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Electronic structure of a vacancy in aluminum

S. P. Singhal and J. Callaway
Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803

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The electronic structure of an isolated atomic vacancy in metallic aluminum is investigated on the basis of solid-state scattering theory. A total scattering phase shift and the change in the sum of the one-electron energies are computed with reference to a band calculation using the LCGO (linear combination of Gaussian orbitals) method. The effects of lattice relaxation are included. The calculation is made approximately self-consistent using a dielectric function calculated (separately) for a perfect aluminum crystal. Problems associated with the calculation of the formation energy are discussed.

I. INTRODUCTION

This paper presents the results of a study of the electronic structure of a single vacancy in metallic aluminum. Realistic potentials are obtained from a self-consistent energy-band calculation for a perfect crystal of aluminum,[1,2] which employed the LCGO (linear combination of Gaussian orbitals) method.[3] The relaxation of the lattice in the vicinity of the vacancy has been computed[4] using the method of lattice statics.[5,6] The displacement of atoms in the first two shells around the vacancy has been included in the calculation of the defect potential. This potential was made approximately self-consistent by screening it with the dielectric function for the perfect aluminum crystal obtained from a separate calculation.[7] This dielectric function includes an explicit exchange correction.

The change in energy of the system in the presence of a vacancy can be split into two parts: the change in the total one-electron energy, and the change in the electron interaction energy. The former is computed here using the procedures of solid-state scattering theory.[8] Modifications have been made in that method to avoid the use of Wannier functions; instead, the local basis functions used in the LCGO band calculation are also used as a basis for the expansion of the modified Bloch functions in the crystal containing the defect.[9] A similar approach has been adopted independently by Bernholc and Pantelides.[10] Special numerical techniques have been developed to facilitate the calculation of the phase shift from the large determinants which occur in this procedure. Integration of the phase shifts over occupied states determines the net change in single-particle energy.

The problem of determining the formation energy is discussed within the framework of the local-density approximation. Difficulties associated with the calculation of the electrostatic interaction are described. A rough estimate of the formation energy at constant volume including only single-particle terms is made using an expression due to Perrot.[11]

The remainder of this introduction attempts to place the present calculation in perspective. Since the pioneering work of Fumi,[12] a rather substantial number of investigations have been devoted to the calculation of the formation energy of a vacancy in a metal. There are two principal types of approaches. The first is based on pseudopotential theory, beginning with the work of Harrison.[13] There have been several studies of this type,[14-22] many of which employ perturbation theory. Frequently, good agreement is obtained between theory and experiment both for monovalent metals and for aluminum. One may question the use of perturbation theory and the free-electron-gas dielectric function. A different attack starts from a jellium model in which the vacancy is initially represented as a hole in the background positive charge.[23-31] The electron gas is then allowed to relax in the presence of this hole. The formation energy is computed using density-functional methods. The effects of considering discrete ions rather than a smooth background charge can be included approximately using perturbation theory. Lattice distortions and electron rearrangement in the presence of ions may not be satisfactorily included. The use of semiempirical interatomic potentials for calculating formation energies of vacancies has been reviewed by Johnson.[32]

Only a few calculations involving realistic potentials of the sort used in band calculations have been reported. Gupta and Siegel have described briefly an augmented-plane-wave (APW) calculation of electron (and positron) densities near a vacancy in aluminum.[33] The present work attempts to move in the direction of more realistic models by using the apparatus developed for band calculations using localized basis functions. We do not claim to have solved the problem of accurately calculating the formation energy of a vacancy in a multivalent metal without introducing greatly simplifying approximations. However, we believe an essential portion of the problem, that of determining the change in the sum of single-particle eigenvalues has been carefully studied, and that the techniques employed here will ultimately lead to precise computations of the total energy.

II. CONSTRUCTION OF THE DEFECT POTENTIAL

Since a vacancy is a missing atom, the first approximation to the change in the crystal potential produced by a vacancy is the negative of a single atomic potential, or pseudopotential. Although this approximation has been employed quite frequently in semiconductors[34] as well as metals, the determination of a single atomic potential in a solid involves significant difficulties, as will be described below. In addition, atoms in the vicinity of the defect readjust their positions and this makes an additional contribution to the potential.

We begin the calculation by defining the potential of the atom removed to be that of a single atom at the end of a self-consistent band calculation. In other words, if the self-consistent crystal potential is $v_{\rm SCF}(r)$ (SCF: self-consistent field), then we write

$$v_{\rm SCF}(\vec{r}) = \sum_{\mu} v_a(\vec{r} - \vec{R}_\mu)\ , \tag{2.1}$$

where the $\vec{R}_\mu$ are direct lattice vectors, and the v_a are the atomic potentials, identical to each other except for location in the crystal. Unfortunately, there are already some ambiguities, as the decomposition of $v_{\rm SCF}$ into a sum of v_a is not unique. In fact, the band calculation on which the present work is based does not give $v_{\rm SCF}(\vec{r})$ directly but rather its Fourier coefficients $v(\vec{K})$

$$v_{\rm SCF}(\vec{r}) = \sum_{K} v(\vec{K}) e^{i\vec{K}\cdot\vec{r}}\ , \tag{2.2}$$

where the $\vec{K}$ are reciprocal-lattice vectors. However, the atomic potential $v_a(\vec{r})$ has Fourier coefficients for all wave vectors $\vec{q}$, not just reciprocal-lattice vectors. More specifically,

$$v_a(\vec{r}) = \frac{1}{N} \sum_{q} v_a(\vec{q}) e^{i\vec{q}\cdot\vec{r}}\ , \tag{2.3}$$

where N is the number of unit cells in the crystal and the $\vec{q}$ are nearly continuous. The $v(\vec{K})$ in (2.2) coincide with the $v_a(\vec{q})$ in (2.3) when $\vec{q}$ is a reciprocal-lattice vector.

We require, however, $v_a(\vec{q})$ for all $\vec{q}$. To this end, we use an analytic expression for $v_a(\vec{q})$ containing parameters which are determined by fitting to the known numerical values of v for wave vectors equal to reciprocal-lattice vectors as found in the calculation of Ref. 2. Both Coulomb and exchange contributions are included. The particular expression used was:

$$v_a(\vec{q}) = [-A/(\vec{q}^{\,2} + \alpha^2)] - B[(\vec{q}^{\,2} + \beta^2)/(\vec{q}^{\,2} + \gamma^2)^2]. \tag{2.4}$$

The real-space form of this potential is simple: it contains two Yukawa terms and one exponential potential. The parameters of this potential are given in Table I. This fit reproduces the specified $v(\vec{K})$ rather accurately: the rms error considering all reciprocal lattice vectors with $K^2 \leq 100\ (2\pi/a)^2$ is 5×10^{-4} Ry. The numerical value of the lattice constant used is 7.635 a.u.

TABLE I. Parameters of the potential of Eq. (2.4) (atomic units, energies in Rydbergs).

A	1.1344
B	1.6003
α	0.7807
β	7.5424
γ	5.3333

The computation of the defect potential includes the contribution from the removal of an atom at the central site and from the displacement of neighboring atoms. Suppose an atom, initially at a site $\vec{R}_\mu$ is displaced to $\vec{R}'_\mu$. The unscreened defect potential, $v_d^{(0)}$ is

$$v_d^{(0)}(\vec{r}) = -v_a(\vec{r}) + \sum_{\mu} [v_a(\vec{r} - \vec{R}'_\mu) - v_a(\vec{r} - \vec{R}_\mu)]\ . \tag{2.5}$$

In principle, all lattice sites are to be included in the sum, but, in practice, the sum is restricted to the first two shells of neighbors.

The lattice relaxation near a vacancy has already been computed in a previous calculation.[4] It is not particularly large. We have included the displacement of the first two shells of neighbors, (1, 1, 0) and (2, 0, 0) in (2.5). Both of these shells are predicted to move radially inward: the first shell by 3.5%, the second shell by 1.8%. In contrast, the third shell is displaced by only 0.4% (not quite radially).

In pricniple, the defect potential (2.5) should serve as input to an iterative self-consistent calculation. The change in charge density produced by the impurity potential at a given stage of the iterative procedure should be used to compute a new impurity potential, and the process should be repeated until convergence is obtained. However, this ideal procedure is not practical for us at the present time. We have therefore simply screened the defect potential (2.5) with an appropriate dielectric function in order to approximate a self-consistent potential. This procedure would be correct if the defect potential were sufficiently weak for linear response theory to be valid. This may not be entirely justified and some corrections to our present results might result in a fully self-consistent calculation. It should be emphasized that the dielectric function employed here is not that for a free-electron gas but rather that obtained in a previous calculation for a perfect aluminum crystal.[7]

The relevant quantity which screens a change in potential energy experienced by an electron is the so-called "electron dielectric function."[35] (The ordinary dielectric function describes the change in potential affecting a test charge.) The electron dielectric function is a matrix, when local-field effects are included, and is given by

$$\tilde{\epsilon}(\vec{p},\omega)=I-[v_C(\vec{p})+v_{xc}]\chi^{(0)}(\vec{p},\omega)\ , \qquad (2.6)$$

in which v_C is a matrix (indices are reciprocal-lattice vectors) representing the Coulomb potential, v_{xc} represents the local exchange-correlation potential, and χ^0 is the polarizability matrix. The screened defect potential has Fourier coefficients

$$v_d^{(s)}(\vec{p}+\vec{K}_j)=\sum_n \tilde{\epsilon}^{-1}(\vec{p},\vec{K}_j,\vec{K}_n,0)v_d^{(0)}(\vec{p}+\vec{K}_n)\ . \qquad (2.7)$$

(The zero among the arguments of $\tilde{\epsilon}$ indicates that we are concerned with the static limit, $\omega=0$.) However, it turns out that the off-diagonal components are substantially smaller than the diagonal elements. This is expected since aluminum is a nearly-free-electron-like material. It is therefore an acceptable approximation to neglect the off-diagonal elements of $\tilde{\epsilon}$. Since the inverse of a diagonal matrix is just a diagonal matrix whose elements are reciprocals of those of the original matrix, Eq. (2.7) simplifies to become, in an obvious notation,

$$v_d^{(s)}(\vec{p}+\vec{K}_j)\approx[1/\tilde{\epsilon}(\vec{p}+\vec{K}_j)]v_d^{(0)}(\vec{p}+\vec{K}_j)\ . \qquad (2.8)$$

We have found it useful to obtain an analytic fit to the computed dielectric function in order to facilitate computation of the matrix elements of v_d. The expression used was

$$\tilde{\epsilon}(\vec{q})=\begin{cases}1+a/\vec{q}^{\,2}-b/(\vec{q}^{\,2}+c^2) & (q^2<q_m^2)\\ 1 & (q^2>q_m^2)\ .\end{cases} \qquad (2.9)$$

TABLE II. Parameters occurring in fit to the dielectric function, Eq. (2.9).

	$0\leq q\leq 1.317$	$1.317<q<q_m=1.810$
a	1.198	1.348
b	7.727	2.682
c	4.115	1.840

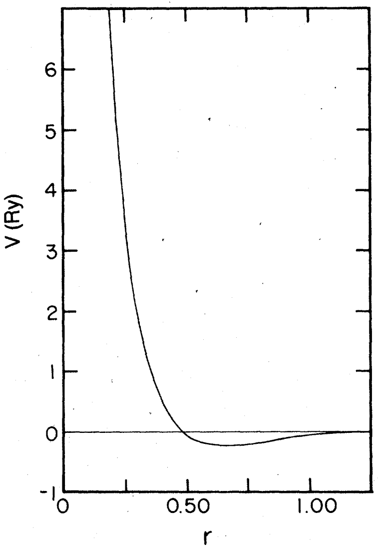

FIG. 1. Contribution from the central atom to the defect potential [from Eqs. (2.10), (2.9), and (2.4)]. The coordinate r is expressed as a fraction of one-half of the lattice constant.

A satisfactory fit to the computed $\tilde{\epsilon}(\vec{q})$ was obtained using the parameters given in Table II.[36]

The analytic fits to $v_a(\vec{q})$ and $\tilde{\epsilon}(\vec{q})$ allow the computation of a screened "atomic" potential $v_a^s(\vec{r})$ in position space

$$\begin{aligned}v_a^s(\vec{r})&=\frac{\Omega}{(2\pi)^3}\int d^3q\,e^{i\vec{q}\cdot\vec{r}}\,\frac{v_a(\vec{q})}{\tilde{\epsilon}(\vec{q})}\\&=\frac{\Omega}{2\pi^2r}\int q\,dq\sin qr\,\frac{v_a(\vec{q})}{\tilde{\epsilon}(\vec{q})}\ .\end{aligned} \qquad (2.10)$$

The integration over angles in (2.10) was immediate because v_a and $\tilde{\epsilon}$ are functions of q^2 only. The negative of the resulting $v_a^s(\vec{r})$ is shown in Fig. 1. The screened defect potential can then be constructed according to Eq. (2.5), using the individually screened atomic potentials $v_a^s(r)$. The reader should note that the same result is obtained regardless of whether the screened atomic potentials are used in (2.5), or if the unscreened potentials are used, and the resulting $v_d^{(0)}$ is inserted in (2.10).

Our calculation of the change in energy produced by the defect requires that we compute matrix elements of this potential connecting the Gaussian orbitals which are the basis functions for our band calculation. Since an enormous number of such matrix elements must be determined, it is essential that the integrals be performed analytically. In order to make this possible, we fit the computed $v_a^s(r)$ as follows

TABLE III. Parameters of the screened potential, Eq. (2.11) (atomic units, energies in Rydbergs).

g_1	6.89	ξ_1	0.676
g_2	14.5	ξ_2	8.05
h_1	−0.39	ζ_1	0.214
h_2	−0.00584	ζ_2	0.0427

$$v_a^s(\vec{r}) = (g_1/r)e^{-\xi_1 r^2} + (g_2/r)e^{-\xi_2 r^2} + h_1 r e^{-\zeta_1 r^2} + h_2 r e^{-\zeta_2 r^2} \; . \tag{2.11}$$

The constants which appear in Eq. (2.11) are listed in Table III. Additional remarks concerning the computation of matrix elements of this potential appear in Sec. IV.

III. FORMAL THEORY FOR THE SINGLE-PARTICLE ENERGY

The calculation of the change in energy of the system produced by the presence of the defect is based on formal scattering theory as developed for solids. The principles of this approach have been described elsewhere,[37] and we state only the essential results here.

The change in the density of single-particle states produced by a single impurity is (for a single direction of electron spin),

$$\Delta G(E) = (1/\pi)(d\delta/dE) \; , \tag{3.1}$$

where δ is a total scattering phase shift (the sum of all partial wave phase shifts with appropriate weights). This quantity is the phase of complex function $D(E)$, the determinantal function,

$$\delta = -\mathrm{Im}\ln D(E) \; , \tag{3.2}$$

$$D(E) = \det(I - \mathcal{G}V) \; . \tag{3.3}$$

Here I is a unit operator, $\mathcal{G}$ is the single-particle Green's function calculated with outgoing wave boundary conditions, and V is the defect potential. Equation (3.3) is formally valid regardless of what particular choice of basis functions are used for the representation of the operators. In previous studies we have used a basis of Wannier functions.[38] However, the construction of Wannier functions for individual bands is difficult,[34] although improved procedures have recently been developed.[39] In this work we have decided to use as a basis the same local orbitals used in the construction of the energy bands. Such a procedure has been developed independently by Bernholc and Pantelides.[10] Thus, the general Bloch wave function in the perfect crystal is written as

$$\psi_n(\vec{k},\vec{r}) = \frac{1}{\sqrt{N}} \sum_i c_{ni}(\vec{k}) \sum_\mu e^{i\vec{k}\cdot\vec{R}_\mu} u_i(\vec{r} - \vec{R}_\mu) \; . \tag{3.4}$$

On this basis, the quantities appearing in (3.3) are matrices in the site and orbital indices,

$$V_{i\mu,j\nu} = \int u_i^*(\vec{r} - \vec{R}_\mu) v_d(\vec{r}) u_j(\vec{r} - \vec{R}_\nu)\, d^3r \; , \tag{3.5}$$

$$\mathcal{G}_{i\mu,j\nu} = \int u_i^*(\vec{r} - \vec{R}_\mu) \frac{1}{E^+ - H_0} u_j(\vec{r} - \vec{R}_\nu)\, d^3r \; . \tag{3.6}$$

The expression for the Green's function can, however, be simplified through use of a relation which is the inverse of (3.4)

$$u_j(\vec{r} - \vec{R}_\nu) = \frac{1}{\sqrt{N}} \sum_{nk} e^{-i\vec{k}\cdot\vec{R}_\nu} c_{nj}^*(\vec{k}) \psi_n(\vec{k},\vec{r}) \; . \tag{3.7}$$

Then

$$\mathcal{G}_{i\mu,j\nu} = \frac{\Omega}{(2\pi)^3} \sum_n \int d^3k\, c_{ni}^*(\vec{k}) c_{nj}^*(\vec{k}) \times \frac{\exp[i\vec{k}\cdot(\vec{R}_\mu - \vec{R}_\nu)]}{E^+ - E_n(\vec{k})} \; . \tag{3.8}$$

The integration covers the Brillouin zone, and Ω is the volume of the unit cell.

The principal formal change resulting from the use of the nonorthogonal local orbitals u_i instead of Wannier functions is the introduction of the eigenvector coefficients into the expression for the Green's-function matrix. These coefficients are real in the present case. Hence the only ambiguity of phase concerns the algebraic sign of a particular eigenvector which can, in a numerical calculation, vary randomly from point to point. However, (3.8) contains the sum over products of elements from a particular vector, so that the ambiguity of sign does not affect the calculation of the Green's function.

We now consider the calculation of the change in total one-electron energy with the aid of (3.1). Other contributions to the change in the total energy will be considered in Sec. V. Let the density of states of the perfect crystal be denoted by $G_0(E)$. The total density of states is

$$G_T(E) = G_0(E) + \Delta G(E) \; . \tag{3.9}$$

Note that G_0 is proportional to N, the total number of atoms in the crystal. The Fermi energy (at zero temperature), E_F^0 is determined by

$$\int_{E_0}^{E_F^0} dE\, G_0(E) = NZ \; , \tag{3.10}$$

in which Z is the valence and E_0 is the energy of the lowest state in the band system. We shall ignore any possible contributions from core electrons to the binding. Now suppose a single atom is removed. We have, in place of (3.10),

$$\int_{E_0}^{E_F'} dE\, [G_0(E) + \Delta G(E)] = Z(N-1) \; . \tag{3.11}$$

The Fermi energy in the presence of the vacancy has been denoted by E_F',

$$E_F' = E_F^0 + \Delta E_F \ . \qquad (3.12)$$

Since the change in the Fermi energy is very small, of order $1/N$, we have, to leading order,

$$G_0(E_F^0)\Delta E_F + \int_{E_0}^{E_F^0} \Delta G(E)\,dE = -Z \ , \qquad (3.13)$$

so that

$$\Delta E_F = -\frac{1}{G_0(E_F^0)}\left(Z + \int_{E_0}^{E_F^0} \Delta G(E)\,dE\right) \ . \qquad (3.14)$$

The change in the total single-particle energy can be computed similarly. Let this energy for the perfect crystal be denoted by $\mathcal{E}_0$,

$$\int_{E_0}^{E_F^0} E G_0(E)\,dE = \mathcal{E}_0 \ ; \qquad (3.15)$$

and the change in this quantity by $\Delta\mathcal{E}_{\text{sp}}$,

$$\mathcal{E}_0 + \Delta\mathcal{E}_{\text{sp}} = \int_{E_0}^{E_F'} E G_T(E)\,dE \ . \qquad (3.16)$$

We obtain

$$\Delta\mathcal{E}_{\text{sp}} = E_F^0 G_0(E_F^0)\Delta E_F + \int_{E_0}^{E_F^0} E\,\Delta G(E)\,dE \ . \qquad (3.17)$$

The change in density of states is given by (3.1), but we should multiply this expression by a factor of 2 to allow for directions of electron spin. Then (3.14) becomes

$$\Delta E_F = -[1/G_0(E_F^0)][Z + (2/\pi)\delta(E_F^0)] \ . \qquad (3.18)$$

This result is inserted into (3.17). The second term in (3.17) can be simplified by means of a partial integration. The result is

$$\Delta\mathcal{E}_{\text{sp}} = -ZE_F^0 - \frac{2}{\pi}\int_{E_0}^{E_F^0} \delta(E)\,dE \ . \qquad (3.19)$$

The results (3.18) and (3.19) deserve some comment. Equation (3.19) contains two terms: the first is the change in energy required to remove Z electrons at the Fermi energy; the second contains the effect of the readjustment of the electron distribution to the defect potential. We should note that if an equivalent Friedel sum rule were satisfied, we would have

$$\delta(E_F^0) = -\tfrac{1}{2}\pi Z \ , \qquad (3.20)$$

so that ΔE_F would vanish. In fact, we find that although (3.20) is not exactly satisfied in our numerical calculation, it is a reasonable approximation.

It must be observed that the change in energy $\Delta\mathcal{E}_{\text{sp}}$ that we have discussed up to this point cannot be directly compared with experiment even if electron interactions are neglected. The physical situation of interest does not correspond to the removal of an atom from the crystal; rather an atom is displaced. We are concerned here with a very large (effectively infinite) crystal. In this work, we shall consider the missing atom to find a new place in the bulk of the crystal—the situation in which a vacancy-interstitial pair is formed will be investigated subsequently.

IV. COMPUTATIONS AND RESULTS

The local orbital basis used in this calculation contains 9- s, 6- p, and 5- d Gaussian-type orbitals on each lattice site. The exponents of these orbitals are listed in Table I of Ref. 1. When the differing possible angular symmetries are included, there are 52 independent functions for each lattice site. We included functions centered on thirteen atomic sites in this calculation—the vacancy site itself and the 12 nearest neighbors. Thus, our basis contains 676 functions, and the matrices $\mathcal{S}, V$ have dimensionality 676×676. The determinant $D(E)$ could be (but was not) factored according to the representations of the point group. Only the total phase shift (sum of the partial-wave phases) is required in the present calculation.

The expression for $D(E)$ is given in Eq. (3.3). The elements of the defect potential matrix were computed according to Eq. (3.5). Explicit formulas for the Gaussian orbitals may be found in Ref. 3. Use of the fit (2.11) to the screened potential enabled rapid evaluation of the matrix elements using analytic formulas. The elements of the Green's-function matrix were computed using the wave functions and energies at 89 points in $\frac{1}{48}$th of the Brillouin zone. A tetrahedral method of integration was employed.[40,41] Since we are only concerned with a relatively small range of energies, only six bands were included in this computation. The integral in (3.8) can be broken into two parts with the aid of the identity

$$[1/(E^+ - E_n(\vec{k}))] = P[1/(E - E_n(\vec{k}))] - i\pi\delta(E - E_n(\vec{k})) \ , \qquad (4.1)$$

(where P denotes the principal value). The contribution to the integral from the δ function term was obtained first: the portion involving the real part was subsequently obtained by a (numerical) Hilbert transformation. The calculation of the Green's function consumed a major portion of the large computer time requirements of this calculation.

It was then necessary to compute the phase shifts. As this involves the determinant of an extremely large complex matrix, special numerical techniques had to be developed. A program was

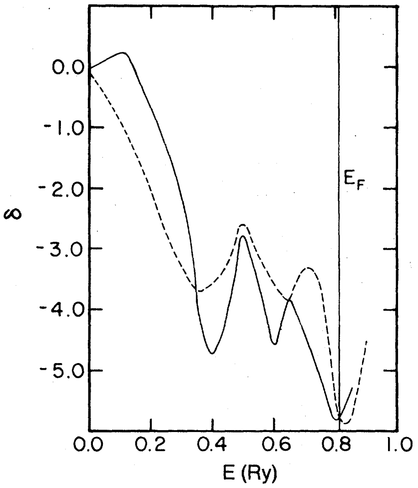

FIG. 2. Energy dependence of the total scattering phase shift (in radians). Solid line: result of the full calculation with 676 basis functions; dashed line, results with a reduced basis of 52 functions. Energies are measured with respect to the bottom of the band; the Fermi energy occurs at 0.812 Ry.

developed which computes the logarithm of the determinant directly avoiding evaluation of the determinant itself. This program was tested using certain large matrices whose determinant had been carefully studied by other methods.

The scattering phase shifts were calculated at energy intervals of 0.05 Ry between the bottom of the band and the Fermi energy. There is a possible ambiguity of π in the value of the phase shift determined from the numerical computations. This was resolved as follows. Since the potential is mostly repulsive, there are no bound states below the bottom of the band. Thus, by Levinson's theorem, the phase shift vanishes there. Then we require the phase shift to be a continuous function of energy.

The phase shifts resulting from our calculation are shown graphically in Fig. 2. We also show the phases obtained from a reduced basis of 52 elements (central cell only). The essential features of the behavior of the phase shift can be understood as follows: as mentioned above, $\delta = 0$ at the bottom of the band. The rise in δ for low energies appears to be a consequence of the weak attraction of the defect potential at large distances from the defect site, as exhibited in Fig. 1. The reader should recall that an attractive potential produces a rising phase shift. As the energy increases, the repulsive portion of the potential at short range becomes dominant, and the phase shift drops rapidly. Near the Fermi energy, the phase shift has fallen to a value $\delta(E_F) = -5.7$. A value of $-\frac{3}{2}\pi$ would be expected if the Friedel sum rule were satisfied. This, however, is not required since charge may be displaced by the lattice distortion. The oscillatory variations of the phase shift are not believed to be calculational artifacts as the positions correlate well with structure in the band density of states.[1]

The phases obtained from a calculation with a smaller basis of functions centered on the vacancy site only show most of the structure of the more complete calculation, and, in particular, the values of the phase shift at the Fermi energy are seen to agree satisfactorily. However, the restricted calculation misses the region of positive δ near the bottom of the band. This is reasonable since we believe the positive phases are due to the weak attractive potential at large distances from the vacancy, which may not be completely included in a calculation involving functions based on a single site. Further, it is suggested that the result of extending this work to additional neighbor sites might be to extend the region of positive phases.

The integral of the phase shift required by Eq. (3.19) was evaluated numerically using Simpson's rule. The result is

$$\frac{2}{\pi}\int_{E_0}^{E_F^0} \delta(E)\,dE = 1.432 \text{ Ry}. \qquad (4.2)$$

We estimate that this result is accurate to about ±0.05 Ry with most of the uncertainty resulting from a few energies where resolution of the ambiguity of π mentioned previously is possible in more than one way. This uncertainty is, unfortunately, quite significant in comparison with the experimental vacancy formation energy. This difficulty could be resolved by calculations on a finer grid of energies. Such calculations are in progress. Our result can be compared with that given by an elementary calculation in which the strength of the effective potential is determined by requiring the Friedel sum rule to be satisfied exactly.[42] This gives

$$\frac{2}{\pi}\int_{E_0}^{E_F^0} \delta(E)\,dE = \tfrac{2}{3}Z(E_F^0 - E_0) = 1.624 \text{ Ry}. \qquad (4.3)$$

The general correspondence between the values given in (4.2) and (4.3) is encouraging.

The numerical value of E_F^0 [required in (3.19)] is -0.469 Ry ($E_F^0 - E_0 = 0.812$ Ry). Our value for the net change in single partial energy is then 2.84 Ry.

V. FORMATION ENERGY, DISCUSSION, AND SUMMARY

We are now ready to estimate the change in total energy. For this purpose, we will follow the procedure discussed by Perrot.[11] The vacancy formation energy at constant volume, E_v, is given by

$$E_v = E_d(N-1, \mathcal{V}) - E_p(N, \mathcal{V}) + E_b \ , \tag{5.1}$$

in which E_p is the energy of the perfect crystal with volume $\mathcal{V}$, and E_d is the energy of the crystal with one atom removed, holding the volume constant. These two terms combine to give the energy required to remove an atom at constant volume. We add to this E_b, the energy necessary to replace the atom in the bulk of the crystal.

The total energy is, unfortunately, not just the sum of the single-electron eigenvalues. Instead, one has, within the present context which employs a local exchange potential, $V_{\text{ex}}(\vec{r})$, of the $X\alpha$ form proportional to the cube root of the charge density,

$$E_{\text{tot}} = \int_{E_0}^{E_F} EG(E)\,dE - \tfrac{1}{2}e^2 \int \frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\, d^3r - \tfrac{1}{4}\int \rho(\vec{r})V_{\text{ex}}(\vec{r})\, d^3r + \tfrac{1}{2}Z^2e^2 \sum_{\mu\neq\nu} \frac{1}{|\vec{R}_\mu - \vec{R}_\nu|} \ , \tag{5.2}$$

in which the coefficient $\frac{1}{4}$ in the third term is a specific consequence of the assumed form of the exchange potential,

$$V_{\text{ex}} = -3e^2\alpha[3\rho(\vec{r})/8\pi]^{1/3} \ , \tag{5.3}$$

where $\alpha = \frac{2}{3}$ in the Kohn-Sham potential used here. The corrections that enable us to relate the total energy to the sum of single-particle energies depend explicitly on the charge density. Unfortunately, there are serious problems involved in evaluating all but the first term in (5.2).

Harrison[13] has calculated the change in the Coulomb contribution to (5.2), which is the sum of the second and fourth terms due to the introduction of a vacancy neglecting lattice distortion and assuming that the charge density is constant ($\rho = Z/\Omega$, where Ω is the volume of the unit cell). His result is

$$Z^2e^2\gamma/3r_s \ , \tag{5.4}$$

where γ is a numerical constant ($\gamma = 1.791\,75$ for a fcc lattice).[43] If one takes $r_s = 2.985$ (a.u.) and $Z = 3$ as are appropriate for aluminum, the result is 3.6015 Ry (50 eV), an enormous effect. In fact, there must be a substantial redistribution of electronic charge in the vicinity of the defect which compensates for most of the contribution above. Evidence for this is the approximate satisfaction of the Friedel sum rule. A quantitative evaluation of electrostatic and exchange terms in (5.2) requires accurate results for the change in the electron density near the vacancy, and the displacement of the positive-ion positions as well. If we denote the charge density in the perfect crystal as ρ_p and that in the presence of the defect as ρ_d,

$$\rho_d = \rho_p + \Delta\rho \ ,$$

then the change in the electron repulsion term in (5.2) is

$$-e^2 \int \frac{\Delta\rho(\vec{r})[\rho_p(\vec{r}\,') + \frac{1}{2}\Delta\rho(\vec{r}\,')]d^3r\,d^3r'}{|\vec{r}-\vec{r}\,'|} . \tag{5.5}$$

This term must be combined with (5.4) to give a formation energy of a reasonable size. The change in charge density, $\Delta\rho$, can in principle be computed using our methods. Procedures which will make such a computation practical must be developed.

If all except the single-particle terms in (5.2) are neglected, we can make a very rough estimate of the formation energy. For this purpose we take for the binding energy of the replaced atom in the bulk simply $1/N$ times the energy of the perfect crystal. This leads to

$$E_v = \Delta\mathcal{E}_{\text{sp}} + \frac{1}{N}\int_{E_0}^{E_F^0} EG_0(E)\,dE \ , \tag{5.6}$$

where $\Delta\mathcal{E}_{\text{sp}}$ is given by (3.19). The integral in the second term of (5.6) has been computed numerically using the density of states obtained from our calculated band structure.[2] The result is

$$\frac{1}{N}\int_{E_0}^{E_F^0} EG_0(E)\,dE = -2.39 \text{ Ry} .$$

The calculated formation energy is then 0.45 Ry (6.1 eV). This is much larger than the experimental value. Recent experimental determinations[44,45] have given formation energies of 0.66 ±0.04 eV, and 0.69 ± 0.03 eV.

Inclusion of the Coulomb and exchange terms can bring the calculated formation energy within range of that observed. This can be seen if we use the results of Stott, Baranovsky, and March[46] for the sum of these corrections. Their calculation is based on a determination of the charge displaced by a self-consistently screened ionic potential in an electron gas. For aluminum, they obtain a Coulomb correction of −0.58 Ry and an exchange correction of +0.26 Ry, for a net effect of −0.32 Ry. If this is added to our single-particle result, the sum is 0.13 Ry or 1.8 eV, considerably closer to the experimental value. This result cannot, however, be taken literally as the model employed by Stott *et al.* is quite different from that used here: it is simply illustrative of the sort of effect to be expected.

Improvement of our present estimates requires first, accurate evaluation of the electrostatic and exchange contributions to (5.2). Second, the use of the dielectric matrix to screen the assumed potential and thereby approximate the potential resulting from a self-consistent calculation needs to be reexamined. It may be that a calculation in which self-consistency is achieved by iteration will be practical. Finally, a factorization of the determinantal function $D(E)$ using symmetrized linear combinations of the Gaussian basis functions would reduce the size of the matrices whose determinants have to be evaluated, and so reduce the possibility of numerical inaccuracies.

In summary, we have evaluated the sum of the phase shifts for the scattering of an electron by a vacancy in aluminum. The calculation employs a realistic impurity potential and includes the effects of lattice distortion. Although approximate self-consistency is achieved through dielectric screening, the dielectric function employed is one computed for the specific metal under study. The Green's function for the scattering calculation was determined from the actual band structure of the metal. The procedures of solid-state scattering theory were modified to replace Wannier functions by the same local orbitals used in the band calculations. Problems associated with the calculation of the formation energy have been discussed. A numerical value is reported for the net change in the sum of single-particle energies.

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