Real Space Cluster Expansion for Total Energies of Pd-Rich PdX (X = Rh, Ru) Alloys, Based on Full-Potential KKR Calculations: An Approach from a Dilute Limit

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We study the accuracy and convergence of the real space cluster expansion (RSCE) for the internal energies in the free energies of Pd-rich PdX (X = Rh, Ru) alloys, being used to study the phase stability and phase equilibria of Pd-rich PdX alloys in fcc structure. In the present RSCE from a dilute limit, the X atoms of minor element are treated as impurities in Pd. The *n*-body interaction energies (IEs) among X impurities in Pd are determined uniquely and successively from the low body to high body, by the *ab-initio* calculations based on the full-potential Korringa-Kohn-Rostoker Green's function method (FPKKR) for the perfect and impurity systems (Pd-host and X_n in Pd, *n* = 1~4), combined with the generalized gradient approximation in the density functional theory. We show that the total energies of the ordered Pd₃X (X = Rh, Ru; X-concentration = 25%) alloys in L1₂ structure, obtained by the screened FPKKR band calculations, are reproduced very well (within the error of ~1 mRy per atom) by the present RSCE including the 2-body IEs up to the 20th nearest neighboring pair (X₂) and the 3-body IEs up to the clusters (X₃) in the two cubic cells in fcc structure. We clarify the contribution from each term (of the 0~4 body terms) in the RSCE to the total energies of Pd-rich PdX alloys, the distance dependence of the 2-body (X₂) IEs, and the cluster-size dependence of 3-body (X₃) and 4-body (X₄) IEs. It is also shown that the contribution from the *n*-body (*n* = 2~4) IEs becomes smaller and smaller with the increase in *n* and that the contribution from the 4-body IEs is very small (less than ~0.2 mRy per atom). [doi:10.2320/matertrans.M2018194]

(Received June 13, 2018; Accepted August 6, 2018; Published September 14, 2018)

Keywords: KKR-Green's function method, GGA, Fermi-Dirac distribution, real space cluster expansion for total energy, phase stability, Pd-rich PdRu alloys, Pd-rich PdRh alloys

1. Introduction

We recently succeeded in reproducing very well the observed X-concentration dependence of the solvus temperatures of the Pd-rich PdX (X = Ru, Rh) alloys in fcc structure,¹⁾ by the free energy calculations based on the cluster variation method (CVM) for the configurational entropy.²⁻⁵⁾ The internal energies in the free energies of the Pd-rich PdX (X = Ru, Rh) alloys, were calculated by the real space cluster expansion (RSCE) from a dilute limit,⁶⁻¹⁰⁾ where the X atoms of minor element were treated as impurities in Pd. The interaction energies (IEs) among X impurities in Pd were calculated by using the full-potential Korringa-Kohn-Rostoker Green's function method (FPKKR) for the perfect and impurity systems (Pd-host and X_n in Pd, *n* = 0~4), combined with the generalized gradient approximation in the density functional theory. We have already clarified the distance dependence of the 2-body IEs, the local lattice relaxation effect, existing even at *T* = 0 K, and both the temperature dependence of (1) the thermal lattice vibration effect by the Debye-Grüneisen model and (2) the electron excitation effect due to the Fermi-Dirac (FD) distribution.³⁻⁵⁾ We found that the temperature (*T*_{FD}) dependence of the electron excitation effect due to the FD distribution, being usually neglected, is very important to reproduce the observed solvus temperatures of the Pd-rich PdX alloys. The present RSCE may be very efficient to calculate the internal energies in the free energies of the

alloys of decomposition type, such as the Pd-rich PdX (X = Ru, Rh) alloys, although we need to examine the accuracy and convergence of the present RSCE.

Differently from the present RSCE approach, there are mainly two other methods to calculate the IEs for predicting the phase stability and phase equilibria in alloys: the approach based on the generalized perturbation method (GPM)¹¹⁾ using the Korringa-Kohn-Rostoker coherent-potential approximation (KKR-CPA),¹²⁾ and the Connolly-Williams (CW) approach.¹³⁾ The GPM combined with the KKR-CPA method starts from the completely disordered states of alloys,¹²⁾ described by the KKR-CPA, and then calculates the 2~4-body IEs by inserting 1~4 specific atoms in the CPA medium. The concentration dependence of the IEs is fully included as a result of the embedding into the CPA medium. However, the KKR-CPA relies on the single-site approximation being not unproblematic for alloys with charge transfer.¹⁴⁾ In addition to this approximation, the 2~4-body IEs are calculated in the frozen-potential approximation and moreover by taking only single-particle energies into account in the GPM. In the present RSCE approach, all these approximations are avoided, which has to be paid off by being restricted to the dilute limit.²⁻⁵⁾

The CW approach determines the IEs by using the total energies of different atomic configurations in the considered alloys. Here the total energies obtained by the supercell calculations with many different configurations in the unit cell are fitted by selected models containing the 2~4-body IEs. The best fit obtained by the smallest number of parameters determines the optional model for the IEs, which

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depends on both of the selections of models and supercells, and therefore cannot be determined uniquely, as discussed in Ref. 12. The present RSCE approach, being the most fundamental among these three approaches, considers only the atomic configurations of impurities, the energy differences of which define uniquely the n -body IEs among impurities. The n -body IEs are determined successively from the low body to high body and are independent on the impurity concentration, as discussed in Sect. 2. Because of an approach from a dilute limit, however, the efficiency of the present RSCE depends very much on the distance dependence of the 2-body (X_2 impurities) IEs and the cluster-size dependence of the 3-body (X_3 impurities) and 4-body (X_4 impurities) IEs. However, we may usually expect that the interactions between distant sites are less important than those between near sites and that the interactions involving many sites are less important than the interactions involving the fewer sites. According to our experiences, the 2-body IEs are very small beyond the 10-th nn pair³⁻⁵⁾ and the n -body IEs become smaller and smaller with the increase in n , and the 4-body IEs is very small compared with 2-body and 3-body IEs.^{2-5,7,8,10)}

The purpose of the present paper is to clarify the accuracy and convergence of the present RSCE for the total energies of the Pd_3X ($X = Ru, Rh$) alloys in $L1_2$ structure, including up to the 4-body IEs. In Sect. 2, we describe the calculation procedures for the FPKKR with the electron excitation effect due to the FD distribution, and the RSCE from a dilute limit. In Sect. 3, we show how the FPKKR band calculation results for the total energies of the ordered Pd_3X alloys (X -concentration = 25%) in $L1_2$ structure are reproduced very accurately (within the error of ~ 1 mRy per atom) by the present RSCE from a dilute limit (X_n impurities in Pd), including the 2-body IEs up to the 20th-nearest neighboring (nn) pair (X_2) and the 3-body IEs up to the clusters (X_3) in the 2 cubic cells in fcc structure. We clarify each contribution from the n -body ($n = 0\sim 4$) IEs in the RSCE, the distance dependence of the 2-body (X_2) IEs, and the cluster-size dependence of 3-body (X_3) and 4-body (X_4) IEs. It is shown that the contribution from the n -body ($n = 2\sim 4$) IEs becomes smaller and smaller with the increase in n and that the contribution from the 4-body IEs is less than ~ 0.2 mRy per atom. Section 4 summarizes the main results of the present paper and discusses the future problems.

2. Calculation Method

2.1 Total energies of impurity systems

The calculations for the total energy of X ($=Ru, Rh$) impurities in Pd metal 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 Pd host, which simplifies very much 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 used the electronic densities obtained self-consistently 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 the Green's function method is that, by the introduction of the host Green's function, the embedding of point defects in an otherwise ideal crystal is described correctly, differently from the usual supercell and cluster calculations. It is noted that the change of the wave functions due to the defects is delocalized over the whole space, although the potential perturbation due to the defects is localized in the vicinity of the defects. The practical advantage in using the 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 energies without the lattice distortion effect, for the impurity system in fcc structure, it may be enough to redetermine self-consistently only the potentials of 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 the Lloyd's formula.^{7,16)} This is also very different from the supercell and cluster calculations where all potentials must be recalculated in each iteration cycle.

In the present method, we introduced the FD distribution into *ab-initio* Green's function calculations. As shown in Ref. 19, this is very useful to simplify the ground state calculations. Based on a contour integration in the complex energy plane we evaluate 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 ($\delta = \pi k T_{FD}$). The total energy is calculated by the grand canonical potential for which a simple formula is given. In all the present calculations, the lattice parameter of Pd host and the T_{FD} for the electron excitation due to the FD-distribution were fixed at 7.40 a.u. and 800 K, respectively.

2.2 Real space cluster expansion for total energies of Pd-rich PdX ($X = Ru, Rh$) alloys

A characteristic feature of the present RSCE for total energies of Pd-rich PdX alloys is that all the terms in the present RSCE are uniquely determined by the combination of total energies in different atomic arrangements of X atoms in Pd. It is noted that the X atoms of minor element are treated as impurities in Pd. In order to study the accuracy and convergence of the present RSCE, we calculate the total energies of the ordered Pd_3X ($X = Ru, Rh$) alloys in $L1_2$ structure (Fig. 1, X -concentration = 25%) and compare them with the band calculation results obtained by the screened FPKKR calculations for the ordered alloys. The RSCE for the total energy (per unit cell) of the ordered Pd_3X alloy in $L1_2$ structure is written as follows:

$$E_{Pd_3X}^{band} = 4E_{Pd}^{band} + \Delta E_{X \text{ in Pd}}^{1-body} + \Delta E^{2-body} + \Delta E^{3-body} + \Delta E^{4-body} + \Delta E^{many-body \text{ IEs beyond 4-body}} \quad (1)$$

where the 1st term is $4 \times$ total energy of Pd atom in Pd fcc metal (0-body), the 2nd term the total energy change due to the insertion of a single X impurity in Pd fcc metal (1-body), the 3 $\sim$ 5th terms correspond to the total contributions from the n -body ($n = 2\sim 4$) IEs among X_n impurities in Pd fcc metal (2 $\sim$ 4 bodies), respectively, and the last term is the sum total of many-body IEs beyond the 4-body. The first

Fig. 1 Pd₃X (X = Ru, Rh) in L1₂ structure.

(0-body) and second (1-body) energies are the quantities characteristic of Pd-host and a single X impurity in Pd, respectively. Thus, these components do not depend on the atomic arrangement of X impurities in Pd. It is noted that $\Delta E^{n\text{-body}}$ ($n \geq 2$) includes many kinds of n -body IEs. For example, $\Delta E^{2\text{-body}}$ includes all the contributions from the 2-body interactions of the (n, l, m) - nn pairs ($n, l, m = \text{integer}$) in unit of the lattice parameter of fcc structure, such as the 2nd (1, 0, 0)-, 4th (1, 1, 0)-, 6th (1, 1, 1)-, 8th (2, 0, 0)-, 10th (1, 2, 0)- nn pairs, which exist in the ordered Pd₃X alloy in L1₂ structure. $\Delta E^{3\text{-body}}$ and $\Delta E^{4\text{-body}}$ also include the contributions from the many 3-body and 4-body IEs of different shaped clusters (of X₃ and X₄ impurities) consisting of (n, l, m) - nn pairs such as the 2nd-, 4th-, and 6th- nn pairs.

Now we explain the definition of the n -body IEs among X_{*n*} impurities in Pd and show how to calculate them. For example, we consider the n -body ($n = 2 \sim 4$) IEs within a square consisting of the four 2nd- nn pairs in L1₂ structure, as shown in Fig. 2. This cluster is the smallest cluster for the 4-body IEs. Figures 2(a)–(f) show the six kinds of Pd_{4-*n*}X_{*n*} square clusters including X_{*n*} ($n = 0 \sim 4$) impurities in Pd fcc metal. There are two kinds of X₂ pairs (the 2nd- and 4th- nn pairs) designated by suffixes (2) and (4). Using the total energies (E_{Pd_4} , $E_{\text{X}_1\text{Pd}_3}$, $E_{\text{X}_2\text{Pd}_2}^{(2)}$, $E_{\text{X}_2\text{Pd}_2}^{(4)}$, $E_{\text{X}_3\text{Pd}_1}$ and E_{X_4}) of these six kinds of clusters in Pd fcc metal, the binding energies of the 2~4 impurities in Pd fcc metal are written as follows,

$$B_{\text{X}_2\text{Pd}_2}^{(2)} = E_{\text{X}_2\text{Pd}_2}^{(2)} - 2E_{\text{X}_1\text{Pd}_3} + E_{\text{Pd}_4} \quad (2)$$

$$B_{\text{X}_2\text{Pd}_2}^{(4)} = E_{\text{X}_2\text{Pd}_2}^{(4)} - 2E_{\text{X}_1\text{Pd}_3} + E_{\text{Pd}_4} \quad (3)$$

$$B_{\text{X}_3\text{Pd}_1} = E_{\text{X}_3\text{Pd}_1} - 3E_{\text{X}_1\text{Pd}_3} + 2E_{\text{Pd}_4} \quad (4)$$

$$B_{\text{X}_4} = E_{\text{X}_4} - 4E_{\text{X}_1\text{Pd}_3} + 3E_{\text{Pd}_4} \quad (5)$$

It is noted that all the potentials in the 37-atom impurity region, including all the Pd host-atoms (totally 34 Pd host-atoms) at the 1st- nn sites around a square cluster, are redetermined self-consistently in the present calculations. By using these binding energies, the 2~4-body IEs within the square cluster are defined as follows,

Fig. 2 Six kinds of square-shaped Pd_{4-*n*}X_{*n*} ($n = 0 \sim 4$) clusters in Pd, shown by the broken lines. $(4 - n) \times \text{Pd}$ and $n \times \text{X}$ atoms are located at vertices of a square consisting of the 2nd- nn pairs (a facet of fcc-cube). There are two kinds of pairs (2nd- and 4th- nn pairs).

$$\begin{aligned} \Delta E^{2\text{-body}(2)} &= B_{\text{X}_2\text{Pd}_2}^{(2)} \\ &= E_{\text{X}_2\text{Pd}_2}^{(2)} - 2E_{\text{X}_1\text{Pd}_3} + E_{\text{Pd}_4} \end{aligned} \quad (6)$$

$$\begin{aligned} \Delta E^{2\text{-body}(4)} &= B_{\text{X}_2\text{Pd}_2}^{(4)} \\ &= E_{\text{X}_2\text{Pd}_2}^{(4)} - 2E_{\text{X}_1\text{Pd}_3} + E_{\text{Pd}_4} \end{aligned} \quad (7)$$

$$\begin{aligned} \Delta E^{3\text{-body}} &= B_{\text{X}_3\text{Pd}_1} - 2\Delta E^{2\text{-body}(2)} - \Delta E^{2\text{-body}(4)} \\ &= E_{\text{X}_3\text{Pd}_1} - 2E_{\text{X}_2\text{Pd}_2}^{(2)} - E_{\text{X}_2\text{Pd}_2}^{(4)} \\ &\quad + 3E_{\text{X}_1\text{Pd}_3} - E_{\text{Pd}_4} \end{aligned} \quad (8)$$

$$\begin{aligned} \Delta E^{4\text{-body}} &= B_{\text{X}_4} - 4\Delta E^{3\text{-body}} - 4\Delta E^{2\text{-body}(2)} - 2\Delta E^{2\text{-body}(4)} \\ &= E_{\text{X}_4} - 4E_{\text{X}_3\text{Pd}_1} + 4E_{\text{X}_2\text{Pd}_2}^{(2)} + 2E_{\text{X}_2\text{Pd}_2}^{(4)} \\ &\quad - 4E_{\text{X}_1\text{Pd}_3} + E_{\text{Pd}_4} \end{aligned} \quad (9)$$

where the binding energy of 2 impurities corresponds to the 2-body IE. It is noted that the n -body IE is obtained by subtracting all the IEs up to $(n - 1)$ -body from the binding energy of n impurities. The other n -body IEs of the cluster with the larger interatomic distances, needed for the RSCE of total energies of the ordered Pd₃X in L1₂ structure, can be calculated in the same way. Thus, the n -body IEs are determined uniquely and successively from the low body to high body and independent on the X concentration.

According to our experiences, the 2-body IEs are very small beyond the 10-th nn pair^{3-5,10} and the n -body IEs become smaller and smaller with the increase in n and the total contribution from the 4-body IEs is very small compared with those from the 2-body and 3-body IEs.^{7,8,10} Thus, in the present paper, we examine the 2-body up to the 20th- nn and the 3-body IEs in two cubes in fcc and the 4-body IEs in one cube in fcc, as shown in Figs. 3 and 4, respectively. The numbers of the n -body ($n = 2 \sim 4$) IEs per atom are determined by considering the atomic arrangement in the ordered Pd₃X alloy at L1₂ structure, shown in Fig. 1.

3. Accuracy and Convergence of Real Space Cluster Expansion for Pd-Rich PdX (X = Ru, Rh) Alloys

We discuss the accuracy and convergence of the present RSCE for the internal energies in the free energies of the Pd-rich PdX (X = Ru, Rh) alloys.²⁻⁵ We show how the total energies for the ordered Pd₃X (X-concentration = 25%, Fig. 1) alloys in L1₂ structure, obtained by the screened-

Fig. 3 Atomic arrangements for X_3 clusters used in the calculations of the 3-body IEs in Pd-rich PdX alloys at $L1_2$ structure. There are three (eleven) kinds of clusters in one cubic cell (two cubic cells) in fcc structure. For example, the 224-cluster means that this cluster consists of two 2nd- nn and one 4th- nn pairs.

Fig. 4 Atomic arrangements for X_4 clusters used in the calculations for the 4-body IEs in Pd-Rich PdX alloys at $L1_2$ structure. There are six kinds of clusters in one cubic cell in fcc structure. For example, the 222244-cluster means that this cluster consists of four 2nd- nn and two 4th- nn pairs.

Table 1 Convergence of the RSCE for the total energies (in Ry) per unit cell (4 atoms) of (a) Pd_3Ru and (b) Pd_3Rh in $L1_2$ structure. The values in parentheses indicate the contributions to the total energy in eq. (1), by the 1st term ($4 \times E_{Pd}^{band}$), the 2nd term ($\Delta E_{X \text{ in Pd}}^{1-body}$), and so on.

	(a) Total energies (Ry) of Pd_3Ru	(b) Total energies (Ry) of Pd_3Rh
0-body	-40374.47003	-40374.47003
($4 \times E_{Pd}^{band}$)	(4×-10093.61751)	(4×-10093.61751)
up to 1-body	-39344.44485	-39851.10469
($\Delta E_{X \text{ in Pd}}^{1-body}$)	(1030.02518)	(523.36534)
up to 2-body	-39344.42363	-39851.10283
(ΔE_{int}^{2-body})	(0.02122)	(0.00186)
up to 3-body	-39344.42898	-39851.10346
(ΔE_{int}^{3-body})	(-0.00535)	(-0.00063)
up to 4-body	-39344.42809	-39851.10344
(ΔE_{int}^{4-body})	(0.00089)	(0.00001)
exact	-39344.43094	-39851.10411
error/cell	(0.00285)	(0.00067)
error/atom	0.00071	0.00017

FPKKR band calculations, are reproduced by the present RSCE approach from a dilute limit (X impurities in Pd). The calculated results for the ordered Pd_3X alloys in $L1_2$ structure, including up to the 4-body IEs among X impurities in Pd, are listed in Table 1 (in unit of Ry), together with the FPKKR band calculation results (bottom line, described as “exact”). In the present RSCE from a dilute limit, we included the 2-body IEs up to the 20th- nn pair and the 3-body and 4-body IEs of the clusters shown in Figs. 3 and 4. It is noted that the 1-body IE is the total energy change due to the insertion of a single X impurity, while the n -body ($n = 2 \sim 4$)

IEs are the total energy change due to the rearrangement of X_n impurities. Thus, the absolute value is very large for the 1-body IE, while very small for the n -body ($n = 2 \sim 4$) IEs, as listed in Table 1. We first show that the band calculation results can be reproduced very well (within the error of 4 mRy per unit cell atom ($=1$ mRy per atom)) by the RSCE including up to the 3-body IEs among X impurities in Pd.

For the Pd_3Rh alloy, we found that the RSCE up to the 1-body term already reproduces very well (by the error of -0.59 mRy per unit cell) the band calculation result since the contribution from the 2-4-body IEs is very small, as listed

Fig. 5 Calculated results for the distance dependence (1~20th- nn pairs) of X_2 (X = Ru, Rh) IEs in Pd. There are two inequivalent sites for the 9th-, 13th-, 16th-, 17th-, and 18th- nn pairs. The 9th-a and 9th-b nn sites are (1.5, 1.5, 0) and (2, 0.5, 0.5), in unit of the lattice parameter, respectively. The (n, l, m) nn pairs (any two of n, l, m are half-integer in unit of lattice parameter of fcc structure), such as 1st (0.5, 0.5, 0)-, 3rd (1, 0.5, 0.5)-, and 5th (1.5, 0.5, 0)- nn pairs, do not exist in the ordered Pd₃X alloy in L1₂, as seen in Fig. 1.

in Table 1. The contribution from the n -body IEs in eq. (1) becomes as small as 1.86, -0.63, and 0.01 mRy per unit cell, with the increase in n ($=2\sim4$). It is noted that the contribution from the 4-body IEs is almost zero. As results, the present RSCE including up to the 3-body IEs reproduce very accurately (by the error of 0.66 mRy per unit cell) the band calculation result for the Pd₃Rh alloy. The change of the RSCE error due to the inclusion of the contribution from the 4-body IEs is very small (from 0.66 to 0.67 mRy per unit cell).

For the Pd₃Ru alloy, the contribution from the 2 body IEs is as large as 21.22 mRy per unit cell, as listed in Table 1. However, the contribution from the n -body ($n = 2\sim4$) IEs in eq. (1) becomes as small as 21.22, -5.35, and 0.89 mRy per unit cell, with the increase in n ($=2\sim4$). The total contribution from the 4-body IEs is less than 1 mRy per unit cell ($=0.25$ mRy per atom). As results, the present RSCE including up to the 3-body IEs reproduces very accurately (by the error of 1.96 mRy per unit cell) the FPKKR band calculation results for the Pd₃Ru alloys in L1₂ structure. The change of the RSCE error due to the inclusion of the contribution from the 4-body IEs is not large (from 1.96 to 2.85 mRy per unit cell). It is noted that the RSCE error is less than 1 mRy per atom for both the ordered Pd₃X (X = Ru, Rh) alloys in L1₂ structure, as listed in Table 1.

We now discuss the details of the contributions from the 2-body to the 4-body IEs. Figure 5 shows the distance dependence of the 2-body IEs (in unit of mRy), up to the 20th- nn pairs for X_2 (X = Ru, Rh) in Pd. The calculated values for the 2-body IEs used in the RSCE are listed in Table 2. The positive value means repulsion, while the negative attraction. It is noted that the (n, l, m)- nn pairs (any two of n, l, m are half-integer) in unit of lattice parameter of fcc structure, such as 1st (0.5, 0.5, 0)-, 3rd (1, 0.5, 0.5)-, and 5th (1.5, 0.5, 0)- nn pairs, do not exist in the ordered Pd₃X alloy in L1₂ structure, as seen in Fig. 1.

First, the attraction of the 1st (0.5, 0.5, 0)- nn pair is dominant, compared with the distant neighbor pairs, for both the impurity systems in Pd. The 2-body IEs beyond the 10th-

Table 2 Calculated results for the 2-body IEs (in mRy) of (a) Ru₂ and (b) Rh₂ impurities in Pd, used in the RSCE of the total energies of ordered Pd₃X (X = Ru, Rh) alloys in L1₂ structure. The numbers of pairs per atom are also shown.

2-body	Number of pairs/atom	(a) 2-body IEs (mRy)	(b) 2-body IEs (mRy)
		Ru ₂ in Pd	Rh ₂ in Pd
100(2nd)	3	1.9641	0.2580
110(4th)	6	2.2095	0.1312
111(6th)	4	-0.1860	0.0038
200(8th)	3	-0.0353	0.0095
210(10th)	12	0.0965	0.0398
211(12th)	12	0.1142	-0.0092
220(15th)	6	-0.1054	-0.0095
221(17th-a)	12	0.0617	-0.0029
300(17th-b)	3	-0.0109	-0.0101
310(19th)	12	0.0268	0.0009

nn pair are considerably small for both the impurity systems. The total contribution of the 2-body IEs up to the 10th- nn is as large as 19.46 (2.08) mRy per unit cell for the total energy of Pd₃Ru (Pd₃Rh) alloy, while that from the 11th- nn to the 20th- nn is as small as 1.76 (-0.22) mRy per unit cell for the total energy of the Pd₃Ru (Pd₃Rh) alloy. As results, the total contribution from the 2-body IEs is 21.22 (1.86) mRy per unit cell for X = Ru (Rh), as listed in Table 1.

Second, the characteristic feature for the distant neighbor interaction depends very much on X, as seen in Fig. 5. The 1st- nn interaction is much stronger for X = Ru (-9.04 mRy) than for X = Rh (-3.52 mRy). We have already shown in Ref. 2 that the X-dependence (X = Zr-Ag) of the 1st- nn (X_2) IEs in 4d fcc metals (Pd and Ag) and 4d bcc metals (Nb and Mo) is understood by the Friedel's band filling mechanism for d-states, in which the dependence of the band width on X metal is taken into account. In addition, the 2-body interaction is long-range for X = Ru and considerably large repulsion for the 2nd (1, 0, 0)-, 4th (1, 1, 0)-, and 9th-a (1.5, 1.5, 0)- nn pairs, against the strong attraction of the 1st- nn pair.³⁾ On the other hand, the 2-body interaction is very short-range for X = Rh, although the interactions of the 2nd-, 4th- and 9th-a- nn pairs remains weakly repulsive.⁴⁾ These results explain the fundamental feature of the experimentally known phase diagrams:¹⁾ (1) the Pd-rich PdX (X = Ru, Rh) alloys are segregated at low temperature and disordered at high temperatures; (2) the solvus temperatures are much higher for X = Ru than for X = Rh.³⁻⁵⁾ The disordered states become stable at high temperatures by the configurational entropy. It is noted that the atomic structures of alloys at low temperatures are determined by the minimization of the total sum of the small n -body IEs ($n \geq 2$), as discussed in Sec. 2.2, and that the total sum of the 2-body IEs may be most important for the atomic structures of alloys. We have already shown that the relative stability among the different atomic structures of the ordered Al-rich AlX (X = Sc-V) alloys and the stability of the atomic structures of AlMn quasicrystal and Zr₇₀Cu₃₀ bulk metallic glass are clarified by using the 2-body IEs.^{9,20,21)} It is also noted that the local lattice distortion effect

Table 3 The same as Table 2 for the 3-body IEs (in mRy) of (a) Ru₃ and (b) Rh₃ impurities in Pd. The numbers of clusters (X₃) per atom are also shown.

3-body	Number of clusters (X ₃) /atom	(a) 3-body IEs (mRy)	(b) 3-body IEs (mRy)
		Ru ₃ in Pd	Rh ₃ in Pd
224	12	-0.1609	0.0269
246	24	0.0604	0.0231
444	8	0.2540	-0.0027
228	3	-0.2886	-0.0138
2410	24	-0.0862	-0.0034
2612	24	-0.0786	-0.0062
2810	24	-0.0649	-0.0135
21012	48	-0.0316	-0.0052
448	12	0.0395	-0.0205
4412	24	0.0966	-0.0034
4610	48	-0.0264	-0.0055
4812	24	-0.0075	0.0002
41010	24	0.0076	0.0011
668	12	-0.0446	-0.0065

always exists in the disordered A-rich AX alloy and becomes usually high for X impurities with a large size-misfit (compared with A atom):^{3,4,22–24} the distortion energy for the 2-body IEs in Pd is as large as ~ -2.6 mRy for X = Ru, and ~ -0.9 mRy for X = Rh and becomes an important factor to reproduce the observed solvus temperatures of Pd-rich PdX alloys, especially for X = Ru, as shown in Refs. 3 and 4.

Table 3 shows the calculated results for the 3-body IEs (in unit of mRy) of X₃ (X = Ru, Rh) impurity clusters in Pd. The atomic arrangements for the 3-body clusters (X₃) are shown in Fig. 3. For example, the 224-cluster means that this cluster consists of two 2nd (1, 0, 0)-nn and one 4th (1, 1, 0)-nn pairs. The calculated results are summarized: (1) the 3-body IEs are smaller by one order of magnitude than the 2nd-nn 2-body IEs (1.96 and 0.26 mRy for X = Ru, Rh), listed in Table 2, except for the three IEs (-0.16 , 0.25 , -0.29 mRy) of 224-, 444-, 228-clusters for X = Ru; (2) the 3-body IEs for X = Rh are much smaller than those for X = Ru, similarly to the 1st-nn 2-body IEs discussed above; (3) the 3-body IEs for the X₃ clusters in the two cubic cells are usually very smaller than those for the X₃ cluster in the one cubic cell, as being expected, although the 3-body IE of the 228-cluster in the two cubic cells is exceptionally large for X = Ru. It is noted however that the contribution of 228-cluster to the total energy of the Pd₃Ru alloy in L1₂ structure is not large because the number (3) of this cluster per atom is small, compared with those of the other X₃ clusters, as listed in Table 3. It is also noted that the total contribution from the

Table 4 The same as Table 2 for the 4-body IEs (in mRy) of (a) Ru₄ and (b) Rh₄ impurities in Pd. The numbers of clusters (X₄) per atom are also shown.

4-body	Number of clusters (X ₄) /atom	(a) 4-body IEs (mRy)	(b) 4-body IEs (mRy)
		Ru ₄ in Pd	Rh ₄ in Pd
222244	3	0.1622	0.0289
222444	8	0.0215	0.0028
222446	24	0.0147	0.0005
224446	24	0.0078	-0.0076
224466	6	-0.0794	0.0067
444444	2	0.0828	0.0179

3-body IEs becomes considerably small by their cancellation due to the rapid oscillating character (between positive and negative values) of the 3-body IEs (see Table 3), depending on the cluster-size. As results, the total contribution from the 3-body IEs is as small as -5.35 (-0.63) mRy per unit cell for X = Ru (Rh), as listed in Table 1. We have already shown that the sign and magnitude of the 3-body IEs are correlated with the shapes of the so-called Guinier-Preston (GP) zones of the age-hardening Al-rich AlX (X = Cu, Zn) alloys, such as the (001) disk in Al-rich AlCu alloys and the spherical shape in Al-rich AlZn alloys.^{6,8}

Table 4 shows the calculated results for the 4-body IEs (in unit of mRy). The corresponding atomic arrangements for the 4-body clusters are shown in Fig. 4. For example, the 222244-cluster means that this cluster includes the four 2nd (1, 0, 0)-nn pairs and two 4th (1, 1, 0)-nn pairs. The calculated values are considerably small except for the 4-body IEs (0.16 mRy) of the 222244-cluster for X = Ru. The contribution of this 4-body IE to the total energy of the Pd₃Ru alloy in L1₂ structure is not large because the number (3) of this cluster per atom is small, as listed in Table 4. We may also expect the cancellation due to the oscillating character (between positive and negative values) of the small 4-body IEs (see Table 4), depending on the cluster-size. For example, for X = Ru, the contribution from the 222244-cluster IEs ($0.1622 \times 3 = 0.4866$ mRy) is cancelled out by that from the 224466-cluster IEs ($-0.0794 \times 6 = -0.4776$ mRy). As results, the total contribution from the 4-body IEs is as small as 0.89 (0.01) mRy per unit cell for X = Ru (Rh), as listed in Table 1.

4. Summary and Future Problems

We studied the accuracy and convergence of the present RSCE from a dilute limit,^{6–10} which calculate the internal energies in the free energies of Pd-rich PdX alloys. In the present RSCE approach, the X atoms of minor element were treated as impurity atoms in Pd. All the interaction energies (IEs) up to the 4-body among X impurities in Pd were determined uniquely and successively from the low body to high body by the FPKKR calculations for the perfect and impurity systems (Pd-host, X_n in Pd, $n = 1 \sim 4$). We found that (1) the interaction is considerably short-range for Rh impurities in Pd, while long-range for Ru impurities in Pd; (2) the 2-body interaction is strongly attractive for the 1st-nn pair, compared with the weak repulsion at the 2nd-, 4th- and

9th-*a-nns*; (3) the contribution from the *n*-body ($n = 2\sim 4$) IEs becomes smaller and smaller with the increase in *n* and the total contribution from the 4-body IEs is less than 1 mRy per unit cell ($=0.25$ mRy per atom); (4) the FPKKR band calculation results for the ordered Pd₃X (X = Rh, Ru; X-concentration = 25%) alloys in L1₂ structure are reproduced very well (within the error of 4 mRy per unit cell ($=1$ mRy per atom)) by the present RSCE including the 2-body IEs up to the 20th *nn* pair (X₂) and the 3-body IEs up to the clusters (X₃) in the two cubic cells in fcc structure. We also found that the total contribution from the 3-body IEs becomes considerably small by their cancellation due to the rapid oscillating character (between positive and negative values) of the 3-body IEs, depending on the cluster-size.

We have already shown in Refs. 3–5 that the present RSCE approach can take into account the lattice distortion effect (always existing in the disordered states) for the IEs among X impurities in Pd, the temperature dependence of the FD distribution, and the thermal vibration effect by the Debye-Grüneisen model: the concentration dependence of the observed solvus temperatures of the Pd-rich PdX (X = Ru, Rh) alloys were reproduced very well by the free energy calculations based on the present RSCE for the internal energies and the cluster variation method (CVM) for the configurational entropy. It is noted that the lattice distortion effect on the 2-body IEs of X ($=$ Ru, Rh) impurities in Pd works attractively and becomes important to reproduce the observed solvus temperatures of the Pd-rich PdX (X = Ru, Rh) alloys.^{3,4)}

The present RSCE approach also allows us to study the stabilities of atomic structures in metallic alloys: the stabilities of atomic structures in Al-rich AlX (X = Sc-V, Mn) alloys including AlMn quasicrystals^{9,20)} are clarified by the distance dependence of the 2-body IEs, while the shapes of GP zones in Al-rich AlX alloys by the sign and magnitude of 3-body IEs of the 1st-*nn*.^{7,8)} Thus, the present RSCE approach may be very efficient in order to study the phase stability and phase equilibria of these metallic alloys.

We are now studying quantitatively the phase stability and phase equilibria of the age-hardenable Al-rich AlX (X = Mg, Cu, Zn) alloys¹⁾ by using the free energy calculations based on the present RSCE for the internal energy and the CVM for the configurational entropy. It is also very interesting to study the effect of another element addition on the kinetics of age-hardening behaviors of Al-rich multi-element alloys, such as Cu in Al-rich AlMgSi alloys.^{25,26)} We plan to develop the calculation program for Monte Carlo (MC) simulations^{6,27–29)} which may be useful as one of material design tools for the high quality of age-hardenable Al-rich multi-element alloys.²⁵⁾ For the mechanical properties of age-hardenable alloys, stability of precipitates is the central concern through nucleation, growth and coalescence processes. We believe Al-rich multi-element alloys offer a good example how thermodynamical calculations can reveal quantitative insight into the underlying age hardening behavior.

As another application of the present RSCE approach for the internal energy, it may be interesting to study the morphology in the nano-scale spinodal decomposition phase,^{30–32)} such as the magnetic network shown in Fig. 17 in Ref. 31, which may occur in the quenching and annealing

process in the dilute magnetic semiconductors such as (Ga,Mn)N and (Ga,Mn)As. At present we can take into account the lattice distortion effect for the chemical and magnetic IEs derived from a dilute limit,^{6,33,34)} which may be important for Mn impurities (at Ga sites) in the GaAs (or GaN) because the difference between the ionic radii (2.67 and 2.38 a.u.) of Ga and Mn atoms in fcc structure is considerably large.³⁵⁾ However, in order to study the morphology, we must further develop, for example, the calculation program for MC simulations with the chemical and magnetic IEs. Morphological features expected by MC simulation with such intriguing energetics will be reported in the future.

Acknowledgement

The authors are grateful for the financial support from the Ministry of the Education, Culture, Sports, Science and Technology (JSPS KAKENHI Grant Nos. 15K06422 and 16K06710). This study was partly supported by New Energy and Industrial Technology Development Organization of Japan (NEDO) Grant (P16010). One of the authors (T. Mohri) appreciates their support. This study was almost completed when T. Hoshino was at the Institute for Material Research, Tohoku University. C. Liu and T. Hoshino would like to express their sincere thanks to the crew of the Center for Computational Materials Science of the Institute for Materials Research, Tohoku University, for their continuous support of the SR16000 supercomputing facilities.

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