

## Anisotropy in the inelastic neutron scattering from fcc NiH

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(received 17 January 2000; accepted in final form 19 May 2000)

PACS. 61.12.-q – Neutron diffraction and scattering.

PACS. 63.20.Dj – Phonon states and bands, normal modes, and phonon dispersion.

PACS. 63.20.Ry – Anharmonic lattice modes.

**Abstract.** – A sample of nearly stoichiometric fcc nickel hydride in the form of polycrystalline plates with strong texture was studied by inelastic neutron scattering (INS) in two different orientations, with the [100] axis of the texture parallel and at an angle of 45° to the direction of neutron momentum transfer. The INS spectra were measured at 5 K with energy transfers  $\omega$  ranging from 26 to 380 meV. In the region of the second and third band of optical hydrogen vibrations, they showed a significant directional dependence. A similar anisotropy was recently observed in the INS spectrum of fcc palladium hydride, and the now available data for NiH and PdH are discussed together.

*Introduction.* – A recent INS study [1] demonstrated that the spectrum of high-energy optical hydrogen vibrations in stoichiometric fcc PdH is strongly anharmonic and anisotropic. The analysis of the observed anisotropy showed that the potential well for hydrogen, which occupies octahedral interstices in the fcc metal lattice of palladium hydride [2, 3], is rather shallow and harmonic along the  $\langle 110 \rangle$  directions and close to the  $\langle 111 \rangle$  directions. Along the  $\langle 100 \rangle$  directions, towards the nearest Pd atom neighbours, the potential well is initially shallow too, but then very steep and thus strongly anharmonic.

Earlier, no significant anisotropy had been observed in the INS spectra of either palladium hydride or any other hydride with cubic local symmetry of the hydrogen positions. The reason may be that an anisotropy like that in PdH is difficult to detect with powder or polycrystalline samples usually used in INS experiments. In PdH, the first (fundamental) optical hydrogen band is practically isotropic and the anisotropy manifests itself only by a strong anharmonicity of the second and higher bands for neutron momentum transfers,  $\mathbf{Q}$ , directed close to one of the  $\langle 100 \rangle$  axes [1]. For other directions of  $\mathbf{Q}$ , the INS spectrum remains nearly harmonic. Averaged over all orientations of  $\mathbf{Q}$ , the contribution from the anharmonic hydrogen vibrations along the  $\langle 100 \rangle$  directions is small, and the high-energy part of the INS spectrum of a powder PdH sample thus exhibits only small deviations from isotropic, harmonic behaviour.

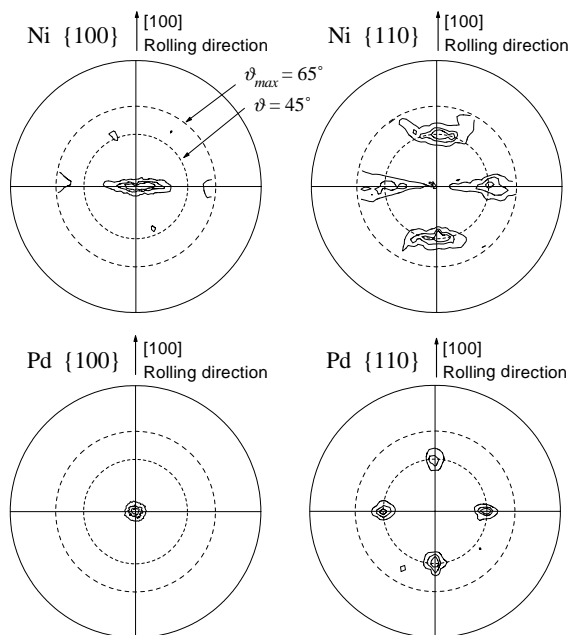


Fig. 1 – Pole figures  $\{100\}$  and  $\{110\}$  of the initial fcc Ni foil used in this work and of the initial fcc Pd foil used in ref. [1]. The isolines are drawn at levels of 0.1, 0.3 and 0.5 of the maximum intensity for each figure.

To reveal anisotropy in the INS spectrum of fcc PdH [1], strongly textured polycrystalline plates of this hydride were studied in two different orientations, with the  $[100]$  axis of the texture approximately parallel and at an angle of  $45^\circ$  to the direction of neutron momentum transfer. In the present work, similar measurements were carried out with textured plates of nearly stoichiometric NiH, another fcc hydride with hydrogen on octahedral sites [4]. The experiment was aimed at answering the question if the anisotropy of the optical hydrogen vibrations is characteristic of more than one single fcc hydride. The INS spectra of polycrystalline samples of nickel hydride measured previously [5–7] had exhibited approximately harmonic behaviour.

*Sample preparation and experimental details.* – The sample was made of a foil of 99.99% pure electrolytic nickel, cold rolled to a thickness of 0.14 mm, annealed in vacuum at  $1000^\circ\text{C}$  for 10 min and quenched in water. Figure 1 shows the pole figures  $\{100\}$  and  $\{110\}$  of this foil and also those of the palladium foil used to prepare the PdH sample in ref. [1] and studied here for comparison. The pole figures were constructed at room temperature by the Schultz method [8] at tilt angles up to  $\vartheta_{\text{max}} = 65^\circ$  using  $\text{MoK}\alpha$  radiation. In both the Ni and the Pd foil, the grain orientations  $(001)[100]$  are dominant, with the  $(001)$  plane parallel to the rolling plane and the  $[100]$  axis parallel to the rolling direction. The  $(001)[100]$  texture is often observed in fcc metals after recrystallisation [9]. The pole figures of the Pd foil are closer to the ideal ones, with the  $\langle 100 \rangle$  pole at  $\vartheta = 0^\circ$  and four  $\langle 110 \rangle$  poles at  $\vartheta = 45^\circ$ , in the directions parallel and perpendicular to the rolling direction. The figures for the Ni foil demonstrate a spread of about  $15\text{--}25^\circ$  in the grain orientations in the plane perpendicular to the rolling direction.

The NiH sample weighing 2.5 g was composed of 40 discs, 8 mm in diameter, cut out of the Ni foil and loaded with hydrogen by a 24 h exposure to a H<sub>2</sub> pressure of 3 GPa at 300 °C and subsequent cooling to 200 K in the high-pressure cell. The hydrogenation method is described elsewhere [10]. Hot extraction gave a H-to-Ni atomic ratio of  $1.05 \pm 0.05$  for the mean hydrogen content of the discs. X-ray diffraction at 100 K showed that the hydrogenated discs were single-phase, homogeneous, and had approximately the same texture as the starting Ni foil. The mean value of the lattice parameter of their fcc metal lattice at 100 K was  $a = 3.732 \pm 0.006$  Å, in agreement with previous data [4]. In order to prevent loss of hydrogen occurring on heating above 250 K, the discs of nickel hydride were stored in liquid nitrogen when not in use and never warmed above 100 K until the end of the INS experiment.

The INS study of the NiH sample was carried out at 5 K with the neutron spectrometer IN1 installed 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 providing an energy resolution of  $\Delta\omega/\omega \approx 6\text{--}8\%$  in the measured range of energy transfer,  $\omega$ , from 26 to 380 meV. The  $\omega$  value was calculated by subtracting 3.5 meV, the mean energy of neutrons that passed through the filter, from the energy of the incoming neutrons. Note that because of this small final energy of the recorded neutrons, the deviation of the momentum transfer vector,  $\mathbf{Q}$ , from the direction of the incident neutron beam was only a few degrees in the range  $\omega > 80$  meV of optical hydrogen vibrations in NiH.

The discs of the NiH sample were placed in a flat aluminium container and arranged in one layer, side by side, randomly with respect to their rolling direction. The INS spectrum was measured first for an angle  $\psi = 0^\circ$  between  $\mathbf{Q}$  and the [100] axis of the sample texture. The sample was then oriented at  $\psi = 45^\circ$  and its INS spectrum was measured again. For these two configurations, the detector was positioned at a neutron scattering angle of  $40^\circ$  (transmission geometry) and  $90^\circ$  (reflection geometry), respectively. Background spectra from an empty container were measured separately under the same conditions and then subtracted from the corresponding raw INS spectra in order to obtain the scattering intensity from the sample alone.

To take the random orientation of the rolling directions of the NiH discs in the container plane into account, the orientation probability density  $P_{hkl}$  has to be averaged over all directions in the sample plane for every given angle  $\psi$ . The relative probability densities for the orientations [100] and [110] at the experimental angles  $\psi = 0^\circ$  and  $45^\circ$  can be estimated by averaging the corresponding pole figure intensities at  $\vartheta = 0^\circ$  and at  $\vartheta = 45^\circ$  (at the centres and along the inner dashed circles in fig. 1). This gives the ratios  $P_{100}(0^\circ)/P_{100}(45^\circ) = 26$  and  $P_{110}(45^\circ)/P_{110}(0^\circ) = 2$  for the Ni foil. For comparison, in the case of the Pd foil used in ref. [1] the same procedure yields  $P_{100}(0^\circ)/P_{100}(45^\circ) = 110$  and  $P_{110}(45^\circ)/P_{110}(0^\circ) = 12$ .

*Results and discussion.* – The obtained INS spectra  $S(Q, \omega)$  for the NiH sample in two different orientations are shown in fig. 2. The spectrum measured at  $\psi = 45^\circ$  agrees with previous data [5–7] and can be interpreted in the same way: The first band of optical hydrogen vibrations consists of a peak centred at  $\omega_0 = 89$  meV and a shoulder towards higher energies, extending up to about 130 meV. The peak is usually ascribed to nearly non-dispersive transverse optical modes, while the shoulder is assumed to arise from longitudinal optical modes, which show significant dispersion due to long-range repulsive H-H interactions. The scattering intensity in the regions 160 to 245 meV and 245 to 335 meV is attributed to the second and third optical band, respectively.

As can be seen in fig. 2, the INS spectrum of NiH measured at  $\psi = 0^\circ$  practically coincides with the  $45^\circ$ -spectrum in the range of the first optical band but differs from it noticeably at higher energies. In particular, the peak at 176 meV, about twice the energy  $\omega_0 = 89$  meV of

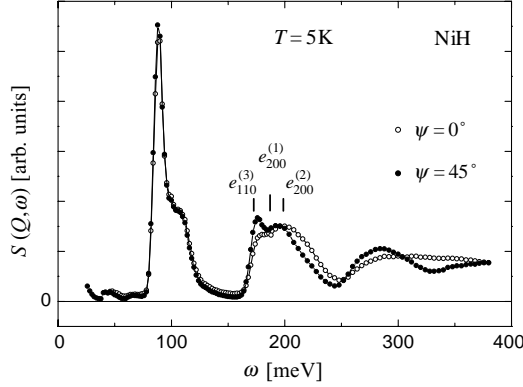


Fig. 2 – The dynamical structure factor  $S(Q, \omega)$  of NiH as a function of the energy loss  $\omega$  of the inelastically scattered neutrons measured at 5 K with the IN1 BeF spectrometer at ILL, Grenoble.  $\psi$  is the angle between the momentum transfer vector,  $Q$ , and the [100] axis of the sample texture.  $e_{nm\ell}^{(i)}$  are the rescaled excitation energies of the  $i$ -fold degenerate oscillator states  $|nm\ell\rangle$  calculated in ref. [13], see text.

the first peak, is reduced for  $\psi = 0^\circ$ . The scattering intensity at energies 200 to 245 meV, on the high-energy side of the second band, is significantly increased. The features at 245 to 380 meV, in the range of the third and fourth band, are smoothed.

A comparison with the data for PdH from ref. [1] presented in fig. 3 shows that the differences between the INS spectra of NiH at  $\psi = 45^\circ$  and  $0^\circ$  are qualitatively the same as those between the spectra of PdH measured under similar conditions. This indicates that the anisotropy in the optical vibrations of hydrogen in NiH is of the same character and, presumably, of the same origin as in PdH.

Figure 3 also shows the contributions from multiphonon neutron scattering (MPNS) calculated in an isotropic harmonic approximation including processes involving up to four phonons. The values for PdH were taken from ref. [1]. The calculation for NiH was done by an iterative technique [11] involving a multiconvolution of the one-phonon spectrum of lattice and optical phonons in the energy region  $\omega \leq 140$  meV. Since the lattice part of the INS spectrum of NiH was not measured in the present work, the necessary data were taken from ref. [7].

As one can see from fig. 3a, the main features of the second and third optical band in the  $45^\circ$ -spectra of both the NiH and the PdH sample are described rather well by the calculated MPNS curves. This indicates that the first three bands of optical hydrogen vibrations in NiH and PdH are approximately harmonic in the directions at  $45^\circ$  to the  $\langle 100 \rangle$  axes. Correspondingly, the potential well for hydrogen in both hydrides is nearly parabolic along these directions, at least at energies up to  $E = (3 + \frac{1}{2})\omega_0$ , where  $E$  is counted from the bottom of the well. With  $\omega_0 = 89$  meV for NiH, this range extends up to  $E \approx 310$  meV and it extends up to  $\approx 200$  meV for PdH with  $\omega_0 = 56$  meV.

In the range of the first optical band, the  $0^\circ$ -spectra of NiH and PdH are very close to the  $45^\circ$ -spectra. This suggests that the first band is nearly isotropic, because the largest deviation from isotropy should be expected at  $\psi = 0^\circ$ , where hydrogen vibrations towards the nearest metal atoms are excited. This may also be taken as an indication that the potential well for hydrogen has approximately the same parabolic shape in all directions at energies below the upper edge of the first band positioned at  $E = 130 + \frac{1}{2}\omega_0 \approx 170$  meV in NiH and at  $E = 90 + \frac{1}{2}\omega_0 \approx 120$  meV in PdH.

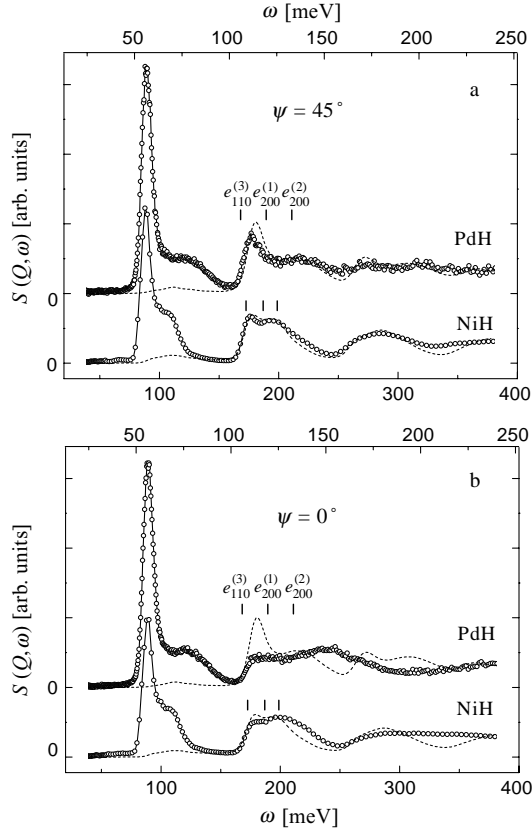


Fig. 3 – The INS spectra of NiH at 5 K (lower energy scale, data of the present work) and of PdH at 25 K (upper energy scale, data of ref. [1]). The dashed lines represent the multiphonon contributions calculated in an isotropic harmonic approximation. The  $e_{nml}^{(i)}$  values are taken from ref. [12] for PdH and from ref. [13] for NiH and rescaled as described in the text.

In the range of the second and third optical bands, the  $0^\circ$ -spectra and the results of the MPNS calculation disagree noticeably (fig. 3b), the differences being most significant at those very places where the  $0^\circ$ -spectra differ from the  $45^\circ$ -spectra. The centres of gravity of both bands are shifted towards higher energies compared to their positions in the calculated harmonic spectra. This points to a larger steepness of the potential well in the  $\langle 100 \rangle$  directions at energies higher than the lower edge of the second band, that is above  $E \approx 210$  meV for NiH and above  $E \approx 130$  meV for PdH.

The above conclusions about the shape of the potential well for hydrogen atoms in nickel and palladium hydrides are in line with the results of *ab initio* calculations by Elsässer *et al.* for fcc PdH [12] and NiH [13]. These authors also calculated hydrogen vibrational states in the first and second optical band, though only for the  $\Gamma$ -point, the centre of the Brillouin zone.

According to refs. [12,13], the vibrational ground state of hydrogen in PdH and NiH is an atom-like  $s_{000}$  state, an oscillator state  $|nml\rangle = |000\rangle$ . The first-excitation states are 3-fold degenerate  $p_{100}$  states with the excitation energy  $e_{100}^{(3)}$  at the  $\Gamma$ -point. The six second-excitation states, which are all degenerate in the case of an isotropic and harmonic oscillator, are split into three groups. These are the 3-fold degenerate  $d_{110}$  states, the single  $s_{200}$  state and the

2-fold degenerate  $d_{200}$  states with energies  $e_{110}^{(3)}$ ,  $e_{200}^{(1)}$  and  $e_{200}^{(2)}$ , respectively. These excitation energies obey the relations  $e_{110}^{(3)} < 2e_{100}^{(3)} < e_{200}^{(1)} < e_{200}^{(2)}$ . The calculated values of  $e_{100}^{(3)}$  for NiH and PdH are higher by about 10% than the experimental  $\omega_0$  values of the first optical peak. Since this peak represents the weakly dispersed transverse modes, its energy can be expected to agree with that of  $\Gamma$ -point vibrations. For easier comparison with experiment, the calculated excitation energies for the states in the second optical band of these hydrides, indicated by vertical bars in figs. 2 and 3, were rescaled by the corresponding factor  $\omega_0/e_{100}^{(3)} \approx 0.9$ . In the case of harmonic vibrations such a rescaling gives correct values for all excitation energies.

Though the calculated data for the  $\Gamma$ -point are still insufficient to describe hydrogen vibrations in NiH and PdH, which display strong dispersion, these data are rather illustrative.

The  $p$  character of the first  $p_{100}$  excitation states calculated by Elsässer *et al.* agrees with experiment in that no anisotropy is observed in the first band of optical hydrogen vibrations. In the case of pure  $p$  wave functions and  $\Gamma$ -point vibrations, the probability of INS processes transferring the hydrogen atom from the ground state to the first excitation state would in fact be perfectly isotropic, since the corresponding transition matrix element between the  $s$  ground state and the appropriate linear combination of the 3 degenerate  $p$  excitation states would be exactly the same. A possible weak anisotropy could still arise from anisotropic dispersion and an admixture of wave functions with different angular symmetry, but was not observed within the accuracy of the experiment.

For similar reasons, the scattering to the second  $s_{200}$  state should only weakly depend on the  $\mathbf{Q}$  direction even in the case of an anisotropic potential well. Scattering to the  $d$ -type states  $d_{110}$  and  $d_{200}$ , on the other hand, should be strongly anisotropic, the scattering intensity being maximum for  $\mathbf{Q}$  parallel to the  $\langle 110 \rangle$  and  $\langle 100 \rangle$  directions, respectively.

With the energies of the  $\Gamma$ -point vibrations indicated in figs. 2 and 3, this suggests that the intensity in the central part of the second band in the INS spectra of the NiH and PdH samples mostly results from scattering to the  $s_{200}$  state and should therefore only weakly depend on  $\psi$ . The intensity of the high-energy part of this band is mainly due to scattering to the  $d_{200}$  states, which has a higher probability at  $\psi = 0^\circ$  than at  $\psi = 45^\circ$ . Since  $e_{200}^{(2)} > 2e_{100}^{(3)}$ , the high-energy edge of the second band in the  $0^\circ$ -spectra should be shifted to higher energies than calculated in the harmonic approximation. This is just what experiment shows.

On the other hand, scattering to the  $d_{110}$  states prevails in the low-energy part of the second band. Here the scattering intensity should be larger at  $\psi = 45^\circ$  than at  $\psi = 0^\circ$  and the low-energy edge of this band in the  $45^\circ$ -spectra of NiH and PdH should be shifted to lower energies compared to the harmonic case because  $e_{110}^{(3)} < 2e_{100}^{(3)}$ . This is also observed in experiment, the effect being most obvious in the  $45^\circ$ -spectrum of PdH (fig. 3a) where the peak of the second band calculated in the harmonic approximation (dashed line) appears at  $\omega_1^{\text{calc}} = 114$  meV while the experimental peak is at  $\omega_1^{\text{exp}} = 112$  meV.

It is worth noting in this connection that  $\omega_1^{\text{calc}}$  for both PdH and NiH is larger than  $2\omega_0$  due to the convolution of the main peak at  $\omega_0$  in the first band with its high-energy shoulder. Interestingly enough, the experimental value of  $\omega_1^{\text{exp}}$  for PdH is almost exactly equal to the ‘‘harmonic’’  $2\omega_0 = 112$  meV, which actually indicates that the harmonic approximation is not fully adequate.

The result of refs. [12, 13] that the peak at  $\omega \approx 2\omega_0$  is mainly due to scattering to the  $d_{110}$  states can also explain why the intensity of this peak in the  $45^\circ$ - and  $0^\circ$ -spectra of NiH differs less than in the spectra of PdH. In fact, the texture of the NiH sample, which had an orientation probability ratio  $P_{110}(45^\circ)/P_{110}(0^\circ) = 2$ , was not as close to the ideal (001)[100] texture as that of the PdH sample with  $P_{110}(45^\circ)/P_{110}(0^\circ) = 12$ .

*Conclusions.* – Despite the cubic symmetry of the octahedral interstitial sites occupied by hydrogen in the fcc metal lattice of NiH, the second and third band of optical hydrogen vibrations are strongly anisotropic. The anisotropy is due to an increase in the steepness of the potential well seen by hydrogen in the  $\langle 100 \rangle$  directions, these being the directions to the nearest metal atom, at energies above the range of the first optical band. A similar anisotropy was earlier observed for the optical H vibrations in fcc PdH [1] and seems thus to be characteristic of the fcc hydrides with octahedral coordination of hydrogen. The directional dependences of the main features of the second optical band in PdH and NiH agree with estimates based on first-principles calculations [12,13].

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This work was supported by the Grants No. 99-02-17299 and 96-15-96806 from the Russian Foundation for Basic Research.

#### REFERENCES

- [1] ROSS D. K., ANTONOV V. E., BOKHENKOV E. L., KOLESNIKOV A. I., PONYATOVSKY E. G. and TOMKINSON J., *Phys. Rev. B*, **58** (1998) 2591.
- [2] BERGSMAN J. and GOEDKOOP J. A., *Physica*, **26** (1960) 744.
- [3] BOND R. A. and ROSS D. K., *J. Phys. F*, **12** (1982) 597.
- [4] IRODOVA A. V., GLAZKOV V. P., SOMENKOV V. A., SHIL'SHTEIN S. SH., ANTONOV V. E. and PONYATOVSKII E. G., *Sov. Phys. Crystallogr.*, **33** (1988) 453.
- [5] WIŚNIEWSKI R., DIMITROVA R., NATKANIEC I. and WASICKI J., *Solid State Commun.*, **54** (1985) 1073.
- [6] DORNER B., BELASH I. T., BOKHENKOV E. L., PONYATOVSKY E. G., ANTONOV V. E. and PRONINA L. N., *Solid State Commun.*, **69** (1989) 121.
- [7] KOLESNIKOV A. I., NATKANIEC I., ANTONOV V. E., BELASH I. T., FEDOTOV V. K., KRAWCZYK J., MAYER J. and PONYATOVSKY E. G., *Physica B*, **174** (1991) 257.
- [8] SCHULTZ L. G., *J. Appl. Phys.*, **20** (1949) 1030.
- [9] WASSERMANN G. and GREWEN J., *Texturen metallischer Werkstoffe* (Springer Verlag) 1962.
- [10] PONYATOVSKII E. G., ANTONOV V. E. and BELASH I. T., *Sov. Phys. Usp.*, **25** (1982) 596.
- [11] ANTONOV V. E., BELASH I. T., KOLESNIKOV A. I., MAYER J., NATKANIEC I., PONYATOVSKII E. G. and FEDOTOV V. K., *Sov. Phys. Solid State*, **33** (1991) 87.
- [12] ELSÄSSER C., HO K. M., CHAN C. and FÄHNLE M., *Phys. Rev. B*, **44** (1991) 10377.
- [13] ELSÄSSER C., KRIMMEL H., FÄHNLE M., LOUIE S. G. and CHAN C., *J. Phys. Condens. Matter*, **10** (1998) 5131.