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Ab initio study on divacancy binding energies in aluminum and magnesium

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The divacancy binding energies in fcc Al and hcp Mg have been examined by *ab initio* calculations based on the density-functional theory. Dense **k**-point meshes and large supercells are used enough to obtained converged values. For Al, the first-nearest-neighbor (1NN) divacancy is indeed unstable with a negative binding energy similar to the recent calculations by Carling *et al.* [Phys. Rev. Lett. **85**, 3862 (2000)]. However, the second-nearest-neighbor (2NN) divacancy is stable with a positive binding energy larger than their value. For Mg, both the 1NN and 2NN divacancies corresponding to the 1NN divacancy in fcc structures are stable with positive binding energies in accordance with the conventional view. The difference in the stability of divacancies in Al and Mg has been analyzed clearly through the calculations of divacancies in hcp Al and fcc Mg. The tendency to form local directional bonds with covalency at defects is the electronic origin of the peculiar nature of divacancies in Al.

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Point defects and their mutual interactions play important roles in various phenomena in metals. Divacancies are considered to be formed by attractive interactions between monovacancies, and are considered to make an important contribution to lattice diffusion at high temperature in metals.[1] Divacancies are also considered an initial step for loop clustering in a vacancy-supersaturated atmosphere. Thus, studies of divacancy properties are of great importance for understanding the properties of metals under high temperature or irradiation.

Many experimental studies on divacancies in metals have been performed for some time in order to obtain precise values of the divacancy binding energies.[2] Recently, Carling *et al.* performed theoretical calculations regarding the divacancy binding energies in Al using an *ab initio* pseudopotential method.[3] To our surprise, Carling *et al.*[3] reported that the first-nearest-neighbor (1NN) divacancy binding energy in Al is -0.08 eV, which means that the 1NN divacancy is unstable against two isolated monovacancies. They also reported that the second-nearest-neighbor (2NN) divacancy binding energy is nearly zero ($+0.004$ eV). These results are completely contrary to the conventional view of previous experimental and theoretical studies in which the 1NN divacancy is considered to be stable due to the simple bond counting model,[4] namely, because of the decrease in the number of unsaturated interatomic bonds as compared with the two isolated monovacancies. In Ref. 3, Carling *et al.* also pointed out that the temperature dependence of the measured vacancy concentration can possibly be explained without considering the presence of divacancies.

The study of Carling *et al.*[3] is a serious challenge to all the preceding experimental and theoretical studies on divacancies in various metals. It is of great importance to examine the validity of their results in Al theoretically and experimentally. As well, it is of great interest to examine this problem in other metals. There emerges a natural question whether the 1NN divacancy is also unstable in metals other than Al, or unstable only in Al. Thus in this paper, first, we perform similar first-principles calculations of the divacancy binding energy in Al using the *ab initio* pseudopotentials method. We use larger supercells and denser **k**-point meshes than those mentioned in Ref. 3. This is because recent studies[5,6] have shown that such conditions, especially the number of **k** points, are essential to obtain converged numerical results. As will be shown, we have found that the 2NN divacancy is stable with a positive binding energy similar to the binding energy of the 1NN divacancy in Cu,[7] although it is nearly zero in Ref. 3. Second, we examine the divacancy binding energy in Mg within the same theoretical framework. Mg is a neighbor of Al in the periodic table, and is a typical simple metal with free-electron-like electrons similar to Al. The properties of Mg are of great scientific and technological importance. Comparison between the results of Al and those of Mg should provide insight into the different nature of two simple metals Al and Mg.

In this study, we use the local density approximation (LDA) in the density function theory[8] (DFT) because our main purpose is to obtain the divacancy binding energy. In Ref. 3, it has been shown that the absolute value of the vacancy formation energy cannot be reproduced with a high degree of accuracy by either LDA or GGA (generalized gradient approximation), because the electron correlation effects near the electronic edges cannot be accurately dealt with by such schemes. However, Ref. 3 has shown that the divacancy binding energy can be obtained adequately by LDA or GGA, because such surface effects are cancelled out. We use norm-conserving Troulier-Martins pseudopotentials.[9] The electronic ground state is efficiently obtained using the conjugate-gradient technique[10] with an effective mixing scheme suggested by Kerker.[11] For the fractional occupancies, we use the Gaussian broadening scheme[12] with the Gaussian half width of 0.2 eV. The present scheme is very efficient for large metallic systems.[13] The cutoff energy for the plane-wave basis is 15 and 10 Ry for Al and Mg, respec-

TABLE I. The monovacancy formation energy H_V^f and divacancy binding energies $H_{2V,i\mathrm{NN}}^b$ in fcc Al, where iNN indicates first neighbor (1NN) or second neighbor (2NN). N_k is the number of **k** points sampled in the BZ. N_a is the number of atoms per cell, and N_{tot} is the effective number of atoms in the crystal. Ω_V is the formation volume of the monovacancy. All the energy values are listed in eV, and the formation volume is listed in units of the bulk atomic volume.

	Unrelaxed	Unrelaxed	Full relaxed	Full relaxed	Exp.
N_a	180	108	108	64, 80	
N_k	64	216	216	216, 144	
N_{tot}	6912	23328	23328	13824, 11520	
H_V^f	0.58	0.80	0.72[a]	0.70[b], 0.54[c]	0.67±0.03[d]
$H_{2V,1\mathrm{NN}}^b$	−0.11	−0.05	−0.05[a]	−0.07[b], −0.08[c]	+0.17±0.05[e]
$H_{2V,2\mathrm{NN}}^b$	+0.01	+0.05	+0.04[a]	+0.005[b], +0.004[c]	
Ω_V			0.69[a]	0.67[b], 0.67[c]	0.62[f]

[a] Best value in this work.
[b] LDA values in Ref. 3.
[c] GGA values in Ref. 3
[d] Recommended value of Ref. 19.
[e] Reference 20.
[f] Reference 21.

tively. Stable atomic configurations are obtained through relaxation according to the Hellmann-Feynman forces. By using stress calculations[14] and generalized Hooke's law,[15] the lattice constants at zero pressure are optimized for each supercell containing vacancies.

The monovacancy formation energy (formation enthalpy at zero pressure) H_V^f is given by

$$H_V^f = E_V[N-1] - \frac{N-1}{N} E[N], \tag{1}$$

where $E_V[N-1]$ is the total energy of the supercell containing $N-1$ atoms and a monovacancy, and $E[N]$ is the total energy of the bulk supercell containing N atoms. Similarly to Eq. (1), the divacancy formation energy $H_{2V,i\mathrm{NN}}^f$ is given. The divacancy binding energy $H_{2V,i\mathrm{NN}}^b$ is given by

$$H_{2V,i\mathrm{NN}}^b = 2H_V^f - H_{2V,i\mathrm{NN}}^f, \tag{2}$$

where iNN indicates a divacancy type such as first-nearest neighbor (1NN).

There are two types of size effects that seriously affect the numerical results. These are the supercell size and the number of **k** points. In contrast to semiconducting systems, many **k** points sampled in the Brillouin zone (BZ) are required for metallic systems, in order to define the Fermi surface and to obtain accurate integrals in the BZ, even if we use Gaussian broadening. The numbers of **k** points required are dependent on the cell size, and there is a trade-off between the cell size and the number of **k** points. The effective total number of atoms in the crystal N_{tot} is useful, and is defined by

$$N_{\mathrm{tot}} = N_a N_k, \tag{3}$$

where N_a is the number of atoms per supercell and N_k is the number of **k** points sampled in the whole BZ based on the concept of Born–von Karman periodic boundary conditions. In this paper, the sampling of **k** points is based on the method suggested by Monkhorst and Pack.[16] Of course, the symmetry operations of the system can reduce the number of **k** points used in actual calculations. In order to obtain converged numerical results, N_{tot} needs to be sufficiently large. Of course, the supercell size, namely, N_a, has to be large so that the distance between divacancies can be long enough.

For Al monovacancies, Chetty *et al.*[5] examined various values of N_a and N_k in the same theoretical framework. According to their study, at least $N_a=32$ and $N_k=512$ ($N_{\mathrm{tot}}=16\,384$) are necessary in order to obtained converged values within ~0.01 eV for the monovacancy formation energy. As will be shown, we have found that the values of $N_a=108$ and $N_k=216$ ($N_{\mathrm{tot}}=23328$) can give well-converged values for divacancies in Al.

Table I lists the results of Al. For unrelaxed values, the lattice constant and atomic positions are fixed at the ideal values of the bulk system. It is clear that the larger values of N_k or N_{tot} are necessary to obtain converged results. The full relaxed value of the monovacancy formation energy decreases by 0.08 eV from the unrelaxed one. However, this relaxation effect is negligible in the divacancy binding energies shown in Table I, because the relaxation effects in the monovacancy and divacancy are canceled each other out. Our results essentially support the results described by Carling *et al.*[3] Our value of the 1NN-divacancy binding energy is indeed negative, and is similar to that shown in Ref. 3. However, there is a remarkable difference in 2NN-divacancy binding energy. Our positive value (+0.04 eV) is larger than the nearly zero value in Ref. 3 (+0.005 eV). It should be noted that a smaller number of **k** points seem to reproduce a smaller value of the 2NN-divacancy binding energy as shown in the first column of Table I. Thus the 2NN-divacancy binding energy in Ref. 3 should be too small because of smaller values of N_k or N_{tot}. We emphasize that the 2NN divacancy is stable in Al in contrast to the unstable 1NN divacancy. Of course, the value of the binding energy is not so large and the stability at high temperature may be affected by the vibrational entropy term. However, it should be noted that the present value of the binding energy of the 2NN divacancy in Al is in a similar range of the 1NN-divacancy binding energy of Cu obtained by recent *ab initio* calculations.[7]

TABLE II. The monovacancy formation energy H_V^f and divacancy binding energies $H_{2V,i\mathrm{NN}}^b$ in hcp Mg, where iNN indicates the kind of divacancies form first neighbor (1NN) to sixth neighbor (6NN). All the energy values are listed in eV and the formation volume is listed in units of the bulk atomic volume.

	Unrelaxed	Unrelaxed	Unrelaxed	Unrelaxed	Full relaxed
N_a	36	96	96	96	96
N_k	294	18	125	294	125
N_{tot}	10584	1728	12000	28224	12000
H_V^f	0.80	0.88	0.75	0.77	0.74[a]
$H_{2V,1\mathrm{NN}}^b$	+0.04	+0.13	+0.04	+0.04	+0.06[a]
$H_{2V,2\mathrm{NN}}^b$	+0.05	+0.16	+0.05	+0.06	+0.07[a]
$H_{2V,3\mathrm{NN}}^b$		+0.07	−0.01	−0.01	−0.01[a]
$H_{2V,4\mathrm{NN}}^b$		+0.07	+0.01	+0.01	+0.01[a]
$H_{2V,5\mathrm{NN}}^b$		+0.07	+0.01	+0.01	+0.01[a]
$H_{2V,6\mathrm{NN}}^b$		+0.06	+0.02	+0.01	+0.01[a]
Ω_V					0.69[a]

[a] Best value in this work.

For Mg, the configurations of divacancies from first to sixth neighbors are schematically shown in Fig. 1. For the ideal hcp structure, the first and second neighbors are separated by the same distance. Both the 1NN and 2NN divacancies in hcp correspond approximately to the 1NN divacancy in fcc. Table II lists the results for Mg. From the four sets of unrelaxed results, it is clear that $N_a = 96$ and $N_k = 125$ can give converged values. From the results of first and second columns, it seems that the value of N_k is more important to obtain converged results. The relaxation effects are rather small as shown in the unrelaxed and relaxed formation energies of a monovacancy. About the full-relaxed values, the 1NN and 2NN divacancies are stable in Mg in contrast to the unstable 1NN divacancy in Al. As well, the binding energies from third to sixth neighbor divacancies are nearly zero. All the results for Mg are consistent with the conventional view.

The binding energy of the 1NN divacancy in fcc Al is negative, although the binding energies of the 1NN and 2NN divacancies in hcp Mg corresponding to the 1NN divacancy in the fcc structure are positive. It is quite interesting to investigate the physical origins of the different features of divacancy binding energies in Al and Mg. There are two factors to be examined. One is the crystal structure, and the other is the electronic properties intrinsic to each metallic species. From this viewpoint, we have examined the binding energies in imaginary hcp Al and fcc Mg. As mentioned earlier, the relaxation effects are negligible in the binding energy. So relaxation is not performed, and the lattice constants of supercells are fixed at the ideal values optimized for the bulk crystals. In order to ensure high accuracy $N_a = 96$ and $N_k = 125$ are used for hcp Al, and $N_a = 108$ and $N_k = 216$ are used for fcc Mg. Table III lists the results. The binding energies of the 1NN and 2NN divacancies in hcp Al are negative, which is consistent with the negative 1NN-divacancy binding energy in fcc Al shown in Table I. The binding energy of the 1NN divacancy in fcc Mg is positive, which is consistent with the positive binding energies of the 1NN and 2NN divacancies in hcp Mg shown in Table II. It should be noted that values of the binding energies of divacancies in the fcc and hcp structures of each metal species are similar to those of the corresponding divacancies in imaginary hcp and fcc structures, respectively. It can be said that the basic electronic structures and properties of simple metals do not strongly depend on the crystal structures, only if it is closed packed fcc or hcp. Thus the features of the

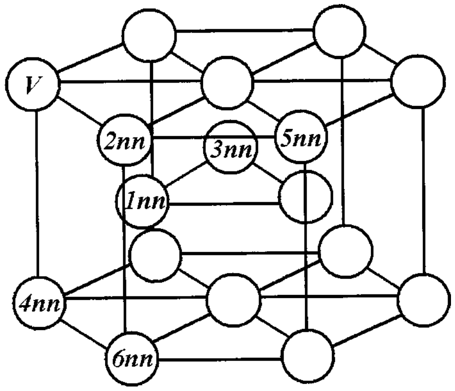

FIG. 1. Configurations of divacancies in hcp structure. Divacancies are formed between a vacancy (V) and a first neighbor (1NN), second neighbor (2NN), third neighbor (3NN), fourth neighbor (4NN), fifth neighbor (5NN), or sixth neighbor (6NN) vacancy.

TABLE III. The monovacancy formation energy H_V^f and divacancy binding energies $H_{2V,i\mathrm{NN}}^b$ in hcp Al and fcc Mg. Results are given without relaxation. All the energy values are given in eV.

	hcp Al	fcc Mg
H_V^f	0.57	0.79
$H_{2V,1\mathrm{NN}}^b$	−0.07	+0.08
$H_{2V,2\mathrm{NN}}^b$	−0.10	+0.01
$H_{2V,3\mathrm{NN}}^b$	−0.03	
$H_{2V,4\mathrm{NN}}^b$	+0.06	
$H_{2V,5\mathrm{NN}}^b$	−0.02	
$H_{2V,6\mathrm{NN}}^b$	−0.01	

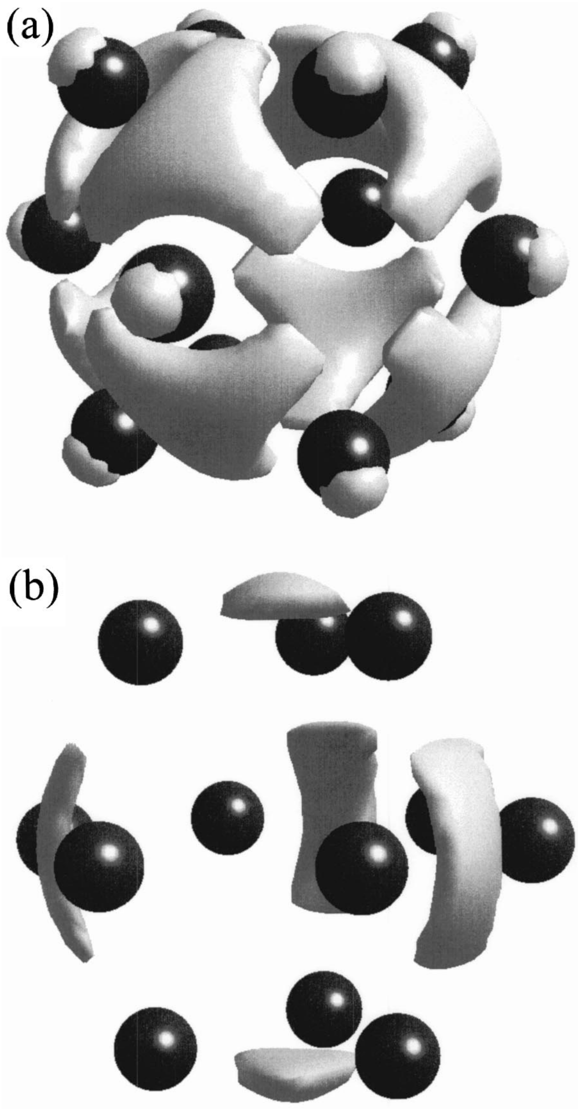

FIG. 2. Three-dimensional representation of the difference of the charge density between with and without a monovacancy in (a) fcc Al and (b) hcp Mg. The gray isosurface indicates the surface of isovalue of the charge-density difference 0.0015 and 0.0007 a.u.$^{-3}$, for Al and Mg, respectively. The black spheres indicate the positions of the nearest neighbor atoms of a monovacancy.

divacancy binding energies should be determined mainly by the electronic properties intrinsic to each metallic species.

The 1NN divacancy is unstable in Al due to the generation of strong directional bonds at the first shell around the monovacancy as pointed out in Ref. 3. Figure 2 clearly shows the charge accumulation between the nearest-neighboring atoms of the monovacancy. It is interesting that the charge density increases at each triangle among each three neighboring atoms. As discussed in Ref. 3, the formation of such directional bonds at the first shell stabilizes the monovacancy and causes the excess energy cost to form the 1NN divacancy. On the other hand, neither such bond formation nor such remarkable charge accumulation are observed around the monovacancy of Mg as clearly shown in Fig. 2. Thus the simple bond counting model[4] seems to be applicable to the divacancies in Mg. It should be noted that several *ab initio* studies have reported that strong directional bonds with covalent characters can be locally formed for Al atoms with reduced coordination numbers at defects or surfaces in Al.[17] This tendency of Al has also been observed in a recent *ab initio* study of the shear deformation of Al.[6] Al is trivalent and is a neighbor of Si in the periodic table. Thus it can be said that Al has a character rather intervening between simple metals and covalent materials, and that Al can form bonds with both metallic and covalent characters according to its environment. Here it should be noted that the 1NN divacancy is thought both experimentally and theoretically to be stable in covalent materials such as Si (Ref. 18) due to a mechanism similar to the simple bond counting model. This point indicates that the unstability of the 1NN divacancy in Al is a rather special case caused by the peculiar electronic nature of Al revealing both metallic and covalent characters. The present results indicate the quite different characters of Al and Mg on local atomic bonding dominating defect energies and structures. Therefore, in developing the effective interatomic potentials for Al and Mg for large-scale simulations, this point should be incorporated.

In summary, we have performed *ab initio* calculations of the divacancy binding energies in fcc Al and hcp Mg, and obtained well-converged values using large supercells and dense **k**-point meshes. For Al, the 1NN divacancy is indeed unstable in a way similar to the results of Carling and coworkers, although the 2NN divacancy is stable with a positive binding energy against their nearly zero values. For Mg, both the 1NN and 2NN divacancies corresponding to the 1NN divacancy in the fcc structure are stable having positive binding energies in accordance with the simple bond counting model. The physical origin of the differing stabilities of the divacancies in Al and Mg has been clearly shown through the calculation of divacancies in hcp Al and fcc Mg and the analysis of the charge density redistribution by vacancies. The origin of the peculiar nature of Al divacancies is their tendency to form local directional bonds with metallic and covalent characters according to the environment, which is intrinsic to Al.

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