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## Short-range order parameter of the disordered alloy $\text{Pd}_{91}\text{Y}_9$ determined from hydrogen absorption

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**Abstract.** Experimental pressure–composition isotherms of hydrogen absorption in the disordered alloy  $\text{Pd}_{91}\text{Y}_9$  have been measured. The isotherms are found to be considerably changed after annealing the sample in a hydrogen atmosphere. This effect is explained quantitatively by the fact that, during the anneal, interstitial hydrogen eliminates the short-range order present in the host metal  $\text{Pd}_{91}\text{Y}_9$ . The isotherms are fitted by a lattice gas model, using Monte Carlo data for the distribution of metal atoms in an alloy with short-range order. From the fit follows an  $\alpha_1$  value of  $-0.07 \pm 0.01$  for the short-range order parameter of  $\text{Pd}_{91}\text{Y}_9$ , a value which is close to the minimum value  $\alpha_1^{\text{min}}$  of  $-0.099$  corresponding to maximum short-range order.

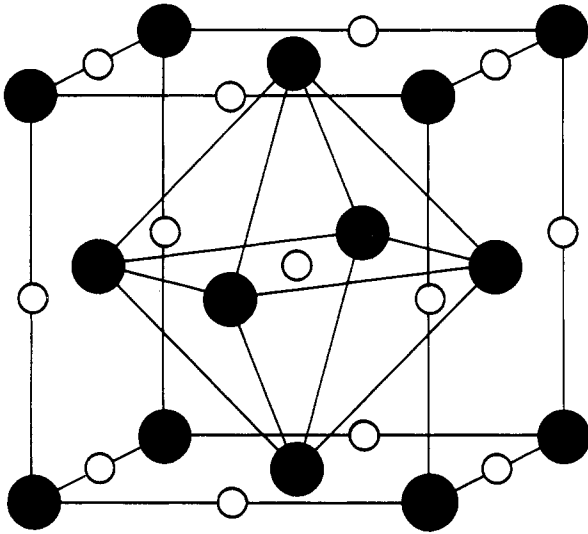
### 1. Introduction

It is well known that many binary metallic alloys  $\text{A}_{1-y}\text{B}_y$  form ordered structures at low temperatures. At higher temperatures (i.e. above the order–disorder temperature) the long-range order in the lattice disappears, but the distribution of the metal atoms is still not completely random, in general. The term short-range order is used for a preference for unlike nearest-neighbour atoms in the alloy (i.e. A–B pairs), while a preference for like nearest-neighbour atoms (i.e. A–A and B–B pairs) is commonly called clustering. In disordered binary alloys, both clustering and short-range ordering has been observed, using the experimental techniques of diffuse x-ray scattering and neutron scattering (Moss and Clapp 1968, Gerold and Kern 1987). The short-range order parameter  $\alpha_1$  of an  $\text{A}_{1-y}\text{B}_y$  alloy is defined by the relation (Haasen 1978)

$$P_{\text{BB}} = \alpha_1 + y(1 - \alpha_1) \quad (1)$$

where  $P_{\text{BB}}$  is the statistical probability of finding a B atom next to a B atom in the alloy. Note that the value  $\alpha_1 = 0$  corresponds to the completely random distribution and that for  $y \leq 0.5$  the value  $\alpha_1 = -y/(1 - y)$  corresponds to maximum short-range order ( $P_{\text{BB}} = 0$ ). In this paper, we show that the short-range order parameter  $\alpha_1$  of the disordered FCC alloy  $\text{Pd}_{91}\text{Y}_9$  can be determined from experimental data for hydrogen absorption.

It has been shown recently (Feenstra *et al* 1988) that atomic hydrogen dissolved in a metallic alloy can be used as a sensitive local probe of structural properties of the host metal. This technique employs the sensitivity of the energy of a hydrogen atom for the local metallic surrounding. Since hydrogen in pure Pd occupies the interstitial octahedral



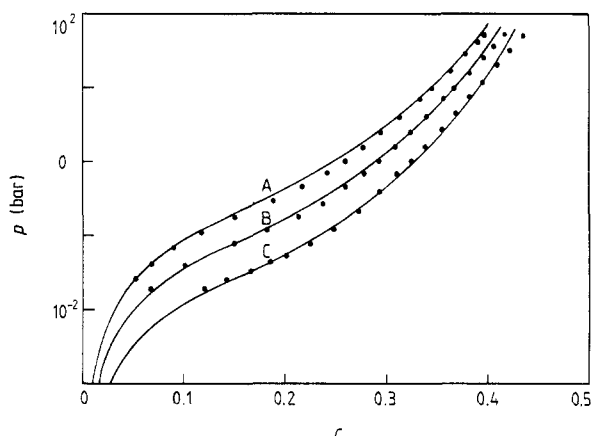
**Figure 1.** Octahedral interstitial sites (○) in the FCC structure.

sites, which are surrounded by six metal atoms (figure 1), one can assume that in a disordered  $\text{Pd}_{1-y}\text{M}_y$  alloy there are seven different types of hydrogen site:  $\text{Pd}_6$ ,  $\text{Pd}_5\text{M}_1, \dots, \text{M}_6$ . Hence a spectrum of seven different site energies  $\varepsilon_i$  for a hydrogen atom is present in the alloy (the index  $i$  denotes the number of solute atoms M in the octahedron). The statistical weight of each site energy  $\varepsilon_i$  is determined by the fraction  $g_i$  of sites of type  $i$ . Obviously the fractions  $g_i$  are functions of the short-range order parameter  $\alpha_1$  of the disordered alloy. Analytical expressions for the fractions  $g_i(\alpha_1)$  of octahedra do not exist, to our knowledge. However, the functions  $g_i(\alpha_1)$  are easily determined by equilibrium Monte Carlo simulations of the nearest-neighbour Ising model for a binary alloy (a nearest-neighbour interaction is the simplest way to introduce short-range order in the alloy).

The procedure in this paper to determine the short-range order parameter of the alloy  $\text{Pd}_{91}\text{Y}_9$  from experimental data for hydrogen absorption is as follows. A multi-site lattice gas model for hydrogen absorption in a disordered alloy (Griessen 1986, Salomons *et al* 1989) is used, with the site energies  $\varepsilon_i$  and the short-range order parameter  $\alpha_1$  as free parameters. In this model the effective mean-field hydrogen–hydrogen interaction accounts for the change in the elastic and electronic properties of the host metal upon hydrogen absorption (Feenstra *et al* 1986). By fitting the model to the experimental data the short-range order parameter  $\alpha_1$  is determined.

The reason why we have chosen  $\text{Pd}_{91}\text{Y}_9$  for this study is the strong lowering of the critical temperature (below which phase segregation of the hydrogen occurs) in this alloy with respect to pure Pd. This implies that spurious hysteresis effects in the hydrogen absorption can be avoided. From the phase diagram of the Pd–Y system (Loebich and Raub 1973) it follows that the composition  $\text{Pd}_{91}\text{Y}_9$  is close to the mixed-phase region corresponding to the ordered  $\text{Pd}_3\text{Y}$  structure. It should be noted that an yttrium atom is considerably larger than a palladium atom, so that a solution of yttrium into palladium results in a sizable lattice expansion. Further, pure yttrium is a much more exothermic hydrogen absorber than is palladium.

In § 2 of this paper the experimental method and results for hydrogen absorption in



**Figure 2.** Experimental pressure–composition isotherms (●) of  $\text{Pd}_{91}\text{Y}_9\text{H}_{100c}$  at three temperatures where the isotherms were measured after annealing the sample in a helium atmosphere at a temperature of 650 K and a pressure of 1 bar, for 40 h: —, model isotherms calculated for  $\varepsilon_i = -7 - 9.5i \text{ kJ (mol H)}^{-1}$  and  $\alpha_1 = 0$  (see text). A, 473 K; B, 443 K; C, 413 K.

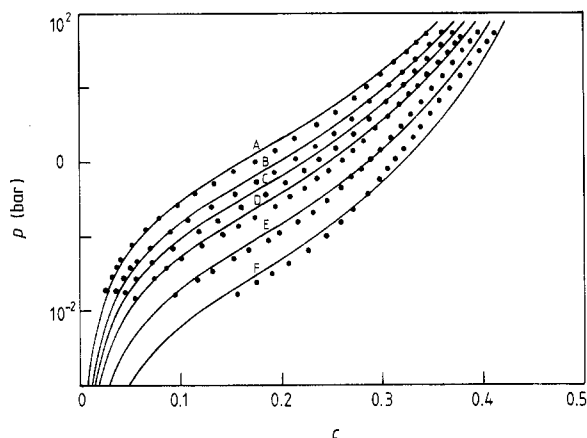
$\text{Pd}_{91}\text{Y}_9$  are presented. Section 3 describes the multi-site lattice gas model and the Monte Carlo simulations for the determination of the fractions  $g_i(\alpha_1)$ . In § 4, we compare the model with the experimental data and discuss the assumptions made in the analysis.

## 2. Experimental method and results

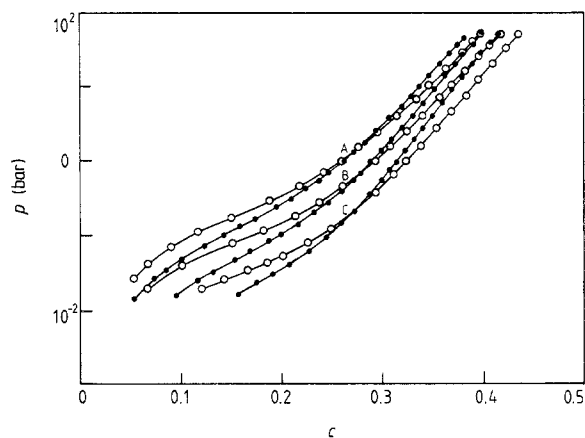
Samples of  $\text{Pd}_{91}\text{Y}_9$  were prepared by melting the pure metals together in an argon atmosphere, followed by an anneal at about 1370 K for 24 h in an argon atmosphere. Using an electron microprobe with a spatial resolution of 4  $\mu\text{m}$  the samples were found to be homogeneous with the composition  $91.0 \pm 0.5 \text{ at.}\%$  Pd and  $9.0 \mp 0.5 \text{ at.}\%$  Y.  $\text{Pd}_{91}\text{Y}_9$  is a substitutional alloy according to the density data of Yoshihara *et al* (1987).

Pressure–composition isotherms of hydrogen absorption in  $\text{Pd}_{91}\text{Y}_9$  were measured using a microbalance with a maximum  $\text{H}_2$  pressure of 50 bar. The microbalance system has been described in detail by Feenstra *et al* (1986). The mass resolution of 1  $\mu\text{g}$  corresponded to a resolution  $\Delta c$  in concentration of  $1 \times 10^{-4}$  for the  $\text{Pd}_{91}\text{Y}_9\text{H}_{100c}$  sample.

In figure 2, three experimental pressure–composition isotherms of  $\text{Pd}_{91}\text{Y}_9\text{H}_{100c}$  are indicated by full circles (the curves correspond to a model calculation described in the next section). It was found that annealing the sample in a hydrogen atmosphere at a temperature of 650 K and a pressure of 20 bar (these conditions correspond to a hydrogen concentration  $c$  of about 0.3 in the sample) considerably changes the isotherms, as indicated in figures 3 and 4. Subsequently annealing the sample in a helium atmosphere at a temperature of 650 K and a pressure of 1 bar restores the original isotherms. It was found that the anneal in the hydrogen atmosphere is complete after about 20 h, while the anneal in the helium atmosphere requires about 40 h. The isotherms of the sample annealed in a helium atmosphere are reversible only for  $T \leq 473 \text{ K}$ , while for  $T > 473 \text{ K}$  a slow relaxation (during the measurements in the hydrogen atmosphere) is observed to the isotherms of the sample annealed in the hydrogen atmosphere. The isotherms of



**Figure 3.** Experimental pressure-composition isotherms (●) of  $\text{Pd}_{91}\text{Y}_9\text{H}_{100c}$  at six temperatures where the isotherms were measured after annealing the sample in a hydrogen atmosphere at a temperature of 650 K and a pressure of 20 bar (corresponding to  $c \approx 0.3$ ) for 20 h: —, model isotherms calculated for  $\epsilon_i = -7 - 9.5i \text{ kJ (mol H)}^{-1}$  and  $\alpha_1 = -0.073$  (see text). A, 543 K; B, 513 K; C, 493 K; D, 473 K; E, 443 K; F, 413 K.



**Figure 4.** Comparison of the experimental data from figure 2 (○) and figure 3 (●). The curves are guides to the eye. A, 473 K; B, 443 K; C, 413 K.

the sample annealed in the hydrogen atmosphere are reversible also for  $T > 473 \text{ K}$ . Obviously a reordering takes place in the sample in the hydrogen atmosphere for  $T \geq 473 \text{ K}$ .

This effect has also been observed (Doyle *et al* (1987) and references therein) for hydrogen in  $\text{Pd}_{92}\text{Y}_8$ . Their experimental isobars changed after the sample had been heated above 610 K. Doyle *et al* attributed the effect to an order-disorder transition. Sakamoto *et al* (1988) measured pressure-composition isotherms of a series of Pd-Y alloys. Since they kept the temperatures below 433 K, these isotherms should agree with the isotherms for annealing in helium, which is indeed the case.

Figure 4 shows that annealing the sample in a hydrogen atmosphere results in steeper

isotherms. This suggests that hydrogen in the lattice enhances the disorder of the host metal Pd<sub>91</sub>Y<sub>9</sub> (see Griessen (1983) for the effect of disorder on pressure–composition isotherms). Since configurational order in a binary alloy originates from the inter-atomic interactions, the enhanced disorder could originate from a weakening of the metal–metal interactions, owing to the hydrogen in the lattice. This can be understood from the fact that hydrogen atoms occupy the interstitial sites in a metal, which are located between the metal atoms. Hence the hydrogen atoms are expected to have a screening effect on the metal–metal interactions. In addition, hydrogen absorption causes a considerable lattice expansion ( $d(\ln V)/dc \approx 0.19$  for Pd alloys (Baranowski *et al* 1971)), which also reduces the inter-atomic interactions.

In the next section we discuss the disordering effect by hydrogen in the lattice in terms of the short-range order parameter of Pd<sub>91</sub>Y<sub>9</sub>.

### 3. Model

In this section, we describe a mean-field multi-site lattice gas model for hydrogen in a disordered alloy (Griessen 1986, Salomons *et al* 1989), which will be used to interpret the experimental pressure–composition isotherms of Pd<sub>91</sub>Y<sub>9</sub>H<sub>100c</sub>.

#### 3.1. Multi-site lattice gas model for hydrogen in a disordered Pd<sub>1-y</sub>M<sub>y</sub> alloy

Since hydrogen in pure Pd occupies the octahedral sites (see figure 1), which are surrounded by six metal atoms, we assume that there are seven different types of site in a disordered Pd<sub>1-y</sub>M<sub>y</sub> alloy: Pd<sub>6</sub>, Pd<sub>3</sub>M<sub>1</sub>, . . . , M<sub>6</sub>. The fraction of sites of type  $i$  in the alloy is denoted by  $g_i$  (the index  $i$  denotes the number of solute atoms  $M$  in the octahedron surrounding the site) and the fractional occupation by hydrogen atoms of sites of type  $i$  by  $x_i$  ( $0 \leq x_i \leq 1$ ). The total hydrogen concentration  $c$  is equal to the number of hydrogen atoms in the lattice divided by the number of octahedral sites (note that the number of octahedral sites is equal to the number of metal atoms in the FCC structure). Hence

$$c = \sum_{i=0}^6 g_i x_i. \quad (2)$$

If hydrogen in a Pd<sub>1-y</sub>M<sub>y</sub> alloy is in equilibrium with molecular hydrogen gas at pressure  $p$  ( $p < 1$  kbar) the occupation  $x_i$  is given by the following mean-field expression (Salomons *et al* 1989):

$$x_i = \llbracket 1 + \exp\{\{\varepsilon_i + \varepsilon(T) + \bar{H}_{\text{elastic}}^*(c) + \bar{H}_{\text{electronic}}^*(c) - T\bar{S}(c) - \frac{1}{2}RT \ln p\}/RT\} \rrbracket^{-1}. \quad (3)$$

Here  $\varepsilon_i$  is the energy at infinite dilution of a hydrogen atom at a site of type  $i$  (with respect to the energy of a hydrogen atom in H<sub>2</sub> gas, at  $T = 600$  K), the function  $\varepsilon(T) = -12 + 0.087T - 0.033 \times 10^{-3}T^2$  kJ (mol H)<sup>-1</sup> contains the excess entropy of hydrogen solution at infinite dilution, and the function  $\bar{S}(c) = -29.23c + 9.15c^2 + 54.83c^3$  J K<sup>-1</sup> (mol H)<sup>-1</sup> is the concentration dependence of the excess entropy of hydrogen solution. The function  $\bar{H}_{\text{elastic}}^*(c)$  represents the elastic hydrogen–hydrogen interaction in Pd<sub>1-y</sub>M<sub>y</sub>H<sub>c</sub>, which is related to the elastic hydrogen–hydrogen interaction  $\bar{H}_{\text{elastic}}(c) = -63.64c + 40.17c^2 - 9.74c^3$  kJ (mol H)<sup>-1</sup> in PdH<sub>c</sub> by the relation

$$\bar{H}_{\text{elastic}}^*(c) = (B_{\text{alloy}}/B_{\text{Pd}})(V_{\text{Pd}}/V_{\text{alloy}})\bar{H}_{\text{elastic}}(c) \quad (4)$$

in which  $B_{\text{Pd}}$  and  $B_{\text{alloy}}$  are the bulk moduli of Pd and  $\text{Pd}_{1-y}\text{M}_y$ , and  $V_{\text{Pd}}$  and  $V_{\text{alloy}}$  are the molar volumes of Pd and  $\text{Pd}_{1-y}\text{M}_y$ . For  $\text{Pd}_{91}\text{Y}_9$ , we calculate the molar volume from the lattice parameter (Paasch and Schaller 1983), and we assume  $B_{\text{alloy}} = B_{\text{Pd}}$  (for several  $\text{Pd}_{1-y}\text{M}_y$  alloys the bulk modulus is found to be only weakly dependent on  $y$  for  $y \ll 1$  (Yoshihara and McLellan 1983, 1985)). The function  $\bar{H}_{\text{electronic}}^*(c)$  represents the electronic hydrogen–hydrogen interaction in  $\text{Pd}_{1-y}\text{M}_y\text{H}_c$ , which is related to the electronic hydrogen–hydrogen interaction  $\bar{H}_{\text{electronic}}(c) = 5.588c + 7.566c^2 - 13.21c^3 + 76.48c^4$  kJ (mol H)<sup>-1</sup> in  $\text{PdH}_c$  by the relation

$$\bar{H}_{\text{electronic}}^*(c) = \bar{H}_{\text{electronic}}(c + \nu y) - \bar{H}_{\text{electronic}}(\nu y) \quad (5)$$

in which  $\nu$  is the valence of the solute M. Equation (5) accounts for the filling of the palladium d band upon alloying. From the susceptibility data of Harris and Norman (1968) follows a valence  $\nu$  of 3 for yttrium in palladium. Obviously equation (5) is an approximation which neglects, for example, the effects of local lattice strains due to yttrium atoms.

Pressure–composition isotherms of a  $\text{Pd}_{1-y}\text{M}_y\text{H}_c$  alloy are determined by equations (2)–(5). For  $\text{PdH}_c$ ,  $\text{Pd}_{1-y}\text{Ag}_y\text{H}_c$  and  $\text{Pd}_{1-y}\text{Cu}_y\text{H}_c$ , model isotherms in good agreement with experimental isotherms were obtained, treating the site energies  $\varepsilon_i$  as free parameters (Salomons *et al* 1989). For the site fractions  $g_i$  the binomial distribution

$$g_i = \binom{6}{i} (1-y)^{6-i} y^i \quad (6)$$

was used, which corresponds to a completely random distribution of the metal atoms (deviations from the binomial distribution, owing to short-range order or clustering, were also discussed).

For  $\text{Pd}_{91}\text{Y}_9\text{H}_{100c}$ , we have seen in the previous section that short-range order in the host metal has a large effect on the isotherms. Therefore we decided to determine the fractions  $g_i$  as a function of the short-range order parameter  $\alpha_1$  by Monte Carlo simulations.

### 3.2. Monte Carlo simulations of an FCC $\text{A}_{91}\text{B}_9$ alloy with short-range order

The short-range order parameter  $\alpha_1$  of a binary alloy was defined in equation (1). For an ideal random FCC alloy,  $\alpha_1 = 0$  and the fractions  $g_i$  of octahedra are given by the binomial distribution (6). For a real alloy,  $\alpha_1$  is different from zero and the fractions  $g_i$  deviate from the binomial distribution, owing to the inter-atomic interactions.

The simplest model of an FCC  $\text{A}_{1-y}\text{B}_y$  alloy with short-range order is the FCC Ising model, with interactions  $J_{\text{AA}}$ ,  $J_{\text{BB}}$  and  $J_{\text{AB}}$  of nearest-neighbour A–A, B–B and A–B pairs, respectively. The total interaction energy of this system is given by

$$E = J_{\text{AA}}N_{\text{AA}} + J_{\text{BB}}N_{\text{BB}} + J_{\text{AB}}N_{\text{AB}} \quad (7)$$

where  $N_{\text{AA}}$ ,  $N_{\text{BB}}$  and  $N_{\text{AB}}$  are the numbers of nearest-neighbour A–A, B–B and A–B pairs, respectively. Equation (7) can also be written as

$$E = JN_{\text{AB}} + J_{\text{AA}}(q/2)(1-y)N + J_{\text{BB}}(q/2)yN \quad (8)$$

with  $q$  the coordination number of the lattice ( $q = 12$  for the FCC structure),  $N$  the total number of atoms, and

$$J \equiv J_{\text{AB}} - \frac{1}{2}J_{\text{AA}} - \frac{1}{2}J_{\text{BB}} \quad (9)$$

the energy of formation of an A–B bond. Note that the last two terms in equation

(8) are constant for a given system, so that the thermodynamic behaviour is entirely determined by the parameter  $J$ .

The FCC Ising model can be solved numerically by Monte Carlo simulation (Binder 1980, Binder *et al* 1981). In order to determine the relation between the fractions  $g_i$  of octahedra and the short-range order parameter  $\alpha_1$  for an FCC  $A_{91}B_9$  alloy we performed simulations of the nearest-neighbour Ising model for several values of the interaction parameter  $J$ . An array of  $4 \times 16 \times 16 \times 16$  elements with periodic boundary conditions was used to represent the FCC alloy ( $16 \times 16 \times 16$  unit cells, each containing four atoms). Initially the A and B atoms were distributed randomly over the lattice. Then nearest-neighbour atoms were allowed to exchange positions according to the transition probability (Binder 1976)

$$W = \begin{cases} \exp(-\Delta E/kT) & \text{if } \Delta E > 0 \\ 1 & \text{if } \Delta E \leq 0 \end{cases} \quad (10)$$

where  $\Delta E$  is the change in interaction energy (8) corresponding to the transition. After a thermalisation time of a few hundreds of Monte Carlo steps per atom, ensemble averages of the octahedron fractions  $g_i$  and the short-range order parameter  $\alpha_1$  (using equation (1)) were determined during another few hundred of Monte Carlo steps per atom.

In figure 5, we show Monte Carlo data for the short-range order parameter  $\alpha_1$  as a function of the interaction parameter  $J/kT$ . The broken straight line in this figure corresponds to the quasi-chemical approximation of the Ising model (Haasen 1978):

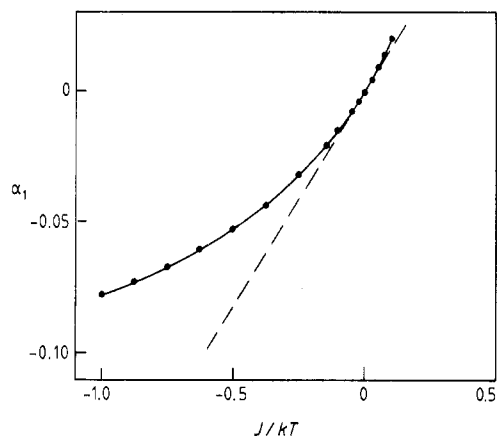
$$\alpha_1 = 2y(1 - y)J/kT. \quad (11)$$

Figure 5 clearly demonstrates that the quasi-chemical approximation is only a first-order approximation of the solution of the Ising model.

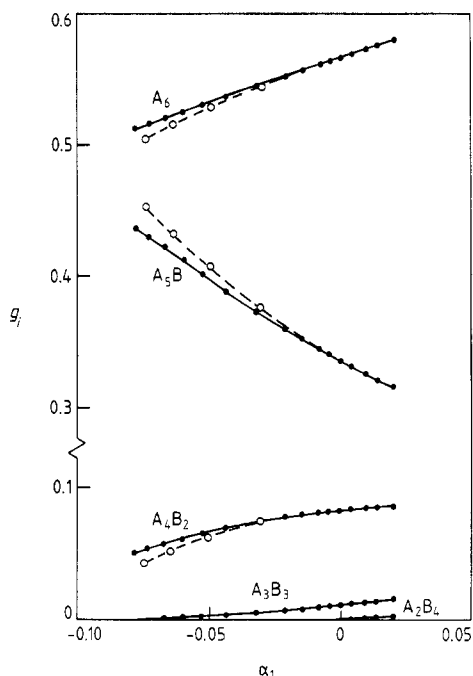
In figure 6, Monte Carlo data for the octahedron fractions  $g_i$  are plotted as a function of the short-range order parameter  $\alpha_1$ . The fractions  $g_5$  and  $g_6$  are too small to be visible on the scale of the figure. For  $\alpha_1 = 0$  the Monte Carlo data are in good agreement with the binomial distribution (6) (the deviations are of the order  $\Delta g_i = 0.0003$ ).

As mentioned above, the nearest-neighbour Ising model is the simplest model for an alloy. In a real alloy the interactions are not restricted to nearest-neighbour atoms. Since the inter-atomic interaction in most real alloys is found to decrease rapidly with increasing inter-atomic distance (Moss and Clapp 1968, Gerold and Kern 1987), our results in figure 6 can be considered as a first-order approximation for a real alloy. In order to determine the effect of a second-nearest-neighbour interaction  $J'$  ( $J' \equiv J'_{AB} - \frac{1}{2}J'_{AA} - \frac{1}{2}J'_{BB}$ , where the prime indicates that the interaction is between second-nearest-neighbour atoms), we performed Monte Carlo simulations of an FCC  $A_{91}B_9$  alloy with nearest-neighbour interaction  $J$  and second-nearest-neighbour interaction  $J' = 0.25J$  (the relation  $|J'/J| \approx 0.25$  appears to be roughly representative for real alloys (Moss and Clapp 1968, Gerold and Kern 1987)). The interaction energy  $E$  of this system is given by an expression similar to equation (8), but now including both first- and second-nearest-neighbour pairs of atoms. The open circles in figure 6 represent the Monte Carlo data for the fractions  $g_i$  of octahedra in this system. The figure shows that the effect of a second-nearest-neighbour interaction on the functions  $g_i(\alpha_1)$  is small, but not negligible.





**Figure 5.** Monte Carlo data (●) of the short-range order parameter  $\alpha_1$  of an FCC alloy  $A_{91}B_9$  with nearest-neighbour interaction  $J$  (see equation (9)): —, guide to the eye; ---, quasi-chemical approximation (see equation (11)).



**Figure 6.** Monte Carlo data of the fractions  $g_i$  of octahedra in an FCC alloy  $A_{91}B_9$  with nearest-neighbour interaction  $J$  (●), and with first- and second-nearest-neighbour interactions  $J$  and  $J' = 0.25J$ , respectively, (○) plotted as a function of the short-range order parameter  $\alpha_1$ : —, --- guides to the eye.

#### 4. Model calculations and discussion

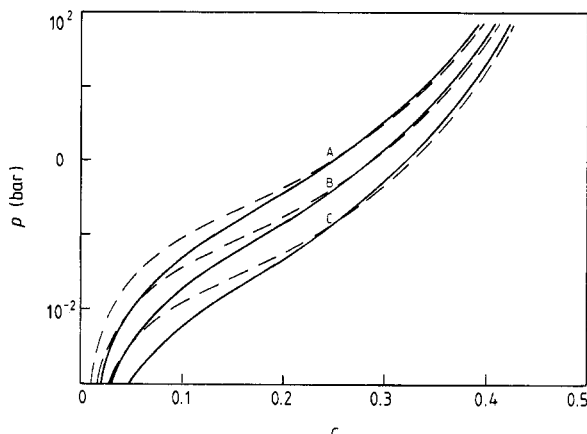
The multi-site lattice gas model described in the previous section can be fitted to the experimental pressure–composition isotherms of  $\text{Pd}_{91}\text{Y}_9\text{H}_{100c}$ , treating the site energies  $\varepsilon_i$  and the short-range order parameter  $\alpha_1$  as free parameters. We make the reasonable assumption that  $\varepsilon_{i+1} < \varepsilon_i$ , since the site energy  $\varepsilon$  in pure yttrium is about  $-80 \text{ kJ (mol H)}^{-1}$  (Griessen and Riesterer 1988) and the site energy  $\varepsilon$  in pure Pd is  $-6.4 \text{ kJ (mol H)}^{-1}$  (Salomons *et al* 1989). For the octahedron fractions  $g_i$ , we use the numerically determined functions  $g_i(\alpha_1)$  for the FCC nearest-neighbour Ising model (figure 6). The experimental isotherms (figures 2–4) cover the concentration range  $0.03 \leq c \leq 0.44$ , so that only the  $\text{Pd}_6$ ,  $\text{Pd}_5\text{Y}$  and  $\text{Pd}_4\text{Y}_2$  sites are relevant for the fits, the small fraction of the remaining sites always having a hydrogen occupation close to unity. In other words, the fits are insensitive for the values of the lowest site energies  $\varepsilon_3$ ,  $\varepsilon_4$ ,  $\varepsilon_5$  and  $\varepsilon_6$ .

The curves in figures 2 and 3 represent our fit to the data, obtained for the following parameters:

$$\varepsilon_i = -7 - 9.5i \text{ kJ (mol H)}^{-1}$$

$$\alpha_1 = -0.073 \quad \text{for the sample annealed in helium (figure 2)} \quad (12)$$

$$\alpha_1 = 0 \quad \text{for the sample annealed in hydrogen (figure 3).}$$



**Figure 7.** Model isotherms calculated for  $\epsilon_i = -7 - 9.5i \text{ kJ (mol H)}^{-1}$ ,  $\alpha_1 = -0.073$  (---) and  $\alpha_1 = 0$  (—) for  $\text{Pd}_{91}\text{Y}_9$ . For the octahedron fractions  $g_i(\alpha_1)$  the data from figure 6 for the alloy with nearest-neighbour interaction were used. A, 473 K; B, 443 K; C, 413 K.

The agreement is remarkably good if one considers that a change of only  $1 \text{ kJ (mol H)}^{-1}$  (which equals about  $0.01 \text{ eV/atom}$ ) in the energy of the hydrogen in the metal corresponds to a change  $\Delta p/p$  in equilibrium pressure of about 0.5, as follows from equation (3). In figure 7 the two sets of model isotherms (for  $\alpha_1 = -0.073$  and  $\alpha_1 = 0$ ) are compared with each other. Comparison with the two sets of experimental isotherms in figure 4 shows that the effect of annealing the sample in a hydrogen atmosphere is quantitatively explained by the elimination of short-range order (the reproduction of this effect by the model isotherms was also used as a criterion for the fit).

While there have been several experimental demonstrations of the effect of long-range order in the host metal on the hydrogen solubility (Phutela and Kleppa 1981, Smith *et al* 1984, Flanagan *et al* 1986), this paper presents an elegant demonstration of the effect of short-range order. This effect has been observed previously for  $\text{Pd}_{92}\text{Y}_8$  by Hughes *et al* (1980) and Doyle *et al* (1987), who ascribed it to an order-disorder transition. The difference between the ordered and disordered state was not specified, however. The model calculation presented above shows that merely a change in short-range order parameter  $\alpha_1$  is sufficient to explain the observed effect. Although data of the short-range order parameter of palladium-rare-earth solid solutions are not available, there are experimental indications for the presence of short-range order in these systems (Hirst *et al* 1976).

Finally we discuss the fitted value of the short-range order parameter  $\alpha_1 = -0.073$  for  $\text{Pd}_{91}\text{Y}_9$  (the sample annealed in helium can be assumed to be representative for 'normal'  $\text{Pd}_{91}\text{Y}_9$ ). As mentioned in § 1, the minimum value  $\alpha_1^{\text{min}}$  of the short-range order parameter corresponding to maximum short-range order is equal to  $-y/(1-y)$ . For  $\text{Pd}_{91}\text{Y}_9$  this yields  $\alpha_1^{\text{min}} = -0.099$ , a value which is close to the fitted value of  $\alpha_1 = -0.073$ .

In order to estimate the accuracy of the fitted value of the short-range order parameter, we note that the largest error is expected to originate from the use of the nearest-neighbour Ising model for the numerical determination of the octahedron

fractions  $g_i(\alpha_1)$ . It follows from figure 6 that the fractions  $g_i$  ( $\alpha_1 = -0.073$ ) for the nearest-neighbour Ising model are equal to the fractions  $g_i$  ( $\alpha_1 = -0.063$ ) for the model with first- and second-nearest-neighbour interactions  $J$  and  $J' = 0.25J$ , respectively. Hence we estimate that the short-range order parameter  $\alpha_1$  is  $-0.07 \pm 0.01$  for  $\text{Pd}_{91}\text{Y}_9$ .

As mentioned above, indications for the presence of short-range order in Pd–Y solid solutions have been reported previously (Hirst *et al* 1976). For other FCC alloys, both positive and negative values of the short-range order parameter have been determined by diffuse x-ray scattering and neutron scattering (Moss and Clapp 1968, Gerold and Kern 1987). The fact that we find a large negative short-range order parameter for  $\text{Pd}_{91}\text{Y}_9$  is probably related to the fact that the composition  $\text{Pd}_{91}\text{Y}_9$  is close to the mixed-phase region corresponding to the ordered  $\text{Pd}_3\text{Y}$  structure (Loebich and Raub 1973).

In summary, experimental pressure–composition isotherms of hydrogen absorption in  $\text{Pd}_{91}\text{Y}_9$  have been presented. The isotherms are found to be considerably changed after annealing the sample in a hydrogen atmosphere (corresponding to a hydrogen concentration  $c$  of about 0.3 in the sample). This effect has been explained by the fact that, during the anneal, interstitial hydrogen eliminates the short-range order present in  $\text{Pd}_{91}\text{Y}_9$ . The isotherms have been fitted by a mean-field multi-site lattice gas model, using Monte Carlo data for the octahedron fractions  $g_i(\alpha_1)$ . From the fit follows a value of  $\alpha_1 = -0.07 \pm 0.01$  for the short-range order parameter of  $\text{Pd}_{91}\text{Y}_9$ .

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