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Corrections to the Fermi level in heavily doped GaAs[†]

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The correction to the chemical potential of a high-density electron gas due to the presence of charged impurities is calculated using Green's-function techniques. In first order, a $r_s^{-1/2}$ correction is determined as compared to the $r_s^{-1/3}$ correction previously determined by Bonch-Breuvich and Zyagin. In either case, however, the contribution is small compared to the contributions from electron exchange and correlation. The upward shift in the Fermi level as a function of impurity concentration is contrasted with optical experiments of Hill on heavily doped GaAs. A discrepancy is noted between experiment and theory.

INTRODUCTION

Theoretical investigations of interacting electron-gas systems have in the past found fruition in the study of heavily doped semiconductors. As has long been realized, many semiconductors doped with moderate impurity concentrations become degenerate at low temperatures. This result is reflected in the parameter r_s which defines the average interelectron spacing in units of effective Bohr radii;

$$r_s = \frac{r_0}{a_0} = \left(\frac{3}{4\pi n}\right)^{1/3} \left(\frac{\hbar^2 \epsilon}{m^* e^2}\right)^{-1},$$

where n is the electron density, m^* is the conduction-band effective mass, and ϵ is the static dielectric constant. The high-density gas regime is defined by concentrations for which r_s is less than unity. In many semiconductors $\epsilon \gg 1$ and $m^* \ll 1$ justifying the assumption $r_s < 1$ for doping of the order 10^{17}–10^{18} cm^{-3}. Thus n and r_s become continuous variables for studying the electron gas in semiconductors with suitable values of ϵ and m^*. The significance of the relation $r_s < 1$ is manifest if one examines the Hamiltonian for an electron gas in an environment containing charged impurities (we neglect lattice effects which are negligible for the physical quantities considered here):

$$H = \sum_i \frac{p_i^2}{2m^*} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{\epsilon |\vec{r}_i - \vec{r}_j|} - \sum_{i,j} \frac{e^2}{\epsilon |\vec{r}_i - \vec{R}_j|}.$$

The first term is the electron kinetic energy, the second and third terms describe the Coulomb interactions between electrons and electrons with ionized impurities, respectively. The Pauli principle restricts not only the momentum space available to electrons but also discourages close proximity in configuration space. The ultimate effect on high-density electron gases is occupation of the higher momentum states subsequently increasing their kinetic energies. The time each electron is in the vicinity of another is reduced. The kinetic energy is considerably larger than the interaction energies, rendering these as perturbations on the nearly-free-electron gas. Field-theoretic techniques can be applied to determine the ground-state energy of the system from infinite perturbation series. Certain contributions to the ground-state energy including kinetic, exchange, and correlation energies, have been calculated and are well known.[1] The electron-impurity interaction however has not been as completely investigated.

A number of experiments have been performed to elucidate the optical properties of III-V semiconductors particularly GaAs.[2-4] GaAs is a direct gap semiconductor—hence it is a system whose optical absorption processes can be simply interpreted with the selection rule $\Delta\vec{k} = 0$. Experimental results in general exhibit a shift in the absorption edge to higher photon energies as doping is increased in n-type material. Burstein originally attributed this shift to a change in the electron's effective mass with impurity concentration causing the absorption edge to progress upward with the Fermi energy.[5,6] Kaiser and Fan derived the formula[7]

$$h\nu(\alpha) = E_g + \left[\zeta - k_B T \ln\left(\frac{\alpha_0}{\alpha} - 1\right)\right] \left(1 + \frac{m_e}{m_n}\right) \quad (1)$$

in an attempt to describe the progression as a function of the absorption coefficient α which in turn is a function of impurity concentration; ζ is the Fermi level, α_0 is the absorption coefficient for pure material and m_e/m_n is the ratio of conduction-band effective mass to heavy-hole valence-band effective mass. Hill measured the optical absorption edge for different doping levels and fitted his experimental results to Kaiser and Fan's expression determining the rise in the Fermi level.[3] The fit, however, gave the anomalously large electron effective mass of $0.12m_e$. Since GaAs has a dielectric constant of 13 and conduction-band effective mass of 0.072, it is a definitive system in which to study the properties of the high-density electron gas when $n \geq 10^{17}\ \text{cm}^{-3}$. One should be able to ascertain the Fermi level using many-body theory and compare this with Hill's experiment.

The chemical potential of an interacting electron gas in the presence of charged impurities has been the object of several theoretical studies. The density of states $\rho(\epsilon)$ is given by Green's-function relation

$$\rho(\epsilon)=\frac{4}{(2\pi)^4}\int \operatorname{Im}G^R(\vec{k},E)\,d\vec{k}\,, \tag{2}$$

where $\operatorname{Im}G^R(\vec{k},E)$ is the imaginary part of the retarded many-body Green's function. Several authors, notably Bonch-Bruevich,[8,9] Kane,[10] Zvyagin,[11] and Wolff[12] have calculated $\rho(\epsilon)$ each deriving similar results regarding the structure of $\rho(\epsilon)$. Kane found a tailing of $\rho(\epsilon)$ into the gap while Wolff found what appeared to be a band-edge shift. Bonch-Bruevich's results indicated the existence of a finite density of states throughout the band-gap, but the contribution in the gap was negligible. Furthermore, Bonch-Bruevich and Zvyagin independently used the relation between the electron density and the density of states

$$n=\int \rho(\epsilon)\,n(\epsilon)\,d\epsilon=\int \frac{\rho(\epsilon)}{e^{\beta(\epsilon-\mu)}+1}\,d\epsilon \tag{3}$$

to calculate μ, the chemical potential as a function of electron density. For heavily doped semiconductors n is equal to the impurity density—hence the effect of doping on μ can be verified. The formulation used by Wolff corresponded to that developed for impurity scattering by Edwards,[13] Kohn and Luttinger,[14] among others.[15,16] Unfortunately, the $\rho(\epsilon)$ calculated using Eq. (2) rendered a rather tedious integration which was numerically evaluated. A deduction of μ from Eq. (3) is inconvenient utilizing Wolff's result.

In this paper an alternative procedure is given to calculate the correction to the Fermi level. It is also predicated on the techniques of Edwards *et al*; however, it differs from Wolff's approach in that we derive the correction to the thermodynamic potential of the interacting gas $\Omega(T,V,\mu)$. The zero-temperature limit then gives the ground-state energy from which μ is determined.

$$\mu=\frac{\partial E(V,N)}{\partial N}\bigg|_V=\frac{\partial}{\partial N}\left(\lim_{T\to 0}\Omega(T,V,\mu)\right)\bigg|_V\,. \tag{4}$$

As with the above theories, the contribution from the electron-impurity interaction is shown to be small compared to those of electron-electron exchange and correlation.

THEORY

In finite-temperatures Green's-function formalism, the expression giving the thermodynamic potential is[17]

$$\Omega(T,V,\mu)=\Omega_0(T,V,\mu)+V\int_0^1\frac{d\lambda}{\lambda}\int\frac{d^3p}{(2\pi)^3}\frac{1}{\beta\hbar}\times\sum_n e^{ip_n\eta}\,\hbar\,\Sigma^\lambda(\vec{p},p_n)G^\lambda(\vec{p},p_n)\,, \tag{5}$$

where $G^\lambda(\vec{p},p_n)$ is the many-body electron Green's function, $\Sigma^\lambda(\vec{p},p_n)$ is the electron self-energy, λ is the coupling constant e^2, and η is a convergence factor whose limit is zero following evaluation of the frequency summation p_n. We write

$$\Sigma^\lambda(\vec{p},p_n)=\Sigma^\lambda_{e-e}(\vec{p},p_n)+\Sigma^\lambda_{e-I}(\vec{p},p_n)\,, \tag{6}$$

where $\Sigma^\lambda_{e-e}(\vec{p},p_n)$ is the self-energy contribution from all electron-electron interactions, including direct, exchange, and correlation energies. Writing $\Sigma^\lambda(\vec{p},p_n)$ in this fashion allows us to take advantage of the extensive properties of Ω and write

$$\Omega(T,V,\mu)=\Omega_0(T,V,\mu)+\Omega_{e-e}(T,V,\mu)+\Omega_{e-I}(T,V,\mu)\,. \tag{7}$$

The contribution of Ω_0 and Ω_{e-e} to the total ground-state energy in the zero-temperature limit has been evaluated and is well documented.[1,17] We designate the result by $E_1(V,N)$ [see Eq. (32)]. Our concern is with $\Sigma^\lambda_{e-I}(\vec{p},p_n)$, the self-energy of the electron-impurity interaction. First we must interpret the exact nature of this contribution. Several authors have discussed $\Sigma^\lambda_{e-I}(\vec{p},p_n)$; we briefly summarize the argument principally of Edwards.[13]

Consider the model Hamiltonian

$$H=H_0+V\,. \tag{8}$$

V is the electron-impurity interaction and has the form

$$V=\sum_j e^{i\vec{R}_j\cdot\vec{q}}\rho(q)V(q)\,, \tag{9}$$

where

$$\rho(\vec{q})=\sum_{\vec{k}} c^\dagger_{\vec{k}+\vec{q}}\,c_{\vec{k}} \tag{10}$$

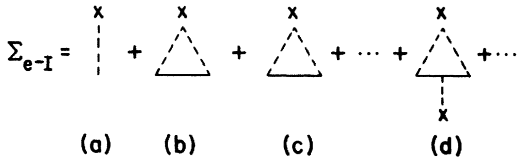

FIG. 1. Diagrams corresponding to Eq. (11) showing the contributions to the self-energy due to electron-impurity interactions.

is the electron-gas density, $V(q)$ is the Fourier transform of the electron-impurity interaction and $\vec{R}_j$ represents impurity positions. H_0 is the unperturbed Hamiltonian which includes the electron-gas kinetic energy and electron-electron interaction. Taking the thermodynamic averages necessary to compute $\Sigma^{\lambda}_{e\text{-}I}(\vec{p}, p_n)$ we discover an explicit dependence on the impurity coordinates $\vec{R}_j$. These coordinates must not appear in the self-energy, as the impurities are assumed randomly distributed; therefore some averaging procedure must be adopted to extricate them. The argument originally due to Kohn and Luttinger[14] and Edwards[13] stipulates that if the fraction of atomic sites occupied by the impurities is small, a configurational average can be carried out which eliminates the coordinates. When this process is completed we obtain a series expansion for $\Sigma^{\lambda}_{e\text{-}I}(\vec{p}, p_n)$, represented by the diagrams in Fig. 1:

$$\Sigma^{\lambda}_{e\text{-}I}(\vec{p}, p_n) = \Sigma^{\lambda}_{I(\mathrm{a})}(\vec{p}, p_n) + \Sigma^{\lambda}_{I(\mathrm{b})}(\vec{p}, p_n) + \Sigma^{\lambda}_{I(\mathrm{c})}(\vec{p}, p_n) + \cdots + \Sigma^{\lambda}_{I(\mathrm{d})}(\vec{p}, p_n) + \cdots , \tag{11}$$

where

$$\Sigma^{\lambda}_{I(\mathrm{a})}(\vec{p}, p_n) = \eta_i V(0) ,$$

$$\Sigma^{\lambda}_{I(\mathrm{b})}(\vec{p}, p_n) = \eta_i \int \frac{d^3p'}{(2\pi)^3} V^{\lambda}(\vec{p}-\vec{p}\,')V^{\lambda}(\vec{p}\,'-\vec{p})G'^{0}(\vec{p}\,', \vec{p}_n) ,$$

$$\vdots$$

$$\Sigma^{\lambda}_{I(\mathrm{d})}(\vec{p}, p_n) \propto \eta_i^2 . \tag{12}$$

η_i is the impurity density and appears for each impurity center in a diagram.

The electron-electron interaction has two effects we must consider before evaluating the above self-energy. First the electron-impurity interaction is screened. Thus the $V(q)$ in Eq. (9) is actually

$$V(q) = \frac{V^0(q)}{\epsilon(\vec{q}, 0)} ; \quad V^0(q) = -4\pi e^2/q^2 , \tag{13}$$

where $\epsilon(\vec{q}, 0)$ is the static dielectric constant, the electron-impurity interaction being a static interaction. This is obtained after summing an infinite set of ring diagrams.

The second effect is to modify the unperturbed electron Green's function $G^0(\vec{p}, p_n)$ given by

$$G^0(\vec{p}, p_n) = \frac{1}{ip_n - \xi_p \hbar^{-1}} , \tag{14a}$$

where

$$\xi_p = \epsilon_p - \mu = \frac{\hbar^2 p^2}{2m^*(r_s)} - \mu . \tag{14b}$$

In writing Eq. 14(b) we have implicitly considered the nonparabolicity of the band in the effective mass $m^*(r_s)$. In the Appendix we derive expression (A3) giving $m^*(r_s)$ as a function of doping density.

Since H_0 contains the electron-electron interaction, our new unperturbed Green's function can be written using Dyson's equation[17]

$$G^{\lambda 0\prime}(\vec{p}, p_n) = G^0(\vec{p}, p_n) + G^0(\vec{p}, p_n)\Sigma^{\lambda}_{e\text{-}e}(\vec{p}, p_n) \times G^{\lambda\prime 0}(\vec{p}, p_n) , \tag{15}$$

or

$$G^{\lambda 0\prime}(\vec{p}, p_n) = \frac{1}{[G^0(\vec{p}, p_n)]^{-1} - \Sigma^{\lambda}_{e\text{-}e}(\vec{p}, p_n)} , = \frac{1}{ip_n - \xi_p \hbar^{-1} - \Sigma^{\lambda}_{e\text{-}e}(\vec{p}, p_n)} . \tag{16}$$

With the above considerations we may evaluate $\Sigma^{\lambda}_{I}(\vec{p}, p_n)$. We note that $\Sigma^{\lambda}_{I(\mathrm{a})}(\vec{p}, p_n)$ cancels the direct term of the electron-electron interaction, since it has the same magnitude but opposite sign. This reflects the charge neutrality of the system. All diagrams representing the multiple scattering from a single impurity other than $\Sigma^{\lambda}_{I(\mathrm{b})}(\vec{p}, p_n)$ are neglected. These diagrams are proportional to η_i; however, they contain powers of e^2 larger than second order and can be shown much smaller than $\Sigma^{\lambda}_{I(\mathrm{b})}(\vec{p}, p_n)$. $\Sigma^{\lambda}_{I(\mathrm{b})}(\vec{p}, p_n)$ also corresponds to the highest-order terms in the coupling constant retained in evaluating $E(V, N)$. We also neglect terms which are greater than first order in η_i. That is, we neglect multiple scattering from different impurities. Since the concentration of impurities is about one in 10^5 atoms of the crystal we expect these multiple-scattering events to be small. However, if there exists clustering or some other preferred arrangement of impurities, the above assumption is rather tenuous. From Eq. (12) we have

$$\hbar\Sigma^{\lambda}_{I(\mathrm{b})}(\vec{p}, p_n) = \eta_i \int \frac{d^3q}{(2\pi)^3} \frac{[V^{\lambda}(q)]^2}{ip_n - \xi_{\vec{p}-\vec{q}} - \hbar\Sigma^{\lambda}_{e\text{-}e}(\vec{p}-\vec{q}, p_n)} . \tag{17}$$

Hence

$$\Omega_I = V \int_0^1 \frac{d\lambda}{\lambda} \int \frac{d^3p}{(2\pi)^3} \frac{1}{\beta\hbar} \sum_n e^{ip_n\eta} \times \hbar \Sigma^\lambda_{I-\mathrm{b}}(\vec{\mathrm{p}}, p_n) G^{\lambda 0\prime}(\vec{\mathrm{p}}, p_n) . \tag{18}$$

We approximate the electron-electron self-energy by the exchange self-energy. This is a reasonable approximation, since $\Sigma^\lambda_x(\vec{\mathrm{p}}, p_n)$ is the largest contribution to $\Sigma^\lambda_{e-e}(\vec{\mathrm{p}}, p_n)$.

$$\hbar \Sigma^\lambda_x(\vec{\mathrm{p}}, p_n) = -(2\pi)^{-3} \int d^3q\, V^\lambda(\vec{\mathrm{k}} - \vec{\mathrm{q}}) n_F(\vec{\mathrm{q}}) . \tag{19}$$

This self-energy is independent of the frequency p_n; hence the Matsubara sum in Eq. (18) can be easily evaluated

$$\Omega_I(T, V, \mu) = \eta_i V \int_0^1 \frac{d\lambda}{\lambda} \int \frac{d^3p}{(2\pi)^3} \int \frac{d^3q}{(2\pi)^3} [V^\lambda(\vec{\mathrm{q}})]^2 \left(\frac{n_F(\vec{\mathrm{p}} - \vec{\mathrm{q}}) - n_F(\vec{\mathrm{p}})}{\xi_{\vec{\mathrm{p}}-\vec{\mathrm{q}}} - \xi_{\vec{\mathrm{p}}} + [\Sigma^\lambda_x(\vec{\mathrm{p}} - \vec{\mathrm{q}}) - \Sigma^\lambda_x(\vec{\mathrm{p}})]\hbar} \right),$$

$$= -2\eta_i V \int_0^1 \frac{d\lambda}{\lambda} \int \frac{d^3p}{(2\pi)^3} \int \frac{d^3q}{(2\pi)^3} [V^\lambda(q)]^2 \frac{n_F(p)}{\xi_{\vec{\mathrm{p}}} - \xi_{\vec{\mathrm{p}}-\vec{\mathrm{q}}} + [\Sigma^\lambda_x(\vec{\mathrm{p}}) - \Sigma^\lambda_x(\vec{\mathrm{p}} - \vec{\mathrm{q}})]\hbar} .$$

The Fermi-Dirac distribution in the zero-temperature limit assumes the form

$$n_F(x) = 1, \quad x < k_F$$
$$= 0, \quad x > k_F \tag{20}$$

where k_F is the Fermi wave number.

$\Sigma^\lambda_x(p)$ can be evaluated in the zero-temperature limit if $V(k)$ is taken to be the screened Coulomb potential in the Thomas-Fermi approximation. The resulting expression is rather unwieldy. Therefore we follow Wolff and expand $\Sigma^\lambda_x(p)$ about $p = 0$.[12] Wolff's self-energy is given by

$$\Sigma^\lambda_x(p) = \Sigma^\lambda_x(0) + \frac{p^2}{2} \Sigma^{\lambda\prime\prime}_x(0) , \tag{21}$$

where

$$\Sigma^\lambda_x(0) = -\lambda \left(\frac{4}{\alpha\pi r_s} \right) \left(\frac{m(r_s)e^4}{2\epsilon^2} \right) = -\delta^\lambda \tag{22a}$$

and

$$\Sigma^{\lambda\prime\prime}_x(0) = \frac{\lambda}{m^*(r_s)} \left(\frac{8\alpha r_s}{3\pi^2} \right) . \tag{22b}$$

Here $\alpha = (4/9\pi)^{1/3}$ and ϵ is the dielectric constant. Wolff states that the above approximation is correct to within 25% of $k = k_F$. $\Sigma^\lambda_x(0)$ represents the downward shift in the band and $\Sigma^{\lambda\prime\prime}_x(0)$ gives the change in the effective mass as a function of r_s. The effect on the integrand of Eq. (20) is to renormalize the band effective mass $m^*(r_s)$;

$$\frac{1}{m^\lambda_1} = \frac{1}{m^*(r_s)} \left(1 + \frac{\lambda 8\alpha r_s}{\pi^2} \right) . \tag{23}$$

The shift δ^λ subtracts out, giving a simple integration over p:

$$\Omega_I(0, V, N) = -\frac{2Nk_Fe^4}{\epsilon^2\hbar^2\pi^2} \int_0^1 \frac{d\lambda}{\lambda m^\lambda_1} \int_0^\infty dq\, q^2 [V^\lambda(q)]^2 \times \left[1 + \frac{k_F}{q} \left(1 - \frac{q^2}{4k_F^2} \right) \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right] . \tag{24}$$

Define

$$\pi(q) = 1 + \frac{k_F}{q} \left(1 - \frac{q^2}{4k_F^2} \right) \ln \left| \frac{2k_F + q}{2k_F - q} \right| .$$

We write for $V^\lambda(q)$ in the random-phase approximation

$$V^\lambda(q) = -\frac{\lambda 4\pi e^2}{q^2 + (\lambda/2)a^2\pi(q)} , \tag{25}$$

where a^2 is the square of the reciprocal Thomas-Fermi screening length

$$a^2 = \left(\frac{4\alpha}{\pi} \right) r_s k_F^2 = 2\beta r_s k_F^2 .$$

Hence

$$\Omega_I = \Omega_0 \int_0^1 \frac{d\lambda\, \lambda}{1 + (4/\pi)\beta r_s \lambda} \int_0^\infty \frac{q^2\pi(q)}{[q^2 + (\lambda/2)a^2\pi(q)]^2} dq , \tag{26}$$

with

$$\Omega_0 = -(4Nk_F/\pi^2) E_d(r_s) ;$$

$$E_d(r_s) = m^*(r_s)e^4/2\epsilon^2\hbar^2 . \tag{27}$$

Set $x = q/k_F$ and the λ integration is immediate:

$$\Omega_I = \left(\frac{\Omega_0}{\beta r_s k_F} \right) \int_0^\infty dx\, f(x, r_s) \left(\frac{1}{1 - (4\beta r_s/\pi) f(x, r_s)} \right) \left(\frac{1}{1 - (4\beta r_s/\pi) f(x, r_s)} \ln \left| \frac{f(x, r_s) + 1}{f(x, r_s)[1 + (4\beta r_s/\pi)]} \right| - \frac{1}{f(x, r_s) + 1} \right) , \tag{28}$$

where

$$f(x, r_s) = x^2/\beta r_s \pi(x) . \tag{29}$$

If the usual Thomas-Fermi approximation is made $\pi(x) \to 2$ and Eq. (26) becomes

$$\Omega_I^0(0, V, N) = \Omega_0 \left(\frac{\pi^2}{2k_F(2\beta r_s)^{3/2}}\right) \times \left[1 - \left(\frac{\pi}{4\beta r_s}\right)^{1/2} \tan^{-1}\left(\frac{4\beta r_s}{\pi}\right)\right] . \tag{30}$$

The ground-state energy of the electron gas is

$$E(V, N) = E_1(V, N) + \Omega_I(V, N) \tag{31}$$

Now $E_1(V, N)$ is given by[18]

$$E_1(V, N) = \frac{Ne^2}{2a}\left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s} + 0.0622 \ln r_s - 0.084\right) . \tag{32}$$

Hence, using Eq. (4), we obtain for the chemical potential

$$\mu = E_d(r_s)\left[\frac{2.21}{r_s^2}\left(\frac{9.24m^*(r_s)}{m} + 1\right) - \left(\frac{0.916}{r_s} + 0.084\right)\left(\frac{9.24m^*(r_s)}{m} - 0.33\right) + 0.0622 \ln r_s \left(\frac{9.24m^*(r_s)}{m} + 0.33\right) - 0.021\right] + \mu_I , \tag{33}$$

where μ_I is given from Eq. (28):

$$\mu_I = -\left(\frac{4E_d(r_s)}{3\pi^2}\right)\frac{1}{\beta r_s}\left\{\int_0^\infty dx\, f(x, r_s)\left[\frac{3 + 27.9m^*(r_s)/m}{1 - (4\beta r_s/\pi)f(x, r_s)}\left(\frac{1}{1 - (4\beta r_s/\pi)f(x, r_s)} \ln \frac{f(x, r_s) + 1}{f(x, r_s)[1 + (4\beta r_s/\pi)]} - \frac{1}{f(x, r_s) + 1}\right) - \frac{1}{1 + (4\beta r_s/\pi)}\ \frac{1}{[f(x, r_s) + 1]^2}\right]\right\} \tag{34}$$

This integral must be numerically evaluated. We note that when $r_s \to 0$ and the Thomas-Fermi approximation [Eq. (30)] is used, the first-order correction μ_I is given by

$$\mu_I^{\mathrm{TF}} = -0.61[E_d(r_s)/r_s^{1/2}] .$$

It is instructive to compare Eq. (33) with the result of Bonch-Bryevich for finite temperatures[8]

$$\mu_{\mathrm{BB}} = E_d(3.68/r_s^2)[1 - 0.322 r_s - 3.95 \times 10^1 k_B T r_s^2 (1 + 0.202 r_s)] . \tag{35}$$

Numerical comparison of Eq. (33) and Eq. (35) with $T = 77$ °K shows agreement with 5% to 10% over most of the r_s range $1 > r_s > 0$, indicating the temperature dependence is unimportant in this temperature regime.

COMPARISON WITH EXPERIMENT

Hill measured the absorption coefficient as a function of the optical absorption edge for both n- and p-type GaAs containing various doping levels. For n-type material he observed a shift in the optical absorption edge to higher energy with increased doping. He fitted his data at fixed absorption coefficient $\alpha = 300$ cm^{-1} to Kaiser and Fan's formula and determined the rise in the absorption edge with Fermi energy. Using the values $T = 77$ °K, $E_g = 1.500$ eV, $m_e/m_n = 0.144$, and $\alpha_0 \approx 9000$ cm^{-1} (as determined from Sturge's data[2]) his fit gave a conduction-band effective mass of 0.12 m_e.

It is possible to extract the progression of the Fermi level with doping from Hill's data in two ways. First, one may use Hill's fit to Eq. (1), where he has plotted the various experimental points at different doping concentrations and obtained a value for the Fermi level at each point. (This corresponds to Hill's Fig. 3). One may obtain the absorption edge directly from Hill's data for the absorption coefficient versus absorption-edge energy at various concentrations. (This is Hill's Figure 2). Fixing α at 300 cm^{-1} we have plotted the absorption-edge threshold as a function of concentration as curve (B) of Figure 2. We have also plotted the absorption edge as determined by the fit to Kaiser and Fan's formula by adding E_g = 1.500 eV to the Fermi level, these points are denoted by X's in Figure 2. Curve (A) gives the theoretical absorption edge obtained by adding E_g to Eq. (33).

We do not add the exciton binding energy since the dense electron gas screens the electron-hole interaction, preventing a bound-exciton state from forming.[4,20] Two immediate observations include the discrepancy between theoretical and experimental absorption edge and the difference in slopes of the two curves. It appears that the contribution from the electron-impurity self-energy is too small. There are a number of diagrams

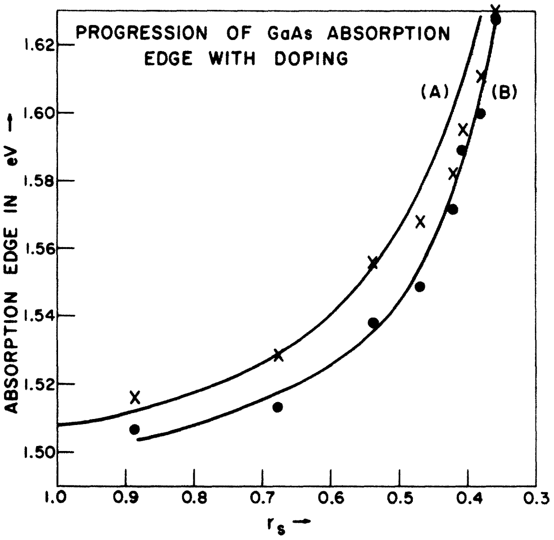

FIG. 2. Theoretical absorption edge [Eq. (33)] plus 1.500 eV given by curve (A). Curve (B) and the solid dots represent the progression determined from Hill's data; the ×'s give the progression obtained by fitting Hill's data to Eq. (1) and adding 1.500 eV.

we neglected, among those are vertex corrections representing higher order exchange effects and diagrams which account for polarization due to the impurities. Since the impurity density is not large, we expect the latter to be unimportant. Vertex contributions have not been fully investigated. One primary concern must be with multiple scattering events from different impurities, that is, those diagrams of order 2 in η_i. Wolff has shown these self-energy terms may contribute corrections of the same magnitude as Eq. (17) for small r_s. The Bohr radius of the electron is about 10^{-5} cm in GaAs; hence for high enough doping levels the electron orbit may encompass several impurities, thereby increasing the probability of multiple scattering. Terms involving the square of the density may therefore be important; indeed the question of convergence has not been fully explored. Wolff[12] has suggested a self-consistent method of eliminating the possible divergences. We are presently examining these self-energy terms.

APPENDIX

Kane determined the deviation of the GaAs band from parabolicity using $\vec{k}\cdot\vec{p}$ perturbation theory.[19] His result for a two-band model is

$$E_c=\frac{\hbar^2k^2}{2m}+\frac{E_g+\frac{1}{3}(E_g^2+8P^2k^2)^{1/2}}{2}. \qquad \text{(A1)}$$

E_c is the conduction-band energy, and P is proportional to the matrix element of the momentum operator between conduction-band and valence-band states at the band edges. The second term in the square root is small for all k up to the Fermi wave vector; hence we may expand the square root to obtain a wave-vector-dependent effective mass:

$$\frac{1}{m^*(k)}\simeq\frac{1}{m}\left(1+\frac{2D}{E_g}-\frac{4D^2}{E_g^3}\frac{\hbar^2k^2}{2m}\right), \qquad \text{(A2)}$$

with

$$2D=(2m/\hbar^2)\tfrac{2}{3}P^2\approx 19.3\text{ eV}.$$

We note that this k^2 dependence will contribute negligibly to the integration in Eq. (24) since the coefficient is small. The significant contribution is when k is equal to the Fermi wave vector, i.e., those electrons involved in optical transitions. We therefore set $k=k_F=1.92/r_0$ and obtain for the effective mass

$$\frac{1}{m^*(r_0)}=\frac{1}{m}\left\{1+\frac{2D}{E_g}\left[1-\frac{2D}{E_g^2}\left(\frac{\hbar^2}{2m}\right)\frac{3.68}{r_0^2}\right]\right\}.$$

The coefficient of the r_0 term is small, thus to a good approximation $m^*(r_0)$ can be written as

$$\frac{1}{m^*(r_s)}=\frac{1}{m}\left\{1+\frac{2D}{E_g}\left[1-\frac{2D}{E_g^2}\left(\frac{m^*}{m}E_d\right)\frac{3.68}{r_s^2}\right]\right\}. \qquad \text{(A3)}$$

Here m^* is the empty conduction-band effective mass $0.072m$ and E_d is the hydrogenic donor depth 0.006 eV.

In summary, we have approximated the correction to the conduction-band effective mass as being equal to the ratio of the density of states for a free-electron gas at the Fermi level to the band gap. From the above considerations this seems a reasonable estimate. However, for r_s less than about 0.2 we must consider higher-order terms in the expansion.

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[1] D. Pines, *The Many-Body Problem* (Benjamin, New York, 1962).

[2] M. D. Sturge, Phys. Rev. 127, 768 (1962).

[3] D. E. Hill, Phys. Rev. 133, A866 (1964).

[4] Several good review articles are to be found in the series *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1966), Vols. I, II, III, and VIII contain reviews by V. L. Bonch-Bruevich, M. Gershenzon, E. J. Johnson, H. B. Beebwith, and E. W. Williams, respectively, which contain relevant information.

[5] E. Burstein, Phys. Rev. 93, 632 (1954).

[6] T. S. Moss, Proc. Phys. Soc. Lond. B 67, 775 (1954).

[7] W. Kaiser and H. Y. Fan, Phys. Rev. 98, 966 (1955).

[8] V. L. Bonch Bruevich, *The Electronic Theory of Heavily Doped Semiconductors*, (Elsevier, New York, 1966).

[9] V. L. Bonch-Bruevich, Fiz. Tverd. Tela 4, 2660 (1963) [Sov. Phys.—Solid State 4, 1953 (1963)].

[10] E. O. Kane, Phys. Rev. 131, 79 (1963).

[11] I. P. Zugagin, Fiz. Tverd. Tela 5, 581 (1963) [Sov. Phys.—Solid State 5, 422 (1963)].

[12] P. A. Wolff, Phys. Rev. 126, 405 (1962).

[13] S. F. Edwards, Philos. Mag. 33, 1020 (1958).

[14] W. Kohn and J. M. Luttinger, Phys. Rev. 108, 590 (1957).

[15] J. S. Langer, Phys. Rev. 120, 714 (1960).

[16] R. C. Klauder, Ann. Phys. (N. Y.) 17, 981 (1961).

[17] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[18] M. Gell-Mann and K. A. Bruekner, Phys. Rev. 106, 364 (1957).

[19] E. O. Kane, J. Phys. Chem. Solids 1, 249 (1957).

[20] R. C. Casella, J. Appl. Phys. 34, 1703 (1963).