Anelastic relaxation of hydrogen in scandium

LETTER TO THE EDITOR

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Abstract. The low-frequency internal friction spectra $Q^{-1}(T)$ of α-ScH(D)$_x$, $0 \leq x \leq 0.3$, reveal a hydrogen-specific peak near $T_p = 200$ K for H and near $T_p = 210$ K for D, the peak temperature increasing slightly with increasing x. The dynamic modulus, G, obtained simultaneously shows a break, $\Delta G/G$, in the temperature dependence corresponding to the peak in Q^{-1}, with $-\Delta G/Gx \simeq 0.3$/atom H(D). The activation energy for the relaxation has been determined to be $E_a = 0.54(3)$–$0.61_5(3)$ eV, increasing with decreasing x. The phenomenon is attributed to a Zener-type process of stress-induced changes in the short-range- and long-range-ordered configurations of the hydrogen sublattice such as are established by neutron scattering.

The solid solution phase of scandium with hydrogen, α-ScH(D)$_x$, is stable down to the lowest temperatures, as it is for a series of other HCP rare earths (R) [1], below a constant concentration limit x_{max} (in the case of Sc, $x_{max}^{Sc} = 0.35$ atoms of H per atom of Sc) [2]. The hydrogen atoms have been found by neutron diffraction [3] to be located in tetrahedral interstitial sites. A resistivity anomaly has been observed near 150–160 K [4], and has been analysed in detail and attributed to short-range ordering into H–H pairs [2]. Recent neutron scattering studies [5, 6] have permitted us to refine this model, in that the pairs are occupying second-neighbour T sites along the c axis surrounding a metal atom and forming quasi-linear chains in the c direction; these chains have a tendency to interact with each other repulsively to create a long-range network. Finally, nuclear magnetic resonance experiments have served to investigate diffusive hopping at high temperatures [7] and localised motion of hydrogen below room temperature [8].

In the present work, we shall investigate the internal friction in the system α-ScH(D)$_x$, for various hydrogen concentrations x, and compare it with results obtained earlier for the analogous system α-LuH(D)$_x$ [9], in view of the rather differing physical parameters in the two cases. Thus, Sc has a much smaller unit cell, a bigger c/a-ratio and a different elastic anisotropy than Lu; its lattice expansion upon hydrogen absorption is inversely anisotropic, i.e. it expands relatively more in the basal plane than along the c axis ($\Delta a/a > \Delta c/c$) while the reverse is true in the case of Lu; hence there is a diminution of the c/a-ratio in α-ScH$_x$ and an increase of c/a in α-LuH$_x$. Furthermore, the binding energy for the H atoms in the ordered configuration of α-ScH$_x$ is about 20% smaller than in other rare-earth hydrogen systems [1], which leads to shorter chain lengths and therefore to stronger interchain interaction [5]. Finally, the hydrogen solubility at low
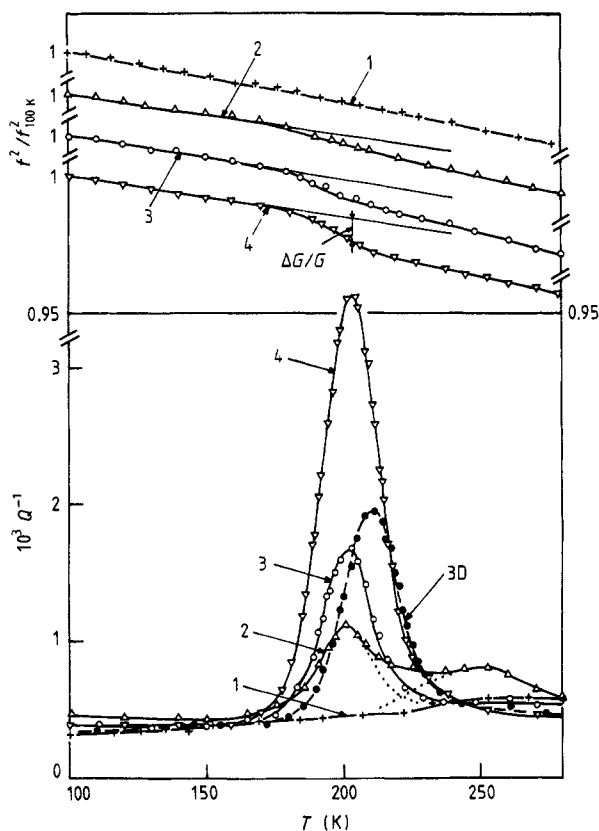
Figure 1. Internal friction spectra $Q^{-1}(T)$ of α-ScH(D)$_x$ at a frequency $f = 1$ Hz, for 1: $x = 0$; 2: $x = 0.1$ H; 3: $x = 0.2$ H; 3D: $x = 0.2$ D; 4: $x = 0.3$ H. Upper part: frequency squared normalised to 100 K (proportional to the dynamic modulus, G) for the same ScH$_x$ specimens.

temperature, x_{max}, being larger in α-ScH$_x$ than in any other R–H system [1], permits us to cover a larger concentration range and to study eventual x-dependent evolution.

4N-grade Sc metal with $\simeq 200$ at.ppm metallic impurities (mainly Lu, Yb, Zr, Gd, Fe, and Y, in order of abundance) and $\simeq 1700$ at.ppm gaseous impurities (H, O, F, and C) were purchased from the Ames Laboratories (Ames IA, USA) and cut into $60 \times 1 \times 0.25$ mm^3 strips. These were loaded with hydrogen (or deuterium) at 550–600 °C, the concentration being determined volumetrically; four specimens of the following concentrations were prepared: ScH$_{0.1}$, ScH$_{0.2}$, ScH$_{0.3}$, and ScD$_{0.2}$.

The internal friction and dynamic modulus were measured by means of an inverted torsional pendulum in the frequency range 0.3 to 2 Hz, between liquid nitrogen and room temperature.

Figure 1 shows the internal friction spectra for all specimens measured at a frequency of 1 Hz in the interval 100 to 280 K, as well as the frequency squared (proportional to the dynamic modulus, G) normalised at 100 K. Hydrogen induces a clear relaxation peak near $T_p \simeq 200$ K, which increases in amplitude with the concentration over the background of the unloaded Sc sample. The latter has a small shoulder centred at 250 K, which has grown into a peak in the case of α-ScH$_{0.1}$ but has disappeared again for the
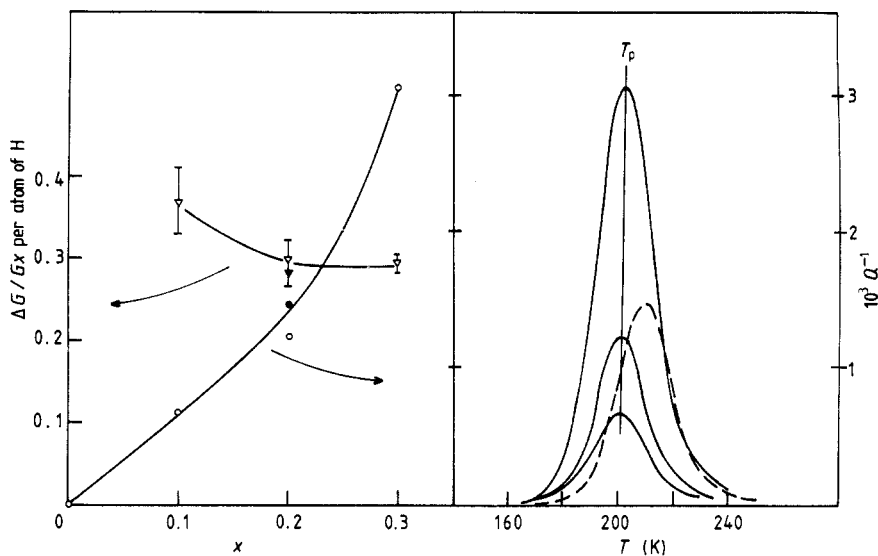
Figure 2. Right hand side: H peak of figure 1 with background subtracted, showing the isotope effect and the dependence on x (the ratio of number of atoms of H(D) to number of atoms of Sc) of T_p. Left hand side: peak amplitude ($\bigcirc$, $\bullet$) and specific modulus variation per atom of H(D) ($\triangledown$, $\blacktriangledown$). Full symbols: $ScD_{0.2}$.

more concentrated specimens. We believe that this is due to deformation introduced during mounting of the sample (its amplitude is, in fact, only poorly reproducible from one run to another) to which the more brittle H-rich specimens are less sensitive. We have therefore extracted the 200 K peak for α-$ScH_{0.1}$ graphically as indicated in figure 1 and are only treating this 'pure' H peak. The internal friction spectrum of the α-$ScD_{0.2}$ sample exhibits an analogous relaxation peak but shifted by roughly 10 K to higher temperatures. The dynamic modulus plotted in the upper part of figure 1 shows a smoothly decreasing behaviour with increasing temperature for pure Sc, within which hydrogen introduces a break, $\Delta G/G$, in the region of T_p.

We have analysed the amplitude of the H-induced effects in more detail in figure 2, where we have included, to the right, the H peak after subtraction of the background. In addition to the above-mentioned isotope effect, we notice a slight but systematic increase of T_p with increasing x. (We recall that the opposite was found in the case of α-$LuH(D)_x$ [9].) Plotting the H-peak amplitude as a function of x (left-hand side of figure 2) we observe a stronger than linear dependence on x, in particular for the sample richest in H with respect to the two less concentrated ones. In the same graph we have also given the calculated specific variation of the dynamic modulus per H atom, $\Delta G/Gx$, showing a slight decrease with increasing x and saturating near

$$\Delta G/Gx \simeq -0.30/\text{atom H(D)}.$$

Comparing with α-$LuH(D)_x$ [9], we note approximately the same peak amplitude per atom of H up to 0.2 H(D) and a stronger increase for higher x, a dynamic modulus variation twice as strong, peak temperatures 15 to 20 degrees lower and a stronger isotope effect on T_p (corresponding well with the observations on the temperature of

Table 1. Relaxation characteristics of α-ScH(D)$_x$.

x	T_p(K) at $f = 1$ Hz	$-\Delta G/Gx$ per atom of H(D)	E_a (eV)	τ_0† (s)
0.1 H	201	0.37(4)	0.61$_5$(3)	7.5×10^{-16}
0.2 H	202	0.30(2)	0.57(3)	7.1×10^{-15}
0.3 H	203.5	0.29$_5$(1)	0.54(3)	3.6×10^{-14}
0.2 D	210.5	0.28(1)	0.58(3)	1.0×10^{-14}

† Within a factor of two.

the resistivity anomaly [2]). We have collected the relevant data on α-ScH(D)$_x$ together in table 1.

We have determined the activation energy, E_a, of the H peak by measuring the variation of the peak temperature with the applied frequency and plotting it in an Arrhenius graph (figure 3) according to

$$1/f = \tau = \tau_0 \exp(E_a/kT_p).$$

The plots are reasonably linear, and the extracted activation energies and relaxation times are given in table 1. The values of E_a for ScH$_{0.2}$ and ScD$_{0.2}$ are the same within the error bars, and the ratio of the jump frequencies $f_0(H)/f_0(D) = \tau_0(D)/\tau_0(H) = 1.4$ is very close to the expected isotope effect, $(m_D/m_H)^{1/2} = \sqrt{2}$. Moreover, the value of $E_a(\text{ScH}_{0.2}) = 0.57(3)$ eV is practically the same as $E_a(\text{LuH}_{0.2}) = 0.56$ eV, while $E_a(\text{LuD}_{0.2}) = 0.64$ eV is significantly higher [9]. Simultaneously, we have a relaxation time τ_0 that is 15 times smaller for ScH$_{0.2}$ than for LuH$_{0.2}$ and one that is 3 times larger for the corresponding D system. Furthermore, while there are no data available for other α-LuH$_x$ concentrations, we can compare here three α-ScH$_x$ samples with each other, and we note a slight decrease of E_a with increasing x and a corresponding increase of the relaxation times. Finally, with the activation energies obtained, one can compare the experimental peak widths at half maximum with that of the corresponding Debye peak of a standard anelastic solid, $\Delta T_{\text{Debye}} = 2.635\ kT_p^2/E_a$, giving in our case $\Delta T_{\text{exp}} = (1.3\text{–}1.4)\Delta T_{\text{Debye}}$.

It is clear that the manifestations of the internal friction phenomena observed in α-ScH(D)$_x$ have the same origin as those described in the earlier work on α-LuH(D)$_x$ [9]. At that time, we had attributed the results to a Snoek effect due to the relaxation of an H–H pair situated on neighbouring tetrahedral sites along the c axis of the HCP lattice, in order to allow for the forbidden symmetry of a single H atom in a T site. In the meantime, diffuse neutron scattering experiments on single crystals of α-LuD$_x$ [10] and α-ScD$_x$ [5] have confirmed the pair configuration as the basic unit of the ordered structure, with the difference that the correlated H atoms were occupying second-neighbour T sites on the c axis and forming quasilinear chains with other H–H pairs. Moreover, new Bragg-type localised reflections indicated an interaction between chains leading to a long-range-ordered hydrogen superstructure.

Therefore, it seems reasonable now to consider the anelastic relaxation in these systems in terms of a Zener effect in the sense of stress-induced changes of directional short-range or long-range order, involving bulk lattice rearrangements of hydrogen interstitials and vacant interstitial sites, such as are, for example, discussed by Mazzolai [11]. The phenomenon is further complicated by the fact that there exist two types of
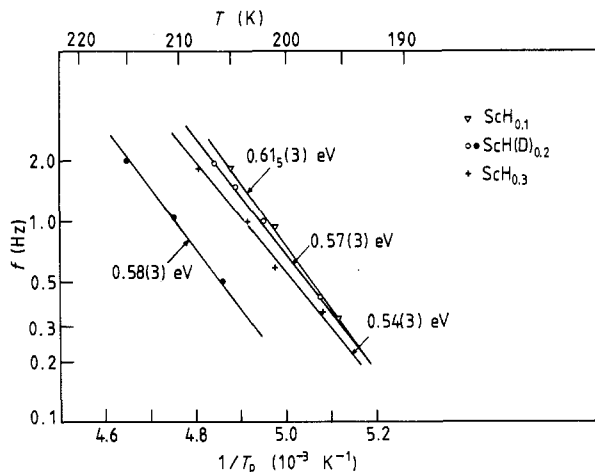
Figure 3. The Arrhenius graph of the peak temperature, T_p, as a function of the applied frequency, f, indicating the activation energies, E_a, obtained.

vacant interstitial site, namely tetrahedral (T) and octahedral (O) and, therefore, two jump types have to be considered: T–T and T–O–T, the latter being triply degenerate in an HCP lattice. Now, recent hydrogen diffusion studies of α-LuH(D)$_{0.05}$ through high-temperature Gorsky effect measurements [12] have yielded exactly the same values for the activation energies and relaxation times as in our earlier internal friction studies of α-LuH(D)$_{0.2}$ [9] establishing the same mechanism as responsible for the IF manifestations. In addition, the analysis of an NMR investigation of hydrogen diffusive hopping in α-ScH$_x$ [7] gave activation energies between 0.49 and 0.55 eV and jump frequencies between 0.3×10^{14} and 1.2×10^{14} Hz, both decreasing with increasing x just like in the present study. As both latter experimental reports [7, 12] show the T–O–T jump mechanism as predominant for the effects, we are inclined to assume that it is also responsible for our anelastic relaxation. The T–T jumps are then reserved for the fast localised motion of hydrogen at low temperatures, such as is detected below 120 K by NMR measurements [8].

   An interesting observation is the inverse dependence on x of the peak temperature T_p in the cases of α-ScH$_x$ and α-LuH$_x$. We had ascribed the decrease of T_p with increasing x in α-LuH$_x$ [9] as due to weakening binding energy of the H–H pairs following the lattice expansion after H absorption. Now, it is possible that the above-mentioned unusual elastic anisotropy of Sc—relative expansion larger in the basal plane than along the c axis, leading to a reduced c/a-ratio for α-ScH$_x$—acts somewhat like a relative compression in the c direction (which is that of the H–H pairs), resulting in a somewhat stronger binding with increasing x.

   As to the concentration dependence of E_a and τ_0 in α-ScH$_x$, corroborated by NMR [7], it could be related to the observed higher chain density (with increasing x) in the ordered H configuration [5], leading to an increased contribution of interchain interference rather than to longer chain lengths (intrachain interference). This could mean a lowering of the potential barrier for diffusion and also a reduction of the attempt jump frequency, f_0, with increasing x. The latter is also somewhat to be expected from the relation between f_0 and the optic mode frequency:

$$f_0 = z(1 - x)f_{opt}$$

where $z = 6$ is the number of adjacent sites available for the jump of a hydrogen atom and x is the probability that such a site is occupied. The local mode in the basal plane, which is the relevant one for a T–O–T jump, has been determined by inelastic neutron scattering [6] for α-ScD$_{0.33}$ to be $f^{a}_{opt} = 107$ meV $= 0.26 \times 10^{14}$ Hz, giving $f_0 = 1 \times 10^{14}$ Hz, which corresponds in the harmonic approximation to $f_0 = 1.4 \times 10^{14}$ Hz in the case of α-ScH$_{0.33}$, in qualitative agreement with our results (table 1).

Finally, the finding that the variation of the dynamic modulus per hydrogen atom in α-ScH(D)$_x$ is twice as strong as that in α-LuH(D)$_x$ is certainly related to the anisotropy ratios being larger in the former—in particular, that between the elastic constants for wave propagation under an angle to the c axis, C_{12}/C_{13}, which is some 35% higher.

Concluding, we wish to stress that α-ScH(D)$_x$ is a further system exhibiting an anelastic relaxation peak of hydrogen, which seems to be a general characteristic of rare-earth hydrogen alloys presenting a solid solution phase at low temperatures. The process can be ascribed to a Zener-type relaxation of hydrogen interstitials with vacant interstitial sites. The qualitative differences between our data on α-ScH(D)$_x$ and the earlier results obtained on α-LuH(D)$_x$ [9] are thought to originate from the difference between the elastic anisotropies of the two systems.

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