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Hydrogen and oxygen motion in yttrium by anelastic relaxation measurements

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Abstract

The role of interstitial hydrogen in the numerous relaxation processes observed in the pure yttrium has been studied by elastic energy loss measurements in the temperature range between 1.1 and 600 K, at vibration frequencies in the kHz range. All the processes below 300 K are caused by hydrogen: the process at liquid He temperature is due to its delocalization whereas three other processes originate from hopping of the H atoms trapped by oxygen (nitrogen) or dragged by dislocations. It is proposed that the effects above room temperature are associated with the motion of oxygen in solid solution.

Keywords: Point defects; Dislocations; Anelasticity

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1. Introduction

The rare earth metal–hydrogen systems have been intensively studied in these last years due to the unexpected stability of their solid solutions down to the lowest temperatures [1] and to the exciting physical properties of their hydrides [2]. Most of the investigations are concerned with the study of these systems at high H concentrations, whilst little attention has been devoted to the properties of pure elements which, for a deeper understanding of their physical properties, should be better characterized. The numerous relaxation processes [3,4] observed in pure yttrium represent a puzzle which has not been exhaustively explained yet, though these effects denote the presence of lattice imperfections.

We report on a preliminary study of the relaxation processes observed in pure polycrystalline yttrium by the elastic energy loss measurements at low concentration of interstitial hydrogen and oxygen and in the presence of plastic deformation, in view to clarify the role of these lattice imperfections in causing the observed relaxation processes.

2. The anelastic relaxation technique and the samples

Anelastic relaxation is an effective tool to investigate lattice imperfections in solids, particularly atomic diffusion and dislocation dynamics. In an oscillating crystal the alternating stress due to the vibration interacts with the local distortion associated with a mobile lattice imperfection perturbing its energy states. As a consequence, the imperfections thermally redistribute themselves among the perturbed states, so giving rise to a relaxation process which manifests itself as a peak of the elastic energy loss Q^{-1} versus temperature. The anelastic relaxation curve is described by the Debye law and displays its maximum at a temperature where the reciprocal of the relaxation time $\tau(T)$(close to the transition time of the imperfection) equals the angular vibration frequency ω:

$$Q^{-1} \propto \frac{c(\Delta\lambda)^2}{k_B T} \frac{\omega\tau}{(1+\omega^2\tau^2)} \tag{1}$$

where c is the concentration of the relaxing entity and $\Delta\lambda$ is the change in the local elastic distortion. The relaxation time $\tau(T)$ generally obeys an Arrhenius-type law $\tau(\mathrm{T}) = \tau_0 e^{\frac{E}{k_B T}}$ characterized by the activation energy E for the transition of the imperfection. From the analysis of the relaxation curve at different vibration frequencies it is possible to evaluate the parameters characterizing the dynamics of the mobile imperfection.

The samples were rectangular bars (≈40×4.4×2 mm^3), cut from different plates of 99.9 at % pure polycrystalline Y purchased from the Ames Laboratory,

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and here labelled as Y0, Y1, Y2. The total amount of the interstitial gaseous impurities of samples, which in the ‘‘as received’’ state was less than 2000 at ppm, was monitored by the residual resistivity ratio (*RRR*). Elastic energy loss measurements were carried out on cooling and heating at a rate lower than 1 K $\min^{-1}$ by electrostatically exciting the samples at different flexural vibration modes in the frequency range 1–33 kHz.

In the thermal treatments for H-outgassing and for reducing the dislocation density, the samples were wrapped in zirconium foils and annealed at 1000 °C in vacuum in the 10^{-8} mbar range; finally they were cooled to room temperature in less than 10 min.

3. Experimental results and discussion

3.1. The relaxation processes below 300 K

Fig. 1 shows the anelastic relaxation spectra on heating of samples Y0 in the ‘‘as received state’’ as cut from a plate (curve 1), of Y1 after annealing (curve 2), and of Y2 after annealing (curve 3) and after 0.4% plastic deformation (curve 4). Between 1 K and room temperature five thermally activated processes appear: P2, P3, P4, P5, P6. It is now accepted that P2 is due to H tunnelling [3,5] and P6 to the formation/dissolution of H pairs [6]; instead, the nature of the other three peaks has not been convincingly clarified yet [3].

A comparison among the relaxation spectra indicates that: (i) in sample Y0 (curve 1), where we expect the lowest O (N) content (*RRR* = 34) and an appreciable dislocation density due to cutting, the H tunnelling peak P2, the H-pair peak P6 and peak P5 are predominant. Moreover, the height of P6 denotes that this sample contains more hydrogen than the other ones; (ii) in sample Y1 (curve 2), the annealing (1 h at 1000 °C, *RRR* = 27) suppresses the processes P2 and P6, reduces P5 and enhances P3 and P4. The *RRR* decreased from 52 in the ‘‘as received’’ state down to 27, indicating O contamination; (iii) in sample Y2 the more intense annealing (1 h 40 min at 1000 °C, *RRR* = 27) markedly reduces all the processes (curve 3). The subsequent plastic deformation (curve 4) does not affect P3 and P4 at all whilst it enhances P2 and the dissipation around P5.

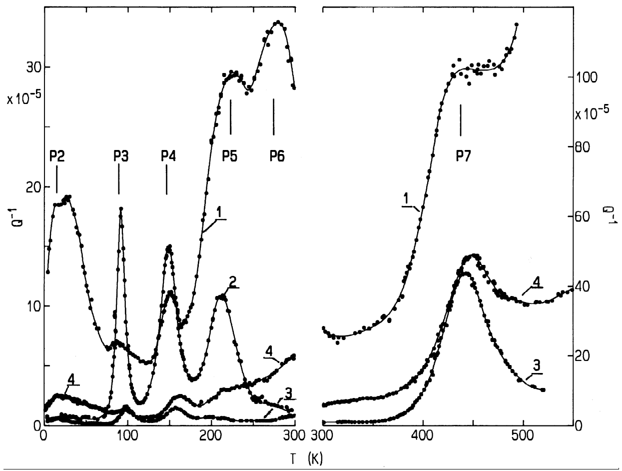

Fig. 1. Anelastic relaxation spectra of the tested samples. Curve 1: Y0 at 1.8 kHz in the received state (*RRR* = 34). Curve 2: Y1 at 2 kHz after the annealing (1 h, 1000 °C, *RRR* = 27). Curves 3 and 4: Y2 at 6.5 kHz after the annealing (1 h 40 min, 1000 °C, *RRR* = 27) and 0.4% plastic deformation, respectively.

Interstitial hydrogen and dislocations were certainly always present in all the samples. Indeed, due to the strong affinity of the rare earths to hydrogen, unwanted quantities of this element can remain in the material even after UHV annealings. Dislocations are produced not only by cutting (sample Y0) and by plastic deformation (sample Y2) but also during the temperature variations, as in *hcp* polycrystals the anisotropic thermal expansion produces plasticity phenomena [7]. Thus, one would be inclined to interpret the intermediate temperature processes by relaxation mechanisms involving dislocations and interstitial atoms. However, the following considerations suggest that only P5 is caused by a mechanism involving dislocations and interstitial hydrogen: (i) the process is more developed in sample Y0 where the dislocation density and the H concentration are higher than in Y1 and Y2; (ii) a relaxation, with similar features, has been observed by Kappesser et al. [4] in plastically deformed polycrystalline Y; (iii) the broadness of the relaxation curve, which is 100% broader than a single Debye peak, and the low value of the attempt frequency τ_0^{-1} (Table 1) are not compatible with point defect relaxation.

The mechanism of peak P5 should be similar to those reported in transition metals (Nb, Ta, V) and attributed to the relaxation of dislocations dragging interstitial H [8]. According to this picture, the observed decrease of P5 can be explained by the concomitant reduction of the dislocation density and H concentration.

Instead, the stress-induced redistribution of point defects has to be invoked for P3 and P4 as suggested by us in a previous investigation [3]. The experimental curves of these two processes can be fitted by a nearly single Debye theoretical curve. In fact, the value of the activation energy E_w assumed for the theoretical curve, is nearly coincident

Table 1
Relaxation parameters of the processes

Process	τ_0 (s)	E_s (eV)	E_w (eV)	E_s/E_w
P3	3×10^{-13}	0.15	0.15	1
P4	5×10^{-12}	0.21	0.18	1.2
P5	1×10^{-10}	0.45	0.23	2
P6	1×10^{-13}	0.60	0.50	1.2
P7	10^{-12}–10^{-14}	0.75	0.70	1.1

with that E_s deduced by the peak shift with frequency, and the attempt frequency τ_0^{-1} is typical of atomic vibrations (Table 1).

Processes P3 and P4 could be due to a classical over-barrier hopping of H between tetrahedral and/or octahedral sites in the environment of a gaseous immobile impurity, more likely O (N). This hypothesis is supported by the fact that P3 and P4 are more pronounced in sample Y1 which has a larger oxygen content. A peculiarity (not shown in the figure) of the intermediate-temperature spectrum is that the heights of P4 and P5 (and of P3 to a less extent) are systematically lower on cooling than on heating; instead, thermal cyclings do not affect process P2 at all. This fact denotes that relaxations P3, P4 and P5 are measured in conditions of non-equilibrium; indeed, the two peaks P4 and P5 occur in the temperature range where resistivity measurements [1] indicated a transition (≈180 K) between mobile and immobile H in the time scale of the usual experiments.

3.2. The relaxation spectrum above room temperature

The extension of the Q^{-1} measurements up to 550 K (in samples Y0 and Y2, Fig. 1) reveals a thermally activated process, P7, around 450 K. The phenomenology of P7 is complex and can be described as follows. The process reaches the highest magnitude (results not reported here) only in the 1st heating run after the UHV annealing at 1000 °C followed by cooling to room temperature in less than 10 min. On subsequently cycling between 300 and 550 K the peak height is progressively reduced (of about 50%) down to nearly stable values (curve 3). The highest magnitude can be restored by repeating the annealing at 1000 °C followed by rapid cooling. The peak height is only partially restored after heating up to 600 K and cooling at 5 K min^{-1}. Curve 1 of sample Y0 (having a lower O(N) content, $RRR = 34$) could be reproduced during the cooling and heating measurements.

A surprisingly good theoretical fit of curve 3 can be achieved in terms of a single-time Debye process (Table 1). This fact and the value of the attempt frequency which is typical of point defects, suggest that process P7 is caused by stress-induced redistribution of interstitial oxygen. The solubility limit of oxygen in yttrium, which is about 3000 at ppm at 550 K [9], practically coincides with the gaseous impurity content (where oxygen is dominant) of our samples. Therefore, the instability of P7 with thermal cyclings could find its explanation in the O precipitation. The attribution of P7 to point defect relaxation is corroborated by the observation that 0.4% plastic deformation in sample Y2 does not affect the height of P7 but introduces a background which strongly increases with temperature. Considering that in a hcp crystal octahedral and tetrahedral sites remain equivalent after application of any type of stress, a simple Snoek-type effect cannot be invoked to explain process P7. Therefore two possible mechanisms are proposed: the redistribution of the O atoms between the octahedral and tetrahedral sites which are non-equivalent, or the formation and dissolution of O–O pairs similarly to that proposed for H in P6. Further investigation is needed to clarify the mechanism.

The rise of dissipation, above 450 K, both in Y0 which contains dislocations due to cutting (curve 1), and in Y2 after plastic deformation (curve 4), could be the tail of a peak, possibly a Snoek–Koester relaxation resulting from dislocations dragging interstitial oxygen.

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