

## Hydrogen interactions as studied by internal friction and solubility measurements in a Pd<sub>3</sub>Mn alloy

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 3377

(<http://iopscience.iop.org/0953-8984/4/13/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 00:08

Please note that [terms and conditions apply](#).

## Hydrogen interactions as studied by internal friction and solubility measurements in a Pd<sub>3</sub>Mn alloy

B Sobha†, B Coluzzi†, F M Mazzolai†, A P Craft‡ and T B Flanagan‡

† Department of Physics, University of Perugia, 06100 Perugia, Italy

‡ Department of Chemistry, University of Vermont, Burlington, Vermont 05405, USA

Received 1 October 1991

**Abstract.** The internal friction (IF) has been measured as a function of the H (D) content in the disordered and ordered Pd<sub>3</sub>Mn system between 90 and 400 K at frequencies in the range 180–5300 Hz. Relaxation processes due to stress-assisted motion of H (D) have been identified and their spectra of relaxation times, heights and temperatures determined as a function of H content and the state of long-range order. The main observations in the case of the alloy in the disordered state are an increase with  $n$  ( $n = \text{H (or D)}/(\text{Pd} + \text{Mn}) \text{ at.}$ ) of the height and width of the peak and a decrease of the peak temperature. These effects have been attributed to progressive filling by H of higher energy I<sub>3</sub> sites (sites having five nearest-neighbour Pd atoms), which differ in terms of atomic arrangements in the second and more distant shells of neighbours. The partial molar enthalpy  $\Delta H_{\text{H}}$  for H solution has also been determined both in the disordered and ordered states of the Pd<sub>3</sub>Mn alloy. In the disordered state  $\Delta H_{\text{H}}$  is found to increase rapidly with  $n$  starting from values of  $n$  as low as 0.01. The concentration dependence of  $\Delta H_{\text{H}}$  as well as of the height of the IF peak reveal strong hydrogen-hydrogen repulsions.

### 1. Introduction

In the last few years there has been an increasing number of studies of the behaviour of H in Pd<sub>3</sub>Mn (Flanagan *et al* 1986, Baba *et al* 1987, 1988, Rodic' *et al* 1989, 1991, Rush *et al* 1989, Sobha *et al* 1991a, b). This is due to the fact that this system can be obtained in states of different order. Quenching from high temperatures results in a disordered metastable form, while slow cooling from above 803 K gives rise to a long-period structure (LPS) of the Al<sub>3</sub>Zr type (Ahlzen *et al* 1989) which can be converted into an L1<sub>2</sub> form by annealing at about 600 K (Flanagan *et al* 1986) in the presence of H<sub>2</sub> gas at pressures of a few MPa. The unit cells of these structures are given in figure 1.

H diffusion coefficients have been derived from recent anelastic measurements on this system over a wide temperature range in the three states of order (Sobha *et al* 1991a, b). The internal friction (IF) peaks associated with H transitions between different interstitial (octahedral) sites (Sobha *et al* 1991a, b) have been characterized. In the present work, changes in the relaxation time spectra of some of these peaks are examined as a function of H content and the state of long-range order of the alloy. The underlying objective of the investigation was to probe H-H and H-Mn interactions. For this purpose complementary measurements of the partial molar enthalpy of H were carried out as a function of H content for the three states of order.

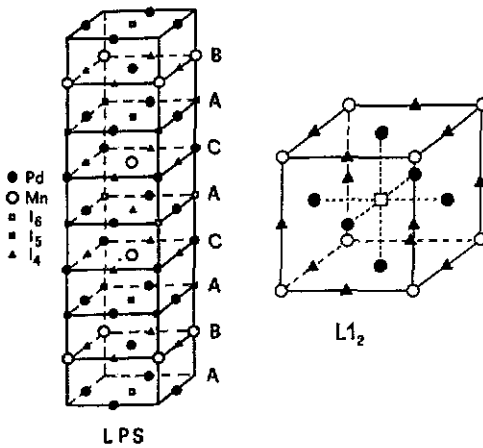


Figure 1. Unit cells of the LPS and L<sub>12</sub> ordered forms of Pd<sub>3</sub>Mn, with I<sub>6</sub>, I<sub>5</sub> and I<sub>4</sub> types of octahedral interstitial sites marked.

## 2. Experimental details

The alloy was prepared by induction melting in argon. The initially disordered state was produced by rapid quenching from 1123 K into ice water. At a later stage the specimens were ordered to the LPS form by annealing *in vacuo* at slowly decreasing temperatures from 800 to 300 K over a period of several days. The L<sub>12</sub> form was obtained by annealing the sample for one week at 600 K under a high H<sub>2</sub> pressure (50 MPa).

### 2.1. Solubility measurements

Hydrogen solubility data were obtained by the gas-phase method which consisted of repeated dosing of the sample under isothermal conditions in a calibrated reaction volume  $V_R$ . The source of ultra-pure hydrogen gas was a hydrided sample of LaNi<sub>5</sub> contained in a stainless steel vessel. A certain amount of gas was admitted from the hydrogen reservoir into a calibrated dosing volume  $V_D$ , which was subsequently connected to  $V_R$ . The pressures in  $V_D$  and  $V_R$  were measured respectively by a Barocel differential manometer and an MKS baratron meter. The specimens used in these experiments were strips of average dimensions 5 mm by 30 mm.

### 2.2. Internal friction measurements

The IF and Young's modulus were measured in flexure by exciting free-free resonant modes of bars; the four specimens used were about 45 mm long, 5 mm wide and of thicknesses: 0.18, 0.28, 1.37 and 3.1 mm, respectively. Hydrogen and deuterium were loaded by gas-phase reaction at appropriate temperatures and H<sub>2</sub> (or D<sub>2</sub>) pressures. The H (or D) content  $n$  ( $n = \text{H(or D)}/(\text{Pd} + \text{Mn})$  at.) was monitored gravimetrically and within the experimental accuracy ( $\delta n = 0.003$ ) was found not to change appreciably during the measurements.

### 3. Results

#### 3.1. Hydrogen solubility

The relative chemical potential of hydrogen dissolved in an alloy is given by the relationship (Atkins 1986)

$$\mu_{\text{H}} = RT(\ln P_{\text{H}_2})^{1/2}. \quad (1)$$

Using this relation, values of  $\mu_{\text{H}}$  were determined at various hydrogen contents  $n$  from pressure-composition isotherms for each of the forms of the alloy. Relative partial molar enthalpies  $\Delta H_{\text{H}}$  of hydrogen at a given hydrogen content were determined from the slopes of  $\mu_{\text{H}}/T$  against  $1/T$  plots over the temperature range 340–533 K. The experimentally deduced enthalpy-hydrogen content relations for the three states of order are shown in figure 2. There it can be seen that in the two ordered forms  $\Delta H_{\text{H}}$  decreases over extended ranges of  $n$ , while in the disordered material it starts increasing at relatively low values of  $n$  ( $n \approx 0.01$ ). The values of  $\Delta H_{\text{H}}$  at infinite dilution as determined from the intercepts at  $n = 0$  of the curves in figure 2 are  $-31.7$  ( $\text{Al}_3\text{Zr}$ ),  $-26.1$  ( $\text{L1}_2$ ) and  $-24.2$  (disord.)  $\text{kJ} (\text{mol H})^{-1}$  and all are much more negative (exothermic) than for Pd ( $-10.1 \text{ kJ} (\text{mol H})^{-1}$ ) (Clewley *et al* 1973).

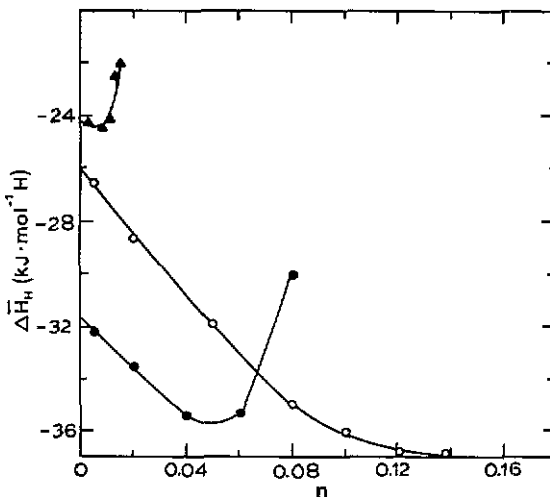


Figure 2. Partial molar enthalpy of hydrogen as a function of hydrogen content for disordered ( $\Delta$ ); LPS ordered ( $\bullet$ ); and  $\text{L1}_2$  ordered ( $\circ$ ) forms of the alloy.

#### 3.2. Internal friction

Figure 3 shows the IF data of the disordered sample 1 after quenching (curve 1), deuterium loading (curve 2) and subsequent partial desorption of deuterium (curves 3 to 6). As can be seen, a broad peak is introduced by D with a maximum occurring at a temperature  $T_{\text{M}}$  ( $240 < T_{\text{M}} < 290 \text{ K}$ ), which for  $n \leq 0.035$  tends to increase

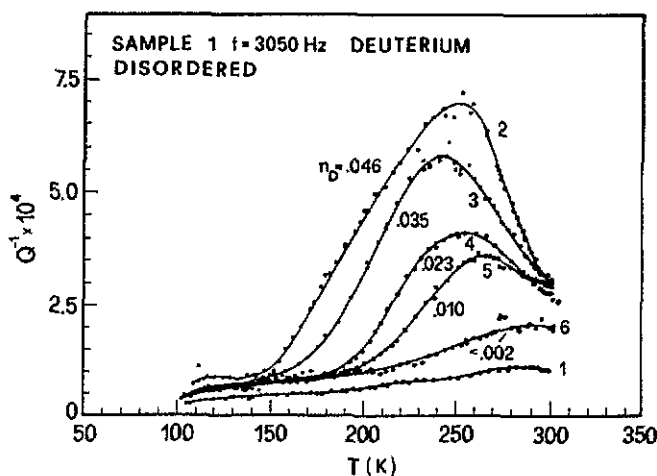


Figure 3. Elastic energy dissipation coefficient  $Q^{-1}$  against  $T$  taken for every successive partial desorption of the disordered sample which was initially deuterium loaded to  $n_D = 0.046$ .

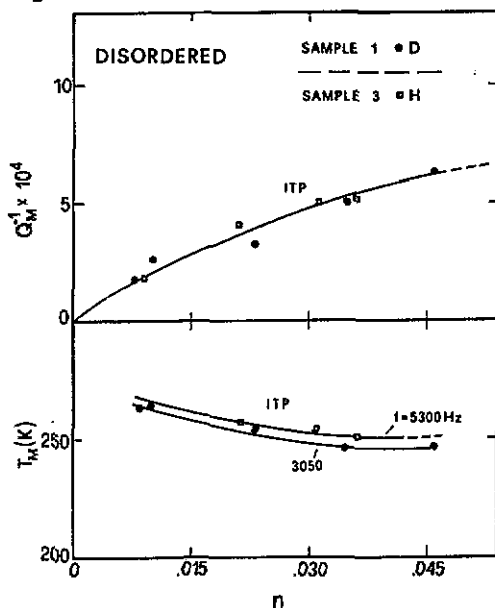


Figure 4. Concentration dependence (H, D) of the height and temperature of the ITP in the case of disordered samples.

with a decrease in the atomic ratio,  $n$ . Results similar to those in figure 3 have been obtained with a thicker sample (sample 3) charged with H.

The dependence of  $Q_M^{-1}$  and  $T_M$  on  $n$  is illustrated in figure 4; data for sample 3 were obtained during subsequent H absorptions. As can be seen,  $Q_M^{-1}$  increases non-linearly with  $n$ , and similarly to  $T_M$ , does not show any appreciable isotopic dependence. The IF behaviour of disordered and ordered (LPS) samples are shown in figure 5, where data taken in different specimens charged with H are compared. Three peaks are observed at about 120, 250 and 350 K in the sample having the LPS type of order, which are labelled LTP, ITP and HTP, respectively. Since the intermediate

temperature peak (ITP) overlaps the peak observed in the disordered state, it seems probable that they are both most likely due to the same structural mechanism. The higher temperature peak (HTP) does not seem to have a counterpart in the disordered material as shown in curve 1 of figure 5 where the measurements cover a more widely extended temperature range than those of figure 3.

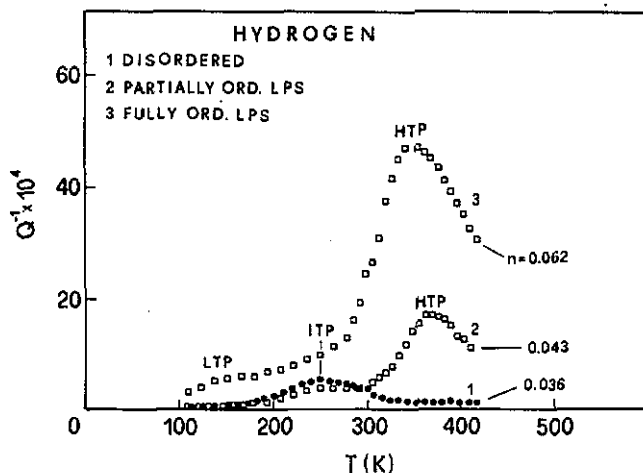


Figure 5. Internal friction of disordered (curve 1), partially ordered LPS (curve 2), and fully ordered LPS forms of the alloy (curve 3).

The ITP was not observed in another specimen which had been separately ordered to the LPS structure (curve 3, figure 5). Results similar to those found here for the LPS type of order have been obtained for the  $L1_2$  structure (Sobha *et al* 1991a, b). It is believed that the appearances of the ITP in the LPS and  $L1_2$  forms are related to an incomplete state of order and does not represent an intrinsic feature of these structures. It is known, for example, that it is difficult to fully order the LPS form (Rodic' *et al* 1991). The LTP, ITP and HTP peaks have been found to be associated with thermally activated relaxation processes whose activation energies  $W$  have been estimated to be 0.29, 0.53 and 0.74 eV, respectively (Sobha *et al* 1991a, b).

The widths of the two more well developed ITP and HTP are found to be greater than that for a theoretical Debye peak associated with a single relaxation time process as shown by figures 6 and 7, where the quantity  $Q^{-1}/Q_M^{-1}$  has been plotted as a function of the universal variable  $(W/k)(1/T - 1/T_M)$ . As can be seen in figure 6 the width of the ITP decreases with a decrease in the D content and is larger than the width of the HTP (figure 7) for comparable values of  $n_D$ .

#### 4. Discussion

Seven octahedral interstitial sites  $I_i$  can be distinguished in a Pd alloy according to the number  $i$  ( $i = 0, 1, \dots, 6$ ) of Pd atoms located in the first shell of the neighbours. Preferential occupancy by H can intuitively be expected of those sites exclusively or predominantly surrounded by Pd because H dissolves more easily in Pd than in Mn. Consistent with this expectation neutron diffraction studies of the ordered forms of  $Pd_3Mn$  alloy have demonstrated that H only occupies  $I_6$  and to a lesser extent  $I_5$  sites (Rodic' *et al* 1989, Rush *et al* 1989).

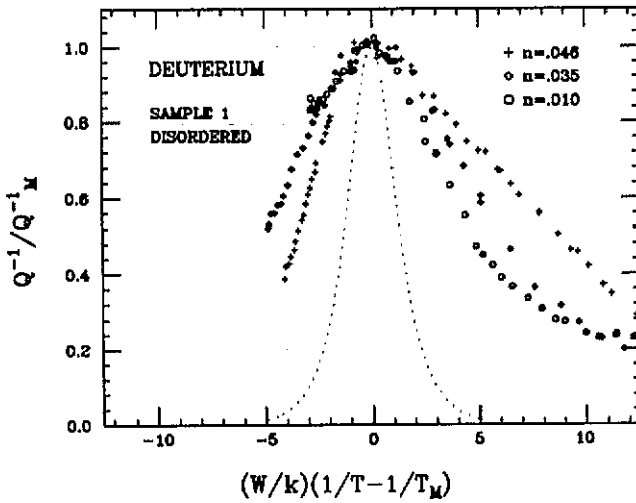


Figure 6. Comparison of normalized relaxation curves (ITP) at different deuterium contents with the theoretical Debye curve of a single-time relaxation process.

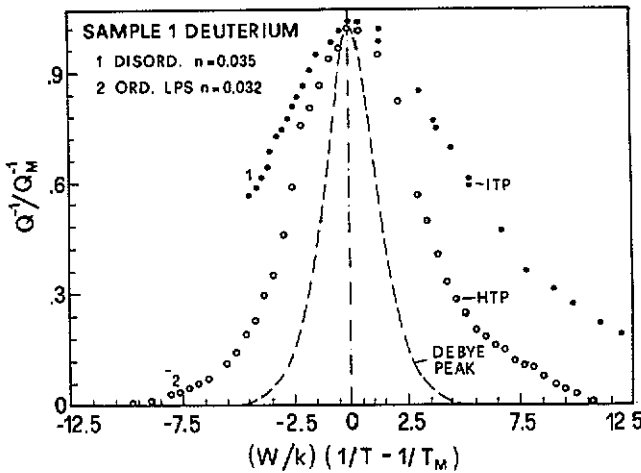


Figure 7. Comparison of normalized relaxation curves for cases of the ITP (disordered) and HTP (LPS ordered) at comparable deuterium contents.

#### 4.1. Solubility data

The main factors which affect the partial molar enthalpy  $\Delta H_H$  of solution of H in a ternary alloy are the site energies  $e_i$  and the H-H interaction. At infinite dilution when H-H interactions are negligible and when hydrogen occupies only the  $I_6$  sites, the partial molar enthalpy gives a measure of the site energy  $e_6$ , which according to the data in figure 2, strongly varies from one form to the other.

The atomic composition and distribution within the second and more distant shells of neighbours may affect  $e_6$  by altering the local electron density and the empty space available for H at the  $I_6$  sites (Salomons *et al* 1990). The average lattice parameter of pure Pd (0.3890 nm) is smaller than the parameters of the three  $Pd_3Mn$  alloys which are all very similar, i.e. 0.3900 nm (disordered), 0.3899 nm ( $AJ_3Zr$ -form) and

0.3901 nm ( $L1_2$ -form) (Flanagan *et al* 1992). The larger lattice parameters for the alloys can only partly account for their greater hydrogen solution exothermicity as compared with pure Pd. As a matter of fact the elastic contributions to changes of  $\Delta H_H$  on alloying as deduced from the formulae given by Salomons *et al* (1990) are much smaller than those observed experimentally. In view of the close coincidence of the lattice parameters, the electronic rather than the volume effect must also be responsible for differences of  $\Delta H_H$  amongst alloys.

The concentration dependences of  $\Delta H_H$  are expected to be mainly affected by preferential site occupancies and H-H interactions. A preferential site occupancy effect alone would predict substantially constant values of  $\Delta H_H$  during the early stages of  $I_6$  site filling and increases at values of  $n$  where the occupancy of other type of sites becomes significant. Clearly these features are not shown by the data, since the two ordered forms of the alloy display unexpected appreciable decreases of  $\Delta H_H$  at the lower values of  $n$  and steep increases for the disordered and the  $Al_3Zr$  ordered forms at values of  $n$  much smaller than expected from the concentrations of the available  $I_6$  sites (0.178 for the disordered form, 0.107 for the  $Al_3Zr$  ordered form). Thus H-H interactions play a major role in determining the concentration dependence of  $\Delta H_H$ .

The decrease of  $\Delta H_H$  with  $n$  in the early stages of H absorption is indicative of predominantly attractive long-range H-H interactions which are due to the lattice expansion caused by H. The subsequent increases with  $n$  observed in the disordered and the LPS ordered forms are associated with strongly concentration dependent short-range repulsive H-H forces, which are presumably electronic in nature.

In the disordered form the H-H repulsive interactions are important even at H concentrations as low as  $\approx 0.01$ , and rapidly increase becoming large enough to prevent any substantial absorption of H above  $n = 0.066$ . These H-H repulsive interactions would seem to arise from the presence of Mn atoms, since they are not present in pure Pd at such low H contents. In this disordered form the Mn atoms, thus, not only act as antitrapping entities by increasing the site energies, but also strongly enhance H-H repulsions and consequently the blocking capability of H atoms, as it will be discussed in detail in section 4.3.

#### 4.2. Internal friction

The relaxation processes associated with the LTP, ITP and HTP peaks have been attributed to the stress-assisted transitions  $I_6 \leftrightarrow I_5$ ,  $I_5 \leftrightarrow I_5$  and  $I_6 \leftrightarrow I_4$ , respectively (Sobha *et al* 1991b). As can be seen in figure 1,  $I_5 \leftrightarrow I_5$  transitions in the LPS structure do not lead to a reorientation of the  $I_5$  tetragonal dipole and these transitions cannot occur in the  $L1_2$  form since there are no  $I_5$  sites. The ITP is thus not expected to occur in these structures in agreement with the experimental findings. The results of a study of long-range diffusion of H using Gorsky relaxation (Sobha *et al* 1991a) support the interpretation of the relaxations given above. A close coincidence was found between the activation energy of the HTP (0.74 eV) and the activation energy for diffusion (0.78 eV) in the  $L1_2$  form. In the case of the LPS structure the activation energy for diffusion (0.46 eV) is found to be close to that of the ITP (0.53 eV). This observation, once the assignment of the ITP to  $I_5 \leftrightarrow I_5$  transitions is accepted, can be taken (Sobha *et al* 1991a) as evidence of a long-range diffusion process occurring over planes containing only  $I_5$  sites (see figure 1). The energy for diffusion in the disordered material is much smaller (0.38 eV) than that in the two ordered forms and is intermediate between those of the LTP (0.29 eV) and ITP (0.53 eV) peaks,



showing that in the disordered form the diffusion of H (D) mainly occurs through  $I_6$  and  $I_5$  sites as would be expected.

Although it is well known that a relaxation due to H-H complexes occurs in  $\alpha'$ -Pd hydride (Zener effect) (Mazzolai et al 1981, Leisure et al 1983), a mechanism of this type has not been considered for the peaks observed in the Pd<sub>3</sub>Mn alloys, because of the relatively low H (or D) concentrations involved and the repulsive H-Mn and H-H interactions, which enhance the randomness in the H (D) distribution.

#### 4.3. Dependence of the height of the ITP on the H (or D) content in the disordered form

The main observations in figure 4 are: (i)  $T_M$  decreases with increasing  $n$ ; (ii)  $Q_M^{-1}$  increases non-linearly with  $n$ . These features are also shown by an anelastic relaxation due to H (or D) in metal glasses (Berry and Pritchett 1989). Using Fermi-Dirac statistics we have recently developed a model (Coluzzi et al 1992) for relaxations due to H in FCC alloys employing the approximation that the symmetry properties are determined only by the atomic arrangements in the first coordination shell. According to this model the relaxation strength,  $S$ , of a single time process due to the reorientation of a tetragonal dipole,  $I_i$ , for the ultrasonic propagation mode  $C'$  in a single crystal is given by

$$S = 2Q_M^{-1} = \frac{2V^*}{3kT}(\lambda_1 - \lambda_2)^2 \pi'_{ii} \quad (2)$$

where  $V^*$  is the atomic volume of the alloy and where  $\lambda_1$  and  $\lambda_2$  are the principal components of the  $\lambda$  tensor associated with the tetragonal dipole  $I_i$ . The factor  $\pi'_{ii}$  represents the concentration of the tetragonal reorientable dipoles  $I_i$ , that is of dipoles that have as nearest neighbour at least one site of type  $I_i$  with its tetragonal axis differently oriented from that of the dipole. The factor  $\pi'_{ii}$  is given by

$$\pi'_{ii} = \alpha_i c_i q_{ii} f_i \quad (3)$$

In this relation,  $\alpha_i$  is the fraction of configurations that lead to dipole reorientation,  $c_i$  is the number  $n_i$  of H atoms on sites  $i$  divided by the total number  $M$  of interstitial sites,  $q_{ii}$  is the probability that a site close to a given dipole  $I_i$  is of type  $i$  and  $f_i$  is the probability that this site is not blocked by other H atoms. Following Brouwer et al (1988)  $c_i$  is given by

$$c_i = \frac{p_i}{s_i + \exp[(e_i - e_F)/kT]} \quad (4)$$

where  $p_i$  is the number of interstitial sites of type  $i$  divided by  $M$ ,  $e_F$  is a quantity that plays a role similar to the Fermi energy for electrons and  $s_i$  is a selective blocking factor indicating the number of sites of type  $i$  blocked by one H atom sitting in a site of type  $i$ . In the case that only nearest-neighbour sites are blocked by a H atom it follows that

$$s_i = 1 + q_{ii} Z \quad (5)$$

where  $Z$  is the number of sites in the first coordination shell ( $Z = 12$  in the case of a FCC lattice and octahedral sites).

The probability  $f_i$  that a site of type  $i$  is not blocked by any other H atom is given by

$$f_i = 1 - \frac{s_i c_i}{p_i} - Z \sum_{j \neq i} \frac{q_{ji} c_j}{p_i} \quad (6)$$

In disordered Pd<sub>3</sub>Mn where only I<sub>6</sub> and I<sub>5</sub> sites are likely to be occupied, the respective probabilities that a site I<sub>6</sub> or I<sub>5</sub> is blocked are given by

$$f_6 = 1 - \frac{s_6 c_6}{p_6} - \frac{Z q_{56} c_5}{p_6} \quad (7.1)$$

$$f_5 = 1 - \frac{s_5 c_5}{p_5} - \frac{Z q_{65} c_6}{p_5} \quad (7.2)$$

Saturation of sites I<sub>6</sub> and I<sub>5</sub> ( $f_5 = f_6 = 0$ ) is obtained for  $c_6^* = 0.007$  and  $c_5^* = 0.057$ , so that  $n \cong c_6^* + c_5^* = 0.064$ . This is in good accord with experimental results which have shown a maximum solubility of H in the disordered alloy of about 0.066.

The quantities  $p_i$  and  $q_{ij}$  in a random alloy can be calculated and depend only on the alloy composition (Coluzzi *et al* 1992); for the disordered alloy Pd<sub>3</sub>Mn,  $p_5$  and  $q_{55}$  are equal to 0.356 and 0.387, respectively.

In order to calculate  $c_i$  as a function of  $n$  the site energies  $e_i$  should be known. This is, however, not the case for the present alloy. Thus, a quantitative comparison of (2) with the experimental data in the upper part of figure 4 is not possible at the moment. The non-linear behaviour of  $Q_M^{-1}$  as a function of  $n$  can, however, be qualitatively accounted for. Thus, assuming that one H atom blocks its twelve nearest interstitial sites, relations (2), (3) and (6) predict that  $Q_M^{-1}$  passes through a maximum for  $c_i = c_{im} = p_i / 2s_i$ .

For  $i = 5$ ,  $s_i$  turns out to be equal to 4.8, equation (5) and  $c_{5m}$  equal to 0.037. Taking for  $c_6$  a value calculated from relation (7.1) and assuming that  $f_6 = 0$  and that  $c_5 = c_{5m}$ , then  $Q_M^{-1}$  would reach its maximum for  $n = 0.053$ . This expectation seems to be in agreement with the trends shown in figure 4.

Relation (2) is only precisely valid for a single crystal and the C' propagation mode and thus, is not immediately applicable to the present experiments. As discussed by Nowick and Berry (1972), however, the relaxation strength measured in polycrystalline material is, to a good approximation, proportional (proportionality constant equal to  $\frac{1}{5}$ ) to the relaxation strength given by (2). Thus, employment of relation (2) should be valid for interpretation of the present data.

#### 4.4. Dependence of the width and peak temperature on $n$ for the ITP in the case of the disordered form

There are two main sources for the spectrum of relaxation times associated with anelastic processes due to H (or D) in alloys. The first source has to do with the multiplicity of the interstitial sites available to H (or D), which may differ from one another depending upon the particular atomic arrangements in the nearest and in the more distant coordination shells. The second source is related to the H-H interactions.

If each of the observed relaxations is due to a well-defined transition, as would be expected for conditions of infinite dilution, a spectrum of relaxation times is related

to metal atom arrangements in the second and more distant shells of neighbours. For perfectly ordered alloys ( $LPS$  and  $L1_2$  forms) the atomic arrangement is unique, thus, at infinite dilution, the HTP should have a single relaxation time. On the other hand at finite H (or D) contents, a spectrum of times is expected which should arise from the presence of H-H interactions. This is consistent with the results in figure 7 which show a wider peak in the case of the disordered as compared with the ordered form. The broadening of the ITP for the lowest D content ( $n = 0.01$ ) in the disordered alloy compared with the single time relaxation curve in figure 6 would seem to be attributable to a distribution of the site energies associated with different atomic arrangements in the more distant coordination shells around an  $I_5$  site. The question now arises however as to whether the increase in width associated with an increase of  $n$  (figure 6) is due to D-D interactions or to an increase in the variety of D jumps due to the occupation of  $I_5$  sites associated with progressively higher energies. In the light of the present results from the solubility and IF data, the broadening of the ITP would seem likely to be due to the occupation of  $I_5$  sites with progressively higher site energies. Such a spectrum of energies of the  $I_5$  sites could arise, of course, from the different atomic arrangements in the second and more distant shells.

The shift of the peak towards lower temperatures shown in figure 4, as the H content is increased, could arise from a lowering of the energy barriers between adjacent  $I_5$  sites. This would lead to the important conclusion that the saddle-point energies are not as sensitive, as the site energies are, to the atomic arrangements in the more distant coordination shells. A possible explanation for this is that the saddle-point energy for an H atom, which hops between a two adjacent octahedral interstitial sites in an FCC lattice, is dominated by the three atoms at the centres of the faces sharing the same corner of the unit cell, and is thus not affected by the atomic distribution in the more distant shells. This would occur because of the relative closeness of the other atoms to the H in the saddle-point configuration.

## 5. Conclusions

The combined investigation of H solubility and IF carried out in this work has provided valuable information on hydrogen-hydrogen and hydrogen-metal atom interactions in the  $Pd_3Mn$  alloy. The concentration dependence of the partial molar enthalpy of H has revealed strong H-H repulsions in the disordered state of the alloy, which have received confirmation from the H concentration dependences of the height and width of the IF peak associated with the stress-induced reorientation of  $I_5$  tetragonal dipoles. With increasing H content,  $I_5$  sites of higher energy become occupied. The differences in the  $I_5$  site energies arise from differences in the atomic arrangements within the second and more distant coordination shells. Progressive site filling results in a broadening of the relaxation-time spectrum. The energies of  $I_5$  sites are more markedly affected by the atomic environment of the more distant shells than are the saddle-point energies. This results in diffusion jumps with lower activation energy with increasing  $n$  and consequently to a shift of the ITP peak towards lower temperatures.

## Acknowledgments

The authors acknowledge financial support from NATO. BS is grateful for a fellowship from ICTP in Trieste.

## References

- Ahlzen P J, Andersson Y, Tellgren R, Rodic' D, Flanagan T B and Sakamoto Y 1989 *J. Phys.: Condens. Matter* **1** 5095
- Atkins P W 1986 *Physical Chemistry* (New York: Freeman)
- Baba K, Niki Y, Sakamoto Y, Flanagan T B and Craft A 1987 *Scr. Metall.* **21** 147
- Baba K, Niki Y, Sakamoto Y, Kraft A P and Flanagan T B 1988 *J. Mater. Sci. Lett.* **7** 1160
- Berry B S and Pritchett W C 1989 *Z. Phys. Chem.* **163** 381
- Brouwer A C, Salomons E and Griessen R 1988 *Phys. Rev. B* **38** 10217
- Clewley J D, Curran T, Flanagan T B and Oates W A 1973 *J. Chem. Soc. Faraday Trans.* **69** 449
- Coluzzi B, Costa C, Biscarini A and Mazzolai F M 1992 *J. Phys.: Condens. Matter* **4** 53
- Flanagan T B, Craft A P, Kuji T, Baba K and Sakamoto Y 1986 *Scr. Metall.* **20** 1745
- Leisure R G, Kanashiro T, Riedi P C and Hsu D K 1983 *Phys. Rev. B* **27** 4872
- Mazzolai F M, Bordoni P G and Lewis F A 1981 *J. Phys. F: Met. Phys.* **11** 337
- Nowick A S and Berry B S 1972 *Anelastic Relaxations in Crystalline Solids* (New York: Academic)
- Rodic' D, Ahlzen P G, Andersson Y and Tellgren R 1989 *Solid State Commun.* **71** 623
- Rodic' D, Ahlzen P J, Andersson Y, Tellgren R and Bouree-Vigneron F 1991 *Solid State Commun.* **78** 767
- Rush J J, Flanagan T B, Craft A P, Clewley J D and Sakamoto Y 1989 *J. Phys.: Condens. Matter* **1** 5095
- Salomons E, Hemmes H and Griessen R 1990 *J. Phys.: Condens. Matter* **2** 817
- Sobha B, Coluzzi B, Costa C, Mazzolai F M, Flanagan T B and Sakamoto Y 1991a *J. Less-Common Met.* **172** 262
- Sobha B, Coluzzi B, Mazzolai F M, Flanagan T B and Sakamoto Y 1991b *J. Less-Common Met.* **172** 254