Self-consistent electronic structure of a vacancy in aluminum

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The electronic structure of a vacancy in Al has been studied using a self-consistent pseudopotential scheme, in which the environment of the vacancy was simulated by a supercell containing 27 atomic sites. The charge-density perturbation due to the vacancy was found to be quite short ranged, indicating that the supercell used was large enough to effectively isolate individual vacancy potentials. At the center of the vacancy, the charge density was 0.27 electrons per atom; this value is compared with the results of previous calculations. The local densities of states at a vacancy and its first- and third-nearest-neighbor shells were investigated, and evidence for a vacancy-associated resonance state was found at ~0.3 Ry below the Fermi energy. Finally, the vacancy-formation energy was also calculated in the ideal (unrelaxed) structure using the $\vec{G}$-space formalism for calculating total energies. A value of 1.9 eV was obtained; this is 2.9 times the experimental value. The effects of lattice relaxation, the supercell method, and defect potentials on the electronic structure and the resulting formation energy are discussed.

I. INTRODUCTION

A knowledge of the detailed electronic structure of atomic defects in metals is of considerable interest for many metal physics applications. In spite of widespread interest in the problem, realistic calculations have been scarce. Two methods have been widely used in dealing with defects in simple metals, (i) jellium calculations and (ii) the pseudo-potential approach with linear screening. The results of these calculations have been summarized and discussed by Evans and Finnis.[1] Their work shows that both methods are inadequate for atomic defect calculations in a polyvalent metal with high electron density such as aluminum. The method of pair potentials has been applied to the study of defects in aluminum by Jacucci et al.[2] They concluded that rescreening effects giving rise to three-body count for differences between their calculated value

of the vacancy-formation energy and their experimental value. A completely realistic self-consistent calculation of the electronic structure of the vacancy in Al has, to our knowledge, never before been attempted. The salient features of a realistic defect calculation are (i) self-consistency of the potential, allowing for proper electronic screening of the defect, as well as for structural relaxation around the defect and (ii) accurate treatment of the electronic structure of the host metal.

Two theoretical approaches have been developed which are capable of incorporating these features in a defect calculation, the supercell[3] and the Green's-function[4] methods. The augmented-plane-wave (APW) calculation in Al by Gupta and Siegel[5] is the only previous application, to our knowledge, of the supercell method to lattice defects in metals. However, this calculation was not self-consistent, a clear limitation when treating the

vacancy. Singhal and Callaway[6] have calculated the energetics of vacancy defect formation in Al by a Green's-function method, but also in a non-self-consistent manner. The electronic structure of various impurities in Cu have been calculated by Zeller and Dederichs[7] using a KKR (Korringa-Kohn-Rostoker) Green's-function scheme, which was partially self-consistent in that the charge density within the defect muffin tin was treated self-consistently. However, the electronic redistribution in neither the interstices nor the neighboring muffin tins was taken into account.

Owing to its simplicity, the supercell approach is very appealing. Its major disadvantage is that significant defect-wave-function overlaps can be present that may give rise to spurious defect-interaction effects. The total charge density and the resulting potential, however, are considerably less affected by such effects. The Green's-function method treats a truly isolated defect, and is superior to the supercell method in that respect. However, the calculation of the total energy of a system is not a simple task in the Green's-function approach, whereas it is relatively simple in the supercell method, once the eigenvalues and eigenfunctions have been determined. Our interest in calculating formation energies of atomic defects in metals prompted us to choose the supercell method for the present work.

In this paper we present the results of calculations of the electronic structure of a vacancy in Al using a self-consistent pseudopotential scheme. Self-consistency in the present context implies the self-consistent electronic response to a given structural model. Lattice relaxations have not been dealt with completely in the present work, but they have been estimated and a scheme for self-consistently evaluating the relaxations is presented. To our knowledge, this is the first self-consistent calculation of this type for defects in metals. The method is not restricted to Al; it can also be readily generalized to treat transition metals. Aluminum was chosen as a test case because of the availability of a host of relevant and realistic experimental data, and the simplicity of its electronic structure.

The remainder of the paper is organized as follows. In Sec. II the self-consistent procedure and the method for evaluating the total energy are reviewed. In Sec. III the results for the electronic structure and the formation energy are presented and discussed, and in Sec. IV the adequacy of the method and further improvements are discussed.

II. CALCULATIONS

A detailed description of the self-consistent pseudopotential scheme applied to a superlattice of vacancies in Si has been presented elsewhere. In this section we give a brief description of the present calculations, which were carried out both in defect-free Al and in Al containing a regular array of vacancies. The infinite Al crystal was divided into large face-centered cubic (fcc) unit cells, each containing 27 atoms for the perfect lattice, or 26 atoms plus a vacancy forming a vacancy superlattice.[5] Test computational runs with smaller supercell sizes indicated that a cell of at least this size is needed to provide the essential physics of the system. In this supercell configuration nearest-neighbor vacancies have common third-nearest-neighbor Al atoms. Hence, to the extent that the perturbaton owing to the vacancy does not extend beyond second-nearest neighbors, the supercell used can effectively isolate the vacancies.

The self-consistent computational loop was initiated with an empirical potential fitted to crystalline properties. This potential was of the form

$$U_{emp}(\vec{G}) = V_{emp}(\,|\vec{G}|\,)S(\vec{G}), \qquad (1)$$

where $\vec{G}$ is a reciprocal-lattice vector and the structure factor

$$S(\vec{G}) = (1/N)\sum_i \exp(-i\vec{G}\cdot\vec{\tau}_i)$$

describes the positions $\vec{\tau}_i$ of the N aluminum atoms in the supercell with or without vacancies. The form factors $V_{emp}(\,|\vec{G}|\,)$ were derived from a continuous interpolation of the form

$$V_{emp}(q) = \frac{a_1(q^2 - a_2)}{\exp[a_3(q^2 - a_4)] + 1}. \qquad (2)$$

The four parameters a_i are given in Table I.[8] Since periodicity is maintained in the system with defects by the use of a superlattice of vacancies, instead of the more natural random distribution, standard pseudopotential methods could be applied to obtain the band structure ϵ_k and the wave function $\psi_k(\vec{r})$, where k represents both the wave vector $\vec{k}$ and the band index n. The total valence charge density was then evaluated from the computed wave functions by summation over the occupied states as

$$\rho(\vec{r}) = \sum_k^{occ} |\psi_k(\vec{r})|^2. \qquad (3)$$

The Hartree screening potential and the Hedin-Lundqvist[9] form of the exchange-correlation potential were obtained from this charge density. The total screening potential was added to an atomic Al^{3+} ionic potential, $U_{ion}(\vec{G}) = V_{ion}(|\vec{G}|) S(\vec{G})$, to form the total input potential for the next iteration. This process was iterated until the potential was self-consistent. For the ionic potential, a local approximation of an Abarenkov-Heine atomic model potential was fitted to the following four-parameter model:

$$V_{ion}(q) = \frac{b_1}{q^2}(\cos b_2 q + b_3)\exp(b_4 q^4) . \qquad (4)$$

The results of a self-consistent bulk band-structure calculation using this potential were in good agreement with those of empirical band-structure calculations.[8] The parameters are presented in Table I. Having been fitted to experimental energy bands, this potential describes wave functions only ap-

TABLE I. Form-factor parameters for the empirical Al pseudopotential [Eq. (2)] and for the ionic Al^{3+} pseudopotential [Eq. (4)].

V_{emp}	V_{ion}
$a_1 = 0.611\,99$	$b_1 = -0.775\,98$
$a_2 = 1.88$	$b_2 = 1.046\,80$
$a_3 = 0.65$	$b_3 = -0.133\,89$
$a_4 = -0.30$	$b_4 = -0.029\,44$

proximately. In Sec. IV we discuss the incorporation of a first-principles ionic pseudopotential, better suited for total energy calculations, into the present scheme.

To calculate the total energy, we applied the recently developed $\vec{G}$-space formalism.[10] The density-functional expression for the total energy associated with the pseudopotential eigenvalue equation is[11]

$$E_{tot} = \sum_k^{occ} \epsilon_k - \frac{1}{2} \int \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}\, d\vec{r}' + \int \rho(\vec{r})[\epsilon_{xc}(\rho(\vec{r})) - V_{xc}(\rho(\vec{r}))] d\vec{r} + \sum_m \sum_n \frac{Z^2}{|\vec{\tau}_m - \vec{\tau}_n|}, \qquad (5)$$

where ϵ_k are the one-electron eigenvalues and the summation in the first term runs only over occupied states. The Hedin-Lundqvist form of the local exchange-correlation potential V_{xc} is related to the exchange-correlation energy ϵ_{xc} by

$$V_{xc} = \epsilon_{xc} + \rho\frac{d\epsilon_{xc}}{d\rho}. \qquad (6)$$

The last term in Eq. (5) is the ion-ion interaction energy with Z the ionic charge. The momentum-space expression for E_{tot}, the total energy per unit cell, developed by Ihm, Zunger, and Cohen,[10] is

$$E_{tot} = \sum_k^{occ} \epsilon_k - \frac{1}{2} \sum_{\vec{G} \neq 0}^{\vec{G}_{max}^{(1)}} V_{Coul}(\vec{G})\rho(\vec{G})$$

$$- \sum^{\vec{G}_{max}^{(1)}} V_{xc}(\vec{G})\rho(\vec{G})$$

$$+ \sum^{\vec{G}_{max}^{(1)}} \epsilon_{xc}(\vec{G})\rho(\vec{G}) + \alpha Z + E_{Ewald}, \qquad (7)$$

where V_{Coul} is the electron-electron repulsion term. The term αZ is a correction due to the pseudonature of the potential and measures the repulsiveness of the potential,

$$\alpha = \lim_{|\vec{G}| \to 0} \left[V_{ion}(\vec{G}) + \frac{8\pi Z}{|\vec{G}|^2} \right]. \qquad (8)$$

The term E_{Ewald} is the Ewald core-core interaction energy.[12] The $|\vec{G}| = 0$ term is excluded from the sum over $V_{Coul}(\vec{G})$, and $\vec{G}_{max}^{(1)}$ denotes the summation limit.

The accuracy of the calculated total energy depends strongly on the accuracy of both the calculated charge density and the eigenvalue spectra. In the remaining part of this section we discuss the convergence properties of the various quantities entering the total energy expression. The computational conditions which govern the precision of the calculated total energy are (i) the number of plane waves (with cutoff $\vec{G}_{max}^{(2)}$) used to expand the crystal wave functions, (ii) the number of Fourier components (cutoff $\vec{G}_{max}^{(3)}$) used to expand the potential and charge density, (iii) the number of k points used to sample the Brillouin zone (BZ) for computing the charge density [Eq. (3)], and (iv) the tolerance criterion for self-consistency. Finally, in the total energy equation, the various terms have to be stablized with respect to the cutoff $\vec{G}_{max}^{(1)}$. The convergence parameter $\vec{G}_{max}^{(2)}$ was varied until the eigenvalues were stabilized to within 10^{-3} Ry (~ 0.01 eV). This required about 500 plane waves corresponding to a kinetic energy cutoff[13] of $E_1 = |\vec{G}_{max}^{(2)}|^2 = 4.6$ Ry; an additional ~ 500 plane waves were included via the Löwdin perturbation scheme.[13]

TABLE II. Components of the total energy per atom of a 27-atom Al supercell with and without a vacancy. All energies are given in Ry. The atomic volume is the same in both systems. V_{scr} denotes the screening field $(V_{Coul} + V_{xc})$. The vacancy formation energy is obtained by taking the difference in the total energy per atom and multiplying by 26. The prime on a summation indicates that the $|\vec{G}| = 0$ term is excluded.

| Quantities	Vacancy	Bulk
$\sum \epsilon_k$	−0.6269	−0.6026
$\frac{1}{2} \sum' V_{Coul}(\vec{G})n(\vec{G})$	0.0582	0.0070
$\sum \epsilon_{xc}(\vec{G})n(\vec{G})$	−1.6239	−1.6171
$\sum V_{xc}(\vec{G})n(\vec{G})$	−2.1090	−2.1000
$-\sum V_{scr}(\vec{G})n(\vec{G})$	1.9926	2.0861
αZ	1.2755	1.2755
E_{Ewald}	−5.3109	−5.3898
E_{tot}	−4.2355	−4.2409
E_{1v}^{F}	0.14 (1.9 eV)	

In aluminum, the variation in charge density across a cell is relatively smooth compared to transition metals, and the number of plane waves needed for reasonable convergence of the screening potential is not too large. We found that about 1400 plane waves were needed to stabilize the various screening potential components to within 10^{-5} Ry. Unlike that in a semiconductor, e.g., Si,[3] the total charge density in Al is not well represented by the charge density from a single symmetry point. The nature of the wave functions varies sufficiently across the cell to warrant a finer sampling of the BZ. We used ten fcc special k points[14] to compute the charge density. The next lower number of two special k points proved to be insufficient in providing the required accuracy; any finer sample proved to be prohibitively expensive. The difference in charge density between two and ten special k points was as much as 10%. The input potential for the nth iteration was taken to be a weighted sum of the input and output potentials of the $(n-1)$th interaction, to damp out fluctuations arising from the divergent nature of the small-$\vec{G}$ components of the Hartree and ionic potentials. The steps of the self-consistency procedure were repeated until the subsequent output potentials were stabilized to within 10^{-5} Ry. The number of iterations needed for this stability was ~ 10. For the total energy summations, it was found that about 1600 plane waves were needed to stabilize all three components of the screening field in Eq. (7) to within 10^{-5} Ry. The repulsive energy was obtained from the $\vec{G}=0$ value of the ionic potential and the Ewald energy was computed as a function of the cell volume, valence charge, and atomic po-

sitions. In order to get a reasonable result for the vacancy-formation energy, extreme accuracy is needed in each of the terms entering the total energy expression (cf. Table II). In the following section we present our results for the charge density, local density of states, and the formation energy of a vacancy in aluminum.

III. RESULTS

The electronic structure of the vacancy was calculated in the unrelaxed lattice structure. The self-consistent valence charge density in the (100) plane is shown in Fig. 1. A necessary condition for simulating noninteracting defects is that the charge density away from the vacancy site resembles the bulk Al charge density. A plot of the difference between the charge density in bulk, defect-free Al and that in Al with a superlattice of vacancies (Fig. 2) illustrates the predominantly local nature of the perturbation, but also gives evidence for some, quite subtle, nonlocal effects. These are seen most clearly in the regions intermediate between nearest-neighbor vacancies in the supercell. The magnitudes of these effects, although small [see Fig. 2(b)], are clearly affected by the size of the present supercell. While such effects could yield a significant contribution to the calculated energy of the defect system described by the supercell, their perturbtaion to the calculated electronic structure is seen to be minimal.

It is interesting to compare the charge-density calculated here with those resulting from the self-consistent jellium calculations of Manninen and Nieminen[15] and the non-self-consistent APW calculations of Gupta and Siegel.[5] The APW value for
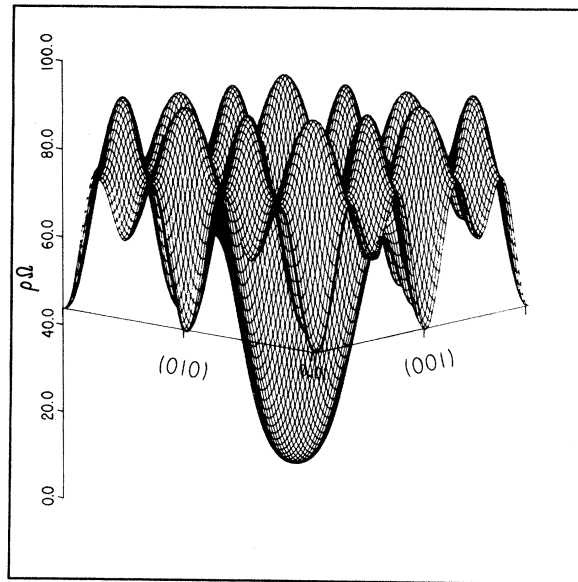
(a)
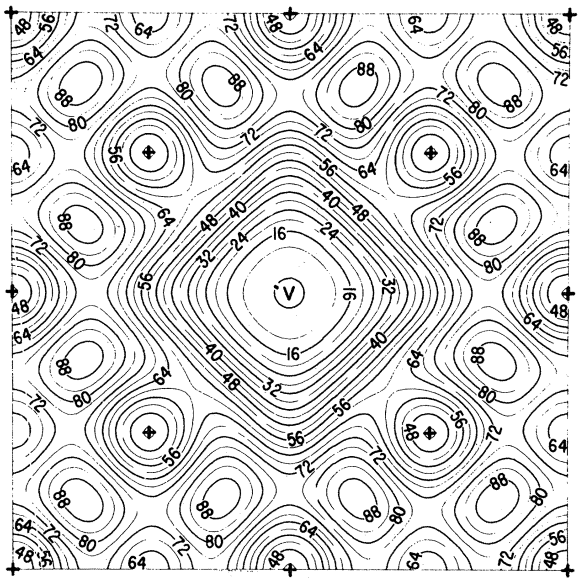
(b)

FIG. 1. (a) Valence charge density $(\rho)\times$ the supercell volume (Ω) around a vacancy in Al on the (100) plane in atomic units; the vacancy sits at the center of the plane. In atomic units, the total valence charge in the supercell is 78; the supercell volume $\Omega=27\Omega_0$, where Ω_0 is the primitive unit-cell volume for Al. (b) Contour plot of the charge distribution shown in (a). The vacancy is marked by V and the atoms by $+$.

the charge density at the center of the vacancy normalized to the supercell volume is 1.87×10^{-3} a.u. (0.21 electrons per atom) as compared to the present value of 2.48×10^{-3} a.u. (0.27 electron per atom). The jellium result for the charge density at the center of the vacancy[15] is 4.12×10^{-3} a.u. (0.46
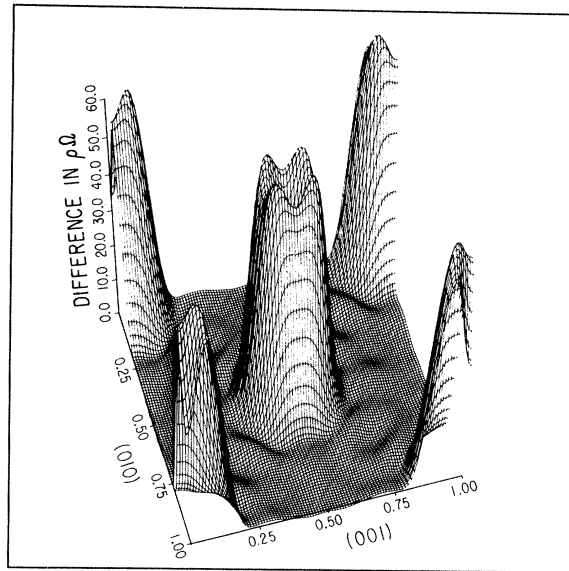
(a)
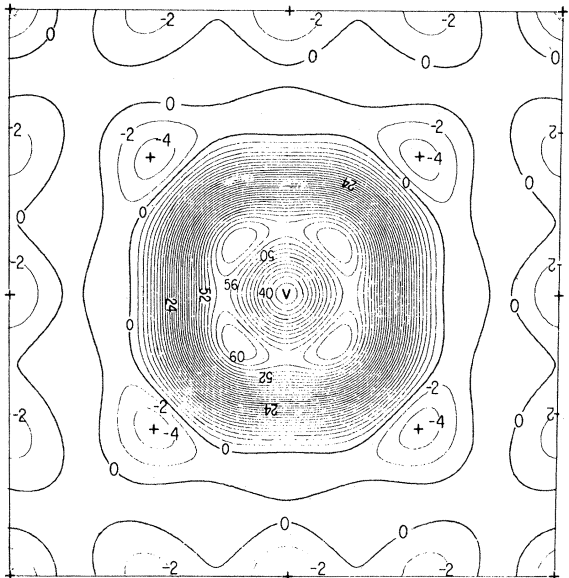
(b)

FIG. 2. (a) Difference in $\rho\Omega$ between the lattice without vacancies and the supercell with vacancies located in the center and corners of the (100) plane, in atomic units. (b) Contour plot of (a) showing only the central 13 atom sites; the atom sites are denoted by $+$ and the vacancy by V (cf. Fig. 1).

electrons per atom). The inclusion of the actual ionic potential thus causes a significant change in the charge density; the effect of self-consistency is smaller. It is interesting to note further that Manninen and Nieminen,[15] by including an average variational potential in conjunction with their pure jellium (a spherical solid model) calculation, were able to bring their value for the charge density at

the center of the vacancy down to 2.5×10^{-3} a.u., in excellent agreement with our result.

While the range of the charge-density redistribution from the vacancy shown in Fig. 2 does not preclude overlap of individual state wave functions of neighboring vacancies in the supercell, it nevertheless does indicate that the supercell used was large enough to effectively isolate the vacancy potentials and the calculated electronic structure of the vacancies. Spherical averages of the various componets of the vacancy potential are shown in Fig. 3. The nonspherical contributions are small. The differences between the starting empirical potential and the final self-consistent potential are significant. The self-consistent potential is shallower than the empirical potential, and the charge inside the vacancy resulting from it is smaller than that from the empirical potential. The long-range tail of the ionic potential is completely screened by the Hartree and exchange-correlation potentials arising from the electronic rearrangement in the vicinity of the vacancy. The total defect potential is quite short ranged and effectively does not extend beyond the nearest-neighbor atom located at 2.9 Å.

The total and local densities of states (LDOS), $\sum_k \delta(\epsilon - \epsilon_k) W_k^{(j)}$, were calculated using the tetrahedron method[16] with 128 tetrahedra in $\frac{1}{48}$th of the BZ. The weights $W_k^{(j)}$ were chosen to be the fraction of the charge of the state k within a sphere of radius R centered at the jth site, with $W_k = 1$ for the total density of states. The value of R was taken to be half the nearest-neighbor distance. The results for the LDOS from the vacancy and from
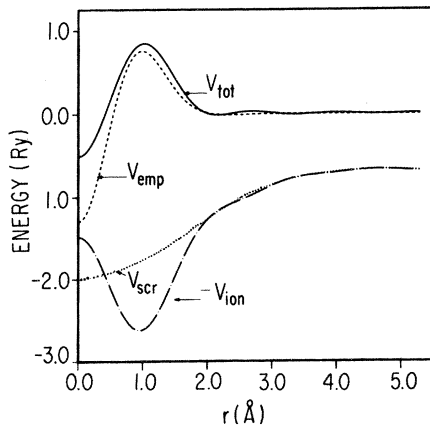
its first- and third-nearest-neighbor shells are shown in Fig. 4, along with the total DOS for the supercell containing vacancies. A variety of structure can be seen in the calculated DOS curves. Each of the peaks was examined for the presence of a related vacancy-associated resonance state; only the peak near -0.3 Ry was found to have one. On comparing the LDOS from the first- and third-nearest-neighbor shells, it can be seen that the small peak in the energy range -0.38 to -0.28 Ry (all energies measured from the Fermi energy) diminishes in magnitude as one moves further away from the vacancy; this points to the existence of a resonance state caused by the vacancy potential. In a nearly free-electron metal like aluminum, the repulsive potential of the vacancy can give rise to a resonance state only in a region of fairly high density of states, i.e., away from band gaps.[17] Resonance states of this nature have a fairly large energy broadening, and fall off only as $1/r$ away from the scattering site.[17] We, therefore, do not expect to see any sharp structure in the density of states, but only a broad peak as observed. Unlike a truly localized state, which falls off exponentially with

FIG. 3. Self-consistent vacancy potentials. The starting empirical potential is V_{emp}, the potential of the missing ion is V_{ion}, the screening potential due to the redistribution of electrons is V_{scr}, and the final self-consistent potential of V_{tot}.
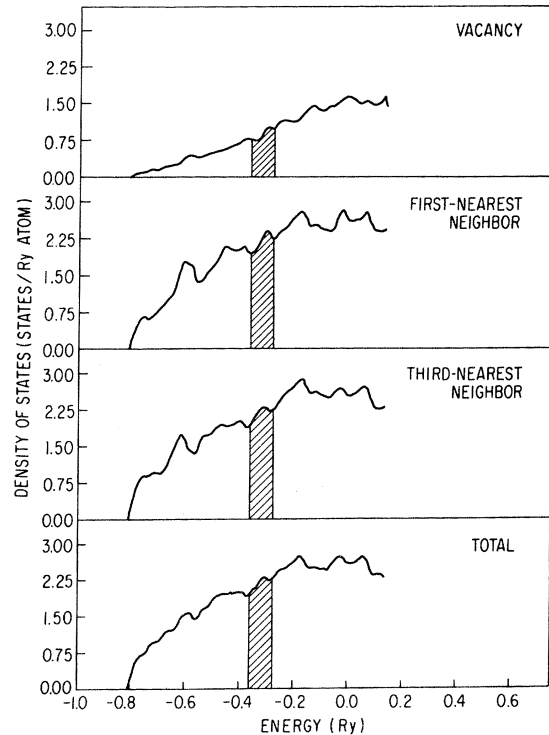

FIG. 4. The local densities of states for the unrelaxed aluminum vacancy and the first- and third-nearest-neighbor shells are compared with the total density of states for the supercell containing vacancies. The resonance region (see text) is crosshatched.
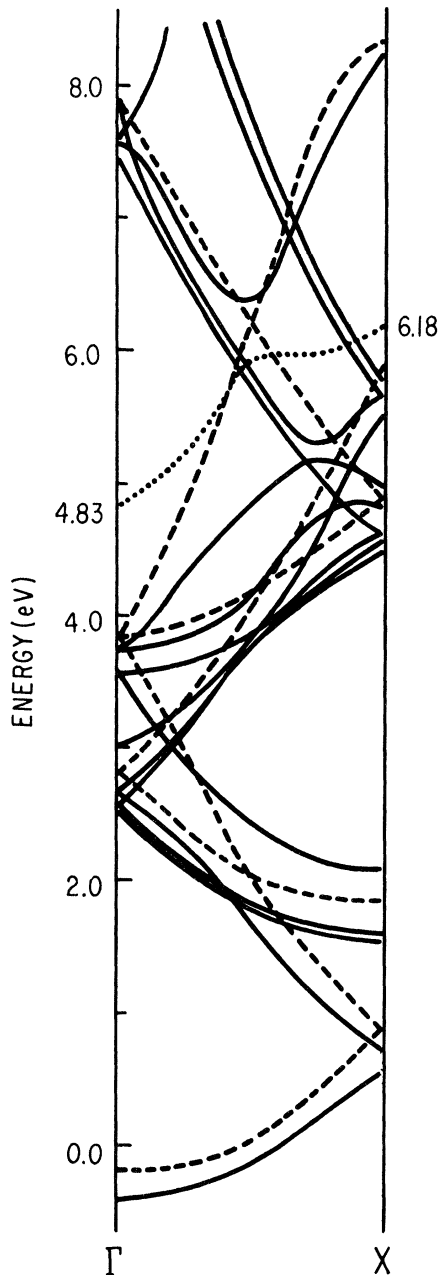
FIG. 5. The energy bands in the Γ-X direction for a 27-atom unit cell of Al (dashed lines) and Al with a superlattice of vacancies (solid lines); the resonant state, between 4.83 and 6.18 eV, associated with the vacancy is indicated by the dotted curve.

distance, these resonance states are fairly extended, and might give rise to some overlap of states from neighboring vacancies in the superlattice.

To investigate further the nature of resonance states associated with a vacancy in Al, states along the Δ direction were compared with those of a defect-free superlattice of Al, as shown in Fig. 5.

A vacancy-related state of Δ_1 symmetry (s-like) was observed; the state is occupied, and has a dispersion of ~ 1.35 eV (~ 0.1 Ry). The position of this state correlates very well with a sharp change in the phase shift calculated by Singhal and Callaway.[6] The charge density related to the vacancy-associated resonance state is shown in Fig. 6. The presence of significant charge near the third-nearest neighbors is clearly seen in Fig. 6(b). This charge lies at the tetrahedrally coordinated interstitial site of the fcc vacancy superlattice, and thus represents a superposition of contributions from four separate vacancies. This clearly indicates that the supercell used was not large enough to completely isolate the individual vacancy resonances. However, while significant spurious contributions to the vacancy-formation energy could result from this overlap, the resulting electronic structure would be perturbed but little, as indicated also by Fig. 2, since the peak magnitudes of the charge density associated with the resonance state from each individual vacancy is rather small in comparison with the total charge-density differences associated with an individual vacancy (cf. Fig. 2).

The total energy calculations were carried out using the reciprocal-space method.[10] The formation energy (E_{1v}^F) of a vacancy is the difference between the energy (E_v) of a system of N atoms with a vacancy occupying a volume Ω' and the energy (E_B) of a perfect crystal of N atoms at the equilibrium volume Ω.[18,19] Thus,

$$E_{1v}^F = E_v(N,\Omega') - E_B(N,\Omega).\qquad(9)$$

Since Ω is the equilibrium volume, Ω' can be replaced by Ω in Eq. (9) causing only an error of order $(1/N)^2$. For the 27-atom supercell used here, this amounts to a correction of ~ 1 mRy. Then,

$$E_{1v}^F = E_v(N,\Omega) - E_B(N,\Omega).\qquad(10)$$

The supercell containing 26 atoms and 1 vacancy was thus taken to have a volume equal to that of a perfect Al lattice containing 26 atoms. This is the closest approximation to the actual constant-pressure experimental environment that could be realized in the calculations. No lattice relaxation was included in the calculation of the formation energy. The lattice constant of Al was taken to be 4.050 Å, the room-temperature value.[20]

The various components of the total energy for the two systems (27 Al atoms and 26 Al atoms plus 1 vacancy) are shown in Table II. The total valence electron contribution to the energy per ion for Al (4.24 Ry) is in good agreement with the experimental value of 4.16 Ry, taken as the sum of
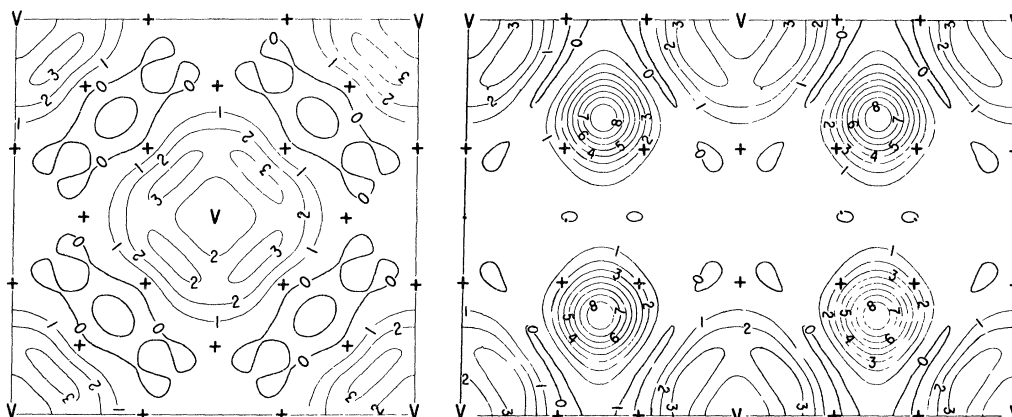
FIG. 6. Charge density of the vacancy-associated resonance state near -0.3 Ry on (a) the (100) plane and (b) the (110) plane. Vacancies are indicated by V and atoms by $+$.

the cohesive energy[21] and the atomic ionization potentials.[22] The calculated vacancy-formation energy (1.9 eV) is larger, by a factor of 2.9, than the experimentally observed value of 0.66 eV.[23,24] For comparison, the only other *ab inito* calculation of E_{1v}^{F} in Al, that of Singhal and Callaway,[6] yielded a value of 6.1 eV for the formation energy. There are three major factors that could have been responsible for the present discrepancy: (i) lattice relaxations around the vacancy, (ii) spurious defect-defect interactions introduced by the supercell, and (iii) inability of the present ionic potential to accurately reproduce variations in the total energy, although the latter is most likely the most important of these. In the next section we discuss these factors in detail.

IV. DISCUSSION

The question of the effect of lattice relaxation on the formation energy has not been addressed in the present work, although it is expected to be small compared with the discrepancy between theory and experiment. A method has been developed, however, which allows the relaxations to be built into the calculation in a self-consistent manner; it is in the process of being applied to Al. The forces on the atoms surrounding the vacancy can be estimated using the Hellman-Feynman theorem for the pseudopotential Hamiltonian,[10,25] once the self-consistent potential is known. This information can be used to estimate the relaxation of the atoms, and the forces can then be recalculated in the new structural configuration. The process can then be repeated until equilibrium is reached.

This method was applied to the vacancy in aluminum. The forces calculated in the unrelaxed

configuration were essentially zero for the second-nearest neighbors and radially inward for the first-nearest neighbors. In the subsequent iterations only the first-nearest-neighbor positions were changed. The forces on the third-nearest-neighbor atoms were not calculated, since each third-nearest-neighbor atom of a vacancy in the 27-atom supercell is also a third-nearest neighbor of two other vacancies. The forces on the first-nearest neighbors were found to change sign between an inward relaxation of 2% and one of 2.5%, implying an equilibrium inward relaxation between these two values.

Minier *et al.*[26] have measured the nuclear quadrupole couplings around a vacancy by the NMR field-cycling technique. Their results seemed to indicate a significant relaxation of the first neighbors, but no quadrupolar transitions were detected which could be associated with the second neighbors. The present estimate of both first- and second-nearest-neighbor relaxations appear to be consistent with their experimental results.[27] Furthermore, the present results appear to be in reasonable agreement with an estimate[28] of the vacancy-relaxation volume in Al extracted from the diffuse x-ray intensity at small scattering angles measured in irradiated samples.[29] Therefore, the relaxation energy is not expected to be very large in this system, and the possibility of its accounting for the large discrepancy in the vacancy-formation energy appears to be slim. For this reason, and because of the uncertainties associated with the supercell size and particularly the ionic potential in the present work, the total energy was not recalculated for each relaxed structure here, since the calculation is expensive. A more thorough investigation of the atomic relaxations will be carried out once these

other uncertainties have been resolved.

The supercell used was not large enough to completely isolate individual vacancy-related states, as was mentioned earlier. The magnitude of the interaction energy coming from nearest-neighbor vacancy-vacancy interactions within the superlattice might be sigificant, but it is not expected to completely account for the difference between theory and experiment. A comparison of the present results with those from a larger supercell would, it is hoped, resolve many of the uncertainties stemming from the supercell method itself; however, the calculations (e.g., for a 64-atom supercell) would be prohibitively expensive at present in the light of the accuracy required for such a comparison.

The third and probably the most significant factor affecting the results of the present calculation is the ionic potential used. A potential fitted to band-structure results cannot be expected to yield accurate wave functions; this might affect the calculated total energy significantly. Although the total valence-electron contribution to the total energy was in good agreement with experiment, the calculated bulk modulus was not. We carried out a total energy calculation for defect-free Al for six values of the lattice parameter (a). The resulting values were than fitted to a polynomial in a. The equilibrium lattice constant obtained was 3.870 Å, which corresponds to 0-K and differs from the extrapolated (0-K) experimental value[30] of 4.045 Å by 4.3%. The bulk modulus was found to be 1.2×10^{12} dyn cm^{-2}, a value which is 36% greater than the experimental value[31] of 0.88×10^{12} dyn cm^{-2}. The ionic potential used in the present work is thus seen to fail in accurately reproducing variations in the total energy. This is most probably the single largest drawback of the present calculations, but is a situation that may now be improved upon.

Ionic potentials to be used for self-consistent calculations of total energies must have more stringent requirements imposed on them. Such first-principles ionic potentials have recently been formulated.[32,33] These potentials have three attractive properties for the present type of calculation: (i) they yield very accurate wave functions outside the core, (ii) they are norm conserving, hence the use of pseudocharge densities as real objects in self-consistent calculations of total energies is justified, and (iii) they have optimum transferability between different environments. This latter property rigorously eliminates the dependence of E_{1v}^F on αZ in a constant-volume calculation such as the present one [cf. Eq. (10)].

A first-principles ionic pseudopotential for aluminum[34] has recently become available. Using this potential, the equilibrium lattice constant and bulk modulus of Al have been calculated by carrying out a total energy calculation at five values of the lattice constant. A value of 4.047 Å was obtained for the equilibrium lattice constant, which is only 0.05% larger than that extrapolated to 0 K from the experimental values. The calculated value for the bulk modulus is 0.99×10^{12} dyn cm^{-2}, about 13% greater than the experimental value. The bulk properties of Al have been calculated before by Janak, Moruzzi, and Williams.[35] Their calculated values for the lattice constant and bulk modulus are 4.015 Å and 0.801×10^{12} dyn cm^{-2}, respectively. The first-principles ionic pseudopotential[34] is thus seen to yield more accurate results for the bulk properties of aluminum. This result is encouraging with respect to using this potential in vacancy calculations. Therefore, formation energy calculations for a vacancy in Al are being initiated with this new potential; the results will be published in a subsequent paper.

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[20]Two aspects regarding this choice of lattice constant might be considered further in future calculations using a more appropriate potential (see Sec. IV): (1) The comparison with experiment would be more appropriate using a lattice constant corresponding to $\sim 250-400\,°C$, from the region in which E^F_{1v} measurements are made, and (2) the effect of using a measured lattice constant as opposed to one obtained from the potential being used in the calculation of E^F_{1v} should be explored. Both of these aspects should yield effects small with respect to the present discrepancy between theory and experiment.

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