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Structural Studies of Hexagonal Mg_2NiH_x

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X-Ray and neutron powder diffraction measurements have been used to study the structural changes when a small amount of hydrogen is absorbed in the hexagonal alloy Mg_2Ni, $a=5.2107$ Å and $c=13.2437$ Å. The unit cell dimensions for saturated Mg_2NiH_x ($x\simeq0.3$) are $a=5.2315$ Å and $c=13.404$ Å. It is shown that the most significant structural change caused by the hydrogenation is an increase in one Mg – Mg distance from 3.062 Å to about 3.73 Å, indicating a hydrogen site between the two Mg-atoms. The result is also in agreement with the assumption that fully ionized H^- is present in $Mg_2NiH_{0.3}$.

The reaction between hydrogen and Mg_2Ni to form the ternary hydride Mg_2NiH_4, proposed as a possible hydrogen storage material, occurs in two consecutive steps, (I) and (II).

$$Mg_2Ni+(\tfrac{x}{2})H_2 \rightleftarrows Mg_2NiH_x \quad (x\simeq0.3) \qquad (I)$$

$$Mg_2NiH_x+(2-\tfrac{x}{2})H_2 \rightleftarrows Mg_2NiH_4 \qquad (II)$$

In the first reaction hydrogen dissolves in hexagonal Mg_2Ni with minor expansions of the unit cell dimensions, primarily of the c-axis (*cf.* Table 1).[1] In the second reaction a complete phase transition takes place, and if the reaction occurs above 235 °C a cubic Mg_2NiH_4(HT) structure, $a=6.490$ Å, of antifluorite type is formed.[2]

It has been proposed in a recent study by Hirata, Matsumoto, Amano and Sasaki [3] that the HT phase is tetragonal, with $a=6.533$ Å and $c=7.499$ Å. An examination of their published data, however, gives scant support for this conclusion. Although the deviations of observed from calculated diffraction angles are smaller for the proposed tetragonal cell than for a cubic cell, the De Wolff figure of merit,[4] M_{20}, is higher for a cubic indexing in an F-centered space group than for the tetragonal indexing. Interestingly, the 9 first lines ($2\theta<85°$) of the 11 measured reflections show positive differences between observed and calculated diffraction angles in a cubic refinement, thus indicating a possible zero point error.

Table 1. Crystal data.

	Mg_2Ni	Mg_2NiH_x ($x\approx0.3$)
Space group	$P6_222$	$P6_222$
Z	6	6
FW	107.33	107.67
a (Å)	5.2107(2)	5.2315(6)
c (Å)	13.2437(5)	13.404(3)
V (Å^3)	311.41	317.70
d_{calc} (g/cm^3)	3.434	≈3.37
M_{20}	193	26

The transformations of Mg_2NiH_4(HT) below 235 °C have been studied by Genossar and Rudman,[5] by Darnaudery, Pezat, Darriet and Hagenmuller [6] and by Noréus and Werner.[7] Although the reaction is not yet fully understood, it seems clear that at 20 °C a monoclinic low-temperature modification Mg_2NiH_4(LT) exists. The unit cell dimensions proposed by the present authors are $a=6.497$ Å, $b=6.414$ Å, $c=6.601$ Å and $\beta=93.23°$, although it was stated that the interpretation of weak lines in the pattern as superstructure lines could not be completely ruled out.[7] Independently, a similar conclusion was drawn by Genossar and Rudman.[5] Darnaudery *et al.*[6] claim that the a-axis should be doubled, 12.99 Å. They have also found an orthorhombic

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Mg_2NiH_4(LT) phase with $a=6.499$ Å, $b=6.415$ Å and $c=6.589$ Å. Unfortunately, however, we have not found it possible to index all diffraction lines in patterns from Mg_2NiH_4 obtained at 20 °C solely by these two unit cells.

The present work was undertaken in an attempt to provide information about the first reaction step, I, in the transformation of Mg_2Ni to a hydrogen containing material. The second reaction, II, will be the subject of a forthcoming study.

EXPERIMENTAL

The Mg_2Ni used in the present study was supplied by MPD-Technology Corp.; it is commercially available as their hydrogen storage alloy, Hystore 301. It contains a slight excess of free magnesium metal in order to prevent the formation of $MgNi_2$ during its preparation.

A sample of 2 g of Mg_2Ni was cycled several times at 400 °C with hydrogen pressures up to 100 bar. Then the pressure was slowly decreased. By monitoring the temperature in the sample, the onset of dehydrogenation could be determined. About 20% of the expected hydrogen content was then very slowly withdrawn. The temperature was lowered to the ambient value, and a sample of a few mg was taken out for X-ray analysis. The hydride was then cycled a few more times to reduce surface oxide contamination. The above procedure was repeated, and each time about 20% more hydrogen was removed from the hydride. Thus, a set of 5 samples with various hydrogen contents was obtained.

The diffraction patterns yielded by the samples contained lines of $Mg_2NiH_{0.3}$, MgH_2 and Mg_2NiH_4(LT). The unit cell dimensions of the constituents remained the same within the standard deviations throughout the set. A number of elusive lines could, however, not be indexed. Their intensities were always very weak, and they diminished at approximately the same rate as those belonging to the monoclinic Mg_2NiH_4(LT). Some of these lines also showed small positional variations, which made it difficult to interpret them as superstructure lines in a simple way. The last sample was used in the subsequent profile refinement.

DATA COLLECTION

The X-ray powder photographs were taken in a subtraction-geometry Guinier-Hägg focussing camera of 80 mm diameter, with strictly monochromatized Cu$K\alpha_1$ radiation ($\lambda=1.5405981$ Å).[8] Single-coated film (CEA Reflex 15) was used in order to avoid superposition of front- and back-layer intensity profiles, and to reduce the background. All measurements of the films were made by means of a computer-controlled single-beam microdensitometer specially designed for X-ray powder diffraction photographs.[9] The slit opening of the collimator was 0.040×2.0 mm and the corresponding measuring step length in the θ-direction on the photographs was about 0.0143°. The θ scale was calibrated by the internal standard technique, using a parabolic correction curve. Silicon [$a=5.430880(35)$ Å at 25 °C] [10] was chosen as standard substance.

The neutron diffraction pattern of Hystore 301 was recorded using one of the diffractometers at the R2 reactor in Studsvik.[11] The incoming wavelength was selected to be 1.1562 Å, allowing a wave vector transfer from 1.0 to 8.4 $Å^{-1}$. To avoid preferred orientation effects the target was rotated during the measurements.

RESULTS AND DISCUSSION

a. Mg_2Ni. Diffraction data from Mg_2Ni, with a slight excess of Mg, was collected by neutron and X-ray powder techniques. Both data sets were refined by the Rietveld profile analysis procedure [12] using program versions for simultaneous refinement of two phases present in a powder sample.[13] Unit cell dimensions for Mg_2Ni, $a=5.2107(2)$ Å and $c=13.2437(5)$ Å, were taken from Ref. 7. The fractional atomic coordinates in space group $P6_222$ used as starting parameters in the refinements were those derived by Schubert and Anderko.[14] No significant differences between the coordinates obtained by the two techniques were found, but the most accurate results were obtained from the neutron diffraction data. The R_F ($=\Sigma|\sqrt{I_{obs}}-\sqrt{I_{calc}}|/\Sigma\sqrt{I_{obs}}$) values obtained from this data set were 0.031 and 0.051 for Mg_2Ni and Mg, respectively. Final position and isotropic thermal parameters are given in Table 2a. Interatomic distances are listed in Table 3a.

b. $Mg_2NiH_{0.3}$. The $Mg_2NiH_{0.3}$ sample, also containing a small amount of MgH_2, was investigated by X-ray diffraction technique. The diffraction patterns obtained were of low quality, however, because of disorder in the structure, caused by the non-stoichiometric hydrogen content. The half-widths of the diffraction lines varied in an

Table 2. Positional and isotropic thermal parameters.

Atom	Site	x	y	z	B (Å^2)
Positional and isotropic thermal parameters for Mg_2Ni					
Ni1	3(b)	0.0	0.0	0.5	0.73(4)[a]
Ni2	3(d)	0.5	0.0	0.5	0.82(4)
Mg1	6(f)	0.5	0.0	0.1158(2)	0.69(5)
Mg2	6(i)	0.1626(6)	0.3252(12)	0.0	0.53(5)
Mg position parameters for $Mg_2NiH_{0.3}$					
Mg1	6(f)	0.5	0.0	0.1391(9)	
Mg2	6(i)	0.160(3)	0.320(6)	0.0	

[a] Estimated standard deviations are given within parantheses.

irregular way. Thus, the prerequisite for a Rietveld refinement, that the half-widths should be described by a second-order polynomial in tg θ, was not well fullfilled. Furthermore, the background was seriously affected by a large amount of amorphous material. It was supposed, however, that because of the simplicity of the structure a refinement could be made, albeit with limited accuracy. Most of the positional coordinates are fixed by the space group symmetry, $P6_222$. The only refinable coordinates are z for Mg1 and x for Mg2 (*cf.* Table 2), as y for Mg2 equals $2x$.

It was found in a number of refinements, using the complete data set up to $2\theta = 88°$, as well as using partial data sets from selected 2θ intervals, that although the R_F values usually were as high as about 0.2, the magnesium coordinates varied only within one standard deviation. Furthermore, if z for Mg1 was fixed at the start value 0.1158 (*cf.* Table 2a), the R_F values increased about 0.1. Therefore, it can be concluded that the transition of Mg_2Ni to $Mg_2NiH_{0.3}$ causes a significant shift in the Mg1 position. It should be realized, however, that the coordinates and distances listed in Tables 2b and 3b, respectively, are derived from a somewhat disordered structure. They should be interpreted as

Table 3. Interatomic metal-metal distances (Å) less than 4.0 Å. Estimated standard deviations are given within parentheses.

(a) Mg_2Ni			
Ni1 – Ni2	2.605(1)		
Ni1 – Mg1	2.691(1)		
Ni1 – Mg2	2.648(3)		
Ni2 – Mg1	2.691(1)		
Ni2 – Mg2	2.679(1)		
Mg1 – Mg1	2.932(2)	3.062(4)	
Mg1 – Mg2	3.255(2)	3.360(2)	3.408(4)
Mg2 – Mg2	2.936(7)	3.045(5)	
(b) $Mg_2NiH_{0.3}$			
Ni1 – Ni2	2.620(1)		
Ni1 – Mg1	2.66(2)		
Ni1 – Mg2	2.646(2)		
Ni2 – Mg1	2.718(8)		
Ni2 – Mg2	2.646(2)		
Mg1 – Mg1	2.722(6)	3.73(3)	
Mg1 – Mg2	3.02(2)	3.53(2)	3.61(3)
Mg2 – Mg2	2.90(4)	3.09(3)	

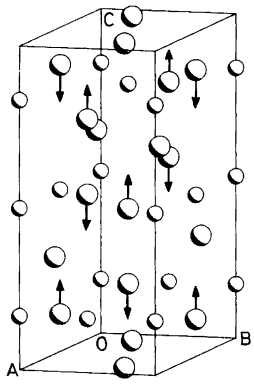

Fig. 1. View of the Mg_2Ni structure. The arrows denote the main directions of distortions induced when hydrogen enters the structure.

Table 4. Observed and calculated 2θ values for $Mg_2NiH_{0.3}$.

$2\theta_{obs}$	$2\theta_{calc}$	$\Delta 2\theta$	d_{obs}	I_{obs}	(*hkl*)
19.603	19.578	0.025	4.525	2354	(100)
19.908	19.855	0.053	4.456	5421	(003)
20.694	20.678	0.016	4.289	3484	(101)
23.717	23.685	0.032	3.7484	1948	(102)
28.072	28.025	0.047	3.1761	890	(103)
34.925	34.920	0.005	2.5670	762	(111)
36.872	36.857	0.015	2.4358	7314	(112)
39.068	39.008	0.060	2.3038	7150	(105)
39.756	39.759	−0.003	2.2655	8725	(200)
{	40.340	0.032			(006)
{ 40.372	40.347	0.025	2.2323	638	(201)
43.912	43.873	0.039	2.0602	1081	(114)
44.783	44.822	−0.039	2.0221	11745	(203)
45.219	45.219	0.000	2.0037	547	(106)
48.628	48.591	0.037	1.8708	179	(115)
51.837	51.791	0.046	1.7623	169	(107)
53.430	53.466	−0.367	1.7135	194	(210)
{ 53.920	53.930	−0.010	1.6991	663	(116)
{	53.936	−0.016			(211)
55.331	55.328	0.003	1.6590	369	(212)
57.600	57.598	0.002	1.5989	190	(213)
57.947	57.930	0.017	1.5902	1205	(206)
58.662	58.704	−0.042	1.5725	115	(108)
60.703	60.685	0.018	1.5244	85	(214)
61.759	61.767	−0.008	1.5009	195	(301)
62.252	62.291	−0.039	1.4902	177	(009)
63.033	63.048	−0.015	1.4736	1627	(302)
64.546	64.522	0.024	1.4426	3602	(215)
65.167	65.151	0.016	1.4304	342	(303)
66.170	66.182	−0.012	1.4111	736	(118)
68.062	68.038	0.024	1.3764	212	(304)
72.147	72.168	−0.021	1.3082	4105	(220)
75.698	75.713	−0.015	1.2554	1163	(223)

giving an average picture of the structure.

The unit cell dimensions of $Mg_2NiH_{0.3}$ determined by the profile refinement are listed in Table 1. An indexed pattern is given in Table 4.

As can be seen from Table 3, the most significant difference between Mg_2Ni and $Mg_2NiH_{0.3}$ is that one short Mg1 – Mg1 distance is increased from 3.062(4) Å in Mg_2Ni to 3.73(3) Å in $Mg_2NiH_{0.3}$. This is symbolized by arrows in Fig. 1, and it may be concluded that the hydrogen enters the structure at the midpoint between these Mg-atoms. In Fig. 2, the assumed hydrogen position is indicated. Interestingly, this point (0,0,1/2), position 3(c) in $P6_222$,[15] is the point in the structure located at maximum distance from the Ni-atoms. Considering that the Mg1 – Mg1, 3.73 Å, in $Mg_2NiH_{0.3}$ represents an average distance because of the disorder, and that Mg – D in MgD_2 is 1.95(2) Å,[16] it may be concluded that hydrogen in $Mg_2NiH_{0.3}$ is present as fully ionized H^-. This is also in agreement with the increase in volume of about 4 Å^3 per H-atom entering Mg_2Ni.

It was concluded by Genossar and Rudman [5] that Mg_2NiH_4 is a weakly ionized structure $Mg_2^{+2\delta}NiH_4^{-\delta}$ with $\delta \rightarrow 0$. Thus, reaction II (see above) should be accompanied by a distribution of the electric charge on H^- over more hydrogen atoms, although the total charge may remain the same.

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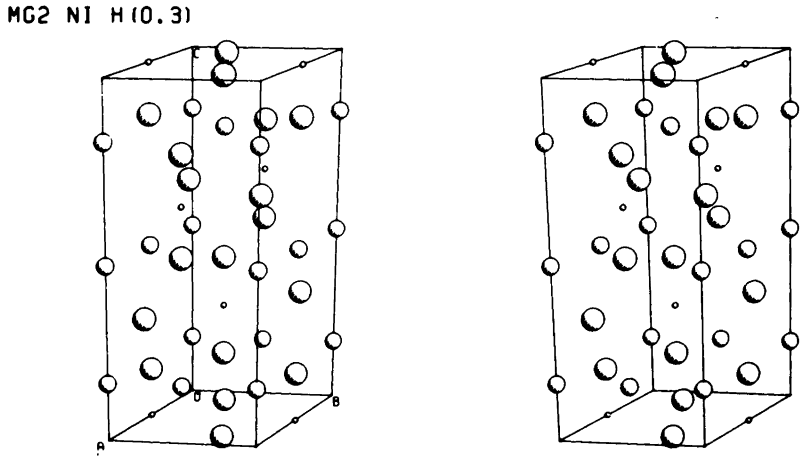

Fig. 2. Stereo view of the $Mg_2NiH_{0.3}$ structure. Small circles = assumed hydrogen sites (occupation factor ≈0.6), medium circles = Ni and large circles = Mg.

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