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Lattice-gas model for the formation of palladium-silver hydrides at pressures up to 100 GPa

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A multisite lattice-gas model is presented that describes the formation of $Pd_{1-y}Ag_y$ hydrides. The parameters entering the model are obtained by generalizing the corresponding parameters of the Pd-H system and by fitting the site energies to the available experimental data. Using the multisite lattice-gas model, pressure-composition isotherms for $Pd_{1-y}Ag_yH_c$ (with $y=0$, 0.1, 0.2, 0.3, 0.4, and 0.5) are calculated for pressures up to 100 GPa.

I. INTRODUCTION

The early transition metals, as well as palladium, the rare earths, the actinides, and many of their alloys and compounds, react readily with hydrogen at room temperature and at pressures of a few bars.[1-3] These systems have a negative heat of formation (i.e., they are exothermic). In contrast to the exothermic systems, the endothermic systems (i.e., with a positive heat of formation) absorb only small quantities of hydrogen at moderate pressures.

For the hydrides of many of the late transition metals, the majority of the simple metals, the noble metals, and many of their alloys and compounds, the heat of formation is positive[3] and are consequently poor hydrogen absorbers. Higher hydrogen concentrations can be obtained in these systems by increasing the chemical potential of the hydrogen. This can be achieved by using high hydrogen pressures.[4]

Until now the formation of endothermic metal hydrides has been studied up to ~7 GPa using different high-pressure techniques.[5-7] The only apparatus capable of reaching substantially higher pressures is the diamond anvil cell (DAC).[8] With the DAC pressures over 100 GPa can be reached. Recently Hemmes et al.[9] developed a technique to prepare metal hydrides at high pressures in a DAC.

The "standard" techniques[5-7] can load samples that are large enough to determine the hydrogen concentration after removing the sample from the high-pressure apparatus. In contrast, the samples in a DAC are so small, typically $100 \times 100 \times 10$ μm^3, that at present, *ex situ* determination of the hydrogen contents is practically impossible.

In order to study the properties of metal hydrides meaningfully in a DAC we need some way to determine the hydrogen concentration. This is, for instance, important in the study of the superconducting properties of the Pd-H and Pd–noble metal–H systems, as the superconducting transition temperature depends strongly on the hydrogen concentration.[10,11]

One way to determine the hydrogen concentration *in situ* is by measuring the volume expansion due to hydrogen absorption. The volume change can be measured using x-ray scattering[8] or an optical technique, using a microscope.[12,13] This technique which requires, however, a knowledge of the dependence of the volume of the sample on the hydrogen concentration and pressure, is at present under development in our laboratory.

Another way is to rely on calculated pressure-composition (*p-c*) isotherms. From measurements of the loading pressure and temperature the concentration can then directly be determined from the *p-c* isotherms. To calculate the *p-c* isotherms we need a model for the thermodynamic properties of hydrogen in a metal and the thermodynamic properties of molecular hydrogen at high pressures. The thermodynamic properties of molecular hydrogen at pressures up to 100 GPa and temperatures between 100 and 1000 K have been determined by Hemmes et al.[4]

Recently the superconducting properties of Pd hydrides and Pd-Ag hydrides, loaded at high pressures in a diamond anvil cell,[14-16] were measured. In the case of the Pd hydrides stoichiometric PdH and PdD were prepared.[15] This could be inferred from the (known) dependence of the superconducting transition temperature (T_c) on the hydrogen concentration. Also the saturation of T_c for increasing H_2 loading pressure indicated that the maximum hydrogen concentration was reached. For the Pd-Ag-H system the concentration dependence of T_c is not well known and stoichiometry of the hydrides is only reached at much higher pressures, if at all. For the analysis of the experimental results on the superconducting properties of the Pd-Ag-H system it is therefore desirable to have an estimate of the hydrogen concentration in the samples. For this reason we developed a multisite lattice-gas model for the description of the hydride formation in palladium-noble metal alloys. Details on this model and its application to Pd-Ag and Pd-Cu alloys are published elsewhere.[17]

In this paper we apply this model to the calculation of thermodynamic properties of hydrogen in a Pd-Ag alloy and present calculations of pressure-composition isotherms up to 100 GPa for a number of alloys and compare the results with experimental results. In Sec. II we give the framework in which the thermodynamic properties of hydrogen in a metal are analyzed and apply this to the Pd-H system. We also discuss the physical interpretation of the quantities emerging from the analysis, as they are important for the generalizations needed to de-

scribe the Pd-Ag-H system. In Sec. III we describe the multisite lattice-gas model for the thermodynamic properties of hydrogen in an alloy. Section IV describes how the site energies, needed in the multisite model, are obtained. Using the developed model and the thermodynamic properties of hydrogen of Hemmes et al.,[4] pressure-composition isotherms of several Pd-Ag alloys are calculated up to 100 GPa. Finally, in Sec. V, the results are discussed.

II. THERMODYNAMICS OF HYDROGEN ABSORPTION IN METALS

Hydrogen may, in principle, be dissolved in any metal. The surrounding molecular hydrogen is then in equilibrium with the metal-hydride phase MH_c and consequently

$$\frac{1}{2}\mu_{H_2}(p,T)=\mu_H(p,T,c) , \tag{1}$$

where μ_{H_2} is the chemical potential of pure molecular hydrogen and μ_H is the chemical potential of atomic hydrogen in solution in the metal, at a given pressure p, temperature T, and hydrogen concentration c. The thermodynamical analysis of the hydride formation of Pd is usually given in terms of enthalpy and entropy.[18−20] We can obtain these quantities from the chemical potential using the standard relations

$$\bar{H}=\frac{\partial(\mu/T)}{\partial(1/T)}\bigg|_{p,n} , \tag{2a}$$

$$\bar{S}=-\frac{\partial\mu}{\partial T}\bigg|_{p,n} . \tag{2b}$$

Here $\bar{H}$ and $\bar{S}$ are the partial molar enthalpy and entropy, respectively, and n is the number of moles. We can now write Eq. (1) in terms of enthalpy and entropy:

$$\frac{1}{2}(\bar{H}_{H_2}-T\bar{S}_{H_2})=\bar{H}_H-T\bar{S}_H . \tag{3}$$

Usually the chemical potential of molecular hydrogen is split into two parts: $\mu_{H_2}=\mu_{H_2}^0(T)+\Delta\mu_{H_2}(p,p_0,T)$, where $\mu_{H_2}^0$ is the chemical potential at a given standard pressure p_0 (usually 1 atm or 1 bar). Equation (3) can then be written as

$$\frac{1}{2}\Delta\mu_{H_2}=\Delta\bar{H}_H-T\Delta\bar{S}_H , \tag{4}$$

where $\Delta\bar{H}_H=\bar{H}_H-\frac{1}{2}\bar{H}_{H_2}^0$ and $\Delta\bar{S}_H=\bar{S}_H-\frac{1}{2}\bar{S}_{H_2}^0$. This notation is especially useful at low pressures ($p\leq 100$ bar), where the hydrogen gas obeys the ideal-gas law and consequently $\Delta\mu_{H_2}(p,T)=RT\ln(p/p_0)$, with p_0 the standard pressure and R the universal gas constant.

The enthalpy $\Delta\bar{H}_H$ and entropy $\Delta\bar{S}_H$ are usually written in terms of a contribution at infinite dilution ($c\to 0$) and a concentration dependent part:[19]

$$\Delta\bar{H}_H=\Delta\bar{H}_H^\infty+\bar{H}(c)+p\bar{V}_H , \tag{5a}$$

$$\Delta\bar{S}_H=\Delta\bar{S}_H^\infty+\bar{S}(c)-R\ln\left[\frac{c}{1-c}\right] . \tag{5b}$$

Here $\Delta\bar{H}_H^\infty=\bar{H}_H^\infty-\frac{1}{2}\bar{H}_H^0$ is the enthalpy at infinite dilution, $\bar{H}(c)$ is the "excess enthalpy" and describes the concentration dependence of the enthalpy, $\bar{V}_H$ is the partial molar volume of hydrogen in the metal, and $p\bar{V}_H$ is the work done in expanding the metal against the pressure p. For the entropy a logarithmic term appears. It is the ideal "configurational" entropy, stemming from the mixing of occupied and empty sites. This term appears naturally in a mean-field lattice-gas treatment of the thermodynamics of hydrogen in metals.[21,22] Because the ideal configurational entropy diverges for $c\to 0$ and $c\to 1$, it is used to extract the "nonideal-configurational" contributions to $\Delta\bar{S}_H$, usually called the excess entropy. In Eq. (5b) $\Delta\bar{S}_H^\infty\equiv\lim_{c\to 0}\bar{S}_H-\frac{1}{2}\bar{S}_{H_2}^0+R\ln[c/(1-c)]$ is the excess entropy at infinite dilution and $\bar{S}(c)$ describes the concentration dependence of the excess entropy.

Equations (4) and (5) give the framework for the usual analysis of "low-pressure"-composition isotherms. In this analysis the ideal-gas approximation is used for $\Delta\mu_{H_2}$ and the $p\bar{V}_H$ term is neglected. In order to analyze and/or calculate "high-pressure"-composition isotherms we have to include the $p\bar{V}_H$ term and cannot use the ideal-gas approximation for $\Delta\mu_{H_2}$ (see, e.g., Refs. 4, 23, and 24). This does not only make the calculations more involved, but the inclusion of the $p\bar{V}_H$ term also leads to a new effect, strongly affecting the hydride formation at high pressures. This effect can be seen most clearly if we differentiate Eq. (1) with respect to pressure, at constant temperature:

$$\frac{1}{2}\frac{\partial\mu_{H_2}}{\partial p}\bigg|_T=\frac{\partial\mu_H}{\partial p}\bigg|_T=\frac{\partial\mu_H}{\partial p}\bigg|_{c,T}+\frac{\partial\mu_H}{\partial c}\bigg|_{p,T}\frac{\partial c}{\partial p}\bigg|_T . \tag{6}$$

By rearranging the terms and using $\partial\mu/\partial p|_T=\bar{V}$, we can rewrite Eq. (6) as

$$\frac{\partial\mu_H}{\partial c}\bigg|_{p,T}\frac{\partial c}{\partial p}\bigg|_T=\frac{1}{2}\bar{V}_{H_2}-\bar{V}_H . \tag{7}$$

From the condition that, in equilibrium, the Gibbs free energy is minimal it follows that $\partial\mu_H/\partial c|_{p,T}\geq 0$, the equality being only satisfied at the critical point.[25] Equation (7) shows that, at constant temperature, as long as $\frac{1}{2}\bar{V}_{H_2}>\bar{V}_H$ the hydrogen concentration increases with pressure, i.e., $\partial c/\partial p|_T>0$. However, if the hydrogen pressure is so large that $\frac{1}{2}\bar{V}_{H_2}<\bar{V}_H$, then $\partial c/\partial p|_T$ changes sign and the hydrogen concentration decreases with increasing pressure. The pressure where the turnover of the p-c isotherms occurs is simply determined by $\frac{1}{2}\bar{V}_{H_2}=\bar{V}_H.$ Because of the small size of $\bar{V}_H$ [typically 1.7 cm^3/mol H (Refs. 26 and 27)], very high hydrogen pressures are needed to satisfy this condition.

In this paper we are mainly concerned with the formation of palladium-silver hydrides. The multisite lattice-gas model presented in Sec. III is a generalization of the single-site lattice-gas model used for the description of the Pd-H system. In the rest of this section we give the results of the analysis of the pressure-composition isotherms of PdH_c in terms of Eqs. (4) and (5). For this we

use the experimental data of Frieske and Wicke[28] and Blaurock.[20] The results given below are optimized to give the best description of the experimental data.

For the enthalpy at infinite dilution we find $\Delta \bar{H}_{H}^{\infty} = -6.4 + 0.020(T - 600)$ kJ/mol H, where T is the temperature in Kelvin. It contains a (constant) contribution of the site energy, i.e., the energy gained by the hydrogen atom when dissolved in the metal, a contribution from the vibrations of hydrogen in the metal, and a contribution of the molecular hydrogen. The last two contributions are temperature dependent.

For the entropy at infinite dilution we find $\Delta \bar{S}_{H}^{\infty} = -47.2 + 0.033(T - 600)$ J/K mol H. It is mainly determined by the hydrogen vibrations in the metal and the molecular hydrogen.

The concentration dependence of the excess entropy, $\bar{S}(c)$, and the excess enthalpy, $\bar{H}(c)$, are shown in Fig. 1. Following Feenstra et al.[19] the concentration dependence of $\Delta \bar{H}_{H}$, i.e., $\bar{H}(c)$ can be written as

$$\frac{d\Delta \bar{H}_{H}}{dc} = \frac{d\bar{H}(c)}{dc} = -\frac{B(c)\bar{V}_{H}^{2}(c)}{V_{m}(c)} + \frac{\alpha}{N(E_{F}(c))} , \qquad (8)$$

where $B(c)$, $V_{m}(c)$, and $N(E_{F}(c))$ are the bulk modulus, the molar volume of the metal, and the electronic density of states at the Fermi level of PdH$_{c}$. The constant $\alpha = 29.62$ kJ/eV mol H is one of the constants appearing in the semiempirical band-structure model of Griessen and Driessen[29] which relates $\Delta \bar{H}_{H}^{\infty}$ to the band-structure parameter $E_{F} - E_{s}$, where E_{F} is the Fermi energy and E_{s} is essentially the center of the lowest s-like conduction band. The first term on the right-hand side of Eq. (8) is called the "elastic" contribution, which accounts for the volume increase during hydrogen absorption at constant pressure. The second term on the right-hand side of Eq. (8) is called the "electronic" term, as it describes the filling of the electronic band structure, at constant volume, by the extra hydrogen electrons. From Eq. (8) it

FIG. 2. Elastic and electronic contributions to the excess enthalpy as a function of hydrogen concentration.
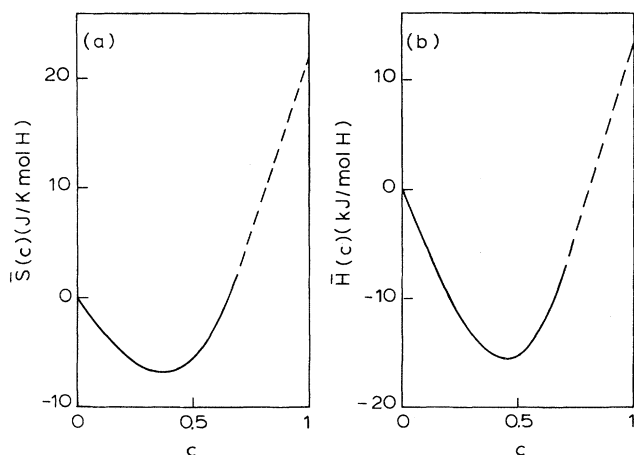
FIG. 1. (a) Excess entropy and (b) excess enthalpy as a function of hydrogen concentration for the Pd-H system. The solid lines represent the values determined from the pressure-composition isotherms of Frieske and Wické (Ref. 28) and Blaurock (Ref. 20). The dashed lines give the (linear) extrapolation for $c > 0.7$.
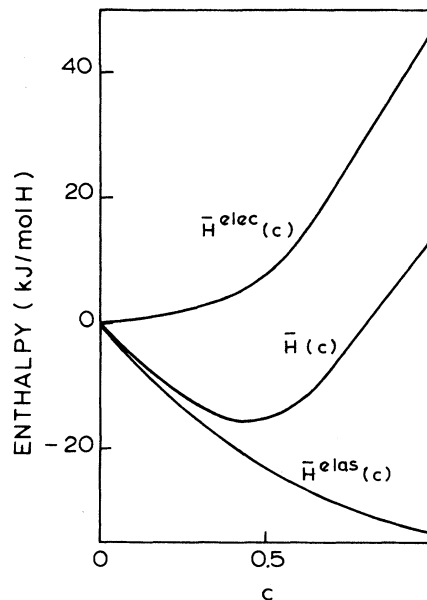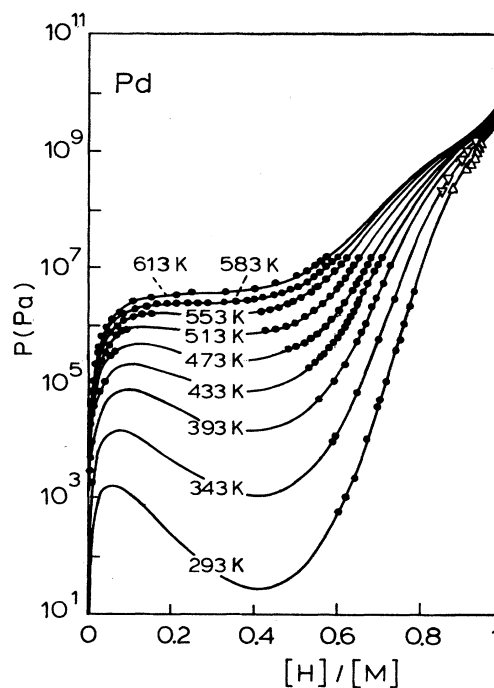
FIG. 3. Pressure-composition isotherms of the Pd-H system. The solid lines are calculated at the indicated temperatures with the parameters indicated in the text. The experimental data at low pressures ($p < 1.5 \times 10^{7}$ Pa), indicated by the solid circles, are from Refs. 19 and 27. The high-pressure data ($p > 1.0 \times 10^{8}$ Pa), indicated by the triangles ($\triangle$, 318 K; ∇, 338 K) is from Baranowski (Ref. 5). The isotherms are calculated at the same temperatures as the low-pressure experimental data.

follows that we can write the excess enthalpy as the sum of an elastic and electronic contribution: $\bar{H}(c) = \bar{H}^{\text{elas}}(c) + \bar{H}^{\text{elec}}(c)$. $\bar{H}(c)$ is determined directly from the experimental data. $\bar{H}^{\text{elas}}$ is defined as the integral of the first term on the right-hand side of Eq. (8) and can be calculated from the known concentration dependence of B, $\bar{V}_H$, and V_m.[19] $\bar{H}^{\text{elec}}(c)$ is then defined as the difference $\bar{H}(c) - \bar{H}^{\text{elas}}(c)$. The enthalpies $\bar{H}^{\text{elec}}, \bar{H}^{\text{elas}}$, and $\bar{H}(c)$ are plotted in Fig. 2 as a function of hydrogen concentration.

Figure 3 shows calculated as well as experimental pressure-composition isotherms for the Pd-H system. $\bar{S}(c)$ and $\bar{H}(c)$ are extrapolated linearly for $c > 0.7$. We see that this extrapolation gives a good agreement between the calculated isotherms at high pressures and the high-pressure experimental data of Baranowski.[5]

III. MULTISITE LATTICE-GAS MODEL

To calculate the pressure-composition isotherms for $Pd_{1-y}Ag_y$ alloys we use a multisite lattice-gas model.[17,21,30-32] We assume that hydrogen occupies the octahedral interstitial sites in the fcc lattice, as in pure Pd, and that there is at most one hydrogen atom at a given site. We further assume that the six metal atoms surrounding an octahedral interstitial site determine its properties. There are seven different types of sites: Pd_6, $Pd_5Ag_1, \ldots, Pd_1Ag_5$, and Ag_6, where only the number of Pd and Ag atoms is important. The fraction x_j ($0 \leq j \leq 6$, with j the number of Ag atoms) of occupied sites, with site energy ε_j, is then given by a Fermi-Dirac distribution:[22,33,34]

$$x_j = \left[\exp \left[\frac{\varepsilon_j + \varepsilon(T) + \bar{H}^* + p\bar{V}_H - T\bar{S}_H^\infty - T\bar{S}^* - \frac{1}{2}\Delta\mu_{H_2}}{RT} \right] + 1 \right]^{-1} . \tag{9}$$

In the special case of just one site, x_j is equal to the total hydrogen concentration c and with $\Delta\bar{H}_H^\infty = \varepsilon_j + \varepsilon(T)$, Eq. (9) is equivalent to Eqs. (4) and (5). For PdH_c we would have $\varepsilon_j = -6.4$ kJ/mol H and $\varepsilon(T) = 0.020(T - 600)$ kJ/mol H. In a multisite system one has to distinguish the total concentration and the partial concentration. The total hydrogen concentration c is defined as the fraction of occupied interstitial sites, irrespective of the type of site. In a fcc lattice there is one octahedral site for each metal atom, so $c = [\text{H}]/[M]$. If g_j is the fraction of interstitial sites with energy ε_j, then the total hydrogen concentration is given by

$$c = \sum_j g_j x_j(\varepsilon_j, c, p, T) . \tag{10}$$

Equation (10) defines an implicit relation between c, p, and T, which can be solved numerically. In an ideal random alloy, g_j is given by a binomial distribution:

$$g_j = \begin{bmatrix} 6 \\ j \end{bmatrix} y^j(1-y)^{6-j} .$$

We will discuss now the quantities appearing in the exponent of Eq. (9).

The site energies ε_j probably depend on the silver concentration, y, of the $Pd_{1-y}Ag_y$ alloy. The contribution of a site (j) to the total hydrogen concentration does not only depend on the value ε_j of the site energy but also on the fraction of sites, g_j, present in the alloy. For example, in the limit $y \to 0$ only the Pd_6 site ($j = 0$) contributes to the p-c isotherms. From these isotherms we can then only determine the site energy of the Pd_6 site at $y = 0$. Similarly for the limit $y \to 1$ we can only determine the site energy of the Ag_6 site at $y = 1$.

The thermal function $\varepsilon(T) = 0.020(T - 600)$ kJ/mol H depends, as discussed in Sec. II, mainly on the vibrations

of the hydrogen in the metal and the properties of molecular hydrogen. Neutron-diffraction studies of the $Pd_{1-y}Ag_yH_c$ system[35,36] have shown that the vibrational properties of hydrogen in Pd do not change significantly when Pd is alloyed with Ag. Since the properties of molecular hydrogen depend only on pressure and temperature, we take $\varepsilon(T)$ to be independent of y. The same arguments apply to the excess entropy at infinite dilution, $\Delta\bar{S}_H^\infty$.

The molar volume of hydrogen does not change when Pd is alloyed with Ag.[26,37] We therefore use the value $\bar{V}_H = 1.77$ cm^3/mol H for all the $Pd_{1-y}Ag_y$ alloys discussed in this paper.

In analogy with the Pd-H system, the excess enthalpy of the alloy, $\bar{H}^*(c)$, is assumed to consist of an elastic and electronic contribution ($\bar{H}_{\text{alloy}}^{\text{elas}}$ and $\bar{H}_{\text{alloy}}^{\text{elec}}$). For the elastic contribution the same form holds as for the Pd-H system. $\bar{H}^{\text{elas}}$ depends on the silver concentration through the bulk modulus and the molar volume of the metal [see Eq. (6)]. The dependence of the bulk modulus and $\bar{V}_H$ of Pd-Ag alloys on the hydrogen concentration is not known. Since we are mainly concerned with Pd-rich alloys we assume for the alloys the same concentration dependence as for the Pd-H system. For a correct behavior at infinite dilution (i.e., at $c = 0$) we scale $\bar{H}_{\text{alloy}}^{\text{elas}}$ with the bulk modulus and the molar volume of the alloy. At higher hydrogen concentration this has, however, only a minor influence on the p-c isotherms. The electronic contribution, $\bar{H}_{\text{alloy}}^{\text{elec}}$, to $\bar{H}^*$, is assumed to describe the filling of electronic bands. Feenstra et al.[19] interpreted $\bar{H}^{\text{elec}}$ for PdH_c as a rise in Fermi level due to the filling of a "rigid band structure" with electrons from the hydrogen atoms. As each silver atom contributes an extra electron to the electronic bands, $\bar{H}_{\text{alloy}}^{\text{elec}}$ does not only depend on the hydrogen concentration c but also on y. Within this picture, the extra electrons from the silver atoms are also

contributing to band filling. Within the rigid band picture we have for a $Pd_{1-y}Ag_y$ alloy an electronic contribution of the form $\bar{H}_{alloy}^{elec}(c,y)=\bar{H}_{Pd}^{elec}(y+c)-\bar{H}_{Pd}^{elec}(y)$, where the term $\bar{H}_{Pd}^{elec}(y)$ is subtracted to ensure $\bar{H}*(c)=0$ at $c=0$, as required by the definition of $\bar{H}*(c)$.

Finally we need an expression for the concentration dependence of the excess entropy $\bar{S}*$. At present since no microscopic interpretation is available for $\bar{S}(c)$ in the Pd-H system we simply put $\bar{S}*(c)=\bar{S}(c)$.

IV. SITE ENERGIES
AND PRESSURE-COMPOSITION ISOTHERMS

In the preceding section practically all quantities needed in the multisite lattice-gas model for the $Pd_{1-y}Ag_y$-H system were obtained from the corresponding quantities for the Pd-H system. Only the site energies ε_j remain to be determined. We use these site energies as free parameters in a fit of the multisite model to the experimental pressure-composition isotherms. This gives us a large number of fit parameters: seven site energies for each alloy. In practice only two site energies can be fitted to the p-c isotherms for each $Pd_{1-y}Ag_y$ alloy. This is due to the limited concentration range of the available experimental data and for a number of sites to fractions, g_j, that are too small to influence the p-c isotherms (e.g., $g_j < 10^{-3}$). In our fits we assume that the seven site energies all have the same (linear) dependence on the silver concentration, i.e.,

$$\varepsilon_j(y)=\varepsilon_j^0+Ky \quad (0\leq j\leq 6) , \tag{11}$$

where ε_j^0 is the energy of site j for $y=0$. These assumptions reduce the number of fit parameters to eight for the whole $Pd_{1-y}Ag_y$-H system, seven site energies and the "slope" K. We further assume that $\varepsilon_j<\varepsilon_{j+1}$, so that sites with more surrounding Ag atoms have a higher site energy (a fit with $\varepsilon_j>\varepsilon_{j+1}$ is easily shown to be incapable of reproducing the experimental data.)

In the limit $y\to0$ only Pd_6 sites exist (i.e., $g_0=1$) and $\varepsilon_0(0)=\varepsilon_0^0$. Since $\varepsilon_0(0)$ is the site energy of a Pd_6 site in pure Pd (i.e., $y=0$), we can obtain ε_0^0 from the analysis of PdH_c isotherms. From the data in Sec. II we find $\varepsilon_0^0=-6.4$ kJ/mol H. Similarly in the limit $y\to1$ only the Ag_6 site is occupied and $\varepsilon_6(1)=\varepsilon_6^0+K$. Since $\varepsilon_6(1)$ is the site energy of a Ag_6 site in pure silver (i.e., $y=1$), we can determine it from the analysis of AgH_c data. We find $\varepsilon_6(1)\approx55$ kJ/mol H.[38,39] We now have a relation [Eq. (11)] between ε_6^0 and K, which further reduces the number of fit parameters to six.

For the fits of the remaining parameters we used the pressure-composition isotherms of $Pd_{1-y}Ag_y$ alloys with $y=0.1$, 0.2, 0.3, 0.4, and 0.5, determined by Brodowsky and Poeschel,[40] Salomons,[41] and Ponyatovskii et al.[6] Because of the limited range of the available data we could only determine four of the six fit parameters. The results of the fits are shown in Figs. 4 and 5. Figure 4 shows the site energies $\varepsilon_j(y)$ as a function of silver concentration. The solid circles indicate the site energies that could be determined from the available experimental data. The parameter $K=-44$ kJ/mol H can be determined from
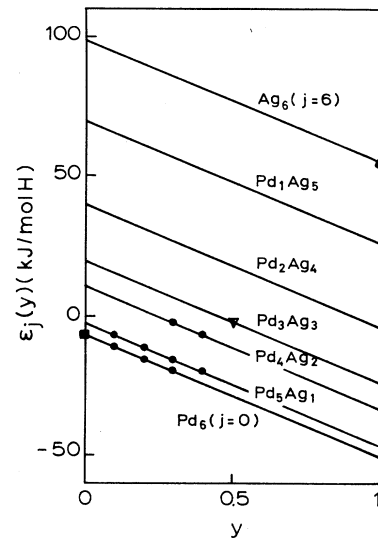

FIG. 4. Site energies ε_j for the $Pd_{1-y}Ag_y$-H system as a function of the silver concentration y. The symbols indicate the site energies that could be fitted to the experimental data [■, Frieske and Wicke (Ref. 28) and Blaurock (Ref. 20); ●, Brodowsky and Poeschel (Ref. 40); ▼, Ponyatovskii et al. (Ref. 6); ◆, Driessen and Griessen (Ref. 38) and McLellan (Ref. 39)]. The solid lines have a slope $K=-44$ kJ/mol H.

the slope of the lines in Fig. 4. Figure 5 shows the site energies (ε_j^0) relative to the energy of the Pd_6 site (ε_0^0). From an interpolation of the fitted site energies we can estimate the two remaining unknown site energies. These are also indicated in Fig. 5 as open circles.

With these site energies and the multisite lattice-gas model described above, we have calculated the pressure-composition isotherms for $Pd_{1-y}Ag_yH_c$ (with $y=0.1$, 0.2, 0.3, 0.4, and 0.5) for pressures up to 100 GPa. The results, together with experimental data, are shown in Figs. 6–10.
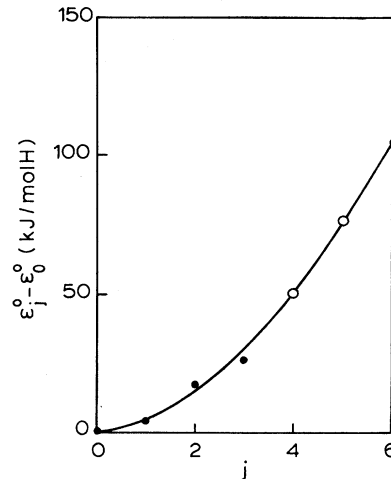

FIG. 5. Site energies ε_j^0 relative to the Pd_6 site energy (ε_0^0). The solid circles indicate site energies fitted to the experimental data. The open circles indicate site energies estimated by interpolation. The solid line is a guide to the eye.
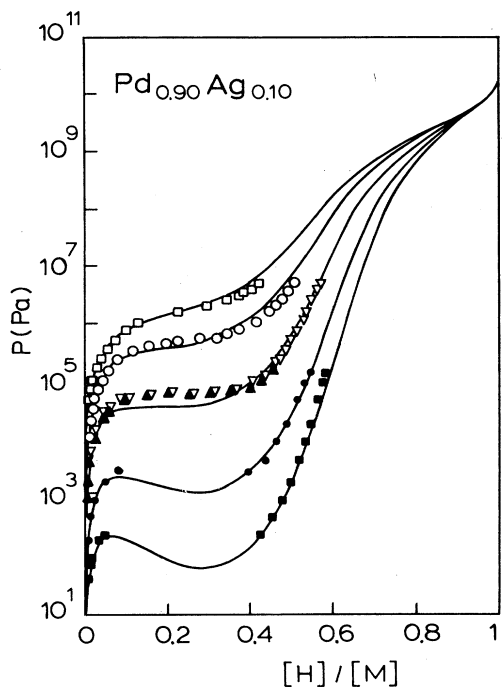
FIG. 6. Pressure-composition isotherms for $Pd_{0.90}Ag_{0.10}H_c$. The solid lines are calculated using the parameters determined in the text. The symbols denote experimental data [■, 303 K; ●, 348 K; ▲, 421 K from Brodowsky and Poeschel (Ref. 40); ▽, 423 K; ○, 513 K; □, 591 K from Salomons (Ref. 41)].
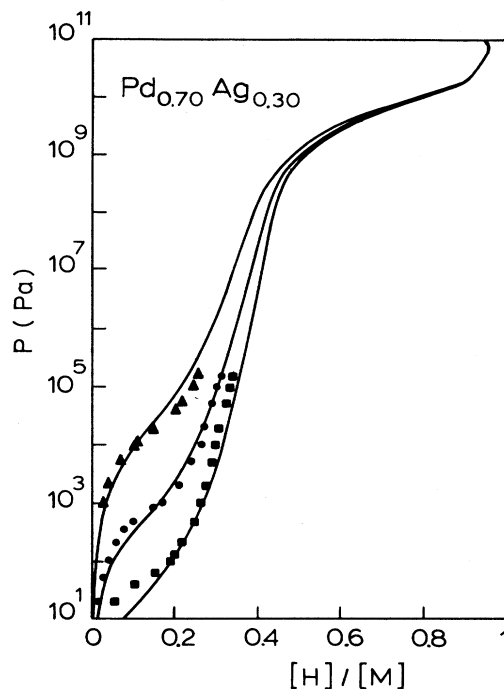

FIG. 8. Pressure-composition isotherms for $Pd_{0.70}Ag_{0.30}H_c$. The solid lines are calculated using the parameters determined in the text. The symbols denote experimental data [■, 303 K; ●, 348 K; ▲, 421 K from Brodowsky and Poeschel (Ref. 40)].

FIG. 7. Pressure-composition isotherms for $Pd_{0.80}Ag_{0.20}H_c$. The solid lines are calculated using the parameters determined in the text. The symbols denote experimental data [■, 303 K; ●, 348 K; ▲, 421 K from Brodowsky and Poeschel (Ref. 40)].
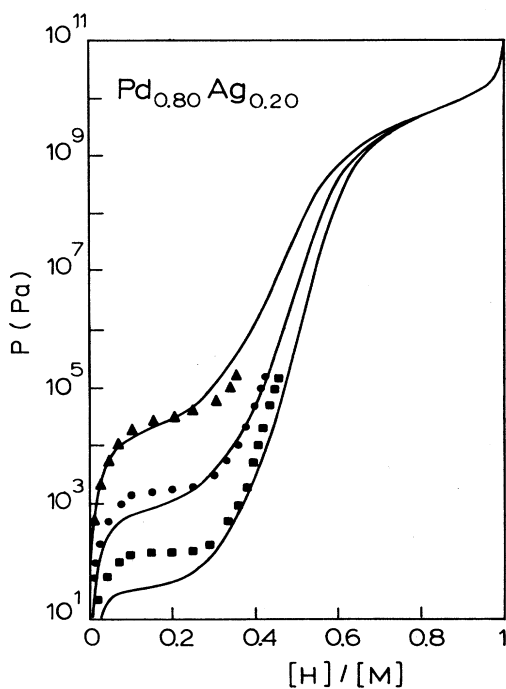

FIG. 9. Pressure-composition isotherms for $Pd_{0.60}Ag_{0.40}H_c$. The solid lines are calculated using the parameters determined in the text. The symbols denote experimental data [■, 303 K; ●,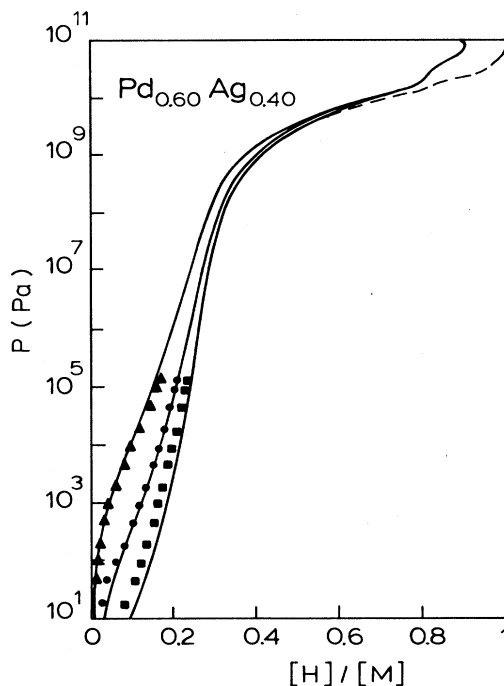 348 K; ▲, 421 K from Brodowsky and Poeschel (Ref. 40)]. A p-c isotherm, calculated at 303 K using a concentration dependent $\overline{V}_H$ ($\overline{V}_H = 1.77 - 0.87 \times c$ cm^3/mol H), is given as a dashed line.
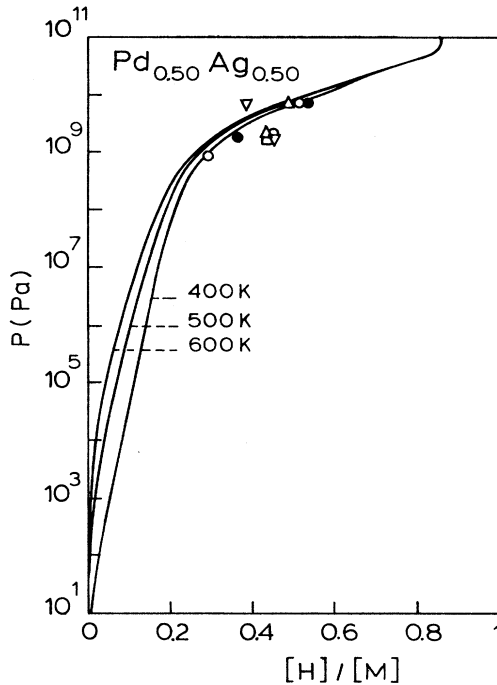
FIG. 10. Pressure-composition isotherms for $Pd_{0.50}Ag_{0.50}H_c$. The solid lines are calculated at the temperatures indicated in the figure, using the parameters determined in the text. The symbols denote experimental data [□, 373 K; ▽, 473 K; △, 573 K; ○, 623 K; ●, 673 K from Ponyatovskii *et al.* (Ref. 6)].

V. DISCUSSION AND CONCLUSION

The calculated *p-c* isotherms for Pd-H and the experimental data, including the high-pressure data of Baranowski,[5] are shown in Fig. 3. As the high-pressure data are not accurate enough for a reliable determination of the temperature derivative, they could not be used to calculate the enthalpy and entropy at high hydrogen concentrations from the isotherms. For $c > 0.7$ we use a linear extrapolation of the excess enthalpy and excess entropy. The calculated *p-c* isotherms agree very well with the high-pressure data.

The calculated *p-c* isotherms for the Pd-Ag-H system, shown in Figs. 6–10, agree reasonably well with the experimental data. Below $\sim 10^7$ Pa the calculated pressures do not deviate more than 20–30% from the experimental pressures. At a temperature of 500 K this corresponds to an error of less than 1 kJ/mol H in the chemical potential. The difference in shape between calculated and experimental isotherms is probably due to the assumptions made for the enthalpy and entropy, in the step from Pd-H to Pd-Ag-H. For instance, the assumption of rigid electronic bands has to break down for Ag-rich alloys, since band-structure calculations show distinct differences in the electronic density of states when going from Pd to Ag.[42] If we compare the scale on which the site energies vary, ~ 100 kJ/mol H, to the energy scale of the differences in calculated and experimental isotherms,

~ 1 kJ/mol H, the agreement between the calculated and experimental *p-c* isotherms is remarkably good.

Around ~ 70 GPa the isotherms show a turnover. At this pressure the molar volume of hydrogen in the metal is equal to that outside the metal, $\overline{V}_H = \frac{1}{2}\overline{V}_{H_2} = 1.77$ cm³/mol H. As a result stoichiometry cannot be achieved for Ag concentrations above ~ 25 at. %.

In the model presented so far we have neglected the dependencies of $\overline{V}_H$ on both the hydrogen concentration and the applied pressure. From measurements on $VH_{0.5}$ up to 50 GPa by Fukizawa *et al.*[43] and Syono *et al.*[44] and predictions of the semiempirical band-structure model[27] we conclude, however, that $\overline{V}_H$ is only weakly pressure dependent. For the hydrogen concentration dependence more care is required.

$\overline{V}_H$ is usually determined from the concentration dependence of the volume of the metal hydride, which is measured by x-ray diffraction.[26] For most metal-hydrogen systems the measured metal volume varies, within the experimental accuracy, linearly with hydrogen concentration, implying thus a constant $\overline{V}_H$. Only recently Feenstra *et al.*[19] managed to determine the concentration dependence of $\overline{V}_H$ for Pd-H in detail by measuring simultaneously the concentration dependence and dilation of PdH_c by means of a microgram balance and a very sensitive capacitive dilatometric technique. They found $\overline{V}_H = 1.77 - 0.87 \times c$ cm³/mol H.

As an example we have calculated a *p-c* isotherm for $Pd_{0.60}Ag_{0.40}$-H with the concentration dependent $\overline{V}_H$ of Pd-H. The result is shown in Fig. 9 as a dashed line. Below 10 GPa the $p\overline{V}_H$ term has little influence on the *p-c* isotherms. Above 10 GPa the equilibrium pressure at a given hydrogen concentration is lowered. Further, because of the decrease in $\overline{V}_H$, the turnover point in the isotherms has shifted to a pressure above 100 GPa. As a result near stoichiometry can be achieved even in Ag-rich alloys.

The foregoing shows clearly that for the calculation of reliable *p-c* isotherms above 10 GPa, one has to know the concentration dependence of $\overline{V}_H$ in detail. From the available experimental data for Pd-Ag hydrides,[26,37] obtained from x-ray measurements, $\overline{V}_H$ appears to be constant. However, because of the accuracy of the technique used, a small concentration dependence of $\overline{V}_H$ cannot be ruled out, as was found for the Pd-H system.

Finally we make some comments on the behavior of the site energies, as shown in Figs. 4 and 5. First we note that, since the site energies have been determined from experimental data below 10 GPa, they are not influenced by the choice of $\overline{V}_H$. The dependence of the site energies on the silver concentration y can be split in two parts. The dependence of ε_j on y, described by the parameter K in Eq. (9), is at least partly caused by the volume changes upon alloying. A quantitative description is, however, hampered by elastic relaxations of the cluster volumes relative to the average volume, for which there is no reliable experimental data (see also Salomons *et al.*[17]). The dependence of the site energy on the number of silver atoms surrounding the interstitial site, shown in Fig. 5, shows a similar behavior as the electronic contribution to

the enthalpy. Apparently the silver atoms also have a "local electronic" effect on the site energy.

In conclusion we have constructed a model from which pressure-composition isotherms for the Pd-Ag-H system can be calculated up to 100 GPa. The calculated p-c isotherms agree very well with the existing experimental data. On the basis of a comparison of the calculated and experimental data for the $Pd_{0.50}Ag_{0.50}$-H system (see Fig. 10) we estimate that the calculated hydrogen concentration at pressures below 10 GPa will be within a few at. % of the actual concentration. Above 10 GPa, however, more experimental data, especially on the concentration dependence of $\bar{V}_H$, are needed if more accurate pressure-composition isotherms are required.

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