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Lattice dynamics of high-pressure hydrides of the group VI–VIII transition metals

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Abstract

Monohydrides of the group VI–VIII transition metals Cr, Mn, Fe, Co, Ni, Mo, Rh and Pd are synthesised under high hydrogen pressures and elevated temperatures and studied by inelastic neutron scattering (INS) at ambient pressure and low temperatures. In the measured INS spectra, the energy of the main optical H peak exhibits a strong monotonic increase as a function of the nearest hydrogen–metal distance in the hydrides of both 3d- and 4d-metals, respectively. The spectra for FCC NiH and PdH appear strongly anisotropic at energy transfers above the fundamental band of optical hydrogen vibrations, while those for FCC PdD do not show a significant directional dependence at energies of the second optical D band. © 2002 Elsevier Science B.V. All rights reserved.

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The technique for compressing gaseous hydrogen to pressures up to 9 GPa at temperatures up to 1000°C [1], developed at the Institute of Solid State Physics RAS, made it possible to synthesise hydrides of all 3d- and 4d-metals of groups VI–VIII (except Ru). The hydrides are unstable at ambient conditions, but they can be removed from the high-pressure cell and studied at ambient pressure in a metastable state if cooled to a lower temperature beforehand. Neutron diffraction studies showed that these metastable hydrides have close-packed metal sublattices with FCC (γ), HCP (ϵ) or DHCP (ϵ') structure, in which hydrogen occupies octahedral interstitial positions [2–4].

The vibrational spectra of most of the hydrides were studied by inelastic neutron scattering (INS) using the beryllium filter spectrometer IN1 BeF installed at the hot source of the high-flux reactor at ILL [5]. This spectrometer combines the highest luminosity among the spectrometers operating in a wide energy-transfer range (25–450 meV) with a rather good resolution (6–8%).

Fig. 1 shows the INS spectra in the range of optical hydrogen vibrations for polycrystalline hydrides of the group VI–VIII transition metals with the maximum hydrogen concentration achieved so far. The first, one-phonon band of optical hydrogen vibrations in these hydrides

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Fig. 1. The dynamical structure factor $S(Q, \omega)$ as a function of the energy loss $\hbar\omega$ of the inelastically scattered neutrons for monohydrides of 3d-metals, ϵ -CrH [6], γ -MnH_{0.41} [7], ϵ -MnH_{0.86} (Ref. [8], Exp. 7-02-58), ϵ' -FeH [9], ϵ -CoH (Ref. [8], Exp. 7-02-47), γ -NiH [6], and 4d-metals, ϵ -MoH [6], γ -RhH (Ref. [8], Exp. 7-02-47) and γ -PdH [10]. The spectrum of γ -PdH was measured at 25 K with the TFXA spectrometer at ISIS, the other spectra at 2–15 K with the IN1 BeF spectrometer at ILL. The curves are shifted along the *y*-axis.

consists of a strong peak with a broad shoulder towards higher energies. Based on results for palladium hydride [11,12], 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 interaction. The second and, if observed, the third optical H band have a more smooth intensity distribution and appear at energies that are approximately multiples of the energy of the fundamental band.

As seen from Fig. 1, the energy $\hbar\omega_0$ of the main optical H peak exhibits a strong monotonic increase with decreasing atomic number of the host metal. Fig. 2 shows this energy as a function of the hydrogen-metal distance R, which also



Fig. 2. The energy $\hbar\omega_0$ of the main optical hydrogen peak vs. the distance *R* between the nearest hydrogen and metal atoms for various dihydrides (crosses) [14] and for monohydrides of 3d-metals (circles) and 4d-metals (squares); see Fig. 1 for references. The dashed curve is a least-squares fit to the data for the dihydrides.

increases monotonically with decreasing atomic number. Also shown are the $\hbar\omega_0(R)$ values for dihydrides with a close-packed fluorite-type structure (an FCC metal lattice with hydrogen in tetrahedral interstices) formed by various d transition metals, rare earths and alkali earths, that were all found earlier [13] to obey the dependence $\hbar\omega_0(R) = A R^{-3/2}$. The $\hbar\omega_0(R)$ values for the monohydrides show a quite different behaviour: they steeply increase with *R* and are significantly different for 3d- and 4d-metals.

The increase in R by itself should weaken interatomic interactions and decrease the vibrational energy. The observed opposite effect is therefore due to a significant increase in the hydrogen-metal interaction with decreasing atomic number of the host metal. This agrees with predictions of first-principles calculations [14] that the reduction of the number of valence electrons from right to left along the transition metal rows in the periodic table should lead to a steepening of the potential well for interstitial hydrogen due to a less efficient screening of the ionic core charges.

Recent INS studies of textured foils of FCC PdH [10] and NiH [15] and single-crystalline



Fig. 3. INS spectra for the PdH (bottom, 25K, TFXA) and NiH (top, 5K, IN1 BeF) samples with cubic texture measured in two orientations, with the neutron momentum transfer vector Q parallel to the [110] axis (solid curve) and the [100] axis (dotted curve) of the texture.

PdH_{0.85} [16] demonstrated that, despite the cubic symmetry of the octahedral hydrogen positions in these hydrides, the second and third band of optical H vibrations are strongly anisotropic (Fig. 3) due to an anisotropy of the potential well for H atoms. Earlier, no significant anisotropy had been observed in the INS spectra of palladium hydride or any other hydride with cubic symmetry of hydrogen positions. The directional dependences of the main features of the second optical band in PdH and NiH agree with estimates based on ab-initio calculations [14,17].

Fig. 4 shows the results of a similar INS investigation of palladium deuteride (see Ref. [8], Exp. 7-02-62) that was prepared from the same Pd foil with cubic texture as in Ref. [10] and had the composition PdD_{0.96}H_{0.04}. We could not avoid a hydrogen contamination of the deuteride, and to isolate its contribution to the INS spectrum (the dashed line in Fig. 4a), we also studied PdD_{1-x}H_x powder samples with x = 0.04, 0.06 and 0.08. As one can see, the peak at $\omega_2^D \approx 72$ meV in the second



Fig. 4. (a) INS spectra for the textured $PdD_{0.96}H_{0.04}$ sample (5 K, IN1 BeF) measured in two orientations, with the neutron momentum transfer vector Q parallel to the [1 10] axis (open circles) and the [1 00] axis (solid circles) of the sample texture. The thin curve at the bottom shows the estimated contribution from 4 at% H. (b) INS spectra for PdD obtained as a difference between the experimental and calculated spectra shown in (a).

D optical band in PdD (Fig. 4b) shows nearly no anisotropy in contrast to the analogous H peak at $\omega_2^{\rm H} \approx 112 \text{ meV}$ in PdH (Fig. 3, bottom). This indicates that the potential well for H and D atoms in palladium is rather isotropic at energies up to $5/4\omega_2^{\rm D} \approx 90 \text{ meV}$, counted from the bottom of the well, and becomes strongly anisotropic only at energies exceeding $5/4\omega_2^{\rm H} \approx 140 \text{ meV}$.

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