Transactions of the Materials Research Society of Japan 30[3] 873-876 (2005)

Full-potential KKR calculations for point-defect interaction energies in Al, based on the generalized-gradient approximation: two-body and many-body interactions

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We present ab-initio results for the interaction energies of impurities (Cu, Zn, Mg) and vacancies in Al, which are required for Monte-Carlo computer simulations for the study of the dynamical process in the initial stage of the formation of the Guinier Preston zones of AlZn and Mg-added AlCu alloys. The calculations are based on the generalized-gradient approximation in the density-functional theory and employ the all-electron full-potential Korringa-Kohn-Rostoker Green's function method for point defects. We show the calculated results for vacancies and impurities (Cu, Zn, Mg) in Al: (1) the two-body interactions are long-ranged; (2) the many-body interactions beyond the three-body, being among the 1st-neighbors, are very small. It is also shown that the agglomerates of defects considered here are reproduced very well by the cluster expansion up to the three-body terms.
Key words: GGA, FPKKR, point-defect interactions, cluster-expansion, many-body interactions

1. INTRODUCTION

Alloys of Al with low-concentrated solute atoms, such as AlX (X=Cu, Zn) have for decades received considerably attention in the material-science community because of their superior technological properties, such as light weight and high strength. It was recently shown by many experiments on precipitation strengthening that the mechanical strength of the above-mentioned Al-based alloys changes very much by the insertion of the other elements.[1, 2] For example, Sato et al showed that the mechanical strength of the AlCu alloy increase by the insertion of Mg.[1] Using the Monte-Carlo computer simulations based on the simple pair interaction model with parameters fitted to the experimental phase diagrams, they also studied the role of the additional microalloying elements at the initial stage of the phase decomposition and discussed an interesting physical picture: the Mg/Cu/Vacancy clusters formed in the initial stage act as effective nucleation sites for Guinier Preston (GP) zones and resultantly accelate the formation of fine and high-density clusters. In order to examine this physical picture and discuss the experimental results quantitatively, we need an accurate interaction-parameter model, which include explicitly the many-body interactions beyond the two-body interactions.[3]

The purpose of our project is to elucidate the micromechanism of binding energies (BEs) of large agglomerates of impurities (Cu, Zn, Mg) and vacancies in Al (fcc) and to construct the interaction-parameter model, using the first-principles calculations. We consider the minority elements of alloys as imputities and divide the BEs of agglomerates into the chemical interaction energies (CIEs) and the lattice distortion energies (LDEs): the CIE is defined as a total-energy change due to the atomic rearrangement on the perfect lattice sites.[3] For the CIE we use the cluster expansion, as discussed in Sec.2. In the present paper we discuss the characteristic features of two-body and many-body interactions in the cluster expansion for the CIEs of the present alloy systems. We show the long-rangeness of two-body interactions and the rapid decreasing order-depenedence of many-body interactions. The calculated results for 1st-neighbor interactions of J-I and I-I pairs in Al (J=vacancy, Cu, Zn; I= Sc-Ge(3d and 4sp), Y-Sn(4d and 5sp)) with the physical mechanisms of their interactions were already reported in Ref.4. The LDEs of impurities and vacancies in Al will be discussed in a separate paper.[5]

2. CALCULATION METHOD AND CLUSTER EXPANSION FOR CHEMICAL INTERACTION ENERGIES (CIEs)

The calculations for CIEs of impurity pairs and impurity clusters are based on the generalized-gradient approximation in density-functional theory. 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 potential. The advantage of the present Green's function method is that the total energies of impurity clusters are calculated accurately without supercell or cluster approximations.[6] In the present calculations, the potentials of impurities and their 1st-nearest neighboring host atoms are calculated self-consistently, while the band-energy changes due to the perturbed wavefunctions over the infinite space are correctly evaluated by using the Lloyd's formula.[7] It is also noted that the present calculations treat accurately the charge transfer effect among impurities of large work-function differences. For the details and accuracy of the present calculations, we refer to Ref.6.

Here we discuss the present approach for the cluster expansion, being different from Connoly-Williams approach:[8, 9] both of which calculate the many-body interaction energies (MBIEs) in the cluster expansion. The present approach, while restricted to the dilute limit,

considers only atomic configurations, the energy differences of which define uniquely the many-body interactions. The MBIEs are determined successively from low-order to high-order interactions,[3] as shown below. The concentration depenendence of MBIEs may also be taken into account by the present calculations combined with the direct configuration averaging.[10]

We give the definition of the MBIEs and show how to determine them. For example, we consider the MBIEs up to the 4th order, of a 1st-nearest-neigboring tetrahedron impurity cluster of same kind. The CIE (B_{4I}^{CIE}) of the tetrahedron impurity cluster, shown in Fig.1(e), can be obtained by use of MBIEs as follows,

$$B_{4I}^{CIE} = 6E_{int}^{Pair} + 4E_{int}^{Triangle} + E_{int}^{Tetrahedron} \quad (1)$$

where E_{int}^{Pair}, $E_{int}^{Triangle}$, and $E_{int}^{Tetrahedron}$ are the two-body, three-body, and four-body interaction energies, determined by Eqs.(2), (3), (4) (see Fig.1). Eq.(1) shows that the CIE of the tetrahedron impurity cluster consists of 6 two-body, 4 triangle three-body, and 1 four-body interaction energies. Each values of the MBIEs are defined by the following equations,

$$E_{int}^{Pair} = E_{IIHH} - 2E_{IHHH} + E_{HHHH} = B_{2I}^{CIE} \quad (2)$$

$$\begin{aligned} E_{int}^{Triangle} &= E_{IIIH} - 3E_{IIHH} + 3E_{IHHH} - E_{HHHH} \\ &= E_{IIIH} - 3E_{int}^{Pair} - 3E_{IHHH} + 2E_{HHHH} \\ &= B_{3I}^{CIE} - 3E_{int}^{Pair} \end{aligned} \quad (3)$$

$$\begin{aligned} E_{int}^{Tetrahedron} &= E_{IIII} - 4E_{IIIH} + 6E_{IIHH} - 4E_{IHHH} + E_{HHHH} \\ &= E_{IIII} - 4E_{int}^{Triangle} - 6E_{int}^{Pair} - 4E_{IHHH} + 3E_{HHHH} \\ &= B_{4I}^{CIE} - 4E_{int}^{Triangle} - 6E_{int}^{Pair} \end{aligned} \quad (4)$$

where $E_{HHHH}, E_{IHHH}, E_{IIHH}, E_{IIIH}, E_{IIII}$ are, respectively, the total energies of the five tetrahedron clusters consisting of impurity and host atoms (see Fig.1), including the total-energy change of the host atoms in the vicinity of the tetrahedron cluster. Eq. (2) shows that E_{int}^{Pair} is a total-energy difference between two states: (1) the initial state where both impurities (I) are infinitely far away and (2) the final state where both impurities are located at the 1st-nearest neigboring sites.[11] It is noted that the n-body interaction energy is obtained by subtracting the MBIEs up to (n-1)-th order from B_{nI}^{CIE}, as shown in Eqs. (3) and (4). Thus, the MBIEs are determined uniquely and successively from low-order to high-order. This point is very different from the Connolly-Williams approach where the MBIEs are determined by fitting to the results of the supercell calculatiuons with many different atomic configurations in the unit cell.[8] It is noted that the MBIEs of Connolly-Williams depends on the choice of the atomic configurations used in the supercell calculations. It is also noted that it may be impossible to reproduce accurately the long-rangeness of two-body interactions by the supercell calculations, as discussed in Ref.3.

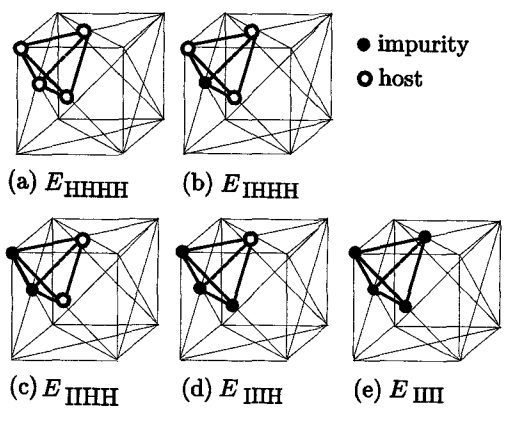


Fig.1 Impurity clusters in fcc metals, used for the calculations of the many-body interactions up to the four-body (a tetrahedron of 1st-neighbors). See text for the details.

3. CALCULATED RESULTS

We present the interaction energies for AlCu (with the insertion of Mg) and AlZn alloys and discuss the characteristic features of those interactions. The elements (Mg, Cu, Zn) of low-concentration are considered as impurities. Since there exist quenched-in excess vacancies (Vacs) in alloys, we practically calculate the CIEs for allgomerates of vacancies and impurities (Cu, Zn, Mg) in Al(fcc). The results for the other impurities in Al-based alloys will be published elsewhere.[12]

3.1 Two-body (pair) interactions

Figure 2 shows the distance depenedence of two-body interaction energies of Cu-Cu, Mg-Mg, Cu-Mg, Cu-Vac, Mg-Vac, Vac-Vac, Zn-Zn, and Zn-Vac,

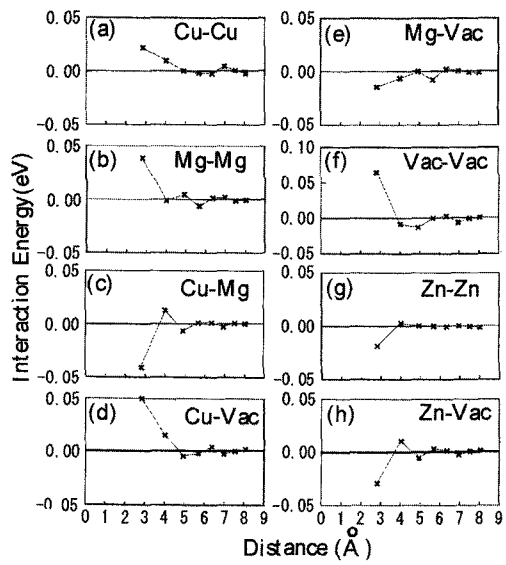


Fig.2 Distance dependence of interaction energies(in eV) of

different pairs in Al. See text for the details.

up to 8th-neighbors: the coordinations of 1~8 neighbors are (1/2,1/2,0), (1,0,0), (1,1/2,1/2), (1,1,0), (1/2,3/2,0), (1,1,1), (1,3/2,1/2), (2,0,0). It is obvious that the interactions are long-ranged except Zn-Zn, although the 1st-neighbor interactions are dominant. It is also noted that the interactions of the present defect pairs are fairy weak compared with the results of the defect pairs including transition-metal impurities, shown in Ref.4. Thus, the elucidation of the physical mechanisms of these weak interactions may be very difficult.

However, we already succeeded in elucidating the micromechanism of repulsion of 1st-neighbor divacancy in Al (Fig.2(f)): we confirmed the recent calculated results of Carling *et al* [13] and showed that the repulsion of 1st-neighbor Vac-Vac interaction, being different from the commonlyaccepted interpretation of the experimental data,[3] is due to the strong screening effect of Al-host. This result may demonstrate that the first-principles calculations play an important role to understand correctly the experimental results of defect interactions. In Sec.4 we discuss qualitatively the role of the additional microalloying element Mg in AlCu, by using the present results for pair interactions.

3.2 Many-body interactions

Figure 3 shows the calculated results of MBIEs up to 6-order. We use the expression $E_{int}^{nI}(n_p)$ for n-body interaction energies, which classifies the different shapes for the same number n of I (=Cu, Zn, Mg, Vac) by the number of 1st-nearest neighboring pairs n_p. We consider the pair (n=2, n_p=1), triangle (n=3, n_p=3), square (n=4,

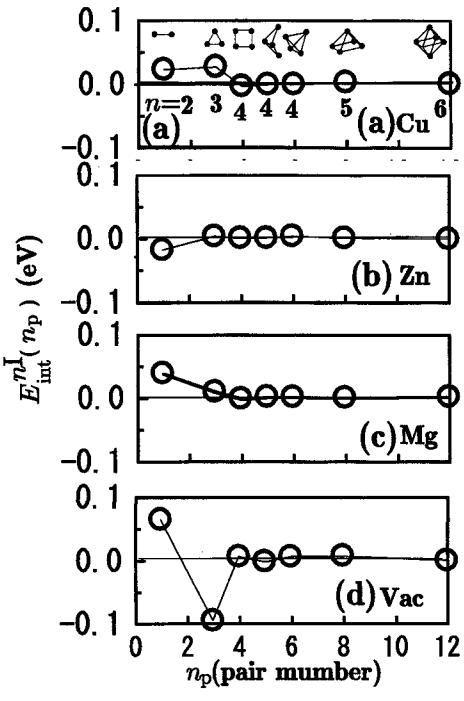
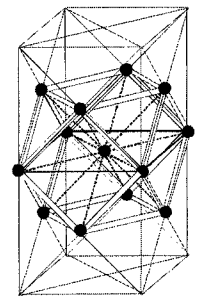


Fig.3 Many-body interaction energies ($E_{int}^{nI}(n_p)$), as a function of a number n of I (I= Cu, Zn, Mg, Vac) and a number of pairs n_p. See text for the details.

n_p=4), bent rhombus (n=4 and n_p=5), tetrahedron (n=4 and n_p=6), pyramid (n=5 and n_p=8) and octahedron (n=6 and n_p=12), of 1st-neighbors, as shown in Fig.3(a). It is noted that the MBIEs beyond the 3-body term are very small for the allgomerates of the vacancies and impurities (Cu, Zn, Mg). For the agglomerates of mixture of different impurity elements, we obtained almost the same results.[12] It is noted that the three-body interactions of 1st-nearest neighbors are very large. We show in Sec.4 that the magnitude and sign of the three-body interaction energies are correlated with the shapes of segregation phases. It is also noted that the weak three-body interaction (0.006, 0.002, 0.0004, -0.002 eV for Vac, Cu, Zn, Mg) of a triangle with one 2nd-neighbor may becomes quantitatively important for large cubic agglomerates because the number of them in the cluster expansion increases rapidly with the size of agglomerates, as shown in the following section.

3.3 Cluster expansion for large agglomeraters of vacancies and impurities (Cu, Zn, Mg)

We discuss the convergence of the cluster expansion or the CIEs (B_{13I}^{CIE}) of the larger allgomerates of 13I (I=Cu, Zn, Mg, Vac), consisting of a center and its 12 neighbors, shown in Fig.4. The cluster expansion up to four-body terms is also shown in Fig.4. It includes



$$B_{13I}^{CIE} \sim 36E_{int}^{2\text{-}(1)} + 12E_{int}^{2\text{-}(2)} + 24E_{int}^{2\text{-}(3)} + 6E_{int}^{2\text{-}(4)} + 32E_{int}^{3\text{-}(1)} + 36E_{int}^{3\text{-}(2)} + 6E_{int}^{4\text{-}(1)} + 24E_{int}^{4\text{-}(2)} + 8E_{int}^{4\text{-}(3)}$$

Fig.4 Agglomerate of 13 bodies, consisting of a central and its 12 1st-neighbors and the cluster expansion of its chemical interaction energy up to the four-body terms. See text for the details.

Table I. Calculated results (in eV) for chemical interaction energies of 13 impurities (Cu, Zn, Mg) and vacancies. The cluster expansion reslts including up to the four-body interaction energies are given together with the exact GGA-FPKKR results. See text for the details.

Up to n-body	n=2	n=3	n=4	Exact
Cu_{13}	1.04	1.96	1.92	1.94
Zn_{13}	-0.63	-0.53	-0.50	-0.49
Mg_{13}	1.43	1.73	1.65	1.60
Vac_{13}	1.90	-0.95	-0.92	-0.95

the pair interactions up to 4th-neighbors ($E_{int}^{2\text{-}(i)}$,i=1~4), MBIEs shown in Fig.3(a) ($E_{int}^{3\text{-}(1)} = E_{int}^{3l}(3)$, $E_{int}^{4\text{-}(1)} = E_{int}^{4l}(4)$, $E_{int}^{4\text{-}(2)} = E_{int}^{4l}(5)$, $E_{int}^{4\text{-}(3)} = E_{int}^{4l}(6)$), and also a three-body interaction energy ($E_{int}^{3\text{-}(2)}$) of triangle with one 2nd-neighbor, discussed in the preceding section. It is noted that the number of $E_{int}^{3\text{-}(2)}$ is large (32) in this 13-body agglomerates, while the number of its cluster is 4 in the pyramid (agglomerates of 5 bodies) and 6 in the octahedron (an agglomerate of 6 body), as shown in Fig.3(a). Thus, the three-body interaction of a triangle with one 2nd-neighbor becomes important for the large cubic agglomerates. Table I shows the convergence of the cluster expansion. It is noted that the inclusion of the three-body terms is important to obtain the nice convergence (0.004 eV per vacancy and impurity atom). These results are compared with the average error (>0.1eV) of the glue models which are very often used to provide interatomic potentials for computer simulations.[14] The comparison of the present cluster expansion with the glue model is discussed in Ref.3. The cluster expansion approach allows us to construct accurately the interaction-parameter model for the computer simulations for the study of the dynamic process in the coherent phases.

4. DISCUSSIONS

We presented the accurate data of the two-body and many-body interaction energies in the cluster expansion for CIEs of large agglomerates of vacancies and impurities(Cu, Zn, Mg) in AlCu (with Mg) and AlZn alloys. The calculations are based on the generalized-gradient approximation in the density-functional formalism and the FPKKR method, which treats the correct embedding of the allgomerates of point defects in an otherwise perfect Al crystal. We showed: (1) the longrangeness of two-body interactions; (2) the many-body interactions beyond the three-body are very small; (3) the CIEs of 13 vacancies and impurities, consisting of a center and its 12 neighbors, are reproduced within the error of 0.004 eV per vacancy and impurity atom. The lattice distortion effect, which is important for the allgomerates of solute atoms of large atomic-radius misfit, compared with the host atoms, is discussed in a separate paper.[5]

At the end we show that the present results are useful to explain qualitatively the experimental results for the formation of the GP zones of Al-Cu (with Mg) and Al-Zn alloys. First we dsicuss the role of the microalloying element Mg at the initial stage of the formation of GP zones of AlCu. As shown in Fig.2, the pair-interactions of Mg-Vac and Mg-Cu are attractive, although the Cu-Vac interaction is repulsive. Thus the role of Mg is very important to make the stable Vac/Mg/Cu complexes. This result may give an justification for the physical picture suggested by Sato's group.[1] 「At the initial stage of age hardening of AlCu, Mg traps a vacancy and retards the diffusion of Cu. After the formation of Mg-Vac, Mg-Vac traps a Cu and forms Vac/Mg/Cu complexs: the stabe Vac/Mg/Cu complexes accelerate the formation of fine and high-density clusters, which increase the strengthening due to the age hardening」. It is also noted that the existence of the Vac/Mg/Cu complexes at the initial stage for the formation of the GP zones of AlCu is consistent with the experimental results obtained by coincidence Doppler broadening of positron annihilation radiation and positron lifetime spectroscopy.[15] In order to study the temperature effect quantitatively, we are trying to carry out the Monte-Carlo simulations with the present interaction-parameter model. It is just our final goal of the present project.

Second we discuss the sign and magnitude of three-body interactions of 1st-neighbors are correlated to the shapes of the GP zones, just as the sign and magnitusde of the two-body interaction energies of 1st –neighbors are connected with the different types of phase diagrams of binary alloys, such as segregation, solid solution, and ordering.[11] For example, the three-body interaction energies of Cu impurities and Zn impurities are, respectively, positive (0.03 eV, repulsion) and zero, which correspond to the (001) disc and the spherical shape of GP zones of AlCu and AlZn, respectively: it is noted that there is no triangle clusters of 1st-neighbors in the (001) layer of fcc structure. The details including the discussion for the shapes of the GP zones of the other Al-based alloys will be given elsewhere.[12]

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(Received December 23, 2004; Accepted April 28, 2005)