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Unified treatment of dielectric enhancement and conduction-electron screening in the Mott transition in semiconductors

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The possibility is discussed that in a heavily doped n-type semiconductor a small but significant fraction of electrons may be released from the donor levels even at 0°K. The theory is based on the model of both the free-electron screening and the donor-electron screening of the potential. The latter screening arises from the neutral-donor polarizability which enhances the dielectric constant via the dipole-dipole interaction. The partial release of electrons into the conduction band starts at such a donor concentration that the bound state would disappear if only the donor electron screening is assumed. The fraction of the released electrons and the binding energy of the donor are calculated for n-type Si and Ge on the basis of a schematic model. Support for the present theory is provided by the magnetic data which are sensitive to the concentration of the conduction-band electrons.

I. INTRODUCTION

It is well known that the binding energy of a shallow donor decreases with increasing donor concentration N_D and that the bound state will disappear at an N_D exceeding a certain critical value N_C, which results in metallic conduction.[1] Concerning this M-I transition Mott[2] has emphasized the importance of the electron correlation effect. One approach to this effect is that of Mott who studied the transition from the metallic side taking into account the free-electron screening. Another approach has been adopted by Hugon and Ghazali[3] for the transition from the insulating side taking into account the polarizability of neutral donors and the dipole-dipole interaction among them. As a result of the dipole-dipole interaction an expression is obtained[3] for the dielectric constant ϵ which represents the Clausius-Mossotti relation. Thus ϵ can be divergent for a certain value of N_D.

The purpose of the present paper is to show the possibility that the likely divergence of ϵ may lead to the partial release of electrons from donor levels into the conduction band, even at 0°K. In this theory potential screening by both the conduction-band electrons and the donor electrons is considered so that the above two approaches are unified.

In Sec. II we first describe the dielectric-constant enhancement due to the neutral-donor polarizability and the mechanism of the electron release into the conduction band. In Secs. III–VI we construct a schematic model for the polarizability of neutral donors, taking into account free-electron screening effects and donor-donor interaction effects. On this basis we study the electron release and the resulting binding energy in Sec. VII. The theory is compared with experiments in Sec. VIII.

II. DESCRIPTION OF DIELECTRIC-CONSTANT ENHANCEMENT AND OF ELECTRON RELEASE

Let us consider isolated hydrogenic donors in the absence of free electrons. Taking account of the Lorentz effective field Castellan and Seitz[4] showed that ϵ will be given by

$$\epsilon = \epsilon_0 + \frac{4\pi N_D \alpha_{D0}}{1-(4\pi/3\epsilon_0)N_D\alpha_{D0}}, \tag{2.1}$$

where ϵ_0 is the static dielectric constant of the host crystal and α_{D0} is the polarizability of a hydrogenic neutral donor. This is the same expression as that obtained by Hugon and Ghazali[3] except that the wave-vector ($\vec{q}$) dependence of α_{D0} is neglected in Eq. (2.1). Considering α_{D0} for a medium of dielectric constant ϵ we have

$$\alpha_{D0} = \tfrac{9}{2} a_B^3 (\epsilon/\epsilon_0)^4 \epsilon_0 , \tag{2.2}$$

where a_B is the Bohr radius given at $\epsilon = \epsilon_0$.

Solving for ϵ as a function of N_D from Eqs. (2.1) and (2.2), we find that there is no positive ϵ solution for donor concentrations exceeding a critical value N_C. Thus there is no bound state. In the range of $N_D \leq N_C$ there are two positive solutions. The smaller of the solutions corresponds to the ground state, noting that the binding energy is proportional to $(\epsilon_0/\epsilon)^2$. The binding energy decreases with increasing N_D down to a certain nonzero value at $N_D = N_C$. Therefore, the transition is of first order in this model. This point has been indicated by Hugon and Ghazali, who obtained $a_B N_C^{1/3} = 0.21$, in contrast to $a_B N_C^{1/3} = 0.119$ obtained in the present calculation. The difference is mainly ascribed to the fact that the $\vec{q}$ dependence of the polarizability is neglected in Eq. (2.1).

The important point to note here is that the above discussions are restricted to the case where all the donors are neutral. Let us assume that a fraction of electrons is in the conduction band. These electrons can screen the polarization field of neutral donors, yielding an effectively reduced polarizability. Then even for $N_D > N_C$ the bound state can exist. The concentration of the released-electron fraction which gives the lowest total energy of the electron system is determined.

This is the essential point of the present theory. In a practical analysis we have more complicated situations, which are mainly related to the nonhydrogenic donor orbit and donor-donor interaction. We adopt a rather schematic model as follows. Let us assume that N_f and N_n electrons/cm^3 are in the conduction band and in the donor ground states, respectively. The sum $N_f + N_n$ is equal to the donor concentration N_D. Our analysis of donor states is based on the effective-mass approximation, considering a conduction band with isotropic effective mass m^* and ν valleys; the valley-orbit interaction is neglected. We also consider the dielectric constants ϵ due to host atoms plus the neutral-donor atoms and the $\epsilon_f(\vec{q})$ due to the conduction-band electrons, which give the total dielectric constant

$$\epsilon_T = \epsilon + \epsilon_f(\vec{q}) . \tag{2.3}$$

In place of Eq. (2.1) we have

$$\epsilon = \epsilon_0 + \frac{4\pi N_n \alpha_D}{1 - (4\pi/3\epsilon_0) N_n \alpha_D} . \tag{2.4}$$

For the time being we neglect the explicit dependence of α_D on $\vec{q}$, but a suitable correction will be given later.

First, we consider isolated donors in the case where there are no screening mobile charges. We have a hydrogenic donor in a medium of dielectric constant ϵ with Bohr radius a_B^* and binding energy E_{b0}^*,

$$a_B^* = \hbar^2 \epsilon / m^* e^2 , \tag{2.5}$$

$$E_{b0}^* = (\hbar^2 / 2m^*)(a_B^*)^{-2} . \tag{2.6}$$

For the special case $\epsilon = \epsilon_0$ we define

$$a_B = \hbar^2 \epsilon_0 / m^* e^2 , \tag{2.7}$$

$$E_{b0} = (\hbar^2 / 2m^*) a_B^{-2} . \tag{2.8}$$

We take the polarizability of a hydrogenic donor to be $(0.119/0.21)^3 \alpha_{D0}$, where α_{D0} is given by Eq. (2.2). The factor $(0.119/0.21)^3$ is empirically given to take account of the $\vec{q}$ dependence of the polarizability. The effective role of the $\vec{q}$ dependence is to reduce the polarizability. The present model closely reproduces the binding energy found by Hugon and Ghazali.

Now we consider the effect of the screening mobile charges and of the donor-donor interaction. We take for the polarizability

$$\alpha_D = (0.119/0.21)^3 \alpha_{D0} h g \eta . \tag{2.9}$$

The factors h and g arise from the presence of the conduction-band electrons. The screening effect of these electrons is to reduce the polarization field and to cause nonhydrogenic behavior of donor electrons. The former and the latter effects are represented by h and g, respectively. In the absence of conduction-band electrons we define $h=1$ and $g=1$. On the other hand we take into account the interaction between neutral donors in terms of η, which is unity in the limit $N_n \to 0$.

III. BINDING ENERGY

We calculate the binding energy of a donor at 0 K for a screened Coulomb potential, which is rewritten from the usual Lindhart result as

$$\mathcal{V}(r) = -\frac{e^2}{r}\frac{2}{\pi}\int_0^\infty dq \frac{1}{\epsilon_T(q)} \frac{\sin(qr)}{q} . \tag{3.1}$$

Here e is the electronic charge and $\epsilon_T(q)$ is given by Eqs. (2.3) and (2.4). The effect of the donor-donor interaction on the binding energy is neglected for simplicity. Let us assume that electrons of zero to k_f wave vector occupy the conduction-band states. We can write

$$\frac{\epsilon_T(q)}{\epsilon} = 1 + \frac{\lambda^2}{q^2}\left(1 + \frac{4k_F^2 - q^2}{4k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right) , \tag{3.2}$$

where

$$\lambda^2 = 4\nu k_F / \pi a_B^* , \tag{3.3}$$

$$k_F = (3\pi^2 N_f / \nu)^{1/3} . \tag{3.4}$$

Equation (3.1) is rewritten

$$\mathcal{V}(r) = -\frac{e^2}{r}\frac{2}{\pi}\int_0^\infty dx \frac{x}{x^2 + \frac{1}{4} v^2 \xi(x)} \sin(2k_F r x) , \tag{3.5}$$

where

$$v^2 = 4\nu / \pi a_B^* k_F , \tag{3.6}$$

$$\xi(x) = \tfrac{1}{2}\left(1 + \frac{1 - x^2}{2x} \ln \left| \frac{1+x}{1-x} \right| \right) . \tag{3.7}$$

To facilitate the analysis we take for $\xi(x)$,

$$\xi(x) = 1/(1 + x^2) . \tag{3.8}$$

This function is found to be quite adequate for the present eigenvalue problem, and it leads to an incorrect expression for the potential only at large distances where the potential is very small. Equation (3.5) is calculated to be

$$\mathcal{V}(r) = -(e^2/\epsilon r)\theta(r) , \tag{3.9}$$

where

$$\theta(r)=e^{(-\lambda_1 r)}\left[\cos(\lambda_2 r)+(v^2-1)^{-1/2}\sin(\lambda_2 r)\right], \tag{3.10}$$

$$\lambda_1=k_F(v+1)^{1/2} \text{ and } \lambda_2=k_F(v-1)^{1/2}, \tag{3.11}$$

in the range $v\geq 1$. Equations (3.9)–(3.11) approximate Eq. (3.5) within a few percent in the r range of practical interest.

Let us calculate the binding energy using Eq. (3.9) on the basis of the variational method which has been formulated by Hulthén and Laurikainen.[5] It is convenient to define κ_b by

$$E_b=(\hbar^2/2m^*)\kappa_b^2. \tag{3.12}$$

For $\kappa_b\ll\lambda_1$ the trial function used by Hulthén and Laurikainen for the Thomas-Fermi screened potential is useful. Analogously we take the ground-state wave function

$$\phi(r)=(1/r)e^{(-\kappa_b r)}(1-e^{(-\lambda_1 r)})(A+Be^{(-\lambda_1 r)}). \tag{3.13}$$

On the other hand, for $\kappa_b\gg\lambda_1$ the function

$$\phi(r)=e^{(-\kappa_b r)}(A+Be^{(-\lambda_1 r)}) \tag{3.14}$$

is appropriate. In the method of Hulthén and Laurikainen the eigenvalue problem is solved choosing e^2/ϵ as an eigenvalue and taking κ_b (or the energy) as a known parameter. Thus A and B are determined so as to give a minimum value for e^2/ϵ. It is found that the value of the binding energy obtained using Eq. (3.13) for $\kappa_b<\lambda_1$ continues smoothly into that obtained using Eq. (3.14) for $\kappa_b>\lambda_1$. In Fig. 1, E_b/E_{b0}^* is plotted as a function of $a_B^* N_f^{1/3}$ for $\nu=1$, 4, and 6. The binding energy vanishes at $a_B^* N_f^{1/3}=0.422$, 0.266, and 0.246 for $\nu=1$, 4, and 6, respectively. These values are considerably larger than those obtained by Krieger and Nightingale[6] (0.29 for $\nu=1$ and 0.23 for $\nu=4$ and 6).

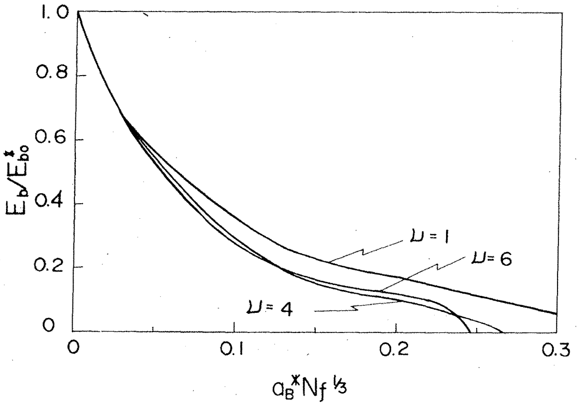

FIG. 1. E_b/E_{b0}^* vs $a_B^* Nf^{1/3}$, calculated for the potential given by Eqs. (3.9)–(3.11) with ν as a parameter.

It is convenient to describe the $E_b-a_B^* N_f^{1/3}$ relation by simulation curves, which are given in the form

$$\frac{E_b}{E_{b0}^*}=\frac{1}{1+Ax}-Bx, \tag{3.15}$$

with $x=a_B^* N_f^{1/3}$, where $A=17.3$ and $B=0.67$ for $\nu=4$ and $A=19.4$ and $B=0.70$ for $\nu=6$. This equation is a good fit to the theroretical curve for $\nu=4$ over the whole range. For $\nu=6$ a smaller value is obtained from Eq. (3.15) only in a restricted range of $a_B^* N_f^{1/3}\gtrsim 0.18$. However, the values of N_f at which E_b vanishes are correctly given by Eq. (3.15) for both $\nu=4$ and $\nu=6$.

IV. SCREENING OF POLARIZATION FIELD

In this section we discuss the reduced polarizability due to screening of the polarization field by the conduction-band electrons and derive an expression for the factor h in Eq. (2.9). The electric displacement $\vec{P}$ in an insulator is given for an electric dipole $\vec{m}$ induced along a uniform field direction, by $\vec{P}=N_n\vec{m}$. In the presence of mobile charges we can define a reduced magnitude of $\vec{P}$ on the basis of the polarization field at a point $\vec{r}=0$ surrounded by a polarized medium. Let the screened potential due to a point charge by $e\theta(r)/\epsilon r$, where $\theta(r)$ has been defined in Eqs. (3.10) and (3.11). Then the screened potential due to an electric dipole located at $\vec{r}=\vec{r}_i$ is given by

$$\Xi(\vec{r}_i)=(1/\epsilon)\vec{m}\cdot\nabla_i\left[(1/r_i)\theta(r_i)\right]. \tag{4.1}$$

The electric field at $\vec{r}=0$ due to all polarized neutral donors is

$$\vec{F}=\sum_i \nabla_i\,\Xi(r_i). \tag{4.2}$$

In performing the summation we consider a uniform distribution of neutral donors. According to the conventional method of Lorentz-field calculation, we consider a spherical cavity of radius t with its center at $\vec{r}=0$. The polarization field is calculated to be

$$\vec{F}=(4\pi/3\epsilon)N_n\vec{m}\,h(t), \tag{4.3}$$

with

$$h(t)=\theta(t)-t\frac{d}{dt}\theta(t). \tag{4.4}$$

If there are no screening charges, we have $h(t)=1$, i.e., the conventional result. We may define a screened polarization field as $\vec{P}=N_n\vec{m}h(t)$. Thus $h(t)$ can be used in Eq. (2.9). Using Eq. (3.10) we obtain

$$h(t)=e^{(-\lambda_1 t)}\left[\left(1+\frac{v}{1+v}\lambda_1 t\right)\cos(\lambda_2 t)+\frac{1}{(v^2-1)^{1/2}}(1+v\lambda_1 t)\sin(\lambda_2 t)\right]. \tag{4.5}$$

There is considerable leave in choosing a value of t for random distributed donors and for large donor orbits. In view of this, the rather arbitrary choice $t=N_t^{-1/3}$ is taken.

V. POLARIZABILITY OF AN ISOLATED NON HYDROGENIC DONOR

For a nonhydrogenic donor which results from the screened Coulomb potential, the polarizability deviates from that of a hydrogenic donor. The deviation is expressed in terms of the factor g in Eq. (2.9). The polarizability is calculated considering a small applied field F in the x direction, which adds the term eFx to the zero-field Hamiltonian. We start from the wave function $\phi(r)(1+\beta x)$, where $\phi(r)$ is the ground-state wave function in the absence of electric field. The ground-state energy in the presence of the applied field is calculated by a suitable choice of β on the basis of the variational principle. From the energy the polarizability is calculated to be

$$\alpha_D=\frac{6\epsilon_0}{a_B}\frac{U^2}{S(S-T)}, \tag{5.1}$$

where

$$S=\int_0^\infty dr\,[\chi(r)]^2, \tag{5.2}$$

$$T=\int_0^\infty dr\,r\chi(r)\frac{d}{dr}\chi(r), \tag{5.3}$$

$$U=\tfrac{1}{3}\int_0^\infty dr\,r^2[\chi(r)]^2. \tag{5.4}$$

In these equations $\chi(r)$ has been defined as $\chi(r)=r\phi(r)$. We note that the expression for α_D is independent of the normalization constant of the wave function.

Especially for the hydrogenic case, i.e., $\phi(r)=e^{-r/a_B}$, we obtain the polarizability

$$\alpha_{D0}=4a_B^3\,(\epsilon/\epsilon_0)^4\epsilon_0, \tag{5.5}$$

which is somewhat different from Eq. (2.2) and is used hereafter for an approximate calculation. For the nonhydrogenic case we use Eq. (3.13), assuming the least important factor $(A+Be^{(-\lambda_1 r)})$ to be unity for simplicity. Figure 2 shows the calculated result (solid line) for

$$(E_b/E_{b0}^*)^2 g=(E_b/E_{b0}^*)^2(\alpha_D/\alpha_{D0})$$

as a function of $\sigma=\kappa_b/\lambda_1$. The theoretical g is well simulated by

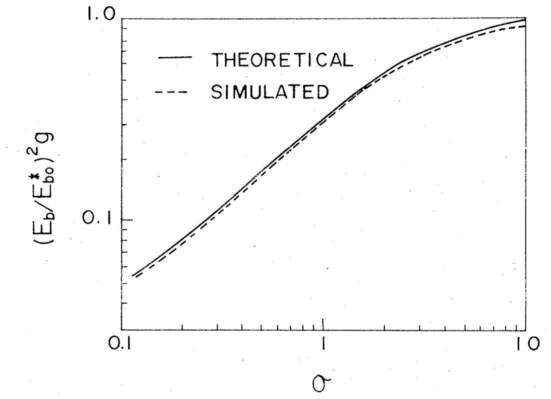

FIG. 2. $(E_b/E_{b0}{}^*)^2 g$ vs σ, calculated from Eqs. (5.1)–(5.4) (—) and from Eq. (5.6) (---) for simulation.

$$g=\tfrac{1}{36}\left(1+\frac{14.7\sigma^{1.3}}{1+0.42\sigma^{1.3}}\right)\left(\frac{E_{b0}^*}{E_b}\right)^2 \tag{5.6}$$

as shown by the dashed curve in Fig. 2. It is to be noted that we have $g=1$ in the limit $N_f \to 0$.

VI. POLARIZABILITIES OF INTERACTING DONORS

Interaction between donors will reduce the polarizability per donor to a value smaller than that for an isolated donor. We define the reduction factor η as the ratio of the polarizability per donor to that of an isolated donor. We calculate η using the somewhat schematic model that the interaction between nearest-neighbor donors is important in determining it.

In a way similar to that followed in the preceding section, the polarizability α_{D-D} of a molecule which is made up of two donors is calculated on the basis of the variational principle. For an electric field in the x direction we obtain

$$\alpha_{D-D}=2e^2G_1/SG_0, \tag{6.1}$$

where

$$S=\int\int d\vec{r}_1\,d\vec{r}_2\,|\Phi_0(\vec{r}_1,\vec{r}_2)|^2, \tag{6.2}$$

$$G_0=-\frac{\hbar^2}{m^*}\int\int d\vec{r}_1\,d\vec{r}_2\,\Phi_0^*(\vec{r}_1,\vec{r}_2)(x_1+x_2)\times\left(\frac{\partial}{\partial x_1}+\frac{\partial}{\partial x_2}\right)\Phi_0(\vec{r}_1,\vec{r}_2), \tag{6.3}$$

$$G_1=\int\int d\vec{r}_1\,d\vec{r}_2(x_1+x_2)^2\,|\Phi_0(\vec{r}_1,\vec{r}_2)|^2. \tag{6.4}$$

In the above equations $\Phi_0(\vec{r}_1,\vec{r}_2)$ is the zero-field two-electron wave function and the two electrons are labeled by the suffices 1 and 2. For $\Phi_0(\vec{r}_1,\vec{r}_2)$ we use the ground-state wave function

$$\Phi_0(\vec{r}_1,\vec{r}_2)=\phi_a(\vec{r}_1)\phi_b(\vec{r}_2)+\phi_a(\vec{r}_2)\phi_b(\vec{r}_1), \tag{6.5}$$

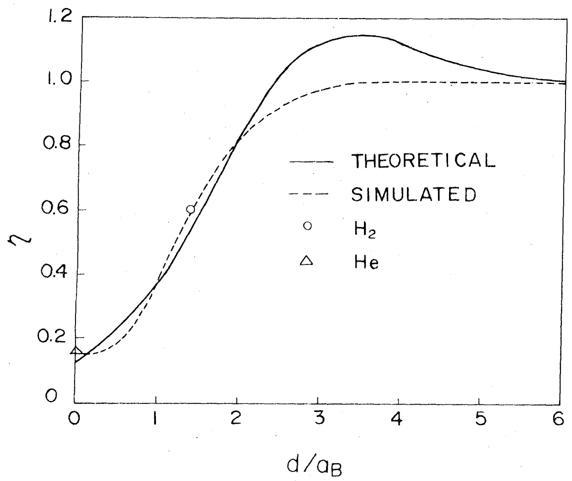

FIG. 3. η vs d/a_B, calculated from Eqs. (6.1)–(6.4) (—) and from Eq. (6.7) (---) for simulation.

given by Rosen[8] for the case of a hydrogen molecule, where

$$\phi_a(\vec{r}_i) = [1 + c(\vec{r}_i - \vec{r}_a)\cdot\hat{n}]\exp(-b|\vec{r}_i - \vec{r}_a|),$$
$$\phi_b(\vec{r}_i) = [1 - c(\vec{r}_i - \vec{r}_b)\cdot\hat{n}]\exp(-b|\vec{r}_i - \vec{r}_b|), \quad (6.6)$$

with $i = 1$ or 2. Here $\hat{n}$ is the unit vector in direction of the molecular axis. The positions of donor atoms are represented by $\vec{r}_a$ and $\vec{r}_b$. The constants c and b are calculated from Figs. 2 and 3 of Ref. 8. Thus we calculate $\eta = \alpha_{D-D}/2\alpha_{D0}$ as a function d/a_B, where d is the average distance between neutral donors, given[7] by $d = [(2\pi N_t)/3]^{-1/3}$, a_B is the Bohr radius, and α_{D0} is given by Eq. (5.5).

The polarizability of the molecule varies with the field direction with respect to the direction of the molecular axis. So we take an average value $\eta = (\eta_\parallel + 2\eta_\perp)/3$, where $\eta_\parallel$ and $\eta_\perp$ are quantities in the cases of field direction parallel and perpendicular to the molecular axis, respectively. The result of the calculation is shown by the solid curve in Fig. 3. The theory is tested using the polarizability data of a hydrogen molecule and of a helium atom. As for the former the interatomic separation is 1.4 times the Bohr radius with $\alpha_\parallel = 0.934$ Å^3 and $\alpha_\perp = 0.718$ Å^3. As for the latter we have $\epsilon = 1.000\,0693$ giving $\alpha = 0.103$ Å^3. On the other hand, rigorous calculation yields $\alpha = 0.663$ Å^3 for the hydrogen atom. The values of η calculated according to the definition are shown in Fig. 3. (○, △). The hump at $\eta > 1$ arises mainly from $a_B b < 1$ only, in the corresponding range of d/a_B, which has been obtained by Rosen.[8] The theoretical curve is simulated by

$$\eta = \frac{(d/a_B)^3}{(d/a_B)^3 + 3} + 0.16\,e^{-d/4a_B}, \quad (6.7)$$

as shown by the dashed curve. We neglect the hump, which is not important in the present discussion.

Now we extend the above case of hydrogenic donors to the case of nonhydrogenic donors. This is done by replacing d/a_B in Eq. (6.7) by $\kappa_b d$, noting that κ_b^{-1} represents the radius of the donor-electron cloud.

VII. DETERMINATION OF DONOR LEVEL AND CONDUCTION-BAND ELECTRON CONCENTRATION

In the present model we consider both conduction-band electrons and neutral donors of concentrations N_f and N_n, respectively, the sum of which gives the donor concentration N_D. The fraction $\rho = N_f/N_D$ of the conduction-band electrons is determined that gives the lowest total energy of the electron system per cm^3,

$$E_T = \tfrac{3}{5} N_f E_f - N_n E_b\,. \quad (7.1)$$

The energy is measured from the conduction-band edge. The first term on the right-hand side of Eq. (7.1) is the total energy of the conduction-band electrons, assuming the band to be filled from zero energy to $E_F = \hbar^2 k_F^2/2m^*$. This assumption will be reasonable since such a distribution may give the lowest total energy. The lowest total energy state can be found by solving for ϵ/ϵ_0 which satisfies the following relations:

$$\frac{\epsilon}{\epsilon_0} = 1 + \frac{4\pi N_n \alpha_D}{1 - \frac{4}{3}\pi N_n \alpha_D}, \quad (7.2)$$

$$\alpha_D = 4a_B^3\left(\frac{\epsilon}{\epsilon_0}\right)^4\left(\frac{0.119}{0.21}\right)^3 \epsilon_0 h g \eta, \quad (7.3)$$

$$h = e^{-\beta}\left\{\left(1 + \frac{v}{1+v}\beta\right)\cos\left[\beta\left(\frac{v-1}{v+1}\right)^{1/2}\right] + \frac{1}{(v^2-1)^{1/2}}(1 + v\beta)\sin\left[\beta\left(\frac{v-1}{v+1}\right)\right]\right\}, \quad (7.4)$$

$$g = \frac{1}{36}\left(1 + \frac{14.7\sigma^{1.3}}{1 + 0.42\sigma^{1.3}}\right)\left(\frac{E_{b0}^*}{E_b}\right)^2, \quad (7.5)$$

$$\eta = \gamma^3/(\gamma^3 + 3) + 0.16\exp(-\tfrac{1}{4}\gamma), \quad (7.6)$$

$$\beta = \left(\frac{9\pi}{2\nu}\right)^{1/3}(v+1)^{1/2}\left(\frac{\rho}{1-\rho}\right)^{1/3}, \quad (7.7)$$

$$\sigma = \frac{(E_b/E_{b0}^*)^{1/2}}{[12\pi(a_B^*)^3 N_f]^{1/4}}, \quad (7.8)$$

$$\gamma = \frac{(E_b/E_{b0}^*)^{1/2}}{(\frac{2}{3}\pi)^{1/3} a_B^* N_n^{1/3}}, \quad (7.9)$$

$$E_b/E_{b0}^* = 1/(1 + A a_B^* N_f^{1/3}) - B a_B^* N_f^{1/3}, \quad (7.10)$$

with $A = 17.3$, $B = 0.67$ for $\nu = 4$ and $A = 19.4$, and

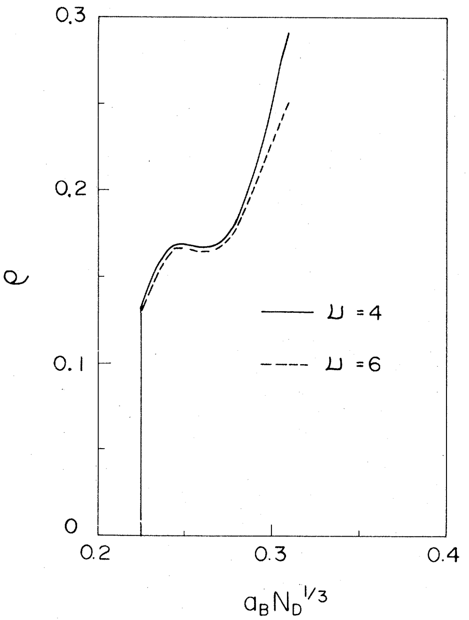

FIG. 4. $\rho (= N_f/N_D)$ vs $a_B N_D^{1/3}$ for $\nu = 4$ (—) and for $\nu = 6$ (- - -).

$B = 0.07$ for $\nu = 6$. For a given value of $a_B N_D^{1/3}$ the solutions are found for various values of ρ in a restricted range. The ground state of the system is determined for the value of ρ which gives the minimum value of E_T.

The ratio ρ thus obtained is shown as a function of $a_B N_D^{1/3}$ in Fig. 4. The conduction-band electrons emerge at $a_B N_D^{1/3} = 0.225$, beyond which the bound state can exist only in the presence of screening mobile charges. The obtained ratio E_b/E_{b0} is shown by the curves in Figs. 5 and 6 as a function of $a_B N_D^{1/3}$. A discontinuity appears at a donor concentration, given by $a_B N_D^{1/3} \doteq 0.225$, where transition to a smaller binding energy occurs. Beyond this concentration an impurity band may be formed, owing to the increased overlap of the wave functions between neutral donors. Thus the calculated binding energy is significant only in an approximate sense. For $a_B N_D^{1/3} \gtrsim 0.31$ the binding energy is so small that the impurity band will completely merge into the conduction band. So the present calculation is useful for $a_B N_D^{1/3} < 0.31$. In Fig. 5 are shown experimental data[9,10] for the binding energy of Ge doped with various donors. Some of the data (●, ▲, △) are calculated from the resistivity-temperature curves. In plotting the data a_B is calculated from values of the binding energy E_{b0} of a donor (see Table I) in a light-doping range, using the relation $E_{b0} = e^2/2a_B\epsilon_0$ based on a hydrogenic picture. We use $\epsilon_0 = 15.36$ for Ge,[11] and $\epsilon_0 = 11.40$ for Si.[11]

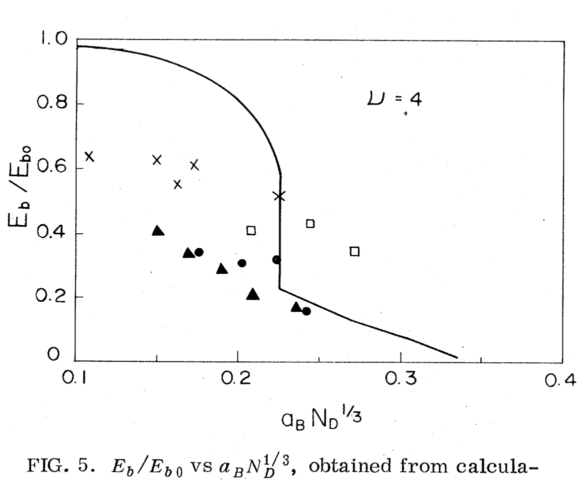

FIG. 5. E_b/E_{b0} vs $a_B N_D^{1/3}$, obtained from calculation (—) for $\nu = 4$ and from experimental data (×, □, ●, ▲) for Ge.

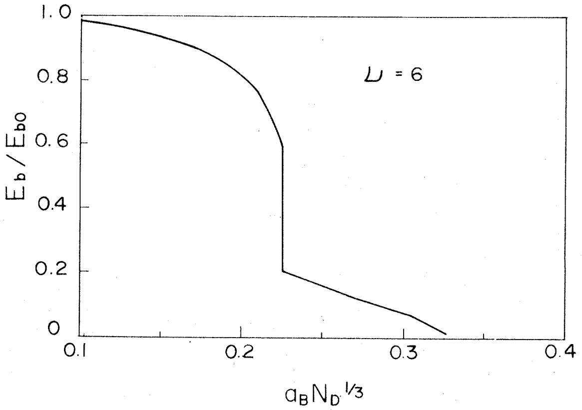

FIG. 6. E_b/E_{b0} vs $a_B N_D^{1/3}$, calculated for $\nu = 6$.

There exists experimental evidence[10,12,13] that the metal-insulator transition occurs at a donor concentration N_C at which the activation energy (conventionally denoted[9] as E_2) vanishes. The values of $a_B N_C^{1/3}$ calculated from the data[10,12,13] are 0.24, 0.24, 0.25, and 0.21 for Ge:P, Ge:As, Ge:Sb and Si:P, respectively. At $N_D = N_C$ the binding energy does not vanish, as is seen from Fig. 5. This situation was theoretically found by Hugon and Ghazali[3] and it is seen also in the present calculation. The reason why the experimental points of E_b lie lower than the theoretical

TABLE I. Parameters for different materials.

Material	E_{b0} (meV) [a]	a_B (Å)
Si:P	45.8	13.8
Ge:P	12.9	36.4
Ge:As	14.2	33.1
Ge:Sb	10.3	45.6

[a] The data are found in Table 9.1 of Ref. 21.

curve for $a_BN_D^{1/3} < 0.225$ will be ascribed to the fact that we have not taken into account the level broadening due to the donor-wave-function overlap and the charge-compensation effect, in calculating the binding energy. Such effects have been considered in Refs. 14 and 15.

The binding-energy gap at a discontinuity point depends on the strength of the free-carrier screening. If stronger screening is assumed, a smaller gap will be obtained. For strong enough screening even a continuous rapid decrease of E_b may occur instead of a discontinuous change. In the present calculation we have taken into account the screening due to the impurity-band electrons only in terms of nearest-neighbor donor interaction. When the impurity band is formed the screening effect will be larger. Thus the actual situation is such that E_b and ρ are larger and smaller, respectively, than those obtained in the present calculation.

VIII. TEST OF THE THEORY

A direct test of the present theory is provided by the magnetic data on the electron system. In Fig. 7 are shown the Knight-shift data[16] on Si:P at 1.6 K together with the theoretical curve. The curve is obtained on the basis of Fig. 4, from which N_f is found to calculate the Knight shift K by the relation $K = AN_f^{1/3}$. The constant A is an adjustable parameter determined at such a high concentration that all donors are ionized. In view of the overestimation of ρ, as discussed above, of the uncertainty in the calculated value of a_B, and of the local-density fluctuation of donors, the present theory describes considerably well the observed qualitative features.

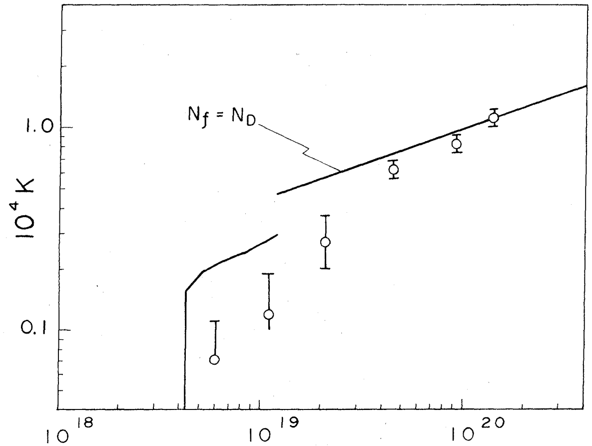

FIG. 7. Knight shift K vs $a_BN_D^{1/3}$ for Si: P. The curve is calculated from $K = 2.1\times10^{-11}N_f^{1/3}$, for which N_f (in cm^{-3}) is found from Fig. 4 for $a_BN_D^{1/3} < 0.31$ and is put equal to N_D for $a_BN_D^{1/3} > 0.31$. Empirical data (○) at 1.6 K are obtained from Ref. 16.

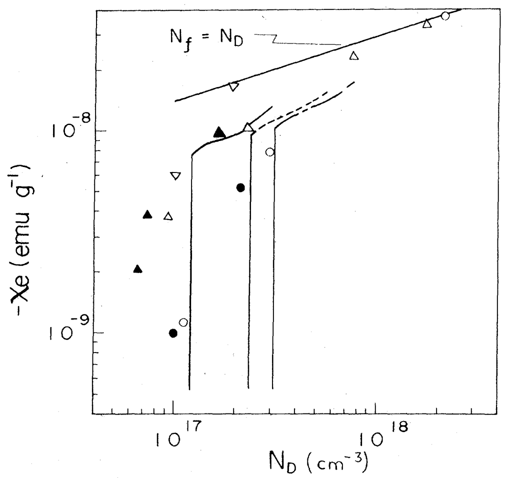

FIG. 8. Magnetic susceptibility χ_e of the electron system vs N_D for Ge: P (– – –), Ge: As (– – –) (●) (Ref. 17) (○) (Ref. 19) and Ge:Sb (—), (▲) (Ref. 17) (△) (Ref. 18) (▽) (Ref. 20). The curves are calculated from $\chi_e = -3.0\times10^{-14}N_f^{1/3}$ emu-g^{-1}, where N_f (in cm^{-3}) is found from Fig. 4 for $a_BN_D^{1/3} < 0.31$. The curve obtained by putting $N_f = N_D$, for which the transition of χ_e occurs at $a_BN_D^{1/3} = 0.225$, is also shown. Empirical data (●○▲△▽) at low temperatures are obtained from Ref. 16.

Figure 8 shows the data, collected in Ref. 16, of the magnetic susceptibility χ_e of the electron system, on Ge doped with various donors. In the figure are shown the theoretical curves obtained on the basis of Fig. 4, assuming χ_e to be determined merely by electrons in the conduction band. Noting the relation $\chi_e = BN_f^{1/3}$, B is again chosen as an adjustable parameter determined at such a high donor concentration that all donors are ionized. In view of the above-mentioned points concerning ρ, a_B, and the local-density fluctuation, the present theory describes considerably well the qualitative features of the observations. Thus the above discussion would indicate a partial release of the donor electrons even at 0 K in the presence of a bound state in a heavily doped semiconductor. The Fermi-Dirac distribution is no longer valid as a result of many-body interaction in the electron system.

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