of Education of Japan (Grant No. 255315).

Registry No. S_4^{2+}, 12597-09-0; Se_4^{2+}, 12310-32-6; Te_4^{2+}, 12597-50-1.

References and Notes

(1) (a) V. V. Walatka, Jr., M. M. Labes, and J. H. Perlstein, *Phys. Rev. Lett.*, **31**, 1139 (1973); (b) C. Hsu and M. M. Labes, *J. Chem. Phys.*, **61**, 4640 (1974).

(2) R. L. Greene, G. B. Street, and L. J. Suter, *Phys. Rev. Lett.*, **35**, 1799 (1975).

(3) For example, see (a) S. R. Ovshinsky, *J. Non-Cryst. Solids*, **2**, 99 (1970); (b) S. R. Ovshinsky and H. Fritzsche, *IEEE Trans. Electron Devices*, **ed-20**, 91 (1973); (c) S. R. Ovshinsky and K. Sapru, *Amorphous Liq. Semicond., Proc. Int. Conf., 5th*, 447 (1974); (d) S. R. Ovshinsky, *Int. Kongr. Reprogr. Inf., 4th*, 109 (1975).

(4) (a) T. Yamabe, K. Tanaka, A. Imamura, H. Kato, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **50**, 798 (1977); (b) K. Tanaka, T. Yamabe, K. Fukui, A. Imamura, and H. Kato, *Chem. Phys. Lett.*, **53**, 452 (1978), and references therein.

(5) (a) I. Chen, *Phys. Rev. B*, **8**, 1440 (1973); (b) T. Shimizu and N. Ishi, *Phys. Status Solidi B*, **74**, K39 (1976); (c) M. Kastner, D. Adler, and H. Fritzsche, *Phys. Rev. Lett.*, **37**, 1504 (1976); (d) A. Tachibana, T. Yamabe, M. Miyake, K. Tanaka, H. Kato, and K. Fukui, *J. Phys. Chem.*, **82**, 272 (1978).

(6) (a) A. Caron and J. Donohue, *Acta Crystallogr.*, **14**, 548 (1961); (b) P. Unger and P. Cherin in "Physics of Selenium and Tellurium", W. C. Cooper, Ed., Pergamon, Oxford, 1969, p 223.

(7) (a) I. Chen, *Phys. Rev. B*, **2**, 1053, 1060 (1970); 7, 3672 (1973); **11**, 3976 (1975); (b) W. R. Salaneck, N. O. Lipari, A. Paton, R. Zallen, and K. S. Liang, *Phys. Rev. B*, **12**, 1493 (1975); (c) W. R. Salaneck, C. B. Duke, A. Paton, C. Griffiths, and R. C. Keezer, *Phys. Rev. B*, **15**, 1100 (1977).

(8) For example, see (a) J. Sharma, D. S. Downs, Z. Iqbal, and F. J. Owens, *J. Chem. Phys.*, **67**, 3045 (1977); (b) R. D. Smith, *Chem. Phys. Lett.*, **55**, 590 (1978); (c) J. Bojes and T. Chivers, *Inorg. Chem.*, **17**, 318 (1978).

(9) For example, see (a) D. R. Salahub and R. P. Messmer, *J. Chem. Phys.*, **64**, 2039 (1976); (b) W. R. Salaneck, J. W-p. Lin, A. Paton, C. B. Duke, and G. P. Ceasar, *Phys. Rev. B*, **13**, 4517 (1976); (c) T. Yamabe, K. Tanaka, K. Fukui, and H. Kato, *J. Phys. Chem.*, **81**, 727 (1977); (d) J. A. Jafri, M. D. Newton, T. A. Pakkanen, and J. L. Whitten, *J. Chem. Phys.*, **66**, 5167 (1977); (e) K. Tanaka, T. Yamabe, A. Tachibana, H. Kato, and K. Fukui, *J. Phys. Chem.*, **82**, 2121 (1978).

(10) (a) C. F. Bucholz, *Gehlen's Neues J. Chem.*, **3**, 7 (1804); (b) G. Magnus, *Ann. Phys. (Leipzig)*, **10** (2), 491 (1827); **14**, 328 (1828); (c) M. H. Klaproth, *Philos. Mag.*, **1**, 78 (1798).

(11) (a) R. J. Gillespie and J. Passmore, *Acc. Chem. Res.*, **4**, 413 (1971); (b) R. J. Gillespie and J. Passmore, *Adv. Inorg. Chem. Radiochem.*, **17**, 49 (1975), and references therein.

(12) C. G. Davies, R. J. Gillespie, J. J. Park, and J. Passmore, *Inorg. Chem.*, **10**, 2781 (1971).

(13) I. D. Brown, D. B. Crump, and R. J. Gillespie, *Inorg. Chem.*, **10**, 2319 (1971).

(14) (a) R. K. McMullan, D. J. Prince, and J. D. Corbett, *Chem. Commun.*, 1438 (1969); (b) R. K. McMullan, D. J. Prince, and J. D. Corbett, *Inorg. Chem.*, **10**, 1749 (1971).

(15) T. W. Couch, D. A. Lokken, and J. D. Corbett, *Inorg. Chem.*, **11**, 357 (1972).

(16) R. Steudel, *Z. Naturforsch., B*, **30**, 281 (1975).

(17) K. Tanaka, T. Yamabe, H. Terama-e, and K. Fukui, *Nouv. J. Chim.*, **3**, 379 (1979).

(18) A. G. MacDiarmid, C. M. Mikulski, P. J. Russo, M. S. Saran, A. F. Garito, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 476 (1975).

(19) I. D. Brown, D. B. Crump, R. J. Gillespie, and D. P. Santry, *Chem. Commun.*, 853 (1968).

(20) (a) A. E. Foti, V. H. Smith, Jr., and D. R. Salahub, *Chem. Phys. Lett.*, **57**, 33 (1978); (b) D. R. Salahub, A. E. Foti, and V. H. Smith, Jr., *J. Am. Chem. Soc.*, **100**, 7847 (1978).

(21) (a) T. Yonezawa, H. Konishi, and H. Kato, *Bull. Chem. Soc. Jpn.*, **42**, 933 (1969); (b) H. Konishi, H. Kato, and T. Yonezawa, *Theor. Chim. Acta*, **19**, 71 (1970); (c) H. Yamabe, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, **44**, 22 (1971); (d) H. Yamabe, H. Kato, and T. Yonezawa, *ibid.*, **44**, 611 (1971).

(22) The two-center Coulomb repulsion integrals are calculated by the Ohno approximation (K. Ohno, *Theor. Chim. Acta*, **2**, 219 (1964)), and the one-center exchange integrals are evaluated by the Slater–Condon parameters estimated by Hinze and Jaffé.[25]

(23) E. Clementi, D. L. Raimondi, and W. P. Reinhardt, *J. Chem. Phys.*, **47**, 1300 (1967).

(24) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(25) J. Hinze and H. H. Jaffé, *J. Chem. Phys.*, **38**, 1834 (1963).

(26) (a) A. G. Turner and F. S. Mortimer, *Inorg. Chem.*, **5**, 906 (1966); (b) M. S. Gopinathan and M. A. Whitehead, *Can. J. Chem.*, **53**, 1343 (1974); (c) K. H. Johnson, *Adv. Quantum Chem.*, 7, 143 (1973); (d) V. Bonačić-Koutecký and J. I. Musher, *Theor. Chim. Acta*, **33**, 227 (1974).

(27) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).

(28) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).

(29) For example, see J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory", Wiley, London, 1965, p 52.

(30) (a) R. C. Paul, J. K. Puri, and K. C. Malhotra, *Chem. Commun.*, 776 (1970); (b) N. J. Bjerrum, *Inorg. Chem.*, **11**, 2648 (1972).

(31) (a) W. J. Taylor, *J. Chem. Phys.*, **48**, 2385 (1968); (b) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Am. Chem. Soc.*, **92**, 3847 (1970).

Contribution from the Nuclear Research Centre, Negev, Beer-Sheva, Israel, and
The Ben-Gurion University of the Negev, Beer-Sheva, Israel

Allotropic Transitions of Mg_2NiH_4

Z. GAVRA, M. H. MINTZ, G. KIMMEL, and Z. HADARI*

Received May 2, 1979

The crystallographic structure and thermal behavior of Mg_2NiH_4 have been studied in the temperature range 25–500 °C. Two allotropic forms of this hydride were identified. An orthorhombic structure with $a = 11.36$ Å, $b = 11.16$ Å, and $c = 9.12$ Å ($P222_1$) containing 16 formula units per cell is stable at ambient temperature. This structure transforms at 210–245 °C to a cubic pseudo-CaF_2-type structure with $a = 6.490$ Å and 4 formula units per cell. The allotropic transition is not accompanied by a change in hydrogen composition which remains the same for both structures (under about a 700-torr hydrogen atmosphere). The enthalpy change associated with this transition was estimated to be 0.80 ± 0.05 kcal/mol of H_2 (1.60 kcal/mol of Mg_2NiH_4).

Introduction

The intermetallic compound Mg_2Ni reacts readily with hydrogen at about 300 °C and moderate pressures.[1] The product of the reaction is a ternary hydride with the formula Mg_2NiH_4.

The high hydrogen weight capacity of this hydride (about 3.6%), its moderate stability, and its fast absorption–desorption kinetics make Mg_2NiH_4 an attractive candidate for hydrogen-storage applications. Thus, for example, Mg_2NiH_4 has been utilized recently as a hydrogen-storage unit in fuel tanks of Mercedes-Benz hydrogen-powered vehicles.[2,3]

It has been reported[1] that Mg_2NiH_4 has a tetragonal structure with $a = 6.464$ Å and $c = 7.033$ Å. No information is available concerning the space group and atomic positions of this structure.

During some thermal analyses which we performed on this compound a reversible allotropic phase transition was observed.

A crystallographic study has thus been carried out on the two allotropic forms of the hydride combined with simulta-

---

*To whom correspondence should be addressed at The Ben-Gurion University of the Negev.

0020-1669/79/1318-3595$01.00/0

Table I. Crystallographic Data for the Low-Temperature Structure of Mg_2NiH_4 Indexed on the Basis of an Orthorhombic Unit Cell

d_{calcd}	d_{obsd}	I_{obsd}	*hkl*
5.68	5.79	5	200
4.56	4.55	30	002
4.22	4.19	<5	012
3.98	4.00	<5	220
3.96	3.95	10	112
3.79	3.81	80	300
3.72	3.75	55	030
3.65	3.68	60	221
2.963	2.969	5	321
2.840	2.840	10	113, 400
2.819	2.820	5	312
2.790	2.790	10	040, 132
2.712	2.721	10	401
2.670	2.675	<5	023, 203
2.439	2.429	10	421, 223
2.380	2.379	20	042
2.305	2.298	100	133
2.293	2.293	90	332
2.280	2.280	80	004
2.247	2.248	20	340
2.174	2.178	10	233
2.056	2.062	5	043
2.050	2.047	10	521
2.022	2.022	10	143
2.005	2.009	5	052
1.978	1.983	15	224
1.945	1.948	<5	423
1.933	1.929	<5	243
1.867	1.869	<5	610
1.777	1.776	<5	153
1.765	1.765	<5	044
1.744	1.741	<5	144
1.644	1.647	5	542
1.621	1.620	<5	135
1.604	1.603	5	344
1.595	1.595	<5	054
1.571	1.571	5	071
1.544	1.542	5	641
1.520	1.520	<5	453
1.503	1.503	<5	334, 552
1.499	1.500	<5	442
1.493	1.493	<5	116
1.488	1.489	5	730
1.464	1.465	<5	363
1.457	1.459	<5	604
1.361	1.361	<5	921
1.330	1.330	<5	472

neous thermogravimetric–differential thermal analyses (TGA–DTA) and differential scanning calorimetry (DSC).

The results of the present study indicate that the crystal structure of the low-temperature allotropic form of Mg_2NiH_4 does not agree with the tetragonal structure reported in the literature.

Experimental Section

Mg_2Ni samples were prepared by melting the corresponding elements in an rf induction furnace in an argon atmosphere. The alloys were characterized by chemical analyses, X-ray diffraction measurements, and combined SEM–EDAX metallography. They contained a small excess of about 2–5% magnesium which during hydrogenation formed MgH_2. The reflections due to the presence of the contaminant MgH_2 phase were identified and served as reference lines. They are not included in the lines summarized in Table I and II. Hydrogenation was carried out with the powdered sample contained in a molybdenum tube placed in a stainless steel reactor. High-purity hydrogen at a pressure of about 70 atm was introduced to the reaction vessel and reacted with the sample at about 350 °C.

The product Mg_2NiH_4 was analyzed by (1) simultaneous TGA–DTA techniques performed under a 700-torr hydrogen pressure in a Mettler thermoanalyzer, (2) differential scanning calorimetry (DSC) performed under a hydrogen flow, and (3) hot-stage X-ray diffraction measurements, performed under a hydrogen atmosphere.

Table II. Crystallographic Data for the Cubic High-Temperature Structure of Mg_2NiH_4

d_{calcd}	d_{obsd}	I_{obsd}	*hkl*
3.747	3.731	90	111
2.295	2.297	100	220
1.957	1.960	35	311
1.623	1.625	15	400
1.489	1.493	10	331
1.325	1.328	15	422

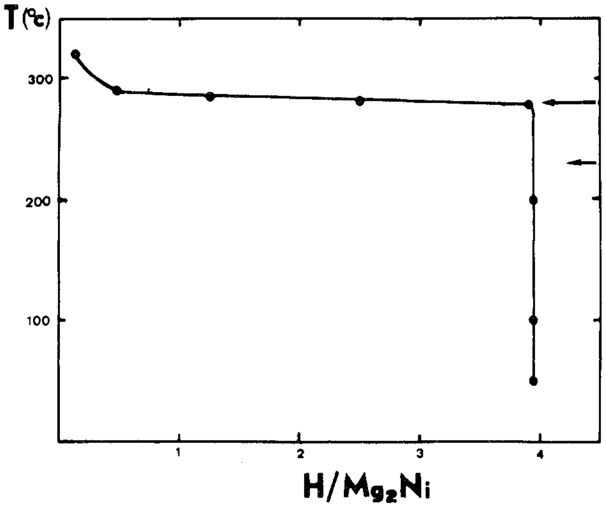

Figure 1. Temperature–composition curve obtained by heating Mg_2NiH_4 under a 700-torr hydrogen atmosphere. The arrows on the right-hand side of the figure present the locations of the maxima of the endothermic peaks obtained by differential thermal analysis.

A Philips PW 1050/30 diffractometer with a graphite monochromator was utilized for the X-ray measurements (Cu Kα radiation).

The densities of the hydride powders were measured by a picnometer, utilizing *n*-dodecane as the displaced liquid.

Results and Discussion

Figure 1 presents a typical thermogram obtained by heating Mg_2NiH_4 under 700 torr of hydrogen pressure. Two endothermic peaks are observed in the DTA curve (indicated by arrows in Figure 1). The peak at 220–245 °C is not accompanied by any change in the H/Mg_2Ni composition ratio and corresponds to an allotropic transition occurring in the hydride. The other peak at about 280–300 °C corresponds to the decomposition of the hydride. The allotropic transition appeared reversibly during repeated heating–cooling cycles as long as the temperature was not raised above the decomposition temperature of the hydride. However, due to the low hydrogen pressure (700 torr) applied to the thermoanalyzer, the decomposition of the hydride at 280–300 °C occurred irreversibly without reabsorption during cooling.

The enthalpy changes associated with these transitions were estimated by differential scanning calorimetry (DSC) performed under a hydrogen flow. From the DSC peaks' area the enthalpy of the allotropic transition was calculated to be 0.80 ± 0.05 kcal/mol of H_2 (1.60 kcal/mol of Mg_2NiH_4) and 11.3 kcal/mol of H_2 for the decomposition of the hydride. The latter value is somewhat lower than the value of 15.4 kcal/mol of H_2, obtained from the pressure–composition isotherms of this system.[1]

Figure 2 presents schematically a sector of the X-ray diffraction pattern of Mg_2NiH_4 obtained below and above the allotropic transition temperature. The reflections are indexed as having the crystal symmetries discussed below.

Table I summarizes the *d* values and relative intensities obtained for the low-temperature allotropic form of the hydride, comparing with the low-temperature structure which is orthorhombic with $a = 11.36$ Å, $b = 11.16$ Å, and $c = 9.12$

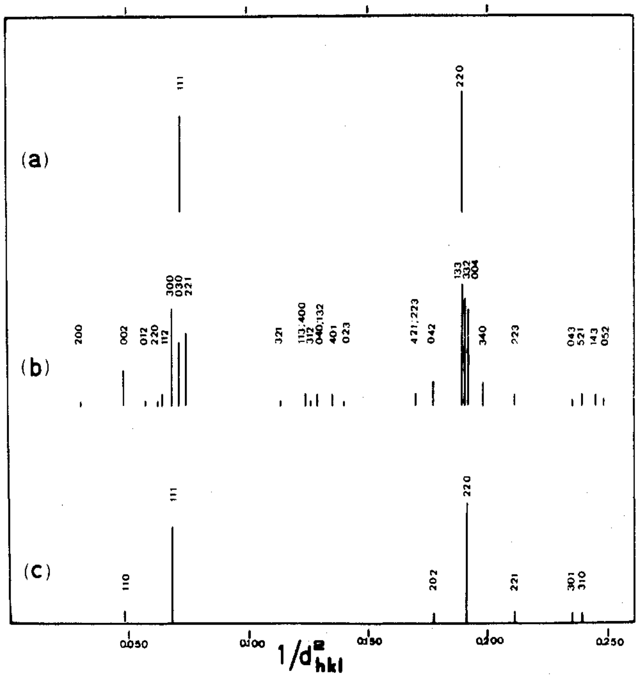

Figure 2. Schematic stick diagrams for the X-ray diffraction patterns obtained for the two allotropic forms of Mg_2NiH_4: (a) high-temperature cubic structure; (b) low-temperature orthorhombic structure; (c) calculated pattern assuming a tetragonal symmetry as reported in ref 1.

Å. The space group $P222_1$ is assumed from the systematic extinctions, resulting in conditions (001), $l = 2n$.

The measured density of Mg_2NiH_4 powder is 2.53 g/cm^3, leading to a value of 16 formula units per orthorhombic cell and to a calculated X-ray density of 2.56 g/cm^3.

It has been reported[1] that Mg_2NiH_4 has a tetragonal structure with $a = 6.464$ Å and $c = 7.033$ Å. The calculated reflections according to such a structure are presented schematically in Figure 2c, from which it is seen that most of the peaks appearing in the measured diffraction pattern (Figure 2b) cannot be indexed according to the tetragonal symmetry. Probably the X-ray measurements reported in ref 1 were performed with a Debye–Scherrer camera leading to a lower resolution pattern in which closely spaced triplet reflections coincided.

The high-temperature phase of Mg_2NiH_4 has a cubic pseudo-CaF_2-type structure where the Ni atoms occupy the cube edges and the cube face centers while the Mg atoms occupy the eight tetragonal positions. Table II summarizes the crystallographic data obtained for this structure. The stoichiometric nature of this hydride suggests the saturation of some 16 hydrogen equivalent interstitial sites. Such an arrangement is possible for the $F\bar{4}3m$ space group with four Ni atoms at sites a, four Mg atoms at sites c, four Mg atoms at sites d, and sixteen hydrogen atoms at sites e. However, without the supporting measurements of neutron diffraction it is not possible to determine unambiguously the positions of hydrogen atoms. Thus, the possibility of the $Fm3m$ space group where hydrogen atoms occupy part of the available interstitial sites in the CaF_2 structure (in the space group $Fm3m$) cannot be excluded.

Acknowledgment. The authors thank Dr. Zevin and Mr. S. Nathan for their assistance in the X-ray diffraction measurements. Thanks are due to Mr. D. Hiershler, Mr. D. Brami, and Mr. H. Maman for preparation of the alloys and hydrides.

Registry No. Mg_2NiH_4, 12362-18-4.

References and Notes

(1) J. J. Reilly and R. H. Wiswall Jr., *Inorg. Chem.*, 7, 2254 (1968).
(2) H. Buchner, International Symposium on Hydrides for Energy Storage, Geilo, Norway, Aug 1977.
(3) H. Buchner, O. Bernauer, and W. Straub, "Proceedings of the 2nd World Hydrogen Energy Conference", Vol. 3, Zurich, Switzerland, 1978, pp 1677–87.

Contribution from the Department of Chemistry,
Ahmadu Bello University, Zaria, Nigeria

Linear Free Energy Relations in Redox Reactions. Oxidation of Iodide Ion by Poly(pyridine)–Iron(III) Complexes and Hexachloroiridate(IV) Ion

C. O. ADEDINSEWO and ADE ADEGITE*

Received October 25, 1978

The rates of oxidation of iodide ion by some poly(pyridine)–iron(III) complexes and by the hexachloroiridate(IV) ion have been measured in aqueous acidic solutions. For the 1,10-phenanthroline– and 2,2′-bipyridyl–iron(III) complexes and the hexachloroiridate ion, the reaction follows second-order kinetics, while for the less reactive substituted poly(pyridine)–iron(III) complexes, the rate law contains an additional term which is first order in the complex but second order in iodide ion. The reaction scheme proposed entails a fast formation of ion pairs between the reactants and a rate-determining intramolecular electron transfer from iodide to the iron(III) or iridium(IV) center or an electron transfer from another iodide ion to the ion pair. The immediate products of the electron-transfer steps are, respectively, the iodide atom or the iodine molecule radical and the reduced form of the complex ion. The variation of rate constants from one oxidant to the other is rationalized on the basis of Marcus' theory. From the results, the homonuclear electron exchange between I· and I^- was estimated as 7×10^7 M^{-1} s^{-1}. When the pertinent work terms are included in the Marcus equation for cross-reactions, excellent agreement between calculated and observed rate constants is obtained for all the oxidants. The higher rate constant often observed for the $[I^-]^2$ term relative to the $[I^-]$ term in iodide reactions is attributed to the more favorable $\Delta G°$ for the formation of $I_2^{-}\cdot$ from I^- and I·.

Introduction

Linear free energy relations have been demonstrated for a large number of redox reactions. The redox reactions of substitution-inert poly(pyridine) complexes of iron in either the ferrous or the ferric state are the most common reactants employed for these investigations.[1-8] Quite recently,[9] Davies and Earley found, using the oxidation of various polycyclic amino acid Cr(II) complexes by $Cr(NH_3)_5Cl^{2+}$, that such linear free energy relations also exist for reactions of the inner-sphere mechanism and, surprisingly, did obtain 0.5 as the slope of ΔG^* vs. $\Delta G°$ plots. The dependence of ΔG^* (the free energy of activation for the redox reaction) on $\Delta G°$ (the

0020-1669/79/1318-3597$01.00/0