CVM-based calculation of the Pd-H Phase Diagram in the High Temperature Region

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By combining the Tetrahedron-Octahedron approximation of the Cluster Variation Method with a phenomenological expression for the atomic interaction energies, the phase diagram of the Pd-H system in the disordered region is calculated. A miscibility gap is confirmed. The phase separation is caused by the configuration-independent atomic interactions originating from elastic interactions. The temperature dependence of the Short Range Order Diffuse Intensity Spectrum is calculated at four special points. It is found that, with decreasing temperature, the short range order diffuse intensity at (1 1/2 0) in \(k\)-space is amplified, implying the existence of a chalcopyrite-type (14\(\bar{a}\)/amd) ordered phase at lower temperatures.

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1. Introduction

Recently, theoretical study of low temperature portion of Pd-H phase equilibria was reported by the present authors.\(^1\) In order to attempt an unified theoretical investigation of phase equilibria for Pd-H system over an entire temperature region based on a single free energy formula, high temperature portion is studied in the present report. Although the body of the theoretical framework was presented in the previous publication, some essential parts are reproduced and further considerations and interpretations are subsidized in the followings.

The thermodynamic properties of concentrated Pd-H alloys may be conveniently discussed in terms of the partial excess chemical potential of \(H\) defined as:

\[
\mu_E^H = RT \cdot \ln \left( \left( \frac{r_m - r}{r} \right)^{1/2} \rho_H^2 \right) - \Delta \mu_H^\circ
\]  

(1)

where \(r\) is the hydrogen/metal ratio, \(r_m\) being a chosen maximum value of \(r\). The relative standard hydrogen potential, \(\Delta \mu_H^\circ\), refers to the infinitely dilute solution and is obtained from:

\[
\Delta \mu_H^\circ = \lim_{r \to 0} \left\{ RT \cdot \ln \left( \left( \frac{r_m - r}{r} \right)^{1/2} \rho_H^2 \right) \right\}.
\]  

(2)

Both \(\Delta \mu_H^\circ\) and \(\mu_E^H\) may be separated into their enthalpic and entropic contributions:

\[
\Delta \mu_H^\circ = \Delta H_H^\circ - T \cdot \Delta S_H^\circ
\]  

(3)

and

\[
\mu_E^H = H_H^E - T \cdot S_H^E.
\]  

(4)

\(\Delta \mu_H^\circ\) has been measured over a wide range of temperature for the Pd-H system. It is found that \(\Delta H_H^\circ\) and \(\Delta S_H^\circ\) vary with temperature, although not to a marked extent below about 500\(^\circ\)C.

The variation of \(H_H^E\) and \(S_H^E\) with \(H\) concentration as assessed by Kuji \textit{et al.}\(^2\) from experimental results, in the temperature range of approximately 0\(^\circ\)C to 300\(^\circ\)C, are reproduced in Figs. 1 and 2. In this assessment, it was assumed that \(H_H^E\) and \(S_H^E\) are independent of temperature, which is unlikely to be a very good approximation. It can be seen that,
in dilute solutions, both \( H_{\text{r}}^E \) and \( S_{\text{r}}^E \) first decrease as the hydrogen concentration increase but that, in more concentrated solutions, both then start to increase.

Interpretations of the \( H_2 \) pressure-composition isotherms for the \( Pd-H \) system or, equivalently, the results shown in Figs. 1 and 2 have continued since the classic work of Lacher,\(^3\) in which the lattice gas model was first applied to a metal-hydrogen system. Lacher considered nearest neighbor pair-wise \( H-H \) interactions with an attractive interaction energy, \( \varepsilon_{\text{HH}} \), and used the point or Bragg-Williams approximation.\(^4\) He also assumed that, in eq. (1), \( r_m = 0.6 \), so that only experimental results below this composition were considered. A linear relation between \( H_{\text{r}}^E \) and \( r \) follows from the Lacher model and \( H_{\text{r}}^E = 6\varepsilon_{\text{HH}}(r/r_m) \) is in very rough agreement with the results shown in Fig. 1. Note, however, that apart from not interpreting the subsequent increase in \( H_{\text{r}}^E \), this two parameter \((\varepsilon_{\text{HH}}, r_m)\) model predicts that \( S_{\text{r}}^E = 0 \), so that the results in Fig. 2 remain unexplained.

In extending the Lacher model so as to include the experimental results at concentrations higher than \( r \approx 0.6 \) (and putting \( r_m = 1 \), Wagner\(^5\) and subsequently Wick and Brodowsky\(^6\)) supplemented the assumed constant \( \varepsilon_{\text{HH}} \) with a configurational independent electron energy term to explain the increase in \( H_{\text{r}}^E \) at higher \( H \) concentrations. Application of the rigid band model gave an apparently plausible physical meaning (an increase in the Fermi energy) to this additional term. This interpretation can be criticized, however, not only on the grounds that the rigid band model is invalid, but also because the additional configurational independent term still cannot explain the variation of \( S_{\text{r}}^E \) with \( H \) concentration shown in Fig. 2. It should be noted that neither Lacher, Wagner nor Wick and Brodowsky were aware of the excess entropy results.

A further significant contribution to our understanding of the thermodynamic properties of the \( Pd-H \) system came from Alefeld,\(^7\) who demonstrated that the major part of the supposed direct attractive \( H-H \) interactions, used by Lacher, Wagner, Brodowsky and Wick, actually results from the expansion of the metal lattice which occurs on the introduction of \( H \). This effect can equally well be regarded as a variation in the energy for \( H \) incorporation (site energy) as a function of \( H \) concentration or, because of the way in which interaction energies are defined, as an indirect \( H-H \) interaction energy. Using continuum linear elasticity theory, Alefeld showed that the indirect \( H-H \) interaction energy gives rise to a contribution to \( \mu_{\text{r}}^E \) which is given by:

\[
\mu_{\text{r}}^E = -\gamma' B V_{xH/r}^2 / \Omega_0 \tag{5}
\]

where \( \gamma' \) is Eshelby coefficient defined as \( \gamma' = \Delta V_D / (\Delta V_D + \Delta V_s) \) with \( \Delta V_D \) the uniform lattice dilatation component and \( \Delta V_s \) the pure shear component, \( B \) the isothermal bulk modulus, \( \Omega_0 \) the crystal volume and \( V_{xH} \) is the partial molar volume of hydrogen.

A relation equivalent to eq. (5) was derived later by Horner and Wagner\(^8\) by using a discrete lattice model in which the host lattice is harmonic and the forces exerted by the \( H \) atoms on the host atoms are assumed constant. Dietrich and Wagner\(^9\) used this model to calculate the direct elastic interaction energies between an isolated pair of \( H \) atoms as a function of separation distance in \( Pd \). The elastic interaction energies were supplemented by direct electronic interaction energies between isolated pairs of \( H \) atoms. Both the elastic and electronic interaction energies extended outwards to include up to the 15th nearest neighbors. The summed elastic and electronic interaction energies were then used in a Monte Carlo calculation of the isotherms and phase diagram. Because, however, of the assumption of constant pairwise interactions, the phase diagram necessarily possess symmetry about the \( r = 1/2 \) composition. Whilst the calculation may be described as an attempt at a more \textit{a priori} approach to calculating the thermodynamic properties of \( Pd-H \) alloys, the assumption that both kinds of interactions are independent of \( H \) concentration is unsatisfactory. The question of the many body nature of the interactions is also ignored. The non-additivity of elastic pairwise \( H-H \) interactions was demonstrated by Oates and Stoneham\(^10\) who used empirical \( Pd-Pd \) and \( Pd-H \) interatomic potentials. They also showed that the magnitudes of the calculated interactions are very sensitive to the interatomic potentials chosen.

The aim of the present work is to calculate a phase diagram for \( Pd-H \) system. Since a configurational excess entropy can arise only in a higher order approximation for the lattice gas calculation, we have used the Cluster Variation Method (CVM).\(^11\) The CVM approach also offers a simple way for introducing many-body interactions into the model, which is important in breaking the symmetry of the phase diagram about \( r = 1/2 \).

Particular emphasis is placed in the present report on the disordered phase in the high temperature region. This is because the experimental phase diagram is well established in the high temperature portion and is well suited for examining the calculation scheme adopted in the present study. In order to refer to the low temperature portion, however, we also calculate diffuse intensity spectrum which provides a clue for predicting the underlying ordered phases. The comparison with recent theoretical study on low temperature phase equilibria\(^1\) facilitates further critical examination of the validity of the present theoretical model.

2. Cluster Variation Method Calculations

Based on the neutron diffraction and proton channeling studies, it has been confirmed that the hydrogen atom in the palladium occupies the octahedral interstitial sites in the face centered cubic lattice\(^12,13\). Since the octahedral sites themselves form an fcc lattice, the phase equilibria of \( Pd-H \) is most conveniently discussed within a lattice gas model applied to the \( H \)-vacancy in fcc sublattice surrounded by \( Pd \) atoms. As was introduced in eq. (1), \( r = x_H/x_{PD} \), the ratio of hydrogen atoms to palladium atoms is equivalent to mole fraction in a binary substitutional alloy system. Hence, no \( H \) atoms are involved when \( r = 0 \), while all the octahedral sites are occupied when \( r = 1 \).

The internal energy of the present model is given as the sum of two contributions, \( E_{NC}(r) \) and \( E_C(\{\xi\}, T) \). The former is the \textit{non-configurational} term indicating that this term is independent of short range order or atomic environment and is determined only by the concentration \( r \). This contribution
originates from elastic interactions and is described as a series expansion in concentration,

\[ E_{NC}(r, T) = \sum_{i=0}^{i_{\text{max}}} a_i(T) \xi_i^r \]

(6)

where the point correlation function, \( \xi_i \), is linearly related to the concentration, \( r \), through \( r = 1/2(1 + \xi_i) \), and the coefficient term \( a_i(T) \) is further expanded in terms of temperature, \( T \), as

\[ a_i(T) = \sum_{n=0}^{n_{\text{max}}} b_n \cdot T^n. \]

(7)

Equation (6) is derived from elasticity considerations\(^{14}\) and the temperature coefficient term, \( b_n \), is determined by a fitting procedure. We note that the satisfactory fittings are achieved with \( i_{\text{max}} = 4 \) and \( n_{\text{max}} = 5 \). With these coefficient terms, the non-configurational energy is calculated via eq. (6). Then, the subtraction of \( E_{NC}(r, T) \) from the experimentally determined enthalpy, assumed equal to the internal energy \( E(r, T) \), gives the remaining contribution of the configuration dependent term, \( E_C(\{\xi_i\}) \). Shown in Fig. 3 are examples at \( T = 450 \text{ K} \). One sees that the non-configurational energy is positive while the configurational dependent energy is negative, indicating that the system has an intrinsically strong tendency to ordering which is nullified by the elastic energy contribution (non-configurational energy).

The configurational dependent energy (or chemical contribution) is further expanded as

\[ E_C(\{\xi_i\}, T) = \sum_{i}^{i_{\text{max}}} v_i \cdot \xi_i, \]

(8)

where \( v_i \) and \( \xi_i \) are the effective interaction energy and correlation function for a cluster specified by subscript \( i \). This equation is nothing but a cluster expansion of the total energy.\(^{15}\) The key to this equation is the fact that a set of correlation functions \( \{\xi_i\} \) spans the orthonormal basis in the configurational space and, therefore, the cluster indicated by \( i \) should be independent each other. In a fully theoretical determination of the effective cluster interaction energies \( \{v_i\} \), one employs electronic structure calculations to obtain total energies for a selected set of ordered compounds and pure elements. Since the atomic arrangements of ordered compounds and pure metals are uniquely determined, the value of the correlation function for each cluster \( i \) is also given in advance. Then, by knowing \( E_C \) which forms a vector and \( \{\xi_i\} \) which is represented as a matrix, one can obtain \( \{v_i\} \) by a matrix inversion.

In the present calculations, however, we used a trial-and-error procedure to determine the effective interaction energies. As will be described shortly, the free energy function in the present study covers the atomic correlations contained in the tetrahedron and octahedron clusters. It is readily shown\(^{16,17}\) that the number of independent clusters involved in these clusters is ten, and \( i \) in eq. (8) runs from 1 to \( i_{\text{max}} = 10 \). Among these clusters, \( i = 1 \) corresponds to a point cluster and \( i = 2 \) and 3 are, respectively, nearest and second nearest neighbor pair clusters. All others are multibody clusters up to the octahedron cluster indicated by \( i_{\text{max}} = 10 \). The determination of effective cluster interaction energies \( \{v_i\} \) for all these ten clusters based on a trial-and-error procedure is a formidable task. However, the number of the clusters participated in the optimization procedure can be reduced in the following way.

It is commonly accepted that the dominant interactions which are responsible for the cohesion of an alloy system are originating from pair-wise interactions. Then, the nearest and next nearest neighbor pair interaction energies are most essential parameters to be adjusted in the present trial-and-error procedure. However, within the concentration independent pair interaction energies which is the case in the present study, it is well known that the resultant thermodynamic quantities are necessarily symmetric around 50 at\%\(^6\). Therefore, in order to reproduce the asymmetric feature of the configurational dependent energy shown in Fig. 3, it is indispensable to introduce multibody interaction energies. Among the remaining seven kinds of multibody interaction energies, the nearest neighbor triangle effective interaction energy is adopted as the third parameter to be optimized and others are set to be null. This is because multibody interactions originating from larger clusters or lower symmetric clusters generally fade away quickly and, therefore, it is deemed safe to renormalize these interactions into the effective interaction of the smallest cluster with the highest symmetry which is the nearest neighbor triangle.

The trial-and-error procedure over a wide temperature range suggests the values for the nearest and second nearest neighbor pairs and triangle interaction energies tabulated in Table 1. It should be noted that \( v_{2,1} \) and \( v_{2,1} \) in Table 1 indicate \( j \)-th nearest neighbor pair and triangle interaction energies which are, respectively, corresponding to \( v_2 \) and \( v_2 \) in Table 1, \( v_3 \) (\( = v_2 \)) and \( v_4 \) (\( = v_3 \)) in eq. (8). The validity of these

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![Figure 3](image-url) Separation of internal energy \((E)\) into non-configurational \((E_{NC})\) and configuration dependent \((E_C)\) contributions at temperature \(T = 450 \text{ K}\). This figure is reproduced from T. Mohri et al.\(^{15}\)

**Table 1** Effective cluster interaction energies determined by the present study. \( v_{2,1} \), \( v_{2,2} \) and \( v_3 \) are, respectively, effective cluster interaction energy for a nearest neighbor, second nearest neighbor and nearest neighbor triangle clusters.

<table>
<thead>
<tr>
<th>( v_{2,1} )</th>
<th>( v_{2,2} )</th>
<th>( v_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 6.08 \times 10^{-3} ) [Ryd]</td>
<td>( 7.60 \times 10^{-4} ) [Ryd]</td>
<td>( -2.84 \times 10^{-3} ) [Ryd]</td>
</tr>
</tbody>
</table>
values are further discussed in the next section. It is noted that our sign convention is that the positive (negative) effective pair interaction enhances the ordering (phase separation) tendency, and that the ratio of $v_{2,2}/v_{2,1}$ is a key factor in predicting the ordered phases appearing at low temperatures as will be discussed in a later section.

In order to determine the equilibrium state, one needs to construct a free energy functional for which the CVM plays a central role. It is emphasized that the basic cluster in the configurational entropy term should contain all the clusters for which effective interactions are explicitly considered in the internal energy term. Since our effective interaction energies contain nearest and second nearest neighbor pairs as well as triangle cluster energies, a relevant basic cluster is the combination of tetrahedron and octahedron clusters. Hence, the Tetrahedron-Octahedron approximation $^{[16,17]}$ is employed for the present study.

The entropy term in the Tetrahedron-Octahedron approximation is given by

$$ S = k_B \cdot \ln \left( \frac{\prod(N \cdot z_{ijk})!}{\prod(N \cdot v_{ijklmn})!} \right) $$

where $x_i$, $y_{ij}$, $z_{ijk}$, $w_{ijkl}$ and $v_{ijklmn}$ are cluster probabilities of finding atomic arrangement specified by subscripts on point, pair, triangle, tetrahedron and octahedron clusters, respectively. In the conventional treatment, the numbers +1 and −1 are usually assigned to subscripts $i$, $j$, $k$, . . . to represent $A$ and $B$ atoms, respectively. The cluster probabilities, $\chi_{\{J\}}$, of atomic arrangement specified by $\{J\}$ is uniquely related to a set of correlation functions through,

$$ \chi_{\{J\}} = \frac{1}{2^n} \left( 1 + \sum_{l \in J} V_{JJ} \cdot \xi_l \right) $$

where $n$ is the number of the lattice points constituting the cluster $V_{JJ}$ is the $V$-matrix which is the sum of products of $i$, $j$, $k$, . . . and this can be more easily grasped with illustrations for the point and tetrahedron cluster probabilities as follows,

$$ x_i = \frac{1}{2} (1 + \xi_1) $$

and

$$ w_{ijkl} = \frac{1}{2^4} \left( 1 + (i + j + k + l) \cdot \xi_1 + (ij + ik + il + jl + kl) \cdot \xi_1 \cdot \xi_2 + (ijk + ilj + ikj + jkl) \cdot \xi_3 + (ijkl) \cdot \xi_4 \right). $$

The details of the correlation function have been amply demonstrated in previous articles $^{[15-17]}$ and will not be reproduced here, but we note that the advantage of correlation functions is due to the fact that an orthonormal basis can be spanned in the thermodynamic configuration space $^{[18]}$ whereas the cluster probabilities are mutually dependent.

Together with eqs. (6)–(9), the configurational free energy functional $F$ of the system is derived. Under a given set of effective interaction energies and temperature, the minimization of the free energy functional with respect to the cluster probabilities with certain constraints originating from reduction relations and normalization conditions provides the equilibrium state. If one employs the correlation functions instead of cluster probabilities, the equilibrium condition is more conveniently described as

$$ \frac{\partial F}{\partial \{\xi_l\} \bigg|_{\{\xi_l\} \neq 0} } = 0, $$

since the set of correlation functions forms independent variables in the thermodynamic configuration space. It is noted that the minimization through eq. (13) provides not only the equilibrium free energy but also the optimized set of correlation functions $\{\xi_{\ell}^{eq}\}$ at the equilibrium state.

3. Results and Discussion

By substituting $\{\xi_{\ell}^{eq}\}$ into eq. (8), the resultant configurational-dependent contribution, $E_C(\{\xi_{\ell}^{eq}\}, T)$ is compared with the experimentally derived one at three temperatures in Fig. 4. The close agreements indicate that the present values for the effective cluster interactions given in Table 1 are quite acceptable.

Based on the free energy with the internal energy expressed by both $E_C$ and $E_{NC}$ in eqs. (6)–(8), a conventional common tangent construction is attempted, and two concentrations to which the phase separation takes place are determined. The same procedure is repeated for other temperatures and the
phase boundary is obtained as shown in Fig. 5. For comparison, the experimental phase diagram reported by Volkl et al.\(^\text{(19)}\) is reproduced in the figure. The agreement is quite acceptable, which suggests that the employed data as well as the thermodynamic model based on the CVM are quite reliable.

As was indicated in the previous section, the pair-wise effective interaction energies, \(v_{2j}\), determined in the present study, implies ordering reactions taking place in the low temperature region. Based on the ground state analysis,\(^\text{(20,23)}\) it has been well known that, at the 1:1 stoichiometry composition of the fcc lattice on which the present study focuses, the most stable underlying ordered phase is the \(L_{10}\) phase when only the nearest neighbor pair interaction is considered. However, inclusion of the second nearest neighbor pair interaction energy lifts the degeneracy of the ordered phases and also stabilizes other types of structure. In fact, the precise ground state analysis has been performed by Cahn and coworkers\(^\text{(20,21)}\) and their results indicate that three types of ordered phases are possibly stabilized at 1:1 stoichiometry depending upon the ratio of \(v_{2j}/v_{21}\) which is termed the \(\alpha\)-value. Note that \(v_{2j}\) in Table 1 is obtained by multiplying \(v_{2j}\) by the number of corresponding parallel per lattice point. When \(\alpha < 0\), the \(L_{10}\) ordered phase is stabilized, whereas for \(0 < \alpha < 1/2\) the Chalcopyrite-type phase \((I_{41}/amd)\) is stabilized and for \(1/2 < \alpha\) the degeneracy is lifted in favor of the \(L_{11}\) ordered phase. Therefore, the present results of \(\alpha = 0.25\) predicts the appearance of Chalcopyrite-type phase. It is, however, noted that because of the quite strong three body interactions the analysis within the pair-wise interactions may be modified. Hence, in order to examine the validity of the prediction, further calculation of short range order diffuse intensity is attempted in the following.

Once the CVM free energy expression is obtained, the first order derivative provides the equilibrium state as shown above, whilst the second order derivative with respect to the correlation functions gives the stability criterion against the fluctuation of the ordering waves.\(^\text{(22,23)}\) Since the matrix of the second order derivative is Hermitian, it is rather straightforward to diagonalize. Then, Fourier transformation is invoked by utilizing the translational symmetry of the disordered phase. The resultant quantity is termed the diffuse intensity,\(^\text{(22,23)}\)

\[
I_{SRO}^{eq}(T, k^*),
\]

formally written as

\[
I_{SRO}^{eq}(T, k^*) \propto k_B \cdot T \cdot |\mathcal{F} \{ \frac{\partial^2 F}{\partial \xi_i \partial \xi_k} \}^{-1}|_{k=k^*},
\]

where \(\mathcal{F}\) represents the Fourier Transformation. The details of the derivation of above formula are outside the scope of the present report, and interested readers should refer to the previous publications.\(^\text{(22,23)}\) We simply provide the physical meaning as follows.

If and only if all the eigen values of a diagonalized matrix are positive, stability prevails, which corresponds to the high temperature disordered state. When the temperature is decreased and as soon as one of the eigen values goes through zero, the system becomes inherently unstable against the excitation and amplification of the concentrated wave associated with the negative eigen value. Then the limit of the stability is formally given by the vanishing condition of the determinant of the 2nd order derivative matrix of the free energy functional. The highest temperature at which this condition is satisfied is termed the instability temperature,\(^\text{(24)}\) while the concentration wave associated with the negative eigen vector is termed the ordering wave.

The diffuse intensities are calculated at a fixed composition of 50 at\%. The results are shown in Fig. 6. One sees that, among the four kinds of ordering waves characteristic of fcc based structures, the amplitude of the [1 1/2 0] ordering wave is intensified with lowering temperature whilst all other waves suggest a decaying tendency. The significance of the short range order diffuse intensity is that a one to one correspondence is possible between the characteristic intensity amplitude and the underlying ordered structure.\(^\text{(23)}\) In fact, [1 1/2 0], [100] and [1/2 1/2 1/2] concentration waves lead to the formation of Chalcopyrite-type \((I_{41}/amd)\), \(L_{10}\) and \(L_{11}\) structures, respectively. Note that a [000] wave is a characteristic of phase separation or clustering with infinite wave length. Hence, the present results shown in Fig. 6 implies that ordered structures appearing in low temperature possess the Chalcopyrite-type structure.

It should be noted that diffuse intensity essentially carries the information of the stability of a system and the present
analysis suggests that the homogeneous disordered solid solution is most unstable against the excitation and amplification of a Chalcopyrite-type concentration wave. In order to determine the transition temperature, one needs to reconstruct a free energy formulae based on sub-lattice division of the entire lattice by taking into account the symmetry of the Chalcopyrite-type structure. This was performed in the previous study\(^1\) and it was confirmed that disorder Chalcopyrite-type order transition takes place at 216 K at 50%.

4. Summary

The Cluster Variation Method in the tetrahedron-octahedron approximation has been used in an empirical way in order to interpret the thermodynamic properties of \(Pd-H\) alloys and the high temperature part of the phase diagram. Both indirect \(H-H\) interactions from the \(H\) induced lattice expansion and composition dependent \(H-H\) interactions have been taken into account. In the low temperature region, the short range order diffuse intensity calculations suggest that, near the 1:1 stoichiometric composition, an ordered phase possessing the Chalcopyrite-type structure (\(I4_1/amd\)), is formed. This is exactly realized in the recent study on low temperature part of phase equilibria.\(^1\)

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