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Strontium dimagnesium iron octahydride, $SrMg_2FeH_8$, containing octahedral $[FeH_6]^{4-}$ complex anions

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Abstract

$SrMg_2FeH_8$ and its deuteride were synthesized by reacting alkaline earth alloy powders of nominal composition $SrMg_{2.2}$ with iron powder at 490–510 °C and 130–140 bar hydrogen (deuterium) pressure, and characterized by X-ray and neutron powder diffraction. The compounds crystallize with a new trigonal structure type, space group $P\bar{3}m1$, and lattice parameters $a=4.5174(2)$ Å and $c=6.5807(4)$ Å (hydride), $a=4.5072(2)$ Å and $c=6.5663(4)$ Å (deuteride). The structure contains two types of deuterium atoms, one surrounding iron in an octahedral configuration with bond distances [Fe–D1] = 1.578(4) Å, and the other situated in a tetrahedral hole formed by one magnesium and three strontium atoms with bond distances [Mg–D2] = 1.919(7) Å, [Sr–D2] = 2.662(1) Å. The limiting ionic formula $SrD_2 \cdot Mg_2^{2+}[FeD_6]^{4-}$ suggests that the transition metal complex conforms to the 18-electron rule.

1. Introduction

Recently we have reported the first quaternary transition metal hydride as found in the Ca–Mg–Ni–H system, *i.e.* $CaMgNiH_4$, containing a tetrahedral $[NiH_4]^{4-}$ 18-electron complex [1]. In this communication we report on the discovery of another such hydride in the Sr–Mg–Fe–H system, *i.e.* $SrMg_2FeH_8$, containing an octahedral $[FeH_6]^{4-}$ 18-electron complex.

2. Experimental details

2.1. Synthesis

Binary alkaline earth metal alloys of nominal composition $SrMg_{2.2}$ were prepared from the elements (strontium, JMG, rod, 1.65 cm, 99%; magnesium, CERAC, 1/8 in pieces, 99.99%) by arc melting. The ingot was powdered and mixed with iron powder (JMC, London, 99.99%) under argon at the ratio $SrMg_{2.2}$:Fe = 1:1, wrapped in molybdenum foil, inserted into an open quartz tube, and placed in a high temperature high pressure autoclave. After evacuation

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of 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 70 bar at room temperature. The temperature was increased to 490–510 °C, yielding a hydrogen (deuterium) pressure of 140 bar. That temperature was held for 7–14 days during which the pressure decreased to about 130 bar, and then the temperature was cooled to room temperature. After the hydrogen (deuterium) pressure (about 50 bar at room temperature) was released the autoclave was opened and the samples were transferred to an argon-filled glove-box. The final products had a green colour and were sensitive to air.

2.2. *X-ray diffraction*

The samples were characterized by X-ray powder diffraction at room temperature (Guinier camera with sealed capillaries and Philips diffractometer, Co Kα radiation; internal standard, silicon powder with $a = 5.4308$ Å). The Guinier films were measured on a computer-controlled microdensitometer [2]. The patterns revealed the presence of a new hydride phase, of small quantities of ternary $SrMgH_4$ [3] and Mg_2FeH_6 [4], and of unreacted elemental iron. After subtraction of the peaks due to these impurity phases, the patterns were indexed on a trigonal lattice with cell parameters $a = 4.5174(2)$ Å and $c = 6.5807(4)$ Å (hydride), and $a = 4.5072(2)$ Å and $c = 6.5663(4)$ Å (deuteride). The reflection intensities were consistent with a metal atom model arrangement of composition $SrMg_2Fe$ as described in space group $P\bar{3}m1$ (No. 164). The model together with the three impurity phases was refined from the diffractometer data by the program DBWS-9006 [5] (see also ref. 6), and converged at the residuals $R_B = 0.061$, $R_p = 0.055$ and $R_{wp} = 0.075$.

2.3. *Neutron diffraction*

The distribution of the hydrogen atoms in the structure was established by neutron diffraction on the DMC powder diffractometer at the SAPHIR reactor at PSI, Villigen (Ge(311) monochromator, neutron wavelengths $\lambda = 1.7013$ Å, angular range 3.0°–135.0°, angular step $\Delta\ 2\theta = 0.1°$, $T = 292$ K [7]). The sample (about 3 g) was enclosed in a cylindrical vanadium container of 8 mm inner diameter and measured in the high resolution mode for 19 h. The profile refinements were performed by using DBWS-9006. The structure of the new deuteride was assumed to contain two symmetry-independent deuterium sites, one (D1) surrounding iron in an octahedral configuration, and the other (D2) situated in a tetrahedral hole formed by one magnesium and three strontium atoms, corresponding to the formula $SrMg_2FeD_8$. The impurity phases iron, Mg_2FeD_6 and $SrMgD_4$ were included in the refinements. The following 24 parameters were allowed to vary: four scale factors, three peak width parameters, one zero correction parameter, seven cell parameters ($SrMg_2FeD_8$, two; iron, one; Mg_2FeD_6, one; $SrMgD_4$, three), eight atomic parameters ($SrMg_2FeD_8$, four positional, four isotropic displacement parameters) and one asymmetry parameter. The atomic parameters of Mg_2FeD_6 and $SrMgD_4$ were fixed at their known values. Preliminary

TABLE 1

Refinement results on neutron diffraction data for trigonal $SrMg_2FeD_8$ ($T = 292$ K)

Atom	Position	x	y	z	Isotropic temperature factor U_{iso} ($\times 100$ Å^2)
Sr	1(b)	0.0000	0.0000	0.5000	0.6(1)
Mg	2(d)	0.3333	0.6667	0.1223(8)	0.46(9)
Fe	1(a)	0.0000	0.0000	0.0000	0.16(7)
D1	6(i)	0.1617(6)	$-x$	0.8557(3)	2.08(4)
D2	2(d)	0.3333	0.6667	0.4146(7)	U_{iso}(D1)

Space group, $P\bar{3}m1$ (No. 164); cell parameters, $a = 4.5072(2)$ Å, $c = 6.5663(4)$ Å; $R_B = 0.038$, $R_p = 0.037$, $R_{WP} = 0.054$ for 85 reflections; form of temperature factor, $T = \exp[-8\pi^2 U_{iso}(\sin\theta/\lambda)^2]$; estimated standard deviations in parentheses.

TABLE 2

Interatomic distances up to 3.6 Å, and D–D contact distances for $SrMg_2FeD_8$ ($T = 292$ K)

Fe–6D1	1.578(4)	D1–Fe	1.578(4)
–6Mg	2.724(2)	–Mg	2.205(6)
–2Sr	3.2832(2)	–2Mg	2.259(6)
Sr–6D1	2.655(3)	–Sr	2.655(3)
–6D2	2.662(1)	–2D1	2.187(5)
–2Fe	3.2832(2)	–2D2	2.869(5)
–6Mg	3.595(4)	D2–Mg	1.919(7)
Mg–D2	1.919(7)	–3Sr	2.662(1)
–3D1	2.205(6)	–6D1	2.869(5)
–6D1	2.259(6)		
–3Fe	2.724(2)		
–3Mg	3.058(4)		
–3Sr	3.595(4)		

Estimated standard deviations in parentheses.

refinements showed that the occupancy factors of the two deuterium sites did not differ significantly from 100%. Thus, they were fixed at unity in the final refinement. Refinement results 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 $SrMg_2FeD_8$ can be described as an intergrowth of slabs of composition Mg_2FeD_6 and sheets of composition SrD_2 (Fig. 2). The Mg_2FeD_6 slabs are built up by octahedral $[FeD_6]^{4-}$ complex anions similar to those in Mg_2FeD_6 [4]. They are surrounded by six magnesium cations in a trigonal antiprismatic configuration such that adjacent antiprisms share edges. The SrD_2 sheets consist of a hexagonal net of metal atoms in which deuterium

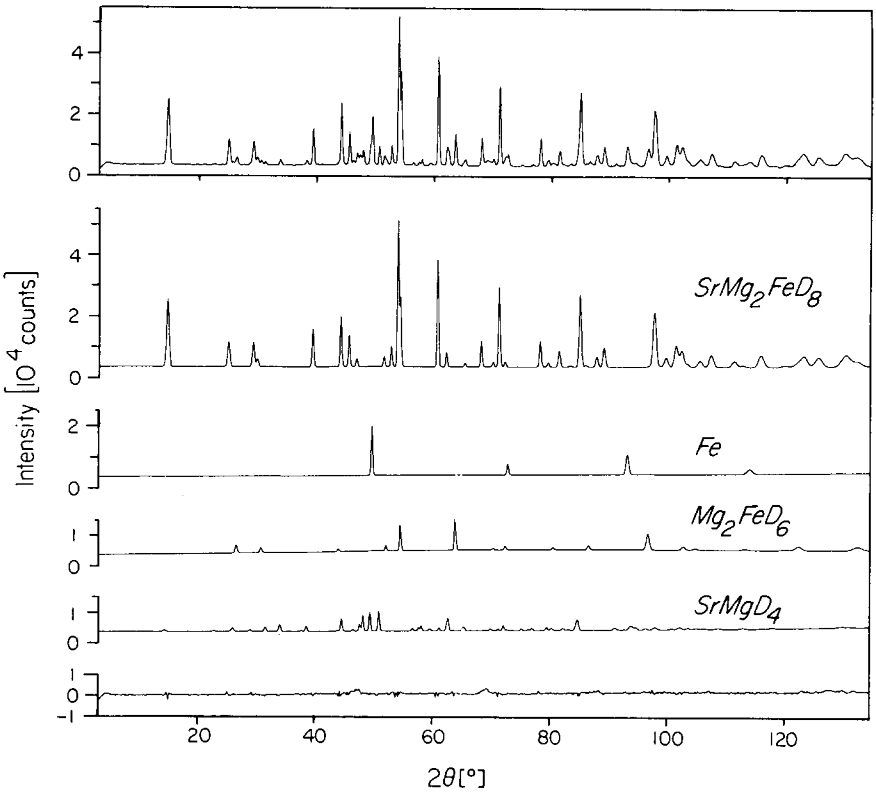

Fig. 1. Observed (top), calculated (middle) and difference (bottom) neutron diffraction patterns of a sample containing $SrMg_2FeD_8$ ($\lambda = 1.7013$ Å).

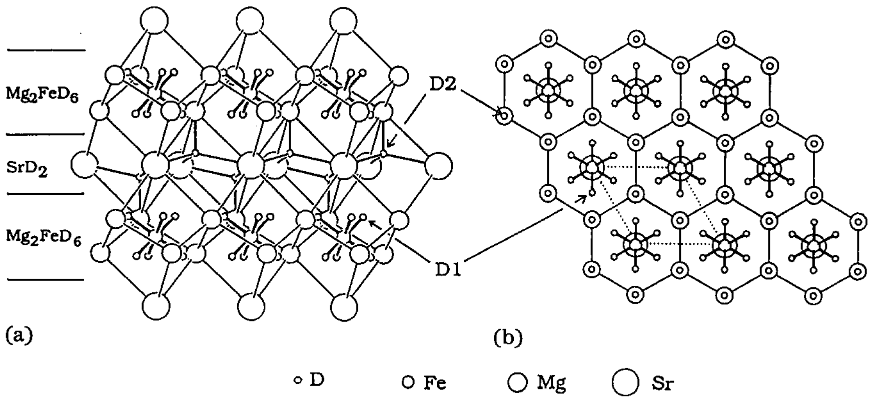

Fig. 2. Structure of $SrMg_2FeD_8$, viewed (a) perpendicular and (b) parallel to the trigonal axis, showing the intergrowth of the Mg_2FeD_6 slabs with the SrD_2 sheets.

is situated slightly above and below the centres of the metal triangles. The connection between the SrD_2 sheets and Mg_2FeD_6 slabs along the trigonal axis is such that the strontium atoms of the former complete the magnesium antiprisms of the latter to form deformed alkaline earth cubes that surround the $[FeD_6]^{4-}$ anions, similar to those in Mg_2FeD_6. The deuterium atoms of the SrD_2 sheets are bonded to the magnesium atoms of the Mg_2FeD_6 slabs to complete the tetrahedral configuration around the alkaline earth atoms. These structural features are consistent with an 18-electron transition metal complex as postulated from the limiting ionic formula $SrD_2 \cdot Mg_2{}^{2+}[FeD_6]^{4-}$. Other known hydride structures containing octahedral 18-electron transition metal complexes are orthorhombic Na_3RhH_6 and congeners [8] and rhombohedral Li_4RuH_6 and congeners [9]. Known examples of complex transition metal deuterides containing differently bound deuterium atoms are tetragonal A_3PtD_5 (A≡K, Rb, Cs) and K_3PdD_3, containing $[PtD_4]^{2-}$ and $[PdD_2]^{2-}$ complexes respectively, and deuteride ions coordinated exclusively by alkali metals [10], and orthorhombic $Mg_6Co_2D_{11}$, containing $[CoD_4]^{5-}$ and $[CoD_5]^{4-}$ complexes, and deuteride ions coordinated exclusively by magnesium [11]. The connection of the transition-metal-centred alkaline earth cubes in the latter compound is identical to that in $SrMg_2FeD_8$.

The metal deuterium distances in the $[FeD_6]^{4-}$ complex of $SrMg_2FeD_8$, [Fe–D1] = 1.578(4) Å, are slightly longer than those in Mg_2FeD_6, [Fe–D] = 1.556(5) Å [4], as expected in view of the relatively expanded alkaline earth matrix surrounding that complex in the former deuteride. The alkaline earth–deuterium bond distances [Mg–D1] = 2.205(6)–2.259(6) Å, [Mg–D2] = 1.918(7) Å, [Sr–D1] = 2.655(3) Å, and [Sr–D2] = 2.662(1) Å, are consistent with the corresponding distances in the ternary deuteride Mg_2FeD_6 ([Mg–D] = 2.22 Å) [4], the elemental deuterides MgD_2 ([Mg–D] = 1.95 Å) and SrD_2 ([Sr–D] = 2.45–2.84 Å [3]), and the recently reported [3] mixed alkaline deuteride $SrMgD_4$ ([Sr–D] = 2.43–2.82 Å, [Mg–D] = 1.87–1.89 Å).

Desorption measurements on $SrMg_2FeH_8$ are in progress to determine its thermal stability.

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