

Neutron spectroscopy of $\text{MnH}_{0.86}$, $\text{NiH}_{1.05}$, $\text{PdH}_{0.99}$ and harmonic behaviour of their optical phonons

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Inelastic neutron scattering spectra from manganese, nickel and palladium hydrides synthesized under a high pressure of gaseous hydrogen have been measured in the energy region of 0–500 meV. The positions and intensities of the peaks in the higher energy parts of the spectra are well described by a contribution from the multiphonon neutron scattering in the harmonic approximation.

1. Introduction

Vibrational spectra for the hydrides of groups III–V transition metals have been extensively studied for a long time using inelastic neutron scattering (INS) techniques, see refs. [1, 2] as a review. As for the group VIII metals, the hydrides were thoroughly investigated only for nonstoichiometric Pd–H [3–7] and Ni–H [8, 9]. Recently, Dorner et al. [10, 11] have studied optical hydrogen vibrations in nearly stoichiometric $\text{NiH}_{1.05}$ and in two hydrides of group VI elements, $\text{CrH}_{1.0}$ and $\text{MoH}_{1.2}$. Here we report the results of the investigation of the vibrational spectra of $\text{MnH}_{0.86}$ (the first example of a hydride of the group VII transition metals) and $\text{NiH}_{1.05}$ and $\text{PdH}_{0.99}$ by the INS method in a wide range of energy transfer (0–500 meV).

The measurement of the entire phonon spectrum was of special interest for the approximately stoichiometric hydride $\text{PdH}_{0.99}$. The Pd–H system has been extensively studied for the past two decades because of the discovery of superconductivity in it [12] with an inverse isotope effect (IIE) for T_c [13]. Ganguly proposed [14] that the IIE could be the result of a strong anharmonicity of the H(D) vibrations in Pd. In fact, the INS experiments have shown [5, 15]

that the Pd–H(D, T) force constant is lower when the mass of the hydrogen isotope increases. Further INS studies by Rush et al. [7] on the α - and β -phases in the Pd–H(D) systems allowed them to conclude that the potential wells for H and D atoms in palladium are very similar and strongly anharmonic. In particular, for $\text{PdH}_{0.014}$ they observed two second excited levels $\omega_2^{(1)} = 2\omega_1$ and $\omega_2^{(2)} = 2\omega_1 + 19$ meV and calculated the anharmonic parameters. Their data were then used in ref. [16] where the anharmonic shape of the interstitial hydrogen–palladium potential well was reanalyzed within first-order perturbation theory.

The present investigation has shown that the fine structure of the “higher vibrational harmonic” in the INS spectra for all the hydrides in question could be explained by multiphonon neutron scattering in an harmonic approximation.

2. Experiment and treatment of data

Manganese powder and nickel and palladium plates 0.3 mm thick were hydrogenated in an atmosphere of high-pressure molecular hydrogen, the method is described elsewhere [17]. The

hydrides obtained are known to have close-packed metal sublattices, hexagonally closed packed for manganese hydride and face centered cubic for nickel and palladium hydrides, with the hydrogen atoms on octahedral interstitial sites [18, 19]. The samples (each of about 5 g) were stored in liquid nitrogen to prevent hydrogen losses: under atmospheric pressure manganese hydride rapidly begins to decompose at about 320 K, while the hydrides of nickel and palladium decompose at about 250 K and 220 K, respectively.

The INS measurements were carried out on the inverted geometry time-of-flight spectrometer KDSOG-M [20] installed at the IBR-2 pulse reactor in Dubna. The incident neutron energy is determined by the reactor-sample flight path 29.7 m long and the energy of the scattered neutrons by the pyrolytic graphite analyzers ($E_f = 4.7$ meV), mounted behind the beryllium filter. The spectra were collected at eight angles ranging from 30° to 140° . The samples were mounted in a top loading cryostat and experiments were performed at different temperatures (see table 1). The neutron transmission through the samples was greater than 90%, so the multiple scattering contributions were negligible. The background from the sample holder and cryostat was subtracted from the INS spectra. The spectra from all the scattering angles were summed, and the generalized vibrational density of states (GVDS) $\theta(\omega)$ was calculated [1] supposing a one-phonon mechanism for the scattering process.

Estimates have shown the scattering by the hydrogen to dominate in the INS spectra for the Mn and Pd hydrides under study, so we assume that these are the spectra of hydrogen atom vibrations. In the case of the nickel hydride, the scattering intensity from the H and Ni atoms is comparable in the region of the lattice phonons, and the experimental spectrum was corrected in order to eliminate the contribution from the Ni atoms and to obtain $\theta(\omega)$ for the H atoms. For this purpose we have measured the INS spectrum for pure Ni at room temperature.

The contributions from the multiphonon neutron scattering (only two- and three-phonon processes were taken into account) were calculated in a harmonic approximation [21] by the multi-convolution of the one-phonon spectrum. The experimental $\theta(\omega)$ in the energy region of the lattice and hydrogen optic phonons was first taken as a one-phonon spectrum. On the second and subsequent steps the one-phonon spectrum was assumed to be the difference between the experimental one and that resulting from the multiphonon processes. For all the spectra the convergence was reached in three or four iterations.

3. Results and discussion

Figures 1 to 3 show the experimental GVDS (points) and calculated, as described above, one-phonon (dashed curves) and multiphonon (solid curves) neutron scattering contributions to the

Table 1
Positions and widths of the peaks of the GVDS of the manganese, nickel and palladium hydrides.

Sample	Temperature (K)	First main peak		Second main peak		
		Energy, ω_1 (meV)	Width, $\Delta\omega_1$ (meV)	ω_2 (meV)		$2\omega_1$ (meV)
				Exper.	Calc.	
MnH _{0.86}	100	111	20	233	231	222
	290	110	25	227	227	220
NiH _{1.05}	15	89	20	196	192	178
	230	90	28	192	190	180
PdH _{0.99}	15	56.0	9.0			
	200	56.0	14.3			

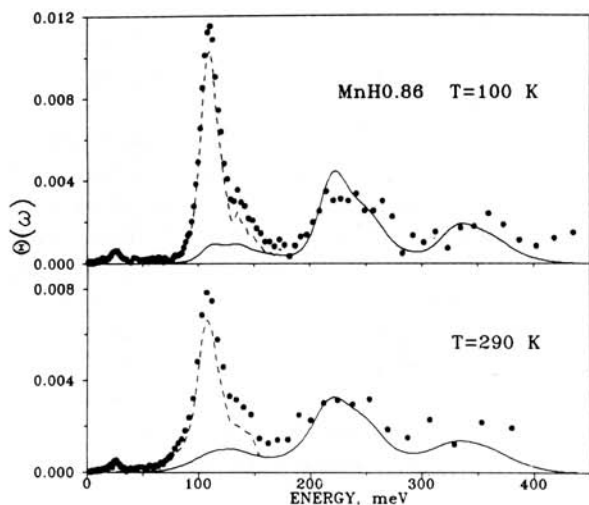


Fig. 1. GVDS spectra for $\text{MnH}_{0.86}$. The dashed and solid curves are the calculated one-phonon and multiphonon neutron scattering contributions, respectively.

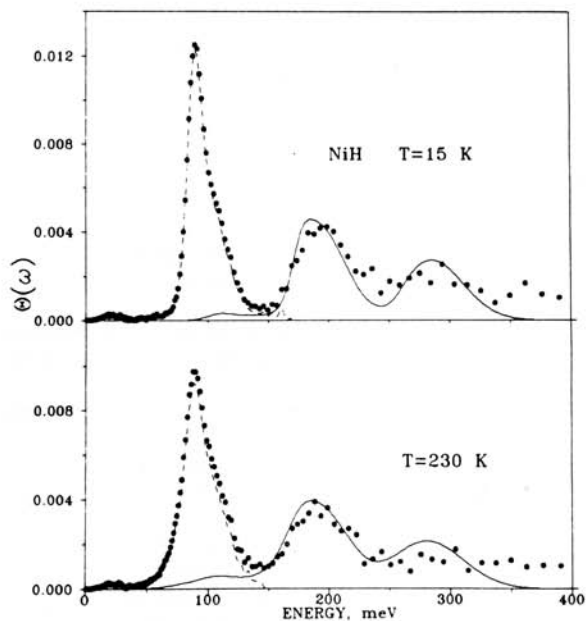


Fig. 2. GVDS spectra for $\text{NiH}_{1.05}$.

spectra for the manganese, nickel and palladium hydrides, respectively. For lattice vibrations in the Mn and Ni hydrides, the Debye energy was estimated by fitting the low-energy acoustic part of the spectrum by a parabola and equating the area under the parabola and under the ex-

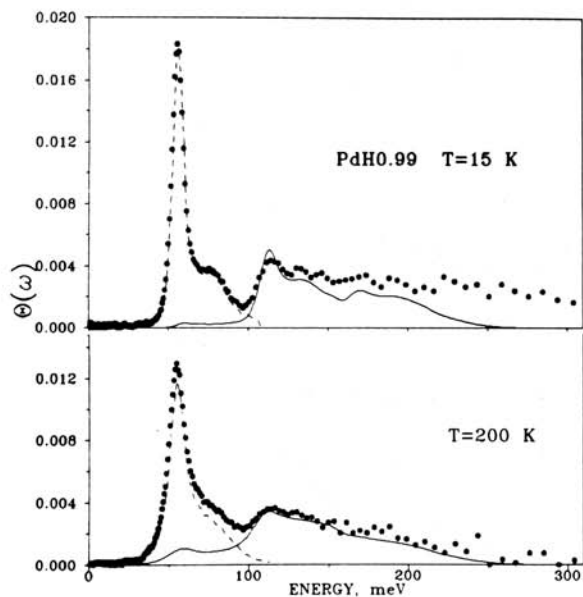


Fig. 3. GVDS spectra for $\text{PdH}_{0.99}$.

perimental spectrum in the region of the lattice vibrations. The Debye energies obtained are $\varepsilon_D = 31 \pm 2$ meV for $\text{MnH}_{0.86}$ (compare with $\varepsilon_D = 34.5$ meV for $\alpha\text{-Mn}$ [22]), 26 ± 2 meV for $\text{NiH}_{1.05}$ and 31 ± 2 meV for Ni (see fig. 4). These results show that the lattice spectra of manganese and nickel, as well as that of palladium [23], become softer after hydrogenation. Moreover, in the case of $\text{PdH}_{0.99}$ (fig. 5), we would like to draw attention to the presence of the non-Debye density of states in the low-energy (2–9 meV) region.

As one can see from figures 1 to 3, despite the cubic symmetry of the hydrogen atom positions in the hydrides, the optical peaks in the spectra have explicit shoulders at the side of the larger energies. We think that these shoulders most probably result from the dispersion of the optical phonon branches, especially in the case of nearly stoichiometric $\text{NiH}_{1.05}$ and $\text{PdH}_{0.99}$.

The positions of the first main optical peaks ω_1 and their widths $\Delta\omega_1$ at half height as well as the positions of the experimental second main peaks and calculated two-phonon peaks are presented in table 1. It is seen (figs. 1–3) that the positions and intensities of the peaks in the spectra in the energy range $\omega > \omega_1$ are well described by contri-

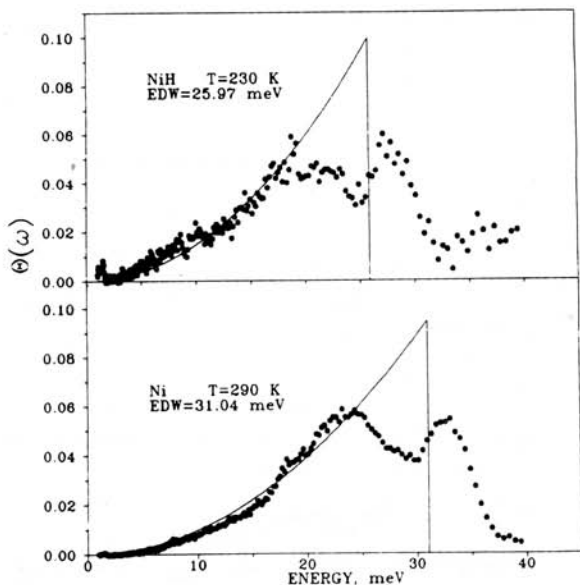


Fig. 4. GVDS spectra for Ni and NiH_{1.05} (in the region of the host lattice modes). The solid curves represent the result of a fit with the Debye model.

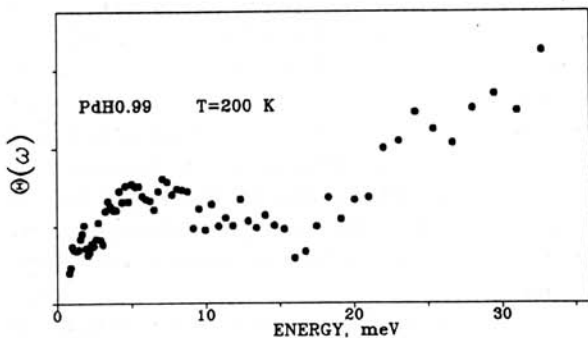


Fig. 5. GVDS spectra for PdH_{0.99} in the low-energy region.

butions from the multiphonon neutron processes. The calculated and experimental positions of the multiphonon peaks in the manganese and nickel hydride spectra differ noticeably from the multiple of ω_1 values (table 1). These differences arise from the asymmetry of the optical peak.

A fine structure of the multiphonon bands in the spectra for PdH_{0.99} is also well reproduced with the calculations in a harmonic approximation. Thus, this approximation turns out to be fairly good even in the case of the noticeably

anharmonic [5, 7, 15] vibrations of H atoms in Pd and, henceforth, could be considered as a simple and useful tool for analyzing the INS spectra for many different hydrides.

As for the origin of the inverse isotope effect in the T_c values of the Pd-H(D) hydrides, it seems worth pointing out here that along with the anharmonic effects other contributions to it are also possible. We mention, for example, the model of Drechsler et al. [24] that accounts for the IIE in metastable hydrides as being caused by the two-level low-energy excitations in these substances. The observed non-Debye density of states (fig. 5) in the low-energy part of the vibrational spectra in our experiments of PdH_{0.99} confirms the latter model.

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References

- [1] Yu.A. Izumov and N.A. Chernoplekov, in: Neutron Spectroscopy, Vol. 3 (Energoatomizdat, Moscow, 1983) p. 328.
- [2] T. Springer and D. Richter, in: Methods of Experimental Physics (Springer-Verlag, Berlin and New York, 1987) pp. 131–186.
- [3] M.R. Chowdhury and D.K. Ross, Solid State Commun. 13 (1973) 229.
- [4] W. Drexel, A. Murani, D. Tocchetti, W. Kley, I. Sosnowska and D.K. Ross, J. Phys. Chem. Solids 37 (1976) 1135.
- [5] A. Rahman, K. Skold, C. Pelizari, S.K. Sinha and H. Flotow, Phys. Rev. B 14 (1976) 3630.
- [6] D.K. Ross, P.F. Martinn, W.A. Oates and R. Khoda Bakhsh, Z. Physik. Chem. NF 114 (1979) 221.
- [7] J.J. Rush, J.M. Rowe and D. Richter, Z. Phys. B 55 (1984) 283.
- [8] J. Eckert, C.F. Majczrak, L. Passell and W.B. Daniels, Phys. Rev. B 29 (1984) 3700.
- [9] R. Wiśniewski, R. Dimitrova, I. Natkaniec and J. Wasicki, Solid State Commun. 54 (1985) 1073.
- [10] B. Dorner, I.T. Belash, E.L. Bokhenkov, E.G. Ponyatovsky, V.E. Antonov and L.N. Pronina, Solid State Commun. 69 (1989) 121.

- [11] B. Dorner, V.E. Antonov, I.T. Belash, E.L. Bokhenkov, E.G. Ponyatovsky and L.N. Pronina, *Z. Physik. Chem. NF* 164 (1989) 1079.
- [12] T. Skoškiewicz, *Phys. Stat. Sol. a* 11 (1972) K123.
- [13] B. Stritzker and W. Buckel, *Z. Physik.* 257 (1972) 1.
- [14] B.N. Ganguly, *Z. Physik.* 265 (1973) 433.
- [15] J.M. Rowe, J.J. Rush, J.E. Schirber and J.M. Mintz, *Phys. Rev. Lett.* 57 (1986) 2955.
- [16] P.M. Oppeneer, A. Lodder and R. Griessen, *J. Phys. F* 18 (1988) 1733.
- [17] E.G. Ponyatovsky, V.E. Antonov and I.T. Belash, in: *Problems in Solid-State Physics*, eds. A.M. Prokhorov and A.S. Prokhorov (Mir, Moscow, 1984) pp. 109–172.
- [18] V.A. Somenkov, V.P. Glazkov et al., *J. Less-Common Metals* 129 (1987) 171.
- [19] A.V. Irodova, V.P. Glazkov et al., *Soviet Phys. Cryst.* 33 (1988) 453.
- [20] G. Baluka et al., *JINR*, P13-84-242, Dubna (1984).
- [21] A.I. Kolesnikov, E.L. Bokhenkov and E.F. Sheka, *Soviet Phys. JETP* 57 (1983) 1270.
- [22] J. de Launay, in: *Solid State Physics*, Vol. 2, eds. F. Seitz and D. Turnbull (Academic Press, New York, 1956).
- [23] J.M. Rowe, J.J. Rush, H.G. Smith, M. Mostoller and H.E. Flotow, *Phys. Rev. Lett.* 33 (1974) 1297.
- [24] S.L. Drechsler, G.M. Vujicic and N.M. Plakida, *J. Phys. F* 14 (1984) L243.