High-Energy-Neutron Vibrational Spectroscopy on β-V_2H

R. Hempelmann
Institut für Festkörperforschung, Kernforschungsanlage Jülich, 5170 Jülich, West Germany

D. Richter
Institut Laue-Langevin, 38042 Grenoble, France

and

D. L. Price
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 10 June 1986)

By means of inelastic neutron scattering we investigated the localized H vibrations in β-V_2H (octahedral H sites). Using a unique single-domain single crystal, for the first time we determined the directions of the fundamental excitations of a hydrogen atom in a metal. Overtones of these vibrations were observed up to the fourteenth order. They establish a well-defined H potential up to more than 1 eV. The sequence of the excitations could be described in terms of an empirical potential.

PACS numbers: 63.20.Pw, 61.12.Gz

The effective hydrogen single-particle potential in metals is one of the important questions in the fundamental research on metal-hydrogen systems; its knowledge is essential for an understanding of a large variety of phenomena like transport properties,[1] superconductivity,[2] and thermodynamics.[3] *Experimentally,* this potential can be determined by neutron vibrational spectroscopy[4]; however, only the fundamental frequencies and one or very few overtones were measured in the past. For PdH_α, e.g., the thus determined potential,[5] when extrapolated to higher energies, leads to serious discrepancies with macroscopic chemical-potential results above room temperature.[6,7] The *theoretical* understanding of the H potential is also still in an early state. We mention the semiempirical approach by Sugimoto and Fukai,[8] who solved the Schrödinger equation using a double Born-Mayer potential, and the first-principles frozen-phonon calculation by Ho, Tao, and Zhu.[9] While the former approach failed to reproduce higher overtones,[10] the latter was able to predict them in accordance with experimental results.[11] A real test of these theories, however, needs experimental information about the potential at higher energies. In this Letter we present this information for β-V_2H and report about the unexpected observation of H vibrational excitations up to the fourteenth order and thus of a well-defined H potential above 1 eV. In addition, by means of a unique sample, a single-domain single crystal, we were able to determine experimentally the directions of the localized vibrations in a hydride.

V_2H is a monoclinic hydride phase where the hydrogen atoms occupy octahedral sites with nearly tetragonal point symmetry and with the pseudotetragonal (001) axis pointing along one of the three cubic axes of the originally bcc host lattice [see Fig. 2(e)]. The sample preparation was performed in two steps. First, single-crystalline slices of vanadium were charged from the gas phase with appropriate amounts of hydrogen. Thus we obtained multidomain single crystals of V_2H. Second, a special heat treatment was applied. It led to the first V_2H crystal of sufficiently large size to allow neutron spectroscopy. The neutron-scattering experiments were performed with the use of the chopper–time-of-flight-spectrometers HRMECS and LRMECS at the IPNS spallation neutron source of the Argonne National Laboratory.[12] The incident neutron energies at HRMECS were 317, 494, 743, and 975 meV. The neutron detectors were positioned at $-14° < 2\theta < +20°$ and at four angles between 86° and 136°. The incident neutron energies at LRMECS were 110 and 1600 meV, while the neutron detectors covered the angular range between $-6°$ and $+90°$.

Figure 1 gives a synopsis of our spectroscopic results. The spectrum with $E_i = 0.5$ eV was taken with the multidomain single crystals, whereas the inset spectrum with $E_i = 1.6$ eV is from the single-domain single crystal. The striking features are (i) the regular repetition of double peaks [at lower energy transfer the splitting is only resolved with lower incident energies; see Fig. 2(b)]; and (ii) the sharp excitation at 223 meV.

Inelastic neutron scattering only observes an excitation if a component of the momentum transfer **Q** is parallel to the vibrational direction. In order to identify the fundamental vibrations, we exploit this directional dependence of the scattered intensity using the single-domain crystal; see Fig. 2. From the observation of only one peak with $\mathbf{Q} \parallel (010)$ [Fig. 2(a)] but of two peaks with $\mathbf{Q} \parallel (1\bar{1}0)$ [Fig 2(b)] we conclude that in the xy plane the normal vibrational modes are in the (100) and (010) pseudotetragonal directions. Thus, the hydrogen atom

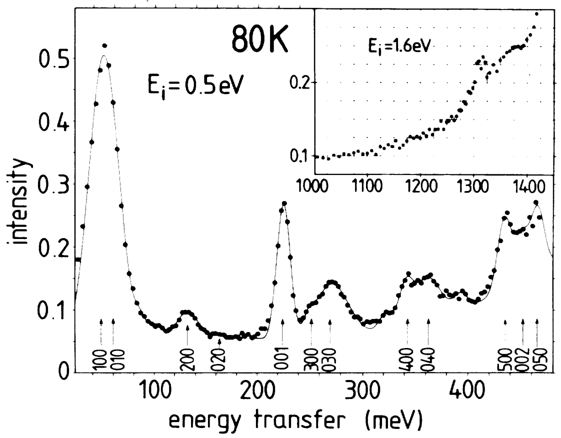

FIG. 1. Neutron spectra from β-V_2H at different incident neutron energies E_i. The line is the result of the fitting of Gaussians to the experimental spectrum in order to define the peak positions. The indices *lmn* mark our assignments for the different transitions.

vibrates with a higher frequency in a direction where the spacing between the metal atoms is smaller. Comparing Figs. 2(c) and 2(d) [with **Q**∥(001) in the former and **Q**⊥(001) in the latter case] we find that the excitation at 223 meV belongs to a vibration in the (001) direction; hence this vibration represents the third fundamental and cannot be an overtone of the peaks around 55 meV. 223 meV is a surprisingly high excitation energy for a fundamental H vibration in a metal; our single-crystalline results prove the suggestion by Klauder *et al.*[14] and terminate a long-lasting discussion about this subject in the scientific community.

Now we consider overtones of these fundamental vibrations. The spectrum of Fig. 1 is a sum of twelve spectra taken at scattering angles between −14° and +14° after background subtraction and shows the first five orders of the (100)/(010) vibrations. In order to see more orders we increased the incident neutron energy successively to 743, 975, and 1600 meV. In this way we necessarily also increased Q. Fortunately, for higher overtones n with higher excitation energies, also the maximum of their form factor, which for a harmonic oscillator is proportional to $Q^{2n}\exp(-\langle u^2\rangle Q^2)$, appears at larger Q. At very high incident energies Q varies strongly with the scattering angle θ. Therefore, the intensity of a given overtone n is concentrated in such a narrow angular range that it appears only in one detector bank. For this reason, the inset spectrum of Fig. 1, recorded at $2\theta = 14.7°$, exhibits as pronounced peaks only the thirteenth order of the (010) and the fourteenth order of the (100) vibrations. Lower excitations, of eleventh and twelfth order, e.g., appear in the spectrum at $2\theta = 6.3°$. We did not subtract a background from the inset spectrum, in order not to increase the noise. The strongly increasing background level at the high-energy side is an artifact of the time-of-flight method which occurs during the transformation from the time-of-flight scale to the energy scale. The excitation energies of the soft (100) vibrations are plotted versus the quantum number in Fig. 3. At high energies the energy levels are practically equidistant and indicate that in this energy range the potential in this direction is rather harmonic. At the lowest energies, however, the spacing resembles nearly that of a square well. Therefore, in the soft direction *qualitatively* the hydrogen potential has to be a parabola with a flattened bottom. In (010), the other soft direction, the potential is very similar. Figure 3 also displays the exci-

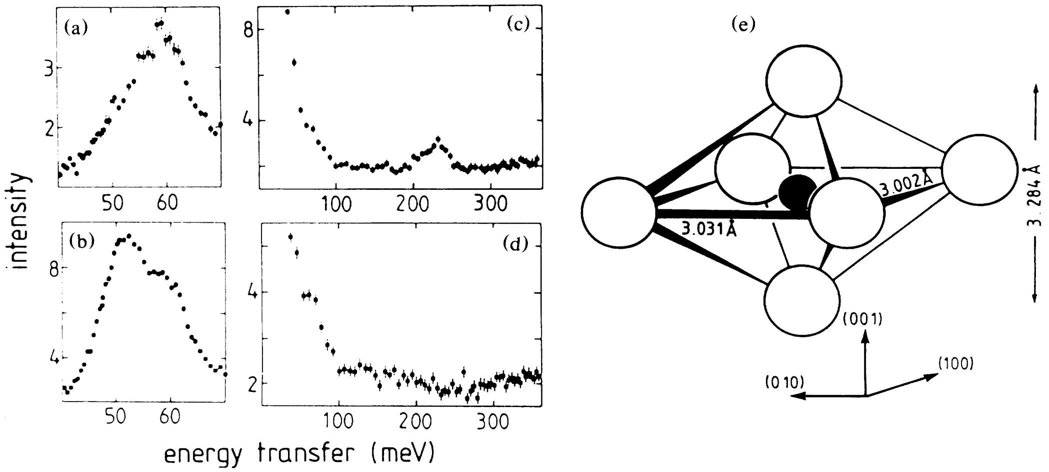

FIG. 2. Directional dependence of the fundamental hydrogen vibrations in β-V_2H: (a) **Q**∥(010), incident neutron energy 110 meV; (b) **Q**∥(0$\bar{1}$0), incident neutron energy 110 meV; (c) **Q**∥(001), incident neutron energy 743 meV; (d) **Q**⊥(001), incident neutron energy 743 meV; (e) geometry of the octahedral hydrogen site in β-V_2H (Ref. 13). The Miller indices are the pseudotetragonal ones.

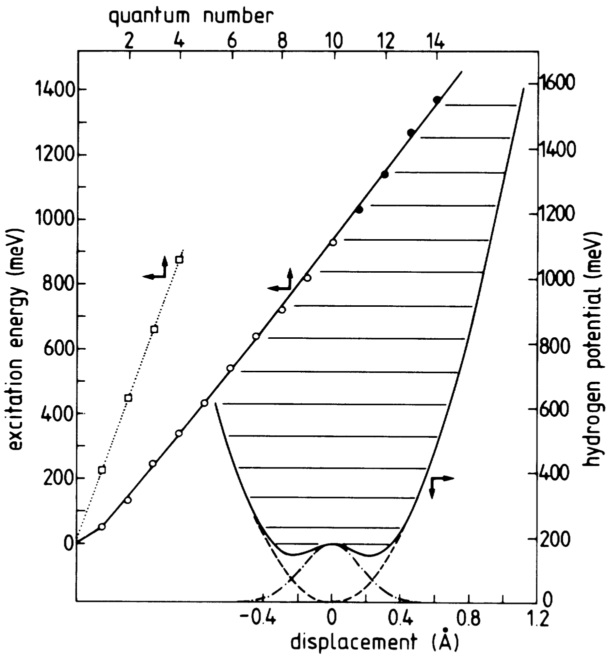

FIG. 3. Left-hand side: Hydrogen excitation energies in the stiff (001) direction (squares) and in the soft (100) direction [multidomain crystal, open circles; single-domain crystal, filled circle; experimental values in millielectronvolts: 50.2(10), 131.8(20), 249.5(30), 340(3), 435(4), 539(6), 639(8), 720(10), 820(10), 930(10), 1140(10), 1270(10), and 1380(10)]. The solid line connects the theoretically calculated frequencies in the (100) direction (50.3, 142.5, 234.4, 232.0, 431.0, 532, 633, 734, 837, 939, 1042, 1145, and 1251), the dotted line those in the (001) direction. Right-hand side: Resulting H potential in the soft (100) direction and the corresponding energy levels.

tation energies in the stiff (001) direction as a function of n. Other than in the xy plane the sequence of the observed vibrations is consistent with a harmonic oscillator potential.

For a more *quantitative* evaluation, we suppose that the hydrogen potential can be described as a superposition of three one-dimensional potentials. Thereby we neglect possible anharmonic coupling effects between different directions of vibration. From the excitation energies found for H on an octahedral site in Pd it was concluded that within experimental accuracy such coupling effects are negligible.[5] In all group Vb metal hydrides the optical H modes do not appear to exhibit any measurable dispersion[4]; i.e., direct H-H interactions are not significant and a single-particle potential is a good approximation. In order to model a harmonic potential with a flattened bottom we make the following *Ansatz:*

$$V(x) = \tfrac{1}{2} m\omega_0^2 x^2 + [b/(2\pi\sigma^2)^{1/2}]\exp(-x^2/2\sigma^2). \qquad (1)$$

An important practical advantage of this *Ansatz* is that, with the use of harmonic-oscillator wave functions as a basis, the matrix elements of the Hamiltonian $\langle n|H|m\rangle$ as well as the transition-matrix elements $\langle n|\exp(iQr)|m\rangle$ can be calculated analytically. Diagonalizing the Hamiltonian matrix we solved the Schrödinger equation and fitted the eigenvalues to the excitation energies. We used eighteen basis functions in order to calculate the lowest fourteen eigenvalues. Calculations with a larger basis did not change the results. Figure 3 compares the theoretical results for the (100) direction with the experimental data (explicitly listed in the figure caption) and displays the resulting potential. For the effective single-particle hydrogen potential of Eq. (1) we find the following parameters: for the (100) direction,

$$\hbar\omega_0 = 104\ \text{meV},\ b = 78.4\ \text{Å meV},\ \sigma = 0.174\ \text{Å};$$

for the (010) direction,

$$\hbar\omega_0 = 107\ \text{meV},\ b = 66.6\ \text{Å meV},\ \sigma = 0.170\ \text{Å};$$

for the (001) direction,

$$\hbar\omega_0 = 223\ \text{meV (harmonic oscillator)}.$$

Obviously our potential consisting of a parabola and a Gaussian reproduces the essential features of the vibrational spectrum of H in V_2H, namely, the nearly equidistant excitation energies at high energy transfers and the reduced spacing of the first overtones. While in general the relative agreement is better than 2%, we notice larger discrepancies for the second and third overtones. They can be removed by introduction of additional fine structure at the potential bottom, but they could also be due to nonlinear coupling effects between different vibrational directions. Independent of details, however, the potential bottom is comparatively flat in the xy directions over distances of about 0.6 Å. Comparing our potential with the semiempirical approach by Sugimoto and Fukai,[8] we find a general agreement with respect to the shape of the potential, both for the stiff as well as for the soft directions. However, quantitatively the width of their flat potential bottom is about 50% larger than our result.

Concerning the intensities we note that the second harmonics at 132 and 162 meV are by a factor of about 5–8 weaker than the two fundamentals around 55 meV. In the low-Q range of our experiment this intensity ratio is compatible with a harmonic oscillator. Surprisingly, however, from the transition-matrix elements $|\langle 0|e^{iQr}|n\rangle|^2$ of our model compared to the harmonic oscillator, we would expect more intense second harmonics. We have studied this shortcoming and found that whenever a one-dimensional harmonic potential is widened at the bottom in the direction of a square well—this is necessary in order to describe the level spacing—the orthogonality requirement for the different wave functions increases the 0-2 compared to the 0-1 transition-matrix element. Thus, we conclude that an accurate description of the H wave function cannot be achieved by a simple factorization into one-dimensional contributions. An answer to this interesting problem requires measurements of the peak intensities over an extended Q range which are in progress.

In summary, this experiment fully utilized the special characteristics of a spallation neutron source in combination with a unique sample: The one-domain single crystal led to an unambiguous assignment of the fundamental vibrations; the availability of high incident neutron energies at small scattering angles allowed an observation of overtones up to the fourteenth order. By means of an empirical one-dimensional potential the observed level spacing could be described.

We would like to thank M. Monkenbusch for helping us to determine the crystal orientation. For kind and skilled support during the experiment we thank C. K. Loong, R. Kleb, and the IPNS operation staff. We gratefully acknowledge partial support from the U. S. Department of Energy under Contract No. W-31-109-ENG-38.

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