

H Tunneling and Trapping in Y by Anelastic Relaxation Measurements

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We present the first evidence by acoustic measurements of H tunneling and trapping by O atoms in a rare-earth-hydride system. The $\text{YO}_{0.0027}\text{H}_{0.016}$ alloy presents three new elastic-energy-loss peaks most likely due to H trapped by O between 1.4 and 330 K. The peak at the lowest temperature is due to tunneling of the trapped H; its relaxation rate strongly depends on temperature, indicating a dominant contribution of multiphonon processes already at a few kelvin. The other two peaks, with activation energies of 0.14 and 0.22 eV, can be attributed to jumps of H in the distorted environment of the O atom.

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RH_x ($R = \text{Y, Sc, Lu, Tm, Er}$) systems have attracted much interest in recent years, especially due to their ability to retain H in solid solution (α phase) up to $x = 0.2\text{--}0.3$ down to 0 K. It is now accepted that H(D) mainly occupies the tetrahedral (T) interstitial sites of the hcp lattice, with little octahedral (O) occupancy; moreover, the H atoms tend to form pairs along the c axis, occupying next-nearest-neighbor (nnn) T sites bridging the metal atoms, and this ordering prevents the formation of the dihydride phase. Such pairs are correlated in chains along the c axis [1,2], and an additional correlation between different chains has been revealed in LuD_x and ScD_x [3].

The motion of H in such systems has been studied by quasielastic neutron scattering (QNS) [4,5], NMR [6,7], inelastic neutron scattering (INS) [8], and the Gorsky effect [9] (anelastic relaxation due to the stress-induced long-range diffusion of H); it is believed that the H long-range diffusion in the α phase occurs via $T\text{--}O\text{--}T$ jumps with an activation energy of 0.5–0.6 eV, the jump rate from the O to the T site being faster than the reverse one, and the nearest-neighbor (nn) $T\text{--}T$ rate being much faster than both.

Recently, this rapid local motion of H between nn T sites has been directly observed by QNS in ScH_x and YH_x [10,11]. The hopping rate is of the order of 10^{11} s^{-1} around 10 K, and exhibits a minimum as a function of temperature as predicted by recent theories on H tunneling [12], and already found for incoherent tunneling of H trapped by O in Nb [13]. Low-temperature relaxations have also been observed by NMR in ScH_x [14] and attributed to $T\text{--}T$ hopping although the observed hopping rates are of the order of 10^8 s^{-1} , i.e., much slower than observed by QNS.

Anelastic relaxation measurements (elastic energy dissipation and dynamic modulus), besides providing the parameters of the long-range diffusion through the Gorsky effect, are effective in investigating H ordering, hopping, and tunneling. In fact, when an atomic jump between

two sites 1 and 2 (or transition between two levels 1 and 2) causes a change $\Delta\lambda$ in the local elastic distortion (elastic dipole), it also gives rise to a Debye peak in the elastic energy dissipation Q^{-1} (inverse of the mechanical quality factor) as a function of temperature [15,16]:

$$Q^{-1} = f(c_1 c_2 / ckT) v_0 (\Delta\lambda)^2 M \omega \tau / [1 + (\omega \tau)^2], \quad (1)$$

where f is a factor of the order of $\frac{1}{2}$ depending on the geometry of the jump and the type of the sample vibration, c the molar concentration of the jumping atoms, c_1 and c_2 their concentrations in the 1 and 2 sites, v_0 the molecular volume, M the elastic modulus, $\omega = 2\pi f$ the angular vibration frequency of the sample, and τ the relaxation time, which is close to the mean time between two subsequent jumps or transitions; τ can be readily evaluated from the position of the maximum of the peak, which occurs for $\omega \tau \sim 1$, when τ varies fast enough with temperature.

A few measurements of this kind were performed at low frequency on Lu and Sc at H(D) concentrations ranging from 5 to 30 at.%, and they all exhibited a peak of Q^{-1} around 200 K, attributed by the authors to the stress-induced changes in the ordered configuration of the H sublattice [17,18].

Considering the variety of phenomena involving H motion in these systems, we extended the acoustic measurements to lower temperatures and H concentrations, looking for new possible anelastic relaxation mechanisms, possibly associated with H tunneling.

Anelastic relaxation measurements have been made on two samples: $\text{YH}_{0.1}$, a single crystal with 540 at. ppm of O and 240 at. ppm of C, and $\text{YO}_{0.0027}\text{H}_{0.016}$, a polycrystal with 300 at. ppm of N as a main impurity. Both samples were electrostatically excited into flexural vibration modes.

Figure 1 presents the elastic energy dissipation Q^{-1} of both samples; the $\text{YH}_{0.1}$ sample was measured at a vibration frequency of 8.6 kHz from 1.4 to 330 K. The large peak at 308 K, labeled here as P6, corresponds to that al-

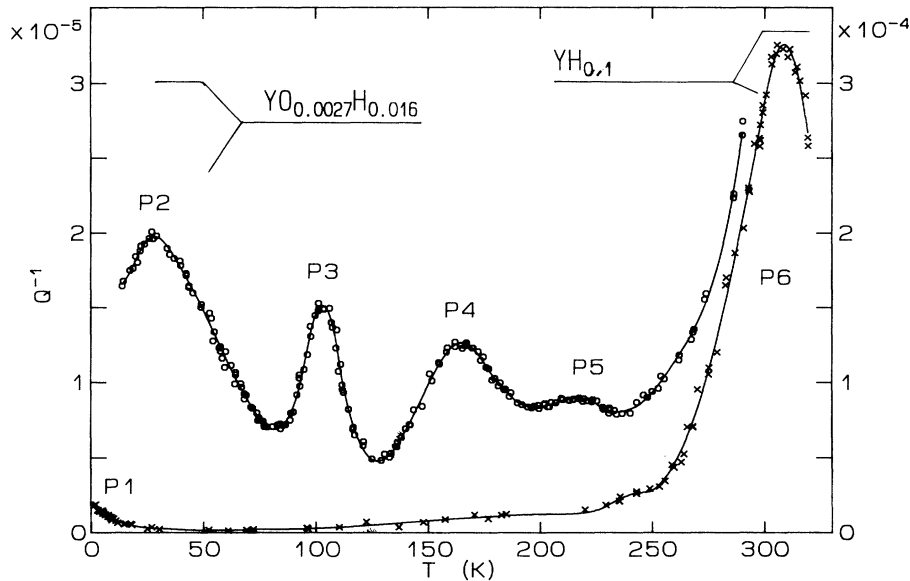


FIG. 1. Elastic energy loss as a function of temperature of $YH_{0.1}$ (right-hand scale) and of $YO_{0.0027}H_{0.016}$ (left-hand scale, enlarged $10\times$).

ready observed at low frequency in Lu, Sc [17,18], and $YH_{0.2}$ at 219 K around 1 Hz [18]. From the shift in temperature due to a change of frequency, an activation energy of about 0.6 eV is estimated, in accord with the value of 0.54 eV obtained by Vajda *et al.* for $YH_{0.2}$. At lower temperature the dissipation curve is flat down to 20 K, where it starts increasing; this is apparently the tail of a process labeled here as P1.

The measurements of the $YO_{0.0027}H_{0.016}$ sample pre-

sented four new peaks, besides P6, labeled as P2, P3, P4, and P5, starting from low temperature. Measurements made at $f=2.6, 13,$ and 32 kHz showed that they are all thermally activated. Figure 2 presents P2 and P3 obtained for the three different frequencies. Peak P2 exhibits a remarkable shift from 9 to 44 K and an increase in height when the frequency increases. The shoulder on its low-temperature side appearing at 32 kHz is apparently due to an additional relaxation process which can be

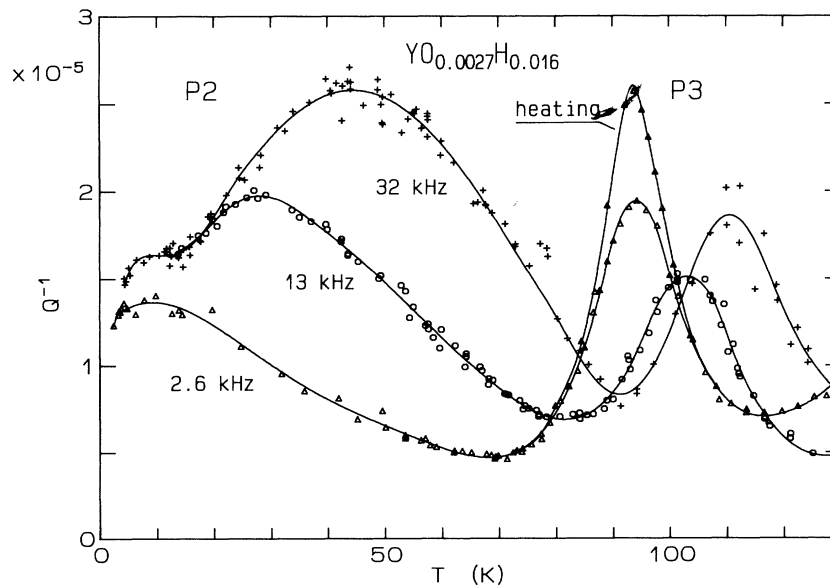


FIG. 2. Elastic energy loss as a function of temperature of $YO_{0.0027}H_{0.016}$ measured at three different vibration frequencies; only peaks P2 and P3 are shown.

hardly resolved, because of its low temperature and small intensity in comparison to P2. Peak P3 is only 10% broader than a single-relaxation-time process with an activation energy $W=0.14$ eV. Peak P4 has $W=0.22$ eV and a broadening of 30%; P5 is only a small bump on the tail of P6, possibly present also in $\text{YH}_{0.1}$, and is also thermally activated. The Q^{-1} curves were retraced on cooling and heating (0.3–1 K/min), except for P3, which was more intense on heating.

The resonant frequency, whose square is proportional to the elastic modulus, is not shown in the figures, but did not show any feature in the whole temperature range, also including the region of the resistivity anomaly [19].

From the comparison of the results obtained in the two samples having different O content it appears that P1, P6, and perhaps P5 are due to untrapped H, whereas P2, P3, and P4 are associated with H close to an O atom; the trapping of H by interstitial or substitutional impurities in metals is a well-known phenomenon [20].

Let us first discuss the possible relaxation mechanisms for untrapped H. As already noted [21], in an hcp lattice all T sites remain equivalent under the application of a homogeneous stress, and the same holds for the O sites; therefore, no relaxation is possible among only T sites or only O sites. Still, stress-induced redistribution of isolated H atoms is possible between T and O sites, because they may have different responses to an applied stress (both hydrostatic and uniaxial), i.e., different elastic dipoles, λ_T and λ_O . According to Eq. (1), the intensity of such a process is proportional to $(\lambda_T - \lambda_O)^2 c_T c_O / c_H$, where c_T and c_O are the concentrations of free H in T and O sites, and c_H is the total H concentration [16]. Another relaxation mechanism which involves untrapped H atoms is the stress-induced formation and dissolution of the H pairs, with intensity proportional to $c_{2T}(\Delta\lambda)^2$, where c_{2T} is the concentration of pairs and $\Delta\lambda$ is the difference in local strain between the formed and dissociated pair. As discussed in detail elsewhere [16], both mechanisms can, in principle, explain P6; however, most experiments indicate that only a few percent of H is in the O sites even above room temperature, while a substantial fraction is paired already at 300 K. Therefore, it seems more likely that P6 is associated with the pairs, as suggested by Vajda *et al.* [17,18].

The dissipation increase observed in $\text{YH}_{0.1}$ below 15 K can be the tail of a relaxation process, called P1 here, whose maximum is well below 1.4 K (the minimum temperature of our measurement), and whose relaxation rate is therefore expected to be much higher than 10^4 s^{-1} already at 1.4 K. Such a process can be the tunneling of free H between two nn T sites, already revealed by INS measurements in ScH_x [6].

We discuss now P2, which is the process at lower temperature among those due to H trapped by O, and therefore is the one with the faster relaxation rate. It seems plausible to associate it with H jumping or tunneling be-

tween nn T sites close to an O atom. Such sites become nonequivalent, because they cannot be symmetrically arranged with respect to an interstitial O atom sitting in any O or T site. From Eq. (1) and Boltzmann statistics one derives that the relaxation intensity for a two-level system (TLS) is proportional to

$$c_1 c_2 / ckT = c / [2kT \cosh^2(E/2kT)],$$

which has a maximum at $kT=0.65E$, where E is the energy separation between the two levels; therefore, by noting that the intensity of P2 is an increasing function of temperature at least up to 50 K, we conclude that the two-site systems giving rise to P2 have $E \geq 80$ K (7 meV).

A semiclassical over-barrier hopping mechanism for H would not be inconceivable *a priori*, in view of the expected very low barrier between nn T sites. We have tried to interpret P2 by supposing that the jump rates of H between the two levels follow simple Arrhenius laws, resulting in

$$\begin{aligned} \frac{1}{\tau} &= \frac{1}{\tau_{12}} + \frac{1}{\tau_{21}} \\ &= \frac{1}{\tau_0} \exp\left(\frac{-W}{kT}\right) \left[\exp\left(\frac{E}{2kT}\right) + \exp\left(\frac{-E}{2kT}\right) \right], \end{aligned}$$

where W is the mean activation energy, and by introducing a distribution of the asymmetries E due to the long-range elastic interactions among the various O and H atoms. It turns out that unrealistically low values of W and $1/\tau_0$ are required in order to reproduce the large shift in temperature of P2 with varying frequency, and therefore we conclude that P2 must be due to a tunnel system.

In all the other known cases of H tunneling in metals, i.e., in the systems $(\text{Nb,Ta})(\text{O,N,C})_x(\text{H,D})_y$, NbTi_xH_y , and ScH_x , the tunnel systems seem to interact mainly with the conduction electrons [10,13,22], and therefore attempts have been made to explain P2 in the same way. However, simple [23] and more elaborate [12] theories of the interactions between TLS and electrons predict a relaxation rate varying linearly or less than linearly with temperature (or even with a negative power), which cannot reproduce the marked shift of P2 with changing frequency. In fact, such a shift is observed when the shape of the Q^{-1} curve is dominated by the Debye part in Eq. (1), which is maximum at $\omega\tau \sim 1$. However, if τ varies slowly with T , the dissipation curve becomes a broad peak around $T \sim E/k$, due to the T dependence of the relaxation intensity of the TLS. The same remark holds for the one-phonon transitions, whose contribution to the relaxation rate has the same temperature dependence as the electron contribution, i.e., $1/\tau \sim \coth(E/2kT)$ [24]. We conclude that already at a few kelvin there is a substantial contribution of two-phonon processes to the transitions of the TLS's giving rise to P2.

The next peak, P3, is also undoubtedly due to H trapped by O atoms, and the fact that it is higher on heating than on cooling is consistent with the rather slow long-range diffusion coefficient of H (its activation energy is ~ 0.55 eV [5,9]): The cooling rate of about 0.3–0.4 K/min did not allow the equilibrium fraction of O-H pairs to be formed during cooling, around 100 K. Regarding the mechanisms of P3 and P4, they are likely due to nearly classical over-barrier jumps among O and T sites in the distorted environment of the O atom; as discussed elsewhere [16], from the fact that their height does not increase with temperature, it is deduced that the energies of such sites cannot differ by more than a few hundred kelvin.

In conclusion, the present anelastic relaxation measurements strongly indicate that oxygen in solid solution in Y is a trap for H, and provides a distorted environment where H can jump faster than in the free lattice. One of the observed relaxation processes is due to an asymmetric TLS which already at few kelvin interacts with the lattice mainly via multiphonon processes, whereas in the other known tunnel systems formed by H in metals the dominant interaction is with the conduction electrons.

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