

## Crystal Structure of TbNiD<sub>3.3</sub>

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**Abstract**—A TbNi-based deuteride has been prepared by hydriding TbNi at a temperature of 297 K and a deuterium pressure no higher than 0.25 MPa. The structure of TbNiD<sub>3.3</sub> differs from that of the parent intermetallic compound, indicating that deuteration causes structural changes in the metallic sublattice. The deuteride has an orthorhombic structure (CrB type, sp. gr. *Cmcm*) in which the deuterium atoms occupy three positions, 4c, 8f, and 4b, with [Tb<sub>3</sub>Ni<sub>2</sub>], [Tb<sub>3</sub>Ni], and [Tb<sub>4</sub>Ni<sub>2</sub>] nearest neighbor environments, respectively.

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### INTRODUCTION

RNi (R = rare-earth metal) intermetallic compounds are capable of reacting with hydrogen under relatively mild conditions (room temperature and low hydrogen pressures) and absorb about three hydrogen atoms per formula unit. RNi-based hydrides have the CrB structure [1–4]. Hydrides with this structure result from the hydrogenation of intermetallic compounds of various structure types: CrB (LaNi, CeNi, PrNi, ZrNi, HfNi, ThCo, ThAl), FeB (ErNi, LuNi), and CsCl (ZrCo, HfCo) [1–8]. Structural data for some of these hydrides [2, 5–7] demonstrate that, near the ABH<sub>3</sub> stoichiometry, the hydrogen atoms occupy positions 8f and 4c. When there are more than three hydrogens per formula unit, the hydrogen occupies the octahedral position 4b.

In this paper, we report an X-ray and neutron diffraction study of the crystal structure of a deuteride prepared by deuteration of TbNi, an intermetallic compound containing a heavy rare earth and differing in structure from earlier studied intermetallics (with the CrB, FeB, and CsCl structures).

### EXPERIMENTAL

TbNi was synthesized by arc-melting an elemental mixture in an argon atmosphere. The alloy was remelted three times in order to improve its chemical homogeneity. Its phase composition and structural parameters were determined by X-ray powder diffraction.

The deuteride was prepared in a Sieverts apparatus. A TbNi sample was placed in an autoclave, which was then pumped for 1 h to a residual pressure of 2–3 Pa. Next, deuterium was introduced into the autoclave in small portions at room temperature. The amount of absorbed deuterium was determined volumetrically from the temperature, autoclave volume, and pressure during the deuteration: D/TbNi = 3.4 ± 0.05.

The phase composition and unit-cell parameters of the intermetallic compound were determined by X-ray diffraction (XRD) on a DRON-2 powder diffractometer (CuK<sub>α</sub> radiation).

The structure of the deuteride was determined by neutron powder diffraction. Diffraction patterns were collected on a DISK neutron diffractometer ( $\lambda = 1.668 \text{ \AA}$ ) at the Russian Research Centre Kurchatov Institute. The deuteride sample was enclosed in a thin-walled vanadium can. The neutron diffraction data were analyzed by the Rietveld method using Fullprof software in order to determine the position of the deuterium atoms.

### RESULTS AND DISCUSSION

It follows from XRD data (Fig. 1) that the synthesized intermetallic compound was low-temperature TbNi [9] (sp. gr. *P2<sub>1</sub>/m*) with lattice parameters  $a = 21.31(2) \text{ \AA}$ ,  $b = 4.211(4) \text{ \AA}$ ,  $c = 5.454(2) \text{ \AA}$ , and  $\beta = 97.43^\circ$ , in reasonable agreement with earlier data ( $a = 21.26(2) \text{ \AA}$ ,  $b = 4.21(4) \text{ \AA}$ ,  $c = 5.45(2) \text{ \AA}$ ,  $\beta = 97.4^\circ$ ).

Neutron diffraction data (Fig. 2) demonstrate that deuteration leads to structural changes in TbNi and that the deuteride has the CrB structure (sp. gr. *Cmcm*) (Fig. 3).

We refined structural parameters (Table 1) and evaluated the deuterium site occupancies and bond distances in the structure of the deuteride (Table 2).

The composition of the synthesized deuteride turned out to be TbNiD<sub>3.3</sub>, instead of the TbNiD<sub>3.4</sub> inferred from volumetry data, which may be due to partial deuterium desorption after the pressure in the autoclave was lowered and the sample was withdrawn. The error of D/TbNi determination is 3% as estimated from the *R*-factor. The deuteration of TbNi increases its unit-cell volume per formula unit by 23.4%. The increase is smaller than those reported for the hydride CeNiH<sub>2.9</sub> (29.5% [2]) and deuteride LaNiD<sub>3.7</sub> (32%

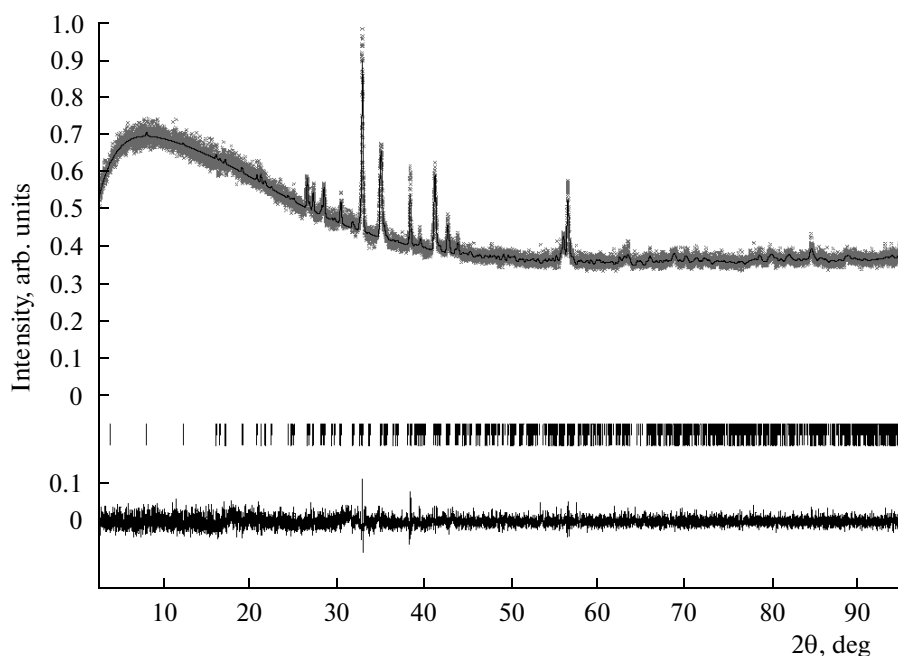


Fig. 1. XRD pattern of the intermetallic compound TbNi.

[7]). A typical increase in unit-cell volume per absorbed deuterium atom (Table 3) in deuterided TbNi is also smaller than those in CeNiH<sub>2.9</sub>, LaNiD<sub>3.7</sub>, and deuterided AB<sub>2</sub> (RNiIn), AB<sub>3</sub> (CeNi<sub>3</sub>, ErNi<sub>3</sub>), and AB<sub>5</sub> (LaNi<sub>5</sub>) intermetallic compounds.

As shown by verifying known structural models for CrB-type deuterides, the deuterium atoms in TbNiD<sub>3.3</sub> reside in three positions, like in the structure of LaNiD<sub>3.7</sub>: 8*f*, 4*c*, and 4*b* (Fig. 3, Table 1). Structure refinement in this model converged at  $R_B = 4.81\%$  and  $R_F = 2.90\%$ .

The coordination polyhedra of the deuterium atoms have the form of a [D(1)Tb<sub>3</sub>Ni] distorted tetra-

hedron, [D(2)Tb<sub>3</sub>Ni<sub>2</sub>] trigonal bipyramid, and [D(3)Tb<sub>4</sub>Ni<sub>2</sub>] distorted octahedron. Analysis of the coordination polyhedra of the deuterium atoms in positions 8*f*, 4*c*, and 4*b* (Fig. 4) demonstrates that deuterium occupies anisotropic sites with a successive increase in coordination number (four in the 8*f* distorted tetrahedron, five in the 4*c* distorted bipyramid, and six in the 4*b* distorted octahedron). Like in other superstoichiometric (H/formula unit > 3) hydrides of this type, position 4*b* is occupied only after positions 4*c* and 8*f*.

The formation of the TbNiD<sub>3.3</sub> deuteride is accompanied by lattice expansion and an increase in bond distances (Table 2). The terbium–deuterium distances are on average comparable to or slightly greater than the analogous distances in the structures of TbD<sub>2</sub> and TbD<sub>3</sub> (Table 3). The largest Ni–D distances are identical to the bond distance in NiD. The La–D and Ni–D distances in the ternary deuteride LaNiD<sub>3.7</sub> slightly exceed those calculated for the deuteride under investigation. This seems to be due to the difference in atomic radius between the rare-earth metals and the stronger lattice expansion because of the higher deuterium content of LaNiD<sub>3.7</sub>.

The Tb–D and Ni–D distances are comparable to the analogous distances in rare-earth nickel deuterides with the AB<sub>2</sub>-, AB<sub>3</sub>-, and AB<sub>5</sub> stoichiometries (Table 3). Thus, the rare-earth-containing intermetallic hydrides have metal–hydrogen bond lengths typical of the binary hydrides of their constituent metals. Similar behavior was reported earlier for transition-metal intermetallic hydrides [18, 19]. The smallest deuterium–deuterium distance in the structure of the

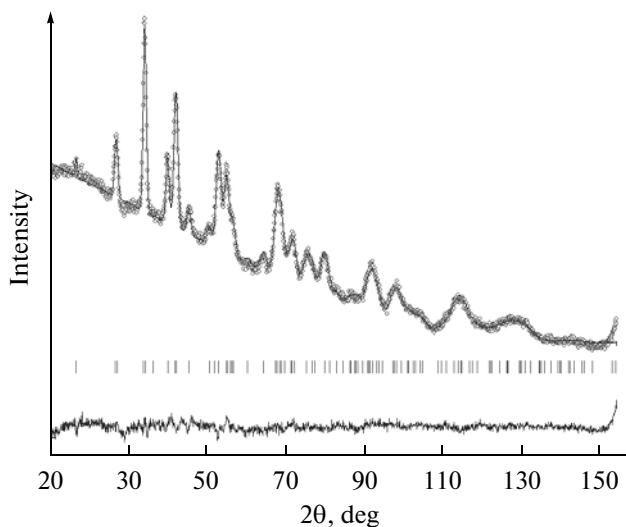
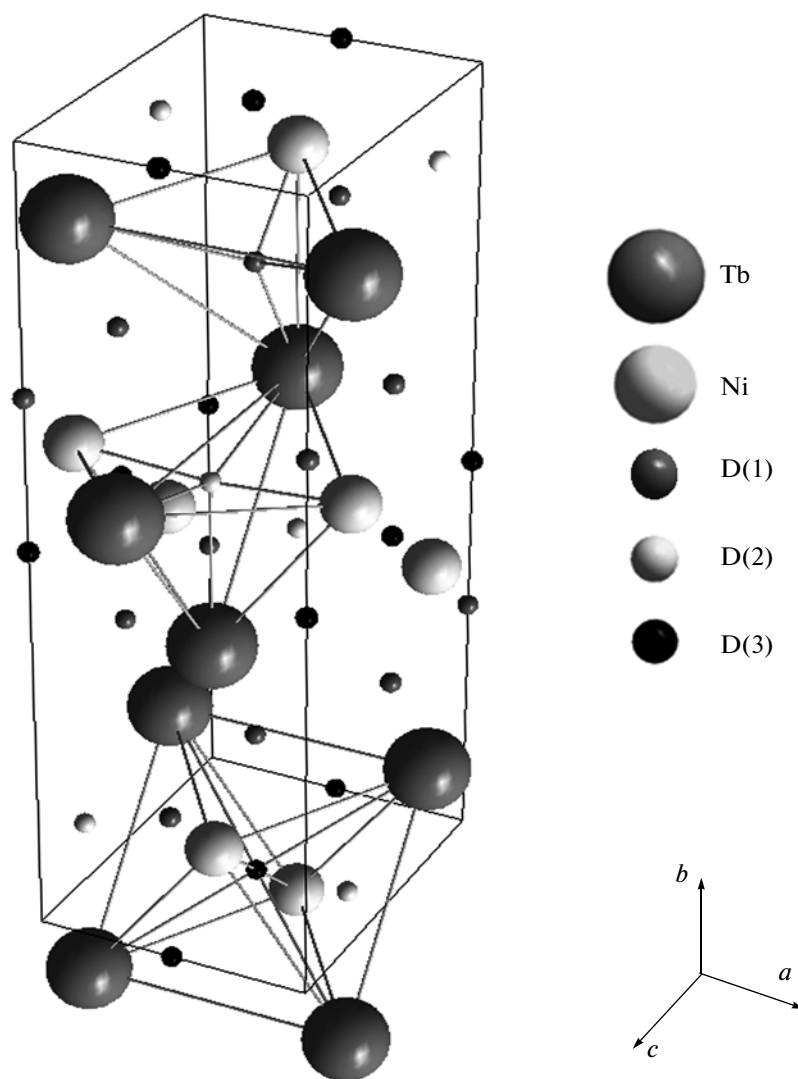


Fig. 2. Neutron diffraction pattern of TbNiD<sub>3.3</sub>.



**Fig. 3.** Crystal structure of deuterided TbNi (CrB type, sp. gr. *Cmc21*) and coordination polyhedra of the deuterium atoms in positions *4c*, *8f*, and *4b*.

deuteride studied here is 2.21 Å, which meets empirical criteria for the formation of hydride phases.

The present results show that TbNi deuteration causes a structural transition in the metallic sublattice:

from the TbNi to the CrB structure. The TbNi and CrB structures are similar in atomic coordination and are made up of the same structural components: nickel-centered trigonal prisms of rare-earth atoms,

**Table 1.** Refined structural parameters of TbNiD<sub>3.3</sub> (CrB structure, sp. gr. *Cmc21*, *Z* = 4)

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub> , Å <sup>2</sup>	Occupancy
Tb	<i>4c</i>	0	0.132	1/4	0.6	1.0
Ni	<i>4c</i>	0	0.410	1/4	1.0	1.0
D(1)	<i>8f</i>	0	0.307	0.497	2.1	1.0
D(2)	<i>4c</i>	0	0.920	1/4	2.7	1.0
D(3)	<i>4b</i>	0	1/2	0	2.1	0.3

Note: *a* = 3.740(2) Å, *b* = 11.435(6) Å, *c* = 4.671(3) Å, *V* = 199.8(4) Å<sup>3</sup>; *R*<sub>B</sub>(TbNiD<sub>3.3</sub>) = 4.81%, *R*<sub>F</sub>(TbNiD<sub>3.3</sub>) = 2.90%.

**Table 2.** Bond distances in the coordination polyhedra of the deuterium atoms and D–D distances in the structure of deuterided TbNi

Atoms	$d, \text{Å}$	Atoms	$d, \text{Å}$	Atoms	$d, \text{Å}$
8f [D <sup>(1)</sup> Tb <sub>3</sub> Ni]		4c [D <sup>(2)</sup> Tb <sub>3</sub> Ni <sub>2</sub> ]		4b [D <sup>(3)</sup> Tb <sub>4</sub> Ni <sub>2</sub> ]	
Tb–D(1)	2.29 2.30(×2)	Tb–D(2)	2.41(×2) 2.42	Tb–D(3)	2.67(×4)
Ni–D(1)	1.64	Ni–D(2)	1.87(×2)	Ni–D(3)	1.56(×2)
Tb–Ni	3.03(×2) 3.17	Tb–Ni	3.03(×4) 3.16(×2)	Tb–Tb	3.74(×2) 3.82(×2)
Tb–Tb	3.74 4.03(×2)	Tb–Tb	3.82(×2) 4.67	Tb–Ni	3.03(×4)
				D(1)–D(1)	2.88
				–D(2)	2.53
				–D(3)	2.36
				D(2)–D(2)	2.27
				–D(3)	2.21
				D(3)–D(3)	2.24

**Table 3.** Bond distances in intermetallic and metal deuterides

Compound	$d(\text{R–R}), \text{Å}$	$d(\text{R–Ni}), \text{Å}$	$d(\text{R–D}), \text{Å}$	$d(\text{Ni–D}), \text{Å}$	$\Delta V/V_0, \%$	$\Delta V/\text{D atom}, \text{Å}^3$	Ref.
TbNi	3.58–3.86	2.58–3.16	–	–	–	–	
TbNiD <sub>3,3</sub>	3.74–4.47	2.95–3.17	2.29–2.65	1.52–1.87	23.4	2.9	
TbD <sub>2</sub>	3.71	–	2.27	–	–	–	[11]
TbD <sub>3</sub>	3.70–3.96	–	2.14–2.52	–	–	–	[12]
NiD	–	–	–	1.87	–	–	[13]
LaNiD <sub>3,7</sub>	3.96–4.24	3.20–3.43	2.41–2.81	1.56–1.99	32	3.8	[7]
LaNiInD <sub>1,22</sub>	3.92	3.25	2.41	1.51	8.5	4.7	[14]
NdNiInD <sub>1,19</sub>	3.83	2.89–3.18	2.35	1.51	7.5	4.1	[14]
TbNiAlD <sub>1,04</sub>	3.76–3.81	2.91–2.99	2.17–2.20	1.54–1.91	5.7	3.2	[15]
CeNi <sub>3</sub> D <sub>3,3</sub>	3.89–4.27	2.85–4.71	2.10–3.04	1.43–2.05	29.7	5.3	[16]
ErNi <sub>3</sub> D <sub>4,0</sub>	3.41–3.42	3.04–3.42	2.38–2.64	1.53–2.16	25.2	3.6	[16]
LaNi <sub>5</sub> D <sub>6,0</sub>	4.28	3.14–3.61	2.30–2.61	1.55–2.73	25.9	3.7	[17]

Note:  $\Delta V/\text{D atom}$  is the change in unit-cell volume per absorbed deuterium atom, and  $\Delta V/V_0$  is the fractional increase in unit-cell volume on deuteration.

arranged in different combinations [10] (Fig. 5a). The structure of TbNi contains asymmetric [Tb<sub>3</sub>Ni] tetrahedral and [Tb<sub>4</sub>Ni<sub>2</sub>] octahedral interstices. Filling the interstices in the structure of TbNi increases their volume and leads to expansion of the crystal lattice as a

whole, eventually resulting in a transformation of the metallic sublattice and a transition to the CrB structure. A similar transition upon the formation of intermetallic hydrides with the CsCl structure was described earlier [18] (Fig. 5b).

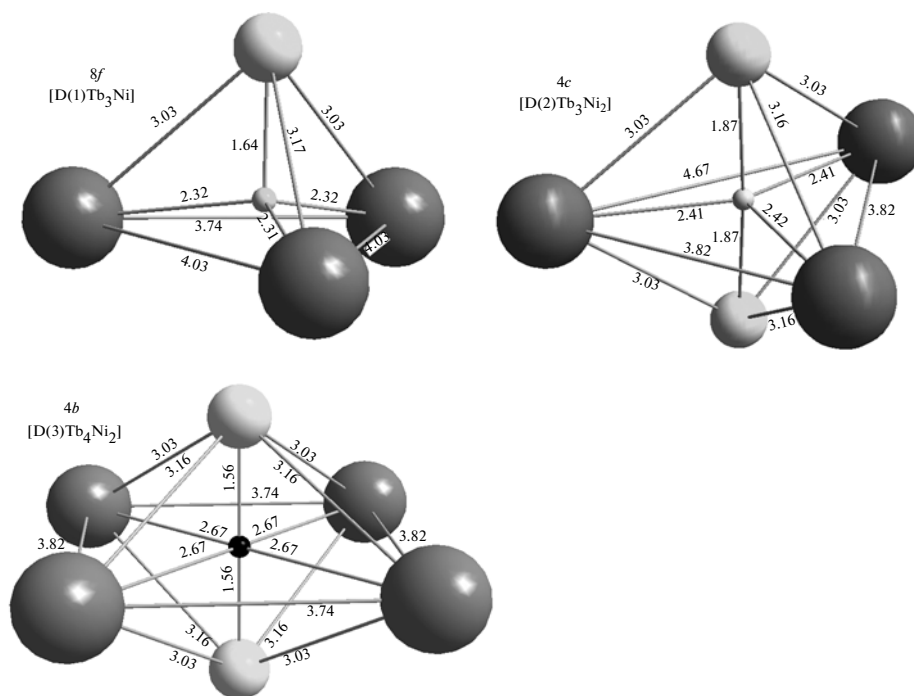


Fig. 4. Coordination polyhedra of the deuterium atoms and bond distances (Å) in the structure of TbNiD<sub>3.3</sub>.

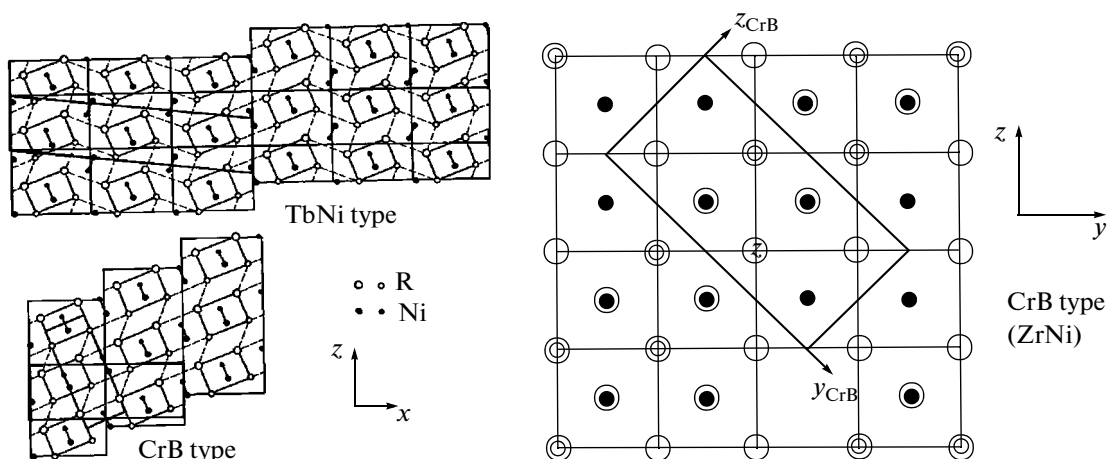


Fig. 5. Structural relationships between the (a) CrB–TbNi [10] and (b) CsCl and CrB types: projection onto the (100) plane [18] (the heavy lines outline the unit cells).

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