Crystal structure and magnetic properties of novel Hf$_3$Ni$_2$Si$_3$-type R$_3$Co$_2$Ge$_3$ compounds (R=Y, Sm, Tb–Tm)

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**A B S T R A C T**

The novel R$_3$Co$_2$Ge$_3$ compounds with R=Y, Sm, Tb–Tm adopt the Hf$_3$Ni$_2$Si$_3$-type structure (ordered variant of the Ca$_3$Ga$_3$-type one, space group Cmcm) [1], similar to Gd$_3$Co$_2$Ge$_3$ [2], R$_3$Co$_2$Si$_3$ and R$_3$Fe$_2$Si$_3$ (R=Sc, Y, Lu, Gd–Tm) [3]. The Hf$_3$Ni$_2$Si$_3$-type structures can be derived from the Mg$_3$type rare-earth ones via orthorhombic distortion of the initial hexagonal rare-earth lattice concomitant with the insertion of transition metals and p elements as shown in [4]. The present Hf$_3$Ni$_2$Si$_3$-type compounds belong to the large family of the two-layer orthorhombic structures with the Cmcm space group symmetry [1–16] (Table 1). The investigation of magnetic ordering in the Hf$_3$Ni$_2$Si$_3$-type compounds permit us to understand the magnetic ordering in this family of the two-layer orthorhombic structures. In the present work, we report on the crystal structure and magnetism of the R$_3$Co$_2$Ge$_3$ phases.

1. Introduction

Structures of many of the rare-earth-rich intermetallic phases can be derived from those of the corresponding rare-earth metals through the insertion of transition metals and p elements. Besides structural changes, incorporation of transition metals and p elements modifies the magnetic interactions between the rare-earth atoms. The novel R$_3$Co$_2$Ge$_3$ compounds with R=Y, Sm, Tb–Tm adopt the Hf$_3$Ni$_2$Si$_3$-type structure (ordered variant of the Ca$_3$Ga$_3$-type one, space group Cmcm) [1], similar to Gd$_3$Co$_2$Ge$_3$ [2], R$_3$Co$_2$Si$_3$ and R$_3$Fe$_2$Si$_3$ (R=Sc, Y, Lu, Gd–Tm) [3]. The Hf$_3$Ni$_2$Si$_3$-type structures can be derived from the Mg$_3$type rare-earth ones via orthorhombic distortion of the initial hexagonal rare-earth lattice concomitant with the insertion of transition metals and p elements as shown in [4]. The present Hf$_3$Ni$_2$Si$_3$-type compounds belong to the large family of the two-layer orthorhombic structures with the Cmcm space group symmetry [1–16] (Table 1). The investigation of magnetic ordering in the Hf$_3$Ni$_2$Si$_3$-type compounds permit us to understand the magnetic ordering in this family of the two-layer orthorhombic structures. In the present work, we report on the crystal structure and magnetism of the R$_3$Co$_2$Ge$_3$ phases.

2. Experimental details

The R$_3$Co$_2$Ge$_3$ samples were prepared by arc-melting the weighed amounts of rare earths, Co (99.9 wt%) and Ge (99.99 wt%). The samples were annealed at 1070 K for 175 h in an argon atmosphere and subsequently quenched in ice-cold water. The quality of the samples was evaluated using powder X-ray diffraction analysis. The X-ray data were obtained on a DRON-3.0 diffractometer (CuK$_\alpha$ radiation, 2, 10, 15, 20, 25 and 30 $\theta$ step). The unit cell data were derived using the Rietan-program [17] in the isotropic approximation. The dc magnetisation was measured on a commercial SQUID magnetometer (Quantum Design) in the temperature range of 5–300 K in applied fields up to 50 kOe.

The neutron diffraction experiments were carried out on the D1B powder diffractometer [18] ($\lambda=0.252$ nm) in zero applied field at the Institute Laue-Langevin, Grenoble, France) at 2, 10, 15, 43, 50, 60 and 222 K. The neutron diffraction patterns were identified and calculated using the FULLPROF-program in terms of traditional crystallographic approach [19].

3. Results and discussion

The X-ray analysis showed that the Y, Sm, Tb–Tm)$_3$Co$_2$Ge$_3$ samples are single phase and confirmed that the R$_3$Co$_2$Ge$_3$ phases adopt the Hf$_3$Ni$_2$Si$_3$-type structure. The refined unit cell data and atomic positions are given in Tables (2) and (3). Unit cell parameters of R$_3$Co$_2$Ge$_3$ increase with the rare-earth atomic radii (Fig. 1).
The shortest Tb–Co, Tb–Ge, Co–Ge, Tb–Tb interatomic distances are close to the sum of metallic radii of pure elements \[20\]. The Co–Co and Ge–Ge distances are larger than the atomic diameters of the elements (Table 4). The shortest interatomic distances are highlighted in a bold character in Table 4. The large “Co–Co” distances preclude the magnetic ordering of the cobalt sublattice.

The paramagnetic susceptibility of the Tb₃Co₂Ge₃, Ho₃Co₂Ge₃, Er₃Co₂Ge₃ and Tm₃Co₂Ge₃ compounds follows the Curie–Weiss law in the temperature range of ca. 20 to 300 K, whereas

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**Table 1**

Summary of the two-layer orthorhombic structures with the Cmcm symmetry. The rare-earth sublattices are classified according to the number and multiplicity of the \( R \) sites. For a given rare-earth sublattice, the structures are classified according to the total number of atoms in the unit cell and then by the formula of the unit cell. Composition of the unit cell is given in square brackets.

<table>
<thead>
<tr>
<th>Rare earth</th>
<th>( \text{Number of atoms in the unit cell} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R )</td>
<td>Structure type</td>
</tr>
<tr>
<td>( \text{Composition of unit cell} )</td>
<td></td>
</tr>
</tbody>
</table>

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**Table 2**

Cell parameters, Weiss temperatures, \( \beta \), effective magnetic moments per formula unit, \( M_{\text{eff}}/\text{fu} \), and Neel temperatures, \( T_N \), for the Hf₃Ni₂Si₃-type \( R \)₃Co₂Ge₃-type phases (space group Cmcm, \( N = 63, oC_{32} \)).

| Compound     | \( a \) (nm) | \( b \) (nm) | \( c \) (nm) | \( R \) (%) | \( \beta \) (K) | \( M_{\text{eff}}/\text{fu} \) (\( \mu_B \)) | \( M_{\text{eff}}/R \) (\( \mu_B \)) | \( T_C,N \) (0.01 T) | \( T_C,N \) (0.5 T) | \( T_C,N \) (1 T) | \( T_C,N \) (2 T) | \( T_C,N \) (5 T) | \( H_c \) (kOe) (5 K) |
|--------------|-------------|-------------|-------------|------------|-------------|---------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \( Y_3\text{Co}_2\text{Ge}_3 \) | 0.41697(2)  | 1.04747(3)  | 1.39336(4)  | 4.3        | \(-270.1\)  | \( 4.14 \)                          | \( 2.41 \)   | \( 60 \) K       | \( 90 \) K       | \( 110 \) K     | \( 130 \) K     | \( 150 \) K     | paramagnet     |
| \( \text{Sm}_3\text{Co}_2\text{Ge}_3 \) | 0.41984(8)  | 1.0606(1)   | 1.3923(4)   | 4.9        | \(-187.0\)  | \( 4.8 \)                          | \( 2.5 \)    | \( 44 \) K       | \( 66 \) K       | \( 86 \) K       | \( 106 \) K      | \( 126 \) K      | paramagnet     |
| \( \text{Gd}_3\text{Co}_2\text{Ge}_3 \) | 0.4214(1)   | 1.0688(1)   | 1.4052(4)   | 5.8        | \(-270.1\)  | \( 4.14 \)                          | \( 2.41 \)   | \( 60 \) K       | \( 90 \) K       | \( 110 \) K     | \( 130 \) K     | \( 150 \) K     | paramagnet     |
| \( \text{Er}_3\text{Co}_2\text{Ge}_3 \) | 0.4258(2)   | 1.0710(2)   | 1.3972(4)   | 6.2        | \(-187.0\)  | \( 5.4 \)                          | \( 2.8 \)    | \( 52 \) K       | \( 72 \) K       | \( 92 \) K       | \( 112 \) K      | \( 132 \) K      | paramagnet     |
| \( \text{Tm}_3\text{Co}_2\text{Ge}_3 \) | 0.4283(3)   | 1.0730(2)   | 1.3994(4)   | 6.5        | \(-187.0\)  | \( 5.7 \)                          | \( 3.2 \)    | \( 63 \) K       | \( 83 \) K       | \( 103 \) K     | \( 123 \) K      | \( 143 \) K      | paramagnet     |

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**Table 3**

Atomic positions in \( \text{Hf}_3\text{Ni}_2\text{Si}_3 \)-type \( R \)₃Co₂Ge₃-type phases (space group Cmcm, \( N = 63, oC_{32} \)). \( R \)₃ = 3.6%, atomic displacement parameters of all atoms \( \beta_{11} = 0.014318 \), \( \beta_{22} = 0.002263 \) and \( \beta_{33} = 0.001280 \).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
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<th>( y/b )</th>
<th>( z/c )</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb₁</td>
<td>8f</td>
<td>0</td>
<td>0.4186(2)</td>
<td>0.1115(2)</td>
<td>1.00</td>
</tr>
<tr>
<td>Tb₂</td>
<td>4d</td>
<td>0</td>
<td>0.1382(2)</td>
<td>1/4</td>
<td>1.00</td>
</tr>
<tr>
<td>Co</td>
<td>4d</td>
<td>0</td>
<td>0.7182(6)</td>
<td>0.0950(6)</td>
<td>1.00</td>
</tr>
<tr>
<td>Ge₁</td>
<td>4d</td>
<td>0</td>
<td>0.8381(4)</td>
<td>1/4</td>
<td>1.00</td>
</tr>
<tr>
<td>Ge₂</td>
<td>8f</td>
<td>0</td>
<td>0.1234(5)</td>
<td>0.0378(4)</td>
<td>1.00</td>
</tr>
</tbody>
</table>

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The shortest Tb–Co, Tb–Ge, Co–Ge, Tb–Tb interatomic distances are close to the sum of metallic radii of pure elements [20]. The Co–Co and Ge–Ge distances are larger than the atomic diameters of the elements (Table 4). The shortest interatomic distances are highlighted in a bold character in Table 4. The large “Co–Co” distances preclude the magnetic ordering of the cobalt sublattice.

The paramagnetic susceptibility of the Tb₃Co₂Ge₃, Ho₃Co₂Ge₃, Er₃Co₂Ge₃ and Tm₃Co₂Ge₃ compounds follows the Curie–Weiss law in the temperature range of ca. 20 to 300 K, whereas
Sm$_3$Co$_2$Ge$_3$ obeys the Curie–Weiss law in the range of ca. 100 to 300 K Fig. 2). The fit yields Weiss temperatures of $-3.4$ K for Tb$_3$Co$_2$Ge$_3$, $-0.6$ K for Ho$_3$Co$_2$Ge$_3$, $3.8$ K for Er$_3$Co$_2$Ge$_3$ and $-1.3$ K for Tm$_3$Co$_2$Ge$_3$, respectively, suggesting weak overall magnetic interactions, whereas $\theta_\text{p} = -270.1$ K for Sm$_3$Co$_2$Ge$_3$ suggesting strong antiferromagnetic interactions. The Y$_3$Co$_2$Ge$_3$ compound demonstrates the Pauli paramagnetism down to $\sim 120$ K (Fig. 2f).

The effective paramagnetic moments derived for Tb$_3$Co$_2$Ge$_3$ and Er$_3$Co$_2$Ge$_3$ are 15.46 and 15.66 $\mu_B$/f.u., respectively, which precludes existence of magnetic moments on Co atoms, assuming Tb and Er taking the theoretical moments of 9.72 and 9.58 $\mu_B$ [21]. But the effective paramagnetic moments of 4.14 $\mu_B$/f.u for Sm$_3$Co$_2$Ge$_3$, 18.77 $\mu_B$/f.u for Ho$_3$Co$_2$Ge$_3$ and 13.28 $\mu_B$/f.u for Tm$_3$Co$_2$Ge$_3$ yield effective paramagnetic moments of 2.77, 2.72 and 1.54 $\mu_B$ per Co atom, respectively, if Sm, Ho and Tm are assumed to have theoretical moments of 0.85, 10.61 and 7.56 $\mu_B$.

The enhanced magnetic moments of $R^3^+$ compared to those of the free ions are often observed in intermetallic phases and stem from the polarization of the rare-earth 5d electrons[22,23]. However, the question of why the 5d electrons contribute to magnetism in some phases and not in others remains unanswered. The Pauli paramagnetism of Y$_3$Co$_2$Ge$_3$ above 120 K confirms the absence of magnetic moments on Co atoms in the $R^3$Co$_2$Ge$_3$ compounds.

3.1. Magnetic transitions

According to the thermomagnetic measurements at 100 Oe, Sm$_3$Co$_2$Ge$_3$ shows an antiferromagnetic-type transitions at 10 and 60 K, whereas Tb$_3$Co$_2$Ge$_3$, Ho$_3$Co$_2$Ge$_3$ and Er$_3$Co$_2$Ge$_3$ compounds show antiferromagnetic-type transitions at ca. 10 K (Fig. 3). We suggest that the 5 K step and the lowest temperature of 5 K used for magnetisation measurements do not provide enough resolution to detect antiferromagnetic transitions for Tb$_3$Co$_2$Ge$_3$ and Er$_3$Co$_2$Ge$_3$ in the field of 100 Oe (Fig. 3b and e). However, their magnetization curves do show some anomaly that could associated with the antiferromagnetic-like transitions around 10 K. Tm$_3$Co$_2$Ge$_3$ remains paramagnetic down to 5 K (Fig. 3f).

The thermal magnetic measurements of Tb$_3$Co$_2$Ge$_3$ at 5, 10, 20 and 50 kOe (temperature step 2 K) indicate presence of the two
Fig. 2. Inverse magnetic susceptibility of (a) Sm$_3$Co$_2$Ge$_3$, (b) Tb$_3$Co$_2$Ge$_3$, (c) Ho$_3$Co$_2$Ge$_3$, (d) Er$_3$Co$_2$Ge$_3$, (e) Tm$_3$Co$_2$Ge$_3$ and (f) Y$_3$Co$_2$Ge$_3$.

Fig. 3. Magnetization vs. temperature for (a) Sm$_3$Co$_2$Ge$_3$, (b) and (c) Tb$_3$Co$_2$Ge$_3$, (d) Ho$_3$Co$_2$Ge$_3$, (e) Er$_3$Co$_2$Ge$_3$ and (f) Tm$_3$Co$_2$Ge$_3$. 
magnetic transitions: high- and low-temperature antiferromagnetic-type ones (Fig. 3c). The temperature of the high-temperature transition decreases from 33 K down to ~29 K when the magnetic field increases up to 20 kOe. At 20 kOe the low-temperature transition becomes a ferromagnetic-type one due to a metamagnetic-like ordering between 10 and 20 kOe. At 50 kOe, the magnetization curve is characteristic of dominant ferromagnetic-type interactions in the mixed AF–F magnetic system. Saturation magnetization at 35 K and in the field of up to 50 kOe indicate that the Tb3Co2Ge3 is a pure paramagnet, whereas at 5 K a critical point is observed at Hc = ~12 kOe (Fig. 4). At 5 K and 50 kOe, the saturation magnetization reaches the value 4.8 µB/Tb (14.5 µB/fu), which less than the theoretical saturation moment of 9.8 µB/Tb. The critical point in Tb3Co2Ge3 may corresponds to a metamagnetic AF–F transition.

Present magnetic measurements demonstrate a complex field-sensitive antiferromagnetic ordering in Tb3Co2Ge3 with an absence of magnetic moment for Co. We suggest that Sm3Co2Ge2, Gd3Co2Ge3, Dy3Co2Ge3, Ho3Co2Ge3, Er3Co2Ge3, and Tm3Co2Ge3 may have antiferromagnetic ordering similar to that of Tb3Co2Ge3.

The results of the magnetic measurements are summarized in Table 2 including Néel temperatures and effective magnetic moments as derived from the paramagnetic state. The present R3Co2Ge3 phases exhibit the antiferromagnetic ordering, similar to the rare-earth compounds of the CrB- [24,25], CeNiSi2 [26,27] and Dy2Co3Si1.8-type [4] as well as other two-layer orthorhombic structures with the Cmcm space group (Table 1). The metamagnetic behavior of Tb3Co2Ge3 may be attributed to the rare-earth lattice that consists of the 4d (symmetry of site Pmcc21) and 8f (symmetry of site Pm) sublattices similar to Dy3Co2.2Si1.8 [4].

3.2. Neutron diffraction study

The Tb3Co2Ge3 structure (space group Cmcm) contains the 4d and 8f sites for terbium, cobalt, and germanium (Table 3). The coordinates for the 4d and 8f sites and symmetry operators for the corresponding terbium lattices are given in Table 5. The “colorless” point groups and “black-white” magnetic point group [28,29] were used for the analysis of neutron diffraction data. Below ~50 K, the set of magnetic reflections reveals the magnetic ordering of Tb3Co2Ge3 (Fig. 5b). The commensurate magnetic reflections correspond to an antiferromagnetic ordering with the Kc = [0, 0, 0] wave vector. The incommensurate low-angle reflections may correspond to a wave vector with a special value [± 1/3, 0, 0], [0, 0, ± 1/8] or [0, ± 0.85, 0]. The magnetic structure with the set of canted, antiferromagnetically-coupled ferromagnetic cones with K1 = [± 1/3, 0, 0] (Antiferromagnet I) is in best agreement with experiment (the cone axis coincides with the commensurate magnetic moment of the Tb atom) (Fig. 6a and b). The symmetry of the commensurate part of the magnetic structure corresponds to the Pmm2c′ = {1, 2, 3} × {1, m} × [1/2, 1/2, 0] × (T × Zj/0, 0, 1/2) magnetic space group. The magnetic unit cell is 3Tb3Co2Ge3 × Tb3Co2Ge3 × Tb3Co2Ge3.

Below ~15 K, the set of magnetic reflections with K2 = [1/2, 0, 0] indicates the second antiferromagnetic transition in Tb3Co2Ge3 (Fig. 5c). The small unindexed reflections (that are marked by a symbol “·” in Fig. 5c) may belong to a small incommensurate magnetic component of Tb3Co2Ge3 or unindexed impurity phases. The magnetic structure becomes the set of the Pb magnetic moments with the Ke, K1, and K2 wave vectors and magnetic unit cell 60Tb3Co2Ge3 × Tb3Co2Ge3 × Tb3Co2Ge3 (Fig. 6c) (Antiferromagnet II):

$$M_{\text{pc}} = i \times [M_{aTb} + M_{cTb} \cos(\pi n) + j \times M_{bTb} \cos(\pi n) + k \times M_{cTb}]$$

$$+ M_{aTb} \cos(2\pi n/3 + \pi x_{Tb}/3) + j \times \sin(2\pi n/3 + \pi x_{Tb}/3)$$

where n = 0, 1, 2, ..., the number of the unit cell along the a axis of Tb3Co2Ge3; i, j, and k are the orthonormal vectors (i coincides with the a axis, j with the b axis and k with the c axis). The cone axis of a flat spiral with the Ke wave vector coincides with the k vector (k = [i × M_aTb + M_cTb \cos(\pi n) + j \times M_bTb + k \times M_cTb] / |[M_aTb + M_cTb \cos(\pi n) + (M_{bTb})^2 + (M_{cTb})^2]|^{1/2}, i, j, and k are the orthonormal vectors. The magnetic components are listed in Table 6. The magnitude of the Tb moment reaches a value of ~8.7 µB/Tb at 2 K, which corresponds well to the 9 µB expected for the free Tb3+ ion [21].

In zero applied field, Tb3Co2Ge3 demonstrates a non-collinear antiferromagnetic ordering. In summary, the sequence of magnetic ordering of Tb3Co2Ge3 is as follows: Paramagnet (symmetry

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Table 5

Coordinates of the 8f and 4d sites in the Cmcm space group (retained by Tb3Co2Ge3) and the corresponding symmetry operators for the crystal and magnetic lattices.

<table>
<thead>
<tr>
<th>N</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Symmetry operator of lattice</th>
<th>M_{Tb}^{00}</th>
<th>M_{Co}^{00}</th>
<th>M_{Ge}^{00}</th>
<th>Symmetry operator of magnetic lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb1</td>
<td>0</td>
<td>+y_{Tb1}</td>
<td>+z_{Tb1}</td>
<td>Pm = {1, m}</td>
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<td>+</td>
<td>+</td>
<td>1</td>
</tr>
<tr>
<td>Tb2</td>
<td>0</td>
<td>−y_{Tb1}</td>
<td>1/2 + z_{Tb1}</td>
<td>m_{Tb}/[0 0 1/2], z_{Tb}/[0 0 1/2]</td>
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<td>+</td>
<td>−</td>
<td>1 × x_{Tb}/[0 0 1/2]</td>
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<td>−y_{Tb1}</td>
<td>−z_{Tb}</td>
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<td>+</td>
<td>−</td>
<td>+</td>
<td>2</td>
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<tr>
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<td>1/2 − z_{Tb}</td>
<td>2_{Tb}/[0 0 1/2], m_{Tb}/[0 0 1/2]</td>
<td>−</td>
<td>+</td>
<td>−</td>
<td>1 × y_{Tb}/[0 0 1/2]</td>
</tr>
<tr>
<td>Tb5</td>
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<td>1/2 + y_{Tb1}</td>
<td>+z_{Tb1}</td>
<td>1/[1/2 1/2 0], m_{Tb}/[1/2 1/2 0]</td>
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<td>+</td>
<td>−</td>
<td>1 × m_{Tb}/[1/2 1/2 0]</td>
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<tr>
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<td>1/2 + z_{Tb1}</td>
<td>m_{Tb}/[1/2 1/2 0], 2_{Tb}/[1/2 1/2 0]</td>
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<td>+</td>
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<td>1/2 − y_{Tb1}</td>
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<td>l/[1/2 1/2 0], 2_{Tb}/[1/2 1/2 0]</td>
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<td>−</td>
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</tr>
<tr>
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<td>1/2 + y_{Tb1}</td>
<td>1/2 − z_{Tb1}</td>
<td>2_{Tb}/[1/2 1/2 0], m_{Tb}/[1/2 1/2 0]</td>
<td>−</td>
<td>+</td>
<td>−</td>
<td>1 × m_{Tb}/[1/2 1/2 0]</td>
</tr>
<tr>
<td>Tb9</td>
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<td>+y_{Tb2}</td>
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<td>Pmc21 = {1, m, z_{Tb}/[0 0 1/2], m_{Tb}/[0 0 1/2]}</td>
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<td>1 × x_{Tb}/[0 0 1/2]</td>
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<tr>
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<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>1 × m_{Tb}/[1/2 1/2 0]</td>
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Fig. 4. Magnetization vs. field for Tb3Co2Ge3 at 5 and 35 K.
$D_{2h}$, Cmcm, size of unit cell $a_{Tb3Co2Ge3} \times b_{Tb3Co2Ge3} \times c_{Tb3Co2Ge3}$ → Antiferromagnet I: an AF component with the $K_0$ wave vector with symmetry $D_{2h}$. Pmm, a flat spiral AF component with the $K_1$ wave vector and a magnetic unit cell of $3a_{Tb3Co2Ge3} \times b_{Tb3Co2Ge3} \times c_{Tb3Co2Ge3}$ → Antiferromagnet II: AF components with the $K_0$ (symmetry $D_{2h}$, Pmm), $K_1$ (flat spiral component) and $K_2$ (collinear component along the a axis) wave vectors and a magnetic unit cell $6a_{Tb3Co2Ge3} \times b_{Tb3Co2Ge3} \times c_{Tb3Co2Ge3}$.

The Tb sublattice consists of the 4d (symmetry of site Pmc21) and 8f (symmetry of site Pm) sublattices (Table 5). The Tb sublattice with the highest 4d symmetry plays a crucial role in the magnetisation of Tb$_3$Co$_2$Ge$_3$, similar to the rare-earth sublattice (4c) of the Mn$_5$Si$_3$-type phases that contain the 4c sublattice of the $D_3$ symmetry and 6g sublattice of the $D_{1h}$ symmetry [30,31]. We suggest that the field-sensitive magnetisation of Tb$_3$Co$_2$Ge$_3$ is due to the structural features of the Tb sublattice. The metamagnetic-like transition of Tb$_3$Co$_2$Ge$_3$ at 5 K and ca. 12 kOe (Fig. 4) possibly corresponds to the ferromagnetic re-orientation of the Tb moments at the 8f site, whereas the Tb sublattice at 4d remains antiferromagnetically ordered. We believe that magnetic structure of other $R_3$Co$_2$Ge$_3$ compounds might be similar to that of Tb$_3$Co$_2$Ge$_3$, but further neutron diffraction studies on other $R_3$Co$_2$Ge$_3$ compounds will be needed to confirm this hypothesis.

4. Conclusion

The novel $R_3$Co$_2$Ge$_3$ phases adopt the Hf$_3$Ni$_2$Si$_3$-type structure. They demonstrate a complex, field-sensitive antiferromagnetic
ordering at low temperatures. The rare-earth sublattice of the 4d site plays a crucial role in the magnetisation of the R₃Co₂Ge₃ compounds. The magnetic structure of Tb₃Co₂Ge₃ has been determined in a wide temperature range.

Acknowledgments

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References


Table 6
Crystallographic and magnetic parameters of the Hf₃Ni₂Si₃-type Tb₃Co₂Ge₃ compound at different temperatures: unit cell data, magnetic moment of flat spiral $M_{ZH}^{SS}$, magnetic moment along the $a$ axis $M_{ZH}^{SS}$, the $b$ axis $M_{ZH}^{SS}$, and magnitude $M_{ZH}^{SS}$ of the magnetic moment of the corresponding atom with the wave vectors $K_{M}=[0,0,0]$, $K_{M}=[1,3,0,0]$ and $K_{M}=[1,2,0,0]$. Magnitude $M_{ZH}^{SS}$ is for one unit cell. $R_{F}$ (crystal structure) and RF (magnetic structure) are reliability factors.

<table>
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<tr>
<th>$T$ (K)</th>
<th>Unit cell data</th>
<th>$R_{F}$ (%)</th>
<th>Atom</th>
<th>$M_{ZH}^{SS}$ (μ₀)</th>
<th>$M_{ZH}^{SS}$ (μ₀)</th>
<th>$M_{ZH}^{SS}$ (μ₀)</th>
<th>$M_{ZH}^{SS}$ (μ₀)</th>
<th>$M_{ZH}^{SS}$ (μ₀)</th>
<th>$M_{ZH}^{SS}$ (μ₀)</th>
<th>$R_{F}$ (%)</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$Tb_{1}$</td>
<td>$Tb_{1}$</td>
<td>$Tb_{1}$</td>
<td>$Tb_{1}$</td>
<td>$Tb_{1}$</td>
<td>$Tb_{1}$</td>
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<tr>
<td>43</td>
<td>$a=0.41745(8)$</td>
<td>4.1</td>
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<td>0.72(7)</td>
<td>0.72(7)</td>
<td>0.72(7)</td>
<td>0.72(7)</td>
<td>0.72(7)</td>
<td>6.8</td>
</tr>
<tr>
<td>2</td>
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<td>Tb$_1$</td>
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<td>0.94(6)</td>
<td>0.94(6)</td>
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<td>0.94(6)</td>
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<tr>
<td></td>
<td>$b=1.0543(1)$</td>
<td></td>
<td>Tb$_1$</td>
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<td>0.94(6)</td>
<td>0.94(6)</td>
<td>0.94(6)</td>
<td>0.94(6)</td>
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<tr>
<td></td>
<td>$c=1.3914(2)$</td>
<td></td>
<td>Tb$_1$</td>
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<td>0.94(6)</td>
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