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PHYSICAL REVIEW B

VOLUME 3, NUMBER 8

15 APRIL 1971

Electronic Structure of the Single Vacancy in Silicon*

Joseph Callaway

Department of Physics, Louisiana State University, Baton Rouge, Louisiana 70803

(Received 21 December 1970)

A technique based on the use of Wannier functions is employed to investigate the electronic structure of the isolated neutral vacancy in silicon. The change in crystal potential produced by the defect is represented as the negative of an atomic pseudopotential. Scattering phase shifts are calculated for states within the valence band. These phase shifts are used to estimate one major contribution to the formation energy of the vacancy; the change in the total one-electron energy, which can be expressed as an integral of the phase shifts over the occupied states. This quantity is computed and found to be equal to 23 eV.

I. INTRODUCTION

The object of this paper is to apply the techniques of solid-state scattering theory¹ to the study of the electronic structure of the single vacancy in silicon. In a previous paper, the formation of localized states in the band gap by both the single vacancy and the divacancy have been studied by similar techniques.² In this paper, we will focus attention on the changes produced in the one-electron wave functions of the occupied states, and on the consequent changes in the total energy of the system.

Because the present approach is different from that which many other workers have employed, it is useful to begin with a brief survey of a previous paper. Most of the existing studies of the vacancy in covalently bonded semiconductors have been based on molecular-orbital theory, whose applicability was initially proposed by Coulson and Kearsley.³ The original calculations concerned vacancies in diamond. Their work has been extended^{4,5} and recently applied to silicon.⁶

The essential idea of the molecular-orbital method as it has been applied to this problem is to separate conceptually the atoms in the immediate neighborhood of the defect from the rest of the crystal. These atoms, together with the defect, are regarded as forming a defect molecule. The energy levels of this molecule are then calculated. Although the concept of atoms in the immediate neighborhood of the defect is ambiguous to some extent, the usual practice has been to consider just the four atoms which are nearest neighbors of the vacancy. The four tetrahedral bonds which were

ruptured when the central atom was removed are employed as basis states for the computation. The orbitals are hybrid sp^3 combinations directed toward the center of the defect. Combinations of these orbitals are constructed which belong to the Γ_1 and Γ_4 representations of the tetrahedral group. Let these combinations be denoted v and t , respectively. A configuration of the defect molecule may be described in terms of occupation of v and t functions, as $v^a t^{n-a}$, where $a=0, 1$, or 2 , and n is the number of electrons in the vacancy molecule ($n=4$ for the neutral vacancy; $n=5$ if there is a net negative charge of unity, etc.). For a given configuration, one now constructs wave functions of proper symmetry (eigenfunctions of S^2 and S_z , where S is the total spin), which transform according to the irreducible representations of the tetrahedral group.

The Hamiltonian used in the molecular-orbital calculation of the structure of the vacancy includes the interaction of each of the n vacancy electrons with the nuclei and other electrons of the atoms which are nearest neighbors of the vacancy, plus the Coulomb repulsion of the valence electrons.⁶ The energies of states coming from a single configuration are determined as the expectation of this Hamiltonian using the wave functions constructed above. If states of the same symmetry occur in different configurations, configuration mixing can be introduced by calculating matrix elements of the Hamiltonian between these states and solving the resulting secular equation. The result is a set of (n -electron) energy states for the system.

The principal objection which can be brought against this procedure involves the concept of a

small isolated defect molecule. Diamond, silicon, and germanium are all broad-band semiconductors, their valence bands being of order 1 Ry wide. When a tight-binding calculation of energy bands is attempted for one of these materials, it is found that the wave functions for the outer electrons placed on atomic sites in the crystals overlap substantially. Quantitative results are not possible in the tight-binding method if just first-neighbor interactions are considered. In contrast, a nearly free-electron approximation with a small number of pseudopotential parameters works quite well for silicon and germanium. Therefore, it seems unreasonable to suppose that an approximation involving strong localization of the wave function for the electrons in the vicinity of the defect could yield quantitative results.

It may be argued in opposition to this view that additional localization could be produced by the defect potential itself. In fact, some effect of this sort will be seen to occur in the calculations reported here in that the defect potential produces scattering resonances in the valence band. However, the phase shifts of states outside the resonance region are substantial, and such states cannot be neglected in a calculation of the energy of formation.

The point which we wish to emphasize is that, in a wide-band material, all states are affected by the presence of the defect. It is convenient to describe this in terms of a change produced in the density of states. The change in density of states can be simply related to the phase shifts for scattering of electrons by the defect. The use of phase shifts to describe this scattering is a rigorous procedure which does not imply an assumption of spherical symmetry for the defect potential nor does it require the use of the differential equations of effective-mass theory, which are not valid in the circumstances of interest to us. Knowledge of the change in the density of single-particle states enables a calculation of the change in the sum of single-particle energies of the system. This alteration of single-particle energies makes a major contribution to the energy required to form the defect. Our procedure is quite similar in principle to a calculation recently reported by Lannoo and Lenglar⁷ for diamond. However, our work is more comprehensive in detail. There is also a (more remote) relation to a *t*-matrix calculation of formation and migration energies by Bennemann.⁸

The plan of this paper is as follows: In Sec. II, we describe the mathematical apparatus of solid-state scattering theory which is used in this calculation. The description of the vacancy in terms of the pseudopotential approach is discussed in Sec. III. Our computational procedures are described in Sec. IV, and our results are presented in Sec. V.

II. THEORY

Let us consider a semiconductor which has a single defect or impurity, located at the origin. We consider the effective single-particle Hamiltonian H which is obtained in principle from Hartree-Fock theory, and determines the energies and wave functions of the one-electron states. This is expressed as

$$H = H_0 + V_s, \quad (1)$$

in which H_0 is the Hamiltonian for the perfect crystal, containing a periodic potential, and V_s is the change in this potential produced by the defect. A one-electron wave function ψ may be expressed as a linear combination of Wannier functions defined in relation to the perfect crystal,

$$\psi = \sum_{n,\mu} B_n(\vec{R}_\mu) a_n(\vec{r} - \vec{R}_\mu). \quad (2)$$

The summation includes all bands (n) and all lattice sites (μ), including the site of the defect (or missing atom).

In an application to a material with the diamond lattice, or more generally, if a material is considered in which there is more than one unit cell, we must note that the Wannier functions involve more than one atom (two for the diamond lattice). To see why this must be the case, we can consider a tight-binding calculation of the band structure. In such a calculation, the number of bands obtained is the product of the number of atomic orbitals considered times the number of atoms in a unit cell. Thus, each band may be pictured as involving contributions from all atoms in the cell. The usual definition of the Wannier function

$$a_n(\vec{r} - \vec{R}_\mu) = \frac{\Omega^{1/2}}{(2\pi)^{3/2}} \int d^3k e^{-i\vec{k} \cdot \vec{R}_\mu} \psi_n(\vec{k}, \vec{r}), \quad (3)$$

which is employed here, will preserve this feature. It is possible to combine Wannier functions from different bands to form functions which are localized about single atoms, but this construction will not be attempted here.

The coefficients $B_n(\vec{R}_\mu)$ satisfy the following equation: Let the energy of the state Ψ be denoted by E ; then

$$\begin{aligned} \sum_\nu [E \delta_{\mu\nu} - \mathcal{G}_n(\vec{R}_\mu - \vec{R}_\nu)] B_n(\vec{R}_\nu) \\ = \sum_{l\nu} (n\mu | V_s | l\nu) B_l(\vec{R}_\nu), \end{aligned} \quad (4)$$

where

$$(n\mu | V_s | l\nu) = \int a_n^*(\vec{r} - \vec{R}_\mu) V_s(\vec{r}) a_l(\vec{r} - \vec{R}_\nu) d^3r, \quad (5)$$

$$\mathcal{E}_n(\vec{R}_\mu) = \frac{\Omega}{(2\pi)^3} \int d^3k E_n(\vec{k}) e^{i\vec{k} \cdot \vec{R}_\mu} \quad (6)$$

where $E_n(\vec{k})$ is the energy-band function for the perfect crystal.

Equation (4) is a matrix equation for the (discrete) coefficients $B_n(\vec{R}_\mu)$. It is desirable to introduce a Green's function $\mathcal{G}_n(\vec{R}_\mu - \vec{R}_\nu)$ which satisfies the equation

$$\sum_\nu [E \delta_{\mu\nu} - \mathcal{E}_n(\vec{R}_\mu - \vec{R}_\nu)] \mathcal{G}_n(\vec{R}_\nu - \vec{R}_\rho) = \delta_{\mu\rho} \quad (7)$$

It is straightforward to show that $\mathcal{G}_n(\vec{R}_\mu)$ may be expressed as

$$\mathcal{G}_n(\vec{R}_\mu) = \frac{\Omega}{(2\pi)^3} \int \frac{e^{i\vec{k} \cdot \vec{R}_\mu}}{E - E_n(\vec{k})} d^3k \quad (8)$$

If E lies in the energy band n , the integrand of (8) will be singular. The manner of treating this singularity must be specified, and this specification corresponds to the imposition of boundary conditions. Usually, a solution representing an excitation moving outward from the scattering center is desired. To obtain this, one may follow the usual procedure of scattering theory and replace E by $E^+ = E + i\epsilon$, where ϵ is allowed to go to zero after the integration has been performed.

Equation (4) may be transformed, with the aid of (7), into

$$B_n(\vec{R}_\mu) = B_n^{(0)}(\vec{R}_\mu) + \sum_{i,\rho} \mathcal{G}_n(\vec{R}_\mu - \vec{R}_\nu) (n\nu | V_s | l\rho) B_l(\vec{R}_\rho) \quad (9)$$

Here, $B_n^{(0)}$ is a solution of the homogenous equation

$$\sum_\nu [E \delta_{\mu\nu} - \mathcal{E}_n(\vec{R}_\mu - \vec{R}_\nu)] B_n^{(0)}(\vec{R}_\nu) = 0 \quad (10)$$

Equation (9) can be regarded as the equivalent in solid-state physics of the Lippmann-Schwinger equation of scattering theory. The solution of this equation and the asymptotic form of the wave functions obtained are described in Ref. 1. The information of interest to us here is contained in the determinantal function

$$\begin{aligned} D(E) &= \det[1 - \mathcal{G}V] \\ &= \det[\delta_{nl} \delta_{\mu\nu} - \sum_\rho \mathcal{G}_n(\vec{R}_\mu - \vec{R}_\rho) (n\rho | V | l\nu)] \end{aligned} \quad (11)$$

It is possible to use this function to determine the energies of bound or localized states associated with the defect, and the change in the one-electron energy produced by the defect.

Bound states are solutions of Eq. (9) with the solution of the homogenous equation $B_n^{(0)}$, set equal to zero. A necessary and sufficient condition for a solution of energy E_0 to exist is

$$D(E_0) = 0 \quad (12)$$

$D(E)$ is given by (11), and the required energy appears in this equation in the Green's function. Solutions of (12) for real E occur outside the band.

Within the band, D is complex, but we have instead

$$\text{Re}D(E_0) = 0 \quad (13)$$

If (13) is satisfied, a scattering resonance may be present.¹ The width of such a resonance is

$$\Gamma = 2 \text{Im}D(E_0) / \text{Re}D'(E_0) \quad (14)$$

where D' is the derivative of D with respect to energy; Im and Re stand for imaginary and real parts, and all quantities are evaluated at the energy for which (13) is satisfied.

It is possible to obtain the change in the sum of the one-electron energies from $D(E)$. A phase shift δ may be defined by

$$\tan \delta = -\text{Im}D(E) / \text{Re}D(E) \quad (15)$$

The change in the density of single-particle states, $\Delta N(E)$, produced by the defect has been shown to be⁹

$$\Delta N(E) = \frac{c}{\pi} \frac{d\delta}{dE} \quad (16)$$

Here c is the concentration of defects, δ being computed for a single one. This result is valid for small concentration, but becomes incorrect when terms of order c^2 must be considered, since then the scattering of Bloch waves by more than one defect must be included. The contribution to the change in the total one-electron energy arising from the band states is

$$\begin{aligned} \Delta E &= \int_0^{E_m} E \Delta N(E) dE \\ &= \frac{c}{\pi} \left[E_m \delta(E_m) - \int_0^{E_m} \delta_T(E) dE \right] \end{aligned} \quad (17)$$

In this equation, E_m is the energy of the highest-occupied band state; the energy of the lowest state being taken as zero. If n localized states of energy ϵ_l are formed and are occupied, their contribution must also be included. Suppose, as is appropriate in the present case, that an entire band plus all localized states formed from it are occupied. Then use Levinson's theorem in the form appropriate to a solid-state problem⁹

$$\delta(0) - \delta(E_m) = \pi n_l \quad (18)$$

Further, since $D(E)$ becomes real at the band edges (we assume that the bands of interest are separated from others by a finite gap) both $\delta(0)$ and $\delta(E_m)$ must approach some integral multiple of π (zero included). Thus, we have

$$\Delta E = c \left[\sum_{i=0}^{n_l} \epsilon_i - E_m \left(\frac{\delta(0)}{\pi} - n_l \right) - \frac{1}{\pi} \int_0^{E_m} \delta(E) dE \right] . \quad (19a)$$

If the occupied bound states are at the top of the band, as may occur for a repulsive potential and is the case for the vacancy, it is convenient to set $\delta(0) = 0$, so that

$$\Delta E = c \left[\sum_{i=1}^{n_l} (\epsilon_i - E_m) - \frac{1}{\pi} \int_0^{E_m} \delta(E) dE \right] . \quad (19b)$$

Phase shifts are negative for a repulsive potential so that the second term will represent the increase in energy of the continuum states. In the opposite situation where an attractive potential produces a bound state below the band, normally $\delta(0) = n_l \pi$. In this case, for which the phase shift is positive,

$$\Delta E = c \left[\sum_{i=1}^{n_l} \epsilon_i - \frac{1}{\pi} \int_0^{E_m} \delta(E) dE \right] . \quad (19c)$$

It should be noted that the change in energy of the system which is considered here is only that involving the sum of the one-electron energies. The change in the electron interaction energy produced by changes in the wave functions has not been included.

The calculation of $D(E)$ can be greatly simplified when the defect potential has some symmetry. In this case, $D(E)$ may be expressed as a product of subdeterminants derived from the irreducible representations (s) of the group of the potential

$$D(E) = \prod_s D_s(E) . \quad (20)$$

Since

$$D(E) = |D| e^{-i\delta(E)} ,$$

and a similar expression holds for each subdeterminant D_s with a phase shift $\delta_s(E)$, the total phase shift δ_T may be expressed as the sum of partial-wave phase shifts:

$$\delta = \sum_s \delta_s(E) . \quad (21)$$

If there is no spin-orbit coupling, each representation will occur twice; once for each spin direction. Also, if representation s is degenerate (degeneracy g_s = number of rows of representation s), the same phase shift will be obtained for each row. In such a case, we write

$$\delta_s(E) = g_s \delta_{sr}(E) , \quad (22)$$

where δ_{sr} is the phase shift for a single row of representation s .

Equation (21) enables us to define a specific contribution to the change in the energies of one-electron states due to scattering in representation s . For example, in the situation in which spin-orbit coupling is neglected and all states are doubly oc-

cupied:

$$\Delta E = 2c \sum_s g_s \Delta E_{sr} ,$$

where, in the case given by (19b), for example,

$$\Delta E_{s,r} = \sum_{i=1}^n (\epsilon_i - E_m) - \frac{1}{\pi} \int_0^{E_m} \delta_{sr}(E) dE , \quad (23)$$

and n is the number of localized states associated with row r of representation s .

It is important to note that the Pauli principle does not impose restrictions on the calculation of the phase shift for a fixed V_s . Although real scattering of an electron in an occupied state must involve excitation to an unoccupied state, the effect with which we are concerned results from the distortion of the wave functions of the occupied states by the potential and will occur even though real scattering is forbidden. If the defect is allowed to have an internal degree of freedom, as in the Kondo problem, the situation would be quite different.

The formulas we have established above are to be used in the calculation of the contribution from the change in the one-electron energies to the formation energy of the single vacancy. This means that a numerical calculation of the Green's-function potential-energy matrix elements, and phase shifts must be made. In most of these respects, the present calculation is similar to that reported in Ref. 2 concerning localized states associated with the vacancy.

III. PSEUDOPOTENTIAL

In this calculation, as well as in the previous paper concerning the localized state, we have used an approximate representation of the single vacancy by a missing atomic pseudopotential. In other words, V_s is the negative of an atomic pseudopotential. It is useful to discuss the content of this approximation.

The pseudopotential representation is obtained by regarding the true Bloch function $|n\vec{k}\rangle$ (band n and wave vector \vec{k}) as being formed from some "smooth" function by projecting out core states. Let these core states be denoted by $|c\vec{k}\rangle$. We also let $|n\vec{k}\rangle$ represent the "smooth" pseudo-Bloch-function. We reserve the indices n, l to indicate bands of interest, while c, d refer to core states. The relation between actual and pseudostates is

$$|n\vec{k}\rangle = Q |c\vec{k}\rangle , \quad (24)$$

where the projection operator Q ($Q^2 = Q$) is given by

$$Q = I - \sum_{c\vec{p}} |c\vec{p}\rangle \langle c\vec{p}| , \quad (25)$$

and I is an identity operator. [Note that $\langle c\vec{p} | n\vec{k} \rangle = 0$ if $\vec{p} \neq \vec{k}$.] The matrix elements of a potential V_T on the basis of the true Bloch functions are equal to

those of an operator V_p on the pseudofunction

$$\langle n\vec{k} | V_T | l\vec{q} \rangle = \langle n\vec{k} | V_p | l\vec{q} \rangle, \quad (26)$$

where

$$V_p = Q V_T Q = V_T - \sum_{c\vec{k}} [|c\vec{k}\rangle \langle c\vec{k}| V_T + V_T |c\vec{k}\rangle \langle c\vec{k}|] \\ + \sum_{c\vec{k}d\vec{p}} |c\vec{k}\rangle \langle c\vec{k}| V_T |d\vec{p}\rangle \langle d\vec{p}|. \quad (27)$$

It should be noted that if this projection process is applied to the full Schrödinger equation, for the perfect crystal, the pseudostates $|n\vec{k}\rangle$ are found to satisfy the Phillips-Kleinman equation¹⁰

$$QHQ | n\vec{k} \rangle = E_n(\vec{k}) Q | n\vec{k} \rangle, \quad (28)$$

or, in terms of wave functions, $(r | n\vec{k} \rangle = \psi_n^{(p)}(\vec{k}, \vec{r})$,

$$H\psi_n^{(p)}(\vec{k}, \vec{r}) - \sum_c [E_c(\vec{k}) - E_n(\vec{k})] \langle c\vec{k} | n\vec{k} \rangle \psi_c(\vec{k}, \vec{r}) \\ = E_n(\vec{k}) \psi_n^{(p)}(\vec{k}, \vec{r}), \quad (29)$$

in which $\psi_c(\vec{k}, \vec{r})$ is the "true" wave function for the core state c .

The preceding argument shows that the matrix elements of the actual defect potential may be calculated exactly in terms of a pseudopotential representation. We proceed as follows: (i) It is assumed that the actual defect potential is, in the case of a vacancy, the negative of a single atomic potential. This assumption neglects the lattice distortion which will occur around the defect site. (ii) A pseudopotential representation is adopted. It is known that the total crystal potential can be represented as the sum of individual atomic pseudopotentials. The vacancy is thus represented as the negative of a single atomic pseudopotential. (iii) The argument above concerning matrix elements of the defect potential relates these to pseudopotential matrix elements found by the procedure of Phillips and Kleinman.¹⁰ We approximate this theoretical pseudopotential by an empirical pseudopotential chosen to give a reasonably good fit to the known band structure of the perfect crystal.¹¹ This, however, introduces a problem: The empirical pseudopotential is specified only by its Fourier coefficients $V(\vec{k})$ for \vec{k} 's which are reciprocal-lattice vectors. The present problem requires knowledge of the entire Fourier transform of the pseudopotential. To obtain this approximately, we fit the empirically determined values of $V(\vec{k})$ to a polynomial. This procedure is described in Ref. 2, which contains the values of the coefficients that we have adopted.

Most of these approximations can be relaxed in more elaborate calculations. Specifically, we note that lattice distortion can be included by modifying the defect pseudopotential to include the displacement of atomic pseudopotentials on sites adjacent to the defect. In principle, it should be possible to determine the lattice distortion by mini-

mizing the energy of the crystal with respect to atomic displacements; but such a calculation is not attempted here.

The Fourier coefficients of the empirical pseudopotential are not determined for $\vec{k}=0$. A finite value for this quantity implies, in the case of a single atom, that a neutral atom is being considered. We follow the prescription of Harrison¹² to determine a value of -0.61 Ry for this quantity.

IV. COMPUTATIONAL PROCEDURES

This calculation employed the same matrix elements of the defect potential used in Ref. 2. In paper work, it was observed that the conduction bands do not make an appreciable contribution to the energy of the localized state, and that the wave function of the localized state is dominated by components in the valence band. It is thus apparently a reasonable approximation to ignore the conduction bands in the calculation; and when this approximation is applied to the localized state, the results appear to be as good as when the conduction bands are included.

Although the potential matrix elements can be used without change in the present paper, the calculation of the Green's function must be extended. For the purpose of calculating the energy of a localized state in the gap, the Green's function is required only within the energy gap, where it is real. Here we need the Green's function for energies corresponding to occupied states. Then we have, from Eq. (8) and the subsequent discussion

$$g_n(\vec{R}_\mu) = \frac{\Omega}{(2\pi)^3} \left[P \int \frac{d^3k}{E - E_n(\vec{k})} e^{i\vec{k} \cdot \vec{R}_\mu} \right. \\ \left. - i\pi \int d^3k e^{i\vec{k} \cdot \vec{R}_\mu} \delta(E - E_n(\vec{k})) \right]. \quad (30)$$

The symmetry of the energy-band function ensures that the first integral is purely real and the second term, purely imaginary.

The calculation of the imaginary part of the Green's function is quite similar to that of the ordinary density of states. Energy levels were obtained using a 15×15 Hamiltonian matrix at 3345 points in $\frac{1}{48}$ of the Brillouin zone, and were used to calculate this quantity by the ordinary technique of counting the number of points for which the energy is within a specified interval (and evaluating $e^{i\vec{k} \cdot \vec{R}}$ for such points). The real part of g cannot be obtained as simply, since if the principal value integral is attempted numerically in accord with the definition $[P(1/x) = \text{Re}(1/x) - i\epsilon = x/x^2 + \epsilon^2]$, the result does not converge readily as $\epsilon \rightarrow 0$. It was found necessary to isolate those cells in which $|E - E_n(\vec{k})|$ is smaller than some assigned value. In such a cell, all quantities other than $[E - E_n(\vec{k})]^{-1}$ can be regarded as constant and an integration is per-

formed on the rapidly varying part. In such a manner, reasonably accurate values of the real part of g can be found.

Symmetrized combinations of Wannier functions belonging to the different irreducible representations were constructed according to the procedures of Ref. 2. Ten lattice sites were considered. We choose the origin at the midpoint of a line joining two atoms in a unit cell, and our Wannier functions are characterized by a direct lattice vector; the relevant symmetry group for our purposes is C_{3v} . As noted earlier, these Wannier functions contain contributions from pairs of atoms. Matrix elements of the potential and of the Green's-function operator can be constructed with the aid of the symmetrized combinations of Wannier functions which allow direct construction of the subdeterminants $D_s(E)$ pertaining to irreducible representations [Eq. (20)]. There are three representations (Λ_1 , Λ_2 , Λ_3). Qualitatively, Λ_1 may be regarded as s -like; the doubly degenerate Λ_3 as p -like and the nondegenerate Λ_2 is d -like. This correspondence is not exact, since C_{3v} does not contain the inversion, and thus Λ_1 mixes functions of p and d nature as well. The localized state described in Ref. 2 belongs to Λ_1 . The real and imaginary parts of D_s were computed, and the scattering phase shifts were found.

It was found in Ref. 2 that it was desirable to determine the energies of localized states as a function of a multiplicative parameter λ which controls the strength of the defect potential. This procedure is also useful here. Specifically, instead of the determinantal function $D(E)$ defined

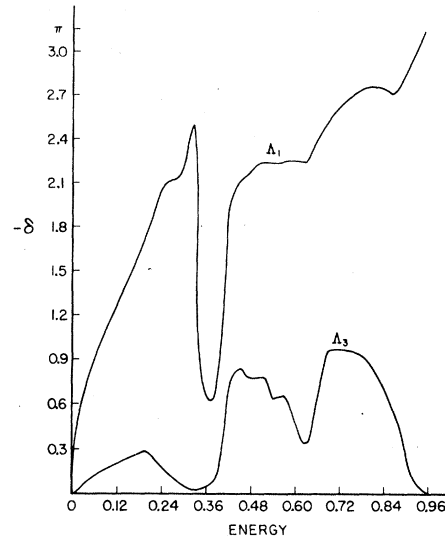


FIG. 2. Negative of the scattering phase shift is shown as a function of energy for $\lambda=1.1$.

in (11), we consider a generalized function

$$D(\lambda, E) = \det[1 - \lambda g V] \quad (31)$$

The energies of localized states, and the change in energy of the system can be obtained as a function of λ . It was seen in Ref. 2 that the defect potential is slightly too weak to produce a localized state above the valence band. A value of λ slightly greater than 1.0 was required. In the present case computations have been made for three values of λ : 0.9, 1.0, and 1.1.

V. RESULTS

The scattering phase shifts for the representations Λ_1 and Λ_3 are shown for the case $\lambda=1$ in Fig. 1. The contribution from Λ_2 is too small to be visible on this graph. The zero of energy is taken as the bottom of the lowest valence band. The phase shifts go to zero at the top of the valence band. In this case no bound state exists above the band. It is interesting to compare the variations of the phase shift with those of the density of states (for the perfect crystal). For this reason, a coarse histogram of the valence-band density of states is also shown in Fig. 1.

A similar presentation of the phase shifts for the case $\lambda=1.1$ is made in Fig. 2. It is to be noted that the phase shift for the Λ_1 representation goes to $-\pi$ at the top of the band. This indicates, according to Eq. (18), the presence of a localized state above the band, and is consistent with the results of Ref. 2. These curves are qualitatively quite similar to those shown by Lannoo and Lenglar from a much less detailed calculation for diamond.⁷ No bound states are found for the Λ_3 representation

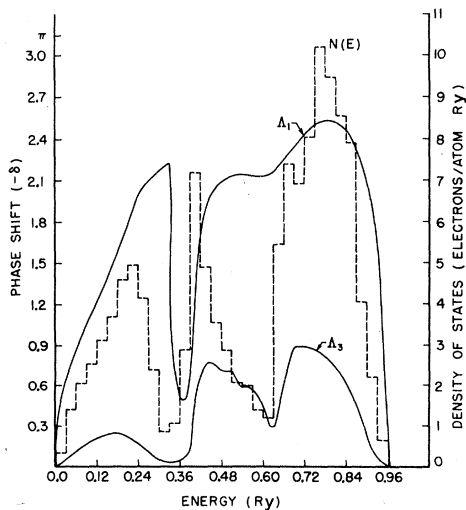


FIG. 1. Negative of the scattering phase shift (in radians) for valence-band states ($\lambda=1.0$) and representations Λ_1 and Λ_3 is shown as a function of energy. Also shown is a histogram representation of the density of states.

for any of the values of λ investigated here.

The rapid (algebraic) increase of the Λ_1 phase shift through $-\frac{1}{2}\pi$ as the energy is varied may indicate the presence of a scattering resonance. In the case $\lambda = 1.0$, two resonances are found, one at $E = 0.219$ Ry, and the other at $E = 0.806$ Ry. For $\lambda = 1.1$, a single resonance is found at $E = 0.223$. As is discussed in more detail in Refs. 1 and 9, a scattering resonance corresponds to an increase in the density of states. Near a resonance, the phase shift follows the Breit-Wigner formula

$$\tan \delta = \Gamma / 2(E_0 - E) \quad , \quad (32)$$

in which E_0 is the resonance position and Γ is the width. These quantities are determined from Eqs. (13) and (14). The width of the low-energy resonance is estimated as 0.02 Ry (for both values of λ), while the high-energy resonance in the case $\lambda = 1.0$ has a width of 0.07 Ry.

The resonances may be interpreted in the following way: If the lowest valence band were separated by a finite gap from the three bands above it, the vacancy would produce a localized state lying in that gap. Actually, there is no gap, although the density of states is seen in Fig. 1 to have a pronounced minimum in that region. As a result, the localized state is partially delocalized, becoming a scattering resonance. That it is relatively narrow indicates that it does retain some local character.

In the case $\lambda = 1.0$, a resonance was found near the top of the valence-band structure. For this value of λ , no localized state appears above the band. The localized state is, however, almost present. It is just the scattering resonance. As the strength of the defect potential is increased through the parameter λ , this state moves out of the band into the gap, and becomes the state discussed in Ref. 2.

We now turn to the determination of the change in total one-electron energy. This calculation employs Eqs. (19). For values of λ such that no bound state is formed, we must do the integral over phase shifts required by this equation, and multiply the result by 2 to allow for the two possible directions of electron spin. When λ is large enough so that a localized state is produced, we must allow for the fact that although the state is doubly degenerate due to spin, it will be occupied by only a single electron. Therefore, we include only a single bound-state contribution in the sum.

The numbers which enter this calculation are presented in Table I. The total energy is seen to vary smoothly with λ . This is in accord with the result of Kohn and Majumdar,¹³ that the properties of the system as a whole are smooth functions of the potential strength, even at those values of λ where a localized state appears. As a result, we

TABLE I. Computation of change in one-electron energy. For each value of λ , columns 1, 2, and 3 give the contribution from each representation to the phase-shift integral (not including spin); column 4 is the contribution from single occupancy of the bound state; and column 5 gives the total change in one-electron energy. All quantities are in Ry.

λ	Λ_1	Λ_2	Λ_3	Bound state	ΔE
0.9	0.468	0.000	0.218		1.372
1.0	0.563	0.000	0.242		1.610
1.1	0.616	0.001	0.265	0.024	1.788

may determine the change in one-electron energy at the value of λ which corresponds to the presence of a bound state at an energy approximately 0.05 eV above the valence band, which is apparently the physical situation.² This value of λ can be roughly estimated by extrapolation of the results of Ref. 2 which give the energy of the localized state as a function of λ , or by interpolation between the upper resonance position determined here and the bound-state energy determined at $\lambda = 1.05$ in Ref. 2. A value of λ of approximately 1.03 or 1.04 can be estimated in this way. Then the interpolated change in one-electron energy is found to be 1.67 ± 0.02 Ry, or approximately 23 eV. This number is the principal result of this paper.

This value is quite close to the energy of 23.6 eV estimated by Seeger and Swanson¹⁴ to be required to break the four bonds connecting a silicon atom to its neighbor. However, in their studies of the formation energy of a vacancy, it is also estimated that this energy is effectively reduced 11.2 eV by the formation of two additional bonds, and raised by 1.8 eV due to the stretching of neighboring bonds, giving a change in energy of 14.2 eV connected with the formation of a vacancy *apart* from that recovered on relocation of the displaced atom on the surface.

The accuracy of the estimates of Seeger and Swanson is difficult to determine, since their work is semiempirical in character. It employs an analysis based on the representation of the energy associated with a bond by a Morse potential. The discrepancy between our result for the change in one-electron energy and their value is probably significant. The present result is incomplete in that we have not considered the change in the energy associated with the coulomb interaction of electrons in the neighborhood of the vacancy. Nor has lattice distortion been included.

A rough estimate of the effects of the Coulomb interaction can be obtained as follows: We approximate the valence electrons by a uniform distribution (for this purpose only). In the unperturbed crystal, each group of four valence electrons in an atomic cell occupies a volume $\frac{1}{8}a^3$ (a being the cubic

lattice constant). When an atom is removed, the volume available to the electrons on the remaining atom in the unit cell is doubled. It is assumed that in this region, four valence electrons occupy a volume of $\frac{1}{4}a^3$. The interaction energy is determined from formulas for the free-electron gas, containing direct, exchange, and correlation terms.¹⁵ Suppose n electrons occupy uniformly a volume $\frac{4}{3}\pi r_s^3$ (this quantity being set equal either to $\frac{1}{8}a^3$ or $\frac{1}{4}a^3$), then their interaction energy is (in Ry)¹⁴

$$E_I = \frac{1.2n^2}{r_s} - \frac{0.916n^{4/3}}{r_s} - nE_c \frac{r_s}{n^{1/3}}. \quad (33)$$

Here, E_c is the correlation function. We employ the formula of Pines¹⁶

$$E_c = -0.115 + 0.031 \ln r_s. \quad (34)$$

However, the contribution from the correlation term

is quite small compared to the direct and exchange terms, so that uncertainties in E_c do not contribute significantly to the uncertainty in the final result.

The decrease in the electron interaction energy computed in this way amounts to 0.83 Ry (11.3 eV). This is quite close to half of the contribution from the one-electron energies. It is quite probably an overestimate, since the electrons are not uniformly spread through the available volume but are partially confined to covalent bonds. The change in energy associated with the formation of a vacancy is thus estimated as 0.84 Ry. This is not, however, the observed formation energy, as the displaced atom must be deposited somewhere (either as an interstitial, or on the surface). Much of this energy is recovered in that process, and a calculation of the formation energy of a vacancy, or of a vacancy-interstitial pair cannot be completed without such considerations. We hope to return to this problem in a future paper.

*Work supported in part by the U. S. Air Force Office of Scientific Research under Grant No. AFOSR-68-1565. Preliminary results were reported by J. Callaway and A. J. Hughes, *Bul. Am. Phys. Soc.* **14**, 440 (1969).

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Impurity Lifetime Broadening on Noble-Metal Fermi Surfaces*

Scott Kirkpatrick

James Franck Institute, The University of Chicago, Chicago, Illinois 60637

(Received 26 October 1970)

A simple theory of lifetime broadening due to scattering from isolated impurities in noble-metal hosts is presented and used to calculate the Dingle temperature observed in de Haas-van Alphen experiments. Details of the scattering anisotropy are easily calculated when the impurity is a transition metal. Numerical estimates of the Dingle temperatures for three extremal orbits are in good agreement with experiments on CuNi and CuZn.

INTRODUCTION

Accurate de Haas-van Alphen measurements of lifetime broadening in dilute alloys¹ now provide a very specific measure of the strength and anisotropy

of electron impurity scattering at the Fermi surface of noble metals. Difficulties in constructing an impurity potential have so far deterred theoretical calculations in the cases where the impurity is of different valence or a transition metal. This