



INELASTIC INCOHERENT NEUTRON SCATTERING SPECTRA
FROM fcc NiH_{1.05}, hcp CrH_{1.0} and hcp MoH_{1.2} at 15K

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Inelastic incoherent neutron scattering spectra from nickel, chromium and molybdenum hydrides, synthesized under high pressure of gaseous hydrogen, have been obtained in the energy region of optical modes of hydrogen vibrations. The measurements have been carried out at the three-axis spectrometer IN1 on the hot source of the ILL High Flux Reactor with the Beryllium filter-detector technique.

In all three cases the frequencies of the fundamental vibrations scale to the observed higher harmonics as 1:2:3. The spectra exhibit a fine structure around the fundamentals as well as around the harmonics. Possible reasons for this effect are discussed.

1. Introduction

In recent years a large number of investigations have been concerned with the problem of hydrogen in transition metals. The method of inelastic incoherent neutron scattering (IINS) is a very effective one for this purpose. Unfortunately an extensive application of this technique to the problem mentioned above was restricted by the absence of samples with a high hydrogen concentration suitable for these investigations.

A technique for compressing gaseous hydrogen to rather high pressures (up to 90 kbar) has been developed at the Laboratory of High Pressure Physics of the Institute of Solid State Physics of the Academy of Sciences of the USSR¹. It enabled the synthesis of solid Me-H solutions on the base of a number of transition metals from the VI-VIII groups of the periodic system². The hydrides produced by means of this method can have an extremely high concentration of hydrogen in their face-centered cubic (fcc) and hexagonal close-packed (hcp) metal sublattices.

In body centered cubic (bcc) metal hydrides it is assumed that the direct interaction between interstitial H-atoms should be weak³ at least as long as the hydrogen occupies tetrahedral sites. In these substances the hydrogens can then be regarded as independent Einstein oscillators with frequencies determined by an effective local potential. On the contrary in close packed metal sublattices (fcc and hcp), where the octahedral sites (one site per metal atom) are occupied first, collective hydrogen vibrations are considered to be important. Unfortunately, only a few experimental investigations are known on the fcc Pd-H system and in some rare earth hydrides^{4,5}.

Here we report on measurements of IINS spectra from hydrides of nickel, chromium and

molybdenum. These hydrides have the following metal sublattices: NiH_{1.05} - fcc, CrH_{1.01} and MoH_{1.2} - hcp^{1,2}.

It is generally accepted that hydrogen occupies the octahedral sites (O-sites) in the metal sublattice for all transition metal hydrides of the VI-VIII groups that have been studied up to now^{6,7}. In hydrides under investigation the O-sites as well as the tetrahedral sites (T-sites) possess cubic symmetry. It should be noted that for hcp structures this type of symmetry is valid only for the lattices with the ideal ratio of cell parameters ($c/a = \sqrt{8/3} \approx 1.633$). Fortunately this value is nearly realized for chromium and molybdenum hydrides: CrH has $a = 2.717 \text{ \AA}$, $c = 4.436 \text{ \AA}$ and $c/a = 1.63$ and MoH has $a = 2.92 \text{ \AA}$, $c = 4.74 \text{ \AA}$ and $c/a = 1.63^8$ at $T = 120\text{K}^{6,7}$.

In view of these facts, we expected for overstoichiometric hydrides to obtain combined spectra one frequency (in the local picture) from the O-sites and one from the T-sites.

2. Sample Preparation

We used the following procedure for the initial preparation of metals:

a) Electrolytical nickel plates were cold-rolled into a foil, then annealed (to remove mechanical stresses) under vacuum at $T = 1100^\circ\text{C}$ during 15 minutes and then quenched in water to obtain a small grain structure. The last property was important for preliminary X-ray diffraction measurements and a phase analysis of the samples after their hydrogenation.

b) High purity single crystal molybdenum foil with electrical resistance ratio $R_{300}/R_{4.2} \approx 1000$ was used for the preparation of the hydride. Earlier experiments have shown that the hydrogen solubility in molybdenum at high pressures of gaseous hydrogen increases noticeably with increasing perfection of the metal.

c) Electrolytical chromium was remelted in an argon-filled induction furnace. Afterwards it was annealed at 1100°C during 15 minutes under vacuum, and then quenched in water. Sample foils were cut from an ingot by spark machining. The damaged surface layer ~ 0.05 mm was ground off, and then a layer ~ 0.03 mm was removed by electropolishing in sulfuric acid.

The samples intended for hydrogenation were stacks of plates about 9 mm in diameter cut from the above foils, each stack weighing about 500 mg. The hydrides were prepared by a 24 h exposure of the samples to an atmosphere of molecular hydrogen at fixed P_{H_2} and T , indicated in Table 1, followed by "quenching" under pressure down to about minus 180°C. The procedure is described in details in².

After every cycle of synthesis a small part of the hydride was analyzed about hydrogen content (three different pieces of 15 mg each). This analysis was performed by measuring the amount of hydrogen liberated in the process of thermal decomposition at temperatures up to 500°C. The synthesis parameters and some characteristics of the samples are given in Table 1. Under atmospheric pressure, all these hydrides are stable relative to decomposition into the metal and molecular hydrogen at liquid nitrogen temperature, but are unstable at room temperature. After high pressure treatment the samples were kept in liquid nitrogen and have never been heated above decomposition temperatures. For the measurement of the IINS spectra we composed samples by adding material from different runs of synthesis to get a total mass of the order of two grams. The scatter of the hydrogen content in the final samples did not exceed the individual experimental error.

3. Experimental Method

We used the three-axis spectrometer IN1BeF⁹ on the hot source of the High Flux Reactor at the Institut Laue-Langevin with a Beryllium filter (thickness 24 cm) before the detector. We used the Cu(220) monochromator to measure the IINS spectra mainly from hydrogen atoms. The instrument resolution is shown in Table 2. To obtain values for transferred energies we subtracted 4 meV as an average final energy¹⁰ from the energies of incident neutrons. The scattering angle was kept constant to 90°. Special precautions were undertaken during the final preparing of the samples. Samples were mounted into rectangular flat aluminium containers (full wall width was 3 mm) under a layer of boiling nitrogen. A special dry cold box was prepared to

avoid the condensation of water vapour. To prevent ice condensing on the container surface the prepared samples were placed into a vessel with liquid nitrogen to transport them close to the cryostat. After putting into a cold, top loading, standard "orange" cryostat⁹ the samples were heated up to 100K and evacuated to avoid solid nitrogen condensation inside the containers. Before the start of the main measurements we restricted the incident beam dimensions down to 53 mm in height and 19 mm in width by means of adjustable diaphragms to increase the signal to background ratio.

4. Results

The IINS spectra of the three investigated hydrides are shown in Fig. 1. These spectra were obtained from the measured ones by subtracting a background from an empty aluminium container. The frequency values of the main peaks and some additional useful information are presented in Table 2.

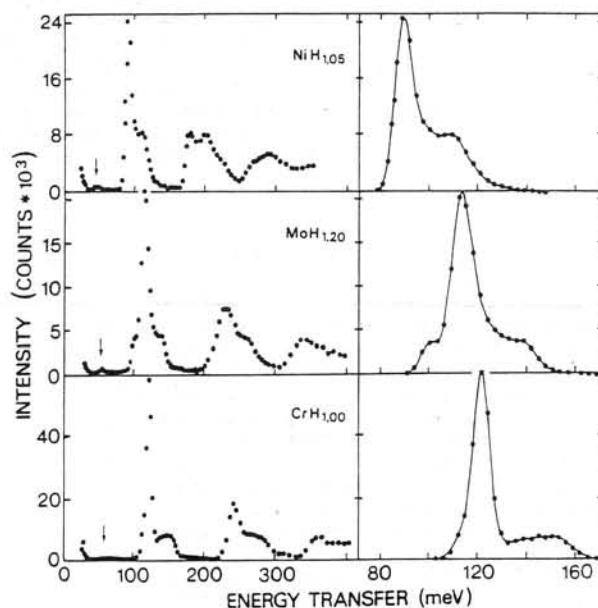


Fig. 1. IINS spectra of three transition metal hydrides at $T = 15K$, measured at the IN1BeF spectrometer. The right hand side presents the signal from the fundamental vibration in an enlarged scale. The solid lines are guides to the eye. The arrows indicate a contamination due to second order neutrons in the monochromatic beam.

Table 1
Parameters of the high hydrogen pressure syntheses and characteristics of samples

Sample	P_{H_2} [kbar]	T [°C]	Mass in one cycle of synthesis [grams]	Total mass of sample, [grams]	Scatter of H content	Thickness of sample, [mm]	Area of sample [cm ²]	IINS measuring time [hour]
NiH _{1.05}	20-30	300-325	0.59	2.20	±0.03	0.30	13	4
MoH _{1.2}	45-55	350	0.59	2.20	±0.06	0.13	20	6
CrH _{1.0}	20-30	325-350	0.66	1.24	±0.04	0.25	7	8

Table 2
Characteristics and results of different samples.

Sample	Distance H-Me in O-sites at 100K, [Å] [1,2]	Frequency of the first main peak, [meV]	Instrumental resolution at the first main peak [meV]	Signal to background ratio at the first main peak
PdH _{0.63} [12]	2.00	57	5 to 9	-
NiH _{1.05}	1.86	89	6.2	19
MoH _{1.2}	2.06	113	7.1	11
CrH _{1.0}	1.92	121	7.4	18

The main peak frequencies of different orders have a regular ratio 1:2:3. It can be distinctly seen for the CrH-spectrum, but it is smeared in the third order for the NiH-spectrum. The quality of the spectra is sufficient for the quantitative analysis of the second order excitations.

As can be seen in Fig. 1 all peaks have a rather complicated structure for every substance. A surprising change is observed for the right-side shoulder of all peaks at raising order of the excitations: its absolute height is nearly equal in the first and second harmonics, while the ratio of its intensity to the main peak height is becoming larger, and this ratio even exceeds unity in the third order for NiH.

NiH_{0.75} has been investigated at room temperature under a pressure of 7kbar¹¹. Only the fundamental frequency could be observed. The shape in the form of a peak with a shoulder is very similar to our result.

5. Discussion

The O-as well as the T-sites have cubic symmetry to a very good approximation ($c/a = 1.633$ for hcp) in all three samples. Therefore there should be only one local fundamental frequency being the same for the three degrees of freedom. This "local" frequencies would appear at very low H concentrations. The observation that the frequencies of the higher harmonics of the H-vibrations are multiples of the fundamentals shows that the potentials are harmonic to a reasonable approximation. The frequency distribution around fundamentals and harmonics needs some detailed consideration.

In PdH_{0.63} dispersion curves have been determined for the D-vibrations¹². Complementary incoherent scattering from PdH_{0.63}¹³ revealed a frequency distribution which could be explained

as well by dispersion curves due to H-H interactions. The assumption of H-H interactions and corresponding dispersion curves for the present systems is the most probable explanation for the fine structure in the spectra. Nevertheless some other possible contributions are also worth mentioning.

First of all we wish to invoke the question about occupation of tetrahedral sites. The theoretical maximum H-concentration is MeH₃ in our cases with one octahedral site occupied first and two tetrahedral sites becoming occupied at higher concentrations for the perfectly ordered metal lattice. Therefore in CrH_{1.0} there is a certain probability that T-sites already become occupied while in NiH_{1.05} and MoH_{1.2} there is a necessity that T are occupied as well as most of the O-sites. As the Me-H distances in T-sites are smaller than in O-sites, the frequencies of H in T-sites should be higher. For the time being we cannot exclude, that part of the structure in the spectra is caused by T-site vibrations.

Within the foregoing remarks it was assumed that the local symmetry is cubic, as found by structure determination. But a small distortion might manifest itself strongly in the frequency spectrum, while it is unobservable in the structure determination.

Another possibility is the assumption of a large number of dislocations and vacancies in the metal lattice. Then the distribution of local H environments would create a distribution of frequencies. The effect of the hydrogenating process on the defect structure can be completely different for different substances. On one side, the hydrogenation of Ni¹⁴ and Co¹⁵ single crystals does not change the defect structures of their metal sublattices significantly. On the other side, the same procedure leads to a creation of an enormous amount of package defects in the case of Nb_{0.75}Ru_{0.25}¹⁶.

Again another explanation for the fine structure is the possibility of coexistence of phases with different compositions. Such phenomena could be expected from the requirement of minimum of configurational entropy.

Last but not least, the multiphonon processes (note that the second harmonic is already a two-phonon process) provide a contribution from the metal lattice modes. These contributions are small at low temperatures but increase strongly with larger momentum transfer¹⁷.

Experimental effects such as higher order contamination in the monochromatic beam,

multiple scattering in the sample and particularities in the background have negligible influence.

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