Journal of Alloys and Compounds, 206 (1994) 73–75
JALCOM 1020

Monoclinic $Sr_2Mg_3H_{10}$ with $Ba_2Ni_3F_{10}$-type structure

F. Gingl and K. Yvon*
Laboratoire de Cristallographie, Université de Genève, 24 Quai E. Ansermet, CH-1211 Geneva 4 (Switzerland)

P. Fischer
Laboratorium für Neutronenstreuung, Eidgenössische Technische Hochschule Zürich und Paul Scherrer Institut, CH-5232 Villigen PSI (Switzerland)

(Received September 28, 1993)

Abstract

$Sr_2Mg_3H_{10}$ and its deuteride were prepared from $SrMg_2$ alloy at 700 K under 75 bar hydrogen (65 bar deuterium) pressure and characterized by X-ray and neutron powder diffraction. They crystallize with the monoclinic $Ba_2Ni_3F_{10}$ structure type in space group *C*2/*m* (No. 12), with the following cell parameters at 295 K: $a = 17.586(5)$ Å, $b = 5.742(2)$ Å, $c = 7.491(2)$ Å, $\beta = 111.51(2)°$, $V = 703.8(2)$ Å^3 (hydride); $a = 17.539(4)$ Å, $b = 5.730(1)$, Å, $c = 7.480(2)$ Å, $\beta = 111.48(2)°$, $V = 699.5(2)$ Å^3 (deuteride); $Z = 4$. The metal–deuterium bond distances range from 1.81 to 2.14 Å (Mg–D) and from 2.49 to 2.96 Å (Sr–D).

1. Introduction

During our work on $SrMgH_4$ [1] we found evidence for the existence of a second ternary phase in the Sr–Mg–H system, which was formed by hydrogenation of SrMg alloys with Sr:Mg < 2:3. In this paper we present the synthesis and crystal structure of this compound, namely $Sr_2Mg_3H_{10}$. Like $SrMgH_4$, it crystallizes with a structure type found in ternary fluorides.

2. Experimental details

2.1. *Synthesis*

$SrMg_2$ alloys were prepared by arc melting 1:2 mixtures of the elements (Sr, Alfa, 99%; Mg, Cerac, $\frac{1}{8}$ in, 99.99%). The ingots were powdered under argon and hydrogenated in a high-temperature, high-pressure autoclave for 6 days at 703(5) K, (693(5) K) and 75(5) bar hydrogen (65(5) bar deuterium) pressure. Alloys with a higher Sr:Mg ratio led to products with a higher content of $SrMgH_4$. The final products are light grey. Because of its sensitivity to air, the thermal stability of $Sr_2Mg_3H_{10}$ could not be determined. However, the conditions of synthesis indicate that it is more stable than MgH_2, but less stable than $SrMgH_4$.

2.2. *X-ray diffraction*

The hydride and deuteride samples were characterized by X-ray powder diffraction at room temperature (Huber 645 Guinier diffractometer [2], Cu Kα_1 radiation, internal standard Si, NBS 640 *a*). The patterns were indexed with DICVOL91 [3] to a monoclinic C-centred cell (refined cell parameters: $a = 17.586(5)$ Å, $b = 5.742(2)$ Å, $c = 7.491(2)$ Å, $\beta = 111.51(2)°$ (hydride); $a = 17.539(4)$ Å, $b = 5.730(1)$ Å, $c = 7.480(2)$ Å, $\beta = 111.48(2)°$ (deuteride)). The metal atom substructure was solved in space group *C*2/*m* [4] using direct methods (programme SHELXS-86 [5]). A preliminary structure refinement was performed on diffractometer data by using the programme DBWS-9006PC [6]. The consistency factors were $R_B = 10.4\%$, $R_{wp} = 13.9\%$ and $S = 2.39$ for the hydride and $R_B = 7.4\%$, $R_{wp} = 13.0\%$ and $S = 2.03$ for the deuteride.

2.3. *Neutron diffraction*

The hydrogen positions were determined from neutron powder diffraction data of a deuterated sample measured on the DMC diffractometer [7] at the reactor SAPHIR, PSI Villigen (Ge (311) monochromator, $\lambda = 1.6984$ Å, 2θ range 3.0°–134.8°, step size $\Delta(2\theta) = 0.1°$, $(\sin\theta/\lambda)_{max} = 0.544$ Å^{-1}, $T = 293$ K). The sample (5.5 g) was enclosed in a cylindrical vanadium container of 9 mm inner diameter and measured in high-resolution mode. The transmission factor was measured ($\mu R = 0.147$) and the data were corrected accordingly. For the structure refinement the F atom coordinates

---

*Author to whom correspondence should be addressed.

SSDI 0925-8388(93)01020-5

TABLE 1. Refinement results on neutron powder diffraction data for $Sr_2Mg_3D_{10}$ (T = 295 K; estimated standard deviations in parentheses)

Atom	Site	x	y	z	U_{iso} ($\times 10^{-2}$ Å^2)
Sr1	4(*i*)	0.2831(6)	0	0.690(1)	0.2(1)
Sr2	4(*i*)	0.3826(7)	0	0.283(1)	U_{Sr1}
Mg1	4(*i*)	0.0757(7)	0	0.438(2)	0.5(1)
Mg2	4(*i*)	0.1710(9)	0	0.023(2)	U_{Mg1}
Mg3	4(*g*)	0	0.260(2)	0	U_{Mg1}
D1	8(*j*)	0.1118(5)	0.269(1)	0.024(1)	2.42(9)
D2	8(*j*)	0.1532(4)	0.246(2)	0.486(1)	U_{D1}
D3	4(*i*)	0.0223(8)	0	0.180(2)	U_{D1}
D4	4(*i*)	0.1361(7)	0	0.743(2)	U_{D1}
D5	4(*i*)	0.2373(8)	0	0.281(2)	U_{D1}
D6	4(*i*)	0.5150(8)	0	0.181(2)	U_{D1}
D7	4(*h*)	0	0.231(2)	$\frac{1}{2}$	U_{D1}
D8	4(*e*)	$\frac{1}{4}$	$\frac{1}{4}$	0	U_{D1}

Space group $C2/m$ (No. 12).
Cell parameters $a = 17.539(4)$ Å, $b = 5.730(1)$ Å, $c = 7.480(2)$ Å, $\beta = 111.48(2)°$, $V = 699.5(2)$ Å^3, $Z = 4$.
$R_B = 4.4\%$, $R_P = 2.9\%$, $R_{wp} = 3.8\%$, $S = 1.94$ for 541 reflections.
Form of the temperature factor: $T = \exp[-8\pi^2 U_{iso}(\sin^2\theta/\lambda^2)]$.

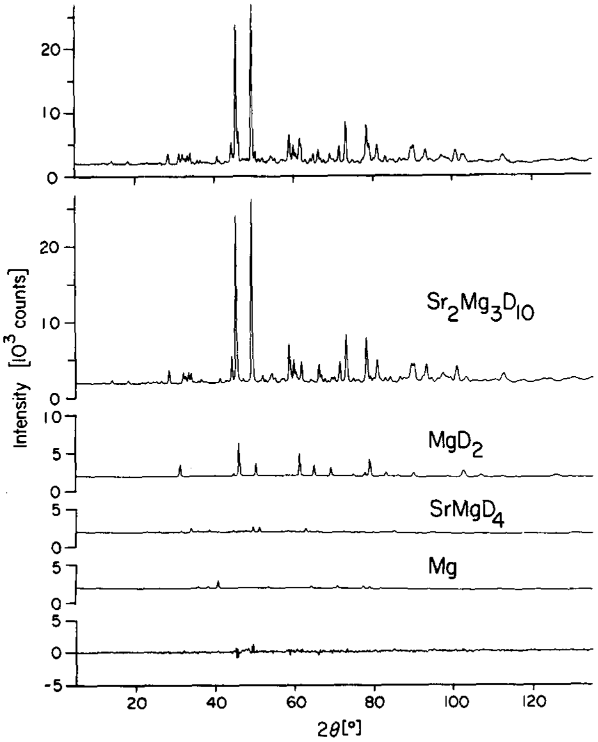

Fig. 1. Observed (top), calculated (middle) and difference (bottom) neutron powder patterns of $Sr_2Mg_3D_{10}$, containing MgD_2, $SrMgD_4$ and Mg impurity phases ($\lambda = 1.6984$ Å).

of $Ba_2Ni_3F_{10}$ [8] were taken as a first model for the deuterium positions. The structures of four phases were refined: monoclinic $Sr_2Mg_3D_{10}$, MgD_2 [9] and traces of $SrMgD_4$ [1] and unreacted Mg. The following 53 parameters were allowed to vary: four scale factors, the θ zero position, six background parameters, four peak shape parameters, 11 cell parameters ($Sr_2Mg_3D_{10}$, four; MgD_2, two; $SrMgD_4$, three; Mg, two), three thermal displacement parameters and 24 positional parameters for $Sr_2Mg_3D_{10}$. Scattering lengths ($b_{Sr} = 7.02$ fm, $b_{Mg} = 5.375$ fm, $b_D = 6.674$ fm) were taken from ref. 10. The results are summarized in Table 1; the atomic coordinates are standardized [11]. The observed, calculated and difference neutron patterns are shown in Fig. 1.

3. Results and discussion

$Sr_2Mg_3D_{10}$ crystallizes with the $Ba_2Ni_3F_{10}$ structure type [8]. The structure (Fig. 2) contains three symmetry-independent Mg atoms, all of them with slightly distorted octahedral deuterium coordination, and two Sr atoms, both with coordination number 12 (see below). The Mg3-centred MgD_6 octahedra are connected via edges to rutile-type chains parallel to the b axis. The Mg2-centred octahedra are connected via corners to zigzag

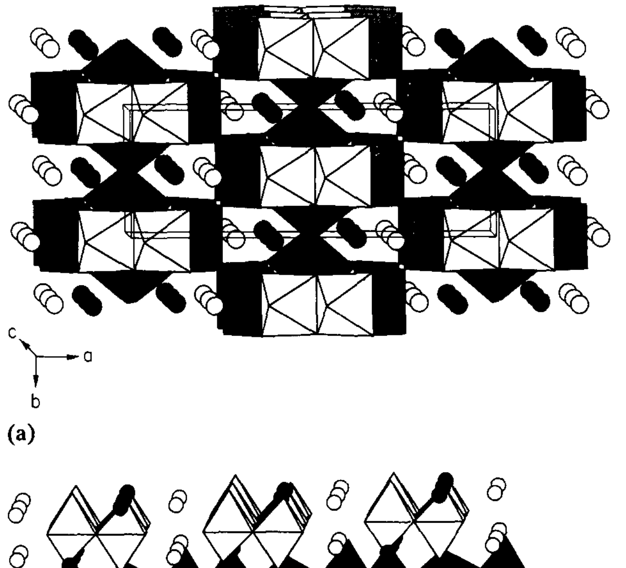

Fig. 2. Projections of $Sr_2Mg_3D_{10}$ (a) along the c axis and (b) along the b axis: open circles, Sr1; filled circles, Sr2; Mg-centred octahedra — light, Mg1; medium, Mg2; dark, Mg3.

TABLE 2. Selected interatomic distances (angstroms) shorter than 3 Å for $Sr_2Mg_3D_{10}$ (estimated standard deviations in parentheses)

Sr1–	2 D2	2.49(1)
	2 D1	2.617(9)
	2 D2	2.64(1)
	D4	2.75(2)
	D5	2.87(2)
	2 D5	2.905(3)
	2 D8	2.961(8)
Sr2–	2 D2	2.51(2)
	D5	2.54(2)
	2 D7	2.61(2)
	2 D1	2.69(1)
	D6	2.70(2)
	2 D4	2.882(2)
	2 D8	2.889(7)
Mg1–	D3	1.81(2)
	2 D2	1.90(1)
	2 D7	2.05(3)
	D4	2.14(2)
Mg2–	D5	1.86(2)
	2 D1	1.86(1)
	D4	1.96(2)
	2 D8	2.04(1)
Mg3–	2 D6	1.88(1)
	2 D1	1.903(9)
	2 D3	1.95(1)
D1–	Mg2	1.86(1)
	Mg3	1.903(9)
	Sr1	2.617(9)
	Sr2	2.69(1)
D2–	Mg1	1.90(1)
	Sr1	2.49(1)
	Sr2	2.51(1)
	Sr1	2.64(1)
D3–	Mg1	1.81(2)
	2 Mg3	1.95(1)
D4–	Mg2	1.96(2)
	Mg1	2.14(2)
	Sr1	2.75(2)
	2 Sr2	2.882(2)
D5–	Mg2	1.86(2)
	Sr2	2.54(2)
	Sr1	2.87(2)
	2 Sr1	2.905(3)
D6–	2 Mg3	1.88(1)
	Sr2	2.70(2)
D7–	2 Mg1	2.05(3)
	2 Sr2	2.61(2)
D8–	2 Mg2	2.04(1)
	2 Sr2	2.889(7)
	2 Sr1	2.961(8)

chains in the *ab* plane, which interconnect two rutile-type chains. The slabs formed by these two types of chains are linked together by pairs of edge-sharing Mg1-centred octahedra. The Sr atoms are located in the cavities of this three-dimensional network and have cuboctahedral (Sr2) and twinned cuboctahedral (Sr1) deuterium coordination. The eight symmetry-independent deuterium sites are coordinated as follows: triangular (D3 [3 Mg]), octahedral with three short distances (D6 [Sr, 2 Mg]), tetrahedral (D1, D7 [2 Sr, 2 Mg], D2 [3 Sr, Mg]), square pyramidal (D4 [3 Sr, 2 Mg], D5 [4 Sr, Mg]) and octahedral (D8 [4 Sr, 2 Mg]). The metal–deuterium bond distances (Table 2) range from 1.81 to 2.14 Å (Mg–D) and from 2.49 to 2.96 Å (Sr–D) and are similar to those found in $SrMgD_4$ [1], SrD_2 [12] and MgD_2 [9]. The shortest D–D distance is 2.49 Å.

$Sr_2Mg_3D_{10}$ is one more example of the structural analogy that exists between hydrides and fluorides [13, 14].

Acknowledgments

We thank J.-L Lorenzoni for technical assistance and Mrs. B. Künzler for help with producing the drawings. This work was supported by the Swiss Federal Office of Energy in the frame of the Swiss Hydrogen Energy Research Programme and the Swiss National Science Foundation.

References

1 F. Gingl, K. Yvon and P. Fischer, *J. Alloys Comp., 187* (1992) 105.
2 J. Ihringer, *J. Appl. Crystallogr., 15* (1982) 1.
3 A. Boultif and D. Louër, *J. Appl. Crystallogr., 24* (1991) 987.
4 Th. Hahn (ed.), *International Tables for Crystallography,* Vol. A, Reidel, Dordrecht, 2nd edn., 1987.
5 G.M. Sheldrick, *Acta Crystallogr. A, 46* (1990) 467.
6 D.B. Wiles and R.A. Young, *J. Appl. Crystallogr., 14* (1981) 149; A. Sakthivel and R.A. Young, *Programs* DBWS-9006 *and* DBWS-9006PC, School of Physics, Georgia Institute of Technology, Atlanta, GA, 1990.
7 J. Schefer, P. Fischer, H. Heer, A. Isacson, M. Koch and R. Thut, *Nucl. Instrum. Methods Phys. Res. A, 288* (1990) 477.
8 M. Leblanc, G. Ferey and R. De Pape, *J. Solid State Chem., 33* (1980) 317.
9 W.H. Zachariasen, C.E. Holley and J.F. Stamper Jr., *Acta Crystallogr., 16* (1963) 352.
10 L. Koester, H. Rauch and E. Seymann, *At. Data Nucl. Data Tables, 49* (1991) 65.
11 L.M. Gelato and E. Parthé, *J. Appl. Crystallogr., 20* (1987) 139.
12 N.E. Brese, M. O'Keeffe and R.B. von Dreele, *J. Solid State Chem., 88* (1990) 571.
13 C.E. Messer, *J. Solid State Chem., 2* (1970) 144.
14 A.J. Maeland and W.B. Lahar, *Z. Phys. Chem., 179* (1993) 181.