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H and D tunnelling systems in diluted $Nb_{1-x}Zr_x$ alloys

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Abstract

The anelastic spectra of a single crystal of $Nb_{0.9955}Zr_{0.0045}$ containing controlled amounts of O and D have been measured to clarify the nature of a narrow peak due to H tunnelling, which appears only at the lowest impurity contents in the dilute Nb substitutional alloys. It is shown that the process is due to Zr–D pairs without the involvement of unwanted O impurities. The saturation of the peak intensity can be understood in terms of the increasing interactions among the H atoms and the consequent broadening of the distribution of the energy asymmetries of the tunnel systems. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: H tunneling; Trapping; Anelasticity

1. Introduction

The dynamics of H trapped by substitutional atoms in bcc metals like Nb, exhibits a very complex phenomenology both when dominated by atomic tunnelling and by overbarrier hopping, as demonstrated by the numerous peaks in the anelastic relaxation spectrum (elastic energy loss coefficient and elastic modulus as a function of temperature) [1–3]. In spite of the simpler geometry of the substitutional-H pair, the resulting anelastic spectrum may be much more complicated than that due to the more asymmetric interstitial-H pairs, like O–H. This is in part due to the fact that the O–H pair in the group 5A metals can be studied at concentrations at most of the order of 1 at%, due to the limited O solubility, whereas the substitutional atoms Ti and Zr have complete solubility. Still, drastic changes of the relaxation spectrum are observed in Nb–Ti and Nb–Zr alloys already at substitutional and H concentrations well below 1 at%. The complexity of the phenomenology is certainly due to fact that four-level tunnel systems (FLS) can be formed, besides or instead of two-level systems (TLS), but a complete explanation of all the features is still lacking. In particular, a puzzling feature observed when H or D are trapped by Ti and Zr is that, below about 1000 at ppm of substitutional-H pairs, a narrow peak is observed at few Kelvin, which at higher concentrations saturates and is covered by a much broader maximum [1–3]. The most simple explanation would be that the narrow peak is due to a small concentration of tunnelling systems that are different from the substitutional-H pairs and that are readily saturated by H; the most likely candidate is H trapped by Zr–O and Ti–O pairs. In order to check this possibility, we measured the anelastic spectra of a single crystal of $Nb_{0.9955}Zr_{0.0045}$ after introducing controlled amounts of O and D.

2. Experimental

The sample was a single crystal of $Nb_{0.9955}Zr_{0.0045}$ cut as a bar ($2\times3\times50$ mm^3) with the longest dimension parallel to the [100] axis. Deuterium was introduced by equilibration in a quartz tube connected with a UHV system with known amounts of 99.8% pure D_2 at 600°C. Oxygen was introduced at 1130°C and the sample was maintained at the same temperature for 18 h to ensure complete homogenization. The O diffusion coefficient in pure Nb at that temperature is 8×10^{-7} cm^2/s, as determined from the Snoek effect [4]. Trapping by substitutional Zr is estimated to lower the diffusion coefficient by a factor $f=\left[1-2c+2c\ e^{E_b/kT}\right]^{-1}$ [5] which, adopting the binding energy $E_b\approx0.3$ eV found by Cantelli and Szkopiak [6], is $f=0.91$. With this diffusion coefficient, the time constant for O to diffuse to the centre of the sample is ≤1 h. The formation of the Zr–O pairs should have occurred during the subsequent charging with D at 600°C for 30 min and further ageing at 250°C for 1 h. The amount of O introduced in the sample was determined as 1100 at ppm

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from the mass variation; this concentration was slightly above the value of 987 at ppm intentionally introduced in the quartz tube. The fact that after such a long treatment above 1000°C only 100 at ppm of additional O was absorbed, ensures that the O contamination during the various H and D charging treatments was negligible.

In order to measure the anelastic spectrum, the sample was suspended in the middle and electrostatically excited on its 1st and 3rd extensional modes (42 and 128 kHz), which are coupled with the $(c_{11}-c_{12})/2$ elastic constant. The elastic energy loss coefficient, or reciprocal of the mechanical Q, is given by:

$$Q^{-1} \propto cD^2 \frac{n_1 n_2}{T} \frac{\omega\tau}{1+(\omega\tau)^2} \tag{1}$$

where c is the concentration of defects, n_i the relative population of the ith state of the defect, $D = \partial(E_2 - E_1)/\partial\varepsilon$ the deformation potential for the strain ε involved in the sample vibration, τ is the relaxation time, close to the mean transition time of the defect between the states 1 and 2 and ω is the angular vibration frequency.

3. Results and discussion

The effect of O doping on the anelastic spectrum of $Nb_{0.9955}Zr_{0.0045}D_x$ is shown in Fig. 1 together with other Q^{-1} curves measured prior to O doping. Only the intensities of the peaks are affected, while their positions and shapes are nearly unchanged. We will only consider the peaks labelled as T1 and H2, which have been ascribed to D tunnelling and hopping within Zr–D pairs [2], and possibly ZrO–D complexes for peak T1.

We chose to measure the spectra with D instead of H, because peak T1 is ~50 times more intense with the heavier isotope. The enhancement of the peak intensity with the isotope mass has been shown [2,3] to be consistent with peak T1 due to transitions between the levels of a TLS or between the 1st and 4th levels of a FLS. In fact, the energy separation between such levels is $E = \sqrt{t^2 + a^2}$ for a TLS and $E = \sqrt{4t^2 + a^2}$ for a FLS, where t is the tunnelling matrix element and a is the shift of the potential minima of the tunnel system, with respect to the perfectly symmetric condition. For very small defect concentrations, as in the present case, a is distributed according to a Lorentzian with width $\bar{a}$. Under the usual hypothesis that the strain modulation of the asymmetry a is much stronger than that of t, the deformation potential in Eq. (1), $D = \partial E/\partial\varepsilon$, becomes negligible for $a < t$. Since $t_D \ll t_H$, all the tunnel systems formed among trap sites with asymmetry $t_D < a < t_H$ will contribute to relaxation when occupied by D but not by H. The resulting increase of the relaxation intensity is amplified in our case by the circumstance that the condition $\omega\tau \approx 1$ for the maximum of the Debye factor in Eq. (1) holds for those nearly symmetric tunnel systems.

The approximate intensities of the two peaks T1 and H2 are plotted against the D concentration in Fig. 2. Excluding the points of the O-doped sample, the intensity of peak H2 scales with the content of D, with some saturation at the highest value, but the intensity of peak T1 at 800 at ppm is even smaller than at 360 at ppm. As a possible explanation of the saturation of peak T1 at such low concentrations, it has been suggested that peak T1 is due to D trapped by Zr–O pairs instead of Zr atoms. In fact, O is the major impurity in these *bcc* metals, and can be unintentionally introduced during the high temperature treatments; since we are dealing with very low concentrations of tunnel systems, few hundreds ppm O would be sufficient to account for the saturation of peak T1. The measurement with 1100 at ppm O demonstrates that this is not the case, since the intensity of peak T1 is much reduced instead of enhanced, and also peak H2 is slightly depressed. This means that the Zr–O complexes can trap D, but do not contribute to the low temperature relaxation spectrum.

Having demonstrated that peak T1 is indeed due to

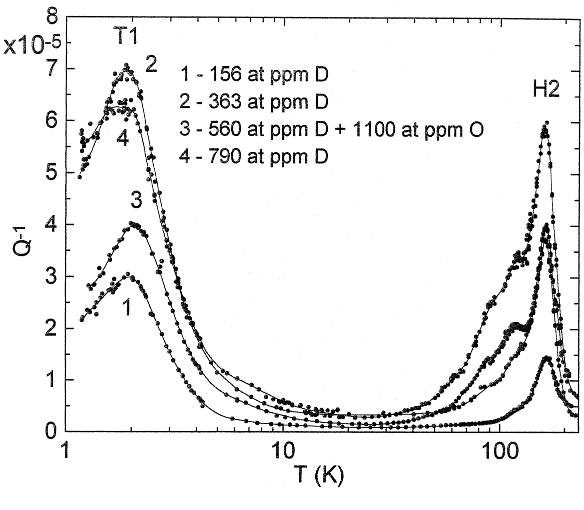

Fig. 1. Anelastic spectra (128 kHz) of $Nb_{0.9955}Zr_{0.0045}$ containing controlled amounts of D and O.

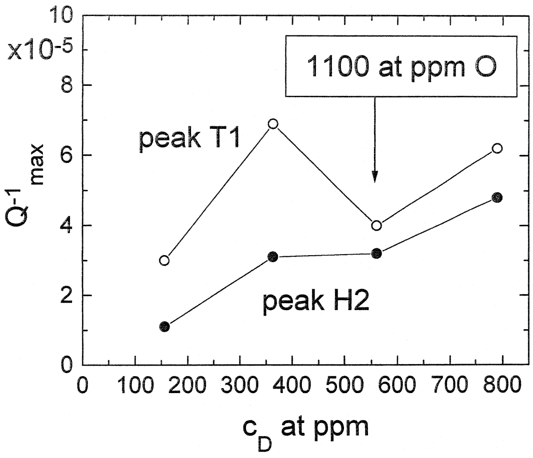

Fig. 2. Intensities of the peaks T1 and H2 as a function of the D content.

Zr–H pairs, it remains to be explained why its intensity saturates at $c_D \ll c_{Zr}$. Again, the presence of Zr–O pairs should be taken into account, since we have just demonstrated that they can trap H atoms at the expenses of the Zr–H pairs. However, the fact that the intensity of peak T1 at $c_D = 790$ at ppm is lower than at $c_D = 360$ at ppm cannot be explained by trapping from Zr–O, since the measurement of the highest intensity with 360 at ppm D was made after that with 790 at ppm, and the content of O can only increase after an additional doping treatment at high temperature. In addition, the saturation of peak T1 has been previously observed on the same sample also by electrolytically doping with H, which does not introduce unwanted O.

We conclude that the decline of the intensity of peak T1 above 500 at ppm D is an intrinsic effect. This effect can be at least partially explained by an increase of the width $\bar{a}$ of the distribution of the site energy asymmetries with increasing D content. The dependence of the asymmetry distribution on the impurity concentration is not known, but from the body of the experimental data on $Nb(O/N)_x(H/D)_y$, O and N interstitials can be estimated to produce site energy shifts of the order of $\bar{a} \approx 3.5 \times 10^{-3}$ K/at ppm [3,7,8]. The specific $\bar{a}$ of the smaller interstitial H(D) is certainly smaller than this value, and that of substitutional Zr should be even less.

The theoretical curves in Fig. 3 show the effect of increasing $\bar{a}$ with values around 1 K, which are compatible with the results for $Nb(O/N)_x(H/D)_y$. The curves are plotted assuming relaxation between the 1st and 4th level of a FLS with $t = 0.15$ K and $\bar{a}$ as shown in the figure; the concentration of FLS was kept fixed. For the relaxation rate, both one-phonon and the electron scattering contributions where considered, with the same coupling parameter to the electrons which was found for the $Nb(O/N)_x(H/D)_y$ systems [3,8]. The specific intensity of the peak decreases for distribution widths exceeding 1 K, and this results in a less than linear dependence of the peak intensity on c_D, if the Zr substitutional atoms alone give rise to $\bar{a} \sim 1$.

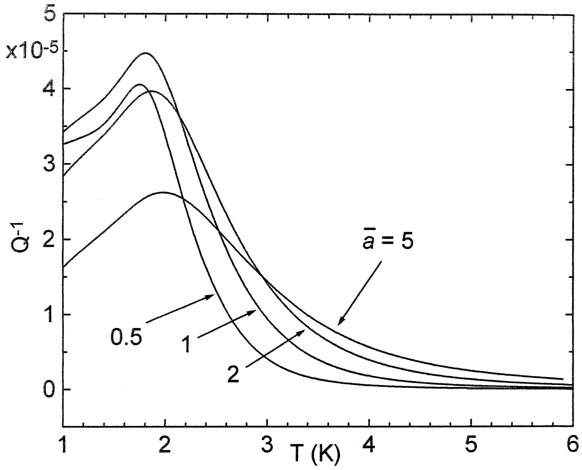

Fig. 3. Theoretical $Q^{-1}(T)$ curves with different values of the width $\bar{a}$ of the lorentzian distribution of site energy shifts; for the other parameters see the text.

4. Conclusions

In conclusion, it has been shown that the narrow peak of the elastic energy loss versus temperature which is observed at the lowest concentrations of H(D) in the dilute $Nb_{1-x}(Zr/Ti)_x$ is indeed due to H tunnelling within substitutional-H pairs, and not to H trapped by (Zr/Ti)–O complexes. The saturation of the intensity of the peak at H concentrations much smaller than the trap concentration can be understood in terms of increase of the interactions among the H atoms, which broaden the distribution of the energy asymmetries of the tunnel systems.

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