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New iron(II) complex metal hydrides with $SrMg_2FeH_8$ type structure

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Abstract

$BaMg_2FeH_8$ and $EuMg_2FeH_8$ were prepared by sintering mixtures of $BaMg_2$ ($EuMg_2$) alloys and Fe at 780–790 K and 120–155 bar hydrogen (deuterium) pressure in a LiH flux. They crystallize with the trigonal $SrMg_2FeH_8$ structure type, space group $P\bar{3}m1$; $BaMg_2FeH_8$: $a = 4.5775(3)$ Å, $c = 6.9263(7)$ Å; $EuMg_2FeH_8$: $a = 4.5078(1)$ Å, $c = 6.5182(2)$ Å. Neutron powder diffraction on the deuteride $BaMg_2FeD_8$ ($a = 4.5683(4)$ Å, $c = 6.9163(3)$ Å) yields the bond distances [Fe–6D1] = 1.577(3) Å for the octahedral $[FeD_6]^{4-}$ complex, and [D2–3Ba] = 1.742(2) Å and [D2–Mg] = 1.916(8) Å for the tetrahedrally coordinated deuterium anions.

Keywords: Quaternary metal hydrides; Neutron powder diffraction; Transition metal hydride complexes; Complex metal hydrides

1. Introduction

The iron based complex transition metal hydrides currently known all contain octahedral 18-electron $[Fe(II)H_6]^{4-}$ anions. Their Fe–D bond distances are strongly influenced by the matrix of the non-transition metal cations [1]. In this communication we present the Ba and Eu analogues of $SrMg_2FeH_8$ [2]. The $[FeH_6]^{4-}$ anions in this structure are surrounded by cubes of cations which consist of six equatorial Mg^{2+} and two apical M^{2+} (M = Sr, Ba, Eu). The cubes are connected via equatorial Mg^{2+} to slabs, and the slabs are connected via apical M^{2+} to a three dimensional matrix. Our structure analysis shows that the Fe–D distances in that matrix are not much influenced by the apical M^{2+}.

2. Experimental details

2.1. Synthesis

Binary alloys of composition MMg_2 (M = Ba, Eu) were prepared from the elements (Ba: JMG, rod, 99%; Mg: CERAC, 1/8″, 99.99%; Eu: Alfa Products, ingots, 3N) by arc-melting. An excess of about 5 at.% Mg was necessary to compensate for evaporation losses. The single phase ingots ($MgZn_2$ type structure) were powdered, mixed with iron powder (CERAC, 400 mesh, 99.6%) and lithium hydride (deuteride) powder (Alfa products, 98%) at the atomic ratios MMg_2:Fe:LiH (LiD) = 1:1:0.30, wrapped into molybdenum foil, and placed in a high-temperature high-pressure autoclave. LiH (LiD) was added as a flux agent. After evacuating to about 10^{-5} bar and flushing several times with argon, the autoclave was charged with hydrogen (deuterium) gas (H_2: Polygaz, 6N; D_2: AGA, 99.8%) to an initial pressure of about 75 bar at room temperature. The temperature was increased to 780–790 K, yielding a hydrogen (deuterium) pressure of 155 bar, held at that level for 6–14 days, during which the pressure decreased to about 120 bar, and then lowered to ambient conditions. After releasing the hydrogen (deuterium) pressure the autoclave was opened and the samples were transferred to an argon-filled glovebox. They had a brownish (Ba sample) or yellow colour (Eu sample), and were sensitive to air.

2.2. X-ray and neutron diffraction

The samples were characterized by X-ray powder diffraction at room temperature (Guinier camera with sealed capillaries, and Guinier diffractometer [3], using Co Kα and Cu Kα_1 radiation, respectively;

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Table 1
Refinement results on neutron or X-ray powder data (T = 295 K)

	$BaMg_2FeD_8$ [a]	$EuMg_2FeH_8$ [b]
Space group	$P\bar{3}m1$	$P\bar{3}m1$
a (Å)	4.5683(4) *4.5775(3)* [b]	4.5078(1)
c (Å)	6.9163(3) *6.9263(7)* [b]	6.5182(2)
M in 1(b): *0, 1, 1/2*		
U_{iso}(Å^2 × 100)	0.3(2)	1.8(1)
Mg in 2(d): 1/3, 2/3, z	0.1147(9)	0.118(2)
U_{iso}(Å^2 × 100)	0.7(1)	0.6(4)
Fe in 1(a): *0, 0, 0*		
U_{iso}(Å^2 × 100)	0.12(8)	0.1(2)
D1 in 6(i): x, $-x$	0.1594(3)	
z	0.8631(4)	
U_{iso}(Å^2 × 100)	2.19(5)	
D2 in 2(d): *1/3, 2/3*, z	0.3917(8)	
U_{iso}(Å^2 × 100)	2.2(1)	
R values: R_B(%)	5.7	7.8
R_p(%)	4.6	5.1
R_{wp}(%)	6.6	6.6

[a] neutron powder diffraction, [b] hydride, X-ray powder diffraction. Form of temperature factor: $T = \exp[-8\pi^2 U_{iso} (\sin \theta/\lambda)^2]$. Estimated standard deviations in parentheses.

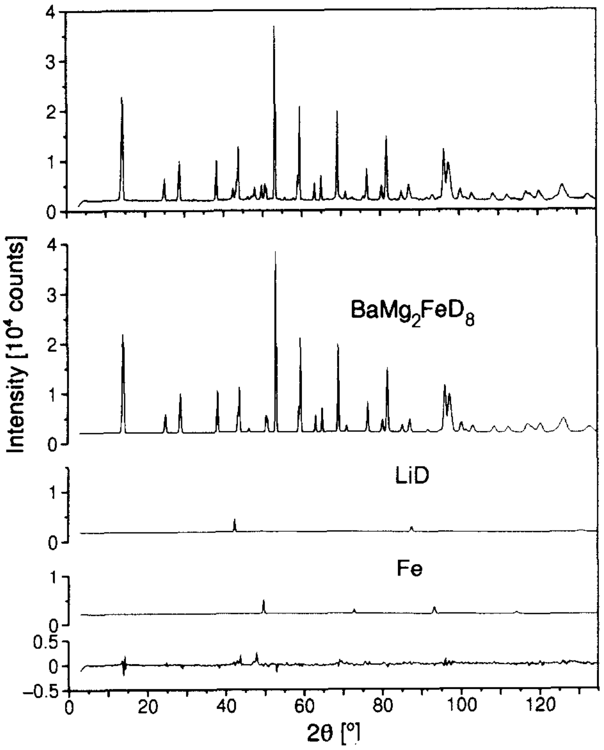

Fig. 1. Observed (top), calculated (middle) and difference (bottom) neutron diffraction patterns of a sample containing $BaMg_2FeD_8$, LiD and Fe (λ = 1.6984 Å).

internal standard: silicon powder, a = 5.4308 Å; computer-controlled microdensitometer [4]). The patterns confirmed the presence of new quaternary hydride phases crystallizing with the trigonal $SrMg_2FeH_8$ type structure [2] (space group $P\bar{3}m1$). The refined cell parameters are summarized in Table 1. The atomic parameters of the Ba compound were refined from neutron powder diffraction data collected on the deuteride by using the DMC diffractometer [5] at the reactor SAPHIR at PSI, Villigen (Ge(311); λ = 1.6984 Å, angular 2θ range 3.0–135.0°, 2θ step 0.1°, T = 295 K; sample size ~ 6 g, cylindrical vanadium container of 8 mm inner diameter, high-resolution mode). The structure was refined (DBWS-9006 [6]) by taking into account the contribution of the impurity phases LiD and Fe. The nuclear scattering lengths (fm), 6.671 (D), − 1.90 (Li), 5.375 (Mg), 9.45 (Fe) and 5.07 (Ba), were taken from Ref. [7]. The occupancy factors of the two deuterium sites were fixed at unity. Refinement results are summarized in Table 1, and the observed, calculated and difference neutron patterns are shown in Fig. 1. Interatomic distances, deuterium – deuterium contact distances, and selected D–Fe–D bond angles are given in Table 2. The metal atom parameters of $EuMg_2FeH_8$ were refined from X-ray data only because of the high absorption cross section of europium for thermal neutrons. The observed, calculated and difference X-ray patterns are shown in Fig. 2.

Table 2
Interatomic distances (Å) up to 3.5 Å, D–D contact distances (Å), and D–Fe–D bond angles (°) for $BaMg_2FeD_8$

Fe–6D1	1.577(3)
6Mg	2.754(2)
2Ba	3.4582(2)
Ba–6D2	2.742(2)
6D1	2.810(3)
2Fe	3.4582(2)
Mg–D2	1.916(8)
3D1	2.219(6)
6D1	2.290(2)
3Fe	2.754(2)
3Mg	3.078(5)
D1–Fe	1.577(3)
Mg	2.219(6)
2Mg	2.290(2)
Ba	2.810(3)
2D1	2.185(3)
D2–Mg	1.916(8)
3Ba	2.742(2)
D1–Fe–2D1	87.7(1) [a]
D1–Fe–2D1	92.3(1) [b]

[a] D1 atoms having the same z coordinate. [b] D1 atoms having different z coordinates. Estimated standard deviations in parentheses.

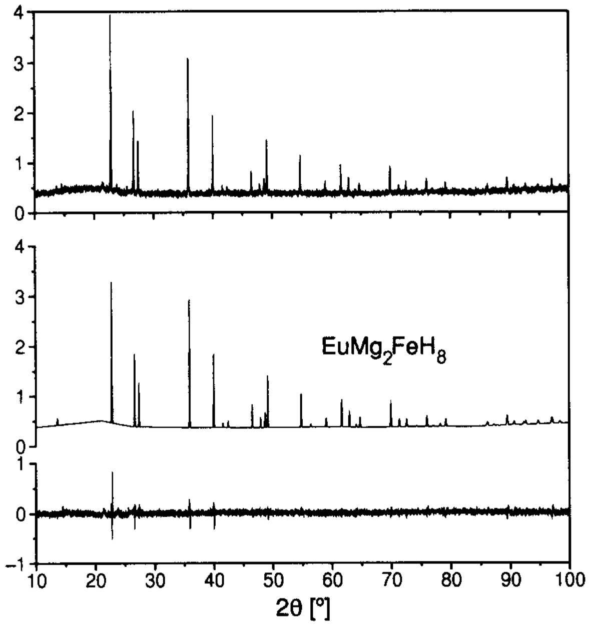

Fig. 2. Observed (top), calculated (middle) and difference (bottom) X-ray diffraction patterns of $EuMg_2FeH_8$ (Cu $K\alpha_1$).

3. Results and discussion

The present study sheds some new light onto the role of the matrix effect in complex transition metal hydrides. Its influence on the Fe–D bond distances in the octahedral $[FeD_6]^{4-}$ groups can be studied from the values listed in Table 3. In cubic M_2FeD_6 (M = Mg, Ca) the M cations surround the complex in a cubic configuration. As the smaller Mg^{2+} ($r = 0.72$ Å [10]) are substituted by the bigger Ca^{2+} ($r = 1.00$ Å [10]), the Fe–D distances increase from 1.56 Å (Mg_2FeD_6) to 1.62 Å (Ca_2FeD_6). In cubic $Ca_4Mg_4Fe_3D_{22}$, the surrounding cations form a distorted cube of interpenetrating Mg and Ca tetrahedra, and the Fe–D distances, 1.58 Å, are intermediate between those in Mg_2FeD_6 and Ca_2FeD_6. In trigonal MMg_2FeD_8 (M = Sr, Ba) the cations form elongated cubes that consist of six equatorial Mg^{2+} and two apical M^{2+}. Interestingly, bond distances and bond angles of the Ba compound, Fe–D1 = 1.577(3) Å, D1–Fe–D1 = 87.7(1)°, 92.3(1)°, do not differ significantly from those of the Sr compound, 1.578(4) Å, 87.7(2)°, 92.3(2)°, and their bond distances are slightly bigger than those in Mg_2FeD_6 (1.556(5) Å). This suggests that the Fe–D bond distances in that structure are mainly determined by the equatorial Mg which connects the complexes to Mg_2FeD_6 type structural slabs parallel to the hexagonal plane (see Fig. 2 in Ref. [2]). This is reflected by the cell parameters, which are commensurate with those in Mg_2FeH_6 ($a\sqrt{2}/2 = 4.556$ Å) and increase only little as the size of M increases (M = Eu: $a = 4.5078(1)$ Å, M = Sr: 4.5172(2) Å, M = Ba: 4.5775(3) Å). The situation perpendicular to the hexagonal plane is quite different. The M–D bond distances are much longer in the Ba compound (D2–3Ba = 2.742(2) Å, D2–Mg = 1.916(8) Å) than in the Sr compound (D2–3Sr = 2.655(3) Å, D2–Mg = 1.919(7) Å). This is reflected by the c/a ratios, which increase strongly as the cation size of M increases (Eu: $c/a = 1.4460$, Sr: 1.4536, Ba: 1.5131). These features can be taken as further evidence for the anisotropic bonding in this structure.

As to their thermal stabilities, $SrMg_2FeH_8$ and $BaMg_2FeH_8$ decompose into the elemental Fe and unknown phases at about 713 K and 723 K under 1 bar hydrogen pressure. Both hydrides are more stable than $Ca_4Mg_4Fe_3H_{22}$ (about 668 K at 1 bar H_2) and $Yb_4Mg_4Fe_3H_{22}$ (about 693 K at 1 bar H_2) [12]. The calculated hydrogen densities are 107 g l^{-1} and 3.2 wt.% for the Ba compound, and 117 g l^{-1} and 3.0 wt.% for the Eu compound.

Table 3
Fe–D bond distances (Å) and point group symmetries of octahedral complexes $[FeD_6]^{4-}$

$BaMg_2FeD_8$	D_{3d}–$\bar{3}m$ 1.577(3) (6×)	this work
$SrMg_2FeD_8$	D_{3d}–$\bar{3}m$ 1.578(4) (6×)	[2]
Mg_2FeD_6	O_h–$m\bar{3}m$ 1.556(5) (6×)	[8]
Ca_2FeD_6	O_h–$m\bar{3}m$ 1.618(5) (6×)	[9]
$Ca_4Mg_4Fe_3D_{22}$	D_{2d} –$\bar{4}2m$ 1.583(3) (4×) 1.562(5) (2×)	[11]
$Yb_4Mg_4Fe_3D_{22}$	D_{2d}–$\bar{4}2m$ 1.586(5) (4×) 1.554(7) (2×)	[12]

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