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High-pressure synthesis of novel europium magnesium hydrides $\stackrel{\text{\tiny}^{\Rightarrow}}{}$

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Abstract

Three new ternary metal hydrides of composition Eu_2MgH_6 , $\text{Eu}_6\text{Mg}_7\text{H}_{26}$ and $\text{Eu}_2\text{Mg}_3\text{H}_{10}$ have been synthesised from mixtures of the binary hydrides in a multi-anvil press at quasi-hydrostatic pressures of up to 3.2 GPa and temperatures of up to 870 K. Crystal structures of the deuterides were determined by joint refinements of neutron and synchrotron powder diffraction data. All structures have alkaline earth and fluorine analogues. Eu₂MgD₆, K₂GeF₆ type structure, space group $P\bar{3}m1$, a=550.644(6) pm, c=410.054(6) pm; Eu₆Mg₇D₂₆, Ba₆Zn₇F₂₆ type structure, I2/m, a=1409.39(4) pm, b=564.55(2) pm, c=1150.90(3) pm, $\beta=90.683(2)^\circ$; Eu₂Mg₃D₁₀, Ba₂Ni₃F₁₀ type structure, C2/m, a=1748.41(5) pm, b=572.31(2) pm, c=736.47(2) pm, $\beta=111.478(2)^\circ$. The coloured compounds are saline and show volume contractions of up to 7.3% upon formation from the binary hydrides. Eu₂MgH₆ shows Curie–Weiss paramagnetic behaviour ($\mu_{eff}=7.88 \mu_B$) and orders ferromagnetic at $T_c=31.6$ K. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, the first ternary europium magnesium hydrides $EuMgH_4$ and $EuMg_2H_6$ have been reported [1,2]. The compounds were synthesised by hydrogenation of intermetallic compounds at 600 K under a hydrogen gas pressure of 5 MPa and structurally characterised by neutron powder diffraction at a wavelength close to the minimum of neutron absorption by a natural isotope mixture of europium. In view of the known existence of ternary alkaline earth hydrides such as A_2MgH_6 (A=Sr [3], Ba [4]), $A_6Mg_7H_{26}$ (A=Ba [5]) and $A_2Mg_3H_{10}$ (A= Sr [6], Ba [7]), some of which (Sr₂MgH₆) were only obtained by application of high quasi-hydrostatic pressure, it was tempting to try the latter method also on the Eu-Mg-H system. Here we report on the successful high pressure synthesis and crystal structure of three novel europium magnesium hydrides of composition Eu₂MgH₆, $Eu_6Mg_7H_{26}$ and $Eu_2Mg_3H_{10}$.

2. Experimental details

2.1. Synthesis

The starting materials were europium ingot (natural isotopic mixture, ^{nat}Eu, Arris International, 99.9%), magnesium powder (Cerac, 99.6%, 400 mesh) and hydrogen (Carbagas, 99.9999%) and deuterium gas (AGA, 99.8%). All materials were handled in an argon-filled glove box since they were sensitive to air. In a first step EuH₂ (EuD_2) powders were prepared by direct hydrogenation (deuteration) of a piece of europium metal at T=600 K and 2 MPa hydrogen (deuterium) pressure during 2 days in an autoclave. MgH₂ (MgD₂) was synthesised by hydrogenation (deuteration) of magnesium powder at T=750 K and 9 MPa hydrogen (deuterium) pressure during 8 days in an autoclave. To complete the reactions the products were reground and the procedure repeated. In a second step mixtures of EuH₂ (EuD₂) and MgH₂ (MgD₂) at various proportions were compacted to pellets and placed in a high-pressure cell. The cell consisted of a boron nitride tube with boron nitride lid as sample container and was surrounded by a graphite tube as external resistance heating and pyrophyllite as pressure transmitting medium [8]. The assembled cube-shaped cells were pressurised by an octahedral anvil press. First, the pressure was increased at a constant rate of typically 50 MPa/min followed by

 $^{^{\}diamond}$ Dedicated to Professor Dr. Horst P. Beck on the occasion of his 60th birthday.

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rapid heating (100 K/min) up to pressures and temperatures of 3.2 GPa and 870 K, respectively (see below). The samples were kept under these p-T conditions for 2 or 3 h and then quenched by switching off the resistance heating while releasing the pressure at a rate of about 50 MPa/ min.

Preliminary experiments suggested the formation of at least three new ternary hydride phases of likely composition Eu_2MgH_6 , $Eu_6Mg_7H_{26}$ and $Eu_2Mg_3H_{10}$ (see Section 2.5). Depending on the molar ratio of the starting materials these phases coexisted in various proportions and were associated with more-or-less non-reacted EuH₂ and MgH₂. Samples containing Eu_2MgH_6 without $Eu_6Mg_7H_{26}$ and $Eu_2Mg_3H_{10}$ were prepared from mixtures of either EuH_2 and MgH_2 or EuH_2 and $EuMgH_4$ by using an excess of EuH₂. Samples containing Eu₆Mg₇H₂₆ in which the $Eu_2Mg_3H_{10}$ content was minimised were prepared at relatively low pressures (1.5-1.7 GPa). However, they always contained Eu₂MgH₆ whose content was reduced by using a slight MgH₂ excess. Samples containing $Eu_2Mg_3H_{10}$ in which the $Eu_6Mg_7H_{26}$ content was minimised were prepared by using an excess of MgH_2 . The simultaneous presence in most samples of all three highpressure phases is presumably due to pressure and temperature gradients in the high pressure cell. Attempts to improve the homogeneity of the starting mixtures did not yield better samples. For the structural and magnetic studies three hydride samples were synthesised at the following conditions (nominal composition, maximum applied pressure and temperature in parentheses): 'Eu₂MgH₆ sample' (EuH₂/MgH₂=2.1/1, 3 GPa, 870 K), $Eu_6Mg_7H_{26}$ sample' (EuH₂/MgH₂=6/7.7, 1.7 GPa, 790) K), 'Eu₂Mg₃H₁₀ sample' (EuH₂/MgH₂=2/4, 3.2 GPa, 760 K). Corresponding deuteride samples were synthesised under the same conditions. Their colour was brown (Eu₂MgH₆), red-brown (Eu₆Mg₇H₂₆) and orange-light brown ($Eu_2Mg_3H_{10}$). The thermal stability was tested by heating the samples under hydrogen atmosphere in an autoclave. The Eu_2MgH_6 sample was found to be stable up to 700 K and to decompose at 750 K into EuH₂ and Mg. The Eu₆Mg₇H₂₆ and Eu₂Mg₃H₁₀ samples decomposed at 700 K into Eu_2MgH_6 and $EuMgH_4$.

2.2. X-ray diffraction

All reaction products were examined by X-ray powder diffraction on a Guinier camera (samples enclosed in sealed glass capillaries of 0.3 mm outer diameter, Co K α_1 radiation, internal Si standard) or on a Bragg–Brentano diffractometer (Philips PW1820, flat samples in a holder for air-sensitive substances, Cu K α radiation, internal Si standard). For structure refinement high-resolution synchrotron powder diffraction data were recorded for the deuteride samples Eu₆Mg₇D₂₆ and Eu₂Mg₃D₁₀ on the Swiss–Norwegian beamline (BM1B) at ESRF (Grenoble, France). The samples were enclosed in sealed glass capillaries (0.2 mm outer diameter) and measured in the range $3^{\circ} \le 2\theta \le 43^{\circ}$, $\Delta 2\theta = 0.005^{\circ}$ and a wavelength of $\lambda = 60.054(1)$ pm during 6 h. They came from the same batches as those investigated later by neutron diffraction (see Section 2.3) and contained three ternary deuteride phases, binary EuD₂ and $\alpha(\gamma)$ -MgD₂, and traces of MgO (for diffraction patterns see Fig. 1a).

2.3. Neutron diffraction

In view of the high absorption cross-section of natural isotope mixtures of europium (^{nat}Eu) for thermal neutrons [9,10], the wavelength was chosen close to the minimum of the absorption cross-section at $\lambda_{\min} = 72.9$ pm [1,2,10]. Data were taken on the high intensity diffractometer D4b installed at the hot source of the reactor at ILL (Grenoble, France). Three deuteride samples were investigated. Whereas the Eu_2MgD_6 sample (0.9 g) was measured at full intensity, the $Eu_6Mg_7D_{26}$ (1.7 g) and $Eu_2Mg_3D_{10}$ (1.6 g) samples could only be measured at 30% intensity due to the non-availability of the hot source. In order to reduce absorption further the samples were filled into doublewalled vanadium cylinders (64 mm length, 9.15 mm inner diameter of the outer tube, 7.95 mm outer diameter of the inner tube, 0.6 mm annular sample thickness). Wavelength and zero-shift corrections were determined from a nickel standard and found to be 70.50(1) pm and $-0.1361(2)^{\circ}$ $(Eu_2MgD_6 \text{ sample})$, and 70.647(8) pm and $-0.1713(3)^{\circ}$ $(Eu_6Mg_7D_{26} \text{ and } Eu_2Mg_3D_{10} \text{ samples})$, respectively. Total data collection times were 11, 32 and 24 h for the Eu_2MgD_6 , $Eu_6Mg_7D_{26}$ and $Eu_2Mg_3D_{10}$ samples, respectively. Due to the low resolution at high diffraction angles only data of the first detector $(4^{\circ} \le 2\theta \le 70^{\circ})$ were used in the structure refinements (for diffraction patterns see Fig. 1b).

2.4. Magnetic susceptibility measurements

The magnetic susceptibility of a Eu₂MgH₆ sample (7.7 mg powder pellet, containing 7% EuH₂ as determined by X-ray phase analysis) was measured on a SQUID magnetometer in the following ranges of temperature and magnetic fields: 10 K \leq T \leq 100 K (*B*=0.01 T) and 50 K \leq T \leq 300 K (*B*=2 T). Curie–Weiss paramagnetism and ferromagnetic ordering at low temperatures was observed (Fig. 2). From the slope and the intercept of the 1/X versus T plot in the paramagnetic region a Curie temperature of T_C=31.6(2) K and an effective magnetic moment for europium of μ_{eff} = 7.88(1) $\mu_{\rm B}$ was derived by correcting for the magnetic EuH₂ impurity.

2.5. Structure determination

The X-ray diffraction patterns of the various samples could be indexed on mixtures of trigonal, orthorhombic and monoclinic unit cells and were consistent with calcu-



Fig. 1. Graphical representation of a joint Rietveld refinement on two synchrotron (a) and three neutron (b) powder diffraction patterns taken on the deuteride samples Eu_2MgD_6 , $Eu_6Mg_7D_{26}$ and $Eu_2Mg_3D_{10}$. The patterns show the following phases: s- $Eu_6Mg_7D_{26}$ (1–5, 8); n- $Eu_2Mg_3D_{26}$ (1–6, 8); s- $Eu_2Mg_3D_{10}$ (1–5, 7, 8); n- $Eu_2Mg_3D_{10}$ (1–8); n- Eu_2MgD_6 (1–3, 7, 8). Phases: (1) Eu_2MgD_6 , (2) EuD_2 , (3) $Eu_6Mg_7D_{26}$, (4) $Eu_2Mg_3D_{10}$, (5) α - MgD_2 , (6) V, (7) γ - MgD_2 , (8) MgO. Observed (crosses), calculated (solid line) and difference patterns (bottom) and Bragg markers of phases 1–8 (from bottom to top). The inserts give a more detailed view of the *d* range 351.5 pm $\geq d \geq 185.0$ pm, which corresponds to $9.80^{\circ} \leq 2\theta \leq 18.68^{\circ}$ for the synchrotron patterns and $11.5^{\circ} \leq 2\theta \leq 22.0^{\circ}$ for the neutron patterns. Wavelengths 70.5–70.6 pm (neutrons), 60.05 pm (synchrontron).

lated patterns based on K2GeF6, Ba6Mg7D26 and Ba2Ni3F10 type structures, respectively. This suggested the presence of ternary hydride phases of composition Eu_2MgH_6 , $Eu_6Mg_7H_{26}$ and $Eu_2Mg_3H_{10}$ isoptypic to the corresponding barium magnesium hydrides [4,5,7]. For the orthorhombic pattern of Eu₆Mg₇H₂₆, however, the synchrotron data revealed a splitting of certain diffraction lines thus indicating a lowering of symmetry. A satisfactory fit was obtained by assuming a monoclinic distortion $(\beta = 90.6^{\circ})$ of the orthorhombic lattice $(\beta = 90^{\circ})$ similar to that in the fluoride $Ba_6Zn_7F_{26}$ [11]. For the sake of comparison with the orthorhombic Ba analogue $Ba_6Mg_7D_{26}$ the non-standard space group setting I2/minstead of standard C2/m was chosen. Refined cell parameters of the hydrides as obtained from laboratory X-ray data are given in Table 3.

Preliminary Rietveld refinements on individual patterns

as performed with FullProf [12] resulted in satisfactory fits and accurate metal positions for the synchrotron data, but in unstable refinements and inaccurate deuterium positions for the neutron data, even when applying severe constraints. In order to make use of the complementary nature of both types of data a joint structure refinement was performed by simultaneous use of all five data sets. Depending on the data set up to eight phases were refined (see Fig. 1). A recent version of GSAS [13] was used that allowed to include the imaginary part of the neutron scattering length, b'', of the highly absorbing ^{nat}Eu. In order to test the programme the crystal structure of EuD₂ which was previously refined [14] without taking into account anomalous dispersion was refined again, but no significant changes for the structure parameters were observed. Starting values for the various atomic parameters were obtained from preliminary refinements on the in-





dividual patterns (Eu₂MgD₆, Eu₆Mg₇D₂₆, Eu₂Mg₃D₁₀) or from the literature (EuD₂ [14], $\alpha(\gamma)$ -MgD₂ [16]). The joint refinement converged and yielded structure parameters of satisfactory precision (Table 1). The background of the synchrotron data was described by a power series with three coefficients and that of the neutron data by interpolation between 10 points. Absorption corrections were applied for the synchrotron data according to Hewat's formula [17,18] and for the neutron data by calculating transmission factors for annular samples by using the programme ABSOR [19]. For the ternary phases all (isotropic) displacement parameters were constrained to be equal for atoms of the same kind. In the final refinement the following 182 parameters were refined: 60 positional (three for Eu_2MgD_6 , 33 for $Eu_6Mg_7D_{26}$, 24 for $Eu_2Mg_3D_{10}$), 11 thermal displacement (three each for



Fig. 2. Temperature dependence of molar magnetic susceptibility, X, of a powder Eu₂MgH₆ sample.

 Eu_2MgD_6 , $Eu_6Mg_7D_{26}$ and $Eu_2Mg_3D_{10}$, one each for EuD₂ and V), 20 cell (all phases), one preferred orientation (March-Dollase model [20,21] for Eu_2MgD_6 in the synchrotron data), 36 background parameters, 33 phase fractions (see above), and 21 profile parameters. For the neutron data the profile parameters of all phases and data sets were constrained to be equal, i.e. only three parameters (Gaussian u, v and w) were refined. This is justified as the reflection widths are determined mainly by the low resolution of the high-intensity diffractometer rather than by intrinsic sample properties. For the synchrotron data only Lorentzian x and y, and asymmetry parameters were refined. The values for phases 3-8 in the synchrotron data were constrained to be equal, i.e. only six sets of x, y and asymmetry parameters were refined. Graphical representations of the Rietveld refinements are given in Fig. 1 and structural results and interatomic distances in Tables 1 and 2, respectively.

It is worth pointing out that absorption effects in the neutron data were still appreciable despite the use of a short-wavelength and annular sample holders (calculated linear absorption coefficients at λ =70 pm: μ =1.56 mm⁻¹ for Eu₂MgD₆, 1.14 mm⁻¹ for Eu₆Mg₇D₂₆ and 1.01 mm⁻¹ for Eu₂Mg₃D₁₀). In particular, the slightly negative displacement parameters of the magnesium sites (Table 1) indicate that the absorption corrections of the synchrotron and neutron data as described above did not completely remove systematic errors due to absorption. As a result the accuracy of the structure parameters (see e.s.d. values in

Tables 1 and 2) does not reach the standard of other metal hydride structures, but is sufficient for the purpose of comparing their crystal chemistry. It should also be noted that the relatively low profile residuals (R_p, R_{wp}) of the neutron data are due to the high background. Finally, it was crucial for the stability of the refinement to keep the number of profile parameters at a minimum and to add new parameters only one by one as the refinement progressed while using a 'damping factor' of 80% for all structure parameters.

3. Results and discussion

There exist five known ternary metal hydrides in the Eu-Mg-H system. Their structural and magnetic properties are summarised in Table 3 and their common structural characteristics are represented in Fig. 3. All compounds contain distorted MgH₆ octahedra that are either isolated (Eu₂MgH₆) or share corners (EuMgH₄, EuMg₂H₆) or edges and corners (Eu₆Mg₇H₂₆, Eu₂Mg₃H₁₀). In contrast to the two low-pressure phases the structures of the three high-pressure phases can be derived by more-or-less close packed europium and hydrogen atom arrangements in which magnesium atoms occupy octahedral voids. The compounds investigated magnetically show Curie–Weiss paramagnetism and ferromagnetic ordering. As expected their Curie temperatures decrease as the minimum Eu–Eu distance increases (Eu₂MgH₆, Eu–

Table 1

Crystal structure data of Eu_2MgD_6 , $Eu_6Mg_7D_{26}$ and $Eu_2Mg_3D_{10}$ from a joint refinement on five synchrotron and neutron diffraction patterns^a

Atom	Wyckoff site	Symmetry	x/a	y/b	z/c	$B_{\rm iso}$ (10 ⁴ pm ²)
Eu ₂ MgD ₆ : space	group P3m1 (No. 164)	, <i>a</i> =550.644(6) pm,	c=410.054(6) pm, Z=	=1		
Eu	2d	3 <i>m</i>	1/3	2/3	0.2641(8)	0.51(3)
Mg	1a	$\bar{3}m$	0	0	0	-0.4(1)
D	6 <i>i</i>	m	0.8221(5)	-x	0.243(2)	3.52(8)
Eu ₆ Mg ₇ D ₂₆ ^b : spa	ace group <i>I2/m</i> (No. 12), a=1409.39(4) pm,	<i>b</i> =564.55(2) pm, <i>c</i> =	1150.90(3) pm, $\beta = 90.6$	683(2)°, Z=2	
Eu1	4i	т	0.3564(4)	0	0.2619(6)	0.17(6)
Eu1'	4i	т	0.6572(4)	0	0.2607(6)	B_{iso} (Eu1)
Eu2	4i	m	0.3498(5)	1/2	0.0040(8)	B_{iso} (Eu1)
Mg1	4i	m	0.229(1)	0	0.019(2)	-1.2(2)
Mg2	4i	m	0.988(1)	0	0.267(2)	B_{iso} (Mg1)
Mg3	4g	2	0	0.250(3)	0	B_{iso} (Mg1)
Mg4	2c	2/m	0	1/2	1/2	B_{iso} (Mg1)
D1	8 <i>j</i>	1	0.243(1)	0.227(4)	0.128(2)	0.6(2)
D1′	8j	1	0.734(2)	0.250(4)	0.124(2)	B_{iso} (D1)
D2	8j	1	0.948(1)	0.180(3)	0.385(2)	B_{iso} (D1)
D3	8j	1	0.994(2)	0.305(3)	0.167(2)	B_{inc} (D1)
D4	4i	т	0.133(3)	0	0.256(3)	B_{inc} (D1)
D4'	4i	т	0.857(2)	0	0.267(3)	B_{int} (D1)
D5	4i	m	0.079(2)	1/2	0.029(3)	B_{int} (D1)
D6	4i	т	0.114(3)	0	0.050(3)	B_{i} (D1)
D7	4i	m	0.348(3)	0	0.051(2)	B_{iso} (D1)
Eu ₂ Mg ₂ D ₁₀ : space	ce group $C2/m$ (No. 12)), $a = 1748.41(5)$ pm.	b = 572.31(2) pm. $c =$	736.47(2) pm. $\beta = 111.4$	$478(2)^{\circ}, Z=4$	
Eu1	4i	m	0.2812(3)	0	0.6874(6)	0.26(6)
Eu2	4i	m	0.3845(3)	0	0.2831(6)	<i>B</i> (Eu)
Mg1	4i	m	0.081(1)	0	0.446(3)	-0.6(2)
Mg2	4i	m	0.170(1)	0	0.009(3)	B. (Mg1)
Mg3	4g	2	0	0.268(3)	0	B_{\cdot} (Mg1)
DI	8i	1	0.100(1)	0.309(3)	0.003(3)	1.3(2)
D2	8j	1	0.145(1)	0.246(5)	0.449(2)	B. (D1)
D3	4i	m	0.032(2)	0	0.190(4)	B_{\cdot} (D1)
D4	4i	m	0.136(2)	0	0.731(5)	B_{\cdot} (D1)
D5	4i	m	0.271(2)	0	0.370(5)	$B_{100} (D1)$
D6	4i	m	0.524(2)	0	0.209(5)	B_{\cdot} (D1)
D7	4h	2	0	0.240(6)	1/2	$B_{100} (D1)$
D8	4 <i>e</i>	Ī	1/4	1/4	0	B_{iso} (D1)
Residuals:	$R_{-}(\%)$	$R_{}(\%)$	Data points			
Data set 1	6.3	8.0	8041			
Data set 2	1.1	1.4	665			
Data set 3	6.6	8.1	7921			
Data set 4	1.1	1.4	665			
Data set 5	0.6	0.8	638			
All data sets	4.2	1.8	17 930	Reduced $\chi^2 = 3.0$		

^a Form of the temperature factor: $T = \exp \left[-B_{iso}(\sin \theta/\lambda)^2\right]$.

^b Non-standard space group setting, atom labels in accordance with Ba₆Mg₇D₂₆ [5].

Eu=372 pm, $T_{\rm C}$ =31.6 K; EuMg₂H₆, Eu-Eu=377 pm, $T_{\rm C}$ =27.2 K; EuMgH₄, Eu-Eu=393 pm, $T_{\rm C}$ =18.7 K). The range of measured effective magnetic moments ($\mu_{\rm eff}$ = 7.54–8.12 $\mu_{\rm B}$) is consistent with the presence of divalent europium (free Eu²⁺ ion, 7.95 $\mu_{\rm B}$). The compounds are colored and can be formulated with limiting ionic formulas based on divalent metal cations (Eu²⁺, Mg²⁺) and hydride anions (H⁻).

All compounds have fluorine analogues. Eu_2MgH_6 and its alkaline earth homologues Sr_2MgH_6 [3] and Ba_2MgH_6 [4] crystallize with the K_2GeF_6 type structure that is also adopted by the fluorides $Ba_2M^{2+}F_6$ (M=Mn, Fe, Co, Ni, Zn, Mg) [22]. All these homologues (except Ba_2MgH_6) can be synthesized under high hydrostatic pressures only. The magnesium site in Eu_2MgH_6 is surrounded by a deuterium octahedron that is compressed along the 3-fold axis (Mg-D=197 pm, D-Mg-D=96.6°), while the europium site has 12 nearest deuterium neighbours (Eu-D=251-276 pm) forming a distorted anti-cuboctahedron. $Eu_6Mg_7H_{26}$ crystallizes with the $Ba_6Zn_7F_{26}$ type structure and can be derived from of its orthorhombic barium hydride homologue by the crystallographic group-subgroup relationship $I2/m 2/m (Ba_6Mg_7D_{26}) \rightarrow t2 \rightarrow I2/m (Eu_6Mg_7D_{26})$. Specifically, the symmetry reduction splits the Bal site in $Ba_6Mg_7D_{26}$ in two crystallographic non-equivalent cation sites that have similar anion coordi-

Table 2

Interatomic distances (angles) and shortest D–D contact distances (pm) in Eu_2MgD_6 , $Eu_6Mg_7D_{26}$ and $Eu_2Mg_3D_{10}$ (Eu–D cut-off value, 300 pm; next longest Eu–D distances, >315 pm)

e	, 1,						
Eu_2MgD_6 :	Eu-3 D	250.7(7) 255.3(7)	Mg-6 D	196.7(6)	D	-Mg	196.7(6) 250.7(7)
	-3 D	233.3(7) 275 7(3)		83 4(5)°		-Eu Eu	255.3(7)
	Average 264	213.1(3)	D-Mg-D	96 6(5)°		-Lu -2 D	255.5(7)
	niverage 201			90.0(3)		-2 Eu	275.7(3)
E. M. D.	E-1 D7	242(2)	M-1 DC	1(7(4)	DI	M-1	190(2)
$Eu_6Mg_7D_{26}$:	2 D1	243(3)	Mg1-D6	10/(4)	DI	-Mg1	180(2)
	-2 D1 2 D3	243(2)	-D7 2 D1	170(4)		-D7 Eu1	210(4) 245(2)
	-2 D3	256(2)	-2 D1	224(3)		-Eu1	2+3(2) 256(2)
	-D5	256(3)	Average 191	224(3)		-Eu2	259(3)
	-2 D4	283.5(3)	Mg2-2 D2	179(3)	D1′	-Mg1	224(3)
	Average 257		-D4'	184(4)		-D4'	230(3)
	Eu1'-2 D1'	239(2)	-D4	206(4)		-Eu2	235(2)
	-2 D1'	246(3)	-2 D3	207(2)		-Eu1'	239(2)
	-2 D3	255(3)	Average 194			-Eu1'	246(3)
	-D4'	282(3)	Mg3-2 D5	182(2)	D2	-Mg2	179(3)
	-2 D4'	284.8(4)	-2 D3	196(2)		-D2	204(4)
	-2 D2	287	-2 D6	221(3)		-Eu2	220(2)
	Average 264		Average 200			-Mg4	235(2)
	Eu2-2 D2	220(2)	Mg4-2 D7	223(4)		-Eu1'	287(2)
	-2 D1'	235(2)	-4 D2	235(2)	D3	-Mg3	196(2)
	-2 D1	259(3)	Average 231			-Mg2	207(2)
	-D4	2/3(3)				-D3	220(4)
	-D4	277(4)				-Eul	250(5)
	-2 D7	267.4(0)			D4	-Eul Ma2	233(3) 206(4)
	Average 250				D4	-Mg2 -D6	239(5)
						-Eu2	237(3) 277(4)
						-2 Eu1	283 5(3)
					D4′	-Mg2	184(4)
						-2 D2	212(3)
						-Eu2	273(3)
						-Eu1'	282(3)
						-2 Eu1'	285(4)
					D5	-2 Mg3	182(2)
						-2 D3	228(4)
						-Eu1	256(3)
					D6	-Mg1	167(4)
						-2 Mg3	221(3)
						-2 D1	239(4)
					D7	-Mg1	170(4)
						-2 D1	216(4)
						-Mg4	223(4)
						-Eu1	243(3)
						-2 EU2	287.4(0)
$Eu_{2}Mg_{3}D_{10}$:	Eu1–D5	228(3)	Mg1–D3	177(4)	D1	-Mg3	176(3)
	-2 D2	240(2)	-2 D2	179(2)		-Mg2	215(3)
	-D4	267(3)	-D4	196(4)		-D1	218(4)
	-2 D1	269(2)	-2 D7	211(3)		-Eu2	247(2)
	-2 D2	278(2)	Average 192	101/10	5.2	-Eul	269(2)
	-2 D8	292.6(4)	Mg2–D4	191(4)	D2	-Mg1	179(2)
	-2 D5	298.7(8)	-2 D8	202(1) 215(2)		-D5	215(3)
	En2 D5	220(2)	-2 D1	213(3) 260(3)		-Eu1 Eu2	240(2) 265(2)
	2 D1	229(3) 247(2)	-D5 Average 214	200(3)		-Eu2 Eu1	203(2) 278(2)
	-2 D1	247(2) 255(2)	Mg3_2 D1	176(3)	D3	-Lui -Mg1	177(4)
	$-2 D^{2}$	265(2)	-2 D6	196(3)	25	-2 Mg3	201(2)
	-D6	269(3)	-2 D3	201(2)		-2D2	260(3)
	-2 D4	288.1(4)	Average 191		D4	-Mg2	191(4)
	-2 D8	288.7(4)	6			-Mg1	196(4)
	Average 265					-2 D2	256(3)
	Ū.					-Eu1	267(3)
						-2 Eu2	288.1(4)
					D5	-2 D2	215(3)
						-Eu1	228(3)
						-Eu2	229(3)
						-Mg2	260(3)
						-2 Eu1	298.7(8)
					D6	-2 Mg3	196(3)
						-2 D1	242(4)
					D7	-Eu2	269(3)
					D/	-2 Mg1	211(3)
						-2 Eu2	255(2)
					50	-2 D2	209(2) 202(1)
					100	-2 mg_2 -2 D1	262(1)
						-2 Eu2	288 7(4)
						-2 Eu1	292.6(4)

Table 3

	Eu_2MgH_6	EuMgH4 ^d	$Eu_6Mg_7H_{26}$	$Eu_2Mg_3H_{10}$	$EuMg_2H_6^d$
Space group type	P3m1	$Cmc2_1$	<i>I2/m</i>	<i>C2/m</i>	P4/mmm
Cell parameters (pm)	a=550.98(4)	a = 392.78(8) b = 1346.3(2)	a = 1410.2(6) b = 566.3(2)	a = 1752.3(6) b = 574.0(2)	a=377.17(2)
	c = 410.99(3)	c = 555.2(1)	c = 1154.0(4) $\beta = 90.61(3)^{\circ}$	c = 738.1(3) $\beta = 111.49(3)^{\circ}$	c=799.44(7)
Cell volume $(10^6 \times pm^3)$	108.1	293.6	921.5	690.8	113.7
Formula units/cell	1	4	2	4	1
ΔV_r^a	-7.3%	-0.4%	-2.6%	-3.1%	+9.5%
Connectivity of	_	Corners	Corners+edges	Corners + edges	Corners
MgH_6 octahedra	MgH ₆	MgH _{2+4/2}	$Mg 1H_{4+1/2+1/3}$ $Mg 2H_{2+4/2}$ $Mg 3H_{4/2+2/3}$ $Mg 4H_{6/2}$	$ \begin{array}{c} Mg IH_{2+3/2+1/3} \\ Mg 2H_{1+5/2} \\ Mg 3H_{4/2+2/3} \end{array} $	MgH _{6/2}
\bar{d} (Mg–D) (pm)	197	196	200	199	197
\bar{d} (Eu ^b –D) (pm)	264 [13]	253 [10]	259 [11,12]	268 [13]	258 [13]
d_{\min} (Eu–Eu) (pm)	372	393	386	385	377
$T_{\rm C}$ (K)	31.6(2)	$18.7(5)^{\circ}$			$27.2(5)^{\circ}$
$\mu_{ m eff}/\mu_{ m B}$	7.88(1)	7.54(2) ^c			8.12(2) ^c

Structural	and	magnetic	data	of euro	pium	magnesium	hydrides:	compounds	synthesised	under	high	pressure	are	given	in i	talics
							-		-							

^a Relative volume change for the reaction $x\text{EuH}_2 + y\text{MgH}_2 \rightarrow \text{Eu}_x\text{Mg}_y\text{H}_{2(x+y)}$, i.e. $\Delta V_r = [V(\text{Eu}_x\text{Mg}_y\text{H}_{2(x+y)}) - xV(\text{EuH}_2) - yV(\text{MgH}_2)]/[xV(\text{EuH}_2) + yV(\text{MgH}_2)]$ with V being the unit cell volume per formula unit. Cell volumes of EuH₂ and α -MgH₂ taken from Refs. [14,15].

^b Coordination numbers of europium given as superscripts.

^c Taken on the deuteride, see Refs. [1,2].

^d Data taken from Refs. [1,2].

nation spheres such as in Ba₆Zn₇F₂₆ [11]. In Eu₆Mg₇D₂₆, however, the smaller Eu cations induce additional atomic shifts that result in fundamentally different anion coordinations. Eu1 and Eu2 shows 10-fold (d(Eu-D)=243-284 pm)(Eu1), 220-287 pm (Eu2)) and Eu1' 11-fold deuterium coordinations (d(Eu'-D)=239-287 pm) (see Fig. 3), in contrast to Ba₆Mg₇D₂₆ (and Ba₆Zn₇F₂₆) that show 12-fold anion coordinations. The coordination polyhedra around Eu1 and Eu2 can be derived from the corresponding cuboctahedra in Ba₆Mg₇D₂₆ and Ba₆Zn₇F₂₆ by removal of two ligands (2D2), and that around Eu1' by removal of two ligands (D5, D7) and addition of one ligand (D4). The four magnesium sites in Eu₆Mg₇D₂₆ are surrounded by strongly distorted deuterium octahedra (Mg-D=167-224 pm (Mg1), 179-207 pm (Mg2), 182-221 pm (Mg3), 223–235 pm (Mg4)) that are tilted and linked by common corners and edges to a three-dimensional network. In contrast to the 12-fold Ba co-ordination in Ba₆Mg₇D₂₆ europium in Eu₆Mg₇D₂₆ is 10-fold (Eu1, Eu2) and 11-fold (Eu1') co-ordinated by deuterium (Eu-D=243-284 pm (Eu1), 239–287 pm (Eu1'), 220–287 pm (Eu2)). A corresponding strontium hydride of composition $Sr_6Mg_7H_{26}$ has so far not been reported. $Eu_2Mg_3H_{10}$ crystallises with the $Ba_2Ni_3F_{10}$ type structure. In contrast to its strontium and barium analogues it can be synthesised at high hydrostatic pressures only. The three magnesium sites are surrounded by distorted deuterium octahedra (Mg-D=177-211 pm (Mg1), 191-260 pm (Mg2), 176-201 pm (Mg3)) that are linked by common corners and edges to a three-dimensional network. The two europium sites have 12-fold deuterium co-ordinations (Eu-D=228-299 pm (Eu1), 229-289 pm (Eu2)) corresponding to slightly distorted cuboctahedra (Eu2) and twinned cuboctahedra (Eu1). The structure can be transformed into that of $Eu_6Mg_7H_{26}$ by condensation of octahedral building blocks as was proposed for the corresponding Ba–Ni fluorides [11].

Interestingly, the ternary hydride phases presented in this work (i.e. those requiring high hydrostatic pressure syntheses) all show considerable volume contractions if compared to the weighted means of the corresponding binary hydrides (see ΔV_r values of up to -7.3% in Table 3). This is in contrast to the hydrides prepared under (moderate) hydrogen gas pressures that show almost no such volume contraction (EuMgH₄, $\Delta V_r = -0.4\%$) or even a strong volume expansion (EuMg₂H₆, ΔV_r =9.5%). The slightly higher contraction of $Eu_2Mg_3H_{10}$ ($\Delta V_r = -3.1\%$) as compared to Eu₆Mg₇H₂₆ ($\Delta V_r = -2.6\%$) is consistent with the fact that high pressure favours the formation of the former compound over the latter at intermediate nominal compositions. On the other hand, the atomic number of the metal constituents also plays a role as expected from Wentorf's pressure homologue rule [23] that states that high pressure conditions favour the formation of phases for which heavier homologues exist. In the alkaline earth series A_2MgH_6 , for example, the heavier homologue (A=Ba) can be prepared under hydrogenation gas pressure [4] unlike the lighter homologue (A=Sr) whose synthesis requires high hydrostatic pressure [3]. In the $A_6Mg_7H_{26}$ series the only member found so far is that for A=Ba which was synthesised under gas pressure [5] and A=Eu (present work) which was synthesised at high hydrostatic pressure. As to the $A_2Mg_3H_{10}$ series its members can be prepared by (low pressure) hydrogenation of binary AMg₂



Fig. 3. Crystal structures of europium magnesium hydrides (deuterides) emphasising the MgD_6 polyhedra (large circles, Eu). Coordination polyhedra of europium drawn separately (Eu–D cut-off value, 300 pm; next longest Eu–D distances, >315 pm; small circles, D). Eu₂MgD₆, **c** axis up; EuMgD₄, view approximately along **a**, **c** axis down; Eu₆Mg₇D₂₆, view approximately along **b**, **a** axis up; Eu₂Mg₃D₁₀, view approximately along **b**, **a** axis to the right; EuMg₂D₆, view approximately along **a**, **c** axis up.

alloys for A=Sr (ΔV_r =-3.8%) [6] and A=Ba (ΔV_r = -5.1%) [7], but only by high pressure reaction between binary hydride mixtures for A=Eu (ΔV_r =-3.1%). Hydrogenation of an EuMg₂ alloy yields EuMg₂H₆ [1,2] that shows a strong volume expansion (ΔV_r =+9.5%). No strontium and barium analogues are known for the latter compound. Finally, the AMgH₄ hydrides (A=Sr, Eu, Ba) can all be obtained under hydrogen gas pressure. Interestingly, the structures for A=Eu [1,2] and Sr [24] are somewhat distorted as compared to that for A=Ba [25].

In conclusion, the structural and magnetic properties of the known ternary metal hydrides in the Eu-Mg-H system are consistent with their description as ionic hydrides. All crystallise with fluorine type structures and have alkaline earth analogues, thus underlining the similarity between the europium and alkaline earth hydride chemistry. The high pressure phases usually show large volume contractions. Those based on europium order magnetically and show Curie-Weiss paramagnetism with magnetic moments consistent with divalent europium. Their Curie temperatures range between 18 and 32 K and scale with the shortest Eu-Eu distances. As to the thermal stability Eu_2MgH_6 appears to be the most stable high pressure phase in view of desorption tests and its easy formation as an unwanted by-product in the high pressure synthesis of other hydride phases.

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