

H and D Tunneling in Niobium

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We performed low-temperature specific-heat measurements investigating tunneling of H and D trapped by O impurities in Nb. The results yield the first experimental values of tunneling matrix elements for both H and D in a metal.

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Low-temperature tunneling of H or D interstitials trapped by O or N in Nb is reported from specific-heat,^{1,2} ultrasonic,³⁻⁵ and neutron-spectroscopic⁶ measurements. In this Letter, we report on specific-heat measurements ($0.04 \text{ K} \leq T \leq 2 \text{ K}$) on a series of NbO_xH_y and NbO_xD_y samples ($0.005 \leq x, y \leq 0.023$) in which we systematically investigated H and D tunneling with respect to (i) its isotope dependence and (ii) its dependence on the concentration of O-H or O-D complexes. Our results yield the first experimental values for the tunneling matrix elements of both H and D in a metal thus providing information on the relevant interatomic potentials, and they demonstrate the decisive influence of stress-induced interaction between different O-H and O-D complexes.

Our samples were prepared from polycrystalline Nb rods (70 mm long, 6 mm in diameter) received from Materials Research GmbH (MARZ grade, 99.99%). To reduce the content of interstitial C and N, the rods were decarburized at $\sim 1700^\circ\text{C}$ in an O_2 atmosphere ($\sim 10^{-4}$ mbar),⁷ and subsequently annealed under UHV conditions ($\sim 2200^\circ\text{C}$, $\sim 10^{-10}$ mbar). Thereupon, for O and H doping, they were again annealed in an appropriate atmosphere first of O_2 ($\sim 1800^\circ\text{C}$, 2×10^{-6} up to 4×10^{-5} mbar),⁷ and then of H_2 or D_2 ($\sim 1200^\circ\text{C}$, 1 up to 700 mbar).⁸ After the last annealing, the rods were quenched to room temperature in order to prevent O precipitation. The O concentrations were determined by residual resistivity measurements⁹ (before H or D doping), and the H or D concentration by vacuum extraction of small pieces cut from the individual rods (the accuracy of the quoted concentrations ranges between 15 and 30%).

Our specific-heat data (experimental accuracy $\sim 5\%$) were taken with a standard quasiadiabatic method¹⁰ in a dilution refrigerator (magnetic fields

were screened to less than 0.02 G). We did not observe any measurable long-time heat release such as that found, e.g., in glasses¹¹ and in H- (D)-doped $\text{Nb Ti}_{0.05}$.¹²

Figure 1 presents our results in a log-log plot versus temperature. Data measured for pure Nb and for Nb doped solely with H are included, as well as specific-heat values (broken line) calculated for pure (superconducting) Nb.¹³ The chief characteristic of Fig. 1 is the large excess specific heat of the samples doped with O-H or O-D complexes. Two features are especially important, (i) the isotope dependence, and (ii) the dependence on the

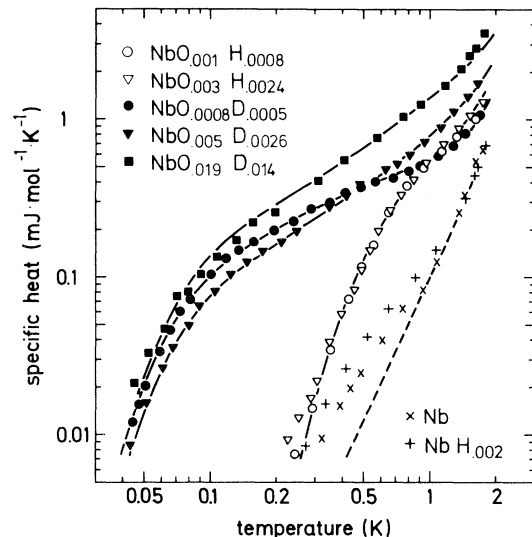


FIG. 1. Specific heat of (superconducting) Nb samples partially doped with O, H, and D. The broken line represents calculated specific heat values for pure Nb (Ref. 13), and the full lines are fits to the data of our samples containing O-H or O-D complexes (the fits for the two samples with O-H complexes are practically identical).

concentration of the complexes. The large isotope dependence establishes the excess specific heat as resulting from tunnel splitting. The concentration dependence is most clearly illustrated by the three D-doped samples. For these samples, the size of the excess specific heat differs at 0.1 K only by a factor of ~ 2 although the concentration of O-D complexes varies by almost a factor of 30. Such a strong nonlinear concentration dependence is also observed for impurity tunneling in alkali halides,¹⁴ and it is straightforward evidence for the existence of (elastic) interaction effects between different tunneling complexes.

Our present results can quantitatively be described in a model according to which the trapped H is tunneling between two equivalent interstitial sites whose respective energies are randomly shifted against each other due to stresses originating from neighboring O-H or O-D complexes. Tunneling between two sites represents the simplest situation possible which is also commonly considered for a description of the low-temperature anomalies observed in glasses.^{15,16} A detailed discussion of possible geometrical configurations for O-H complexes in Nb is given in Magerl *et al.*¹⁷ According to this reference, the trapped H is located in tetrahedral sites, and most likely in sites that correspond, e.g., to $(\frac{1}{4}, \frac{1}{2}, 1)$ or $(\frac{1}{2}, \frac{3}{4}, 1)$ positions if the O atom is assumed to be in an octahedral $(1, 0, \frac{1}{2})$ position. (See also Fig. 4 in Ref. 17.) There are in total sixteen tetrahedral trap sites around an O atom. It is important that they are grouped into eight sets (tunneling systems) each of which consists of only two nearest-neighbor tetrahedral sites [the two $(\frac{1}{4}, \frac{1}{2}, 1)$ and $(\frac{1}{2}, \frac{3}{4}, 1)$ sites discussed above represent, e.g., one of the eight sets of tunneling systems]. The distance $d \approx 1.17 \text{ \AA}$ between the two sites within a given tunneling system is much smaller than the distance from each one of these sites to any other one of the remaining sites (the smallest of the latter distances is $\sim 3.3 \text{ \AA}$). Since tunneling matrix elements decrease exponentially with increasing distance, the relevant tunneling process observed in the present experiments can, therefore, be concluded to take place only between two nearest-neighbor tetrahedral sites within one tunneling system.

For the considered two-site tunneling systems, the energy difference E between the two vibrational ground states of the H is given by^{15,16}

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

where J is the tunneling matrix element, and ϵ is the energy shift between the two sites due to

stresses caused by neighboring O-H complexes. Since the O-H complexes are randomly distributed within the sample, we need to consider a distribution function $Z(\epsilon)$ for the energy shifts which is assumed to be a Lorentzian line,¹⁸

$$Z(\epsilon) = \frac{1}{\pi} \frac{\epsilon_0}{\epsilon_0^2 + \epsilon^2}. \quad (2)$$

The width ϵ_0 of this line characterizes also a typical energy shift between the two sites. According to Eq. (1), the distribution function $Z(\epsilon)$ in the energy shift ϵ implies a distribution function $Z(E)$ for the energy differences E ,

$$Z(E) = \frac{2}{\pi} \frac{E}{(E^2 - J^2)^{1/2}} \frac{\epsilon_0}{\epsilon_0^2 + E^2 - J^2}, \quad (3)$$

which is defined in the energy range $E \geq J$.

The present tunneling model is closely related to that commonly discussed for glasses.^{15,16} However, there is an important difference. In the case of glasses, a broad distribution is considered in the values of both the energy shifts ϵ and the matrix elements J , and the additional distribution in J effects the essentially linear temperature dependence of the observed specific heat. In contrast to this, identical matrix elements are assumed for all the tunneling systems in the present Nb samples (this seems justified by the fact that, except for symmetry operations, these systems also exhibit identical geometries). The distribution function $Z(E)$ in Eq. (3) has, therefore, a low-energy cutoff at $E = J$ which is responsible for a characteristic exponential decrease of the excess specific heat towards lower temperatures below $T \approx 0.4J/k_B$. The fact that no additional distribution function needs to be considered for J makes, compared to glasses, the present tunneling situation more transparent. At the same time, it facilitates any theoretical description (and its experimental verification) since the number of adjustable parameters is reduced. O-H and O-D complexes in Nb may, therefore, represent an attractive model system for experimental studies on tunneling excitations, since the responsible atomic species (H, D) is clearly identified and can readily be varied in its isotopic mass, and since the number of tunneling systems is widely adjustable by changing O-H or O-D concentration.

In the present experiments, the measured excess specific heat C_{exc} is the sum of the specific-heat contributions of all the O-H complexes (tunneling systems) with their respective energy differences E . Under consideration of the distribution function

$Z(E)$, C_{exc} can be written as

$$C_{\text{exc}} = Nk_B \int dE Z(E) \left(\frac{E}{k_B T} \right)^2 \frac{\exp(-E/k_B T)}{[1 + \exp(-E/k_B T)]^2}, \quad (4)$$

where N is the total number of O-H complexes.

Using Eq. (4), we made fits to the measured excess specific heat of our samples doped with O and either H or D (full lines in Fig. 1). The background specific heat (phonons and electrons) was assumed as calculated for pure Nb (broken line).¹³ For each of the five samples, we obtained two fit parameters, (i) the tunneling matrix element J , and (ii) the energy shift parameter ϵ_0 defined in Eq. (2).

Independently of the concentration of O-H or O-D complexes, the matrix element was found to be $J_H = 0.19 \pm 0.02$ meV for the two H-doped, and $J_D = 0.021 \pm 0.002$ meV for the three D-doped samples. These values are very precisely determined from the data in the temperature regime below $T \approx 0.4J/k_B$ where the specific heat decreases exponentially towards lower temperatures because of the low-energy cutoff in the distribution function $Z(E)$ at $E = J$ [Eq. (3)]. The significance of the results for J_H and J_D will be discussed at the end of this Letter.

The energy shift parameter ϵ_0 shows a strong dependence on the concentration of O-H or O-D complexes. Figure 2 presents the results for this quantity in a plot versus the O concentration of the individual samples (lattice expansion and, therefore, stress-induced interaction due to O are more than twice those caused by H^{19,20}). As expected in the case of stress-induced energy shifts from neighboring complexes, ϵ_0 increases with rising O con-

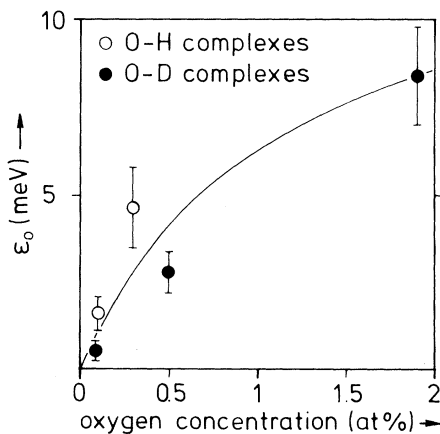


FIG. 2. The energy-shift parameter ϵ_0 in a plot vs the O concentration of our samples. The full line indicates an eye fit to the data.

centration. In agreement with the result found already in Ref. 6, the values of ϵ_0 exceed by far those of J_H and J_D , which demonstrates the importance of stress-induced interaction for the present tunneling systems.

We conclude this Letter with comments on our results for J_H and J_D . The present value of J_H confirms convincingly that determined previously by neutron spectroscopy [$J_H = 0.19 \pm 0.04$ meV (Ref. 6)]. The value of J_D establishes for the first time the isotope dependence of the tunneling matrix element. The present experimental results can finally quantitatively be compared with matrix elements calculated within a one-dimensional approximation for a sinusoidal potential contour. Under these conditions, the matrix element for both H and D may be written as²¹

$$J = \frac{4}{\pi} \hbar \omega \left(\frac{md^2\omega}{\pi\hbar} \right)^{1/2} \exp\left(-\frac{2}{\pi^2} \frac{md^2\omega}{\hbar}\right), \quad (5)$$

where d is the distance between the two tunneling sites, and m is the mass and ω the vibrational frequency of the H or D. The frequency $\omega = \omega_H$ for H corresponds to 107 or 163 meV,¹⁷ and the respective frequencies ω_D for D will be assumed to be smaller by a factor of $\sqrt{2}$. With the distance d between nearest-neighbor tetrahedral sites in Nb ($d = 1.17 \text{ \AA}$), we obtain $J_H = 0.36$ or 0.016 meV, and $J_D = 0.016$ or 0.00015 meV, depending on whether the lower or the upper values are used for the respective vibrational frequencies.

In view of the large inaccuracies inevitably involved in rough estimates like those given above, the agreement between calculation and experiment is quite satisfactory. However, it is pointed out that the calculated values are smaller than actually required for a full quantitative agreement in particular since the bare matrix element in Eq. (5) should be reduced by a polaron factor $e^{-s} \approx 0.1$ in order to appropriately take account of the H- or D-induced lattice relaxation.²¹ This fact is likely to be indicative for the existence of strong anharmonicities in the potential contour between two nearest-neighbor tetrahedral sites as already theoretically suggested from model calculations.²² The present results provide, therefore, a solid experimental basis for the application of refined interatomic model potentials in metal-H systems.

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