phys. stat. sol. (a) <u>65</u>, K43 (1981) Subject classification: 18.2; 21.1.1 Institute of Solid State Physics, Academy of Sciences of the USSR, Chernogolovka¹) <u>Magnetization of Iron Hydride</u> By V.E. ANTONOV, I.T. BELASH, E.G. PONYATOVSKII,

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Introduction At T = 523 K and P_{H} = 45 kbar a phase transformation occurs in iron followed by a jump-like increase in the hydrogen solubility /1/. The hydrogen content in the Fe-H samples obtained by quenching down to \approx 95 K after hydrogenation for 10 h at $P_{H} = 67$ kbar and T = 523 K was within the H-to-metal atomic ratio n = 0.65 to 0.81. The X-ray study has shown that the hydride thus synthesized has an iron h.c.p. sublattice with the parameters a = (2.686 ++0.003)^A, c = (4.380 + 0.005)^A, c/a = 1.631 + 0.003 at T \approx 80 K and atmospheric pressure. The scattering found for the n-values (from 0.65 to 0.81) seemed to be due to the hydrogen losses from the Fe-H samples during manipulations at atmospheric pressure before a chemical analysis, since at P = 1 bar the rate of hydrogen liberation from iron hydride became noticeable even at $T \approx$ \$150 K, and at T = 180 K the main quantity of hydrogen escaped from the samples in a few seconds. After complete liberation of hydrogen, iron recovers the initial b.c.c. crystal structure but becomes very brittle. The samples in the form of rods of 1.1 mm diameter and 5 mm length prepared from iron purified by zone melting followed by refining in hydrogen at T = 1140 K for 100 h (the content of impurities and details of the purification technique are given in (2/)were used for the measurement.

Just the similar specimens hydrogenated under the same conditions (10 h at $P_{H_2} = 67$ kbar and T = 523 K) were used in the present work for the investigation of the magnetization (σ) behaviour at atmospheric pressure and $4.2 \le T \le \le 80$ K in a pulsed magnetic field H up to 320 kOe, the pulse duration being ≈ 0.01 s. Immediately after the magnetic measurement the Fe-H sample was placed in a previously cooled scaled glass vessel filled up by benzine. Then this vessel was heated to room temperature, hydrogen liberated from the sample

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Fig. 1. Dependences of the magnetization σ upon magnetic field H at T = 4.2 K. (1) Fe, (2) Fe-H solid solution with n = 0.75 + 0.03

and partially expelled benzine from the vessel. The content of the Fe-H sample was determined by the volume of released hydrogen with an accuracy of 4%. After a complete liberation of hydrogen, the magnetization of the iron sample was measured again in order to calibrate the measuring installation. The investigation has shown that several hydrogenation-dehydrogenation cycles do not change the $\sigma(H)$ dependences for iron specimens in the studied T and H intervals, and this additional calibration permitted to attain a relative accuracy of 2% in the measurement of iron hydride magnetization.

Results and discussion A typical $\sigma(H)$ dependence is shown in Fig. 1 for the Fe-H sample with $n = 0.75 \pm 0.03$. One can see that at H < 150 kOe the $\sigma(H)$ curve for iron hydride lies perceptibly below the similar curve for b.c.c. iron, the hydride magnetization being essentially dependent on H. At further H increase the hydride magnetization approaches saturation and within the experimental error coincides with that for the pure iron sample. The dependence of σ' upon H observed for iron hydride at H < 150 kOe seems to be caused by a large value of the magnetic anisotropy energy that can be associated with, for example, a large magnitude of internal stresses /3/ occurring at hydrogenation. Note that the nearest analogue of the iron hydride - the ferromagnetic manganese hydride with h.c.p. manganese sublattice - also exhibits a rather large field of technical saturation exceeding 60 kOe /4/.

In the investigated temperature range 4.2 to 80 K the $\sigma(H)$ dependence for iron hydride (as well as for pure b.c.c. iron) is independent of temperature within the experimental error. Hence, its Curie point $T_c \gg 80$ K and the value of spontaneous magnetization at 4.2 $\leq T \leq 80$ K is approximately equal to σ_c at T = 0 K. The presence of a large region of a non-linear $\sigma(H)$ dependence for the hydride (Fig. 1) impedes a correct determination of the spontaneous magnetization. One may only state that $\sigma_0 \lesssim 2.22 \ \mu_B/\text{atom} = \sigma_0^{Fe}$, where μ_B Bohr magneton. Note that although the Fe-H sample with n = 0.75 may contain a considerable amount of pure iron phase (without hydrogen) /1/, this cannot change the above result due to the proximity of the σ_0 values for iron hydride and b.c.c. iron.

Hydrogenation leads to a strong deformation of the band structure of transition metals. The investigation of hydrogen solid solutions on the base of the f.c.c. metal sublattice has shown, however, that the behaviour of their magnetic properties may be described assuming an increase in the degree of occupation of the host metal 3d-band to be the main effect on hydrogenation, hydrogen being a donor of a fractional number of electrons $\eta < 1$ electron/proton /5, 6/. As a theoretical basis for such an approach the band structure calculations may serve to some extent. These calculations show (see, for instance, /7, 8/) that at $n \leq 1$ no new (hydrogen) band is formed below the Fermi energy, metal d-states change weakly whereas the energy of sp-states strongly decreases. The latter leads to an increase of the number of states below the Fermi level. Thus, a part of electrons supplied by hydrogen atoms into the conduction band is spent to fill those additional states.

Consider to what degree the description /5, 6/, which can be called a "rigid d-band" model, is useful for hydrogen solid solutions on the base of the h.c.p. metal sublattice.

The conclusion that it is an increase in the degree of occupation of the dband which has a main effect on the magnetic properties of 3d-metal alloys at hydrogenation was based on the fact that the dependences of these properties upon hydrogen content in alloys of 3d-metals situated close to each other in the Periodic Table proved to be similar to that on changing the composition of these alloys toward an increase in the average number N^e of 3d + 4s electrons per atom /5, 6/. It is worth noting that, in its turn, the assumption of a dominating role of the degree of d-band filling for the alloys of this kind in varying the magnetic properties with composition in rather wide concentration intervals ($\Delta N^e \approx 0.5$ electrons/atom) has been confirmed while investigating hydrogen solid solutions on their base. The values of σ_0 for the f.c.c. alloys of 3d-metals closely arranged in the Periodic Table as a function of N^e fall onto a single curve (the Pauling-Slater curve). While decreasing N^e down to ≈ 8.8 electrons/atom σ_0 increases approximately linearly with the slope $\partial \sigma_0 / \partial N^e \approx -1 \mu_B$ /electron (Ni-Cu, Ni-Co, and Ni-Fe alloys), then reaches a maximum and begins decreasing. At N^e \approx ≈ 8.35 electrons/atom the alloys become paramagnetic down to helium temperature, at further N^e decrease antiferromagnetic ordering occurs and the Néel point increases monotonously up to T_N ≈ 440 K at N^e = 7.65 electrons/atom (Fe₆₅(Ni_{1-x}Mn_x)₃₅ alloys)/9, 5/.

The data concerning the $\sigma_0(N^e)$ dependence for the alloys with h.c.p. crystal lattice are very rare. Nevertheless, it seems to have similar character in this interval of N^e magnitudes. The h.c.p. Fe-Mn alloys ($N^e = 7.71$ to 7.82 electrons/atom) are antiferromagnetics with $T_N \approx 230$ K/10/. Extrapolation from Fe-Ru and Fe-Os alloys shows that at atmospheric pressure the h.c.p. iron ($N^e = 8$ electrons/atom) should also be antiferromagnetically ordered, but exhibit a lower Néel point $T_N \approx 100$ K/11/. Sufficiently correct data on the concentration dependence of magnetic properties for the 3d-metal h.c.p. alloys with $8 < N^e < 9$ electrons/atom) is a ferromagnetic with $\sigma_0 = 1.72 \ \mu_B/atom/12/$ that is near the σ_0 -value for f.c.c. cobalt. At further N^e increase up to ≈ 9.28 electrons/atom (h.c.p. Co-Ni alloys /13 to 15/) σ_0 decreases approximately linearly with the slope $\partial \sigma_0/\partial N^e \approx -1 \ \mu_B/electron$.

Thus, at $7.7 \leq N^e \leq 9.28$ electrons/atom the magnetic properties and their concentration dependences seem to be close for the 3d-metal alloys with f.c.c. and h.c.p. crystal structures. Investigation of hydrogen solid solutions on the base of h.c.p. cobalt has shown the hydrogenation to result in a decrease of σ_0 with an initial slope $\partial \sigma_0 / \partial n \big|_{n=0} \approx -0.6 \,\mu_B / H$ atom that agrees with the predictions of the "rigid d-band" model. If this model is valid for the description of the Fe-H solutions, an increase of hydrogen content in h.c.p. iron should lead (as it has been observed at the hydrogenation of the Fe₆₅(Ni_{1-x}Mn_x)₃₅ f.c.c. alloys /5/) to the suppression of antiferromagnetic ordering, the appearance of spontaneous magnetization at a certain value of n = n_f, and then to a monotonous increase of σ_0 and T_c. The transformation of the antiferromagnetic h.c.p. ≈ 80 K at

 $n \approx 0.8$ found in the present work agrees qualitatively with such a dependence of magnetic properties upon hydrogen content.

For the Fe-H system it is possible, following /5/, to introduce the coefficient of an "effective" number of electrons supplied by hydrogen into the d-band of the metal $G = \Delta N^e / \Delta n$, relating the changes in N^e and n resulting in similar changes of iron magnetic properties. By analogy with the $\sigma_0(N^e)$ dependence for the f.c.c. alloys one should expect that at $8 < N^e < 9$ electrons/atom the $\sigma_0(N^e)$ curve passes through a maximum. So, at $n \approx 0.8$ the point $\sigma_0(N^e_{Fe} + Gn) \approx 2.2 \mu_B/atom$ either falls onto the prolongation of the linear dependence $\sigma_0(N^e)$ with the slope $\varphi = \partial \sigma_0/\partial n \approx -1 \mu_B/electron$, which is valid for h.c.p. Co-Ni alloys, or lies below this line. Hence,

$$\sigma_{0}^{Co} - \left[N_{Co}^{e} - (N_{Fe}^{e} + Gn)\right] \varphi \gtrsim 2.2 \mu_{B} / atom,$$

from whence G ≤ 0.6 electrons/H atom that is a reasonable estimate.

Thus, as well as in the case of the f.c.c. alloys /5, 6/, the behaviour of iron magnetic properties at hydrogenation may be described under the assumption that these properties are mainly affected by the degree of d-band filling, and the "rigid d-band" model gives the correct sign and the order of magnitude of the observed effects.

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