All-electron first-principles supercell total-energy calculation of the vacancy formation energy in aluminum*

M.J. Mehl and B.M. Klein
Complex Systems Theory Branch
Condensed Matter and Radiation Sciences Division
Naval Research Laboratory
Washington, DC, 20375-500, USA

Abstract

We use the first-principles all-electron linearized augmented plane-wave (LAPW) method to perform self-consistent total-energy electronic structure calculations for the vacancy formation energy in aluminum in the supercell approximation. The method makes no uncontrolled approximations for the shape of the potential. Supercells with 4, 8, 16, and 27 sites are used. When no relaxation is allowed, the formation energy is 0.87, 0.88, 0.89 and 0.86 eV for the 4-, 8-, 16-, and 27-site supercells, respectively. When some of the atoms are allowed to relax about the vacancy the formation energy is lowered by 0.05 eV in the 16-site cell and 0.03 eV in the 27-site cell. These results are in semiquantitative agreement with the experimental formation energy of 0.66 eV. The dependence of the formation energy on cell size is discussed.

*Appears in *Physica B* **172**, 211 (1991).

1 Introduction

Point defects in metals are of interest in many applications of metal physics. In particular, the problem of calculating the formation energy of a vacancy in aluminum has received considerable attention.[1, 1, 3, 4] These calculations were all carried out with various forms of pseudopotentials, on supercells including up to 27 sites. As shown by Jansen and Klein[4] the formation energy is extremely sensitive to the choice of the pseudopotential. We can, however, perform all-electron calculations on these supercells, and since there need be no fitting to a pseudopotential, the resulting formation energy is unambiguous if the supercell is large enough. Thus, all-electron total-energy calculations can be of use not only in their own right, but also as benchmarks for pseudopotential calculations and empirical schemes such as the embedded-atom method.[5]

The strain field associated with the vacancy is of interest in elasticity theory. We can gain some insight into the range of the field by noting that the 16- and 27-site supercells allow some of the atoms to relax about the vacancy. This relaxation can be calculated by determining the configuration of the supercell that minimizes the total energy consistent with the allowed symmetry around the vacancy.

This paper presents a first-principles all-electron calculation of the vacancy formation energy in aluminum. We model the local neighborhood of the vacancy by removing aluminum atoms from the room temperature equilibrium FCC lattice, forming a periodic supercell. In general, the interaction between the vacancies will cause the calculated formation energy to depend upon the size of the supercell. In an effort to determine the size of this interaction we study supercells containing 4, 8,16, and 27 FCC sites. Larger supercells are computationally difficult because of the constraints of computer memory and available execution time. The self-consistent charge density and total energy are calculated within the local-density approximation (LDA) to density functional theory (DFT)[6] by a full potential version of the linearized augmented plane-wave (LAPW) method.[7, 8] The method makes no uncontrolled approximations other than the LDA. In particular, there is no shape approximation to the potential.

Table 1: The supercell parameters.

Number of sites	Supercell symmetry	Cubic lattice constant (Å)	Distance between vacancies (Å)	Relaxation Allowed	
				First neighbors	Second neighbors
4	SC	4.05	4.05	No	No
8	FCC	8.10	5.73	No	No
16	BCC	8.10	7.01	Yes	No
27	FCC	12.15	8.59	Yes	Yes

2 Theory

We study the vacancy in aluminum by a supercell method; that is, we begin with the periodic FCC aluminum lattice and remove atoms in a periodic array so that each supercell of the lattice contains one vacancy. The supercells used are listed in Table 1 and shown in Figure 1. For a supercell containing N sites, the energy required to form a vacancy is

$$E_{\text{Fermi}} = E(N-1,1) - [(N-1)/N]E(N,0) \ , \tag{1}$$

where $E(N-V,V)$ is the total energy of an N-site supercell with V vacancies. In the limit of large N this will converge to the formation energy for an isolated vacancy. All calculations were carried out at constant volume, in this case at the experimental FCC lattice constant $a_{\text{FCC}} = 4.05$Å. In this we follow the procedure of Jansen and Klein.[4] The computations could also have been done at constant Al density,[3] but in the limit of large supercells the methods must agree. We choose the constant-volume method because we want the environment around the vacancy to mimic that of the isolated vacancy as closely as possible.

Calculations were done using the first-principles LAPW method[7, 8] to solve the equations of density functional theory in the LDA.[6] No other uncontrolled approximations were made. Inside the muffin tins the wave functions were expanded to include all angular momenta up to $\ell = 8$, and the potential was expanded up to $\ell = 4$. In the interstitial the potential was expanded into a Fourier series using approximately 400 plane waves for the primitive FCC lattice. Brillouin zone sums were determined using a k-point mesh generated by the method of Monkhorst and Pack[9] and

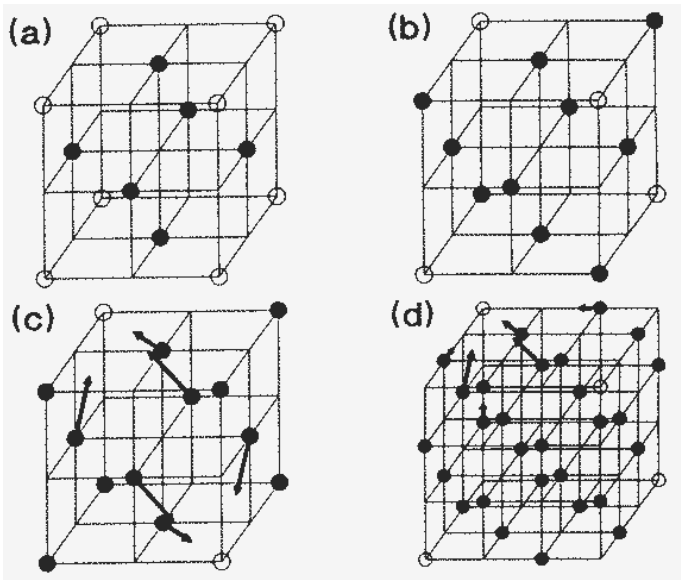

Figure 1: The supercells used in the calculations are shown. The solid circles represent the occupied sites, the open circles the vacancies. The supercells contain (a) 4, (b) 8, (c) 16, and (d) 27 sites. For clarity in (b)-(d) only one eighth of the cubic unit cell is shown. The other parts of the cube may be generated by applying the cubic symmetry operations about the vacancy in the upper left-hand corner in each cell. The arrows in (c) and (d) show the possible relaxations of the atoms around the vacancies (not to scale). In (d) we show the possible relaxations around only one of the vacancies.

checked for satisfactory convergence by doing the calculations for various k-point meshes. To facilitate k-point convergence, the electronic states were populated by weighting with a Fermi distribution function corresponding to a fictitious temperature of 0.002 Ry. We chose the plane-wave cut-off so that there were approximately 40 LAPW basis functions per atom. While this is rather small, previous calculations showed that this is an adequate basis set for calculation of such properties as the elastic constants.[10]

The initial calculations were done without relaxation. That is, all of the atoms occupied FCC lattice sites, even in the presence of the vacancy. As we shall see, this produces the major contribution to the formation energy. Further calculations allowed the atoms nearest to the vacancy to relax. The only restriction placed on the relaxation was that the vacancy remain a point with the full lattice symmetry. Because of this restriction, relaxation is allowed only for supercells with 16 or more sites. In the 16-site lattice there is one free parameter, d_1, the distance between the vacancy and the atoms on the nearest-neighbor sites. When we increase the supercell to 27 sites we add a new parameter d_2, the distance between the vacancy and the second-neighbor atoms. When there is no relaxation we have

$$d_1 \rightarrow d_{10} \equiv a/\sqrt{2} \ , \tag{2}$$

and

$$d_2 \rightarrow d_{20} \equiv a \tag{3}$$

where a is the lattice parameter of the simple FCC lattice. For each lattice we calculated the total energy at various values of the free parameters. We then fitted these energies to polynomials in x and y, where

$$d_1 = d_{10}(1-x) \ , \tag{4}$$

and

$$d_2 = d_{20}(1-y) \ , \tag{5}$$

with y vanishing identically for the 16-site supercell. These polynomials were then minimized to determine the minimum-energy structure, characterized by the parameters x_0 and y_0. We can then calculate the change in energy resulting from relaxation:

$$E_R(N) = E(N,0,0) - E(N,x_0,y_0) \ , \tag{6}$$

Table 2: Unrelaxed formation energies

Number of sites	Number of k-points	E_{form} (eV)
4	56	0.856
4	165	0.866
8	28	0.860
8	85	0.882
16	20	0.855
16	55	0.895
27	10	0.781
27	28	0.933
27	60	0.862
27	110	0.864

where E(N, x, y) is the self-consistent total energy of the N-site supercell with vacancy-neighbor distances given by (4) and (5). The formation energy can then be calculated from the expression

$$E_{\text{form}}(N) = E^{(0)}_{\text{form}}(N) - E_R(N) \ , \tag{7}$$

where $E^{(0)}_{\text{form}}(N)$ is the formation energy (1) of the unrelaxed lattice.

3 Results

We used the LAPW method to calculate the vacancy formation energy for supercells of 4, 8, 16, and 27 atoms, as shown in Table 1 and Figure 1. Our first set of calculations did not allow the atoms close to the vacancy to relax, even when this was allowed by symmetry. To determine the formation energy accurately we did our calculations for at least two different k-point meshes in each of the supercells. As seen in Table 2, when the k-point mesh is dense enough, the unrelaxed formation energy is 0.88 0.02 eV, independent of the supercell size, at least for supercells containing up to 27 sites. This behavior is in agreement with the findings of Jansen and Klein[4] although we do not obtain their value for the formation energy.

The 16- and 27-site supercells allow some relaxation about the vacancy. As outlined in the preceding section, we determined the values of (x, y) that

Table 3: Relaxation about the vacancy: $d_1 = 2.86(1-x)$Å, $d_2 4.05(1-y)$Å.

Number of sites	Number of k-points	x_0	y_0	E_R (eV)	E_{form}, (eV)
16	20	0.015	0	0.059	0.796
16	55	0.014	0	0.052	0.843
27	10	0.012	0.003	0.037	0.744
27	28	0.010	0.003	0.027	0.906
27	60	0.010	≈ 0.0	0.026	0.836

minimized the total energy. As can be seen in Table 3, the relaxation energy is approximately 0.05 eV in the 16-site supercell and 0.03 eV for the 27-site cell, both in the direction lowering the formation energy. These energy differences are somewhat smaller than the values found by Gillan[3] (0.098 and 0.084 eV, respectively). In any case, the relaxation energy changes the formation energy by a very small amount. Useful information can also be gained from the parameters (x_0, y_0) themselves. In the 16-site supercell the nearest neighbors contract around the vacancy, d1 changing by a little more than 1%. In the 27-site cell the contraction is also approximately 1%, while the second-nearest neighbors contract by a smaller amount. The amount of this small contraction is very sensitive to the k-point mesh, and the value of 0.3% must be regarded as preliminary.

4 Discussion

Including relaxation, our 16- and 27-site supercell results indicate that the vacancy formation energy in aluminum is 0.84 eV, and that the atoms nearest the vacancy relax towards the vacancy, reducing d_1 by about 1%. Consideration of the k-point convergence in Tables 2 and 3 leads us to conclude that the numerical error in the formation energy is no greater than 0.04 eV. Thus, our calculated formation energies are in semi-quantitative agreement with the accepted experimental value of 0.66 eV[11, 12, 13] and the theoretical predictions of Gillan[3] (0.56 eV) or Jansen and Klein[4] (0.52 eV).

The difference between the various theoretical calculations is not surprising. Jansen and Klein showed that the formation energy was sensitive

to the choice of pseudopotential. Their value of 0.52 eV was determined using Hamann-Schluter-Chiang[14] pseudopotentials fitted to the Bachelet-Hamann-Schluter form.[15] However, when the actual Bachelet *et al.* pseudopotentials[15] were used, the formation energy was found to be 1.0 eV. Our all-electron calculation should not suffer from these difficulties.

Supercell size effects may play an important roll. An embedded-atom functional fitted to an aluminum vacancy formation energy of 0.73 eV yields a formation energy of 0.91 eV in the unrelaxed 16-site supercell, lowering to 0.885 eV when d_1 is allowed to relax.[16] Since these energies are in rather good agreement with our calculation, it seems likely that even in the 27-site supercell there is a significant vacancy-vacancy interaction, on the order of 0.1 eV. This would lower our calculated formation energy to 0.74±0.04 eV, in much better agreement with experiment. In this case, the results of Table 2 and the calculations of Jansen and Klein[4] indicate that the vacancy-vacancy interaction is approximately independent of distance for periodically ordered vacancies separated by less than about 10Å. We may not be able to confirm this result by first-principles calculations in the near future. The next supercell in this system has 32 sites with the vacancies sitting on a simple cubic lattice of side $a = 2a_{\mathrm{FCC}}$8.10Å. Unfortunately, the vacancy-vacancy distance is smaller than in the 27-site supercell, where the "close-packed" vacancies are separated by 8.59Å. The next larger supercell contains 64 sites, with the vacancies sitting on an FCC lattice of side $a = 3a_{\mathrm{FCC}}$. Since the computer-memory requirements of the all-electron methods scale as the square of the number of atoms and the execution time scales as the cube, the 64-site supercell will strain the capabilities of the current generation of supercomputers. Further use of the embedded-atom method[5] may be needed to model the behavior of the formation energy as a function of cell size. Other first-principles methods, such as Greens functions approaches, may be more appropriate for improved accuracy in the calculation of the isolated vacancy formation energy.[17]

Acknowledgements

This work was partially supported by the Office of Naval Research, US Department of Defense. Computer support for the 27-site supercell calculations was provided by the San Diego Supercomputing Center.

References

[1] B. Chakraborty, R. W. Siegel and W. E. Pickett, *Phys. Rev. B* **24**, 5445 (1981).

[2] B. Chakraborty and R. W. Siegel, in *Point Defects and Defect Interactions in Metals*, eds. J. Takamura, M. Doyama and M. Kiritani (North-Holland, Amsterdam, 1982), p. 93.

[3] M. J. Gillan, *J. Phys. Condens. Mat.* **1**, 689 (1989).

[4] R. W. Jansen and B. M. Klein, *J. Phys. Condens. Mat.* **1**, 8359 (1989).

[5] M. S. Daw and M. I. Baskes, *Phys. Rev. B* **29**, 6443 (1989).

[6] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

[7] O. K. Andersen, *Phys. Rev. B* **12**, 3060 (1975).

[8] S.-H. Wei and H. Krakauer, *Phys. Rev. Lett.* **55**, 1200 (1985).

[9] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).

[10] M. J. Mehl, J. E. Osburn, D. A. Papaconstantopoulos and B.M. Klein, *Proc. 1990 Spring Meeting of the Materials Research Society, Alloy Phase Stability and Design*, in press.

[11] W. Triftshäuser, *Phys. Rev. B* **12**, 4634 (1975).

[12] A. S. Berger, S. T. Ockers and R. W. Siegel, *J. Nucl. Matter*, 734 (1978). (1978) 734.

[13] M. J. Fluss, L. C. Smedskjaer, M. K. Chason, D. G. Legnini and R. W. Siegel, *Phys. Rev. B* **17**, 3444 (1978).

[14] D. Hamann, M. Schluter and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).

[15] G. B. Bachelet, D. R. Hamann and M. Schluter, *Phys. Rev. B* **26**, 4199 (1982).

[16] M. J. Mehl, M. Pederson, D. Farkas and B. M. Klein, in preparation.

[17] U. Klemradt, B. Drittler, R. Zeller and P. H. Dederichs, *Phys. Rev. Lett.* **64**, 2803 (1990).