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# Crystal structure and lattice dynamics of chromium hydrides

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### Abstract

Samples of fcc ( $\gamma$ ) CrH and hcp ( $\varepsilon$ ) CrH have been prepared by cathodic electrodeposition of chromium and studied by powder neutron diffraction at 8 K and by inelastic neutron scattering (INS) at 5 K in the range of energy transfers 6–400 meV. A profile analysis of the neutron diffraction patterns showed that hydrogen occupies octahedral interstitial sites in the fcc metal lattice of  $\gamma$ -CrH with a = 3.854(3) Å and in the hcp metal lattice of  $\varepsilon$ -CrH with a = 2.719(3) Å and c = 4.433(4) Å. No magnetic ordering was detected in either hydride at 8 K. The INS investigation demonstrated that the fundamental band of optical hydrogen vibrations in both hydrides consists of a strong peak with a broad shoulder towards higher energies. The peak position is 118 meV for  $\gamma$ -CrH and 122 meV for  $\varepsilon$ -CrH.

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## 1. Introduction

Chromium hydrides with compositions close to CrH can be produced electrolytically - by cathodic electrodeposition of chromium [1,2] – and under high hydrogen pressure [3,4]. Depending on the synthesis conditions, the hydrides can have a hcp ( $\varepsilon$ ) or fcc ( $\gamma$ ) metal lattice [2,4]. A room-temperature neutron diffraction investigation of the  $\varepsilon$ -CrH produced electrolytically showed that hydrogen atoms occupy octahedral interstitial positions in the hcp chromium lattice and that the hydride is not magnetically ordered [5]. The vibrational spectrum of hydrogen in a high-pressure  $\varepsilon$ -CrH sample was studied by inelastic neutron scattering (INS) at 15 K in the range of energy transfers 40–500 meV [6]. The  $\gamma$ -CrH hydride has never been studied by neutron scattering. Experiments on nuclear magnetic resonance and magnetic susceptibility revealed no signs of magnetic ordering in electrolytically prepared  $\gamma$ -CrH and  $\varepsilon$ -CrH at temperatures down to 3 K [2].

In the present work, the  $\gamma$ -CrH and  $\varepsilon$ -CrH hydrides were prepared electrolytically and studied by neutron diffraction and INS at liquid helium temperatures.

## 2. Sample preparation and experimental details

The samples of  $\gamma$ -CrH and  $\varepsilon$ -CrH, each weighing about 1.5 g, were prepared from 99.99% CrO<sub>3</sub> by cathodic electrodeposition as described in [2,7]. Chromium hydrides produced in this way are rather stable at room-temperature and do not noticeably loose hydrogen during a few hours [7]. The  $\gamma$ -CrH and  $\varepsilon$ -CrH samples were ground in an agate mortar and, when not in use, stored in liquid nitrogen to prevent thermal decomposition. A small portion of a few milligrams of each sample was analysed by X-ray diffraction and hot extraction.

The room-temperature X-ray diffraction examination (SIEMENS D-500 diffractometer, monochromated Cu K $\alpha_1$  radiation) showed that the  $\varepsilon$ -CrH sample was a single-phase  $\varepsilon$ -CrH compound, while the  $\gamma$ -CrH sample contained a few percent admixture of  $\varepsilon$ -CrH and Cr metal. The hot extraction into a calibrated volume at temperatures up to 500 °C gave the atomic

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H-to-metal ratio x = 0.98(4) for the  $\varepsilon$ -CrH sample and x = 0.93(4) for the  $\gamma$ -CrH sample.

Both samples were studied by neutron diffraction at 8 K with the time-of-flight DN-2 diffractometer at JINR in Dubna. A powdered sample was enclosed in a cylindrical, thin-walled vanadium can and placed in a helium refrigerator. The background was determined in a separate empty-can measurement and subtracted from the measured diffraction patterns. The diffraction data were analysed with a computer program [8] based on the Rietveld profile refinement technique.

Both CrH samples were also investigated by INS at 10 K in the range of neutron energy transfers 6–400 meV using the invertedgeometry time-of-flight spectrometer KDSOG-M at JINR. The  $\gamma$ -CrH sample was additionally studied by INS at 5 K and energies from 40 to 400 meV using the IN1-BeF neutron spectrometer installed at the hot source of the high-flux reactor at ILL, Grenoble. In the case of the IN1-BeF spectrometer, the energy lost by the neutrons was calculated by subtracting 3.5 meV, the mean energy of neutrons transmitted through the cooled Be filter, from the incident neutron energy. With both spectrometers, the background spectrum from an empty flat sample holder made of thin aluminium foil was measured separately and then subtracted from the raw INS spectrum of the sample.

### 3. Neutron diffraction

## 3.1. Experiment

The neutron diffraction patterns of the  $\varepsilon$ -CrH and  $\gamma$ -CrH samples and the results of their profile analysis are presented in Figs. 1 and 2, respectively. The smooth background has been subtracted from the shown spectra to allow a better visual comparison with the calculated profiles. The samples proved to be rather well-crystallised and homogeneous. Most diffraction lines were well resolved and the profile fit of the pattern required the Debye–Waller factors  $B_{Cr} = 0.4 \text{ Å}^{-1}$  and  $B_{H} = 2.0 \text{ Å}^{-1}$ . Similar values of *B*-factors are typical of powder d-metal hydrides prepared by gas-phase absorption and this suggests a comparable degree of lattice disorder in our electrolytical samples.

As seen from Fig. 1, the neutron diffraction pattern of the single-phase  $\varepsilon$ -CrH sample contains no new lines in addition to the lines of the hcp structure. The crystal structure of this phase therefore belongs to the same space group, P63/mmc, as the hcp structure of its metal lattice. In the hcp structure, there are two types of highly symmetrical interstitial positions conforming to the  $P6_3/mmc$  space group. These are the octahedral positions (which are as many as the metal sites) and tetrahedral positions (which are twice as many). As can be seen from the difference curve b in Fig. 1, a model assuming that hydrogen occupies every octahedral site gives a satisfactory profile fit of the experimental spectrum. At the same time, this spectrum is qualitatively different from profile c calculated for hydrogen randomly distributed over the tetrahedral sites. Correspondingly, any admixture of tetrahedral hydrogen makes the agreement between the calculation and experiment worse, and the model allowing partial occupancy of sites of both types converges to 100% occupancy of the octahedral ones.



Fig. 1. Neutron powder diffraction pattern of the  $\varepsilon$ -CrH sample measured for 10 h at 8 K with the time-of-flight DN-2 diffractometer at JINR in Dubna (open circles) and results of its Rietveld analysis (lines). Curve (a) is the profile fit calculated for the NiAs-type  $P6_3/mmc$  structure with a = 2.719(3) Å, c = 4.433(4) Å and hydrogen atoms occupying every octahedral site in the hcp Cr lattice. Curve (b) is the difference between the experimental (circles) and calculated (curve a) spectra. Curve (c) is the spectrum calculated for x = 1 hydrogen atoms randomly occupying one half of the tetrahedral interstices in hcp Cr, the other fitting parameters being the same as for curve (a). The dashed curve labelled "magnetic as  $\varepsilon$ -MnD<sub>0.8</sub>" shows the calculated profile of the magnetic contribution, which would be observed in addition to the structure lines of  $\varepsilon$ -CrH if it were an antiferromagnet with the same magnetic structure and magnetic moments of 0.73  $\mu$ B/metal atom as  $\varepsilon$ -MnD<sub>0.83</sub> [14].



Fig. 2. Neutron powder diffraction pattern of the  $\gamma$ -CrH sample measured for 10 h at 8 K with the DN-2 diffractometer (open circles) and results of its Rietveld analysis (lines). Curve (a) presents the sum of calculated profiles for  $\gamma$ -CrH (86 mol.%) and  $\varepsilon$ -CrH (11 mol.%, curve (c)) and *bcc* Cr metal (3 mol.%, curve (d)). The profile for  $\gamma$ -CrH is calculated assuming a NaCl-type  $Fm\bar{3}m$  structure with a = 3.854(3) Å and hydrogen atoms occupying every octahedral site in the fcc Cr lattice. Curve (b) is the difference between the experimental (circles) and calculated (curve a) spectra. Curve (e) is the profile calculated for x = 1 hydrogen atoms randomly occupying one half of the tetrahedral interstices in fcc Cr, the other fitting parameters being the same as in the model with hydrogen on octahedral sites. The dashed curve labelled "magnetic as  $\gamma$ -Mn" shows the calculated profile of the magnetic contribution, which would be observed in addition to the structure lines of  $\gamma$ -CrH if it were an antiferromagnet with the same magnetic structure and magnetic moments of 2.4  $\mu_B$ /metal atom as  $\gamma$ -Mn [15].

In agreement with the preliminary X-ray examination, the neutron diffraction pattern of the  $\gamma$ -CrH sample (Fig. 2) presents a superposition of diffraction lines of  $\gamma$ -CrH and  $\epsilon$ -CrH and chromium metal. The  $\gamma$ -CrH phase shows no new lines in addition to those of the fcc structure therefore the structure of this hydride belongs to the same space group,  $Fm\bar{3}m$ , as its fcc metal lattice. In full analogy with the said about the  $\varepsilon$ -CrH phase, there are octahedral and tetrahedral interstitial sites in the metal lattice of the  $\gamma$ -CrH phase. A model with hydrogen atoms occupying the tetrahedral sites is qualitatively inapplicable (see the calculated profile d in Fig. 2), while a model with octahedral hydrogen allows a satisfactory profile fit. Assuming the octahedral hydrogen co-ordination in the  $\gamma$ -CrH phase, the profile analysis of the experimental spectrum gives a mixture of 86 mol.%  $\gamma$ -CrH and 11 mol.% E-CrH and 3 mol.% bcc Cr metal for the phase composition of the  $\gamma$ -CrH sample.

The lattice parameters of  $\varepsilon$ -CrH and  $\gamma$ -CrH determined in the present work well agree with X-ray results of Ref. [9]. The NiAs-type crystal structure of  $\varepsilon$ -CrH agrees with earlier neutron diffraction data [5]. The octahedral hydrogen coordination established for both  $\varepsilon$ -CrH and  $\gamma$ -CrH is characteristic of all hydrides with close-packed metal lattices that are formed by transition metals of groups VI–VIII (see review [10] and recent paper on  $\gamma$ -CoH [11]).

## 3.2. Implications for the magnetic properties of 3d-metals

Of special interest are the magnetic properties of chromium hydrides because chromium is the leftmost 3d-metal in the periodic table that shows magnetic ordering. This problem, however, needs introductory remarks.

Concentration dependences of the spontaneous magnetization  $\sigma_0$  at T = 0 K (for ferromagnets) and of the Néel temperature  $T_{\rm N}$  (for antiferromagnets) of fcc ( $\gamma$ ) alloys of 3d-metals which are close neighbours in the periodic table, are well described by the rigid band model and can be represented as unique functions of the average number  $N^{e}$  of external (3d + 4s) electrons per atom of the alloy (the so-called Slater-Pauling curves). These dependences are plotted by thin solid lines in Fig. 3. Our studies of  $\gamma$ hydrides of fcc Ni-based and Fe-based alloys showed [12] that the magnetic properties varied with increasing hydrogen content as if the hydrogen were merely a donor of a fractional number of  $\eta \approx 0.5$  electrons per H atom in the otherwise unchanged metal dband. This approximation, which we call the rigid d-band model for brevity, is a rather straightforward consequence of the available ab initio band structure calculations, and its applicability to alloys with different types of band structure has been thoroughly discussed in [12]. In particular, if the properties of the alloy obey the rigid band model, the properties of its  $\gamma$  hydrides considered as functions of the effective electron concentration  $N^{e}(x) = N^{e}(0) + \eta x$  are described by the thin lines of Fig. 3.

Due to the relatively narrow intervals of mutual solubility of 3d-metals in hexagonal phases, the concentration dependences of their magnetic properties (two segments of thick solid line in Fig. 3) are known to a much lesser extent than those of the fcc alloys. However, if the available experimental points for hexagonal hydrides are added to the graph as a function of  $N^{e}(x)$  with



Fig. 3. Slater–Pauling curves for fcc ( $\gamma$ ) alloys (experiment—thin solid lines) and hcp ( $\varepsilon$ ) alloys (experiment—two sections of thick solid lines; an estimation—dashed lines) of 3d-metals that are nearest neighbours in the periodic table. The symbols for hydrides show experimental data presented as a function of the effective electron concentration,  $N^{\text{e}}(x) = N^{\text{e}}(0) + \eta x$ , where *x* is the H-to-metal atomic ratio and  $\eta = 0.5$  electrons per H atom: (1)  $\sigma_0$  of  $\varepsilon$ -CoH<sub>x</sub> solid solutions; (2)  $\sigma_0$  of  $\varepsilon'$ -FeH with a *double hcp* metal lattice; (3)  $\sigma_0$  of  $\varepsilon$ -Ore<sub>1.2</sub> of  $\varepsilon$  of  $\varepsilon$ -Fe<sub>0.776</sub>Mn<sub>0.224</sub>H<sub>x</sub> solid solutions; (6)  $T_{\text{N}}$  of  $\varepsilon$ -Fe; (7)  $\sigma_0$  of  $\varepsilon$ -FeH<sub>0.42</sub> (references to the original experimental papers are given in Ref. [13]); (8)  $T_{\text{N}}$  of  $\varepsilon$ -MnD<sub>0.83</sub> [14]; (9)  $T_{\text{N}}$  of  $\gamma$ -Mn [15]; (10)  $T_{\text{N}}$  of  $\varepsilon$ -CrH and  $\gamma$ -CrH ([2] and this work).

 $\eta = 0.5$  electrons per H atom, the properties of both hexagonal metals and hydrides can be described by the same curves (dashed lines in Fig. 3). These curves are similar to those for the  $\gamma$  alloys and are likely to represent the Slater–Pauling plot for the (hypothetical) hexagonal alloys [13].

As seen from Fig. 3, the Néel points of the hexagonal alloys monotonically increase from 0 K at  $N^e \approx 8.1$  el./metal atom to 350 K at  $N^e \approx 7.4$  el./metal atom (the point for  $\varepsilon$ -MnD<sub>0.83</sub>), and the Néel points of the fcc alloys increase from 0 K at  $N^e \approx 8.3$  el./metal atom to 660 K at  $N^e = 7$  el./metal atom (the point for  $\gamma$ -Mn). Both  $\varepsilon$ -CrH and  $\gamma$ -CrH have  $N^e \approx 6.5$  el./metal atom. The dashed curves labelled "magnetic as . . ." in the upper parts of Figs. 1 and 2 show the calculated profiles of the magnetic contribution, which would be observed in addition to the structure lines if  $\varepsilon$ -CrH and  $\gamma$ -CrH were antiferromagnets with the same magnetic structures and magnetic moments as the earlier studied phases with the nearest  $N^e$ -values, namely  $\varepsilon$ -MnD<sub>0.83</sub> [14] and  $\gamma$ -Mn [15].

The calculated magnetic contribution to the neutron diffraction pattern of  $\varepsilon$ -CrH (Fig. 1) is too small to be seen against the background. The magnetic contribution to the pattern of  $\gamma$ -CrH (Fig. 2) is significant, and the absence of corresponding diffraction lines in the experimental pattern of  $\gamma$ -CrH measured at 8 K therefore corroborates the conclusion [2] that this hydride is paramagnetic down to helium temperatures. Assuming, in accordance with the NMR data [2], that  $\varepsilon$ -CrH and  $\gamma$ -CrH are not magnetically ordered at temperatures down to 3 K, the Néel points of antiferromagnetic hcp and fcc 3d-alloys as a function of decreasing electron concentration should reach a maximum and then go down to helium temperatures at the  $N^{e}$  values not less than 6.5 el./metal atom. This is schematically shown by the dashed curves in Fig. 3.

Fig. 3 therefore presents the Slater–Pauling curves for hcp and fcc 3d-alloys delineated over the entire range of electronic concentrations, where the alloys undergo magnetic ordering. Interestingly, the steep decrease in the Néel temperature (and, correspondingly, in the magnetic moments) of antiferromagnetic fcc alloys with  $N^{e}$  decreasing in the range 7.0–6.5 el./atom is similar to the steep decrease in  $\sigma_{0}$  of ferromagnetic fcc alloys occurring in the invar range 8.8–8.4 el./atom. One can speculate that the strong dependence of magnetic properties on the electron concentration suggests their strong dependence on the interatomic distances, and the antiferromagnetic fcc phases (for example, hydrides of Cr–Mn alloys) in the range 7.0–6.5 el./atom would show invar anomalies as well.

## 4. Inelastic neutron scattering

#### 4.1. Experiment: studies with the KDSOG-M spectrometer

Fig. 4 shows the INS spectra  $S(Q,\omega)$  of the  $\gamma$ -CrH and  $\varepsilon$ -CrH samples measured at 10 K with the KDSOG-M spectrometer at JINR in Dubna. The two spectra are much the same and look similar to the spectra of monohydrides of all other 3d- and 4d-metals of groups VI–VIII studied so far (see [16] and references therein). Like all those, the spectra of  $\gamma$ -CrH and  $\varepsilon$ -CrH are composed of the range of lattice modes ( $\hbar\omega < 40 \text{ meV}$ ) and optical H vibrations ( $\hbar\omega > 90 \text{ meV}$ ). The first, fundamental band of optical H vibrations consists of a strong peak centred at  $\hbar\omega_0 \approx 120 \text{ meV}$  with a shoulder towards higher energies extending up to about 170 meV. The second and the third optical H band resulting from



Fig. 4. The dynamical structure factor  $S(Q,\omega)$  of the  $\gamma$ -CrH (solid circles) and  $\varepsilon$ -CrH (open circles) powder samples as a function of the energy loss  $\hbar\omega$  of the inelastically scattered neutrons. Each sample was measured for 20 h at 10 K with the KDSOG-M spectrometer at JINR in Dubna. The horizontal bars indicate the energy resolution. The thick solid line in the inset shows the low-energy 'lattice' part of the spectrum used to calculate the multiphonon contributions to the INS spectra of  $\gamma$ -CrH and  $\varepsilon$ -CrH measured with the IN1-BeF spectrometer at ILL, Grenoble.

multiphonon neutron scattering have a smoother intensity distribution and appear at energies approximately two and three times the energy of the fundamental band, respectively.

The INS spectra of chromium hydrides mainly originate from neutron scattering on hydrogen atoms. In the case of lattice vibrations, the contribution from chromium atoms is less than 4% because of the large incoherent neutron scattering cross-section of H atoms [17], and this contribution further decreases below  $2 \times 10^{-3}$ % for the optical vibrations due to the mass dependence of polarisation vectors of the corresponding vibrational modes. The INS spectra of the hydrides therefore well represent the density of states for H vibrations.

As seen from Fig. 4, the spectrum of the  $\gamma$ -CrH and, to a lesser extent,  $\varepsilon$ -CrH sample show scattering intensity in the range  $40 < \hbar \omega < 90$  meV between the bands of lattice modes and optical H vibrations. This is not characteristic of hydrides and demonstrates the presence of impurities in our samples prepared by electrolysis of CrO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub>. The presence of a small amount of paramagnetic impurities (presumably, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·*n*H<sub>2</sub>O sulfates) in  $\gamma$ -CrH and  $\varepsilon$ -CrH samples prepared in the same way was earlier detected by magnetisation measurements [2].

Despite the impurities, the lattice parts of the INS spectra of  $\gamma$ -CrH and  $\varepsilon$ -CrH can be rather reliably recovered from the experimental spectra. First of all, these parts should be approximately the same for both hydrides because of the nearly coinciding arrangements of neighbouring chromium atoms in the fcc and hcp modifications of CrH. Assuming the same type of impurities in the  $\gamma$ -CrH and  $\varepsilon$ -CrH sample, the difference between the spectra of these samples is therefore proportional to the impurity spectrum in the range of lattice modes. This proportionality also holds true at higher energies of 40–90 meV, where the scattering intensity from the hydrides should be small.

To get the spectrum of lattice modes, the impurity spectrum thus obtained was scaled to fit the INS spectrum of the  $\varepsilon$ -CrH sample at 40 <  $\hbar\omega$  < 90 meV and then subtracted from it. The resulting spectrum (thin solid curve in the inset in Fig. 4) had a satisfactory statistical accuracy at 15 <  $\hbar\omega$  < 50 meV. It was smoothed in this energy range, set equal to zero at higher energies and extended to lower energies using a Debye approximation (a dependence of the vibrational density of states quadratic in frequency).

The obtained profile is shown with the thick solid line in the inset in Fig. 4. Its double-peak shape in the range of lattice modes is typical of monohydrides with close-packed metal lattices, for example,  $\gamma$ -PdH [18] and  $\gamma$ -NiH [19]. By analogy with the spectrum of  $\gamma$ -PdH [18], the peaks at energies of 25 and 33 meV in the spectrum of chromium hydrides can be attributed to the transverse and longitudinal acoustic zoneboundary modes, respectively. A high-energy cutoff of the lattice modes is observed at approximately 38 meV.

## 4.2. Experiment: studies with the IN1-BeF spectrometer

The INS spectrum of the  $\gamma$ -CrH sample was additionally measured with a better statistical accuracy in the energy range 40–400 meV at T = 5 K using the high-luminosity IN1-BeF spectrometer at ILL, Grenoble (Fig. 5). Earlier [6], the INS spectrum



Fig. 5. The INS spectrum of  $\gamma$ -CrH. The open circles connected by a solid line in (a) represent the spectrum of the powder  $\gamma$ -CrH sample measured for 11 h at 5 K with the IN1-BeF spectrometer at ILL, Grenoble. The dashed line depicts the contribution from 11 mol.%  $\varepsilon$ -CrH in the sample. The horizontal bars indicate the energy resolution. The open squares in the inset give the difference between the spectra of the  $\gamma$ -CrH sample measured with the IN1-BeF (open circles) and KDSOG-M (dashed fair curve) spectrometer. The thick solid line in the inset shows the calculated contribution from the neutrons of half the wavelength contaminating the monochromated incoming beam. The solid curve in (b) is a combination of the 'lattice' part of the spectrum from the inset in Fig. 4 ( $\hbar\omega$  <40 meV) and the optical part from (a) after subtracting the contribution from 11 mol.%  $\varepsilon$ -CrH ( $\hbar\omega$  >90 meV). The dashed curve in (b) shows the calculated multiphonon contribution.

of an impurity-free  $\varepsilon$ -CrH sample synthesised at high hydrogen pressure was also measured with IN1-BeF under similar conditions (Fig. 6).

Unlike the time-of-flight KDSOG-M spectrometer, the IN1-BeF spectrometer works with a monochromated beam of incoming neutrons. The beam is slightly contaminated with neutrons of half the wavelength. In the case of chromium hydrides, two- and three-phonon scattering of the  $\lambda/2$  neutrons gives spurious intensity in the range 40–90 meV as shown in the insets in Figs. 5 and 6 by the thick solid lines. As seen from the inset in Fig. 5, such a line well describes the difference between the spectra of the  $\gamma$ -CrH sample measured with the KDSOG-M and IN1-BeF spectrometer. The spectrum of the  $\varepsilon$ -CrH sample measured many years ago [6] shows some additional scattering intensity in the 40–90 meV range (see the inset in Fig. 6) along with the  $\lambda/2$ contribution, but this additional intensity is also small and, presumably, spurious.



Fig. 6. The INS spectrum of  $\varepsilon$ -CrH. The open circles connected by a solid line in (a) represent the spectrum of the powder  $\varepsilon$ -CrH sample measured at 15 K with the IN1-BeF spectrometer at ILL, Grenoble [6]. The thick solid line in the inset shows the calculated contribution from the  $\lambda/2$  neutrons. The solid curve in (b) is a combination of the 'lattice' part of the spectrum shown by the thick solid line in the inset to Fig. 4 ( $\hbar\omega$  < 40 meV) and the optical part from (a) ( $\hbar\omega$  > 100 meV). The dashed curve in (b) shows the calculated multiphonon contribution.

We therefore conclude that the INS spectra of both  $\gamma$ -CrH and  $\varepsilon$ -CrH hydrides in the energy range 0–90 meV are best represented with the profile, which is shown in the inset in Fig. 4 with the thick solid line and has zero intensity at energies from 40 to 90 meV. The INS spectrum of  $\varepsilon$ -CrH composed of this profile at  $\hbar \omega \leq 90$  meV and the experimental INS spectrum  $S(Q,\omega)_{\varepsilon}$  of the  $\varepsilon$ -CrH sample measured with IN1-BeF at higher energies is plotted in Fig. 6b by the solid line. The INS spectrum of  $\gamma$ -CrH drawn with the solid line in Fig. 5b combines the above profile at  $\hbar \omega \leq 90$  meV and the difference spectrum  $[0.97S(Q,\omega)_{\gamma} - 0.11S(Q,\omega)_{\varepsilon}]/0.86$  at higher energies.  $S(Q,\omega)_{\gamma}$  is the INS spectrum of the  $\gamma$ -CrH sample measured with IN1-BeF, and the difference spectrum takes into account the presence of 11 mol.%  $\varepsilon$ -CrH in that sample.

With the "composite" INS spectra of  $\gamma$ -CrH and  $\varepsilon$ -CrH hydrides shown in Figs. 5b and 6b, respectively, the contribution from multiphonon neutron scattering (MPNS) was calculated in an isotropic and harmonic approximation using an iterative technique [19]. The calculation procedure consisted in finding a self-consistent deconvolution of the INS spectrum in the interval 0–180 meV into the sum of a one-phonon and multiphonon



Fig. 7. One-phonon optical spectra of  $\gamma$ -CrH (solid line) and  $\varepsilon$ -CrH (dashed line). The horizontal bars indicate the energy resolution of the IN1-BeF spectrometer.

contribution. The calculated MPNS spectra are shown in Figs. 5b and 6b with the dashed curves. As one can see from the figures, MPNS adds a little intensity to the shoulder of the main optical peak and rather well describes the main features of the experimental spectra at energies above 180 meV.

## 4.3. One-phonon spectra of optical hydrogen vibrations

The one-phonon optical spectra of  $\gamma$ -CrH and  $\varepsilon$ -CrH hydrides obtained by subtracting the calculated MPNS spectra from the IN1-BeF experimental data are shown in Fig. 7. A high-energy shoulder of the main peak is clearly seen in each spectrum. Such a shoulder is characteristic of the vibrational spectra of all hydrides of the VI–VIII group transition metals studied so far. Based on results for palladium deuteride [20], the main peak is usually ascribed to nearly nondispersive transverse optical modes, while the shoulder is assumed to arise from longitudinal optical modes, which show significant dispersion due to longrange repulsive H–H interactions.

As seen from Fig. 7, the main optical peak is centred at  $\hbar\omega_0 = 118$  meV in the spectrum of  $\gamma$ -CrH and at  $\hbar\omega_0 = 122$  meV in the spectrum of  $\varepsilon$ -CrH. Both peaks have a full width at half maximum of about 9 meV, which virtually coincides with the resolution  $\Delta \approx 8$  meV of the IN1 BeF spectrometer in this energy range. The similar sharpness of these and other features in the optical spectra of the  $\gamma$ -CrH and  $\varepsilon$ -CrH phases suggests the similar degree of their homogeneity and crystallinity. Together with the results of earlier NMR studies of electrolytically prepared  $\gamma$ -CrH and  $\varepsilon$ -CrH samples [2], this also suggests that the impurities trapped in our electrolytical  $\gamma$ -CrH sample should have formed isolated inclusions without contaminating the material of the hydride phase.

The energy  $\hbar\omega_0$  of the main optical hydrogen peak in the INS spectra of monohydrides of 3d-metals studied so far monotonically increased with decreasing atomic number of the host metal. Plotted as a function of the hydrogen-metal distance R (Fig. 8), these  $\hbar\omega_0$  values fall onto a single and approxi-



Fig. 8. Energy of the main optical hydrogen peak,  $\hbar\omega_0$ , vs. the shortest hydrogen–metal distance *R* for various dihydrides with a fluorite-type structure (crosses) [21] and for monohydrides of 3d-metals (open circles) and 4d-metals (solid circles) (see [16] for references and discussion; the point for  $\gamma$ -CoH is from later work [11]). The dashed curve is a least-squares fit to the data for the dihydrides.

mately linear dependence, irrespective of the structure of the metal lattice: fcc ( $\gamma$ ), hcp ( $\varepsilon$ ) or dhcp ( $\varepsilon$ '). The INS results for the two different modifications of chromium hydride,  $\gamma$ -CrH and  $\varepsilon$ -CrH, with identical compositions and similar *R*-values strongly corroborate the generality of this observation. As seen from Fig. 8, the points for  $\gamma$ -CrH and  $\varepsilon$ -CrH are in fact close to each other and well agree with the  $\hbar\omega_0(R)$  dependence for other monohydrides of 3d-metals. Moreover, the slightly lower  $\hbar\omega_0$  value for  $\gamma$ -CrH can be attributed, at least partly, to the longer interatomic distances *R* in this hydride resulting in a weaker interatomic interaction. Specifically, R = a/2 = 1.927 Å for  $\gamma$ -CrH and  $R = \sqrt{a^2/3 + c^2/16} = 1.922$  Å for  $\varepsilon$ -CrH.

The independence of the  $\hbar\omega_0$  values upon the crystal structure suggests that the position of the main optical peak in the monohydrides is solely determined by H interaction with the nearest metal atoms, because the arrangements of atoms in farther coordination spheres of fcc and hcp hydrides are significantly different.

Another noteworthy feature of the  $\hbar\omega_0(R)$  dependence for monohydrides of 3d-metals and, most likely, that for 4d-metals is the steep increase in  $\hbar\omega_0$  with increasing *R*. This is quite different from the behaviour of the well-known  $\hbar\omega_0(R)$  dependence [21] for dihydrides with a close-packed fluorite-type structure (an fcc metal lattice with hydrogen on tetrahedral interstices) also shown in Fig. 8. In the case of fcc dihydrides of various d transition metals, rare earths and even alkali earths, the energy of the main optical hydrogen peak monotonically decreases with increasing *R* and obeys the dependence  $\hbar\omega_0 \propto R^{-3/2}$  plotted with the dashed line.

The factors resulting in the  $\hbar\omega_0 \propto R^{-3/2}$  dependence common for all the fluorite-type dihydrides are not well under-

stood yet [21–23]. What can be said is that the increase in *R* by itself should decrease the strength of the interatomic interaction in a hydride and should therefore decrease  $\hbar\omega_0$ . The opposite behaviour of the  $\hbar\omega_0(R)$  values of the monohydrides with increasing *R* and, respectively, decreasing atomic number of the host metal therefore indicates a significant strengthening of the hydrogen-metal interaction in the series of the 3d-metals Ni  $\rightarrow$  Co  $\rightarrow$  Fe  $\rightarrow$  Mn  $\rightarrow$  Cr and also of the 4d-metals Pd  $\rightarrow$  Mo. This effect agrees with the results of first-principles calculations [24,25] predicting a monotonic increase in the steepness of the potential well for interstitial hydrogen in transition metals from right to left in the periodic table due to a less efficient screening of the ionic core charges by the decreasing number of valence electrons.

## 5. Conclusions

Phases of fcc ( $\gamma$ ) CrH and hcp ( $\varepsilon$ ) CrH prepared electrolytically using the technique of Ref. [7] show a good homogeneity and crystallinity comparable to those of  $\varepsilon$ -CrH samples prepared by gas-phase absorption at high pressure. A small amount of paramagnetic impurity (presumably, chromium sulfates) entrapped in the electrolytical samples only reveals itself by the occurrence of a low-intensity featureless background in the INS spectra at energies below the fundamental optical band.

The present neutron diffraction investigation and earlier NMR investigation [2] of electrolytically prepared samples showed  $\gamma$ -CrH and  $\varepsilon$ -CrH to be magnetically disordered down to helium temperatures. This allowed completing the construction of the Slater–Pauling curves for fcc and hcp 3d-alloys over the entire range of electronic concentrations, where the alloys undergo magnetic ordering (see Fig. 3).

The INS study demonstrated that the energies  $\hbar\omega_0$  of the main peak in the fundamental band of optical H vibrations in  $\gamma$ -CrH and  $\varepsilon$ -CrH are approximately the same. With the two modifications of chromium hydride having identical compositions and nearly equal hydrogen-metal interatomic distances *R*, this result strongly corroborates the conjecture [16] that the  $\hbar\omega_0(R)$  values for all close-packed monohydrides of 3d-metals fall onto a single and approximately linear dependence, irrespective of the structure of the metal lattice (Fig. 8). This, in particular, suggests that the position of the main optical peak in such monohydrides is determined by H interaction with the nearest metal atoms.

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