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Hydrogen relaxation in lutetium

P. Vajda, J. N. Daou
E.R.A. 720 du CNRS, Bât. 350, Université de Paris-Sud, F-91405 Orsay, France
and P. Moser
Section de Physique du Solide, DRF, Centre d'Études Nucléaires, F-38041 Grenoble, France

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Résumé. — Nous avons mesuré le frottement intérieur et le module dynamique entre 4,2 et 470 K dans le système α-LuH(D)x, pour x = 0 à 0,2. On observe à 215-225 K dans des échantillons bien recuits un pic (H) dont l'amplitude dépend linéairement de x et qui présente un effet isotopique pour l'énergie d'activation et le temps de relaxation. Il est attribué à une relaxation de type Snoek de paires H-H se réorientant dans le réseau Lu. L'effet isotopique est interprété dans un modèle utilisant l'effet tunnel à partir de différents niveaux excités pour LuHx et LuDx. La déformation introduit un pic (d-H) à 250-260 K seulement dans les échantillons contenant H(D), montrant aussi un effet isotopique ; il est attribué à une relaxation du type Snoek-Köster pour H(D) piégé sur des dislocations. Deux pics (d1,2) à 160 K et 215 K, observés uniquement dans le métal pur, et un pic (d) centré à 350 K dans tous les échantillons déformés sont attribués à la migration de décrochement géométrique et à la formation de décrochements doubles sur un réseau de dislocations vis, respectivement.

Abstract. — The internal friction and the dynamic modulus have been measured between 4.2 and 470 K in the system α-LuH(D)x, with x = 0 to 0.2. In well annealed specimens, an (H)-peak is observed at 215-225 K, which has a linearly x-dependent amplitude and exhibits an isotope effect on its activation energy and relaxation time. It is attributed to a Snoek-like relaxation of H-H pairs reorienting in the Lu-lattice. The isotope effect is interpreted in a model of tunnelling from different excited levels for LuHx and LuDx. Deformation introduces a (d-H)-peak at 250-260 K in H(D)-containing samples only, also exhibiting an isotope effect; it is attributed to a Snoek-Köster type relaxation of H(D) trapped on dislocations. Two (d1,2)-peaks at 160 and 215 K, which occur in the pure metal only, and a (d)-peak centred near 350 K in all deformed specimens are ascribed to geometrical kink migration and to double-kink generation on a screw dislocation network, respectively.

1. Introduction. — The trivalent h.c.p. rare-earth metals, R, form solid solutions with hydrogen or deuterium, α-R(H, D), at high temperatures. Below a certain limit, Tα, hydrogen has precipitated into the β-phase (dihydride phase), Tβ, decreasing with increasing atomic number of the lanthanide : from roughly 700 K for La to 400 K for Dy. The three heaviest trivalent rare earths — Er, Tm and Lu — possess as a characteristic property the ability to retain hydrogen in solution at room temperature and below in important amounts : upto 3, 11 and 20 at. % respectively [1]. The α → β transition is blocked and all hydrogen atoms which are dissolved in the α-phase at 400 K remain there down to 0 K, designating these metals as excellent candidates for the study of hydrogen behaviour at low temperatures.

In the temperature range 160-200 K the electrical resistivity of the α-phases Er(H, D)x, Tm(H, D)x and Lu(H, D)x exhibits an anomaly characterized by a sharp minimum of the derivative, dp/dT, as a function of T. This phenomenon has been investigated in detail in a series of publications [2-7], and a wealth of information has been accumulated using various techniques such as low-temperature electron irradiation and quench across the anomaly. An ion channelling study [8] served to determine the deuterium location as being in the tetrahedral sites of the h.c.p. cell in the whole temperature range between 25 and 425 K. The results have been interpreted in terms of a model implying the condensation of isolated H-atoms into pairs through short-range ordering when cooling the specimens below the anomaly temperature. In this model, attractive interaction between H-atoms occupying the centres of two adjacent tetrahedra joined by their faces should take place and lead to the formation of H-H pairs oriented along the c-axis of the unit cell [9]. Additional evidence for the exis-
tence of uniaxially oriented pairs at low temperature had been drawn from experiments where the influence of hydrogen upon the magnetic properties of Er [10] and Tm [2, 11, 12] was investigated.

It seemed, therefore, interesting in this context to undertake an internal friction study of such a system and to draw conclusions inter alia about the symmetry properties of the dissolved hydrogen and its relaxation parameters. Similar investigations of anelastic effects of hydrogen in metals have in their great majority concerned the body-centred cubic metals of the groups Va and Vla of the periodic system and α-Fe, because of a straightforward interpretation of the observed phenomena in the framework of the Snoek effect (for a recent compilation, see ref. [13] and references therein). As the symmetry of the interstitial sites in f.c.c. and h.c.p. lattices is unfavourable to the introduction of directional distortion by interstitial solute atoms, the occasional observation of hydrogen relaxation was usually accounted for in terms of atom associations. Thus, internal-friction peaks in f.c.c. Pd(H, D) had been attributed either to hydrogen pairing [14] or to a Zener-type rearrangement of H-interstitials and vacant interstitial sites [15], while a peak in H-charged austenitic stainless steel was ascribed to a hydrogen-substitutional solute atom pair [16]. The investigations of h.c.p. metals concerned primarily the systems α-Zr-H [17, 17a] and α-Ti-H [18]. There, the observed peaks were explained either by a stress induced redistribution of H-atoms on tetrahedral sites or by ordering between octahedral-tetrahedral sites.

The present study of internal friction of hydrogen in h.c.p. lutetium (1) is therefore not only of specific interest to the α-phases of the heavy rare earths, but also of general importance for the elucidation of H-relaxation phenomena in the whole family of h.c.p. metals. Lutetium was selected among the three lanthanides, Mg, Si and Fe. The residual hydrogen has been eliminated by an anneal at 1000 °C; the absorbed quantities were determined volumetrically. The final specimens had the approximate dimensions of 60 × 1.0 × 0.25 mm³ and included : Lu; LuH₀.₀₅, LuH₀.₁, LuH₀.₂; LuD₀.₀₅, LuD₀.₁, LuD₀.₂.

Internal friction and dynamic modulus were measured by means of a low-frequency inverted torsional pendulum [19](in the range 0.1 to 1 Hz) working in the temperature region between 4.2 and 470 K. Cold work was introduced through torsional deformation in situ at room temperature.

3. Results. — 3.1 Annealed Specimens : Hydrogen Related Observations. — In figure 1 we show the internal friction spectra and the reduced frequency square (proportional to the dynamic modulus, \( G \)) in the temperature range 78 to 470 K for well annealed specimens of LuHₓ (\( x = 0 \) to 0.2). No structure had been detected between 4.2 and 78 K during preliminary runs, therefore the great majority of the following experiments had been started from liquid-nitrogen temperatures only, the heating rate being of the order of 2-3 K/min. The dynamic modulus variation had been normalized to 78 K, \( f^2(T)/f^2(78K) \), and furthermore adjusted such that all curves coincided between 78 K and 160 K (well below the appearance of the peak in the \( Q^{-1} \) spectra). This has been done to clarify the picture and to avoid multiple crossing over of the curves, since the temperature variation of \( f^2 \) for the hydrogen loaded specimens becomes gradually slower with increasing H-contents. As the diminution of the modulus with increasing temperature is generally due to the crystal lattice vibrations and to the ensuing modification of the interatomic forces due to the ther-

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(1) Part of this work has been communicated at the 7th International Conference on Internal Friction and Ultrasonic Attenuation in Metals, Lausanne, July 1981.
mal expansion, the introduction of point defects in the form of interstitial H-atoms renders the metal lattice brittle counteracting slightly the vibrational mechanism. (For comparison, the thermal expansion coefficient, $\alpha_v = \frac{1}{c} \frac{dc}{dT}$, along the c-axis of the unit cell is about 50% bigger in the case of Lu metal than for LuHo$_2$ in this temperature range [20].)

The only significant structure showing up in figure 1 is a peak appearing in the hydrogen loaded specimens which is centred around 215 K. The peak is growing with the H-concentration in the sample, and the temperature of its maximum, $T_p$, seems to decrease slightly at the same time. The peak is well reproducible, i.e. it does not change its amplitude and/or position after an anneal at 470 K. We shall designate this structure as the (H)-peak. We have tested the cooling-rate dependence of the spectra in several quenching runs, since we have been conscious of the sensitivity of the resistivity anomaly near 170 K (4, 9) to such a treatment. No additional structures or changes upon the (H)-peak were observed.

The dynamic modulus, which behaves smoothly in the case of Lu metal (curve 1), exhibits a break in the hydrogenated samples right in the region of the (H)-peak — this break gradually increasing with the concentration, H/Lu. From the size of the break we can estimate the contribution of one atom of hydrogen to the modulus decrease:

$$\frac{\Delta G}{G_{H}} = -0.14 \pm 0.01,$$

where $c_H = H/Lu$ is the H-concentration in the sample.

Hence, the activation energy of the (H)-peak has been measured for the two richest specimens, LuH$_{0.2}$ and LuD$_{0.3}$ by varying the applied frequency by about a factor of 10. From the Arrhenius plot corresponding to figure 4

$$\frac{1}{T} = \tau = \tau_0 \exp(E_a/kT_p)$$

one finds in the case of the hydrogenated sample:

$$E^H_a = (0.56 \pm 0.05) \text{ eV},$$
$$\tau^H_0 = 1 \times 10^{-13\pm1} \text{ s},$$

and for the deuterated sample (where the precision is better):

$$E^D_a = (0.64 \pm 0.03) \text{ eV},$$
$$\tau^D_0 = 3.7 \times 10^{-15\pm0.5} \text{ s}.$$
Fig. 4. Arrhenius plot of the peak temperature as a function of frequency for LuHo.2 (○) and LuDo.2 (●) in the case of the (H)-peak.

Thus, we observe not only an isotope effect on the peak temperature, which could be related to a difference in jump frequencies only, but also different activation energies for the (H)-peak mechanism in LuHo.2 and LuDo.2. With the above obtained values for $E_a$, we can estimate the half width of the corresponding Debye peak from $\Delta T_{\text{Debye}} = 2.635 \, kT_p^2 / E_a$ as 19 K and 17.5 K for LuHo.2 and LuDo.2 respectively. The experimental half widths, $\Delta T_{\text{exp}}^H = 24.5$ K and $\Delta T_{\text{exp}}^D = 26$ K, are thus 30 to 50% higher than for a standard anelastic solid. At the same time, the above formula permits the evaluation of an apparent activation energy for samples with various hydrogen concentrations from the peak half width: from figure 3 one finds that $E_{a,\text{app}}$ increases with increasing $c_{H,D}$ indicating a growing interaction strength between the H-atoms.

3.2 INFLUENCE OF COLD WORKING. — In order to check the influence of cold work upon the (H)-peak and eventually upon the rest of the internal friction spectrum, we have applied torsional deformation to all the specimens. In figure 5, we exhibit as a typical example, the $Q^{-1}$ spectra and the normalized dynamic modulus, $f^2(T)/f_{78K}^2$, for the deuterated samples, LuD$_x$ with $x$ as parameter, after the torsion through a half turn, corresponding to a maximum strain $\varepsilon = 3.2$ %. As in figures 1 and 2, the internal friction curves of LuD$_x$ have been adjusted such as to possess the same background for $T \leq 160$ K, and that of the pure Lu sample was made to start together with the others at 78 K. This normalization was done to permit a minimum of comparison between specimens of various histories (initial deformation present, shape dependence of the strain, etc.). The comparison remains still quite relative, but the qualitative features are very explicit:

— For $x = 0$, i.e. the pure Lu sample, one notes two flat peaks centred near 160 K and 220 K and designated (d$_1$) and (d$_2$); a big structure, named (d)-peak shows up above room temperature, with a maximum near 350 K.

For $x \neq 0$, i.e. the deuterated samples, the (d$_1$), (d$_2$)-peaks have disappeared, and the (d)-peak has remained roughly the same as in the case of the metal; between 200 and 300 K, however, there takes place an evolution of a double peaked structure, whose low-temperature part (centred near 225 K) seems to be the (H)-peak of the annealed specimens (cf. Fig. 2), superposed by a peak of deformational origin (centred near 260 K) designated (d-H)-peak since it is not present in Lu metal.

Figure 6 demonstrates the strain dependence of the internal friction spectra for one selected specimen, LuHo.1. One can follow very distinctly the growth of the (d-H)-peak upon the spectrum of the undeformed
specimen (curve 1 in Fig. 6 corresponds to curve 3 of Fig. 1) dragging the (H)-peak behind, until the latter shows up as a mere shoulder of it. Note that there is also an isotope effect on the peak temperature of (d-H) : $T_{p_D} \approx T_{p_H} + 5$ K (cf. curve 4 of Fig. 6 and curve 3 of Fig. 5). Another observation is a slight shift of $T_p$ towards lower values with increasing strain. This is also true, even to a higher degree, for the (d)-peak : $\Delta T \approx -15$ K for a strain increase by 12 % (twisted by 1/8 turn to 2 turns) — cf. insert in figure 6. Moreover, there seems to be a saturation in the peak growth for higher deformations : this is particularly true for the (d)-peak and is also visible in the modulus evolution around 350 K (overlap for the curves 5 and 6).

The amplitudes of all stress-induced peaks are strongly reduced after an anneal at 470 K : 75-80 % of the (d1) and (d2)-peaks have recovered in Lu as well as 50 % of the (d)-peak in LuDx and 60-65 % in Lu and LuHx ; 60 % of the (d-H)-peak in LuDx and up to 80 % in LuHx. A detailed investigation of the influence of aging upon the heights of the (d-H) and the (d)-peak for a selected specimen has yielded the data of figure 7. The striking result is a begin of the peak decrease at the very first annealing points, indicating their inherent instability after room-temperature deformation.

Fig. 7. — Evolution of peak heights with annealing temperature for the LuHo,1 specimen twisted by 1/2 turn at room temperature. — (d-H)-peak ; - - - (d)-peak.

In figure 8 we have plotted the amplitudes of the deformation peaks as observed in the pure metal specimen after background subtraction, as a function of the applied strain on a semilogarithmic scale. After an initially uniform increase, the peak heights reach saturation values for strains above roughly 3 %.

The strain dependence of the deformation-induced peaks (d-H) and (d) in the hydrogen loaded specimens is presented in figure 9 : i.e. in figure 9a for the case of LuHx and in figure 9b for LuDx (Curves not drawn upto the highest applied strain values correspond to specimens which broke before reaching the full torsional deformation of 2 turns.) The evolution of the peak amplitudes is qualitatively similar for the two groups of specimens : the uniform-growth region of the (d)-peaks extends farther than for the metal (cf. Fig. 8) turning towards saturation at $\varepsilon \sim 10\%$. The (d-H)-peaks saturate above $\varepsilon \sim 5\%$. In the cases where comparison is possible it seems that the LuDx specimens have somewhat larger peak amplitudes than the LuHx samples. This is not unreasonable in view of the slightly more expanded lattice of the latter : a deformation will have more effect in a denser structure ; the smaller effect in the metal sample, on the other hand, is due to its « softer » lattice, with no interstitial hydrogen to strain it.

4. Discussion. — 4.1 RELAXATION MECHANISM FOR THE (H)-PEAK. — The fact that the (H)-peak exists only in the hydrogen loaded specimens, its nearly linear concentration dependence and, finally, the isotope effect on its temperature are all clear indications for hydrogen relaxation in the lutetium lattice. An interaction with foreign atoms as its origin can be excluded in view of the high H-concentrations invol-

![Fig. 8. — Strain dependence of the (d1)-peaks and the (d)-peak for Lu metal. Note the semi-logarithmic scale.](image-url)
dium — made at the Ames Laboratories [42], and which was an order of magnitude cleaner, have revealed the same type of resistivity anomaly as in our heavy lanthanides, which — as shall be shown below — is believed to be closely related to the here discussed H-relaxation. We propose, therefore, a Snoek-type relaxation mechanism for the process in question.

As already indicated in the introduction chapter, the problem with Snoek-type relaxation effects in a hexagonal close packed (and also in a face-centred cubic) lattice is that the symmetry of a normal interstitial site (tetrahedral and octahedral) is not compatible with the appearance of internal friction peaks. Now, it had been determined earlier [8] that the preferential location of a deuterium atom in the Lu lattice was the interstitial tetrahedral site (T-site) independent of temperature in the whole range of 25 to 425 K, thus covering the here investigated domain. The problem had already been encountered in the past in investigations of the systems zirconium-hydrogen [17, 17a] and titanium-hydrogen [18]. In the former, Povolo and Bisogni suggested a stress-induced redistribution of hydrogen between O and T-sites — no evidence for an O-site occupation had been noticed in the ion-channelling study of the system Lu-D [8]. On the other hand, it had been theoretically excluded [21] to have stress-induced ordering of solute atoms in one type of site in h.c.p. structures, as had been proposed at one moment [18]. Similarly, a redistribution of H atom — H vacant site (Zener-type relaxation) should not give rise to anelastic effects unless there exists long-range ordering of the H-atoms: this is not the case in the solid solutions treated in this experiment. A further possibility had been discussed by Beshers [22]: in h.c.p. metals with a \( (c/a) \)-ratio deviating from the ideal value 1.63, the symmetry of the interstitial sites would be lowered and could give rise to anelastic phenomena. This is, in principle, the case with our specimens \( (c/a) = 1.59 \) [20], but we do not believe the effect to be strong enough to be responsible for the Snoek-peak manifestation as observed here.

Finally, we should like to propose for the explanation of the internal friction of hydrogen in lutetium a model where the H-atoms condense into H-H pairs below the anomaly region \( (\lesssim 200 \text{ K}) \), which has already been used to interpret the quench and irradiation experiments [3-7, 9] and the results of the magnetic measurements [10-12]. This model has the advantage to obey the selection rules for anelasticity [23], which permit the existence of an anelastic effect for orthorhombic defects in an h.c.p. crystal. The fact that the concentration dependence is linear rather than quadratic as expected [24] in a system under equilibrium, is due to the thermodynamically metastable (frozen-in) situation of the H-H pairs at low temperature (for a discussion cf. ref. [9]): all H-atoms are supposed through short-range ordering to condense into pairs if cooled down slowly enough across the anomaly, and no singles exist in parallel. It is only in the region of the anomaly and just above \( (\gtrsim 200 \text{ K}) \) that the pairs become mobile enough (before being broken apart through thermal agitation) to relax mechanically and to give rise to anelastic effects. This hydrogen relaxation is probably reorientational rather than diffusional: the (H)-peak is quite narrow and the relaxation time \( \tau_0 \) compatible with this mechanism. This interpretation explains also why a quenching across the anomaly — quite efficient in resistivity measurements [4, 9] — does not give observable changes in the internal friction spectra. Supposing in our model that quenching introduces frozen-in isolated H-atoms at low temperature, these « defects » have sufficient possibility to recover in the annealing stage just at the onset of the anomaly, near 160 K, recombining to the H-H pairs responsible for the (H)-peak (Anyway, the symmetry of the H-singles would not permit their detection.) Thus, even if the initial concentration of pairs might depend on the cooling (or heating) rate, at the time of the peak appearance we shall again find the same number. Indeed, the intensity of the (H)-peak is independent of treatment and also of the measuring frequency (Fig. 4), since its \( T_p \) is always high enough above the critical range. (Tran [7] has observed hysteresis effects on the anomaly depending on the heating and cooling rate, but its manifestations were completed at 200 K).

An interesting problem is posed by the isotope effect. As was shown in chapter 3, there is a difference of

\[ \Delta E_0 = E_0^D - E_0^H = 0.08 \pm 0.06 \text{ eV} \]

for the activation energies, together with a ratio of the relaxation times

\[ \tau_0^H/\tau_0^D = 28 \]

between the hydrogenated and the deuterated specimens. Similar effects have been reported in the literature for the systems Pd-H, D [14], Fe-H, D [25], Nb-H, D [26]. They have also been observed and treated in detail in investigations of magnetoelastic relaxation by means of the magnetic aftereffect of

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**Fig. 9.** — Strain dependence of the amplitudes for the (d-H)-peak (—) and for the (d)-peak (- - -). (a) : LuH\(_x\); (b) : LuD\(_x\).
hydrogen in ferromagnets (for a review, see e.g. ref. [27]). A particularly interesting case for its analogy with the here proposed H-H pairs is the magnetic aftereffect of diatomic C-H(D) complexes in Ni [28]. There, the reorientational relaxation exhibited an isotope effect with roughly the same difference in parameters as in our case. It was interpreted through a mass-dependent tunnelling probability from thermally excited discrete energy levels across a potential barrier (saddle-point configuration). In our case, the pairs could represent self-trapped states giving rise to a relaxation peak, whose activation energy corresponds to the deformation energy necessary to produce a symmetrical configuration for two neighbouring potential wells. The relaxation time of an orthorhombic defect in a hexagonal crystal, $\tau_0 = 1/3 \, \nu_0$, can be calculated for an H-H pair in the approximation of an harmonic oscillator from

$$\nu_0 \approx \frac{4 \, V_0}{(m_{H,D})^{1/2}},$$

where the amplitude of the oscillation potential, $V_0$, is of the order of the experimental activation energies, $E_{H,D}^x \approx 0.6 \, \text{eV}$, and $d$ is the internuclear distance between the atoms in a pair, $d = 1.3 \, \text{Å}$ for two nearest-neighbour T-sites in Lu, giving $V_0^{H,D}$ of the order of $2 \times 10^{-15} \, \text{s}$ and $\tau_0^{H,D} \approx 2^{-1/2}$, which is far off the experimental findings of chapter 3. On the other hand, both these discrepancies and the observed isotope effect for $E_x$ can be accounted for in a model of tunnelling protons or deuterons from differently excited energy levels, $E_{H,D}^x = h\nu_{H,D}^{x}(n + 1/2)$, with a jump frequency

$$\nu_{H,D}^{x} = \sum_{n=0}^{\infty} \nu_{H,D}^{x}(E_{n}^{H,D}) \exp\left(-\frac{E_{n}^{H,D}}{kT}\right),$$

where $P_n$ is the tunnelling probability from the $n$-th level, by fitting a potential $V(r)$ such as to reproduce the experimental $E_x^H$ and $E_x^D$.

The concentration dependence of $T_p$ for the (H)-peak (Fig. 3) is certainly related to the same phenomenon which gives rise to the temperature shift of the resistivity anomaly with varying $c_{H,D}$ [3-7]: a binding energy of the H-H pairs which decreases with increasing $c_H$ because of the expanding lattice. In terms of the tunnelling process discussed above, this would correspond to weakening oscillator forces resulting in a change in the discrete energy level positions. An indication for such a possibility had been observed [29] in a study of the Manninen-Jena effect in the system Lu(H, D)$_x$: there, the deviation from Matthiessen’s rule for the hydrogen resistivity was also $c_H$-dependent and was caused by a changing excitability to higher excited states.

As to the manifestation of the hydrogen relaxation upon the dynamic modulus, we have found a specific modulus change per H(D)-atom of

$$\frac{\Delta G}{G_{H}} = -0.14$$

and

$$\frac{\Delta G}{G_{D}} = -0.16.$$ 

The small isotope effect has probably the same origin as in the case of the slightly higher amplitudes for the deformational peaks in LuD$_x$ when compared to LuH$_x$: the slightly denser structure of the former material.

An estimate made for H in Pd using the elastic modulus measurements by Mazzolai et al. [15] gives values of several tenths per atom H, i.e. of the same order of magnitude. On the other hand, determinations of $\Delta G/G_{F}$ — the modulus change per unit concentration of Frenkel pairs — in zirconium [30], yielded a value of $-25$, i.e. two orders of magnitude higher than our value for hydrogen. This is a clear sign for a much bigger anelastic perturbation by a Frenkel pair, which is not surprising, also when one compares the corresponding specific resistivities: the added resistivity of an H-atom in Lu, $\rho_H^\text{L} \approx 3 \times 10^{-4} \, \text{ohm cm}/\text{H} [1]$, is 50 times smaller than the Frenkel pair resistivity $\rho_F^\text{L} \approx 150 \times 10^{-4} \, \text{ohm cm}/\text{F} [31]$. One arrives to similar conclusions concerning the interrelationship between $\Delta G/G_{F,Lu}$ and $\rho_{H,Lu}$ in the system tantalum-hydrogen when perusing the data by Cannelli-Cantelli [43] and Watanebe-Fukai [44].

4.2 THE INTERACTION OF HYDROGEN WITH DEFORMATIONAL PEAKS: (d-H)-PEAK. — The dislocations produced by the cold work exert an attraction upon hydrogen which is caused by elastic interaction resulting in the possible manifestation of the Snoek-Köster effect. Such effects have been mainly observed with N and C dissolved in b.c.c. metals [cf. ref. [23]], but hydrogen has also been more recently made responsible for its appearance. Most results have been obtained with iron [33-36], but also with Nb [37], Ni [38] and other metals. According to Schoeck’s model [32], the anelastic strain responsible for the showing up of the effect is due to the diffusion-controlled bowing out of pinned dislocation segments, the binding energy between the interstitial impurity and the dislocation giving rise to a higher activation energy (and higher $T_p$) than that of the Snoek peak.

The saturation effect expected for the amplitude of the Snoek-Köster peak with growing H-concentration due to the filling of all available dislocation sites is not always clearly visible in our experiment (a positive example is given in the insert of Fig. 5), probably because the hydrogen concentrations are already very high compared to the dilute alloys for which the theory was initially developed. For the same reason, there is also no clear evidence for a $T_p$-shift to higher values with growing $c_{H,D}$. On the other hand, there seems...
to be a slight tendency towards decreasing $T_p$ with increasing strain (insert of Fig. 6), which can be understood as a structure sensitivity of either or both the frequency factor $\tau_0^{-1}$ and the activation energy $E_a^{(d-H)}$ of the bound hydrogen atoms, through [32]

$$\tau = \frac{2kTc_d}{l^2bG}\exp\left(-\frac{E_a^{(d-H)}}{kT}\right) = \frac{\tau_0\exp(E_a^{(d-H)}/kT)}{c_d},$$

where $a$ is of the order of unity, $b$ the magnitude of the Burgers vector, $G$ the shear modulus, $C_d$ the concentration of the bound H-atoms at the dislocation and $D_o$ their diffusion coefficient; $l_0$ is the average dislocation segment length between locking points such as dislocation intersections and precipitate particles.

The annealing behaviour of the (d-H)-peak (strong reduction after aging at 470 K) goes conform with observations made in a channelling study on low-temperature D-implanted Lu-specimens [8], where the hydrogen atoms were sufficiently mobile at room temperature to quit their trapping sites in the investigated surface region for the bulk. Hence, significant amounts of bound H-atoms will escape from the dislocations leading to the disappearance of the peak, as manifested in figure 7. An alternative explanation would be a reduction of the density of the screw dislocations which, according to a model by Seeger [45], are involved in the Snoek-Köster relaxation. This mechanism is also applied below for the description of the (d)-peak annealing.

4.3 Pure cold work peaks : (d$_{1,2}$) and (d).

4.3.1 (d$_1$) and (d$_2$)-peaks. — These structures occur only in the pure Lu specimen and are relatively unstable : 75-80% recovery after aging at 470 K. Their width is indicative of a multiplicity of relaxation times; this and their temperature domain design the (d$_{1,2}$)-peaks as analogues to the $\alpha$, $\alpha'$ or $\delta$-peaks of the b.c.c. metals (for a review see e.g. ref. [39]). These intrinsic low-temperature peaks of dislocational origin are usually attributed to geometrical kink migration or to double-kink formation in dislocations with edge component; they are frequently inhibited by interaction with impurities or masked by Snoek-Köster relaxation. In our case, it seems that hydrogen doping pins the dislocations down and blocks the relaxation mechanism.

An alternative explanation for the (d$_{1,2}$)-peaks could be a Snoek-Köster type mechanism with residual oxygen and/or nitrogen (though they appear somewhat too large for it), again inhibited in the hydrogenated specimens by the interaction H-O and H-N. An argument against this interpretation is the lack of a Snoek peak corresponding to O or N in the H-free specimens, but here again the symmetry of the defect could be responsible for its non-observation.

4.3.2 (d)-peak. — The (d)-peak is present in all deformed specimens and its occurrence, form and evolution make it a candidate for a Bordoni peak or $\gamma$-peak analogue as observed in f.c.c. and b.c.c. metals [39]. As suggested by Seeger [40], double-kink generation on screw dislocations could account for most of the observed features. The instability of the peak (in our case 60-65% recovery for LuH$_x$ and 50% recovery for LuD$_x$ after aging at 470 K) is well described in the model by Astie [41] through the thermal instability of the screw-dislocation network in the internal stress field, where the screw part of the dislocation decreases causing a disappearance of the $\gamma$-peak. This rearrangement of the screw-dislocation network is in our case supported by the modulus defect (cf. Figs. 5 and 6) accompanying the (d)-peak manifestation, which is a clear indication for an anelastic effect. It is interesting to note that the corresponding lattice « softening » is much stronger in the H-containing specimens than in the pure metal (Fig. 5) showing that the H-atoms represent important anchoring centres for the screw dislocations and that their release contributes efficiently to the relaxation process.

5. Summary and conclusions. — Measurements of the internal friction and the dynamic modulus in the system $\alpha$-Lu(H, D)$_x$ with $x = 0$ to 0.2, have revealed several structures designated and interpreted as follows :

— (H)-peak, in the region 215-225 K. The peak amplitude is in a roughly linear dependence on $x$; its temperature $T_p$ decreases slightly with increasing $x$ and exhibits an isotope effect ($T_p^{\text{H}} \approx T_p^{\text{D}} + 6$ K). The relaxation mechanism of the (H)-peak is attributed to a Snoek effect of hydrogen in the h.c.p. Lu-lattice, where the H(D)-atoms occupying tetrahedral interstitial sites are condensed in pairs below $T \approx 200$ K. The process giving rise to the peak is a reorientational relaxation of these pairs; the isotope effect is interpreted in the framework of a tunnelling mechanism from thermally excited states resulting in a difference in activation energies, $E_a^{\text{H}} - E_a^{\text{H}} = 0.08$ eV, and in relaxation times, $\tau_0^{\text{H}}/\tau_0^{\text{H}} = 28$.

— (H)-peak, in the region 250-260 K. This peak occurs after deformation in the hydrogenated specimens only; its $T_p$ exhibits a similar isotope effect as in the case of the (H)-peak and diminishes somewhat with increasing strain $x$. The peak amplitude goes towards saturation at higher $x$. The (H)-peak is interpreted as due to a Snoek-Köster mechanism, where the anelastic strain stems from the bowing out of dislocation segments pinned by the hydrogen atoms and dislocation intersections.

— (d$_1$) and (d$_2$)-peaks, centred at 160 K and 215 K and occurring only in the deformed metal. They are attributed to geometrical kink migration or to double-kink formation in dislocations with edge component; they are inhibited in the hydrogen doped specimens through pinning down of the dislocations.

— (d)-peak, centred near 350 K, occurring in all deformed specimens. By analogy to the Bordoni
and γ-peaks in f.c.c. and b.c.c. metals, the (d)-peak is attributed to double-kink generation on screw dislocations and the rearrangement of its network.

As a general conclusion, we suggest that observations of hydrogen relaxation in h.c.p. (and probably f.c.c.) structures are related to diatomic associations either in the form of H-H pairs or, if available, with other interstitial or substitutional impurities.

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References