

# Reorientation of diatomic H–Y complexes in dilute Pd–Y alloys

M. Ege, G. Hauptmann, W. Ulfert and H. Kronmüller

Max-Planck-Institut für Metallforschung, Institut für Physik, Heisenbergstr. 1, D-70569 Stuttgart (Germany)

## Abstract

The reorientation of diatomic H–Y complexes in hydrogen-doped dilute Pd<sub>100-x</sub>Y<sub>x</sub> alloys ( $x=1, 2, 4.5, 8$ ) has been studied by means of internal friction (IF) in an inverted torsion pendulum and in a vibrating reed apparatus. As reported earlier, the internal friction of hydrogen-doped dilute Pd<sub>100-x</sub>Y<sub>x</sub> alloys shows three maxima that are identified as the Zener peak, the reorientation peak of diatomic H–Y complexes and the Snoek–Köster peak. The width of the reorientation peak exceeds that of a single Debye maximum, and increases with the Y content as well as with the hydrogen content of the sample. For a fixed hydrogen content, the maximum shifts to higher temperatures if the Y content of the alloys increases; in contrast, for a fixed Y content, there is a shift to lower temperatures caused by an increasing hydrogen content. The measured reorientation peak can be fitted by a superposition of Debye maxima using a constant pre-exponential factor and spectra of activation enthalpies for the relaxation times. The analysis of the hydrogen content dependence of the relaxation strength yields a value of  $|\lambda_1 - \lambda_2| = 0.036$  for the elastic anisotropy of the diatomic H–Y complexes. The activation parameters for the relaxation time of the reorientation of an isolated complex are 0.18 eV and  $3 \times 10^{-12}$  s. The properties of the activation enthalpy spectra can be interpreted in terms of a model which takes into account the elastic long-range interaction between an H–Y complex and the Y atoms in the vicinity of this complex.

## 1. Introduction

Whereas the internal friction (IF) caused by the reorientation of hydrogen-substitutional (HS) pairs is well established in b.c.c. host metals [1, 2], in the past, a similar demonstration could not be given for f.c.c. host metals. In contrast, measurements of the magnetic after effect (MAE) in several b.c.c. and f.c.c. transition metals [3, 4] have given evidence for HS reorientation jumps in both types of lattice. As reported recently [5], the lack of evidence mentioned above could be made up now by the observation of a dissipation effect in H-doped dilute Pd–Y alloys, which was attributed to the reorientation of diatomic H–Y complexes. Below we will present new experimental data of this effect, concerning its dependence on the hydrogen and Y contents, which show clearly that there is no contribution of higher order complexes in the concentration range investigated.

## 2. Experimental procedure

The relaxation of H in dilute Pd–Y alloys Pd<sub>100-x</sub>Y<sub>x</sub> ( $x=1, 2, 4.5, 8$ ) has been studied by measurements of the IF. The measurements have been carried out using an inverted torsion pendulum and a vibrating reed apparatus. The preparation of the alloys was reported

earlier [5]. The polycrystalline samples used for the torsion pendulum had a cylindrical shape with a diameter of 2.0 mm and a length of 25 mm. The vibrating part of the samples for the vibrating reed apparatus was in the shape of a rectangular parallelepiped with a length of 20 mm, a width of 3.5 mm and a thickness varying between 0.5 and 1.5 mm, resulting in vibration frequencies of 660 up to 1900 Hz.

The doping of the samples with hydrogen was performed in an H<sub>2</sub> atmosphere at a temperature of  $T=350$  K. The applied H<sub>2</sub> pressures ranged from 0.5 to 150 Torr and the doping times were between 3 and 24 h. The weight of the samples was measured before and after doping, which made it possible to determine the hydrogen content exactly. For degassing, the samples were annealed in a high vacuum at a temperature of 1273 K for 12 h.

## 3. Experimental results and discussion

Figure 1 shows the IF of hydrogen-doped Pd<sub>99</sub>Y<sub>1</sub> and Pd<sub>92</sub>Y<sub>8</sub> samples measured in the vibrating reed apparatus. For convenience in the following, we use the notation Pd<sub>100-x</sub>Y<sub>x</sub>H<sub>c</sub> for a Pd<sub>100-x</sub>Y<sub>x</sub> alloy containing  $c$  hydrogen atoms per 100 metal atoms.

Depending on the hydrogen and the Y content of the samples, three different maxima can be identified

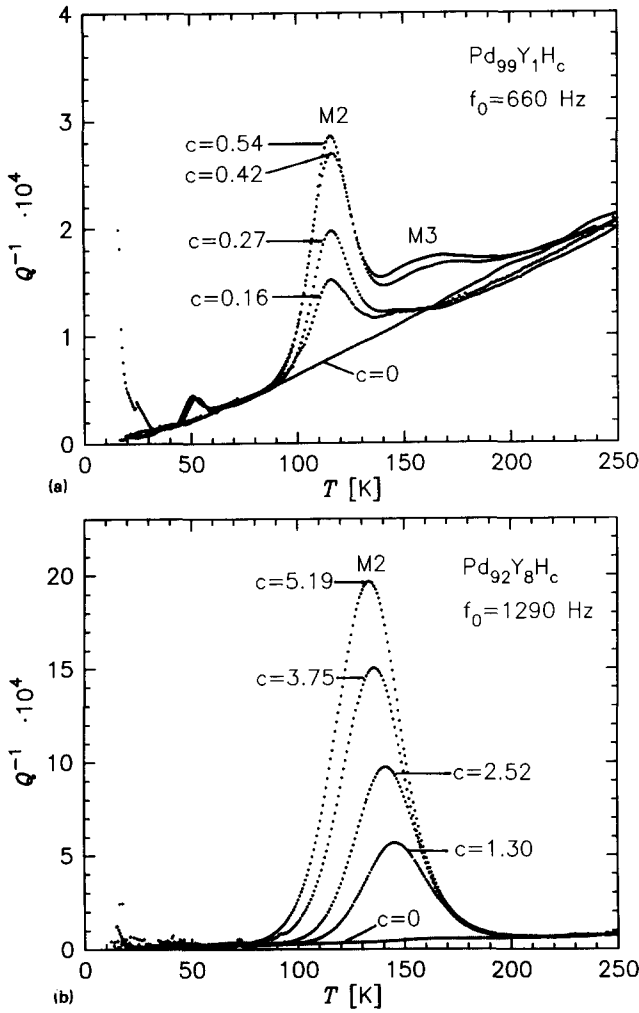


Fig. 1. IF spectra of hydrogen-doped dilute Pd-Y alloys measured in a vibrating reed apparatus: (a)  $\text{Pd}_{99}\text{Y}_1\text{H}_c$ ,  $f_0=660$  Hz; (b)  $\text{Pd}_{92}\text{Y}_8\text{H}_c$ ,  $f_0=1290$  Hz.

TABLE 1. Hydrogen saturation concentration  $c^s$  of the reorientation maximum in  $\text{Pd}_{100-x}\text{Y}_x\text{H}_c$

Alloy	$\text{Pd}_{99}\text{Y}_1$	$\text{Pd}_{98}\text{Y}_2$	$\text{Pd}_{95.5}\text{Y}_{4.5}$
Hydrogen content $c^s$	0.6	1.6	4.8

[5]. For low hydrogen contents, a Snoek-Köster peak (denoted by M3 in Fig. 1(a)) and a maximum M2 attributed to the reorientation of H-Y complexes are observed. The Snoek-Köster peak does not occur in alloys with higher Y contents ( $x=4.5, 8$ ), owing to the pinning of dislocations by substitutional Y atoms, resulting in a smaller mean dislocation length.

The peak height of the reorientation maximum M2 increases with the hydrogen content of the samples but saturates at higher hydrogen contents  $c^s$ , whose value depends on the Y content (Table 1). This saturation is accompanied by the occurrence of a third maximum M1 (Zener maximum), which lies at lower temperatures

(80 K for frequencies of about 1 Hz, and 100 K for frequencies of about 1 kHz) and whose peak height increases monotonically with increasing hydrogen content.

In the following, the reorientation maximum M2 will be the subject of our discussion. For all the alloys studied, the width of this peak exceeds that of a single Debye maximum. To account for the broadening of the peak a superposition of Debye maxima is assumed.

$$Q^{-1}(\omega, T) = \int_{-\infty}^{\infty} p_s(\ln(\tau)) \frac{\omega\tau}{1 + (\omega\tau)^2} d(\ln(\tau)) \quad (1)$$

Here,  $\tau$  is the relaxation time,  $\omega$  the angular frequency and  $T$  the temperature.

The spectral relaxation strength  $p_s(\ln(\tau))$  describes the contribution  $p_s(\ln(\tau)) d(\ln(\tau))$  of the relaxation processes in the interval  $[\ln(\tau), \ln(\tau) + d(\ln(\tau))]$  to the total relaxation strength  $\Delta$ . Therefore, the total relaxation strength  $\Delta$  is given by

$$\Delta = \int_{-\infty}^{\infty} p_s(\ln(\tau)) d(\ln(\tau)) \quad (2)$$

The relaxation time  $\tau$  is given by an Arrhenius law

$$\tau = \tau_0 \exp(H_a/kT)$$

which means that a spectrum of  $\tau$  can be the result of a distribution of the pre-exponential factor  $\tau_0$  as well as of the activation enthalpy  $H_a$ . The values of the pre-exponential factor  $\tau_0$  for the reorientation maximum obtained from Arrhenius plots are listed in Table 2. Within experimental accuracy, the value of  $\tau_0$  can be treated as being constant for all the alloys as well as for all the hydrogen contents. A mean value of  $\tau_0 = 3 \times 10^{-12}$  s is obtained from Table 2.

Therefore, the fitting of eqn. (1) to the measured reorientation peak can be performed using a spectrum of activation enthalpies  $H_a$  but a constant pre-exponential factor of  $\tau_0 = 3 \times 10^{-12}$  s. The fitting has been carried out by an iterative method, yielding a distribution  $p_s(H_a)$  for the spectral relaxation strength and the total relaxation strength  $\Delta$  given by eqn. (2).

Figure 2 shows the dependence of the total relaxation strength  $\Delta$  on the hydrogen content  $c$ . Figure 2(a) gives the results obtained with the torsion pendulum, whereas Fig. 2(b) shows the values obtained from the measurements in the vibrating reed apparatus. The tem-

TABLE 2. Pre-exponential factor  $\tau_0$  of the reorientation maximum in hydrogen-doped Pd-Y alloys

	$\text{Pd}_{99}\text{Y}_1\text{H}_c$	$\text{Pd}_{98}\text{Y}_2\text{H}_c$	$\text{Pd}_{95.5}\text{Y}_{4.5}\text{H}_{0.7}$	$\text{Pd}_{95.5}\text{Y}_{4.5}\text{H}_{3.6}$
$\tau_0$ (s)	$5 \times 10^{-12 \pm 0.5}$	$1 \times 10^{-12 \pm 0.5}$	$4 \times 10^{-12 \pm 0.5}$	$4 \times 10^{-12 \pm 0.5}$

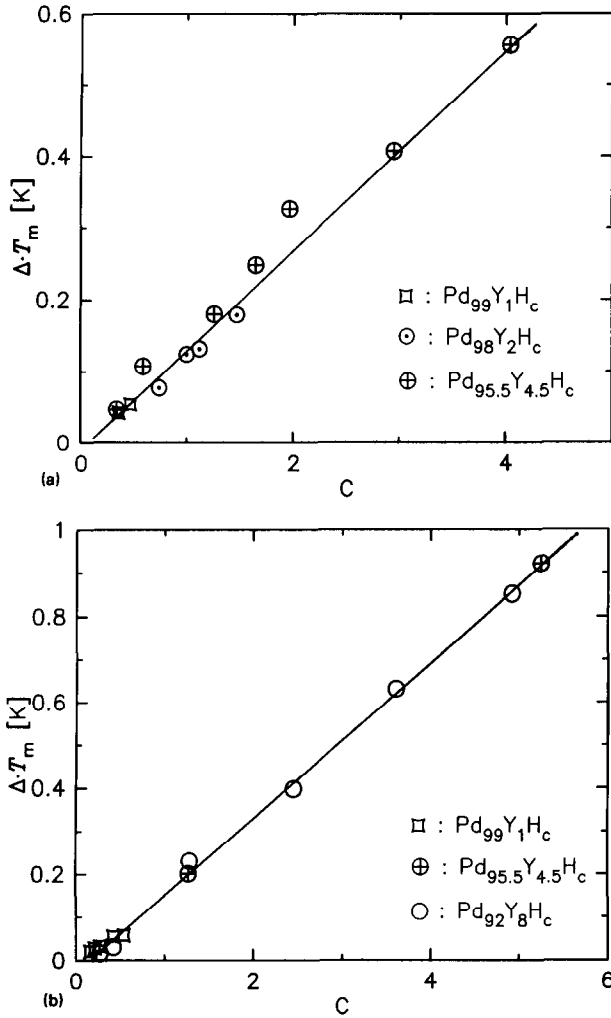


Fig. 2. Dependence of  $\Delta$  on hydrogen content  $c$ , as determined by relaxation of distortion in (a) torsion and (b) bending mode.

perature  $T_m$  denotes the peak temperature. In both cases, the values lie on straight lines.

The fact that the values of  $\Delta$  lie on the same straight line for all hydrogen contents is evidence that we have to deal with only one sort of H-Y complex in the hydrogen concentration range investigated. Table 1 shows that the saturation of the reorientation maximum is reached when the atomic hydrogen content is approximately equal to the Y content of the sample, which means that the observed complexes are diatomic H-Y complexes. Using the theoretical relationship between the total relaxation strength  $\Delta$  and the concentration,  $c$ , of tetragonal defects in a cubic polycrystalline material allows us to determine the elastic anisotropy  $|\lambda_1 - \lambda_2|$  of the H-Y complexes, *i.e.*

$$\Delta = \beta \frac{c}{100} \frac{v_0}{kT_m} M_{\text{poly}} (\lambda_1 - \lambda_2)^2 \quad (3)$$

In this equation, where  $k$  is the Boltzmann constant and  $v_0$  the atom volume of the host lattice,  $M_{\text{poly}}$  is

the shear modulus  $G_{\text{poly}}$  (and  $\beta=4/15$ ), if the peak is observed in torsion, whereas it is the Young modulus  $E_{\text{poly}}$  (and  $\beta=4/45$ ) if the peak is observed in flexure. From Fig. 2(a), a value of  $|\lambda_1 - \lambda_2|=0.035$  is obtained; Fig. 2(b) yields  $|\lambda_1 - \lambda_2|=0.037$ .

The distribution of the spectral relaxation strength  $p_s$  for  $\text{Pd}_{99}\text{Y}_1\text{H}_c$  (Fig. 3(a)) is very sharp and its peak is located at an activation enthalpy  $H_a=0.18$  eV, which remains the same for all hydrogen contents. With increasing Y content, the width of the distribution increases and the peak of the distribution shifts to higher values of  $H_a$ . In addition, the alloys with higher Y contents show a shift of the spectral relaxation strength to lower values of  $H_a$  with increasing hydrogen content (Fig. 3(b)), which is accompanied by a small increase in the peak width.

To understand these features, we consider a model that takes into account the elastic long-range interaction between a given H-Y complex and the Y atoms in its environment. For this purpose, we consider a random

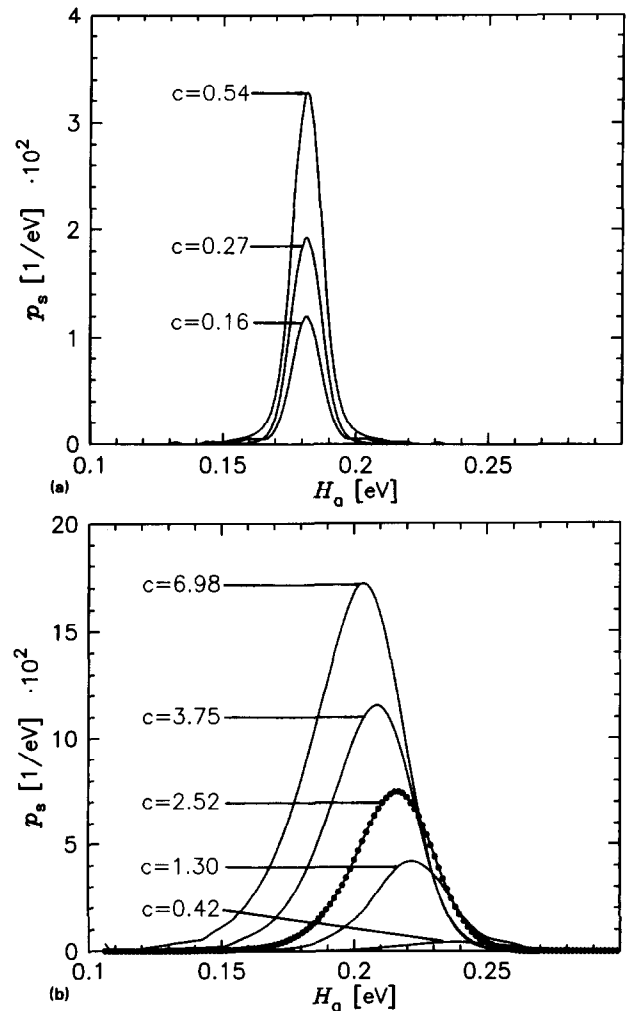


Fig. 3. Spectral relaxation strength  $p_s$  of (a)  $\text{Pd}_{99}\text{Y}_1\text{H}_c$  and (b)  $\text{Pd}_{92}\text{Y}_8\text{H}_c$ .

distribution of substitutional Y atoms in the Pd lattice. Then, a single hydrogen atom is placed on an octahedral site next to an Y atom, forming a diatomic H-Y complex. The elastic interaction between this hydrogen atom and further Y atoms is calculated using an equation [6] for elastic point defects in a cubic lattice. This interaction, which can be of either sign, changes the site enthalpy of the hydrogen atom under consideration.

In our calculations, we considered all Y atoms within a sphere with a radius of 40 lattice constants. Doing this calculation for a lot of H-Y complexes leads to a distribution  $P$  of site enthalpies  $H_{H-Y}$  in comparison with the enthalpy  $H_{H-Y}^0$  of an isolated H-Y complex (Fig. 4). Under the assumption of a constant saddle-point enthalpy for the reorientation jumps, these distributions can explain qualitatively the observed features of the spectral relaxation strength.

In the case of low Y contents, we obtain a very sharp distribution  $P$  corresponding to nearly isolated H-Y

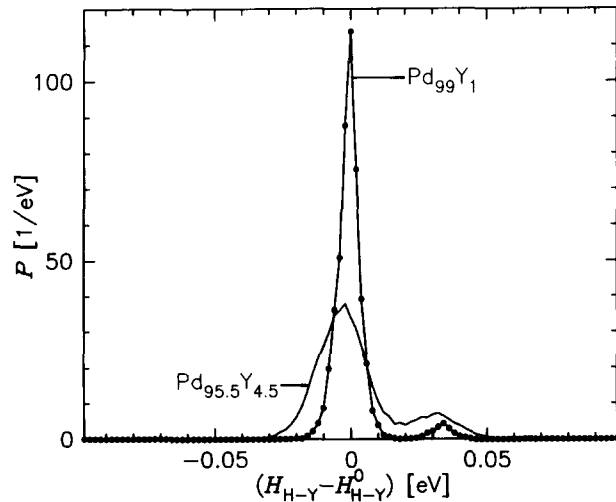


Fig. 4. Distribution of site enthalpies  $H_{H-Y}$  of diatomic H-Y complexes in  $\text{Pd}_{99}\text{Y}_1$  and  $\text{Pd}_{95.5}\text{Y}_{4.5}$ .

complexes and resulting in a spectral relaxation strength resembling a delta function. In the case of higher Y contents, the distribution  $P$  comprises a wide range of site enthalpies.

On doping such a lattice with hydrogen atoms, the hydrogen atoms will fill the sites with the lowest enthalpies first. These sites are characterized by the highest activation enthalpies. As shown in Fig. 4, there are sites in  $\text{Pd}_{95.5}\text{Y}_{4.5}$  with lower enthalpies than those in  $\text{Pd}_{99}\text{Y}_1$ . Therefore, we expect a higher activation enthalpy for the reorientation of the H-Y complex, which is found experimentally as a shift of the reorientation maximum towards higher temperatures. From Fig. 4, we also expect a broader maximum in alloys with higher Y contents, owing to the fact that, in these alloys, the distribution  $P$  is not as sharp as in alloys with very low Y contents, which leads to a broader site enthalpy spectrum of the occupied sites.

With increasing hydrogen content in the alloy, the hydrogen atoms will successively fill the sites with higher site enthalpies. These sites are characterized by lower activation enthalpies, and the reorientation of these hydrogen atoms gives rise to contributions on the side of low activation enthalpies  $H_a$  in the spectral relaxation strength. In the experiment, this is observed as a shift of the maximum towards lower temperatures.

## References

- 1 G. Cannelli, R. Cantelli and F. Cordero, *J. Phys. F*, **16** (1986) 1153.
- 2 S. Tanaka and M. Koiwa, *Scr. Metall.*, **15** (1981) 403.
- 3 H. Kronmüller, G. Higelin, P. Vargas and R. Lässer, *Z. Phys. Chem. NF*, **143** (1985) 161.
- 4 B. Höhler and H. Kronmüller, *Philos. Mag. A*, **45** (1982) 607.
- 5 G. Hauptmann, W. Ulfert and H. Kronmüller, *Mater. Sci. Forum*, **119-121** (1993) 109.
- 6 P.H. Dederichs and J. Pollmann, *Z. Phys.*, **255** (1972) 315.