

much truth in the picture of a change in anisotropy with statistical fluctuations, and we feel that any further synthesis of the band and atomic methods must take this picture into account.

ACKNOWLEDGMENTS

I wish to thank Dr. C. Zener of Westinghouse Research Laboratories and my colleagues E. Gerjuoy and A. M. Portis for a number of stimulating discussions.

Interaction of Impurities and Mobile Carriers in Semiconductors*

GUY W. LEHMAN† AND HUBERT M. JAMES
Purdue University, West Lafayette, Indiana

(Received July 29, 1955)

The interaction of mobile carriers in semiconductors with impurity atoms and ions tends to reduce the impurity activation energy. This effect is studied using the familiar model of the semiconductor as a uniform medium of dielectric constant K in which randomly distributed impurity ions appear as fixed unit charges and the mobile carriers as charges with opposite sign and effective mass m^* . The treatment is based on the solution of Hartree equations for nonlocalized orbitals ψ_i describing mobile carriers and localized orbitals φ_j describing electrons trapped in the neighborhood of impurity ions. Determination of the individual nonlocalized orbitals is made unnecessary by a method that expresses the fluctuation in mobile carrier density approximately as a linear functional of the fluctuations in electronic potential due to impurity atoms and ions. On use of this relation, Poisson's equation becomes a linear integro-differential equation for the electronic potential energy, which can be solved in terms of integrals involving the localized orbitals φ_j . All localized orbitals are taken to have the same form φ , satisfying an integro-differential equation obtained by averaging the potential energy for a trapped electron over all configurations of the other impurities; this is solved by a variational procedure. All orbitals in the theory

depend on temperature T , the Fermi level ζ , and the impurity density N/V , since the distribution of quantum numbers of the occupied orbitals depends on these quantities. The free energy F of the system, first expressed in terms of the orbitals, T , and ζ , is then reduced to a function of ζ , T , and N/V . For given T and N/V , the physically significant ζ is determined as that which minimizes F ; the carrier density and the effective impurity activation energy are then computed as functions of T and N/V . The theory differs from all others in predicting a marked T -dependence of the activation energy, especially for high impurity concentrations. This appears because the polarizability of the mobile carrier distribution, which has an important effect on the interaction of impurities and mobile carriers, is temperature dependent in the present theory, and is completely ignored in earlier theories. For moderately high T the reduction in impurity activation energy predicted by the present theory is of the order of that predicted by Shifrin, and by Pearson and Bardeen; at low temperatures it is much less. Existing data on germanium and silicon suggest that the theory underestimates the reduction in activation energy at high impurity concentrations.

1. INTRODUCTION

THE first theoretical attempt to compute the ionization energy of impurity atoms in a semiconductor as a function of concentration was made by Shifrin.¹ Shifrin used the hydrogenic model of the impurities, which pictures the neutral atom as consisting of a single potential carrier (hole or electron) with appropriate effective mass m^* , moving about a fixed point charge (the atom core) in a medium of dielectric constant K . The ionization energy of an isolated impurity is then

$$E_0 = E_H m^* / m K^2, \quad (1.1)$$

where m is the true electronic mass and E_H the ionization energy of a hydrogen atom; the "radius" of the atom in the ground state is

$$a_0 = a_H K m / m^*, \quad (1.2)$$

where a_H is the Bohr radius. Shifrin assumes that in the impure semiconductor the impurity states with

principal quantum number n merge with the continuum, and form its lower bound, when the "radius" $n^2 a_0$ of the corresponding orbitals is the radius of a sphere of volume V/N , where N/V is the density of impurity atoms. He thus concludes that the activation energy of the impurity is given as a function of impurity density by

$$\Delta E_S = E_0 \left[1 - \left(\frac{4\pi}{3} a_0^3 \right)^{\frac{1}{3}} \left(\frac{N}{V} \right)^{\frac{1}{3}} \right]. \quad (1.3)$$

A less schematic calculation has been made by Pearson and Bardeen² who note that the energy required to remove an electron from an impurity atom is reduced by the interaction of the resulting ion with the free carriers in the system. Treating the free carrier distribution as unaffected by the presence of the ions, and assuming that almost all impurities are ionized, they arrive at a formula resembling that of Shifrin:

$$\Delta E_{PB} = E_0 \left[1 - 3.29 \left(\frac{4\pi}{3} a_0^3 \right)^{\frac{1}{3}} \left(\frac{N}{V} \right)^{\frac{1}{3}} \right]. \quad (1.4)$$

Like Shifrin, they thus conclude that the decrease in

* Based in part on a thesis presented by G. W. Lehman in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Purdue University, January, 1954.

† Now at North American Aviation, Inc., Downey, California.

¹ K. S. Shifrin, J. Theoret. Phys. (U.S.S.R.) 14, 43 (1944).

² G. L. Pearson and J. Bardeen, Phys. Rev. 75, 865 (1949).

the activation energy is proportional to $(N/V)^{1/3}$. Castellán and Seitz³ point out that it is usually not sufficiently accurate to equate the density of free carriers to the impurity density, and suggest other changes in the theory. They conclude, consequently, that the factors considered by Pearson and Bardeen will not reduce the activation energy simply proportionally to $(N/V)^{1/3}$, and cannot account for the experimental results of Pearson and Bardeen. They examine a number of other possible mechanisms, but do not succeed in fully explaining the observed effects.

The present theory again uses as the model of the semiconductor a uniform medium of dielectric constant K , in which randomly distributed impurity ions appear as fixed unit charges, and the mobile carriers as charges of opposite sign and effective mass m^* . (For simplicity in terminology, the carriers will henceforth be thought of as electrons, and the ions as positively charged donor ions.) It attempts to go beyond earlier theories in giving a more systematic and consistent treatment of what appears to be the dominant factor in reducing the activation energy: the interactions of impurity ions with trapped and with mobile carriers. This treatment is based on the determination of one-electron orbitals by solution of Hartree equations. It is unusual, however, in that the electronic orbitals depend on the temperature and carrier density as parameters. In treating conduction electrons as free, one describes a given state of electronic motion by the same orbital, regardless of what other orbitals are occupied. When the electrons are subject to external forces, such as interactions with ions or atoms, this is no longer a satisfactory approximation. One must expect solutions of the Fock or Hartree equations to yield orbitals depending on the quantum numbers of all orbitals involved in describing the system—as is the case, for example, in atomic and molecular problems. In the present problem a change in the quantum numbers of any single occupied orbital would have an insignificant effect on any single other orbital; all that matters in determining the form of an orbital is the distribution of the quantum numbers of the other occupied orbitals. This distribution is essentially the same for almost all ψ 's that might describe the crystal at any given T , and is sufficiently defined when one gives the energy level distribution in the conduction band, the density n_e of free carriers, and the temperature. Thus the form of the orbitals comes to depend on the parameters n_e and T .⁴

Determination of this dependence adds another element of complexity to the problem. The determination of the quantum numbers to be used in solving the Hartree equations for the orbitals involves statistical considerations; these considerations, in turn,

involve energies that have to be determined by solution of the Hartree equations. Thus the statistical and wave-mechanical aspects of the problem must be developed in a self-consistent way.

A characteristic feature of the present theory is the predicted temperature dependence of the impurity activation energy. The formal basis of this temperature dependence will be clear from the preceding paragraphs; the physical basis can be pictured as follows. The mobile carriers form a polarizable charge distribution, made nonuniform by its interaction with the impurity ions and atoms. The polarizability of this charge distribution depends on the distribution of electrons over the continuum states—on the electron density, and on the temperature as well. Around each positive ion is an induced average charge distribution of total amount $-e$, which tends to shield the positive ion. In the neighborhood of each neutral impurity atom there is also an induced average charge distribution of total amount zero, which modifies the effective potential acting on the trapped electron, and thus the activation energy, in a temperature dependent way. Further, each mobile carrier is regarded as moving in the field of the fixed charges plus the associated temperature-dependent induced electronic distributions. These interactions modify the energy levels in the conduction band, changing the position of the band edge and the distribution of the levels within the band in temperature-dependent ways. This again affects the activation energy, in a way that appears to be much more important than the change of energy of the trapping states. The two effects are not, however, treated separately in the theory, but appear as interdependent factors in a self-consistent formalism.

The complexity of the calculation makes it desirable to give a preliminary survey of the procedure used here. Solution of the Hartree equations is based on the assumption that the system can be properly described by use of two types of orbitals: orbitals ψ_i that extend throughout the very large volume of the crystal and describe conduction electrons, and $1s$ orbitals φ_j that describe electrons trapped in localized states about the impurity atoms (Sec. II). Each conduction electron moves in a potential field due to the trapped electrons, the impurity centers, and rest of the conduction electrons. For very large systems this differs negligibly from the potential energy $V_c(\mathbf{r})$ of an electron interacting with the total average charge distribution of the system; thus one can assume that all conduction orbitals obey the same Hartree equation with potential energy $V_c(\mathbf{r})$. On the other hand, it would involve a large error to proceed as if the electron in the localized orbital φ_j interacted with its own average charge distribution, as would be the case if the effective potential energy for this electron were taken to be V_c . Hence one must use a different effective potential energy for computing each trapped orbital,

³ G. W. Castellán and F. Seitz, *Semiconducting Materials* (Butterworth Publications, London, 1950), p. 8.

⁴ Formal treatments of such problems have been given by several authors; e.g., K. Husimi, *Phys.-Math. Soc. Japan* **22**, 264 (1940); W. M. MacDonald III and J. M. Richardson, *Phys. Rev.* **96**, 18 (1954).

that required for the calculation of φ_j being

$$V_{ij}(\mathbf{r}) = V_c(\mathbf{r}) - \frac{e^2}{K} \int d\mathbf{r}' \frac{|\varphi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}. \quad (1.5)$$

For any given form of $V_c(\mathbf{r})$, one could in principle compute the corresponding nonlocalized orbitals; given the distribution of electrons over these orbitals, one could then compute the total average density $n_e(\mathbf{r})$ of untrapped electrons in the system. In practice, such a procedure is out of the question. An approximation method, developed in Sec. III, gives $n_e(\mathbf{r})$ directly in terms of $V_c(\mathbf{r})$, the Fermi level ζ , and T , it being assumed that the distribution of electrons over the levels of the conduction band is of the Boltzmann form.

One could determine $V_c(\mathbf{r})$ by solving Poisson's equation, if one were given the positions of the impurity ions, the forms of the occupied localized orbitals φ_j , and the density $n_e(\mathbf{r})$ of the conduction electrons. Substitution of the form of $n_e(\mathbf{r})$ mentioned above converts Poisson's equation into an integro-differential equation for V_c , which also involves the position of the impurity ions and atoms, the orbitals φ_j , ζ , and T . Section IV shows how this determines $V_c(\mathbf{r})$ and $n_e(\mathbf{r})$ as a sum of contributions associated with the individual impurity atoms and ions, and expresses these contributions in terms of ζ , T , and the localized orbitals φ_j .

The form of the localized orbitals would, ideally, depend somewhat on the positions of nearby atoms and ions. To simplify the problem, the effective potential $V_{ij}(\mathbf{r})$ for the orbital φ_j is averaged over all configurations of the impurities (Sec. V). There results an integro-differential equation for φ_j , the same for all j , which is later (Sec. IX) solved approximately by a variational method. In Secs. VI and VII the total energy, free energy, and carrier density are expressed in terms of T , ζ , and the averaged form φ of the localized orbitals. Simplifying approximations, discussed in Secs. VIII and IX, then lead to complicated, but usable, expressions for the free energy F and for n_e in terms of T , ζ , and the impurity density (Sec. X). For given T and impurity density, the significant value of ζ is that which minimizes F ; when this is known, the carrier density can be computed immediately.

2. FORMULATION OF THE HARTREE EQUATIONS

In formulating the wave mechanical treatment of our model, we start from the standard form of the Hartree equations for N carriers of charge $-e$, effective mass m^* , interacting with N fixed charges $+e$, in a medium of dielectric constant K :

$$\left\{ -\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{K} \sum_{i=1}^N \frac{1}{|\mathbf{R}_i - \mathbf{r}|} + \frac{e^2}{K} \int \frac{d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \sum_{i' \neq i}^N |\psi_{i'}(\mathbf{r}')|^2 \right\} \psi_i(\mathbf{r}) = E_i \psi_i(\mathbf{r}). \quad (2.1)$$

Here \mathbf{R}_j and \mathbf{r} are vectors giving the positions of positive and negative charges, respectively; ψ_i is the normalized orbital to which the i th electron is assigned, and E_i is the corresponding energy parameter. The total energy of the system is, in the Hartree approximation,

$$E = \sum_{i=1}^N \int d\mathbf{r} \psi_i^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{K} \sum_{j=1}^N \frac{1}{|\mathbf{R}_j - \mathbf{r}|} \right] \psi_i(\mathbf{r}) + \sum_{i \neq i'}^N \sum_{i' \neq i}^N \frac{e^2}{2K} \int \int \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} |\psi_i(\mathbf{r})|^2 |\psi_{i'}(\mathbf{r}')|^2 + \sum_{i \neq j'}^N \sum_{j' \neq i}^N \frac{e^2}{2K} \frac{1}{|\mathbf{R}_j - \mathbf{R}_{j'}|}, \quad (2.2)$$

or

$$E = \sum_i^N E_i - \sum_{i \neq i'}^N \sum_{i' \neq i}^N \frac{e^2}{2K} \int \int \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} |\psi_i(\mathbf{r})|^2 |\psi_{i'}(\mathbf{r}')|^2 + \sum_{i \neq j'}^N \sum_{j' \neq i}^N \frac{e^2}{2K} \frac{1}{|\mathbf{R}_j - \mathbf{R}_{j'}|}. \quad (2.3)$$

The quantity on the right of Eq. (2.2) is stationary to variations of the ψ_i that maintain normalization.

It is well known that the Hartree equations may possess solutions that are without physical significance: for example, Pekar⁵ has pointed this out in connection with the treatment of an assemblage of hydrogen atoms. We shall assume that in the system under consideration the physically significant solutions of the Hartree equation involve orbitals of two types:

(a) orbitals localized about individual impurity ions, representing electrons trapped by these ions. We shall denote a $1s$ -orbital localized about the j th impurity ion by $\varphi_j(\mathbf{r})$. We shall neglect the possibilities that electrons might be trapped in excited localized states of other types, or that two electrons might be trapped by a single impurity atom.

(b) orbitals extending through the whole system, representing mobile carriers in the conduction band. Henceforth the symbol $\psi_i(\mathbf{r})$ will be reserved for orbitals of this type.

We shall write the particle density due to trapped electrons as

$$n_i(\mathbf{r}) = \sum_{j=1}^N a_j |\varphi_j(\mathbf{r})|^2, \quad (2.4)$$

where

$$a_j = \begin{cases} 0 & \text{if orbital } \varphi_j \text{ is empty,} \\ 1 & \text{if orbital } \varphi_j \text{ is occupied.} \end{cases} \quad (2.5)$$

The particle density due to conduction electrons is, of course, $\sum |\psi_j(\mathbf{r})|^2$, where the sum is over all orbitals occupied by the conduction electrons. Because of the nonlocalized character of the ψ orbitals, no single term makes an appreciable contribution to this sum. We

⁵ S. I. Pekar, *Abhandlungen aus der Sowjetischen Physik, Folge II* (Verlag Kultur, und Fortschritt, Berlin, 1951), pp. 61-72.

shall therefore take as the particle density due to conduction electrons

$$n_e(\mathbf{r}) = \sum_i f(E_i) |\psi_i(\mathbf{r})|^2, \quad (2.6)$$

where $f(E_i)$ is the fraction of occupied orbitals ψ_i in a small energy range about E_i , and the sum is over all nonlocalized orbitals of both spins. The error involved in using Eq. (2.6), with $f(E_i)$ a smoothly varying function, will be negligible for all statistically important distributions of conduction electrons over the nonlocalized states. The average potential energy of interaction of an electron with the total electronic distribution and the fixed positive charges is then

$$V_c(\mathbf{r}) = -\frac{e^2}{K} \sum_{j=1}^N \frac{1}{|\mathbf{R}_j - \mathbf{r}|} + \frac{e^2}{K} \int d\mathbf{r}' \frac{[n_i(\mathbf{r}') + n_e(\mathbf{r}')] }{|\mathbf{r} - \mathbf{r}'|}. \quad (2.7)$$

The potential energy term in Eq. (2.1) differs from this primarily in the restriction $i' \neq i$ in the sum over electronic states.

In using Eq. (2.1) to determine a conduction orbital ψ_i , one will make only an error of relative magnitude $1/N$ if one includes the term $i' = i$ in the electronic potential energy, thereby including a spurious interaction of the conduction electron with its own averaged charge density. To this approximation, all conduction orbitals satisfy the same wave equation, which we write as

$$\left[-\frac{\hbar^2}{2m^*} \nabla^2 + v_c(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (2.8)$$

where

$$v_c(\mathbf{r}) = V_c(\mathbf{r}) - \langle V_c(\mathbf{r}) \rangle, \quad (2.9)$$

$$\epsilon_i = E_i - \langle V_c(\mathbf{r}) \rangle. \quad (2.10)$$

Thus $v_c(\mathbf{r})$ and E_i are the electronic potential energy and the energy parameter of the orbital, measured from $\langle V_c \rangle$, the average value of V_c in the crystal, which will henceforth be taken as the zero of energy. Important use will later be made of the obvious relation

$$\langle v_c(\mathbf{r}) \rangle = 0. \quad (2.11)$$

Since the potential due to an electron trapped by an ion is large just where the localized orbital is large, it would be a serious error to include in Eq. (2.1) the interaction of a trapped electron with itself. The effective potential energy for an electron in the localized orbital $\varphi_j(\mathbf{r})$ must therefore be obtained by subtracting from V_c the potential energy due to an electron in the orbital φ_j , to obtain $V_{tj}(\mathbf{r})$, as given in Eq. (1.5). We write the corresponding wave equation as

$$\left[-\frac{\hbar^2}{2m^*} \nabla^2 + v_c(\mathbf{r}) - \frac{e^2}{K} \int \frac{d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} |\varphi_j(\mathbf{r}')|^2 \right] \varphi_j(\mathbf{r}) = \mu_j \varphi_j(\mathbf{r}), \quad (2.12)$$

where μ_j denotes the energy parameter of the j th localized orbital, as distinguished from the energy parameters ϵ_i of the conduction orbitals.

Equation (2.12), taken for each impurity j with a trapped electron, and Eq. (2.8) for the conduction orbitals, constitute the Hartree equations used in this theory. Since $V_c(\mathbf{r})$ involves implicitly the parameters a_j and the function $f(\epsilon)$, as well as the orbitals themselves, the solution of this system of equations will depend on which ions are assumed to have trapped electrons, and on the energy distribution of the untrapped electrons.

In terms of the quantities thus far introduced, Eq. (2.3) for the total energy of the system can be written as

$$E = \sum_i f(\epsilon_i) \epsilon_i + \sum_{j=1}^N a_j \mu_j + N \langle V_c \rangle + \sum_{j \neq j'}^N \sum_{j'=1}^N \frac{e^2}{2K} \frac{1}{|\mathbf{R}_j - \mathbf{R}_{j'}|} - \frac{e^2}{2K} \int \int \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \times [n_e(\mathbf{r}) n_e(\mathbf{r}') + \sum_{j \neq j'}^N \sum_{j'=1}^N a_j a_{j'} |\varphi_j(\mathbf{r})|^2 |\varphi_{j'}(\mathbf{r}')|^2 + 2n_e(\mathbf{r}) n_i(\mathbf{r}')]. \quad (2.13)$$

In the first term, the sum over occupied conduction orbitals has been replaced by a sum over all conduction orbitals, just as this was done in formulating Eq. (2.6). The first term in the double integral includes one half the interaction of every electron with its own average charge distribution. This corrects only in part for the inclusion of such self-interaction terms in Eq. (2.8), used in calculating the ϵ_i , but the fractional error is negligibly small in any case, being of the order of $1/N$.

In using the Hartree equations and the energy expression of Eq. (2.13), we shall be neglecting the exchange and correlation energies that play an important role in the theory of metals. The reasonableness of this, as concerns the exchange energy in nondegenerate semiconductors, is easily checked. Wigner and Seitz⁶ have shown that in the case of a completely degenerate free-electron gas the exchange energy per electron is

$$E_{\text{ex}} = -0.458 e^2 / r_s, \quad (2.14)$$

where r_s is defined in terms of the electron density N/V by

$$(4\pi/3) r_s^3 = V/N. \quad (2.15)$$

If one regards the electrons as moving in a medium of dielectric constant K , as in the present model, an extra factor of $1/K$ will appear on the right in Eq. (2.14). By similar methods it can be shown that for a nondegenerate gas of electrons with effective mass m^* , in a medium with dielectric constant K , having a Boltzmann distribution of energies corresponding to tempera-

⁶ E. Wigner and F. Seitz, Phys. Rev. 46, 509 (1934).

ture T , the exchange energy per electron is

$$E_{\text{ex}} = -\frac{3}{4} \frac{e^2}{r_s} \frac{1}{K} \frac{m}{m^*} \frac{E_H}{kT} \left(\frac{a_H}{r_s} \right)^2, \quad (2.16)$$

where a_H is the Bohr radius. $E_H = e^2/2a_H$ is the ionization energy of the hydrogen atom, and m is the true electronic mass. As an example we take $N/V = 10^{18}/\text{cm}^3$, $K = 13$, $T = 187^\circ\text{K}$, $m^* = 0.45m$. Then Eq. (2.16) yields $E_{\text{ex}} = -0.0018$ ev, compared with the impurity activation energy -0.036 ev found by use of the hydrogenic model.

3. CALCULATION OF SUMS OVER STATES

In solving our problem, it will be necessary to evaluate certain sums over the conduction orbitals, such as $n_e(\mathbf{r})$ [Eq. (2.6)]. Even if $v_c(\mathbf{r})$ were known to begin with, it would obviously be impracticable to do this by solving Eq. (2.8) explicitly for the individual ψ_i and ϵ_i , and then summing. Fortunately, when the distribution of electrons in the conduction band is of the Boltzmann form,

$$f(\epsilon_i) = \exp[-(\epsilon_i - \zeta)/kT], \quad (3.1)$$

such sums are easily expressed directly in terms of integrals involving the electronic potential energy $v_c(\mathbf{r})$.

We shall assume that Eq. (2.8) is to be solved within the very large volume V of the crystal, surrounded by an infinite potential barrier. (Our theory will, however, neglect surface effects due to the bounding barrier.) Let

$$Z(\mathbf{r}', \mathbf{r}; t) = \sum \psi_i^*(\mathbf{r}') \psi_i(\mathbf{r}) \exp(-\epsilon_i t), \quad (3.2)$$

where the sum is over all *spin-free* solutions of Eq. (2.8) normalized to 1 in the volume V . We shall assume that Eq. (2.8) has only nonlocalized solutions,⁷ and can then write

$$n_e(\mathbf{r}) = 2e^{\zeta/kT} Z(\mathbf{r}, \mathbf{r}; 1/kT). \quad (3.3)$$

The factor 2 enters because Eq. (2.6) involves a sums over spins, whereas Eq. (3.2) does not

In principle, $Z(\mathbf{r}', \mathbf{r}; t)$ can be determined by solving a diffusion problem. It follows from Eqs. (2.8) and (3.2) that, for $t > 0$,

$$-D\nabla^2 Z(\mathbf{r}', \mathbf{r}; t) + v_c(\mathbf{r})Z(\mathbf{r}', \mathbf{r}; t) = -\partial Z/\partial t, \quad (3.4)$$

where

$$D = \hbar^2/2m^*. \quad (3.5)$$

From the closure property⁸ of the ψ 's, it follows that

$$Z(\mathbf{r}', \mathbf{r}; 0) = \delta(\mathbf{r}' - \mathbf{r}), \quad (3.6)$$

⁷ In principle, Eq. (2.8) might possess localized solutions, which would be without physical significance [since any localized orbital should satisfy an equation of the type of Eq. (2.12)] and should therefore be excluded from the sum over conduction orbitals. In the practical cases under consideration here K is large and the binding energy of localized solutions of Eq. (2.12) is small. Localized solutions of Eq. (2.8) will have even smaller binding energy, and their contribution to the sums seems safely negligible compared to that of the numerous nonlocalized solutions.

⁸ D. Bohm, *Quantum Theory* (Prentice-Hall, Inc., New York, 1951), p. 221.

where δ is the Dirac delta function. The presence of the infinite potential barrier at the surface S of the crystal requires $\psi_i(\mathbf{r}) = 0$ and

$$Z(\mathbf{r}', \mathbf{r}; t) \equiv 0, \text{ for } \mathbf{r} \text{ on } S. \quad (3.7)$$

For each \mathbf{r}' , $Z(\mathbf{r}', \mathbf{r}; t)$ could be obtained by solving Eq. (3.4), subject to the initial condition of Eq. (3.6) and the boundary condition of Eq. (3.7). If the parameter t is interpreted as time, $Z(\mathbf{r}', \mathbf{r}; t)$ can be interpreted as the density of a system of diffusing particles at point \mathbf{r} , at time t , per particle released at point \mathbf{r}' at time $t=0$, when the following conditions are satisfied: (a) the diffusion constant is D ; (b) a particle at point \mathbf{r}'' may disappear with probability $v_c(\mathbf{r}'')$ per unit time if $v_c(\mathbf{r}'') > 0$, or give rise to another particle with probability $-v_c(\mathbf{r}'')$ per unit time if $v_c(\mathbf{r}'') < 0$; (c) any particle reaching the surface S is withdrawn from the system.

An alternative interpretation of these equations makes it easy to write down an equivalent integral formulation of the problem. One can regard $Z(\mathbf{r}', \mathbf{r}; t)$ as the average density of particles at point \mathbf{r} at time t , due to release of one particle at point \mathbf{r}' at time $t=0$, plus the release of $-v_c(\mathbf{r}'')Z(\mathbf{r}', \mathbf{r}''; t')$ particles per unit volume and per unit time, for all \mathbf{r}'' in V and all $t' > 0$; as before, any particle reaching the surface S is withdrawn from the system. Let $Z_0(\mathbf{r}', \mathbf{r}; \Delta t)$ denote the average density at \mathbf{r} at time t per particle released at \mathbf{r}' at time $t - \Delta t$. Then the total particle density due to the system of sources described above is obviously

$$Z(\mathbf{r}', \mathbf{r}; t) = Z_0(\mathbf{r}', \mathbf{r}; t) - \int_0^t dt' \int_V d\mathbf{r}'' v_c(\mathbf{r}'') \times Z(\mathbf{r}', \mathbf{r}''; t') Z_0(\mathbf{r}'', \mathbf{r}; t - t'). \quad (3.8)$$

From the character of the diffusion problem, it is evident that for $|\mathbf{r} - \mathbf{r}'|$ small compared to the distance of \mathbf{r} and \mathbf{r}' from the surface S of the crystal, and for not too large t , the nature of the solution will be negligibly changed by ignoring the boundary condition on S , Eq. (3.7). Then $Z_0(\mathbf{r}', \mathbf{r}; t)$ can be taken as the solution of Eq. (3.4), with $v_c(\mathbf{r}) \equiv 0$, subject to the initial condition of Eq. (3.6): that is, it can be replaced by the familiar diffusion function

$$Z_0(|\mathbf{r} - \mathbf{r}'|; t) = [4\pi Dt]^{-3/2} \exp[-|\mathbf{r} - \mathbf{r}'|^2/4Dt]. \quad (3.9)$$

Making this approximation, we write

$$Z(\mathbf{r}', \mathbf{r}; t) = Z_0(|\mathbf{r} - \mathbf{r}'|; t) - \int_0^t dt' \int_{\infty} d\mathbf{r}'' v_c(\mathbf{r}'') \times Z(\mathbf{r}', \mathbf{r}''; t') Z_0(\mathbf{r} - \mathbf{r}''; t - t'). \quad (3.10)$$

This equation can be solved by a familiar iterative method. Writing

$$Z(\mathbf{r}', \mathbf{r}; t) = \sum_{\tau} Z_{\tau}(\mathbf{r}', \mathbf{r}; t), \quad (3.11)$$

where Z_τ is of the τ th order in $v_c(\mathbf{r})$, substituting this into Eq. (3.10), and equating terms on the two sides that are of the same order in v_c , one finds

$$Z_{\tau+1}(\mathbf{r}', \mathbf{r}; t) = - \int_0^t dt' \int_{\infty} d\mathbf{r}'' v_c(\mathbf{r}'') \times Z_\tau(\mathbf{r}', \mathbf{r}''; t') Z_0(\mathbf{r} - \mathbf{r}''; t - t'). \quad (3.12)$$

The successive integrations over t' can be carried out without difficulty. One finds

$$Z_1(\mathbf{r}', \mathbf{r}; t) = - \frac{1}{4\pi D} \int d\mathbf{r}_1 v_c(\mathbf{r}_1) \left[\frac{|\mathbf{r} - \mathbf{r}_1| + |\mathbf{r}_1 - \mathbf{r}'|}{|\mathbf{r} - \mathbf{r}_1| |\mathbf{r}_1 - \mathbf{r}'|} \right] \times Z_0(|\mathbf{r} - \mathbf{r}_1| + |\mathbf{r}_1 - \mathbf{r}'|; t), \quad (3.13)$$

$$Z_2(\mathbf{r}', \mathbf{r}; t) = \frac{1}{(4\pi D)^2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 v_c(\mathbf{r}_1) \times v_c(\mathbf{r}_2) \left[\frac{|\mathbf{r} - \mathbf{r}_1| + |\mathbf{r}_1 - \mathbf{r}_2| + |\mathbf{r}_2 - \mathbf{r}'|}{|\mathbf{r} - \mathbf{r}_1| |\mathbf{r}_1 - \mathbf{r}_2| |\mathbf{r}_2 - \mathbf{r}'|} \right] \times Z_0(|\mathbf{r} - \mathbf{r}_1| + |\mathbf{r}_1 - \mathbf{r}_2| + |\mathbf{r}_2 - \mathbf{r}'|; t); \quad (3.14)$$

the generalization is obvious.

If $v_c \equiv 0$, one has $Z_\tau = 0$, for $\tau > 0$. If $v_c(\mathbf{r})$ is constant, it follows easily from the definition in Eq. (3.2), together with the fact that introduction of a constant potential v_c changes every ϵ_i by this same amount, that

$$Z(\mathbf{r}', \mathbf{r}; t) = Z_0(|\mathbf{r} - \mathbf{r}'|; t) \exp[-v_c t]. \quad (3.15)$$

On the other hand, Eqs. (3.11) to (3.14) yield

$$Z(\mathbf{r}', \mathbf{r}; t) = Z_0(|\mathbf{r} - \mathbf{r}'|; t) [1 - v_c t + \frac{1}{2}(v_c t)^2 - \dots]. \quad (3.16)$$

Roughly speaking, then, Eq. (3.11) gives an expansion of Z in terms of increasing order in $v_c(\mathbf{r})t$. It is easily shown that, for bounded $v_c(\mathbf{r})$ and for $t > \epsilon > 0$, the series in Eq. (3.11) is uniformly convergent in t ; it will not, however, be rapidly convergent if $v_c(\mathbf{r})t$ is large at many points. As applied in the present work, Eq. (3.11) will yield expansions in powers of $v_c(\mathbf{r})/kT$; the practical necessity for dealing with only the first few terms of the expansions will then limit the accuracy of the results more severely the lower the value of T .

It follows from these results, together with Eq. (3.3), that

$$n_e(\mathbf{r}) = 2e^{\xi/kT} \left\{ \left(\frac{2\pi m^* kT}{h^2} \right)^{\frac{3}{2}} - \frac{4\pi m^*}{h^2} \int d\mathbf{r}_1 \frac{v_c(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} \times Z_0(2|\mathbf{r} - \mathbf{r}_1|; 1/kT) + \left(\frac{2\pi m^*}{h^2} \right)^2 \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{v_c(\mathbf{r}_1)v_c(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_1| |\mathbf{r}_1 - \mathbf{r}_2| |\mathbf{r}_2 - \mathbf{r}|} R Z_0(R; 1/kT) - \dots \right\}, \quad (3.17)$$

where

$$R = |\mathbf{r} - \mathbf{r}_1| + |\mathbf{r}_1 - \mathbf{r}_2| + |\mathbf{r}_2 - \mathbf{r}|. \quad (3.18)$$

In the present theory it is impractical to use terms beyond those explicitly written out in Eq. (3.17). In fact, this expression will be further simplified by replacing the last term by its average over \mathbf{r} , thus retaining only the first-order fluctuations in $n_e(\mathbf{r})$, given by the first integral on the right. Since the average value of $v_c(\mathbf{r})$ is zero by definition [Eq. (2.9)], the average value of the first integral in Eq. (3.17) is zero. The average value of the second integral is easily obtained by integrating in elliptic coordinates with \mathbf{r}_1 and \mathbf{r}_2 as foci. One finds, to our approximation,

$$\langle n_e \rangle = 2e^{\xi/kT} \left\{ \left(\frac{2\pi m^* kT}{h^2} \right)^{\frac{3}{2}} + \frac{2\pi m^*}{h^2 kT} \frac{1}{V} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{v_c(\mathbf{r}_1)v_c(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} Z_0(2|\mathbf{r}_1 - \mathbf{r}_2|; 1/kT) \right\}, \quad (3.19)$$

$$n_e(\mathbf{r}) - \langle n_e \rangle = - \frac{8\pi m^*}{h^2} e^{\xi/kT} \int d\mathbf{r}_1 \frac{v_c(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} \times Z_0(2|\mathbf{r} - \mathbf{r}_1|; 1/kT). \quad (3.20)$$

Important simplifications and some characteristic features of the present theory arise from the linearized relation of $n_e(\mathbf{r})$ to $v_c(\mathbf{r})$, as given in Eq. (3.20).

4. CALCULATION OF THE ELECTRONIC POTENTIAL ENERGY

The potential energy $v_c(\mathbf{r})$ of an electron in the crystal is related to the total charge density by Poisson's equation, which can here be written as

$$\nabla^2 v_c(\mathbf{r}) = \frac{4\pi e^2}{K} [\sum_j \delta(\mathbf{r} - \mathbf{R}_j) - n_e(\mathbf{r}) - n_i(\mathbf{r})]. \quad (4.1)$$

Using Eqs. (2.4) and (3.20), one can reduce this to the form

$$\nabla^2 v_c(\mathbf{r}) - \kappa e^{\xi/kT} \int_{\infty} d\mathbf{r}_1 \frac{v_c(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} Z_0(2|\mathbf{r} - \mathbf{r}_1|; 1/kT) = \frac{4\pi e^2}{K} \left\{ -\langle n_e \rangle + \sum_j (1 - a_j) \delta(\mathbf{r} - \mathbf{R}_j) + \sum_j a_j [\delta(\mathbf{r} - \mathbf{R}_j) - |\varphi_j(\mathbf{r} - \mathbf{R}_j)|^2] \right\}, \quad (4.2)$$

where

$$\kappa = 32\pi^2 m^* e^2 / K h^2. \quad (4.3)$$

This constitutes a linear integro-differential equation for $v_c(\mathbf{r})$, which is to be solved subject to the condition that $\langle v_c(\mathbf{r}) \rangle = 0$.

The bracket on the right of Eq. (4.2) describes what may be regarded, at this stage of the problem, as the fixed charges in the crystal: the average electronic charge density, the charges of impurity ions without trapped electrons, and the charge distributions of the

impurity "atoms"—ions plus trapped electrons. The total fixed charge is zero.

Because of the linear character of Eq. (4.2), its solution is easily expressed in terms of the solution of a similar equation with a single fixed point charge. We write

$$\nabla^2 V_i(\mathbf{r}) - \kappa e^{\zeta/kT} \int_{\infty} d\mathbf{r}_1 \frac{V_i(\mathbf{r}_1)}{|\mathbf{r}-\mathbf{r}_1|} Z_0(2|\mathbf{r}-\mathbf{r}_1|; 1/kT) = \frac{4\pi e^2}{K} \delta(\mathbf{r}), \quad (4.4)$$

to be solved for V_i subject to the boundary condition that $V_i(\mathbf{r}) \rightarrow 0$ as $r \rightarrow \infty$. $V_i(\mathbf{r})$ can be regarded as the electronic potential energy that would be produced in the crystal by a single impurity ion placed at the origin; it is the potential energy of interaction of an electron with the ion itself, plus its energy of interaction with the distribution of mobile electrons, of density $P_i(\mathbf{r})$, induced by presence of the ion. V_i and P_i must obviously satisfy the relations

$$\nabla^2 V_i(\mathbf{r}) = \frac{4\pi e^2}{K} \{\delta(\mathbf{r}) - P_i(\mathbf{r})\}, \quad (4.5)$$

$$V_i(\mathbf{r}) = \frac{e^2}{K} \left[-\frac{1}{r} + \int d\mathbf{r}_1 \frac{P_i(\mathbf{r}_1)}{|\mathbf{r}-\mathbf{r}_1|} \right]. \quad (4.6)$$

Comparison of Eqs. (4.4) and (4.5), with use of Eqs. (4.3) and (3.5), shows also that

$$P_i(\mathbf{r}) = -\frac{1}{\pi D} e^{\zeta/kT} \int d\mathbf{r}_1 \frac{V_i(\mathbf{r}_1)}{|\mathbf{r}-\mathbf{r}_1|} \times Z_0(2|\mathbf{r}-\mathbf{r}_1|; 1/kT). \quad (4.7)$$

From Eq. (4.5), and the boundary condition on $V_i(\mathbf{r})$, it follows that

$$\int d\mathbf{r} P_i(\mathbf{r}) = 1; \quad (4.8)$$

the total charge of the ion and the induced electronic distribution that surrounds it is zero.

Equation (4.4) is easily solved by Fourier transform methods. One finds

$$V_i(\mathbf{r}) = -\frac{e^2}{2\pi^2 K} \int_{\infty} d\mathbf{p} \frac{e^{i(\mathbf{p}\cdot\mathbf{r})}}{p^2 + H(\mathbf{p})}, \quad (4.9)$$

where

$$H(\mathbf{p}) = \kappa e^{\zeta/kT} \int_{\infty} d\mathbf{r}_1 \frac{e^{-i(\mathbf{p}\cdot\mathbf{r}_1)}}{r_1} Z_0(2r_1; 1/kT). \quad (4.10)$$

On substituting Eq. (4.9) into Eq. (4.7), one finds

$$P_i(\mathbf{r}) = \frac{1}{(2\pi)^3} \int_{\infty} d\mathbf{p} e^{i(\mathbf{p}\cdot\mathbf{r})} \frac{H(\mathbf{p})}{p^2 + H(\mathbf{p})}. \quad (4.11)$$

Calculation of V_i and P_i for given ζ and T is thus reduced to a matter of quadratures. These functions will be discussed in Sec. VIII.

It will also be convenient to define the electronic potential energy $V_a(\mathbf{r})$ produced in the crystal by an atom—ion plus trapped electron—at the origin. This satisfies the relation

$$\nabla^2 V_a(\mathbf{r}) - \kappa e^{\zeta/kT} \int_{\infty} d\mathbf{r}_1 \frac{V_a(\mathbf{r}_1)}{|\mathbf{r}-\mathbf{r}_1|} Z_0(2|\mathbf{r}-\mathbf{r}_1|; 1/kT) = \frac{4\pi e^2}{K} \{\delta(\mathbf{r}) - |\varphi(\mathbf{r})|^2\}, \quad (4.12)$$

where φ is the orbital of the trapped electron. $V_a(\mathbf{r})$ consists of terms representing the interaction of an electron with the ion, with the trapped electron, and the distribution of mobile electrons, of density $P_a(\mathbf{r})$, induced by presence of the atom:

$$V_a(\mathbf{r}) = \frac{e^2}{K} \left[-\frac{1}{r} + \int d\mathbf{r}_1 \frac{|\varphi(\mathbf{r}_1)|^2}{|\mathbf{r}-\mathbf{r}_1|} + \int d\mathbf{r}_1 \frac{P_a(\mathbf{r}_1)}{|\mathbf{r}-\mathbf{r}_1|} \right]. \quad (4.13)$$

Comparison of Eq. (4.12) with the obvious analog of Eq. (4.5) shows that

$$P_a(\mathbf{r}) = -\frac{1}{\pi D} e^{\zeta/kT} \int d\mathbf{r}_1 \frac{V_a(\mathbf{r}_1)}{|\mathbf{r}-\mathbf{r}_1|} \times Z_0(2|\mathbf{r}-\mathbf{r}_1|; 1/kT). \quad (4.14)$$

Comparison of Eqs. (4.4) and (4.12) shows that

$$V_a(\mathbf{r}) = V_i(\mathbf{r}) - \int d\mathbf{r}_1 |\varphi(\mathbf{r}_1)|^2 V_i(\mathbf{r}-\mathbf{r}_1), \quad (4.15)$$

while comparison of Eqs. (4.7) and (4.14) yields

$$P_a(\mathbf{r}) = P_i(\mathbf{r}) - \int d\mathbf{r}_1 |\varphi(\mathbf{r}_1)|^2 P_i(\mathbf{r}-\mathbf{r}_1). \quad (4.16)$$

From Eqs. (4.15) and (4.16) it follows that

$$\int d\mathbf{r} P_a(\mathbf{r}) = \int d\mathbf{r} V_a(\mathbf{r}) = 0; \quad (4.17)$$

both the net charge in the mobile electron distribution induced by a neutral impurity atom and the average potential due to the whole set of charges will vanish.

We shall assume that all the localized orbitals φ have the same form. Then from Eqs. (4.4) and (4.12), and the linear character of Eq. (4.2), it follows that

$$v_c(\mathbf{r}) = \sum_{\text{atoms } j} V_a(\mathbf{r}-\mathbf{R}_j) + \sum_{\text{ions } j} V_i(\mathbf{r}-\mathbf{R}_j) - \langle n_c \rangle \int d\mathbf{r} V_i(\mathbf{r}). \quad (4.18)$$

Similarly, the mobile electron density is

$$n_e(\mathbf{r}) = \sum_{\text{atoms}} P_a(\mathbf{r}-\mathbf{R}_j) + \sum_{\text{ions}} P_i(\mathbf{r}-\mathbf{R}_j). \quad (4.19)$$

Thus the mobile electron density is expressed as the sum of contributions associated with each atom and ion; the potential energy fluctuation $v_e(\mathbf{r})$ is similarly expressed as a sum of contributions from the atoms and ions, minus the average value of these contributions. The possibility of expressing $v_e(\mathbf{r})$ and $n_e(\mathbf{r})$ in this way depends entirely on the linearization of the theory resulting from the assumption, expressed in Eq. (3.20), that the mobile carrier density is a linear functional of the potential energy fluctuation. It is this linearization of the theory that gives it a relatively simple form, but restricts its applicability to sufficiently small $v_e(\mathbf{r})$.

5. HARTREE EQUATION FOR LOCALIZED ORBITALS

In the preceding section we have seen how to determine the form of $v_e(\mathbf{r})$ for any specified ζ , T , and any distribution of trapped electrons in localized orbitals φ_j , by a series of quadratures. Physically, one would expect the localized orbitals to have slightly different forms and energy parameters μ_j , because of the different relative positions of the other impurity ions and atoms with which the trapped electron interacts. To make the problem more tractable, we shall replace the interaction of each trapped electron with the neighboring impurities by an average interaction—the average taken over all trapped electrons in a fixed random arrangement of impurity atoms and ions, or, what is equivalent, an average taken over all configurations of the impurities surrounding a given trapped electron. We shall accordingly write

$$\varphi_j(\mathbf{r}) = \varphi(\mathbf{r}-\mathbf{R}_j). \quad (5.1)$$

Combining Eqs. (2.12) and (4.18), one can express the Hartree equation for an electron trapped by an impurity ion at the origin as

$$\left\{ -\frac{\hbar^2}{2m^*} \nabla^2 + \sum_{\text{atoms}} V_a(\mathbf{r}-\mathbf{R}_j) + \sum_{\text{ions}} V_i(\mathbf{r}-\mathbf{R}_j) - \langle n_e \rangle \int d\mathbf{r} V_i(\mathbf{r}) - \frac{e^2}{K} \int d\mathbf{r}_1 \frac{|\varphi(\mathbf{r}_1)|^2}{|\mathbf{r}-\mathbf{r}_1|} \right\} \varphi(\mathbf{r}) = \mu \varphi(\mathbf{r}). \quad (5.2)$$

Averaging over all configurations of the neighboring impurities, or over all \mathbf{R}_j (except that of the ion under consideration), one obtains

$$\langle \langle V_a(\mathbf{r}-\mathbf{R}_j) \rangle \rangle = 0, \quad (5.3)$$

by Eq. (4.17), and

$$\langle \langle V_i(\mathbf{r}-\mathbf{R}_j) \rangle \rangle = \frac{1}{V} \int d\mathbf{r} V_i(\mathbf{r}), \quad (5.4)$$

where V is the volume of the crystal, and the configura-

tion average is indicated by double angular brackets. This averaging removes from Eq. (5.2) all terms representing interactions with neighboring atoms, while the average value of the interaction with the N_i ions in the crystal cancels out against the fourth term. Thus one obtains

$$\left\{ -\frac{\hbar^2}{2m^*} \nabla^2 + V_a(\mathbf{r}) - \frac{e^2}{K} \int d\mathbf{r}_1 \frac{|\varphi(\mathbf{r}_1)|^2}{|\mathbf{r}-\mathbf{r}_1|} \right\} \varphi(\mathbf{r}) = \mu \varphi(\mathbf{r}). \quad (5.5)$$

The dependence of this equation on φ can be made completely explicit by use of Eq. (4.15) for V_a :

$$\left\{ -\frac{\hbar^2}{2m^*} \nabla^2 + V_i(\mathbf{r}) - \int d\mathbf{r}_1 |\varphi(\mathbf{r}_1)|^2 \times \left[V_i(\mathbf{r}-\mathbf{r}_1) + \frac{e^2}{K} \frac{1}{|\mathbf{r}-\mathbf{r}_1|} \right] \right\} \varphi(\mathbf{r}) = \mu \varphi(\mathbf{r}). \quad (5.6)$$

Use of Eq. (4.13) instead yields

$$\left\{ -\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{Kr} + \frac{e^2}{K} \int d\mathbf{r}_1 \frac{P_a(\mathbf{r}_1)}{|\mathbf{r}-\mathbf{r}_1|} \right\} \varphi(\mathbf{r}) = \mu \varphi(\mathbf{r}), \quad (5.7)$$

which expresses the effective potential energy for the trapped electron as the sum of contributions from its interaction with the nucleus and with the mobile carrier distribution P_a induced by presence of the nucleus plus trapped electron.

In connection with Eq. (5.7), it may be well to emphasize the significance of the present application of the Hartree approximation. The induced distribution of mobile carriers is here treated as determined by the time-average distribution $|\varphi(\mathbf{r})|^2$ of positions of the trapped electron, rather than its instantaneous position. In effect, the trapped electron is treated as moving rapidly as compared with the conduction electrons. In consequence of this approximation, the induced distribution of mobile carriers, $P_a(\mathbf{r})$, is treated as static, and like the inducing atom, has zero net charge. The electronic potential energy due to $P_a(\mathbf{r})$ falls off exponentially as r increases; thus the effective potential energy for the trapped electron assumes the Coulomb form $-e^2/Kr$ at large r . This is in contradiction to another natural picture of the situation (inconsistent with the Hartree approximation) which would have the trapped electron moving slowly at large r in the field of an ion effectively screened by the conduction electron distribution induced by the ion alone. At least for large r , the present theory appears to underestimate the effect of shielding by the conduction electrons, by overestimating the effectiveness of the trapped electron in keeping the conduction electrons away from the nucleus.

6. TOTAL ENERGY OF THE SYSTEM

An expression for the total energy of the system has been given in Eq. (2.13). By use of Eqs. (2.4) and (4.19)

this can be expressed in terms of the localized orbitals φ and the distributions of mobile carriers P_a and P_i induced about impurity atoms and ions, respectively. To this expression we apply the process of configuration averaging, as discussed in the preceding section. The calculation is elementary, but requires a little care. Let N_a and N_i denote the number of impurity atoms and ions, respectively. Then one finds

$$\begin{aligned} \langle\langle E \rangle\rangle = & \langle\langle \sum_i f(\epsilon_i) \epsilon_i \rangle\rangle + N_a \mu \\ & - N_i \frac{e^2}{2K} \iint \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} P_i(\mathbf{r}) P_i(\mathbf{r}') \\ & - N_a \left[\frac{e^2}{2K} \iint \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} P_a(\mathbf{r}) P_a(\mathbf{r}') \right. \\ & \left. + \frac{e^2}{K} \iint \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} |\varphi(\mathbf{r})|^2 P_a(\mathbf{r}') \right]. \quad (6.1) \end{aligned}$$

As usual, the total energy appears as the sum of the Hartree parameters of the occupied orbitals, corrected by subtraction of the interaction terms that are duplicated when one considers each electron in turn. Here the configuration average of these subtracted terms is expressed as the sum of the self energies of the mobile carrier distributions induced by each ion and atom, plus the energy of interaction of each trapped electron with the carrier distribution induced about the same center.

Configuration averaging has removed from Eq. (6.1) all terms that refer explicitly to interactions of charge distributions associated with different impurities. The interaction of impurities is now entirely implicit in the dependence of $P_i(\mathbf{r})$ and $P_a(\mathbf{r})$ on ζ , which depends on N_i and T , and is ultimately determined by T and the total impurity concentration.

The relation between the number N_i of mobile electrons and the parameter ζ is implicit in Eq. (3.19). To average this equation over all configurations of the impurities, one can use Eqs. (4.18), (5.3), and (5.4) to find

$$\begin{aligned} \langle\langle v_c(\mathbf{r}_1) v_c(\mathbf{r}_2) \rangle\rangle = & N_a \langle\langle V_a(\mathbf{r}_1) V_a(\mathbf{r}_2) \rangle\rangle \\ & + N_i \langle\langle V_i(\mathbf{r}_1) V_i(\mathbf{r}_2) \rangle\rangle, \quad (6.2) \end{aligned}$$

after neglect of the quantity $-N_i \langle\langle V_i \rangle\rangle^2$, which is of higher order in $1/V$. Insertion of Eq. (6.2) into Eq. (3.19), and application of Eqs. (4.7) and (4.14) yields

$$\begin{aligned} N_i/V = \langle\langle n_e \rangle\rangle = & n_0(\zeta, T) - \frac{1}{2kT} \left[\frac{N_a}{V} \int d\mathbf{r} P_a(\mathbf{r}) V_a(\mathbf{r}) \right. \\ & \left. + \frac{N_i}{V} \int d\mathbf{r} P_i(\mathbf{r}) V_i(\mathbf{r}) \right], \quad (6.3) \end{aligned}$$

where

$$n_0(\zeta, T) = 2 \left(\frac{2\pi m^* kT}{h^2} \right)^{\frac{3}{2}} e^{\zeta/kT} \quad (6.4)$$

is the electron density in an ideal unperturbed semiconductor with the given ζ and T . For a fixed number of impurity atoms,

$$N = N_a + N_i, \quad (6.5)$$

Eq. (6.3) provides an implicit relation between N_i and ζ that depends on the values of N and T . (The dependence of the integrals on ζ must not be forgotten.) The complexity of this relation, as compared with the usual Eq. (6.4), arises from the fact that the theory takes some account of the change in the energy distribution of the conduction levels caused by interaction of the conduction electrons with the impurity atoms and ions.

A quantity of fundamental interest in the theory is the average energy change per electron removed from a localized level:

$$\frac{\partial \langle\langle E \rangle\rangle}{\partial N_i} \Big|_{N, T} = \frac{\partial \langle\langle E \rangle\rangle}{\partial N_i} \Big|_{N, \zeta, T} + \frac{\partial \zeta}{\partial N_i} \Big|_{N, T} \frac{\partial \langle\langle E \rangle\rangle}{\partial \zeta} \Big|_{N, N_i, T}. \quad (6.6)$$

The first term on the right could be computed from Eq. (6.1), after properly expressing $\langle\langle f(\epsilon_i) \epsilon_i \rangle\rangle$ as a function of N , N_i , ζ , and T ; it represents the average energy required to bring into the conduction band an electron trapped by an isolated impurity, ζ being held constant. The second term could be computed by use of Eqs. (6.1) and (6.3); it represents the additional energy required, on the average, because of the change in the interaction of the ionized impurity with the other impurities, and the associated changes in the self-energies of the charge distributions around those other impurities. It would be complicated and unnecessary to disengage these terms from each other before completing the calculation.

7. CALCULATION OF THE FREE ENERGY

In preceding Sections we have seen how to calculate $\langle\langle E \rangle\rangle$, the contribution of mobile and trapped carriers to the internal energy of the system, as a function of N , T , and ζ or N_i . It remains to determine the physically occurring values of ζ or $\langle N_i \rangle$ as a function of N and T . These are the values that minimize the free energy

$$F(N, T, \zeta) = \langle\langle E \rangle\rangle - TS(N, T, \zeta). \quad (7.1)$$

The entropy S is given by

$$S = k \ln W = k \ln W_e + k \ln W_i, \quad (7.2)$$

where W is the number of ways of choosing occupied orbitals, localized and unlocalized, consistent with the specified values of N , T , and ζ , and W_e and W_i are the number of ways of choosing conduction and trapping orbitals, respectively.

The number of ways of distributing $N_a = N - N_i$ electrons over N impurities is

$$W_i = \frac{N!}{N_i!(N - N_i)!}, \quad (7.3)$$

the last factor taking account of the two spin possibilities for each electron. The corresponding term in the entropy can be written, using Sterling's approximation, as

$$S_i = k \ln W_i = k \{ (N - N_i) [\ln 2 - \ln(1 - N_i/N)] - N_i \ln(N_i/N) \}. \quad (7.4)$$

The other entropy term, S_c , can be expressed in terms of the distribution function $f(\epsilon)$ [Eq. (3.1)] by familiar methods.⁹ Let $\rho(\epsilon)$ be the density of conduction band levels, both spins included. Then W_c is the number of ways of distributing $Z_i = f(\epsilon_i)\rho(\epsilon_i)\Delta\epsilon_i$ electrons over $N_i = \rho(\epsilon_i)\Delta\epsilon_i$ levels in each of the energy ranges $\Delta\epsilon_i$, and

$$S_c = k \ln W_c = -k \int d\epsilon \rho(\epsilon) \times \{ f(\epsilon) \ln f(\epsilon) + [1 - f(\epsilon)] \ln [1 - f(\epsilon)] \}. \quad (7.5)$$

Separate calculation of this quantity is unnecessary: it is more convenient to associate it with the corresponding term in $\langle\langle E \rangle\rangle$,

$$\langle\langle \sum_i f(\epsilon_i)\epsilon_i \rangle\rangle = \int d\epsilon \rho(\epsilon) f(\epsilon)\epsilon, \quad (7.6)$$

and to compute

$$F_c = \langle\langle \sum_i f(\epsilon_i)\epsilon_i \rangle\rangle - TS_c. \quad (7.7)$$

With the assumed Boltzmann form of $f(\epsilon_i)$, this becomes

$$F_c = \int d\epsilon \rho(\epsilon) \{ \zeta f(\epsilon) + kT [1 - f(\epsilon)] \ln [1 - f(\epsilon)] \}. \quad (7.8)$$

Treating f as small throughout the conduction band, one can replace $(1 - f) \ln(1 - f)$ by f ; the integration then yields

$$F_c \cong N_i (\zeta - kT). \quad (7.9)$$

With this approximation we have

$$F = N_i \left\{ \zeta - kT [1 - \ln(N_i/N)] - \frac{e^2}{2K} \int \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} P_i(\mathbf{r}) P_i(\mathbf{r}') \right\} + (N - N_i) \left\{ \mu - kT [\ln 2 - \ln(1 - N_i/N)] - \frac{e^2}{2K} \int \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} P_a(\mathbf{r}) [P_a(\mathbf{r}') + 2|\varphi(\mathbf{r}')|^2] \right\}, \quad (7.10)$$

where μ , P_i , P_a , and φ all depend implicitly on ζ , and ζ and N_i are related by Eq. (6.3).

⁹ H. A. Bethe and A. Sommerfeld, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 2, p. 34.

8. THE MOBILE CARRIER DISTRIBUTION $P_i(\mathbf{r})$ INDUCED BY AN IMPURITY ION

The calculations in the present work have been based on use of a simple analytical approximation to the distribution function $P_i(\mathbf{r})$, which must now be discussed.

The exact form of $P_i(\mathbf{r})$ is given by Eqs. (4.10) and (4.11). On substituting into Eq. (4.10) the form of Z given in Eq. (3.9), and carrying out the integration over directions of \mathbf{r} , one obtains

$$H(\mathbf{p}) = \frac{2\pi\kappa n_0(\zeta, T)}{p} \int_0^\infty dr \sin(pr) \exp(-kTr^2/D). \quad (8.1)$$

Let

$$q = \frac{1}{2} p (D/kT)^{\frac{1}{2}}, \quad (8.2)$$

and define¹⁰

$$q\Theta(q) = \int_0^\infty dx \sin(2qx) \exp(-x^2) = \exp(-q^2) \int_0^q dx \exp(x^2). \quad (8.3)$$

One can then write

$$H(\mathbf{p}) = n_0(\zeta, T) \cdot \frac{4\pi e^2}{KkT} \cdot \Theta(q). \quad (8.4)$$

The function $q\Theta(q)$ has been tabulated and discussed by Rosser.¹¹ Here it is sufficient to note that

$$\Theta(0) = 1, \quad (8.5)$$

$$\Theta(q) \cong 1/2q^2, \quad \text{for } q > 10. \quad (8.6)$$

In the classical limit, $h \rightarrow 0$, $D \rightarrow 0$, and $q \rightarrow 0$. In this limit one can replace $H(\mathbf{p})$ in Eqs. (4.9) and (4.11) by

$$\frac{1}{r_f^2} = \frac{4\pi e^2}{KkT} n_0(\zeta, T), \quad (8.7)$$

and carry out the integrations without difficulty, to obtain

$$V_{ic}(\mathbf{r}) = -(e^2/Kr) \exp(-r/r_f), \quad (8.8)$$

$$P_{ic}(\mathbf{r}) = (1/4\pi r_f^2 r) \exp(-r/r_f). \quad (8.9)$$

The potential V_{ic} due to an ion in the crystal thus appears as a shielded Coulomb potential, with range of the order of the distance r_f . The length r_f is identical with the characteristic length that appears in the classical theory of potential fluctuations in semiconductors.¹² The infinity in $P_{ic}(\mathbf{r})$ at the origin is a

¹⁰ The equivalence of the two forms for $I = q\Theta(q)$ can be established by noting that both satisfy the first-order equation $dI/dq = 1 - 2qI$ and assume the value 0 when $q = 0$.

¹¹ J. B. Rosser, Office of Scientific Research and Development Report OSRD No. 5861 (unpublished).

¹² G. W. Lehman, M.S. thesis, Purdue University, 1950 (unpublished); also available as a Signal Corps Report.

peculiarity of the classical limiting form, and appears neither in the exact quantum-mechanical result, nor in the approximate one next to be derived.

Convenient analytical approximations to $P_i(\mathbf{r})$ and $V_i(\mathbf{r})$ can be obtained by introducing a simple approximation to $\Theta(q)$. Equations (8.5) and (8.6) suggest that one may be able to approximate $\Theta(q)$, with sufficient accuracy for present purposes, by an expression of the form $1/(1+dq^2)$. Here it is desirable to choose d so that the approximation has its first and second derivatives correct at the origin.

$$\Theta_a(q) = 1/(1 + \frac{2}{3}q^2). \quad (8.10)$$

This is a good approximation for small q , but it is in error by a factor of 3 when q is large. For large q , however, $\Theta(q)$ is small, and contributes little to the denominator in Eq. (4.9). We write this denominator as

$$p^2 + H(\mathbf{p}) = \frac{4kT}{D} \left\{ q^2 + \frac{3}{2} \frac{\xi^2}{(\xi^2 + 1)^2} \Theta(q) \right\}, \quad (8.11)$$

where ξ is a parameter defined by

$$\frac{6kT}{D} \frac{\xi^2}{(\xi^2 + 1)^2} = \frac{4\pi e^2}{KkT} n_0(\zeta, T) = \frac{1}{r_f^2}, \quad 0 \leq \xi \leq 1. \quad (8.12)$$

Numerical checks show that replacement of Θ in Eq. (8.11) by Θ_a will introduce an error of no more than $1\frac{1}{2}$ percent for any q , so long as $\xi \leq \frac{1}{4}$, as is the case in most of our calculations; the corresponding approximate forms of $V_i(\mathbf{r})$, and $P_i(\mathbf{r})$ should be correspondingly accurate. With this approximation, the integrations in Eqs. (4.9) and (4.11) are easily performed by contour integration. One finds

$$V_i(\mathbf{r}) = -\frac{e^2}{K(1-\xi^2)r} \times [\exp(-r/r_s) - \xi^2 \exp(-r/\xi r_s)], \quad (8.13)$$

$$P_i(\mathbf{r}) = \frac{1}{4\pi(1-\xi^2)r_s^2 r} \times [\exp(-r/r_s) - \exp(-r/\xi r_s)], \quad (8.14)$$

where

$$r_s = r_f / (1 + \xi^2)^{\frac{1}{2}}. \quad (8.15)$$

These approximations will be used henceforth. Elementary integration yields

$$\int d\mathbf{r} V_i(\mathbf{r}) P_i(\mathbf{r}) = -\frac{e^2}{2Kr_s} \frac{1 + \xi + \xi^2}{(1 + \xi)^3}. \quad (8.16)$$

The approximate forms in Eqs. (8.13) and (8.14) satisfy Eq. (4.5), and hence Eq. (4.6); applying the

latter equation and integrating, one finds

$$\begin{aligned} & \frac{e^2}{K} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} P_i(\mathbf{r}) P_i(\mathbf{r}') \\ &= \int d\mathbf{r} \left\{ V_i(\mathbf{r}) + \frac{e^2}{Kr} \right\} P_i(\mathbf{r}) \\ &= \frac{e^2}{2Kr_s} \frac{1 + 3\xi + \xi^2}{(1 + \xi)^3}. \end{aligned} \quad (8.17)$$

9. APPROXIMATE FORM OF THE LOCALIZED ORBITALS

Having determined the form of $V_i(\mathbf{r})$, one can turn to the solution of Eq. (5.6) for the localized orbital $\varphi(\mathbf{r})$. A variational method will be used here to determine a simple approximate form for this orbital.

Solution of Eq. (5.6) is equivalent to finding functions $\varphi(\mathbf{r})$ that make

$$\begin{aligned} H(\varphi) &= \int d\mathbf{r} \varphi^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m^*} \nabla^2 + V_i(\mathbf{r}) \right] \varphi(\mathbf{r}) \\ &\quad - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' |\varphi(\mathbf{r})|^2 |\varphi(\mathbf{r}')|^2 \\ &\quad \times \left\{ V_i(\mathbf{r} - \mathbf{r}') + \frac{e^2}{K} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right\} \end{aligned} \quad (9.1)$$

stationary to variations of $\varphi(\mathbf{r})$ that maintain its normalization. The corresponding value of μ can be written in terms of integrals involving $V_i(\mathbf{r})$, or, as is most quickly evident from Eq. (5.7), as

$$\begin{aligned} \mu(\varphi) &= \int d\mathbf{r} \varphi^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{Kr} \right] \varphi(\mathbf{r}) \\ &\quad + \frac{e^2}{K} \iint \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} P_a(\mathbf{r}) |\varphi(\mathbf{r}')|^2. \end{aligned} \quad (9.2)$$

We are interested in the form of φ that makes $H(\varphi)$ an absolute minimum. The functional $\mu(\varphi)$ is not stationary with respect to deviations of φ from this form, but, as in any Hartree calculation, the total energy of the system is stationary with respect to variations of the orbitals φ , if the other orbitals ψ (and thus P_i and P_a) are held constant.

Equation (5.7) expresses the effective potential energy for a trapped electron as the sum of a Coulomb term and a contribution due to the presence of an induced distribution of carriers about the impurity atom. Since the inducing charge distribution has total charge zero, the induced distribution $P_a(\mathbf{r})$ of carriers will have total charge zero, and, moreover, will tend to be small in magnitude everywhere. Thus the potential energy term due to the induced carrier distribution can

be expected to be very small; the total effective potential will be nearly of Coulomb form, and $\varphi(\mathbf{r})$ will be approximately of hydrogenic form. For simplicity, we shall base our calculation on the use of an approximate orbital of hydrogenic form,

$$\varphi(\alpha; \mathbf{r}) = \left[\frac{\alpha^3}{8\pi r_s^3} \right]^{1/2} \exp(-\alpha r/2r_s), \quad (9.3)$$

where α is an adjustable parameter so chosen as to extremalize $H(\varphi)$. The adequacy of this approximation will appear later.

On using this form of φ , together with our approximations for V_i and P_i , one can compute the free carrier distribution about a neutral impurity by use of Eq. (4.16). One finds

$$P_a(\mathbf{r}) = \frac{1}{4\pi(1-\xi^2)r_s^3} \cdot \frac{1}{x} [-A_1 \exp(-x) + A_2 \exp(-x/\xi) + (A_1 - A_2 - A_3\alpha x/2) \exp(-\alpha x)], \quad (9.4)$$

where

$$x = r/r_s, \quad (9.5)$$

$$A_1 = \frac{\alpha^4}{(\alpha^2 - 1)^2} - 1,$$

$$A_2 = \frac{\alpha^4 \xi^4}{(\alpha^2 \xi^2 - 1)^2} - 1, \quad (9.6)$$

$$A_3 = \alpha^2 \left[\frac{\xi^2}{\alpha^2 \xi^2 - 1} - \frac{1}{\alpha^2 - 1} \right].$$

The contribution of this induced carrier distribution to the electronic potential energy is

$$V_{ia}(\mathbf{r}) = \frac{e^2}{2Kr} [B_1 \exp(-x) - B_2 \exp(-x/\xi) + (B_2 - B_1 + B_3\alpha x) \exp(-\alpha x)], \quad (9.7)$$

where

$$\begin{aligned} B_1 &= 2A_1/(1-\xi^2), \\ B_2 &= 2\xi^2 A_2/(1-\xi^2), \\ B_3 &= A_3/\alpha^2(1-\xi^2). \end{aligned} \quad (9.8)$$

A tedious calculation based on Eq. (9.1) yields

$$H(\varphi) = E_0 \left[\left(\frac{\alpha}{\alpha_0} \right)^2 - \frac{5}{8} \frac{\alpha}{\alpha_0} - \frac{1}{8(1-\xi^2)} \frac{\alpha}{\alpha_0} \times \{f(\alpha) - \xi^2 f(\xi\alpha)\} \right], \quad (9.9)$$

where E_0 is, as previously defined, the ionization energy of an isolated impurity, α_0 is defined by the relation

$$\frac{\alpha_0}{2r_s} = \frac{1}{a_0} = \frac{E_0}{e^2/2K}, \quad (9.10)$$

and

$$f(\alpha) = \frac{11\alpha^4 + 28\alpha^3 + 15\alpha^2}{(1+\alpha)^4}. \quad (9.11)$$

To minimize $H(\varphi)$, one must have

$$\frac{\alpha}{\alpha_0} = 1 + \frac{1}{16} \frac{\alpha^{-2}}{1-\xi^2} \{g(\alpha) - \xi^2 g(\xi\alpha)\}, \quad (9.12)$$

where

$$g(\alpha) = \frac{75\alpha^3 + 119\alpha^2 + 65\alpha + 13}{(1+\alpha)^5}. \quad (9.13)$$

For $\xi \leq \frac{1}{4}$ and $a_0 \geq 4$, the cases in which we shall be particularly interested, Eq. (9.12) shows that α/α_0 is very nearly equal to 1; at worst, for $\xi = \frac{1}{4}$, $\alpha_0 = 4$, one has $\alpha/\alpha_0 = 1.007$. We shall therefore take $\alpha = \alpha_0$ in all the calculations that follow. Equations (9.3) and (9.10) show that this amounts to neglecting the change in form of the trapped electron orbital due to the free carrier distribution induced about the neutral impurity. The small deviation of α from α_0 suggests that the use of hydrogenic orbitals is an adequate approximation, and this is confirmed by test calculations of V_{ia} , which show that this quantity is small and roughly constant in the region where φ is large.

The total electronic potential due to an impurity atom is V_{ia} plus the potential due to the unshielded impurity atom:

$$V_a(\mathbf{r}) = V_{ia}(\mathbf{r}) - \frac{e^2}{Kr} \left(1 + \frac{\alpha r}{2r_s} \right) \exp(-\alpha r/r_s). \quad (9.14)$$

In calculating N_i/V by Eq. (6.3) and F by Eq. (7.10) we shall neglect the very small integral

$$\iint \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} P_a(\mathbf{r})P_a(\mathbf{r}') = \int d\mathbf{r} V_{ia}(\mathbf{r})P_a(\mathbf{r}). \quad (9.15)$$

To this approximation one finds

$$\int d\mathbf{r} V_a(\mathbf{r})P_a(\mathbf{r}) \cong \frac{e^2}{2Kr_s} \cdot \frac{1}{8\alpha(1-\xi^2)} \times [h(\alpha) - h(\xi\alpha)], \quad (9.16)$$

where

$$h(\alpha) = \frac{25\alpha^2 + 36\alpha + 13}{(1+\alpha)^4}. \quad (9.17)$$

With our choice of $\varphi(\mathbf{r})$, Eq. (9.2) for μ becomes

$$\mu = -E_0 + \frac{e^2}{K} \iint \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} P_a(\mathbf{r}) |\varphi(\mathbf{r}')|^2. \quad (9.18)$$

The last integral in this expression also appears explicitly in Eq. (7.10) for F , but cancels out when this value for μ is introduced. Evaluation of this integral is therefore unnecessary unless it is desired to determine μ as a function of N_i and T .

10. PARAMETRIC EXPRESSIONS FOR THE FINAL RESULTS

The calculations and approximations described in previous sections bring the problem into the following form. The conduction electron density is related to T , ζ , and the impurity density N/V by Eq. (6.3). By use of Eqs. (8.16) and (9.16), this can be written as

$$\langle\langle n_e \rangle\rangle \left\{ 1 - \frac{e^2}{4KkTr_s} \left[\frac{1+\xi+\xi^2}{(1+\xi)^3} + \frac{1}{8\alpha_0(1-\xi^2)} \right] \times (h(\alpha_0) - h(\xi\alpha_0)) \right\} = n_0(\zeta, T) - \frac{N}{V} \frac{e^2}{4KkTr_s} \frac{1}{8\alpha_0(1-\xi^2)} (h(\alpha_0) - h(\xi\alpha_0)), \quad (10.1)$$

where $h(\alpha)$ is defined by Eq. (9.17), and n_0 , ξ , r_s , and α_0 are defined as functions by T and ζ by Eqs. (6.4), (8.12), (8.15), and (9.10), respectively. The electronic free energy per unit volume, as given by Eq. (7.10), becomes, on use of Eqs. (8.17) and (9.18) and neglect of the smallest integral,

$$\frac{F}{V} = \langle\langle n_e \rangle\rangle \left\{ \zeta - kT [1 - \ln(V\langle\langle n_e \rangle\rangle/N)] - \frac{e^2}{4Kr_s} \frac{1+3\xi+\xi^2}{(1+\xi)^3} \right\} + \left\{ \frac{N}{V} - \langle\langle n_e \rangle\rangle \right\} \times \{-E_0 + kT \ln[(N - V\langle\langle n_e \rangle\rangle)/2N]\}. \quad (10.2)$$

The physically significant value of ζ is that which minimizes F , for fixed T and N/V . Given this, all other quantities of interest can be calculated.

The carrier density depends on T , N/V , and the two constants that characterize our model of the pure semiconductor: K and m^* , or the binding energy E_0 and radius a_0 of the impurity orbitals at zero impurity concentration, as defined by Eqs. (1.1) and (1.2). The present theory establishes a relation between just three dimensionless parameters:

$$\tau = \frac{3}{2} kT/E_0, \quad (10.3)$$

which characterizes the temperature of the system, and

$$\eta_i = (N/V) \cdot 3\pi a_0^3, \quad (10.4)$$

$$\eta_e = \langle\langle n_e \rangle\rangle \cdot 3\pi a_0^3, \quad (10.5)$$

which characterize the impurity and carrier densities, respectively. Except for a numerical factor of the order of 1, introduced to simplify numerical calculations, η_i and η_e are the average number of impurities and free carriers in the volume occupied by a trapped electron orbital.

For practical calculations it is convenient to replace ζ as the adjustable parameter by ξ [see Eq. (8.12)]:

$$(6\pi\tau)^{\frac{1}{2}} \xi^2 / (1+\xi^2)^2 = \exp(\zeta/kT), \quad 0 < \xi < 1. \quad (10.6)$$

In terms of ξ , one has

$$\alpha_0^2 = (1+\xi^2)/\xi^2\tau, \quad (10.7)$$

$$n_0(\zeta, T) = \tau^2 \xi^2 / 3\pi a_0^3 (1+\xi^2)^2, \quad (10.8)$$

$$r_s^2 = a_0^2 (1+\xi^2) / 4\tau \xi^2. \quad (10.9)$$

Equation (10.1) assumes the form

$$\eta_e \left\{ 1 - \frac{3}{2\alpha_0\tau} \left[\frac{1+\xi+\xi^2}{(1+\xi)^3} + \frac{1}{8\alpha_0(1-\xi^2)} (h(\alpha_0) - h(\xi\alpha_0)) \right] \right\} = \frac{\xi^2\tau^2}{(1+\xi^2)^2} \frac{3\eta_i}{16\alpha_0^2\tau(1-\xi^2)} (h(\alpha_0) - h(\xi\alpha_0)), \quad (10.10)$$

and Eq. (10.2) the form

$$\frac{F}{V} = \frac{kT}{3\pi a_0^3} \left[\eta_e \left\{ \ln[(6\pi\tau)^{\frac{1}{2}} \xi^2 / (1+\xi^2)^2] - 1 + \ln(\eta_e/\eta_i) - \frac{3}{2\alpha_0\tau} \frac{1+3\xi+\xi^2}{(1+\xi)^3} \right\} + (\eta_i - \eta_e) \left\{ -\frac{3}{2\tau} + \ln((\eta_i - \eta_e)/2\eta_i) \right\} \right]. \quad (10.11)$$

The last two equations define $3\pi a_0^3 F/VkT$ as a function of τ , η_i , and ξ only. Solution of

$$(\partial F/\partial \xi)_{\tau, \eta_i} = 0 \quad (10.12)$$

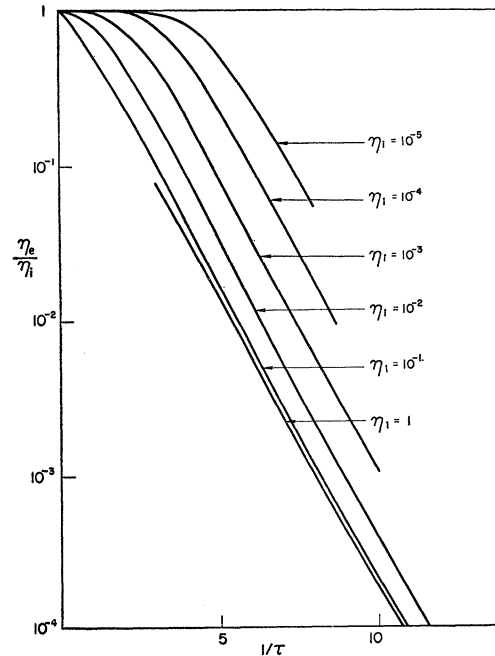


FIG. 1. Ratio of carrier concentration to impurity concentration, plotted against reciprocal temperature for various impurity concentrations η_i [see Eqs. (10.3), (10.4)].

fixes ξ as a function of τ and η_i , whereupon Eq. (10.10) gives η_e as a function of these quantities.

11. RESULTS AND CONCLUSIONS

The calculations described in the preceding paragraph have been carried out on the punched card digital computer of the Purdue Statistical Laboratory, using a method of successive approximations. They have been limited to ranges of the parameters for which $\xi \lesssim \frac{1}{4}$, to assure the accuracy of the approximations for V_i and P_i [Eqs. (8.13) and (8.14)], and for which $\zeta < -2kT$, to assure reasonable accuracy for the assumption of classical statistics for the electrons in the conduction band. The basic results of the calculations are presented graphically in Fig. 1, where the ratio of carrier to impurity concentration is plotted as a function of $1/\tau$ for various impurity concentrations. Curves for $\eta_i=10$ and $\eta_i=100$ would be scarcely distinguishable from that for $\eta_i=1$.

The difference between the present theory and earlier ones appears more clearly in Fig. 2. The relation between the densities of carriers and impurities at a given T can be expressed in terms of an effective ionization energy:

$$\Delta E = -kT \ln \left[\left(\frac{h^2}{2\pi m^* kT} \right)^{\frac{3}{2}} \frac{n_e^2}{N/V - n_e} \right]. \quad (11.1)$$

As thus defined, ΔE is the ionization energy required in the usual model of noninteracting impurities if a concentration N/V of impurities is to give rise to a concentration n_e of carriers at temperature T . The ratio of ΔE to the ionization energy at zero impurity concentration, expressed in terms of our dimensionless parameters, is

$$w = -\frac{2\tau}{3} \ln \left[\left(\frac{24\pi}{\tau^3} \right)^{\frac{3}{2}} \frac{\eta_e^2}{\eta_i - \eta_e} \right]. \quad (11.2)$$

Figure 2 shows w as a function of impurity concentration, for a series of values of temperature; it shows also

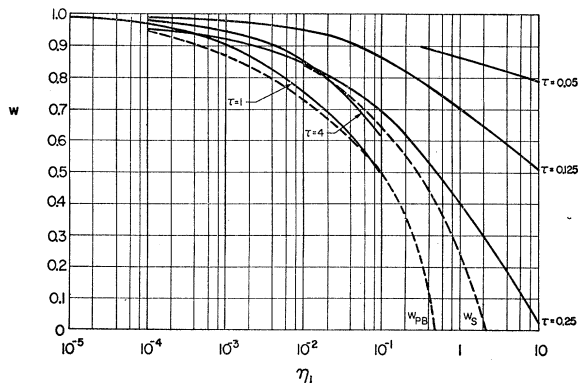


FIG. 2. Solid lines give $\Delta E/E_0$ as a function of impurity concentration, for several temperatures τ , according to the present theory. Dashed lines indicate the temperature-independent results of the theories of Shifrin and of Bardeen and Pearson.

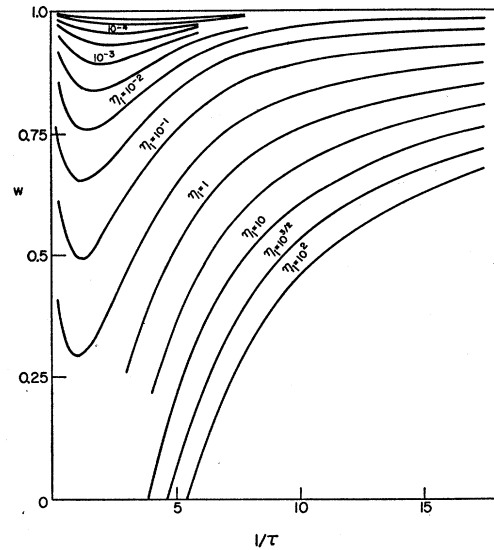


FIG. 3. Dependence of $\Delta E/E_0$ on reciprocal temperature, for various impurity concentrations.

the temperature-independent values given by the theories of Shifrin and of Pearson and Bardeen. The present theory gives about the same reduction in activation energy by impurity interaction as do the other theories when the temperature is relatively high, but a much smaller reduction at low temperatures, where the carrier concentration is low.

The most striking result of the present theory is the strong predicted dependence of effective activation energy on temperature, when the impurity concentration is high. This is shown most clearly in Fig. 3, where w is plotted against reciprocal temperature for various impurity concentrations. The existence of a minimum in the curves, for not-too-high impurity concentrations, is easily understood. When τ is reduced from its value at the minimum, w tends to increase because the carrier concentration is decreasing, and with it the shielding effects that tend to reduce the activation energy. On the other hand, w increases when τ is raised, because the relatively smaller increase in carrier concentration is overbalanced by the decrease in polarizability of the electron distribution, which also tends to diminish the shielding effects. The curves for the larger values of η_i presumably approach 1 as $1/\tau$ goes to zero, but no attempt has been made to compute this part of the curves.

The theory predicts that the family of plots of $\ln n_e$ against $1/T$, for different impurity concentrations, will always have the same form for all semiconductors with the simple band structure discussed here, and for all impurities describable by the hydrogenic model. More precisely, the plots will differ only by a vertical displacement determined by the value of a_0 or Km/m^* , and by a horizontal scale factor determined by the value of E_0 or m^*/mK^2 . If K and m^* are known from other sources, a family of theoretical curves can be super-

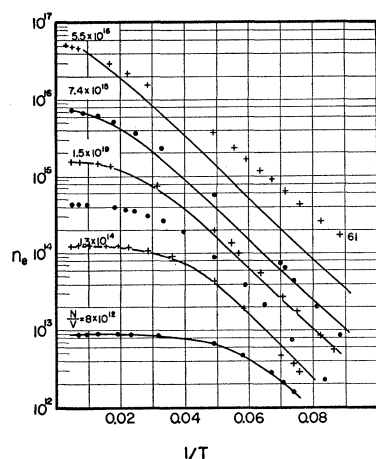


FIG. 4. Solid lines give carrier concentration as a function of $1/T$, for various impurity concentrations in a semiconductor with $K=16$, $m^*=0.25m$, according to the present theory. The points give experimental data on six samples of n -type germanium, as obtained by Debye and Conwell.

imposed on a family of experimental curves without arbitrary adjustment of any factors. Figure 4 shows such a family of curves, drawn for $K=16$, $m^*/m=1/4$.

Even though the band structure of germanium and silicon is more complex than that assumed in the present model,¹³ it is tempting to compare experimental data for these materials with the theory, anticipating that the tensor effective mass may be replaceable by some mean m^* . As an example, we take the carefully analyzed data of Debye and Conwell¹⁴ for n -type germanium. Figure 4 shows experimental data taken from their work (Fig. 10), in comparison with theoretical curves calculated for the observed value of K and a generally appropriate value of m^* —actually that used in the theoretical analysis of Debye and Conwell. In the case of the purer samples the fit is generally satisfactory, except that the observed carrier densities begin to fall more rapidly than is indicated by theory as $1/T$ becomes large. That this effect is due to the presence of acceptor impurities is already indicated by both the mobility and the concentration data of Debye and Conwell. On the other hand, the experimental data on the less pure sample 61 of Debye and Conwell deviates from the experimental curves in a way that cannot be attributed to the presence of acceptor impurities. Debye and Conwell fit a theoretical curve to this data by assuming a decidedly lower activation energy (0.007 ev) than is predicted by the present theory. It seems clear that the present theory, at least as applied to germanium, underestimates the decrease in activation energy at high impurity concentrations.

The observations of Morin and Maita¹⁵ on n -type silicon deviate from the theory in a somewhat similar way; for instance, the behavior of their sample 126 of silicon doped with arsenic suggests that the impurity activation energy is temperature dependent and considerably lower than would be predicted by the present theory. (The larger value of E_0 and the smaller value of a_0 make the continuous dielectric model of the semiconductor less reliable here than in the case of germanium.)

Replacement of the scalar m^* by a tensor effective mass would make it easier to compare the theory with observations on germanium and silicon. It is probable, however, that the most serious approximation in the present theory is the use of a linearized relation between the carrier density fluctuation and the potential fluctuation [Eqs. (3.19) and (3.20)], and that this is responsible for the underestimate of the decrease in activation at high impurity concentrations. It appears that this approximation can be removed by use of the methods of Friedel,¹⁶ together with other simplifications suggested by the outcome of the present work. In principle, the theory can also easily be extended to materials containing both donor and acceptor impurities—an extension that is certainly required if careful quantitative comparison is to be made with existing experimental results.

Morin and Maita have shown that it is often, though not invariably, possible to obtain impressive agreement between experimental data on carrier concentration and a theory based on the assumption of constant activation energy, if one uses as parameters adjustable separately for each sample the concentration of majority and minority impurities, the activation energy of the majority impurity and, independently, the effective mass of the carriers. However, in view of the strong indication given by the present theory that the effective activation energy is strongly temperature dependent when the impurity concentration is high, it seems reasonable to attribute their success in part to the multiplicity of their parameters, and to doubt the physical significance of the exact values assigned to these parameters. This is in line with the doubts expressed by Morin and Maita as to the significance of the mass parameter determined by their method. It therefore seems to the authors that further theoretical study of the dependence of impurity activation energy on concentration and temperature is called for.

¹³ The present calculation can be extended to band structures such as those of n -type Ge and Si without appreciable difficulty.

¹⁴ P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954).

¹⁵ F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).

¹⁶ J. Friedel, Phil. Mag. (7) **43**, 153 (1952); Ann. phys. **9**, 158 (1954).