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Crystallographic and magnetic structure of TbPtGa

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Abstract

Structural parameters and the magnetic structure of TbPtGa are determined from neutron powder diffraction performed in white beam time-of-flight technology. The crystallographic space group is *Pnma* with four formula units per cell and Tb, Pt and Ga at sites 4*c*(*x*, 1/4, *z*) each. Refined lattice constants, atomic positional parameters and interatomic distances are presented. At 25 ± 1 K TbPtGa undergoes a magnetic phase transition into a collinear antiferromagnetic structure with propagation vector $k = [0, 1/2, 0]$. Terbium magnetic moments of 7.4(1) μ_B are oriented along the *b* axis.

1. Introduction

TbPtGa belongs to the major class of equiatomic ternary rare earth (R)–transition metal (T) gallides, where T may be either a 3d-, 4d- or 5d-element and where a large variety of different magnetic structures can be expected. For the present, we concentrate on compounds with Ni, Pd and Pt, which correspond to each other chemically as group VIII elements of the periodic table. While RNiGa compounds crystallize in the orthorhombic $CeCu_2$-type structure [1], the structure of both RPdGa and RPtGa compounds is a $PbCl_2$-type derivative (see ref. 2).

So far, the magnetic structures of two nickel compounds have been determined by neutron powder diffraction. TbNiGa shows a classical collinear antiferromagnetic moment configuration [3]; HoNiGa is characterized by a more complex sine-modulated spin alignment of a linear transverse wave mode [4]. No magnetic moments were found on the nickel atoms. The present neutron diffraction study is concerned with TbPtGa in order to determine both the crystallographic parameters and the magnetic structure.

2. Experimental details

Polycrystalline material was prepared by arc-melting equal amounts of Tb, Pt and Ga under a helium atmosphere. The ingot was remelted several times to guarantee homogeneity. The specimen was pulverized, filled into a cylindrical vanadium container of 8 mm diameter and inserted into a helium refrigerator cryostat equipped with vanadium windows. Measuring temperatures were 300, 200, 100, 50 and 18 K.

The neutron diffraction measurements were performed at the ROTAX neutron beam facility at the pulsed spallation source ISIS at RAL. The experimental setup was that of an angular dispersive time-of-flight diffractometer with the sample positioned directly in the primary white beam; the configuration is described in ref. 5. One unit of the position-sensitive scintillation detector JULIOS was positioned in forward scattering geometry to register diffracted neutrons with respect to both time-of-flight and position corresponding to wavelength and Bragg angle respectively. The total neutron flight path from moderator to detector was 16 m and the wavelength band used was from 0.495 to 3.441 Å; the detector covered Bragg angles 2θ from 15.2° to 55.7°. The total *d*-spacing coverage during the experiment was from 0.5 to 12.0 Å; the most relevant section of the 300 K pattern is shown in Fig. 1.

The analysis of the *d*-spacing dependent diffraction patterns was performed with the intensity formulae given in ref. 6. Structure analysis and refinement was done according to the two-step method [7]; integrated intensities of single reflections and groups of nonre-

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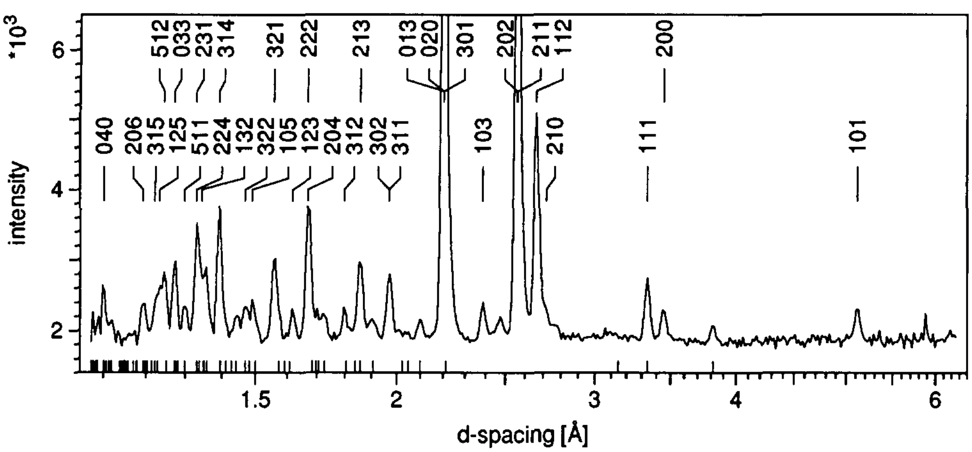

Fig. 1. Neutron diffraction *d*-spacing pattern of TbPtGa taken at 300 K; the indexing is based on an orthorhombic unit cell according to *Pnma*.

solved reflections were refined simultaneously using the least-squares program POWLS [8]. Nuclear scattering lengths used were $b(\mathrm{Tb})=7.38$ fm, $b(\mathrm{Pt})=9.60$ fm and $b(\mathrm{Ga})=7.288$ fm [9].

3. Crystal structure

According to X-ray powder diffraction photographs TbPtGa is known to crystallize in the orthorhombic TiNiSi-type structure in space group *Pnma* with Tb, Pt and Ga on 4*c* positions $(x, 1/4, z)$ each [2]. The 300 K neutron Bragg intensities were used to determine the free atomic positional parameters; the refined values are:

$x(\mathrm{Tb})=0.975(10)$ $z(\mathrm{Tb})=0.697(3)$
$x(\mathrm{Pt})=0.215(3)$ $z(\mathrm{Pt})=0.107(11)$
$x(\mathrm{Ga})=0.327(3)$ $z(\mathrm{Ga})=0.415(14)$

The refinement calculations are based on 13 observations with a total of 35 *hkl* planes; the reliability value is R (Bragg) = 4.7%. Lattice parameters are refined from the observed *d*-spacings to $a=6.887(3)$ Å, $b=4.399(2)$ Å and $c=7.621(4)$ Å. Interatomic distances of the crystallographic TbPtGa structure (Fig. 2) are summarized in Table 1.

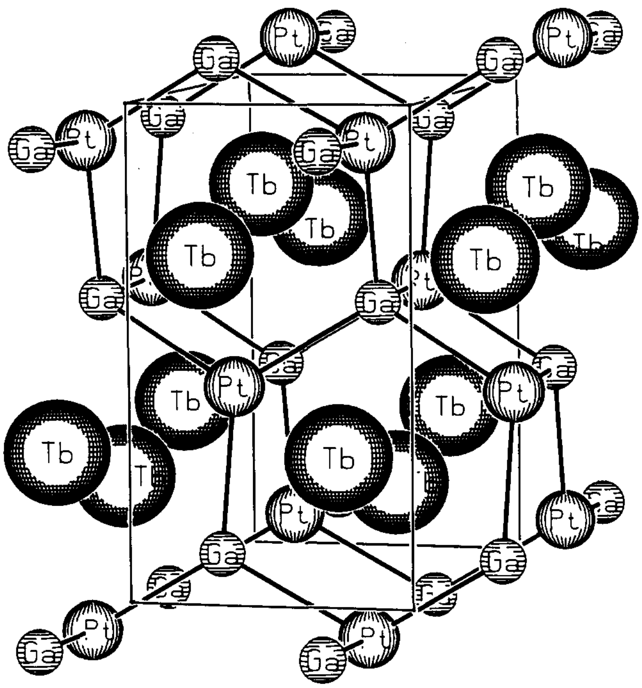

Fig. 2. Crystal structure of TbPtGa. The orthorhombic unit cell is depicted in standard crystallographic setting with *b* and *c* axes oriented horizontally and vertically respectively.

TABLE 1. Interatomic distances *dd* in Å up to *dd*(max) = 4.0 Å and corresponding atomic coordination numbers *cn*

Atoms	*dd*	*cn*	*dd*	*cn*	*dd*	*cn*	*dd*	*cn*
Tb–Tb	3.537	2	3.738	2				
Tb–Pt	2.928	1	2.963	2	3.141	2	3.535	1
Tb–Ga	3.075	2	3.128	1	3.145	2	3.240	1
Pt–Ga	2.471	1	2.658	2	2.677	1		
Ga–Ga	3.492	2						

4. Magnetic structure

The diffraction pattern taken at 18 K (Fig. 3) is characterized by additional reflections originating from an ordered magnetic structure. The magnetic reflections can be indexed by doubling the *b* axis of the chemical unit cell. The symmetry positions of the magnetic terbium atoms are (x, y, z), $(-x, -y, -z)$, $(1/2-x, 1/2-y, 1/2+z)$ and $(1/2+x, 1/2+y, 1/2-z)$ with parameters $x=0.975$, $y=0.125$, $z=0.697$ on sites A and

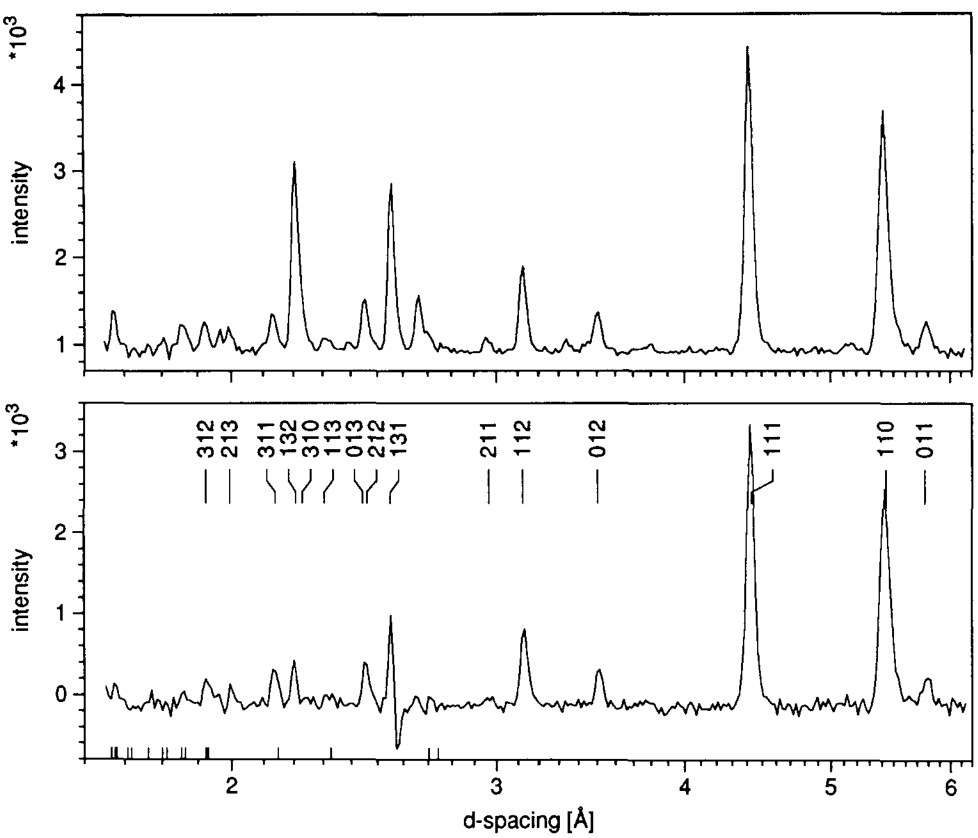

Fig. 3. Neutron diffraction *d* spacing pattern of TbPtGa taken at 18 K (above) and the temperature difference pattern (18–50 K) (below) containing only magnetic intensities. The indexing is based on the enlarged magnetic unit cell (compare text).

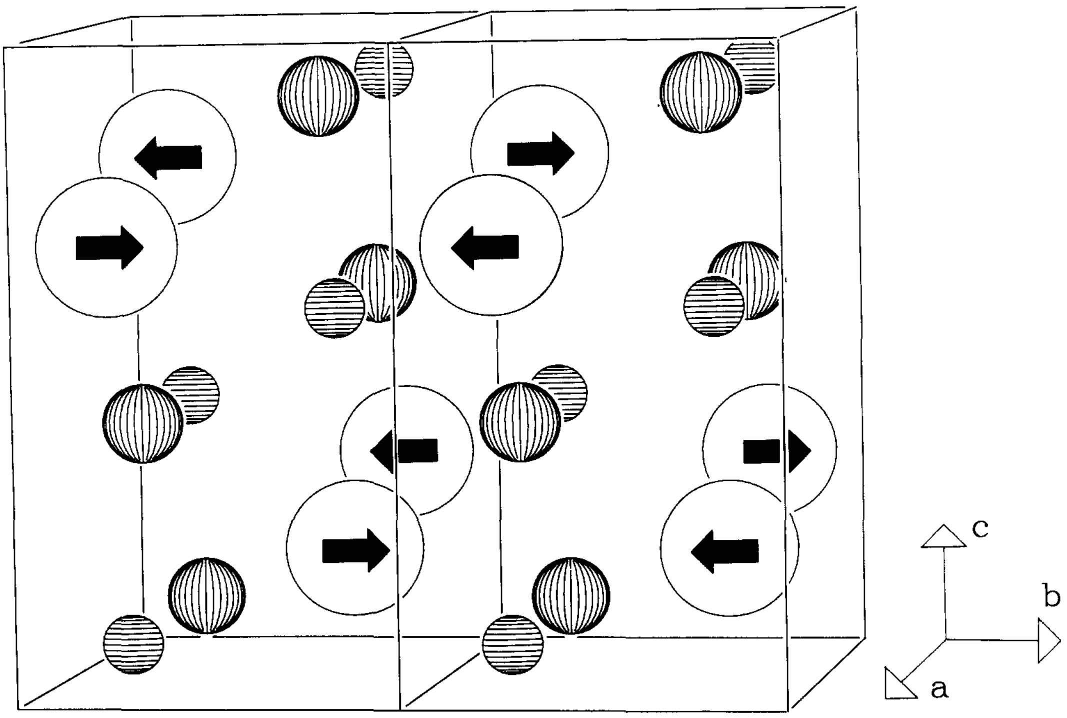

Fig. 4. Antiferromagnetic unit cell of TbPtGa with arrows indicating the ordered terbium moments; nonmagnetic Pt and Ga atoms are shown by medium and small circles respectively.

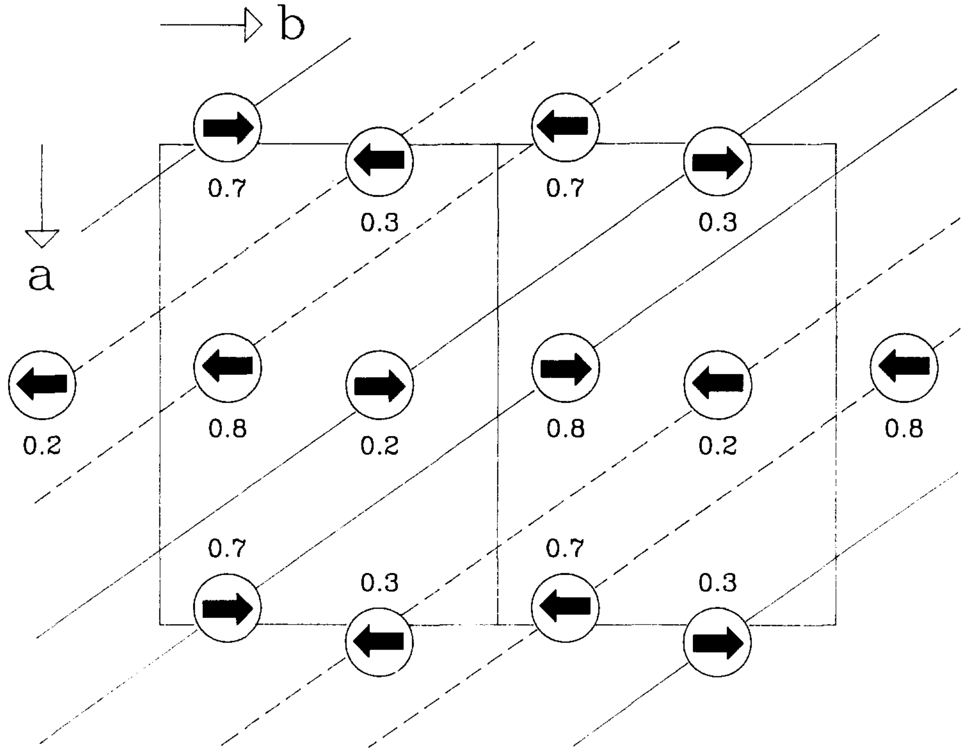

Fig. 5. Antiferromagnetic terbium moment configuration shown as a projection onto the *a*–*b* plane. (110) planes are marked by continuous and broken lines to symbolize pairs of ferromagnetic planes of terbium moments coupled antiferromagnetically.

$x=0.975$, $y=0.625$, $z=0.697$ on sites B. The observed reflections are in accordance with a collinear antiferromagnetic configuration with spin sequences $(++++)$ and $(----)$ of terbium moments on sites A and B respectively. The antiferromagnetic unit cell containing 8 terbium atoms is shown in Fig. 4. The magnetic structure can be described by ferromagnetic (110) planes, which are coupled pairwise antiparallel to each other (Fig. 5). The refinement of the magnetic intensities reveals a moment orientation along the *b* axis. The magnitude of the magnetically ordered terbium moments is 7.4(1) μ_B at the measuring temperature of 18 K. The refinement calculation, performed with a Tb^{3+} form factor taken from [10], is based on 20 observations with a total of 55 magnetic reflections; the final *R*-value is 5.5%. A comparative list of observed and calculated intensities is given in Table 2. Temperature variable measurements between 50 and 18 K revealed a Neel temperature of 25 ± 1 K.

TABLE 2. Comparison of integrated observed *I*(obs) and calculated *I*(calc) magnetic neutron intensities due to the POWLS refinement of the 18 K TbPtGa data

hkl	*I*(obs)	*I*(calc)
011	1342	1492
110	12731	12541
101	473	342
111	13616	13980
021, 002	336	287
012, 200	2008	2067
121, 102	409	429
112	3499	3499
211	504	509
220, 130, 122	2786	2867
221, 202, 131	6401	6726
212, 013	2290	1824
103	342	257
032, 113	766	734
230, 310,...023	8131	7629
231, 311	1887	1406
213, 321, 302	1500	1438
232, 312,...004	1256	1317
014, 240,...330	1365	1632
401, 233,...411	1453	1565

5. Discussion

Our neutron diffraction data confirm the crystallization of TbPtGa in the orthorhombic TiNiSi-type structure, which is a derivative of the $PbCl_2$-type structure of binary compounds. There is a large variety of chemical compounds with very different bonding conditions, including also metallic bonding, to be found in these structure types. The atomic constituents of TbPtGa are found in three different well-ordered sites (x, 1/4, z) of space group *Pnma* without indications of random distributions. The atomic coordinations are different for Tb, Pt and Ga (compare Table 1). A detailed discussion of crystallographic sites and different coordinations in TiNiSi-type structure compounds, *e.g.* ScRhSi, ScPtSi and YNiSi, is given in ref. 2. A characteristic feature of TiNiSi-type compounds is found in the free adjustable positional parameters of the atoms; the sum value $\Sigma(x)$ of the x-coordinates of the transition element and Si (or in our case Ga) is almost the same as the sum value $\Sigma(z)$ of the corresponding z-coordinates for a given compound but differ for different compounds. For TbPtGa we find

$$\Sigma(x)=x(\mathrm{Pt})+x(\mathrm{Ga})=0.215(3)+0.327(3)=0.542(6)$$

$$\Sigma(z)=z(\mathrm{Pt})+z(\mathrm{Ga})=0.107(11)+0.415(14)=0.522(25)$$

Corresponding values for the platinum compound ScPtSi are $\Sigma(x)=0.5048$ and $\Sigma(z)=0.4905$; those for ScRhSi are $\Sigma(x)=0.4425$ and $\Sigma(z)=0.4471$.

At low temperature, TbPtGa undergoes a magnetic phase transition into a collinear antiferromagnetic structure. The ordering temperature of 25 ± 1 K results from the observed appearance and disappearance of the magnetic peaks during a cooling-down and warming-up procedure of the sample, respectively. The Neel temperature of TbPtGa is very similar to that of TbNiGa with 23 K [3]. The value of 7.4(1) μ_B at 18 K for the ordered Tb moment in TbPtGa is significantly below the free ion value of Tb^{3+}. The magnitude of the magnetic moment may be compared with 6.8(4) μ_B at 5 K in TbNiGa [3].

Analogous to the findings in TbNiGa and HoNiGa, in TbPtGa also only rare earths are concerned with the magnetic ordering process. The transition metal Pt and Ga do not carry any magnetic moment. We assume that the platinum 5d shell is totally filled by the compound conduction electrons.

Both TbPtGa and TbNiGa are classical antiferromagnets with collinear spin orientations along one basis axis of the orthorhombic unit cells according to the TiNiSi- and $CeCu_2$-type structures of space group *Pnma* and *Imma* respectively. There is a correspondence in the crystal structures especially with respect to the coordination of the Tb sites (compare ref. 2). The spin configurations of TbPtGa and TbNiGa can be described by ferromagnetic (110) planes in the enlarged magnetic cells, where pairs of subsequent planes are coupled antiparallel to each other (see Fig. 5). In both compounds the moments are oriented perpendicular to the c axes; in TbPtGa the orientation is along the propagation vector [0, 1/2, 0], in TbNiGa perpendicular to the propagation vector [1/2, 0, 0].

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