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Anelastic spectroscopy study of very diluted Zr–D tunnel systems in Nb single crystals

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Abstract

The anelastic spectrum of the $Nb_{1-x}Zr_xD_y$ alloy has been studied in the high dilution limit, down to $x = 1300$ ppm and $y = 150$ ppm. It was thus possible to single out the peaks associated with the most symmetric four-level systems (FLS). A narrow peak at 6 K (40 kHz) has been identified with the transitions between the intermediate levels of the FLS. The fact that such transitions are much slower than those between levels 1 and 4 and are not caused by the scattering with the conduction electrons is explained in terms of a vanishing matrix element for first order transitions involving the intermediate states of a centrosymmetric FLS.

Keywords: Anelastic spectroscopy; Symmetric four-level systems

1. Introduction

Tunneling of H near an interstitial impurity (O, N, C) in Nb and Ta has been thoroughly studied by several techniques over more than 20 years and is now well explained by the existing theory in terms of a two-level system (TLS) with prevalent interaction with the conduction electrons [1,2]. When trapped in the more symmetric environment of a substitutional impurity (Ti, Zr), H can delocalize over the four tetrahedral sites of a face of the cubic cell, giving rise to a more complex phenomenology, mainly studied by anelastic spectroscopy [2]. A four-level system (FLS) model has been developed [2,3] in order to explain the dependence of the intensities of the elastic energy absorption peaks on the symmetry of the applied stress, of the H isotope mass and of the substitutional concentration. Recently, the dissipative dynamics of such a FLS model has been analyzed, finding interesting differences with respect to a TLS [4]. Still, the intriguing phenomenology of the anelastic spectrum of $Nb_{1-x}Zr_x(H,D)_y$, even in the range $x,y < 0.005$, is not yet explained. A complication in the interpretation of the anelastic spectra comes from the fact that they are particularly sensitive to the tunnel systems which are made asymmetric by the elastic interactions among the impurities. As a consequence, with increasing impurity content one observes not only broadening but also qualitative changes of the spectra. Here we present anelastic spectroscopy measurements on single crystals of $Nb_{1-x}Zr_x$ charged with D at such low impurity contents that the spectra should be close to those for the infinite dilution case. New indications are thus found on the nature of the various peaks, and the observations fit well, at least qualitatively, the FLS model.

2. Experimental

The samples are two single crystals of $Nb_{1-x}Zr_x$ with $x = 0.0013$ and 0.0045, hereafter called sample 1 and 2 respectively, cut as bars ($0.2 \times 0.3 \times 5$ cm^3) with the longest dimension parallel to the [100] axis. After cutting, they were annealed for 8 min at 1800°C in a vacuum better then 10^{-7} mbar for annealing the residual dislocations. Deuterium was introduced by equilibration with a controlled amount of 99.8% pure D_2 at 600–660°C in a UHV system. Some results from sample 2 have already been published [5,6]. The impurity content of sample 1 was checked by resistivity; the ratio $R(273\ K)/R(0\ K) = 90$ yields a residual resistivity $\rho_0 = 0.13$ $\mu\Omega$ cm, in perfect agreement with 1300 at ppm of substitutional Zr (whose specific resistivity is [7] 1.0×10^{-4} $\mu\Omega$ cm/at ppm) and

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negligible O content (5×10^{-4} μΩ cm/at ppm, Ref. [8]).

In order to measure the anelastic spectrum, the sample was suspended in the middle and electrostatically excited on its 1st extensional mode (38 kHz), so obtaining the complex Young's modulus M^* in the [100] direction, which coincides with the reciprocal of the s_{11} compliance; s_{11} can be expressed as $\frac{1}{3}(s_{11}+2s_{12})+\frac{2}{3}(s_{11}-s_{12})$, and the anelastic response is expected to come mainly from the shear component $(s_{11}-s_{12})$. We will discuss the elastic energy loss coefficient, Q^{-1}, which is related to the dynamic modulus by M''/M'. A monodispersive relaxation process, like hopping or transitions between two sites or energy levels α and β with a relaxation time τ contributes to M'' with [2]

$$M'' = \frac{c}{v_0}\frac{n_\alpha n_\beta}{k_B T}(\gamma_\beta - \gamma_\alpha)^2 \frac{\omega\tau}{1+(\omega\tau)^2} \qquad (1)$$

where c is the total concentration of tunnel systems, n_α the population and $\gamma_\alpha = \partial E_\alpha / \partial \varepsilon$ the deformation potential of the level E_α. A FLS has three relaxation modes, corresponding to the modulation of different combinations of the n_α (Ref. [9]); however, if the transition rates between different pairs of energy levels are very different, some simplification in the description of the relaxation kinetics is possible, and it can be meaningful to adopt the above expression.

The measurements on sample 1 were exceedingly difficult, possibly due to a polydomain structure of the sample, and only the 1st extensional mode could be measured.

3. Results

Fig. 1 compares the anelastic spectrum of sample 1 (1300 ppm Zr) charged at $y = 150$ ppm D with those from sample 2 (4500 ppm Zr) charged at $y = 363$ ppm and $y = 1400$ ppm. At the lowest impurity content four peaks are clearly visible, labeled T1, T2, H1 and H2 starting from low temperature. All of them are observed also at higher impurity concentrations, although with very different relative weights. Peaks H1 and especially T2 are strongly depressed by the increase of Zr content and T2 reappears in sample 2 only for $y > 800$ ppm. The peak at 6 K in sample 2 with $y = 1400$ ppm has the same position and shape of peak T2 in sample 1 with $y = 150$ ppm, with an intensity only 1.3 times greater. In the assumption of a peak intensity proportional to y (all D is trapped by Zr) this means that peak T2 is about seven times smaller in sample two than in sample 1. The transition to the superconducting state ($T_c = 9.25$ K) produces a discontinuity in the slope of the elastic modulus versus temperature (not shown here), but no observable effect in the dissipation curves.

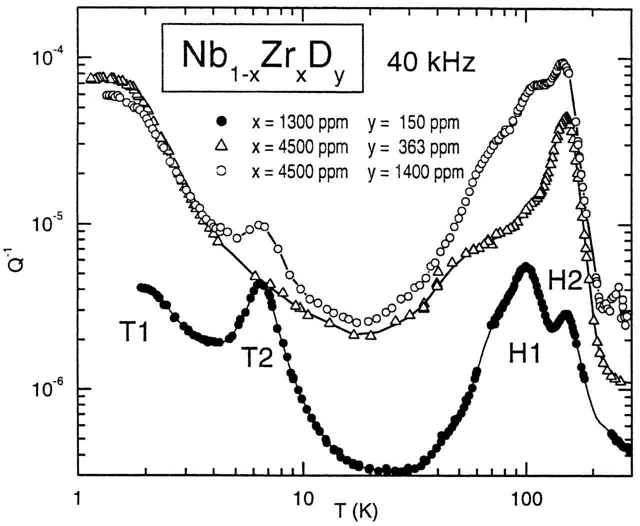

Fig. 1. Elastic energy loss coefficient of $Nb_{1-x}Zr_xD_y$ crystals excited on the [100] extensional mode at different impurity contents.

4. Discussion

This is the first time that the anelastic spectrum of a substitutional Nb alloy at such low impurity concentrations is measured. Even though the presence of O impurities at the level of few hundreds ppm cannot be excluded, all the four peaks present in sample 1 have to be attributed to Zr–D complexes. In fact, it had already been shown that Zr–O pairs may trap the D atoms, but the resulting complexes do not contribute to the anelastic relaxation [6]. We can also exclude the presence of O–D and O–H pairs, [10] since the peak due to the reorientation of the O–D pairs at 38 kHz should be centered at 130 K, where there is no peak in Fig. 1. Peak H1 is centered at a temperature close to that of the O–H peak, but it is also the most intense process and therefore cannot be due to contamination from O and H: the O–H peak should be much smaller than the O–D one, which already is undetectable.

Fig. 2 demonstrates that the shape of the anelastic spectrum is determined by the concentration x of substitutional Zr, and independent of the D content y, for $y \ll x$. In fact, the two curves measured at the lowest D contents on sample 2 have practically the same shape and scale with the D concentration: the curve for $y_1 = 156$ ppm coincides with that for $y_2 = 363$ ppm if multiplied by $y_2/y_1 = 2.35$. This means that at such low impurity levels the D atoms statistically fill the trap sites around the Zr atoms, which alone determine the site energy distribution. In Fig. 2 the spectrum of sample 1 has been multiplied by 18, in order to have the intensity of peak H2 coincident with that in the curves of sample 2. In this way it is apparent that the increase of lattice disorder due to the Zr substitutional atoms increases peaks T1 and H2 at the expenses of T2 and H1.

The phenomenology of Fig. 2 suggests that peaks T2 and H1 are those which would be present in the ideal

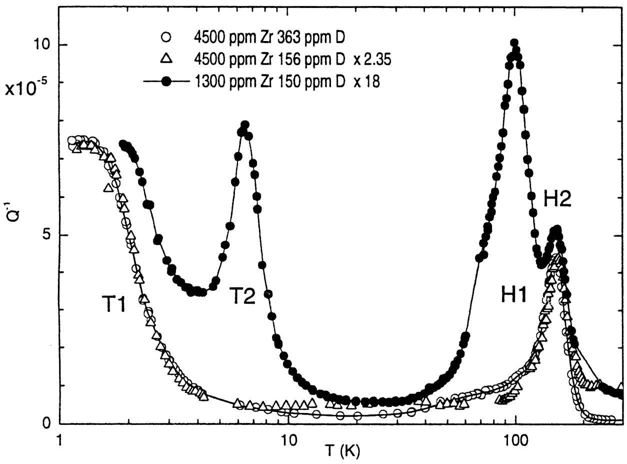

Fig. 2. Comparison of the anelastic spectra of $Nb_{1-x}Zr_xD_y$ at low y. The spectra of sample 2 coincide after normalization according to the D concentration; the curve of sample 1 has been normalized after the intensity of peak H2. The multiplication factors are indicated in the legend.

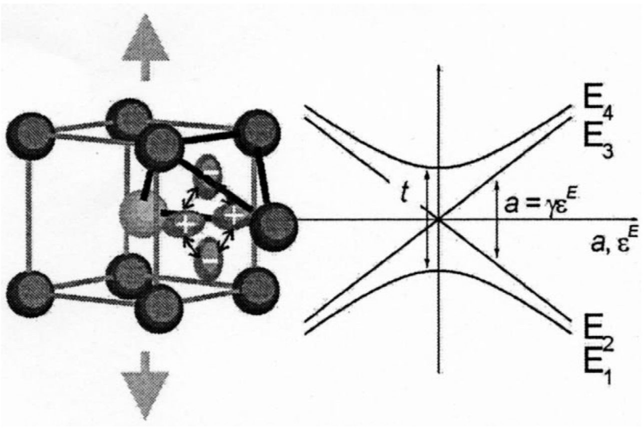

Fig. 3. Niobium cell with a substitutional atom in the center and four tetrahedral sites over which H can delocalize; a tetrahedron of host atoms surrounding a site is evidenced. The ellipsoids represent the strain tensor (elastic dipole) associated with the H occupation in each site. An E-type strain, like that indicated by the arrows, changes the site energies by $\pm a/2$, as indicated by the signs within the ellipsoids. The diagram of the energy levels $E_i(a)$ is presented on the right hand side.

infinite dilution case, and therefore they are due to D atoms trapped at Zr atoms with a particularly symmetric environment. With the addition of Zr atoms, the fraction of distorted sets of trap sites around Zr increases at the expenses of the ‘regular’ trap sites, so that the absolute number of the latter decreases and causes a reduction of T2 and H1. Peaks T1 and H2 would be due to D trapped at the newly formed disturbed sets of trap sites.

4.1. Nearly centrosymmetric FLS and peak H1

We propose the following picture, which can explain several experimental features. Similarly to the TLS formed by H near O in Nb, [1,2] we neglect the effect of strain on the tunneling energy; therefore, a FLS over the four tetrahedral sites of a cube face in a perfect *bcc* lattice would be affected only by a strain that is coupled with the elastic dipole tensors of the tetrahedral sites, having tetragonal symmetry [9]. Since the pairs of opposite sites have the same elastic dipole, they are perturbed of the same amount $\pm a/2$, where a is the asymmetry energy of the centrosymmetric FLS; in addition, E-type ($\varepsilon^E = \varepsilon_1 - \varepsilon_2$, $2\varepsilon_3 - \varepsilon_1 - \varepsilon_2$) but not F type ($\varepsilon^F = \varepsilon_4$, ε_5, ε_6) shears affect the energies of the tetrahedral sites, [9] so that $a = \gamma\varepsilon^E$ in the perfect lattice. Fig. 3 shows the geometry of the FLS with an E-type uniaxial strain. The proximity to the substitutional trap and the non-homogeneity of the static strain due to a high impurity concentration cause non-centrosymmetric perturbations to the FLS, which however are supposed to be smaller. A basis for a phenomenological but quantitative treatment of this kind can be found in Ref. [2]. It should be noted that the effect of the trapping impurity is not negligible at all, since peak H2 and a broad dissipation maximum below 30 K at high impurity contents are observable also exciting F-type vibration modes [3]. When passing from E- to F-type vibration, the intensity of H2 and of the broad maximum decrease by about three times, whereas the intensity of peak T1 at low doping and H1 decrease by 20 times [3,5]; this demonstrates that a stress of F-type affects the energies of the sites near Zr, but T1 at low doping and H1 involve states whose symmetry cancels the non-centrosymmetric perturbations to the site energy. This is exactly what happens with the eigenstates of a nearly centrosymmetric FLS, [2,3] whose energies do not change under F-type strain even if the latter changes the individual site energies.

The extension of this selection rule to peak H1, attributed to hopping among different FLS, implies that also at 100 K there is an averaging effect of the site energy perturbation over a centrosymmetric wave function. At that temperature tunneling is incoherent, impairing a treatment in terms of coherent wave functions, but it has recently been shown [4] that even in the incoherent regime a centrosymmetric FLS should maintain long lived oscillations within pairs of opposite sites.

4.2. Peak T1: transitions with the 1st and 4th levels of centrosymmetric FLS

The main features of peak T1 resulting from the present and previous [2,3,5,6] studies are: (i) it is relatively narrow and centered around 2 K; (ii) its intensity decreases of 50–80 times when passing from D to H (Refs. [2,5]); (iii) its intensity increases by ~7.6 times when the concentration of the substitutional Zr atoms passes from 1300 to 4500 ppm (Fig. 2). All these features can be explained in terms of transitions between the 1st and 4th levels of nearly centrosymmetric FLS (Fig. 3) or between the two levels of TLS: both pairs of levels have similar dependence on the asymmetry $a = \gamma\varepsilon^{\mathrm{E}}$, and tunneling matrix element t between adjacent sites: $E_{1,2}^{\mathrm{TLS}} = \pm\frac{1}{2}\sqrt{t^2 + a^2}$, $E_{1,4}^{\mathrm{FLS}} = \pm\frac{1}{2}\sqrt{4t^2 + a^2}$, which implies vanishing $(\partial E_i/\partial\varepsilon - \partial E_j/\partial\varepsilon)^2 \propto (a/E)^2\gamma^2$, in the relaxation strength (1) for $a < t$. Then, in terms of FLS, the reduction of the intensity passing from D to H is explainable in terms of a distribution of asymmetries with a width $\bar{a} \sim 2t_{\mathrm{H}}$ but $\bar{a} > 2t_{\mathrm{D}}$, so that the FLS with $2t_{\mathrm{D}} < a < 2t_{\mathrm{H}}$ have negligible $\partial E_i/\partial\varepsilon$ for H but not for D [5]. On the other hand, the relaxation strength for these transitions averaged over a distribution of asymmetries increases with $\bar{a}$ until it saturates for $\bar{a} > 2t$. This explains the increase of T1 observed in Fig. 2, when passing from sample 1 to sample 2 with the same D content $y =$ 150 ppm, if $\bar{a} < 2t_{\mathrm{D}}$ for $x =$ 1300 ppm.

We tried to reproduce the above features by calculating the elastic energy dissipation due to the 1↔4 transitions of a FLS from Eq. (1) with $\tau(T)$ determined [2] by the scattering with the conduction electrons with coupling $K =$ 0.07–0.2 and one-phonon transitions with coupling $\gamma =$ 500–1000 K equal to the coupling to ε^{E}, $t_{\mathrm{D}} =$ 0.1–0.3 K, $t_{\mathrm{H}} =$ 1–3 K, and $\bar{a} = 0.1$–5 K. With the parameters in these ranges, which are comparable with those found for the O–H and O–D pairs in Nb, [1] one always obtains a maximum around 0.7–2 K, similar to peak T1. It is also possible to separately obtain the above effects (ii) and (iii) with slightly different sets of the parameters, but not both effects with the same parameters. This fact can be due to an oversimplification of the description of tunneling systems. For example, it is possible that Zr atoms with more asymmetric environment give rise to delocalization over TLS instead of FLS, which have different expressions of the relaxation strength and rate. This fact has not been taken into account.

4.3. Peak T2: transitions involving the intermediate levels of centrosymmetric FLS

Peak T2, like H1, is clearly associated with FLS with a particularly regular environment, which therefore should closely satisfy the conditions of a centrosymmetric Hamiltonian. Contrary to peak T1, its intensity increases when the lattice disorder and therefore $\bar{a}$ are reduced to very low levels passing from sample 2 to sample 1. This rules out 1↔4 transitions of a FLS or TLS, but is compatible with transitions involving the intermediate levels $E_{2,3} = \pm a/2$ of FLS, [2,3] which do not suffer from the vanishing strain dependence at $a < t$. The peak can be described by a relaxation rate $\tau^{-1} \propto T^5$, and does not show any anomaly at T_{c}, indicating that the scattering from the conduction electrons is not involved in these transitions. This is exactly what one would expect from transitions involving the intermediate levels of a centrosymmetric FLS. In fact, both the one-phonon and the electronic contribution to the transition rate from a state $|i\rangle$ to $|j\rangle$ of the FLS involve the square of the matrix element $\langle i|V|j\rangle$, where the perturbation V is the modulation of the asymmetry a from the phonon field or the scattering of the electrons. It is easy to calculate $\langle i|V|j\rangle$ between the eigenstates of centrosymmetric FLS [2,3] and to find that it vanishes if $i = 2,3$. This means that there are no first order transitions involving the intermediate levels, but only two-phonon and higher order transitions. The resulting much slower rate explains the presence of a peak well separated from T1, and is in agreement with a $\tau^{-1} \propto T^5$ law. In addition, it justifies the approximation of separating the relaxation modes of a FLS into $n_4 - n_1$ mode with a rate τ_{14}^{-1} and a slower independent mode involving n_2 and n_3.

5. Conclusion

The anelastic spectrum of the $\mathrm{Nb}_{1-x}\mathrm{Zr}_x\mathrm{D}_y$ alloy has been measured at the lowest Zr and D contents tested up to now, $x = 1300$ ppm and $y = 150$ ppm. The low impurity level allowed the peaks characteristic of the ideally infinite dilution situation to be singled out. The peak around 100 K (40 kHz) has been confirmed to be due to the hopping between nearly centrosymmetric FLS, and the persistence of the symmetry of the eigenstates of a FLS at such high temperature seems to be justified by a recent theoretical analysis of the FLS [4]. A narrow peak at 6 K has been identified with the transitions involving the intermediate levels of the FLS. Such transitions are much slower than those between the fundamental and upper levels and are not caused by the scattering with conduction electrons; this is explained in terms of a vanishing matrix element for first order transitions involving the intermediate states of a centrosymmetric FLS.

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