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A ^{57}Fe MÖSSBAUER STUDY OF THE HIGH PRESSURE HYDRIDE PHASES OF Fe AND Co

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Hydrides of iron and cobalt prepared at pressures between 4.0 and 9.5 GPa were studied by ^{57}Fe Mössbauer spectroscopy at 4.2 K. Iron hydride was found to be nearly stoichiometric FeH. The two iron sites in its dhcp lattice have hyperfine fields of 33.8 and 28.8 T. Practically the same results were found for the deuteride. In hcp ϵ-CoH$_x$, the hyperfine fields decrease with hydrogen content by about 6% between $x = 0$ and $x = 0.5$. In all studied hydrides the electron densities at the ^{57}Fe nuclei are smaller than in the pure metals.

1. Introduction

Both iron and cobalt form hydrides at temperatures around 300 °C and hydrogen pressures exceeding about 5 GPa for Fe and 2 GPa for Co [1–4]. Iron hydride was initially thought to have a hcp structure with the hydrogen in the octahedral interstices, but later shown [5] to rather have a dhcp stacking of closepacked planes, as had been suggested by Mössbauer experiments [6] with samples that were only partially hydrogenated. We now present Mössbauer data for virtually pure ϵ-FeH$_x$ as well as first results for the corresponding deuteride.

In hcp cobalt, hydrogen forms a continuous series of ϵ-CoH$_x$ solid solutions up to a hydrogen-to-metal atomic ratio of about $x = 0.6$ [1,4]. At higher hydrogen contents, the fcc γ-phase with $x \approx 1.0$ begins to form. Like the hydride of iron, both hydride phases of cobalt are ferromagnetic [1,4], but the spontaneous magnetization of CoH$_x$ decreases with the hydrogen content. The present ^{57}Fe Mössbauer results confirm these findings and show that between the iron probes and the hydrogen in CoH$_x$ there is no strongly repulsive interaction like, for instance, in β-NiH$_x$ at $x \approx 1.0$ [7].

2. Experimental details

At normal pressure and ambient temperature, the hydrides of iron, and to a lesser extent also those of cobalt, decay quickly into the metals and hydrogen. All Mössbauer experiments were therefore performed at 4.2 K. The hydrides were prepared at pressures between 4 and 9.5 GPa as described elsewhere [1] and cooled with liquid N_2 while still in the high-pressure cell. Between the preparation and the Mössbauer experiments, and during the transfer into the Mössbauer cryostat, the samples were kept at liquid N_2 temperature. The hydrogen contents were determined by outgassing after the Mössbauer measurements. Iron hydride and deuteride were prepared from 25 μm thick iron foils, the hydrides of cobalt from 25 μm thick foils containing 0.5% of enriched ^{57}Fe.

3. Results and discussion

Mössbauer spectra of the hydride and deuteride of iron are shown in fig. 1. The hydride was prepared at a pressure of 8.5 GPa and a temperature of 350 ° C. It exhibits two magnetic hyperfine patterns with hyperfine fields of $B_{\mathrm{hf}} = 33.8(1)$ and 28.8(1) T. Both have very small effective quadrupole interactions, $\frac{1}{4}eQV_{zz}(3\cos^2\theta - 1) = -0.053(5)$ and $+0.030(5)$ mm/s, respectively. This is not surprising since the c/a ratio of ϵ-FeH$_x$ is very close to the ideal value [1,2,5,8]. The isomer shifts of both patterns are also practically the same, $IS = +0.364(5)$ and $+0.370(5)$ mm/s with respect to the source of ^{57}Co in Rh at 4.2 K, or about $+0.49$ mm/s with respect to α-iron. The hydrogen content of the sample was found to be $x = 1.01(3)$. According to the Mössbauer spectrum, the sample still contains 3.6(5)% of α-iron. For the ϵ-FeH$_x$ phase one therefore obtains $x = 1.05(4)$. This is compatible with a virtually stoichiometric FeH composition of the hydride, which explains the narrow Mössbauer lines of the hydride phase. The FeD$_x$ sample was prepared at 7.0 GPa and 350 ° C and still contained about 70% of α-iron. The hyperfine fields. $B_{\mathrm{hf}} = 33.5(2)$ and 29.0(2) T, as well as the isomer

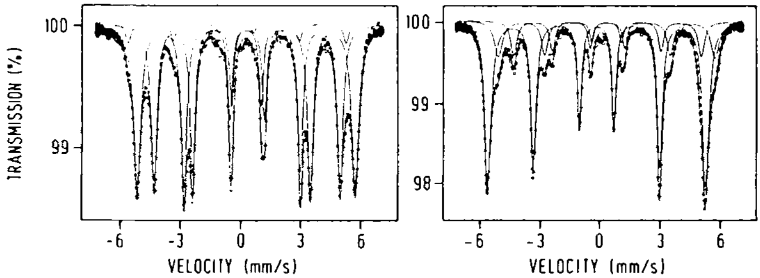

Fig. 1. Mössbauer spectra of iron hydride (left) and iron deuteride (right) measured with a source of ^{57}Co in Rh with the source and absorber at 4.2 K. Both samples still contain α-iron, which is the weakest component in the hydride but dominant in the deuteride.

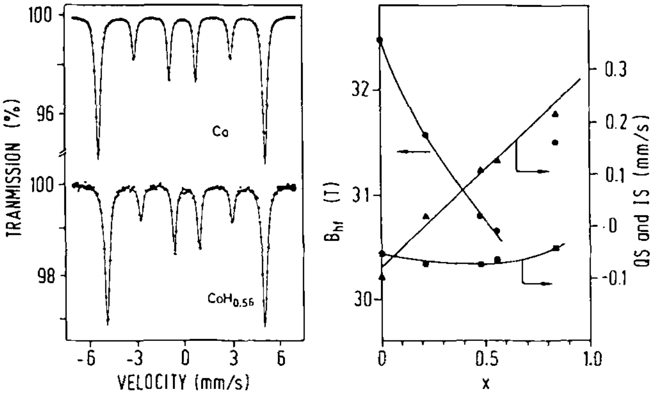

Fig. 2. Mössbauer results for the hydrides of cobalt. On the left, spectra of ^{57}Fe in hcp Co and CoH$_{0.56}$ are shown. The diagram on the right shows the dependence of the hyperfine field (dots), the isomer shift with respect to the ^{57}Co : Rh source (triangles) and the projected electric quadrupole interaction, $\frac{1}{4}eqV_{zz}(3\cos^2\theta - 1)$, (squares) on the hydrogen-to-metal ratio x.

shifts and quadrupole interactions of the deuteride are nearly the same as those of the hydride. The hydrogen content of the FeD$_x$ phase could not be determined because of the high α-iron content, but the Mössbauer data indicate that it is also virtually stoichiometric FeD. The two magnetic hyperfine patterns in both the hydride and the deuteride can be attributed to the cubic and hexagonal layers of the dhcp structure, but it is impossible to tell which of the two sites has the larger hyperfine field.

With $B_{hf} = 32.4(2)$ T, $\frac{1}{4}eQV_{zz}(3\cos^2\theta - 1) = -0.055(3)$ mm/s and $IS = -0.101(3)$ mm/s, the spectrum of the rolled ^{57}Fe : Co foil (fig. 2) used to prepare the hydrides is typical for the hcp low temperature phase of Co [9,10]. Samples of ϵ-CoH$_x$ prepared at 350 °C and 4, 5 and 6 GPa reveal a decrease of the hyperfine field and an increase of the isomer shift with increasing hydrogen content (fig. 2), while the quadrupole splitting hardly changes. Although the hydrides are non-stoichiometric, their Mössbauer lines are but slightly wider than those of the pure Co sample. The Co sample loaded at 8.2 GPa ($x = 0.84(4)$) should be a mixture of hcp ϵ-CoH$_x$ with $x \approx 0.65$ and of fcc γ-CoH$_{\approx 1.0}$ [1,4]. The Mössbauer spectrum, however, does not show any contribution of the ϵ-phase and rather indicates that the sample is pure but understoichiometric fcc γ-CoH$_x$. The line broadening is larger than in the ϵ-phase hydrides. The shape of the spectrum indicates that this is due to a distribution of isomer shifts rather than hyperfine fields.

The decrease of the hyperfine field with hydrogen content by about 6% between ^{57}Fe in pure Co and in ϵ-CoH$_{0.5}$ is somewhat smaller than the 13% decrease of the magnetic moment per Co atom in the same composition range [4]. On formation of the fcc γ-CoH$_x$ at higher hydrogen concentrations, the hyperfine field increases again, revealing structural influences in addition to those of the hydrogen. The isomer shift increases nearly linearly with x and extrapolates to about $+0.40$ mm/s at $x = 1.0$ with respect to ^{57}Fe : Co. The approximately linear dependence on x as well as the absolute value of the shift as compared to that of ϵ-$FeH_{1.0}$ indicate that iron probes in CoH_x may experience a slightly repulsive interaction with the hydrogen, but certainly not a strong repulsion like that found, e.g., for ^{57}Fe in NiH_x [7] or PdH_x [11].

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