Mössbauer study of hydrides and deuterides of iron and cobalt

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Abstract

Hydrides and deuterides of iron and hydrides of cobalt prepared at pressures between 4 and 9 GPa and temperatures near 350 °C were studied by ⁵⁷Fe Mössbauer spectroscopy. The d.h.c.p. ε -FeH_{z1.00} phase was found to have a deuteride analogue with nearly the same Mössbauer parameters. In addition to ε -FeH_{z1.00} and ε -FeD_{z1.00}, three novel hydride (deuteride) components were observed in the Mössbauer spectra, one of them non-magnetic at 4.2 K. In h.c.p. ε -CoH_x the magnetic hyperfine field decreases by about 6% between x = 0 and x = 0.5. In f.c.c. γ -CoH_x it is about 3% higher than in the ε phase. The electron density at the ⁵⁷Fe nuclei decreases with increasing hydrogen content without a discontinuity between the ε and the γ phase.

1. Introduction

Both iron and cobalt form hydrides when they are exposed to hydrogen pressures in the GPa range [1-7]. The ferromagnetic iron hydride, ε -FeH_x, has recently been shown by X-ray diffraction to have a close-packed d.h.c.p. (4H) structure [8]. The Mössbauer spectra of ε -FeH_x exhibit two magnetic hyperfine patterns arising from the two different iron sites in the d.h.c.p. structure [9, 10].

In the Co-H system, two phases have been identified [6, 7], namely h.c.p. (2H) ε -CoH_x with $0 < x \le 0.65$, and f.c.c. γ -CoH_x with $x \ge 0.9$. The former phase forms at hydrogen pressures between 2 and 7 GPa and temperatures near 350 °C. The f.c.c. γ phase is obtained at pressures near or above 9 GPa, while hydrogenation at pressures between 7 and 9 GPa results in the coexistence of both phases [6, 7]. All hydrides of cobalt have been found to be ferromagnetic up to 200 K, but their Curie temperatures could not be determined because of the instability of the hydrides at higher temperatures and ambient pressure. In the present paper we report on 57 Fe Mössbauer studies of the Fe-H, Fe-D and Co-H systems. A preliminary account of some of these results has been given elsewhere [11].

2. Experimental details

All hydrides were produced in high pressure cells using MnH_x or MnD_x as a donor of hydrogen or deuterium [7], the latter containing a few per cent of hydrogen impurities. The cells were cooled with liquid nitrogen while still under pressure. The samples were then removed and kept in liquid nitrogen until they were transferred into the Mössbauer cryostat without being warmed above liquid nitrogen temperature. The iron hydrides were prepared from natural iron foils 25 µm thick, the cobalt hydrides from foils of cobalt 25 µm thick containing 0.5 at.% of isotopically enriched ⁵⁷Fe. The Mössbauer spectra were measured with both the absorber and the source of ⁵⁷Co in rhodium at 4.2 K, and fitted with appropriate superpositions of Lorentzian lines. Structure determinations were made at 100 K with iron K_x X-rays. The hydrogen-to-metal ratio was determined by outgassing after the Mössbauer measurements. In order to avoid premature hydrogen losses, the samples were transferred from the Mössbauer cryostat into the outgassing apparatus without being warmed above liquid nitrogen temperature.

3. Results and discussion

3.1. Hydrides and deuterides of iron

Figure 1 shows Mössbauer spectra of iron loaded with hydrogen and deuterium, respectively. These spectra consist of three magnetic six-line patterns, one of which is that of α -Fe, while the other two represent the two iron sites in d.h.c.p. ε -FeH_x or ε -FeD_x (Table 1). According to the area in the Mössbauer spectrum, the hydride contained only 4% of α -Fe. The mean hydrogen-to-metal ratio was found to be $\bar{x} = 1.01 \pm 0.03$. This corresponds to $x = 1.05 \pm 0.03$ for the ε phase, which thus is practically stoichiometric FeH.

The deuteride still contained a large amount of α -Fe, but its Mössbauer parameters are practically the same as for FeH_{\$1.00} (Table 1), indicating that it is nearly stoichiometric FeD. A direct determination of the deuterium content of ε -FeD_x was impossible, because only a lower limit for the mean deuterium content of the sample could be determined due to a contamination of the specimen with debris from the high pressure cell.

The two iron sites in d.h.c.p. ε -FeH_x (ε -FeD_x) have practically the same isomer shift. The sites designated as (1) have the larger hyperfine field and a negative effective electric quadrupole interaction, $\Delta E_Q = \frac{1}{2}eQV_{zz}$ ($3\cos^2\theta - 1$) [12], while sites (2) have the smaller field and a positive ΔE_Q . One can only guess which pattern corresponds to the sites with a "cubic" (c) coordination between two differently stacked close packed metal layers and which to the



Fig. 1. 57 Fe Mössbauer spectra of iron hydride and iron deuteride, showing the two magnetic patterns of the d.h.c.p. (4H) phase and the sextet of α -Fe, which is very weak in the hydride but dominant in the deuteride sample. All spectra were measured at 4.2 K with a source of 57 Co in rhodium at the same temperature.

sites with "hexagonal" (h) coordination between two equally stacked layers, but it is tempting to identify sites (1) as the hexagonal ones because for them the electric quadrupole interaction is negative as in h.c.p. ϵ -CoH_x (see below).

The area under pattern (1) is about 20% larger than that under pattern (2)[†]. It is unlikely that the Lamb-Mössbauer factors for the two sites differ that much. More probably, the intensity difference arises becauses sites (1) occur more often than sites (2) owing to faults in the ideal d.h.c.p. (4H) stacking sequence. For hydrides of Fe-Cr alloys, X-ray diffraction has shown [8] that the fraction of c sites increases with the iron content from zero in h.c.p. (2H) CrH_x through about 0.33 in $(Fe_{0.95}Cr_{0.05})H_x$ with approximate 9R stacking, to 0.5 in d.h.c.p. (4H) ε -FeH_x. A moderate density of stacking faults in the d.h.c.p. structure can explain the intensities observed in the Mössbauer patterns. If sites (1) are indeed the hexagonal ones, the hexagonal coordination is favoured over the cubic one, indicating that the transition from 9R to 4H stacking is incomplete. It is interesting to note that the linewidths for pattern (1) are always somewhat larger than those for pattern (2). This may be the case because the excess planes will have one h and one c plane as neighbours, whereas the normal planes in the d.h.c.p. lattice are

[†]In addition to the one listed in Table 1, four independently prepared samples of ε -FeH_x showed the same effect, which had already been observed in the first Mössbauer experiments on iron hydrides [9, 10].

TABLE 1

р _{Н2} (HGPa)	S (mm s ⁻¹)	ΔE_Q (mm s ⁻¹)	B _{hf} (T)	W (mm s ⁻¹)	RI (%)	Assignment
Nearly pu	ure ε-FeH, ; x	= 1.01(3)				
8.5	+0.364(5)	-0.053(5)	33.8(1)	0.44(1)	53(1)	D.h.c.p. & FeH _{1.05} , site (1)
	+0.370(5)	+0.030(5)	28.8(1)	0.37(1)	43(1)	D.h.c.p. ɛ-FeH _{1.05} , site (2)
	-0.122(5)	0.0	33.8(1)	0.37(1)	4(1)	B.c.c. α-Fe
c-FeD, an	d α -Fe; $\bar{x} > 0$.14				
7.5	+0.382(5)	-0.051(5)	33.5(2)	0.44(1)	17(1)	D.h.c.p. ϵ -FeD _{s10} , site (1)
	+0.372(5)	+0.024(5)	29.0(2)	0.29(1)	13(1)	D.h.c.p. ε-FeH _10, site (2)
	-0.123(5)	+0.003(2)	33.8(1)	0.37(1)	70(1)	B.c.c. a-Fe
Hydride o	ontaining th	e non-magnet	ic phase			
8.2*	-0.021(5)	_		0.68(1)	16(2)	Non-magnetic phase
	+0.422(5)	+0.064(7)	31.7(1)	1.00(2)	45(2)	Disordered phase
	-0.136(5)	0.0	33.6(1)	0.40(1)	39(2)	B.c.c. a-Fe
Deuteride	containing	the non-magn	etic phase	!		
9.0	-0.037(5)	_	_	0.50(2)	41(2)	Non-magnetic phase
	+0.422	+0.064	31.7	1.00	4(2)	Disordered phase
	+0.058	+0.013	36.0	0.46	11(2)	High-field phase
	-0.128(5)	0.0	33.7(1)	0.39(1)	44(2)	B.c.c. a-Fe
Same as a	above after c	old-working a	ıt 77 K			
9.0	-0.023(5)	_		0.50(1)	17(2)	Non-magnetic phase
	+0.422	+0.064	31.7	1.00	5(2)	Disordered phase
	+0.058(5)	+0.013(6)	36.0(1)	0.43(2)	30(1)	High-field phase
	-0.120(5)	0.0	33.4(1)	0.34(1)	48(1)	B.c.c. α -Fe
Same afte	r cold-worki	ng at 77 K an	d annealii	ng at 150 K	for 10	min
9.0	-0.017(5)		_	0.43(2)	11(2)	Non-magnetic phase
	+0.422	+0.064	31.7	1.00	7(2)	Disordered phase
	-0.123(5)	0.0	33.4(1)	0.32(1)	82(2)	B.c.c. α -Fe

Mössbauer results for hydrides and deuterides of iron

The samples were loaded at a hydrogen (deuterium) pressure $p_{\rm H_2}$ and 350 °C (325 °C when there is an asterisk behind the $p_{\rm H_2}$ value) for 24 h. When the mean hydrogen-to-metal ratio \bar{x} is not given, it could not be determined because the sample had lost hydrogen during or after the Mössbauer experiments. S is the isomer shift with respect to the source of ⁵⁷Co in rhodium at 4.2 K, ΔE_Q the effective quadrupole interaction, $B_{\rm hf}$ the magnetic hyperfine field, W the mean width at half maximum of the outermost lines of the magnetic pattern or the full width of the non-magnetic component, and RI the relative intensity of the individual components. Experimental uncertainties are given in parentheses; values without errors were fixed during a least squares fitting procedure.

stacked between two equal planes. This argument holds for excess h planes as well as for excess c planes.

The Mössbauer spectra of some of the studied FeH_x and FeD_x specimens were different from those typical for the ε phase, although there was no evident difference in sample preparation. Such spectra (Fig. 2) are characterized by a strong non-magnetic component and the absence of the twin patterns of the ε phase. In addition to the ubiquitous pattern of α iron, the



Fig. 2. (a) ⁵⁷Fe Mössbauer spectra of iron hydride and iron deuteride samples exhibiting a strong non-magnetic component, but no ε phase. (b) Spectra of the deuteride whose spectrum is shown on the left after cold-working at 77 K and again after the cold-worked sample at 150 K for 10 min. All spectra were measured at 4.2 K with a source of ⁵⁷Co in rhodium at the same temperature.

hydride spectrum contains a strong pattern with broad lines indicating a distribution of hyperfine fields, and a mean hyperfine field lying between the field values of the ε phase. The isomer shift of this component is practically the same as that of ε -FeH_{≈ 1.00} (Table 1), indicating that the broad magnetic pattern also arises from a phase with a hydrogen-to-metal ratio close to unity. This is reminiscent of the Mössbauer spectra of the iron hydrides produced by implantation of high doses of H⁺ ions into iron films [13], which have been attributed to a phase with a disordered stacking of close-packed layers. Obviously polytypes with a high density of stacking faults yielding such spectra can also form during high pressure loading.

The non-magnetic component has an isomer shift of only about $+0.10 \text{ mm s}^{-1}$ with respect to α -Fe (Table 1). This indicates that it arises from a phase containing less hydrogen than the ε phase or the disordered one. Considering that (hypothetical) hydrogen-free h.c.p. iron at ambient pressure is expected [14] to have an isomer shift of about -0.10 mm s^{-1} with respect to α -Fe, the total change of the isomer shift of the non-magnetic component with respect to such iron is about $+0.20 \text{ mm s}^{-1}$, compared to $+0.60 \text{ mm s}^{-1}$ for ε -FeH. Assuming that the isomer shift increases linearly with the hydrogen content, the non-magnetic phase should thus have a hydrogen-to-metal ratio of $x \approx 0.3$. With only about one third of the interstitial sites occupied, the relatively large width of the non-magnetic peak can be attributed to a

distribution of isomer shifts arising from a distribution in the number of hydrogen neighbours around the individual iron atoms [15, 16].

To test the stability of the non-magnetic and the disordered hydride phases, the deuteride was cold-worked, *i.e.* ground in a mortar under liquid nitrogen. After this treatment, the intensity of the non-magnetic component had decreased (Fig. 2), and in its place a new magnetic component with a larger hyperfine field than those of the ε phase had appeared (Fig. 2 and Table 1). According to the isomer shift, which is but slightly larger than that of the non-magnetic component, the high-field phase should have a deuterium content of $x \approx 0.4$. In fact, the spectrum of the as-prepared sample already contains a small amount of this component (Fig. 2 and Table 1).

The stability of ε -FeH_{≈ 1.00} against cold-working under liquid nitrogen was also tested, but this phase turned out to be quite stable. A slight increase of the α -Fe fraction in the Mössbauer spectrum may be due to decomposition caused by the cold-working, but could also be explained by the diminution of the particles, which may have laid open some α -Fe that had been inaccessible to the 14.4 keV γ -rays inside the rather coarse grains of the as-prepared hydride.

The thermal stability of the new phases was studied by annealing the cold-worked deuteride at increasing temperatures and taking Mössbauer spectra at 4.2 K between the annealing steps. Already on annealing at 125 K for a few minutes, half of the high-field component had decayed to α -Fe. On annealing at 150 K for 10 min, the high-field phase had disappeared altogether, while the disordered and non-magnetic phases were still weakly visible (Fig. 2 and Table 1). After 20 min at 160 K, practically all hydride components had transformed into α -Fe. Similar thermal decomposition properties have been observed for ϵ -FeH [9, 10] and for the hydride formed by ion implantation [13].

In addition to the isomer shifts, the decomposition of the high-field and non-magnetic phases into α -Fe between 120 and 150 K shows that these are indeed hydrides or deuterides, but their nature remains a matter of speculation. The non-magnetic component appears to be a hitherto unknown phase with a hydrogen (deuterium) content near x = 0.3. It could be an f.c.c. phase, but since X-ray patterns taken immediately after the preparation of the samples could be interpreted as arising from an h.c.p. (or d.h.c.p.) phase and α-Fe, a hexagonal polytype appears to be more probable. Hexagonal iron is expected to become ferromagnetic only if the number of electrons per metal atom is increased by incorporation of a sufficient amount of hydrogen [8]. The hydrogen-to-metal ratio of $x \approx 0.3$ may be too low to render the hydride ferromagnetic. If cold-working results in a disproportionation into some α-Fe and a hexagonal hydride with a slightly higher hydrogen content ($x \approx 0.4$), the system may become ferromagnetic. In this case, the rigid-band model predicts a higher magnetization and hyperfine field than observed at higher hydrogen contents [7, 8]. This would account for the high-field phase, which then differed from the non-magnetic one only by a minor increase in the hydrogen or deuterium content. The occurrence of only one hyperfine field and rather narrow lines in the high-field state indicates that this phase, and

Mössbaue	r results for	hydrides of (cobalt						
ĸ	$^{P_{\mathrm{H}_{z}}}_{\mathrm{(GPa)}}$	a (Å)	c (Å)	S (mm s ¹)	ΔE_{Q} (mm s ⁻¹)	$B_{ m hf}$ (T)	W (mm s ⁻¹)	RI (%)	Assignment
0.00	and the second se	2.503	4.064	-0.101(5)	-0.054(5)	32.4(1)	0.33(1)	100	H.c.p. cobalt
0.22(2)	4.0	2.538	4.104	+0.018(5)	-0.074(5)	31.6(1)	0.46(1)	100	E-CoH,
0.48(2)	5.0	2.575	4.164	+0.108(5)	-0.077(5)	30.7(1)	0.37(1)	100	e-CoH,
0.56(2)	6.0	2.590	4.183	+0.123(5)	-0.065(5)	30.7(1)	0.36(1)	100	E-CoH
0.67(3)	9,0*	2.594	4.184	+0.171(5)	-0.065(5)	30.6(1)	0.36(1)	69(2)	e-CoH _{≈ne}
		3.723	ţ	+0.206(5)	-0.018(5)	31.8(1)	0.29(1)	31(2)	γ-CoH _{z0} ,
0.84(2)	8.1	3.72	l	+0.215(5)	-0.041(5)	31.5(1)	0.54(1)	100	γ-CoH,
0.90(4)	0.6	3.722		+0.245(5)	-0.038(5)	31.5(1)	0.46(1)	100	γ-CoH _γ
The samp hydrogen- 100 K. S h hyperfine componen	tes were load to-metal ratic s the isomer s field, W the m	ed at a hyd ss ž were de shift with re lean width ai bauer specti	rogen pressu termined by spect to the t half maxim rum. Experir	rre p_{H_2} and 350 outgassing after source of 57 Co ir um of the outerm nental uncertain	C (325 C when the Mössbauer 1 rhodium at 4.2 ost lines of the m ties are given in	there is an as experiments, $a K$, AE_{q} the effective patter parter parter parentheses.	terisk behind th and c are the fective quadrup ns, and RI the r	he $p_{H_{u}}$ value) lattice parame ole interaction elative intensi	for 24 h. The mean term determined at Ω_{hf} the magnetic ty of the respective

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TABLE 2	Möschaner



Fig. 3. 57 Fe Mössbauer spectra of CoH_x samples measured at 4.2 K with a source of 57 Co in rhodium at the same temperature.

presumably also the non-magnetic one, has a simple h.c.p. (2H) structure rather than being a more complicated stacking polytype.

3.2. Hydrides of cobalt

The Mössbauer results for the hydrides of cobalt (Table 2 and Fig. 3) show a decrease of the hyperfine field on hydrogenation in h.c.p. ϵ -CoH_x by about 6% between x = 0 and x = 0.60, which is about half of the relative decrease of the spontaneous magnetization in the same concentration range [6, 7]. For $0.6 \leq x \leq 0.9$, one expects the h.c.p. and the f.c.c. hydride phases to coexist [6, 7]. The two components distinguishable in the Mössbauer spectrum at a mean hydrogen content of $\bar{x} = 0.67$ (Fig. 3) can be attributed to the ϵ and γ phases, respectively. The isomer shift increases linearly with the hydrogen content, without a noticeable discontinuity between the ϵ and the γ phase. Since iron is a dilute probe atom in CoH_x, it may be surrounded by fewer nearest hydrogen neighbours than the cobalt atoms. Compared to the shift observed in ϵ -FeH_{z1.00} (see above), the magnitude of the isomer shifts for ⁵⁷Fe in CoH_x indicates that the iron probes indeed interact repulsively with the hydrogen, but much more weakly than, for instance, in PdH_x or NiH_x [15, 16].</sub>

The effective electric quadrupole interaction, ΔE_Q , in h.c.p. ε -CoH_x is negative and slightly larger in magnitude than in pure h.c.p. cobalt (Table 2). In f.c.c. γ -CoH_x one also observes a non-vanishing effective electric quadrupole interaction (Table 2). This is surprising even if the iron probes are surrounded by fewer than six nearest hydrogen neighbours and therefore are subject to small local electric field gradients, because ΔE_Q measures only the projection of the electric field gradient on the direction of the magnetic hyperfine field [12]. A non-vanishing value of ΔE_Q therefore requires a correlation between the direction of magnetization and the geometrical arrangement of the hydrogen surrounding the iron atoms. Such correlations may arise from magnetostrictive or electronic interactions and cause, for instance, the magnetic after-effect [17].

The decrease of the magnetic hyperfine field in ε -CoH_x with increasing hydrogen content can be explained as a consequence of the filling of the 3d band with electrons donated by the hydrogen [7, 8]. A similar behaviour is expected for the f.c.c. γ phase, but the concentration range in which this phase could be observed is too narrow for drawing definite conclusions. The hyperfine fields in the γ phase are, however, generally higher by about 1 T than in the ε phase. This is reminiscent of the behaviour of pure cobalt, where ⁵⁷Fe hyperfine field is also larger in the f.c.c. phase than in the h.c.p. phase [18].

4. Conclusions

The Mössbauer spectra of the hydrides of cobalt can be explained by the existence of the ε and γ phases. The dependence of the magnetic hyperfine fields on hydrogen concentration is in agreement with the expectations of the rigid-band model, and the isomer shifts indicate that there is a weakly repulsive interaction between the iron probes and the hydrogen.

Both the nature and the conditions of formation of the new phases observed in the Fe-H and Fe-D systems require further clarification, not only by Mössbauer spectroscopy, but also by X-ray diffraction and other methods. The Mössbauer results indicate that in addition to a disordered stacking polytype with a hydrogen-to-metal ratio close to unity, there is a phase with $x \approx 0.3$, whose structure appears to be h.c.p. (2H), and whose hydrogen content is close to the threshold at which ferromagnetism sets in, such that it becomes ferromagnetic when the hydrogen content increases slightly.

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