

# PHYSICAL REVIEW B

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### Local modes in dilute metal-hydrogen alloys

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We report on measurements of the local modes of H in the transition metals V, Nb, and Ta with particular emphasis on low-concentration alloys. The excitations appear as very broad peaks in the neutron scattering spectrum even at a level of  $< 1$  at. % H, in contrast to the narrow density-of-states peaks normally expected for such interstitial defects. The lower vibration peak in  $\text{NbH}_{0.0055}$  reveals, within the  $\alpha$  phase between 295 and 210 K, an unexpected continuous shift from 106 to 118 meV. Several possible mechanisms to explain these unusual observations are discussed and evaluated.

#### INTRODUCTION

The local modes of hydrogen (H) absorbed in a metal provide direct information about interatomic potentials. The strength of the force field and its symmetry have been used as a probe of H-site occupancies.<sup>1</sup> In fact, this spectroscopic evidence can often provide greater sensitivity than diffraction experiments, particularly for disordered or mixed occupancy systems, or for low H concentrations. Recently, improved instrumentation has stimulated an upsurge in studies of the dynamics of hydrogen in metals and has allowed (1) measurements of higher-order transitions and the determination of anharmonicity parameters in the ordered low-temperature phases<sup>2</sup>; (2) probing of the potential at tetrahedral sites in  $\beta$ -phase Nb by measurement of the local-mode frequencies for the three isotopes  $^1\text{H}$ ,  $^2\text{H}$ , and  $^3\text{H}$  (Ref. 3); and (3) spectroscopy of H trapped at low concentration by defects such as O and Ti in Nb.<sup>4</sup>

In spite of this progress, no conclusive explanation has been given for the intrinsic linewidths of the H modes in disordered phases. In triple-axis measurements of H vibrations in the  $\alpha'$  phase of  $\text{NbH}_x$ ,<sup>5</sup> a pronounced change of the linewidths with temperature and crystallographic phase was noted. This technique keeps the wave-vector transfer  $Q$  relatively small, so that multiphonon scattering is minimized. The energy resolution can be improved at the expense of increased  $Q$  values by using a Be filter as an analyzer. Such an instrument was used recently to study the H modes of high-concentration  $\text{NbH}_x$  and  $\text{NbD}_x$  at the  $\alpha' \rightarrow \beta$  phase transition (disorder  $\rightarrow$  order).<sup>2</sup> It was proposed that the large linewidths observed in the

$\alpha'$  phase reflect locally varying H-H interactions due to the short-range order in the  $\alpha'$  phase.

In this paper we report on measurements of the local H modes in V, Nb, and Ta in the dilute  $\alpha$  phases. For  $\text{TaH}_x$  we have also studied the concentration dependence of the vibrational spectrum, and for  $\text{NbH}_{0.0055}$  we have followed the evolution of the spectrum at low temperatures until the ordered  $\beta$  phase is reached. These data provide the first direct information about the microscopic mechanism leading to the large linewidths in the dilute  $\alpha$  phase, and models proposed earlier can be reevaluated within the framework of the present results.

#### EXPERIMENTAL DETAILS

The measurements on dilute H in metals were made possible by the development of a new Be-filter spectrometer at the National Bureau of Standards (U.S.) research reactor, which has an excellent signal-to-background ratio. This is achieved by taking advantage of large solid angles at the analyzer both horizontally and vertically in combination with a well-shielded detector of  $15 \times 15 \text{ cm}^2$ . The distance from the sample to the detector is 1.1 m. A cold Be filter with a cutoff of 5.2 meV serves as analyzer. The incident energy is varied using a Cu(220) monochromator, with collimations of  $40'$  before and after the monochromator.

Some spurious peaks were originally observed in the case of a single crystal of  $\text{NbH}_{0.0055}$ . They originated from neutrons Bragg-scattered by the sample into the filter. Because of thermalization in the Be some neutrons could pass the filter, creating misleading peaks which

reached about half the height of the first H excitation in  $\text{NbH}_{0.0055}$  at 300 K. This problem was overcome when this sample was cut into 50 pieces to effectively create a polycrystal and the spectra were measured at various scattering angles between  $40^\circ$  and  $100^\circ$ . Similar difficulties were not encountered with the other specimens measured.

The samples contained 40 g V, 25 g Nb, and 70 g Ta, respectively. Nb and Ta were purified at 2200 and 2500°C, respectively, in a vacuum of  $10^{-10}$  Torr. Because of its low melting point, V cannot be purified efficiently in the same way. The metals were loaded in the usual way in a H atmosphere of appropriate pressure at 700°C to  $\text{VH}_{0.012}$ ,  $\text{NbH}_{0.0055}$ ,  $\text{NbH}_{0.030}$ , and  $\text{TaH}_{0.180}$ . These concentrations were determined by the weight increases of the samples. After a first set of measurements, the  $\text{TaH}_{0.180}$  specimen was mounted in a furnace on the spectrometer to partially degas the sample. In this way the H concentration could be monitored continuously via the lattice constant. The final concentration was  $\text{TaH}_{0.037}$ . The measurements at low temperature were performed with the sample mounted in a controlled temperature cryostat. Spectral measurement time varied from a few hours for  $\text{TaH}_{0.18}$  to 2 days for  $\text{NbH}_{0.0055}$ .

It should be noted that over the energy range scanned the wave vector varies from approximately 6 to  $9 \text{ \AA}^{-1}$ . However, the observed counts are a very good approximation to the density of states  $g(E)$  for the conditions under which the spectra are measured, because of a cancellation of two terms in the one-phonon cross section. There is a contribution to the scattering from multiphonon processes, but this effect has been shown not to seriously distort the results even in  $\text{PdH}_{0.005}$ , a system in which the effect is larger than in the present case.<sup>6</sup>

## RESULTS

Figure 1 shows spectra measured at room temperature for  $\text{VH}_{0.012}$ ,  $\text{NbH}_{0.030}$ , and  $\text{TaH}_x$  with  $x=0.180$  and 0.037, after the fast-neutron background has been subtracted. In all cases the energy widths of both excitations are considerably broader than the instrumental resolution, which is 7 and 9 meV full width at half maximum (FWHM) for an energy transfer of 110 and 160 meV, respectively. The vibrational peaks are broadest for  $\text{VH}_{0.012}$ . The first excitation is centered at about 106 meV, whereas the position of the second maximum can be indicated only tentatively at about 170 meV. For  $\text{NbH}_{0.030}$  the vibrational peaks are better defined and their positions are centered at 107 and 163 meV. Figure 2(a) shows a spectrum for  $\text{NbH}_{0.0055}$ , again measured at room temperature. Within the counting statistics there is a little difference in the spectra for these hydrogen concentrations. For  $\text{TaH}_{0.037}$  [Fig. 1(c)] we again find two well-defined peaks, at 114 and 154 meV. Also shown is a spectrum for  $\text{TaH}_{0.180}$ . This spectrum has been measured with improved statistical accuracy due to the much higher H concentration, and details of the line shape become clearly observable, including a shoulder on the low-energy side of the first peak. This is likely to be due to a multiphonon-scattering process involving acoustic lattice

modes and will not be discussed further in this paper. The salient feature in Fig. 1(c) is the fact that the position of the second peak is shifted to a higher energy of 164 meV, whereas the first mode remains at 114 meV. The data also indicate a slight difference in the general shape of peaks, more noticeable at the high-energy end. This, however, we attribute to multiphonon contributions which give rise to a smooth and monotonically increasing background underneath the scattering from the H motions. This background becomes less important at higher concentration, where the scattering from the H dominates the scattering from the metal.

Figure 2 shows spectra for  $\text{NbH}_{0.0055}$  between 295 and 78 K. Because of the long counting times necessary at these low concentrations, only the first excitation peak has been measured at the intermediate temperatures. The po-

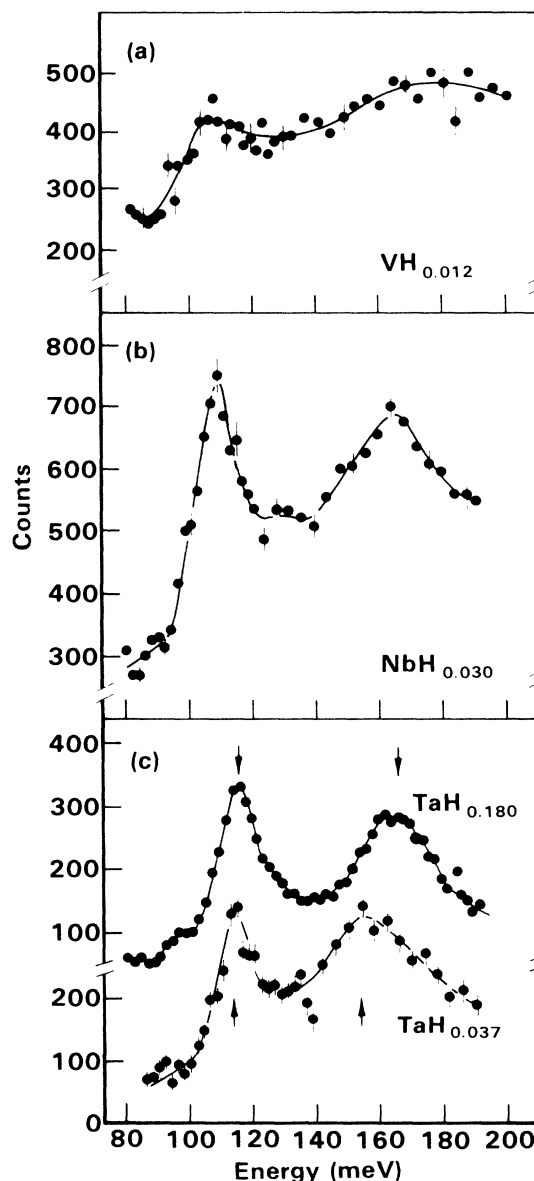


FIG. 1. Spectra of the local H modes measured at room temperature. The fast-neutron background has been subtracted.

sition of this peak at 295 K is indicated by an arrow and it is also marked at the lower temperatures by the open symbol, whereas the actual peak position is indicated by a solid symbol. The striking feature we observe is a continuous shift of the position of the peak between 295 and 210 K from 106 to 118 meV. The highest-energy value is essentially the same as that measured previously for ordered hydride phases at low temperature, as is also demonstrated by a 78-K spectrum in Fig. 2, at which the hydrogen must be entirely in the ordered  $\delta$  phase. Howev-

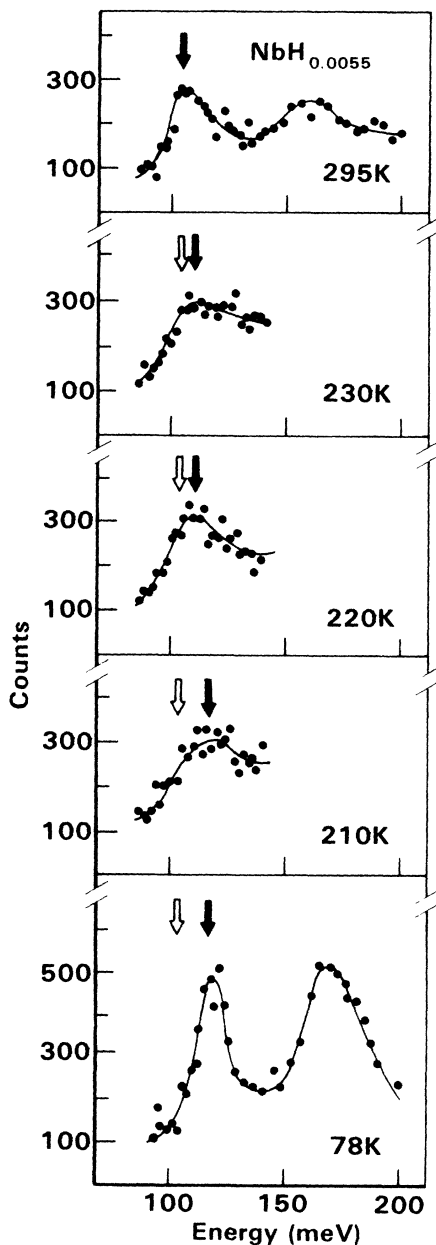


FIG. 2. Temperature dependence of the local H modes of  $\text{NbH}_{0.0055}$ . Down to 210 K the sample remains in the homogeneous  $\alpha$  phase, whereas the H is totally precipitated into an ordered, high-concentration  $\delta$  phase at 78 K. The solid arrow shows the actual peak position at a given temperature; the open arrow indicates the peak position at 295 K.

er, in  $\text{NbH}_{0.0055}$ , no H precipitation occurs above 200 K,<sup>7</sup> so that down to 210 K the sample remains in the homogeneous  $\alpha$  phase. Moreover, the peak shape is quite different from that observed for H in the ordered phase.

## DISCUSSION

The results shown in Figs. 1 and 2 reveal several novel aspects of the vibrational spectrum of hydrogen dissolved at low concentration in refractory metals: (1) large intrinsic linewidths of the observed  $\alpha$ -phase peaks even at the low H concentration studied, (2) an anomalous temperature dependence of the first excitation in very-low-concentration  $\text{NbH}_{0.0055}$ , and (3) a different concentration dependence of the two local-mode frequencies in  $\alpha\text{-TaH}_x$ .

### Linewidths

The measured linewidths for these dilute  $\alpha$ -phase samples are much too large to be related to the H diffusion in these metals;<sup>2</sup> broadened peaks have also previously been reported for  $\alpha$ -phase samples of  $\text{NbH}_x$  at much higher concentrations.<sup>2,5</sup> An explanation of the width in  $\text{NbH}_{0.0055}$  by local variations of the force constants<sup>2</sup> due to the random occupation of tetrahedral sites in the  $\alpha$  phase is unlikely in view of the low concentration in the present experiment. Moreover, a reduction of the H concentration in Ta from 18 to 3.7 at. % increases the average H-H distance by 70% without a noticeable change in the line shape. Other tentative explanations have been given previously for the large linewidths of the H modes, such as dispersion of the optical branches or electron-phonon coupling. The first possibility can be rejected in view of the low concentrations employed in these measurements. The second possible explanation is more difficult to evaluate because there are no model calculations for transition-metal hydrides. However, considering the small changes observed in the phonon spectrum at the  $\alpha'$ - $\beta$  phase transition in  $\text{NbH}_x$  (Ref. 1) in contrast to the strong reduction of the width of the H modes at this phase transition, it is not likely that the widths in  $\alpha$  phase are due to electron-phonon coupling.

As an alternative possibility it may be speculated that the linewidths are due to hydrogen delocalization. Tunneling of H trapped at low temperature by a heavier interstitial atom is well established now, both by specific-heat measurements<sup>8</sup> and by neutron spectroscopy.<sup>9</sup> Recently, it has been shown that the pocket states for the trapped H resemble closely tetrahedral positions of the pure  $\alpha$  phase.<sup>4</sup> The heavy defect atom mainly prevents H precipitation into an ordered hydride structure in which delocalization would be suppressed by the high H concentration. The measured ground-state energy for  $\text{NbO}_x\text{H}_x$ ,  $x < 0.01$ , amounts to about 0.20 meV. If one assumes a double-well potential, such a splitting of the vibrational ground state suggests a splitting of the first and second H local-mode frequencies of  $\sim 4$  and  $\sim 6$  meV, respectively.<sup>10</sup> Indeed, the local modes of trapped H reveal widths of 5–10 meV, of the same order as the widths observed in the pure  $\alpha$  phase. Anharmonicities can further increase these splittings, and a delocalization involving more than two pocket states will result in broad bandlike states, as

shown in a recent paper.<sup>11</sup> Furthermore, the use of such a model to explain the observed vibration bandwidths by hydrogen delocalization is also consistent with the observation of significantly larger widths for  $\alpha$ -VH<sub>0.012</sub> than for H in Nb and Ta. The lattice parameter for bcc V is 9% smaller than that for Nb and Ta, so that the H tetrahedral sites are closer together. Excited vibrational levels whose widths are due to "tunneling" or delocalization would be highly sensitive to the distance between potential minima and would yield relative vibration bandwidths consistent with our observations.

Such tunneling phenomena are well known for molecular crystals containing methyl groups or ammonium ions.<sup>12</sup> In general, the ground-state splittings are much smaller than for H trapped in Nb and tunneling is only observable below 50 K. In this temperature range the vibrational modes of the tunneling unit become damped due to coupling to the phonon bath of the crystal. However, for metal hydrides the local-mode frequencies are well above the acoustic-phonon spectrum, so that a delocalization may be observable up to considerably higher temperatures. Thus, the observation of broadened vibration peaks for interstitial H in metals even at low "defect" concentrations (< 1 at. %) is consistent with a delocalization of the excited states.

#### Temperature dependence

Perhaps the most surprising result concerns a gradual increase of the energy of the first vibrational band of NbH<sub>0.005</sub> in the  $\alpha$  phase between room temperature and 210 K, at which temperature it has reached a peak energy equal to that observed for the high-concentration ordered phases.<sup>1</sup> Throughout this temperature range the peak remains very broad. The measured fractional frequency shift of 0.13%/deg is far too large to be explained by the usual lattice anharmonicity of a high-melting-point material like Nb. Alternatively, one could assume fluctuations in the hydrogen short-range order with a local structure resembling the ordering in the low-temperature phase. Such short-range "ordering" has never before been directly observed over such a large temperature range ( $\approx 40$  K). Such fluctuating clusters could lead to a continuous shift of the average vibrational energy, toward the value of the  $\beta$  phase, as the phase boundary is approached. A neutron small-angle-scattering study on NbH<sub>0.005</sub> did show some changes in the scattering pattern close to the precipitation temperature, but these results did not provide evidence of any large regions (> 10 Å) of H "clusters" growing in size as the phase boundary is approached.<sup>13</sup> On the other hand, at much higher H concentrations ( $\alpha'$  phase) Burkel *et al.* identified in an x-ray experiment diffuse peaks several hundred degrees kelvin above the precipitation temperature, which they related to the short-range deuterium arrangements close to that in the low-temperature phases.<sup>14</sup>

It is interesting to note that NbH<sub>x</sub> exhibits other unusual properties in the temperature range considered here.

Around 250 K the activation energy for H diffusion changes from a high-temperature value of 106 meV to a low-temperature value of 68 meV.<sup>15</sup> The reason for this is not understood, although, in general, it is associated with the quantum-mechanical aspects of H diffusion becoming manifest at this temperature. A recent quasielastic neutron-scattering experiment indicates that in the same temperature range hydrogen diffusion can no longer be described by a jump motion between nearest tetrahedral sites.<sup>16</sup> Although a direct connection between these unusual features is not obvious at present, their occurrence in the same temperature range suggests the existence of short-range-correlated arrangements of hydrogen atoms which exist considerably above the phase boundary, even at very dilute concentrations in the  $\alpha$  phase.

#### Concentration dependence

Figure 1(c) shows a change of a local-mode frequency in a homogeneous phase with H concentration. Although not reported earlier, the increase of the higher-energy peak by 6% with increasing H content is perhaps not too surprising. In an earlier work on TaH<sub>0.180</sub> and TaD<sub>0.220</sub>, it has been shown that the acoustic modes increase by an average of 0.3% per 1 at. % H.<sup>17</sup> From this point of view it is more surprising that there is *no* observable shift for the first peak, which is due to eigenmodes with a displacement vector in the direction of an octahedral site (the higher-energy peak is due to the degenerate eigenmodes in the orthogonal directions). These results clearly underline the need to describe the H modes by microscopic models with realistic coupling between the host lattice and the H. Recently, first calculations for the dynamics of single-H defects have been presented<sup>18</sup> and at present the model is being refined to improve the description of the details of the experimental results.<sup>19</sup>

#### SUMMARY

In conclusion, we have extended measurements of local H vibrational modes in the transition metals V, Nb, and Ta to low-concentration alloys ( $\leq 1$  at. %). Even at the lowest H concentration, the vibrational peaks show large widths, comparable to those observed for high-H-concentration compounds. Reviewing various explanations for the widths, we propose that they originate from a bandwidth of the excited states (excited-state tunneling transitions). Surprisingly, the energy of the first mode in NbH<sub>0.005</sub> increases in the  $\alpha$  phase continuously from 106 meV at room temperature to 118 meV at 210 K. The peak remains very broad over the entire temperature range. H-density fluctuations with a local symmetry resembling the ordering of the low-temperature phases are proposed to account for this unusual feature. Measurements of TaH<sub>x</sub> at concentrations of  $x=0.037$  and 0.180 reveal a shift only for the high-energy excitation with concentration, whereas the widths for both excitations appear independent of the amount of H.

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