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## Hydrogen wave functions in the metal hydrides ZrH<sub>2</sub> and NbH<sub>0.3</sub>

Susumu Ikeda†, Michihiro Furusaka†, Toshiharu Fukunaga‡ and A D Taylor§

† National Laboratory for High Energy Physics, Oho, Tsukuba-shi, Ibaraki-ken 305, Japan

‡ Department of Crystalline Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

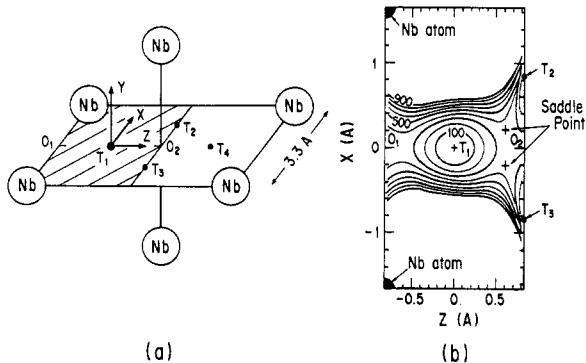
§ Rutherford Appleton Laboratory, Oxfordshire, UK

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**Abstract.** The hydrogen local vibrational modes of ZrH<sub>2</sub> and NbH<sub>0.3</sub> were observed by using a chopper neutron spectrometer coupled with a pulsed spallation neutron source. From the momentum transfer dependence of their modes, it was confirmed that the hydrogen wave functions for the first, second and third excited states in ZrH<sub>2</sub> are completely harmonic, and found that those for  $\epsilon = 220$  meV and  $\epsilon = 161$  meV in NbH<sub>0.3</sub> are very different from simple harmonic, although that for the first excited state ( $\epsilon = 115$  meV) seems to be harmonic.

### 1. Introduction

Measurements of the hydrogen vibrational local modes in metal hydrides [1–8] have provided important information about the hydrogen potential which strongly depends on the chemical and topological environments around a hydrogen atom. In the early investigations [5, 6], the hydrogen potential was discussed simply in terms of an anharmonic parameter,  $\beta$ . If the shape of the hydrogen potential,  $V(X)$ , in a given direction  $X$  is expressed as  $V(X) = A_2X^2 + A_4X^4$ , the  $n$ th excitation energy,  $\epsilon_n$ , can be approximated as  $\epsilon_n = n\hbar\omega + \beta(n^2 + n)$ , with  $\omega^2 = 2A_2/m$  and  $\beta = 3\hbar^2A_4/4m^2\omega^2$ . The term  $A_4X^4$  shifts the  $n$ th excitation energy relative to the harmonic energy,  $n\hbar\omega$ , by the amount  $\beta(n^2 + n)$ . Therefore, the hydrogen potential can be classified according to the value of  $\beta$  into three types: harmonic ( $\beta = 0$ ), trumpet-like ( $\beta < 0$ ) and well-like ( $\beta > 0$ ). In fact, detailed measurements of the local vibrational modes had been performed, and their anharmonic parameters determined, for example, the  $\beta$ -values of TiH<sub>2</sub> and ZrH<sub>2</sub> were almost zero (harmonic); the  $\beta$ -values of NbH<sub>0.31</sub> and TaH<sub>0.1</sub> were determined to be  $-5$  meV and  $-11$  meV, respectively (trumpet-like); the  $\beta$ -value of VH<sub>0.33</sub> was determined to be  $+11$  meV (well-like) [8]. Recently, a more exact approach for metal hydrides NbH and TaH has been taken, assuming that the hydrogen motion is like a three-dimensional (3D) anharmonic oscillator, where the  $x$ ,  $y$  and  $z$  motions of the hydrogen are no longer decoupled [7]. A similar approach with some modifications has been applied to NbH<sub>0.31</sub> and VH<sub>0.33</sub>, in order to extract the parameters of their hydrogen potentials using the measured excitation energies of the local modes [8]. From this



**Figure 1.** T and O sites in NbH<sub>0.3</sub> (a) and a two-dimensional display of the hydrogen potential proposed in [8] (b).

approach, it was found that the ground state and the first excited state in NbH<sub>0.3</sub> can be approximately described as harmonic [8]. The hydrogen potential,  $V(x, y, z)$ , for NbH<sub>0.3</sub> was also derived as

$$V(x, y, z) = m\omega_x^2 x^2/2 + m\omega_y^2 y^2/2 + m\omega_z^2 z^2/2 + ez(x^2 - y^2) + fx^2y^2 + g(x^2 + y^2)z^2 + C_{4x}(x^4 + y^4) + C_{4z}z^4 + C_{6z}z^6$$

where  $\hbar\omega_x = 147$  meV,  $\hbar\omega_y = 130$  meV,  $e = 1.246$  eV Å<sup>-4</sup>,  $f = 30.77$  eV Å<sup>-4</sup>,  $g = -4.23$  eV Å<sup>-4</sup>,  $C_{4x} = 1.373$  eV Å<sup>-4</sup>,  $C_{4z} = -3.807$  eV Å<sup>-4</sup> and  $C_{6z} = 2.272$  eV Å<sup>-6</sup>. However, there were a few assumptions made in this approach: that the potential also has minima at the T<sub>2</sub> and T<sub>3</sub> sites in NbH<sub>0.3</sub> (see figure 1); that the calculations are performed only considering diagonal terms; and that the wave function can be described by linear combinations of harmonic functions. If the actual hydrogen wave functions of the ground and excited states are, for example, extremely different from harmonic functions, the previous approach should be improved. It is, therefore, required to confirm the proposed potential and wave functions by using other approaches.

The aim of the present work was to observe the momentum transfer dependence ( $Q$ -dependence) of local vibrational mode intensities in NbH<sub>0.3</sub> and ZrH<sub>2</sub>, and to derive the wave functions directly. In the case of an excitation energy  $\gg kT$ , without any contribution from the host metal vibration, the inelastic neutron scattering intensity of the local modes of a powder sample,  $I(Q, \varepsilon_n)$ , is given by the transition probability from the initial state ( $\phi_0(X)$ ,  $\exp(ik_i \cdot X)$ ) to the final state ( $\phi_\mu(X)$ ,  $\exp(ik_f \cdot X)$ ), where  $\exp(ik_i \cdot X)$  and  $\exp(ik_f \cdot X)$  are the wave functions of the incident and scattered neutrons, respectively.  $\phi_0(x)$  is the wave function of the ground state and  $\phi_\mu(x)$  is that of an excited state with a transition energy from the ground state of  $\varepsilon_n$ . Since the interaction between a neutron and the hydrogen nucleus is given by a constant value ( $=V_0$ ),  $I(Q, \varepsilon_n)$  can be expressed as

$$I(Q, \varepsilon_n) = N_0 \sum_{\mu} \left\langle \left| \int (\phi_{\mu}(X) \exp(ik_f \cdot X))^* V_0 \exp(ik_i \cdot X) \phi_0(X) dX \right|^2 \right\rangle = AP(Q, \varepsilon_n)$$

and

$$P(Q, \varepsilon_n) = \sum_{\mu} \left\langle \left| \int \phi_{\mu}(X) \exp(iQ \cdot X) \phi_0(X) dX \right|^2 \right\rangle \quad (1)$$

where  $Q = k_i - k_f$  and  $A = N_0 V_0^2$ .  $N_0$  is the number of hydrogen nuclei in a sample.  $\langle \dots \rangle$

indicates averaging over the angle between  $Q$  and the direction of motion of the hydrogen. It should be noted that  $I(Q, \epsilon_n)$  is explicitly expressed in terms of the wave functions of the hydrogen. Therefore, measurements of  $I(Q, \epsilon_n)$  make possible a direct investigation of the wave functions. In the following sections we report on measurements of  $I(Q, \epsilon_n)$  for  $ZrH_2$  and  $NbH_{0.3}$ , and applications of (1) for estimating their wave functions.

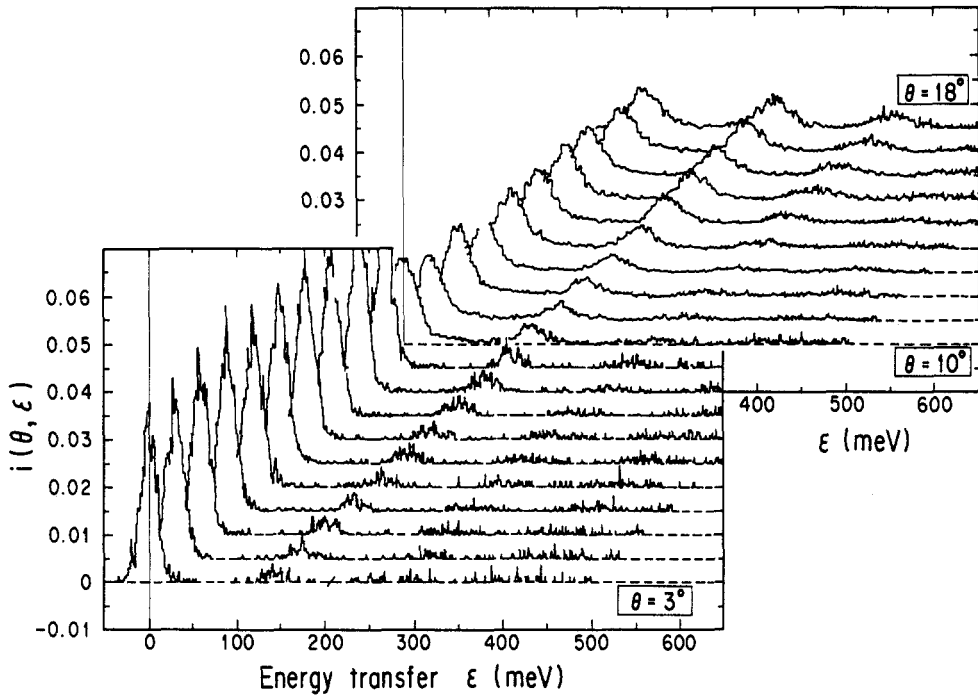
## 2. Measurements

Experiments were performed using the chopper neutron spectrometer HET at the Rutherford Appleton Laboratory. In the chopper spectrometer, the incident energy  $E_i$  was fixed and the final energy  $E_f$  was determined by the time of flight of the scattered neutrons. The energy transfer ( $\epsilon$ ) and momentum transfer ( $\hbar Q$ ) at a scattering angle of  $\theta$  were obtained from

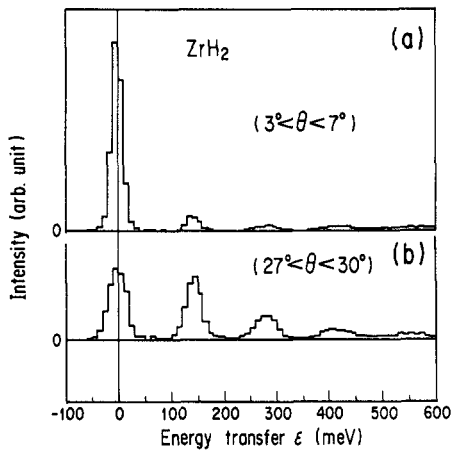
$$\epsilon = E_i - E_f \quad \hbar^2 Q^2 = E_i + E_f - 2\sqrt{E_i E_f} \cos(\theta). \quad (2)$$

In the HET, 10 detector banks were installed in the small-angle region,  $3^\circ < \theta < 7^\circ$ , and 25 detector banks were set up in the large-angle region,  $10^\circ < \theta < 30^\circ$ . Therefore, in one experiment we could measure  $I(Q, \epsilon_n)$  ( $n = 1, 2, \dots$ ) for 35 different values of  $Q$ . A powder sample of  $ZrH_2$  was packed into many small holes, each with diameter 1 mm, in a boron nitride plate with 1 mm thickness (area  $50 \times 50 \text{ mm}^2$ ), in order to reduce multiple scattering, and fixed in aluminium sample holders. The sample holder was cooled down to about 20 K. A powder sample of  $NbH_{0.3}$  was also packed into holes, each with a diameter of 3 mm. The incident energy used in both measurements was about 630 meV. Each neutron scattering spectrum of  $ZrH_2$  and  $NbH_{0.3}$  was obtained by subtracting the scattering from the sample holder, including the boron nitride plate, and normalised using the vanadium scattering intensity. Here no multiple-scattering correction was made.

Figure 2 shows local mode spectra of  $ZrH_2$  observed in both the small-angle and large-angle regions. The first, second and third excitations were observed at about 147, 294, 441 meV, respectively, consistently with previous measurements [8]. Figure 3 shows typical spectra summed over the small-angle (a) and large-angle (b) regions. In this figure, it is clear that the intensities of the local modes become larger at larger angles (i.e. for higher  $Q$ ). The neutron scattering intensity  $I(Q, \epsilon_n)$  can be given by  $(k_i/k_f)i(Q, \epsilon_n)/\eta(E_f)$ , where  $i(Q, \epsilon_n)$  is the observed intensity of the local mode and  $\eta(E_f)$  the detector efficiency. In order to achieve good statistics, the spectra observed at the two detector banks were summed, and the  $i(Q, \epsilon_n)$  ( $n = 1, 2, 3$ ) were obtained by integrating the intensity of each local mode around the peak. Figure 4 shows the measured  $I(Q, \epsilon_n)$  for  $ZrH_2$ . Here, the  $Q$  are calculated from (2) using the centre energies of the peaks and the centre angles of the detector banks. (Note that the scattering intensities for different energy levels,  $I(Q, \epsilon_n)$ , as shown in figure 4 are plotted on the same scale although the figure is given in arbitrary units.) In the case of  $NbH_{0.3}$ , the local mode spectrum was obtained by summing over 10 detector banks in the small-angle region and by summing over 5 detector banks in the large-angle region. Figure 5 shows typical raw data obtained by this method. One can see three peaks at 115, 160 and 220 meV, which correspond to the first excitation of the  $z$  motion, that of the  $x$  and  $y$  motions and the second excitation of the  $z$  motion. The  $I(Q, \epsilon_n)$  of  $NbH_{0.3}$  were obtained by fitting their peaks to Gaussians (see figure 5), and are shown in figure 6.



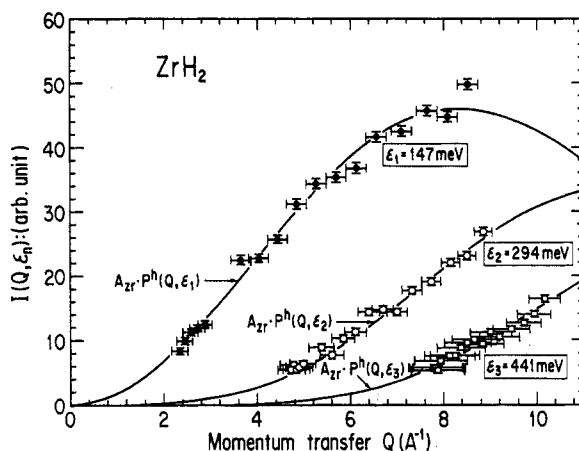
**Figure 2.** Neutron scattering spectra of  $\text{ZrH}_2$  obtained from a chopper spectrometer. The 10 spectra on the left-hand side of the figure were observed in the small-angle region, and the others were observed in the large-angle region.



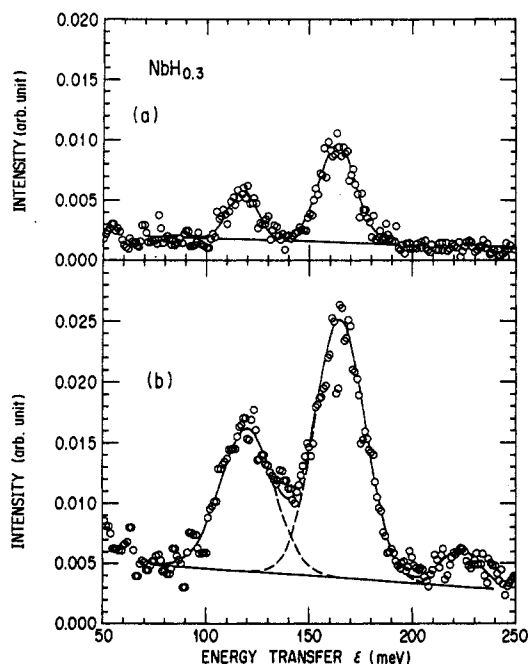
**Figure 3.** Typical spectra of  $\text{ZrH}_2$  obtained at small and large angles. (a) Spectrum summed over the region  $3^\circ < \theta < 7^\circ$ . (b) Spectrum summed over the region  $27^\circ < \theta < 30^\circ$ .

### 3. Discussion

At the start of the present approach, we can confirm that the  $Q$ -dependence of the local modes observed using the neutron scattering spectrometer HET can be completely described by (1). We selected a powder sample of  $\text{ZrH}_2$  as the standard sample to be

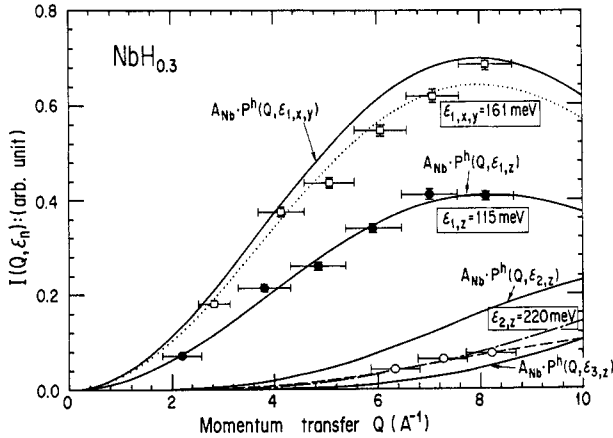


**Figure 4.** The neutron scattering intensity  $I(Q, \epsilon_n)$  of  $ZrH_2$ . Closed circles, open circles and open squares show observed values of  $I(Q, \epsilon_n)$  for  $\epsilon = 247, 294$  and  $441$  meV, respectively.



**Figure 5.** Typical spectra of  $NbH_{0.3}$  at small and large angles. (a) Spectrum summed over the region  $3^\circ < \theta < 10^\circ$ . (b) Spectrum summed over the region  $27^\circ < \theta < 30^\circ$ . Full and broken curves indicate the results of the fitting.

used in this approach. Since the anharmonic parameter  $\beta$  of  $ZrH_2$  is almost zero and no large split in the peaks at  $\epsilon = 147, 294$  and  $441$  meV has been observed, the hydrogen motion in  $ZrH_2$  can be considered as being an isotropic harmonic oscillator. Therefore, the hydrogen wave functions are described as being of harmonic type,  $\phi_{ijk}(X) = \Psi_i(\omega_x, x)\Psi_j(\omega_y, y)\Psi_k(\omega_z, z)$ , with a normal vibration of  $\hbar\omega$  ( $=\hbar\omega_x = \hbar\omega_y = \hbar\omega_z$ ) =  $147$  meV [8]. In such a simple case, one can easily calculate  $P^h(Q, \epsilon_n)$ . The suffix h indicates that  $P(Q, \epsilon_n)$  in (1) is calculated using harmonic wave functions. Since the



**Figure 6.** The neutron scattering intensity  $I(Q, \varepsilon_n)$  of  $\text{NbH}_{0.3}$ . Closed circles, open squares and open circles show observed values of  $I(Q, \varepsilon_n)$  for  $\varepsilon = 115, 161$  and  $220$  meV, respectively.

peaks observed at  $\varepsilon = 147, 294$  and  $441$  meV are considered to correspond to the transitions from the ground state to  $i + j + k = 1, 2$  and  $3$  states, the  $Q$ -dependence of local modes,  $I(Q, \varepsilon_n)$ , can be obtained as  $A_{Zr} P^h(Q, \varepsilon_n)$ , where  $A_{Zr}$  is a constant for this  $\text{ZrH}_2$  sample. The  $P^h(Q, \varepsilon_n)$  ( $n = 1, 2, 3$ ) are derived from (1) as follows:

$$\begin{aligned} P^h(Q, \varepsilon_1 = 147 \text{ meV}) &= (Q^{*2}/2) \exp(-Q^{*2}/2) \\ P^h(Q, \varepsilon_2 = 294 \text{ meV}) &= (Q^{*4}/8) \exp(-Q^{*2}/2) \\ P^h(Q, \varepsilon_3 = 441 \text{ meV}) &= (Q^{*6}/48) \exp(-Q^{*2}/2) \end{aligned} \quad (3)$$

where  $Q^* = Q/\alpha$  and  $\alpha = \sqrt{m\omega/\hbar}$ . It is remarkable that the  $Q$ -dependence of the transition probability for the isotropic harmonic oscillator can be scaled by  $1/\alpha$ . The three full curves in figure 4 indicate  $A_{Zr} P^h(Q, \varepsilon_n)$  ( $n = 1, 2, 3$ ) calculated with  $\hbar\omega = 147$  meV [8] and  $A_{Zr} = 12.5$ . The consistency between the measured and calculated values is very good. This result makes clear that the wave functions for the first, second and third excited states in  $\text{ZrH}_2$  are perfectly harmonic, and strongly indicates that the wave function can be directly investigated by measurements of  $I(Q, \varepsilon_n)$ .

Let us apply this approach to a more general system:  $\text{NbH}_{0.3}$ . In this case, the three peaks observed at 115, 161 and 220 meV correspond to the first excitation of the  $z$  motion, that of the  $x$  and  $y$  motion, and the second excitation of the  $z$  motion, respectively. The results of the previous approach [8] have suggested that the wave functions of the ground and excited states can be approximately expressed using harmonic forms,  $\phi_{ijk}(X) = \Psi_i(\omega_x, x)\Psi_j(\omega_x, y)\Psi_k(\omega_z, z)$ , with two kinds of normal vibration:  $\hbar\omega_z = 130$  meV and  $\hbar\omega_x (= \hbar\omega_y) = 147$  meV [8]. From (1) we can also derive  $P^h(Q, \varepsilon_n)$  for the first, second and third excitations of the  $z$  motion, and the first excitation of  $x$  and  $y$  motion. These are  $P^h(Q, \varepsilon_{1,z})$ ,  $P^h(Q, \varepsilon_{2,z})$ ,  $P^h(Q, \varepsilon_{3,z})$  and  $P^h(Q, \varepsilon_{1,x,y})$ :

$$\begin{aligned} P^h(Q, \varepsilon_{1,z}) &= (Q^2/2\alpha_z^2) \exp(-\Delta) \frac{1}{2}(I_0(\gamma) + I_1(\gamma)) \\ P^h(Q, \varepsilon_{1,x,y}) &= (Q^2/2\alpha_x^2) \exp(-\Delta)(I_0(\gamma) - I_1(\gamma)) \\ P^h(Q, \varepsilon_{2,z}) &= (Q^4/8\alpha_z^4) \exp(\Delta) \left( \frac{3}{4}I_0(\gamma) + 2I_1(\gamma) + \frac{1}{2}I_2(\gamma) \right) \end{aligned}$$

$$\begin{aligned}
P^h(Q, \varepsilon_{3,z}) = & (Q^6/48\alpha_z^6) \exp(-\Delta) \left[ \frac{5}{8} I_0(\gamma) + 4I_1(\gamma) \right. \\
& + \frac{3}{2} I_2(\gamma) + (8/\pi) \exp(-\gamma) B\left(\frac{3}{2}, \frac{3}{2}\right) {}_1F_1\left(\frac{3}{2}; 4; 2\gamma\right) \\
& \left. - (4/\pi) \exp(-\gamma) B\left(\frac{3}{2}, \frac{3}{2}\right) {}_1F_1\left(\frac{3}{2}; 3; 2\gamma\right) \right] \quad (4)
\end{aligned}$$

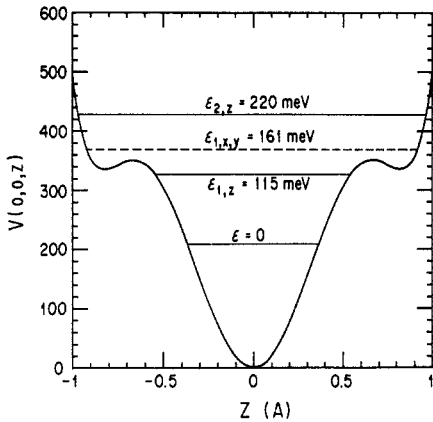
where  $\alpha_x = \sqrt{m\omega_x/\hbar}$ ,  $\alpha_z = \sqrt{m\omega_z/\hbar}$ ,  $\gamma = Q^2(\frac{1}{4}\alpha_z^2 - \frac{1}{4}\alpha_x^2)$  and  $\Delta = Q^2(\frac{1}{4}\alpha_z^2 + \frac{1}{4}\alpha_x^2)$ .  $I_n(x)$  ( $n = 0, 1, \dots$ ) is a modified Bessel function,  ${}_1F_1$  a hypergeometric function and  $B$  a  $B$ -function. In the previous study [8], it was concluded that the wave functions for the ground and first excited state of the  $z$  motion ( $\varepsilon = 115$  meV) are almost harmonic. Therefore, we calculated  $A_{Nb}P^h(Q, \varepsilon_{1,z})$ , using  $\hbar\omega_z = 130$  meV and  $\hbar\omega_x (= \hbar\omega_y) = 147$  meV obtained in a previous work [8]. The results are shown by a full curve in figure 6. Here,  $A_{Nb}$  was 36. The consistency between the measured and calculated values is fairly good. This means that the ground state and the first excited state of the  $z$  motion should be represented by harmonic functions. This is perfectly consistent with the previous result [8].  $A_{Nb}P^h(Q, \varepsilon_{1,x,y})$  and  $A_{Nb}P^h(Q, \varepsilon_{2,z})$  were also calculated using the same values of  $\hbar\omega_x (= \hbar\omega_y)$ ,  $\hbar\omega_z$  and  $A_{Nb}$ . These results are shown as full curves in figure 6. There is a clear difference between the calculated and measured values. This means that the wave functions of the excited states are very different from the 'normal' harmonic ones. In order to determine the difference,  $0.92A_{Nb}P^h(Q, \varepsilon_{1,x,y})$  and  $0.47A_{Nb}P^h(Q, \varepsilon_{2,z})$  were plotted and are shown in figure 6 as a dotted curve and a broken curve, respectively. The consistency between the modified lines and the measured values is good. This result can be explained well if the wave functions of the second excited state of the  $z$  motion and the first excited state of the  $x$  ( $y$ ) motion are 'small' harmonic functions with two normal frequencies of  $\hbar\omega_x (= \hbar\omega_y) = 147$  meV and  $\hbar\omega_z = 130$  meV, but with small amplitudes. In the previous study [8], the hydrogen potential of  $NbH_{0.3}$  was classified as a trumpet-like potential and numerically estimated as  $V(x, y, z)$  (see figure 1). The estimated potential  $V(0, 0, z)$  is displayed with the energy levels of the ground and excited states in figure 7. This figure indicates that the potential deforms at a height of about 350 meV (from the bottom) and that excited states higher than  $\varepsilon = 161$  meV exist above 350 meV although the ground state and the first excited state with  $\varepsilon = 115$  meV exist below. Moreover, figure 1 shows that there are saddle points with a height of about 350 meV (from the bottom) between the  $T_1$  site and the other T sites. It is, therefore, expected that the hydrogen waves for the excited states at energies higher than  $\varepsilon = 161$  meV can 'escape' from the  $T_1$  site to the  $T_2$  and  $T_3$  sites or, at least, change from being harmonic. Assuming a linear combination of one-dimensional harmonic wave functions,  $\varphi_i(x) = p\Psi_i(\omega, x) + q\Psi_i(\omega, x - a)$ , we will calculate the  $Q$ -dependence of

$$P_i(Q) = \left| \int \varphi_i(x) \exp(iQ \cdot x) \Psi_0 dx \right|^2.$$

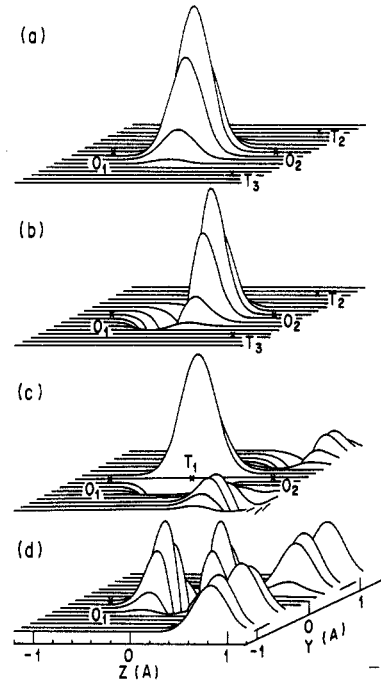
Here,  $p^2 + q^2 = 1$  and  $a$  is the distance between T sites.  $P_1(Q)$  is expressed as

$$\begin{aligned}
P_1(Q) = & \left| \int \varphi_1(x) \exp(iQ \cdot x) \Psi_0(\omega, x) dx \right|^2 \\
= & P_1(\text{normal}) [p^2 + q^2(1 + \alpha^4 a^2/Q^2) \exp(-\alpha^2 a^2/2) \\
& + 2pq(\cos(aQ/2) - \alpha^2 a/Q \sin(aQ/2)) \exp(-\alpha^2 a^2/4)] \quad (5)
\end{aligned}$$





**Figure 7.** The hydrogen potential and excited level in NbH<sub>0.3</sub>. The full lines of the energy levels indicate the ground state ( $\epsilon = 0$ ) and the excited states of the  $z$  motion ( $\epsilon = 115$  and  $220$  meV), and the broken line the excited state of  $x$  ( $y$ ) motion ( $\epsilon = 161$  meV).



**Figure 8.** Hydrogen wave functions in NbH<sub>0.3</sub>. (a) ground state; (b) excited state of  $\epsilon = 115$  meV; (c) excited state of  $\epsilon = 161$  meV; (d) excited state of  $\epsilon = 220$  meV.

where  $\alpha = \sqrt{m\omega/\hbar}$ .  $P_1(\text{normal})$  is  $Q^2/2\alpha^2 \exp(-Q^2/2\alpha^2)$ , which is the transition probability of a normal harmonic oscillator without ‘escape’. If  $a = 1.155 \text{ \AA}$  and  $\hbar\omega = 130 \text{ meV}$  (in the case of NbH<sub>0.3</sub>),  $P_1(Q)$  can be approximated as

$$P_1(Q) = P_1(\text{normal}) p^2 (1 + O(10^{-2})) \quad (\text{for } Q > 1 \text{ \AA}^{-1}). \quad (6)$$

Generally, a relation similar to (6) can be obtained for  $P_i(Q)$  ( $i = 2, 3, \dots$ ). It indicates that the probability of transition to an excited state,  $\varphi_i(x) = p\Psi_i(\omega, x) + q\Psi_i(\omega, x - a)$ , has a  $Q$ -dependence analogous to that of the normal case, although the amplitude is decreased by a factor  $p^2$ . This feature is just that of  $I(Q, \epsilon = 160 \text{ meV})$  and  $I(Q, \epsilon = 220 \text{ meV})$  observed for NbH<sub>0.3</sub>. It may therefore be reasonable to define the excited states due to  $\epsilon = 160$  and  $220 \text{ meV}$ ,  $\varphi_1^x(X)$  (and  $\varphi_1^y(X)$ ) and  $\varphi_2^z(X)$ , by  $p\phi_{ijk}(X) + q\phi_{ijk}(X - X_2) + q\phi_{ijk}(X - X_3)$ , where  $p^2 + 2q^2 = 1$  and  $X_2$  and  $X_3$  are the coordinates of the T<sub>2</sub> and T<sub>3</sub> sites. Since the values obtained for  $p^2$  for  $\epsilon = 160$  and  $220 \text{ meV}$  are 0.92 and 0.47, respectively, their wave functions should be described as

$$\varphi_1^x(X) = 0.96\phi_{100}(X) + 0.2\phi_{100}(X - X_2) + 0.2\phi_{100}(X - X_3)$$

and

$$\varphi_2^z(X) = 0.69\phi_{002}(X) + 0.51\phi_{002}(X - X_2) + 0.51\phi_{002}(X - X_3) \quad (7)$$

where  $\phi_{ijk}(X) = \Psi_i(\omega_x, x)\Psi_j(\omega_y, y)\Psi_k(\omega_z, z)$ ,  $\phi_{ijk}(X - X_2) = \Psi_i(\omega_x, z - b)\Psi_j(\omega_y, y)\Psi_k(\omega_z, x - b)$  and  $\phi_{ijk}(X - X_3) = \Psi_i(\omega_x, -z - b)\Psi_j(\omega_y, y)\Psi_k(\omega_z, -x - b)$ .

Here,  $b$  is  $0.825 \text{ \AA}$ . The proposed hydrogen wave functions on the  $x = 0$  plane are shown in figure 8. From these proposed wave functions, the same values as for the dotted and broken curves shown in figure 6 can also be obtained. These results indicate that it is possible to propose (7) as the wave function for  $\varepsilon = 161$  and  $220 \text{ meV}$ . Note that the value of  $p$  in  $\varphi_1^{\pm}(X)$  is approximately 1. That the wave function for  $\varepsilon = 161 \text{ meV}$  is approximately harmonic is not so very different from the previous result [8]. Sugimoto and Fukai [9] assumed a double Born–Mayer potential and calculated the wave functions for the ground and excited states ( $\Psi_0$ ,  $\Psi_1^{\pm}$  and  $\Psi_2^{\pm}$  in [9]) by the method of Kimball and Shortley [10]. Their results (figure 3(a) and (b) in [9]) also show that the small portion of the hydrogen wave corresponding to  $\varepsilon = 161 \text{ meV}$  exists at the neighbouring pair of T sites, although the ground state and the first excited state corresponding to  $\varepsilon = 115 \text{ meV}$  are completely localised at the original T site. The feature of ‘escape’ at  $\varepsilon = 161 \text{ meV}$  estimated by the present measurement corresponds to their result very well.

Since the wave functions for  $\varepsilon = 220 \text{ meV}$ , unfortunately, have not been explicitly discussed, we cannot here compare our result with the others. Note that the wave functions for  $\varepsilon = 220 \text{ meV}$  are still not identified exactly by the present measurements. For example, if  $\varphi_2^{\pm}(X)$  is given by a ‘mixture’ state  $r\phi_{002}(X) + s\phi_{003}(X)$ ,  $I(Q, \varepsilon_n = 220 \text{ meV})$  should be expressed as  $r^2 A_{Nb} P^h(Q, \varepsilon_{2,z}) + s^2 A_{Nb} P^h(Q, \varepsilon_{3,z})$ , where  $r^2 + s^2 = 1$ . The chain curve in figure 6 shows calculated values for the case where  $r^2 = 0.3$ . In order to identify it exactly, one must observe the  $Q$ -dependence in a wider  $Q$ -range, for example,  $1 < Q < 12 \text{ \AA}^{-1}$  (see figure 6). However, the present measurement at least suggests that the wave function for  $\varepsilon = 220 \text{ meV}$  is very different from the simple harmonic wave function, and that it should be calculated by a more exact method.

Generally, if one wants to obtain exact wave functions from the local mode spectrum, one must observe many local mode peaks, assume a very complicated potential with many parameters and calculate the energy levels with a large linear combination of the harmonic wave functions. Since the wave functions are indirectly determined under the many assumptions used in this procedure, it seems difficult to investigate their exact features. In principle, our present approach makes a direct investigation of the wave function possible. This point is a big advantage and the best use of this may be in ascertaining whether the wave functions proposed on the basis of other experimental results and theories are appropriate or not.

In this paper we reported on the  $Q$ -dependence of local modes, confirmed that the hydrogen wave functions for the first, second and third excited states in  $ZrH_2$  are completely harmonic, and proposed for the first time the wave functions due to the higher excited state of  $NbH_{0.3}$ . Our results suggest that the measurement of the  $Q$ -dependence is very useful for confirmation or estimation of wave functions.

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## References

- [1] Kai K, Ikeda S, Fukunaga T, Watanabe N and Suzuki K 1983 *Physica B* **120** 342

- [2] Richter D 1984 *Proc. Workshop on High Energy Excitation in Condensed Matter (Los Alamos, 1984)* LA-10227 p 559
- [3] Richter D and Shapiro S M 1980 *Phys. Rev. B* **22** 599
- [4] Richter D, Rush J J and Rowe J M 1983 *Phys. Rev. B* **27** 6227
- [5] Ikeda S, Watanabe N and Kai K 1983 *Physica B* **120** 131
- [6] Hempelmann R, Richter D and Kollmar A 1981 *Z. Phys. B* **44** 159
- [7] Eckert J, Goldstone J A, Tonks D and Richter D 1983 *Phys. Rev. B* **27** 1980
- [8] Ikeda S and Watanabe N 1987 *J. Phys. Soc. Japan* **56** 565
- [9] Sugimoto H and Fukai Y 1981 *J. Phys. Soc. Japan*. **50** 3709
- [10] Kimball G E and Shortley G H 1934 *Phys. Rev.* **45** 815