Isotope Dependence of Hydrogen Tunneling in Niobium

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We present ultrasonic experiments on the low-temperature tunneling of H and D interstitials in Nb. Strong isotope effects are observed in the sound velocity and the attenuation. From the temperature dependence of these quantities we determine tunneling matrix elements and relaxation rates for both isotopes. We demonstrate that this isotopic behavior is adequately described by present theories on nonadiabatic interaction of tunneling systems with conduction electrons in the weak-coupling regime.

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Low-temperature tunneling of trapped H interstitials in Nb has been intensively investigated by specific-heat,[1-3] acoustic,[4-9] and neutron spectroscopic[10,11] measurements. In these measurements H was trapped by O or N impurity atoms under formation of O-H or N-H pairs. The results are well explained by the H atom occupying a double-well potential consisting of two nearest-neighbor tetrahedral interstitial sites. Tunneling of the H gives rise to two-level systems with energy splitting $E=(\Delta_0^2+\Delta^2)^{1/2}$. Δ_0 is the tunneling matrix element and Δ is an energy shift between the two potential wells arising from lattice strains caused by neighboring O-H or N-H pairs. The dynamical properties of the H tunneling systems are dominated by nonadiabatic interaction with conduction electrons.

The two-level systems formed by trapped H exhibit a close similarity to the intrinsic tunneling system in glasses.[12] There are, however, two important differences. First, the tunneling matrix elements in glasses are broadly distributed whereas they are nearly identical for all the H atoms in Nb as a consequence of the crystallinity of the metal host. Second, hydrogen allows a detailed investigation of isotopic effects with the highest possible atomic mass ratio. Both facts make trapped hydrogen a discriminative model system for an experimental test of theoretical predictions on the dynamical properties of tunneling systems. Although these properties can be studied by both neutron spectroscopy and acoustic measurements, only acoustic experiments presently allow the investigation of isotope effects.

In this Letter, we report on results of ultrasonic experiments in which we specifically investigated the isotopic behavior of the tunneling systems formed by N-H and N-D pairs in Nb. The measured quantities, sound velocity and attenuation, reflect the resonant and the relaxation processes characteristic of the interaction between tunneling systems and sound waves. For both isotopes we determine the tunneling matrix elements from the sound velocity and the relaxation rates from the attenuation. We demonstrate for the first time experimentally that the relaxation rate obeys the theoretically predicted isotope effect for a dominant interaction with conduction electrons.

Our ultrasonic experiments were carried out between 0.01 and 20 K. Below the superconducting transition temperature of Nb ($T_c=9.2$ K) they were performed in both the superconducting state and the normal conducting state retained by a magnetic field of 1 T. We applied a pulse-echo method with phase-sensitive detection. Absorption and relative change of sound velocity were measured with resolutions of 0.01 dB/cm and $<10^{-6}$, respectively. We studied longitudinal sound waves generated by a sputtered ZnO transducer and propagated in the [100] direction of the Nb single crystal. The crystal was doped with 0.15 at.% N and 0.3 at.% H. After the first part of the measurements H was extracted and the sample was subsequently doped with 0.24 at.% of the heavier isotope D. This procedure guarantees an identical N content and thus the same distribution of strain fields for the investigation of both hydrogen isotopes. Details of the doping procedures were described previously.[2]

Figure 1 shows our results for the sound velocity. Above 10 K the sound velocity decreases due to anharmonicity of the host lattice. The data of the doped samples merge at higher temperatures with those of an undoped sample. Below 10 K we observed a strongly isotope-dependent reduction of the sound velocity relative to pure Nb. The temperature-dependent reduction is the result of two different interaction processes be-

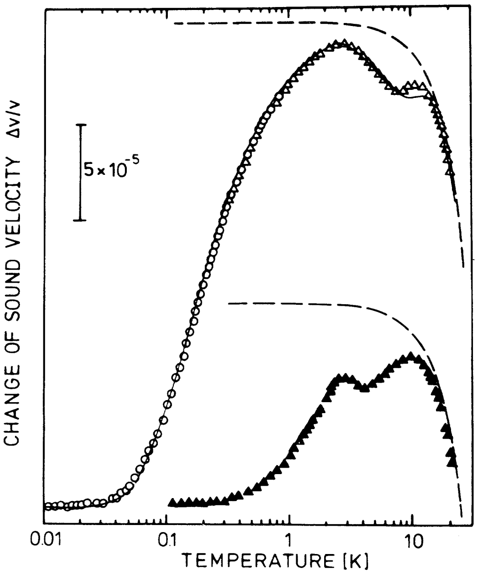

FIG. 1. Temperature dependence of the sound velocity of NbN$_{0.0015}$H$_{0.003}$ at 90 MHz (▲) and NbN$_{0.0015}$D$_{0.0024}$ at 980 MHz (○) and 110 MHz (△). Broken lines represent data of a hydrogen-free sample. The data are shifted for clarity so that the sound velocities of the hydrogenated and the deuterized sample are equal for $T \to 0$. The material is superconducting below $T_c = 9.2$ K. The solid line is a fit including resonant and relaxation processes and the lattice anharmonicity.

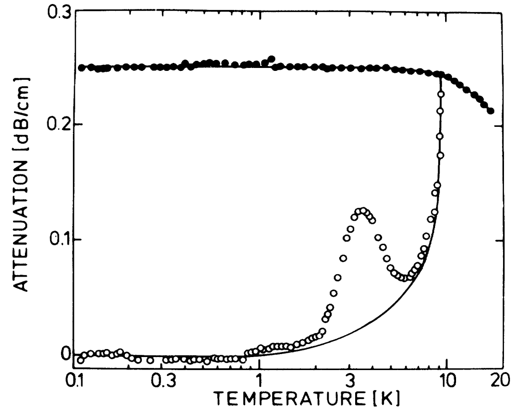

FIG. 2. Temperature dependence of ultrasonic attenuation in NbN$_{0.0015}$H$_{0.003}$ at 90 MHz: (○), superconducting; (●), normal conducting. Solid lines are data of a hydrogen-free sample.

tween sound waves and tunneling systems: a relaxation process as discussed below and a resonant process.[13] The resonant process causes a reduction of the sound velocity proportional to the temperature-dependent population difference of the two levels. The relative change $\Delta v/v$ of the sound velocity is given by[13]

$$\frac{\Delta v}{v} = -\frac{n_0 \gamma^2}{\rho v^2}\left(\frac{\Delta_0}{E}\right)^2 \frac{1}{E} \tanh\left(\frac{E}{2k_B T}\right), \tag{1}$$

where n_0 is the concentration of tunneling systems, ρ is the density, and v is the sound velocity of the material. $\gamma = \delta\Delta/\delta e$ is the variation of the asymmetry energy Δ with respect to the strain e. For a double-well potential consisting of two nearest-neighbor tetrahedral sites γ is determined by the anisotropy $A - B$ of the double force tensor of a H or D on these sites of tetragonal symmetry.[14] For longitudinal sound waves in the [100] direction as in our experiment $\gamma^2 = 2(A-B)^2/3$. Equation (1) applies only if the phase coherence time of the tunneling particle is much longer than h/E which holds for temperatures well below the superconducting transition.[15,16] Recent measurements on Nb doped with O and H were analyzed with Eq. (1) and actually provided the first values for the energy splitting of H tunneling systems.[5] For a more precise analysis, however, we have to consider a distribution function $n(\Delta)$ for the asymmetry energy Δ which is caused by lattice strains from the randomly distributed neighboring N trap centers. The tunneling matrix elements Δ_0 for both hydrogen isotopes are assumed to be single valued, reflecting the crystallinity of the host lattice. For the distribution of Δ we choose a Lorentzian[2,10] with a characteristic width $\bar{\Delta}$:

$$n(\Delta) = \frac{n_0}{\pi} \frac{\bar{\Delta}}{\bar{\Delta}^2 + \Delta^2}. \tag{2}$$

From our sound velocity data we determine the tunneling matrix elements for both hydrogen isotopes as the result of a fit according to Eq. (1) in which we substituted $n(\Delta)$ for n_0 and integrated over Δ. Up to 2.5 K for the H-doped and up to 3 K for the D-doped sample the resonant process of Eq. (1) is sufficient to describe excellently our sound velocity data. For the tunneling matrix elements of H and D we find $\Delta_0(\mathrm{H}) = 1.4 \pm 0.1$ K and $\Delta_0(\mathrm{D}) = 0.18 \pm 0.01$ K in good agreement with recent specific-heat experiments.[3] We point out that our analysis allows an extremely precise determination of the tunneling matrix element since the distribution in the energy splitting E has a singularity for $E = \Delta_0$ and is additionally weighted with $(\Delta_0/E)^2$. Above 2.5 K in the H-doped sample and above 3 K in the deuterized material a decrease of the sound velocity is observed which is caused by relaxation of the tunneling systems in the sound field. We would like to discuss this process in the next paragraphs in more detail together with our attenuation measurements. A complete fit (solid line in Fig. 1) of the sound velocity including both processes yields $\bar{\Delta} = 3$ K for both hydrogen isotopes and values of γ equal to those obtained from the relaxation absorption.

Figure 2 shows our results for the ultrasonic attenuation in the superconducting and normal conducting states of the H-doped sample together with data of a sample containing no hydrogen. The dominant absorption mechanism is the electron-phonon coupling[17] causing a temperature-independent attenuation in the normal state

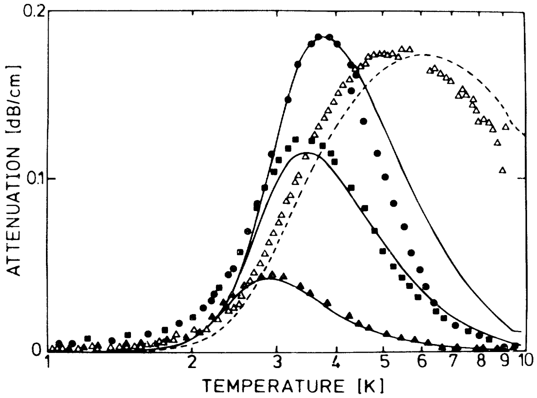

FIG. 3. Ultrasonic attenuation of superconducting Nb doped with H at (▲) 30 MHz, (■) 90 MHz, (●) 150 MHz, or with D at (△) 110 MHz. Damping due to electron-phonon coupling is subtracted from the data. Lines show calculations described in the text.

when the electron mean free path becomes constant at low temperatures. In the superconducting state this mechanism freezes out because the conduction electrons condense into Cooper pairs. We observe, however, in the H-doped sample an absorption peak approximately 3.5 K which is absent if the material is normal conducting. This behavior has been found previously and was discussed as a proof of the existence of a nonadiabatic interaction of H tunneling systems with conduction electrons.[6] Figure 3 shows, for three different ultrasonic frequencies, this attenuation peak in the superconducting state after subtraction of the background determined in the H-free sample. The figure also shows attenuation data of the D-doped crystal measured at 110 MHz. These data will be discussed later.

The attenuation maximum is caused by relaxation of the tunneling systems in a sound field due to strain-induced modulation of the asymmetry energy Δ.[18] The relaxation attenuation is given by

$$\alpha = \frac{n_0 \gamma^2}{\rho v^3} \frac{1}{k_B T} \left(\frac{\Delta}{E} \right)^2 \frac{\omega^2 \tau}{1+\omega^2 \tau^2} \operatorname{sech}^2 \left(\frac{E}{2k_B T} \right) . \quad (3)$$

As usual Eq. (3) has a maximum when the temperature-dependent relaxation rate τ^{-1} becomes equal to the ultrasound angular frequency ω. According to the theory developed for metallic glasses[19] nonadiabatic interaction of tunneling systems with conduction electrons results in a relaxation rate which in the superconducting state is[20]

$$\tau^{-1} = \frac{\pi}{\hbar} 2K \left(\frac{\Delta_0}{E} \right)^2 \frac{k_B T}{1+\exp(\Delta_S / k_B T)} . \quad (4)$$

The dimensionless constant K describes the electron-tunneling system coupling and Δ_S is the BCS superconducting gap parameter. Equation (4) is valid for $E \ll k_B T_c$. The freezing of the relaxation rate in the superconducting state has already been verified experimentally for amorphous metals.[21] Note the quadratic dependence of the relaxation rate on Δ_0 which gives a key to the isotopic effect. In the normal conducting state the relaxation rate of the tunneling systems due to their coupling to conduction electrons is high enough to provide $\omega\tau \ll 1$ down to $T = 0$ K, thus resulting in a negligible absorption contribution.

Our objective now is the determination of the coupling constant K from a fit to the attenuation data of the H-doped sample in Fig. 3. The fit has been carried out by integrating Eq. (3) over Δ after insertion of Eqs. (4) and (2). The fitted curves resulting for the three ultrasonic frequencies are indicated in Fig. 3 by solid lines. For the tunneling matrix element we use the value $\Delta_0(\mathrm{H}) = 1.4$ K as determined from the sound velocity. For the width of the distribution of asymmetry energies we take $\bar{\Delta} = 3$ K as for our fit to the sound velocity. From the absolute value of the absorption we derive the deformation potential of the H tunneling system $\gamma_\mathrm{H} = 0.023$ eV assuming that n_0 is given by the nominal concentration of trapping centers.[22] The fit finally yields the value $K = 0.07$ for the dimensionless coupling constant of the interaction between H-tunneling systems and conduction electrons.

Our present result for K agrees with that reported in previous neutron scattering experiments.[10,11] K is considerably smaller than its limiting value of 0.5 and thus indicates a weak-coupling situation.[23] It is theoretically expected to be essentially isotope independent. This allows a presently unique test of the validity of the theoretical concepts for the nonadiabatic coupling between tunneling systems and conduction electrons by a consistent description of the isotope dependence of the acoustic properties. In fact, we can quantitatively predict the temperature dependence of the ultrasonic attenuation for the D-doped sample using $\Delta_0(\mathrm{D}) = 0.18$ K as determined from our sound velocity measurements. With values $K = 0.07$ and $\bar{\Delta} = 3$ K as for the H-doped sample the result of this calculation is shown by the dashed line in Fig. 3. For the deformation potential we use the value $\gamma_\mathrm{D} = 0.032$ eV—again under the assumption that n_0 is given by the concentration of N traps. We consider the deformation potential to be the only adjustable parameter in calculating the attenuation. It enters only as a constant multiplicative factor.

It is seen from Fig. 3 that the calculated (dashed) curve represents a fair description of the measured attenuation of the D-doped sample. This proves that the theoretical concepts above do indeed adequately predict the experimentally observed isotopic behavior. Because of its Δ_0 dependence the relaxation rate of the dominantly contributing tunneling systems (which have $E \sim \Delta \gg \Delta_0$) decreases by almost 2 orders of magnitude when going from H to D. Thus the agreement between theory and experiment must be regarded as remarkably good. Considering the fact that appreciable differences exist in the vibrational amplitudes of the investigated hydrogen isotopes we can actually not exclude a small isotope dependence of the coupling constant K. This may explain why the calculated attenuation is slightly shifted to higher temperatures as compared to the experimental data. The different vibrational amplitudes of H and D can also possibly explain the measured isotope differences in γ.

In summary, we studied the isotopic behavior of hydrogen tunneling systems in Nb with ultrasonic experiments. We determine the tunneling matrix elements of the two isotopes H and D from the temperature dependence of the sound velocity which is—below 2.5 K—caused by resonant interaction of the sound wave with the tunneling systems. From the ultrasonic attenuation due to relaxation of the H tunneling systems we obtain $K=0.07$ for the dimensionless constant describing the nonadiabatic coupling between the tunneling systems and conduction electrons. Finally we predict quantitatively the experimentally observed attenuation for the isotope D from our results for K and the tunneling matrix element. This proves that the present theoretical concepts for the interaction between a tunneling particle and conduction electrons describe the isotopic behavior adequately.

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