Int. J. Hydrogen Energy, Vol. 14, No. 6, pp. 371–377, 1989.
Printed in Great Britain.

0360–3199/89 $3.00 + 0.00
Pergamon Press plc.

CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF HIGH-PRESSURE PHASES IN THE Fe–H AND Fe–Cr–H SYSTEMS

V. E. Antonov, I. T. Belash, V. F. Degtyareva, D. N. Mogilyansky, B. K. Ponomarev and V. Sh. Shekhtman

Institute of Solid State Physics, U.S.S.R. Academy of Sciences, 142432, Chernogolovka, Moscow district, U.S.S.R.

(*Received for publication* 6 *December* 1988)

Abstract—Isotherms of hydrogen solubility at $T = 325°\mathrm{C}$ and $P_{\mathrm{H}_2} \leqslant 7$ GPa were plotted for the Fe–Cr alloys with 50, 25 and 5.3 at %Cr. At $T = 350°\mathrm{C}$ and $P_{\mathrm{H}_2} = 9$ GPa, nearly single-phase samples of iron hydride with H/Me $\approx$ 0.9 were synthesized. At atmospheric pressure, the hydrides obtained were X-rayed ($T = 90$ K) and their magnetization measured ($80 \leqslant T \leqslant 180$ K, $H \leqslant 5$ T). The hydrides of the alloys with 50 and 25 at %Cr were shown to have an hcp (2H) metal lattice. The hexagonal metal lattice of hydrides of the alloy with 5.3 at %Cr contains stacking faults partly ordered to the Sm-type (9R) structure, and the iron hydride has a dhcp (4H) lattice. The hydrides of iron and the alloys with 5.3 and 25 at %Cr are ferromagnetics, the values of their spontaneous magnetization being in accordance with the predictions of the rigid *d*-band model.

INTRODUCTION

The iron hydride was first synthesized under hydrogen pressure of 6.7 GPa at $T = 250°\mathrm{C}$ [1]. The X-ray investigation of the Fe–H samples at atmospheric pressure and $T \approx 80$ K has shown them to contain a considerable amount of the starting α-Fe. Besides the α-Fe lines, there were other 8 lines in the diffraction patterns referred to the iron hydride and indexed in the hcp (ε) cell. At an atmospheric pressure the iron hydride is extremely thermally unstable and decomposes rapidly to H_2 and α-Fe at $T \geqslant -120°\mathrm{C}$, and it was not clear whether the presence of α-Fe in the samples was due to a partial decomposition of the hydride while transferring the samples to the X-ray cryostat at atmospheric pressure or due to the incompleteness of the process of the hydride formation at a high hydrogen pressure.

It has been shown in [2] that the iron hydride is a ferromagnetic with spontaneous magnetization σ_0 at $T = 0$ K close to that of α-iron and the Curie temperature $T_c \gg 80$ K, that does not contradict the rigid *d*-band model for the ε-hydrides [3]. The Mössbauer investigation [4] of the Fe–H samples, synthesized under the same conditions as in [1], has given, however, unexpected results. Along with the magnetic sextet, corresponding to α-Fe, the spectra displayed two additional sextets with approximately equal intensities instead of one sextet which could have been expected for a ferromagnetic ε-hydride. As a most probable explanation of the observed spectra, it has been assumed in [4] that the crystal structure of iron hydride has two non-equivalent positions of iron atoms with equal multiplicity factors.

Therefore, the data available on the hydrogen content of the iron hydride as well as on its crystal structure were not reliable.

The present work was aimed at elucidating these characteristics of the iron hydride by studying the composition and crystal structure of hydrides forming under high hydrogen pressure on the base of the iron–chromium alloys and by further extrapolation of the data obtained to the zero chromium content. Under high hydrogen pressure chromium forms an ε-hydride [5] which is much more stable at atmospheric pressure than the iron hydride ($T_{\mathrm{decomp}} \approx -30°\mathrm{C}$ [5, 6]); thermal treatment permits production of sufficiently homogeneous bcc (α) Fe–Cr alloys in the whole range of concentrations from Fe to Cr [7]. So, one could hope that hydrides of the Fe–Cr alloys will also be more stable at atmospheric pressure than the iron hydride, and that changes in their crystal structure, if any, with increasing the iron content of the alloys will be restricted to modifications of the ε-lattice. According to the rigid *d*-band model [3], the ε-hydrides of Fe–Cr alloys containing up to ≈ 30 at %Cr, must be ferromagnetically ordered, and along with the structural studies we have examined the magnetic properties of the synthesized hydrides.

Besides, an analysis of the data obtained upon investigating phase transformations in the Fe–Cr–H systems allowed us to clear up the reasons of the presence of α-Fe in the earlier synthesized Fe–H samples. As a result, nearly single-phase samples of iron hydride were synthesized and their X-ray examination performed.

EXPERIMENTAL

The ingots of the Fe–Cr alloys containing 50, 25 and 5.3 %Cr were melted from Armco-iron and electrolytical chromium in an induction furnace in vacuum. After a 24 h homogenization in vacuum at 1100°C and water-quenching these ingots and also an ingot of Armco-iron were cold-rolled into 0.2 mm thick strips, then subjected to stress-relief annealing in vacuum at

Table 1. Pressure of the synthesis at 325°C, composition, spontaneous magnetization at $T=0$ K†, structure and parameters of the metal lattice at $T=90$ K for the Fe–Cr alloys and their hydrides

At %Cr	P_{H_2} (GPa)	n	σ_0† (μ_B atom^{-1})	Metal lattice	a(Å)	c(Å)	c/a	V_a (Å^3 atom^{-1})	ΔV_a (Å^3 atom^{-1})	$\Delta V_a/n$ (Å^3 H atom^{-1})
0	—	0	2.22 [9]	bcc	2.865	—	—	11.76	—	—
	9*	0.88	2.2 [2]	4H(dhcp)	2.683	8.775	3.270	13.67	1.91	2.17
5.3	—	0	2.10	bcc	2.867	—	—	11.78	—	—
	7	0.92	1.45	9R(?)	2.690	19.70	7.32	13.72	1.94	2.11
25	—	0	1.56	bcc	2.869	—	—	11.81	—	—
	2.8	0.63	$\lesssim 0.03$	2H(hcp)	2.626	4.225	1.609	12.62	0.81	1.29
	7	1.01	≈ 0.55	2H(hcp)	2.689	4.333	1.611	13.57	1.76	1.74
50	—	0	0.97	bcc	2.871	—	—	11.83	—	—
	1.8–3.2	0.77	$\lesssim 0.01$	2H(hcp)	2.679	4.297	1.604	13.35	1.52	1.97
	4.5–7	1.15	$\lesssim 0.01$	2H(hcp)	2.700	4.342	1.608	13.71	1.88	1.63

* Synthesis temperature is 350°C.

† Values extrapolated from $T \geqslant 80$ K.

1100°C for 15 min and again quenched in water. The obtained strips had a bcc lattice, the values of their unit-cell parameters and σ_0 (see the lines for $n = 0$ in Table 1, n is H/Me atomic ratio) well agreed with the literature data [8, 9]. The samples intended for hydrogenation weighed about 50 mg and were made up of $\approx 3 \times 3$ mm^2 plates cut from the strips.

Hydrogenation of the alloys was carried out by a 24 h exposure in a hydrogen atmosphere at 325°C and pressures up to 7 GPa with subsequent quenching down to ≈ -170°C (the method is given in [3]). The error in estimating the pressure grew from ± 0.05 GPa at $P_{H_2} \lesssim 1$ GPa to ± 0.3 GPa at $P_{H_2} \approx 7$ GPa, the temperature being measured accurate to ± 10°C.

Thermal stability of the synthesized hydrides at atmospheric pressure decreased with decreasing chromium concentration in the alloys, from $T_{\text{decomp}} \approx +20$°C for the alloy with 50 at %Cr to $T_{\text{decomp}} \approx -(60\text{–}80)$°C for the alloy with 5.3 at %Cr. The hydrogen content of the samples was determined with a relative accuracy of 3%, the method is given in [10].

An X-ray study was performed by a phototechnique using a DRON-2.0 diffractometer with FeK_α radiation. The magnetization of the samples was measured with 5% error in a pulsed magnetic field up to 6 T by the induction method [11] in the temperature range 80–200 K, the pulse duration being ≈ 0.01 s.

When not in use, the Fe–H and Fe–Cr–H samples were stored in liquid nitrogen to prevent hydrogen losses. The installation permitted loading the samples without their heating much above liquid nitrogen temperature.

STRUCTURAL STUDIES

For each of the three Fe–Cr–H systems, isotherms of hydrogen solubility in the metal at $T = 325$°C and $P_{H_2} \lesssim 7$ GPa were plotted. The phase composition of the synthesized samples and the crystal structure of metal sublattice of the forming phases were studied at atmospheric pressure and $T = 90$ K. The basic results are presented in Figs 1–3 and Tables 1, 2. The X-ray data in Figs 1(b) and 3(b) are given in the form of dependences $\Delta V_a = V_a(n) - V_a(0)$ upon the pressure of synthesis and the hydrogen content of the samples, respectively, where V_a is the volume per metal atom in the phase under study. For the Me–H phases on the base of a great number of different transition metals and their alloys, the dependences $\Delta V_a(n)$ are approximately linear and close to each other within wide concentration ranges [3, 12], and determination of the ΔV_a-values is useful, in particular, for estimating the hydrogen concentration of the phases in multi-phase samples.

The $Fe_{50}Cr_{50}$–H *system*

As is seen from Fig. 1, an increase in the hydrogen pressure to ≈ 0.8 GPa at 325°C induces growth of the hydrogen concentration in the α-alloy $Fe_{50}Cr_{50}$ up to $n \approx 0.03$, the parameter of the bcc alloy lattice somewhat increasing, and at higher pressures solid ε-solutions (hydrides) with $n \gtrsim 0.75$ and an hcp metal lattice are formed. Dependences $n(P_{H_2})$ and $\Delta V_a\ (P_{H_2})$ are characterized by the presence of two plateaux in the pressure ranges ≈ 2 to 3 GPa and ≈ 4 to 7 GPa, separated by the region of a rather steep increase in the both parameters.

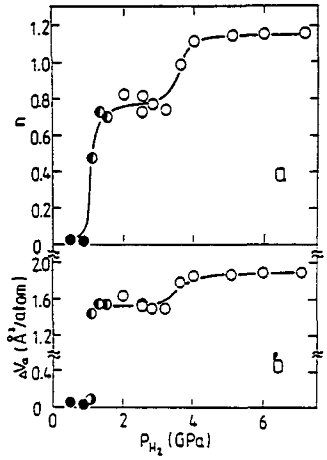

Fig. 1. Hydrogen content, n, (a) and an increase in the volume per metal atom, $\Delta V_a = V_a(n) - V_a(0)$ for the $Fe_{50}Cr_{50}$–H solid solutions produced by a 24 h exposure at 325°C and under the hydrogen pressures indicated on the abscissa. ●—data for α-solutions (bcc metal lattice), ○—for ε-solutions (hcp metal lattice), half-blackened symbols refer to two-phase ($\alpha + \varepsilon$) samples.

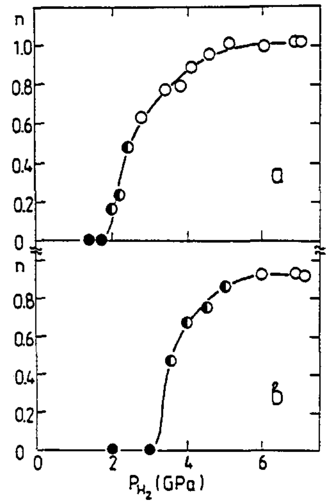

Fig. 2. Hydrogen content, n, vs pressure, P_{H_2}, of the samples synthesis (24 h at 325°C) for the $Fe_{75}Cr_{25}$–H (a) and $Fe_{94.7}Cr_{5.3}$–H (b) solid solutions. ●—α-solutions, ○—hydrides (based on the hcp metal lattice (a) and on the lattice with stackings partly ordered to the 9R structure (b)), half-blackened symbols stand for the two-phase samples.

Table 2. Experimental ($T = 90$ K) and calculated values of lattice spacings, d, and integral intensities of the X-ray diffraction maxima, I, for the hydrides of iron and Fe–Cr alloy with 5.3 at %Cr. The values of the unit cell parameters from Table 1 have been used in the calculation

$Fe_{94.7}Cr_{5.3}$–H, n=0.92±0.03									Fe–H, n=0.88±0.03					
Experiment			Calculation						Experiment			Calculation		
			2H (hcp)			9R (Sm-type)						4H (double hcp)		
No.	d (Å)	I	hkl	d (Å)	I/I_{max}(%)	hkl	d (Å)	I/I_{max}(%)	No.	d (Å)	I/I_{max}(%)	hkl	d (Å)	I/I_{max}(%)
1	2.32	m	100	2.330	26	101	2.313	42	1	2.328	10	100	2.324	8
2	2.25	w				012	2.267	16	2	2.250	60	101	2.246	48
3	2.19	m	002	2.189	28	009	2.189	54	3	2.201	66	004	2.194	35
4	2.05	m,b	101	2.057	100	104	2.106	100	4	2.058	100	102	2.053	100
						015	2.005	86	5*	2.029	2			
5	1.80	vw				107	1.795	7	6	1.823	30	103	1.819	22
						018	1.692	13	7	1.600	10	104	1.595	5
			102	1.595	13				8*	1.436	<1			
						10.10	1.504	9	9	1.404	12	105	1.400	10
						01.11	1.420	3	10	1.341	58	110	1.342	24
6	1.345	m	110	1.345	14	110	1.345	35	11	1.238	30	106	1.238	25
7	1.266	vw			10.13	1.270	22	12*	1.171	<1				
			103	1.237	17				13	1.152	12	201	1.152	9
						01.14	1.204	22	14	1.145	40	114	1.144	12
			200	1.165	3				15	1.124	25	202	1.123	23
8	1.145	m	112	1.146	21	119	1.146	30	16	1.080	10	203	1.080	18
						024	1.134	55						
9	1.125	w,b	201	1.127	32	205	1.117	45						

* Lines of α-iron.
Designation: m—medium, w—weak, vw—very weak, b—broadened.

In the vicinity of $P_{H_2} = 3.5$ GPa, dependences $n(P_{H_2})$ and $\Delta V_a(P_{H_2})$ are very similar to supercritical ones for the isomorphous $\varepsilon_1 \rightleftarrows \varepsilon_2$ transformation terminated at a critical point at $T < 325$°C. At the present stage of investigation the $Fe_{50}Cr_{50}$–H system one cannot neglect other possible explanations of the observed anomaly either, for instance, it may be due to the ordering of the solutions with $n \approx 0.75$ to the Me_4H_3 type.

The $Fe_{75}Cr_{25}$–H *system*

Figure 2 shows that at $T = 325$°C the hydrogen solubility in the α-alloy $Fe_{75}Cr_{25}$ at $P_{H_2} \lesssim 1.7$ GPa is very low ($n \lesssim 0.005$), and at higher pressures ε-solutions are formed with the hydrogen concentrations growing monotonically from $n \approx 0.6$ at $P_{H_2} = 2.8$ GPa to $n \approx 1$ at $P_{H_2} = 7$ GPa.

As is seen from Fig. 3, the ΔV_a-values of the single-phase ε-samples increase linearly with the hydrogen concentration. In the two-phase ($\alpha + \varepsilon$) samples, the α-phase has $\Delta V_a \approx 0$ (that points to low hydrogen solubility in this phase) and the ΔV_a-value of the ε-phase (and, consequently, the hydrogen concentration of the ε-phase) is independent of the relative content of the phase in the samples within the experimental error and constitutes ≈ 0.6 Å^3 atom^{-1}. The intersection of the linear prolongation of dependence $\Delta V_a(n)$ for the single-phase ε-samples with the line $\Delta V_a = 0.6$ Å^3 atom^{-1} (see Fig. 3b) gives $n \approx 0.55$ for the composition of the ε-phase in the two-phase samples and, accordingly, for the minimum hydrogen concentration in the ε-solutions forming at $T = 325$°C and high hydrogen pressures, Fig. 2a.

The extrapolation of the linear dependence ΔV_a (n) for the ε-solutions to even less values of the hydrogen concentrations (dotted line in Fig. 3b) produces an unexpected result. The extrapolation suggests that formation of ε-solutions (virtual) with $n \lesssim 0.3$ should cause a decrease in V_a instead of its increase. Such an effect has not been observed so far in any of the

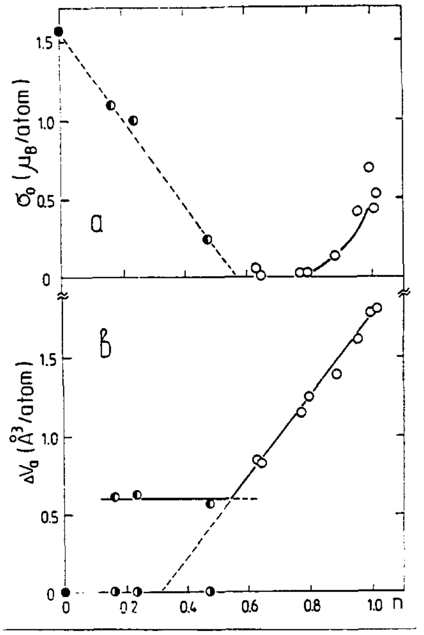

Fig. 3. Spontaneous magnetization, σ_o, at $T = 0$ K (in Bohr magnetons per metal atom) (a) and ΔV_a (b) as functions of the hydrogen content, n, of the $Fe_{75}Cr_{25}$–H samples. ●—data for α-solutions, ○—for ε-solutions, half-blackened symbols refer to two-phase samples. The σ_o-values were obtained by extrapolation from $T \geqslant 80$ K.

d-metal–hydrogen systems investigated. Moreover, in the most systems (for example, Pd–H, Ni–H and on the base of their alloys [3, 12]) the derivative $\partial V_a/\partial n > 0$ and decreases with the hydrogen concentration (i.e., $\partial^2 V_a/\partial^2 n < 0$); as one can see from the ΔV_a-values listed in Table 1, this is valid for $Fe_{50}Cr_{50}$–H ε-hydrides too.

The $Fe_{94.7}Cr_{5.3}$–H *system*

At $T = 325$°C, the equilibrium hydrogen concentration in α-solutions $Fe_{94.7}Cr_{5.3}$–H did not exceed $n \approx 0.005$, and starting with $P_{H_2} \approx 3.5$ GPa, the appearance of a hydride with an hcp metal lattice was observed in the samples, see Fig. 2(b). At $3.5 \lesssim P_{H_2} \lesssim 4.5$ GPa (that is, in the pressure range where the produced samples consisted of a mixture of the α-phase and the hydride), the parameters of the hcp metal lattice of the hydrides somewhat increased with the pressure of synthesis, and for the single-phase hydride samples obtained at $6 \lesssim P_{H_2} \lesssim 7$ GPa neither the lattice parameters, nor the hydrogen content depended on P_{H_2}.

X-Ray patterns for the $Fe_{94.7}Cr_{5.3}$–H hydrides had peculiarities (see Table 2) distinguishing them qualitatively from those for the $Fe_{50}Cr_{50}$–H and $Fe_{75}Cr_{25}$–H hydrides: (i) the lines with indices (101) and (201) were broadened and had lower integral intensity, and lines (102) and (103) were absent; (ii) three additional weak lines were observed to which fractional indices of the $(10l/m)$ type can be ascribed in the hexagonal cell.

The broadening of the $(h0l)$ type diffraction lines with $h \neq 3n$ is typical for the hcp metals with chaotic stacking faults. An estimation of the density of stacking, α_{st}, by the experimental value $\Delta(2\theta)_{101} \approx 1°$ of the (101) line width, according to the formula [13]

$$\alpha_{st} = \Delta(2\theta)_{101} \times \frac{c^2}{4\lambda^2} \times \sin 2\theta$$

gave $\alpha_{st} \approx 0.3$ for the $Fe_{94.7}Cr_{5.3}$–H hydride (θ is the Debye angle, c is the hcp cell parameter, λ is the wavelength of the radiation used).

The presence of lines with the $(10\,l/m)$ type indices in the hcp cell suggests formation of a multilayer close-packed structure (polytype). The shortest repetition units along the c axis are characteristic of the polytype 4H (double hcp structure consisting of alternating cubic (c) and hexagonal (h) layers, *chchch*. . . , and polytype 9R (Sm-type structure) with the sequence of layers *chhchhchh*. . . Taking into consideration the value $\alpha_{st} \sim 1/3$ of the density of stacking faults in the $Fe_{94.7}Cr_{5.3}$–H hydride, it seems quite probable that the presence of the $(10l/m)$ type lines in the X-ray patterns of this hydride is due to the partial ordering of the stackings just to the 9R type, see Table 2.

The Fe–H *system*

Figures 1 and 2 show that as the chromium content of the Fe–Cr alloys decreases, the pressure for a hydride to start forming at 325°C increases monotonically from $P_{H_2} \approx 1$ GPa for the alloy with 50 at %Cr to ≈ 3.5 GPa for the alloy with 5.3 at %Cr, and the interval of the transition (where the forming Fe–Cr–H samples are two-phase mixtures) comprises ≈ 0.5 GPa for the alloys with 50 and 25 at %Cr and extends to ≈ 2 GPa for the alloy with 5.3 at %Cr. An examination of the T–P_{H_2} phase diagram of the Fe–H system showed [14] that at $T \approx 250$ to 350°C the iron hydride starts forming at $P_{H_2} \approx 5$ to 5.5 GPa. If one assumes the interval of the transition in the Fe–H system, as well as in the $Fe_{94.7}Cr_{5.3}$–H system, to be ≈ 2 GPa, then the pressures of ≈ 7–7.5 GPa, exceeding those used in [1, 4], are required to synthesize single-phase samples of the iron hydride.

In this work we succeeded in preparing nearly single-phase samples of the iron hydride (see Table 2) by a 24 h exposure to a hydrogen pressure of 9 GPa at $T = 350$°C. Therefore, the main reason lying behind the presence of α-Fe in the Fe–H samples studied in [1, 4] was incompleteness of the process of hydride formation under the conditions of synthesis.

As is seen from Table 2, all the diffraction lines of the iron hydride obtained are well indexed in the double hcp cell (structure 4H). A higher intensity of the (hkl) type lines, as compared to the calculated one, is likely to be related to the sample texture (we could not get rid of the texture, since grinding the Fe–H samples even in liquid nitrogen causes considerable losses in hydrogen).

It is apparently the particular texture of the samples (bits of the 1.1 mm dia. rod) that was responsible for the absence of "superstructural" lines of the 4H polytype in X-ray photographs of the iron hydride in [1]. The two-phase Fe–H sample with $n = 0.70 \pm 0.03$, synthesized in the present experiment under the same conditions as in [1] (10 h at $P_{H_2} = 6.7$ GPa and $T = 250°C$), exhibited these lines.

An additional argument in favour of the choice of the 4H cell to describe the metal lattice of the iron hydride is the existence of two non-equivalent positions of atoms with equal multiplicity factors in the 4H structure, since it agrees with the existence of the two magnetic sextets in the Mössbauer spectra of the iron hydride, observed in [4]. It is also worth noting that in the sequence of the polytype structures 2H (hcp) → 9R → 4H, proposed for the Fe–Cr–H hydrides, an increase in the fraction of cubic (*c*) layers with decreasing the chromium content of the alloys is monotonous: zero—for the 2H structure (*ccccc*. . .) 1/3—for 9R (*chhchhchh*. . .) 1/2—for 4H (*chchch*. . .). The sequence of structures 2H → 9R → 4H is characteristic of the systems with the decreasing energy of stackings.

Extrapolation of properties of the Fe–Cr–H hydrides is also useful for elucidating the hydrogen concentration in the iron hydride which is somewhat uncertain due to the presence of the α-phase in the investigated Fe–H samples with $n \approx 0.88$, see Table 2. As follows from Figs 1 and 2 and Table 1, the characteristics of the Fe–Cr–H hydrides practically stop changing at $P_{H_2} \gtrsim 6$ GPa. Figure 4 depicts the data for the Fe–Cr–H hydrides synthesized at $P_{H_2} = 7$ GPa and the iron hydride (to make it easier to compare the X-ray data, a doubled distance between the close-packed planes, as in the hcp lattice, is taken as a *c* parameter for the $Fe_{94.7}Cr_{5.3}$–H (+) and Fe–H (×) hydrides where it constitutes 2/9 and 1/2 of the repetition period, respectively). One can see that the values ΔV_a and c/a for the iron hydride well agree with the extrapolated ones. This suggests that the hydrogen content of the iron hydride does not much differ from the extrapolated value, $n \approx 0.9$, either, and the Fe–H samples with $n \approx 0.88$ obtained in the experiment are practically single-phase indeed, i.e. the texture does not distort the X-ray data in this respect.

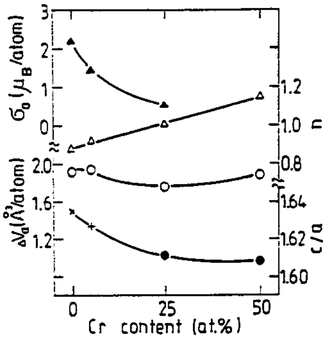

Fig. 4. Values of σ_o (▲), ΔV_a (○), n (△) and the ratio c/a for the hcp cell (●) and hcp pseudocell (+, ×—see the text) as functions of chromium concentration in the Fe–Cr alloys, for the hydrides synthesized at maximum hydrogen pressures (7 GPa, 325°C for Fe–Cr–H hydrides and 9 GPa, 350°C for iron hydride; the σ_o-value for iron hydride is taken from [2]).

MAGNETIC MEASUREMENTS

The values of spontaneous magnetization, σ_s,. did not change within the experimental error in the temperature range 80 to 180 K for all the investigated samples, $Fe_{50}Cr_{55}$–H and $Fe_{77}Cr_{25}$–H hydrides with very low $\sigma_s \approx 0.01$ to 0.03 μ_B (metal atom)$^{-1}$ among them. The observed behaviour of σ_s is indicative of high (much above 180 K) temperatures of magnetic disordering of the samples that allows us to consider their values σ_s (80 K) as σ_o at $T = 0$ K, without introducing any essential error.

The σ_o-values for the α-solutions of hydrogen in the Fe–Cr alloys coincided with those for the starting alloys. The results of magnetic measurements for the samples with a higher hydrogen content can be illustrated on an example of the $Fe_{75}Cr_{25}$–H system (Fig. 3a).

It is seen that the σ_o-values for the single-phase $Fe_{75}Cr_{25}$–H ε-solutions increase from $\sigma_o \lesssim 0.03$ μ_B atom^{-1} at $n \approx 0.6$ to 0.8 to $\sigma_o \approx 0.5$ μ_B atom^{-1} at $n \approx 1$. Magnetization of the two-phase ($\alpha + \varepsilon$) samples is proportional to the content of the ferromagnetic α-phase. The approximation by a straight line (dotted line in Fig. 3a) provides for $\sigma_o = 0$ the value $n \approx 0.57$, which is close to the minimum hydrogen concentration $n \approx 0.55$, in the single-phase ε-samples, determined from the X-ray measurements.

An analogous dependence $\sigma_o(n)$ for the two-phase ($\alpha + \varepsilon$) samples was observed in the $Fe_{50}Cr_{50}$–H system. All the single-phase $Fe_{50}Cr_{50}$–H ε-samples with $0.75 \lesssim n \lesssim 1.15$ had $\sigma_o \lesssim 0.01$ μ_B atom^{-1}.

For the case of the $Fe_{94.7}Cr_{5.3}$–H system the hydride was ferromagnetic, and the σ_o-values for the two-phase samples displayed an approximately linear decrease from 2.10 μ_B atom^{-1} for the starting $Fe_{94.7}Cr_{5.3}$ alloy down to 1.45 μ_B atom^{-1} for the hydride with $n \approx 0.92$.

As for the interpretation of the data obtained, the following should be noted. The magnetic properties of the fcc (γ) and hcp (ε) alloys of 3*d*-metals, which are the closest neighbours in the Periodic Table, are well described by the rigid band model [9]. The concentration dependences of σ_o for the ferromagnetic alloys and the Néel points, T_N, for the antiferromagnetic ones are plotted in Fig. 5, the composition of the alloys being given in the N^e units of the average number of external ($3d + 4s$) electrons per atom of the alloy (the so-called Pauling–Slater curves).

At present a large scope of the data on magnetic properties of γ- and ε-hydrides of 3*d*-metals and their alloys is available, see [3]. An analysis of these data permitted formulating the phenomenological rigid *d*-band model [3] to describe concentration dependences

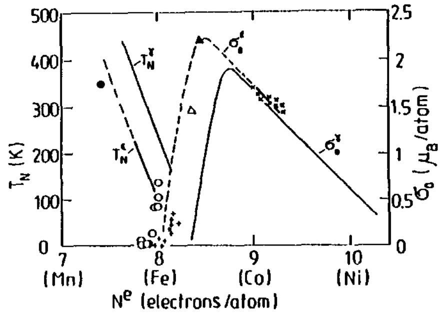

Fig. 5. Concentration dependences of σ_0 and Néel temperature, T_N, for the fcc (γ) (thin lines, experimental data [9]) and hcp (ε) (sections of solid lines, experimental data [9], and dotted lines, an estimation [3]) alloys of 3*d*-metals that are nearest neighbours in the Periodic Table, and also the experimental values of T_N for the manganese ε-hydride [16] (●) and of σ_0 for the ε-solutions Co–H [17] (×) and $Fe_{77.6}Mn_{22.4}$–H [3] (+), iron hydride [2] (▲), ε-hydrides of $Fe_{75}Cr_{25}$ alloy (○) and $Fe_{94.7}Cr_{5.3}$–H hydride (△), data of the present paper, at η = 0.5 electron per H atom, see the text.

of the magnetic properties of such hydrides. The essence of the model is that the change in these properties upon hydrogenation is mainly caused by the increase in the degree of filling up the *d*-band of the host metal with electrons, hydrogen being considered as the donor of a fractional number of electrons $\eta \approx 0.3$ to 0.7 electrons per H atom. Thus, according to the model, in the case of formation of γ- or ε-hydrides on the basis of the alloys of 3*d*-metals which are close neighbours in the Periodic Table, their magnetic properties should be described by the curves given in Fig. 5, provided the quantity $N^e_{eff} = N^e + \eta n$ is taken as the electron concentration.

The η-values may differ considerably for the hydrides of different metals and alloys. The values of η for some of the γ-hydrides (in particular, for the Pd and Ni hydrides [15]) were obtained directly from the quantum-mechanical calculation of their band structure, but those for the ε-hydrides we are interested in, have not been estimated yet.

Having chosen $\eta = 0.5$ electrons per H atom, we plotted in Fig. 5 the values of T_N and σ_0 for all the ε-hydrides studied earlier and also for the hydrides of iron and $Fe_{75}Cr_{25}$ and $Fe_{94.7}Cr_{5.3}$ alloys. One can see that these values well fit the dependences $T_N(N^e)$ and $\sigma_0(N^e)$ for the hcp alloys.

If the observed agreement is not assumed to be of a random character, then we have:
(i) the magnetic properties of the virtual Fe–Cr alloys with an hcp lattice and polytypes on its basis are described satisfactorily by the rigid band model for the chromium concentrations up to 25 at% at least; (ii) the properties of their hydrides are mainly determined by the degree of filling up the *d*-band of these alloys with the electrons supplied by hydrogens, the value of η being of the order of 0.5 electrons per H atom.

In case this is valid for the $Fe_{50}Cr_{50}$ alloy (N^e = 7 electrons per atom = N^e_{Mn}) too, its ε-hydrides, as is seen from Fig. 5, should be antiferrogmagnetics with high Néel points. Note, that the presence of stacking faults (and the hydrides of Fe–Cr alloys are liable to it) in an ε-antiferromagnetic must lead to a decompensation of its magnetic sublattices that gives rise to a relatively small spontaneous moment only slightly depending on temperature at $T \ll T_N$. Maybe the small spontaneous moment of the $Fe_{50}Cr_{50}$–H ε-hydrides (Table 1) is just of this origin.

Acknowledgements—The authors are grateful to V. G. Glebovsky in whose laboratory the Fe–Cr alloys were melted and I. M. Romanenko for the chemical analysis of these alloys.

REFERENCES

1. V. E. Antonov, I. T. Belash, V. F. Degtyareva, E. G. Ponyatovsky and V. I. Shiryaev, *Dokl. Akad. Nauk SSSR* **252**, 1384 (1980).
2. V. E. Antonov, I. T. Belash, E. G. Ponyatovskii, V. G. Thiessen and V. I. Shiryaev, *Phys. Status Solidi (a)* **65**, K43 (1981).
3. E. G. Ponyatovsky, V. E. Antonov and I. T. Belash, In A. M. Prokhorov and A. S. Prokhorov (eds), *Problems in Solid State Physics*, p. 109, Mir, Moscow (1984).
4. R. Wordel, F. E. Wagner, V. E. Antonov, E. G. Ponyatovskii, A. Permogorov, A. Plachinda and E. F. Makarov, *Z. Phys. Chem. Neue Folge* **145**, 121 (1985).
5. B. Baranowski and K. Bojarski, *Roczn. Chem.* **46**, 525 (1972).
6. E. G. Ponyatovsky and I. T. Belash, *Dokl. Akad. Nauk SSSR* **229**, 1171 (1976).
7. M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York (1958).
8. W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, p. 532, Pergamon Press, Oxford (1964).
9. S. V. Vonsovsky, *Magnetizm*, Izd. Nauka, Moskva (1971) (in Russian).
10. V. E. Antonov, T. E. Antonova, I. T. Belash, V. Yu. Malyshev, E. G. Ponyatovsky and V. I. Rashupkin, *Fiz. Tverd. Tela* **28**, 2352 (1986).
11. I. S. Jacobs and P. E. Lawrence, *Rev. Sci. Instrum.* **29**, 713 (1958).
12. H. Peisl, Topics in applied physics, In G. Alefeld and J. Völkl (eds), *Hydrogen in Metals I*, Vol. 28, p. 53. Springer, Berlin (1978).
13. A. Guinier, *Théorie et Technique de la Radiocristallographie*, Dunod, Paris (1956).
14. V. E. Antonov, I. T. Belash and E. G. Ponyatovsky, *Scripta Metall.* **16**, 203 (1982).
15. A. C. Switendick. *Ber. Bunsenges. physik. Chem.* **76**, 535 (1972).
16. A. V. Irodova, V. P. Glazkov, V. A. Somenkov, S. Sh. Shilstein, V. E. Antonov and E. G. Ponyatovsky, *Fiz. Tverd. Tela* **29**, 2714 (1987).
17. I. T. Belash, V. Yu. Malyshev. B. K. Ponomarev, E. G. Ponyatovsky and A. Yu. Sokolov. *Fiz. Tverd. Tela* **28** 1317 (1986).