Polish J. Chem., **71**, 1792–1796 (1997)

The Inelastic Neutron Scattering Spectrum of dhcp Iron Hydride*

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(Received July 2nd, 1997)

The optic phonon modes of hydrogen in dhcp iron hydride (FeH_x with x close to 1) were investigated by neutron spectroscopy. The optic phonons have energies between ~70 and ~140 meV. The average energy of the optic phonons is ~105 meV.

Key words: hydrides, neutron spectroscopy, optic phonons, high pressure

The properties of hydrogen interstitials in iron are subject of intensive research activities since many years, chiefly focused on the mechanical behavior and degradation effects, that structural iron and steel components show in the presence of hydrogen (see [1–4] and references therein). Because of the extremy low solubility of hydrogen in iron at atmospheric hydrogen-gas-pressures, the investigated hydrogen concentrations were usually very small. It was not before 1980 that a hydride FeH_x, with x close to 1 was synthesized in a high-pressure cell (67 kbar H_2 gas, 250°C) [5]. One important reason, why both synthesis and properties of this specific hydride are of broad general interest, is that it was repeatedly suggested to represent a main constituent of the core of the earth [6,7]. Iron hydrides are thermodynamically stable only at high hydrogen gas pressures, and they decompose into Fe and H_2 gas under ambient conditions. However, they can be frozen in a low-temperature metastable state without high hydrogen gas pressures if they are cooled below about 150 K under high-pressure conditions and subsequently are kept below this temperature. Because of this fact, the properties of iron hydrides have been studied both in the presence of high hydrogen gas pressures [5,6,8–12] and in metastable low-temperature states, where high hydrogen gas pressures were not required [13–17].

The temperature hydrogen-gas-pressure phase diagram of iron hydride is complex and exhibits bcc, fcc, hcp and dhcp (double hcp with a stacking sequence ABAC) structures for the iron host lattices. Particularly in the metastable low-temperature states below 150 K, iron hydrides with dhcp and hcp host lattices were observed. A recent low-temperature neutron diffraction study [17] on such metastable iron hydrides and deuterides demonstrated further that the hydrogen or deuterium atoms

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* Dedicated to Prof. B. Baranowski on the occasion of his 70th birthday.

occupy octahedral sites in both the dhcp and the hcp host lattices. An important characteristic of these octahedral sites is that they exhibit cubic symmetry (i), if we consider only the six nearest-neighbor iron atoms and (ii) if we neglect any deviations from an ideal *c/a* ratio between the lattice parameters *a* and *c* (the ideal ratio is $2\cdot\sqrt{8/3} = 3.266$ for a dhcp and $\sqrt{8/3} = 1.633$ for a hcp host lattice).

In this paper, we report the results of a study in which we determined the vibrational energies of the optic phonon modes of the hydrogen atoms in dhcp iron hydride. The experiment was carried out by inelastic neutron scattering on a sample that was in a frozen-in metastable low-temperature state.

EXPERIMENTAL

The investigated sample was polycrystalline FeH_x with a hydrogen concentration x close to 1 and a mass of ~170 mg. It was prepared in a high-pressure cell from iron foils (~0.12 mm thick), that were exposed to hydrogen gas pressures up to 92 kbar at temperatures up to 350°C. The cell with the sample was subsequently cooled below 100 K under pressure before the sample was removed from the cell and stored in liquid nitrogen. A more detailed description of the sample preparation technique is given in [18]. However, an important point to mention is that in all our later investigations the sample never was allowed to surpass 150 K in order to maintain its frozen-in metastable state.

Neutron diffraction measurements carried out at ~90 K [17] demonstrated that the iron host lattice of the FeH_x sample had dhcp structure with lattice parameters $a = 2.679$ Å and $c = 8.77$ Å, yielding an almost ideal *c/a* ratio of 3.274. The measurements showed also a small contamination of the sample with α-Fe (lattice parameter $a = 2.863$ Å). However, since this α-Fe contamination was practically free of hydrogen, it did not impair the measurement of the energies of the optic phonon modes of the hydrogen interstitials in iron hydride.

The inelastic neutron scattering measurements were carried out with the three-axis spectrometer IN1 at the hot source of the high flux reactor at the Institute Laue-Langevin in Grenoble. The spectrometer was operated in the beryllium filter mode, with a fixed scattering angle of 44°. The Cu(200) and Cu(220) monochromators were used for neutron energies below and above ~120 meV, respectively. The energy resolutions were ~7% (Cu(200) monochromator) and ~10% (Cu(220) monochromator) of the neutron energies [19,20].

The investigated FeH_x sample was enclosed in a stair-like folded aluminum foil that was in a flat aluminum container. Before and after the neutron scattering measurements, the container was kept in a liquid nitrogen bath. For the measurements the container was quickly mounted into a cooled cryostat (standard orange cryostat of the Institute Laue-Langevin), which subsequently was evacuated and heated to ~90 K in order to remove any condensated nitrogen inside of the sample container. After this, the sample was cooled to ~2 K, the temperature at which our neutron data were taken.

RESULTS AND DISCUSSION

Figure 1 presents the neutron spectrum obtained from our FeH_x sample (full circles), together with a background spectrum, taken from an empty aluminum container (open circles). The abscissa shows the neutron energy loss of the inelastically scattered neutrons. This energy loss is given by the neutron energy after the monochromator, reduced by the average final neutron energy of 4.7 meV after the beryllium filter. The fact that the scattering cross section of hydrogen exceeds that of iron by far [21] means that the scattering intensity from our sample is dominated by the hydrogen atoms. This holds in particular for the energy range above 60 meV, which is of present interest, since the vibrational energies of the host lattice iron atoms are much lower. For this reason, the difference between the two spectra in Fig. 1 represents practically exclusively scattering processes from the hydrogen in our FeH_x sample.

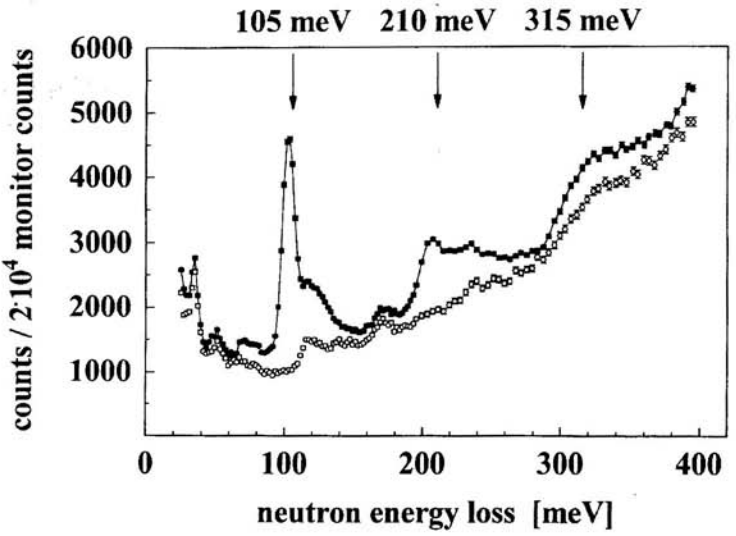

Figure 1. Neutron spectrum of the dhcp FeH_x powder sample (full data points), together with the background spectra of the sample environment (open data points). The spectra show the respective counts normalized to the monitor counts in a plot *versus* the energy loss of the neutrons.

The spectrum of our FeH_x sample in Fig. 1 shows three energy regions around 105, 210 and 315 meV, where distinct inelastic scattering intensity from the hydrogen is observed (arrows in the upper abscissa). For the lowest energy region around 105 meV, the inelastic scattering intensity consists of a peak with a width that does not exceed very much the energy resolution of ~7 meV. Further, there is a small shoulder at lower energies, extending down to ~70 meV, and a large shoulder at higher energies, extending up to ~140 meV. It seems interesting to mention, that the shape of the scattering intensity around 105 meV is similar to that of palladium hydride (PdH_x with $x = 0.99$) [22], if we reduce the energy scale by a factor ~1.75. For our later discussion, it is of further interest to compare the total intensities of the hydrogen-induced scattering in the three different energy regions. These total scattering intensities scale 1 to 0.75 to 0.59, if we integrate hydrogen-induced counts from 69 to 142 meV (region around 105 meV), 183 to 271 meV (region around 210 meV) and 282 to 383 meV (region around 315 meV), respectively.

The chief characteristics of the neutron spectrum from our sample can be understood if we assume, that the hydrogen atoms in iron hydride are located in a harmonic isotropic potential. This means, that the presence of the hydrogen atoms leads to local (dispersionless) optic phonon modes with a common threefold degenerated energy $\hbar\omega_0$. Considering the low temperature of our measurements, we can assume $\hbar\omega_0 >> k_B T$, so that phonons can only be created, but not annihilated, in a scattering process. In this case, the scattering law can be written as [23]

$$S(Q,\omega) = \sum_{n=1}^{\infty} \exp\left(-\frac{\hbar Q^2}{2M\omega_0}\right) \cdot \frac{1}{n!} \cdot \left(\frac{\hbar Q^2}{2M\omega_0}\right)^n \cdot \delta(\hbar\omega - n \cdot \hbar\omega_0) \qquad (1)$$

where $\hbar Q$ and $\hbar\omega$ are the momentum and the energy loss of the scattered neutron, M is the mass of a hydrogen atom, $\delta(x)$ is the delta function and n is the number of created phonons.

The assumption of an isotropic and harmonic potential for the hydrogen atoms is a first and crude approximation. It holds if the symmetry of the octahedral sites, which are occupied by hydrogen, is essentially determined by the six nearest-neighbor iron atoms, and if the (small) deviations from an ideal *c/a* ratio can be neglected. In this case, the octahedral sites have cubic symmetry, which leads to a threefold degeneracy of local optic modes. Further, as long as the vibrational amplitudes are sufficiently small, the lattice potential of the hydrogen is harmonic and isotropic. Finally and most importantly, we have to assume that interaction effects between the hydrogen atoms, which cause a dispersion in the optic phonon modes, can be neglected. Even in the absence of any direct hydrogen-hydrogen interaction, an indirect interaction will arise from the hydrogen-induced lattice strains.

Considering again our data in Fig. 1, we can identify the inelastic intensities in the three energy regions around 105, 210 and 315 meV with scattering processes in which, according to (1), one, two or three optic phonons are created. This means that the average energy of the optic phonons of hydrogen is ~105 meV. The inelastic intensities are much broader than the energy resolution. This broadening reflects the dispersion in the optic phonon modes due to hydrogen-hydrogen interaction, and it may also result from deviations of the octahedral sites from cubic symmetry, which lifts the threefold degeneracy of the local modes. A further small broadening effect is caused by the band modes of the hydrogen [24,25] which are discussed below.

The band modes reflect the fact that the hydrogen atoms participate also in the vibrations of the iron host lattice atoms [24,25]. The vibrational energies of the band modes are much lower than those of the optic modes, so that scattering processes with a creation solely of a band mode phonon do not contribute to the scattering intensity in the energy range where the optic modes are observed. However, multiphonon scattering processes with the creation of both optic and band mode phonons will contribute to this scattering intensity. We can estimate the influence of the band modes for a Debye spectrum of these modes with a typical Debye temperature of 420 K, assuming that the vibrational amplitudes of hydrogen are identical to those of the iron host-lattice atoms [24]. For the energy region around 105 meV, where one optic phonon is created, such an estimate yields, for instance, that only ~6% of the total measured intensity is caused by scattering processes where a band mode phonon is involved. The estimate shows that the influence of the band modes can essentially be neglected in our determination of the average energy of the optic phonons.

A final and important aspect of our data are the total scattering intensities in the energy regions around 105, 210 and 315 meV (creation of one, two or three optic phonons, respectively). According to (1), the total intensities in these regions should scale 1 to 0.73 to 0.61, under consideration of the appropriate Q values. This prediction agrees excellently with the experimental result given above and supports, therefore, strongly the present data analysis. The use of the scattering law in (1) (instead of the scattering cross section [23]) is appropriate for the calculation of the total scattering intensities, because our spectra are normalized to monitor counts and

because the sensitivity of the monitor is inversely proportional to the wavevector of the neutrons. We mention, finally, also that band mode scattering processes do not influence the total scattering intensities since the decrease of the Debye-Waller factor, due to the band modes, compensates precisely the additional multiphonon processes in which band modes are involved.

Acknowledgement

The present work was supported by the Russian Foundation for Basic Research under the grants No. 96-02-17522 and 96-15-96806.

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