

Full-potential KKR calculations for point defects in Al, based on the generalized-gradient approximation: chemical interaction and lattice distortion

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We give systematic *ab-initio* calculations for the solution energies of single impurities (Na-Si, Cu, Zn, Zr-Ag) in Al. 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. In order to study the lattice distortion effect, we performed the calculations with and without the lattice distortion. The chemical interaction energies, being the parts without the distortion effect, agree very well with the available experimental data for the solution energies of Mg and Si, because the distortion effect is very small for these impurities. It is shown that the lattice distortion effect of single impurities can be easily understood in terms of the size of impurities compared with the host atom. As an example of defect pairs, we also study the distortion effect for the formation of a 1st-nearest-neighboring divacancy in Al: the distortion effect is repulsive as well as the chemical interaction [Phys. Rev. B70, 094118(2004)], although it is very weak due to the cancellation of both the distortion effects around the monovacancy and divacancy.

Key words: GGA, FPKKR, point-defect interactions, cluster-expansion, lattice distortion

1. INTRODUCTION

The study of the initial stage of the temperature-dependent dynamical process of the formation of Guinier-Preston (GP) zones of low-concentrated Al-based alloys such as $Al_{1-c}X_c$ ($X=Cu, Zn$; $c < 0.05$) is strongly requested for the design of new materials of light and high strength.¹ At present the Monte-Carlo simulations are possible for such problems. However, almost all of them use the simple pair-interaction model with the parameters fitted to the experimental data of the phase diagrams.² Since the calculated results depend on the accuracy of the interaction-parameter model, the construction of the interaction-parameter model is essential. Recently it has been shown that the first-principles calculations, based on the generalized-gradient approximation (GGA) in density-functional theory, reproduce almost completely the experimental data for defect properties as well as the bulk properties of materials and elucidate the micromechanism of defect properties.³⁻⁷ Thus, it may be expected that the first-principles calculations replace experiments as a major source of information for many properties of materials. It is noted that the first-principles calculations can provide the input data including the total energies of metastable and hypothetical structures, being not measured experimentally, which are important to construct the accurate interaction-parameter model. Among the different band-calculation methods, the all-electron full-potential Korringa-Kohn-Rostoker (FPKKR) Green's function method used in the present work is most useful.^{6,8,9} The advantage of the Green's function

method is that due to 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. Now it is possible to calculate the energetics of point defects in complex periodic systems because the host Green's function of complex periodic systems with a large number of atoms per unit cell can be calculated by the screened FPKKR (SFPKKR) method.^{10,11} We plan to construct the accurate interaction-parameter model for the above-mentioned alloys, using the GGA-FPKKR calculations. Practically we calculate the binding energies (BEs) of vacancies and impurities in Al, corresponding to the internal energies of low-concentrated alloys. In the present work, we divide the BE into the chemical interaction energy (CIE) and the lattice distortion energy (LDE): the CIE is defined as a total-energy change due to the atomic rearrangement on the ideal lattice. For the CIE we use the cluster expansion. In a separate paper,¹² we show that the CIE of agglomerates of vacancies and impurities (Cu, Zn, Mg) are reproduced very well by use of the many-body interaction energies up to the four-body terms.⁴ For the LDE we plan to construct the size- and shape-dependent model for agglomerates of defects: we must perform systematic *ab-initio* calculations for the LDEs for different atomic arrangement of vacancies and impurities. For example, in order to construct the interaction-parameter model for the computer simulations, which are required for the dynamical process of GP zones of AlCu, we need, at least, the calculations for single, pair, and square of Cu impurities

in (001) plane in Al. Although the study for the lattice distortion effect around point defects is very difficult because of the requirements of accurate calculations for total energies or forces, it is now possible by the calculations based on the GGA-FPKKR method.^{13,14,15} The difficulty arises mainly from the fact that the LDE is generally very small (an order of 0.01eV), being compared with the cohesive energy (~5eV) of solids.

In the present paper, as a first application for the systematic study of the lattice distortion, we show the calculated results for the lattice distortion effect of solution energies of single impurities (Na-Si, Cu, Zn, Zr-Ag) in Al. We also discuss the lattice distortion effect for the formation of a 1st-nearest-neighboring divacancy in Al, as an example of defect pairs in Al.

2. CALCULATIONAL METHOD

The calculations for solution energies of single impurities in metals 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.^{5,8,9} In the present calculations for the CIEs, being the total-energy changes due to the atomic rearrangement on the ideal lattice, the potentials of impurities and their 1st-nearest-neighboring host atoms are recalculated 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.⁹ the potential perturbation due to point defects in metals is very short-ranged because of the strong screening effect of host electrons. On the other hand, the study for the lattice distortion effect demands the self-consistent calculations for the potentials in the larger region because the potentials at the host atoms connected to the relaxed host atoms around the single impurities are also perturbed: the perturbation region depends on the largeness of the distortion. For example, we recalculate the potentials up to the 5th-nearest-neighboring sites of point defects, as discussed in section 4.

Here we discuss how to calculate the solution energies of impurities in Al. The formation energy of a binary alloy A_{1-c}B_c, where c is the atomic concentration of B atoms, is defined by

$$E(c) = E_{A_{1-c}B_c} - (1 - c)E_A - cE_B \tag{1}$$

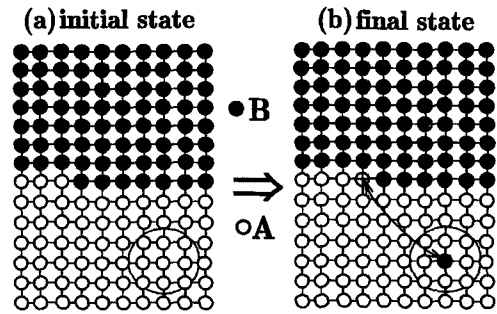


Fig.1 The solution energy of one B impurity in an A metal is defined as a total-energy difference between two states: (a)

the initial state without a impurity and (b) the final state with a single impurity.

Here $E_{A_{1-c}B_c}$ is the total energy of the alloys, and E_A and E_B are the energies of the pure metals. Thus the solution energy $E_{B \text{ in } A}^{\text{sol}}$ of one B impurity in an A metal is given by derivative dE/dc in the dilute limit $c \rightarrow 0$:

$$E_{B \text{ in } A}^{\text{sol}} = \frac{d}{dc} E_{A_{1-c}B_c} \Big|_{c=0} + E_A^{\text{bulk}} - E_B^{\text{bulk}} \tag{2}$$

$$\frac{d}{dc} E_{A_{1-c}B_c} \Big|_{c=0} = \Delta E_{A_{n-1}B} = E_{A_{n-1}B} - E_{A_n} \tag{3}$$

where $\Delta E_{A_{n-1}B}$ is the energy difference between an A metal with a substitutional B impurity and the pure B metal: n is a number of atoms in the region of the perturbed potentials and is set to be 13 (one center and 1st-nearest-neighboring host atoms in fcc) in the present calculations.⁵ In view of a chemical bond picture, the $E_{B \text{ in } A}^{\text{sol}}$ is expressed by

$$E_{B \text{ in } A}^{\text{sol}} = 12E_{A-B \text{ in } A}^{\text{bond}} - 6E_{A-A \text{ in } A}^{\text{bond}} - 6E_{B-B \text{ in } B}^{\text{bond}} \tag{4}$$

where $6E_{A-A \text{ in } A}^{\text{bond}}$ (<0) and $6E_{B-B \text{ in } B}^{\text{bond}}$ (<0) are the cohesive energies of pure A and B metals with the opposite sign, respectively. For the solution of one B impurity in an A metal, 12 A-B bonds are created, while 6 A-A and 6 B-B bonds of pure metals are broken. This is easily understood because $E_{B \text{ in } A}^{\text{sol}}$ is a total-energy difference between the two states, as shown in Fig.1: (a) the initial state without an impurity and (b) the final state with a single impurity.

3. CALCULATED RESULTS FOR COHESIVE ENERGIES (Na-Si,Cu, Zn, Zr-Ag)

Figure 2 shows the calculated results for the atomic structures, cohesive energies, and Wigner-seitz radii for pure crystals (Na-Si, Cu, Zn, Zr-Ag) , which were obtained by use of the GGA-SFPKKR calculations.^{10,11} It includes the experimental data. It is noted that the present calculations reproduce very well the experimental data for the atomic structures of ground states, Wigner-Seitz radii, cohesive energies for all

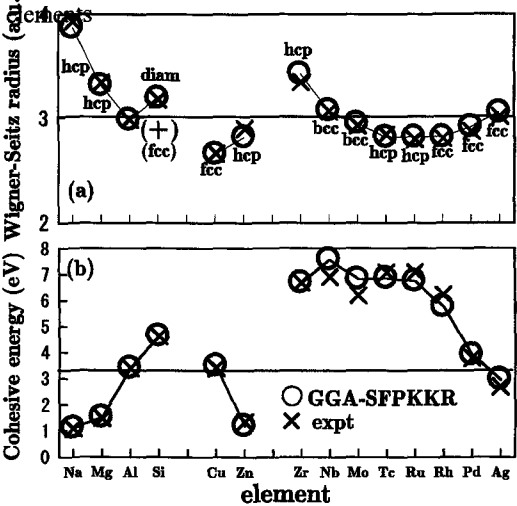


Fig.2 Atomic structure and Wigner-Seitz radius (a), cohesive

energy (b) of pure metals, obtained by the GGA-SFPKKR calculations, together with the experimental data. See text for details.

considered here, as shown in Fig.2, although the small discrepancies occur for the cohesive energies of transition metals (Mo and Tc). For Si, we show the Wigner-Seitz radii in diamond (ground state) and fcc structures because the nature of cohesion in fcc (metallic bonding) is very different from that in diamond (covalent bonding): the Wigner-Seitz radius for fcc is smaller than that of Al. We will discuss that the lattice relaxations of the host atoms around single impurities, being relaxed inward or outward, are understood by comparing the Wigner-Seitz radii of the host atom and impurities, in the metallic bonding.

4. CALCULATED RESULTS FOR SOLUTION ENERGIES OF SINGLE IMPURITIES (Na-Si, Cu, Zn, Zr-Ag) IN Al

In subsection 4.1 we show the CIEs for the solution of single impurities in Al, while in subsection 4.2 the LDEs.

4.1 Chemical interaction energies (CIEs)

Figure 3 shows the CIEs (and LDEs discussed in the next subsection) for the solution of single impurities in Al. It includes the experimental data for Mg and Si.^{17,18} The calculated results are summarized as follows.

- (1) The available experimental data agree very well with the CIEs.
- (2) The chemical interaction for Na and Si is strong repulsive.
- (3) The chemical interaction for Cu is very weak.
- (4) The chemical interactions for Zr-Pd are attractive and strongest around Rh.

We explain briefly the calculated results. The strong repulsion (positive value) for Na may be due to the much weaker Na-Al bond, compared with Al-Al bond. On the other hand, the strong repulsion for Si may be due to the break-up of the strong Si-Si bonds. For Cu, the weak repulsion means that the bond strength doesn't change very much for Al-Al, Cu-Cu, and Al-Cu: the bond strength of Al-Al and Cu-Cu is almost same, as shown in Fig.2. On the other hand, the attraction (negative value) for Zr-Pd is due to the creation of the strong Al-X (X=Zr-Pd) bonds, compared with Al-Al and X-X bonds. This is consistent with the calculated results for the impurity-impurity interactions of X-X in Al, as discussed in Ref.7.

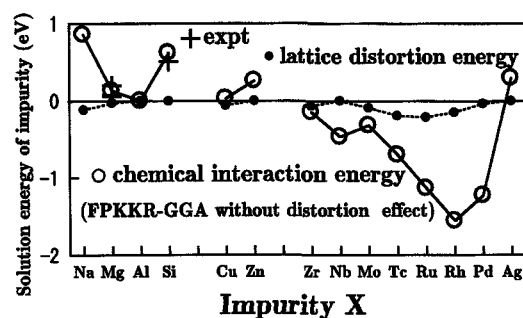


Fig.3 Solution energies of impurities in Al. The calculated

results for the chemical interaction energies and distortion energies are shown, together with the experimental data for Mg and Si.

4.2 Lattice distortion energies (LDEs)

If a defect (impurity or vacancy) is inserted in a metal, the forces are induced on the host atoms around the defect. Figure 4 shows the calculated Hellmann-Feynman (HF) forces on the host atoms at ideal atomic positions in the vicinity of a defect X (X=vacancy, Cu). The negative means the inward relaxation around a defect. We show the calculated results obtained by use of the impurity clusters including up to the 5th (78 host atoms+X) and 14th (296 host atoms+X) neighbors, where the potentials are redetermined self-consistently. The equilibrium atom positions may be determined by the condition of vanishing forces, although the full-optimization of atomic positions for the distant-neighboring host atoms is very time-consuming. Figure 4 shows: (1) the HF forces are long-ranged and show the Friedel-type oscillation, although the forces on the 1st-neighbors are dominant; (2) the forces up to

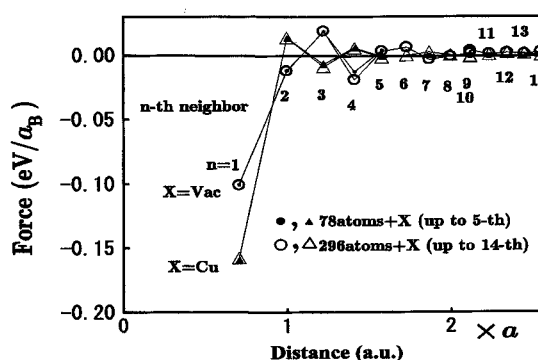


Fig.4 HF forces for a vacancy and a Cu in Al, obtained by use of the impurity clusters of (78 host atoms+X) and (295 host atoms + X). See text for details. a is a lattice parameter.

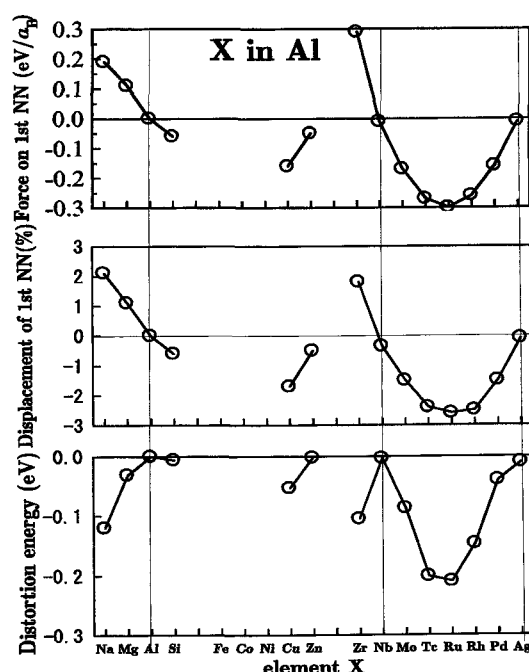


Fig.5 HF forces at ideal positions of the 1st-nearest-neighboring

host atoms of single impurities, the resultant displacements of the 1st-nearest-neighboring host atoms, and are distortion energies. See text for details.

5th-neighbors are reproduced very well by the smaller cluster (78 host atoms+X), where all the host atoms connected to the 1st-neighbors or 2nd-neighbors of a defect are included. Thus we believe that the main part of the distortion effect may be treated by using the smaller cluster (78 host atoms + X) and by considering only the lattice relaxation effect of the 1st-neighbors of a defect. In order to study the LDEs in the solution of impurities, we use both the approximations. Figure 5 shows the the calculated results for the HF forces at ideal positions, displacements of the 1st-nearest-neighboring host atoms around impurities X (X=Na-Si, Cu, Zn, Zr-Ag), and the distortion energies. The characteristic features are summarized as follows:

- (1) The LDEs are very small compared with the CIEs, as seen in Fig.3.
- (2) The LDEs increase with the magnitude of the displacements.
- (3) The displacements increase with the HF forces at the ideal positions.
- (4) The signs and magnitudes of the forces at the ideal positions are correlated to the differences between the Wigner-Seitz radii of the host atom and impurities, shown in Fig.2.

These results mean that the behavior of the distortion effect is very simple because it can be explained by use of the differences between the Wigner-Seitz radii of the host atom and impurities.

5. LATTICE DISTORTION ENERGY(LDE) FOR THE FORMATION OF A 1ST-NEAREST-NEIGHBORING-DIVACANCY IN Al

We already showed that the chemical interaction for the formation of a 1st-nearest-neighboring divacancy in Al is repulsion ($\sim 0.06\text{eV}$),⁴ differently from the commonly accepted interpretation "attraction due to the decrease of dangling bonds".

Here we show the calculated result for the lattice distortion effect for the formation of a divacancy in Al. In order to study the lattice distortion effect, we used the the impurity cluster (100 host atoms + 2 vacancies) of C_{2v} symmetry point group. This cluster includes the host atoms up to 5th-neighbors of vacancies. We tried the full-optimization for the atomic positions in the impurity cluster, although it is very time-consuming. The LDE of a monovacancy is as large as -0.052 eV . For a divancy, the LDE is almost the sum total (-0.100 eV) of the distortion energies of two monovacancies. As a result, the lattice distortion effect for the formation of a divacancy is almost zero (0.004 eV), due to the cancellation of both the distortion effects of the monovacancy and divacancy. However, it is noted that the distortion effect is as repulsive as the chemical interaction.

6. SUMMARY

We showed that the experimental data for solution energies of impurities in Al are reproduced very well by the present GGA-FPKKR calculations. The solution energies are divided into the CIEs and LDEs. It was found that the LDEs are very weak compared with the

CIEs. As an example for defect pairs, we also calculated the LDE for the formation of a 1st-nearest-neighboring divacancy in Al: the distortion effect is repulsive, although it is very weak due to the cancellation of both the lattice distortion effects of the monovacancy and divacancy.

It was also shown that the behavior of the LDEs for single impurities is very simple: it is understood in terms of the size of impurities compared with the host atom. If the behavior of the LDEs of agglomerates of impurities and vacancies is similar to that obtained for single impurities, we can construct the distortion-energy model in the simple functional form. The calculations for the LDEs of 2~13 impurities in Al are in progress.

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