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[24] Usually $\alpha = 1$ unless the recombination strongly depends on compressive deformation and the recombination time is short. The dependence of α on ω has not been developed in view of the uncertainties involved. Even though computations were made with values of α other than unity, the final analysis uses $\alpha = 1$ only.

[25] *Materials Used in Semiconductor Devices*, edited by C. A. Hogarth (Interscience, New York, 1965), pp. 135, 150.

[26] E. F. Steigmeir and B. Abeles, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors* (Academic, New York, 1965), p. 701.

[27] For acceptor doping levels such that indium antimonide is degenerate at liquid-helium temperatures, it is expected that an "impurity band" is formed in which there could be a conduction mechanism at least as efficient as the hopping of electrons from one impurity site to another. The carriers in this band, which for acceptor impurity concentrations above 2×10^{17} cm^{-3} overlap the valence band [R. F. Broom and A. C. Rose-Innes, Proc. Phys. Soc. (London) B69, 1269 (1956)], have a small conductivity which should increase with increased doping.

[28] The condition $\sigma_2{}^0 < \sigma_1{}^0$ does not induce the same relationship between the σ_i. For the impurity band, the conditions $ql_2 < ql_1$ and $\omega\tau_2 < \omega\tau_1$ yield $\sigma_2' > \sigma_1'$, and this may give values of σ_1 and σ_2 of comparable magnitude. It is expected that in the present case $\sigma_2 < \sigma_1$, where index 1 refers to the heavy-hole band and index 2 refers to the impurity band.

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Dielectric Screening and the Mott Transition in Many-Valley Semiconductors

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We show that the donor density N_c required for the Mott transition to occur in a many-valley semiconductor is given by $a_0(N_c)^{1/3} = 0.25C(\nu)$, where a_0 is the radius of the first Bohr orbit in the material, ν is the number of equivalent conduction-band valleys occupied by electrons, and $C(\nu) = \nu^{-2/3}$ in the Thomas-Fermi (TF) approximation. This result is identical to Mott's for $\nu = 1$ and is in good agreement with experiment for that case, but predicts an N_c which is smaller than the experimental results for Ge ($\nu = 4$) and Si ($\nu = 6$). This discrepancy is attributed to the fact that the TF approximation does not include the result, predicted by the dielectric-screening theory, that only those Fourier components of the potential for which $q \lesssim 2k_F$ are effectively screened by the conduction electrons. This is of increased significance in the many-valley case due to the decrease of k_F for a given N. We have calculated the condition for zero activation energy assuming dielectric screening and find $C(1) = 1.14$, $C(2) = 0.96$, and $C(4) = C(6) = 0.92$ in good agreement with the available experimental results. We also note that it may be possible to observe a metal-to-insulator transition when stress is applied to a degenerately doped Ge crystal.

I. INTRODUCTION AND CONCLUSIONS

It is well known that as the density of donors in a semiconductor increases, the activation energy decreases owing to the electron-electron interaction and that for sufficiently high donor concentrations the activation energy will vanish resulting in metallic conduction.[1] It was Mott who first pointed out that this insulator-to-metal transition might be abrupt with a definite critical density which experimentally appears to be slightly smeared out because of the variation in the local density of donors about the average density.[2]

In order to get an estimate of the critical density N_c at which the transition would occur, Mott assumed Thomas-Fermi screening of the donor atoms by the electrons and found the condition for zero activation energy, i.e., when the binding energy of the electron to the donor is zero. The result was

$$a_0 N_c^{1/3} \cong 0.25, \tag{1}$$

where a_0 is the first Bohr orbit in the material. Mott[3] and Mott and Twose[4] found that there was good agreement between theory and experiment for heavily doped Ge and Si, the constant on the right-hand side of Eq. (1) being approximately 0.2. More recently Alexander and Holcomb[5] have made a detailed analysis of the transport data on Si : P,[6] Ge : Sb,[7–9] Ge : P,[8] Ge : As[8] and found that the average value of the constant in Eq. (1) is 0.22. In each case, the value of the effective mass appearing in a_0 was taken as the one that gave the experimentally observed binding energy of an electron bound to a donor in the light-doping range for each particular dopant.

Alexander and Holcomb[5] also show that the width of the transition region can be understood assuming a Poisson distribution of local donor densities in the semiconductor. In fact, the width of the transition region estimated in this way is larger than the experimental width because, as they point out, the direct current requires a connected conduction path through the sample, and thus, clusters of impurities with local concentrations above N_c will only contribute to the direct current if they are connected.

Mikoshiba,[10] assuming a Poisson distribution of impurity concentrations and Thomas-Fermi screening of the donors in the metallic density regions, has succeeded in explaining, at least qualitatively, the anomalous behavior of the magnetoresistance, the spin susceptibility, and the static susceptibility above the insulator-metal (Mott) transition for heavily doped Ge and Si crystals. There thus appears to be considerable evidence for the validity of using the Thomas-Fermi screening theory to predict the approximate critical density and, together with assuming a Poisson distribution of metallic density regions, to gain an understanding of other properties of these materials.

Nevertheless, the present work demonstrates that when the Thomas-Fermi theory is correctly applied to many-valley semiconductors such as Ge and Si, the predictions of the critical density are different from that given in Eq. (1) and are substantially in disagreement with experiment. In Sec. II we show that the Thomas-Fermi theory predicts that the critical density satisfies

$$a_0 N_c^{1/3} \cong 0.25\, C(\nu), \tag{2}$$

with

$$C(\nu) = \nu^{-2/3},$$

where ν is the number of equivalent valleys in the conduction band. Since $\nu = 4$ for Ge and $\nu = 6$ for Si, this result lowers the predicted critical density by a factor of 16 and 36, respectively, for these materials. The physical reason why the critical density is lowered in the many-valley Thomas-Fermi case arises from the fact that by spreading the electrons over more than one valley their Fermi energy is decreased and they move more slowly. Since slow electrons can linger in the vicinity of the impurity longer, they tend to screen more effectively and hence the critical density decreases.

However, the Thomas-Fermi theory does not take into consideration the fact, predicted by the dielectric-screening theory, that the Fourier components of the potential $V(q)$ are not effectively screened for $q > 2k_F$, where k_F is the magnitude of the Fermi wave number. This has a small effect on the conductivity of a degenerate electron gas interacting with screened ionized impurities because in the first Born approximation the transition rate depends only on $V(q)$ for $0 \le q \le 2k_F$. However, the calculation of the binding energy requires the use of $V(q)$ for all q. Furthermore, since distributing a given number of electrons over several valleys lowers k_F, then the difference between the potential predicted by the Thomas-Fermi theory and dielectric-screening theory increases as the number of valleys increases and the attraction to the donor atom becomes progressively larger than the Thomas-Fermi theory would suggest. This effect thus requires heavier doping to obtain zero binding energy than that given by the many-valley Thomas-Fermi theory.

In Sec. III, assuming dielectric screening, we calculate the binding energy of an electron bound to a donor as a function of the electron density in the conduction band at $T = 0\,^\circ\mathrm{K}$ for $\nu = 1$, 2, 4, and 6. We find that $C(1) = 1.14$ which is similar to the value predicted by the Thomas-Fermi theory (but larger, as expected) and agrees well with a numerical self-consistent calculation performed for InSb by Li *et al.*[11] Furthermore, $C(4) = C(6) = 0.92$, which yields a predicted value of N_c in better agreement with experiment[5] than that given by Eq. (1).

II. CALCULATION OF BINDING ENERGY AND CRITICAL DENSITY: THOMAS-FERMI APPROXIMATION

Using a simple hydrogenic wave function with a single variational parameter, Krieger[12] has calculated $\overline{E}/\epsilon_0$ as a function of $a_0\lambda$, where $\overline{E}$ is the binding energy in the presence of Thomas-Fermi screening. Here ϵ_0 is the binding energy for zero screening, $a_0 = \hbar^2\kappa/m^* e^2$ is the radius of the first Bohr orbit in the material, and λ is the Thomas-Fermi inverse-screening length which at $T = 0\,^\circ\mathrm{K}$ is given by

$$\lambda^2 = (4\pi e^2/\kappa)\, g(\epsilon_F), \tag{3}$$

where $g(\epsilon_F)$ is the electron density of states at the Fermi energy and κ is the static dielectric constant of the host crystal. The broken curve in Figs. 1 and 2 is a graph of the results. The critical density corresponds to

$$a_0\lambda = 1, \tag{4}$$

which is precisely Mott's result.

Now for electrons occupying ν equivalent valleys in the conduction band,

$$g(\epsilon_F) = \nu\, g_1(\epsilon_F), \tag{5}$$

where $g_1(\epsilon_F)$ is the density of states for the electrons in any one of the valleys and for parabolic bands is given by

$$g_1(\epsilon_F) = 3n_1/2\epsilon_F. \tag{6}$$

Here n_1 is the electron concentration in a single valley. Thus, from Eqs. (5) and (6) we have

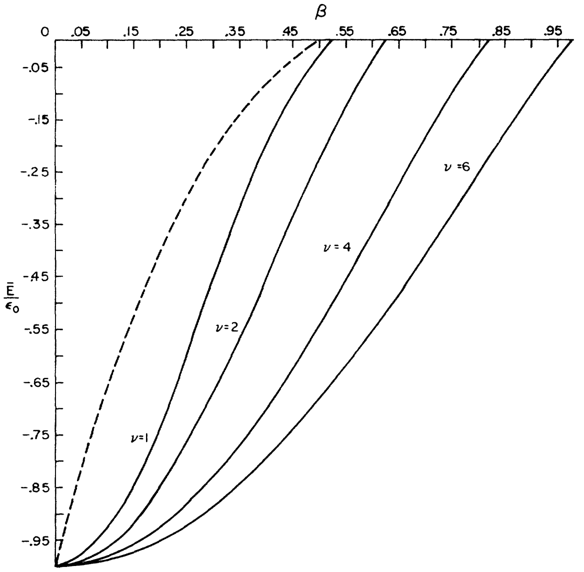

FIG. 1. $\bar{E}/\epsilon_0$ vs β for $\nu = 1, 2, 4$, and 6, assuming approximate dielectric function given by Eq. (14). The dotted curve is the result for all ν given by the Thomas-Fermi approximation.

$$g(\epsilon_F) = 3N/2\epsilon_F, \tag{7}$$

where N is the total electron concentration. Assuming each equivalent valley has an isotropic band structure, then

$$\epsilon_F = \hbar^2 k_F^2/2m^*, \qquad k_F = (3\pi^2 n_1)^{1/3} = (3\pi^2 N/\nu)^{1/3}. \tag{8}$$

Then from Eqs. (3) and (6)–(8) we have

$$a_0\lambda = [a_0 N^{1/3} 4\nu^{2/3}(3/\pi)^{1/3}]^{1/2}, \tag{9}$$

which yields, using Eq. (4),

$$a_0 N_c^{1/3} \simeq 0.25\nu^{-2/3} \tag{10}$$

for the critical density which, as noted above, is different from the usual result by the factor $\nu^{-2/3}$ and yields results for the critical density which are no longer in agreement with experiment for Si and Ge.

III. CALCULATION OF BINDING ENERGY AND CRITICAL DENSITY: DIELECTRIC-SCREENING APPROXIMATION

In this case we seek the ground-state energy of the Schrödinger equation in the effective-mass approximation, i.e.,

$$-(\hbar^2/2m^*)\,\nabla^2\psi(\vec r) + V(\vec r)\,\psi(\vec r) = E\,\psi(\vec r),$$

where the Fourier transform of the potential is given by

$$V(\vec q) = V_c(q)/\epsilon(\vec q). \tag{11}$$

Here $\epsilon(\vec q)$ is given in the Hartree approximation by

$$\epsilon(\vec q) = 1 + \frac{4\pi e^2}{\kappa q^2}\,\frac{3N}{2\epsilon_F}\left(\frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q}\ln\left|\frac{2k_F + q}{2k_F - q}\right|\right). \tag{12}$$

The latter is obtained by summing the contributions to $\epsilon(\vec q)$ from all ν valleys which leads to a factor $n_1\nu = N$ in the second term. The factor κ in $\epsilon(\vec q)$ arises from the fact that the impurity is imbedded in a medium with a static dielectric constant different from unity.

As in the case of the Thomas-Fermi potential, no analytic solution of the Schrödinger equation has been found for this potential. Furthermore, it is not possible to obtain an analytical function for $V(\vec r)$ by taking the Fourier transform of $V(\vec q)$. The first difficulty is eliminated by employing the variational principle for the energy with the usual hydrogenic wave function

$$\psi(\vec r) = (\pi a^3)^{-1/2}\, e^{-r/a},$$

where a is a variational parameter. The second difficulty is circumvented by taking the Fourier transform of $\psi^*\psi$ and then finding the average potential energy by performing an integration in $\vec q$ space. The result is

$$\bar{E} = \frac{\hbar^2}{2m^* a^2} - \frac{32 e^2}{\kappa\pi a^4}\int_0^\infty \frac{1}{(q^2+\eta^2)^2}\,\frac{dq}{\epsilon(q)}, \tag{13}$$

where $\eta = 2/a$.

However, it is not possible to perform the required integration analytically. Since we require the a that minimizes $\bar{E}$ for a range of electron concentrations and for several different ν, it is useful

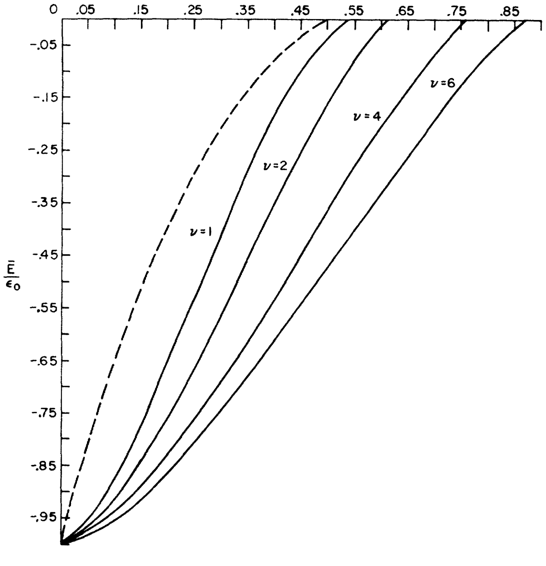

FIG. 2. $\bar{E}/\epsilon_0$ vs β for $\nu = 1, 2, 4$, and 6, assuming dielectric screening given by Eq. (12). The dotted curve is the result for all ν given by the Thomas-Fermi approximation.

to perform the calculation first with an approximate $\epsilon(q)$ which permits Eq. (13) to be evaluated analytically. Examination of $\epsilon(q)$ shows that[13]

$$\epsilon(q) \to 1 + \lambda^2/q^2, \quad q \ll 2k_F$$
$$\epsilon(q) \to 1, \quad q \gg 2k_F$$

and that the transition between these two regions occurs over a small range of values around $q = 2k_F$. We thus take as our approximate dielectric function

$$\begin{aligned} \epsilon(q) &= 1 + \lambda^2/q^2, \quad q < 2k_F \\ \epsilon(q) &= 1, \quad q > 2k_F . \end{aligned} \tag{14}$$

The result for the energy with this approximation is

$$\frac{\bar{E}}{\epsilon_0} = \alpha^2 - 2\alpha - \frac{16\alpha^3}{\pi}\left[\frac{\alpha\beta}{2(\alpha^2-\beta^2)^2}\tan^{-1}\left(\frac{\pi\beta}{\nu}\right) + \frac{\beta^2(3\alpha^2-\beta^2)}{4\alpha^2(\alpha^2-\beta^2)^2}\tan^{-1}\left(\frac{\pi\beta^2}{\nu\alpha}\right) + \frac{\pi\beta^4}{4\nu\alpha(\alpha^2-\beta^2)[\alpha^2+(\pi\beta^2/\nu^2)]}\right], \tag{15}$$

where we have defined the dimensionless quantities α and β by

$$\alpha \equiv a_0/a, \quad \beta \equiv [(\nu/\pi)a_0 k_F]^{1/2} = a_0\lambda/2, \tag{16a}$$

and

$$\epsilon_0 \equiv m^* e^4/2\hbar^2\kappa^2. \tag{16b}$$

For a given number of valleys, ν, it is easy to compute numerically the minimum value of $\bar{E}$ for a given β. Figure 1 shows a graph of the results obtained in this way for $\nu = 1$, 2, 4, and 6. Furthermore, substituting Eqs. (16) into Eq. (13) we find

$$\frac{\bar{E}}{\epsilon_0} = \alpha^2 - \frac{8\alpha^4\nu^3}{\pi^4\beta^6}\int_0^\infty \frac{1}{(x^2+\nu^2\alpha^2/\pi^2\beta^4)^2}\,\frac{dx}{\epsilon(x)},$$

where

$$\epsilon(x) \equiv 1 + \frac{\nu^2}{\beta^2 x^2}\left[\frac{1}{2} + \frac{4(1-x^2)}{x}\ln\left|\frac{1+x}{1-x}\right|\right],$$

which, when minimized for a given ν, yields a function of β. Since the approximate dielectric function given by Eq. (14) is close to the Hartree dielectric function, we expect the results of the two calculations to be nearly the same. The minimization of the energy is thus easily accomplished by varying the value of α about the value that made $\bar{E}$ a minimum when the approximate dielectric function was employed. Figure 2 shows a graph of these results which are indeed closely approximated by the curves in Fig. 1.

IV. DISCUSSION OF RESULTS

The broken curve in Fig. 2 gives the result of $\bar{E}/\epsilon_0$ as a function of $\beta = \frac{1}{2}a_0\lambda$ in the Thomas-Fermi approximation for all ν.[12] It is clear that when the dielectric-screening theory is employed, the binding energy is greater for any given density of conduction electrons and any number of valleys, the difference between the Thomas-Fermi results and the latter increasing as ν increases. In the low-density limit the binding energy changes much more slowly than predicted by the Thomas-Fermi theory and for $\nu = 1$ the results are similar to those obtained by Li *et al.*[11] using a self-consistent Hartree potential.

If $\beta_c(\nu)$ is the critical density for ν valleys, then from the definition of β we have

$$[(\nu/\pi)a_0 k_{Fc}]^{1/2} = \beta_c$$

and therefore

$$a_0 N_c^{1/3} \cong \beta_c^2(\nu)/\nu^{2/3} = 0.25\,C(\nu),$$

where

$$C(\nu) = 4\beta_c^2(\nu)/\nu^{2/3}.$$

From the graph we have $C(1) = 1.14$, $C(2) = 0.96$, $C(4) = 0.92$, and $C(6) = 0.92$, which yield for both Ge and Si

$$a_0 N_c^{1/3} \cong 0.23,$$

which is in excellent agreement with the experimental results[5] given by

$$a_0 N_c^{1/3} \cong 0.22.$$

The fact that the derivation of the correct equation for the critical density in the many-valley case cannot be obtained from the Thomas-Fermi theory, but instead requires the introduction of dielectric screening, indicates that a quantitative theory of other anomalous effects[10] in these materials will also require similar considerations.

Finally, we note that when uniaxial stress is applied to a many-valley semiconductor, the degeneracy of the equivalent valleys in the conduction band can be removed.[14] In Ge it is possible to lower one or two valleys relative to the others.[14,15] The present calculation indicates that the critical density in the two-valley case is only about 15% higher than in the four-valley case which is small compared to the smearing of the critical density due to the random distribution of the impurities. However, if stress is applied such that one valley is lowered relative to the other three, then the critical density is increased by about a factor of 2 over the four-valley case and it may be possible to observe an inverse Mott transition, i.e., the unstressed degenerately doped crystal can make a transition to the nonconducting state when stress is applied. In Si, this effect is expected to be unobservable because the degeneracy of at least two conduction-band valleys cannot be removed by the application of stress and the change from six to two occupied valleys increases the critical density by only approximately 15%.

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Free-to-Bound and Bound Exciton Transitions at Isoelectronic Impurities: GaP(Zn,O)

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We show, for sufficiently high temperatures and sufficiently weak majority-carrier binding energies, that the dominant radiative transition at an isoelectronic acceptor (donor) in p-type (n-type) material consists of the recombination of singly trapped minority carriers (bound by central-cell forces) with free majority carriers attracted by a Coulomb interaction. There are two reasons why the radiative recombination rate of the free-to-bound process is greater than the bound exciton process, which dominates at lower temperatures: (i) The population of free majority-carrier states greatly exceeds that of exciton states at higher temperatures, and (ii) the oscillator strength of the free-to-bound transition is greatly enhanced by the Coulomb attraction between the free carrier and the charged isoelectronic impurity. This enhancement is important for isoelectronic centers and is easily calculable from existing exciton models. We show that the free carrier attracted by a Coulomb interaction can be viewed as a continuum excited state of the bound exciton. When we apply the results of our calculations to the GaP(Zn, O) system, we find that the major part of the room-temperature luminescence from nearest-neighbor isoelectronic Zn-O complexes results from free-to-bound recombination and not exciton recombination as has been thought previously. Recent experiments on impulse excitation of luminescence in GaP(Zn, O) are reevaluated in the light of our calculations and are shown to be consistent with a strong free-to-bound transition. For deep isoelectronic centers with weakly bound majority carriers, we predict an overwhelming dominance of the free-to-bound process at 300 °K.

I. INTRODUCTION

Isoelectronic impurities have three distinct and coupled occupation or charge states, i.e., empty (neutral), singly occupied (charged), and exciton occupied (neutral). The three-state nature of isoelectronic impurities greatly complicates the recombination processes occurring at these impurities, as discussed in detail elsewhere.[1-3] It has been amply demonstrated[4] over the past several years that isoelectronic impurities are important radiative recombination centers in many wide-band-gap semiconductors. At low temperatures, where free carriers are absent, the luminescence from isoelectronic centers is due principally to excitonic recombination. However, at high temperatures, where thermally generated free-carrier concentrations are large and where thermal dissociation of excitons occurs, we find that excitonic recombination becomes less probable, while at the same time free-to-bound recombination originating from the singly charged state becomes increasingly more probable. As a result, we anticipate that the high-temperature emission from isoelectronic centers will in general be made up of a combination of excitonic and free-to-bound emissions. These two processes are manifestations of the same basic interaction. That is, the excitonic process involves radiative recombination of Coulomb-attracted bound electron-hole pairs, whereas the free-to-bound pro-