indicative of a critical ordering temperature is observed above 50°K.

When no external magnetic field is present, the torsion modulus has a minimum near 105°K, Fig. 2, but this disappears when the sample is saturated. It is thus a domain wall motion effect and is associated with changes in magnetostriction and permeability.

The longitudinal internal friction was also measured near 275 kc/sec. The measurements, not shown, are less reliable than those for the lower frequency since the experimental conditions were not as satisfactory, but the internal friction appeared to peak at a temperature 3 to 7° higher than the 83-kc/sec measurements. This corresponds to an activation energy of between 0.055 and 0.026 ev per electron jump. The value obtained from ferromagnetic resonance line widths[5] is within this range.

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Theory of Donor and Acceptor States in Silicon and Germanium

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An exact theory of impurity states in crystals is developed, and an evaluation is given of the applicability of the Wannier equation to the donor states in Si and Ge in view of the multiple energy minima in the conduction band. The theory is extended to include degenerate bands, and it is shown by two different methods that the Wannier equation is to be replaced by a set of coupled wave equations. The theory is applied to acceptor states in Si and Ge. The agreement with experiment is fairly good for both donors and acceptors.

$\mathbf{W}$E are concerned here with the calculation of the ionization energies of the shallow donor and acceptor impurity states in silicon and germanium. The ionization of these levels is largely responsible for the charge carrier concentrations observed at room temperature and below. The central experimental facts[1] are that the approximate ionization energies of electrons associated with pentavalent substitutional impurities are 0.04 ev in Si and 0.01 ev in Ge, and the ionization energies of holes associated with trivalent substitutional impurities are about 0.05 ev in Si and 0.01 ev in Ge. The general picture which one has of the donor and acceptor ground states is that their wave functions are spread out over a hydrogenic $1s$ orbital with a large effective radius, of the order of 20 A or more. The loose binding is thought to be the result of the high dielectric constant of the crystals and the light effective masses of the carriers. We recall that the radius R_0 of the first Bohr orbit of an electron of mass m^* moving in a medium of dielectric constant ϵ around a fixed charge $|e|$ is

$$R_0 = \epsilon \hbar^2/m^* e^2 = (\epsilon m/m^*) a_H, \qquad (1)$$

where $a_H = \hbar^2/m e^2$ is the usual Bohr radius. As an example, $R_0 \approx 50 a_H \approx 25$ A if $\epsilon = 16$ and $m^* = 0.3m$. The effective nuclear charge is taken as $\pm e$ for pentavalent or trivalent substitutional impurities in silicon or germanium.

Our interest in the problem was heightened by the striking circumstance that in both Si and Ge the ionization energies of donors are approximately equal to the ionization energies of acceptors. This is the more remarkable because the forms of the conduction and valence bands are known from cyclotron resonance experiments[2] to be entirely different from each other. The principal energy bands for silicon are shown in Fig. 1. The conduction band energy surfaces are spheroids in k space along $\langle 111 \rangle$ axes in Ge and along $\langle 100 \rangle$ axes in Si, of the form

$$E(\Delta \mathbf{k}) = \hbar^2 \left[\frac{(\Delta k_{\shortparallel})^2}{2m_1} + \frac{(\Delta k_{\perp})^2}{2m_2} \right], \qquad (1)$$

where $\Delta \mathbf{k} = \mathbf{k} - \mathbf{k}_i$, with $\mathbf{k}_i$ at one of the set of equivalent energy minima. The valence band energy surfaces for both crystals consist of two fluted or warped spheres[3] degenerate at $k = 0$:

$$E(\mathbf{k}) = A k^2 \pm [B^2 k^4 + C^2 (k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)]^{\frac{1}{2}}. \qquad (2)$$

The numerical calculations given below suggest that the apparent equality of donor and acceptor energies is only accidental, without fundamental significance.

IMPURITY STATE THEORY

The unusual character of the energy surfaces in Si and Ge makes one hesitant about applying the Wannier theorem[4] without further examination. We have

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[1] See, for example, J. A. Burton, Physica (to be published).

[2] For a review of this work, see papers by Kip, Lax, and Kittel, Physica (to be published).
[3] Dresselhaus, Kip, and Kittel, Phys. Rev. **95**, 568 (1954).
[4] G. H. Wannier, Phys. Rev. **52**, 191 (1937); J. C. Slater, Phys. Rev. **76**, 1592 (1949); G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954); for further references, see J. Friedel, J. phys. et radium **15**, 28 (1954).

developed a method for determining the applicability of the Wannier theorem and for estimating the importance of the corrections associated with the multiplicity of the conduction band energy minima and the approximate degeneracy of the valence band energy surfaces. Our general method is exact in principle and leads to an enhanced understanding of the Wannier theorem. After completing our development we found that the basic idea had been anticipated in one of the methods given by Adams.[5] Our development is more revealing for the present applications, which have not been considered previously.

The line of attack is to compare the Wannier effective Hamiltonian in a plane wave representation with the exact Hamiltonian in a Bloch function representation. The Schrödinger equation of one electron in the perturbed periodic lattice is

$$(\mathcal{3C}_0+\delta V)\Psi=W\Psi, \tag{3}$$

where $\mathcal{3C}_0$ refers to the unperturbed lattice and δV is the perturbation. The equation of the unperturbed problem is

$$\mathcal{3C}_0\psi_{\mathbf{k}}{}^l=E^l(\mathbf{k})\psi_{\mathbf{k}}{}^l, \tag{4}$$

where

$$\psi_{\mathbf{k}}{}^l=u_{\mathbf{k}}{}^l(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \tag{5}$$

is the Bloch function with wave vector $\mathbf{k}$ and belonging to the lth energy band. The solutions Ψ of the perturbed problem may be expressed as sums over the complete set of $\psi_{\mathbf{k}}{}^l$:

$$\Psi=\sum_{l,\mathbf{k}} a_{\mathbf{k}}{}^l\psi_{\mathbf{k}}{}^l. \tag{6}$$

We substitute this expansion in Eq. (3), multiply through by Ψ^* and integrate over coordinate space. We find directly

$$W=\sum_{l,\mathbf{k}} |a_{\mathbf{k}}{}^l|^2E^l(\mathbf{k})+\sum_{l',\mathbf{k}'l,\mathbf{k}} a_{\mathbf{k}'}{}^{l'*}a_{\mathbf{k}}{}^l(\psi_{\mathbf{k}'}{}^{l'},\delta V\psi_{\mathbf{k}}{}^l). \tag{7}$$

It is useful to expand the perturbation in a Fourier series:

$$\delta V=\sum_{\mathbf{K}} b_{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}}. \tag{8}$$

The matrix element in Eq. (7) may now be written

$$(\psi_{\mathbf{k}'}{}^{l'},\delta V\psi_{\mathbf{k}}{}^l)=\sum_{\mathbf{K}} b_{\mathbf{K}}\int u_{\mathbf{k}'}{}^{l'*}u_{\mathbf{k}}{}^le^{i(-\mathbf{k}'+\mathbf{K}+\mathbf{k})\cdot\mathbf{r}}d\mathbf{r}. \tag{9}$$

It is the well-known property of periodic functions that the integral cannot be different from zero unless

$$\mathbf{k}'=\mathbf{k}+\mathbf{K}. \tag{10}$$

We use the reduced zone convention, according to which all wave vectors $\mathbf{k}$ and $\mathbf{k}'$ lie in the central Brillouin zone. If the sum $\mathbf{k}+\mathbf{K}$ would lie otherwise outside the central zone, we may subtract 2π times the

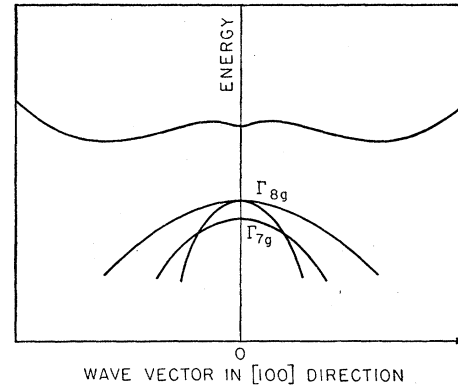[5] E. N. Adams II, J. Chem. Phys. 2013 (1953); see also S. Pekar, J. Phys. (U.S.S.R.) 10, 431 (1946).

FIG. 1. Energy band scheme for silicon as determined by cyclotron resonance. The bands will not really cross.

appropriate reciprocal lattice vector to bring it into the central zone.

We have now the result

$$W=\sum_{l,\mathbf{k}} |a_{\mathbf{k}}{}^l|^2E^l(\mathbf{k})+\sum_{l'}\sum_{l,\mathbf{k}}\sum_{\mathbf{K}} a_{\mathbf{k}+\mathbf{K}}{}^{l'*}a_{\mathbf{k}}{}^lb_{\mathbf{K}}\Delta_{\mathbf{k}+\mathbf{K},\mathbf{k}}{}^{l'l}, \tag{11}$$

where

$$\Delta_{\mathbf{k}+\mathbf{K},\mathbf{k}}{}^{l'l}=\int u_{\mathbf{k}+\mathbf{K}}{}^{l'*}u_{\mathbf{k}}{}^ld\mathbf{r}. \tag{12}$$

It is to be emphasized that Eq. (11) is an exact result. The energy eigenvalues may be found as the roots of the secular equation associated with the diagonalization of Eq. (11).

The Wannier equation follows when a simple and revealing assumption is made. We know that, by the orthogonality property of the Bloch functions,

$$\Delta_{\mathbf{k},\mathbf{k}}{}^{l'l}=\delta_{l'l}. \tag{13}$$

Thus, if we may neglect $\mathbf{K}$ in Eq. (12), the fundamental equation (8) becomes

$$W=\sum_{l}\{\sum_{\mathbf{k}} |a_{\mathbf{k}}{}^l|^2E^l(\mathbf{k})+\sum_{\mathbf{k}}\sum_{\mathbf{K}} a_{\mathbf{k}+\mathbf{K}}{}^{l*}a_{\mathbf{k}}{}^lb_{\mathbf{K}}\}. \tag{14}$$

In this approximation different bands l are entirely independent. We now show that this equation is equivalent to the Wannier equation.

We consider the problem of a free particle (not in the crystal) moving in the potential δV. We take the effective kinetic energy operator to be $E^l(-i\nabla)$, understood to be the same function of $-i\nabla$ as the energy eigenvalue $E^l(\mathbf{k})$ in Eq. (4) is of $\mathbf{k}$. The Wannier equation in the usual form is

$$[E^l(-i\nabla)+\delta V]\phi=W\phi. \tag{15}$$

We can transform this to look like Eq. (14). We consider ϕ in the plane wave representation:

$$\phi=\sum_{\mathbf{k}} a_{\mathbf{k}}{}^le^{i\mathbf{k}\cdot\mathbf{r}}. \tag{16}$$

Then Eq. (15) becomes

$$W = \sum_{k} |a_k{}^l|^2 E_l(\mathbf{k}) + \sum_{k} \sum_{K} a_{k+K}{}^{l*} a_k{}^l b_K, \qquad (17)$$

giving a secular equation identical with the factored part for the l th band of the secular equation associated with Eq. (14).

It is seen that the Wannier theorem is rigorous in an approximation which can be stated precisely, namely, the approximation that

$$\int u_{k+K}{}^{l'*} u_k{}^l d\mathbf{r} = \int u_k{}^{l'*} u_k{}^l d\mathbf{r}. \qquad (18)$$

The following two sections of this paper consider the applicability of this approximation to our semiconductor problems.

DONOR STATES

The conduction band edge of silicon consists of six equivalent spheroids oriented along the set of six equivalent $\langle 100 \rangle$ directions in $\mathbf{k}$ space. The conduction band edge of germanium consists of eight (or four, if centered at the zone boundary) equivalent spheroids oriented along the set of eight equivalent $\langle 111 \rangle$ axes in $\mathbf{k}$ space.

The first question to investigate is the effect of multiple minima in $E^l(\mathbf{k})$ on the solutions of the Wannier equation. The forms (14) or (17) show that the impurity state problem may be factored into separate problems relating to each energy spheroid separately if the condition is satisfied that the important a_{k+K} all lie comfortably within the same region of $\mathbf{k}$ space as the a_k from which they originate. In other words, we require that the sum

$$\sum_{k} \sum_{K} a_{k+K}{}^{l*} a_k{}^l b_K \qquad (19)$$

should group into the appropriate number of separate parts, each part clustered about a different band edge point $\mathbf{k}_i$, with only insignificant cross terms between the different parts. When this condition is met we can confidently calculate the donor energy by taking one energy spheroid by itself and know that the resulting value will not be affected by including states from the other equivalent spheroids. The actual eigenstates will involve all spheroids, but the energy can be calculated from one spheroid. The eigenstates must transform as irreducible representations of the symmetry group of the Wannier Hamiltonian.

We now look into the Fourier coefficients a_k, b_K. For an order-of-magnitude estimate we consider the analysis of the function

$$\phi = e^{-r/R_0}, \qquad (20)$$

as for the ground state of hydrogen. For this function the k dependence is given by

$$a_k \sim 1/(1 + k^2 R_0{}^2)^2, \qquad (21)$$

and for a Coulomb potential $\delta V \sim 1/r$ we have

$$b_K \sim 1/K^2. \qquad (22)$$

We note that $b_K K^2 dK$ is constant. It is now obvious that the convergence of the sum (19) is excellent when $kR_0 \gg 1$. From Eq. (1) we know that R_0 is of the order of $50a_H$, while the values of $(\Delta k)_0$ connecting separate energy minima of the conduction band are presumably of the order of 2π times the reciprocal lattice parameter, or $(\Delta k)_0 \approx 0.5/a_H$. Therefore $(\Delta k)_0 R_0 \approx 25$, assuring good convergence for the donor ground state problem when solved around a single energy minimum with a surface of the form (1).

Having disposed of the problem of the multiple minima, we must now consider the applicability of the approximation

$$\Delta_{k+K,\,k}{}^{l'l} \cong \delta_{l'l}, \qquad (23)$$

which led to the Wannier equation. This question arises, of course, in any application of the Wannier equation. We restrict ourselves in this section to a study of the situation in the neighborhood of one spheroidal energy minimum of the conduction band.

We use the property that it is possible to obtain u_{k+K} from u_k to the first order in $\mathbf{K}$ by the equation

$$u_{k+K}{}^l = u_k{}^l - (i\hbar^2/m) \sum_{l'} \frac{\mathbf{K} \cdot \int u_k{}^{l'*} \nabla u_k{}^l d\mathbf{r}}{E^l(\mathbf{k}) - E^{l'}(\mathbf{k})} u_k{}^{l'}. \qquad (24)$$

The normalization is not affected to first order in K, so that

$$\Delta_{k+K,\,k}{}^{ll} = 1 + O(K^2). \qquad (25)$$

However,

$$\Delta_{k+K,\,k}{}^{l'l} = \delta_{l'l} + \frac{i\hbar^2}{m} \frac{\mathbf{K} \cdot \int u_k{}^l \nabla u_k{}^{l'*} d\mathbf{r}}{E^{l'}(\mathbf{k}) - E^l(\mathbf{k})} + O(K^2), \qquad (26)$$

while in this approximation the effective mass tensor is given by

$$\left(\frac{1}{m^*} \right)_{ij} = \frac{\delta_{ij}}{m} + \left(\frac{\hbar^2}{m^2} \right) \frac{\partial^2}{\partial K_i \partial K_j}$$
$$\times \sum_{l'} \frac{|\mathbf{K} \cdot \int u_k{}^{l'*} \nabla u_k{}^l d\mathbf{r}|^2}{E^l(\mathbf{k}) - E^{l'}(\mathbf{k})}. \qquad (27)$$

We can make an estimate of the right-hand side of Eq. (26), along a principal axis of the energy surface, if we make the assumption that perturbations by a single band l' determine the effective mass in the band l; we also assume for convenience that $(1/m^*) \ll (1/m)$. Then, in the principal direction,

$$\frac{1}{m^*} \approx \frac{2\hbar^2}{m^2} \frac{|\int u_k{}^{l'*} \nabla u_k{}^l d\mathbf{r}|^2}{E^l(\mathbf{k}) - E^{l'}(\mathbf{k})}. \qquad (28)$$

Using Eq. (26),

$$\frac{1}{m^*} \approx \frac{2}{\hbar^2 K^2} [E^l(\mathbf{k}) - E^{l'}(\mathbf{k})] |\Delta_{k+K,\,k}{}^{l'l}|^2, \qquad (29)$$

so that

$$\Delta_{k+K, k}{}^{l'l} \approx \left[\frac{\hbar^2 K^2/2m^*}{E^l(\mathbf{k}) - E^{l'}(\mathbf{k})}\right]^{\frac{1}{2}}. \quad (30)$$

The range of $\mathbf{K}$ of importance is of the order of $1/R_0$, where R_0 is the orbital radius. We can expect therefore for the important terms,

$$\Delta^{l'l} \approx \left[\frac{\text{impurity ionization energy}}{\text{band gap, taken at } k}\right]^{\frac{1}{2}}, \quad (31)$$

so that $\Delta^{l'l}$ may be of the order of 0.1 for Si and Ge. We are going to neglect it in the calculations reported directly below, but it is useful to realize that the error introduced by the neglect may be of the order of 10 percent of the effective potential δV.

The next question to consider is that of the effective potential energy. We shall use as the potential energy of an electron in the field of a donor atom

$$\delta V = -e^2/\epsilon r, \quad (32)$$

where ϵ is the dielectric constant. At the relevant energies ($W_{\text{ionization}} \ll W_{\text{gap}}$) the static dielectric constant may be used. We are not aware that a careful analysis has ever been carried out of the applicability of Eq. (32) to the circumstances of the present problem. It is tempting to let $\epsilon \to 1$ for small r well within the outer shells of the donor atom. We are not entirely certain, however, that the Wannier equation can be used to describe effects so restricted in range. Pauling gives the ionic radius of P^{5+} as 0.34A, so that at this point e^2/r is much greater than the important interband energies. There is undoubtedly some increase in binding and a pileup of charge near the donor nucleus, but we will have to omit these effects because we do not yet know how to treat them with a rigor comparable to that of the rest of the present calculation. The eigenvalue equation is

$$-\frac{\hbar^2}{2m}\left[\frac{1}{\alpha_1}\frac{\partial^2}{\partial x^2}+\frac{1}{\alpha_2}\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\right]\phi-\frac{e^2}{\epsilon r}\phi=W\phi, \quad (33)$$

where $m_i^* = \alpha_i m$. This equation is not separable completely for $\alpha_1 \neq \alpha_2$. We determine an upper bound to the ground-state energy W_0, relative to the bottom of the conduction band continuum, by a variational calculation. The variational function was of the form

$$\phi=\left[\frac{ab^2}{\pi r_0^3}\right]^{\frac{1}{2}}\exp\{-[a^2x^2+b^2(y^2+z^2)]^{\frac{1}{2}}/r_0\}, \quad (34)$$

where $r_0 = \epsilon\hbar^2/me^2$. We obtain

$$W_0=-3\left(\frac{me^4}{2e^2\hbar^2}\right)(\rho^2+1)\left[\frac{\rho^2+1}{\alpha_1}+\frac{2}{\alpha_2}\right]^{-1}\left(\frac{\tan^{-1}\rho}{\rho}\right)^2, \quad (35)$$

where ρ is to be chosen to minimize W_0. We then deter-

mine a and b from

$$b=3(\rho^2+1)^{\frac{1}{2}}\left[\frac{\rho^2+1}{\alpha_1}+\frac{2}{\alpha_2}\right]^{-1}\frac{\tan^{-1}\rho}{\rho}$$

and

$$a=(\rho^2+1)^{\frac{1}{2}}b.$$

The results were as follows:

For $n-$ Ge with $\alpha_1 = 1.58$, $\alpha_2 = 0.082$, $\epsilon = 16$:

$$W_0 = -0.00905 \text{ ev}, \quad a^2 = 0.135, \quad b^2 = 0.0174.$$

For $n-$ Si with $\alpha_1 = 1$, $\alpha_2 = 0.2$, $\epsilon = 12$:

$$W_0 = -0.0298 \text{ ev}, \quad a^2 = 0.216, \quad b^2 = 0.0729.$$

Using the four-parameter variation function,

$$\psi=N[a+bx^2+c(y^2+z^2)]\exp\{-[dx^2+e(y^2+z^2)]^{\frac{1}{2}}\},$$

the energy was not lowered by as much as one percent. It may be noted that the extent of the Ge ground state in the yz plane is of the order of 60 A.

DISCUSSION OF RESULTS

Burstein, Oberly, and Davisson[6] report that the donor ionization energy in silicon is 0.04 ev, based on measurements of the infrared photoconductive response. Morin, Maita, Shulman, and Hannay[7] report for Si the values 0.039 ev for P donor atoms; 0.049 ev for As; 0.039 ev for Sb. Their values are derived from Hall coefficient data. A representative experimental value may be taken to be 0.04 ev, although it is not clear why the arsenic donors give 0.049 ev. Our calculated lower bound to the numerical value of the ionization energy is 0.030 ev and is in fair agreement therefore with the observations. There is some uncertainty in principle in the interpretation of all the observations.

Burton[8] reported at the 1954 Amsterdam conference on semiconductors the following ionization energies for donor atoms in Ge, based on Hall effect measurements:

P, 0.0120 ev; As, 0.0127 ev; Sb, 0.0096 ev.

The calculated lower limit to the ionization energy is 0.0090 ev. This is also somewhat lower than the experimental values.

ACCEPTOR STATES

As shown in Fig. 1, the valence band actually consists of two bands which are degenerate at the center of the Brillouin zone; there is also a third band which at the center of the zone is lower in energy by the amount of the spin-orbit coupling energy. To terms in k^2, the energy surfaces are described by

$$E_{1,2}(\mathbf{k})=Ak^2\pm[B^2k^4+C^2(k_x^2k_y^2+k_y^2k_z^2+k_z^2k_x^2)]^{\frac{1}{2}}, \quad (36)$$

[6] Burstein, Oberly, and Davisson, Phys. Rev. 89, 331 (1953).
[7] Morin, Maita, Shulman, and Hannay, Phys. Rev. 96, 833(A) (1954).
[8] J. A. Burton, reference 1; T. H. Geballe and F. J. Morin, Phys. Rev. 95, 1085 (1954).

and

$$E_3(\mathbf{k}) = -\Lambda + Ak^2, \tag{37}$$

where Λ is the separation between bands at $\mathbf{k}=0$.

When the energy minimum of a band is at or close to a point in k space at which several bands are degenerate, the theory of impurity states has to be revised and the Wannier equation replaced by a set of coupled differential equations. The unperturbed Hamiltonian and the impurity perturbation should be in effect diagonalized simultaneously. We develop the necessary theory below.

We suppose that we have n orthogonal states ϕ_0^i degenerate at $\mathbf{k}=0$. We make an arbitrary choice of the ϕ_0^i once and for all. By perturbation theory we obtain a set of functions $\phi_\mathbf{k}^i$. To first order in $\mathbf{k}$,

$$\phi_\mathbf{k}^j = \left\{ \phi_0^j - (i\hbar^2/m) \sum_l \frac{\mathbf{k} \cdot \int \psi_0^{l*} \nabla \phi_0^j d\mathbf{r}}{E^j(0) - E^l(0)} \psi_0^l \right\} e^{i\mathbf{k} \cdot \mathbf{r}}. \tag{38}$$

The sum is over all bands l, but in our applications the matrix elements connecting the degenerate functions ϕ_0^i will vanish. It is important to recognize that the $\phi_\mathbf{k}^i$ defined by (38) are eigenfunctions of the crystal translation operator and have the eigenvalue $e^{i\mathbf{k}\cdot\mathbf{r}}$. The $\phi_\mathbf{k}^i$ are *not*, in general, eigenfunctions of the crystal Hamiltonian $\mathcal{3C}_0$. The eigenfunctions $\psi_\mathbf{k}^j$ of $\mathcal{3C}_0$ are linear combinations of the $\phi_\mathbf{k}^i$:

$$\psi_\mathbf{k}^j = \sum_i c_\mathbf{k}^{ji} \phi_\mathbf{k}^i. \tag{39}$$

The coefficients $c_\mathbf{k}^{ji}$ may be fairly complicated functions of $\mathbf{k}$; for this reason our theory is simpler when set up first in terms of the $\phi_\mathbf{k}^i$.

We call the $\phi_\mathbf{k}^i$ *pseudo-Bloch* functions, as they obviously share some of the properties of Bloch functions. The functions given by Eq. (38) are approximately orthogonal, and we may treat them as orthogonal for our purposes. The pseudo-Bloch functions are of value even in the unperturbed problem, as the secular equation in the pseudo-Bloch representation is identical with that obtained less directly with the usual method of Van Vleck and Shockley.

We now look for a solution to the perturbed problem in the form

$$\Psi = \sum_{i, \mathbf{k}} a_\mathbf{k}^i \phi_\mathbf{k}^i. \tag{40}$$

We neglect other bands l except as they are already mixed in the $\phi_\mathbf{k}^i$ by Eq. (38). We are trying to establish a modified Wannier equation. Taking matrix elements of $\mathcal{3C}_0 + \delta V$, we have

$$(\phi_\mathbf{k}^j | \mathcal{3C}_0 + \delta V | \Psi) = a_\mathbf{k}^j W = \sum_i a_\mathbf{k}^i (\phi_\mathbf{k}^j | \mathcal{3C}_0 | \phi_\mathbf{k}^i)$$
$$+ \sum_{i, \mathbf{k}'} a_{\mathbf{k}'}^i (\phi_\mathbf{k}^j | \delta V | \phi_{\mathbf{k}'}^i). \tag{41}$$

Writing $\delta V = \sum b_\mathbf{K} e^{i\mathbf{K} \cdot \mathbf{r}}$,

$$(\phi_\mathbf{k}^j | \delta V | \phi_{\mathbf{k}'}^i) = b_\mathbf{K} \Delta_{\mathbf{k}, \mathbf{k}-\mathbf{K}}^{ji}, \tag{42}$$

where Δ is defined by Eq. (12). To a good approximation

for our n bands,

$$\Delta_{\mathbf{k}, \mathbf{k}-\mathbf{K}}^{ji} \cong \delta_{ji}; \tag{43}$$

this approximation is better than the earlier one of neglecting mixing of higher bands. The secular equation takes the form

$$W a_\mathbf{k}^j = \sum_i a_\mathbf{k}^i \mathcal{3C}^{ji}(\mathbf{k}) + a_{\mathbf{k}-\mathbf{K}}^j b_\mathbf{K}, \tag{44}$$

where

$$\mathcal{3C}^{ji}(\mathbf{k}) = (\phi_\mathbf{k}^j | \mathcal{3C}_0 | \phi_\mathbf{k}^i);$$

to the second order in $\mathbf{k}$,

$$\mathcal{3C}^{ji}(\mathbf{k}) = A^{ii} \delta_{ji} + \sum_{p, q} B_{pq}^{ji} k_p k_q, \tag{45}$$

where p, q run over x, y, z.

We now propose that for degenerate situations the Wannier equation should be replaced by the following set of coupled wave equations:

$$\sum_i \mathcal{3C}^{ji}(-i\nabla) U^i(\mathbf{r}) + \delta V U^j(\mathbf{r}) = W U^j(\mathbf{r}), \tag{46}$$

where $\mathcal{3C}^{ji}(-i\nabla)$ is a differential operator derived from $\mathcal{3C}^{ji}(\mathbf{k})$ by replacing $\mathbf{k}$ by $-i\nabla$. We note that $\mathcal{3C}^{ji}$ is a much simpler operator in the pseudo-Bloch representation $\phi_\mathbf{k}^i$ than in the diagonalized Bloch representation $\psi_\mathbf{k}^i$. The proof of Eq. (46) follows readily from the secular equation (44). We suppose that the U^i may be expanded in plane waves,

$$U^i(\mathbf{r}) = \sum_\mathbf{k} a_\mathbf{k}^i e^{i\mathbf{k} \cdot \mathbf{r}}. \tag{47}$$

The secular equation which results from Eq. (46) is identical with Eq. (44). This completes the proof.

It is now desirable to establish a physical interpretation of the functions $U^i(\mathbf{r})$. To do this we must start out with a new derivation of our modified Wannier equation Eq. (46). We follow the lines of the usual proof of the Wannier theorem for a single band, generalizing as required. We define a set w^i of pseudo-Wannier functions for the bands degenerate at $\mathbf{k}=0$:

$$w_n^i = w^i(x - x_n) = N^{-\frac{1}{2}} \sum_k e^{-ikx_n} \phi_k^i(x); \tag{48}$$

$$\phi_k^i(x) = N^{-\frac{1}{2}} \sum_n e^{ikx_n} w^i(x - x_n). \tag{49}$$

We look for a solution of the perturbed problem in the form

$$\Psi = \sum_{i, n} U^i(x_n) w^i(x - x_n). \tag{50}$$

We treat this function exactly as in the standard derivation for the nondegenerate problem, using the approximation (for δV slowly varying)

$$\int w_m^{j*} \delta V \sum_{i, n} U^i(x_n) w_n^i dx \cong \delta V(x_m) U^j(x_m), \tag{51}$$

and at the appropriate stage making use of the fact that $\mathcal{3C}^{ji}(\mathbf{k})$ is periodic in the reduced zone scheme:

$$\mathcal{3C}^{ji}(k) = \sum_s A^{ji}(x_s) e^{-ikx_s}, \tag{52}$$

so that

$$\mathcal{H}^{ii}(-id/dx)=\sum_s A^{ii}(x_s)e^{(-x_s d/dx)}. \qquad (53)$$

We are led to the set of coupled wave equations

$$\sum_i \mathcal{H}^{ji}(-i\nabla)U^i(\mathbf{r})+\delta V U^j(\mathbf{r})=WU^j(\mathbf{r}), \qquad (54)$$

identical with Eq. (46). We now have, however, the interpretation in Eq. (50) of the U^i as envelope functions of the pseudo-Wannier functions $w^i(x-x_n)$.

We have established above the important result that for degenerate bands the ordinary Wannier equation is replaced by the set of coupled differential equations[9]

$$\begin{bmatrix} Ak^2+Bk_z{}^2+\delta V-W & -Dik_zk_+ & Ek_+{}^2+Jk_-{}^2 & 0 \\ Dik_zk_- & Ck^2-Bk_z{}^2+\delta V-W & 0 & Ek_+{}^2+Jk_-{}^2 \\ Ek_-{}^2+Jk_+{}^2 & 0 & Ck^2-Bk_z{}^2+\delta V-W & Dik_zk_+ \\ 0 & Ek_-{}^2+Jk_+{}^2 & -Dik_zk_- & Ak^2+Bk_z{}^2+\delta V-W \end{bmatrix} U=0. \qquad (55)$$

The constants A, B, C, D, E, J can be expressed in terms of three constants F, G, H related to sums of matrix elements squared over energy denominators. The relations are known from unpublished work by Dresselhaus. The constants can be determined from cyclotron resonance results.

The perturbation $\delta V=-e^2/\epsilon r$ is invariant under time reversal, so that by the Kramers theorem the eigenvalues of (54) must occur in pairs. This means that for real trial functions it is reasonable to take $U_1=U_4$; $U_2=U_3$. In a magnetic field the Kramers degeneracy is lifted, and four different functions are required in principle.

Consideration of the expression (2) for the unperturbed energy shows[10] that the 4×4 matrix operator may be factored into two identical 2×2 non-Hermitian matrices which do not contain square roots of differential operators. The elements of these matrices are

$$\mathcal{H}_{11}=-\left[A+\left(B^2+\frac{1}{3}C^2\right)^{\frac{1}{2}}\right]\nabla^2-\frac{e^2}{\epsilon r}-W,$$

(54). We now consider the application to the valence band edge in germanium and silicon. It is known from cyclotron resonance that the highest state in the valence band is 4-fold degenerate and transforms as the irreducible representation Γ_{8g} of the cubic group. We have then to deal with a set of four coupled wave equations, analogous to the Dirac equations. The band associated with $\Gamma_{7g}(J=\frac{1}{2})$ does not mix in.

We choose a system of representation in which the $\phi_0{}^i$ transform as $m_J=\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$. The matrix operator becomes, symbolically,

$$\mathcal{H}_{22}=-\left[A-\left(B^2+\frac{1}{3}C^2\right)^{\frac{1}{2}}\right]\nabla^2-\frac{e^2}{\epsilon r}-W,$$

$$\mathcal{H}_{12}=-\mathcal{H}_{21}{}^*=\frac{C}{3^{\frac{1}{2}}}\left(\frac{\partial^2}{\partial x^2}+\omega\frac{\partial^2}{\partial y^2}+\omega^2\frac{\partial^2}{\partial z^2}\right),$$

where $\omega^3=1$ and A, B, and C are defined by Eq. (2). If we treat the off-diagonal elements as perturbations, we obtain in the zeroth-order approximation two hydrogen-like equations with different effective masses. The larger effective mass and ionization energy that we obtain are $m^*=0.58m$, $W_0=0.055$ ev for Si, and $m^*=0.42m$, $W_0=0.022$ ev for Ge. A second-order perturbation calculation lowered the energy by less than one percent in both cases.

The result is not reliable, however, as noncommutability was neglected in the transformation.

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[9] J. M. Luttinger and W. Kohn (private communication) have found independently a result of this type.

[10] This factorization was performed by G. Dresselhaus.