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Determination of frustrated and non-frustrated magnetic structures of hexagonal and orthorhombic TbPdAl

A. Dönni[a,*], H. Kitazawa[a], L. Keller[b], P. Fischer[b], P. Javorsky[c], F. Fauth[d,b], M. Zolliker[e,b]

[a] National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan
[b] Laboratory for Neutron Scattering, ETH Zurich and Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
[c] Charles University, Faculty of Mathematics and Physics, Department of Condensed Matter Physics, Ke Karlovu 5, 121 16 Prague 2, Czech Republic
[d] BM16-CRG/Consorci Laboratori Llum Sincrotro (LLS), c/o European Synchrotron Radiation Facility (ESRF), F-38043 Grenoble, France
[e] Laboratory for Development and Methods, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

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ABSTRACT

TbPdAl is of particular interest, because different heat treatment allows to transform it from a geometrically frustrated hexagonal modification to a non-frustrated orthorhombic modification. Using powder neutron diffraction, we have determined the complex magnetic structures of the two TbPdAl modifications, both with two successive phase transitions at $T_{N1} \approx 43$ K and $T_{N2} \approx 22$ K. In orthorhombic TbPdAl, the magnetic Tb^{3+} ions form a three-dimensional network of zigzag chains running along the *a*-axis and the *b*-axis. The magnetic structure below T_{N1} corresponds to a propagation vector $\boldsymbol{k}_1 = [0.271(1), 0.523(1), 0]$ with incommensurate modulations along all chain directions. At T_{N2} a lock-in transition to a commensurate structure with $\boldsymbol{k}_2 = [0, 1/2, 0]$ occurs. Large Tb moments of 8.6(1) μ_B at saturation are ordered along the chains with a "+−" sequence (*a*-axis) and a "++−−" sequence (*b*-axis). In hexagonal TbPdAl, the magnetic Tb^{3+} ions form a triangular lattice in the basal plane and geometrically frustrated magnetic structures are observed. Two third of non-frustrated Tb moments order at T_{N1} with a commensurate structure ($\boldsymbol{k}_1 = [1/2, 0, 1/2]$) and a large saturation value of 8.7(2) μ_B. One third of frustrated Tb moments change from a commensurate structure with $\boldsymbol{k}_1$ below T_{N1} to a purely incommensurate structure with $\boldsymbol{k}_{2i} = [0.50(1), 0.12(1), 1/2]$ below T_{N2}. A strong sample dependence is observed for the very unusual magnetic properties of the frustrated Tb moments.

1. Introduction

The ternary intermetallic compounds, in which a rare earth metal is alloyed 1:1:1 with a transition metal and a *p*-electron metal, form a large group and many of such compounds adopt the hexagonal ZrNiAl-type structure (space group $P\bar{6}2m$, No. 189, $Z = 3$) or the orthorhombic TiNiSi-type structure (space group *Pnma*, No. 62, $Z = 4$). TbPdAl is a member of the series, which is of particular interest, because different heat treatment [1,2] allows to transform it from the hexagonal modification (with geometrically frustrated unusual magnetic properties) to the orthorhombic modification (with non-frustrated magnetic properties).

Hexagonal TbPdAl, illustrated in Fig. 1a, has a distinct-layered character. It consists of a strongly distorted hexagonal close packing (ABAB), with the A layers containing Tb on site (3f) and Pd on (1a), and the B layers Pd on (2d) and Al on (3 g). The magnetic Tb^{3+} ions in the hexagonal basal plane form a triangular lattice, which resembles a twisted *kagomé* lattice. Orthorhombic TbPdAl, illustrated in Fig. 1b, can be regarded as a distorted hexagonal ZrNiAl-type structure. All atoms are on (4c) sites. The magnetic Tb^{3+} ions form a three-dimensional network of zigzag chains running along the *a*-axis (Tb1–Tb4–Tb1... and Tb2–Tb3–Tb2...) and the *b*-axis (Tb1–Tb3–Tb1... and Tb2–Tb4–Tb2...). The structural parameters of hexagonal and orthorhombic TbPdAl have been reported in Ref. [2].

In TbPdAl an isostructural phase transition near 98 K has been observed in the hexagonal modification but not in the orthorhombic modification [2]. Such a structural instability of the hexagonal ZrNiAl-type lattice has been found in several ternary (GdNiAl [3,4], GdPdAl [5,6] and TbNiAl [7,8]) and pseudo-ternary ($TbPd_{1-x}Ni_xAl$ [8,9], $DyNi_{1-x}Cu_xAl$ [10], $ErNi_{1-x}Cu_xAl$ [11] and $Ce_{1-x}Y_xPdAl$ [12]) compounds at the temperature, where the ratio c/a of the hexagonal lattice parameters reaches a small interval of unstable values [9,13]. With decreasing temperature, these materials exhibit an anisotropic thermal expansion with the lattice parameters *a* (intralayer distance) *decreasing* and *c* (inter-layer distance) *increasing*. At the isostructural phase transition, abrupt changes of *a* and *c* in

* Corresponding author. Tel.: +81 29 859 2857/90 3435 7667 (mobile); fax: +81 29 859 2801.
E-mail address: DOENNI.Andreas@nims.go.jp (A. Dönni).

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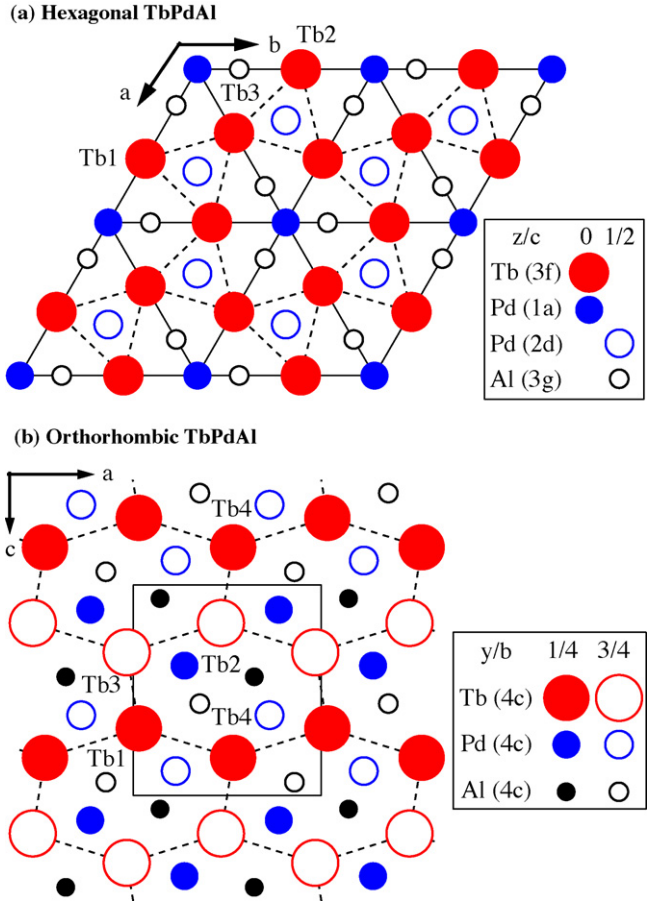

Fig. 1. The hexagonal high-temperature modification (HTM) and the orthorhombic low-temperature modification (LTM) of TbPdAl. (a) ZrNiAl-type crystal structure shown as a projection along the hexagonal *c*-axis. (b) TiNiSi-type crystal structure shown as a projection along the orthorhombic *b*-axis.

opposite directions give rise to a first-order phase transition from a "low-*c*/*a* phase" at higher temperature to a "high-*c*/*a* phase" at lower temperature.

The close structural relationship between hexagonal and orthorhombic TbPdAl is shown in Table 5 of [2]. Although for the magnetic Tb^{3+} ions, the local site symmetry is higher in the hexagonal modification (*m*2*m*) than in the orthorhombic phase (.*m*.), the number of nearest neighbors around the Tb^{3+} ions is similar and both compounds undergo two successive magnetic phase transitions with almost the same Néel temperatures $T_{N1} \approx 43$ K (second-order) and $T_{N2} \approx 22$ K (first-order).

Some magnetic properties have been reported for hexagonal TbPdAl [14–19] but not for orthorhombic TbPdAl. In this paper we present a systematic determination of the complex magnetic structures of orthorhombic and hexagonal TbPdAl samples based on powder neutron diffraction data. In addition we performed specific heat measurements to compare the magnetic phase transitions in the two TbPdAl modifications.

2. Experimental

Polycrystalline TbPdAl samples were prepared by arc-melting stoichiometric amounts of the pure elements (Tb 3N; Pd 4N; Al 5N) in an argon atmosphere as described in Ref. [2]. For as-cast TbPdAl material, X-ray powder diffraction measurements confirmed the presence of the hexagonal high-temperature modification (HTM). The orthorhombic low-temperature modification (LTM) was obtained by annealing as-cast TbPdAl material at 900 °C for 120 h. The hexagonal high-temperature modification (HTM) was prepared by annealing as-cast TbPdAl material at 1050 °C for 120 h and rapid quenching to room temperature.

Specific heat measurements were performed at NIMS between 4 K and room temperature for orthorhombic TbPdAl (on a small bulk piece) and for hexagonal TbPdAl (on a pressed powder sample of as-cast material) with a PPMS instrument, which uses the two-τ relaxation method to determine the heat capacity. Attempts to measure the specific heat of hexagonal TbPdAl on a small bulk piece failed because the sample lost the thermal contact with the holder when cooling through the isostructural phase transition near 98 K.

Neutron diffraction experiments were performed between 1.5 and 60 K to determine the magnetic structures of three different TbPdAl samples (orthorhombic, as-cast hexagonal and annealed hexagonal). Measurements were done partly at the high-flux reactor of the Institute Laue-Langevin (ILL) in Grenoble, France, within the Collaborating Research Groups (CRG) program on the powder diffractometer D1A (neutron wavelength $\lambda = 2.478$ Å) and IN3 (operated in the two-axis mode with $\lambda = 2.36$ Å), and partly at the neutron spallation source SINQ at the Paul Scherrer Institute (PSI) in Villigen, Switzerland, on the powder diffractometer DMC ($\lambda = 2.453$ Å). Large amounts of the TbPdAl samples were ground to a fine powder and enclosed under helium atmosphere into vanadium cylinders of 12 mm diameter (D1A) and 9 mm diameter (DMC) or into an aluminum cylinder of 10 mm diameter (IN3).

Rietveld refinements of the neutron diffraction patterns were carried out with the program FullProf [20], using the internal scattering length and magnetic form factor tables. The background was modeled by a sixth-order polynomial and the intensity profiles by the Thompson–Cox–Hastings pseudo-Voigt function [21].

3. Results and discussion

3.1. Magnetic structures of orthorhombic TbPdAl

Fig. 2 shows the D1A neutron diffraction pattern of orthorhombic TbPdAl LTM collected at 60 K (in the paramagnetic state), at 28 K (between T_{N1} and T_{N2}) and at 1.5 K (below T_{N2}). The observed magnetic Bragg peaks can all be indexed with an incommensurate antiferromagnetic propagation vector $\boldsymbol{k}_1 = [0.271(1), 0.523(1), 0]$ at 28 K and with a commensurate antiferromagnetic propagation vector $\boldsymbol{k}_2 = [0, 1/2, 0]$ at 1.5 K.

The unit cell of the TiNiSi-type crystal structure contains four Tb^{3+} ions on site (4c), which are located at Tb1 (0.03, 1/4, 0.68), Tb2 (0.47, 3/4, 0.18), Tb3 (0.97, 3/4, 0.32) and Tb4 (0.53, 1/4, 0.82) as illustrated in Fig. 1b. We performed a group theoretical calculation with the program MODY [22], known as the symmetry analysis method, to find all models of magnetic structures that are compatible with the symmetry of the paramagnetic phase. Here the magnetic representation $\boldsymbol{S}(\boldsymbol{r})$ is an axial vector function which can be presented as a direct sum of irreducible representations $\psi_\lambda^{\nu n}$ of the paramagnetic symmetry group *G*:

$$\boldsymbol{S}(\boldsymbol{r}) = \sum_{\nu\lambda n} c_\lambda^{\nu n} \psi_\lambda^{\nu n} \quad (1)$$

Table 1
Magnetic modes calulated by the program MODY [22] for space group *Pnma* (No. 62), site (4c) and magnetic propagtion vectors $\boldsymbol{k}_1 = [k_x, k_y, 0]$ and $\boldsymbol{k}_2 = [0, 1/2, 0]$. $\phi = k_x \cdot \pi$.

TbPdAl LTM		Tb1 (*x*, *y*, *z*)	Tb2 (*x*, *y*, *z*)	Tb3 (*x*, *y*, *z*)	Tb4 (*x*, *y*, *z*)
$\boldsymbol{k}_1$, representation τ_2:					
G($\boldsymbol{k}_1$) Orbit 1	ψ^{11}	(0, 1, 0)			(0, −exp[*i*ϕ], 0)
G($\boldsymbol{k}_1$) Orbit 2	ψ^{12}		(0, −exp[−*i*ϕ], 0)	(0, 1, 0)	
$\boldsymbol{k}_2$, representation τ_2:					
G($\boldsymbol{k}_2$) Orbit 1	ψ^{21}	(0, 1, 0)	(0, −*i*, 0)	(0, *i*, 0)	(0, −1, 0)
G($\boldsymbol{k}_2$) Orbit 1	ψ^{21*}	(0, 1, 0)	(0, *i*, 0)	(0, −*i*, 0)	(0, −1, 0)