PHYSICAL REVIEW B VOLUME 22, NUMBER 2 15 JULY 1980

Study of the temperature dependence of the localized vibrations of H and D in niobium

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(Received 16 January 1980)

The second harmonic of the local deuterium vibration in $NbD_{0.85}$ has been observed for the first time. Its energy $\hbar\omega = 170$ meV is 7 meV below the harmonic value of twice the lower local-mode energy, $2\hbar\omega_1$. The measured isotope effect for the lowest local-mode energy is $\omega_1^H/\omega_1^D = 1.365 \pm 0.005$ which differs from the harmonic value of $(M_D/M_H)^{1/2} = \sqrt{2}$. The temperature dependence of the local modes for both the deuteride and hydride system exhibit pronounced precursor effects prior to the $\beta \rightarrow \alpha'$ order-disorder phase transition.

I. INTRODUCTION

The investigation of the dynamics of H and D in the bcc metals, Ta, Nb, and V has attracted scientific interest over a long period of time.[1] Of particular interest is the measurement of the local-mode energies since this provides information about the potential seen by the light atoms. Accurate knowledge of H potential is of particular importance in view of the possible quantum-mechanical origin of the fast H diffusion in these metals.[2,3] Most earlier experiments have been carried out by either neutron transmission[4] or time-of-flight technique[5,6] which have poor energy resolution. For $NbH_{0.85}$ in the ordered β phase, Pan *et al.*[7] reported two vibrational levels at 120 and 165 meV. The resolution-corrected width was estimated at 18 ± 3 meV for both levels. More recently, coherent scattering experiments on $NbD_{0.6}$ single crystals in the disordered α' phase revealed dispersionless optic modes at 79.3 ± 2 meV and 111.5 ± 2 meV (Ref. 8) and no intrinsic linewidths. Similarly, Lottner *et al.*[9] found local modes at 86 and 120 meV in the β phase of $NbD_{0.75}$. However, there has been no systematic investigation of the temperature dependence of these modes near the order-disorder phase transition nor have the higher harmonics of the local modes been observed.

In this paper, we report a high-resolution study of the localized H (D) vibrations in $NbD_{0.85}$ and $NbH_{0.82}$. We measure the temperature dependence of both the linewidth and the positions of the local modes in the neighborhood of the β-α' order-disorder phase transition. At low temperatures, a well-defined second harmonic of the lower D vibration is observed. This indicates a very stiff potential in spite of the low activation energy for diffusion.[10]

II. THEORY

Hydrogen dissolved in niobium occupies tetrahedral interstitial sites. According to their tetragonal point symmetry, the localized H vibrations are split into two levels, the upper one being twofold degenerate. Considering only coupling to the next nearest four Nb atoms by a longitudinal force constant f the dynamical matrix ϕ for the localized vibrations has the form

$$\phi = \tfrac{4}{5} f \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} . \tag{1}$$

For the case of only longitudinal forces, the ratio between the upper and lower frequencies, ω_2/ω_1, is given by $\sqrt{2}$.

The apparent absence of dispersion even at high D concentrations[8,9] indicates that direct interactions between the D (H) atoms are small. Thus, as a first step, we can treat the hydrogen or deuterium excitations as uncoupled oscillators. The double-differential neutron cross section $\partial^2\sigma/\partial\omega\partial\Omega$ can be calculated analytically for a harmonic oscillator with tetragonal point symmetry and including all higher harmonics.[11,12]

$$\frac{\partial^2\sigma}{\partial\omega\partial\Omega} = \frac{\sigma^{\text{tot}}}{4\pi}\frac{k_f}{k_i}\exp[-2W(Q)]\exp(\tfrac{1}{2}\hbar\omega\beta) \times \sum_{\substack{n=-\infty \\ m=-\infty}}^{\infty} I_n(y_1)I_m(y_2)\delta(\hbar\omega - n\hbar\omega_1 - m\hbar\omega_2) \tag{2}$$

with the Debye-Waller factor

$$2W(Q) = \frac{\hbar Q^2}{6M}\left(\frac{1}{\omega_1}\coth(\tfrac{1}{2}\hbar\omega_1\beta) + \frac{2}{\omega_2}\coth(\tfrac{1}{2}\hbar\omega_2\beta)\right)$$

and the argument

$$y_{1\,(2)}=(2)\frac{\hbar Q^2}{6M\omega_{1\,(2)}}\operatorname{csch}(\tfrac{1}{2}\hbar\omega_{1\,(2)}\beta)\,.$$

σ^{tot} is the total neutron cross section, k_i and k_f are the incident and scattered neutron wave vectors, M is the H (D) mass, $\beta=1/k_BT$, $\hbar\vec{Q}=\hbar(\vec{k}_i-\vec{k}_f)$ is the momentum transferred to the sample, and $I_n(y)$ is the modified Bessel function of the first kind. For $\hbar\omega\gg k_BT$ and small arguments, Eq. (1) yields for energy-loss processes

$$\frac{\partial^2\sigma}{\partial\omega\partial\Omega}=\frac{\sigma^{\text{tot}}}{4\pi}\frac{k_f}{k_i}\exp[-2W(Q)]\sum_{\substack{n=0\\m=0\\m+n>0}}^{\infty}\frac{1}{n!}\frac{1}{m!}\left(\frac{\hbar^2Q^2}{6M\omega_1}\right)^n\left(\frac{\hbar^2Q^2}{3M\omega_2}\right)^m\delta(\hbar\omega-n\omega_1-m\omega_2)\,. \tag{3}$$

Equation (3) allows the calculation of the intensity relation between the different harmonics for H (D) in Nb under the assumption of a harmonic potential. For our experiment, where Q is essentially defined by the incident energy, the intensity ratio between the first and second harmonic of the lower D vibration $I(\omega_1^{\text{D}})/I(2\omega_1^{\text{D}})=6.4$. For ω_2^{D}, the intensity ratio is $I(\omega_2^{\text{D}})/I(2\omega_2^{\text{D}})=3.6$.

Now let us consider small anharmonic disturbances to the potential of the form $c_3x^3+c_4x^4$ where c_3 and c_4 are the corresponding force constants. The value of c_4 affects the frequency in first-order perturbation theory and c_3 in second-order perturbation theory. Both contributions have the same order of magnitude. The influence on the frequencies is twofold: (i) They shift the phonon frequencies relative to the ground state by an amount[13]

$$\Delta E=-\frac{3}{2}\frac{\hbar^2}{Mc_2}\left(\frac{5}{2}\frac{c_3^2}{c_2}-c_4\right)(n^2+n)=-\frac{\alpha}{M}(n^2+n)\,, \tag{4}$$

where c_2 is the harmonic force constant, and (ii) assuming that the potentials for H and D are identical[14] the anharmonic terms also cause deviations from the harmonic isotope effect. For the first level we obtain

$$\hbar\omega_1^{\text{H (D)}}=\hbar\left(\frac{4}{5}\frac{f}{M^{\text{H (D)}}}\right)^{1/2}-\frac{2\alpha}{M^{\text{H (D)}}}\,. \tag{5}$$

In the next step we estimate the influence of the forces mediated by the elastic H-H interaction on the localized vibrations. Since the detailed form of the elastic interaction, in particular its angular dependence, is very complicated, we give only an order-of-magnitude estimate for the longitudinal force constants which can be calculated as the second derivatives of the elastic potential, $V(r)$:

$$V(r)=-\frac{\Delta}{r^3}\,. \tag{6}$$

We approximate the interaction strength Δ by the values calculated by Horner and Wagner[15] who evaluated the H-H interaction energies for dilute systems from the Kanzaki forces by using the phonon Green's functions for Nb. Owing to the angular dependence of $V(r)$, Δ is different for each crystal direction and can be attractive or repulsive. The longitudinal force constant between an H (D) atom at $r=0$ and $r=r_i$ is then given by

$$c_i=\frac{1}{2!}\left.\frac{\partial^2V}{\partial r^2}\right|_{r_i}=-\frac{6\Delta}{r_i^5}\,. \tag{7}$$

In the β phase the H (D) atoms are ordered along chains in [110] direction causing a slight orthorhombic distortion.[16] The polarization of the lower-lying optic mode thereby is perpendicular to the chain axis. The largest longitudinal force-constant coupling with this mode stems from H (D) atoms in adjacent chains. Its value of about 300 dyn/cm is smaller than 1% of the corresponding Nb-H (D) force constant $\frac{4}{5}f\,(f\simeq73000$ dyn/cm) and far outside experimental detectability. The longitudinal force constant in the chain direction would be ~−900 dyn/cm which again is too small to be measured.

Above room temperature at 390 K, there is a β-α' order-disorder phase transition and precursor effects are known to occur. H (D) atoms leave their sites along the chains and occupy "forbidden" interstitials. Measurements of the β-phase superstructure reflection $(1,\frac{1}{2},\frac{1}{2})$ on a $\text{NbH}_{0.82}$ powder sample revealed a remarkable intensity decrease prior to the phase transition. The probability to occupy a non-β site was found to increase to about 17% before the phase transition takes place.[17] The elastic forces caused by the disordered H (D) atoms can vary considerably and depend upon the sites which are occupied. For example, an H (D) atom displaced by one jump from its proper site approaches more closely at least one other H (D) atom. The result of the elastic interaction would be a longitudinal force constant of −3000 dyn/cm which would decrease the frequency by about 5%. Since the H-H interaction between close neighbors is generally attractive,[15-18] it tends to lower the local-mode frequency. Thus, the onset of disorder is expected to shift the frequencies to lower values and to broaden the spectra by an amount similar to the shift reflecting the distribution of environments. At short distances, in addition to the elastic forces, electronic contributions due to the Friedel oscillations caused by the shielded proton charge will also contribute. However, as the analysis of structure data shows,[18] the net effect is still attractive for close H distances.

III. EXPERIMENTAL

The experiments have been performed at the Brookhaven High Flux Beam Reactor using a triple-axis spectrometer. The instrument was operated by varying the incident energy and using a 15-cm cooled Be filter as an analyzer. Be (002) and Be (110) reflections were used as monochromators. The collimation in front of the monochromator, between monochromator and sample, and sample and Be filter was varied between 20-20-20, 40-20-40, and 40-40-40 min. The Be-filter technique for inelastic scattering works on the basis of the filter characteristics of Be which transmits only neutrons in the energy range $0 \leqslant E \leqslant 5.2$ meV. For the cooled Be, the cutoff is quite sharp and the transmission below 5.2 meV is better than 90%. This results in high-energy resolution combined with high-intensity at the required energy transfers between 70 and 180 meV. Since $k_f = 1.1\,(+0.4, -1.1)$ is small and fixed by the filter, constant-Q scans are possible only over limited energy ranges in this technique. Energy transfers in the range of $50 < \hbar\omega < 200$ meV were performed both at constant Q using three values of Q (5.34, 6.38, 6.99 Å^{-1}) and at constant angle.

Using the Be filter as an analyzer and the appropriate Be reflection for the monochromator, the energy resolution of monochromator and analyzer parts of the instrument can be made comparable. The resolution function was calculated by folding the filter transmission curve, approximated by a step function between 0 and 5.2 meV, with the resolution function of the monochromator. Resolution widths between 6 and 10 meV FWHM (full width at half maximum) are obtained depending on monochromator, incident energy, and collimation.

The experimental results were fitted with a resolution-convoluted superposition of two Lorentzians. The intensity of the higher-energy vibration was kept fixed at twice the energy of the lower one according to Eq. (2). In order to accommodate for the intensity variation due to changes in Q, a phonon form factor, $Q^2 \times \exp[-2W(Q)]$, was taken into account. The Debye-Waller factor $2W(Q)$ was evaluated on the basis of a Debye model for Nb [to account for the band modes of the H (D)] and the contributions from the localized vibration itself [Eq. (2)]. The background was allowed to vary linearly with energy transfer. The agreement of the results for linewidth and position obtained under different experimental configurations confirms the method of data evaluation.

The $\text{NbD}_{0.85}$ sample was a single crystal cylindrical in shape with a diameter of 2.5 cm and of 2.5 cm a height, while the $\text{NbH}_{0.82}$ sample consisted of small single crystalline pieces 0.1–0.2 cm thick stacked together in a random manner. The total weight of the $\text{NbH}_{0.82}$ sample was 6 g.

IV. RESULTS

Figure 1 presents spectra obtained on $\text{NbD}_{0.85}$ for several temperatures. At 10 and 300 K, the D atoms are ordered, whereas at 422 K the sample is in the disordered α' phase and the D atoms

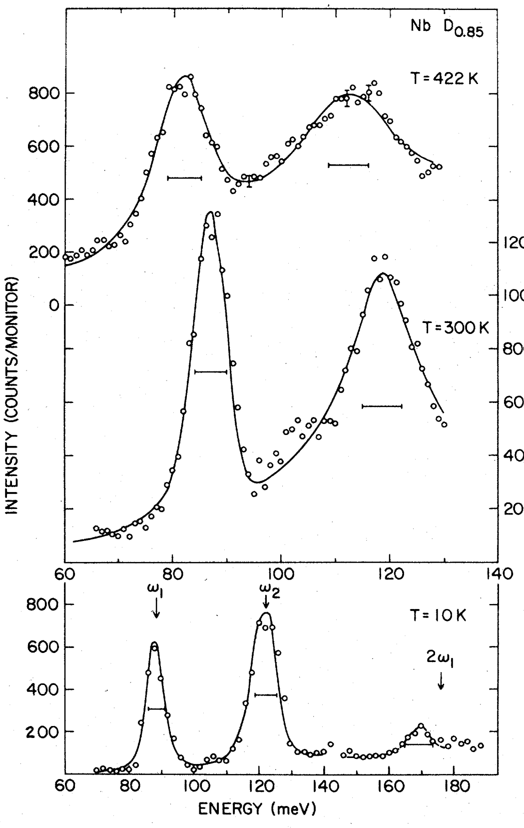

FIG. 1. Inelastic spectra obtained from $\text{NbD}_{0.85}$ at three different temperatures. Typical counting times varied from 5 min at 70 meV to 60 min near 200 meV. The bars give the resolution width for each peak. The arrow at $2\omega_1$ shows the position of the second harmonic expected for a harmonic oscillator. The solid lines are the result of the fitting procedure.

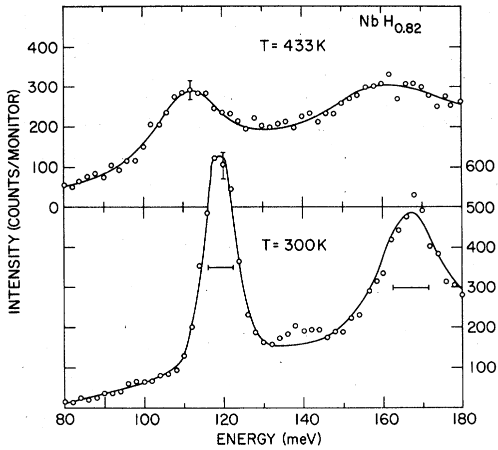

FIG. 2. Inelastic spectra obtained from $NbH_{0.82}$. The bars give the resolution of the peak positions; the solid line is a result of the fitting procedure.

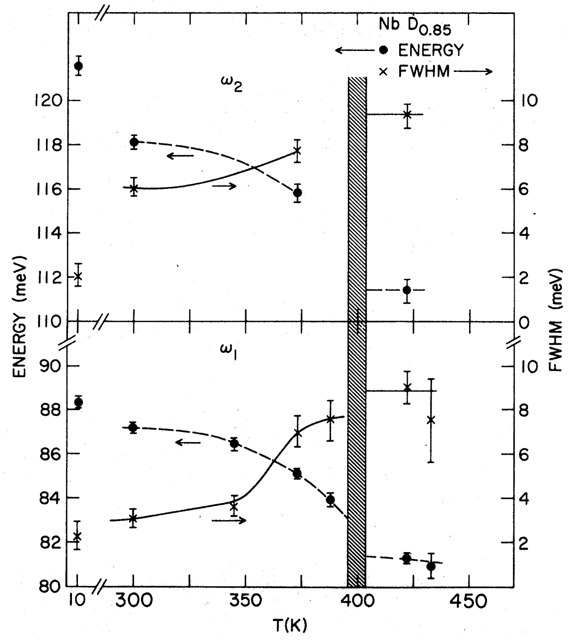

FIG. 3. Temperature dependence of linewidth and peak position for the two local excitations in $NbD_{0.85}$. The shaded area indicates the two-phase region. The solid and the dashed lines are guides to the eye.

are randomly distributed over the tetrahedral sites. For 10 and 300 K, the two D vibrations have narrow linewidths, but considerable broadening is present in the disordered phase at 422 K. This broadening is accompanied by a shift of the peak positions by ~10% to lower frequencies. At low temperatures, a third peak is observed at 170 meV whose intensity is about a factor of 4 weaker than that of the peak at 88.4 meV. The linewidth is close to the resolution width of 10 meV at this energy. This peak also appears in the spectrum at 300 K (see Fig. 4 below), but due to background problems its quantitative evaluation is connected with larger uncertainties. Again, its intensity seems to be about 4 times weaker than that of the low-energy excitation. The linewidth now appears broader than the resolution of the instrument.

Figure 2 shows the spectra obtained from $NbH_{0.82}$ in the ordered and disordered phase. At 300 K the lines are narrow, but a strong broadening is observed above the phase transition. The positions

TABLE I. Linewidths and position of the local vibrational modes in $NbD_{0.85}$ and $NbH_{0.82}$ as a function of temperature.

T (K)	$\hbar\omega_1$ (meV)	FWHM (meV)	$\hbar\omega_2$ (meV)	FWHM (meV)
		$NbD_{0.85}$		
10	88.4 ± 0.3	2.3 ± 0.6	121.6 ± 0.4	4.2 ± 0.9
300[a]	87.2 ± 0.2	3.1 ± 0.4	118.1 ± 0.3	12.2 ± 0.7
300[b]	86.6 ± 0.2	3.4 ± 0.5	118.1 ± 0.4	11.4 ± 0.8
345	86.5 ± 0.3	3.7 ± 0.5		
373	85.1 ± 0.4	7.0 ± 0.7	115.8 ± 0.4	15.3 ± 0.9
388	83.9 ± 0.2	7.5 ± 0.9		
422	81.3 ± 0.2	9.0 ± 0.7	111.4 ± 0.5	18.6 ± 0.9
433	80.9 ± 0.5	7.5 ± 1.8		
		$NbH_{0.85}$		
300	119.0 ± 0.2	4.7 ± 0.5	166.8 ± 0.5	14.6 ± 1.0
347	118.0 ± 0.1	4.3 ± 0.5		
368	117.6 ± 0.2	6.7 ± 0.5		
337	112.0 ± 0.4	19.0 ± 1.7	160.4 ± 1.0	34.0 ± 2.2

[a] $\vec{q}$ was mainly along [100].
[b] $\vec{q}$ was mainly along [110].

of the lines shift again towards lower energies in the α' phase. The results for D and H samples are summarized in Table I. The harmonic result for the isotope effect is obeyed for the higher-energy mode at 300 K

$$\omega_2^H/\omega_2^D = 1.412 \pm 0.006 .$$

However, the lower vibrational level shows considerable deviation from the harmonic value: $\omega_1^H/\omega_1^D = 1.365 \pm 0.005$.

Figure 3 displays the temperature dependence of the position and linewidth for the two excitations in $NbD_{0.85}$. The vertically shaded area indicates the two-phase region. The striking feature is that a precursor to the phase transition is seen by the localized vibrations. The peak position shows most of the softening in the one hundred degrees prior to the phase transition. Likewise, most of the broadening occurs prior to the phase transition.

V. DISCUSSION

We identify the excitation observed at 170 meV in $NbD_{0.85}$ as the second harmonic of the low-energy vibration $\hbar\omega_1$ in NbD_x. It appears about 7 meV below the energy $2\hbar\omega_1$ expected for a harmonic oscillator. Thus, it is easily distinguished from multiple-scattering processes which would peak at $2\hbar\omega_1$. They could be the origin for the shoulder observed on the high-energy side of the 170-meV vibration. Background problems as well as this high-energy shoulder limit the accuracy in the determination of the intensity ratio between the two harmonics. Under these circumstances, however, the estimated value of 4 is in reasonable agreement with the ratio 6.4 calculated from Eq. (3). Both multiple-scattering and anharmonic effects, which manifest themselves in the frequency shift, tend to decrease the calculated ratio.

Another possibility for a peak in this frequency range has to be watched carefully. About 1.5% H in the deuterated sample would give rise to an equally intense $\hbar\omega_2^H$ peak in the frequency range in question. Beside the fact that purity of the D used was much better than 98.5%, Fig. 4 gives further evidence that $\hbar\omega_2^H$ and the second harmonic of $\hbar\omega_1^D$ are at different energies. In Fig. 4 we compare the spectra of H and D in Nb at room temperature. The $\hbar\omega_2^H$ is clearly at a different position than the second harmonic in NbD_x.

The deviation of the second harmonic from $2\hbar\omega_1$ and the observed nonharmonic isotope effect can be described consistently by the anharmonic correction $\alpha/M^{H\,(D)}$ of Eqs. (4) and (5). The observed peak is at 170 meV and from Eq. (5) we find $\alpha/M^D = 3.3$ meV. From this quantity we calculate for the isotope effect $\omega_1^H/\omega_1^D = 1.370$ which compares well with the observed value 1.365 ± 0.005. Since the third- and fourth-order terms in the potential affect line shift and isotope effect in the same manner, their separate evaluation is impossible. The isotope effect for the upper vibrational level $\omega_2^H/\omega_2^D = 1.411 \pm 0.006$ is very close to the harmonic value. It is not understood why the isotope effect should be different for the two modes.

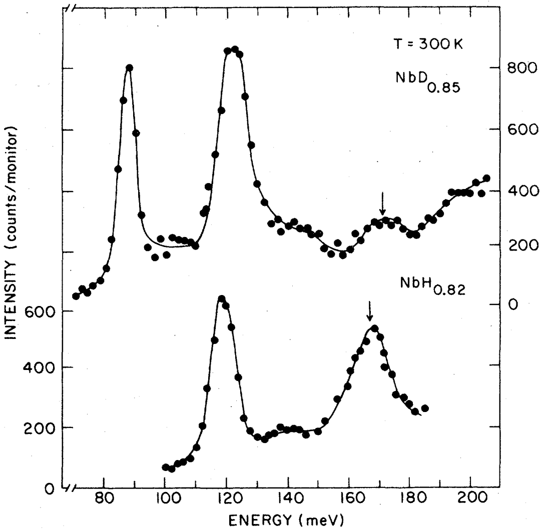

FIG. 4. Spectra obtained on $NbD_{0.85}$ and $NbH_{0.82}$ at room temperature. The arrows indicate the positions of the second harmonic of the lower D vibration ω_1^D and of the higher H vibration ω_2^H. The two are clearly at different energies.

The ratio between the lower and upper D vibration $\omega_2^D/\omega_1^D = 1.35 \pm 0.005$ deviates strongly from $\sqrt{2}$ which would result from only longitudinal springs between the D and its nearest Nb neighbors [Eq. (1)]. The corresponding ratio for the case of hydrogen is given by $\omega_2^H/\omega_1^H = 1.40 \pm 0.005$. The ratio ω_2/ω_1 should be the same for H and D if the potential well is truly harmonic. This can be seen if we take the renormalized harmonic part of the potential for $\hbar\omega_1$ in Eq. (5): $\hbar\omega_{1h}^{H\,(D)} = \hbar\omega_1^{H\,(D)} + 2\alpha/M^{H\,(D)}$ (where ω_{1h} is the harmonic frequency) then the ratio $\omega_{2h}/\omega_{1h} = 1.26$ for both H and D. The difference in the observed ratio is another manifestation of the anharmonicity of the potential well.

While the observed frequencies are not in disagreement with the earlier experiments which had less accuracy, there are striking differences with respect to the linewidths. Pan *et al.*[7] reported the same 18 ± 3 meV linewidth for both H levels in the β and α' phases. Magerl *et al.* in Ref. 1 found widths between 24 and 40 meV for the lower vibration and 36 to 60 meV for the upper H vibration in Nb. These widths are considerably broader than we measured, but with the limited energy resolution of their technique the multiphonon contribution to the background could be large and affect the measured linewidths. For D in Nb, the experiments reported only resolution-limited linewidths.[8,9] We find significant linewidths for H (D) in Nb and a considerable change between the ordered and disordered phases.

The small linewidths observed at 10 K could originate from weak dispersion effects. For example, from a linear chain of alternating H and Nb atoms a 1% effect on the linewidth arises due to the coupling to the Nb vibrations. On the other hand, the linewidths measured along the [100] and [110] directions (see Table I) do not differ significantly. This suggests an intrinsic damping mechanism rather than dispersion effects. This is also supported by the strong increase of linewidths between 10 and 300 K, well below the $\beta \rightarrow \alpha'$ transition. Since, at these temperatures within the β phase, the protons are completely ordered, H diffusion cannot be the process which limits the lifetime of the localized vibration. Additionally, we can estimate the damping caused by the lifetime of the proton in its well. This is of the order $\hbar/\tau$, where τ^{-1} is the jump rate of the proton. For the β phase, $\hbar/\tau$ has values on the order of μ eV[10] which increases in the α' phase to 0.1–0.3 meV[10], far below the experimental widths. On the other hand, the precursor to the phase transition observed above room temperature cannot be caused by a pure damping mechanism which would increase the linewidth but would not measurably shift the frequencies. There is also no lattice expansion which could be responsible for the softening of the optical modes. At this point, we suggest that the elastic H-H interaction discussed above causes the simultaneous frequency shift and line broadening. The order of magnitude of the frequency shift is in agreement with the estimates given earlier. The accompanying linewidth would then reflect the frequency distribution due to disorder. While this picture explains reasonably well the situation for NbD_x, the much larger linewidths in the α' phase of NbH_x requires an additional source of broadening. This could be increased coupling to acoustic phonons due to the large amplitude of the H vibration. A weak point of this picture is the missing isotope effect in the frequency shift which would be expected for a harmonic potential.

Further information on the influence of the elastic interaction could be obtained from a careful study of the concentration dependence of the localized-mode frequencies and linewidths. Also more quantitative theoretical considerations would be desirable.

VI. CONCLUSION

In conclusion, we can state that for the first time (i) a higher harmonic of an H vibration has been observed in a bcc metal. (ii) The accurate determination of the anharmonic isotope effect together with the observed shift of the second harmonic from $2\hbar\omega_1$ gives a quantitative estimate of the anharmonicity of the H potential. (iii) In view of an activation energy for H diffusion comparable with the vibrational energy of the first harmonics the existence of a well-defined higher harmonic demonstrates that the diffusive process is not simply a motion over a barrier provided by the vibrational potential. (iv) Optical-mode frequency as well as linewidth exhibit a clear precursor to the order-disorder phase transition. The observed softening is related to the elastic H-H interaction of disordered H atoms.

ACKNOWLEDGMENTS

The authors would like to thank H. K. Birnbaum for preparation of the sample and J. M. Rowe and A. Magerl for helpful discussions. Research at Brookhaven was supported by the Division of Basic Energy Sciences, Department of Energy under Contract No. DE-AC02-76CH00016.

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