Ab-Initio Calculations for Solvus Temperatures of Pd-Rich PdRu Alloys: Real-Space Cluster Expansion and Cluster Variation Method

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We present the ab-initio calculations for the solvus temperatures (T_{solvus}) of $\text{Pd}_{1-c}\text{Ru}_c$ ($0.03 \leq c \leq 0.12$), in which the interaction energies (IEs) among the Ru impurities in Pd are determined by the full-potential Korringa-Kohn-Rostoker Green's function method, combined with the generalized gradient approximation in the density functional theory. The configurational entropy calculations are based on the cluster variation method (CVM) within the tetrahedron approximation. In order to take into account the long-range 2-body IEs, we renormalized the 1st-nearest neighbor (*nn*) IE by including the 2–10th-*nn* IEs. We also take into account the following three effects on the IEs among the Ru impurities; (1) the local lattice distortion for the 1st-*nn* IE, existing even at $T = 0$ K, (2) the lattice thermal vibration by the Debye-Grüneisen model, and (3) the T -dependence of the electron excitation due to the Fermi-Dirac distribution. The calculated results for the T_{solvus} agree fairly well with the experimental results at low Ru-concentrations (up to ~6%), while the discrepancy between the calculated and experimental results becomes significant for the high Ru-concentrations (8–12%). We discuss that the discrepancy may be corrected by the CVM calculations with the large basic cluster including up to the 4th-*nn* IE. [doi:10.2320/matertrans.M2017292]

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1. Introduction

Ab-initio calculations along with the cluster variation method (CVM) used to evaluate the configurational entropy have attracted broad attention as a theoretical approach for drawing the phase diagrams of alloys.^{1,2)} The phase stability and phase equilibria for many binary alloys have been successfully described by the CVM. For example, using the cluster variation method within the tetrahedron approximation (CVMT), the experimentally determined transition temperature (1023 K) of FePd alloys was reproduced very well (1030 K) by including the lattice thermal vibration effect.¹⁾ The free energy in these calculations was divided into two parts (internal energy and configurational entropy). The effective cluster interaction energies (ECIEs), used in the calculations of the internal energy, were determined from the combination of the total energies of a set of selected ordered and elemental metals, following the Connolly-Williams approach.³⁾ For the configurational entropy by the CVMT, three fcc-based ordered alloys (A_3B , AB , AB_3) and two fcc elemental metals (A and B) were chosen for the AB alloys to determine the five kinds of ECIEs up to the tetrahedron formed from the 1st-nearest neighbor (*nn*) pairs.

On the other hand, we also succeeded in reproducing the observed solvus temperatures, T_{solvus} (820–860 K), of the $\text{Pd}_{1-c}\text{Rh}_c$ fcc alloys ($0.09 \leq c \leq 0.12$) by the free energy calculations based on the CVMT⁴⁾, although the local lattice distortion effect, existing even at $T = 0$ K, and the thermal vibration effect were not taken into account. The Rh atoms were treated as impurities in Pd. It has been experimentally

reported that the Rh impurities are segregated at low temperatures and disordered at high temperatures due to the configurational entropy.^{4,5)} As discussed later, the 2–4 body interaction energies (IEs)⁴⁾ among the Rh impurities, up to the tetrahedron formed by the 1st-nearest neighbor (*nn*) pairs, were uniquely determined by the real-space cluster expansion (RSCE) based on the Korringa-Kohn-Rostoker Green's function (KKR) method for perfect and impurity systems, different from the Connolly-Williams approach. It is noted that the spherical potential approximation for the KKR method was used in the previous study. We found that the 2-body interaction between the Rh impurities in Pd is considerably short-range (see Fig. 4 in Ref. 4)), and the 3-body and 4-body interactions of the tetrahedron formed by the 1st-*nn* pairs are considerably weak, as discussed in Ref. 4). We have shown that the observed T_{solvus} of the $\text{Pd}_{1-c}\text{Rh}_c$ alloys may be well reproduced by the free energy calculations based on the CVMT, using these 2–4 body IEs for the internal energy, if the attractive 1st-*nn* 2-body IE is renormalized by including the weakly repulsive 2–8th-*nn* 2-body IEs. It is noted that the small reduction of the attractive 1st-*nn* 2-body IE is very important to accurately reproduce the observed T_{solvus} of the $\text{Pd}_{1-c}\text{Rh}_c$ alloys, as shown in Ref. 4). These successful results based on the CVMT may be mainly due to the short-range nature of the IEs used in the calculations of the internal energies of the considered alloys.

In this paper, we present the *ab-initio* calculations for the observed T_{solvus} (1000–1600 K) of the $\text{Pd}_{1-c}\text{Ru}_c$ ($0.03 \leq c \leq 0.12$) fcc alloys⁵⁾, in which the Ru atoms are treated as impurities in Pd. In the present calculations, we carried out the *ab-initio* calculations based on the full-potential Korringa-

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Kohn-Rostoker Green's function (FPKKR) method, different from the previous calculations with the spherical potential approximation. Since the present approach is an approach from a dilute limit, we concentrated on studying the low-concentrated $\text{Pd}_{1-c}\text{Ru}_c$ alloys ($c \leq 0.12$). We found that the 2-body interaction of the Ru impurities is very long-range and considerably repulsive at the 2nd-, and 4th-, and 9th-*nn*s in comparison to the strong attraction at the 1st-*nn*, as described in this paper.⁶⁾ Since the 2-body interaction between impurities in metals seem to be usually long-range, as shown in Refs. 4), 7), and 8), it is very important to study the T_{solvus} of the $\text{Pd}_{1-c}\text{Ru}_c$ alloys as a typical example of binary alloys with the long-range 2-body interaction. It is also noted that the observed T_{solvus} (1000~1600 K) of the $\text{Pd}_{1-c}\text{Ru}_c$ ($0.03 \leq c \leq 0.12$) alloys significantly changes, different from the observed T_{solvus} (820~860 K) of the $\text{Pd}_{1-c}\text{Rh}_c$ ($0.09 \leq c \leq 0.12$) alloys. In the previous calculations for the Rh impurities in Pd,⁴⁾ the temperature (T_{FD}) of the Fermi-Dirac (FD) distribution was fixed at 800 K, which agrees with the observed T_{solvus} (820~860 K). We also found that the local lattice distortion effect may be more important for the Ru impurities in the Pd metal, compared to the Rh impurities in Pd.⁶⁾ Thus, in addition to the 2-body long-range IEs up to the 20th-*nn*, in the present study we investigated the following three effects on the IEs of the Ru impurities in Pd; (1) the local lattice distortion for the 1st-*nn* Ru-Ru IE, existing even at $T = 0$ K, (2) the lattice thermal vibration at finite temperatures, and (3) the T_{FD} -dependence for the electron excitation due to the FD distribution.

In order to determine the n -body ($n = 1 \sim 4$) IEs among the Ru impurities in Pd, we used the RSCE for the total energies of the alloys,⁹⁻¹²⁾ different from the Connolly-Williams Approach.³⁾ The present approach, while restricted to the dilute limit, considers only atomic configurations, the energy differences of which uniquely define the n -body IEs. The n -body IEs are successively determined from the low-order to high-order and are independent of the concentration.^{4,10)} On the other hand, the Connolly-Williams approach determines the ECIEs from different atomic configurations, in which the results of the supercell calculations with different configurations in the unit cell are fitted by models containing the ECIEs. Thus, the ECIEs depend on the selected set of ordered and elemental metals, as shown in Ref. 13). To verify the accuracy and convergence of the present approach for the Pd-rich PdRu alloys, it is very important to clarify the distance dependence of the 2-body (pair) IEs and the cluster-size dependence of the 3- and 4-body (trimer and tetramer) IEs among the Ru impurities in Pd. We already examined how the total energies of the Pd-rich PdRu alloys can be accurately reproduced by the present RSCE including up to the 4-body IEs among the Ru impurities in Pd and found that the band calculation results for the Pd_3Ru alloy in the L1_2 structure, as one example of the Pd-rich PdRu alloys, may be reproduced within the error of 1 mRy per atom by the RSCE including the 2-body IEs up to the appropriate neighbors (for example, up to 20th-*nn*) and the 3-body IEs up to the appropriate size of the clusters (for example, up to the 3-body clusters in the 2cubes in the fcc structure). The contribution from the n -body IEs becomes less and less with the increase in n , as discussed in Ref. 9). The calculated re-

sults will be published in a subsequent paper.¹⁴⁾

In Sect. 2, we discuss the calculation procedures for the FPKKR method with the electron excitation effect due to the FD distribution and the thermal vibrational free energy. In Sect. 3, the calculated results for the T_{solvus} of the $\text{Pd}_{1-c}\text{Ru}_c$ ($0.03 \leq c \leq 0.12$) alloys are discussed. We show that the calculated CVMT results agree fairly well with the observed T_{solvus} for the low Ru-concentrations (up to ~6%), while the discrepancy (overestimation) between the calculated and experimental results becomes high for the high Ru-concentrations (8~12%). We also show that this discrepancy may be corrected by the calculations based on the cluster variation method within the tetrahedron-octahedron approximation (CVMTO), in which the 2nd-*nn* IE is renormalized by including the 4th-*nn* IE. We also found that, in addition to the local lattice distortion and the lattice thermal vibration effects, the T_{FD} dependence of the IEs due to the electron excitation of the FD distribution is very important to reproduce the observed T_{solvus} (1000~1600 K) of $\text{Pd}_{1-c}\text{Ru}_c$ ($0.03 \leq c \leq 0.12$). We will show that the electron excitation effect due to the FD distribution attractively works for the 2-body IEs and increases T_{solvus} . Section 4 summarizes the main results of the present paper. It is also discussed that the CVM calculations for the larger basic clusters is strongly claimed to quantitatively study the phase diagrams of the long-range interaction systems, such as the present Pd-rich PdRu alloys.

2. Calculation Method

2.1 Total energies of impurity systems

The calculations for the total energy of the Ru impurities in Pd are based on the density functional theory (DFT) in the generalized gradient approximation (GGA).^{15,16)} In order to solve the Kohn-Sham equations, we used a multiple scattering theory in the form of the KKR Green's function method for the full-potentials (FP). We used the screened version of the FPKKR band calculations for the Pd host, which significantly simplifies the numerical calculations by introducing the short-range structural Green's functions.^{17,18)} In order to simplify the total energy calculations in the GGA formalism, we use the electronic densities self-consistently obtained by the local spin density approximation in the DFT. The accuracy of the present GGA calculations was discussed in Refs. 15) and 16).

The advantage of Green's function method is due to the introduction of the host Green's function and the embedding of point defects in an otherwise ideal crystal is correctly described, differently from the usual supercell and cluster calculations. It is noted that although the potential perturbation due to the defects is localized in the vicinity of the defects, the change in the wave functions due to the defects is delocalized over the whole space. The practical advantage in using Green's function method is to exploit this short-range nature of the defect potential. For example, in order to obtain the accurate and converged total energy of the impurity system without the lattice distortion in the fcc structure, it is sufficient to self-consistently redetermine only the potentials of the impurities and their 1st-*nn* host atoms, if the total energy change due to the perturbed wave functions over the infinite space is correctly evaluated by using Lloyd's for-

mula.^{16,19)} This is also very different from the supercell and cluster calculations in which all the potentials must be recalculated in each iteration cycle.

As discussed in Sect.3 and Appendix 2, in order to calculate the Ru-concentration dependence of the T_{solvus} of the $\text{Pd}_{1-c}\text{Ru}_c$ alloys, we must first calculate the total energy difference between the disordered and segregated states. The total energy (per tetrahedron basic cluster of the 1st-*nn* pairs) of the disordered state, within the CVMT approximation, is written as follows:

$$E_{\text{dis}} = 2 \sum_{i,j,k,l} E_{ijkl} \omega_{ijkl} \quad (1)$$

where i, j, k , and l distinguish Pd or Ru, E_{ijkl} is the total energy (per tetrahedron basic cluster), and ω_{ijkl} is the cluster probability. E_{ijkl} is calculated using the IEs up to the 4-body of the tetrahedron cluster, obtained in the RSCE. The definitions and calculation procedure of the IEs up to the 4-body are described in Refs. 4), 10), 12), and 14). The total energy of the segregated state is also expressed by using the cluster probability of the segregated state ($\omega_{\text{RuRuRuRu}} + \omega_{\text{PdPdPdPd}} = 1$, Ru-concentration = ω_{RuRuRuRu} , Pd-concentration = ω_{PdPdPdPd}), as discussed in Appendix 2.

In the present study, we describe the T_{FD} dependence of the IEs due to the electron excitation of the FD distribution. As shown in Ref. 20), the introduction of the FD distribution into the *ab-initio* Green's function calculations is very useful to simplify the ground state calculations. Based on a contour integration in the complex energy plane, we evaluated the residues at a few Matsubara frequencies, while the remaining integral is analyzed by the Sommerfeld expansion. The imaginary part (δ) in the complex energy plane is related to T_{FD} of the FD distribution ($\delta = \pi k T_{\text{FD}}$). The total energy is calculated by the grand canonical potential for which a simple formula is given. Since the total energy change due to the electron excitation is usually expected to be negligible, the FD distribution, usually with $T_{\text{FD}} = 800$ K for metals, has been expediently used to efficiently perform the ground state calculations.^{15,16,20)} In the present study, we evaluated the T_{FD} -dependence for the IEs among the Ru impurities in Pd and show that the effect due to the FD distribution becomes very important to reproduce the concentration dependence of the observed high T_{solvus} .

In the present study, we also evaluated the local lattice distortion effect for the 1st-*nn* Ru-Ru IE in Pd.^{21,22)} The local lattice distortion energy is defined as the total energy change caused by the lattice distortion around the impurities.²³⁾ It is noted that the local lattice distortion energy for the 1st-*nn* Ru-Ru IE is defined as the difference between the local lattice distortion energies of the two states: (1) the final state where two impurities are located at the 1st-*nn* sites, and (2) the initial one where both impurities are infinitely apart. As discussed in Refs. 21)–24), the treatment of the lattice distortion is very cumbersome in the present KKR method. In order to study the lattice distortion effect, we must self-consistently redetermine the potentials in the larger region compared to the calculations for the impurity systems without the local lattice distortion, because the potentials of the host atoms surrounding the displaced host atoms may be strongly perturbed. Since the local lattice distortion up to the

1st-*nn* host atoms around the 1st-*nn* Ru-Ru impurity pair in Pd is taken into account in the present calculations, we self-consistently redetermined the potentials in the 102-atom impurity cluster in Pd, as discussed in Ref. 24). In the present calculations, the positions of the displaced atoms are determined by the condition of the Hellmann-Feynman forces = 0. The detailed discussion for the local lattice distortion and the accuracy of the present calculations are reported in Ref. 21).

2.2 Vibrational free energy

In addition to the local lattice distortion effect due to the difference in the atomic size, existing even at $T = 0$ K, the effect of the lattice softening due to the thermal vibration at finite temperatures is considered in the present study. The vibrational free energy for the lattice softening is calculated by using the Debye-Grüneisen model which is based on the quasi-harmonic approximation. By following Ref. 1), the vibrational free energy, $F_{\text{vib}}^{(n)}(a, T)$, of each phase (n) consisting of the basic cluster, $\text{Pd}_{4-n}\text{Ru}_n$ ($n = 0 \sim 4$), used in the CVMT (see Fig. 2 in Ref. 4), H = Pd and I = Ru), is written as follows:

$$F_{\text{vib}}^{(n)}(a, T) = E_{\text{vib}}^{(n)}(a, T) - T S_{\text{vib}}^{(n)}(a, T) \quad (2)$$

where $E_{\text{vib}}^{(n)}(a, T)$ is the vibrational internal energy and $S_{\text{vib}}^{(n)}(a, T)$ is the vibrational entropy depending on the lattice parameter (a), temperature (T), and the phase (n) specified by the basic cluster ($\text{Pd}_{4-n}\text{Ru}_n$). These terms are given by the following formulae:

$$E_{\text{vib}}^{(n)}(a, T) = \frac{9}{8} k_B \cdot \Theta_D^{(n)} + 3 k_B \cdot T \cdot D \left(\frac{\Theta_D^{(n)}}{T} \right) \quad (3)$$

$$S_{\text{vib}}^{(n)}(a, T) = 3 k_B \cdot \left[\frac{4}{3} D \left(\frac{\Theta_D^{(n)}}{T} \right) - \ln \left\{ 1 - \exp \left(- \frac{\Theta_D^{(n)}}{T} \right) \right\} \right] \quad (4)$$

where $\Theta_D^{(n)}$ is the Debye temperature of the phase (n) consisting of the basic cluster $\text{Pd}_{4-n}\text{Ru}_n$ (fcc structure for Pd_4 and Ru_4 , $\text{L}1_2$ for Pd_3Ru and PdRu_3 , and $\text{L}1_0$ for Pd_2Ru_2), determined by using the lattice parameter dependence of the total energy. The calculation procedure for the total energy ($E_{\text{Pd}_{4-n}\text{Ru}_n}$) per basic cluster is described in Appendix 1. $D(x)$ is a Debye function and the first term of the vibrational internal energy (eq. (3)) represents the zero-point energy.

3. Solvus Temperatures of $\text{Pd}_{1-c}\text{Ru}_c$

We discuss the *ab-initio* calculations for the Ru-concentration dependence of the T_{solvus} of the $\text{Pd}_{1-c}\text{Ru}_c$ ($0.03 \leq c \leq 0.12$) alloys. In the present study, we calculated the free energy difference (eq. (5)) between the disordered and segregated states,

$$\Delta F(a, T) = \Delta E(a, T) - T S_{\text{conf}}(a, T) \quad (5)$$

$$\Delta E(a, T) = E_{\text{dis}}(a, T) - E_{\text{seg}}(a, T) \quad (6)$$

where $E_{\text{dis}}(a, T)$ and $E_{\text{seg}}(a, T)$ are the internal energies corresponding to the disordered and segregated states, respectively, depending on the lattice parameter (a) and tempera-

ture (T), and include the contributions from the electron excitation due to the FD distribution and the lattice thermal vibration effect (eq. (2)) based on the Debye-Grüneisen model, discussed in Sect. 2. The $S_{\text{conf}}(a, T)$ is the configurational entropy calculated by the CVMT. The $S_{\text{conf}}(a, T)$ and $\Delta E(a, T)$ are expressed by the cluster probabilities $\{\omega_{ijkl}\}$ of the tetrahedron, where i, j, k , and l distinguish Pd or Ru. Thus, by minimizing the free energy difference (eq. (5)) with respect to the cluster probabilities $\{\omega_{ijkl}\}$, we can determine the cluster probabilities in the equilibrium state. The calculation procedure for the minimization of $\Delta F(a, T)$ is described in Appendix 2. The Ru-concentration limit to a given temperature (T_{solvus}) is calculated by using the calculated

values for $\{\omega_{ijkl}\}$, as the Ru-concentration = $\sum_{j,k,l=\text{Pd,Ru}} \omega_{\text{Ru}, jkl}$. In the present calculations, the equilibrium lattice parameter of $\text{Pd}_{1-c}\text{Ru}_c$ at a given T is approximated by the equilibrium lattice parameter of the Pd-host determined by the minimization of $E_{\text{Pd}_4}(a, T)$ with the electron excitation due to the FD distribution and the lattice thermal vibration effect, since the difference between the equilibrium lattice parameters ($a(T, c)$ and $a(T, 0)$) of $\text{Pd}_{1-c}\text{Ru}_c$ and Pd at a given T may be small for the low Ru-concentration, as seen in Fig. 3. The error caused by this approximation will be discussed in the last paragraph of this section.

In the CVMT approximation, we can treat IEs exactly up to the 4-body in a tetrahedron formed from the 1st- nn pairs. However, we have found that the 2-body interaction is long-range for the Ru impurities in Pd, as shown in Fig. 1, and may be important up to the 10th- nn interaction; the positive (repulsive) IEs at the 2nd-, 4th-, and 9th- nn s are comparatively large.⁶⁾ It is noted that the 1st(0.5,0.5,0)-, 4th(1,1,0)-, and 9th-a(1.5,1.5,0)- nn s align along the $\langle 110 \rangle$ direction, although we have not understood the micro-mechanism of the rather large repulsion at the 9th-a nn . Thus, as the first approximation, we renormalized the strong and attractive 1st- nn IE (negative value) as follows, as discussed in Ref. 4):

$$\Delta \tilde{E}_1^{2\text{-body}} = \Delta E_1^{2\text{-body}} + \frac{6}{12} \Delta E_2^{2\text{-body}} + \frac{24}{12} \Delta E_3^{2\text{-body}} + \dots + \frac{24}{12} \Delta E_{10}^{2\text{-body}} \quad (7)$$

Fig. 1 Calculated results for the distance dependence (1~20th- nn) of the Ru-Ru IEs in Pd for the lattice parameter of 7.40 a.u., with the FD distribution at $T_{\text{FD}} = 800$ K. There are two nonequivalent sites for the 9th-, 13th-, 16th-, 17th-, and 18th- nn s. The 9th-a and 9th-b nn sites are (1.5, 1.5, 0) and (2, 0.5, 0.5) in the unit of the lattice parameter (7.40 a.u.), respectively. See the text for details.

where the coefficient in the n th- nn term is the ratio of the coordination number of the n th- nn shell to that of the 1st- nn shell. It is noted that the sum total of the long-range 2-body IEs up to the 10th- nn is maintained in the renormalized 1st- nn IE. In the present paper, the CVMT calculations with the 1st- nn IE renormalized by the IEs up to the 10th- nn are written as CVMT10. The lattice thermal vibration effect for the renormalized 1st- nn IE is taken into account in the present calculations, as discussed in the last paragraph of Appendix 1.

The 3-body and 4-body IEs are listed in Table 1 as their lattice parameter (a) dependence and T_{FD} -dependence for the FD distribution. These values are considerably small compared to the 2-body IEs. It is also noted that the contributions from the 3-body and 4-body are proportional to the 3rd- and 4th-power of the Ru-concentration. Thus, in the present study for the low Ru-concentration, we do not consider the contributions from the 3-body and 4-body IEs of the larger clusters. Figure 2 shows the calculated results for the distance (1~10th- nn) and T_{FD} ($= 800, 1000, 1200, 1400, 1600$ K)-dependence of the 2-body IEs, for the lattice parameter of 7.40 a.u. We find that the T_{FD} -dependence is not

Table 1 Calculated results (in eV) for the 3-body and 4-body IEs among the Ru impurities in Pd, shown in Fig. 2 (I = Ru, H = Pd) in Ref. 4), for seven lattice parameters ($a = 6.8 \sim 8.0$ a.u., in interval of 0.2 a.u.) and at three temperatures ($T_{\text{FD}} = 800, 1200, 1600$ K) for the FD distribution. See the text for details.

a (a.u.)	$T_{\text{FD}} = 800$ K		1200 K		1600 K	
	$E_{\text{int}}^{3\text{-body}}$	$E_{\text{int}}^{4\text{-body}}$	$E_{\text{int}}^{3\text{-body}}$	$E_{\text{int}}^{4\text{-body}}$	$E_{\text{int}}^{3\text{-body}}$	$E_{\text{int}}^{4\text{-body}}$ (eV)
6.8	0.0128	0.0085	0.0140	0.0092	0.0151	0.0090
7.0	0.0125	0.0085	0.0136	0.0090	0.0146	0.0084
7.2	0.0124	0.0086	0.0134	0.0086	0.0142	0.0076
7.4	0.0125	0.0085	0.0134	0.0080	0.0138	0.0067
7.6	0.0128	0.0084	0.0133	0.0073	0.0132	0.0057
7.8	0.0131	0.0081	0.0132	0.0064	0.0125	0.0049
8.0	0.0134	0.0076	0.0129	0.0056	0.0117	0.0041

Fig. 2 Calculated results for the distance (1~10th- nn) dependence of the Ru-Ru IEs in Pd with the FD distribution at $T_{\text{FD}} = 800, 1000, 1200, 1400$, and 1600 K. The lattice parameter is fixed at 7.40 a.u. The repulsive 2nd- nn IE becomes smaller and smaller with the increasing T_{FD} . The enlarged view around the 2nd- nn is inserted in Fig. 2. See the text for details.

as small as we have usually been expecting it to be.²⁵) It is noted that the repulsive interaction at the 2nd-*nn* becomes considerably weak with the increasing T_{FD} . This means that the temperature effect of the electron excitation due to the FD distribution attractively works for the 2-body IEs of the Ru impurities in Pd. As shown later, this effect is very important to reproduce the observed T_{solvus} .

The vibrational internal energy (eq. (3)) and vibrational entropy (eq. (4)) for the basic cluster ($\text{Pd}_{4-n}\text{Ru}_n$, $n = 0\sim 4$) used in the CVMT were calculated using the Debye temperatures which were determined from the lattice parameter dependence of the total energies per $\text{Pd}_{4-n}\text{Ru}_n$, as discussed in Sect. 2.2. The lattice parameter dependences (6.8~8.0 a.u.) of the total energies ($E_{\text{Pd}_{4-n}\text{Ru}_n}$, $n = 0\sim 4$) at $T_{\text{FD}} = 1200$ K without the thermal vibration effect are shown in Fig. 3(a), and those with the thermal vibration effect at $T_{\text{vib}} = 800, 1200$ and 1600 K are shown in Figs. 3(b), (c) and (d). For the lattice parameter dependence, the FPKKR calculations were done in intervals of 0.1 a.u. Table 2 shows the calculated results for the renormalized 1st-*nn* IE with the thermal vibration effect. It is noted that the negative values of IE become larger with the increasing T_{vib} . This means that the thermal vibration effect works attractively.

In the present calculations, we also take into account the local lattice distortion effect for the 1st-*nn* Ru-Ru IE. The calculated lattice distortion energies (negative values) for the 1st-*nn* Ru-Ru IEs at $a = 7.5$ and 7.6 a.u., with the FD distribution at $T_{\text{FD}} = 800, 1000, 1200, 1400$ and 1600 K, are listed in Table 3. We found that the local lattice relaxation effect also works attractively for the 1st-*nn* Ru-Ru interaction and that both the dependences on a and on T_{FD} are very small. In the following calculations for T_{solvus} , the lattice distortion energies for the equilibrium lattice parameters ($a_0 = 7.54$,

7.56, 7.59, 7.61, 7.63 a.u.), corresponding to the given temperatures ($T = 800, 1000, 1200, 1400, 1600$ K), are estimated by interpolating or extrapolating the two values at 7.5 and 7.6 a.u., as listed in Table 3.

We now discuss the calculated results for the Ru-concentration dependence of the T_{solvus} of the $\text{Pd}_{1-c}\text{Ru}_c$ ($0.03 \leq c \leq 0.12$) alloys. In order to clarify the lattice thermal vibration effect, we carried out two kinds of calculations without and with the thermal vibration effect. For the calculations without the thermal vibration effect, the lattice parameter is constant at 7.46 a.u., obtained by the FPKKR cal-

Table 2 Calculated results (in eV) for the renormalized 1st-*nn* IEs with the thermal vibration at $T_{\text{vib.}} = 800, 1200$, and 1600 K. These calculations were executed with the FD distribution at $T_{\text{FD}} = 800, 1200$, and 1600 K, respectively. See the text for details.

T_{FD}	renormalized 1st- <i>nn</i> IEs (eV)		
	$T_{\text{vib.}} = 800$ K	1200 K	1600 K
800 K	-0.0662	-0.0681	-0.0705
1200 K	-0.0825	-0.0833	-0.0841
1600 K	-0.0987	-0.0993	-0.1000

Table 3 Calculated results (in eV) for the local lattice distortion energies for the 1st-*nn* Ru-Ru IEs in Pd. These calculations were executed for two lattice parameters ($a = 7.5, 7.6$ a.u.) with the FD distribution at $T_{\text{FD}} = 800, 1000, 1200, 1400$ and 1600 K, respectively. See the text for details.

a (a.u.)	local lattice relaxation energies (eV)				
	$T_{\text{FD}} = 800$ K	1000 K	1200 K	1400 K	1600 K
7.5	-0.0336	-0.0340	-0.0342	-0.0344	-0.0346
7.6	-0.0346	-0.0349	-0.0353	-0.0367	-0.0361

Fig. 3 Lattice parameter dependence (6.8~8.0a.u.) of the total energies ($E_{\text{Pd}_{4-n}\text{Ru}_n}$) per basic cluster of five phases, $\text{Pd}_{4-n}\text{Ru}_n$ ($n = 0\sim 4$), discussed in Appendix 1: (a) total energies without thermal vibration effect; (b), (c) and (d) those with the thermal vibration effect at $T_{\text{vib.}} = 800, 1200$ and 1600 K, respectively. All the calculations were executed with the FD distribution at $T_{\text{FD}} = 1200$ K. See the text for details.

Fig. 4 Concentration dependence of the T_{solvus} of the $\text{Pd}_{1-c}\text{Ru}_c$ ($0.3 \leq c \leq 0.12$) alloys obtained by the two kinds of CVMT10 calculations: (a) without and (b) with the thermal vibration effect. The calculated results are shown for the five temperatures ($T_{\text{FD}} = 800, 1000, 1200, 1400$, and 1600 K). See the text for details.

Table 4 Experimental results for the Ru-concentration dependence of the T_{solvus} of the $\text{Pd}_{1-c}\text{Ru}_c$ alloys.⁵⁾

$c \times 100(\%)$	2.7	4.4	7.8	12.0
T_{solvus} (K)	1000	1200	1400	1600

calculations at $T_{\text{FD}} = 800$ K. We found that the equilibrium lattice parameter is almost independent of T_{FD} . Figure 4 (a) shows the CVMT10 results without the thermal vibration effect using the IEs at $T_{\text{FD}} = 800, 1000, 1200, 1400$, and 1600 K together with the experimental results listed in Table 4.⁵⁾ It was found that T_{solvus} become higher and higher with the increasing T_{FD} . These results are easily understood by considering that the IEs (positive values, repulsion) at the 2nd-, 4th, 9th-a-nns become smaller (less repulsive) with the increasing T_{FD} by the effect of the electron excitation due to the FD distribution, as already discussed. It is noted that, in the present calculations, the observed T_{solvus} (x) for a given Ru-concentration should agree with the calculated result (●) obtained by using $T_{\text{FD}} = T_{\text{solvus}}$. We then compared the calculated results (●) with the experimental results (x) for T_{solvus} to the given Ru-concentration, listed in Table 4. For the observed $T_{\text{solvus}} = 1000$ and 1200 K, corresponding to the Ru-concentration limits of 2.7% and 4.4%, the CVMT10 calculations underestimate the experimental results by ~ 110 and ~ 80 K, respectively. For the observed $T_{\text{solvus}} = 1400$ K, corresponding to the Ru-concentration limit of 7.8%, the CVMT10 result agrees with the observed result. On the

other hand, for the observed $T_{\text{solvus}} = 1600$ K, corresponding to the Ru-concentration limit of 12.0%, the CVMT10 calculations overestimate the experimental result by ~ 100 K.

Figure 4(b) shows the CVMT10 results with the thermal vibration effect. We found that the calculated T_{solvus} considerably increases with the thermal vibration effect, resulting in the good agreement with the observed T_{solvus} for the low Ru-concentration up to $\sim 4\%$ and the higher overestimation ($100 \sim 260$ K) for the higher Ru-concentrations ($8 \sim 12\%$), corresponding to the higher $T_{\text{solvus}} = 1400 \sim 1600$ K. The increase in T_{solvus} is understood by considering that the renormalized attractive 1st-*nn* IE (negative value, attraction) increases with the increasing T_{vib} , for examples, as -0.066 , -0.083 , and -0.100 eV for $T_{\text{vib}} = T_{\text{FD}} = 800, 1200$, and 1600 K, respectively, as listed in Table 2. As a result, we can conclude that, as shown in Fig. 4(b), the CVMT10 calculations reproduce fairly well (within the error of ~ 50 K) the observed T_{solvus} for the low Ru-concentration up to $\sim 6\%$, while the discrepancy (overestimation) between the calculated and observed results becomes greater for the higher Ru-concentrations ($8 \sim 12\%$). The overestimation is as high as ~ 260 K around the observed $T_{\text{solvus}} = 1600$ K. This discrepancy may be caused by the CVMT10 calculations with the insufficient renormalization (eq. (7)) of the long-range 2-body IEs.

According to the Monte Carlo simulations of Schweika,^{26,27)} the overestimation due to the insufficient renormalization (eq. (7)) becomes higher and higher with the increasing concentration of the minor element, for the alloys with the competitive 2-body IEs (the strongly attractive IE at the 1st-*nn* and the considerably repulsive IE at the 2nd-*nn*), being similar to the present $\text{Pd}_{1-c}\text{Ru}_c$ alloys. It now appears obvious that the suitable treatment for the repulsive IEs at the 2nd- and 4th-, and 9th-nns is important to correct the high discrepancy toward the higher T_{solvus} , especially for the 4th-*nn* IE because it is highly repulsive in the high T_{FD} ($1400 \sim 1600$ K) and the 4th-nns brings the higher coordination number (12) compared to the 2nd-nns.

In order to clarify the influence of the renormalization for the 2-body IEs on the overestimation of T_{solvus} , we carried out the calculations based on the cluster variation method within the tetrahedron-octahedron approximation (CVMTO), in which the 1st- and 2nd-*nn* IEs can be taken into account. We treat the repulsive IE at the 2nd-*nn*, independently from the attractive IE at the 1st-*nn*, and renormalize the 1st-*nn* IE by including the 3-10th-*nn* IEs (eliminating the 2nd-*nn* part from eq. (7)). In the present paper, the CVMTO calculations with the 1st-*nn* IE renormalized by the IEs up to the 10th-*nn* are written as CVMTO10. The thermal vibration effect for the 2nd-*nn* IE is calculated by the way similar to that discussed in Sect.2.2 with the basic cluster ($\text{Pd}_{6-n}\text{Ru}_n$) of the octahedron. However, we found by comparing Fig. 5(a) with Fig. 4(b) by the CVMT10 calculation, that the improvement by introducing the CVMTO10 approximation is inadequate, especially for the high T_{solvus} around 1600 K, although the overestimation around $T_{\text{solvus}} = 1400 \sim 1600$ K is reduced from $100 \sim 260$ K to $85 \sim 225$ K. It is noted that the T_{solvus} below 1200 K, corresponding to the low Ru-concentration ($2 \sim 4\%$), is almost unchanged. The inadequacy around $T_{\text{solvus}} = 1600$ K is mainly caused by the

fact that the repulsive (positive) IE at the 2nd-*nn* becomes very small with the increasing T_{FD} , as shown in Fig. 2. In order to obtain a good agreement with the experimental results for the high T_{solvus} around 1600 K, we may need the correct treatment not only for the 2nd-*nn* IE, but also for the strongly repulsive 4th-*nn* IE even at the high T_{FD} .

In order to suitably include the effect of the repulsive 4th-*nn* IE, we then renormalized the repulsive 2nd-*nn* IE by including the 4th-*nn* IE, while the 1st-*nn* IE by including the 3- and 5-10th-*nn* IEs (eliminating the 2nd- and 4th-*nn* parts from eq. (7)), since we cannot exactly take into account the 4th-*nn* IE by the CVMTO calculation. The CVMTO10 results with this renormalization (2nd $\leftarrow$ 4th) for the 1st and 2nd IEs are shown in Fig. 5(b). In contrast to the result in Fig. 4(b) (the overestimation ($\sim$ 260 K) around $T_{solvus} = 1600$ K), the results in Fig. 5(b) (2nd $\leftarrow$ 4th) agree very well with the experimental results. It is noted that the overestimation around $T_{solvus} = 1600$ K is less than $\sim$ 50 K. Figure 5(b) also shows the calculated results obtained by the different renormalization (2nd $\leftarrow$ 3~5th) for the 1st- and 2nd-*nn* IEs, where the 2nd-*nn* IE is renormalized by including the 3~5th-*nn* IEs and the 1st-*nn* IE is renormalized by including the 6~10th-*nn* IEs. The calculated result shows the low underestimation ($\sim$ 55 K) around $T_{solvus} = 1600$ K. This means that the CVMTO10 calculations with the suitably renormalized 1st-*nn* and 2nd-*nn* IEs may reproduce the observed T_{solvus} up to the higher Ru-concentration ($\sim$ 12%). Thus, we may conclude that the exact treatment for the repulsive

4th-*nn* IE, beyond the CVMTO approximation, is very important to quantitatively study the observed T_{solvus} around 1400~1600 K, corresponding to the high Ru-concentration limits (8~12%).

We now discuss the error caused by using the equilibrium lattice parameter ($a(T, 0)$) of Pd instead of that ($a(T, c)$) of $Pd_{1-c}Ru_c$ at a given T . In order to take into account the Ru-concentration dependence of the equilibrium lattice parameter of $Pd_{1-c}Ru_c$, we prepared the equilibrium lattice parameter $a(T, c)$ by fitting the five equilibrium lattice parameters of $Pd_{4-n}Ru_n$ ($n = 0\sim 4$), shown in Fig. 3. The Ru-concentration limit at a given T is self-consistently determined using the obtained $a(T, c)$. The CVMTO10 results for the T_{solvus} are shown in Fig. 6 and compared to the CVMTO10 results in Fig. 4(b), being obtained using the lattice parameters ($a(T, 0)$) of Pd. For the low Ru-concentrations ($c = 0.027\sim 0.044$), the calculated results shown in Fig. 6 are almost the same to those obtained using the lattice parameter $a(T, 0)$ of Pd and agree very much with the experimental results. On the other hand, for the higher Ru-concentrations, we found that the discrepancies between the calculated and experimental results are reduced by 35 K (100 K $\rightarrow$ 65 K) and 60 K (260 K $\rightarrow$ 200 K), respectively, at $c = 0.078$ ($T_{solvus} = 1400$ K) and 0.12 ($T_{solvus} = 1600$ K). However, the high discrepancy (overestimation) between the calculated and experimental results still remains in the high Ru-concentrations ($c = 0.078\sim 0.12$). Thus, it is concluded that the results obtained by using the equilibrium lattice parameters ($a(T, c)$) of $Pd_{1-c}Ru_c$ may almost be unchanged from all of the above-mentioned results obtained by using the lattice parameters ($a(T, 0)$) of Pd.

4. Summary and Future Problem

We presented the ab-initio calculations for the T_{solvus} of the $Pd_{1-c}Ru_c$ ($0.03 \leq c \leq 0.12$) alloys, in which the Ru atoms are treated as impurities in Pd. The internal energies in the free energies are calculated by the present RSCE with the impurity IEs up to the 4-body, all of which are uniquely and accurately determined by the FPKKR calculations for perfect and impurity systems.^{9-12,14} The configurational entropy calculations are based on the CVMTO and CVMTO.

We firstly showed that the 2-body interaction is long-

Fig. 5 Concentration dependence of the T_{solvus} of the $Pd_{1-c}Ru_c$ ($0.3 \leq c \leq 0.12$) alloys obtained by the CVMTO10 calculation. In (a), the CVMTO10 results with the 1st-*nn* IE renormalized by the 3~10th-*nn* IEs except the 2nd-*nn* IE, and with the FD distribution at $T_{FD} = 800, 1000, 1200, 1400$, and 1600 K, are shown. In (b), the CVMTO10 results due to the different renormalization for the 1st- and 2nd-*nn* IEs are shown. For (b), T_{FD} is fixed at 1600 K. See the text for details.

Fig. 6 Concentration dependence of the T_{solvus} of the $Pd_{1-c}Ru_c$ ($0.3 \leq c \leq 0.12$) alloys, obtained by the CVMTO10 calculations. The Ru-concentration is self-consistently determined by using lattice parameters ($a(T, c)$) of $Pd_{1-c}Ru_c$. See the text for details.

range, and comparatively repulsive at the 2nd-, 4th-, and 9th-*nn*s against the strong attraction at the 1st-*nn*. We also found that the following three effects attractively work on the IEs of the Ru impurities in Pd: (1) the local lattice distortion for the 1st-*nn* Ru-Ru IE, (2) the lattice softening due to the thermal vibration at high temperatures, and (3) the electron excitation due to the FD distribution, being usually neglected in the *ab-initio* calculations. During the solvus temperature calculations, we realized that these three effects are very effective in reproducing the observed T_{solvus} .

We secondly showed the T_{solvus} of the $\text{Pd}_{1-c}\text{Ru}_c$ ($0.03 \leq c \leq 0.12$) alloys by the free energy calculations based on the CVM. We found that the results obtained by the CVMT10 calculations, in which the 1st-*nn* IE is renormalized by including the 2~10th-*nn* IEs, agree fairly well (within the error of ~50 K) with the observed T_{solvus} of the $\text{Pd}_{1-c}\text{Ru}_c$ alloys, for the low Ru-concentrations up to ~6%, while the discrepancy (overestimation) between the calculated and experimental results becomes high for the high Ru-concentrations (8~12%). We also found that the CVMT010 calculations, in which the 1st- and 2nd-*nn* IEs can be taken into account, may correct the discrepancy in the high Ru-concentration (8~12%), if the 2nd-*nn* IE is suitably renormalized by including the 4th-*nn* IE.

Thus, we believe that the CVM calculations with the larger basic cluster such as the ~13 atom clusters,²⁸⁾ at least exactly treating the IEs up to the repulsive 4th-*nn* IE, can reproduce very well the observed T_{solvus} of the $\text{Pd}_{1-c}\text{Ru}_c$ alloys, even for the high Ru-concentrations up to ~12%. The CVM calculations with the larger basic cluster including up to the 4th-*nn* IE is strongly claimed to quantitatively determine the phase diagrams such as the concentration dependence of the observed T_{solvus} of the long-range interaction systems.

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Appendix

Appendix 1: Lattice parameter dependence of total energy per basic cluster of each phase consisting of the basic cluster used in the CVM calculations

In order to calculate the thermal vibration free energy using the Debye-Grüneisen model,¹⁾ we must prepare some

potential surfaces for the thermal vibration, that is, the lattice parameter dependences of the total energy per basic cluster, of each phase consisting of the basic cluster used in the CVM calculations. For the CVMT calculations, there are five kinds of basic clusters, as shown in Fig. 2 in Ref. 4) ($H = \text{Pd}$, $I = \text{Ru}$), where four atoms ($\text{Pd}_{4-n}\text{Ru}_n$, $n = 0 \sim 4$) are located at the 1st-*nn* tetrahedral sites. We show how to estimate the total energy $E_{\text{Pd}_{4-n}\text{Ru}_n}(a)$ per basic cluster of each phase consisting of the basic cluster $\text{Pd}_{4-n}\text{Ru}_n$ depending on the lattice parameter (a). We can simply calculate $E_{\text{Pd}_{4-n}\text{Ru}_n}(a)$ as follows:

$$E_{\text{Pd}_{4-n}\text{Ru}_n}(a) = 4 \times E_{\text{Pd}}(a) + \Delta E_{\text{Ru}_n \text{ in Pd}}(a) \quad (\text{A.1})$$

where $E_{\text{Pd}}(a)$ is the total energy of the Pd host per atom and $\Delta E_{\text{Ru}_n \text{ in Pd}}(a)$ is the total energy change due to the presence of the Ru_n impurities in Pd, all of which are obtained by the present *ab-initio* calculations. Of course, the interaction among the Ru impurities is restricted within a basic cluster, and no interaction among an infinite number of Ru_n in the separate basic clusters is included in eq. (A.1). However, if the equilibrium lattice parameter and the lattice parameter dependence of E obtained by eq. (A.1) agree with those in the dense cluster system, where an infinite number of basic clusters ($\text{Pd}_{4-n}\text{Ru}_n$) are arranged over the whole space, the Debye-Grüneisen model may be applicable for the dilute limit calculations presented here.

In order to give validity to the present approach, we compared the present results with the calculated results obtained from the periodic system of the basic $\text{Pd}_{4-n}\text{Ru}_n$ ($n = 0 \sim 4$) clusters in the fcc unit cell. We noted in Fig. A.1 that the lattice parameter dependence of E (including the value of the equilibrium lattice parameter of the total energy minimum), obtained by the present approach, agrees very well with those obtained by the periodic band calculations for each basic cluster. It is noted that all the energy minima are shifted to zero because the absolute value of the energy has no effect on the thermal vibration. These results show that the contribution from the interaction among Ru_n in the arrayed basic clusters, being ignored in the present approach, may be not important for the lattice parameter dependence of $E_{\text{Pd}_{4-n}\text{Ru}_n}(a)$. As a result, we may conclude that the important effect for the lattice parameter dependence of the total energy $E_{\text{Pd}_{4-n}\text{Ru}_n}(a)$ may be estimated by the present approach.

We now discuss how to treat the thermal vibration effect for the long-range 2-body IEs. The m -th *nn* IE is written as follows:

$$E_m^{2\text{-body}}(a) = \Delta E_{\text{Ru}_2 \text{ in Pd}}^{m\text{-th neighbor}}(a) - 2 \times \Delta E_{\text{Ru}_1 \text{ in Pd}}(a) \quad (\text{A.2})$$

where $\Delta E_{\text{Ru}_2 \text{ in Pd}}^{m\text{-th neighbor}}(a)$ is the total energy change due to the presence of the m -th *nn* Ru-Ru impurity pair in Pd. We renormalized $\Delta E_{\text{Ru}_2 \text{ in Pd}}(a)$ in eq. (A.1) by including these long-range 2-body IEs up to the 10th-*nn*. Using the resultant $E_{\text{Pd}_2\text{Ru}_2}(a)$, we calculated the thermal vibration free energy using the Debye-Grüneisen model discussed in Sect. 2.2. Thus, within the CVMT approximation, we can take into account the thermal vibration effect for the long-range 2-body IEs.

Fig. A.1 Lattice parameter dependence of the total energies ($E_{\text{Pd}_{4-n}\text{Ru}_n}$) per basic clusters ($\text{Pd}_{4-n}\text{Ru}_n$, $n = 0 \sim 4$) used in the CVMT approximation obtained by the present approach. The calculated results by the band calculations with the unit cells ($\text{Pd}_{4-n}\text{Ru}_n$, $n = 0 \sim 4$) are also shown for comparison. All these calculations were executed with the FD distribution at $T_{\text{FD}} = 800$ K. There is almost no difference between the calculated results obtained by the two approaches. See the text for details.

Appendix 2: Calculation procedure for temperature dependence of solid solubility limit

In order to calculate the configurational entropy in the disordered state (in eq. (5)) at a given temperature, we used the cluster variation method within the tetrahedron approximation (CVMT) introduced by Kikuchi.²⁹⁾ Kikuchi also designed the natural iteration (NI) technique for the minimization of the grand potential of the disordered state. As shown in Ref. 29), the grand potential per atom is written in the following form:

$$\Omega = F_{\text{dis}} - \sum_i \mu_i \times x_i \quad (\text{A.3})$$

where F_{dis} is the free energy of the disordered state, and μ_i and x_i are the chemical potential and concentration of the i -element (here, $i = \text{Pd}$ or Ru), respectively. It is noted that Ω is the function of cluster probabilities $\{\omega_{ijkl}\}$, temperature (T) and chemical potentials $\{\mu_i\}$, as shown in Ref. 29).

In order to minimize the free energy difference, ΔF (eq. 5), we can use this formalism by regarding the 2nd term in eq. (A.3) as the internal energy of the segregation state, which is written as,

$$E_{\text{seg}} = 2 \times (E_{\text{Pd}_4} \times x_{\text{Pd}} + E_{\text{Ru}_4} \times x_{\text{Ru}}) \quad (\text{A.4})$$

where E_{Pd_4} (E_{Ru_4}) is the total energy of the tetrahedron cluster Pd_4 (Ru_4) in the Pd host, discussed in Sect. 2.1. and factor 2 means that the N-lattice points constitute $2 \times N$ tetrahedrons in the fcc structure. As a result, it is shown that Ω

equals ΔF (eq. 5) as follows:

$$\begin{aligned} \Omega &= F_{\text{dis}} - \sum \mu_i \times x_i \\ &= F_{\text{dis}} - 2 \times (E_{\text{Pd}_4} \times x_{\text{Pd}} + E_{\text{Ru}_4} \times x_{\text{Ru}}) \\ &= \Delta F \end{aligned} \quad (\text{A.5})$$

It is noted that μ_i ($i = \text{Pd}$ or Ru) is replaced by $2 \times E_{iiii}$. Equation (A.5) may also be transformed as follows,

$$\begin{aligned} \Omega &= F_{\text{dis}} - (E_{\text{Pd}_4} + E_{\text{Ru}_4}) \times (x_{\text{Pd}} + x_{\text{Ru}}) \\ &\quad - (E_{\text{Pd}_4} - E_{\text{Ru}_4}) \times (x_{\text{Pd}} - x_{\text{Ru}}) \\ &= F_{\text{dis}} - (E_{\text{Pd}_4} + E_{\text{Ru}_4}) - (E_{\text{Pd}_4} - E_{\text{Ru}_4}) \times (x_{\text{Pd}} - x_{\text{Ru}}) \end{aligned} \quad (\text{A.6})$$

where we used the relation $x_{\text{Pd}} + x_{\text{Ru}} = 1$. Since the origin of the energy can be changed, we used the origin of eq. (A.6) to satisfy the following relation

$$E_{\text{Pd}_4} + E_{\text{Ru}_4} = 0 \quad (\text{A.7})$$

Then, eq. (A.6) is transformed into

$$\begin{aligned} \tilde{\Omega} &= F_{\text{dis}} - (E_{\text{Pd}_4} - E_{\text{Ru}_4}) \times (x_{\text{Pd}} - x_{\text{Ru}}) \\ &= F_{\text{dis}} - (\tilde{\mu}_{\text{Pd}} \times x_{\text{Pd}} + \tilde{\mu}_{\text{Ru}} \times x_{\text{Ru}}) \end{aligned} \quad (\text{A.8})$$

where $\tilde{\mu}_{\text{Pd}} = -\tilde{\mu}_{\text{Ru}} = E_{\text{Pd}_4} - E_{\text{Ru}_4}$. It is noted that the final formula (eq. (A.8)) is a function of the cluster probabilities $\{\omega_{ijkl}\}$ and temperature T . Thus, using the NI technique along with the total energies $\{E_{ijkl}\}$ of the tetrahedron clusters in the Pd host, we can easily obtain $\{\omega_{ijkl}\}$ by minimizing eq. (A.8) with respect to $\{\omega_{ijkl}\}$ at a given temperature T .

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