

Description of Impurity Ionization in Semiconductors by Chemical Thermodynamics

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The phenomenon of impurity ionization is considered on the basis of exact thermodynamics, involving an extension of the usual mass-action formalism. To make possible the evaluation of quantities of interest in the two-band model of covalent semiconductors, comparison is made with the statistical formulation of ionization equilibrium. Particular consideration is given to the concentration dependence of the impurity ionization energy. Interactions between ionized impurities and mobile carriers are treated by the Debye-Hückel theory of strong electrolytes; the treatment involves only one parameter which must be determined from experimental carrier densities. Very good agreement is found for arsenic-doped germanium using the detailed data and analysis of Debye and Conwell.

INTRODUCTION

IMPURITY ionization equilibria have usually been treated by combining quantum statistics with a so-called "mass action" formalism. This treatment has the disadvantage that interactions other than exclusion effects are inserted in an *ad hoc* manner as corrections to the ionization energy. In a treatment based on chemical thermodynamics, on the other hand, particle interactions are included naturally and, indeed, constitute an essential part of the formulation.

In any rigorous approach a distinction must be made between the equilibrium constant K , involving thermodynamic activities, or "effective concentrations," and the analogous quantity K' , involving actual concentrations. Depending upon impurity content, K' for impurity ionization reactions in semiconductors may, in fact, exceed K by several orders of magnitude. In the language of chemical thermodynamics, the variation of K' with impurity content is ascribed to deviations from ideal particle behavior.

Particle interactions leading to a concentration dependence of K' include specific (short-range) forces and, for charged particles, long-range electrostatic forces. The exclusion principle constitutes an additional interaction, whose relative importance depends upon particulars of the band structure. Measurements of the electrical properties of boron- and phosphorus-doped silicon by Pearson and Bardeen¹ and of arsenic-doped germanium by Debye and Conwell² showed that interactions between mobile carriers and ionized impurities in silicon and germanium outweigh exclusion effects, at least for hole or electron concentrations below about 10^{18} cm⁻³; as a result, impurity ionization energies decreased to zero with increasing impurity content.

The concentration dependence of the impurity ionization energy in semiconductors is of particular interest. Lehman and James³ state that the first attempt to derive the dependence of the ionization energy on impurity

content was made by Shifrin,⁴ employing a hydrogen-like model of the impurity atom. Shifrin concluded that the ionization energy should decrease linearly as $N^{1/2}$, where N is the concentration of impurity. An empirical relation of the same form was found by Pearson and Bardeen¹ to fit their measurements on silicon; these authors provided a theoretical interpretation based on the decrease in the average potential energy of an electron or hole, resulting from attraction between it and the ionized impurity center. Subsequently, Debye and Conwell² found closer agreement with their own experimental data when the total donor concentration of the Pearson and Bardeen expression was replaced by the concentration of ionized donors.

The variation of impurity ionization energies in semiconductors has also been considered theoretically by Pincherle⁵ and, more recently, by Chetkarov.⁶ The most comprehensive treatment is that due to Lehman and James³; their intricate theory is based on the determination of one-electron orbitals by solution of Hartree equations and leads to results in fair agreement with the data of Debye and Conwell. The present paper describes an alternate approach, based on chemical thermodynamics, which gives very satisfactory agreement with the data. The procedure consists of evaluating the difference between the actual and the ideal free energy change for the ionization of an impurity atom. Two contributions to this difference are recognized: The first, arising from electrostatic interactions, is treated by the Debye-Hückel theory⁷⁻⁹ of strong electrolytes (see Teltow¹⁰ for an account of the literature on applications of the Debye-Hückel theory to defect interactions in solids); the contribution of exclusion is obtained by comparing thermodynamic and quantum-statistical expressions for the concentration product K' .

⁴ K. S. Shifrin, *Zhur. Tekh. Fiz.* **14**, 43 (1944).

⁵ L. Pincherle, *Proc. Phys. Soc. (London)* **A64**, 663 (1951).

⁶ M. L. Chetkarov, *Zhur. Tekh. Fiz.* **28**, 962 (1958).

⁷ P. Debye and E. Hückel, *Physik. Z.* **24**, 185 (1923).

⁸ R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, New York, 1960), Chap. IX.

⁹ R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Butterworths Publications Ltd., London, 1959), 2nd ed., Chaps. 4 and 9.

¹⁰ J. Teltow, *Halbleiter Probleme*, edited by W. Schottky (Friedrich Vieweg und Sohn, Braunschweig, 1956), Vol. III, pp. 26-58.

* Operated with support from the U. S. Army, Navy, and Air Force.

¹ G. L. Pearson and J. Bardeen, *Phys. Rev.* **75**, 865 (1949).

² P. P. Debye and E. M. Conwell, *Phys. Rev.* **93**, 693 (1954).

³ G. W. Lehman and H. M. James, *Phys. Rev.* **100**, 1698 (1955).

THERMODYNAMIC FORMULATION

Chemical equations for the ionization of a donor or acceptor impurity may be generalized by writing

$$\sum \nu_j S_j = 0, \quad (1)$$

where the S_j denote chemical symbols and the ν_j are the stoichiometric coefficients, taken as negative for reactants. The equilibrium constant of the reaction is

$$K = \prod a_j^{\nu_j}, \quad (2)$$

and the equilibrium concentration product is

$$K' = \prod c_j^{\nu_j}. \quad (3)$$

The quantities c_j and a_j are the equilibrium particle concentrations and thermodynamic activities, respectively.

For the generalized impurity ionization reaction (1), the change in the Helmholtz free energy at constant temperature and total volume is

$$\Delta F = \sum \nu_j \mu_j = \sum \nu_j \mu_j^0 + kT \sum \nu_j \ln a_j, \quad (4)$$

where $\mu_j = \mu_j^0 + kT \ln a_j$ is the chemical potential of the j th particle, and $\mu_j^0(T)$ is its chemical potential in the standard state of unit activity. It is convenient for our purposes to choose the standard state such that the particle, present at unit concentration (one particle per cm^3), has the properties it would possess at the given temperature in the absence of all other solute particles.

If there were no interactions (other than the chemical reaction considered), the free energy change would be

$$\Delta F_{\text{ideal}} = \sum \nu_j \mu_j^0 + kT \sum \nu_j \ln c_j. \quad (5)$$

The difference between (4) and (5) will be referred to as the *deviation free energy*:

$$\Delta F_{\text{dev}} = \Delta F - \Delta F_{\text{ideal}} = kT \sum \nu_j \ln(a_j/c_j). \quad (6)$$

For the case where each a_j has its equilibrium value,

$$\sum \nu_j \mu_j = 0, \quad (7)$$

so that, from (4),

$$\sum \nu_j \ln a_j = - \sum \nu_j \mu_j^0 / kT \equiv \ln K, \quad (8)$$

which is identical with (2).

Since each $\mu_j^0 = \mu_j^0(T)$, the equilibrium constant K is seen from (8) to be a function of temperature only. The quantity K' , on the other hand, varies with composition owing to the concentration dependence of the quantities a_j/c_j :

$$\ln K' = \sum \nu_j \ln a_j - \sum \nu_j \ln(a_j/c_j) = \ln K - \Delta F_{\text{dev}}/kT. \quad (9)$$

By virtue of our choice of standard states for the reacting particles, each $a_j \rightarrow c_j$ (whence $K' \rightarrow K$) as $\sum c_i \rightarrow 0$, the summation extending over *all* solute species. In principle, provided sufficient data are available, K may be obtained from K' by extrapolation. For the impurity ionization reaction which we shall consider in some detail, it will be found that K' approaches K asymptotically. A theoretically sound expression relating K' to

concentration is then essential for reliable extrapolation.

To see why it is desirable to evaluate K , we note that the standard¹¹ energy change ΔE^0 is obtained from the temperature dependence of K according to

$$\Delta E^0 = -k \frac{d \ln K}{d(1/T)}. \quad (10)$$

The energy change ΔE for an arbitrary composition is similarly related to K' :

$$\Delta E = -k \frac{\partial \ln K'}{\partial(1/T)}. \quad (11)$$

However, the experimental data will not generally be sufficiently extensive for the direct evaluation of ΔE , since the temperature dependence of K' for a particular set of values of the concentrations c_i is required in (11). Therefore, ΔE must be obtained indirectly; the evaluation of K at several temperatures is involved in the procedure. [Unlike (10), the relation (11) is not of general thermodynamic validity, but applies to the problem at hand since the concentrations employed are not arbitrarily chosen, but are equilibrium values and, as will be shown, K' can be expressed as a function of $N_A + n$ and T].

For the ionization of a simple donor, present at the concentration N_D , (1) and (3) become respectively

$$D = D^+ + e^-, \quad (12)$$

$$K_D' = (c_{D^+})(c_{e^-})/c_D = (c_{D^+})n/(N_D - c_{D^+}), \quad (13)$$

where n has been written for the concentration of electrons. If the semiconductor also contains the concentration N_A of acceptor impurity, the exact formulation of K_D' in terms of N_D and N_A is

$$K_D' = \frac{[N_A + n - p + (K_{np}'/nK_A')(n - p)]n}{N_D - N_A - n + p + (K_{np}'/nK_A')(N_D - n + p)}, \quad (14)$$

where p has been written for the hole concentration c_{e^+} , $K_{np}' = np$, and $K_A' = (c_{A^-})p/c_A$. For a sufficient excess of donors over acceptors and at the lower temperatures corresponding to incomplete ionization of the donor impurity, (14) reduces to

$$K_D' = (N_A + n)n/(N_D - N_A - n), \quad (15)$$

the expression usually employed. In what follows, K_D' will be written without the identifying subscript.

COMPARISON WITH STATISTICAL FORMULATION

The application of Fermi-Dirac statistics to the donor ionization equilibrium (12) is straightforward and

¹¹ Refers to the reaction under conditions where the impurity atom, impurity ion, and electron are in their respective standard states; ΔE^0 is the value of the energy change for the ionization reaction in the limit of vanishingly small impurity content.

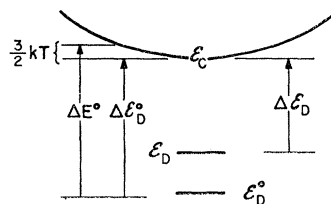


FIG. 1. Electron energy diagram illustrating the energy changes attending transitions between donor states and conduction band (simple model).

leads to

$$K' = (2\pi mkT/h^2)^{3/2} \exp(-\Delta\mathcal{E}_D/kT) \times 2\pi^{-1/2} \exp(-\eta) F_{1/2}(\eta), \quad (16)$$

with $\Delta\mathcal{E}_D = \mathcal{E}_C - \mathcal{E}_D$, $\eta = (\mathcal{E}_F - \mathcal{E}_C)/kT$, and

$$F_{1/2}(\eta) = \int_0^\infty x^{1/2} [1 + \exp(x - \eta)]^{-1} dx.$$

\mathcal{E}_C , \mathcal{E}_D , and \mathcal{E}_F are the energies of an electron at the bottom of the conduction band, at the donor level, and at the Fermi level, respectively, and m is the density-of-states effective mass for conduction band electrons.

As the impurity content is progressively decreased, $F_{1/2}(\eta) \rightarrow (\pi^{1/2}/2) \exp(\eta)$,¹² $\Delta\mathcal{E}_D \rightarrow \Delta\mathcal{E}_D^0$ and K' becomes equal to

$$K = (2\pi mkT/h^2)^{3/2} \exp(-\Delta\mathcal{E}_D^0/kT), \quad (17)$$

so that (16) may be rewritten as

$$K' = K \exp\left(\frac{\Delta\mathcal{E}_D^0 - \Delta\mathcal{E}_D}{kT}\right) \times 2\pi^{-1/2} \exp(-\eta) F_{1/2}(\eta). \quad (18)$$

On comparing (17) with (10), it is found that the standard energy change ΔE^0 (of the system) is related to the standard donor ionization energy $\Delta\mathcal{E}_D^0$ by

$$\Delta E^0 = \Delta\mathcal{E}_D^0 + \frac{3}{2}kT + \frac{3}{2}kT^2 \frac{\partial \ln m}{\partial T} - T \frac{d\Delta\mathcal{E}_D^0}{dT}. \quad (19)$$

If we neglect any temperature variation of $\ln m$ and $\Delta\mathcal{E}_D^0$, (19) shows that ΔE^0 exceeds $\Delta\mathcal{E}_D^0$ by $\frac{3}{2}kT$, i.e., by the average thermal energy of an electron in the standard state. It does not follow, however, that ΔE and $\Delta\mathcal{E}$ also differ by $\langle \mathcal{E} - \mathcal{E}_C \rangle_{av}$; ΔE cannot be represented on an electron energy diagram (Fig. 1).

Referring to the earlier discussion of interactions contributing to departures from ideal behavior, we write the deviation free energy as the sum of contributions of electrostatic and quantum-mechanical effects:

$$\Delta F_{dev} = \Delta F_{elec} + \Delta F_{excl}, \quad (20)$$

so that, from (9)

$$K' = K \exp\left(-\frac{\Delta F_{elec}}{kT}\right) \exp\left(-\frac{\Delta F_{excl}}{kT}\right). \quad (21)$$

As indicated above, the product of terms to the right of the cross in (18) increases with decreasing n , becoming unity in the classical limit. The identification of ΔF_{excl} is thus readily made (cf., Reiss¹³ and Rosenberg¹⁴) as

$$\Delta F_{excl} = -kT \ln[2\pi^{-1/2} \exp(-\eta) F_{1/2}(\eta)], \quad (22)$$

whereupon it follows that

$$\Delta F_{elec} = \Delta\mathcal{E}_D - \Delta\mathcal{E}_D^0. \quad (23)$$

The concentration dependence of ΔE is more complicated than that of $\Delta\mathcal{E}_D$, but can be derived using the thermodynamic identity $\Delta E = -\partial(\Delta F/T)/\partial(1/T)$; the general relation is

$$\Delta E = \Delta E^0 + \partial(\Delta F_{dev}/T)/\partial(1/T), \quad (24)$$

and the contribution of exclusion to ΔE is evaluated as

$$\frac{\partial(\Delta F_{excl}/T)}{\partial(1/T)} = \frac{3}{2}kT \left(F_{1/2}(\eta) \frac{d\eta}{dF_{1/2}(\eta)} - 1 \right). \quad (25)$$

It is interesting that $\frac{3}{2}kTF_{1/2}(d\eta/dF_{1/2})$ is not the average kinetic energy of an electron, $kTF_{1/2}/F_{1/2}$,¹² although both quantities reduce to $\frac{3}{2}kT$ for sufficiently negative values of η . Whereas electrostatic interactions between electrons and ionized donors decrease both ΔE and $\Delta\mathcal{E}_D$ (though not by the same amount), exclusion operates to increase ΔE by forcing electrons into higher levels in the conduction band.

EVALUATION OF ELECTROSTATIC EFFECTS BY THE DEBYE-HÜCKEL THEORY

In applying the Debye-Hückel theory⁷⁻⁹ to impurity ionization, mobile carriers and ionized impurities will be identified only by their charges, except that for pairs of particles there is in the theory a characteristic parameter a which is nominally the distance of closest approach of their centers. We imagine the indicated change of state to be carried out by a two-step process. In the first step, the ionization reaction takes place, yielding the donor ion and electron without their respective charges. For this step, the free energy change is $\Delta F_{ideal} + \Delta F_{excl}$. In the second step, the particles become charged. If a way can be conceived of charging the particles reversibly to their respective potentials, then the work performed can be equated to the decrease in free energy for this step and, therefore, to $-\Delta F_{elec}$ for the over-all ionization reaction.

In the charging process devised by Güntelberg,^{8,9,15} the ions are charged simultaneously, allowing the ion atmospheres to adjust to each incremental addition of charge; the electrical free energy is then obtained by integration. The evaluation is particularly straightforward in the present application, wherein all that is required is to charge one donor ion and one electron in the presence

¹² J. McDougall and E. C. Stoner, Phil. Trans. Roy. Soc. (London) A237, 67 (1938).

¹³ H. Reiss, J. Chem. Phys. 21, 1209 (1953).

¹⁴ A. J. Rosenberg, J. Chem. Phys. 33, 665 (1960).

¹⁵ E. Güntelberg, Z. phys. Chem. 123, 199 (1926).

of all of the other ions. For this purpose we require the electrical potential at each j ion due to the remaining ions, i.e., to its ion atmosphere. According to the Debye-Hückel theory, this quantity is

$$\psi_j' = -\frac{z_j e}{\epsilon} \frac{\kappa}{1 + \kappa a}, \quad (26)$$

where $z_j e$ is the charge of the j ion, ϵ is the dielectric constant, a is the mean effective distance of closest approach of the ion centers, and κ is defined by

$$\kappa^2 = (4\pi e^2 / \epsilon k T) \sum c_i z_i^2, \quad (27)$$

the indicated summation extending over *all* charged species.

In an impurity semiconductor with N_D donors, N_A ionized acceptors and n electrons per cm^3 , the sum in (27) is equal to (consistent with over-all electroneutrality)

$$c_{D^+} + c_{A^-} + n = 2c_{D^+} = 2(N_A + n). \quad (28)$$

If at any given stage in the charging process the j ion has acquired the fraction λ of its final charge, the potential due to its atmosphere is $\lambda\psi_j'$, whereupon ΔF_{elec} for the reaction $\sum v_j S_j = 0$ may be evaluated as

$$\int_0^1 \sum v_j (\lambda \psi_j') z_j e d\lambda = - \sum v_j z_j^2 \frac{e^2}{\epsilon} \frac{\kappa}{1 + \kappa a} \int_0^1 \lambda d\lambda. \quad (29)$$

For the ionization of a single impurity atom $\sum v_j z_j^2 = 2$, whence

$$\Delta F_{\text{elec}} = - \frac{e^2}{\epsilon} \frac{\kappa}{1 + \kappa a}. \quad (30)$$

The concentration dependence of $\Delta \mathcal{E}_D$ follows immediately as¹⁶

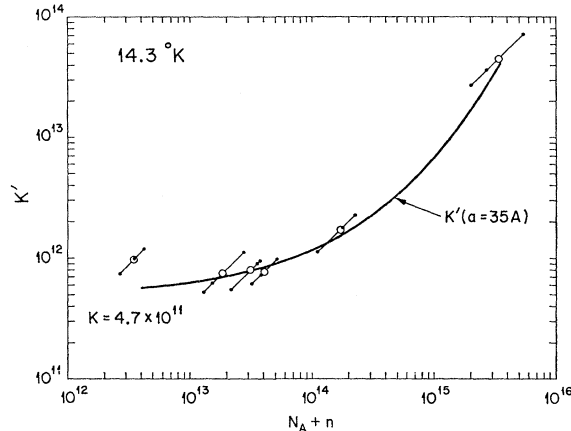


FIG. 2. Evaluation of the equilibrium constant K at 14.3°K for arsenic ionization in germanium. Dots show K' calculated for the different values of N_A estimated for each of their samples by Debye and Conwell.² Circles show K' for an averaged value of N_A .

¹⁶ The electrostatic contribution to the variation of ΔE is, from (24) and (30),

$$\frac{\partial(\Delta F_{\text{elec}}/T)}{\partial(1/T)} = - \frac{e^2}{\epsilon} \frac{\kappa}{1 + \kappa a} \frac{3 + 2\kappa a}{2(1 + \kappa a)}.$$

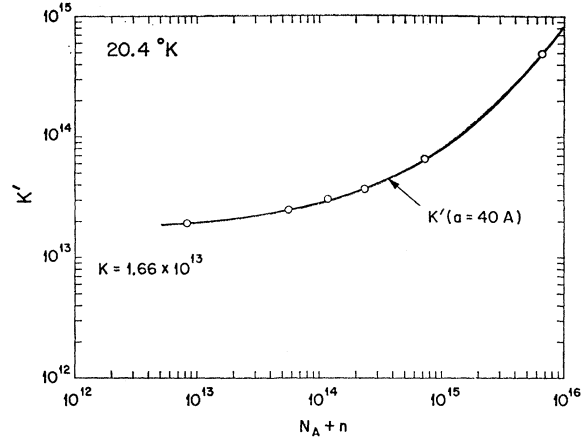


FIG. 3. Evaluation of the equilibrium constant at 20.4°K for arsenic ionization in germanium using the data of Debye and Conwell.²

$$\Delta \mathcal{E}_D = \Delta \mathcal{E}_D^0 - \frac{e^2}{\epsilon} \frac{\kappa}{1 + \kappa a}, \quad (31)$$

and that of K' as

$$K' = K \exp\left(\frac{e^2}{\epsilon k T} \frac{\kappa}{1 + \kappa a}\right) \times 2\pi^{-\frac{1}{2}} \exp(-\eta) F_{\frac{1}{2}}(\eta). \quad (32)$$

COMPARISON WITH THE EXPERIMENTAL DATA OF DEBYE AND CONWELL

The concentration product K' was calculated for the Debye and Conwell samples at a series of temperatures between 12.5°K and 25.0°K using their tabulated values of $N_D - N_A$ and N_A , and reading n from their Fig. 10. At each temperature, K' for different samples was found to be a smooth function of $N_A + n$ in agreement with the indicated concentration dependence of κ . Figures 2 and 3 show typical plots of K' vs $N_A + n$. As noted earlier, K' approaches a limit asymptotically, so that graphical extrapolation is not a reliable method for obtaining K . At the lower temperatures, the calculated concentration products are sensitive to the values selected for N_A ; the procedure adopted was to base the computation on the average of the three estimates of N_A (see Fig. 2) listed for each sample by Debye and Conwell.

In fitting the curves the abridged relation,

$$\ln K' = \ln K + \frac{e^2}{\epsilon k T} \frac{\kappa}{1 + \kappa a}, \quad (33)$$

was used, since calculation showed the additional term in (32) to be smaller than the uncertainty in other quantities; for example, the value of $(2/\pi^{\frac{1}{2}}) \exp(-\eta) F_{\frac{1}{2}}(\eta)$ is 0.98 for the largest experimental value of n employed in the calculations. The value of a at each temperature was selected so as to result in the smallest average deviation of $\ln K$. "Best" values of the equilibrium constants and the parameter a are tabulated below.

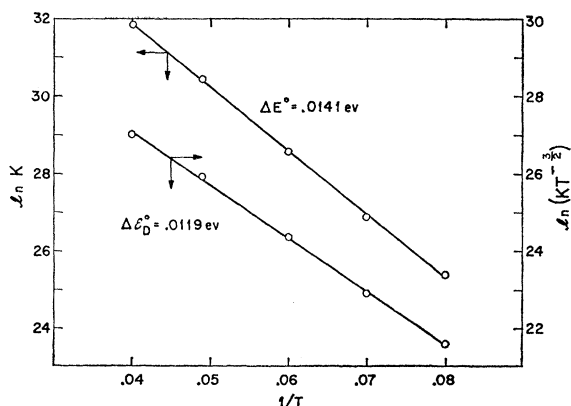


FIG. 4. Temperature dependence of ΔE^0 and $\Delta \mathcal{E}_D^0$ for arsenic-doped germanium.

In Fig. 4, $\ln K$ is plotted vs reciprocal absolute temperature. The value of ΔE^0 obtained from the slope of the least-squares straight line drawn through the points is shown in the figure. However, it is unlikely that ΔE^0 is actually constant as suggested by Fig. 4, since this would require that the standard entropy change for the ionization reaction be independent of temperature over the same range and, moreover, that K approach a finite limit as the temperature is increased indefinitely (n would not then become equal to $N_D - N_A$). If, instead, the more reasonable assumption is made that $\Delta \mathcal{E}_D^0$ is constant and equal to $\Delta E^0 - \frac{3}{2}kT$, a plot of $\ln(KT^{-3/2})$ vs $1/T$ should be a straight line of slope $-\Delta \mathcal{E}_D^0/k$. The value of $\Delta \mathcal{E}_D^0$ obtained from the least-squares slope of Fig. 4 is in reasonably good agreement with the value 0.0127 eV obtained by Geballe and Morin.¹⁷ It is not possible within the probable error of the calculated points to distinguish between constant ΔE^0 and constant $\Delta \mathcal{E}_D^0$ over the limited temperature interval of Fig. 4; both quantities may in fact exhibit some variation, consistent with (19).

In Fig. 5, $\Delta \mathcal{E}_D$ calculated by (31) is plotted against the concentration of ionized donors. The concentration dependence of $\Delta \mathcal{E}_D$ is seen to be not very different from that of the semi-empirical expression in $(N_A + n)^{1/2}$ adopted by Debye and Conwell. Their corresponding plot (Fig. 12 of reference 2) applies to a range of tem-

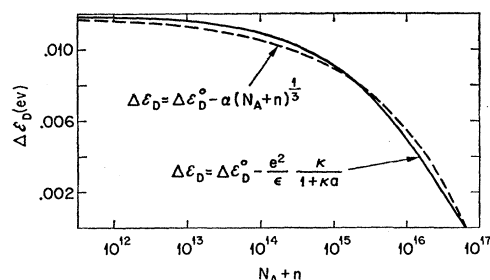


FIG. 5. Concentration dependence of $\Delta \mathcal{E}_D$ calculated for arsenic in germanium at 20.4°K and $a=35$ Å.

¹⁷ T. H. Geballe and F. J. Morin, Phys. Rev. **95**, 1085 (1954).

peratures, so a detailed comparison is not warranted. Apart from the good agreement between the $\Delta \mathcal{E}_D^0$ values, Fig. 5 indicates that at 20.4°K, $\Delta \mathcal{E}_D$ becomes zero at a lower net donor concentration than their sample 59.

In essence, the Debye-Hückel theory of ionic interaction has been used for smoothing and extrapolating experimental values of K' for arsenic ionization in germanium. The over-all formulism was tested by calculating n at a series of temperatures according to the expanded equation

$$\ln \frac{(N_A + n)n}{N_D - N_A - n} = \text{const} - \frac{\Delta \mathcal{E}_D^0}{kT} + \frac{3}{2} \ln T + \frac{(e^2/\epsilon kT)[(8\pi e^2/\epsilon kT)(N_A + n)]^{1/2}}{1 + a[(8\pi e^2/\epsilon kT)(N_A + n)]^{1/2}}, \quad (34)$$

and comparing with experiment (Fig. 6). The first two terms on the right were obtained from Fig. 4, the value 16.1 was used for ϵ , and a was taken to be 35 Å for all samples and all temperatures. The extraction of n was performed by the IBM 7090 computer.

In contrast to the theory of Lehman and James, the fit at the higher impurity contents is very good. The somewhat poorer fit for the purest sample is partly the result of a discrepancy between the tabulated value of $N_D - N_A$ and the limit of the experimental points. In future applications, careful consideration should be given to the estimation of carrier densities from measured Hall coefficients, since somewhat different values of the various parameters will be obtained depending upon the ratio of Hall to conductivity mobility.

DISCUSSION

The Debye-Hückel theory treats only the electrostatic part of the total interaction between charged particles; the neglect of interactions other than electrostatic and exclusion effects restricts the treatment to "dilute" solutions. As seen in Fig. 5, the ionization energy of arsenic in germanium becomes zero at an ionized impurity concentration of about $6 \times 10^{16} \text{ cm}^{-3}$ (10^{-4} molar solution); it is probably valid to neglect short-range effects at this and lower concentrations. At higher concentrations, such short-range interactions as may exist would be swamped by exclusion effects.

A more specific limitation to the applicability of the theory results from dropping terms higher than ψ_j^2 in the expansion of the assumed Boltzmann distribution of ions about a central ion:

$$c_i' = c_i \exp(-z_i e \psi_j / kT). \quad (35)$$

In (35), c_i' is the time-average local concentration of i ions, and ψ_j is the time-average local electrostatic potential (including that due to the j ion). The approximation is valid for $(z_i e \psi_j / kT) < 1$, i.e., for the electrostatic potential energy of an ion small in comparison to

its thermal energy. The maximum physically possible value of ψ_j , given by the theory as

$$\psi_j = \frac{z_j e \exp(\kappa a) \exp(-\kappa r)}{\epsilon (1 + \kappa a) r}, \quad (36)$$

occurs at the distance a from the j ion, leading to

$$\left| \frac{e\psi_j}{kT} \right|_{\max} = \frac{e^2}{\epsilon kT} \frac{1}{(1 + \kappa a)a}. \quad (37)$$

Calculated values of $|e\psi_j/kT|_{\max}$ vary from 23.6 for the most lightly doped sample at 12.5°K to 9.1 for the most heavily doped sample at 25.0°K. It might therefore appear that the Debye-Hückel theory applies better to the phenomenon of impurity ionization than one has a right to expect. However, for the two extreme cases cited, the calculated average separations of charged particles are 7050 Å and 410 Å, respectively, at which distances the magnitudes of $e\psi_j/kT$ are only 0.028 and 0.016. The quadratic approximation to c_i' probably involves no serious errors in the present application.

Two further considerations may be mentioned. In the Debye-Hückel theory, the dielectric constant is taken to be that of the pure semiconductor; small influences of impurities on the polarization (see Castellan and Seitz¹⁸) may be absorbed in the a . Of greater concern is the question of applicability of the theory to systems in which some of the ions are fixed. Reiss *et al.*¹⁹ were confronted with a similar question in applying the concept of ion pairing to semiconductors containing both mobile donors and immobile acceptors. Reiss²⁰ was able to show rigorously that the same equations apply to the equilibrium condition as in the more general case of all ions mobile.

Although mobility does not appear explicitly in the Debye-Hückel theory (it is implied by the etymology of the word "ion"), it is essential that the equilibrium distribution of ions about any given ion be describable by Boltzmann factors. This presents no problem for electrons (or holes) about an impurity ion,²¹ but the converse requires some thought. To an observer following an electron about in its peregrinations, attracted by

¹⁸ G. W. Castellan and F. Seitz, *Semiconducting Materials* (Butterworths Publication Ltd., London, 1951), pp. 8-25.

¹⁹ H. Reiss, C. S. Fuller, and F. J. Morin, *Bell System Tech. J.* **35**, 535 (1956); see especially pp. 565, 566.

²⁰ H. Reiss, *J. Chem. Phys.* **25**, 400 (1956).

²¹ Laura Roth has suggested to the author that the distribution of electrons about a donor ion should obey Fermi-Dirac statistics, leading to

$$n' = n \int_0^\infty x^{\frac{1}{2}} f_0(x - e\psi_j) dx / \int_0^\infty x^{\frac{1}{2}} f_0(x) dx,$$

where x has been written for $(\epsilon - \epsilon_c)/kT$. A linear approximation to $f_0(x - e\psi_j)$ gives

$$n' = n \left[1 + \frac{1}{2} \frac{F_{-1}(\eta)}{F_{\frac{1}{2}}(\eta)} \frac{e\psi_j}{kT} \right],$$

and modifies κ^2 to equal $(4\pi e^2/\epsilon kT) \{2N_A + n[1 + \frac{1}{2}(F_{-1}/F_{\frac{1}{2}})]\}$. In the classical limit, the foregoing expressions reduce to those employed in the text.

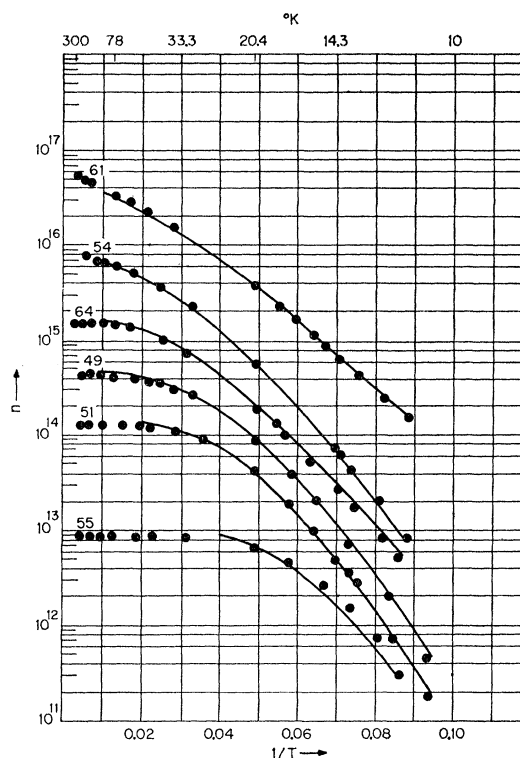


Fig. 6. Comparison between theory and experiment for six samples of n -type germanium. The points are from the corresponding figure of Debye and Conwell.²

ionized donors and avoiding ionized acceptors and other electrons, the fixed ions would appear to be distributed in the proper way *relative to the moving electron*. Moreover, in the range of temperature corresponding to incomplete ionization, the simultaneous capture of electrons by some donor ions and release of electrons by others lends a certain effective mobility to ionized (and neutral) donors. The exact distribution of impurities is probably unimportant at large average separations, although the theory may run into difficulty at appreciable concentrations of compensating impurity.

The pragmatic justification for including the fixed ions lies in comparison with experiment: The formulation does not fit the data unless the *total* concentration of charged particles is used in the Debye screening length $1/\kappa$. Lax and Mengert²² refer to quantum mechanical calculations by P. A. Wolff of correlations introduced by Coulomb forces; for separations large compared to a thermal de Broglie wavelength, the expressions are stated to reduce to those obtained on describing the correlations in terms of the classical Debye-Hückel theory. However, the Debye screening length employed by Lax and Mengert contains $n + p$ rather than the total concentration of charged particles. Furthermore, the Debye-Hückel limiting law, which applies for $\kappa a \ll 1$, was

²² M. Lax and P. Mengert, *J. Phys. and Chem. Solids* **14**, 248 (1960).

TABLE I. Donor equilibrium constants and values of the Debye-Hückel parameter a for arsenic-doped germanium.^{a, b}

T (°K)	$\ln K$	K	$a \times 10^8$ (cm)
12.5	$25.35 \pm 0.15_0$	$1.0_3 \times 10^{11}$	35-36
14.3	25.877 ± 0.046	$4.7_0 \times 10^{11}$	31-32
16.7	28.561 ± 0.039	2.53×10^{12}	36
20.4	30.442 ± 0.014	1.662×10^{13}	40
25.0	31.848 ± 0.024	6.78×10^{13}	34

^a Derived from the published data of Debye and Conwell.²
^b $\epsilon = 16.1$.

used in place of the more general expression, so that it is not clear to what extent the restriction to very large separations applies. Similar comments hold for the application of the Debye-Hückel theory made by Herring and Nichols.²³

The average value of a for the Debye and Conwell samples is 35 Å (Table I). This figure is about half the radius of the lowest Bohr orbit for an electron bound to a group V impurity in germanium (calculated by averaging the cyclotron resonance effective masses²⁴ according to $3/m^* = 2/m_t + 1/m_l$) and an order of magnitude smaller than the de Broglie wavelength of a thermal electron [averaging the effective masses according to $m^* = (2m_t + m_l)/3$]. For ions in liquid media, the distance of closest approach of the excess charges is given roughly by the sum of the ionic radii. The same physical model obviously does not apply to encounters between electrons and arsenic ions in germanium, since a is an order of magnitude greater than a lattice spacing.

In applying the chemical reaction approach, bound electrons and free electrons have been treated separately; it has been assumed, moreover, that the excited bound states are populated to a negligible extent. On this basis, it seems reasonable that the region about the donor ion from which free electrons are excluded would be defined approximately by the orbit of the bound electron. A large value of the minimum distance a is also compatible with the wave mechanical treatment in that, due to orthogonality to the bound state, the wave functions of electrons in the conduction band tend to avoid the impurity atom (see exposition by Slater²⁵). The quantity a may thus measure the separation at which the "repulsive force" due to orthogonality overcomes the attractive field of the positively charged arsenic ion.

If excited impurity states are not negligibly populated, k' calculated by (15) will be too small at the higher impurity concentrations (see Conwell²⁶). Consequently, a larger value of a would be required to fit the

data, and $\Delta\mathcal{E}_D$ would decrease less rapidly than indicated in Fig. 5.

As we have shown, the decrease of the ionization energy of arsenic in germanium can be accounted for entirely by electrostatic effects, according to the Debye-Hückel theory of ionic interactions. The theory was also applied to the measurements of Pearson and Bardeen¹ on boron-doped silicon, although here the data were not sufficiently extensive and precise to permit as detailed an analysis as for the Debye and Conwell data. Morin and Maita²⁷ used the Debye-Hückel limiting law to estimate the decrease in the gap energy due to electrostatic interactions of holes and electrons in the intrinsic range of germanium; the correction is important at elevated temperatures, where intrinsic carrier concentrations are high.

It is not unreasonable to expect the same considerations to apply to extrinsic germanium and silicon at intermediate temperatures, where impurities are com-

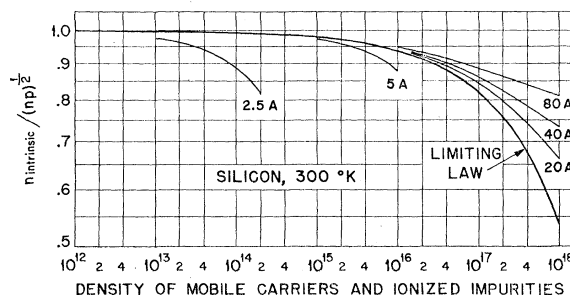


FIG. 7. Calculated concentration dependence of the intrinsic ionization product of silicon at room temperature for various assumed values of the Debye-Hückel parameter a . The lines for a equal to 2.5 Å and 5 Å were calculated approximately by the Bjerrum theory²⁸ of ion-pairing and are included mainly for interest.

pletely ionized. The electrostatic contribution to the deviation free energy for the intrinsic ionization reaction will be given by (30) with the Debye screening length determined by the total concentration of impurities and mobile carriers. In consequence of a decrease in the gap energy, np will be somewhat greater than its intrinsic value. Calculations have been made for silicon at room temperature for various assumed values of the parameter a (Fig. 7).

At high impurity contents, exclusion effects will bring about a reversal in sign of the concentration dependence of $\Delta\mathcal{E}$ for the intrinsic ionization reaction, so that a maximum in np may result. At somewhat lower concentrations, say 10^{17} cm^{-3} , the np product may exceed its intrinsic value by some 20% (Fig. 7). By the same reasoning, np should be less for uncompensated material than for partially compensated material of the same net donor or acceptor concentration. It is suggested that the indicated effects be looked for, although it is rec-

²² C. Herring and M. H. Nichols, *Revs. Modern Phys.* **21**, 185 (1949); see especially p. 255.

²⁴ R. N. Dexter, H. J. Zeiger, and B. Lax, *Phys. Rev.* **104**, 637 (1956).

²⁵ J. C. Slater, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 19, pp. 1-136; see especially pp. 78-80.

²⁶ E. M. Conwell, *Phys. Rev.* **99**, 1195 (1955).

²⁷ F. J. Morin and J. P. Maita, *Phys. Rev.* **94**, 1525 (1954).

²⁸ See, for example, pertinent sections in references 8 and 9.

ognized that they may be difficult to distinguish from other effects, as for example, changes in mobility.

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Solution of Schrödinger Equation for a Periodic Lattice

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We present a new method for solving the problem of one electron in a periodic potential; it is discussed in this paper mainly for $\mathbf{k}=0$, although it can be generalized to other \mathbf{k} . The periodic potential is considered to be generated by spherically symmetric "atomic" potentials at each lattice site; this does not mean of course that the total potential near a lattice site need be spherically symmetric. The method has its origin in the observation that (for $\mathbf{k}=0$) the equation for $C(\mathbf{K}_i)$, the Fourier coefficient of the wave function, becomes just the momentum-space Schrödinger equation when the lattice spacing becomes infinite. This latter equation is separable into a radial part, and an angle-dependent part expressible in spherical harmonics. This suggests that it would be advantageous to expand the $C(\mathbf{K}_i)$ for finite lattice spacing similarly, into radial functions $C_l(K_m)$, where K_m is the magnitude of the m th smallest reciprocal lattice vector, and into an angle-dependent part expressible (for cubic lattices) by Kubic harmonics. We do this and the Schrödinger equation for the system becomes a set of homogeneous linear equations for the $C_l(K_m)$, with a corresponding secular determinant for the eigenvalues.

We have tested the method numerically, as a function of lattice spacing and potential strength, for S -like states, when the "atomic" potentials are exponential ones, and the lattice is body-centered cubic. In many cases it turns out that one can solve the periodic potential case more easily and more accurately than one can solve for the isolated atom. This is because as the lattice spacing gets large the successive K_m became more and more closely spaced and this leads to larger and larger secular equations. The wave functions as well as energies are given for most lattice spacings to considerable accuracy (three to seven significant figures).

When the lattice spacing gets large and the equations approach those for the isolated atom, we show how one can use the atomic momentum space functions as variational functions, in the same spirit as the usual tight-binding approximation (as applied for $\mathbf{k}=0$). The present method has the considerable advantage that it bypasses the usual difficulties with that approximation—near-neighbor approximations and calculation of overlap integrals—and permits an easy and accurate evaluation of the variational expression as a sum over the K_m .

I. INTRODUCTION AND THE BASIC EQUATIONS

THE one-electron band structure problem, i.e., the problem of solving the Schrödinger equation for an electron in a periodic lattice, is an old one with an extensive literature.¹ In this paper, we look at some old equations for this problem in a new light, and are led to a new and accurate method for solving it. We are also led to a new way of doing the "tight-binding" approximation which bypasses the multi-center integrals that occur in the usual formulation of this method.

To begin, we consider a monatomic periodic lattice at each lattice site of which there is an "atomic" potential; this gives rise, of course, to a periodic space potential. For simplicity, we shall assume that these "atomic" potentials are spherically symmetric, although one can generalize to potentials which are not spherically sym-

metric in a straightforward way. This assumption does *not* mean, of course, that an electron sees a spherically symmetric *total* potential, for near any lattice site it will see the local "atomic" potential plus the tails of the potentials that are at other sites. We choose an origin of coordinates at one of the potentials and in this coordinate system let \mathbf{r} be a position vector to a point \mathbf{P} in space. The site of the i th potential is specified by a vector \mathbf{d}_i of the form

$$\mathbf{d}_i = i_1 \mathbf{a}_1 + i_2 \mathbf{a}_2 + i_3 \mathbf{a}_3,$$

where $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are three basis vectors for the crystal and i_1, i_2, i_3 are integers. At each lattice site, we set up a coordinate system oriented similarly to the coordinate system at the origin, and let \mathbf{r}_i be the position vector in the i th system to the point \mathbf{P} in space. Then obviously we have

$$\mathbf{d}_i + \mathbf{r}_i = \mathbf{r}.$$

As usual, we define the basis vectors \mathbf{b}_j of the reciprocal lattice by

$$\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij}$$

* Operated with support from the U. S. Army, Navy, and Air Force.

¹ For a review article with extensive references to the literature see, for example: Joseph Callaway, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1958), Vol. 7.