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Local hydrogen vibrations in Nb in the presence of interstitial (N,O) and substitutional (V) impurities

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We have measured the hydrogen vibrations in $NbV_{0.008}H_{0.005}$, $NbN_{0.004}H_{0.003}$, and $NbO_{0.011}H_{0.010}$ between 295 and 4 K. In the case of $NbV_{0.008}H_{0.005}$, these spectroscopic measurements suggest a down shift of the phase boundary for H precipitation by about 30 K. At low temperatures we find excitations at 117 and 166 meV, which are characteristic of an ordered hydride phase. On the contrary, O or N interstitial defects totally suppress the precipitation of H due to trapping. The vibrational energies of H trapped by N (or O) are 106 (107) and 160 (163) meV, which are very close to energies measured for free H in $NbH_{0.005}$ at 295 K. This clearly indicates that H atoms in these systems are trapped at relatively unperturbed tetrahedral-type sites. The peak shapes are distinctly different for the trapping and the nontrapping defects. Several mechanisms that can cause the large widths observed are discussed.

INTRODUCTION

Numerous investigations have shown that interstitial impurities such as O and N in group-V*b* transition metals can act as trapping centers for dissolved H. This was first indicated by H solubility measurements, which revealed deviations from Sievert's law due to O impurities in Ta and V.[1,2] In the case of Nb, internal friction measurements by Baker and Birnbaum[3] showed the existence of a relaxation peak due to H trapped by O or N. Gorsky-effect measurements by Münzing *et al.*[4] demonstrated that N defects cause a considerable decrease in the H diffusion rate in Nb. Furthermore, they tend to suppress the reduction in activation energy for diffusion found below room temperature for H in pure Nb.[5] From resistivity measurements by Pfeiffer and Wipf,[6] it was concluded that one N atom can bind only one H atom and that at low temperatures any excess H precipitates into an ordered hydride phase. More recently, Richter and Springer[7] reported two-component peaks in a quasielastic neutron scattering study of Nb containing H and N impurities, which they associated with the simultaneous observation of H diffusing in a more or less unperturbed host lattice and H escaping from a trapping center. In summary, both the macroscopic and neutron scattering data show the existence of an attractive potential for the interstitial traps, with a binding enthalpy comparable to or larger than the precipitation enthalpy for the ordered hydride phase.

Internal friction measurements[3,8] and their dependence on crystal orientation have been used to suggest models for the symmetry of the H-impurity pairs. In particular, Zapp and Birnbaum[8] proposed second-neighbor ⟨100⟩ pairs with monoclinic symmetry or, alternatively, ⟨100⟩ pairs coexisting with third-neighbor pairs having ⟨110⟩ monoclinic symmetry. These measurements were also interpreted to suggest tunnel states associated with hydrogens situated on rings centered around octahedral sites. On the other hand, channeling experiments on the analogous TaN_xD_y defect system suggested trapping sites in between tetrahedral and octahedral positions.[9] Very recently, tunneling transitions for H trapped by N and O in Nb were detected both by specific-heat measurements[10] and by inelastic neutron scattering.[11]

The interpretation of all these results is sensitive to the details of the interatomic potentials and local strain field experienced by the H. Neutron spectroscopy of the H dynamics is a unique method for probing these potentials on an atomic scale. In the present paper we report the first measurements of H vibrations in a metal (Nb) doped both with interstitial (O and N) and substitutional (V) impurities. Surprisingly, the local-mode energies of H trapped by interstitial impurities resemble very closely the *H* modes in the α phase of pure Nb. This similarity clearly suggests that the H atoms are trapped on interstitial sites that are closely related to a tetrahedral position in a relatively weakly distorted Nb environment. The substitutional V impurities, on the other hand, were found to bind H less strongly so that precipitation is not prevented at low *T*.

EXPERIMENTAL

$NbN_{0.004}H_{0.003}$ and a $NbN_{0.004}$ "blank" sample, both with a weight of 125 g, 240 g of $NbO_{0.011}H_{0.010}$, and 50 g of $NbV_{0.008}H_{0.005}$ were used. The $NbN_{0.004}$ and the $NbN_{0.004}H_{0.003}$ samples each consisted of a bundle of 250 Nb wires (1.6 mm diameter, 30 mm long), which were prepared in four steps: (1) the 99.99% pure Nb wires were decarbonated and subsequently degassed in ultrahigh vacuum, yielding resistivity ratios above 2000; (2) nitrogen doping was performed under equilibrium conditions out of the gas phase; (3) the samples were quenched to 500 °C in about 20 sec in order to maintain N in solid solution; (4) hydrogen loading was also carried out from the gas phase. Residual resistivity measurements before and after H loading, as well as inspections by electron microscope and Snoek-effect measurements, were performed in order to ensure that there was no formation of N precipitates or subnitrides. For a more detailed description of the sample preparation, we refer to Ref. 7. The O-doped samples consisted of seven single crystalline rods (12 mm diameter, 35 mm long). The sample preparation was similar to that of the NbN_xH_y samples with the exception that H loading was performed at 1200 °C while the O was still in solid solution under equilibrium conditions. For more details we refer to Ref. 11.

The V-doped samples were prepared by electron-beam melting of a mixture of Nb and V powder of appropriate weights. H loading was performed afterwards from the gas phase, and the concentration was determined from the weight increase. The V concentration and homogeneity were monitored by mass spectroscopy and atomic absorption spectroscopy. Chemical analysis after preparation

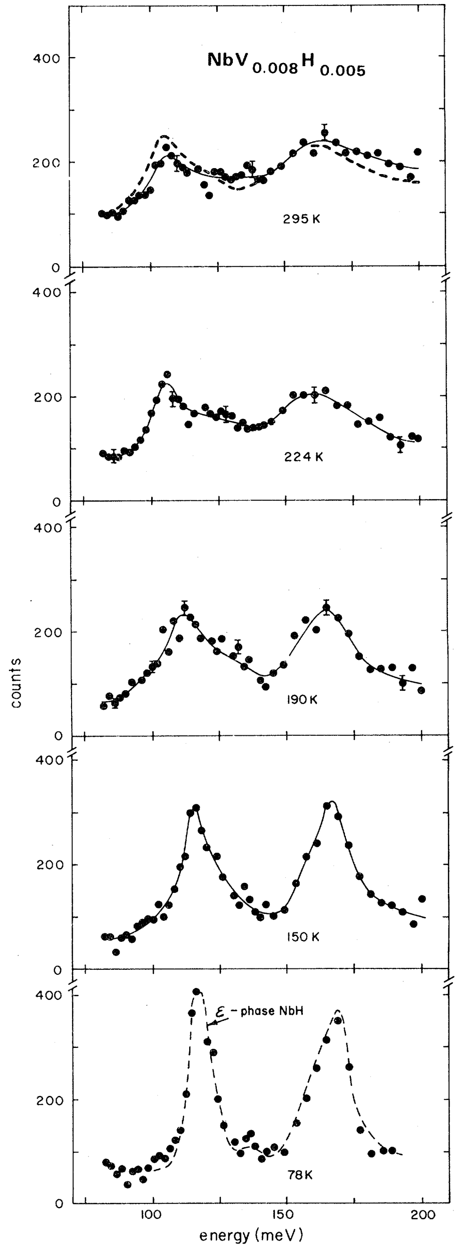

FIG. 1. Spectra from $NbV_{0.008}H_{0.005}$. Fast-neutron background and scattering from host metal subtracted. Also shown as dashed curves are the measured spectra (normalized) for the α and ϵ phases of NbH_x at 295 and 78 K, respectively. The ϵ phase is the phase expected if hydride precipitation occurs for any H concentration between 0 and 70%.

showed that the sum of other metal impurities in the sample was an order of magnitude less than the vanadium concentration, while oxygen was present at concentrations $\lesssim 300$ ppm.

The experiments were performed on the BT-4 triple-axis spectrometer at the Natl. Bur. Stand. (U.S.) Research Reactor. Copper [220] was used as a monochromator, and a polycrystalline Be filter at liquid-N_2 temperature was used as an analyzer. Collimations before and after the monochromator were 40′. Under these conditions the energy resolution of the instrument changes from 6.5 meV [full width at half maximum (FWHM)] at 100 meV to 9.5 meV at 170 meV energy transfer. The cold Be analyzer has been installed recently. It yields a high signal:background ratio by combining a well-shielded detector (225 cm^2) with large vertical and horizontal divergences.

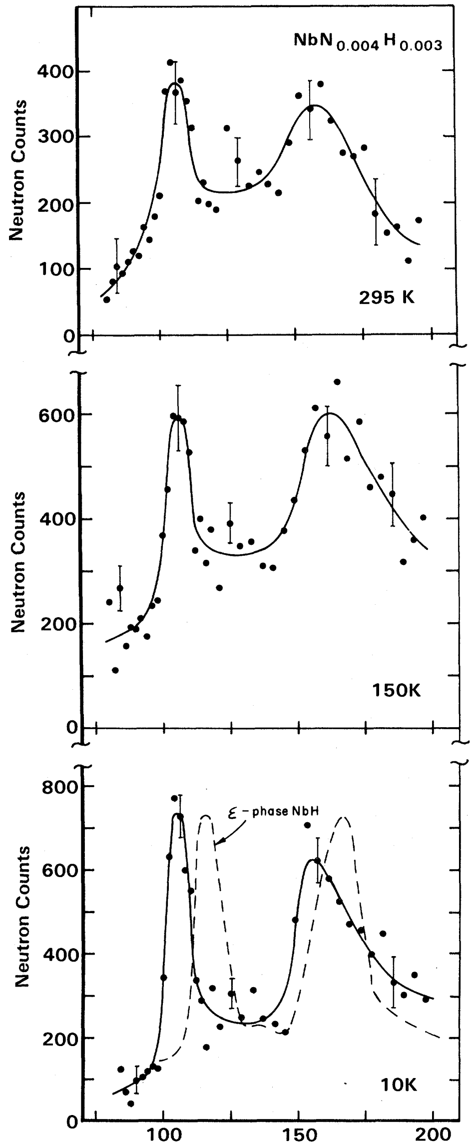

FIG. 2. Spectra from $NbN_{0.004}H_{0.003}$. Fast-neutron background and scattering from host metal subtracted. Dashed curve represents ϵ phase results, as in Fig. 1.

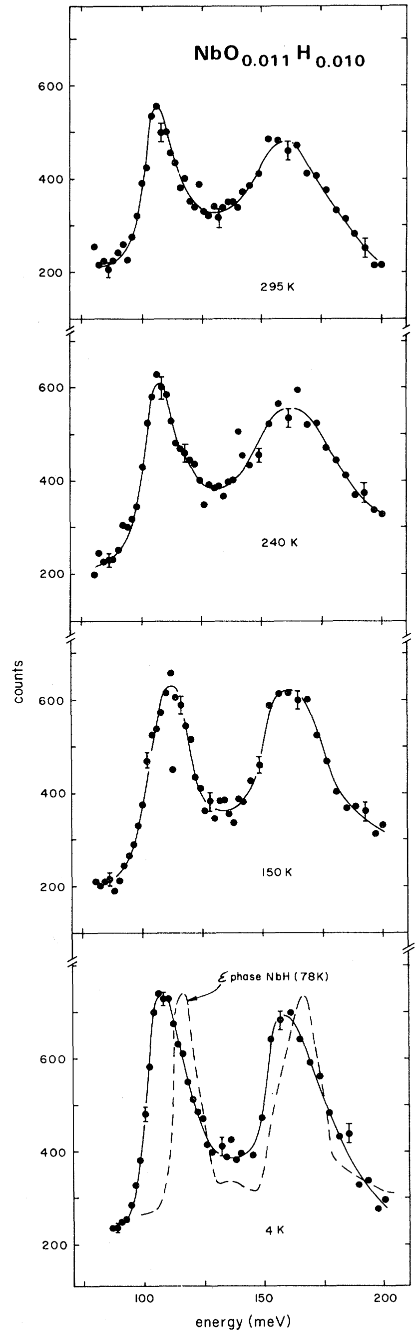

FIG. 3. Spectra from $NbO_{0.011}H_{0.010}$. Fast-neutron background subtracted. Dashed curve represents ϵ-phase results, as in Fig. 1.

TABLE I. Energies and measured linewidths (FWHM) (in meV) of the neutron peaks determined from Figs. 1—3.

$NbV_{0.008}H_{0.005}$[a]					$NbN_{0.004}H_{0.003}$					$NbO_{0.011}H_{0.010}$				
T (K)	$\hbar\omega_1$	Γ_1[b]	$\hbar\omega_2$	Γ_2	T (K)	$\hbar\omega_1$	Γ_1	$\hbar\omega_2$	Γ_2	T (K)	$\hbar\omega_1$	Γ_1	$\hbar\omega_2$	Γ_2
295	108±3	×[c]	~164	×	295	106±2.0	15	159±3.0	30	295	107±1.5	15	160±3	35
224	106±3	×	~162	×						240	107±1.5	18	163±3	35
190	112±2.0	25[d]	165±3	23[d]	150	106±1.5	12	163±3.0	29	150	112±1.5	22	162±3	30
150	116±1.5	14[d]	167±2.5	20[d]	10	106±1.0	11	157±2.5	22	4	108±1.5	22	159±3	28
78	117±1.0	11	168±2.0	16										

[a] Peak energies observed for α-phase $NbH_{0.0055}$ are at 106 and ~163 meV; values for the ordered phase at 78 K are 117±1 and 167±2 meV, with corresponding widths of 12 and 18 meV.

[b] Quoted widths are not corrected for instrumental resolution and have estimated errors of 1—2 meV.

[c] Peaks for which the width is given by × were too broad to allow a reliable estimate of their width.

[d] Two components.

RESULTS

Figures 1, 2, and 3 show the spectra of $NbV_{0.008}H_{0.005}$, $NbN_{0.004}H_{0.003}$, and $NbO_{0.011}H_{0.010}$, respectively, measured from 80 to 200 meV at various temperatures. The fast-neutron background has been subtracted from all spectra. In addition, scattering from the Nb metal has been substracted in Figs. 1 and 2 with the use of a spectrum measured for the $NbN_{0.004}$ sample and normalized according to the relative weights of the samples. In all spectra we observe two peaks. The positions and the peak shapes are markedly different for the three systems. Table I summarizes the peak positions and the measured linewidths of the excitations.

At 295 and 224 K, $NbV_{0.008}H_{0.005}$ shows two very broad density-of-states peaks centered at about 107 and 163 meV. (The α-phase spectrum for $NbH_{0.005}$ is shown for comparison.) As the temperature is decreased, the peaks sharpen somewhat and the peak positions become better determined. Simultaneously, we find a continuous shift of the peak positions (particularly the lower-energy peak) toward higher energies. At 150 K the spectrum appears to be composed of broad and narrow components, indicating a two-phase situation. At 78 K the two excitations are centered at 117 and 166 meV. The observed widths are greatly reduced to 11 and 17 meV (FWHM). The measured spectrum for the ordered (ϵ) phase NbH at 78 K (Ref. 12) is shown superimposed on the low-temperature $NbV_{0.008}H_{0.005}$ data.

$NbN_{0.004}H_{0.003}$ shows a completely different behavior. Even at 295 K we find well-defined peaks in the spectrum. The position of the first peak remains unchanged at 106 meV from 295 K down to 10 K. However, the width of this peak decreases from 15 to 11 meV. The second peak shifts slightly from about 158 meV at 295 K to 163 meV at 150 K. At 10 K its position is decreased again to about 158 meV. In addition, we find a reduction in the width from 29 to 24 meV between 150 and 10 K.

$NbO_{0.011}H_{0.010}$ shows an intermediate behavior between the V-doped and the N-doped samples. At 295 K the general features of both interstitial impurity samples are similar; the two systems show well-defined peaks and the values for the corresponding widths are about the same. Lowering the temperature to 150 K, we find an increase of the energy of the first peak from 106 to 112 meV, which is similar to that observed for the $NbV_{0.008}H_{0.005}$ system. The width increases from 16 to 23 meV. At 4 K the peak position is again decreased to 108 meV with a large width of 22 meV. The position of the second peak at about 163 meV changes little over the whole temperature range. A large width of 27 meV is still observed at 4 K. The spectrum at 4 K is significantly different from the spectrum of ordered-phase niobium hydride (dashed curve).

DISCUSSION

In the analysis that follows we make use of the fact that the vibrational frequency spectrum of the ordered ϵ phase of NbH has a characteristic shape that is quite different from the solute-phase spectrum, as shown by the dashed lines in Figs. 1–3. When low-concentration samples are cooled below the (α-ϵ) coexistence temperature, the hydrogen migrates to clusters of pure ϵ phase (fully ordered) in a matrix of the cubic phase metal. The relative volumes of the two phases is, of course, just the total hydrogen concentration in the sample. Since the hydrogen is in stoichiometric regions, the dynamics are those appropriate to a high-concentration sample, and the defect concentration within these regions is less than 1%. At this concentration, the defects cannot shift the normal modes of the hydrogen optic frequencies significantly. Since the neutron incoherent scattering comes *only* from the hydrogen, this method of observation is inherently much more sensitive than, e.g., diffraction techniques, in which the scattering will be dominated by the scattering from the host-metal matrix. Of course, in the α phase (or trapped state), the concentration of defects is approximately equal to that of the hydrogen, and no *a priori* statements can be made about the effects of the impurities on the dynamics of the hydrogen, although as discussed below the present results indicate a surprisingly small effect.

Substitutional impurity

A comparison of the temperature dependence of the spectra of $NbV_{0.008}H_{0.005}$ with recent measurements for pure $NbH_{0.0055}$ (Ref. 12) reveals several interesting features:

(1) α-phase samples both with and without V defects show rather broad density-of-states peaks at 295 K. In fact, the lower-energy peak for $NbV_{0.008}H_{0.005}$ appears even broader. (See Fig. 1.)

(2) At 190 K, where the solubility limit for α-phase NbH_x is $x \simeq 0.003$,[6] we find little evidence for hydrogen in a precipitated, ordered phase [such a phase would provide sharp density-of-states peaks at 117 and 167 (Refs. 12 and 13)], although it is not possible to rule out a small amount of precipitation.

(3) At 150 K the lower-energy peaks appears to be composed of a narrow and a broad component. We associate the broad component with H still in the α phase and the narrow component with precipitated H. At 78 K the peak positions and widths are characteristic of H precipitated in an ordered, low-temperature phase.[12,13] This is shown directly by the almost identical vibration spectrum observed for the ordered ϵ-phase niobium hydride, which is plotted as the dashed curve in Fig. 1.

The results summarized above strongly suggest that while the interaction of V defects with H in Nb is not strong enough to prevent precipitation, it does appear to have shifted the phase boundary for precipitation of the ϵ-phase hydride to a lower temperature. An estimated trapping energy of about 100 meV has been derived for this system from quasielectric neutron scattering measurements.[14] On the other hand, hydrogen-pressure measurements versus temperature for Nb doped with a larger concentration (6%) of V have been interpreted to suggest a binding energy of about 70 meV.[15] However, it should be noted that at this concentration each atom has a 50% probability of having another V as a nearest neighbor. Assuming a hydride-phase component at 150 K with the same line shapes as those observed for 78 K (Fig. 1), we estimate that only about 50% of the hydrogen is precipitated. This would indicate a downshift of the solubility limit by ~30 K.

Interstitial impurities

The salient feature in the results obtained for $NbN_{0.004}H_{0.003}$ (Fig. 2) is the invariance of the peak positions with temperature. The frequencies at 295 K, where less than half of the H is trapped, remain unchanged down to 10 K, where all the H is trapped. A similar behavior is found for $NbO_{0.011}H_{0.010}$ (Fig. 3). The peak positions at 295 and 4 K are practically the same. These results demonstrate that N as well as O act as effective traps down to low temperatures and prevent H precipitation. The low-temperature spectra for both interstitial traps are distinctly different from that for the ordered phase of NbH_x (see Fig. 3). For example, the peak energies are ~10 meV different in each case (Table I), and the width of the low-energy peak for $NbO_{0.011}H_{0.010}$ is about double that for the spectrum of a precipitated hydride phase. Furthermore, there is no evidence of a shoulder in either trapped hydrogen spectrum, which would indicate the presence of a precipitated phase.

The $NbO_{0.011}H_{0.010}$ system shows a more complex behavior in the intermediate temperature regime when compared with $NbN_{0.004}H_{0.003}$. At 150 K the position of the first peak is increased from 107 meV at 295 K to 112 meV. At the same time the linewidth reaches a maximum. The peak shift as well as the line broadening may be associated with the existence of more than one type of trapping site available for occupation at this temperature. However, the possibility that these effects are caused by the higher defect concentration as compared to the N defects cannot be excluded. At low temperature, where only the energetically most favorable site can be occupied, the measured peak positions for H trapped by O or N interstitials are practically the same.

The vibrational energies of H depend sensitively on the occupied interstitial site; e.g., in bcc V the lowest energy modes for H at octahedral sites are found about 50% lower than those for H at tetrahedral sites.[13,16] In addition, for an octahedral site in a bcc lattice, the first excitation is doubly degenerate, whereas for a tetrahedral site the second excitation is degenerate.[17] Therefore, the spectrum of a H that is not occupying a tetrahedral site will exhibit both a characteristic frequency shift and a lifting of the degeneracy of the upper mode. From the present results, we find clear evidence that the sites occupied by trapped H are similar to the tetrahedral positions in a relatively undisturbed Nb environment.

The occupation of tetrahedral sites is in disagreement with a suggestion by Zapp and Birnbaum.[8] They assumed that H atoms are spread out over the four tetrahedral and four triangular sites on the face of a cube as proposed earlier by Flynn and Birnbaum for untrapped H in pure Nb.[18] According to the present results, this model cannot be correct since no significant triangular site occupation is observed. In fact, the model seems inappropriate as it involves tunneling of H between inequivalent sites. The energy levels of H on these sites would be predicted to vary too strongly, due to the H-impurity interaction, to allow a delocalization. From channeling experiments on TaN_xD_y,[9] Carstanjen concluded that the trapped D occupies a position in between a tetrahedral and an octahedral site. The present observation of H trapped by O or N in Nb excludes such a position. However, it should be pointed out that the trapping energy suggested for N in Ta (Ref. 19) is only about half that of O or N in Nb, so that the geometry of the N-D defect in Ta may be different.

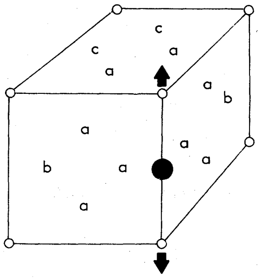

FIG. 4. Schematic representation of possible H sites associated with interstitial impurity on an octahedral site (●) in a bcc lattice. Refer to text for further explanation.

Recently Sugimoto and Fukai performed a quantum-mechanical calculation of the self-trapped state of H in Nb.[20] In order to model the vibrational properties of H as well as its well-known isotropic distortion field, they had to assume a strong, short-range interaction potential together with a long-range tail. As a consequence of the short-range part, the hydrogen vibration should be very sensitive to lattice distortions. As the nearest-neighbor Nb atoms (with respect to an octahedral O or N interstitial defect) are heavily displaced (see Fig. 4), it seems unlikely that the first-neighbor tetrahedral sites of these Nb atoms (marked *a*) are H positions. This suggests that both the first- and second-neighbor sites of the interstitial impurity located at an octahedral site (marked *a* in Fig. 4) are excluded.

Specific-heat[10] and inelastic neutron scattering experiments[11] have revealed a tunnel-split vibrational ground state of the trapped H. To explain these results, a double-well potential connecting two equivalent sites has been used. For these sites the nearest possible positions with respect to the O or N defect according to the discussion above (marked *b* in Fig. 4) need to be rejected, since their separation of about 3.5 Å is too large. The nearest sites that seem to fulfill all requirements are marked *c*. They are crystallographically equivalent with respect to the impurity and are not first neighbors of heavily displaced Nb atoms. In addition, the relatively large distance between the interstitial impurity and the proposed H positions would explain the lack of a substantial direct (electronic) force constant between them. Such a force constant would change the tetrahedral symmetry of the force field at the H site and lift the degeneracy of the upper mode.

Linewidths

All peak shapes measured in the present investigation are determined by intrinsic widths and not by the experimental resolution. A remarkable feature of the present results is that at room temperature both samples with interstitial impurities have smaller linewidths than low-concentration α-phase $NbH_{0.0055}$,[12] whereas the sample with the substitutional impurity V has a larger apparent linewidth than that of the pure metal-hydrogen system.

The relatively small widths observed for $NbV_{0.008}H_{0.005}$ at 78 K, where the H is precipitated into a high-concentration hydride phase, may result from a small dispersion of the optic modes. Similar widths have been observed for H in pure Nb.[12,13,21]

However, dispersion certainly cannot explain the widths for dilute H trapped by impurities, especially since the widths observed for the trapped H are even larger than the widths for ordered hydrides. At the low temperatures involved the origin of the widths is unlikely to be found in lifetime effects. Several mechanisms are possible to explain the large widths observed even at low temperatures:

(1) The statistical distribution of the impurities causes spatially varying strain fields. This was found to cause the relatively small fraction of undisturbed tunneling protons at similar impurity concentrations in measurements of the H tunnel states.[10,11] Moreover, the mean strain field at a trapped site was found to increase with impurity concentration in specific-heat measurements.[22] These strain fields may also result in a distribution of force constants determining the H vibrations. In this case the linewidths should depend on the impurity concentration. Indeed, we find the width for the first excitation for 1.1% O about twice as large as the width for 0.4% N.

(2) The presence of an interstitial impurity associated with a H atom disturbs the tetrahedral symmetry, thereby disturbing the eigenstates for the degenerate second excitation. As outlined above, the deviations from a tetrahedral symmetry cannot be strong. However, a contribution from such a disturbance to the widths cannot be excluded.

(3) A ground-state splitting of 0.19 meV has been observed spectroscopically[11] for $NbO_{0.01}H_{0.01}$ in accordance with specific-heat measurements.[10,22] From this, a splitting of 4 and 6 meV can be calculated for the first and second vibrational excitation, respectively, for an harmonic potential.[23] This suggests significant contributions to the observed linewidths. Moreover, a consideration of anharmonic effects will increase the splitting. A mean value for the strain-induced energy difference of the two pocket states of $\epsilon = 3.7$ meV was found for an impurity concentration of 1.3 at. % O in Ref. 11. Because this value is much larger than the ground-state splitting, only about 1 at. % of the H was found to be delocalized. In contrast, the splittings for the excited states are comparable to or larger than ϵ. This implies that a large fraction of H in the excited state will be delocalized. It also suggests that the effect of the excited-state tunneling, possibly in contrast to the ground-state tunneling, is easily observable at the temperatures measured.

SUMMARY

We have shown, by neutron spectroscopy of H vibration modes, that 0.8 at. % V as a substitutional impurity in Nb lowers the phase boundary for H precipitation by ~ 30 K. In contrast, the interstitial defects O and N trap H down to 4 K. Surprisingly, the local-mode energies of "free" H at 295 K and of trapped H at low temperature are almost equal. The data provide direct evidence that trapped H occupies sites which have a close resemblance to tetrahedral interstices in pure Nb. Thus the electronic H-N or H-O interaction must be rather small. Taking into account theoretical considerations of the range of the Nb-H potential and the requirement of a tunnel-split vibrational ground state, we suggest the pair configuration c-c' as the most likely trapping sites (Fig. 4). These sites are energetically lowered with respect to other tetrahedral sites in the host matrix, and therefore, a precipitation of the hydride phases is suppressed. The trapping, however, appears to have a relatively small effect on the force field effective for the H vibrations. The linewidths for trapped H are quite large. Several mechanisms that can contribute to the widths are discussed. It is likely that a significant contribution to the widths results from tunnel-split excited states.

Note added in proof. Results similar to those shown in the present paper for $NbV_{0.008}H_{0.005}$ (Fig. 1) have recently been observed for H associated with Cr substitutional defects in $NbCr_{0.01}H_{0.01}$ [Richter, Rush, and Rowe (unpublished)]. In these experiments, more extensive measurements of the line shape versus temperature of the broad lower energy band have revealed the existence of a trapped state with a vibrational energy *higher* than that observed in either the α or ϵ phases. As in $NbV_{0.008}H_{0.005}$, however, this trapping state does not surpress precipitation of the ordered ϵ phase. It is possible that the broad lower energy band in Fig. 1 at temperatures down to 190 K is indicative of the same phenomenon.

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