Full-Potential KKR Calculations for Point Defect Energies in Metals, based on the Generalized-Gradient Approximation: II. Impurity-Impurity Interaction Energies and Phase Diagrams

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We present systematic first-principles calculations for impurity-impurity interaction energies ($E_{\text{int}}$) of 4d elements in 4d bcc metals Nb and Mo, and 4d fcc metals Pd and Ag. The calculations are based on the generalized-gradient approximation in density-functional formalism, proposed by Perdew and Wang in 1991 (PW91-GGA), and apply the full-potential Korringa-Kohn-Rostoker (FPKKR) Green’s function method for point defects, developed by the Jülich group. First we examine the distance dependence, from 1st to 8th neighbors, of $E_{\text{int}}$ and show that for most cases, the 1st nearest-neighboring impurity-impurity interaction energies ($E_{\text{int}}^1$) are dominant. Second it is shown that most of the types of phase diagrams of binary alloys of impurity and host elements, such as segregation, solid solution, and order, known experimentally, may be very well discriminated by use of the sign and magnitude of $E_{\text{int}}^1$. Third we show that the temperature dependence of solid solubility limit of Rh in Pd, which is segregated at low temperatures and becomes disordered at high temperatures, are reproduced fairly well by the free-energy calculations based on the cluster variation method with the present results for $E_{\text{int}}$ (up to the 8th neighbor). It is also shown that the inclusion of the impurity-cluster interaction energies up to the four-body (a tetrahedron of 1st-nearest neighbors) being also determined by the present first principles calculations, leads to the complete agreement with the experimental result. We also show that the chemical trend for $E_{\text{int}}^1$ is understood by use of the Friedel’s band filling mechanism for d-states, if the dependence of the band width on element is taken into account in the model.

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1. Introduction

The interactions of point defects in solids are still the subject of numerous experimental studies because the knowledge of the interactions is indispensable for the understanding of many basic physical processes, such as diffusion, short-range order, segregation, ordering, etc. It is obvious that the diffusion properties of impurities in metals depend strongly on the defect energies, such as vacancy formation energies and vacancy-solute interaction energies.1,2 Most interesting, from technological point of view as well as fundamental point of view, are the effective-interatomic-cluster-interaction-energies (EICIEs) in alloys, which are essential for the understanding of phase diagrams.3,4

At present there are mainly two theoretical approaches to obtain the EICIEs, both of which are based on density functional theory.4,5 One is the so-called Connolly-Williams method,6,7 which assumes that the total energy can be written as a sum of the configurational independent EICIEs multiplied by the multi-site correlation functions. The other is the generalized perturbation method,8,9 which uses a perturbation treatment about the completely disordered state determined by the Korringa-Kohn-Rostoker coherent-potential-approximation.10 However, both methods have their characteristic drawbacks. The EICIEs cannot be determined uniquely in the first one,9,10 while the second one is problematic for alloys with charge transfer because it relies on the single-site approximation and takes into account only the band-energy changes for total-energy changes.11-13

In a preceding paper14 it was shown that the defect energies such as vacancy formation energies as well as the bulk properties such as equilibrium lattice parameters and bulk moduli are calculated very accurately by the full-potential (FP) Korringa-Kohn-Rostoker (KKR)15,16 Green’s function method for point defects,17-25 developed by the Jülich group, based on density functional theory (DFT) in the generalized-gradient approximation, proposed by Perdew and Wang in 1991 (PW91-GGA),24,25 The KKR Green’s function method for point defects allows us to determine the EICIEs uniquely and exactly by calculating the total-energy changes due to the rearrangement of atoms.15 We have already calculated the impurity-impurity interaction energies $E_{\text{int}}$, up to the 2nd neighbor, of 4d (3d) elements in fcc metals Pd and Ag (Ni and Cu) and showed that the fundamental features of phase diagrams of binary alloys of impurity and host elements, known experimentally,26,27 are discriminated very well by the sign and magnitude of the calculated results of $E_{\text{int}}$, although the local-spin-density approximation (LSDA)28-30 for DFT and the spherical approximation for potentials were used for solving the Kohn-Sham equations.31,32 We have also shown that the concentration dependence of EICIEs of low-concentrated alloys (≤10%) may be accurately calculated by using the present KKR-Green’s function method for the impurity cluster consisting of ~30 atoms, which includes the host atoms around impurities; the charge transfer is determined self-consistently in the impurity cluster and the alloy effect in the
impurity cluster is treated accurately by the direct configurational averaging.\textsuperscript{13,32}

The purpose of the present work is to calculate $E_{\text{int}}$ of 4$d$ elements in bcc metals Nb and Mo, and fcc metals Pd and Ag, by using the FPKKR method for point defect systems, combined with the PW91-GGA and study the fundamental features of binary alloys of impurity and host elements. In Section 2 we give a brief description of the calculational procedure. In Section 3 we show the calculated results for $E_{\text{int}}$ of 4$d$ elements in Nb, Mo, Pd, and Ag. The distance dependence of $E_{\text{int}}$, from 1st to 8th neighbors, are examined in detail. It is shown that the 1st nearest-neighboring impurity-impurity interaction energies ($E_{\text{int}}^1$) are dominant for most cases and that most of the types of phase diagrams of binary alloys, consisting of impurity and host elements, such as segregation, solid solution, and order, may be very well discriminated by use of the sign and magnitude of $E_{\text{int}}^1$. The chemical trend of $E_{\text{int}}^1$ is understood by use of the Friedel’s band-filling mechanism for $d$-states,\textsuperscript{33} if the dependence of the band width on element is taken into account. In Section 4 we show that the experimental result for temperature dependence of solid solubility limit of Rh impurities in Pd, which is segregated at low temperatures and becomes disordered at high temperatures, is reproduced almost completely by the free-energy calculations based on the cluster variation method\textsuperscript{34,35} with the pair (up to the 8th neighbor) to the four-body (a tetrahedron of 1st-nearest neighbors) interaction energies. Section 4 summarizes the main result and gives discussions on the possibilities of the present method to calculate the EICIEs of high-concentrated alloys.

2. Method of Calculations

The calculations for impurity-pair and impurity-cluster interaction energies are based on density-functional theory\textsuperscript{4,5} in the LSDA\textsuperscript{26-30} and the PW91-GGA.\textsuperscript{24,28} In order to solve the Kohn-Sham equations we use multiple scattering theory in the form of the KKR-Green’s function method for full potentials, developed by Dritter et al.\textsuperscript{11-25} This method is already discussed in a preceding paper.\textsuperscript{14}

The impurity-impurity interaction energies ($E_{\text{int}}^n$) between the $n$-th nearest-neighboring impurities in the host (H) is defined as the total-energy difference between two states, as shown in Fig. 1: (1) the initial state where both impurity (I) atoms are infinitely far away and (2) the final state where the two impurity atoms are located at $n$-th nearest-neighboring sites. Thus $E_{\text{int}}^n$ is given by

$$E_{\text{int}}^n = E_{\text{II}} - 2E_{\text{IH}} + E_{\text{HH}}$$  \hspace{1cm} (1)

where $E_{\text{XY}}$ (X, Y = I or H) represents the total energy of the system with the X-Y pair in the center of the impurity cluster. All the energies $E_{\text{XY}}$ are calculated by using the impurity cluster including host atoms up to 1st (2nd) neighbor around impurities, for fcc (bcc) metals, as discussed in Ref. 31); the potentials in the impurity cluster are re-determined self-consistently. In view of a chemical bond picture, eq. (1) means that as a result of impurity-pair formation, the impurity-impurity (II) and host-host (HH) bonds are created and two impurity-host (IH) bonds are broken.

Next we discuss the calculations for the impurity-cluster interaction energies in fcc metals, such as triangle 3-body ($E_{\text{int}}^\text{Triangle}$), and tetrahedron 4-body ($E_{\text{int}}^\text{Tetrahedron}$), which are defined by the total-energy differences as\textsuperscript{30}

$$E_{\text{int}}^\text{Triangle} = E_{\text{III}} - 3E_{\text{IIH}} + 3E_{\text{IHH}} - E_{\text{HHH}}$$  \hspace{1cm} (2)

$$E_{\text{int}}^\text{Tetrahedron} = E_{\text{IIII}} - 4E_{\text{IIHI}} + 6E_{\text{IHHH}} - 4E_{\text{IIHH}} + E_{\text{HHHH}}$$  \hspace{1cm} (3)

where $E_{\text{III}}, E_{\text{IIH}}, E_{\text{IH}}$, and $E_{\text{HH}}$ represent the total energies of the impurity clusters, consisting of 28 atoms, shown in Fig. 2. All the total energies are calculated by using the GGA-KKR-Green’s function method for point defects. The method takes the advantages of the Green’s function method to embed correctly the impurity cluster in the bulk, differently from an isolated cluster. The potentials inside the impurity cluster are calculated self-consistently, while the band-energy changes, induced by impurities, are determined by Lloyd’s formula summing up all the changes of the local

Fig. 1. The $n$-th nearest-neighboring impurity-impurity interaction energy is defined as the total-energy difference between two atomic configurations: (a) the initial state where both impurities are infinitely far away and (2) the final state where the two impurity atoms are located at $n$-th nearest-neighboring sites.

Fig. 2. Impurity clusters in fcc metals, used for the calculations of the impurity cluster interaction energies up to the four-body (a tetrahedron of 1st-nearest neighbors). See the text for details.
density of states over the infinite space.\textsuperscript{12} For impurities in bcc metals Nb and Mo, we carried out FPKKR calculations with the maximum angular momentum ($l_{\text{max}}$) = 4. On the other hand, for impurities in fcc metals Pd and Ag, for simplicity we used the spherical potential approximation (called the SHP)\textsuperscript{14,22} with $l_{\text{max}} = 3$, but the full charge density for the total energies. We believe that for $E_{\text{int}}$ the SHP results with $l_{\text{max}} = 3$ don’t differ very much from the FP results with $l_{\text{max}} = 4$. We have already found that for $E_{\text{int}}(n = 1, 2)$ in Fe the SHP calculations with $l_{\text{max}} = 3$ reproduce very well the results obtained by the FP calculations with $l_{\text{max}} = 4$, differently from vacancy formation energies in metals.\textsuperscript{14}

It is also noted that in the present calculations the PW91-GGA total-energy functional is evaluated with self-consistent LSDA spin-densities as input. This avoids the slowly converging self-consistency iterations for the PW91-GGA Kohn-Sham equations, and yields the same accuracy of the total energies as a fully self-consistent PW91-GGA treatment calculations, as shown in Refs. 22 and 37).

3. Calculated Results for Impurity-Impurity Interaction Energies

Figure 3 and Table 1 show the PW91-GGA results for the $E_{\text{int}}$ of 4d impurities in Nb, Mo, Pd, and Ag. The LSDA results are also listed in Table 1. Figure 4 shows the dependence from 1st to 8th neighbors. Positive energies mean repulsive interaction between the impurity atoms, while negative ones attractive interaction. First we find that the non-local effect beyond the LSDA, being included in the PW91-GGA density functional, is very small for $E_{\text{int}}$ (see Table 1), although these small differences become important for the quantitative discussions for solid solubility limit of impurities in metals, as shown in the next subsection 4.1. Second it is seen in Fig. 4 that $E_{\text{int}}$ are dominant for most cases, although the interactions are rather long-ranged for the systems including early 4d transition-metal elements.

Here we show that the types of experimental phase diagrams,\textsuperscript{26,27} shown in Table 2, are divided into the four groups, which are characterized by the sign and magnitude of $E_{\text{int}}$ as follows,\textsuperscript{31,38,39}

1. Ordered compound (O in Table 2) corresponds to $E_{\text{int}} \gg 0$ (strong repulsion between impurities) because the similar atoms repel each other and each impurity is surrounded with the atoms of the host element.

2. Homogeneous solid solution (H in Table 2) corresponds to $E_{\text{int}} \approx 0$ because the difference between individual characters of host and impurity elements is very small, leading to the random distribution of impurities in the host metals.

3. Segregation at low temperatures ($\leq 1000$ K) and disorder at high temperatures ($\geq 1000$ K) ($S^*$ in Table 2) corresponds to $E_{\text{int}} \approx -0.1$ (small attraction between impurities) because the impurities attract each other at low temperatures (segregation of impurities) and become

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Zr</th>
<th>Nb</th>
<th>Mo</th>
<th>Tc</th>
<th>Ru</th>
<th>Rh</th>
<th>Pd</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-host</td>
<td>0.01</td>
<td>—</td>
<td>0.06</td>
<td>0.22</td>
<td>0.37</td>
<td>0.36</td>
<td>0.16</td>
<td>—</td>
</tr>
<tr>
<td>(0.01)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-host</td>
<td>0.23</td>
<td>—</td>
<td>(0.08)</td>
<td>—</td>
<td>0.04</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(0.24)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd-host</td>
<td>1.45</td>
<td>1.06</td>
<td>0.40</td>
<td>—</td>
<td>—</td>
<td>0.26</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(1.45)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag-host</td>
<td>0.13</td>
<td>—</td>
<td>(0.53)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(0.05)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![PW91-GGA](image)

**Fig. 3** Interaction energies between two 4d impurities in Nb, Mo, Pd, and Ag, obtained by the PW91-GGA calculations. The 1st nearest-neighbor impurity-impurity interaction energies are shown. The FPKKR calculations were carried out for impurities in Nb and Mo, while the spherical potential approximation was used for 4d impurities in Pd and Ag. See the text for details.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Zr</th>
<th>Nb</th>
<th>Mo</th>
<th>Tc</th>
<th>Ru</th>
<th>Rh</th>
<th>Pd</th>
<th>Ag</th>
</tr>
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<tbody>
<tr>
<td>Nb-host</td>
<td>S*</td>
<td>—</td>
<td>H</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>?</td>
</tr>
<tr>
<td>Mo-host</td>
<td>O</td>
<td>H</td>
<td>—</td>
<td>H</td>
<td>S*</td>
<td>S*</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Pd-host</td>
<td>O</td>
<td>O</td>
<td>H</td>
<td>S*</td>
<td>S*</td>
<td>—</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>Ag-host</td>
<td>O</td>
<td>?</td>
<td>S*</td>
<td>S*</td>
<td>H</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

![Table 2](image)

**Table 2** Observed structures for binary alloys of host elements (Nb, Mo, Pd, Ag) and impurity elements (Zr ~ Ag). S, H, and O represent segregation, homogeneous solid solution (or high solid solubility of impurities), and ordered compounds, respectively. S* means segregaton at low temperatures, but disorder at high temperatures. ? means no experimental data available.
disordered at high temperatures, due to the increase of the configurational entropy effect.

(4) Segregation up to high temperatures corresponds to $E_{\text{int}} \ll -0.1\text{ eV}$ (strong attraction between impurities) because the attraction between impurities is stronger than the effective repulsion caused by the configurational entropy at high temperatures.

Now we compare the calculated results (Table 1) with the experimental results (Table 2) for phase diagrams of binary alloys,\cite{26,27} consisting of host and impurity elements. For Ag host, the large negative values of $E_{\text{int}}$ for AgMo and AgRu, seen in Table 1 and Fig. 3, correspond to segregation up to
high temperatures (group 4); there are no data for AgNb and AgTc. The homogeneous solid solution of AgPd is understood by the small positive value of $E_{1\text{int}}^1$ (group 2). For Pd host, the large positive values of $E_{1\text{int}}^1$ of PdZr, PdNb, and PdMo, seen in Table 1 and Fig. 3, correspond to ordered compound (group 1). The negative and small values of PdRu and PdRh correspond to the segregation at low temperatures and disorder at high temperatures because of the configurational entropy effect (group 3). For Mo host, the large negative values of $E_{1\text{int}}^1$ for MoRh, MoPd, and MoAg correspond to the segregation up to high temperatures (group 4). The large positive values of MoZr correspond to the ordered compound. For Nb host the large positive values of NbTc, NbRu, NbRh, and NbPd correspond to the ordered compounds (group 1).

The experimental result of PdTc (H in Table 2) contradicts with the structure predicted by the present calculation result (a small and negative value of $E_{1\text{int}}^1$ corresponds to $S^*$). However, it is noted that for a Tc pair $E_{1\text{int}}^n$ (n = 2 ~ 4) are positive and their magnitudes are larger than $E_{1\text{int}}$ (see Fig. 4(c)). Thus, the distant-neighbor interactions for the impurity pairs become important. In order to take into account the effect of $E_{1\text{int}}^n$ (n ≥ 2), we may consider the effective impurity-impurity interaction energy ($\bar{E}_{\text{int}}$) as follows,

$$\bar{E}_{\text{int}} = E_{1\text{int}}^1 + \frac{6}{12} E_{2\text{int}}^2 + \frac{24}{12} E_{3\text{int}}^3 + \frac{12}{12} E_{4\text{int}}^4 + \cdots$$

(4)

where the coefficient in the n-th term is the ratio of the coordination number of the n-th neighbor shell to that of the 1st neighbor shell. It is noted that the sum of $E_{1\text{int}}^n$, being distributed over the whole space, is kept in the renormalized impurity-impurity interaction energy $\bar{E}_{\text{int}}$. The usefulness of $\bar{E}_{\text{int}}$ is discussed in the next subsection 4.1. The $\bar{E}_{\text{int}}$ for impurities in Nb, Mo, Pd, and Ag are shown in Fig. 5. It is noted that $\bar{E}_{\text{int}}$ becomes a positive value for Tc in Pd, leading to the agreement with the experimental result at low Tc-concentrations (high solid solubility of Tc). We will show in the next subsection 4.1 that the interactions between the impurities on the distant neighbors become important for the temperature dependence of solid solubility limit of impurities in metals.

Lastly we discuss the chemical trend of $E_{1\text{int}}^1$. We consider the simple bond version for the Friedel’s band-filling model for d-state,\(^{30}\) which was suggested for understanding the parabolic behavior in the cohesion across 4d series. According to Friedel, if the density of d-states is assumed to be rectangular, the band energy per atom may be written as follows,

$$E_{\text{band}} = -\frac{W}{20} n_d (10 - n_d)$$

(5)

where $n_d$ is the number of valence d electrons and W is the band width of the d-state. Following this, the bond energy per one bond is written by

$$E_{\text{bond}} = -\frac{W}{20\zeta} n_d (10 - n_d) \times 2$$

(6)

where the number $\zeta$ is a coordination number (12 for fcc and 8 for bcc). The use of a factor 2 is understood by considering that the bond energy is contributed from two atoms. Now we discuss the three kinds of bond energies in eq. (1). The HH bond may be written as follows, by use of eq. (6)

$$E_{\text{bond}}^{\text{HH}} = -\frac{W_H}{10\zeta} n_d^H (10 - n_d^H)$$

(7)

where $n_d^H$ is the number of valence d electrons of the H-element metal (host), while $W_H$ the band width of d-states.

On the other hand we need the approximations for II and IH bond energies. The II bond energy may be approximated as follows,

$$E_{\text{bond}}^{\text{II}} = -\frac{W_I}{10\zeta} n_d^I (10 - n_d^I)$$

(8)

where $n_d^I$ is the number of valence d electrons of the I-element metal, while $W_I$ the band width of d-states. For the IH bond energy there seem to be many approximations. In the present work, for simplicity we use the following approximation,

$$E_{\text{bond}}^{\text{IH}} = -\frac{\sqrt{W_{1}} W_{\text{III}}}{10\zeta} \frac{(n_d^I + n_d^H)}{2} \left(10 - \frac{(n_d^I + n_d^H)}{2}\right)$$

(9)

where the band width $\sqrt{W_{1}} W_{\text{III}}$ is approximated by the geometrical average of the band widths of I-element and H-element metals, while the number of d electrons by the arithmetic average of d electrons. Presumably this bond energy corresponds to that of the binary alloys of I and H elements. The values of the d band width may be taken from the first-principles calculations,\(^{40}\) shown in Table 3. The calculated results by this simple bond model is written in Fig. 6. It is noted that the chemical trend for $E_{\text{int}}^1$ obtained by the present first-principles calculations, are fairly well reproduced by this simple model, although there are large differences, between the results obtained by the first-principles calculations and the model calculations, for Ru, Rh, Pd in Mo. If the band widths of impurity elements are same to that of the host element, we can get the parabolic behavior for $E_{\text{int}}^1$ shown in Fig. 6 (broken lines), being same to the parabolic behavior in the cohesion across 4d series; it is noted that the minimum of the parabolic behavior obtained by the simple bond model, is always zero and located at the host element. From these results, it may be concluded that the dependence of the band width on element is very important to understand the chemical trend for $E_{\text{int}}^1$.

4. Temperature Dependence of Solid Solubility Limit of Rh in Pd

We show first-principles calculations for the temperature dependence of solid solubility limit of impurities in metals, which is segregated at low temperatures and becomes disordered at high temperatures (S* in Table 2). As an example for S*,\(^{31,41}\) we treat Rh in Pd. In order to calculate the free energy of the disorder state, we use the cluster variation method (CVM) up to tetrahedron-octahedron (TO) approximation for the configurational entropy,\(^{34,35}\) and includes the many-body...
interaction energies up to the four-body (of a tetrahedron of 1st-nearest neighbors) in the internal energy. In subsection 4.1, we discuss the results obtained by use of the pair approximation for the internal energy, while in subsection 4.2 we discuss the importance of many-body interaction effect quantitatively.\(^{42}\)

### 4.1 Pair approximation for internal energy

As shown in Table 1, \(E_{\text{int}}^1\) for Rh in Pd is \(-0.05\) eV, which predicts correctly the structure of PdRh alloy at low temperatures \((S^*\text{ in Table 2})\). However, this small attraction between impurities is overcome, at high temperatures, by the configurational entropy which becomes large with temperature. Thus, we can easily expect that the disorder structure occurs at high temperatures. Before discussing the calculated results for the solvus temperatures (separating two phases of segregation and disorder), we explain the pair approximation used in the present work. The internal-energy change between the disordered and segregated phases of Rh in Pd may be written in the pair approximation as follows,

\[
\Delta E = -6E_{\text{int}}^1p_1 - 3E_{\text{int}}^2p_2 - 12E_{\text{int}}^3p_3 - 6E_{\text{int}}^4p_4 - \cdots
\]

(10)

where the coefficients in the \(n\)-th term is half of the coordination number, while \(p_n\) is a \(n\)-th nearest-neighboring pair probability of Rh–Pd. In order to treat the configurational entropy, however, we use the tetrahedron (T) approximation of the CVM, shown by CVMT in Fig. 7, which can treat only \(E_{\text{int}}^1\) exactly: the terms beyond the first one is neglected in the T approximation of the CVM. In order to take into account the effect of \(E_{\text{int}}^n(n \geq 2)\), we use \(\tilde{E}_{\text{int}}\), defined by eq. (4), in-
Fig. 7 PW91-GGA results for the concentration dependence of the solvus temperatures of Rh in Pd, together with the experimental result. The pair approximation is used for the internal energy. See the text for details.

Fig. 8 PW91-GGA results for the concentration dependence of the solvus temperatures of Rh in Pd, together with the experimental results. The many-body interaction energies up to a tetrahedron of 1st-nearest neighbors are included in the calculations. See the text for details.

stead of $E^1_{\text{int}}$. This approximation seems to be allowed for low concentration of impurities and at high temperatures where the impurity atoms are distributed at random and the probability of Rh–Pd pair does not change with the distance. Assuming $p_1 = p_2 = p_3, \ldots$, eq. (10) is written as follows,

$$\Delta E = -6E^1_{\text{int}} p_1,$$

(11)

The distant-neighbor interaction energies are accurately taken into account by using this approximation formula (eq. (11)) for the internal-energy change between the disordered and segregated phases, as discussed in the end of this subsection.

Now we discuss the calculated results for the concentration dependence of the solvus temperatures of Rh in Pd. Figure 7 shows the calculated results together with the experimental result. The CVMT1 calculations, which include only $E^1_{\text{int}}$ ($= -0.05$ eV), overestimate the solvus temperatures, compared with the experimental result. This means that the attraction between impurities (segregation effect) is overestimated. This overestimation is reduced by the CVMT2 calculations (see Fig. 7), which include the $E^n_{\text{int}}$ up to $n = 2$, because the positive value of $E^2_{\text{int}}$ ($= 0.01$ eV), shown in Fig. 4(c), weakens the segregation effect due to $E^1_{\text{int}}$ ($= -0.05$ eV). The inclusion of $E^n_{\text{int}}$ ($n \geq 3$) doesn’t change the CVMT2 result because $E^n_{\text{int}}$ ($n \geq 3$) is very small, as seen in Fig. 4(c); for example, the CVMT8 result, shown in Fig. 8, including $E^n_{\text{int}}$ up to $n = 8$, doesn’t differ from the CVMT2 result. However, the CVMT2 result still overestimates the solvus temperatures, compared with the experimental results. It will be shown in the next subsection 4.2 that the remaining discrepancies between theory and experiment may be almost completely corrected by including the many-body interaction energies of impurities (up to the four-body).

In order to examine the validity of the two approximations (CVMT and eq. (11)) used in the present calculations, we carried out the more accurate calculations, based on the TO approximation of the CVM, called the CVMT0. As seen in Fig. 7, the CVMT01 result, which includes only $E^1_{\text{int}}$ in the internal energy and the TO probabilities for the configurational entropy, is in complete agreement with the CVMT1. This means that the T approximation for the configurational entropy is enough for low concentrated alloys, at least, less than 10%. Next we examine the validity of eq. (11), where $E^n_{\text{int}}$ ($n \geq 2$) are included in $E_{\text{int}}$. As seen in Fig. 7, the CVMT02 result, which is obtained by treating exactly $E^1_{\text{int}}$ and $E^2_{\text{int}}$ in the internal energy and the TO probabilities for the configurational entropy, agrees very well with the CVMT2 result. This demonstrates the validity of eq. (11). However, it was also shown by Schweik's 49) that this approximation becomes wrong towards high concentrated alloys.

4.2 Many-body interaction effect

Figure 8 shows the calculated results, including the many-body interaction effect, for the temperature dependence of solid solubility limit of Rh in Pd together with the experimental result. The effect of the three-body (a triangle of 1st-nearest neighbors) interaction, defined in Section 2 (see Fig. 2), makes smaller the discrepancy between the CVMT2 and experimental results because of the positive values ($E_{\text{Triangle}} = 0.005$ eV): the positive value of $E_{\text{Triangle}}$ weakens the segregation effect of impurities and reduces the overestimation for the solvus temperatures. It is also noted that the four-body (a tetrahedron of 1st-nearest neighbors) interaction energy is also positive ($E_{\text{Tetrahedron}} = 0.008$ eV). The inclusion of $E_{\text{Tetrahedron}}$ leads to the complete agreement between theory and experiment. It is also noted that the PW91-GGA calculations improve the LSDA results, as shown in Fig. 9.

5. Summary and Future Problem

We have examined the distance dependence of the impurity-impurity interaction energies ($E_{\text{int}}$) in bcc metals Nb and Mo, and fcc metals Pd and Ag. For most cases, the 1st nearest-neighboring impurity-impurity interaction energies ($E^1_{\text{int}}$) are dominant, although the interactions are long-ranged for the systems including early 4d transition-metal elements. It is shown that most of the types of phase diagrams
of binary alloys, consisting of host and impurity elements, known experimentally, are understood by the sign and magnitude of $E_{\text{int}}$. The experimental results for temperature dependence of solid solubility limit of Rh in Pd is also reproduced very well by the free-energy calculations based on the CVM with the pair (up to the 8th neighbor) and many-body (up to a tetrahedron of 1st-nearest neighbor) interaction energies, all of which are determined by the present first-principles calculations. It is noted that the PW91-GGA calculations improve the LSDA results for the solvus temperatures of Rh in Pd, as have been discussed for bulk properties and vacancy formation energies in fcc and bcc metals (Li−Au). 14 We have also shown that the chemical trend of calculated results for $E_{\text{int}}$ is understood by the Frdél’s band-filling mechanism of d-states, 13 if the dependence of band width on element is taken into account in the model.

At the end we would like to state that the present FPKKR-Green’s function method for point defects is useful for the calculations of the accurate effective-iteratomic-cluster-interaction-energies (EICIEs) in transition-metal alloys. We already showed that for low-concentrated alloys (≤ 10%) the EICIEs may be accurately calculated by use of the present KKR-Green’s function method for the impurity cluster consisting of ∼ 30 atoms, which includes the host atoms around impurities; the charge transfer is determined self-consistently in the impurity cluster and the alloy effect in the impurity cluster is taken into account by the direct configurational averaging method. 13 Using the impurity cluster of the same size (∼ 30 atoms), we already succeeded in reproducing the experimental results of the concentration dependence of vacancy formation energies in low-concentrated Cu-based transition-metal alloys. 14 If the impurity cluster with a number of atoms larger than ∼ 100 is treated by the present method, we can presumably obtain the accurate EICIEs even for high-concentrated alloys. The real-space screened (tight-binding) KKR-Green’s function method (order-N method in density-functional electronic-structure calculations) 45−47 was already developed by Zeller and can treat the supercell with a number of atoms larger than ∼ 500 by exploiting the freedom in the choice of the reference system related to the impurity system through the Dyson equations. This method may also become useful for the study of EICIEs of high-concentrated alloys because we can use the short-ranged structure constants (for example, being zero beyond the 1st-neighboring sites) to solve the Dyson equations of the system with the large impurity cluster; it is noted that the long-ranged structure constants for the perfect crystal may be easily transformed to the short-ranged structure constants by introducing the appropriate repulsive potential in the large impurity cluster, as the free-space structure constants are transformed into the short-ranged structure constants, as shown in Ref. 45.

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