

Excited-state vibrational tunnel splitting of hydrogen trapped by nitrogen in niobium

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Abstract. – High-resolution inelastic-neutron-scattering spectra of hydrogen trapped by interstitial nitrogen impurities in $\text{NbN}_{0.007}\text{H}_{0.004}$ have been measured to study the vibrational lineshape of the broad 105 meV feature previously observed for $\text{NbN}_{0.004}\text{H}_{0.003}$. The spectrum measured at 4.2 K exhibits clear evidence of a doublet that disappears at higher temperatures. We interpret this result as the first spectroscopic observation of excited-state tunnel splitting of light-atom (H) vibrations in a solid-state double-well potential. We also show that both the observed excited-state splitting of 4.0 ± 0.3 meV and the previously measured ground-state splitting are well represented by a hardened-harmonic-well potential.

The trapping of hydrogen by interstitial and substitutional impurities in niobium provides a fundamental example of H tunnelling in metals at low temperature [1, 2] and represents a model system for atomic transfer studies relevant to quantum diffusion theory [3-6]. Hydrogen trapped by interstitial oxygen impurities in NbO_xH_y ($y \approx x$) has been widely studied by specific heat [7-9] (and ultrasonic or anelastic measurements [10-15]), which provided the first evidence of quantised H motions at very low temperatures. Subsequently, direct measurement of ground-state tunnelling transitions of ~ 0.1 – 0.2 meV for H trapped by O [16-20], N [21], and C interstitial impurities [22] as well as Ti substitutional impurities [23] has been achieved by cold-neutron spectroscopy. These results and related local diffusion studies at higher temperatures have been associated with non-adiabatic coupling of hydrogen to the conduction electrons (Kondo effect) [5, 6, 18, 20].

In the light of the ground-state tunnelling results, a previous low-resolution, incoherent-inelastic-neutron-scattering (IINS) study [24] of $\text{NbN}_{0.004}\text{H}_{0.003}$ has suggested that the large peak widths observed for the hydrogen normal-mode vibrations might be associated with

unresolved *excited-state* tunnel splitting. Such splitting has been previously reported in the substitutional-trap system $\text{NbTi}_{0.01}\text{H}_{0.0095}$ [23] although a more complex array of tunnelling levels results from apparent hydrogen delocalisation over four or six trap sites. In this letter, we present spectroscopic evidence of excited-state tunnel splitting for the simpler interstitial N-trap system via high-resolution IINS measurements of the fundamental singlet vibration of H in $\text{NbN}_{0.007}\text{H}_{0.004}$. We believe that these measurements represent the first spectroscopic observation of excited-state tunnel splitting of light-atom (H) vibrations in an interstitial defect system. We also show that these results are surprisingly well represented by a relatively simple double-well potential, in distinct contrast to the measurements of split H vibrations due to substitutional Ti metal defects [23].

A detailed description of the sample preparation is given elsewhere [25]. Briefly, $\text{NbN}_{0.007}\text{H}_{0.004}$ and $\text{NbN}_{0.007}$ samples consisted each of a (25 mm diameter \times 30 mm length, 86 g) cylindrical bundle of approximately 170 Nb (99.99% metals purity, 1.6 mm diameter) wires. After decarbonation in low-pressure oxygen and ultrahigh-vacuum degassing at 2573 K, the Nb wires were doped with nitrogen by equilibrium gas-phase absorption at 1993 K and subsequently quenched rapidly to 773 K to retain N in solid solution. Hydrogen loading was also accomplished by gas-phase absorption at 773 K using a calibrated dose volume to titrate the desired concentration. Residual resistivity measurements before and after H loading, as well as inspections by electron-microscope and Snoek-effect measurements, were performed to corroborate the absence of N precipitates and subnitrides. The prepared samples were supported in thin-walled Al containers and mounted into a liquid-helium-cooled cryostat for spectral analysis.

The IINS measurements were performed at the Neutron Beam Split-Core Reactor (NBSR) at the National Institute of Standards and Technology using the BT-4 triple-axis spectrometer. Incident neutron energies were selected using a Cu(220) monochromator. For the low-resolution measurements, 40' collimations before and after the monochromator were used in conjunction with a Be-filter analyser; for the high-resolution measurements, 20' pre- and post-collimations were used in conjunction with a composite Be-graphite-Be-filter analyser. In the latter configuration, the instrumental resolution was about 2.6 meV (full width at half-maximum, FWHM) at 105 meV energy transfer, much better than the 6.3 meV FWHM resolution obtained from the low-resolution configuration, which was also the configuration used in the previous $\text{NbN}_{0.004}\text{H}_{0.003}$ study [24].

The low-resolution IINS spectrum of the fundamental H vibrational modes in $\text{NbN}_{0.007}\text{H}_{0.004}$ at 4.2 K is shown in fig. 1 along with a schematic representation of the bcc Nb structure depicting a single hydrogen trapped by nitrogen at sites as indicated previously [24]. The lower-energy (≈ 105 meV) and higher-energy (≈ 157 meV) bands are associated, respectively, with the singlet and doubly degenerate hydrogen vibrations for an interstitial (irregular) tetrahedral site in a bcc metal lattice. For $\text{NbN}_{0.007}\text{H}_{0.004}$, however, the local symmetry surrounding the H is distorted by the strain field induced by the presence of the N trapping atom in the nearby tetrahedral interstice, so that the otherwise degenerate modes are likely split [24]. As noted in the previous $\text{NbN}_{0.004}\text{H}_{0.003}$ study, both the low- and high-energy peaks are markedly broader than the instrumental resolution (*e.g.*, ≈ 10 meV FWHM peak width for the low-energy singlet).

To probe the source of this peak broadening, we have measured the singlet peak with much better instrumental resolution. Figure 2 shows the high-resolution IINS spectra of the low-energy H vibrational mode for $\text{NbN}_{0.007}\text{H}_{0.004}$ measured at 4.2, 77, and 296 K. Featureless background contributions from the metal host lattice were removed by subtraction of a least-squares fit of the $\text{NbN}_{0.007}$ blank spectrum measured under identical conditions. At 4.2 K, a definite spectral splitting is resolved by the present measurement. At 77 and

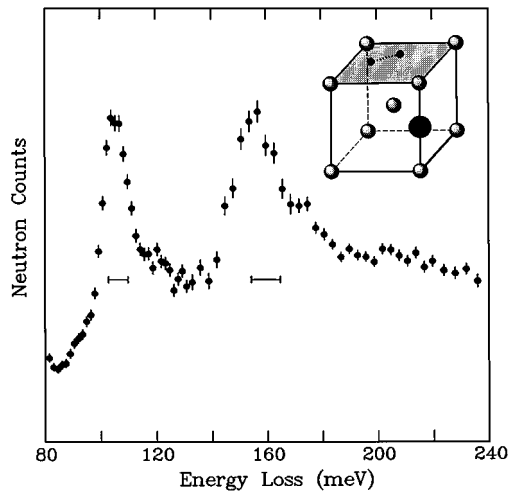


Fig. 1

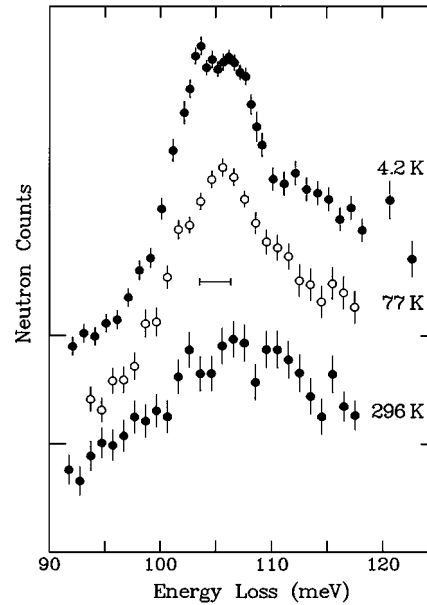


Fig. 2

Fig. 1. – Low-resolution IINS spectrum of $\text{NbN}_{0.007}\text{H}_{0.004}$ at 4.2 K. The instrumental resolution (FWHM) is illustrated by the horizontal bars beneath the spectra. Spectral energies are determined assuming an average neutron final energy of 3 meV. Inset: Schematic depicting the location of the pair of tetrahedrally coordinated H trapping sites (small black circles) due to the presence of an octahedrally coordinated, interstitial N impurity (large black circle) in the bcc lattice of Nb (shaded circles). At low temperature, a single trapped H atom tunnels between the sites.

Fig. 2. – High-resolution IINS spectra of the low-energy H vibrational mode in $\text{NbN}_{0.007}\text{H}_{0.004}$ at 4.2, 77, and 296 K after removing the $\text{NbN}_{0.007}$ blank spectrum. The horizontal tick marks correspond to the offset baselines for the 4.2 K and 77 K spectra. The instrumental resolution (FWHM) is illustrated by the horizontal bar beneath the spectra. Spectral energies are determined assuming an average neutron final energy of 1 meV.

296 K, it is clear that this splitting has disappeared. The peak in the 4.2 K spectrum was fit by various schemes to bracket the magnitude of the splitting. Lorentzian, Gaussian, and combination (*i.e.*, pseudo-Voigt) lineshapes were attempted to describe the components of the doublet. In addition, the presence of the multiphonon band on the higher-energy side was modelled by the convolution of the main doublet with the phonon density of states previously measured for Nb [26], which possesses a low-energy peak maximum near 16 meV. From the various fitting procedures, a peak splitting of 4.0 ± 0.3 meV was obtained with a median peak energy of 105.1 meV. This peak splitting is of the same magnitude as the multiple splittings found for the analogous yet more complex vibrational band near 109 meV for hydrogen in $\text{NbTi}_{0.01}\text{H}_{0.0095}$ [23].

A splitting of similar magnitude has also been observed [27-31] for the *c*-polarised vibration of tetrahedrally coordinated interstitial hydrogen in α -phase solid solution with the rare-earth metals Y, Sc, and Lu. Yet, unlike the H atoms in nitrogen-doped Nb, which are to first order isolated by the dilute nitrogen traps [32], the H atoms in these rare-earth-hydrogen α -phase systems have a tendency to form zigzag chains of next-nearest-neighbour H-H pairs along the *c*-direction. Hence, the vibrational splitting encountered in these systems is a direct

manifestation of the dynamic coupling between H atoms within the c -directed chains due to H-H interactions. This type of splitting also demonstrates a different temperature dependence than is seen for the splitting of the singlet vibration of nitrogen-trapped H in Nb. In particular, the splitting observed for the rare-earth-hydrogen α -phase systems persists up to relatively higher temperatures (≈ 200 K), and its disappearance coincides with the breakdown of H-H pairing order. In contrast, the splitting observed for unpaired, nitrogen-trapped H in Nb at 4.2 K is already absent in the 77 K spectrum. This is in agreement with the theoretical prediction [6] of a crossover from coherent tunnelling motion between trap sites below 10 K to local jump diffusion processes at higher temperatures. Such a result is consistent with the previously observed disappearance of the ground-state splitting in this system, which was shown to only exist below 10 K in the superconducting state [18].

It should be pointed out that, although a definite peak splitting is observed for $\text{NbN}_{0.007}\text{H}_{0.004}$, its appearance is affected by the distribution of perturbations to the double-well potentials due to the strain fields generated by the N interstitials. The component tunneling bands exhibit non-Gaussian peakshapes consisting of sharp central components with significant spectral wings. The observed shapes reflect the distribution of asymmetries from N-induced lattice distortions [1]. The sharp central components are indicative of a substantial fraction of symmetric and near-symmetric double-well potentials within the broad overall distribution of asymmetries. The width and shape of this distribution is dependent on the dopant concentration. Decreasing this concentration is known to narrow the energy-shift distribution function, as evidenced by the sharpening of ground-state tunnelling peaks [18,21].

It is useful at this stage to inquire to what extent the splitting of the hydrogen vibrational singlet in $\text{NbN}_{0.007}\text{H}_{0.004}$ can be understood in terms of an elementary one-dimensional, symmetric, double-well potential for the motion along the line joining the two sites in the trap, even recognising that, in undoped Nb, the singlet vibrational direction makes a 45° angle with this line. Such a model needs to account simultaneously for the observed vibrational energy and splittings, which is a significant constraint on possible potential shapes when the distance between wells is fixed at or close to the distance between nearest-neighbour tetrahedral sites. Two well-known candidates for trial are the double harmonic well and the double quartic well. The double harmonic well is formed by the abutment of two parabolic wells: $V_h(x) = \min[v(x-a), v(x+a)]$, where $v(x) = 1/2kx^2$, k is an adjustable force constant, and $2a$ is the distance between minima. Its low-lying spectrum is known in detail [33,34], but it is incapable of describing the present case. Essentially, the double harmonic oscillator proves to be too soft: the ratio of the first-excited-state splitting to the vibrational energy between the ground-state and first-excited-state levels is much larger than is required to explain the data. The standard double quartic well has the form $V_q(x) = V_0 - ax^2 + \beta x^4$, where α and β are positive adjustable parameters. This potential form, while harmonic near its minima, proves to be too hard because of its quartic sides. Numerical analysis, discussed below, shows that the splitting/vibration ratio is much smaller than is needed to rationalise the data. Thus we have been led to consider a simple model that can interpolate these extremal shapes using only one additional parameter. It is the convex sum of the two double-well shapes described above,

$$V(x) = (1 - \mu)V_h(x) + \mu V_q(x), \quad (1)$$

where $\mu = 0$ corresponds to the double harmonic well and $\mu = 1$ gives the double quartic well. We fix both double-well functions to have the same site separations and barrier heights, V_0 , defined in each case as the potential at $x = 0$ (thus, in the harmonic well, $k = 2V_0/a^2$, while in the quartic well, $\alpha = 2V_0/a^2$, and $\beta = V_0/a^4$). Then $V(0) = V_0$ in eq. (1), and the interpolating model is completely specified by three parameters: $2a$, the site separation, V_0 ,

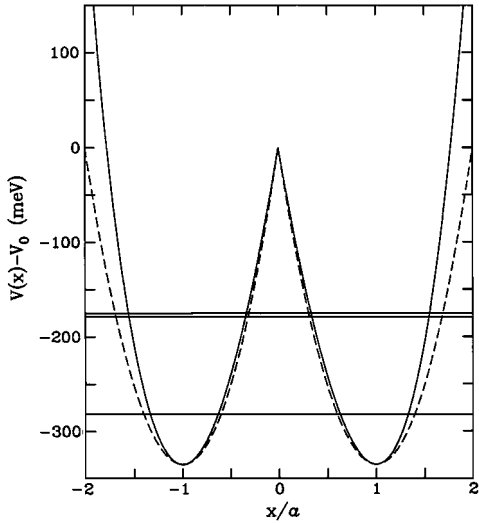


Fig. 3

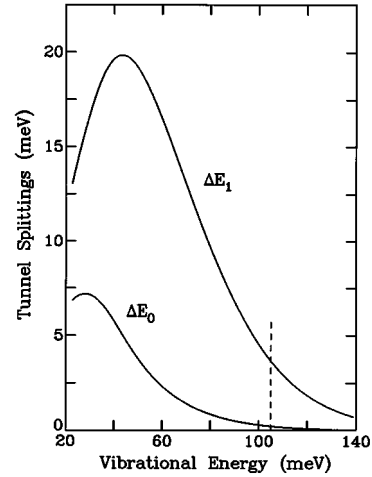


Fig. 4

Fig. 3. – The model potential and energy levels resulting from the fit of the experimental splitting and vibrational energy using eq. (1) with $\mu = 0.1$ and $2a = 1.13 \text{ \AA}$. N.B., the ground-state splitting is unresolved on the scale used in the figure. The dashed line shows the double harmonic well (*i.e.*, $\mu = 0$) for reference.

Fig. 4. – The ground-state and first-excited-state splittings *vs.* the vibrational energy for $\mu = 0.1$ and $2a = 1.13 \text{ \AA}$. The experimentally observed vibrational energy of 105 meV is marked by the dashed line.

the barrier height, and μ , the shape admixture parameter.

For each realisation of the model, the Schrödinger equation was solved numerically using the Kimball and Shortley iterative method [35] on a fine mesh of points along the x -axis. The algorithm finds the lowest energy eigenfunction in a given manifold. Once the ground state has been computed, it is projected out of the manifold using Schmidt orthogonalisation or parity, as appropriate, and the next highest state (*i.e.*, the lowest in the new manifold) is found, and so on. The method is accurate and stable for a small number of states, such as we deal with here, but eventually the need for explicit orthogonalisation degrades numerical stability.

For given μ and V_0 , the Schrödinger equation can be solved along the unitless x/a axis, and the resulting energies can be rescaled to physical dimensions, a convenience which facilitates searching the parameter space. We found the model spectra to be sensitive to all three adjustable parameters, especially the well separation, $2a$. By visual inspection, we sought good agreement between the observed excited-state splitting and the vibrational energy, a very restrictive requirement, as discussed above. To find a fit, we varied μ for fixed a values, and then by varying V_0 , examined the excited-state splittings associated with vibrations near 100 meV. In fig. 3, we show the model (eq. (1)) and resulting spectrum for our estimate of fit. In fig. 4, we show the graph of ground-state and first-excited-state splittings as a function of vibrational energy for our choice of admixture, $\mu = 0.1$. While this represents a relatively small admixture of the quartic component, it significantly alters the shape of the double-harmonic potential, effectively hardening it, as can be seen in fig. 3, and is necessary to get agreement. We found that $2a = 1.13 \text{ \AA}$, which is near the equilibrium spacings of 1.17 \AA for the nearest-neighbour tetrahedral-site separation in Nb [36], allowed the best agreement. The

calculated excited-state splitting of a 105 meV vibration is 3.7 meV, in very good agreement with the measurement. The barrier height for this potential is approximately 330 meV, which also is a reasonable value. Moreover, the resulting ground-state splitting of 0.22 meV is in good agreement with the experimental peak energy of ≈ 0.18 meV observed for the more dilute Nb(NH)_{0.0005} trap system [21]. It should be noted that our simple model does not consider the effects of concentration-dependent strains on the observed tunnelling levels [18, 21], but these effects are expected to be relatively small and will have little impact on the excited-state tunnel splitting. Further, despite the success of our relatively simple one-dimensional model in reproducing the key features of this tunnelling system, we stress that our potential is only meant to represent the dominant one-dimensional effects of the actual three-dimensional H potential.

In closing, we would note that investigations of excited-state tunnel splitting are currently being extended to other metal-hydrogen systems possessing either substitutional or interstitial traps in order to determine if the presence of a more extensive hydrogen delocalisation with its more complex set of tunnelling levels is typical of the substitutional-trap systems compared to the interstitial-trap systems.

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