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A study of hydrogen diffusion in hexagonal YH_x single crystals ($x \leq 0.10$) by mechanical spectroscopy

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Abstract

We studied the diffusion of H in hcp YH_x single crystals ($x \leq 0.1$), by mechanical spectroscopy (vibrating-reed technique, 280 to 1750 Hz). In agreement with previous data from polycrystalline YH_x, we find an anelastic relaxation peak at ~280 K. Our single crystals show a large anisotropy in the relaxation strength which demonstrates that this peak results from a Zener relaxation of H pairs. Two types of H jumps determine the relaxation kinetics. Comparison with previous quasielastic neutron scattering data identifies the jumps that cause the relaxation, showing further that their jump rates follow, over ten orders of magnitude, an Arrhenius law with an activation energy of (0.60 ± 0.03) eV.

Keywords: Metal–hydrogen systems; Hydrogen diffusion in metals; Mechanical spectroscopy; Internal friction; Zener relaxation

1. Introduction

The α-phase (hcp) systems YH_x, ScH_x and LuH_x are the subjects of a large number of investigations because of the high solid–solution range of the H even at low temperatures (up to $x = 0.2$ for YH_x), the formation of H pairs and the existence of H jumps with widely different jump rates [1].

The H occupies in α-phase YH_x, ScH_x and LuH_x predominantly tetrahedral (T) interstitial sites, with little or no octahedral (O) occupancy at room temperature and below [1]. The H pairs (binding enthalpy ~0.06 eV) occupy two next-nearest-neighbor T sites along the c-axis with a bridging metal atom in between [1]. Such a pair configuration is shown in Fig. 1. The figure shows also the existence of two types of H jumps between the T sites, type-1 jumps between nearest-neighbor T sites (jump rate ν) and type-2 jumps between non-nearest-neighbor T sites (jump rates Γ_i).

Above 400 K, H diffusion in hcp YH_x has been investigated by quasielastic neutron scattering (QNS) [2,3] and nuclear magnetic resonance (NMR) [4,5]. The QNS experiments yielded $\nu \geq 100 \cdot \Gamma_i$, which agrees with a similar conclusion from Gorsky effect [6] and QNS [7] data for hcp LuH_x and ScH_x. Below 320 K, H diffusion in hcp YH_x was studied by mechanical spectroscopy [8–10]. The studies were performed on polycrystals, yielding an anelastic relaxation peak, e.g., at ~280 K for a frequency of 500

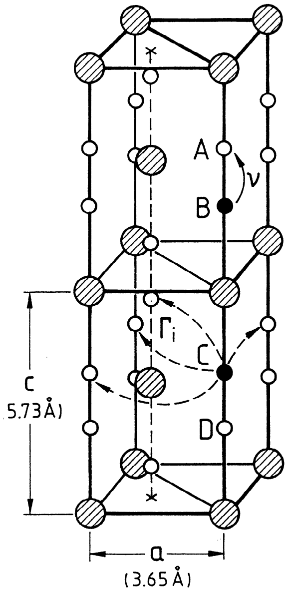

Fig. 1. Two unit cells of hcp rare-earth metals. The large hatched circles are metal atoms. The small (open and full) circles indicate tetrahedral (T) interstitial sites. The small full circles show a H pair, and *A*, *B*, *C* and *D* refer to T sites discussed in the text. The lattice constants hold for Y.

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Hz. For symmetry reasons, the peak cannot result from a Snoek relaxation of the H on T (or O) sites [11], so that it was explained either by a stress-induced creation or annihilation of H pairs (Zener relaxation [12]) or by a stress-induced change of the H distribution between T and O sites [1,8–10,13].

This paper reports on a mechanical spectroscopy study on hcp YH_x single crystals, demonstrating that the above relaxation peak results from a Zener relaxation of the H pairs. A further topic of the study is the kinetics of this relaxation process.

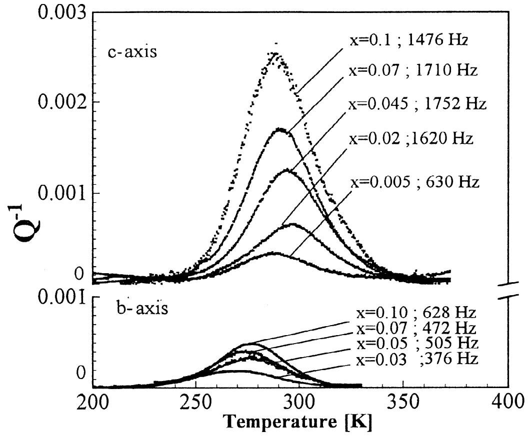

Fig. 2. Elastic energy dissipation Q^{-1} measured from the *c*-axis and the *b*′-axis crystals in a plot versus temperature. A linear background is substracted for each spectrum. The vibrational frequencies at the peak maxima and the H concentrations are indicated.

2. Experimental details

We investigated two Y single crystals (18×5×0.2 mm^3) doped with H up to x=H/Y=0.1. The long sides (18 mm) of the crystals were oriented in *c*-axis or *b*′-axis direction, respectively (*c*-axis and *b*′-axis crystal, where the *b*′-axis is normal to the *a*- and *c*-axes). The elastic-energy dissipation was measured with a vibrating-reed apparatus (electrostatic drive, detection via frequency-modulation [12]) in which the crystals were fixed in a clamp at variable positions along their long side, thus allowing a change of the vibrational frequencies (flexural sample vibrations, 280 to 1750 Hz). Depending on the investigated sample, the relaxation of Young's modulus either in the *c*-axis direction (*c*-axis crystal) or in the *b*′-axis direction (*b*′-axis crystal) was measured.

H doping was performed at ~1100°C in an UHV system into which H_2 gas was introduced. The H concentrations were determined from the amount of the absorbed gas and by vacuum extraction after the measurements were completed.

3. Experimental results and discussion

Fig. 2 shows the energy dissipation, Q^{-1}, measured on both crystals for various H concentrations ($0.005 \leq x \leq 0.1$). The data do not include a linear background damping in order to make it easier to see the dependence of the relaxation strength on both H concentration and crystal orientation. In agreement with previous results [9,10], the relaxation strength is essentially proportional to H concentration (this contradicts only seemingly a Zener relaxation of H pairs [1,13]). The important aspect of the present study is the strong anisotropy of the relaxation strength, expressed by the fact that this quantity is about five times larger for the *c*-axis than for the *b*′-axis crystal, for the same H concentration. This anisotropy is strongly indicative of Zener relaxation of the H pairs, since a stress in *c*-axis direction, which changes maximally the distance between the two atoms of a pair, will also maximally change its binding enthalpy and, consequently, cause a maximum relaxation. Therefore, we conclude that the observed relaxation process is in fact a Zener relaxation of the H pairs.

For the discussion of the kinetics of the relaxation process, we assume that the relevant relaxation rate τ_{rel}^{-1} at the temperature of a peak maximum is the angular vibrational frequency (τ_{rel} is the relaxation time). Fig. 3 presents an Arrhenius plot of our τ_{rel}^{-1}, together with corresponding data from previous mechanical spectroscopy [8–10], QNS [2,3] and NMR [4,5] experiments on hcp YH_x. The solid line in Fig. 3 shows that the present and the previous mechanical spectroscopy results are well

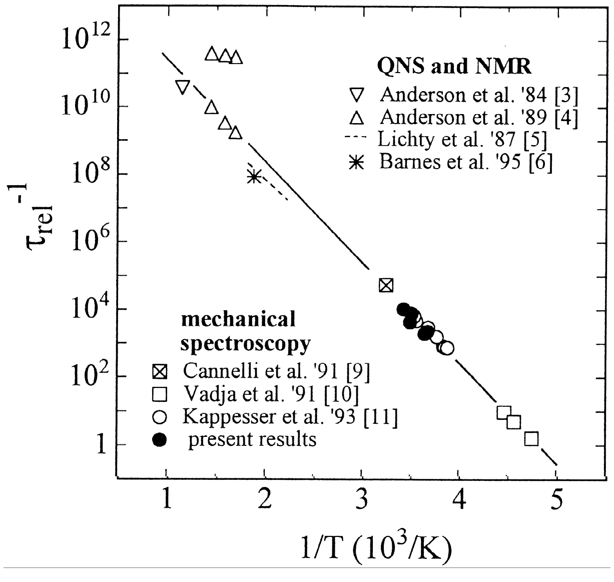

Fig. 3. The relaxation rates τ_{rel}^{-1} of the present experiments in an Arrhenius plot versus reciprocal temperature. The figure shows also relaxation rates from previous mechanical spectroscopy studies [9–11] on hcp YH_x, plus relaxation rates calculated from QNS [3,4] and NMR [5,6] measurements on hcp YH_x.

described by an Arrhenius relation with an activation energy of (0.60±0.03) eV.

Before discussing the QNS and NMR data in Fig. 3, we consider first the relaxation rates we expect for a Zener relaxation of the H pairs. Since all the pairs have the same orientation, the relaxation rate is completely determined by the time dependence of the diffusive decay of an initial pair like that in Fig. 1 [12,14]. This decay depends crystallographically differently on jumps of type-1 and type-2 in that type-1 jumps occur only locally between two nearest-neighbor T sites, so that the H cannot leave these sites and long-range diffusion cannot take place. Therefore, the sole presence of type-1 jumps annihilates the pair only at given times (i.e. partially) since subsequent type-1 jumps will create the pair again. On the other hand, type-2 jumps result in long-range H diffusion so that these jumps alone cause a complete pair annihilation. For the present situation where type-1 jumps (jump rate ν) are much faster than type-2 jumps (jump rates Γ_i), a quantitative calculation of the relaxation spectrum [14] shows the simultaneous existence of two relaxation processes, a fast one with the relaxation rate $\tau_{\mathrm{rel}}^{-1} \simeq 2.7\nu$ and a slow one with the rate $\tau_{\mathrm{rel}}^{-1} \simeq 1.4\Gamma$, where $\Gamma = \sum_i \Gamma_i$ is the total jump rate for type-2 jumps. These results demonstrate that the fast and the slow relaxation processes are in fact caused by the fast type-1 and the slow type-2 jumps, respectively.

We return to Fig. 3 now. The figure shows the τ_{rel}^{-1} calculated from QNS [2,3] and NMR [4,5] results. The data above and below 10^{11} s^{-1} describe the fast and the slow relaxation, respectively. The QNS studies allow either a direct calculation of τ_{rel}^{-1} for both relaxation processes from the quoted residence times τ_{TO} and τ_{TT} ($\Gamma = 3/\tau_{\mathrm{TO}}$, neglecting back jump processes, and $\nu = 1/\tau_{\mathrm{TT}}$) [3], or an estimate of τ_{rel}^{-1} for the slow relaxation process from the quoted self diffusion coefficient, D_s, of the H in a polycrystalline sample ($\Gamma \simeq 5D_s/a^2$ [6], with $a = 3.65$ Å as lattice parameter) [2]. Fig. 3 shows that a high-temperature extrapolation of the τ_{rel}^{-1} data from mechanical spectrometry fits the QNS data for the slow relaxation process very well. This demonstrates that it is this process that has been studied by mechanical spectroscopy, and that its relaxation rate τ_{rel}^{-1} (or the jump rate Γ) follows an Arrhenius law over ten orders of magnitude.

The NMR data in Fig. 3 are τ_{rel}^{-1} values for the slow relaxation process, derived from jump rates of type-2 jumps determined in spin–lattice relaxation rate measurements (the NMR jump rates and Γ are assumed equal) [4,5,15]. It is seen that these values are also consistent with the high-temperature extrapolation of the mechanical spectroscopy data.

Finally, we mention that an anelastic relaxation from H (or D) jumps of type-1 is reported from low-temperature mechanical spectroscopy studies on the related hcp systems YD_x [16] and $\mathrm{ScH(D)}_x$ [17]. For ScH_x, the relaxation rates (~10^7 s^{-1}) measured at ~25 K are four orders of magnitude smaller than the jump rates ν that were observed by QNS [7] for the same system between 10 and 300 K. This discrepancy cannot be explained by the effect of the binding energy in a Zener relaxation that involves H pair annihilation (or creation) since, in such a case, a binding enthalpy $\epsilon \simeq 0.06$ eV [1] would reduce the relaxation strength to such an extent that it would be undetectable at 25 K [13,17]. The observed relaxation was, therefore, attributed to a Zener relaxation of other spatial H configurations [17].

4. Conclusion

We performed a mechanical spectroscopy study on hcp YH_x single crystals. The strongly anisotropic relaxation strength identifies the observed anelastic relaxation as a Zener relaxation of H pairs. This Zener relaxation consists of two simultaneous relaxation processes in different frequency ranges, determined by the jump rates of H jumps of type-1 and -2. Comparison with QNS [2,3] data shows that the observed relaxation is controlled by type-2 H jumps, and that their jump rate follows an Arrhenius law that holds over ten orders of magnitude.

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