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Tunnelling of H trapped by substitutional Zr in Nb: an investigation on its geometry

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Abstract

We carried out an investigation on the symmetry of the tunnel system of H trapped by Zr in b.c.c. Nb. We measured the elastic energy dissipation of two $NbZr_{0.0045}H_x$ single crystals excited with extensional and torsional vibrations along their [100] and [111] directions at frequencies around 40 kHz. Below 40 K at least two processes are observed under ⟨110⟩ shear ($c_{11}-c_{12}$); under other types of stress the intensity of the main contribution is reduced by about a factor of 5, while a smaller peak around 2 K is completely suppressed.

Tunnelling over two or four sites in the perturbed region close to the substitutional impurity is considered; the absence or strong reduction of relaxation under ⟨100⟩ shear can be explained by the symmetry of a four-site tunnel system.

1. Introduction

Most of the investigations on tunnelling of H in metals have been focused on H trapped by interstitial O in Nb. At present it is believed that H delocalizes over two tetrahedral sites which are symmetric with respect to O, and such a model explains most of the experimental observations made by several techniques, sometimes even quantitatively [1–4].

The substitutional atom–H pair has a higher symmetry, with four equivalent tetrahedral sites on each face of the cube containing the substitutional atom (Fig. 1). Tunnelling over all 24 sites can be excluded because of the presence of anelastic relaxation processes associated with slow jumps (activation energy of about 0.14 eV [5]) around the substitutional atom; such jumps would occur between different tunnel systems. Reasonable tunnelling configurations are that H delocalizes over two or four tetrahedral (or close-to-tetrahedral) sites which are equivalent with respect to the Zr atom. Although some experimental observations favour the four-site geometry [6], no conclusive evidence has been provided yet. Here we consider the dependence of the anelastic relaxation strength of the tunnel system on the stress symmetry.

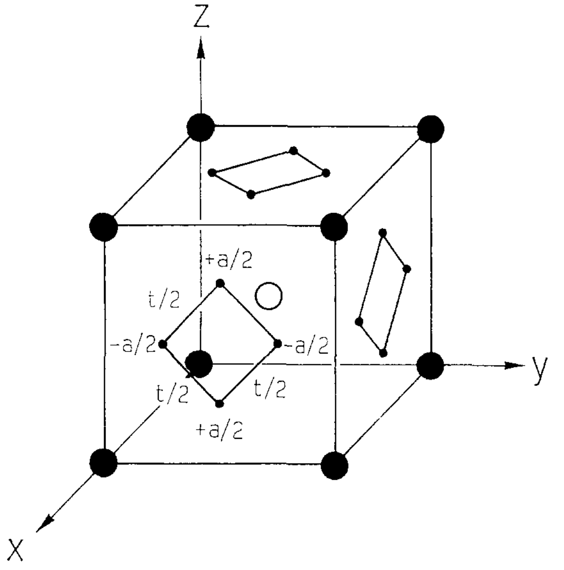

Fig. 1. Niobium cell containing a substitutional atom in the centre (open circle). The small circles are the tetrahedral site nearest neighbours to Zr. Also represented are the site and tunnelling energies of a centrosymmetric FLS.

2. Experimental details and results

The samples were two single crystals of $NbZr_{0.0045}$ approximately $2 \times 3 \times 50$ mm^3 in size, with the [100]

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and the [111] axis parallel to the longer dimension within 3°, and containing less than 400 at.ppm O and N after the last annealing treatment. Hydrogen was introduced electrolytically. They were suspended in the middle and electrostatically excited on their odd extensional (E) and torsional (T) vibration modes at frequencies around 40 kHz.

Two processes are observed below 40 K under ⟨100⟩ E and ⟨111⟩ T vibrations (Fig. 2): a small peak around 2 K, labelled A, whose intensity is already saturated at about 1000 at.ppm H, and a broader contribution, labelled B, which becomes predominant at higher concentrations. Also shown is the dissipation of the H-free [111] sample. The inflection of the dissipation curves at the onset of superconductivity is a common feature of the H tunnel systems, whose relaxation rates are controlled by the interaction with the conduction electrons. In the case of the H-free sample the step is likely due to the reduction of the absorption from the electron–phonon interaction ($f = 28$ kHz).

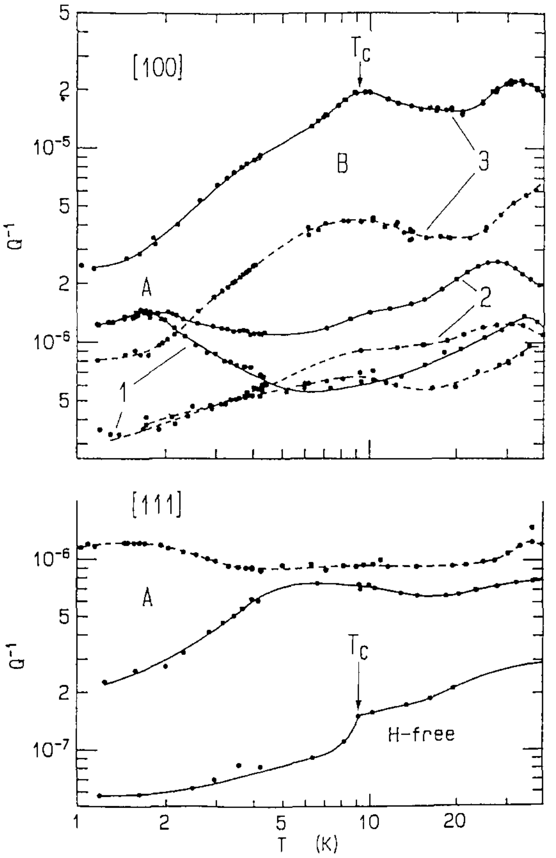

Fig. 2. Elastic energy loss of $NbZr_{0.0045}H_x$ under extensional (continuous curves) and torsional (dashed curves) vibrations. The frequencies are included between 28 and 50 kHz; T_c indicates the normal–superconductor transition. Lower part: [111]-oriented sample, H free and with $x = 0.0011$. Upper part: [100]-oriented sample with $x = 0.00065$ (curves 1), $x = 0.0013$ (curves 2) and $x = 0.0027$ (curves 3).

Under ⟨100⟩ T and ⟨111⟩ E vibrations peak A is completely suppressed, while the intensity of B is reduced by about a factor of 5. The effect shown in Fig. 2 is only due to the change in the stress symmetry, since all the vibration frequencies are included between 28 and 50 kHz. In terms of the symmetric stress components of the cubic systems, processes A and B are excited by the ⟨110⟩ shear ($c_{11} - c_{12}$) elastic constant), which contributes to the ⟨100⟩ E and ⟨111⟩ T vibrations, but are not at all or much less sensitive to the ⟨100⟩ shear (c_{44}) and hydrostatic stresses.

While it seems rather obvious to associate peak B with tunnelling of H close to a Zr atom, some doubts may arise about the nature of peak A, whose intensity saturates already below 1000 at.ppm H. Since the samples contained up to 400 at.ppm O and O is trapped by Zr, it is possible that peak A is due to tunnelling of H trapped by a Zr–O pair. It cannot be identified as one of the two processes observed in the presence of O–H complexes, whose maxima at the same frequency are respectively below 1 K and around 3 K [7].

Even in the case of H trapped by a Zr–O pair, symmetric four-site tunnelling could be possible. In fact, a reasonable configuration of the O–Zr–H complex, which minimizes the elastic energy and still has a fourfold symmetry, is that H and O occupy opposite faces with respect to Zr (O occupies octahedral sites in the centers of the cube faces and edges).

3. Discussion

We will discuss the dependence of the relaxation strength on the stress symmetry in the case of two-site tunnelling (two-level system, TLS) between any pair of sites equivalent with respect to Zr and in the case of four-site tunnelling (FLS) over a cube face (Fig. 1).

The relaxation strength Δ_{ij} between any two energy levels E_i and E_j of a multilevel system due to the application of a strain ε is proportional to the square of the difference in the strain derivatives of the two levels [8, 9]:

$$\Delta_{ij} \propto \left(\frac{\partial E_i}{\partial \varepsilon} - \frac{\partial E_j}{\partial \varepsilon} \right)^2 \qquad (1)$$

In order to compute the energy levels of a tunnel system, we need to diagonalize its hamiltonian H. It is convenient to express H in the localized representation as a function of the site energy $a_h/2$ of the hth site (a stands for asymmetry) and the tunnelling energy $t_{hk}/2$ between sites h and k (the factors $\frac{1}{2}$ are in accordance with the notation used in most of the literature on TLSs). Since the tunnelling energies are of the order of a few kelvins [1–4, 6, 7] while the perturbations to the site energies due to internal strains are one or two orders of magnitude higher [3], we must include such perturbations in the hamiltonian. This means that $a_h \neq a_k$ even for symmetric tunnel systems, owing to the long-range elastic interactions.

The case of a TLS with site energies $\pm a/2$ gives the well-known result [10]

$$E_{1,2} = \mp\tfrac{1}{2}(a^2+t^2)^{1/2} = \mp\frac{E}{2} \longrightarrow \Delta_{12} = 4\left(\alpha\frac{a}{E} + \tau\frac{t}{E}\right)^2 \qquad (2)$$

where $\alpha = \mathrm{d}a/\mathrm{d}\varepsilon$ and $\tau = \mathrm{d}t/\mathrm{d}\varepsilon$; τ is generally neglected in comparison with α in accordance with the smallness of t with respect to a. From eqn. (2) we see that a strain ε gives rise to relaxation (changes the energy levels) if it changes the asymmetry a of the TLS.

In the case of an FLS the first approximation in which the local strain is taken into account is to make the FLS centrosymmetric instead of symmetric, since strain is a centrosymmetric tensor. The centrosymmetric hamiltonian is

$$H = \frac{1}{2}\begin{bmatrix} a & t & 0 & t \\ t & -a & t & 0 \\ 0 & t & a & t \\ t & 0 & t & -a \end{bmatrix} \qquad (3)$$

with eigenvalues

$$E_{1,4} = \mp\tfrac{1}{2}(a^2+4t^2)^{1/2} = \mp\frac{E}{2}, \qquad E_{2,3} = \mp\frac{a}{2} \qquad (4)$$

and eigenfunctions

$$|1,4\rangle = \frac{1}{2[E(E\pm a)]^{1/2}}\begin{bmatrix} 2t \\ -(a\pm E) \\ 2t \\ -(a\pm E) \end{bmatrix}$$

$$|2\rangle = \frac{1}{2^{1/2}}\begin{bmatrix} 0 \\ 1 \\ 0 \\ -1 \end{bmatrix}, \qquad |3\rangle = \frac{1}{2^{1/2}}\begin{bmatrix} 1 \\ 0 \\ -1 \\ 0 \end{bmatrix} \qquad (5)$$

The application of an external strain ε perturbs H by δH, whose elements are α_h and $\tau_{hk} = \tau_{kh}$; the resulting changes in the energy levels are $\delta E_i = \langle i|\delta H|i\rangle$:

$$\frac{\partial E_{1,4}}{\partial\varepsilon} = \bar{\alpha} \mp \left(\frac{a}{2E}\,\delta + 4\,\frac{t}{E}\,\bar{\tau}\right), \qquad \frac{\partial E_{2,3}}{\partial\varepsilon} = \bar{\alpha} \mp \delta \qquad (6)$$

where $\bar{\alpha}$ and $\bar{\tau}$ are the mean values of all the α_h and τ_{hk}, and $\delta = (\alpha_1 + \alpha_3 - \alpha_2 - \alpha_4)/4$. The relaxation strength is obtained by introducing eqn. (6) into eqn. (1) and turns out to be proportional to δ^2; the perturbations to the tunnelling energies contribute to the relaxation only if their mean value is different from zero, and can anyhow be neglected in comparison with δ. The difference δ in the variation in the energies of the pairs of opposite sites is analogous to the asymmetry change α of the TLS (eqn. (2)).

We will show now by symmetry arguments that under the application of a ⟨100⟩ shear, δ is null while α is not; in other words, an FLS would not relax while a TLS would. If we neglected the presence of the substitutional atom and assumed that H occupies sites with perfect tetragonal symmetry, then also a TLS would not be affected by such a shear. In fact, the tetragonal elastic dipole would couple only with the diagonal components of stress [8] and no interaction would be expected with the ⟨100⟩ shear. However, it does not seem appropriate to completely discard the perturbation from the Zr atom. An obvious indication of the importance of such a perturbation is the fact that anelastic relaxation from H is only observed in the presence of the substitutional atom. Therefore we will suppose that the site energy change α_h induced by the applied strain can be parametrized with the variation in the distance between site h and the Zr atom. Taking into account additional distances would not change the qualitative picture.

Figure 3 shows the effect of the [001] extensional and torsional vibrations on the Nb cell. In the first case the FLSs on the z faces of the cell are symmetrically affected and do not contribute to relaxation ($\delta = 0$), while the distances between Zr and the opposite pairs of sites of the other FLSs change by opposite quantities. Therefore, if a_2 and a_4 change by α, then a_1 and a_3 change by $-\alpha$, resulting in $\delta = \alpha$ and a finite relaxation strength (the same result is obtained without the substitutional atom).

The effect of the [001] torsional vibration is shown in Fig. 3(b); it results in a shear strain $\varepsilon = \varepsilon_0(\hat{t}\hat{k} + \hat{k}\hat{t})/2$, where $\hat{t}$ assumes all the directions perpendicular to the [001] axis, $\hat{k}$, depending on the position of the cell in the sample. By inspecting Fig. 3(b), which represents the particular case of $\hat{t}$ parallel to a crystal

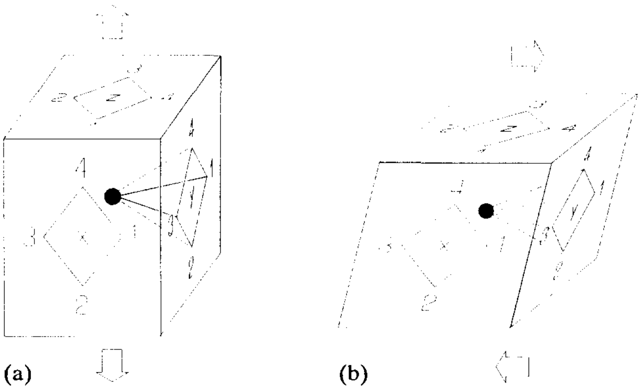

Fig. 3. Distortion of the Nb unit cell under (a) [001] extensional and (b) [001] torsional stresses.

axis, we see that the energies of the sites of all the faces change as $\alpha_1 = \alpha_3 = 0$ and $\alpha_2 = -\alpha_4$, resulting in $\delta = 0$. For a generic direction of $\hat{t}$ the sites of the z faces change as $\alpha_1 = -\alpha_3$ and $\alpha_2 = -\alpha_4$, and δ is again zero. Moreover, pairs of adjacent (x and y faces) or opposite (z faces) sites are affected in the opposite way, resulting in a null $\bar{\tau}$.

We conclude that no relaxation is expected for a centrosymmetric FLS subjected to ⟨100⟩ shear, even taking into account the changes in the tunnelling energies. Instead, a TLS constituted by any pair of sites close to the Zr atom would relax, because there would always be a pair oriented in such a way as to be asymmetrically affected.

The above analysis is only qualitative but shows that an FLS is expected to have a relaxation strength much lower than a TLS under ⟨100⟩ torsional and ⟨111⟩ extensional vibrations, as observed experimentally for peak A. Peak B is also observed under such stresses, though with an intensity reduced by about a factor of 5; such a process may be due to the additional existence of TLSs or to Zr–H complexes where the local distortion is such that the FLSs are no longer centrosymmetric.

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