Neutron-Spectroscopic Evidence for Hydrogen Tunneling States in Niobium

H. Wipf
Physik-Department der Technischen Universität München, D-8046 Garching, Germany

and

A. Magerl
National Bureau of Standards, Washington, D. C. 20234

and

S. M. Shapiro, S. K. Satija, and W. Thomlinson
Brookhaven National Laboratory, Upton, New York 11973

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Inelastic neutron scattering measurements demonstrating H tunneling states for O-H pairs in $NbO_{0.013}H_{0.016}$ are presented. The tunneling matrix element found is 0.19 ± 0.04 meV.

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The most direct experimental evidence for H (D) tunneling in metals was obtained from low-temperature specific heat,[1,2] thermal conductivity,[3] and anelasticity measurements[4,5] for N-H (N-D) and O-H (O-D) pairs in Nb. In this Letter we present the first spectroscopic experiments showing H tunneling in a metal. They are also the first experiments showing tunneling-induced inelastic scattering in a system where sizable polaron[6,7] (lattice distortion) effects are expected for the tunneling atoms. These effects, which are of central importance for hydrogen diffusion in metals,[6,7] are negligible in systems in which rotational tunneling has been observed.[8] From our results we obtain a value of the tunneling matrix element and an estimate of the strain-induced interaction between different pairs.

The experiments were performed on a 90-g polycrystalline sample of $NbO_{0.013}H_{0.016}$ consisting of seven rods (diameter 6 mm, length 45 mm). For O and H doping, the pure Nb crystals (MRC, 99.99% purity) were annealed first in an O_2 atmosphere (~1800 °C, 2×10^{-5} mbar O_2, 16 h) and then in a H_2 atmosphere (~1150 °C, 330 mbar H_2, 15 min). After the last annealing, the rods were quenched to room temperature in order to prevent O clustering. The O concentration was determined by residual resistivity measurements[9] (before H doping), and the H concentration by vacuum extraction of small pieces cut from the individual rods. Because of the excess H, our sample contained, besides O-H pairs (1.3 at. %), small amounts (0.3 at. %) of precipitated H at low temperatures (tunneling is not observed[2] for precipitated H).

The neutron scattering experiments were performed on a triple-axis spectrometer at the Brookhaven high-flux–beam reactor. Pyrolytic graphite crystals were used as monochromator and analyzer, and the collimations were 20′-40′-20′-40′ (from reactor to detector). The incident energy was kept fixed at 4.5 meV, and higher-order contamination was removed by a cooled Be filter. The energy resolution measured with vanadium had a full width at half maximum (FWHM) of 0.10 ± 0.01 meV, which agrees with the calculated value. It was very well Gaussian also in its tails. All energy scans were performed at constant $q = 2.5$ Å^{-1}. The sample was mounted in a ^{3}He/^{4}He dilution refrigerator, and spectra were obtained at $T = 0.09$ and 5 K.

Figure 1(a) shows the spectrum obtained at $T = 0.09$ K. Energy-gain processes are not observed at this low temperature, and the intensity on the energy-loss side is evidence for an inelastic scattering process. As the temperature is raised to 5 K [Fig. 1(b)], the data indicate an intensity increase on the energy-gain side, and a *decrease* on the energy-loss side. This proves directly that the scattering is not due to phonons since, in such a case, the intensity on the energy-loss side should increase strongly between 0.09 and 5 K (by a factor of 3 for one-phonon processes and by an even larger factor for multiphonon processes). We propose that the inelastic scattering results from energy transfer to H tunneling states. Because of the small incoherent scattering cross section of Nb, the elastic scattering is primarily due to incoherent scattering from H atoms. This elastic scattering is about 100 times stronger than the observed inelastic scattering.

Our present results can be understood quanti-

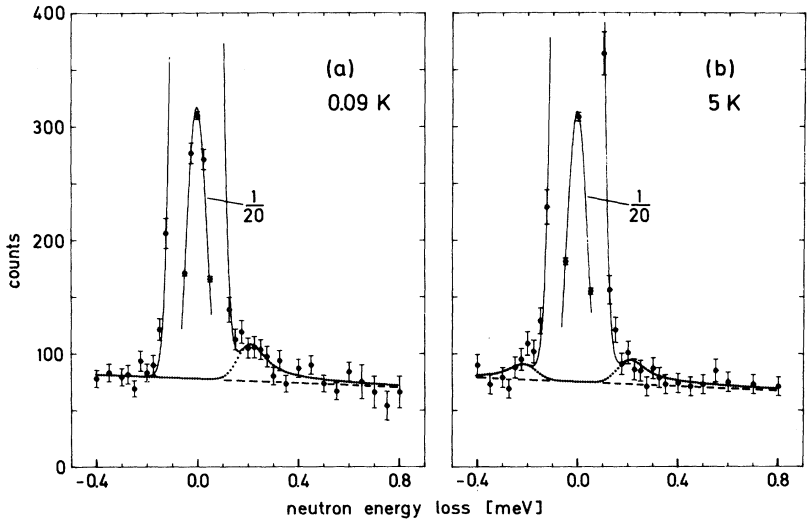

FIG. 1. Inelastic neutron spectra of $NbO_{0.013}H_{0.016}$ at (a) 0.09 K and (b) 5 K. The counting time is 84 min (the counts and standard deviations for data points measured with different counting times are appropriately corrected). The full, dotted, and broken lines indicate fits explained in the text.

tatively in terms of H tunneling between two equivalent interstitial sites[10] whose energies differ randomly by a shift ϵ resulting from strain-induced interaction effects between different O-H pairs.[2] For a statistical spatial pair arrangement, the distribution function $Z(\epsilon)$ of ϵ is Lorentzian,[11]

$$Z(\epsilon)=\pi^{-1}\epsilon_0/(\epsilon_0^2+\epsilon^2), \quad (1)$$

where ϵ_0 characterizes a typical energy difference between the two sites.

For a given shift ϵ, the energy difference ΔE between the two lowest eigenstates in a tunneling system is[12-14]

$$\Delta E=(J^2+\epsilon^2)^{1/2}, \quad (2)$$

where J is the effective tunneling matrix element. For a tunneling system consisting of two harmonic potential wells, J is given approximately by[12,15,16]

$$J=f\hbar\omega_H(m\omega_H d^2/\pi\hbar)^{1/2}\exp(-m\omega_H d^2/4\hbar), \quad (3)$$

where m is the H mass, d is the distance between the two potential wells, and ω_H is the vibrational frequency of the H within a well [ω_H corresponds to 110 or 170 meV (Ref. 17)]. The factor f ($f \approx 0.1$)[7] accounts for the local (polaron) lattice relaxations.

The present model is closely analogous to the two-site tunneling system discussed for glasses.[13] However, since the spatial configuration of the tunneling sites is identical for each O-H pair, J is essentially the same for all tunneling systems because this quantity usually is not significantly modified by strain-induced energy shifts.[15,18] Therefore, contrary to glasses, the energy difference ΔE in Eq. (2) has a lower bound value J for those pairs for which ϵ is fortuitously zero.

For the tunneling systems considered, the incoherent cross sections for inelastic and elastic scattering from H atoms are[12,19]

$$\left(\frac{d^2\sigma}{d\Omega\, d(\hbar\omega)}\right)_{\text{inel}}=\frac{\sigma_{\text{inc}}}{4\pi}\frac{k_f}{k_i}e^{-2W}\left(\frac{1}{2}-\frac{\sin(qd)}{2qd}\right)\int_{-\infty}^{+\infty}d\epsilon\, Z(\epsilon)\frac{J^2}{J^2+\epsilon^2}\frac{\delta(\hbar\omega+\Delta E)+\delta(\hbar\omega-\Delta E)}{1+\exp(-\hbar\omega/k_B T)} \quad (4a)$$

and

$$\left(\frac{d^2\sigma}{d\Omega\, d(\hbar\omega)}\right)_{\text{el}}=\frac{\sigma_{\text{inc}}}{4\pi}e^{-2W}\left[\epsilon_0+J\left(\frac{1}{2}+\frac{\sin(qd)}{2qd}\right)\right]\frac{\delta(\hbar\omega)}{\epsilon_0+J}, \quad (4b)$$

where σ_{inc} is the incoherent cross section of H, k_i and k_f are the wave vector of the incident and scattered neutrons, $\hbar\omega$ is the energy, and $\hbar q$ is the momentum transferred during scattering;

e^{-2W} is the Debye-Waller factor, which is close to 1 for the present q values.[17] Equation (4) takes account of both the energy-shift distribution $Z(\epsilon)$ and the orientational averaging required for polycrystalline samples. From Eq. (4), the ratio between the integrated inelastic and total scattering intensities I_{inel} and I_{tot} found in a constant-q scan is

$$\frac{I_{\text{inel}}}{I_{\text{tot}}} = \frac{J}{\epsilon_0 + J}\left(\frac{1}{2} - \frac{\sin(qd)}{2qd}\right), \tag{5}$$

where the term k_f/k_i is neglected since it is nearly unity for the present $\hbar\omega$ range. According to Eq. (5), the inelastic scattering is a maximum for $q \approx 4.5/d$ and $\epsilon_0 \ll J$. The inelastic scattering is a much smaller fraction of the total scattering if $\epsilon_0 \gg J$, as will be found to be the case in the present experiment.

The resolution function as measured with a vanadium standard was convoluted with Eq. (4) and a least-squares fit with the data at $T = 0.09$ K was performed. The variation of the resolution with energy was not taken into account; however, this correction would not substantially change the results. The parameters varied were J and the normalization parameters for Eq. (4), which effectively are I_{inel} and I_{tot}. A sloping background was also included in the fitting procedure. The fits are shown in Fig. 1(a) as dotted, full, and dashed lines representing the calculated inelastic, total, and background scattering, respectively. The parameters obtained are $J = 0.19 \pm 0.04$ meV and $I_{\text{inel}}/I_{\text{tot}} = 0.011 \pm 0.003$. With these values fixed, the spectrum at $T = 5$ K was calculated by varying only T in Eq. (4) [Fig. 1(b)]. The fit is reasonable within the counting statistics, but can be improved by reducing J. This reduction of the tunneling matrix element with increasing T may indicate the influence of coupling of phonons to the H tunneling states when $k_B T \gg J$.

The characteristic energy shift ϵ_0 was not an explicit fit parameter since the fit is insensitive to this quantity as long as $\epsilon_0 \gg J$. In fact, all the fit parameters vary insignificantly (J by less than 1%) for any fixed ϵ_0 larger than 1 meV. Therefore, the results given above and the curves in Fig. 1 are valid for $\epsilon_0 \geq 1$ meV.

The present result, $J \approx 0.19$ meV, agrees well with the value deduced from the specific-heat measurements.[2,20] It also allows an estimate for the distance d between the two tunneling sites. From Eq. (3), we find $d = 0.87$ and 0.73 Å, using 110 and 170 meV, respectively, for $\hbar\omega_H$ and $f = 0.1$. These distances are considerably smaller than the 1.17-Å distance between the tetrahedral sites occupied by H in pure Nb. Once d is obtained we can use Eq. (5) to calculate ϵ_0 by using the measured ratio $I_{\text{inel}}/I_{\text{tot}} \approx 0.011$. For an average $d \approx 0.8$ Å, and increasing the experimental intensity ratio by ~20% to take account of the precipitated H, we obtain $\epsilon_0 \approx 3.7$ meV. This value, which is much larger than J, demonstrates the importance of the strain-induced interaction effects. It agrees well with the estimates given in Ref. 2.

In summary, we have presented the first spectroscopic evidence for H tunneling states in a metal. We plan to investigate in more detail the q dependence of the tunneling states as well as their temperature dependence. This temperature dependence is particularly interesting in connection with H diffusion theory[6,7] since it opens the way for neutron spectroscopy to explore the transition between coherent (bandlike) and incoherent quantum transport, which is characterized by a destruction of the tunneling states because of a coupling to phonons.

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Frequency-Dependent Dielectric Response in Polar Liquids

E. L. Pollock and B. J. Alder

University of California, Lawrence Livermore National Laboratory, Livermore, California 94550

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Molecular-dynamics computations for point dipolar particles of the time-dependent polarization fluctuations allow evaluation of the dielectric properties. From these the collective effects in the longitudinal component (dipolarons) analogous to the plasma oscillations (plasmons) in Coulomb systems can be readily identified. The transverse mode, by contrast, is strongly damped.

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The relaxation of the total polarization of a polar liquid, quantitatively expressed in terms of the frequency-dependent dielectric tensor, is theoretically predicted to have two kinds of collective effects.[1] One corresponds to a transverse mode for which the transverse component of the dielectric tensor has a pole and the other corresponds to a self-sustained longitudinal collective mode for which the longitudinal component of the dielectric tensor vanishes. The prediction of this longitudinal collective mode in dipolar fluids, called a dipolaron, analogous to the plasma oscillations in Coulomb systems, has stimulated experimental work, which, though very suggestive, is not completely conclusive.[2] In this Letter, molecular-dynamics (MD) simulations of the polarization fluctuations confirm the existence of such collective modes for a model polar fluid.

The relation between the dielectric tensor $\vec{\epsilon}(k, \omega)$, and the time-dependent polarization fluctuations[3,4] at any nonzero wave vector, k, follows from linear-response theory:

$$[\epsilon_L(k, \omega)]^{-1} = 1 + 4\pi\rho\mu^2\beta\int_0^\infty [dg_L(k, t)/dt]\, e^{i\omega t}\, dt \qquad (1)$$

and

$$\epsilon_T(k, \omega) = 1 - 4\pi\rho\mu^2\beta\int_0^\infty [dg_T(k, t)/dt]\, e^{i\omega t}\, dt \qquad (2)$$

for the longitudinal (L) and transverse (T) components, where

$$\vec{g}(k, t) = (N\mu^2)^{-1}\langle \vec{\mathbf{M}}_k(t)\vec{\mathbf{M}}_{-k}(0)\rangle, \qquad (3)$$

$$\vec{\mathbf{M}}_k(t) = \textstyle\sum_i \vec{\mu}_i(t)\exp[ik\cdot r_i(t)], \qquad (4)$$

and the angular brackets denote an ensemble average. In the long-wavelength limit, $k = 0$, the polarization fluctuations depend on boundary effects (e.g., sample shape). The appropriate formula in that limit, where the transverse and longitudinal components become identical, is given by Eq. (2) if periodic boundary conditions