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## The *ab initio* calculation of defect energetics in aluminium

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**Abstract.** A detailed study of the energetics and electronic structure of the vacancy point defect in bulk aluminium is presented. The calculations are based on a norm-conserving *ab initio* pseudopotential and the supercell approach, the energy functional minimization being performed with the conjugate gradients technique, with full relaxation of all ionic positions. Calculated results for the formation and migration energies and the volume of formation are in close agreement with experiment. The screening-charge distribution around the vacancy is found to be highly localized. Preliminary results are also given for the aluminium self-interstitial.

### 1. Introduction

The ability to make reliable and accurate calculations on the energetics of materials has made remarkable strides in recent years. Rapid advances in pseudopotential techniques and in methods for achieving electronic self-consistency have led to standard procedures for calculating the cohesive energy, equilibrium lattice constant, elastic constants and phonon dispersion relations of perfect crystals. Attention is now turning increasingly to the problem of performing reliable calculations on the energetics of materials containing defects and impurities. This is often a difficult problem, because of the need to treat systems of many atoms, and to relax the atomic positions to mechanical equilibrium.

The purpose of this paper is to describe a detailed study of the energetics of the isolated vacancy in aluminium. The vacancy in aluminium is a particularly important test system for *ab initio* methods, because it is one of the simplest examples of a defect in a technologically important material. In spite of its apparent simplicity, this system has proved difficult to deal with. Early attempts to treat it by a perturbation expansion in the strength of the pseudopotential proved hopelessly inadequate, as shown by Evans and Finnis (1976). Full *ab initio* calculations also initially failed to give satisfactory results for the formation energy (Chakraborty *et al* 1981, Chakraborty and Siegel 1983) and it was only fairly recently that the first successful results were obtained from a full electronically self-consistent pseudopotential treatment (Gillan 1989). These recent calculations were based on an empirical local pseudopotential which, although fairly realistic, cannot be regarded as fully satisfactory. Our purpose here is to re-examine the problem of the vacancy in aluminium using a fully *ab initio* non-local pseudopotential. We shall present results for the energy and volume of formation of the fully relaxed vacancy, and the energy of vacancy migration (i.e. the

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energy barrier involved in the vacancy diffusion process). Results will be given for the relaxation of the neighbouring ions and the self-consistent valence electron charge distribution. We also present results for the energy of formation of the fully relaxed self-interstitial. We note that one of the aims of this work is to prepare the way for *ab initio* pseudopotential calculations on hydrogen in aluminium which will be reported in a companion paper.

As in our previous work (Gillan 1989), the calculations are performed in periodically repeated geometry, using up to 27 atomic sites in the unit cell, with a plane-wave basis set. Simultaneous relaxation of the electronic and ionic coordinates to the global energy minimum is performed using the conjugate gradients technique. Brillouin zone sampling is performed by the Monkhorst–Pack scheme (Monkhorst and Pack 1976), with the Fermi surface smoothing method developed by Gillan (1989). The non-local pseudopotential we use is that due to Bachelet *et al* (1982), in the Kleinman–Bylander representation (Kleinman and Bylander 1982), with *s* and *p* non-locality.

The plan of the paper is as follows. In section 2 we summarize in more detail the techniques used and the definitions of the quantities we have calculated. Section 3 presents our results. In the final section 4 we discuss the comparison of our results with experiments. In the past two years, there have been a number of other studies of the aluminium vacancy. We comment in section 4 on the relation between the present work and these other studies.

## 2. Techniques and definitions

### 2.1. Techniques

We briefly summarize the standard aspects of our calculations before describing some special technical features of the work. The total ground state energy involved in the minimization procedure has the usual form:

$$E = E_K + E_H + E_{XC} + E_C + E_I \quad (1)$$

as a function of the ionic coordinates in the supercell and of the plane-wave coefficients of the occupied orthonormal electron orbitals. Here  $E_K$ ,  $E_H$ ,  $E_{XC}$ ,  $E_C$  and  $E_I$  represent the kinetic, Hartree, exchange–correlation, electron–core, and Madelung core energies. We adopt the usual local density approximation for  $E_{XC}$  as calculated by Ceperley and Alder (1980) and parametrized by Perdew and Zunger (1981). The electron–core pseudopotential in  $E_C$  is represented in the fully non-local form due to Kleinman and Bylander (1982) (KB). We have constructed our KB pseudopotential from the semi-local pseudopotential  $V^{BHS}$  of Bachelet *et al* (1982):

$$V^{BHS} = V^L + \sum_{l=0}^{\infty} V_l^{BHS} P_l \quad (2)$$

with  $V^L$  the local potential and  $P_l$  the projector onto states of angular momentum  $l$  in the non-local summation. For third row elements such as aluminium, it is accurate enough to terminate the series as

$$V'^{BHS} = V'^L + \sum_{l=0}^1 V_l'^{BHS} P_l \quad (3)$$

where  $V_2^{\text{BHS}}$  has been added to the local and subtracted from the non-local terms in (2), and where all the other terms for which  $l > 2$  have been disregarded. Denoting  $\chi_l(r)$  the reference atomic pseudo-wavefunctions, the plane wave matrix elements of the KB pseudopotential  $V^{\text{KB}}$  are given by the separable form:

$$\langle k | V^{\text{KB}} | k' \rangle = V'_{\mathbf{k}-\mathbf{k}'} + \sum_{l,m} A_l Y_l^m(k) Y_l^{m*}(k') \phi_l(k) \phi_l(k') \quad (4)$$

where

$$\phi_l(k) = \int d\mathbf{r} j_l(kr) V_l^{\text{BHS}}(r) \chi_l(r) \quad (5)$$

and

$$A_l = \left( \int d\mathbf{r} \chi_l(r)^2 V_l^{\text{BHS}}(r) \right)^{-1}. \quad (6)$$

This form of the pseudopotential allows one to avoid double summations over  $k$ -vector indices in the evaluation of the non-local energy contribution to  $E_C$ .

In fact, the form we have adopted here is very close to the KB pseudopotential for aluminium reported by Stumpf *et al* (1990). These authors show that the pseudopotential is free of the 'ghost' states that sometimes afflict the KB form, and that it closely reproduces the logarithmic derivatives of the all electron wavefunctions within a range of about one Hartree from the reference energy levels. We therefore expect our pseudopotential to have good transferability properties.

The calculations are performed in periodic boundary conditions using plane-wave basis sets, with repeating cells containing 8, 16 and 27 regular lattice sites, respectively, corresponding to FCC, BCC and FCC superlattice symmetries. Brillouin zone integration is performed on the standard Monkhorst-Pack grid (Monkhorst and Pack 1976) reduced by symmetry to the inequivalent subset of weighted sampling points. In order to increase integration efficiency we perform a Fermi surface smoothing with variable orbital occupation numbers (Gillan 1989). This smoothing technique is equivalent to treating the electron system at finite temperature within the fixed supercell volume. The functional being minimised is the free energy  $A$

$$A = E - TS \quad (7)$$

where

$$S = -2k_B \sum_i [f_i \ln(f_i) + (1 - f_i) \ln(1 - f_i)] \quad (8)$$

instead of  $E$  itself,  $S$  being the entropy associated with the  $i$ -orbital occupation numbers  $f_i$  at temperature  $T$ . When  $A$  is minimised, the quantity  $(A + E)/2$  deviates from the ground state energy only by a term of order  $\sim T^3$ . In all the calculations to be reported later, we take  $k_B T$  equal to one tenth of the Fermi energy of jellium at the same electron density. Tests at different values of  $T$  show that the deviation of  $(A + E)/2$  from the zero temperature value of  $E$  are at most a few hundredths of an eV per atom. When we refer later to results for ground state 'energies' we always mean the calculated values of  $(A + E)/2$ .

The calculation scheme for determining the electronic ground state is the conjugate gradients method described by Gillan (1989). Like the Car-Parrinello scheme (Car and Parrinello 1985), the method involves minimization of the total energy functional (actually the free energy  $A$  in this case) with respect to all the plane wave coefficients, with the constraint that all the occupied orbitals remain orthonormal. We note here the main principles of the method; for full details the paper cited above should be consulted.

The electrons are iteratively relaxed to the ground state with a succession of displacements of the vector of plane-wave coefficients  $a_{q,i,G}$  (sampling vector  $q$ , orbital  $i$ , plane wave  $G$ ). The method guarantees that every such displacement results in a decrease of free energy. A displacement has two components, which are respectively within and orthogonal to the subspace spanned by the current orbitals. The displacement within the subspace is a unitary rotation, chosen so that ultimately the Kohn-Sham Hamiltonian becomes diagonal. The orthogonal displacement is constructed using conjugate gradients. If  $F_{q,i,G}$  are the components of the force vector acting on the wavefunctions:

$$F_{q,i,G} = -\partial E / \partial a_{q,i,G}^* \quad (9)$$

and if  $F_{q,i,G}^\perp$  denotes the projection of the force into the orthogonal subspace, then the new search direction  $S_{q,i,G}$  for the orthogonal displacement of the plane-wave coefficients is given by

$$S_{q,i,G} = F_{q,i,G}^\perp + \beta S'_{q,i,G} \quad (10)$$

where  $S'_{q,i,G}$  is the previous search direction and the coefficient  $\beta$  is determined by the standard conjugate gradients algorithm.

The relaxation of the ionic coordinates is performed by the method outlined by Gillan (1989): once an electronic displacement has been completed, all ions are relaxed by steepest descents, holding the orbital coefficients fixed. This relaxation procedure is terminated when the energy decrease due to ionic displacements falls below a specified small fraction of the decrease due to the last electronic displacement.

The global minimisation procedure makes full use of the symmetry of the system. The point sub-group of symmetry operations characterizing the defect system is maintained at each iteration step by direct symmetrization of the charge density and the non-local component of the forces over the ions. By using symmetry in this way we economize on effort, but prevent the system escaping from its initial symmetry. This means that in cases where the energy could be lowered by symmetry breaking, our technique would not yield the true ground state. However, symmetry breaking is exceedingly unlikely for any of the situations studied in the present work.

## 2.2. Definitions

When referring to the energy of formation  $E_f$  of the vacancy, we shall mean, as usual, the energy change when an atom is removed from the perfect bulk crystal and replaced on a new bulk lattice site. The exact definition of  $E_f$  depends on the conditions under which the vacancy is formed. There are at least three natural conditions: we can consider the vacancy to be formed with the pressure, the total volume or the lattice parameter held fixed. Denoting by  $E(N, \nu; \Omega)$  the energy of

the system of  $N$  atoms and  $\nu$  vacancies occupying  $N + \nu$  lattice sites in the volume  $\Omega$ , the energy of formation at constant volume  $E_f^\nu$  is:

$$E_f^\nu = E(N, 1; \Omega) - E(N, 0; \Omega). \quad (11)$$

The quantity of physical interest is obtained for  $N \rightarrow \infty$ , the limit being taken with  $\Omega/N$  held fixed. The energies of formation  $E_f^p, E_f^e$  at constant pressure and lattice parameter are defined in an analogous way.

The relation between  $E_f^\nu$  and  $E_f^p$  involves the vacancy volume of formation  $\Omega_f$ , defined as the volume change of the whole system when a vacancy is formed at constant pressure. If  $\Omega(N, \nu; p)$  denotes the equilibrium volume of the system of  $N$  atoms and  $\nu$  vacancies at pressure  $p$ , then

$$\Omega_f = \Omega(N, 1; p) - \Omega(N, 0; p). \quad (12)$$

The energy of formation at constant pressure can therefore be written as

$$E_f^p = E(N, 1; \Omega_0 + \Omega_f) - E(N, 0; \Omega_0) \quad (13)$$

where  $\Omega_0 = \Omega(N, 0; p)$ . Expanding  $E$  up to quadratic order in the small change  $\Omega_f$ , we obtain:

$$E_f^p = E_f^\nu + \Omega_f \frac{\partial E}{\partial \Omega}(N, 1; \Omega_0) + \frac{1}{2} \Omega_f^2 \frac{\partial^2 E}{\partial \Omega^2}(N, 1; \Omega_0) \quad (14)$$

which can be rewritten in terms of pressure  $p$  and bulk modulus  $B$  in the vacancy system as

$$E_f^p = E_f^\nu + p\Omega_f + \frac{1}{2} \Omega_f^2 B / \Omega. \quad (15)$$

An analogous relation can be given for  $E_f^e$

$$E_f^e = E_f^p + p(\Omega_c - \Omega_f) + \frac{1}{2} (\Omega_c - \Omega_f)^2 B / \Omega \quad (16)$$

where  $\Omega_c$  is the equilibrium atomic volume in the perfect system at pressure  $p$ . Given these simple relations, it does not particularly matter which of the formation energies we aim to calculate. If  $p = 0$ , the case of usual interest, they are all equal in the limit  $N \rightarrow \infty$ : given one, we can obtain the others.

In practical calculations  $N$  is finite, and the definition to be adopted should be taken as the one which gives the most rapid convergence to the thermodynamic limit with increasing system size. In a previous paper (Gillan 1989) we have given perturbation theory arguments which suggest that the formation energy at constant atomic volume converges within a few hundredths of an electron volt by the time the size of a 27-atom supercell is reached, and we therefore calculate  $E_f^\nu$ . We can however estimate through equation (15) the difference that would arise if we calculated  $E_f^p$ .

Because of the periodic boundary conditions, we are forced to perform calculations on the perfect and defective systems having the same number of lattice sites.  $E_f^\nu$  is therefore actually calculated as

$$E_f^\nu = E(N - 1, 1; (N - 1)\Omega/N) - \frac{N - 1}{N} E(N, 0; \Omega). \quad (17)$$

When comparing our calculated formation energy with experiment, we have to bear in mind that the quantity derived from experiment is the enthalpy of formation at high temperature, not the energy of formation at zero temperature. We return to this question in section 4.

Similar remarks apply to the formation energy of the self-interstitial, which we define to be the energy change in going from a perfect crystal of  $N$  lattice sites to a system of  $N - 1$  lattice sites occupied by  $N - 1$  atoms with an atom on an interstitial site. We calculate the formation energy at constant volume.

Finally, we calculate the migration energy of the vacancy. This is the energy barrier that has to be surmounted in moving a vacancy from one site to a neighbouring site. We assume that in the saddle-point configuration the migrating atom is midway between two nearest-neighbour lattice sites. The migration energy  $E_m$  is then the energy difference between this fully relaxed saddle-point configuration and the fully relaxed system in which the vacancy is on a regular site.

### 3. Results

#### 3.1. The perfect crystal

As a preliminary test of our methods we have determined the equilibrium lattice parameter  $a_0$  and bulk modulus  $B$  of the perfect crystal. Calculations have been performed at a series of values of  $a_0$  with a constant number of plane waves, using a cut-off energy which is 13 Hartree when  $a_0$  has the experimental value of 7.64 au. The calculations were performed on the 16-atom system using two sampling points in the irreducible wedge. We used five uniformly spaced values of  $a_0$ , with a rather small difference of 0.025 au between successive values. This allowed us to deduce values for the equilibrium  $a_0$  and  $B$  from a simple parabolic fit to the five values of energy. Our calculated values  $a_0 = 7.66$  au and  $B = 0.722$  Mbar are in close agreement with the experimental values 7.64 au and 0.722 Mbar (see Chakraborty and Siegel 1983 and references therein), as previous work would lead one to expect. This agreement confirms the technical adequacy of the methods used here.

#### 3.2. The equilibrium vacancy

We have calculated the ground state energy of the perfect crystal and of the unrelaxed and relaxed vacancy for systems containing 8, 16 and 27 lattice sites; we note that for the 8-site vacancy system the ions are constrained by symmetry to be exactly on their regular sites, so relaxation effects cannot be studied in this case. In all cases, the lattice parameter in the perfect system is taken to have the experimental value 7.64 au.

In accordance with the discussion of section 2, we evaluate the formation energy from the total energy of the vacancy system whose lattice parameter is chosen so that the number of atoms per unit volume is the same as in the perfect crystal.

We note here that in calculations of this kind the energy of interest is obtained as the difference of much larger energies. Moreover, these large energies come from calculations on systems having different numbers of electrons. It is therefore important to ensure the best possible cancellation of errors.

Given the very large cut-off energy we use, the error due to incompleteness of the basis set should be negligible. We believe that the most important remaining source

of numerical error is the imperfection of the Brillouin zone sampling. However, a correction can be made for this, which we now outline. In a nearly-free-electron metal like aluminium, the error in the total energy due to imperfect sampling will be similar to the error which would be incurred in a calculation on jellium. Now the quantity  $E(N-1, 1; (N-1)\Omega/N) - (N-1)E(N, 0; \Omega)/N$  defined in equation (17) would be exactly zero in a calculation on jellium using perfect sampling: we subtract the total energy for equal numbers of electrons in jellium at the same electron density. Hence, the value of this difference for calculations on jellium with the sampling actually used gives us an estimate of the sampling error. We call this the 'jellium correction'  $\Delta E_{\text{jell}}$ , and we subtract it as a systematic error from the values of  $E_f^v$  as calculated from equation (17).

We present in table 1 results for the vacancy formation energy, the relaxation energy, and the magnitude of the inward displacement of the nearest neighbours of the vacancy.

Table 1. Calculated values of the fully relaxed vacancy formation energy in aluminium for different sizes of repeating cell. Results are given both without (uncorrected) and with (corrected) the jellium correction. Values of the relaxation displacement of vacancy neighbours are given in units of the nearest neighbour distance.

No of sites in the cell	8	16	27
Relaxed (uncorrected) $E_f^v$ (eV)	0.768	0.882	0.590
Jellium correction $\Delta E_{\text{jell}}$ (eV)	0.103	-0.260	-0.043
Relaxed (corrected) $E_f^v$ (eV)	0.871	0.622	0.547
Relaxation energy (eV)	—	-0.060	-0.075
Relaxation displacement	—	0.011	0.014

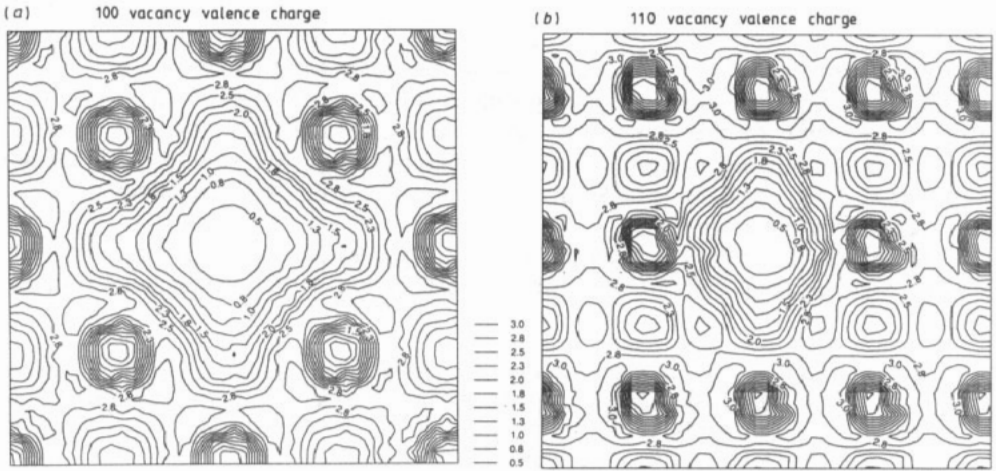
We expect our most reliable result for  $E_f^v$  to be the value for the 27-site system, namely 0.55 eV. This should be compared with the experimental enthalpy of formation of 0.66 eV. The significance of this quite close agreement and a comparison with the results of other recent calculations will be discussed later.

We have calculated the volume of formation  $\Omega_f$  from the defining equation (12). This requires a knowledge of the volume for which the pressure in the vacancy system is zero. To determine this, we have calculated the ground state energy of the 16-site vacancy system for a series of lattice parameters and performed a parabolic fit as we did before for the perfect lattice. We find that the equilibrium volume of the 16-site vacancy system is less than that of the 16-site perfect crystal by  $0.29\Omega_c$ , where  $\Omega_c$  is the atomic volume. The volume of formation  $\Omega_f$ , obtained by adding  $\Omega_c$ , is thus  $0.71\Omega_c$ , which is quite close to the experimental values  $(0.60 \pm 0.02)\Omega_c$  (Emrick and McArdle 1969),  $0.55\Omega_c$  (Babić *et al* 1970) and  $(0.68 \pm 0.1)\Omega_c$  (Harrison and Wilkes 1971) as reviewed by Seeger *et al* (1971).

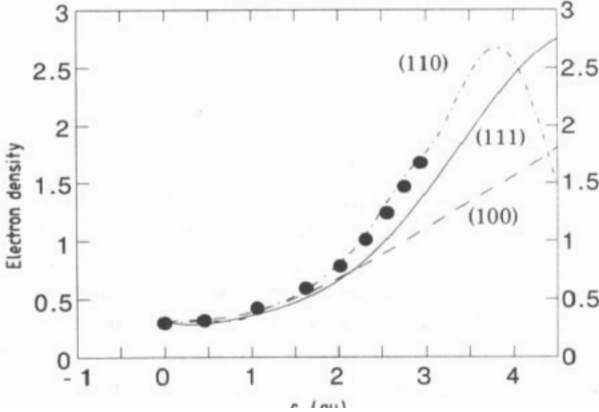
We show in figure 1 the valence electron distribution around the relaxed vacancy in the 27-site system, on the (100) and (110) planes passing through the vacancy site. The strong deviation of the valence charge density from its bulk value in the region of the vacancy, and the spatial anisotropy both within and between the two planes are in accord with the results of previous workers. Figure 2 shows a comparison of our calculated valence charge density in the vacancy region with the results of Chakraborty and Siegel (1983) as reported by Pickett and Klein (1984), which were also obtained by a calculation using a supercell and an *ab initio* pseudopotential. The



very close agreement is of interest in view of the poor value for the vacancy formation energy obtained by those authors.



**Figure 1.** Full valence electron density around the relaxed vacancy in the 27-site system. The density is shown in (a) the (100) plane; (b) the (110) plane, with the vacancy site at the centre of the plot. Values of the density are in  $10^{-2}$  au; in these units the average Al valence density is 2.7.



**Figure 2.** Valence electron density as a function of distance from the centre of the vacancy along the (100), (110) and (111) direction lines, compared with the results of Chakraborty and Siegel (1983) reported by Pickett and Klein (1984) (full circles). Same units as in figure 1.

We have also used these results to study the deviation of the electron density from its perfect crystal value in the region surrounding the vacancy. This is displayed in figure 3. The difference of charge density is obtained by subtracting the perfect lattice density from the density in the unrelaxed vacancy system, both systems having the same lattice parameter. It can be seen that the two contour plots still retain some of the geometrical features of the underlying 'subtracted' lattice, modulating the zero

contour lobes of the oscillating electron charge displacement. The small absolute values of the displaced charge density away from the vacancy strongly suggest that the electronic interaction between vacancies in the 27-site supercell should be negligible.

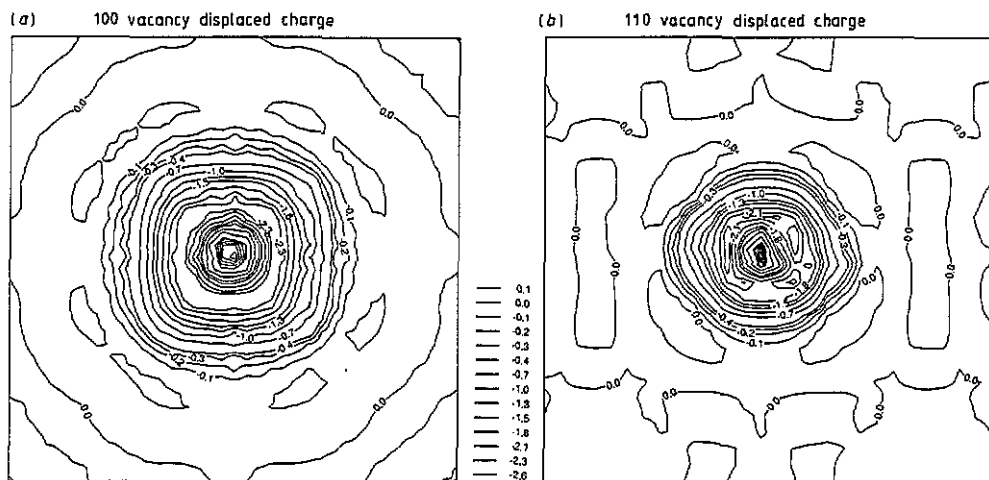


Figure 3. Displaced charge density around the unrelaxed vacancy in the 27-site system. The density is shown in (a) the (100) plane; (b) the (110) plane. Length scales and density units are the same as in figure 1.

To check how much the calculated final formation and relaxation energies depend on the definitions adopted in the biggest system investigated, we make use of the relations (15) and (16) discussed in section 2 to estimate  $E_f^p$  and  $E_f^a$  from our computed value of  $E_f^v$ . The results (without jellium correction) are reported in table 2. In order to verify that the relations (15) and (16) give adequate estimates, we have made a direct calculation of  $E_f^a$  for the 27-site cell, the result of which is also given in table 2. We also include the values of  $E_f^a$  and  $E_f^v$  calculated for the same system without ionic relaxation, and the related relaxation energies.

Table 2. Vacancy energies of formation and relaxation energies for the 27-atom cell from full calculations at constant volume and lattice parameter. Estimates of the formation energy at constant pressure and at constant lattice parameter from equations (15) and (16) are also provided. Jellium correction is not included here.

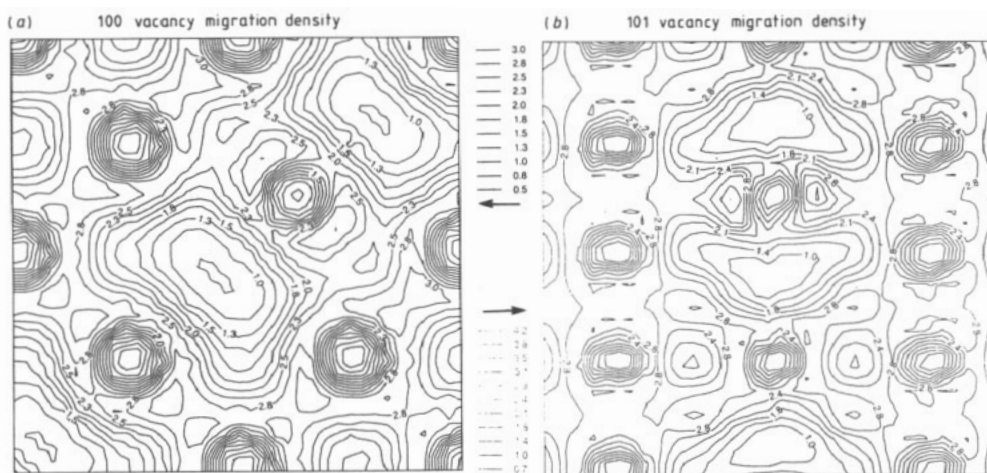
	$E_f^v$ (eV)	$E_f^a$ (full calc) (eV)	$E_f^a$ (est) (eV)	$E_f^p$ (est) (eV)
Ions relaxed	0.589	0.500	0.487	0.483
Ions unrelaxed	0.664	0.552	—	—
Relax. energy	-0.075	-0.052	—	—

### 3.3. Vacancy migration

We have calculated the ground state energy of the relaxed system in which a migrating aluminium atom is fixed midway between two vacancies located in nearest neighbouring perfect lattice sites. We report here results for the 16- and 27-site

systems at the lattice parameters used for the constant volume equilibrium vacancy calculations. From the difference of the total energies we find the migration energy to be respectively  $E_m = 0.59$  eV and  $E_m = 0.57$  eV, to be compared with the experimental value of 0.62 eV (Seeger *et al* 1971).

The role played in the energy evaluation by the (symmetry constrained) ionic relaxation is here, as expected, much bigger than in the monovacancy system. The mid-vacancy location of the migrating ion has the effect of pushing the nearest neighbour ions (the ones in a tetrahedral arrangement with the two lattice vacancy sites) and pulling the second nearest neighbours (the ones at the closest vertices of the cubic faces containing the two vacancies) by the fractions 0.041 and 0.015 of the nearest neighbour distance, to be compared with the equilibrium vacancy results in table 1. Contour plots for the total valence charge density for this unstable equilibrium ionic configuration are provided in figure 4, for the (100) and (110) planes.



**Figure 4.** Full valence electron density for vacancy migration in the 27-site relaxed system. The density is shown in (a) the (100) plane; (b) the (110) plane. The migrating ion is mid-way between the two vacant sites. Same units as in figure 1.

### 3.4. The self-interstitial

We include here preliminary results for the aluminium self-interstitial, calculated for a single interstitial ion placed at the octahedral site, the calculation being performed in the 27-site supercell at the usual cut-off energy (13 Hartrees) adopted elsewhere in this work.

The technical difficulty of the calculation resides mainly in the strong long range ionic displacement field, which makes extremely troublesome the convergence with respect to the system size. For the self-interstitial system in the geometry described we obtain from calculation a formation energy at constant volume of 2.8 eV, to be confronted with the experimental value  $3.2 \pm 0.5$  eV (Schilling 1978) obtained from the Frenkel defect formation energy of  $3.9 \pm 0.5$  eV, and the vacancy formation energy 0.66 eV. The same formation energy as obtained without relaxing the ions is found to be 9.7 eV, which leads to a very large relaxation energy of 6.9 eV. The calculated displacement of the six nearest neighbour atoms amounts to 19% of

the distance from the self-interstitial. Some details about the present theoretical and experimental understanding of this system will be given in the next section.

#### 4. Discussion

In order to provide a framework for the discussion of our results, we summarize in table 3 our calculated values of the vacancy formation and migration energies, the vacancy formation volume and the octahedral site self-interstitial formation energy, together with the experimental values and the results of other recent calculations.

**Table 3.** Comparison of our calculated results for the vacancy formation and migration energies  $E_f$  and  $E_m$ , the vacancy formation volume  $\Omega_f$  in terms of the atomic volume  $\Omega_c$ , and the formation energy  $E_f^{self}$  of the self interstitial, with experimental and other theoretical results. Note that the calculation of Jansen and Klein do not include lattice relaxation.

	$E_f$ (eV)	$E_m$ (eV)	$\Omega_f/\Omega_c$	$E_f^{self}$ (eV)
Theory	0.52 <sup>a</sup>	—	—	10.2 <sup>a</sup>
	0.84 <sup>b</sup>	—	—	—
	0.73 <sup>c</sup>	0.7 <sup>c</sup>	0.66 <sup>c</sup>	3.4 <sup>c</sup>
	0.55 <sup>d</sup>	0.57 <sup>d</sup>	0.72 <sup>d</sup>	2.8 <sup>d</sup>
Experiment	0.66 <sup>e</sup>	0.62 <sup>f</sup>	0.62 <sup>g</sup>	3.2 <sup>f</sup>

<sup>a</sup> Pseudopotential calculation of Jansen and Klein (1989).

<sup>b</sup> APW calculation of Mehl and Klein (1990).

<sup>c</sup> APW calculation of Denteneer and Soler (1990).

<sup>d</sup> Present work.

<sup>e</sup> Fluss *et al* (1978).

<sup>f</sup> Schilling (1978).

<sup>g</sup> Emrick and McArdle (1969).

For all four quantities we find close agreement with the experimental values and the calculated results, where these exist. This is extremely encouraging, since it suggests that the technical problems which troubled earlier calculations have now been largely resolved. The agreement between our pseudopotential results and the APW results is particularly satisfactory. Both approaches are based on the LDA, but apart from that they involve very different approximations. If these other approximations had been reduced to insignificance, the two approaches would give identical results. The fairly small size of the differences, while certainly no cause for complacency, indicates that the approximations in both approaches are under reasonably good control.

In judging the agreement with experiment, it should be noted that experimental values for  $E_f$ ,  $E_m$  and  $\Omega_f$  come from measurements at high temperature, whereas our calculations refer to zero temperature. General arguments suggesting that the temperature dependence of formation and migration enthalpies should be very weak have been given by Gillan (1981) and Harding (1985, 1990). However, the only direct evidence we have on aluminium comes from molecular dynamics simulations of Jacucci *et al* (1981), which indicate that the enthalpy of formation of the vacancy might be increased by as much as 0.1 eV on going from zero temperature to 860 K. This difference is not negligible, but would not affect any of our conclusions.

We believe that the most serious source of inaccuracy in our calculations is the incompleteness of BZ sampling, a problem that also appears to affect the calculations of Denteneer and Soler (1990). The error is most significant for the calculation of  $E_f$ , since this relies on the energies of systems containing different numbers of electrons, so that sampling errors will not cancel. Our 'jellium correction', which is designed to compensate for these errors, turns out to be negligible for our largest cell, but it would still be desirable to improve this aspect of the method. The  $k \cdot p$  technique recently developed by Robertson and Payne (1990) may be the way to do this.

In the present type of calculation, the results should, in principle, be extrapolated to infinite system size, and there is an uncertainty involved in doing this. This problem is related to the question of the exact definition to be adopted for such quantities as the energy of formation, which we have discussed in section 2.2. Although the energies of vacancy formation under conditions of constant volume, pressure or lattice parameter become identical for an infinite system, the differences between them are not negligible for computationally tractable systems. As we have shown (see table 2), the vacancy formation energy may be affected by the definition adopted by as much as 0.1 eV, even for the 27-site system.

The encouraging preliminary results for the self-interstitial which we compare in table 3 with other theoretical predictions are now being followed up by a more detailed examination of this problem, in which we plan to study the stable configuration of this defect, which both experiment and previous calculations indicate is not the octahedral configuration treated here (Schilling 1978, Sindzingre 1988), though the energy differences between competing configurations are expected to be small. We also note that we have used the present methods in a detailed study of the energetics of hydrogen in aluminium, the results of which will be reported in a companion paper.

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### References

- Babić E, Girt R, Krsnik R, Leontić B and Zorić I 1970 *Phys. Lett.* 33A 368  
 Bachelet G B, Hamann D R and Schlüter M 1982 *Phys. Rev. B* 26 4199  
 Car R and Parrinello M 1985 *Phys. Rev. Lett.* 55 2471  
 Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* 45 566  
 Chakraborty B, Siegel R W and Pickett W E 1981 *Phys. Rev. B* 24 5445  
 Chakraborty B and Siegel R W 1983 *Phys. Rev. B* 27 4535  
 Denteneer P J H and Soler J M 1990 *Preprint*  
 Emrick R M and McArdle P B 1969 *Phys. Rev.* 188 1156  
 Evans R and Finnis M W 1976 *J. Phys. F: Met. Phys.* 6 483  
 Fluss M J, Smedskjaer L C, Chason M K, Legnini D G and Siegel R W 1978 *Phys. Rev. B* 17 3444  
 Gillan M J 1981 *Phil. Mag.* A 43 301  
 Gillan M J 1989 *J. Phys.: Condens. Matter* 1 689  
 Harding J H 1985 *Phys. Rev. B* 32 6861  
 Harding J H 1990 *Rep. Prog. Phys.* 53 1403  
 Jacucci G, Taylor R, Tenenbaum A and van Doan N 1981 *J. Phys. F: Met. Phys.* 11 793

- Jansen R W and Klein B M 1989 *J. Phys.: Condens. Matter* **1** 8359  
Kleinman L and Bylander D M 1982 *Phys. Rev. Lett.* **48** 1425  
Mehl M J and Klein B M 1990 *Preprint*  
Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188  
Perdew J and Zunger A 1981 *Phys. Rev. B* **23** 5048  
Pickett W E and Klein B M 1984 *Phys. Rev. B* **29** 1588  
Robertson I J and Payne M C 1990 *J. Phys.: Condens. Matter* **2** 9837  
Schilling W 1978 *J. Nucl. Mater.* **69** 465  
Seeger A, Wolf D and Mehrer H 1971 *Phys. Status Solidi b* **48** 481  
Sindzingre P 1988 *Phil. Mag.* **57** 877  
Stumpf R, Gonze X and Scheffler M 1990 *Research Report of the Fritz Haber Institute*