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## Diffusivity of H and D in palladium–platinum alloys via Gorsky relaxation

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**Abstract.** The macroscopic diffusion coefficient of H and D has been measured using Gorsky relaxation in the temperature range 225–350 K for H (D) atomic ratios  $n = 0.03$  and  $n = 0.29$ , where  $n = H(D)/(Pd+Pt)$ . The data are analysed in terms of a diffusion model originally proposed by Griessen and co-workers, which has been adapted to apply to FCC alloys. The site energy calculations show that in the Pd<sub>85</sub>Pt<sub>15</sub> alloy only  $I_6$  and, to a minor extent,  $I_5$  sites are occupied and contribute to diffusion in the temperature range investigated. A match of Gorsky and Zener relaxation data indicates the existence of an upwards deviation in the diffusion coefficient when plotted against  $1/T$ . This deviation cannot be accounted for by classical diffusion models.

### 1. Introduction

Recently, hydrogen diffusion in alloys has attracted considerable attention, and a substantial amount of work has been done both theoretically and experimentally. Among other achievements, statistical models have been developed that can now provide a better understanding of macroscopic observations in terms of microscopic hopping transitions and site occupancies (Kirchheim 1982, Brouwer *et al* 1988, 1989, Brouwer and Griessen 1989). A promising way to test such models, or to use them to understand H–metal atom interactions, is to apply combined investigation techniques that are sensitive to the single microscopic jump processes and to collective long-range diffusion, respectively (Sobha *et al* 1991a,b). It is well known that anelastic techniques are suitable for investigating symmetry properties of lattice defects and, consequently, atomic arrangements around the octahedral sites occupied by H, thus proving to be particularly useful for studying alloy systems. These techniques are usually only able to monitor local motions of H taking place over one or a few atomic distances. However, one anelastic relaxation exists (the Gorsky relaxation) that can also probe long-range diffusion of H under applied stresses that cause strains ( $\epsilon_{ij}$ ) associated with a non-vanishing gradient of the dilation  $\delta$  ( $\delta = \epsilon_{11} + \epsilon_{22} + \epsilon_{33}$ ) (Schaumann *et al* 1968, 1970, Völkl 1972, Cantelli *et al* 1969, 1973). Besides the dynamic aspects of the H behaviour, the relaxation strength of this anelastic effect can also provide information on thermodynamic properties of metal–H systems, in particular on H–H interactions.

An anelastic study has been undertaken on PdPt alloys involving ultrasonic and internal friction (IF), as well as elastic-after-effect experiments, respectively designed

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to investigate local motions of H and to detect Gorsky relaxation. These new investigations follow some previous preliminary work, which had revealed the existence of a well developed internal friction peak at low temperatures (Mazzolai *et al* 1987).

The data concerning ultrasonic experiments are reported elsewhere (Coluzzi *et al* 1991), as well as some new low-frequency IF results obtained at temperatures lower than 100 K (Coluzzi *et al* 1992). Here, only high-temperature data ( $T > 225$  K) on Gorsky relaxation will be discussed.

## 2. Experimental procedure

The elastic after-effect due to long-range diffusion of H and D was monitored after removal of a bending stress applied to a specimen in the cantilever configuration. The displacements were measured as a function of time at constant temperature by using a General Radio capacitance bridge (model 1615-A), with a sensitivity high enough to reveal displacements of less than  $1 \mu\text{m}$ . The average bending strain  $\langle \epsilon \rangle$ , which is given by

$$\langle \epsilon \rangle = dh/l^2 \quad (1)$$

was found to have values of the order of  $10^{-5}$ . In relation (1),  $d$  is the displacement of the free end of the sample,  $h$  the thickness and  $l$  the free length.

The specimen was a thin bar of dimensions  $0.14 \times 22 \times 3 \text{ mm}^3$ , which was prepared by cold-rolling a slab cut from the  $\text{Pd}_{85}\text{Pt}_{15}$  single crystal supplied by Materials Research and used in the ultrasonic experiments. After annealing *in vacuo* ( $p = 4 \times 10^{-4} \text{ Pa}$ ) at  $800^\circ\text{C}$ , the sample was electrolytically loaded with H or D at room temperature. The H and D contents  $n$ , where  $n = \text{H(D)}/(\text{Pd}+\text{Pt})$  atomic, were monitored through weight changes before and after electrolysing, as well as between consecutive measurement runs. Within the limits of the experimental accuracy ( $\delta n = \pm 0.003$ ) these checks did not reveal any appreciable losses of H or D.

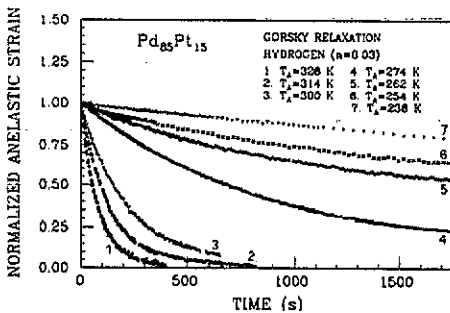


Figure 1. Isothermal normalized strain relaxation curves associated with the Gorsky effect due to hydrogen.

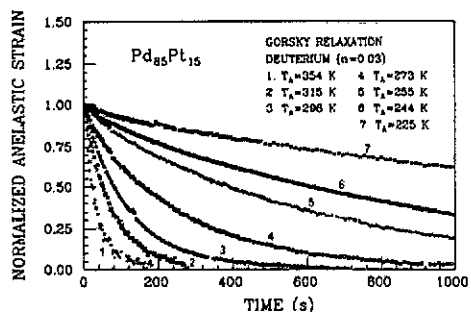


Figure 2. The same as in figure 1, but for deuterium.

### 3. Results

Normalized strain relaxation curves of the Gorsky effect due to H and D are displayed in figures 1 and 2, respectively. The temperature range spanned is approximately 225–350 K, and the relaxation times fall between about 30 and 5000 s. Within the limit of experimental error the strain relaxation curves are exponential. A comparable content ( $n = 0.03$ ) was used for both H and D in order to check for isotopic effects. In the case of H, data were also taken at a value of  $n$  ( $n = 0.29$ ) equal to that used in the ultrasonic and internal friction experiments. The strain curves are similar to those of figures 1 and 2 and are omitted. The expected critical content  $n_c$  and temperature  $T_c$  for this alloy are about 0.08 and 225 K, respectively (Carson *et al* 1960). Thus, the sample was in a single homogeneous phase over the entire temperature range of the present measurements.

#### 3.1. Relaxation strength

The theory of hydrogen density fluctuations developed by Wagner and Horner (1974), Horner and Wagner (1974), Bausch *et al* (1975) and Wagner (1978) predicts that the relaxation strength  $S_m$  of the Gorsky effect depends on the density mode, determined by the applied stress, the shape and the orientation of the crystal according to a relation of the type

$$S_m = \frac{R_m E_m}{a(T, \bar{\rho}) - E_m}. \quad (2)$$

Here the index  $m$  denotes the macroscopic density mode (foil and wire bending modes will be identified with indices  $f$  and  $w$ , respectively),  $\bar{\rho} = 4n/a^3$  is the average number of H atoms per unit volume,  $a$  is the lattice parameter,  $R_m$  and  $E_m$  are quantities depending on the elastic constants  $C_{lk}$  and on the trace  $3P$  of the elastic dipole moment tensor  $P_{lk}$  (Horner and Wagner 1974), and  $a(T, \bar{\rho})$  is a coefficient that appears in the series expansion in powers of  $\tilde{\rho}$  ( $\tilde{\rho} = \bar{\rho} - \rho(x)$ ) of the minimum total work  $\Delta F$  required to alter the H density at any position  $x$  from the value  $\bar{\rho}$  to the value  $\rho(x)$ . Under the limiting conditions discussed by Wagner (1978), relation (2) can be approximated by

$$S_m = S_0(\bar{\rho}) \frac{R_m E_m}{T - T_m} \quad (3)$$

which shows a temperature dependence approximately of the Curie–Weiss type;  $T_m$  is the spinodal temperature relative to mode  $m$ .

The strength  $S_f$  of the process was deduced from the strain relaxation curves of our foil-shaped sample as the ratio of the anelastic (time-dependent) and the elastic (instantaneous) strains.  $S_f$  could only be determined for the higher H content ( $n = 0.29$ ) and was found to increase with decreasing temperature. A fit of the data to a Curie–Weiss type of temperature dependence gave  $T_f = 190 \pm 25$  K. The mean value of  $S_f$  for atomic per cent (at.%) of H was found to be  $0.6 \times 10^{-2}$ .

#### 3.2. Macroscopic diffusion coefficient

According to the theory of density fluctuations the mode dependent effective (macroscopic) diffusion coefficient  $D_m^*$  is related to the mobility  $M(T, \bar{\rho})$  by the expression

$$D_m^* = \bar{\rho} M(T, \bar{\rho}) [a(T, \bar{\rho}) - E_m]. \quad (4)$$

Using the well known Einstein relation between the tracer diffusion coefficient  $D^+$  and the mobility

$$D^+ = k_B T M(T, \bar{\rho}) f_c(\bar{\rho}) \quad (5)$$

as well as expression (2) for the relaxation strength, we get

$$D^+ = D_m^* \{k_B T / \bar{\rho} [a(T, \bar{\rho}) - E_m]\} f_c(\bar{\rho}) = D_m^* (k_B T S_m / \bar{\rho} R_m E_m) f_c(\bar{\rho}). \quad (6)$$

In the above relations  $k_B$  is the Boltzmann constant and  $f_c$  is the correlation factor, which accounts for the higher probability for a jumping atom to return to its original position rather than to proceed by random diffusion (Murch 1982). For diffusion of interstitials this factor only depends weakly on  $\bar{\rho}$  and its value is expected to be only slightly smaller than one (Hempelmann *et al* 1988, Potzel *et al* 1984). To a first approximation in the following analysis of the data  $f_c$  will be taken as unity. To investigate the concentration dependence of the individual hopping transitions of H and D atoms, it is convenient to introduce the reduced diffusion coefficient  $D_r$ , defined as

$$D_r = D^+ / (1 - n) \quad (7)$$

where the factor  $1 - n$  represents the probability of finding empty the arrival site for the hopping atom. It can be seen from (6) and (7) that the simultaneous measurements of  $D_m^*$  and  $S_m$  can provide the mode-independent reduced diffusion coefficient  $D_r$ . For the bending mode of a foil the following relation holds (Wagner 1978) between  $D_r^*$  and the relaxation time  $\tau_G$  of the Gorsky effect

$$D_r^* = h^2 / (10\tau_G). \quad (8)$$

The values of  $D_r^*$  measured for H and D are compared in figure 3, where a reverse isotopic effect is observed similar to that displayed by the H and D macroscopic diffusion coefficients  $D_w^*$  associated with the bending mode of a wire in the  $\alpha$ -phase of the Pd-H(D) system (Völkl *et al* 1971), which are also shown in figure 3. The effective diffusion coefficient for H at  $n = 0.03$  is lower than at  $n = 0.29$ , as shown in figure 4. An increase of the diffusion coefficient with concentration has also been observed in a Pd<sub>75</sub>Ag<sub>25</sub> alloy containing deuterium for atomic ratios  $n \leq 0.30$  (Hickman 1969). Possible sources of such an increase are the interstitial-interstitial interactions and/or the lattice expansion induced by H or D.

The values of the product  $R_r E_r$  in (6) have been calculated for the two orientations of a foil-shaped single crystal subjected to a bending torque examined by Bausch *et al* (1975). The value 9.9 eV was used for the trace  $3P$  of the H dipole moment tensor as obtained from the following relation:

$$\Delta a/a = 4n P/a^3 (C_{11} + 2C_{12}) \quad (9)$$

where the elastic constants  $C_{ik}$  were taken from Coluzzi *et al* (1989), while the relative volume change  $\Delta a/a$  for at.% of H was deduced from density measurements and turned out to be  $5.7 \times 10^{-4}$ . The two calculated values of  $R_r E_r$  are close to each other (their ratio is 1.36 (or 0.73)), and their average value ( $R_r E_r = 0.102 \times 10^{-11} P^2$ ) has been taken to calculate  $D_r$  from relations (6) and (7). The results

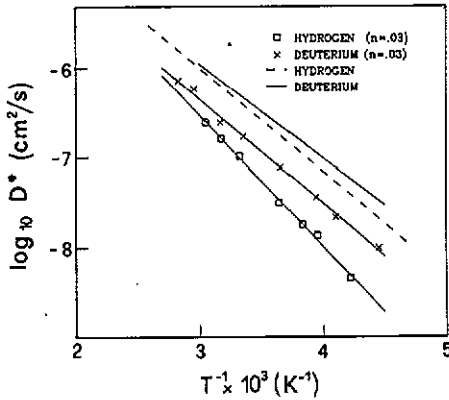


Figure 3. Macroscopic diffusion coefficients  $D_f^*$  ( $\times$ ,  $\square$ ) for  $Pd_{85}Pt_{15}$  alloy and  $D_w^*$  (—, —) for pure Pd taken from Völkl *et al* (1971).

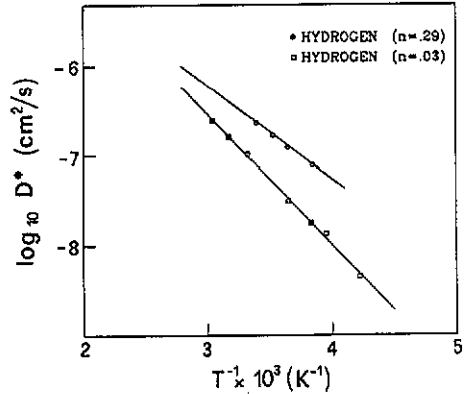


Figure 4. Comparison between effective diffusion coefficients  $D_f^*$  at  $n = 0.03$  and  $n = 0.29$ .

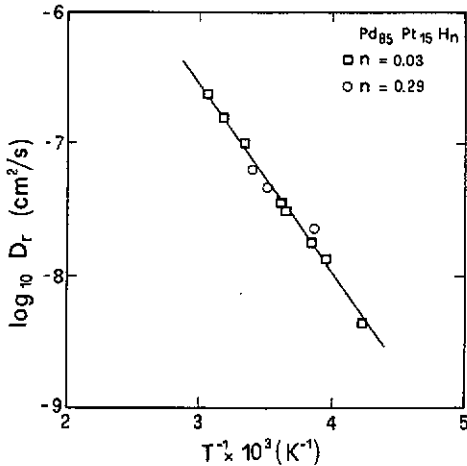


Figure 5. Comparison between  $D_f^*$  for  $n = 0.03$  and  $D_r$  for  $n = 0.29$ .  $D_r$  has been calculated using relations (6) and (7) in the text and data in figure 4.

obtained for  $n = 0.29$  are shown in figure 5, where the values  $D_f^*$  at  $n = 0.03$  are also plotted. The two sets of data are in close coincidence, thus indicating a weak concentration dependence of the H mobility  $M(T, \bar{p})$ . Actually, a linear fit through the experimental points would give an activation energy lower for  $D_r$  ( $n = 0.29$ ) than for  $D_f^*$  ( $n = 0.03$ ). However, the estimate of the spinodal temperature is not accurate enough to allow final conclusions to be derived from this comparison.

It is of interest to compare the data in figure 5 with those for  $D_r$  deduced from the relaxation time  $\tau_z$  of the Zener effect (Mazzolai *et al* 1980, 1981, Leisure *et al* 1983) by using the following relation (Mazzolai and Züchner 1981)

$$\tau_z = Ea^2/[12D_r(1 - n)]. \tag{10}$$

Here  $E$  is a proportionality constant, which is expected to be of the order of unity, but which is actually not exactly known. The two sets of data could be matched assuming

for  $E$  the value 1.75. As can be seen, the combined plot seems to indicate the existence of a deviation from a single-exponential behaviour, as previously reported for the Pd  $\alpha'$ -hydride (Mazzolai and Züchner 1981), for which data are also shown in figure 6. Unfortunately, the information available so far is confined to temperatures higher than 110 K, making the deviation not as well evidenced as for the Pd  $\alpha'$ -hydride. In a preceding paper, when only data on the Zener effect were available, the experimental points have been fitted to a single straight line (Coluzzi *et al* 1991), giving an activation energy for diffusion of 0.24 eV.

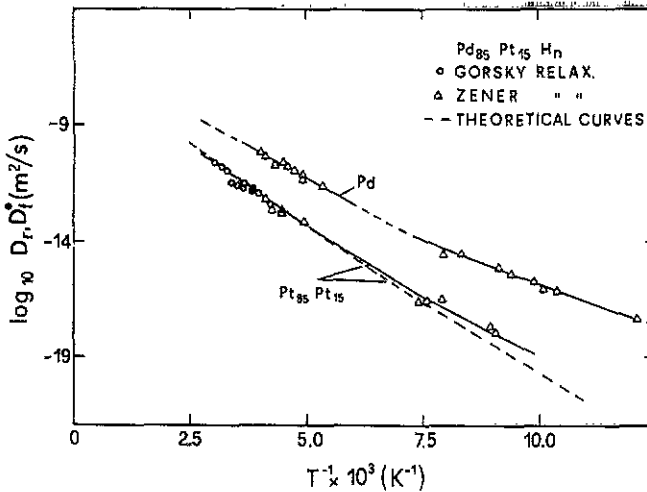


Figure 6. Comparison between the experimental data of figure 5 (O) and the values of  $D_r$  calculated from relation (11) in the text (---). The diffusion parameters were:  $W_{Pd} = 0.245$  eV,  $W_{Pt} = 0.46$  eV,  $D_{Pd}^0 = 2.7 \times 10^{-7}$  m<sup>2</sup> s<sup>-1</sup>,  $D_{Pt}^0 = 8.4 \times 10^{-6}$  m<sup>2</sup> s<sup>-1</sup>; ( $\Delta$ ) data from the Zener effect.

#### 4. Discussion

In the following discussion use will be made of a model similar to that originally developed by Griessen and co-workers (Griessen 1986, Brouwer *et al* 1988, 1989) for BCC alloys. According to this model, the reduced diffusion coefficient  $D_r$  can be expressed in terms of quantities related to the interstitial sites  $I_i$ , assumed to differ from each other only in the number  $i$  ( $i = 0$  to 6) of Pd atoms in their first coordination shell.  $D_r$  is given by

$$D_r = \frac{1}{(1-n)n} \sum_i \sum_j D_{ij}^0 c_i q_{ij} \left(1 - \frac{c_j}{p_j} s_j\right) \exp\left(-\frac{E_{ij}}{k_B T}\right). \quad (11)$$

Here  $E_{ij}$  is the activation energy for diffusion from an interstitial site of type  $i$  to one of type  $j$ ,  $q_{ij}$  is the probability of finding a site of type  $j$  next to a site of type  $i$ ,  $p_j$  is the number  $m_j$  of interstitial sites of type  $j$  divided by the total number of interstitial sites  $N$ ,  $s_j$  is a selective blocking factor indicating the number of sites of type  $j$  blocked by one H atom sitting in a site of type  $j$ ,  $D_{ij}^0$  are diffusion constants

Table 1. Site energies calculated from the embedded cluster model.

$i$	0	1	2	3	4	5	6
$e_i$ (eV)	0.54	0.43	0.31	0.20	0.10	0.00	-0.10

depending on the type of sites involved in an H jump, and  $c_i$  is the number  $n_i$  of interstitial atoms on sites of type  $i$  divided by  $N$ ;  $c_i$  is given by

$$c_i = \frac{p_i}{\llbracket s_i + \exp\{[e_i + f(n) - \mu]/k_B T\} \rrbracket} \quad (12)$$

where  $e_i$  is the site energy,  $f(n)$  is an effective interstitial-interstitial interaction and  $\mu$  the chemical potential of H.

The site energies can reliably be deduced from p-n-T isotherms (Feenstra *et al* 1988, Salomons *et al* 1990a,b), which are, however, not available for PdPt alloys over a wide enough temperature range. These quantities have thus been calculated following a procedure developed by Griessen (1986) and Brouwer and Griessen (1989), which assimilates the first coordination shell of an interstitial site to a cluster of composition  $\text{Pd}_i\text{Pt}_{6-i}$  embedded in a matrix of average composition  $\text{Pd}_{1-y}\text{Pt}_y$ , by using the relation

$$e_i(y) = e_i^* - (BV_H/V_m)[\Omega_i(y) - \Omega_i^*] \quad (13)$$

The site energy  $e_i^*$  of the free cluster, that is a cluster located in an alloy with average composition identical to that of the cluster itself, has been deduced from relation (13) of Brouwer and Griessen (1989), taking for the quantities related to the electronic band structure of Pd and Pt the values given by Griessen and Driessen (1984a) and by Andersen (1970) and for the bulk modulus  $B$ , the molar volume  $V_H$  of H in solution and the molar volume  $V_m$  of the alloy the values measured in the course of the present experiments:  $B_{290} = 2.027 \times 10^{11}$  Pa,  $V_H = 1.3 \text{ cm}^3 \text{ mol}^{-1}$  H and  $V_m = 8.9 \text{ cm}^3 \text{ mol}^{-1}$ . The molar volume  $\Omega_i(y)$  of the embedded cluster has been deduced from that ( $\Omega_i^*$ ) of the free cluster by using the following relation (Brouwer and Griessen 1989):

$$\Omega_i(y) = (1-d)\bar{\Omega}(y) + d\Omega_i^* \quad (14)$$

where  $\bar{\Omega}(y)$  is the average cluster volume in the alloy and  $d$  a parameter that represents the force constant between nearest-neighbour atoms. This parameter has been calculated, for an FCC alloy and for octahedral site occupancy by H, following a procedure similar to that of Brouwer and Griessen (1989), which is outlined in the appendix. The obtained expression for  $d$  is

$$d = 0.812I' \quad (15)$$

where  $I'$  is a quantity that measures the average deviations of the mean lattice spacings in an alloy. A value of 0.31 was estimated for this parameter from figure 1 of Froyen and Herring (1981) using our elastic constant data (Coluzzi *et al* 1989). The site energies calculated from (13) are found to change linearly with the number of Pt atoms in the cluster, as shown in table 1 and in the lower part of figure 7. The difference between the site energies of  $\text{Pd}_5\text{Pt}_1$  and  $\text{Pd}_6\text{Pt}_0$  is found to be 0.10 eV, which compares favourably with a previous estimate of 0.11 eV made by Griessen and Driessen (1984b). The calculated site energy  $e_6$  (-0.104 eV) is in close coincidence with the enthalpy of H solution,  $\Delta H$ , for  $\text{Pd}_{35}\text{Pt}_{15}$  alloy as deduced from data by Clewley *et al* (1977) ( $\Delta H \simeq -0.096$  eV) at infinite dilution of H.



In order to get a complete picture of the H diffusion in an alloy, the matrix of the saddle-point energies  $Q_{ij}$  has to be determined. To a first approximation, the two diagonal elements  $Q_{66}$  and  $Q_{00}$  can be taken as the sum  $e_6 + W_{Pd}$  and  $e_0 + W_{Pt}$  of the site and the diffusion energies of H in Pd and Pt, respectively. The values 0.23 and 0.46 eV have been assumed as the best estimates of  $W_{Pd}$  (Völkl and Alefeld 1975) and  $W_{Pt}$  (Yoshihara and McLellan 1986), as indicated in the lower part of figure 7.  $Q_{66}$  and  $Q_{00}$  turn out to be appreciably different from each other, contrary to what happens for the couple Nb and V (Brouwer et al 1988). To a first approximation, the remaining diagonal elements can be estimated by assuming a linear dependence on  $i$  of  $Q_{ii}$ , between the extreme values  $Q_{66}$  and  $Q_{00}$ , as indicated again in the lower part of figure 7. For  $i \neq j$  an intermediate value between  $Q_{ii}$  and  $Q_{jj}$  is taken for  $Q_{ij}$ . From the  $Q_{ij}$  and the  $e_i$ , the diffusion barriers  $E_{ij}$  are obtained; the resulting energy scheme is shown in the upper part of figure 7.

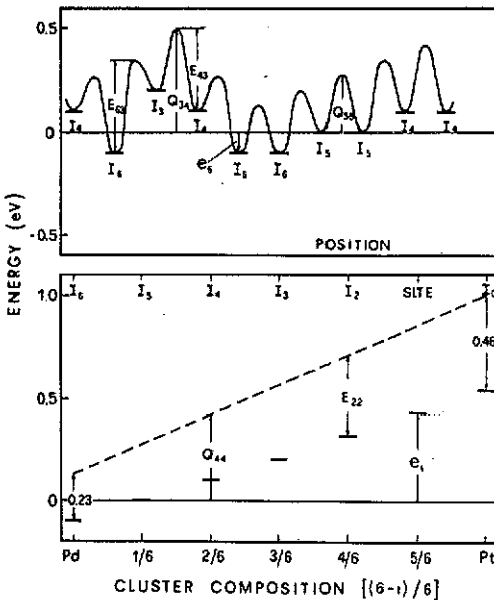


Figure 7. Site ( $e_i$ ) and saddle-point ( $Q_{ij}$ ) energies and activation energies ( $E_{ij}$ ) for H diffusion in the  $Pd_{85}Pt_{15}$  alloy are shown in the lower part of the figure. The  $e_i$  are calculated assimilating the first coordination shell of an interstitial site to a cluster embedded in the  $Pd_{85}Pt_{15}$  alloy. The  $Q_{ij}$  were obtained from a linear interpolation between the known extreme values  $Q_{66} = 0.13$  eV (Pd) and  $Q_{00} = 1.0$  eV (Pt). The upper part of the figure shows the energy scheme constructed with the values of  $e_i$ ,  $Q_{ij}$  and  $E_{ij}$ .

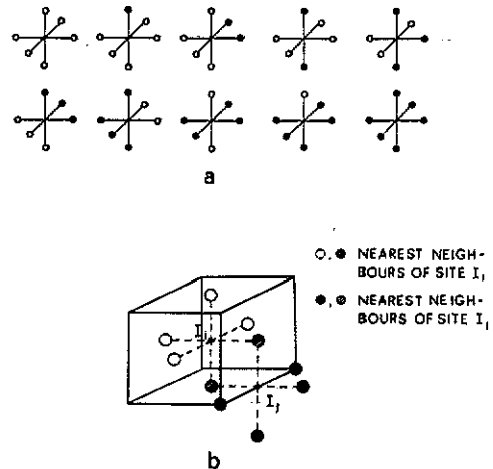


Figure 8. (a) Distinguishable interstitial octahedral sites in an FCC binary alloy AB: (○) atom of type A, (●) atom of type B. (b) Pair of nearest-neighbour octahedral interstitial sites,  $I_i$  and  $I_j$ , and associated first coordination shells sharing the two hatched atoms.

Unlike the case of the BCC alloys NbV and TiV, in the PdPt system filling of progressively higher energy sites results in an increase of the activation energy for diffusion and, consequently, in a decrease of the diffusion coefficient. Thus, the higher values of  $D^*$  observed in figure 4 at  $x = 0.29$  cannot be associated with a site filling

process.

In order to use relation (9), the probabilities  $q_{ij}$  of finding a site of type  $j$  next to one of type  $i$  have been calculated for a binary FCC alloy  $A_{1-y}B_y$ . As shown in figure 8(a), 10 distinguishable arrangements of the two types of atoms in the first coordination shell are allotted (Hohler and Kronmüller 1982) and a pair of nearest-neighbour (NN) sites share two of their six NN atoms, as indicated in figure 8(b) (hatched circles). Thus, given a site  $I_i$ , the type of  $I_j$  is determined by the nature of its remaining four NN atoms (full circles). The  $q_{ij}$  values have been calculated taking into account the 10 possible configurations of figure 8(a) and are given as a function of Pt content in table 2.

The fractions of the occupied sites  $c_i$  have been determined by inserting in (12) the values of  $p_i$  deduced from the binomial formula and assuming the selective blocking factors  $s_i$  to be unity. This assumption appears reasonable for Pd, where limiting concentrations close to one can be obtained. In the  $Pd_{85}Pt_{15}$  alloy the maximum amount of H that can be loaded by electrolysis is lower and corresponds to an atomic ratio of about 0.54. This reduction in the absorption capability results from site filling difficulties, rather than from blocking effects. The unknown quantity  $f(n)-\mu$  has been used as a normalizing parameter to fulfil the condition  $\sum_i c_i = n$ . The results of these calculations show that, in the temperature range of the present measurements, only  $I_6$  and, to a lesser extent,  $I_5$  sites are occupied. This result, combined with the previous estimates of the saddle-point energies, leads to the conclusion that in the sum in relation (11) the overwhelming contributions come from the  $I_6-I_6$  and  $I_6-I_5$  jumps.

The site-dependent diffusion constants  $D_{ij}^0$  in (11) have been estimated from those of Pd ( $D_{Pd}^0 = 2.9 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ ) (Völkl and Alefeld 1975) and Pt ( $D_{Pt}^0 = 8.4 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ ) (Yoshihara and McLellan 1986), according to the following averaging formula:

$$D_{ij}^0 = D_{Pd}^0(i+j)/12 + D_{Pt}^0[12 - (i+j)]/12 \quad (16)$$

and are found to differ appreciably from each other.

The reduced diffusion coefficient has been deduced from relation (11) by using  $W_{Pd}$  and  $D_{Pd}^0$  as fitting parameters ( $D_r$  is relatively insensitive to  $D_{Pt}^0$  and  $W_{Pt}$ ). A good fit to the high temperature data is obtained (figure 6) with  $W_{Pd} = 0.245 \text{ eV}$  and  $D_{Pd}^0 = 2.7 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$ . Within the limits of the experimental uncertainty these values coincide with those reported in the literature (Völkl and Alefeld 1975).

At lower temperatures an upwards deviation from the theoretical curve is indicated by the experimental points. This aspect is still under investigation and seems likely to be due to quantum effects, which will be discussed elsewhere (Coluzzi *et al* 1992).

This deviation does not seem to be related to the multiplicity of jumps and sites available in the alloy, since it is also observed in the pure Pd  $\alpha'$ -hydride (Mazzolai and Züchner 1981), or to the fact that Gorsky and Zener relaxations may monitor different processes. Namely, in the case of Pd the deviation is seen even when only data for the Zener effect are used, as shown in figure 6. We draw attention to the close phenomenological similarity of the deviation discussed here and that more widely known to occur in the diffusion coefficient of Nb and Ta (Qi *et al* 1983). It seems likely that they have the same origin.

Table 2. Probability  $q_{ij}$  of finding an octahedral site of type  $j$  as nearest neighbour of site of type  $i$  for FCC binary alloys.

$i \setminus j$	6	5	4	3	2	1	0
6	$(1-y)^4$	$4(1-y)^3y$	$6(1-y)^2y^2$	$4(1-y)y^3$	$y^4$	0	0
5	$\frac{2}{3}(1-y)^4$	$\frac{1}{3}(1-y)^4 + \frac{8}{3}(1-y)^3y$	$\frac{4}{3}(1-y)^3y + 4(1-y)^2y^2$	$2(1-y)^2y^2 + \frac{2}{3}(1-y)y^3$	$\frac{2}{3}y^4 + \frac{1}{3}(1-y)y^3$	$\frac{1}{3}y^4$	0
4	$\frac{2}{3}(1-y)^4$	$\frac{8}{3}(1-y)^4 + \frac{8}{3}(1-y)^3y$	$\frac{15}{3}(1-y)^4 + \frac{12}{3}(1-y)^3y + \frac{12}{3}(1-y)^2y^2$	$\frac{15}{3}(1-y)^3y + \frac{12}{3}(1-y)^2y^2 + \frac{6}{3}(1-y)y^3$	$\frac{2}{3}y^4 + \frac{12}{3}(1-y)y^3 + \frac{2}{3}(1-y)^2y^2$	$\frac{10}{3}y^4 + \frac{1}{3}(1-y)y^3$	0
3	$\frac{1}{2}(1-y)^4$	$\frac{3}{2}(1-y)^4 + \frac{1}{2}(1-y)^3y$	$\frac{11}{2}(1-y)^4 + \frac{12}{2}(1-y)^3y + \frac{6}{2}(1-y)^2y^2$	$\frac{1}{2}(1-y)^3y + \frac{18}{2}(1-y)^2y^2 + \frac{5}{2}(1-y)y^3$	$\frac{1}{2}y^4 + \frac{12}{2}(1-y)y^3 + \frac{6}{2}(1-y)^2y^2$	$\frac{2}{3}y^4 + \frac{1}{3}(1-y)y^3$	$\frac{1}{3}y^4$
2	$\frac{1}{12}(1-y)^4$	$\frac{1}{12}(1-y)^4y + \frac{8}{12}(1-y)^3y$	$\frac{2}{3}(1-y)^4 + \frac{12}{3}(1-y)^3y + \frac{3}{3}(1-y)^2y^2$	$\frac{8}{3}(1-y)^3y + \frac{18}{3}(1-y)^2y^2 + \frac{12}{3}(1-y)y^3$	$\frac{1}{3}y^4 + \frac{12}{3}(1-y)y^3 + \frac{3}{3}(1-y)^2y^2$	$\frac{10}{12}y^4 + \frac{1}{6}(1-y)y^3$	$\frac{2}{3}y^4$
1	0	$\frac{1}{3}(1-y)^4$	$\frac{2}{3}(1-y)^4 + \frac{1}{3}(1-y)^3y$	$\frac{5}{3}(1-y)^3y + 2(1-y)^2y^2$	$\frac{4}{3}(1-y)^2y^2$	$\frac{1}{3}y^4 + \frac{2}{3}(1-y)y^3$	$\frac{2}{3}y^4$
0	0	0	$(1-y)^4$	$4(1-y)^3y$	$6(1-y)^2y^2$	$4(1-y)y^3$	$y^4$

## 5. Conclusions

Long-range diffusion has been investigated for the first time by Gorsky relaxation in the  $\text{Pd}_{85}\text{Pt}_{15}$  alloy over a relatively wide temperature range. This technique has proved to be particularly useful for testing the diffusion model developed by Griessen and co-workers for alloys. The Griessen model has been extended to FCC alloys, for which the quantities needed have been calculated for the first time. It is found that the high-temperature data for the reduced diffusion coefficient can be accounted for reasonably well by theory. The results have revealed an upwards deviation in the diffusion coefficient at low temperatures, which is probably due to quantum effects.

A further result of this work is that, in the  $\text{Pd}_{85}\text{Pt}_{15}$  alloy, only the  $I_6$  and, to a lesser extent, the  $I_5$  sites are occupied and contribute to diffusion below 300 K.

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## Appendix

For an FCC binary alloy AB the combination of relations (25) and (13) of Froyen and Herring (1981) results in expressions for the average changes  $u_{AA}$ ,  $u_{BB}$  and  $u_{AB}$  in the average nearest-neighbour separation, which differ from those for a BCC alloy (relations (A1a), (A1b), (A1c) of Brouwer and Griessen (1989)) only in a numerical factor ( $\frac{1}{8}$  instead of  $\frac{1}{4}$ ).

In the FCC lattice a cluster  $\text{Pd}_i\text{Pt}_{6-i}$  contains 12 bonds between nearest neighbours with average separation  $u$  and three bonds between next nearest neighbours with average separation  $u\sqrt{2}$ . Following Brouwer and Griessen (1989) the average change  $\delta a$  in the average lattice parameter  $a$  is given by

$$\delta a = \frac{1}{15} \left( \frac{12}{15} + \frac{3}{15}\sqrt{2} \right) (k_1 u_{AA} + k_2 u_{BB} + k_3 u_{AB}) \quad (\text{A1})$$

where  $k_1$ ,  $k_2$  and  $k_3$  represent respectively the numbers of AA, BB and AB bonds in the cluster and are given by

$$k_1 = i(i-1)/2 \quad k_2 = (6-i)(6-i-1)/2 \quad k_3 = i(6-i). \quad (\text{A2})$$

Relation (A8) of Brouwer and Griessen (1989) now becomes

$$d[(6-i)/6 - y] = (I'/200)(4 + \sqrt{2})[-2k_1 y + k_2(2 - 2y) + k_3(1 - 2y)] \quad (\text{A3})$$

to give for  $d$  the final expression

$$d = 0.812I' \quad (\text{A4})$$

which does not depend on the cluster and alloy compositions.

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