Non-collinear magnetic structures of TbCoO$_3$ and DyCoO$_3$

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The orthoperovskites TbCoO$_3$ and DyCoO$_3$ with Co$^{3+}$ in a non-magnetic low-spin state have been investigated by neutron diffraction down to 0.25 K. Magnetic ordering is evidenced below $T_N = 3.3$ K and 3.6 K, respectively, and the ordered arrangements are of canted type, $A_g G_u$ for TbCoO$_3$ and $G_g A_g$ for DyCoO$_3$ in Bertaut’s notation. The experiments are confronted with the first-principle calculations of the crystal field and magnetism of Tb$^{3+}$ and Dy$^{3+}$ ions, located in the $Pbnm$ structure on sites of $C_1$ point symmetry. Both these ions exhibit an Ising behavior, which originates in the lowest energy levels, in particular in accidental doublet of non-Kramers Tb$^{3+}$ ($4f^8$ configuration) and in ground Kramers doublet of Dy$^{3+}$ ($4f^9$) and it is the actual reason for the non-collinear AFM structures. Very good agreement between the experiment and theory is found. For comparison, calculations of the crystal field and magnetism for other systems with Kramers ions, NdCoO$_3$ and SmCoO$_3$, are also included.

PACS numbers:
Keywords:

I. INTRODUCTION

The perovskite cobaltites of LaCoO$_3$ type are systems with closeness in energy of different local state of the octahedrally coordinated cobalt ions. The ground state is generally based on non-magnetic low spin state of Co$^{3+}$ (LS, $S = 0, t^6_2 0^6_0$), and the paramagnetic high spin Co$^{3+}$ (HS, $S = 2, t^4_2 c^2_2$) species are populated by thermal excitation, which process becomes observable for LaCoO$_3$ above $\sim 40$ K and achieves the highest rate at $T_{magn} = 70$ K as documented by a maximum of the specific heat excess and anomalous expansion. The resulting non-uniform phase is characterized by HS/LS nearest neighbor correlations [1,2]. A further change is observed at about 530 K where the correlations are melted by thermal agitation, which is accompanied with a drop of electrical resistivity reminding the insulator-metal transition. In related systems with smaller rare-earth or yttrium ions, the magnetic transition shifts to higher temperatures and finally merges with the electrical transition, in particular for TbCoO$_3$ and DyCoO$_3$ at $T_{magn} = 735$ K and 740 K, respectively [3]. Such increased stability of LS Co$^{3+}$ means that the low-temperature magnetic properties are governed by Tb$^{3+}$ and Dy$^{3+}$ local moments and depend on the crystal field splitting of respective $4f^8$ and $4f^9$ levels, as well as on the rare-earth intersite interactions.

Early studies have shown that TbCoO$_3$ and DyCoO$_3$ undergo a non-collinear antiferromagnetic (AFM) ordering below $T_N = 3.3$ K and 3.6 K due to interactions that are for the most part of a classical dipole-dipole nature [4,5]. The present study revisits both systems. The crystal and magnetic structures are refined based on the high-resolution powder neutron diffraction, and the electronic levels of rare-earth ions are determined together with their magnetic characteristics, using a novel ab-initio approach. It appears that the observed magnetic arrangements reflect the Ising nature of rare-earths moments associated with the lowest energy levels, namely the ground Kramers doublet of Dy$^{3+}$ and accidental doublet of non-Kramers Tb$^{3+}$.

II. EXPERIMENT AND CALCULATIONS

Samples TbCoO$_3$ and DyCoO$_3$ were prepared by a solid state reaction from stoichiometric amounts of Co$_2$O$_3$ and respective oxides Tb$_2$O$_3$ and Dy$_2$O$_3$. The precursor powders were mixed, pressed in the form of pellets and sintered at 1200°C for 100 hours under air. The product was checked for phase purity and its structural and physical properties were extensively probed. Both compounds were identified as distorted perovskite structure of the orthorhombic $Pbnm$ symmetry.

The powder neutron diffraction was performed on diffractometer Hb2a at Oak Ridge National Laboratory. The scans were recorded at selected temperatures between the 0.25 and 150 K. Two crystal monochromators (Ge113 and Ge115) were used, providing neutron wavelengths $\lambda = 2.408$ Å and 1.537 Å, respectively. Data were collected between $8^\circ$ and $126^\circ$ of $2\theta$ with the step of 0.08°. To overcome the problem with rather high absorption of dysprosium, the neutrons path length through the DyCoO$_3$ sample was minimized by use of an annular container, where the powder was placed between two concentric aluminium cylinders. Structural refinements were done by Rietveld profile analysis using program FULLPROF (Version 5.30-Mar2012-ILL JRC).

The determination of the Tb$^{3+}$ and Dy$^{3+}$ electronic structure was performed in two steps. First, the crystal field parameters were calculated using a novel method based on the first-principles band structure and Wan-
The eigenenergies differ by only 0.025 meV, representing a quasi-doublet. This specific kind of accidental degeneracy has important consequences. Firstly, a relatively modest magnetic field of external or molecular nature will mix the eigenstates into a form of two pseudospins with the main weight of \{6, +6\} and \{6, –6\} ionic states, respectively. This results in large magnetic moment of Tb\(^{3+}\) ions of about 8.4 \(\mu_B\). Secondly, these moments have essentially an Ising-like character, which is a source of large local anisotropy.

In the case of Dy\(^{3+}\) in electronic configuration \(4f^9\), the lowest lying free-ion term is \(^7H_{15/2}\) (\(L = 5, S = 5/2, J = 15/2\)), and it is split by the low-symmetry crystal field to 8 Kramers doublets. The ground doublet is spanned by two pseudospins with dominant contribution of \(15/2, +15/2\) and \(15/2, -15/2\) ionic states, pointing also to the Ising character.

The results of present first-principle approach are summarized in Appendix, where the calculated single-electron CFP for non-Kramers Tb\(^{3+}\) and Kramers Dy\(^{3+}\) are displayed including two other ions possessing Kramers degeneracy, Nd\(^{3+}\) (\(4f^8\)) and Sm\(^{3+}\) (\(4f^6\)) (see Table III). Using these parameters in the 'lanthanide' program, the splitting of \(4f^n\) levels for each rare-earth ion is determined. It is seen below in Table VII that the two lowest singlets for Tb\(^{3+}\) in TbCoO\(_3\) are separated in energy by only 0.002 meV. Next two singlets are situated at much larger energy, 22.9 and 23.1 meV. For Dy\(^{3+}\) all the states are true doublets and the first excited doublet is situated at energy of 29.8 meV above the ground doublet. Similar separation between the ground and excited doublet is found for Sm\(^{3+}\), 29.6 meV, while a somewhat lower separation 13.2 meV is obtained for Nd\(^{3+}\) (see also [7]).

The application of external magnetic field brings two effects on the rare-earth electronic levels (see e.g. [7]). One is a linear splitting of the doublets that defines the relevant magnetic moments and represents Zeeman energy. Except very low fields, the splitting of the Tb\(^{3+}\) pseudodoublet is also linear, as illustrated for several orientations of applied field in upper panel of Fig. 1 . The corresponding g-factors are strongly anisotropic, they are in fact of Ising character with principal components \(g_x = 17.78\), \(g_y \sim 0\), \(g_z \sim 0\), where the local z-axis is defined by symmetry along the perovskite c axis and the Ising x-axis in c-plane makes an angle \(\alpha_g = \pm 37.1^\circ\) with the orthorhombic a axis. (Here \(\pm\) refers to two inequivalent rare-earth sites in the structure.)

An analogous calculation for the ground doublet of Dy\(^{3+}\) (see lower panel of Fig. 1) gives principal components \(g_x = 19.44\), \(g_y \sim 0\), \(g_z \sim 0\) and orientation of the Ising axis in c-plane under the angle \(\alpha_g = \pm 64.0^\circ\) to the a-axis.

The g-factors for Sm\(^{3+}\) and Nd\(^{3+}\) are much less anisotropic with principal in-plane components \(g_x = 0.703\), \(g_y = 0.588\), out-of-plane component \(g_z = 0.322\) and orientation of the x-axis under the angle \(\alpha_g = \pm 33.2^\circ\) for SmCoO\(_3\). The respective values for NdCoO\(_3\) are \(g_x = 2.818\), \(g_y = 1.228\), \(g_z = 3.015\) and angle \(\alpha_g = \pm 62.3^\circ\).
TABLE I: The crystallographic data summary for TbCoO$_3$ and DyCoO$_3$ at selected temperatures. Space group $Pbnm$.

| T (K) | TbCoO$_3$ | DyCoO$_3$ |
|-------|------------|------------|
|       | 0.25  | 5.5  | 150 | 0.25  | 5.5  | 150 |
| a (Å) | 5.2034(3) | 5.2034(3) | 5.1995(2) | 5.1644(3) | 5.1650(3) | 5.1655(3) |
| b (Å) | 5.3890(3) | 5.3898(3) | 5.3945(2) | 5.4165(3) | 5.4161(3) | 5.4143(4) |
| c (Å) | 7.4050(4) | 7.4052(4) | 7.4102(3) | 7.3806(4) | 7.3813(4) | 7.3866(5) |
| V (Å$^3$) | 207.64(2) | 207.68(2) | 207.84(2) | 206.46(2) | 206.48(2) | 206.59(2) |

Selected bond distances and angles.

| Co-O1 (Å) | ×2 | 1.916(2) | 1.916(1) | 1.917(1) | 1.904(3) | 1.912(2) | 1.911(2) |
| Co-O2 (Å) | ×2 | 1.935(4) | 1.935(3) | 1.932(2) | 1.932(8) | 1.945(6) | 1.946(6) |
| Co-O2 (Å) | ×2 | 1.938(4) | 1.942(3) | 1.942(2) | 1.979(8) | 1.965(6) | 1.964(6) |
| Co-O1-Co(°) | ×1 | 150.0(4) | 150.1(3) | 150.1(2) | 151.5(8) | 149.6(6) | 150.1(6) |
| Co-O2-Co(°) | ×2 | 150.5(4) | 150.1(3) | 150.5(2) | 146.2(8) | 146.3(6) | 146.2(6) |

The neutron diffraction data at the lowest temperature ($T = 0.25$ K) and above $T_N$ ($T = 5.5$ K) are displayed in Fig. 2. Presence of AFM ordering is manifested in appearance of magnetic peaks below $T_N$ at positions $hkl$ with $h + k = 2n + 1$, in particular 100+010 and 101+011. These peaks are indicative for the A- and G-types of AFM arrangement in the sample, depending whether $l = 2n$ or $2n + 1$. Let us note that the presence of higher lying states and is at the root of van Vleck paramagnetism. In systems with non-Kramers ions, this term is generally manifested at low temperatures as a practically constant susceptibility, independent up to very high fields. The well known example is the paramagnetic contribution of Pr$^{3+}$. A similar contribution exists also for Kramers ions, where van Vleck susceptibility represents a small addition to dominant, strongly temperature dependent Curie susceptibility that arises due to thermal redistribution within the split levels of ground doublet. In particular for DyCoO$_3$, the principal values of the van Vleck susceptibility tensor associated with Dy$^{3+}$ are calculated to $\chi_{\xi} = 0.0143$, $\chi_{\eta} \approx 0$ for the in-plane components, and $\chi_{\zeta} = 0.0526 \mu_B/T$ for the out-of-plane component and the orientation of $\xi$ axis is defined by $\alpha_{vV} = \pm 22.2^\circ$ with respect to the $a$-axis. Let us note that there is also van Vleck contribution of LS Co$^{3+}$, which is of the order $\sim 0.0004 \mu_B/T$ ($\sim 0.0002$ emu·mol$^{-1}$·Oe$^{-1}$) and brings thus little effect.

C. Magnetic ordering

![FIG. 1: Zeeman splitting of the TbCoO$_3$ low-energy pseudodoublet and the DyCoO$_3$ ground doublet.](image)
FIG. 2: Neutron diffraction patterns of TbCoO$_3$ and DyCoO$_3$ at 0.25 and 5.5 K ($\lambda = 2.408$ Å).

of both components indicates a canting, which is an inevitable consequence of the Ising character of Tb$^{3+}$ and Dy$^{3+}$ moments, and the inclination of easy axes $\pm \alpha$ in the $ab$-plane of the orthoperovskite structure.

The results of the Rietveld refinement of the rare-earth moments are presented in Fig. 3. The estimated Néel temperatures of the AFM ordering $T_N$ are 3.3 K and 3.6 K for TbCoO$_3$ and DyCoO$_3$, respectively, are in agreement with previous studies and are oriented in the $ab$-plane of the orthoperovskite structure.

The ordered moments are oriented in the $a$, $b$-plane of the orthoperovskite structure and reach $m(A_x) = 6.5\mu_B$ and $m(G_y) = 5.1\mu_B$ for TbCoO$_3$ and $m(G_x) = 4.3\mu_B$ and $m(A_y) = 8.0\mu_B$ for DyCoO$_3$.

IV. DISCUSSION

Based on the present study, Néel temperatures of the AFM ordering in TbCoO$_3$ and DyCoO$_3$ is estimated to $T_N = 3.3$ K and 3.6 K, and the ordering is of $A_xG_y$ and $G_xA_y$ type, respectively. This is in agreement with earlier findings on these cobaltites and is also close to AFM temperatures in analogous aluminates. The arrangements in the $a$, $b$-plane of the orthoperovskite structure are depicted in Fig. 4 and the coupling along the $c$-axis is purely AFM. The ordered moments for TbCoO$_3$ have a magnitude of $m = 8.3\mu_B$ and are inclined from the orthorhombic $a$-axis to angle $\pm 38^\circ$. For DyCoO$_3$, the magnitudes of moments is $m = 9.1\mu_B$ and their inclination is $\pm 62^\circ$.

The experimental magnitudes and directions of the magnetic moments are confronted with calculated values in Table II. Calculated magnitudes of the moments are by 7 and 6 % larger than the experimental ones in TbCoO$_3$ and DyCoO$_3$, respectively. Taking into account that theory contains no parameter to fit the experiment

FIG. 3: The AFM ordered moments deduced from neutron diffraction patterns of TbCoO$_3$ and DyCoO$_3$. The dashed lines are guides to the eyes.

FIG. 4: Schematic view of octahedral tilts and the magnetic structures of TbCoO$_3$ and DyCoO$_3$. The CoO$_6$ octahedrons are centered at the $c = 0$ level; the displayed rare-earth moments are located at $c = 1/4$ while those at $c = 3/4$ are oppositely oriented.
the agreement may be regarded as good for the magnitudes of the moments and excellent for their directions. As pointed out by Bidaux and Meriel for DyAlO$_3$ [12], there are two variants depending in which sense the moments could be inclined, which cannot be distinguished in neutron diffraction experiment. On the other hand, theory allows an unambiguous assignment of the sign of angle $\alpha_g$ to the RE crystal site. Regarding the agreement of the experimentally determined angles and the orientation of Ising axes in our calculations, we may state that, with respect to CoO$_6$ tilts, the actual orientation is as shown in Fig. [1]

As mentioned above, the origin of observed AFM arrangement, $A_2G_y$ for TbCoO$_3$ and $G_xA_y$ for DyCoO$_3$ in Bertaut’s notation, can be associated with dipolar interactions, which dominant role can be understood in view of large magnitude of the Tb$^{3+}$ and Dy$^{3+}$ long-range ordered moments, $\sim 8$ and $9 \mu_B$, respectively. There are, however, strong indications that the superexchange interactions of purely spin nature must be also acting and may eventually decide on final magnetic arrangement in the rare-earth cobaltites, aluminates or gallates. In particular, AFM ordering at $T_N = 1.5$ K is stabilized for SmCoO$_3$, though the spin and orbital components of the Sm$^{3+}$ moment nearly cancel ($L = 5$, $S = 5/2$, $J = L - S = 5/2$), and dipolar interactions are thus negligible.

Acknowledgments. This work was supported by Project No. P204/11/0713 of the Grant Agency of the Czech Republic. We acknowledge the Oak Ridge National Laboratory (Tennessee, United States) for providing access to the neutron beams and for all technical support during the experiments.

Appendix A: Electron states and magnetism of lanthanide ions in orthocobaltites

The crystal field parameters, obtained by first-principle calculations with a use of experimental crystallographic data for NdCoO$_3$ [14], SmCoO$_3$ [15], TbCoO$_3$ and DyCoO$_3$ (see Table [1]), are summarized in Table [III] The energies of Kramers doublets and respective $\hat{q}$ and $\hat{v}^{\pm}$ tensor components for Nd$^{3+}$, Sm$^{3+}$ and Dy$^{3+}$ are presented in Tables [IV] [V] and [VI]. The diagonal tensor components refer to axes $a$, $b$ and $c$ of the orthorhombic space group $Pbnm$, while the index $\omega$ stands for the field orientation along $110$.

The energies of thirteen levels of the $^7F_g$ multiplet of the non-Kramers Tb$^{3+}$ are given in Table [VII]. It appears that there are five pairs of states with close energy possessing a quasi-doublet character, i.e. allowing sizeable Zeeman splitting when the strength of external field exceeds the energy gap. The remaining three singlets are non-magnetic and their response to external field is of the van Vleck character.

| RE | TbCoO$_3$ | DyCoO$_3$ |
|----|-----------|-----------|
|    | ND calc. | ND calc. |
| $\alpha_g(\degree)$ | $\pm 38(1)$ | $-37.1$ | $\pm 62(1)$ | $-64.0$ |
| $m_{RE}(\mu_B)$ | $8.3(2)$  | $8.9$    | $9.1(2)$   | $9.7$    |

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TABLE V: Sm$^{3+}$ ion in SmCoO$_3$. Energy of three Kramers doublets originating from $^6H_{5/2}$ multiplet, $\hat{g}$ and $\hat{\chi}^{\mu\nu}$ tensor components along the orthorhombic axes and $\omega$ direction. Energy $\varepsilon(0)$ is in meV, $\hat{\chi}^{\mu\nu}$ is units of $\mu_B/T$.

| doublet | $\varepsilon(0)$ | $g_{aa}$ | $g_{bb}$ | $g_{cc}$ | $g_{\omega}$ | $\chi^{\mu\nu}_{aa}$ | $\chi^{\mu\nu}_{bb}$ | $\chi^{\mu\nu}_{cc}$ | $\chi^{\mu\nu}_{\omega}$ |
|---------|------------------|----------|----------|----------|-------------|-------------------|-------------------|-------------------|-------------------|
| 1       | 0.00             | 1.701    | 2.560    | 3.015    | 1.442       | 0.0149            | 0.0106            | 0.0118            | 0.0024            |
| 2       | 13.19            | 1.773    | 2.208    | 2.432    | 0.813       | -0.0072           | -0.0020           | 0.0040            | 0.0054            |
| 3       | 25.66            | 3.596    | 2.524    | 1.666    | 3.800       | 0.0026            | 0.0018            | -0.0062           | -0.0013           |
| 4       | 64.37            | 2.964    | 3.950    | 1.659    | 4.372       | -0.0012           | -0.0022           | 0.0008            | 0.0016            |
| 5       | 84.60            | 2.576    | 2.152    | 3.009    | 1.605       | -0.0068           | -0.0057           | -0.0081           | -0.0063           |

TABLE VI: Dy$^{3+}$ ion in DyCoO$_3$. Energy of eight Kramers doublets originating from $^8H_{15/2}$ multiplet, $\hat{g}$ and $\hat{\chi}^{\mu\nu}$ tensor components along the orthorhombic axes and $\omega$ direction. Energy $\varepsilon(0)$ is in meV, $\hat{\chi}^{\mu\nu}$ is units of $\mu_B/T$.

| doublet | $\varepsilon(0)$ | $g_{aa}$ | $g_{bb}$ | $g_{cc}$ | $g_{\omega}$ | $\chi^{\mu\nu}_{aa}$ | $\chi^{\mu\nu}_{bb}$ | $\chi^{\mu\nu}_{cc}$ | $\chi^{\mu\nu}_{\omega}$ |
|---------|------------------|----------|----------|----------|-------------|-------------------|-------------------|-------------------|-------------------|
| 1       | 0.00             | 8.52     | 17.47    | 0.03     | 6.33        | 0.0124            | 0.0029            | 0.0526            | 0.0123            |
| 2       | 29.75            | 6.68     | 14.90    | 0.22     | 5.82        | 0.0176            | 0.0049            | 0.0210            | 0.0174            |
| 3       | 59.02            | 7.42     | 11.35    | 0.38     | 2.84        | 0.0259            | 0.0161            | 0.0490            | 0.0364            |
| 4       | 80.47            | 8.66     | 6.92     | 0.07     | 1.34        | 0.0321            | 0.0434            | 0.1143            | 0.0553            |
| 5       | 90.14            | 18.65    | 0.47     | 0.02     | 13.48       | 0.0298            | 0.0623            | -0.0087           | 0.1136            |
| 6       | 96.11            | 7.52     | 4.40     | 6.98     | 7.28        | -0.0818           | -0.0677           | -0.0911           | -0.1653           |
| 7       | 114.61           | 9.89     | 7.37     | 0.30     | 12.08       | -0.0212           | -0.0151           | 0.2774            | -0.0164           |
| 8       | 124.22           | 10.58    | 11.99    | 2.62     | 15.95       | -0.0227           | -0.0455           | -0.4132           | -0.0522           |
TABLE VII: Tb$^{3+}$ ion in TbCoO$_3$. Energy of five magnetic quasidoublets and three singlets originating from $^7F_6$ multiplet, $\hat{g}$ tensor components along the orthorhombic axes and $\omega$ direction, in high field ($\sim 1$ T) limit. Energy $\varepsilon(0)$ is in meV.

| singlet | $\varepsilon(0)$ | $g_{aa}$ | $g_{bb}$ | $g_{cc}$ | $g_\omega$ |
|---------|------------------|----------|----------|----------|------------|
| 1+2     | 0.000+0.002      | 14.18    | 10.71    | 0        | 2.40       |
| 3+4     | 22.897+23.063    | 1.59     | 4.34     | 0        | 0.08       |
| 5       | 33.264           | -        | -        | -        | -          |
| 6       | 35.889           | -        | -        | -        | -          |
| 7+8     | 41.325+41.334    | 3.82     | 0.39     | 0        | 1.76       |
| 9       | 43.185           | -        | -        | -        | -          |
| 10+11   | 43.59+44.491     | 0        | $\sim 0.04$ | 0.31    | 0          |
| 12+13   | 68.797+68.824    | 13.30    | 5.97     | 0        | 14.66      |