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Structural Studies of the Hydrogen Storage Material Mg_2NiH_4.
1. Cubic High-Temperature Structure

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The structure of the high-temperature modification of Mg_2NiD_4 has been determined from neutron powder diffraction data collected at 280 °C. It is face-centered cubic (space group *Fm*3*m*, with $a = 6.507$ (2) Å) with the metal atoms occupying anti-fluorite positions and the D atoms surrounding the Ni atoms in a disordered configuration of yet unknown local symmetry. The average structure resembles the K_2PtCl_6 structure type. The average metal–deuterium distances are d(Ni–D) = 1.49 (3) Å and d(Mg–D) = 2.305 (3) Å.

Introduction

Magnesium–nickel alloys are considered promising materials for energy storage applications.[2a] A compound of central interest is Mg_2Ni because it forms a ternary hydride Mg_2NiD_4[2b] having a favorable hydrogen-to-metal weight ratio of 3.8% and because its presence improves considerably the hydriding kinetics of the binary hydride MgH_2.

Contrary to other hydrogen storage materials such as FeTi[3-5] and $LaNi_5$[6] structural information on this compound is scarce. Gavra et al.[7] have shown from an X-ray study that Mg_2NiH_4 forms a cubic high-temperature (HT) phase with lattice constant $a = 6.490$ Å which transforms between 245 and 210 °C into a low-temperature (LT) phase of low symmetry. The metal atom arrangement of the HT phase was suggested to be of the anti-fluorite type. The positions of the H atoms and the overall symmetry of the structure have not been determined.

In this article we report on final neutron diffraction results on the HT (β') phase of the deuteride $Mg_2NiD_{3.9}$, corresponding to improved experimental conditions with respect to a preliminary account of the results which has been presented recently.[8] Moreover, in the present article the bonding of $Mg_2NiD_{3.9}$ will be discussed and compared to that in similar systems.

Table I. Crystal Data for the High-Temperature Phase (β') of $Mg_2NiD_{3.9}$ at 280 °C and 22 bar of D_2

space group	*Fm*3*m* (No. 225)
lattice const	$a = 6.507$ (2) A
atom positions	4 Ni in (4a) 0, 0, 0 etc.
	8 Mg in (8c) 1/4, 1/4, 1/4 etc.
	~16 D in (24e) x_D, 0, 0
fractional coord x_D	0.229 (1)[a] (0.229 (5))[b]
occupancy of D atom sites	0.69 (2)[a] (0.77 (10))[b]
temp factors	
B(Ni,Mg)	1.3 (2) A²[a] (1.2 (8) A²)[b]
B(D)	7.6 (3) A²[a] (9 (2) A²)[b]
R factors	5.6%[a] (8.1%)[b]

[a] Based on simultaneous profile refinement[9] of $Mg_2NiD_{3.9}$ and MgD_2.[15] [b] Based on least-squares refinement of integrated neutron intensities.

Experimental Section

The sample preparation is described in ref 8. In order to avoid large Bragg peaks from the container, we filled a Cu-coated vanadium tube with the sample and kept it under a constant pressure of 22 bar of D_2. This tube was placed into a second, coaxial vanadium tube which was evacuated and heated by electrical current to temperatures up to 300 °C. The assembly was mounted on a two-axis diffractometer ($\lambda = 2.346$ Å) at the reactor Saphir in Würenlingen, Switzerland, and a neutron diffraction pattern was recorded at $T = 280$ °C (Figure 1a). The pattern was analyzed by a special profile refinement technique[9] in which the contributions due to the MgD_2 impurity phase were taken into account. As shown in Figure 1b, 11 reflections were retained for the structure determination of $Mg_2NiD_{3.9}$. The results

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Table II. Interatomic Distances (Å)

	$Mg_2NiD_{3.9}$[a]				Sr_2IrD_5[b,c]				Sr_2RuD_6[c]		
atom	Mg	Ni	D	atom	Sr	Ir	D	atom	Sr	Ru	D
Mg	3.254 (1)	2.818 (1)	2.305 (3)	Sr	3.81	3.30	2.70	Sr	3.80	3.29	2.69
Ni		4.601 (2)	1.49 (3)	Ir		5.40	1.70	Ru		5.37	1.69
D			[2.11 (5)],[d,f] [2.51 (6)][e]	D			[2.4],[d] [3.0][e]	D			2.4,[d] 3.0[e]

[a] Based on least-squares refinement of integrated intensities. [b] Assuming $x(D) = 0.223$ and not 0.233 as given in ref 10. [c] Reference 10. [d] Between different transition metal-ligand spheres. [e] Within the transition metal-ligand sphere. The values in brackets do not correspond to interatomic distances but to distances between average atomic positions.

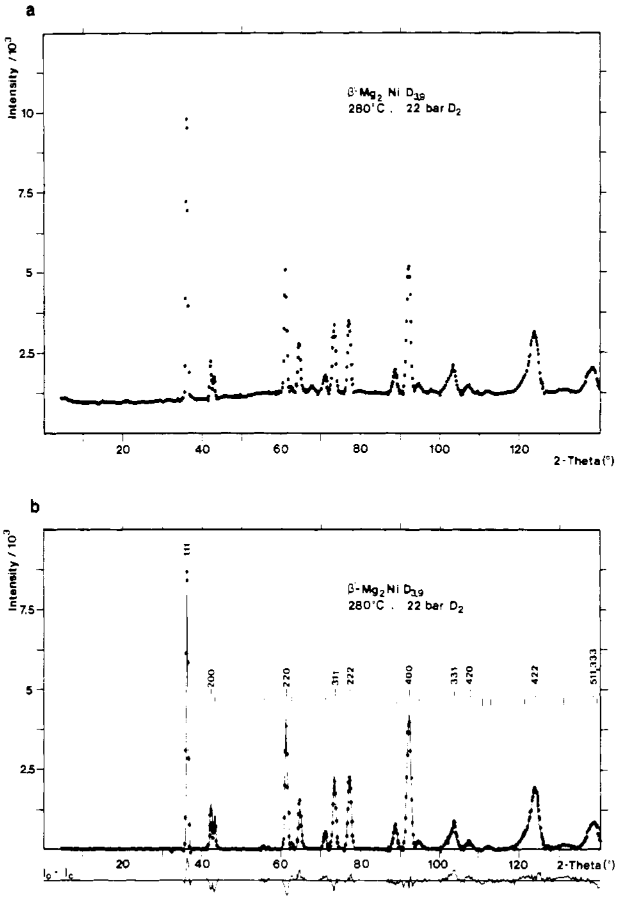

Figure 1. (a) Observed and absorption corrected and (b) calculated neutron diffraction pattern of the high-temperature phase (β′) of $Mg_2NiD_{3.9}$ at 280 °C and 22 bar of D_2 pressure (λ = 2.346 (1) Å). Nonlabeled peaks belong to the MgD_2 phase.[15]

are summarized in Table I, where they are compared with the results obtained from a least-squares refinement of integrated neutron intensities. Except for the standard deviations, which are much higher and presumably more realistic in the least-squares refinement than in the profile refinement, both methods yield practically the same results.

Results and Discussion

As can be seen from the structure shown in Figure 2, the Ni and Mg atoms occupy the cation and anion sites, respectively, of fluorite CaF_2, whereas the D atoms are distributed in a statistical manner over six equivalent sites forming an octahedron around the Ni atoms. This arrangement is identical to that found[10,11] for M_2RhH_5 and M_2IrH_5 (M = Ca, Sr, Eu) except that these hydrides have one more H atom on the average, in the coordination sphere of the transition-metal atom. Compounds having six H atoms in the coordination sphere, i.e., showing fully occupied H atom sites, are M_2RuH_6 (M = Ca, Sr, Eu, Yb).[12,13] Their atomic arrangement corresponds to the K_2PtCl_6 structure type.

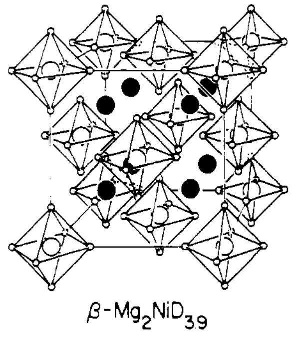

Figure 2. Average crystal structure of the disordered high-temperature phase (β′) of $Mg_2NiD_{3.9}$. Large filled circles represent Ni atoms and dotted spheres Mg atoms. The small open circles represent the average positions of the D atoms. Their average occupancy is 0.69.

As can be seen from Table II, the transition metal–deuterium distances in Mg_2NiD_4, Sr_2IrD_5, and Sr_2RuD_6 are relatively short and indicative of covalent bonding, whereas the alkaline earth–deuterium distances are relatively long and comparable to those in the ionic binary hydrides and deuterides (for SrH_2, $d(Sr-D) = 2.35$ (×3) and 2.71 (×4) Å;[14] for MgD_2, $d(Mg-D) = 1.95$ (×6) Å[15]). Thus from a bonding point of view it is useful to describe this series of compounds by an arrangement of divalent cations M^{2+} (M = Mg, Ca, Sr, Yb, Eu) and tetravalent complex anions of average formula $(TH_6)^{4-}$ (T = Ru), $(TH_5)^{4-}$ (T = Rh, Ir), and $(TH_4)^{4-}$ (T = Ni). Interestingly the H content of these complex anions decreases as the group number of the transition element increases such that they can all be characterized by 18 valence electrons in the metal–ligand bonding system. Thus the upper limit of the H concentration found in "H-deficient" compounds such as Sr_2IrD_5,[10] Eu_2IrH_5,[11] and Mg_2NiH_4[2] seems to be governed mainly by electronic factors which depend on the valency of the metal atoms. If this is correct, it should be possible to increase the maximum H content in, e.g., Mg_2NiH_{4-x} by partially replacing Ni with a transition metal of lower valency such as Mn, Fe, and Co or Mg by a non transition metal of higher valency such as Al.

As to the local composition of the complex anions and the local configuration of the D atoms around the transition-metal atoms, no statement can be made on the basis of the neutron diffraction data presently available because the structures are all disordered. In particular one cannot exclude the possibility that Ni has locally a tetrahedral D atom configuration and that the octahedral configuration as observed by the diffraction techniques above corresponds only to a thermal average of orientationally disordered $[NiD_4]^{4-}$ complex ions. An analysis

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of the low-temperature modification of $Mg_2NiD_{\sim 4}$ is therefore desirable.

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MCD Spectra of $M(CO)_5L$ Complexes (M = Cr, Mo, W; L = N Donor, P Donor)

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MCD spectra are reported and discussed for $M(CO)_5L$ complexes (M = Cr, Mo, W; L = PCl_3, $P(Ph)_3$, PMe_3, thiazole, pyridine, pyrazine, pyridazine, piperidine, and NMe_3). The results were used to assign the absorption bands of the $M(CO)_5L$ complexes. From the sign of the *A* term belonging to the lowest ligand field transition, it could be deduced that this transition is directed to the d_{z^2} orbital, a result that is of importance for the understanding of the photochemistry of these complexes. Furthermore, the magnitude of this *A* term decreases going from piperidine to NMe_3, thiazole, pyridine, pyrazine, and pyridazine. The MCD spectrum of $Cr(CO)_5PCl_3$ closely resembles that of $Cr(CO)_6$, indicating that the electron distribution within the metal d orbitals of this pentacarbonyl complex has nearly octahedral symmetry.

Introduction

The photochemistry of $M(CO)_5L$ complexes (M = Cr, Mo, W; L = N-donor ligand, P-donor ligand) has been investigated both in solution and in rare gas matrices at 10 K.[1-5] The complexes show release of CO upon high-energy excitation and loss of L upon low-energy irradiation.

$$M(CO)_5L \xrightarrow[X]{h\nu} M(CO)_5X + L$$

$$M(CO)_5L \xrightarrow[X]{h\nu'} M(CO)_4LX + CO$$

X = ligand in solution, "vacancy" in the matrix; $\nu' > \nu$

This photochemical behavior has been explained by means of the one-electron d-orbital energy diagram shown in Figure 1.

The relative positions of the occupied d orbitals were derived from photoelectron spectra of these complexes.[6] Furthermore, the wavelength dependence of the photochemical behavior could only be explained on the assumption that the excited state, in which the d_{z^2} orbital (a_1) is occupied, has a lower energy than the corresponding state with an occupied $d_{x^2-y^2}$ (b_1) orbital.[1,2,4] However, since no proof for this assumption has been given, we found it necessary to establish the order of the d_{z^2} and $d_{x^2-y^2}$ orbitals with MCD spectroscopy. So far only a few metal carbonyl complexes have been studied with MCD. Zandstra et al. reported a MCD study of $Mn(CO)_5Br$ and used this technique for the assignment of the LMCT transition $Br(\pi) \rightarrow d_{z^2}$.[7]

In the course of our investigations Zink et al. reported some preliminary results of the MCD spectra of $W(CO)_5L$ complexes (L = Br^-, CS, N_3^-). In agreement with the results for $Mn(CO)_5Br$[7] the lowest CT transition was assigned.[2] Preliminary MCD results concerning the lowest LF band and its assignment to the $^1E_a(b_2^2e^3a_1) \leftarrow {}^1A_1(b_2^2e^4)$ transition have been communicated by Schreiner[8] and Boxhoorn.[9] In this article we discuss the assignment of this lowest LF transition in detail. Also other bands in the spectra of the $M(CO)_5L$ complexes are assigned, and the influence of L on the magnetic moment of the lowest LF transition is described.

Results

The absorption spectra of the $Cr(CO)_5$ N-donor complexes show only one CT band at about 250 nm, which corresponds with a positive *A* term in the MCD spectrum in conflict with the assignment $^1A_1 \leftarrow {}^1A_1$ (CT transition) by Wensky.[10] A LF transition is detected at about 420 nm, which coincides with a positive *A* term in the MCD spectra for L = piperidine and NMe_3 (Figure 2). For L = thiazole, pyridine, pyrazine, and pyridazine the center of this *A* term does not coincide with the maximum of the absorption band. This is caused by the fact that these ligands possess low-lying π^* orbitals leading to CT transitions from the metal to the ligand L. These transitions show in contrast to the LF transitions a solvent dependence and give rise to a *B* term in the MCD spectra, close to the *A* term of the LF transition (Figure 3, Table II). For $Cr(CO)_5pyr$ (pyr = pyrazine) a MCD term corresponding to the MLCT transition could hardly be observed. $Cr(CO)_5pyr$ shows some weak intraligand transitions, but no MCD effect

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