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Synthesis and structure of $Yb_{19}Mg_8H_{54}$, a new salt-like ternary metal hydride

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Abstract

The structure of $Yb_{19}Mg_8H_{54}$ was established from X-ray single-crystal and neutron powder diffraction and found to be of a new type. It has cubic symmetry, space group $Im\bar{3}$ (No. 204), $Z = 2$, hydride: $a = 12.1066(8)$ Å (X-ray single-crystal data at 295 K), deuteride: $a = 12.0974(2)$ Å (X-ray powder data at 295 K), and 12.0666(2) Å (neutron powder data at 50 K), and consists of a distorted body-centred cubic cation arrangement in which the deuteride anions occupy four types of tetrahedral interstices, $2\times[Yb_4]$, $[Yb_3Mg]$, $[Yb_2Mg_2]$. The Yb sites have eight-, ten- and twelve-fold, and the Mg site six-fold deuterium coordination. The metal–deuterium bond distances range from 1.95 to 2.00 Å (Mg–D), and from 2.19 to 2.49 Å (Yb–D).

Keywords: Ytterbium magnesium hydrides; Neutron powder diffraction; Saline hydrides; Ternary metal hydrides

1. Introduction

Recently we have reported the first ternary compound in the ytterbium magnesium hydrogen system. It has the composition $Yb_4Mg_3H_{14}$ [1], and crystallizes with a hexagonal structure in which four symmetry-independent hydrogen atoms have tetrahedral, trigonal bipyramidal and triangular metal coordinations. During the investigation of the Yb–Mg–Co–H system [2], we have accidentally found a single crystal of another ternary metal hydride. It has the composition $Yb_{19}Mg_8H_{54}$ and crystallizes with a body-centred cubic structure. In this communication we report on its synthesis in bulk form and on its structure analysis by X-ray and neutron diffraction.

2. Experimental details

2.1. Synthesis

Binary alloys of nominal composition YbMg and $Yb_{19}Mg_8$ were prepared from the elements (Yb: Alfa, 99.9%; Mg: CERAC, 1/8 in pieces) by arc-melting. YbMg powder was mixed with LiH powder, wrapped into molybdenum foil, and placed in an autoclave. The autoclave was charged with hydrogen gas (Polygaz, Genève, Switzerland; 99.9999%) 75 bar at room temperature. The temperature was increased to 803 K, yielding a hydrogen pressure of 150 bar, held at that temperature for 3 weeks, during which the pressure decreased to 100 bar, and then cooled to room temperature. The samples contained dark grey translucent single crystals which were later identified as $Yb_{19}Mg_8H_{54}$.

Powder samples of the deuteride were obtained from the reaction of binary alloy powders of nominal composition $Yb_{19}Mg_8$ with deuterium (AGA, 99.8%) at 798 K and 90–100 bar pressure for 6 days. Treatments at lower temperatures and/or higher pressures favoured the formation of the previously reported deuteride $Yb_4Mg_3D_{14}$, whereas treatments at higher temperatures and/or lower pressures led to a segregation into binary YbD_2 and Mg metal. In all cases the final products had a blackish colour and were stable in air.

2.2. X-ray diffraction

A single crystal of irregular shape (~0.12 mm) was mounted on a Philips PW1100 automatic four-circle diffractometer (Mo Kα radiation, graphite mono-

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chromator). The cell parameter ($a = 12.1066(8)$ Å) was refined from 2θ values of 34 reflections. 6183 reflections were collected out to $(\sin\theta/\lambda) = 0.746$ Å^{-1} ($-18 < h < 18$, $-18 < k < 18$, $0 < l < 18$) in the ω-2θ scan mode. The reflection conditions ($h + k + l = 2n + 1$) and symmetry-equivalent reflections were consistent with the cubic space groups $I23$, $I2_13$, $Im\bar{3}$ ($R_{int} = 6.9\%$). The intensities of the reflections ($3h$ $3k$ 0), ($6h$ 0 0), ($6h$ $3k$ $3l$) etc. were relatively strong, thus suggesting the heavy metal atoms occupy the sites (~ 0.33, ~ 0.33, 0), (~ 0.33, 0, 0) and (0, 0, 0) etc. The magnesium positions were obtained from electron density maps. The structure model as described in the space group $Im\bar{3}$ was refined from 509 unique reflections and yielded the residuals $R = 5.9\%$ and $wR = 7.5\%$ (see Table 1). None of the hydrogen sites could be identified, since electron density peaks of up to 4.6 eÅ^{-3} occurred in the difference Fourier map near the metal atom positions. The calculations were performed by using the XTAL 3.2 system [3].

The deuteride samples were characterized by X-ray powder diffraction (Huber 645 Guinier diffractometer [4], Cu Kα_1 radiation). They contained $Yb_{19}Mg_8D_{54}$ with cell parameter $a = 12.0974(2)$ Å as the main phase, and $YbD_{2.6}$ (cubic high pressure phase [5] with $CeD_{\sim 3}$-like structure [6]), $Yb_4Mg_3D_{14}$ [1], and YbD_2 (orthorhombic low pressure phase with $PbCl_2$-type structure [7]) as secondary phases. Profile refinements as performed by DBWS-9006 [8] converged at residuals $R_B = 7.6\%$, $R_{wp} = 15.4\%$, $R_p = 11.6\%$. The atomic parameters obtained are in good agreement with the X-ray values of the hydride single-crystal.

Table 1
Refinement results of $Yb_{19}Mg_8D_{54}$ on neutron powder data ($T = 50$ K) and comparison with X-ray single crystal data on hydride (second lines, $T = 295$ K)

Atom	Position	x	y	z	U_{iso}(Å^2 × 100)
Yb1	*24(g)*	0	0.3134(5)	0.3456(6)	0.81(6)
		0	*0.3113(2)*	*0.3472(2)*	*1.60(5)*
Yb2	*12(d)*	0.3343(9)	0	0	U_{Yb1}
		0.3323(1)	*0*	*0*	*0.46(6)*
Yb3	*2(a)*	0	0	0	U_{Yb1}
		0	*0*	*0*	*0.56(6)*
Mg	*16(f)*	0.154(1)	0.154(1)	0.154(1)	U_{Yb1}
		0.1582(5)	*0.1582(5)*	*0.1582(5)*	*0.9(2)*
D1	*48(h)*	0.3137(7)	0.1142(6)	0.171(1)	2.1(1)
D2	*24(g)*	0	0.400(1)	0.186(1)	U_{D1}
D3	*24(g)*	0	0.168(1)	0.108(1)	U_{D1}
D4	*12(e)*	0.121(2)	1/2	0	U_{D1}

Space group $Im\bar{3}$ (No. 204).
Cell parameter $a = 12.0666(2)$ Å (deuteride powder, neutrons, $T = 50$K);
$a = 12.1066(8)$ Å (hydride single crystal, X-rays, $T = 295$ K).
Agreement indices:
neutron data $R_B = 4.6\%$, $R_p = 5.3\%$, $R_{wp} = 6.8\%$, $S = 0.98$.
X-ray data $R_F = 5.9\%$, $R_w = 7.5\%$.
Form of temperature factor: $T = \exp[-8\pi^2 U_{iso}(\sin\theta/\lambda)^2]$.

Estimated standard deviations in parentheses.

2.3. Neutron diffraction

The atomic positions and displacement amplitudes of hydrogen were established by neutron powder diffraction on the deuteride sample by using the D1A diffractometer at the reactor ORPHEE at CEN Saclay (Ge(511) monochromator, neutron wavelength $\lambda = 1.9980$ Å, angular range 3.0–160.0°, angular step $\Delta 2\theta = 0.05°$, $T = 50$ K, sample size about 4 g, cylindrical vanadium container with 8 mm inner diameter). (The diffractomer D1A, belonging to the Institute Laue–Langevin (ILL), was installed at a cold neutron guide of the Laboratoire Léon Brillouin during the refurbishment of the ILL reactor.) The deuterium atom arrangement was solved by trial and error, and found to involve four tetrahedral metal interstices. The structures of four phases were refined by the Rietveld method (program DBWS-9006), $Yb_{19}Mg_8D_{54}$, $Yb_4Mg_3D_{14}$ [1], $YbD_{2.6}$ and YbD_2. Their relative amount was estimated from the relation [9]:

Table 2
Selected bond lengths (Å) up to 2.9 Å, and the shortest D–D contact distances (Å) in $Yb_{19}Mg_8D_{54}$ ($T = 50$ K, neutron powder data)

Yb1–D2	2.19(1)
–2D2	2.220(9)
–2D1	2.24(1)
–D4	2.287(7)
–2D1	2.420(9)
Yb2–2D2	2.38(1)
–2D3	2.39(2)
–2D4	2.48(2)
–4D1	2.49(1)
Yb3–12D3	2.41(1)
Mg–3D3	1.95(1)
–D1	2.00(1)
D1–Mg	2.00(1)
–Yb1	2.24(1)
–Yb1	2.420(9)
–Yb2	2.49(1)
–D2	2.47(1)
D2–Yb1	2.19(1)
–2Yb1	2.220(9)
–Yb2	2.38(1)
–D2	2.41(2)
–2D1	2.47(1)
–D4	2.62(2)
D3–2Mg	1.95(1)
–Yb2	2.39(2)
–Yb3	2.41(1)
–D3	2.52(1)
D4–2Yb1	2.287(7)
–2Yb2	2.48(2)
–2D2	2.62(2)

Estimated standard deviations in parentheses.

$$W_p = S_p(ZMV)_p / \sum_i S_i(ZMV)_i$$

where S, Z, M and V are, respectively, the Rietveld scale factor, the number of formula units per unit cell, the molar mass and the unit-cell volume, and found to be ~48 wt.% for $Yb_{19}Mg_2D_{54}$, ~22 wt.% for $YbD_{2.6}$, ~22 wt.% for YbD_2 and ~8 wt.% for $Yb_4Mg_3D_{14}$. The following 39 parameters were allowed to vary: 1 zero; 4 scale; 6 background; 6 half-width; 1 mixing; 7 lattice; 12 positional; 2 thermal displacement. The nuclear scattering lengths (fm), 6.671 (D), 5.375 (Mg), 12.43 (Yb), were taken from Ref. [10]. Preliminary refinements showed that the occupancy factors of the four deuterium sites in $Yb_{19}Mg_8D_{54}$ did not differ significantly from 100%. Thus, they were fixed at unity in the final refinement.

Refinement results on neutron and X-ray diffraction data are summarized in Table 1. Selected bond distances and deuterium–deuterium contact distances for $Yb_{19}Mg_8D_{54}$ are given in Table 2. The observed, calculated and difference neutron patterns are shown in Fig. 1, and a structure drawing is given in Fig. 2.

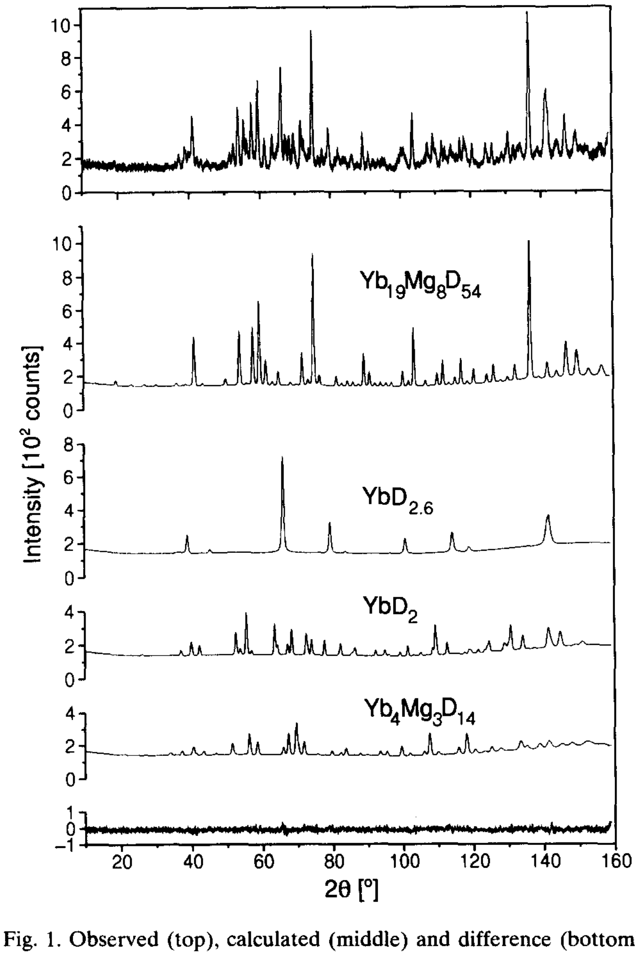

Fig. 1. Observed (top), calculated (middle) and difference (bottom) neutron diffraction patterns of a sample containing $Yb_{19}Mg_8D_{54}$ (main phase), and $YbD_{2.6}$, YbD_2 and $Yb_4Mg_3D_{14}$ (secondary phases) ($\lambda = 1.9980$ Å, $T = 50$ K).

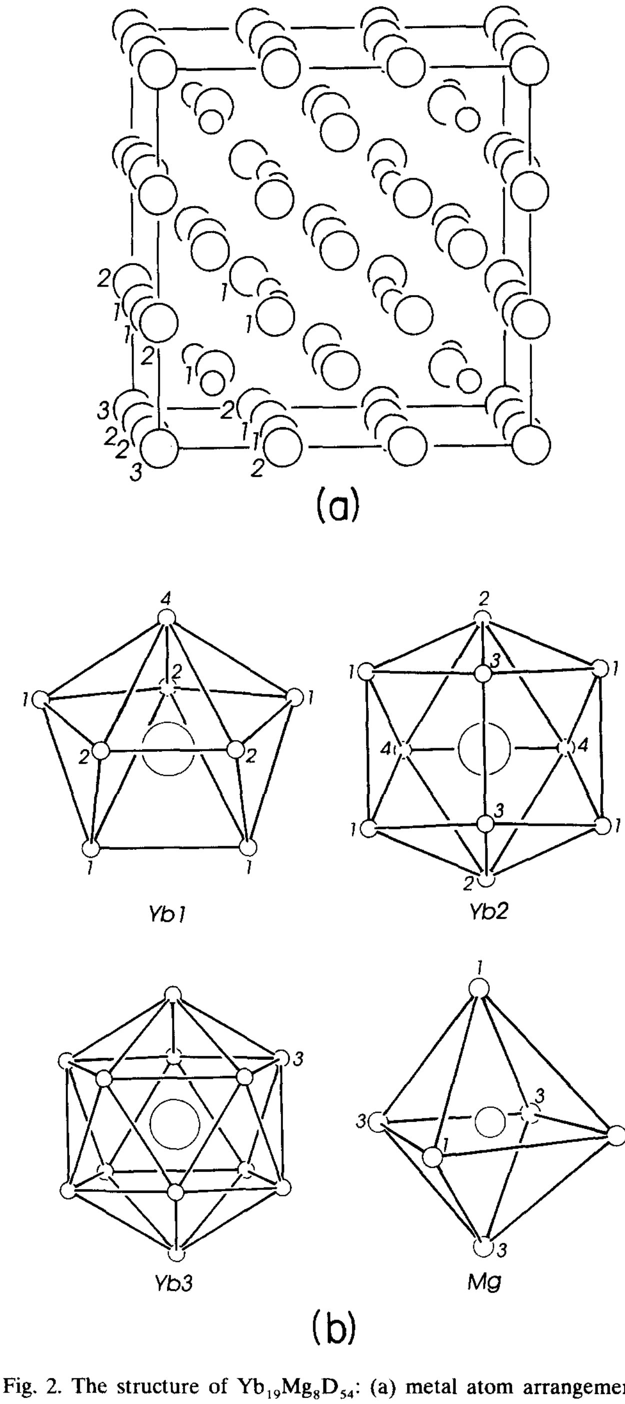

Fig. 2. The structure of $Yb_{19}Mg_8D_{54}$: (a) metal atom arrangement with distorted W-type structure (Yb sites numbered), (b) deuterium coordination polyhedra around the metal atoms (D sites numbered); large, medium and small circles are Yb, Mg and D atoms, respectively.

3. Results and discussion

$Yb_{19}Mg_8D_{54}$ is a new and presumably salt-like ternary metal deuteride in which ytterbium is divalent. In contrast to most other salt-like deuterides it has no known fluoride analogue. Its structure can be described as a body-centred cubic metal atom arrangement with distorted W-type structure (Fig. 2(a)). It contains three ytterbium sites which have eight-fold irregular (Yb1: [4D1, 3D2, D4]), ten-fold irregular (Yb2: [4D1, 2D2, 2D3, 2D4]) and twelve-fold icosahedral (Yb3: [12D3]) deuterium configurations, compared to the nine-fold irregular deuterium configuration in YbD_2 [7], and one magnesium site which has a distorted octahedral deuterium coordination similar to the regular one in binary MgD_2 (rutile structure) (Fig. 2(b)). The deuteride anions occupy four types of tetrahedral interstice: D1, [3Yb, Mg]; D2, [4Yb]; D3, [2Yb, 2Mg]; D4, [4Yb]. The shortest magnesium–deuterium bond distances (1.95 Å) are close to those in binary MgD_2 (1.95 Å), and longer than those in the ternary $Yb_4Mg_3D_{14}$ (1.84 Å) [1]. The shortest ytterbium–deuterium bond distance (2.19 Å) is shorter than that in YbD_2 (2.33 Å) [7] and $Yb_4Mg_3D_{14}$ (2.27 Å) [1].

As to the thermal stability, preliminary experiments suggest that $Yb_{19}Mg_8H_{54}$ is more stable than $Yb_4Mg_3H_{14}$. This correlates with their different Yb/Mg ratios, and the fact that ytterbium forms a more stable binary hydride (YbH_2: $\Delta H = -178$ kJ per mol H_2 [12]) than magnesium (MgH_2: $\Delta H = -74$ kJ per mol H_2 [12]). The calculated hydrogen densities are 101 g l^{-1} and 1.5 wt%.

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References

[1] F. Gingl, K. Yvon and P. Fischer, *J. Alloys Comp.*, *201* (1993) 105.
[2] B. Huang, K. Yvon and P. Fischer, *J. Alloys Comp.* (1995) in press.
[3] S.R. Hall, H.D. Flack and J.M. Stewart (eds), *XTAL 3.2 Users Manual*, Universities of Western Australia, Geneva and Maryland, 1993.
[4] J. Ihringer, *J. Appl. Crystallogr.*, *15* (1982) 1.
[5] W. Iwasieczko, H. Drulis and R.M. Frak, *J. Alloys Comp.*, *180* (1992) 265, and references therein.
[6] J. Schefer, P. Fischer, W. Hälg, J. Osterwalder, L. Schlapbach and J.D. Jorgensen, *J. Physics C: Solid State Physics*, *17* (1984) 1575.
[7] P. Fischer, J. Schefer and K. Tichy, *J. Less-Common Met.*, *94* (1983) 151.
[8] D.B. Wiles and R.A. Young, *J. Appl. Crystallogr.*, *14* (1981) 149; see also A. Sakthivel and R.A. Young, *Programs DBWS-9006 and DBWS-9006PC;* School of Physics, Georgia Institute of Technology, Atlanta, GA 30332, 8 June 1990.
[9] R.J. Hill and C.J. Howard, *J. Appl. Crystallogr.*, *20* (1987) 467.
[10] V.F. Sears, *Neutron News*, *3*(3) (1992) 26.
[11] J.P. Bastide, A. Bouamrane, J. Carré, P. Claudy, J.M. Letoffé and D. Mourksi, *J. Alloys Comp.*, *191* (1993) 21.
[12] R. Griessen and T. Riesterer, in L. Schlapbach (ed.), *Hydrogen in Intermetallic Compounds I, Topics Appl. Phys.*, Vol. 63, Springer, Berlin, 1988, p. 219.