

20.

Finally we would like to comment on the interpretation of Cowley's values on the linewidth. We presently treat these values⁶ as *half-width at half-intensity*, based on Table 7 of Ref. 12. Other workers have taken these values as *full width at half-intensity*. It is essential to use the correct interpretation of these values, inasmuch as a factor of 2 affects the conclusions derived from the

comparison of theory and experiment, as per Fig. 1.

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Isolated Interstitials in Silicon[†]

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An isolated interstitial in silicon at the nominal site is investigated using a procedure based on the expansion of the wave function in terms of the Wannier functions of the perfect crystal and using a pseudopotential for the defect potential. Scattering phase shifts are calculated for states within the valence band and a search is made for bound states within the band gap. We discover that there is no bound state in the band gap associated with this defect. The change in the one-electron energy arising from the interstitial is calculated and combined with the corresponding quantity for a single vacancy. We find this major contribution to the formation energy of the vacancy interstitial pair to be 13.6 eV.

I. INTRODUCTION

An imperfection or an impurity in a semiconductor may produce a state with an energy within the band gap of the crystal. A general method of study of these defect states and of the change in the density of states was given by Callaway.^{1,2} In this

approach, the wave function of the defect state is expanded in terms of the Wannier functions for the perfect crystal. Matrix elements on the Wannier-function basis are formed both for the defect potential and the Green's function. Solutions of a determinantal equation yield the bound state. The scattering phase shifts defined in terms of real

and imaginary parts of this determinant are related to the change in the density of states due to the defect.²

This method has been used to calculate the localized states for an isolated single vacancy and for the divacancy in silicon,³ with successful results. Recently, the formation energy of the vacancy was calculated⁴ using these techniques. However, the results obtained could not be compared directly with values inferred from experiment because the calculation was incomplete in that it did not include the changes due to the accompanying interstitial and the lattice distortion.

In this work, we use the techniques of solid-state scattering¹ to investigate an isolated single interstitial silicon atom at the nominal site, namely, the body center of the cubic lattice.

Two major results are obtained in this calculation. One is the absence of a bound state in the band gap, which possibly can explain the lack of any direct evidence of the existence of an interstitial in silicon. The other is the change in the one-electron energy arising from the vacancy-interstitial pair formation. However, to obtain the formation energy we still need the effect of lattice distortion and the change in the interaction energy.

In Sec. II we give a summary of the mathematical theory of solid-state scattering,¹ the phase shifts,² and their relationship with the change in density of states. In Sec. III we give the method of evaluating the wave function used (plane-wave coefficients in the expansion of Bloch function) and the pseudopotential coefficients. Section IV deals with the potential to describe the interstitial and the symmetry relations between various matrix elements of the defect potential; and the computational details are given in Sec. V. Finally in Sec. VI we present the results of this investigation.

II. REVIEW OF METHOD

The single-particle Hamiltonian H can be written as

$$H = H_0 + V, \quad (2.1)$$

where H_0 is the Hamiltonian for the perfect crystal containing a periodic potential, and V is the change caused in this potential by the defect.

The eigenvalues and eigenfunctions of H_0 are given by

$$H_0 \psi_n(\vec{k}, \vec{r}) = E_n(\vec{k}) \psi_n(\vec{k}, \vec{r}), \quad (2.2)$$

where $\psi_n(\vec{k}, \vec{r})$ is the Bloch function and $E_n(\vec{k})$ is the energy as a function of \vec{k} , n being the band index. The Wannier functions (involving all atoms in the unit cell) are given by

$$a_n(\vec{r} - \vec{R}_\mu) = \frac{\Omega^{1/2}}{(2\pi)^{3/2}} \int d^3k e^{-i\vec{k} \cdot \vec{R}_\mu} \psi_n(\vec{k}, \vec{r}), \quad (2.3)$$

and provide an excellent set of basis functions for expanding the solution of

$$(H_0 + V) \psi(\vec{r}) = E \psi(\vec{r}), \quad (2.4)$$

i. e.,

$$\psi(\vec{r}) = \sum_{n, \mu} B_n(\vec{R}_\mu) a_n(\vec{r} - \vec{R}_\mu), \quad (2.5)$$

where the sum includes all bands (n) and all lattice sites (μ), including the site (or sites) of the defect.

The coefficients $B_n(\vec{R}_\mu)$ are required to satisfy the equation

$$\begin{aligned} \sum_{\nu} [E \delta_{\mu\nu} - E_n(\vec{R}_\mu - \vec{R}_\nu)] B_n(\vec{R}_\nu) \\ = \sum_{i, \nu} (n\mu | V | l\nu) B_i(\vec{R}_\nu), \end{aligned} \quad (2.6)$$

where

$$(n\mu | V | l\nu) = \int a_n^*(\vec{r} - \vec{R}_\mu) V(\vec{r}) a_l(\vec{r} - \vec{R}_\nu) d^3r \quad (2.7)$$

and

$$E_n(\vec{R}) = \frac{\Omega}{(2\pi)^3} \int d^3k E_n(\vec{k}) e^{i\vec{k} \cdot \vec{R}}. \quad (2.8)$$

Now we introduce the Green's function $G_n(\vec{R}_\mu - \vec{R}_\nu)$ which satisfies the equation

$$\sum_{\nu} [E \delta_{\mu\nu} - E_n(\vec{R}_\mu - \vec{R}_\nu)] G_n(\vec{R}_\nu - \vec{R}_\rho) = \delta_{\mu\rho}. \quad (2.9)$$

It can also be expressed as

$$G_n(\vec{R}) = \frac{\Omega}{(2\pi)^3} \int \frac{e^{i\vec{k} \cdot \vec{R}}}{E - E_n(\vec{k})} d^3k, \quad (2.10)$$

where E is replaced by $E + i\epsilon$ and ϵ is allowed to go to zero after the integration is performed, to treat the case when E lies within the band n .

The coefficients B_n are now the solutions of

$$\begin{aligned} B_n(\vec{R}_\mu) = B_n^{(0)}(\vec{R}_\mu) + \sum_{\nu, l, \rho} G_n(\vec{R}_\mu - \vec{R}_\nu) \\ \times (n\nu | V | l\rho) B_l(\vec{R}_\rho), \end{aligned} \quad (2.11)$$

where $B_n^{(0)}(\vec{R}_\mu)$ is a solution of the homogeneous equation

$$\sum_{\nu} [E \delta_{\mu\nu} - E_n(\vec{R}_\mu - \vec{R}_\nu)] B_n^{(0)}(\vec{R}_\nu) = 0. \quad (2.12)$$

Equation (2.11) is analogous to the Lippmann-Schwinger equation of formal scattering theory. The solutions and the asymptotic form of the wave functions are described in Ref. 1.

The information needed to locate the bound states and the change in the one-electron energy arising from the defect is contained in the determinant

$$D(E) = \det[I - GV]$$

$$= \det[\delta_{nl} \delta_{\mu\nu} - \sum_{\rho} G_n(\vec{R}_{\mu} - \vec{R}_{\rho})(n\rho | V | l\nu)] . \quad (2.13)$$

The bound states of the defect are present at real energies E_0 , such that

$$D(E_0) = 0 , \quad (2.14)$$

and occur outside the band. For energies inside the band D is complex but we have a scattering resonance¹ whenever

$$\text{Re}D(E_0) = 0 , \quad (2.15)$$

and the width of the resonance is

$$\Gamma = 2 \left[\text{Im}D(E_0) / \text{Re} \left(\frac{dD(E)}{dE} \right) \Big|_{E_0} \right] . \quad (2.16)$$

The change in the density of single-particle states, $\Delta N(E)$, produced by the defect has been shown to be²

$$\Delta N(E) = \frac{c}{\pi} \frac{d\delta}{dE} , \quad (2.17)$$

where c is the concentration of defects (c must be small, i. e., terms of order c^2 can be neglected) and δ is the phase shift for a single defect given by

$$\tan \delta = - \text{Im}D(E) / \text{Re}D(E) . \quad (2.18)$$

The contribution to the change in the total one-electron energy arising from the band states is

$$\Delta E = \int_0^{E_m} E \Delta N(E) dE , \quad (2.19)$$

where E_m is the energy of the highest occupied band state (zero of the energy is set at the bottom of the band).

Since $D(E)$ is real outside the band, $\delta(0)$ and $\delta(E_m)$ must approach some integral multiple of π (zero included).

For a repulsive potential (for example, vacancy) the change in energy is given by

$$\Delta E = c \left(\sum_{l=1}^n (\epsilon_l - E_m) - \frac{1}{\pi} \int_0^{E_m} \delta(E) dE \right) , \quad (2.20)$$

where n is the number of bound states due to the defect (all occupied) with energies ϵ_l ($l = 1, \dots, n$). For the opposite case of attractive potential (interstitial, for example), one has the result

$$\Delta E = c \left(\sum_{l=1}^n \epsilon_l - \frac{1}{\pi} \int_0^{E_m} \delta(E) dE \right) . \quad (2.21)$$

III. ENERGY BANDS AND WAVE FUNCTIONS

In order to evaluate the matrix elements of the defect potential using (2.7), we need an expression for the defect potential V and a way to determine the Wannier functions (also the energy bands for evaluating the Green's function).

The true potential of a silicon atom is quite

strong and gives rise to core states as well as the valence states of interest. The wave functions for the valence states must be orthogonal to those of the core states. This can be conveniently achieved by the use of pseudopotential.³⁻⁵ This will simplify the calculation of energy bands in perfect crystal and the evaluation of the matrix elements by representing V in terms of the atomic pseudopotential.

The pseudopotential is local in the sense that its matrix elements between two plane waves are functions only of the wave-vector difference, i. e.,

$$\langle \vec{k} | V_{ps} | \vec{q} \rangle = U(\vec{q} - \vec{k}) \quad (3.1)$$

and

$$V_{ps} | \vec{q} \rangle = \sum_{\mu, j} v_{ps}(\vec{r} - \vec{R}_{\mu j}) | \vec{q} \rangle , \quad (3.2)$$

where $v_{ps}(\vec{r} - \vec{R}_{\mu j})$ is the atomic pseudopotential for an atom at the j th site in the unit cell located at \vec{R}_{μ} and V_{ps} is the total crystal pseudopotential.

The pseudopotential coefficients needed in our calculation are the Fourier coefficients of v_{ps} , i. e.,

$$U_{at}(\vec{k}) = \frac{2}{\Omega} \int e^{i\vec{k} \cdot \vec{r}} v_{ps}(\vec{r}) d^3r \quad (3.3)$$

for all values of \vec{k} in the Brillouin zone. We shall use the analytical expression given by Callaway and Hughes,³ derived by matching with Brust's⁵ coefficients for k values equal to the reciprocal-lattice vectors and Harrison's⁶ prescription to evaluate U_{at} at $k=0$. Thus we have

$$U_{at}(\vec{k}) = -(0.61) + (0.177311)q^2 - (0.016250)q^4 + (0.000530)q^6, \quad q^2 < 12 \quad (3.4a)$$

and

$$U_{at}(\vec{k}) = 0, \quad q^2 \geq 12 \quad (3.4b)$$

where

$$q = |\vec{k}| a / 2\pi . \quad (3.4c)$$

To obtain the band structure we expand the Bloch function in the form

$$\psi_n(\vec{k}, \vec{r}) = \frac{1}{(2\pi)^{3/2}} \sum_s b_n(\vec{k}, \vec{K}_s) e^{i(\vec{k} + \vec{K}_s) \cdot \vec{r}} , \quad (3.5)$$

in which \vec{K}_s is the reciprocal-lattice vector. The quantities b_n are the momentum wave functions for band n and satisfy the orthonormality relation

$$\sum_s b_n^*(\vec{k}, \vec{K}_s) b_l(\vec{k}, \vec{K}_s) = \delta_{n,l} . \quad (3.6)$$

We shall choose the origin at the point halfway between the two atoms in the unit cell, such that the atoms in the unit cell at the origin ($\vec{R}_{\mu} = 0$) are at points $|\vec{r}| = \pm d$. This choice of the origin makes b_n 's real.

The functions b_n 's are the eigenvectors of the matrix H_{ij} whose elements are

$$H_{ij}(\vec{k}) = \begin{cases} (\hbar^2/2m)(\vec{k} + \vec{K}_i)^2 - 0.61, & i=j \\ U_{at}(\vec{K}_i - \vec{K}_j) \cos[(\vec{K}_i - \vec{K}_j) \cdot d], & i \neq j \end{cases} \quad (3.7)$$

To limit the computational labor involved, we terminated the sum in (3.5) to 15 reciprocal-lattice vectors which included the vector (000), eight vectors of the type (111), and six of the type (200) (units of $2\pi/a$).

The eigenvalues $E_m(\vec{k})$ obtained by diagonalizing the matrix $H_{ij}(\vec{k})$ are not the energy bands. It is found that usually two or three subscripts will be involved in obtaining a band over the entire zone. Of course, we need to consider only the $\frac{1}{48}$ subzone of the Brillouin zone with the bounding interior planes for the subzone D used being $k_x = 0$, $k_x = k_y$, and $k_y = k_z$.

The energy bands are now identified in the subzone D by taking some reference point and following the symmetry and behavior of the wave function as we move from point to point in D . During the course of this, we find that the label m on the numerical eigenvalue changes. The wave functions at two points in the k space are connected by the relation (for \vec{k} such that we have isolated energy bands)

$$b_n(\alpha\vec{k}, \vec{K}_s) = \chi_n^{(j)}(\alpha) b_n(\vec{k}, \alpha^{-1}\vec{K}_s) e^{-i\vec{K}_s \cdot \vec{t}_\alpha}, \quad (3.8)$$

where α is an operation of the cubic group, \vec{t}_α is nonprimitive translation corresponding to α , and $\chi_n^{(j)}(\alpha)$ is the character for the operation α in the j th one-dimensional representation of the point group. Both $\chi_n^{(j)}(\alpha)$ and $e^{-i\vec{K}_s \cdot \vec{t}_\alpha}$ have the numerical value ± 1 (in the case of diamond lattice).

We may use the relation (3.8) to determine $\chi_n^{(j)}(\alpha)$ by considering the specific case of an α that leaves \vec{k} unchanged and $\vec{K}_s = 0$ (say). Thus we have

$$b_n(\vec{k}, 0) = \chi_n^{(j)}(\alpha) b_n(\vec{k}, 0), \quad (3.9a)$$

where

$$\alpha_1 \vec{k} = \vec{k}. \quad (3.9b)$$

Thus, we have if $b_n(\vec{k}, 0) \neq 0$, $\chi = 1$. In order to have $\chi = -1$, we must have $b_n(\vec{k}, 0) = 0$.

At points \vec{k} where we have double (or higher-order) degeneracy of energy bands, the relationship between the b_n 's is not as simple. For an operation α (with associated nonprimitive translation \vec{t}_α) belonging to $G(\vec{k})$, the symmetry group of the point of degeneracy \vec{k} , we now have⁷

$$b_n(\vec{k}, \alpha^{-1}\vec{K}_s) e^{-i\vec{K}_s \cdot \vec{t}_\alpha} = \sum_m \Gamma_{mn}^{(l)}(\alpha) b_m(\alpha\vec{k}, \vec{K}_s), \quad (3.10)$$

where $\Gamma_{mn}^{(l)}(\alpha)$ is the mn th matrix element of the operation α in the l th irreducible representation of $G(\vec{k})$. For the cases we deal with in here, we have at most a twofold degeneracy involving the mixing

of the wave functions for two bands. Thus $\Gamma_{mn}^{(l)}(\alpha)$ is replaced by $\Gamma_{mn}(\alpha)$ where m and n take values 1 and 2.

IV. ISOLATED INTERSTITIAL

As mentioned in Sec. III, we can represent the defect potential V by just the atomic pseudopotential at the position of the defect. We consider here the case of the nominal interstitial, i. e., the interstitial silicon atom is placed at the point

$$\vec{d} = \frac{1}{8}a(3, -1, -1), \quad (4.1)$$

where a is the lattice constant for Si (equal to 5.418×10^{-8} cm) and the regular atomic sites for this cell are $\pm \frac{1}{8}a(1, 1, 1)$. The defect potential is

$$V(\vec{r}) = v_{ps}(\vec{r} - \vec{d}). \quad (4.2)$$

A. Equivalent Sites

If for an operation β (with $\vec{t}_\beta = 0$) in the cubic group we have

$$\beta\vec{d} = \vec{d} - \vec{R}_\beta, \quad (4.3)$$

where \vec{R}_β is a lattice vector, the result of the operation is simply to transfer the interstitial to an equivalent site, i. e., the new position $\beta\vec{d}$ has the same relative position for another cell as \vec{d} for the cell at origin. Consequently, we are able to connect the matrix elements $(n\mu | V | l\nu)$ with $(n\mu' | V | l\nu')$ where R_μ and R_ν are related to R_μ and R_ν through β .

From (4.3) and the fact that the pseudopotential depends only on the magnitude of \vec{r} , we find

$$v_{ps}(\vec{r} - \vec{d}) = v_{ps}(\beta\vec{r} + \vec{R}_\beta - \vec{d}) \quad (4.4a)$$

or

$$V(\vec{r}) = V(\beta\vec{r} + \vec{R}_\beta). \quad (4.4b)$$

Making use of the transformation properties of the Wannier functions,³ namely,

$$a_n(\vec{r} - \vec{R}_\nu) = \chi_n^{(j)}(\alpha) a_n[\alpha(\vec{r} - \vec{R}_\nu)], \quad (4.5)$$

we find

$$(n\mu | V | l\nu) = (n\mu' | V | l\nu') \chi_n(\beta) \chi_l(\beta), \quad (4.6)$$

where

$$\vec{R}_{\mu'} = \beta\vec{R}_\mu + \vec{R}_\beta, \quad \vec{R}_{\nu'} = \beta\vec{R}_\nu + \vec{R}_\beta \quad (4.7a)$$

or

$$\vec{R}_{\mu'} = \beta^{-1}(\vec{R}_\mu - \vec{R}_\beta), \quad \vec{R}_{\nu'} = \beta^{-1}(\vec{R}_\nu - \vec{R}_\beta). \quad (4.7b)$$

Thus we find that the matrix elements for different cell-site vectors \vec{R}_μ break into groups such that a vector \vec{R}_μ can be connected with the others in the same group by the use of (4.7). Table I gives the distances from the defect for the different \vec{R}_μ 's for three site groups (actually, they should be referred to as four groups but since site number

TABLE I. Lattice-site vectors (\vec{R}_μ) and the corresponding distances squared from the interstitial site (\vec{d}) for the three site groups, with a total of ten cells.

Site group	Site No.	\vec{R}_μ (units $\frac{1}{2}a$)	$ \vec{R}_\mu - \vec{d} ^2$ [units $(\frac{1}{2}a)^2$]
1	1	(000)	$\frac{11}{16}$
	2	(1-10)	
	3	(10-1)	
2	4	(110)	$1 \frac{11}{16}$
	5	(101)	
	6	(200)	
	7	(0-1-1)	
3	8	(01-1)	$2 \frac{11}{16}$
	9	(0-11)	
	10	(2-1-1)	

7 forms a group by itself but has the same distance from the defect as site numbers 4-6, we have included it in site group 2).

For the ten lattice-site vectors listed in Table I,

we have a total of 25 site pairs for which matrix elements must be evaluated. Table II gives a list of these pairs and the number of total matrix elements to be evaluated in both three-band and six-band problems.

On the basis of previous results in cases of a single vacancy and divacancy,³ we use only the first three valence bands for the phase-shift part and only the lowest three conduction bands when we look for a bound state (in vacancy, a bound state was expected above the top of the bands, so the valence bands were used). (Here we expect the bound state below the bands, if any, and so must use the conduction bands.)

V. COMPUTATIONAL DETAILS

With the use of (2.3) and (3.5) we obtain

$$a_n(\vec{r} - \vec{R}_\mu) = \frac{\Omega^{1/2}}{(2\pi)^3} \sum_s \int d^3k b_n(\vec{k}, \vec{K}_s) \times e^{i(\vec{k} + \vec{K}_s) \cdot (\vec{r} - \vec{R}_\mu)}, \quad (5.1)$$

TABLE II. Twenty-five types of potential matrix elements which must be considered for the three site-groups problem with the ten lattice vectors of Table I. Columns 4 and 5 give the number of matrix elements that must be evaluated for the problem with three and six bands, respectively. The last column gives the number of matrix elements that are obtained through the use of symmetry relations for the three-band problem.

Site pair No.	Matrix element	Band indices	No. of matrix elements to be calculated		No. of matrix elements available from use of (4.6)
			3 bands	6 bands	3 bands only
1	$(n, 000 V l, 000)$	$n \leq l$	6	21	27
2	$(n, 1-10 V l, 000)$	$n \leq l$	6	21	54
3	$(n, 110 V l, 110)$	$n \leq l$	6	21	27
4	$(n, 110 V l, 101)$	$n \leq l$	6	21	54
5	$(n, 200 V l, 000)$	$n \leq l$	6	21	36
6	$(n, 000 V l, 200)$	$n < l$	3	15	18
7	$(n, 110 V l, 000)$	$n \leq l$	6	21	72
8	$(n, 000 V l, 110)$	$n < l$	3	15	36
9	$(n, 0-1-1 V l, 0-1-1)$	$n \leq l$	6	21	9
10	$(n, 110 V l, 0-1-1)$	$n \leq l$	6	21	36
11	$(n, 0-1-1 V l, 110)$	$n < l$	3	15	18
12	$(n, 0-1-1 V l, 000)$	$n \leq l$	6	21	36
13	$(n, 000 V l, 0-1-1)$	$n < l$	3	15	18
14	$(n, 01-1 V l, 01-1)$	$n \leq l$	6	21	27
15	$(n, 01-1 V l, 0-11)$	$n \leq l$	6	21	54
16	$(n, 01-1 V l, 000)$	$n \leq l$	6	21	72
17	$(n, 000 V l, 01-1)$	$n < l$	3	15	36
18	$(n, 01-1 V l, 1-10)$	$n \leq l$	6	21	36
19	$(n, 1-10 V l, 01-1)$	$n < l$	3	15	18
20	$(n, 01-1 V l, 110)$	$n \leq l$	6	21	36
21	$(n, 110 V l, 01-1)$	$n < l$	3	15	18
22	$(n, 01-1 V l, 101)$	$n \leq l$	6	21	72
23	$(n, 101 V l, 01-1)$	$n < l$	3	15	36
24	$(n, 01-1 V l, 0-1-1)$	$n \leq l$	6	21	36
25	$(n, 0-1-1 V l, 01-1)$	$n < l$	3	15	18
Totals			123	471	900

which are either purely real or purely imaginary depending upon the band index n (as indicated in Table III of Ref. 3). The defect-potential matrix elements are given by [using (4.2) for the defect potential]

$$\begin{aligned} \langle n\mu | V | l\nu \rangle &= \frac{\Omega}{(2\pi)^6} \sum_{s,t} \iint b_n(\vec{k}, \vec{K}_s) b_l(\vec{p}, \vec{K}_t) \\ &\times e^{i(\vec{k} + \vec{K}_s) \cdot \vec{R}_\mu - i(\vec{p} + \vec{K}_t) \cdot \vec{R}_\nu} \\ &\times \left[\int e^{-i(\vec{k} + \vec{K}_s) \cdot \vec{r}} v_{ps}(\vec{r} - \vec{d}) \right. \\ &\left. \times e^{i(\vec{p} + \vec{K}_t) \cdot \vec{r}} d^3r \right] d^3k d^3p. \quad (5.2) \end{aligned}$$

Using the pseudopotential Fourier coefficients given by (3.3), we can rewrite (5.2), i. e.,

$$\begin{aligned} \langle n\mu | V | l\nu \rangle &= \frac{\Omega^2}{2(2\pi)^6} \\ &\times \sum_{s,t} \iint \exp \{ i[(\vec{k} + \vec{K}_s) \cdot (\vec{R}_\mu - \vec{d}) \\ &- (\vec{p} + \vec{K}_t) \cdot (\vec{R}_\nu - \vec{d})] \} b_n(\vec{k}, \vec{K}_s) b_l(\vec{p}, \vec{K}_t) \\ &\times U_{at}(\vec{p} + \vec{K}_t - \vec{k} - \vec{K}_s) d^3k d^3p. \quad (5.3) \end{aligned}$$

In (5.3) the \vec{k} and \vec{p} integrals extend over the whole of the first Brillouin zone. To evaluate these integrals, one could take points only in the $\frac{1}{48}$ sub-zone (D described earlier and used in Ref. 3) and replace \vec{k} by $\beta\vec{k}$ with a sum over the operations β (similarly $\vec{p} \rightarrow \gamma\vec{p}$ and a sum over γ). This leads to the expression (after some mathematical rearrangement)

$$\begin{aligned} \langle n\mu | V | l\nu \rangle &= \frac{\Omega^2}{2(2\pi)^6} \int_D d^3k \\ &\times \int_D d^3p \sum_{s,r} \chi_l(\gamma) U_{at}(\vec{k} - \gamma\vec{p} + \vec{K}_s) \\ &\times \sum_{\beta} \left\{ \begin{array}{l} \cos \\ i \sin \end{array} \right\} [(\beta\vec{R}_\mu \cdot \vec{k} - \beta\vec{R}_\nu \cdot \gamma\vec{p}) \\ &- (\vec{k} - \gamma\vec{p} + \vec{K}_s) \cdot \beta\vec{d}] e^{i\vec{R}_s \cdot \vec{r}_\beta} \chi_l(\beta) \chi_n(\beta) \\ &\times \sum_t b_l(\vec{p}, \gamma^{-1}\vec{K}_t) b_n(\vec{k}, \vec{K}_s + \vec{K}_t) e^{-i\vec{K}_t \cdot \vec{r}_\gamma}, \quad (5.4) \end{aligned}$$

where the sums β and γ extend over all operations of the cubic group (however these sums can be reduced to a smaller number depending upon the symmetry groups of \vec{k} and \vec{p} points used, respectively),

the sum over t includes the 15 values of inverse lattice vectors chosen, and the sum over s now extends to 65 vectors formed by taking the difference of two vectors \vec{K}_i and \vec{K}_j , each going over the 15 values. Also the sum over t is limited to only those values of \vec{K}_t which give $\vec{K}_s + \vec{K}_t$ belonging to the original 15 values. The choice of ($i \sin$) or (\cos) depends on the pair of bands n, l being used.

In Ref. 3 the expression (5.4) has been used and ten points in the subzone were taken to do the \vec{k} and \vec{p} integrals. Even that limited number of points required about 6 min of high-speed computer time for each matrix element.

In the present work we have improved the accuracy by using a different technique. We use here Houston's method⁸ to evaluate the integral over the solid angles and then the Gaussian method for the k -magnitude integral.

Houston's method of evaluating integrals over the Brillouin zone consists of expanding the integrand (which possesses the symmetry of the cubic group) in terms of cubic harmonics of von der Lage and Bethe,⁹ and then using the orthogonality of these harmonics to evaluate the integral. If, for example, we are interested in an integral

$$I = \int F(\vec{q}) d^3q, \quad (5.5)$$

we expand $F(\vec{q})$ using coefficients a_j 's

$$F(\vec{q}) = \sum_j a_j(q) K_j(\theta, \phi) \quad (5.6)$$

such that

$$I = (4\pi)^{1/2} \int dq q^2 a_1(q), \quad (5.7)$$

where $a_1(q)$ is given by inverting (5.6). If we terminate the expansion (5.6) with N terms, we find

$$a_1(q) = \sum_{i=1}^N (Q^{-1})_{1i} F(q, \theta_i, \phi_i). \quad (5.8)$$

In (5.8) $F(q, \theta_i, \phi_i)$ is the value of the integrand at the value q (for the magnitude) and in the direction defined by the angles θ_i, ϕ_i . The quantities $(Q^{-1})_{1i}$ are the "weight factors" for these directions and are evaluated by inverting the matrix formed from the cubic harmonics. The values of these quantities for choices of N up to 16 are given in Ref. 8.

In the present case the integrand in (5.3) does not possess the cubic symmetry but it does in (5.4). So we shall use expression (5.4) and the change

$$\int_D d^3k = \frac{1}{48} \int d^3k, \quad (5.9)$$

where the integral on the right-hand side is over the whole zone. In changing from the Brillouin zone to Houston's method we also replace the Brillouin zone by an equivalent sphere which introduces

certain errors. However, in the case of a face-centered cubic lattice the errors involved are quite small (for other lattices, one can use methods similar to those suggested by Ganesan and Srinivasan¹⁰). Thus we get

$$\begin{aligned}
 (n\mu | V | l\nu) = & \frac{\Omega^2}{2(2\pi)^6(48)^2} \sum_{\mathbf{k}} k^2 \omega_{g_{\mathbf{k}}} \sum_{\hat{\mathbf{k}}} \omega_{h_{\hat{\mathbf{k}}}} \\
 & \times \sum_{s,p} p^2 \omega_{g_p} \sum_{\hat{p}} \omega_{h_{\hat{p}}} \sum_{\gamma} \chi_l(\gamma) U_{at}(\vec{\mathbf{k}} + \vec{\mathbf{K}}_s - \gamma\vec{p}) \\
 & \times \left(\sum_{\beta} e^{i\vec{\mathbf{R}}_s \cdot \vec{\mathbf{t}}_{\beta}} \chi_l(\beta) \chi_n(\beta) \begin{cases} \cos \\ i \sin \end{cases} \right) \\
 & \times [\beta\vec{\mathbf{R}}_{\mu} \cdot \vec{\mathbf{k}} - \beta\vec{\mathbf{R}}_{\nu} \cdot \gamma\vec{p} - (\vec{\mathbf{k}} + \vec{\mathbf{K}}_s - \gamma\vec{p}) \cdot \beta\vec{\mathbf{d}}] \\
 & \times \left(\sum_{\mathbf{t}} b_l(\vec{p}, \gamma^{-1}\vec{\mathbf{K}}_l) b_n(\vec{\mathbf{k}}, \vec{\mathbf{K}}_s + \vec{\mathbf{K}}_l) e^{-i\vec{\mathbf{K}}_l \cdot \vec{\mathbf{t}}_{\gamma}} \right), \quad (5.10)
 \end{aligned}$$

where $\omega_{g_{\mathbf{k}}}$ is the weight factor for the k magnitude in the Gaussian integration and $\omega_{h_{\hat{\mathbf{k}}}}$ is the weight factor for the $\hat{\mathbf{k}}$ direction in the Houston's method.

With the choice of five terms in both the Gaussian and Houston integration, it took about 10 min of IBM 360/65 computer time with the most efficient programming. Even though five terms are not much, it should be able to accommodate changes in the integrand for a polynomial up to the tenth degree.

The evaluation of the Green's function was also done in a similar way for E values below the conduction bands, but since it does not use enough points it was not used for E values within the valence band where one has to do principal-value

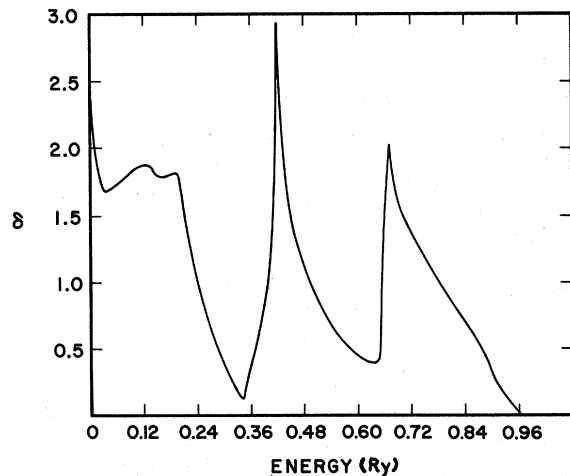


FIG. 1. Plot of the scattering phase shift (in radians) for valence-band states as a function of energy. The zero of energy corresponds to the bottom of the valence band.

TABLE III. Results for four different values of λ , the strength of the potential. Listed are the location of the bound state (zero of the energy is at the bottom of the valence band), the contribution to the change in one-electron energy from the phase shifts ($\Delta E_{\text{ph.s.}}$), and the total contribution (ΔE) from the interstitial. Last four lines give the locations (E_{01} and E_{02}) and widths (Γ_1, Γ_2) of the two scattering resonances found inside the valence band. All quantities are in rydbergs.

λ	0.9	1.0	1.04	1.1
Bound state	-0.005	-0.011	-0.013	-0.014
$\Delta E_{\text{ph.s.}}$	-0.576	-0.635	-0.658	-0.692
ΔE	-0.581	-0.646	-0.671	-0.706
E_{01}	0.407	0.406	0.406	0.406
Γ_1	0.013	0.010	0.009	0.008
E_{02}	0.668	0.663	0.661	0.659
Γ_2	0.08	0.043	0.034	0.028

integrals. In that case, the method outlined in Ref. 4 was used.

VI. RESULTS

The scattering-phase shifts, as defined by (2.18), were evaluated for the three valence bands. The results for the three site groups, listed in Table I, are shown in Fig. 1. The bottom of the valence bands is taken as the zero of the energy scale. Phase shifts are zero at the top of the valence band and rise towards π at the bottom of the band, indicating the presence of a bound state below the band.

The study of the determinant (2.13) below the band does indeed show the presence of such a bound state. The energy of this bound state is -0.011 Ry (i. e., 0.14 eV below the valence band).

Two resonances are indicated by the rapid increase of the phase shift through $\frac{1}{2}\pi$ as the energy is increased. The position (E_0) of such a resonance is given by the vanishing of the real part of the determinant, i. e.,

$$\text{Re}D(E_0) = 0, \quad (6.1)$$

or the energy at which the phase shift goes through $\frac{1}{2}\pi$ during the process of increasing. The change in the density of states follows the Breit-Wigner formula^{1,2}

$$\Delta N \sim \Gamma / [(E - E_0)^2 + (\frac{1}{2}\Gamma)^2], \quad (6.2)$$

where

$$\Gamma = 2 \text{Im}D(E_0) / \left(\frac{d}{dE} \text{Re}D(E) \right) \Big|_{E_0} \quad (6.3)$$

is the width of the resonance. The two resonances for the case shown are at energies 0.406 and 0.663 Ry with widths 0.01 and 0.043 Ry, correspondingly.

The change in the total one-electron energy is the sum of the contribution from the phase shifts and the occupied bound states, i. e.,

$$\Delta E = \Delta E_{\text{ph.s.}} + \Delta E_{\text{bs}}, \quad (6.4)$$

where

$$\Delta E_{\text{ph.s.}} = -(2/\pi) \int_0^{E_m} \delta(E) dE \quad (6.5)$$

and

$$\Delta E_{\text{bs}} = N \sum_{i=1}^n \epsilon_i. \quad (6.6)$$

The contribution from the phase shift has an extra factor of 2, as compared to result (2.21), to allow for the two possible directions of electron spin. The factor N in bound-state contribution has a value of 1 or 2 depending upon whether it is occupied by one or two electrons. However, since this contribution is negligibly small, we can ignore this difference.

Studies were made for different potential strengths by just replacing V by λV . Table III shows the results for four values of λ .

From the study of the single vacancy,^{3,4} it was concluded that a value of $\lambda = 1.04$ is required. The

change in the one-electron energy for this case is now found to be -0.67 Ry. The corresponding value for the single vacancy⁴ is 1.67 Ry. Thus we get a net change for a vacancy-interstitial formation of 1.00 Ry or 13.6 eV.

To evaluate the actual formation energy of the vacancy-interstitial pair, one has still to consider the change in the energy associated with the Coulomb interaction of electrons in the neighborhood of the vacancy and the interstitial and the lattice distortion in the two areas.

We searched for a possible bound state in the gap below the conduction bands. None was found. This can possibly explain the lack of direct evidence of the presence of an interstitial in silicon.

Further study on other possible interstitial locations is in progress.

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Experimental Determination of the Electron Temperature from Burstein-Shift Experiments in Gallium Antimonide[†]

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The shift of the Fermi energy because of an applied electric field is determined from Burstein-shift measurements in GaSb at 77 K up to field strengths of 150 V/cm. By comparison with results of the Burstein shift at lattice temperatures up to 105 K without an electric field, the electron temperature is obtained as a function of the electric field. Calculations of the electron temperature, based on a two-band model, are compared with the experimental results.

I. INTRODUCTION

Hot-electron experiments in semiconductors with large electron concentrations are often interpreted by assuming a Maxwellian or a Fermi distribution function with an electron temperature T_e , which is

higher than the lattice temperature. Methods of an experimental determination of T_e from Shubnikov-de Haas measurements¹ and Raman scattering² due to hot electrons have been reported. However, Shubnikov-de Haas experiments are restricted to low temperatures and high magnetic fields, and