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## Hydrogen spectroscopy of $\text{Pd}_{1-y}\text{Ag}_y$ and $\text{Pd}_{1-y}\text{Cu}_y$ alloys

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**Abstract.** Thermodynamic data for hydrogen absorption in  $\text{Pd}_{1-y}\text{Ag}_y$  and  $\text{Pd}_{1-y}\text{Cu}_y$  alloys, including pressure–composition isotherms and enthalpies and excess entropies of solution, are described by a multi-site lattice gas model. The distributions of site energies of hydrogen in these alloys are obtained by fitting to the data. It is found that the site energy at a  $\text{Pd}_{6-i}\text{M}_i$  octahedral site ( $\text{M} \equiv \text{Ag}, \text{Cu}; i = 0, \dots, 6$ ) is not a linear function of the index  $i$ . It is suggested that this non-linear behaviour originates from a local electronic effect related to the filling of the Pd d band by Ag or Cu electrons.

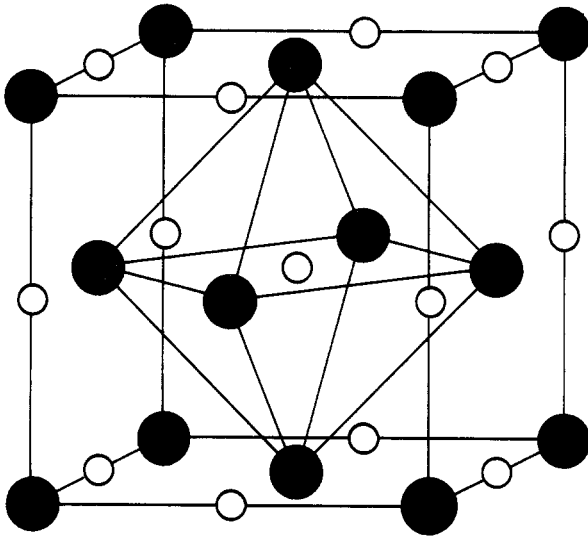
### 1. Introduction

It has been shown recently that local properties of disordered metallic alloys can be investigated using atomic hydrogen as a sensitive probe (Feenstra *et al* 1988). From experimental data for hydrogen absorption in  $\text{Nb}_{1-y}\text{V}_y$  alloys a spectrum of site energies corresponding to different metallic surroundings of a hydrogen atom was determined. From the spectrum the local inter-atomic spacings of Nb–Nb and V–V nearest-neighbour pairs could be determined.

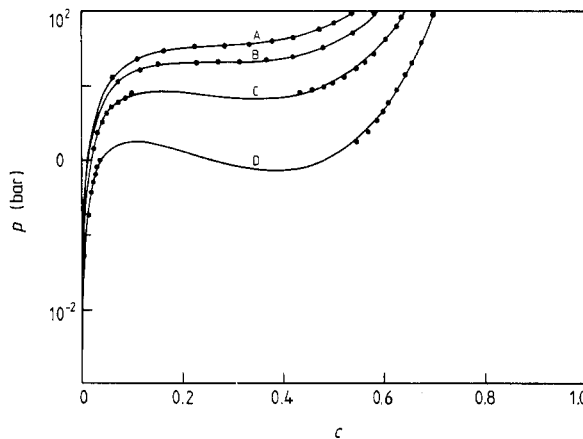
For  $\text{Pd}_{1-y}\text{Ag}_y$  and  $\text{Pd}_{1-y}\text{Cu}_y$  alloys a similar analysis can be made. We have chosen the systems  $\text{Pd}_{1-y}\text{Ag}_y$  and  $\text{Pd}_{1-y}\text{Cu}_y$  because of the large amount of experimental data available for hydrogen absorption in these alloys. It should be noted that the noble metals Ag and Cu absorb much less hydrogen than does the transition metal Pd (whereas the transition metals Nb and V react almost identically with hydrogen).

Most previous studies of hydrogen in Pd alloys considered only non-local elastic and electronic effects. It has been established that the filling of the Pd d band upon alloying has a drastic effect on the hydrogen absorption (Wicke and Brodowsky 1978). The fact that a distribution of local site energies is present in these alloys, however, has not been established (Griessen 1986). Since hydrogen in Pd occupies the octahedral sites, which are surrounded by six metal atoms (figure 1), one can assume that there are seven different types of site in a disordered Pd alloy. Hence the site energy spectrum consists of seven discrete site energies, the statistical weight of each site energy being determined by the random distribution of the metal atoms. To relate this site energy spectrum to thermodynamic data for hydrogen absorption, a multi-site lattice gas model (Griessen 1986) will be used.

Section 2 of this paper presents this multi-site lattice gas model for hydrogen in Pd alloys. From fits to experimental data the site energy spectra of  $\text{Pd}_{1-y}\text{Ag}_y$  and  $\text{Pd}_{1-y}\text{Cu}_y$  alloys are determined. Section 3 shows that a spectrum with only one site energy cannot



**Figure 1.** Octahedral interstitial sites (○) in an FCC metal.



**Figure 2.** Model isotherms (—) of hydrogen in palladium, and experimental data (●) of Blaurock (1985). The temperatures are indicated in the figure. For simplicity the Maxwell construction has not been applied to the model isotherms. A, 613 K; B, 573 K; C, 513 K; D, 433 K.

be fitted to the data. This section also demonstrates that another model, in which the effective hydrogen–hydrogen interaction also has a local effect on the hydrogen energy, cannot be fitted to the data. In § 4 we discuss how the site energy spectra are modified by a deviation from the random distribution of the metal atoms in the alloy (owing to short-range ordering) or by a broadening of the energy peaks in the spectrum (owing to an effect on the hydrogen energy by the metal atoms surrounding the octahedra). In § 5 the site energy spectra of  $\text{Pd}_{1-y}\text{Ag}_y$  and  $\text{Pd}_{1-y}\text{Cu}_y$  are discussed in terms of elastic and electronic alloy properties.

## 2. Model for hydrogen in Pd<sub>1-y</sub>M<sub>y</sub>

It is well known that the thermodynamic behaviour of hydrogen in metals can be described by a lattice gas model (Lacher 1937, Hill 1956, 1960, Manchester 1976). The fact that the properties of the metal change upon hydrogen absorption can be taken into account as an effective mean-field interaction between the hydrogen atoms. For hydrogen in Pd this interaction contains an elastic contribution corresponding to the lattice expansion upon hydrogen absorption and an electronic contribution corresponding to the filling of the Pd d band (Feenstra *et al* 1986). For hydrogen in a Pd<sub>1-y</sub>M<sub>y</sub> alloy, one should also account for the presence of the spectrum of site energies, as mentioned in the previous section. In this section we shall first describe a mean-field lattice gas model for hydrogen in Pd and then generalise this model for hydrogen in a disordered Pd<sub>1-y</sub>M<sub>y</sub> alloy.

### 2.1. Hydrogen in Pd

Let us consider the situation where atomic hydrogen in pure Pd is in equilibrium with molecular hydrogen gas. We have then the following equilibrium condition:

$$\mu_{\text{H}}(c, p, T) = \frac{1}{2}\mu_{\text{H}_2}(p, T) \quad (1)$$

where  $\mu_{\text{H}}$  is the chemical potential of H in Pd,  $\mu_{\text{H}_2}$  is the chemical potential of H<sub>2</sub> gas,  $c$  is the hydrogen concentration ( $c \equiv N_{\text{H}}/N_{\text{sites}}$ , in which  $N_{\text{H}}$  is the number of hydrogen atoms in the lattice and  $N_{\text{sites}}$  is the number of octahedral sites; note that  $N_{\text{sites}}$  is equal to the number of metal atoms in the FCC lattice),  $p$  is the gas pressure and  $T$  is the absolute temperature. In this paper, only pressures  $p$  up to 100 bar are considered, so that the pressure dependence of  $\mu_{\text{H}}$  is negligible (Hemmes *et al* 1989). Using a mean-field lattice gas model for  $\mu_{\text{H}}$  (Griessen 1986), equation (1) can be written as

$$\Delta\bar{H}^{\infty}(T) - T\Delta\bar{S}^{\infty}(T) + \bar{H}(c) - T\bar{S}(c) + RT \ln\left(\frac{c}{1-c}\right) = \frac{1}{2}RT \ln p \quad (2)$$

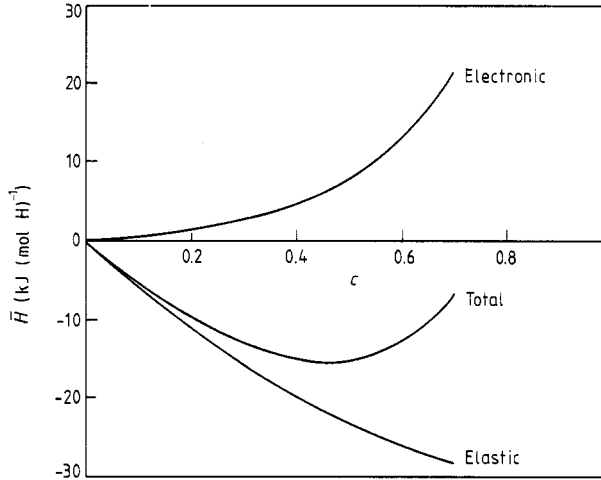
in which  $\Delta\bar{H}^{\infty}$  and  $\Delta\bar{S}^{\infty}$  are the partial molar enthalpy and excess entropy of hydrogen solution at infinite dilution (i.e.  $c \rightarrow 0$ ), and  $\bar{H}(c)$  and  $\bar{S}(c)$  are the concentration dependences of  $\Delta\bar{H}^{\infty}$  and  $\Delta\bar{S}^{\infty}$ , respectively (with  $\bar{H}(0) = 0$  and  $\bar{S}(0) = 0$ ). We write

$$\Delta\bar{H}^{\infty}(T) - T\Delta\bar{S}^{\infty}(T) = \varepsilon_0 + \varepsilon(T) \quad (3)$$

in which the constant  $\varepsilon_0$  is called the site energy of hydrogen in Pd (for hydrogen in an alloy we shall see below that there is a distribution of site energies  $\varepsilon_i$ ) and the function  $\varepsilon(T)$  contains both the entropy of solution at infinite dilution and the temperature dependence of the enthalpy of solution at infinite dilution. For the site energy  $\varepsilon_0$ , we use the value of  $\Delta\bar{H}^{\infty}(T)$  at  $T = 600$  K, so that the site energy is measured with respect to the energy of a hydrogen atom in molecular hydrogen gas at a temperature of 600 K.

The excess enthalpy  $\bar{H}(c)$ , which can be considered as an effective mean-field hydrogen-hydrogen interaction, is split into an elastic part and an electronic part (Feenstra *et al* 1986):

$$\bar{H}(c) = \bar{H}_{\text{elastic}}(c) + \bar{H}_{\text{electronic}}(c) \quad (4)$$



**Figure 3.** The partial molar excess enthalpy  $\bar{H}(c)$  of hydrogen in palladium (curve labelled 'Total'). The separate elastic and electronic contributions are also shown.

with

$$\bar{H}_{\text{elastic}}(c) = -\int_0^c B(c') \frac{\bar{V}_{\text{H}}^2(c')}{V_{\text{m}}(c')} dc' \quad (5)$$

in which  $B$  and  $V_{\text{m}}$  are the bulk modulus and the molar volume of the metal, and  $\bar{V}_{\text{H}}$  is the partial molar volume of hydrogen in the metal. Since  $\bar{H}_{\text{elastic}}(c)$  is given by equation (5),  $\bar{H}_{\text{electronic}}(c)$  can be determined from experimental data using equation (4). The experimental data of Kuji *et al* (1983), Blaurock (1985) and Feenstra *et al* (1986) for  $\text{PdH}_c$  can be represented by equation (2) using the following functions ( $c \leq 0.7$ ):

$$\begin{aligned} \varepsilon_0 &= -6.4 \\ \varepsilon(T) &= -12 + 0.087T - 0.033 \times 10^{-3} T^2 \\ \bar{H}_{\text{elastic}}(c) &= -63.64c + 40.17c^2 - 9.74c^3 \\ \bar{H}_{\text{electronic}}(c) &= 5.588c + 7.566c^2 - 13.21c^3 + 76.48c^4 \\ \bar{S}(c) &= -29.23c + 9.15c^2 + 54.83c^3 \end{aligned} \quad (6)$$

with  $T$  in kelvins, energies and enthalpies in kilojoules per mole of atomic hydrogen and entropies in joules per kelvin per mole of atomic hydrogen (as everywhere in this paper). It should be noted that the functions  $\varepsilon(T)$  and  $\bar{H}_{\text{electronic}}(c)$  were optimised to obtain best agreement with the (tabulated) isotherms of Blaurock (figure 2). In figure 3 the functions  $\bar{H}(c)$ ,  $\bar{H}_{\text{elastic}}(c)$  and  $\bar{H}_{\text{electronic}}(c)$  are shown.

Finally we write equation (2) in a different form:

$$c = \llbracket 1 + \exp\{\{\Delta\bar{H}^\infty(T) - T\Delta\bar{S}^\infty(T) + \bar{H}(c) - T\bar{S}(c) - \frac{1}{2}RT \ln p\}/RT\} \rrbracket^{-1} \quad (7)$$

which is most suitable for the generalisation for a multi-site lattice gas.

2.2. *Hydrogen in a Pd<sub>1-y</sub>M<sub>y</sub> alloy*

To describe the absorption of hydrogen in a disordered Pd<sub>1-y</sub>M<sub>y</sub> alloy, equation (7) has to be modified as follows (Griessen 1986):

$$c = \sum_{i=0}^6 g_i x_i \tag{8}$$

in which  $x_i$  is the hydrogen occupation of sites of type  $i$ , which is given by

$$x_i = [1 + \exp\{\Delta\bar{H}_i^z(T) - T\Delta\bar{S}^z(T) + \bar{H}^*(c) - T\bar{S}(c) - \frac{1}{2}RT \ln p\}/RT\}]^{-1} \tag{9}$$

and  $g_i$  is the fraction of sites of type  $i$ , which is given by the binomial distribution

$$g_i = \binom{6}{i} (1-y)^{6-i} y^i \tag{10}$$

We assume that there are seven different types  $i$  of octahedral site in a Pd<sub>1-y</sub>M<sub>y</sub> alloy: Pd<sub>6</sub> ( $i = 0$ ), Pd<sub>5</sub>M<sub>1</sub> ( $i = 1$ ), . . . , M<sub>6</sub> ( $i = 6$ ), and consequently seven different enthalpies  $\Delta\bar{H}_i^z(T)$ . Analogous to equation (3), we write

$$\Delta\bar{H}_i^z(T) - T\Delta\bar{S}^z(T) = \varepsilon_i + \varepsilon(T) \tag{11}$$

in which the energies  $\varepsilon_i$  will be referred to as the site energies of hydrogen in the alloy. We assume that the functions  $\varepsilon(T)$  and  $\bar{S}(c)$  are not affected by the alloying (i.e. they are given by the same functions (6) as for pure Pd). This implies that we assume that the hydrogen vibrational frequency does not depend on the solute content, in good agreement with neutron scattering studies on hydrogen in Pd<sub>1-y</sub>Ag<sub>y</sub> alloys (Chowdhury and Ross 1973, Hunt and Ross 1976). Implicitly in equations (8) and (9) there is, however, a configurational change in entropy upon alloying, as will be shown below.

The excess enthalpy  $\bar{H}^*(c)$  of hydrogen in Pd<sub>1-y</sub>M<sub>y</sub> is related to the excess enthalpy  $\bar{H}(c)$  of hydrogen in Pd, as will be described now. We write again

$$\bar{H}^*(c) = \bar{H}_{\text{elastic}}^*(c) + \bar{H}_{\text{electronic}}^*(c) \tag{12}$$

From equation (5) it follows that approximately

$$\bar{H}_{\text{elastic}}^*(c) = (B_{\text{alloy}}/B_{\text{Pd}})(V_{\text{Pd}}/V_{\text{alloy}})\bar{H}_{\text{elastic}}(c) \tag{13}$$

in which  $B_{\text{alloy}}$  and  $B_{\text{Pd}}$  are the bulk moduli of the alloy and Pd (evaluated at  $c = 0$  for simplicity) and  $V_{\text{alloy}}$  and  $V_{\text{Pd}}$  are the molar volumes of the alloy and Pd (also evaluated at  $c = 0$ ). It has been assumed that the partial molar volume of hydrogen in the alloy is the same as in Pd, in agreement with experimental data (Baranowski *et al* 1971). Values of the bulk modulus of Pd<sub>1-y</sub>Ag<sub>y</sub> and Pd<sub>1-y</sub>Cu<sub>y</sub> alloys were reported by Yoshihara and McLellan (1983, 1985), and values of the molar volume were calculated from the lattice parameters (Pearson 1958).

For the electronic interaction an assumption in the spirit of the rigid-band approximation is used (Griessen 1986):

$$\bar{H}_{\text{electronic}}^*(c) = \bar{H}_{\text{electronic}}(c + \nu y) - \bar{H}_{\text{electronic}}(\nu y) \tag{14}$$

in which  $\nu$  is the valence of the solute M ( $\nu = 1$  for M  $\equiv$  Ag, Cu), and  $\nu y$  is the so-called valence electron concentration. As the valence of atomic hydrogen is 1,  $c + \nu y$  is the total number of valence electrons per metal atom in the alloy (with respect to the number in pure Pd). It has been assumed in equation (14) that the valence electrons of the solute M play the same role in the electronic interaction as the hydrogen electrons (remember

that the electronic interaction is in fact an effective interaction, which accounts for the change of the electronic properties of the metal upon hydrogen absorption).

Using the model described above expressions will now be derived for the change upon alloying of the average enthalpy and excess entropy of hydrogen solution at infinite dilution. Especially the (configurational) change in excess entropy will appear to be a sensitive parameter in the determination of the site energy spectrum from experimental data.

The partial molar enthalpy  $\bar{H}_H$  and entropy  $\bar{S}_H$  of hydrogen in a metal are given by

$$\bar{H}_H = \left( \frac{\partial(\mu_H/T)}{\partial(1/T)} \right)_{c,p} \quad (15)$$

and

$$\bar{S}_H = - \left( \frac{\partial\mu_H}{\partial T} \right)_{c,p}. \quad (16)$$

The partial molar enthalpy and excess entropy of hydrogen solution are given by

$$\Delta\bar{H} = \bar{H}_H - \frac{1}{2}\bar{H}_{H_2}^0 \quad (17)$$

and

$$\Delta\bar{S} = \bar{S}_H + R \ln\left(\frac{c}{1-c}\right) - \frac{1}{2}\bar{S}_{H_2}^0 \quad (18)$$

where  $\bar{H}_{H_2}^0$  and  $\bar{S}_{H_2}^0$  are the molar enthalpy and entropy of  $H_2$  gas (at pressure  $p = 1$  bar). From equations (8), (9), (11), (15) and (17) the change upon alloying in the partial molar enthalpy of solution at infinite dilution is obtained as an average over the site energies:

$$\Delta\bar{H}^\infty(y) - \Delta\bar{H}^\infty(y=0) = \left( \sum_{i=0}^6 g_i \zeta_i \varepsilon_i \right) - \varepsilon_0(y=0) \quad (19)$$

with

$$\zeta_i \equiv \exp\left(-\frac{\varepsilon_i}{RT}\right) / \left[ \sum_j g_j \exp\left(-\frac{\varepsilon_j}{RT}\right) \right]. \quad (20)$$

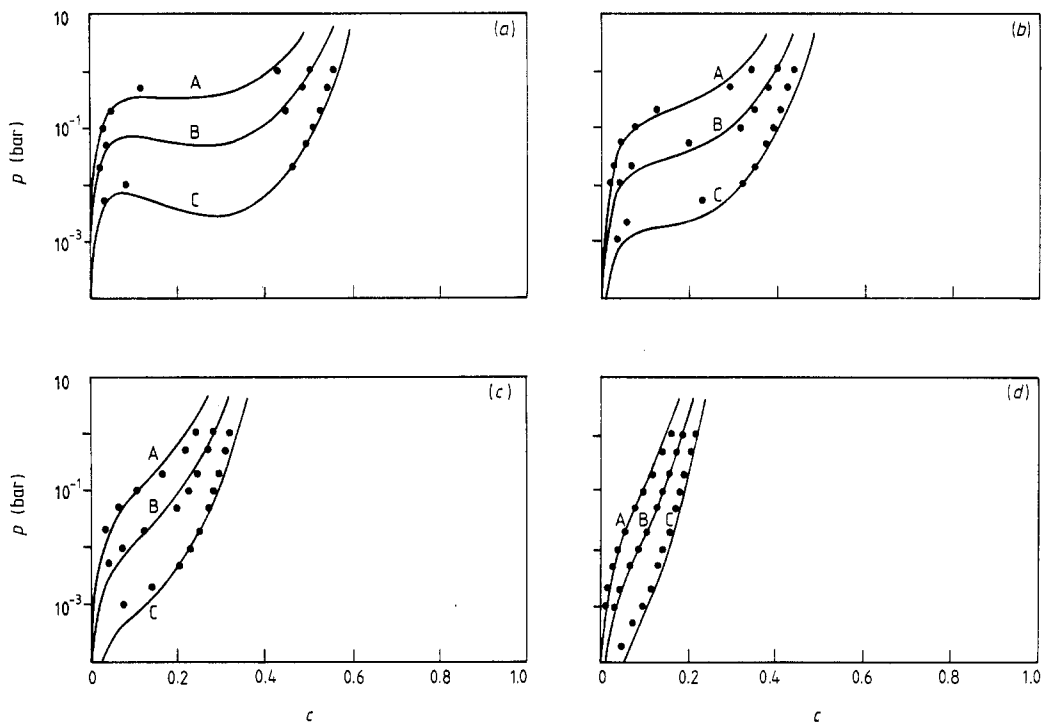
From equations (8), (9), (11), (16) and (18) the change upon alloying in the partial molar excess entropy of solution at infinite dilution is obtained:

$$\Delta\bar{S}^\infty(y) - \Delta\bar{S}^\infty(y=0) = -R \sum_{i=0}^6 g_i \zeta_i \ln \zeta_i. \quad (21)$$

This change in excess entropy is due to the non-random distribution of hydrogen in an alloy. It is important to note that  $\Delta\bar{H}^\infty(y) - \Delta\bar{H}^\infty(y=0)$  and  $\Delta\bar{S}^\infty(y) - \Delta\bar{S}^\infty(y=0)$  according to equations (19) and (21) depend only on the site energies  $\varepsilon_i$  and are independent of the functions  $\varepsilon(T)$ ,  $\bar{H}_{\text{elastic}}^*(c)$ ,  $\bar{H}_{\text{electronic}}^*(c)$  and  $\bar{S}(c)$ .

### 2.3. Site energy spectra of $Pd_{1-y}Ag_y$ and $Pd_{1-y}Cu_y$

In this section the site energy spectra (i.e. the site energies  $\varepsilon_i$  in equation (11)) of  $Pd_{1-y}Ag_y$  and  $Pd_{1-y}Cu_y$  will be determined by fitting equations (8) plus (9), (19) and (21) to experimental pressure–composition isotherms and data for the enthalpy and excess entropy of solution at infinite dilution. We make the reasonable assumption that

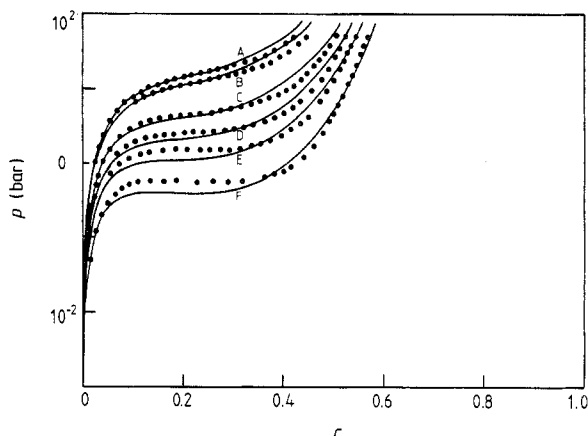


**Figure 4.** Model isotherms (—) of hydrogen in  $Pd_{1-y}Ag_y$  alloys for (a)  $y = 0.1$ , (b)  $y = 0.2$ , (c)  $y = 0.3$  and (d)  $y = 0.4$ , and experimental data (●) of Brodowsky and Poeschel (1965). A, 421 K; B, 373 K; C, 323 K.

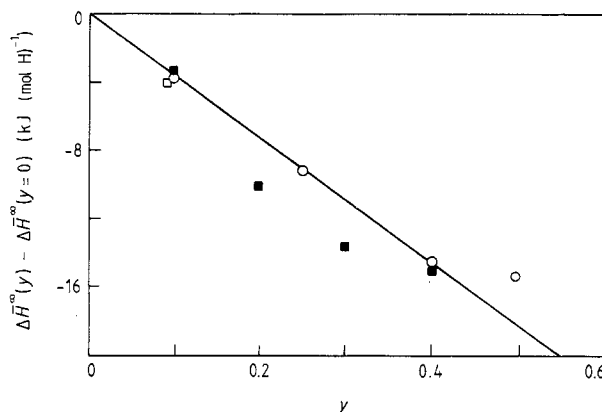
$\epsilon_i < \epsilon_{i+1}$ , so that octahedra with more Ag or Cu atoms have a higher site energy. Unfortunately the experimental data cover only a limited range of hydrogen concentrations  $c$ , and also a limited range of solute content  $y$ . Therefore only the lowest three site energies  $\epsilon_0$ ,  $\epsilon_1$  and  $\epsilon_2$  can be determined, the fits being insensitive for the actual values of the higher site energies. We show elsewhere (Hemmes *et al* 1989) that the site energy  $\epsilon_3$  for  $Pd_{1-y}Ag_y$  can be determined from high-pressure data (for  $y = 0.5$ ).

In figures 4–7 the fits to the experimental data for  $Pd_{1-y}Ag_y$  are shown, while the corresponding site energy spectrum is represented in figure 8. Figure 4 contains the experimental pressure–composition isotherms of Brodowsky and Poeschel (1965), together with model isotherms calculated using equations (8) and (9). The experimental pressure–composition isotherms in figure 5 were measured by Salomons (1988). Although the fits to the experimental isotherms are not perfect, the deviations are acceptable if one considers the fact that a change in equilibrium pressure of one decade corresponds to a change in chemical potential of about  $4 \text{ kJ (mol H)}^{-1}$  (at  $T = 400 \text{ K}$ ). In other words, the isotherms are very sensitive for small changes in the site energies. It should be noted that the experimental isotherms shown in figure 5 are in agreement with the isotherms measured on  $Pd_{90}Ag_{10}$  by Buck and Alefeld (1972). In figure 6 the accurate experimental data of Picard *et al* (1979) for the partial molar enthalpy of solution at infinite dilution are shown (with respect to the value of pure Pd), while the curve corresponds to equation (19). In figure 7, experimental data for the partial molar excess entropy of solution at infinite dilution are shown (with respect to the value of Pd), while





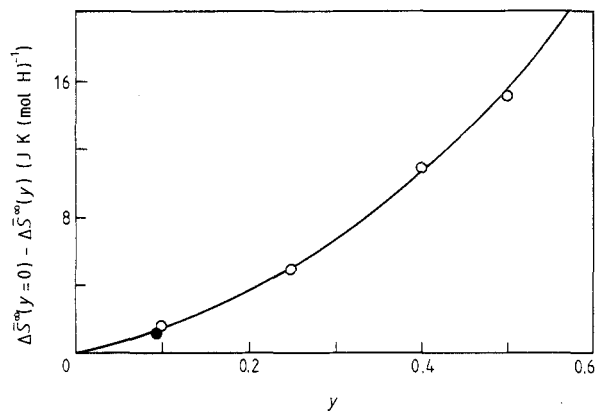
**Figure 5.** Model isotherms (—) of hydrogen in  $\text{Pd}_{90.5}\text{Ag}_{9.5}$  and experimental data (●) of Salomons (1988). A, 591 K; B, 573 K; C, 513 K; D, 483 K; E, 458 K; F, 423 K.



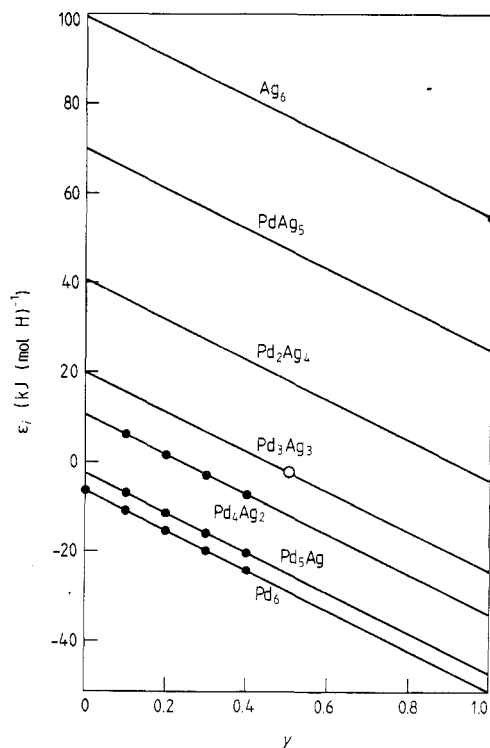
**Figure 6.** The partial molar enthalpy (—) of hydrogen solution at infinite dilution for  $\text{Pd}_{1-y}\text{Ag}_y$ , with respect to the value for Pd ( $T = 500$  K), and experimental data of Picard *et al* (1979) (○), Brodowsky and Poeschel (1965) (■) and Salomons (1988) (□).

the curve corresponds to equation (21). The enthalpy of solution at infinite dilution decreases with increasing silver content  $y$ , which corresponds to the decrease in the site energies  $\varepsilon_i$  as a function of  $y$  shown in figure 8. In figure 8 the site energies  $\varepsilon_4$  and  $\varepsilon_5$  were determined by interpolation between  $\varepsilon_3$  and  $\varepsilon_6$  (see figure 14 later), and the value of  $\varepsilon_6$  for  $y = 1$ , i.e. the site energy in pure Ag, was taken from Driessen and Griessen (1989). It has been assumed that all the site energies have the same linear dependence on  $y$ , which is suggested by the fact that the three fitted site energies (for  $y \leq 0.5$ ), given by  $\varepsilon_0 = -6.4 - 44y$ ,  $\varepsilon_1 = -2.4 - 44y$  and  $\varepsilon_2 = 10.6 - 44y$ , have the same linear dependence on  $y$ .

In figures 9–11 the fits to the experimental data for  $\text{Pd}_{1-y}\text{Cu}_y$  are shown, and the corresponding site energy spectrum is represented in figure 12. The experimental isotherms in figure 9 were measured by Salomons (1988). Note that the equilibrium pressure

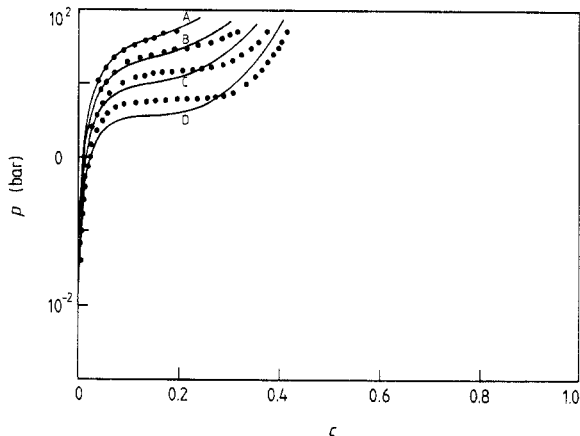


**Figure 7.** The partial molar excess entropy (—) of hydrogen solution at infinite dilution for Pd<sub>1-y</sub>Ag<sub>y</sub>, with respect to the value for Pd ( $T = 555$  K), and experimental data of Picard *et al* (1979) (○) and Salomons (1988) (●).

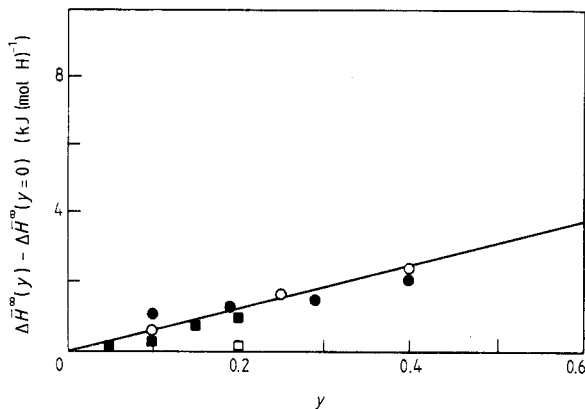


**Figure 8.** The site spectrum (—) of Pd<sub>1-y</sub>Ag<sub>y</sub>, corresponding to the fits shown in figures 4-7: ●, site energies used for figure 4 and site energies for pure Pd and Ag; ○, site energy  $\epsilon_3$  for  $y = 0.5$  determined by Hemmes *et al* (1989) from high-pressure data.

(at a fixed concentration of, for example,  $c = 0.2$ ) is higher for Pd<sub>1-y</sub>Cu<sub>y</sub> than for Pd, whereas for Pd<sub>1-y</sub>Ag<sub>y</sub> it is lower than for Pd. This opposite behaviour is generally attributed to the fact that the lattice parameter (and hence the interstitial volume)



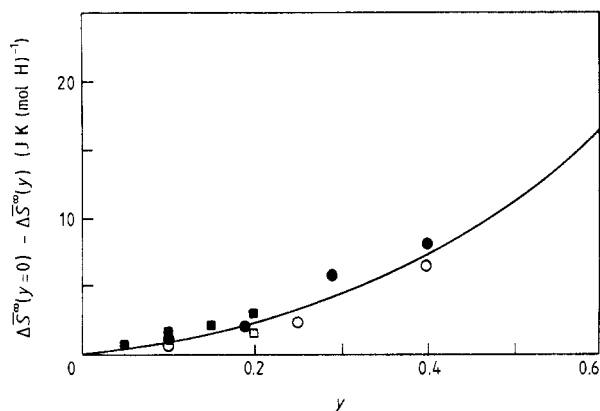
**Figure 9.** Model isotherms (—) of hydrogen in  $\text{Pd}_{79.5}\text{Cu}_{20.5}$ , and experimental data (●) of Salomons (1988). A, 513 K; B, 473 K; C, 433 K; D, 393 K.



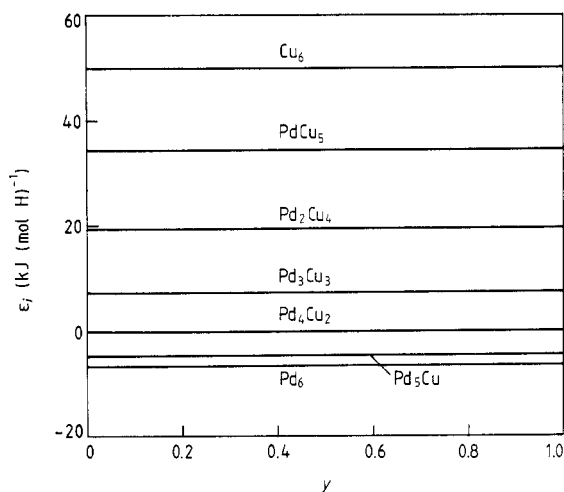
**Figure 10.** The partial molar enthalpy (—) of hydrogen solution at infinite dilution for  $\text{Pd}_{1-y}\text{Cu}_y$  with respect to the value of Pd (at  $T = 400$  K), and experimental data of Kleppa *et al* (1979) (○), Fisher *et al* (1977) (●), Burch and Buss (1975) (■) and Salomons (1988) (□).

decreases for  $\text{Pd}_{1-y}\text{Cu}_y$  with increasing  $y$  but increases for  $\text{Pd}_{1-y}\text{Ag}_y$  (see also § 5). In figures 10 and 11, data for the partial molar enthalpy and excess entropy of solution at infinite dilution are shown (with respect to the values for Pd), together with the fits. The rather weak variation with  $y$  in the enthalpy of solution at infinite dilution corresponds to site energies which are independent of  $y$  (figure 12). In figure 12 the site energies  $\epsilon_3$ ,  $\epsilon_4$  and  $\epsilon_5$  were determined by interpolation between  $\epsilon_2$  and  $\epsilon_6$  (see figure 14 later), and the value of  $\epsilon_6$  for  $y = 1$ , i.e. the site energy in pure Cu, was taken from Driessen and Griessen (1989). It has been assumed that all the site energies are constant as a function of  $y$ , which is suggested by the fact that the three fitted site energies (for  $y \leq 0.4$ ), given by  $\epsilon_0 = -6.4$ ,  $\epsilon_1 = -4.4$  and  $\epsilon_2 = 0$ , are constant as a function of  $y$ .

The quality of the fits in figures 4–7 and 9–11 is rather satisfactory, if one considers the assumptions made in the lattice gas model. The assumption that the effective hydrogen interaction can be split simply into an elastic and an electronic part is an



**Figure 11.** The partial molar excess entropy (—) of hydrogen solution at infinite dilution for  $Pd_{1-y}Cu_y$  with respect to the value for Pd (at  $T = 400$  K), and experimental data of Kleppa *et al* (1979) (○), Fisher *et al* (1977) (●), Burch and Buss (1975) (■) and Salomons (1988) (□).



**Figure 12.** The site energy spectrum of  $Pd_{1-y}Cu_y$ , corresponding to the fits shown in figures 9–11.

approximation, of course. The most important approximation is equation (14) for the band-filling effect of the solute electrons on the electronic hydrogen interaction.

### 3. Different models

In this section, two slightly different models for hydrogen in a  $Pd_{1-y}M_y$  alloy are discussed briefly. It will be shown that these models cannot be fitted to the experimental data.

### 3.1. Single-site model

The single-site model is identical with the model described in § 2, but with the assumption that all the site energies in the alloy are equal. Such a model should be applicable to the case where the differences between the site energies are small. It describes a  $\text{Pd}_{1-y}\text{M}_y$  alloy as a pure metal which differs from Pd only in the values of the energy parameters (6). Although it has been shown already that the differences between the site energies are not small, it is instructive to see why this model cannot be fitted to the data. The failure of the model is most clearly demonstrated by considering the partial molar excess entropy of solution at infinite dilution. It follows from equation (21) that  $\Delta\bar{S}^x(y) - \Delta\bar{S}^x(y=0) = 0$  in this case, in sharp contrast with the experimental data shown in figures 7 and 11. We also tried to fit this model to the isotherms of  $\text{Pd}_{1-y}\text{Ag}_y$ , and obtained a reasonable agreement, although not as good as with the model described in § 2. However, a site energy  $\varepsilon$  of  $-6.4 - 21y$  had to be used for these fits ( $\varepsilon = \varepsilon_i$ ,  $i = 0, 1, \dots, 6$ ), which implies that  $\Delta\bar{H}^x(y) - \Delta\bar{H}^x(y=0) = -21y$ . The experimental data in figure 6 show a significantly larger dependence on  $y$  of  $\Delta\bar{H}^x(y) - \Delta\bar{H}^x(y=0) \approx -35y$ . Hence it is concluded that the single-site model cannot be fitted to the data.

### 3.2. A model with local hydrogen-hydrogen interactions

The electronic interaction  $\bar{H}_{\text{electronic}}(c)$  of hydrogen in Pd (figure 3) is closely related to the band structure of  $\text{PdH}_c$ . This was demonstrated by Feenstra *et al* (1986), using the semi-empirical band-structure model of Griessen and Driessen (1984) for the enthalpy of hydrogen solution:

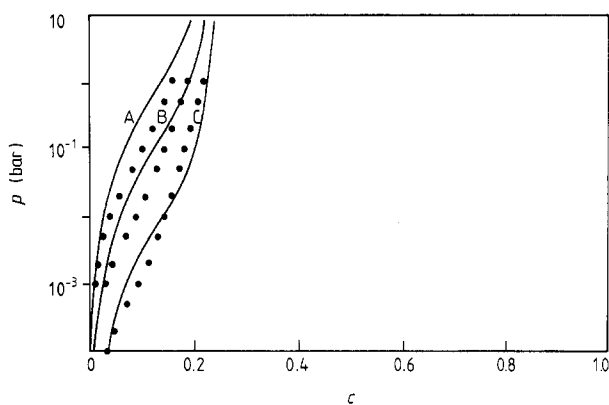
$$\Delta\bar{H} = \alpha(E_F - E_s) + \beta \quad (22)$$

where  $E_F$  is the Fermi energy and  $E_s$  is the energy for which the integrated density of states is equal to unity (this is near the bottom of the d band),  $\alpha = 29.62 \text{ kJ eV}^{-1} (\text{mol H})^{-1}$  and  $\beta = -135 \text{ kJ} (\text{mol H})^{-1}$ . Upon increasing the hydrogen concentration the Fermi energy rises, and hence also the enthalpy of the hydrogen. It was also demonstrated by Feenstra *et al* (1986) that conversely realistic values for the electronic density of states in  $\text{PdH}_c$  can be deduced from the experimentally determined function  $\bar{H}_{\text{electronic}}(c)$ .

To determine the electronic interaction  $\bar{H}_{\text{electronic}}^*(c)$  of hydrogen in a  $\text{Pd}_{1-y}\text{Ag}_y$  alloy (or  $\text{Pd}_{1-y}\text{Cu}_y$  alloy) it has been assumed that the valence electrons of the Ag atoms produce a shift in the Fermi energy and hence in  $\bar{H}_{\text{electronic}}(c)$  (see equation (14)). This argument neglects, however, the fact that these valence electrons remain in the vicinity of the Ag atoms. This might result in a local effect on the electronic interaction. Although the Fermi energy is constant in an alloy, it is possible that  $E_F - E_s$  in equation (22) varies with the local concentration of Ag atoms, owing to local shifts of  $E_s$ . Therefore we replaced the non-local function  $\bar{H}_{\text{electronic}}^*(c)$  according to equation (14) by the local function

$$\bar{H}_{\text{electronic}}^*(c; i) = \bar{H}_{\text{electronic}}(c + i/6) - \bar{H}_{\text{electronic}}(i/6) \quad (23)$$

for the electronic excess enthalpy of hydrogen at a site of type  $i$ , with local Ag concentration  $i/6$ . We tried again to fit this model to the experimental data. In figure 13 the best fit to the isotherms of  $\text{Pd}_{60}\text{Ag}_{40}$  is shown, which was calculated for  $\varepsilon_0 = -25$ ,  $\varepsilon_1 = -15$  and  $\varepsilon_2 = 0 \text{ kJ} (\text{mol H})^{-1}$ . The model isotherms show a considerably larger deviation from the data than do the isotherms shown in figure 4. Also the partial molar excess entropy of solution at infinite dilution calculated for this site energy distribution deviates



**Figure 13.** Isotherms (—) according to the model with local hydrogen–hydrogen interactions (§ 3.2), and the data of Brodowsky and Poeschel (1965) (●), for  $Pd_{60}Ag_{40}$ . A, 421 K; B, 373 K; C, 323 K.

significantly from the experimental data. Hence it is concluded that this model also cannot be fitted to the data. This implies that the electronic hydrogen–hydrogen interaction in a Pd alloy should be considered as a non-local contribution to the enthalpy of the hydrogen.

#### 4. Deviations from the ideal site energy spectrum

In the foregoing it has been shown that a spectrum consisting of seven discrete site energies, the statistical weight of each site energy being determined by the binomial distribution of the metal atoms, gives good agreement with the experimental data. This section discusses possible deviations from this ideal spectrum.

##### 4.1. Deviations from the binomial distribution

In § 2 it was assumed that the metal atoms in a binary alloy are randomly mixed. The metal atoms in a real alloy, however, are in general not randomly mixed, owing to the effects of inter-atomic interactions. In binary FCC alloys, both short-range ordering (i.e. a preference for unlike nearest-neighbour atoms) and clustering (i.e. a preference for like nearest-neighbour atoms) has been observed (Moss and Clapp 1968, Gerold and Kern 1987). For a random distribution of the metal atoms the octahedron fractions  $g_i$  are given by the binomial distribution in equation (10). For a non-random distribution the fractions deviate from the binomial distribution. To study this deviation quantitatively, we have performed Monte Carlo simulations of binary FCC alloys with nearest-neighbour interactions.

For the simulations a computer array of  $4 \times 16 \times 16 \times 16$  elements was used to represent the lattice ( $16 \times 16 \times 16$  unit cells, each containing four atoms), while periodic boundary conditions were used to avoid edge effects. First the A and B atoms of an

**Table 1.** Monte Carlo data for the octahedron fractions  $g_i$  and the short-range order parameter  $\alpha_1$  of an FCC  $A_{60}B_{40}$  alloy for different values of the nearest-neighbour B–B interaction  $J$ . The binomial distribution (the exact solution for  $J/kT = 0$ ) is also indicated.

	$J/kT = -0.3$	$J/kT = 1.0$	$J/kT = 0$	Binomial
$\alpha_1$	0.10740	-0.13428	-0.00115	0
$g_0$	0.09226	0.01108	0.04609	0.04666
$g_1$	0.20315	0.13402	0.18666	0.18662
$g_2$	0.25159	0.40445	0.31114	0.31104
$g_3$	0.22195	0.35167	0.27776	0.27648
$g_4$	0.14537	0.09209	0.13806	0.13824
$g_5$	0.06786	0.00656	0.03632	0.03686
$g_6$	0.01779	0.00010	0.00394	0.00410

$A_{1-y}B_y$  alloy were distributed randomly over the lattice. Then nearest-neighbour atoms were allowed to exchange positions according to the transition probability (Binder 1976)

$$W = \begin{cases} \exp(-\Delta E/kT) & \text{if } \Delta E > 0 \\ 1 & \text{if } \Delta E \leq 0 \end{cases} \quad (24)$$

where  $\Delta E$  denotes the change in energy corresponding to the transition. For simplicity, we used only an interaction  $J$  between nearest-neighbour B atoms. After a thermalisation time of a few hundreds of Monte Carlo steps per atom, ensemble averages of the octahedron fractions  $g_i$  and also of the short-range order parameter  $\alpha_1$  (Haasen 1978) were determined during another few hundreds of Monte Carlo steps per atom. As an example, table 1 presents Monte Carlo results obtained for an  $A_{60}B_{40}$  alloy, for both  $J/kT = 1.0$  (ordering) and  $J/kT = -0.3$  (clustering). The values for the short-range order parameter of  $\alpha_1 = -0.134$  and  $\alpha_1 = 0.107$  are of the same order of magnitude as those reported in real FCC alloys. Although in a real alloy the interactions are not restricted to nearest-neighbour atoms, our Monte Carlo data should, however, give reasonable estimates for the octahedron fractions in alloys with these values of  $\alpha_1$ .

Using these data for the cluster fractions, we have fitted again the pressure–composition isotherms and the enthalpy and excess entropy at infinite dilution for  $Pd_{1-y}Ag_y$ . Since no values for the short-range order parameter  $\alpha_1$  of  $Pd_{1-y}Ag_y$  alloys have been reported to our knowledge, we have investigated the cases of both clustering for  $J/kT = -0.3$  and short-range ordering for  $J/kT = 1.0$ . For  $J/kT = 1.0$  we found a good fit to all the data for a site energy distribution with  $\varepsilon_0 = -6.4 - 50y$ ,  $\varepsilon_1 = -1.4 - 50y$  and  $\varepsilon_2 = 9.1 - 50y$ , which differs only slightly from the distribution shown in figure 8. For  $J/kT = -0.3$  we found a good fit for a distribution with  $\varepsilon_0 = -6.4 - 40y$ ,  $\varepsilon_1 = -3.4 - 40y$  and  $\varepsilon_2 = 20.6 - 40y$ , which differs from the distribution shown in figure 8 mainly in the value of  $\varepsilon_2$ . Both fits yield a very small difference between  $\varepsilon_0$  and  $\varepsilon_1$ , similar to the difference  $\varepsilon_1 - \varepsilon_0 = 4 \text{ kJ (mol H)}^{-1}$  obtained from the fits using the binomial distribution for the octahedron fractions. We conclude that the site energy spectra in figures 8 and 12 would be modified only slightly by the effect of short-range ordering or clustering.

#### 4.2. Broadening of the peaks in the site energy spectrum

In § 2 it was assumed that the site energies  $\varepsilon_i$  are determined only by the numbers of Pd atoms and Ag or Cu atoms in the octahedron surrounding the site. The effect on the

hydrogen energy of the more distant metal atoms around the octahedron has been neglected. One expects, however, that these more distant metal atoms affect both the volume and the local electronic structure of the octahedron (and hence the site energy). The fluctuation of the Ag or Cu concentration in the shell of atoms surrounding the octahedrons (this shell contains, for example, the eight atoms at the corners of the unit cell shown in figure 1) causes therefore a broadening of the seven peaks in the ideal site energy spectrum. In this section it is investigated how much this broadening affects the positions of the peaks.

To simulate the broadening, we have split each site energy  $\varepsilon_i$  with weight  $g_i$  into three energies:

$$\begin{aligned} \varepsilon_{i,1} &= \varepsilon_i && \text{with weight } g_{i,1} = \frac{1}{2}g_i \\ \varepsilon_{i,2} &= \varepsilon_i + \Delta\varepsilon && \text{with weight } g_{i,2} = \frac{1}{4}g_i \\ \varepsilon_{i,3} &= \varepsilon_i - \Delta\varepsilon && \text{with weight } g_{i,3} = \frac{1}{4}g_i \end{aligned} \quad (25)$$

so that there are 21 types of site instead of seven. The energy difference  $\Delta\varepsilon$  is determined by the fluctuations in the Ag or Cu concentration in the shell around the site. For a randomly mixed alloy, one can derive that the standard deviation of the Ag or Cu concentration in a cluster is proportional to  $\sqrt{y(1-y)}$ . We write therefore

$$\Delta\varepsilon = \Delta\varepsilon_0 \sqrt{y(1-y)} \quad (26)$$

so that  $\Delta\varepsilon = 0$  for  $y = 0$  and  $y = 1$ , as required.

For the more or less arbitrarily chosen value of  $\Delta\varepsilon_0 = 8 \text{ kJ (mol H)}^{-1}$ , we have again fitted the experimental data for Pd<sub>1-y</sub>Ag<sub>y</sub>. A good fit was obtained for a distribution with broadened site energies at  $\varepsilon_0 = -6.4 - 40y$ ,  $\varepsilon_1 = -3.4 - 40y$  and  $\varepsilon_2 = 6.6 - 40y$ . From a comparison with the site energy distribution shown in figure 8, it follows that the broadening of the site energy peaks has only a small effect on the positions of the peaks.

## 5. Discussion of the spectra

The main results of this paper are the site energy spectra of hydrogen in Pd<sub>1-y</sub>Ag<sub>y</sub> (figure 8) and Pd<sub>1-y</sub>Cu<sub>y</sub> (figure 12). Previous thermodynamic studies of hydrogen in these Pd alloys have neglected the presence of a site energy distribution, with two exceptions. Picard *et al* (1979) concluded that the change  $\Delta\bar{S}^\infty$  in excess entropy of solution with increasing silver concentration (figure 7) could be explained by a site energy spectrum with  $\varepsilon_0 = \varepsilon_1$  and  $\varepsilon_2, \dots, \varepsilon_6 = \infty$ , which they rejected as 'unphysical'. Note, however, that this spectrum resembles in a qualitative sense the more 'physical' spectrum shown in figure 8 (which gives a better fit to the data for  $\Delta\bar{S}^\infty(y)$ ). Griessen (1986) used the semi-empirical band-structure model (22) to calculate the site energy spectrum of hydrogen in Pd<sub>1-y</sub>Ag<sub>y</sub> and Pd<sub>1-y</sub>Cu<sub>y</sub> alloys. At present, we are working on an extension of this model to predict local site energies (Griessen 1989). A discussion of the spectra obtained in the present work in the light of this local model will be published elsewhere.

Next we shall try to interpret the spectra in figures 8 and 12. Most striking is the difference between Pd<sub>1-y</sub>Ag<sub>y</sub> and Pd<sub>1-y</sub>Cu<sub>y</sub>. While the site energies  $\varepsilon_i$  in Pd<sub>1-y</sub>Ag<sub>y</sub> decrease with increasing  $y$ , they are constant for Pd<sub>1-y</sub>Cu<sub>y</sub>. Since approximately the same trend is observed in the enthalpies  $\Delta\bar{H}^\infty(y)$  of solution for both systems, this



difference was also recognised in studies which neglected the presence of a site energy spectrum. One can write in general

$$d\varepsilon_i/dy = (d\varepsilon_i/dy)_{\text{elastic}} + (d\varepsilon_i/dy)_{\text{electronic}} \quad (27)$$

where  $(d\varepsilon_i/dy)_{\text{elastic}}$  represents the effect of the change in lattice parameter upon alloying, and the term  $(d\varepsilon_i/dy)_{\text{electronic}}$  contains the remaining (electronic) effects. This separation of the hydrogen energy in Pd alloys was also suggested by Burch and Buss (1975).

To calculate the elastic term in equation (27), we first note that the volume dependence of the partial molar enthalpy of hydrogen solution is given by (Griessen and Feenstra 1985)

$$[\partial(\Delta\bar{H})/\partial(\ln V)]_c = -B\bar{V}_H. \quad (28)$$

In analogy with this relation we write

$$d\varepsilon_i/d(\ln \Omega_i) = -B\bar{V}_H \quad (29)$$

where  $\Omega_i$  is the volume of the octahedron  $\text{Pd}_{6-i}\text{M}_i$  in the alloy  $\text{Pd}_{1-y}\text{M}_y$  ( $\text{M} \equiv \text{Ag, Cu}$ ). In general, this local volume  $\Omega_i$  differs from the average volume  $\Omega$  of the octahedra in the alloy, since the atoms in a random alloy do not form a perfect lattice. Therefore we introduce a parameter  $D$  by the relation

$$\Omega_i(y) = (1 - D)\Omega(y) + D\Omega_i^{\text{free}} \quad (30)$$

where the 'free' volume  $\Omega_i^{\text{free}}$  is the volume of an octahedron  $\text{Pd}_{6-i}\text{M}_i$  in an alloy  $\text{Pd}_{1-y}\text{M}_y$  with solute content  $y = i/6$ . The parameter  $D$  (with  $0 \leq D \leq 1$ ) is a measure of the lattice relaxation with respect to the perfect (or average) lattice. From equations (29) and (30), one obtains (using  $\Omega_i \approx \Omega$ )

$$(d\varepsilon_i/dy)_{\text{elastic}} = -B\bar{V}_H(1 - D) d(\ln \Omega)/dy \quad (31)$$

or

$$(d\varepsilon_i/dy)_{\text{elastic}} = -B\bar{V}_H(1 - D)3 d(\ln a)/dy \quad (32)$$

where  $a$  is the lattice parameter of the alloy. The parameter  $D$  is simply related to the parameter  $I_1$  of Froyen and Herring (1981) as  $D = \frac{3}{4}\sqrt{2}I_1$ . For Pd, Ag and Cu,  $I_1 \approx 0.3$ , so that  $D \approx 0.3$ . We obtain then

$$(d\varepsilon_i/dy)_{\text{elastic}} \approx -30y \quad \text{for Pd}_{1-y}\text{Ag}_y$$

$$(d\varepsilon_i/dy)_{\text{elastic}} \approx +40y \quad \text{for Pd}_{1-y}\text{Cu}_y.$$

From figures 8 and 12 it follows that

$$d\varepsilon_i/dy = -44y \quad \text{for Pd}_{1-y}\text{Ag}_y$$

$$d\varepsilon_i/dy = 0 \quad \text{for Pd}_{1-y}\text{Cu}_y.$$

From equation (27), one obtains then

$$(d\varepsilon_i/dy)_{\text{electronic}} = -14y \quad \text{for Pd}_{1-y}\text{Ag}_y$$

$$(d\varepsilon_i/dy)_{\text{electronic}} = -40y \quad \text{for Pd}_{1-y}\text{Cu}_y.$$

These negative electronic contributions to the site energy should originate from the change in the electronic structure on alloying. It is interesting that the electronic contribution is considerably larger for  $\text{Pd}_{1-y}\text{Cu}_y$  than for  $\text{Pd}_{1-y}\text{Ag}_y$ . This difference might be related to the fact that for  $\text{Pd}_{1-y}\text{Cu}_y$  a narrowing of the d band with increasing  $y$

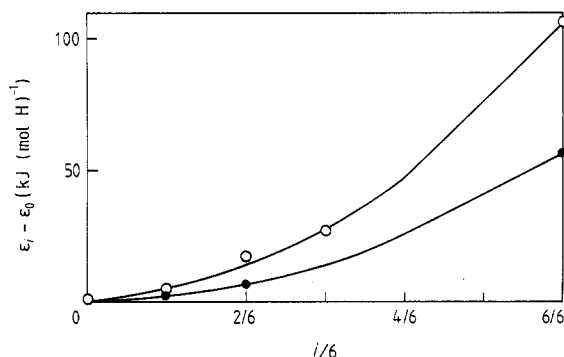


Figure 14. Plot of  $\epsilon_i - \epsilon_0$  from figures 8 and 12 against the local (○) or Cu (●) concentration  $i/6$  (at constant  $y$ ).

occurs, whereas for  $Pd_{1-y}Ag_y$  the d band width is approximately constant as a function of  $y$  (Winter and Stocks 1983, Winter *et al* 1986).

A different way to look at the site energy distributions is shown in figure 14. In this figure the difference  $\epsilon_i - \epsilon_0$  is plotted as a function of  $i/6$  (at constant  $y$ ). There is a remarkable similarity of  $\epsilon_i - \epsilon_0$  as a function of  $i/6$  to the electronic enthalpy  $\bar{H}_{\text{electronic}}$  as a function of  $c$  (see figure 3).

This suggests that the band filling by Ag or Cu electrons has a local effect on the site energies, although it was shown in § 3 that this band filling does not have a local effect on the effective electronic hydrogen-hydrogen interaction. To understand this difference, it should be remembered that the site energy is related to the occupation of the site by a hydrogen atom, while the electronic interaction is related to the accommodation of the hydrogen electrons at the Fermi level. The energy of a hydrogen atom at a site appears to be affected by the local electronic density of states. In addition, one expects that the site energies are affected by the local volume changes in the octahedra in the alloy, as mentioned above. This latter effect explains (partly) the difference between the curves for  $Pd_{1-y}Ag_y$  and  $Pd_{1-y}Cu_y$  in figure 14, as follows from equation (32).

In summary, the site energy spectra of hydrogen in  $Pd_{1-y}Ag_y$  and  $Pd_{1-y}Cu_y$  alloys have been determined from available experimental data, using a mean-field multi-site lattice gas model for hydrogen in a disordered alloy. To determine the highest site energies, additional data are required at higher hydrogen concentrations and/or higher solute concentrations  $y$ . The spectra suggest that the electronic band filling by Ag or Cu electrons has a local effect on the site energies. We are at present working on a local version of the semi-empirical band-structure model (Griessen 1989) to explain this effect.

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