

Synthesis and crystal structure of the new $\text{Mg}_8\text{Rh}_4\text{BD}_{3.5}$ deuteride

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The crystal structure of the $\text{Mg}_8\text{Rh}_4\text{BD}_{3.5}$ deuteride has been investigated by both X-ray and neutron powder diffraction at 300 and 10 K. Deuterium absorption by $\text{Mg}_8\text{Rh}_4\text{B}$ proceeds through isotropic expansion of the unit cell volume by 4.1% in the same cubic structure ($Fd-3m$) as the parent compound. The deuterium atoms mostly occupy tetrahedral $32e$ sites with Mg_3Rh surrounding (93.5% of the total D content), however, a small occupancy of octahedral $16d$ sites (Mg_6) was also observed.

Metal hydride / Magnesium compounds / Crystal structure / X-ray and neutron powder diffraction

1. Introduction

The Ti_2Ni structure type is often found in different binary and ternary systems containing transition metals [1-3]. In the structure of the Ti_2Ni type, the titanium atoms occupy $16c$ and $48f$ sites, while the Ni atoms are located in $32e$ sites forming the formula $\text{Ti}^{(1)}_{48}\text{Ni}^{(2)}_{32}\text{Ti}^{(3)}_{16}$. An interesting feature of this structure is the ability to incorporate non-metal elements, such as C, N, O, etc. [4-7]. Many compounds reported with the Ti_2Ni structure type are stabilized by a small amount of these non-metals (e.g. $\text{Ti}_4\text{Fe}_2\text{O}_x$, $\text{Zr}_3\text{V}_3\text{O}_x$, $\text{Zr}_4\text{Fe}_2\text{O}_x$, $\text{Hf}_4\text{Ni}_2\text{O}_x$ and many others) [8-10]. Structure studies of the oxygen-, nitrogen- or carbon- containing phases have shown that the non-metal atoms occupy octahedrally coordinated $16d$ (or $8a$) interstitial sites [2,3]. Such phases belong to the so-called $\eta\text{-Fe}_3\text{W}_3\text{C}$ ($\text{W}_{48}\text{Fe}_{132}\text{Fe}_{216}\text{C}_{16}$) structure type [1], a filled version of the Ti_2Ni type. The oxygen and nitrogen stabilization results in the formation of $\text{Ti}_2\text{M-Zr}_2\text{M}$ or $\text{Zr}_2\text{M-Hf}_2\text{M}$ ($M = \text{Fe, Co, Ni}$) continuous solid solutions [8-11]. These modified Ti_2Ni -type phases are more stable than the TiZrM ternary compounds (MgZn_2 -type structure) without non-metal additives [8-10]. A number of such binary and ternary intermetallic compounds, as well as O-, C-, and N-stabilized phases, have been studied with respect to their hydrogenation properties as promising hydrogen storage or MH-electrode materials. The capability of the Ti_2Ni -type compounds to incorporate hydrogen atoms is related to the occupancy of the tetrahedral,

octahedral or triangular interstices. Different types of interstices in the Ti_2Ni structure are shown in Fig. 1 and their calculated coordinates are collected in Table 1. To our best knowledge, structural investigations have been performed for the following deuterides: Ti_2NiD_x [12-14], $\text{Hf}_2\text{FeD}_{1.8-4.4}$ [15], $\text{Ti}_4\text{Fe}_2\text{OD}_{2.25}$ [16], $(\text{Ti,Zr})_4\text{Fe}_2\text{O}_x\text{D}_y$ [9], $\text{Zr}_3\text{V}_3\text{OD}_{1.85-4.93}$ [17], $\text{Zr}_3\text{V}_3\text{O}_{0.25}\text{D}_{9.6}$ [18], $\text{Zr}_3\text{V}_3(\text{B}_2\text{O}_3)_x\text{D}_y$ [19], and $\text{Zr}_4\text{Pd}_2\text{OD}_{4.5}$ [20].

$\text{Mg}_2\text{RhD}_{1.14}$ and $\text{Mg}_3\text{MnNi}_2\text{D}_{0.23/1.83}$ are the only known hydrides (deuterides) of Mg-based intermetallic compounds with Ti_2Ni -type structure [21,22]. The hydride $\text{Mg}_2\text{RhH}_{1.1}$ can be considered as the first example of hydrogen-stabilized binary metal compounds, because the parent Mg_2Rh compound has not been observed in the Mg-Rh binary system. Systematic studies of the Mg-Rh-B system are presented in [23-25]. This system is characterized by the existence of eleven ternary compounds. The structures of four phases have been fully investigated. Among them the boride $\text{Mg}_8\text{Rh}_4\text{B}$ with a structure related to that of Ti_2Ni (space group $Fd-3m$) [23,24] paid our attention due to possible hydrogenation and interesting structural features in comparison with similar hydrides.

The experimental observations revealed differences between the Ti,Zr,Hf-based and Mg-based systems. The former form a number of O-, C-, and N-stabilized compounds, whereas for the latter only H- and B-stabilized compounds are known. No Mg-based intermetallic compounds stabilized by O, C or N have been reported so far. The present paper is

focused on neutron diffraction studies of the crystal structure of the $\text{Mg}_8\text{Rh}_4\text{BD}_{3+x}$ deuteride. The obtained structural results are compared with the structures of the hydrides of both Ti,Zr,Hf- and Mg-based compounds.

2. Experimental details

The $\text{Mg}_8\text{Rh}_4\text{B}$ alloy was prepared by sintering a mixture of pure elemental powders ($\geq 99.9\%$) at high temperature in purified argon. The alloy was annealed at 500°C for 10 days. Hydrogenation was performed in a Sieverts-type apparatus under a hydrogen pressure of 0.1-4.5 MPa at 100°C after preliminary activation

of the sample by heating in vacuum at 350°C for 15 min. The amount of absorbed hydrogen was determined by the volumetric method.

Phase and structural analyses of the alloy and its hydride (deuteride) were performed on X-ray diffraction data collected using DRON-3.0 and Brucker D8 ($\text{Cu K}\alpha$) diffractometers. The neutron powder diffraction (NPD) data of the deuteride at 300 K and 10 K were collected on the 3T2 diffractometer at the Laboratoire Léon Brillouin (LLB) at Saclay. The wavelength was 1.225 \AA and the angular range $5^\circ < 2\theta < 120^\circ$ with a step of 0.05° . The obtained XRD and NPD data were refined by the Rietveld method, using the FullProf program [26].

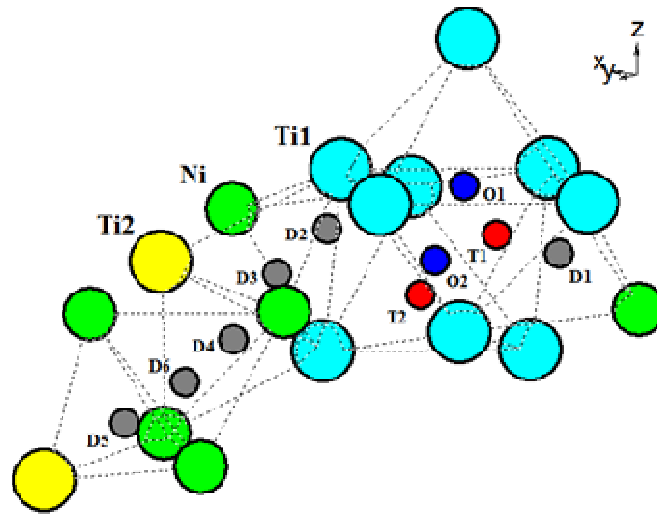


Fig. 1 Tetrahedral (D), octahedral (O) and triangular (T) interstices in the structure type Ti_2Ni .

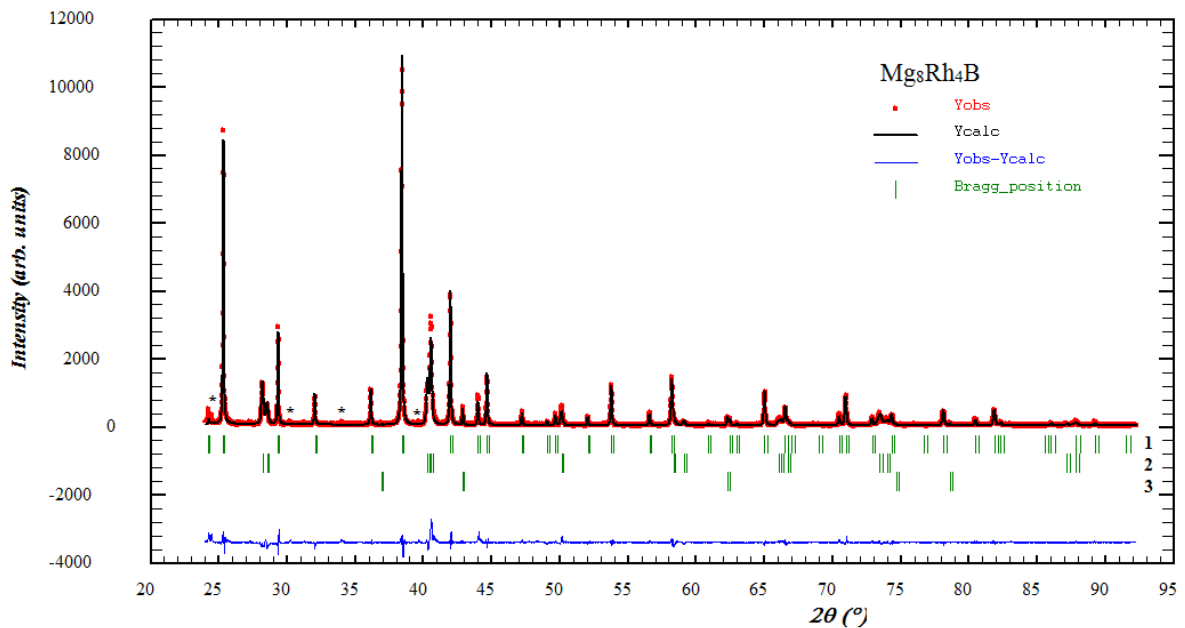


Fig. 2 X-ray diffraction pattern of the as-prepared $\text{Mg}_8\text{Rh}_4\text{B}$ sample (1 – main phase, 2 – MgRh, 3 – MgO, * – unidentified phases).

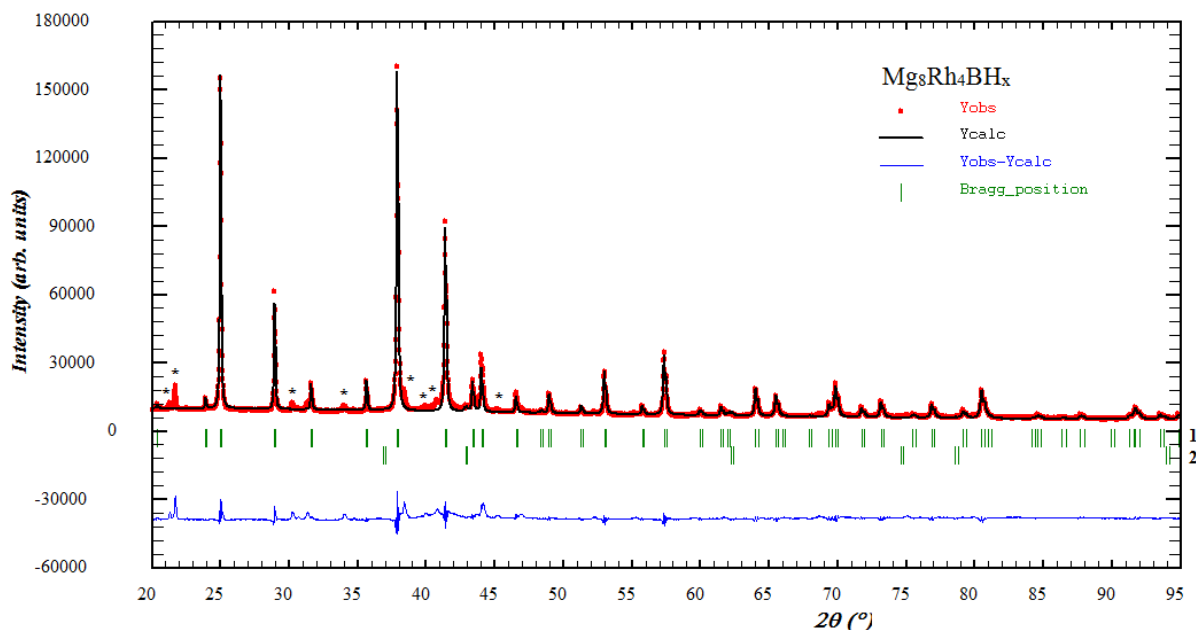


Fig. 3 X-ray diffraction pattern of the $\text{Mg}_8\text{Rh}_4\text{B}$ sample after hydrogenation (1 – main phase, 2 – MgO , * – unidentified phases).

3.1. Results and discussion

3.1. Crystal structure and hydrogenation properties of the $\text{Mg}_8\text{Rh}_4\text{B}$ boride

An X-ray diffraction pattern of the as-prepared $\text{Mg}_8\text{Rh}_4\text{B}$ sample is presented in Fig. 2. The calculated lattice parameter $a = 12.1646(3)$ Å for $\text{Mg}_8\text{Rh}_4\text{B}$ is in good agreement with literature data [23]. The small additional peaks observed in the XRD pattern could not be attributed to any known binary or ternary (Mg–Rh–B) compound, and may belong to an unknown ternary phase. The volumetric method indicated a hydrogen content of 10 H/f.u. at 4.3 MPa, whereas the deuterium content was estimated to be close to 3.3 D/f.u. at 3 MPa and 298 K. It was found that upon hydrogenation of $\text{Mg}_8\text{Rh}_4\text{B}$ the cubic symmetry of the parent compound is preserved (Fig. 3). The XRD patterns of the hydride and deuteride are very similar, with close cubic cell parameters ($a = 12.3346(2)$ Å and $12.3295(2)$ Å, respectively) and a cell volume expansion of 4.1–4.3%. No hydrogen desorption was observed up to at least 2 weeks for the hydride, which means that at atmospheric pressure and room temperature the H and D content is stabilized around $3+x$ H(D)/f.u.

3.2. Crystal structure of $\text{Mg}_8\text{Rh}_4\text{BD}_{3+x}$ at 300 and 10 K

The results of the Rietveld refinement of the neutron diffraction patterns of the $\text{Mg}_8\text{Rh}_4\text{BD}_{3+x}$ deuteride are presented in Fig. 4. The atomic parameters are given in Table 2. In the structure of the $\text{Mg}_8\text{Rh}_4\text{BD}_{3+x}$ deuteride (Fig. 5), the Mg atoms occupy two independent positions, 48f and 16c; the rhodium atoms are in the 32e sites. The B atoms fully occupy the 8a sites.

Deuterium atoms were found to fill the 16d (D1) and 32e (D2) sites by 11% and 81%, respectively. The total refined D content of 3.45(6) D/f.u. is close to that estimated by the volumetric method.

Coordination polyhedra of the atoms in the $\text{Mg}_8\text{Rh}_4\text{BD}_{3+x}$ structure are shown in Fig. 6. Ignoring the deuterium atoms, deformed 14-vertex Frank-Kasper polyhedra can be considered for the Mg1 and Mg2 atoms, *i.e.* $[\text{Mg}_{10}\text{Rh}_4]$ and $[\text{Mg}_6\text{Rh}_6\text{B}_2]$, respectively. The rhodium atoms are surrounded by four-capped deformed trigonal prisms, $[\text{Mg}_9\text{B}]$. The boron atoms are located at the centers of two nested tetrahedra, $[\text{Mg}_4\text{B}_4]$. Octahedral environment, $[\text{Mg}_8]$, can be seen for the D1 atoms, while the D2 atoms are located at the centers of $[\text{Mg}_3]$ triangles, or tetrahedra $[\text{Mg}_3\text{Rh}]$ if the neighboring rhodium atom is included.

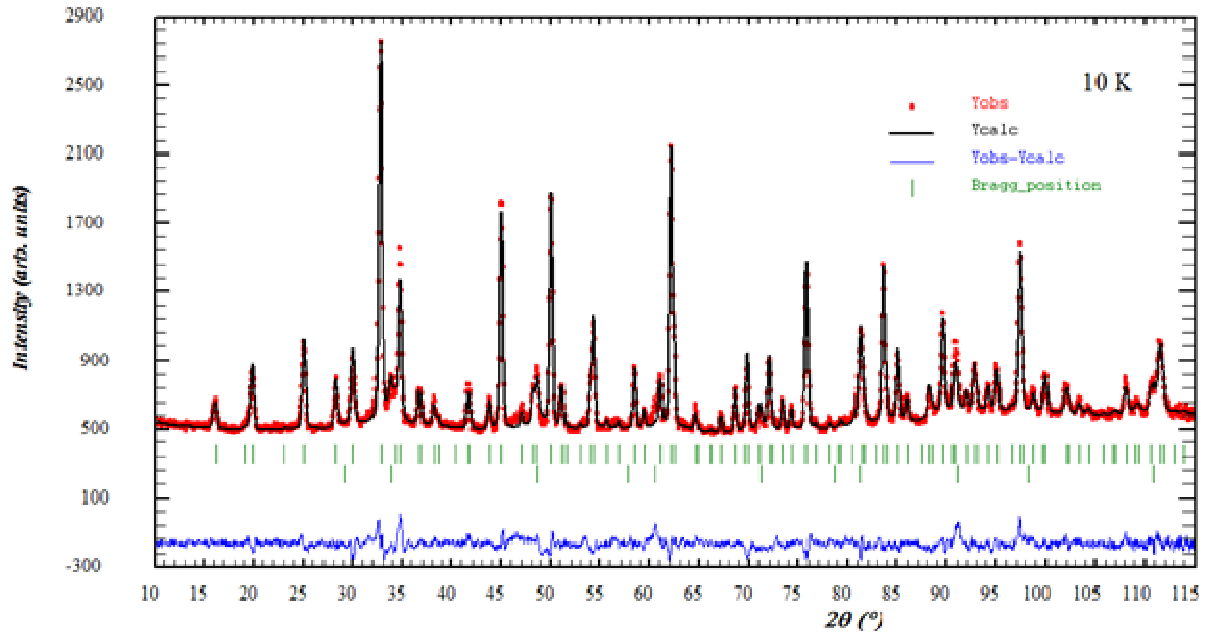
The interatomic distances and the coordination numbers are presented in Table 3. The analysis of the interatomic distances clearly indicates strong Mg–Mg, Mg–Rh and Rh–B interactions. These distances are considerably shorter than the sum of the atomic radii of the corresponding elements [22]. The Mg–D distances are in good agreement with the sum of the atomic radii of Mg and D (2.06 Å). The Mg–B distances are somewhat longer than the sum of $r_{\text{Mg}} + r_{\text{B}}$ (2.51 Å).

3.3. Comparison with other structures

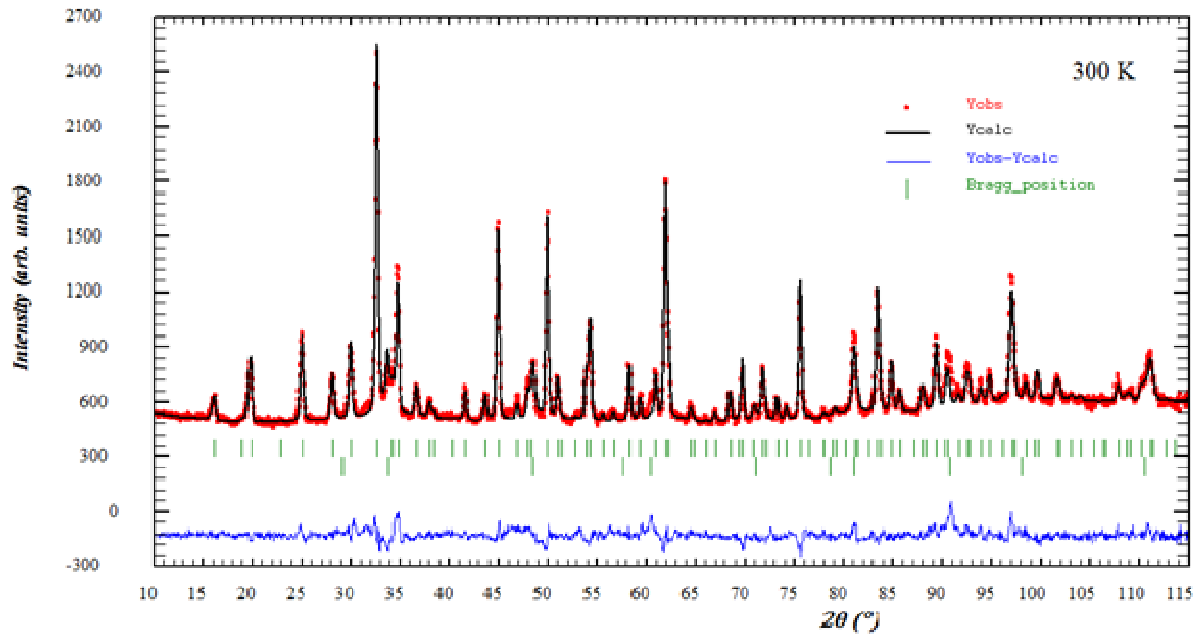
It is worth mentioning that the structures of the three studied Mg-based deuterides, $\text{Mg}_2\text{RhD}_{1.1}$, $(\text{Mg}_{1.5}\text{Mn}_{0.5})\text{NiD}_{0.92}$ ($=\text{Mg}_3\text{MnNi}_2\text{D}_{1.83}$) and $\text{Mg}_2\text{Rh}(\text{B}_{0.25}\text{D}_{0.86})$ ($=\text{Mg}_8\text{Rh}_4\text{BD}_{3.45}$), are close to each other and characterized by a $\text{Mg}_2\text{M}/(\text{D},\text{B})$ ratio ~ 1 (Table 4). Similarly to the Ti_2Ni structure, the magnesium and transition metal atoms, Ni, Mn and

Rh, occupy three independent sites, $48f$, $32e$ and $16c$. In the $\text{Mg}_3\text{MnNi}_2\text{D}_{1.83}$ phase only two interstitial sites, octahedral $16d$ [Mg_6] and tetrahedral $32e$ [Mg_3Ni], are filled by deuterium atoms with preferred occupation of the octahedral position. The same sites accommodate the deuterium atoms in the $\text{Mg}_8\text{Rh}_4\text{BD}_{3.45}$ structure, and one more, the tetrahedral $8a$ site [Rh_4], is fully

occupied by boron. An interesting difference can be seen for the $\text{Mg}_2\text{RhD}_{1.1}$ phase, where the D atoms also partially occupy octahedral $8b$ [Mg_6] and tetrahedral $8a$ [Rh_4] interstices. It should be noted that in both the binary $\text{Mg}_2\text{RhD}_{1.1}$ and ternary $\text{Mg}_8\text{Rh}_4\text{BD}_{3.45}$ deuterides, the deuterium atoms prefer to occupy the tetrahedral [Mg_3Rh] site.



(a)



(b)

Fig. 4 Observed (\bullet), calculated (line) and difference (bottom line) Rietveld profiles for neutron powder diffraction of the $\text{Mg}_8\text{Rh}_4\text{BD}_{3+x}$ deuteride at 10 K (a) and 300 K (b).

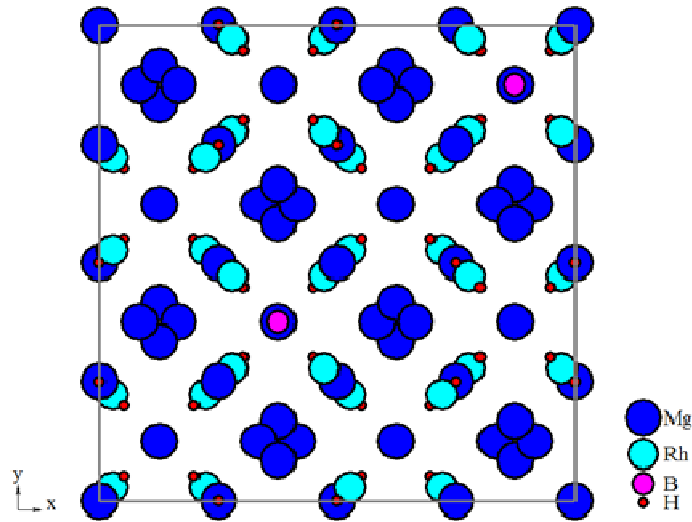


Fig. 5 Projection of the structure of $\text{Mg}_8\text{Rh}_4\text{BD}_{3+x}$ onto the XY plane.

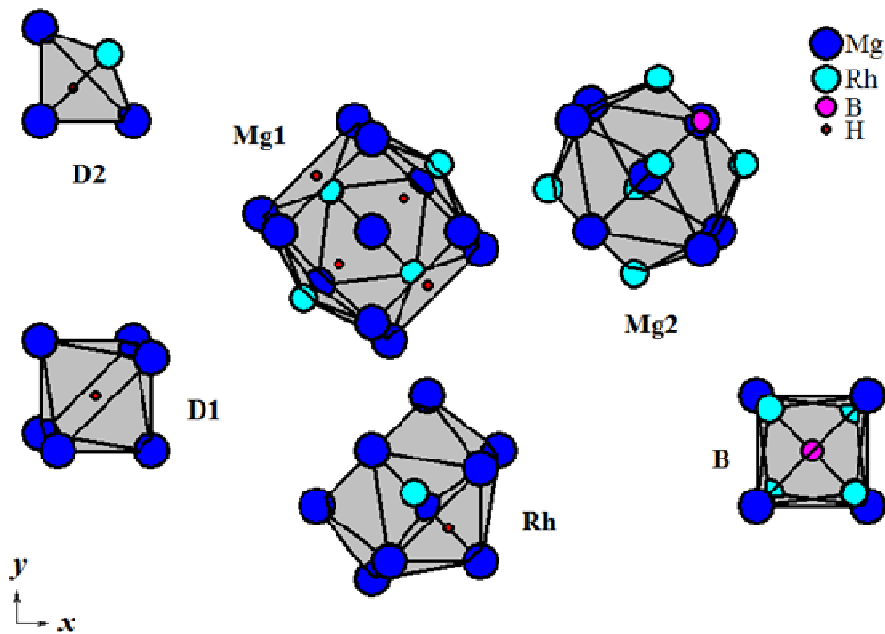


Fig. 6 Atomic environments in the structure of $\text{Mg}_8\text{Rh}_4\text{BD}_{3+x}$.

Table 1 Atom positions and coordinates of the interstices in the Ti_2Ni structure.

Atom	Site	x	y	z	Polyhedron
Ti1	48f	0.4360	$\frac{1}{8}$	$\frac{1}{8}$	–
Ti2	16c	0	0	0	–
Ni	32e	0.2130	x	x	–
O1	8b	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	[Ti ₆]
O2	16d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	[Ti ₆]
D1	32e	0.28725	x	x	[Ti ₃ Ni]
D2	96g	0.02525	x	0.34975	[Ti ₃ Ni]
D3	192i	0.00925	0.11900	0.31850	[Ti ₂ Ti ₂ Ni]
D4	96g	0.09375	x	0.97200	[Ti ₁ Ti ₂ Ni ₂]
D5	32e	0.07175	x	x	[Ti ₂ Ni ₃]
D6	8a	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	[Ni ₄]
T1	96g	0.02133	x	0.39533	[Ti ₃]
T2	32e	0.43800	x	x	[Ti ₃]

Table 2 Crystallographic data for the Mg₈Rh₄BD_{3+x} deuteride at 10 (top) and 300 K (bottom).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} (Å ²)	Occupancy
Mg1	48 <i>f</i>	0.41539(16)	1/8	1/8	0.46(3)	1
Mg2	16 <i>c</i>	0	0	0	0.46(6)	1
Rh	32 <i>e</i>	0.22218(11)	<i>x</i>	<i>x</i>	0.35(4)	1
B	8 <i>a</i>	1/8	1/8	1/8	0.56(9)	1
D1	16 <i>d</i>	1/2	1/2	1/2	0.91(5)	0.11(-)
D2	32 <i>e</i>	0.30156(13)	<i>x</i>	<i>x</i>	0.91(5)	0.81(-)

a = 12.2868(3) Å, R_B = 6.90%, R_F = 5.09%, R_p = 2.77%, R_{wp} = 3.71%, χ^2 = 3.61 (10 K).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso} (Å ²)	Occupancy
Mg1	48 <i>f</i>	0.41515(21)	1/8	1/8	0.88(5)	1
Mg2	16 <i>c</i>	0	0	0	0.38(7)	1
Rh	32 <i>e</i>	0.22191(13)	<i>x</i>	<i>x</i>	0.54(5)	1
B	8 <i>a</i>	1/8	1/8	1/8	1.06(12)	1
D1	16 <i>d</i>	1/2	1/2	1/2	2.00(11)	0.11(1)
D2	32 <i>e</i>	0.30078(17)	<i>x</i>	<i>x</i>	2.00(11)	0.81(1)

a = 12.3147(4) Å, R_B = 8.87%, R_F = 7.21%, R_p = 2.81%, R_{wp} = 3.92%, χ^2 = 3.91 (300 K).

Refined composition: Mg₈Rh₄BD_{3.45(6)} (300 K).

Table 3 Interatomic distances (*d*, Å) and coordination numbers (CN) in the structure of Mg₈Rh₄BD_{3+x}.

Atoms		<i>d</i> _{10K}	<i>d</i> _{300K}	CN
Mg1:	2D2	2.104(2)	2.112(3)	18
	2D1	2.408(1)	2.415(1)	
	2Rh	2.746(1)	2.756(2)	
	2Rh	2.913(2)	2.917(3)	
	2Mg2	2.974(1)	2.979(2)	
	4Mg1	3.151(1)	3.157(1)	
	4Mg1	3.642(1)	3.655(3)	
Mg2:	2B	2.660(1)	2.666(1)	14
	6Rh	2.772(1)	2.776(2)	
	6Mg1	2.974(1)	2.979(2)	
Rh:	1D2	1.689(2)	1.682(3)	11
	1B	2.068(1)	2.067(2)	
	3Mg1	2.746(1)	2.756(2)	
	3Mg2	2.772(1)	2.776(2)	
	3Mg1	2.913(2)	2.917(3)	
B:	4Rh	2.068(1)	2.067(2)	8
	4Mg2	2.660(1)	2.666(1)	
D1:	8Mg1	2.408(1)	2.415(1)	8
D2:	3Mg1	2.104(2)	2.112(3)	4
	1Rh	1.689(2)	1.682(3)	

Table 4 Coordinates of the metal positions and occupied interstices in deuterides with Ti₂Ni-type substructure.

Deuteride	Mg ₂ RhD _{1,1}	Mg ₃ MnNi ₂ D _{1,83}	Mg ₈ Rh ₄ BD _{3,45}
<i>Metal positions:</i>			
48f ($x \frac{1}{8} \frac{1}{8}$) $x \sim 0.42$	1 Mg	1 Mg	1 Mg
32e ($x x x$) $x \sim 0.22$	1 Rh	1 Ni	1 Rh
16c (0 0 0)	1 Mg	1 Mn	1 Mg
<i>Interstitial sites:</i>			
8a ($\frac{1}{8} \frac{1}{8} \frac{1}{8}$)	0.64D	-	1B
8b ($\frac{3}{8} \frac{3}{8} \frac{3}{8}$)	0.09D	-	-
16d ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$)	0.31D	0.72D	0.11D
32e ($x x x$) $x \sim 0.29$	0.80D	0.55D	0.81D

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