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Hopping rates of H(D) bound to heavy interstitials in Ta as investigated by mechanical spectroscopy at MHz frequencies

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Abstract

The stress-induced reorientation of O(N)–H(D) pairs has been investigated at MHz frequencies in Ta by propagating longitudinal ultrasonic pulses along a <111> crystal lattice direction. The resulting anelastic relaxation is found to be composed of two processes which are attributed to two distinct configurations of the pair. A comparison of the transition rates of free and trapped H(D) atoms in Nb and Ta suggests that both processes observed in Ta involve transitions of H(D) atoms between equivalent nn sites, which are probably slightly displaced from normal tetrahedral sites (dis-1T↔dis-1T transitions). In Nb bound H(D) atoms should be in a state delocalized over two equivalent sites, probably slightly displaced from normal tetrahedral sites (dis-2T state), and the reorientation in this metal would take place via (dis-2T↔dis-2T) transitions.

Keywords: Anelastic relaxation; Ultrasonic attenuation; Point defects interactions

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1. Introduction

It is well known that H(D) in refractory bcc metals Ta, Nb and V can be trapped by the heavy interstitials O and N. The diatomic complex I–H(D) (I stands here for O or N) forms an elastic dipole, which can be reoriented by an applied stress field, thus giving rise to an anelastic relaxation that has been extensively investigated in Nb [1–10] and to a lesser extent in Ta [1,2,11] and V [12,13]. Attention has recently been paid also to TaNb alloys containing H and O [14,15].

In the course of the above investigations it has clearly been shown that hopping rates of free and bound H(D) do not match over common temperature ranges. This mismatch has usually been attributed to partial dissociation of the I–H(D) complex during the reorientation process induced by an applied stress. More recently [15], however, the assumption has been made that this mismatch may also reflect differences in the state (localized/delocalized) of free and trapped H(D). This idea has originated from the observation that the hopping rate of free H(D) is higher in Nb than in Ta while the reverse is found to be true for trapped H(D). The existence of these differences in the hopping rates, however, have only been observed at low temperatures, since measurements in Ta containing H(D) and O(N) have only been carried out at kHz frequencies and below. In view of their relevance ultrasonic measurements were extended in this work to the MHz frequency range.

2. Experimental

The marz grade tantalum specimen used in this experiment was a cylinder of diameter $\Phi=6$ mm and length $l=25.9$ mm supplied by MRC. The axis of the cylinder was oriented along a <111> crystal direction. The single crystal was doped with O and N by annealing the sample at about 1000 °C in poor vacuum ($P\cong 10^{-3}$ torr) for about 72 h. To facilitate H(D) absorption a thin Pd film was subsequently evaporated on the lateral surface of the sample at a temperature of 950 °C. Under the above doping conditions the equilibrium concentration of O and N is expected to coincide with the terminal solubilities of these impurities in Ta at 1000 °C, that is, $n_{\mathrm{N,O}}=\mathrm{I/Ta}\cong 0.02$ at. Deuterium was introduced at a concentration $n_{\mathrm{D}}=\mathrm{D/Ta}=0.008$ at. by annealing the sample in a D_2 atmosphere at appropriate pressures and temperatures. After various series of ultrasonic measurements at low temperatures the specimen was outgassed from D and, then, repeatedly

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charged with H to H contents $n_H=0.002$, 0.0065, 0.01 and 0.037 at.. Ultrasonic attenuation was measured using a pulse echo technique at frequencies between 5 and 75 MHz. Longitudinal pulses were propagated along the <111> principal lattice direction.

3. Results

The energy dissipation coefficient Q^{-1}, as derived from the attenuation coefficient A ($Q^{-1}=A$(dB μs^{-1})/ 8.7πf(MHz)) at various frequencies for the O(N) and D doped material, is plotted against T^{-1} in Fig. 1 after background subtraction. As can be seen, an internal friction (IF) peak is observed at temperatures which increase with increasing the ultrasonic frequency. No peak was observed in the sample after deuterium degassing nor was it observed in the absence of O(N). These observations confirm that the relaxation responsible for the IF peak is due to stress-induced reorientation of I–D pairs. Remarkable features of data in Fig. 1 are: (a) the marked reduction in the peak height associated with an increase in the frequency of the ultrasonic pulses; (b) the strong asymmetry of the peak.

Similar results were obtained with H at 10, 30 and 75 MHz as shown by Fig. 2. Again the height of the peak decreases with increasing the frequency and the peak is asymmetric; in the case of H the $Q^{-1}(T^{-1})$ curves at 30 and 75 MHz clearly indicate the existence of a bump on the lower temperature side of the main peak, the height of which, as measured at 10 MHz, linearly increases with increasing D content.

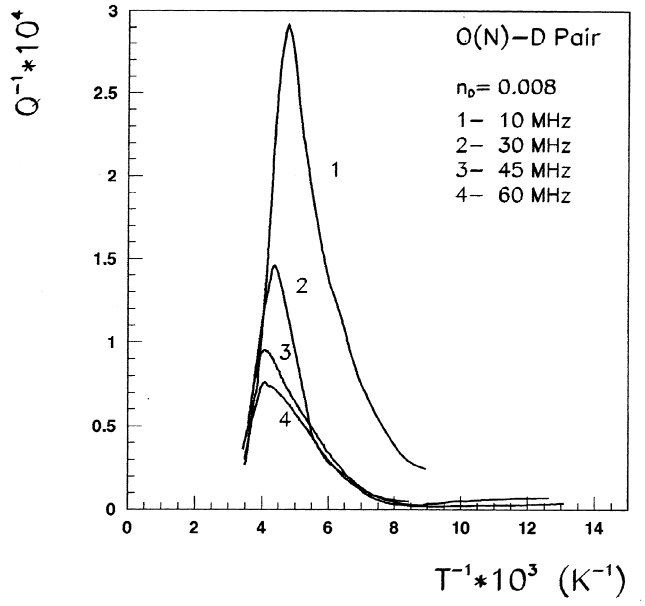

Fig. 1. Temperature dependence of IF at different frequencies in O(N) and D doped sample.

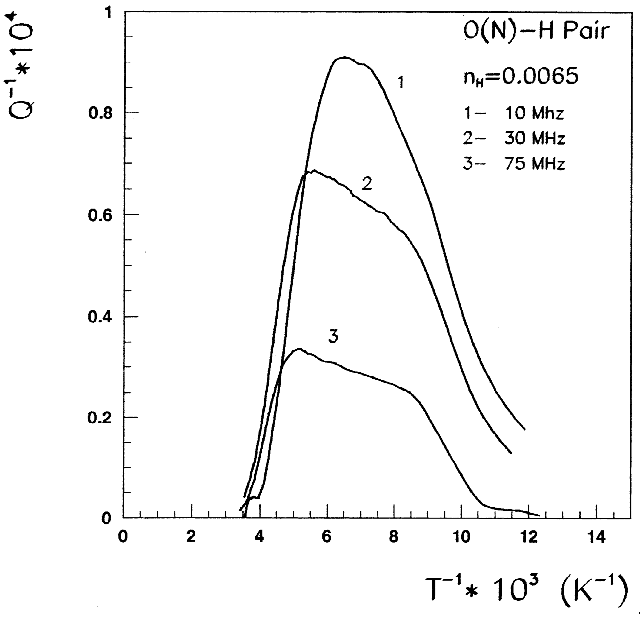

Fig. 2. Temperature dependence of IF at different frequencies in O(N) and H doped sample.

4. Discussion

The structure of the I–H(D) pair in Nb, Ta and V has not been unambiguously identified so far [7]. From a number of experimental observations (for a review see Ref. [16]), it follows that in Nb, at liquid helium temperatures, an H(D) atom trapped at an O or N impurity is in one (or more than one) tunnel-split state formed by simultaneous occupancy by H(D) of two equivalent sites (see Fig. 3). Presumably, these occupied sites are slightly displaced from normal tetrahedral sites (dis-2T state) and are located far away from the trapping impurity [17]. The occurrence at liquid helium temperatures of a (dis-2T) state has also been found in Ta by ultrasonic attenuation measurements [18,19].

Oxygen and nitrogen atoms as trapping centers appear to behave quite similarly giving rise to anelastic processes

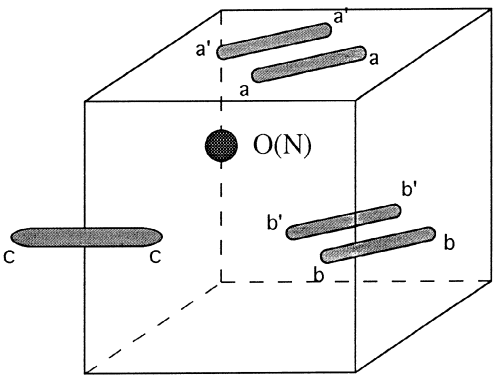

Fig. 3. Some possible configurations of the O(N)–H(D) pair.

that are expected to perfectly overlap when observed at MHz frequencies [8]; thus, the O–H(D) and N–H(D) pairs are assumed to be undistinguishable from one another as far as the present measurements are concerned.

The strength and time of a relaxation due pairs are given by

$$\Delta_{\mathrm{I-H(D)}} = \Delta^0_{\mathrm{I-H(D)}} \frac{C_{\mathrm{I-H(D)}}}{T - T_s};\ \tau_{\mathrm{I-H(D)}} = \tau^0_{\mathrm{I-H(D)}} \exp\left(\frac{W_{\mathrm{I-H(D)}}}{kT}\right) \tag{1}$$

where $C_{\mathrm{I-H(D)}}$ is the concentration of the I–H(D) pairs; T_s is a self-ordering temperature which accounts for the interactions among pairs; $\Delta^0_{\mathrm{I-H(D)}}$ and $\tau^0_{\mathrm{O(N)-H(D)}}$ are constants.

An exact calculation of $C_{\mathrm{I-H(D)}}$ has been carried out only recently [20] and gives

$$C_{\mathrm{I-H(D)}} = \frac{\alpha n_{\mathrm{I}} + \alpha' n_{\mathrm{H}} + (1-\alpha')\beta - \{[\alpha n_{\mathrm{I}} + \alpha' n_{\mathrm{H}} + (1-\alpha')\beta]^2 - 4\alpha' n_{\mathrm{I}} n_{\mathrm{H}}\}^{\frac{1}{2}}}{2\alpha'} \tag{2}$$

with

$$\alpha = 1 - \exp\left(-\frac{B_{\mathrm{I-H(D)}}}{kT}\right);\ \alpha' = 1 - \frac{\exp\left(-\frac{B_{\mathrm{I-H(D)}}}{kT}\right)}{z} \tag{3}$$

where n_{I} and n_{H} are the atomic ratios I/Ta and H/Ta, respectively; $B_{\mathrm{I-H(D)}} > 0$ is the binding energy of the pair; $z = 4$ is the coordination number; $\beta = 6$ is the ratio between the number of interstitial tetrahedral sites and of metal atoms. A fit of Eqs. (1)–(3) to all the experimental curves in Figs. 1 and 2 has been attempted by using $B_{\mathrm{I-H(D)}}$ and $\Delta^0_{\mathrm{I-H(D)}}$ as fitting parameters and attributing to T_s the value of 25 K, which is suggested by data obtained in a $\mathrm{Ta_{75}Nb_{25}}$ alloy [15], and to $W_{\mathrm{I-H(D)}}$ and $\tau^0_{\mathrm{I-H(D)}}$ the values deduced from composite Arrhenius plots of the present and previous data at temperatures higher than about 100 K ($W_{\mathrm{I-H}} = 0.125$ eV, $W_{\mathrm{I-D}} = 0.194$ eV, $\tau^0_{\mathrm{I-H}} = 1{*}10^{-12}$s and $\tau_{\mathrm{I-D}} = 3{*}10^{-13}$s). The fit turned out to be rather poor, probably due to uncertainties in the subtraction of background attenuation, nonetheless, it reproduced all the main features of plots in Figs. 1 and 2, giving: $B_{\mathrm{I-H}} \cong B_{\mathrm{I-D}} \cong 0.08$ eV, $\Delta^0_{\mathrm{I-H}} \cong 4$ and $\Delta^0_{\mathrm{I-D}} \cong 25$. To further improve data analysis, the high temperature side of some of the curves of Fig. 1 ($f = 10$, 45 and 60 MHz) and Fig. 2 ($f = 10$, 30 and 75 MHz) were separately fitted to Eqs. (1)–(3) taking $\tau^0_{\mathrm{I-H(D)}}$ and $\Delta^0_{\mathrm{I-H(D)}}$ as parameters and assuming: $T_s = 25$ K, $B_{\mathrm{I-H}} \cong B_{\mathrm{I-D}} \cong 0.08$ eV, $W_{\mathrm{I-H}} = 0.125$ eV and $W_{\mathrm{I-D}} = 0.194$ eV. An example of such a fit is given in Fig. 4, which clearly shows the existence at lower temperatures of a second relaxation, the main features of which are: $B_{\mathrm{I-H}} \cong B_{\mathrm{I-D}} \cong 0.08$eV, $\Delta^0_{\mathrm{I-H}} \cong 2$, $\Delta^0_{\mathrm{I-D}} = 3$, $W_{\mathrm{I-H}} = 0.06$ eV, $W_{\mathrm{I-D}} = 0.09$eV, $\tau^0_{\mathrm{I-H}} = 3{*}10^{-11}$s and $\tau_{\mathrm{I-D}} = 2{*}10^{-11}$s. Here the activation energies have been deduced from the widths and the limiting times from the widths and positions of the peaks. The two component peaks, which are shown in Fig. 5, exhibit similar trends with increasing the measuring frequency: (a) they both shift towards higher temperature and (b) they are considerably reduced in height. This implies that the peaks are of the same nature, probably originating from two different configurations of the pair.

The cumulative plots of Figs. 6 and 7 show all the collected IF data so far available in the literature con-

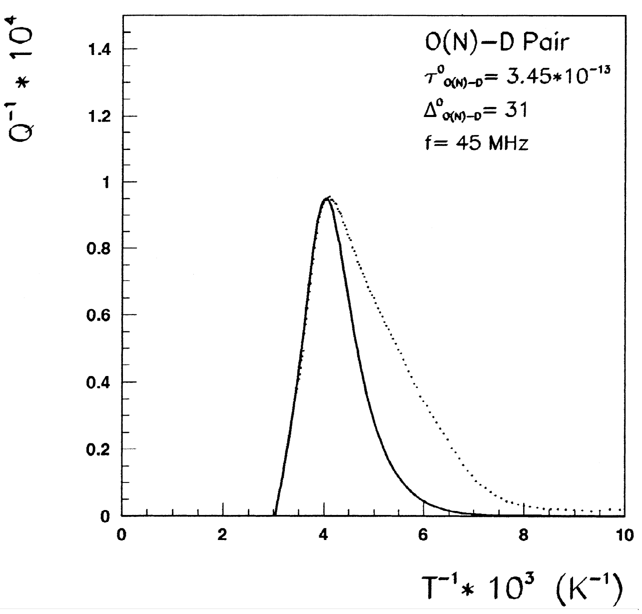

Fig. 4. Fit to the experimental curve at 45 MHz of Eqs. (1)–(3).

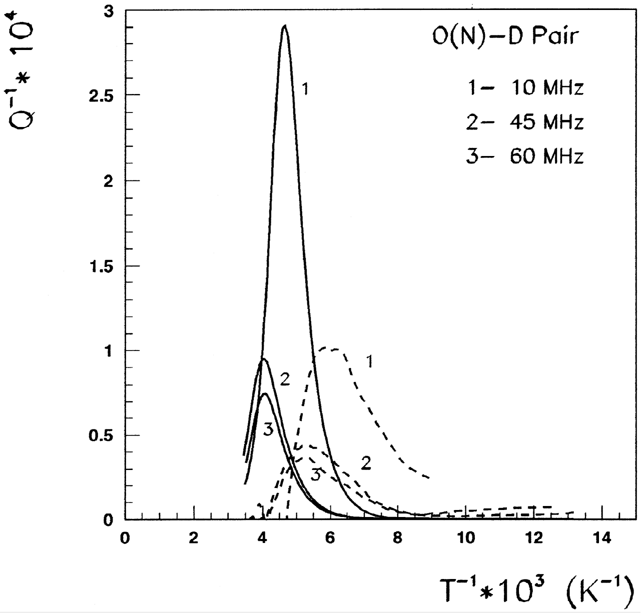

Fig. 5. Component relaxations as obtained by subtracting the main peak from the experimental curves.

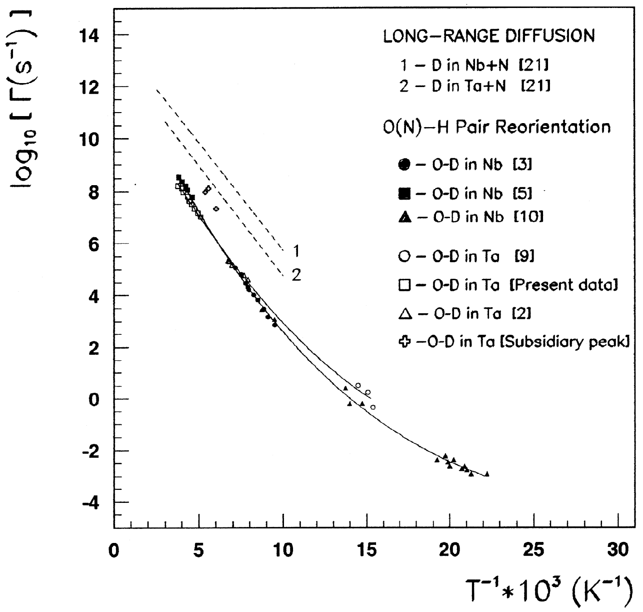

Fig. 6. Hopping rate vs. T^{-1} of free (- - -) Ref. [21] and trapped (data points) D atoms in Nb and Ta.

cerning the I–H(D) pair reorientation and also some long-range diffusion results. As can be seen, the jump frequencies deduced from the lower temperature peak reported here are comparable to those associated with free H and D. This implies that in the reorientation of the corresponding pair jumps similar to those of free H(D) are involved, as well as similar states of the H(D) atoms. This means that the trapped H(D) atom is localized at a single site, probably displaced from the regular T site (dis-1T state), and that the transitions take place between nn T sites (dis-1T ↔dis-1T transition).

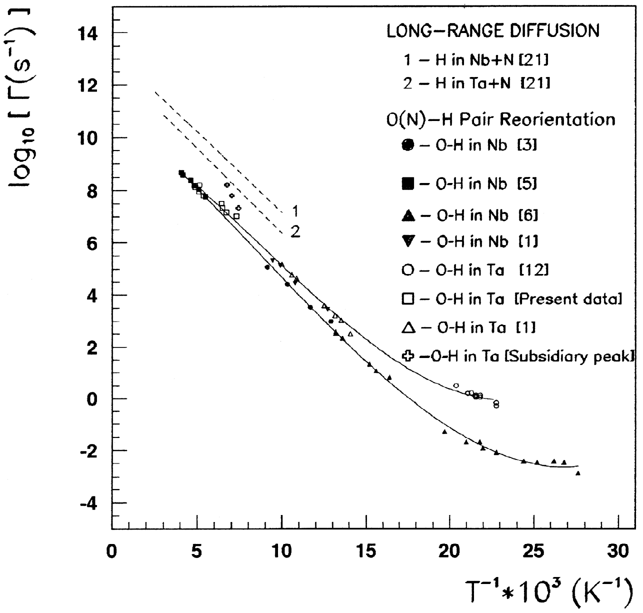

Fig. 7. Hopping rate vs. T^{-1} of free (- - -) Ref. [21] and trapped (data points) H atoms in Nb and Ta.

Inspection of Figs. 6 and 7 shows also that the jump frequencies of bound H in Ta is higher than in Nb, while those of bound D are about the same in these two metals. The opposite happens for free H and D, the jump frequencies of which are both sensibly higher in Nb than in Ta. These observations suggest that the structure of the pairs is different in the two metals, probably being of type dis-1T in Ta and dis-2T in Nb.

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