phases with very close oxygen content, but not the same degree of its ordering among the apical positions. This leads to different crystal structures described in Fig. 1. Magnetic diffraction pattern from this sample is nothing more, but a sum of two patterns due to magnetic ordering in two crystallographic phases. As the unit cell parameters have always a common multiple, the parameter \(a_p\) of the pseudocubic perovskite cell, one may easily take additional magnetic reflections for those of the main phase. A wrong magnetic structure is suggested as a result. This may even happen when studying a single crystal, as the phase separation depends on the degree of oxygen ordering.

In our case, sample II that has been annealed in the oxygen flow has one double perovskite phase \(a_p\times2a_p\times2a_p\) at 400 K [Fig. 1(a)] with only a small part of vacant sites in pyramids occupied by oxygen (see Table III). Some unrecognized weak reflections have been observed, but they do not change essentially the differential diffraction patterns. The perfection of oxygen ordering, although not ideal, is manifested in both magnetic and neutron diffraction measurements showing three phase transitions at about 290 K, 255 K, and 170 K. The differential diffraction pattern \(I(265)\) - \(I(300)\) contains only one type of magnetic reflections corresponding to the \(a_1=2a_p\), with the cell doubling being a result of the structural phase transition from \(Pmmn\) to \(Pmma\) symmetry above the temperature of magnetic ordering \(T_N=290\) K. With this crystallographic unit cell the wave vector of spin structure in the high-temperature magnetic phase is \(k_{19}=0\). Consequently, additional magnetic reflections observed for the sample I at 265 K and shown in Fig. 9(a) arise due to magnetic ordering in the erroneous phase \(a_p\times a_p\times2a_p\) [Fig. 1(b)]. Actually, the quality of the main phase \(a_p\times2a_p\times2a_p(Pmmn)\) in the sample I is as good as in the sample II (compare Tables I and III). Although there is no second maximum observed at about 170 K on the magnetization temperature dependence (Fig. 2), the intensity behavior of the magnetic reflection (1,1,2) is similar to that shown in Fig. 8 for sample II. We should be reminded that in Ref. 5 this reflection appeared at \(T_N=275\) K, went through a flat maximum at about 230 K, and gradually fell with the further temperature decrease. The spontaneous moment was ignored. The reflection (0,0,1), as indexed in the cell \(2a_p\times2a_p\times4a_p\), appeared at \(T=230\) K, which was considered as the point of spin state ordering in the octahedral sites.

As discovered in our experiment, the moments in all three phases are collinear along the [1,0,0] axis. The difference is in their values and in the sequence of the signs. Only in phase 1 every moment has six nearest neighbors with the opposite sign, i.e., so called \(G\)-structure is realized, although with different moment values. Except phase 3, both sublattices are composed of the same basis function \(f_\gamma\) of irreducible representation \(\tau_1\) shown in Table IV. The difference between the phases 1 (260 K) and 2 (230 K) is in the mutual orientation of the pairs 1, 4 and 2, 3, \((f_1,-f_3)\) and \((f_1,f_3)\), respectively. The moment values obtained as a result of the best fit are collected in Table VIII for all 16 Co\(^{3+}\) ions under the numbers \(N=1-4, 9-12\) and \(N=5-8, 13-16\) for the Py1, Py2 and Oc1, Oc2 sites, respectively, in accordance with Fig.
10. As can be concluded by comparing Table VI and VIII, magnetic structure of the pyramidal sublattice in the phase 3 is given by $F_x, -F_x$ and belongs to irreducible representation $\tau_{72}$, while for the octahedral one it is given by $A_2, -A_2$ of the representation $\tau_{22}$. We should point out that the moments in the limits of one sublattice are transformed according to a single irreducible representation.

The weak ferromagnetism of Dzyaloshinskii-Moriya-type suggested in a number of publications,22–24 is forbidden in phase 1 by symmetry even with the wave vector $k_{\parallel} = 0$. It needs at least two basis functions, one of which is ferromagnetic, to be mixed in one irreducible representation. Eq. (2), which is also valid for $k_{\parallel} = 0$, shows that this is not the case. As follows from Table VIII, the spontaneous moment is a result of ferrimagnetism, i.e., antiparallel spin ordering in two nonequivalent pyramidal positions. (Very weak moment may also result from the octahedral sites.) The spontaneous moment value that is obtained from the neutron diffraction data at $T = 260–265$ K is $M_{\parallel} = 0.60(6) \mu_B$ per one Co$^{3+}$ ion in the pyramidal sublattice, or $M_{\parallel} = 0.30(3) \mu_B$ per a Co$^{3+}$ ion in general. The moment $M_{\parallel}$ is parallel to the [1,0,0] direction. Unfortunately, we cannot compare this value either with $M_{\parallel}$ = 0.186 $\mu_B$ (Fig. 2) or with $M_{\parallel}$ = 0.085 $\mu_B$ (Fig. 3) measured on the polycrystalline samples I and II, respectively. Apparently, a proper value is $M_{\parallel}$ = 0.35 $\mu_B$ that has been obtained7 by extrapolation to zero field of magnetization measured along the [1,0,0] axis on a detwinned single crystal of GdBaCo$_2$O$_{5.5}$.

One may assume that a complicated character of the isothersms in the phases 2 and 3 (Fig. 4) is a consequence of different spin state in both pyramidal and octahedral sublattices, which may result in quite different exchange parameters. The superexchange between two pyramids with a vacancy in between should be very weak. Then a spin-flip transition may occur in the field of a few tesla, in spite of the high Ising-type anisotropy, as found for GdBaCo$_2$O$_{5.5}$ in Ref. 7.214407-12

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one may expect to be almost spherically symmetric, are de-
phase 2. The basis function of irreducible representations of the group \(G_\alpha\) has been constructed for each phase. It is shown that the spontaneous moment in the phase 1 cannot be due to the Dzyaloshinskii-Moriya spin canting, which is forbidden by symmetry. A spontaneous moment \(M_0 = 0.30(3) \mu_B/Co\) is found to be due to ferrimagnetism, i.e., antiparallel order of the spins in two nonequivalent pyramidal sites.

The weak antiferromagnetism, i.e., hidden spin canting due to Dzyaloshinskii-Moriya interaction is allowed in both octahedral and pyramidal sublattices in the phase 3.

The moment values and the ion-ligand distances determined from the neutron diffraction experiment indicate possible spin-state/orbital ordering at all temperatures. The experiments on single crystals would allow determination of the orbital ordering at all temperatures.

We suppose that all these results, being reproducible for two different samples, one of which contains considerable amount of erroneous phase, reflect the actual spin/spin-state/orbital ordering in TbBaCo\(_2\)O\(_{5.5}\).

When resubmitting the manuscript, we have learned that no magnetic order, or “poor long-range magnetic order” exists in NdBaCo\(_2\)O\(_{5.5}\), while a long-range spin order has been found in this material below \(T_C \approx 170\) K in Ref. 30.

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