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Anelastic relaxation of H trapped by Zr in Nb single crystals

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Abstract

The anelastic relaxation due to the reorientation of the Zr–H pair has been measured in two Nb single crystals at low H and Zr contents. The two crystals were oriented with the longer dimension along the [100] and [111] directions, and were excited in their extensional, torsional and flexural modes. The observed dissipation between 50 and 200 K consists of at least two peaks. One of them is not observed under [100] torsional and [111] extensional vibrations, and this is interpreted as due to the redistribution of H among four-site tunnel systems over the faces of the cube containing the Zr atom. The other peak is predominant and is always observed, implying the occupation of additional sites.

1. Introduction

Interstitial H in Nb is trapped by substitutional Ti [1] and Zr [2] and gives rise to anelastic relaxation due to reorientational jumps [1–3] and transitions within tunnel systems [4, 5]. The phenomenology is rather complex and not yet explained. The main dissipation peak, attributed to the reorientation of a single H atom around the substitutional position, shifts to lower temperature with increase in the H content. Such a phenomenon has been explained by supposing that the peak contains contributions also from complexes with more than one H atom [3], or by supposing that the long-range distortions around the substitutional atoms cause a distribution of the site (but not saddle-point) energies; the trap sites with higher energy are filled at higher concentrations, resulting in a decrease in the mean activation energy [6]. The latter model also explains why the temperature shift is higher at higher substitutional contents.

Regarding the geometry of the substitutional–H pair, the observation of tunnel systems implies that the slower relaxation at liquid nitrogen temperature is not simply due to H reorientation among tetrahedral or octahedral sites. Rather, the reorientation occurs among different tunnel systems and possibly additional types of sites.

We measured two single crystals of $NbZr_{0.0045}$ under different types of stress, in order to have information on the geometry of the Zr–H pair.

2. Experimental details and results

The samples were two Nb single crystals approximately 2 mm×3 mm×50 mm in size, with the longer dimension parallel to the [100] and [111] directions. They contained 4500 at.ppm Zr and less 400 at.ppm O and N, which constituted the main impurities. The samples were electrostatically excited in their flexural (F), torsional (T) and extensional (E) vibration modes, ranging from 2 to 125 kHz.

Figure 1 shows the dependence of the main dissipation peak on the vibration mode, with 0.2 at.% H. The [100] E and [111] T modes exhibit not only higher dissipation but also an additional peak around 105 K. The vibration modes of Fig. 1 have nearly the same frequency, so that the differences in dissipation are due only to the symmetry of the applied stress.

When the H concentration x is increased to 0.002, the shape of the peaks shown in Fig. 1 changes little, and their maximum shifts to lower temperature by a few kelvin. Above that concentration, the temperature shift becomes larger and an additional broad peak develops just below 100 K.

3. Discussion

We will limit the analysis to low H concentrations, when the dominant relaxation is that shown in Fig. 1. From the quasi-linear dependence of its intensity on x, such a relaxation can be ascribed to a single H atom trapped by Zr. The above-mentioned temperature shifts

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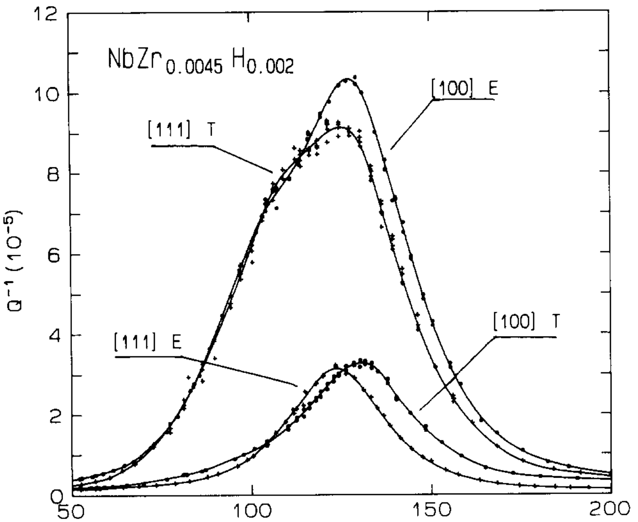

Fig. 1. Elastic energy loss coefficient of $NbZr_{0.0045}H_{0.002}$ under [100] extensional (41 kHz), [100] torsional (46 kHz), [111] extensional (28 kHz) and [111] torsional (52 kHz) vibrations.

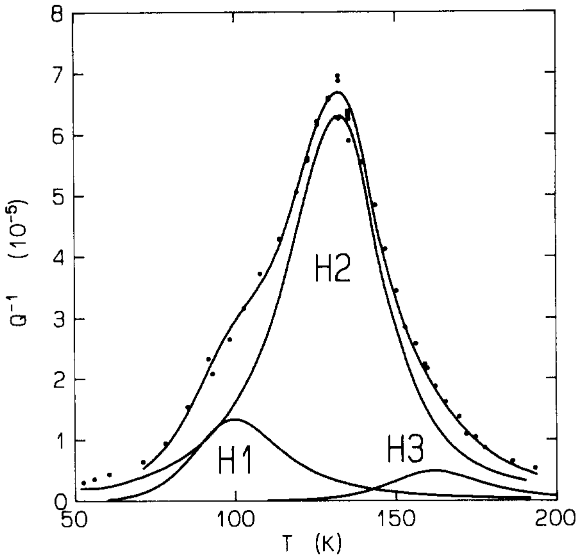

Fig. 2. Decomposition of the peak measured on $NbZr_{0.0045}H_{0.0013}$ under [100] extensional stress. Peak H2 is the rescaled curve measured under torsional stress, while the remaining peaks are fitted with Debye curves with $\tau=\tau_0\exp(E/kT)$; $\tau_0=1.5\times10^{-9}$ s, $E/k=800$ K for H1 and $\tau_0=1.5\times10^{-11}$ s, $E/k=2000$ K for H3.

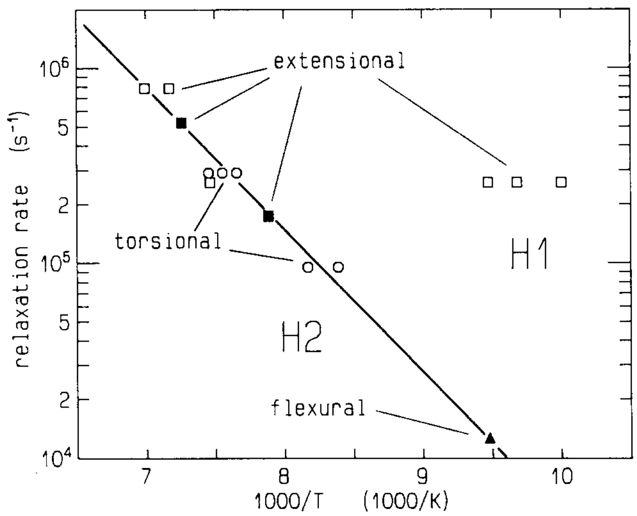

Fig. 3. Arrhenius plot of the relaxation rate ($2\pi f$) of H2, from different vibration modes and H concentrations; ○, □, [100] sample; ■, [111] sample. The apparent activation energy of 1670 K is estimated from the [111] flexural and extensional vibrations of $NbZr_{0.0045}H_{0.002}$.

with varying x may be explained in a manner analogous to the Ti case, *i.e.* as due to a distribution of the site energies resulting from the long-range disturbances from the Zr atoms [6]. This explanation seems to be favoured with respect to an explanation based on the interaction between H atoms, at least for the $Nb_{1-y}Ti_yH_x$ case, because the effect increases with y. For $Nb_{1-y}Zr_yH_x$ there are no data as a function of y yet.

In order to analyse the Zr–H peak, we will take advantage of the fact that the first extensional and the third torsional vibration modes of the [100] sample (relaxation of c' and c_{44} respectively) have nearly the same frequency (41 and 46 kHz). This allows us to compare directly the shapes of the peak in both cases, by subtracting the rescaled narrower torsional peak from the extensional peak, so obtaining the part which relaxes under [100] E but not [100] T stress. Figure 2 shows such a subtraction for the case $x=0.0013$. The peak measured under the [100] E vibration has been decomposed into the same peak measured under [100] T stress, labelled as H2, plus two peaks, H1 and H3, which have been fitted with two Debye peaks, as specified in the figure. The background dissipations of both the E and the T measurements have been taken into account, but do not affect the fit much. The line passing through the experimental points is the sum of the three peaks, the background being included in the H2 curve. The same decomposition for other values of x up to 0.002 gives similar results, with the weight of H1 slightly increasing with x, whereas the intensity of H3 remains nearly constant or even decreases with increasing x. Although we do not expect any of these peaks to be a simple Debye process, we estimate H2 to be about 30% broader than a single peak, from its width and apparent activation energy (Fig. 3).

The case of the [111] sample cannot be treated in the same simple manner, because its extensional and torsional modes differ too much in frequency. Nonetheless, it is easy to identify H2 with the [111] E peak in Fig. 1 and H1 with the low temperature shoulder of the [111] T peak. To help with the identification, one can look at the Arrhenius plot in Fig. 3, where the peak temperatures of H2 and H1 at different H concentrations are reported. The apparent activation energy of H2 is 1670 K, as estimated from the [111] flexural and extensional vibrations of $NbZr_{0.0045}H_{0.002}$. For H1, only the peak temperatures resulting from the analysis of the [100] sample are shown. The spread in peak temperatures reflects the shifts with the H content.

We consider now the possible geometries which could give rise to the observed peaks. Since at lower temperatures dissipation from H tunnel systems is observed, we suppose that such tunnel systems are among the configurations between which H can redistribute. The sites involved in tunnelling are not yet known, the most probable being pairs of nearest-neighbour tetrahedral (T) sites or the ring of the four T sites on a face of the cube containing the Zr atom. The dependence of the relaxation strength on the applied stress and especially specific heat measurements favour the existence of four-site tunnelling [4, 5]. Since the transition rates within such four-level systems (FLSs) are much higher than that for reorientation around Zr, the symmetry of the FLS is that of the ring of T sites, *i.e.* $\langle 100 \rangle$ tetragonal, like for an octahedral (O) site. Defects with that symmetry are all equally affected by $\langle 111 \rangle$ uniaxial stress and therefore they do not relax under a [111] extensional vibration. Moreover, it can be shown that the total energy of the FLS should not change under the application of a shear stress of the F type (ϵ_4, ϵ_5, ϵ_6) [5], just like a $\langle 100 \rangle$ tetragonal defect; therefore, no relaxation is expected under a [100] torsional vibration.

The absence of relaxation under [100] T and [111] E stresses (c_{44} elastic constant) is exactly what is observed for peak H1, which therefore we attribute to the redistribution of H among FLSs.

Peak H2 is observed under any stress, and is also more intense than H1. We must conclude that H also occupies lower symmetry sites, such as the octahedral second-nearest neighbours to Zr, or that it mostly forms two-site tunnel systems (two-level systems (TLSs)) instead of FLSs. The formation of TLSs is probably near Zr atoms with a much distorted environment. From our measurements it is not easy to distinguish between the above possibilities. Moreover, one should consider several types of relaxations, *i.e.* redistribution within the additional sites, or TLSs, or both, and between the different types of occupations. Such an analysis was made by Koiwa [7] for the similar case of an interstitial trapped by a substitutional in the octahedral sites of a b.c.c. crystal. Although this analysis cannot be applied in a straightforward manner to our case, some remarks should still hold. (In our case the octahedral (O) sites that are nearest neighbours to the Zr atom would correspond to the FLSs; however, the latter are not affected by a σ_4 stress, whereas the O sites are. Also, TLSs could not be modelled as O sites.) In particular, the decomposition in Debye peaks is valid, but their relaxation strengths are temperature dependent and their relaxation rates do not coincide with but are functions of the various jumping rates involved. This could explain the fact that peak H2 is well described by a Debye peak only about 30% broader than a single peak, but its wings are not.

We finally consider the small peak H3, whose dependence on the H content suggests that it is associated with some scarce traps, such as Zr–O, which are immediately saturated. The only question is its absence in the [100] T mode, which would imply a rather symmetric defect.

4. Conclusion

The anelastic relaxation of H trapped by Zr has been measured in Nb single crystals at low H and Zr concentrations, in order to minimize the interactions between the various complexes. The main dissipation peak associated with a single H atom trapped by Zr has been shown to contain at least two processes, which are differently affected by the symmetry of the applied stress. The smaller peak is not observed under [100] torsional and [111] extensional vibrations (c_{44} elastic constant); this fact can be explained by supposing redistribution of H among four-site tunnel systems over the faces of the cube containing the Zr atom. The other peak is predominant and is always observed, implying the occupation of additional sites or of two-site tunnel systems.

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