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$Ca_4Mg_4Fe_3H_{22}$, a new quaternary transition metal hydride containing octahedral $[FeH_6]^{4-}$ complex anions

B. Huang and K. Yvon
Laboratoire de Cristallographie, Université de Genève, 24 Quai E. Ansermet, CH-1211 Genève (Switzerland)

P. Fischer
Labor für Neutronenstreuung, ETH Zürich-PSI, CH-5232 Villigen PSI (Switzerland)

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Abstract

$Ca_4Mg_4Fe_3H_{22}$ and its deuteride were synthesized by reaction of binary CaMg with iron wire at 500–530 °C and 100–155 bar hydrogen (deuterium) pressure. The cubic structure was established from X-ray single-crystal and neutron powder diffraction: space group $P\bar{4}3m$, $a = 6.7151(6)$ Å (hydride) and 6.7016(4) Å (deuteride) at 295 K. It contains three types of deuterium atoms: two surrounding iron octahedrally with bond distances [Fe–4D1] = 1.583(3) Å and [Fe–2D2] = 1.562(5) Å, and one situated in a tetrahedral hole formed by one magnesium and three calcium atoms with bond distances [Mg–D3] = 1.808(7) Å and [Ca–D3] = 2.388(9) Å.

1. Introduction

Our efforts to synthesize new metal hydrides suitable for hydrogen storage have recently led to the discovery of quaternary hydrides containing a transition element and two alkaline earth elements. Examples are nickel-based $CaMgNiH_4$ [1] and its analogues [2] and iron-based $SrMg_2FeH_8$ [3]. The nickel-based hydrides form tetrahedral $[NiH_4]^{4-}$ complex anions whereas the iron-based hydride forms a mixture of octahedral $[FeH_6]^{4-}$ complex anions and hydride H^- anions. As with most ternary transition metal hydrides, the transition metal complexes conform to the 18-electron rule.

In this paper we report another iron-based quaternary metal hydride. It contains octahedral transition metal complexes conforming to the 18-electron rule, and H^- hydride anions.

2. Experimental details

2.1. *Synthesis*

Binary alloys of nominal composition CaMg, $CaMg_{1.15}$ and Li_2Ca were prepared from the elements (calcium, Cerac Inc., Milwaukee, WI, USA, −4 mesh, 99.5%; magnesium, Cerac Inc., $\frac{1}{8}$ inch pieces, 99.99%; lithium, Johnson–Matthey, Zürich, Switzerland, rod, 99.8%) by arc melting and powdered under a protective argon atmosphere. Iron wires (Goodfellow, UK, 99.5%) were surrounded by powder mixtures of CaMg and LiH (Johnson–Matthey, 98%) in the ratios Fe:CaMg:LiH = 1:1:0.25 (hydride) and Fe:$CaMg_{1.15}$:Li_2Ca = 1:1:0.12 (deuteride), wrapped in molybdenum foil and placed in a high temperature, high pressure autoclave. Lithium (or LiH) was added to the samples because it was found to favour the growth of single crystals [4]. After evacuating the autoclave to about 10^{-2} mbar and flushing with argon, it was charged with hydrogen (deuterium) gas (Polygaz, Genève, Switzerland, 99.9999% for H_2; AGA, 99.8% for D_2) to an initial pressure of about 50 (75) bar at room temperature. The temperature of the autoclave was increased to 500–510 (520–530 °C), yielding a hydrogen (deuterium) pressure of 100 (155) bar, held at that temperature and 104–96 (155–140) bar pressure for 21 (10) days and then cooled to room temperature. After the hydrogen (deuterium) pressure has been released, the autoclave was opened and the samples transferred to an argon-filled glove-box. The iron wire was found to be covered by a layer of brownish powder and small quantities of $Ca_4Mg_3H(D)_{14}$ impurity phase [5]. The unreacted parts of the iron wire (about 26 at.%) and the impurity phase were mechanically removed.

Single crystals were obtained from the reaction of binary alloy powders of nominal composition CaMg with iron wires and LiH as a fluxing agent (CaMg:LiH = 1:0.5) at 500–510 °C and 100 bar hydrogen

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pressure for 3 weeks. The crystals had a brownish colour and were translucent.

TABLE 1. Refinement results of X-ray single-crystal and neutron powder diffraction for $Ca_4Mg_4Fe_3D_{22}$(T=295 K)

Atom	Position	x	y	z	U_{iso} (Å^2)×100
Ca	4(e)	0.7090(11)	x	x	2.6(3)
		0.7067(2)^a	x	x	1.11(4)^a
Mg	4(e)	0.2153(7)	x	x	1.1(2)
		0.2104(3)^a	x	x	1.16(6)^a
Fe	3(d)	0.5	0	0	0.16(6)
		0.5	0	0	0.76(4)^a
D1	12(h)	0.2362(5)	0.5	0	2.06(7)
D2	6(f)	0.2670(8)	0	0	2.5(1)
D3	4(e)	0.3711(7)	x	x	2.9(2)

Space group	$P\bar{4}3m$(No. 215)
Cell parameters	a=6.7016(4) Å (deuteride) a=6.7159(8) Å (hydride, single crystal)
Agreement indices	
neutron data	R_B=6.9%, R_p=5.4%, R_{wp}=7.3%
X-ray data	R=4.1%, wR=4.2%
Form of temperature factor	$T=\exp\,[-8\pi^2U_{iso}(\sin\,\theta/\lambda)^2]$

Estimated standard deviations in parentheses.

[a] Data from refinements of X-ray single-crystal diffraction on the hydride.

2.2 X-ray diffraction

The samples were characterized by X-ray powder diffraction at room temperature (Guinier camera, Co Kα radiation; internal standard, silicon powder with a=5.4308 Å). The Guinier films were measured on a computer-controlled microdensitometer [6]. The patterns showed the presence of a new quaternary hydride phase and were indexed on a cubic lattice with cell parameters a=6.7151(6) Å (hydride) and a=6.7016(4) Å (deuteride). The reflection intensities were consistent with a primitive cubic cell, space group $P\bar{4}3m$ (No. 215), with a metal atom arrangement similar to that found in Mg_2FeD_6 [7]. In the new compound there appeared to be an ordered substitution of the alkaline earths on two fourfold positions 4(e); the iron appeared to be located on the onefold 1(b) and threefold 3(d) positions. However, the consistency indices obtained were not satisfactory and the interatomic distances between the alkaline earths and the onefold iron site were too short.

A single crystal of cubic shape (dimensions 0.08×0.08×0.08 mm^3) was mounted on a Philips PW1100 automatic four-circle diffractometer (Mo Kα radiation, graphite monochromator). The cell parameter, refined from 2θ values of 15 reflections (a=6.7159(8) Å), is in good agreement with that obtained from Guinier patterns. A total of 1796 reflections were collected out to $(\sin\theta/\lambda)=0.704$ Å^{-1} ($-10<h<10$, $-10<k<10$, $0<l<10$) in the ω–2θ scan mode, yielding 194 unique reflections, R_{int}=9.4%. The metal atoms were placed on the positions derived from X-ray powder diffraction, except for iron on site 1(b) which was omitted. The structure refinements based on $|F|$ values converged at the residuals R=4.7% and wR=5.6%. After including three symmetry-independent hydrogen atoms with fixed positions (H1 and H2 surrounding iron in an octahedral configuration, H3 situated in a tetrahedral hole formed by one magnesium and three calcium atoms), the residuals decreased to R=4.1% and wR=4.2%. The calculations were performed using the XTAL 3.0 system [8].

2.3. Neutron diffraction

The positions and displacement amplitudes of the hydrogen atoms were refined from neutron powder diffraction on the deuteride sample by using the DMC diffractometer [9] at the reactor SAPHIR at PSI, Villigen (Ge(311) monochromator, neutron wavelength λ=1.6995 Å, angular range 3.0°–135.0°, angular step Δ (2θ)=0.1°, T=295 K). The sample (about 3 g) was enclosed in a cylindrical vanadium container of 8 mm inner diameter and measured in the high resolution mode. The profile refinements were performed using DBWS-9006 [10]. The structure model established from single-crystal X-ray diffraction was refined by including two impurity phases: LiD and MgD_2. the following 21 parameters were allowed to vary: three scale factors, three peak width parameters, one zero-correction parameter, two cell parameters ($Ca_4Mg_4Fe_3D_{22}$, one; LiD, one), 11 atomic parameters ($Ca_4Mg_4Fe_3D_{22}$, five positional, six isotropic displacement parameters) and one asymmetry parameter. The nuclear scattering lengths (10^{-12} cm), 0.490 (calcium), 0.5375 (magnesium), 0.954 (iron), 0.6674 (deuterium) and −0.203 (lithium), were taken from ref. 11. The lattice and atomic parameters of MgD_2 were fixed at their known values. Preliminary refinements showed that the occupancy factors of the three deuterium sites did not differ significantly from 100%. Thus they were fixed at unity in the final refinement.

Refinement results of both X-ray and neutron diffraction are summarized in Table 1. Interatomic distances and deuterium–deuterium contact distances are given in Table 2. The observed, calculated and difference neutron patterns are shown in Fig. 1.

3. Results and discussion

The structure of $Ca_4Mg_4Fe_3D_{22}$ is closely related to that of Mg_2FeD_6 [6]. As shown in Fig. 2, its basic building block is a strongly deformed cube of alkaline earth cations centred by octahedral $[FeD_6]^{4-}$ complex

TABLE 2. Interatomic distances (angstroms) up to 3.5 Å and D–D contact distances (angstroms) for $Ca_4Mg_4Fe_3D_{22}$ (T=295 K) from neutron data)

Fe–2D2	1.562(5)	D1–Fe	1.583(3)
–4D1	1.583(3)	–2Mg	2.396(5)
–4Mg	2.794(5)	–2Ca	2.429(7)
–4Ca	3.093(7)	–2D2	2.224(5)
Ca–3D3	2.388(9)	–2D1	2.239(3)
–6D1	2.429(7)	D2–Fe	1.562(5)
–3D2	2.763(7)	–2Mg	2.070(5)
–3Fe	3.093(7)	–2Ca	2.763(7)
–3Mg	3.386(9)	–4D1	2.224(5)
–3Mg	3.468(9)	–4D2	2.531(5)
Mg–D3	1.808(7)	D3–Mg	1.808(7)
–3D2	2.070(5)	–3Ca	2.388(9)
–6D1	1.396(5)	–3D3	2.443(7)
–3Fe	2.794(5)		
–3Ca	3.386(9)		
–3Ca	3.468(9)		

Estimated standard deviations in parentheses.

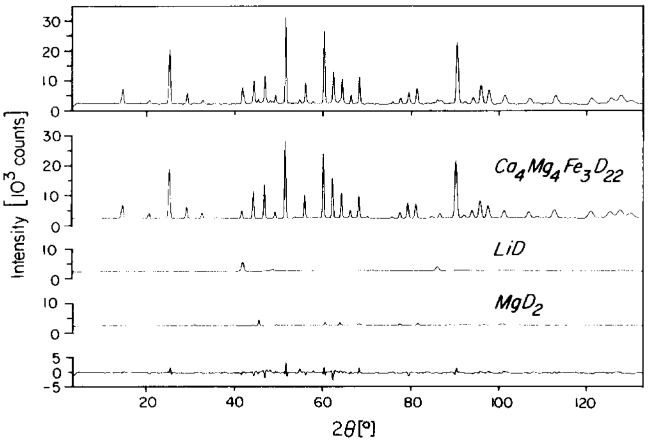

Fig. 1. Observed (top), calculated (middle) and difference (bottom) neutron diffraction patterns of a sample containing $Ca_4Mg_4Fe_3D_{22}$ and impurity phases LiD and MgD_2 ($\lambda = 1.6995$ Å).

anions, similar to the non-deformed cube of magnesium cations in Mg_2FeD_6. In $Ca_4Mg_4Fe_3D_{22}$ four corners of the magnesium cube are substituted by calcium in a tetrahedral configuration. The two deuterium sites (D1, D2) surrounding iron octahedrally have bond distances [Fe–4D1] = 1.583(3) Å and [Fe–2D2] = 1.562(5) Å, similar to those in Mg_2FeD_6([Fe–6D] = 1.56 Å [6]) and Ca_2FeD_6([Fe–6D] = 1.62 Å [12]).

In $Ca_4Mg_4Fe_3D_{22}$ the filled alkaline earth cubes are connected via edges to sheets (Fig. 2(a)) as in Mg_2FeD_6 (Fig. 2(b)). In contrast to Mg_2FeD_6, however, half of the $[FeD_6]^{4-}$ complex anions in every second layer of $Ca_4Mg_4Fe_3D_{22}$ are missing. The missing complexes are substituted by four deuterium atoms (D3) occupying tetrahedral holes in the strongly deformed alkaline earth cube. Assuming anionic D^-, their four negative charges formally replace the fourfold negative charge

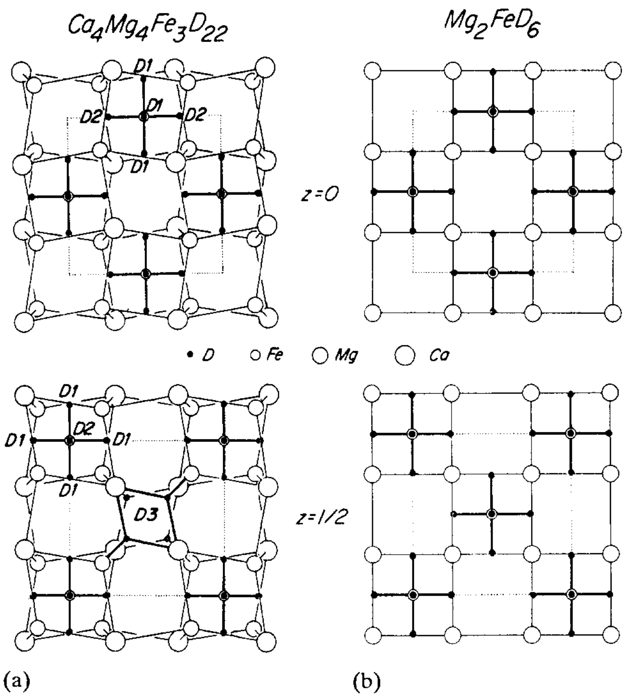

Fig. 2. Structure slabs of (a) cubic $Ca_4Mg_4Fe_3D_{22}$ centred at $z=0$ (top) and $z=\frac{1}{2}$ (bottom), and comparison with (b) cubic Mg_2FeD_6, all viewed parallel to the fourfold axes.

of the $[FeD_6]^{4-}$ complex. Their bond distances to magnesium, [D3–Mg] = 1.808(7) Å, and calcium, [D3–3Ca] = 2.388(9) Å, are consistent with those in the corresponding binary deuterides. Calcium has 12 nearest deuterium neighbours forming a deformed cubo-octahedral configuration, of which nine belong to $[FeD_6]^{4-}$ complexes and three form a group of D^- ions, whereas magnesium has 10 nearest deuterium neighbours forming a configuration which derives from that around calcium by substituting the group of three D^- ions by a single D^- ion.

These structural features confirm the presence of an 18-electron transition metal complex corresponding to the limiting ionic formula $Ca_4Mg_4Fe_3D_{22} = 2CaD_2 \cdot 3(Ca_{2/3}{}^{2+}Mg_{4/3}{}^{2+}[FeD_6]^{4-})$. The only other iron-based quaternary compound known to contain both 18-electron transition metal hydride complexes and D^- ions is $SrMg_2FeD_8$ [3]. Its octahedral $[FeD_6]^{4-}$ complex centres a trigonally deformed alkaline earth cube of composition Mg_6Sr_2, in which two strontium atoms occupy opposite corners, and its D^- ions are tetrahedrally surrounded by one magnesium and three strontium atoms. Its [Fe–6D] bond distances (1.58 Å) do not much differ from those in $Ca_4Mg_4Fe_3D_{22}$ (1.56–1.58 Å) and Mg_2FeD_6 (1.56 Å). Its limiting ionic formula can be written as $SrMg_2FeD_8 = SrD_2 \cdot Mg_2{}^{2+}[FeD_6]^{4-}$.

Measurements of pressure–composition isotherms on both hydrides are in progress to determine their thermal stabilities.

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