trum in iron-doped $SrTiO_3$ in addition to the normal cubic spectrum. This axial spectrum was attributed by them to the presence of near-neighbor oxygen vacancies.

In addition to the quadrupole-split Fe^{3+} spectrum, we observe the temperature-dependent quadrupole-split Fe^{2+} spectrum in this highly reduced sample. This suggests that the Mössbauer spectrum reveals the existence of the Fe^{3+} state as well as the Fe^{2+} state. The previous question of whether any of these states are nonequilibrium ones arises. We have discussed this in our earlier paper on $BaTiO_3$,[15] and following Craig's work,[36] we conclude that both of these are equilibrium states in the lattice, Fe^{2+} being stabilized because of large deviation from stoichiometry. The variation of the quadrupole splitting of the Fe^{2+} state with temperature is shown in Fig. 7.

ACKNOWLEDGMENTS

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Magnetic-Field-Induced Mott Transition in Semiconductors*

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The influence of an applied magnetic field on semiconductor impurity states is calculated, including the effects of screening of the impurity-ion potential by free carriers. When the screening is sufficiently great so that no bound states occur at zero field, they are introduced at some critical field. If the semiconductor is extrinsic, then the appearance of bound states at the critical field results in a Mott transition as the field is increased. Free carriers are entrapped at impurity sites and the electrical conductivity is markedly reduced as the magnetic field is increased beyond the critical value.

INTRODUCTION

ELECTRONIC energy levels in semiconductors associated with impurity ions can frequently be described by an effective-mass formalism in which wave functions and energy levels of the hydrogen atom describe an electron of mass m^*, the effective mass of the electron in the crystal, and a nucleus with charge Ze/K, the excess charge of the impurity ion decreased by the dielectric constant K of the medium.

Now consider this model in a magnetic field. A convenient measure of the strength of the field is the dimensionless parameter

$$\gamma = \hbar\omega_c/(2\ \mathrm{Ry}^*).$$

ω_c is the cyclotron frequency of a free electron with mass m^*, and 1 Ry* is the Rydberg constant appropriate to m^* and K, which will be called the effective Rydberg. γ is the ratio of the lowest energy of a free electron in a magnetic field to the lowest energy level of the hydrogen atom in zero field.

When $\gamma \ll 1$, the wave functions and energy levels can be calculated accurately by considering the magnetic field as a perturbation. For the hydrogen atom itself, $\gamma < 1$ for magnetic fields as great as 10^9 G, and magnetic fields large enough so that $\gamma \gg 1$ are not realizable experimentally. However, the situation may be different for impurity levels in a semiconductor. If we consider for example indium antimonide, where $m_e^* \sim 0.01 m_e$ and $K \sim 16$, then $\gamma \gg 1$ at 50 kG. Thus the effect of even moderate magnetic fields on impurity levels cannot be considered as a perturbation.

Qualitatively, the effect of a magnetic field on an electron bound to an impurity ion can be understood as follows. The application of a magnetic field shifts the atomic energy levels upward (atomic diamagnetism). However, the unbound electronic states are also shifted upward, and by a greater amount. Hence the net effect of the magnetic field is to *increase* the binding energy of the impurity level.[1]

If the impurity levels are sufficiently shallow, there may be a large enough number of electrons in the conduction band so that screening of the impurity potential shifts the levels. A similar atom model can be retained if the impurity potential is described in some manner which will take account of the electron screening. Binding energy decreases continuously as the concentration of screening electrons is increased, and at some critical concentration, the lowest bound state will have zero

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[1] Y. Yafet, R. W. Keyes, and E. N. Adams, J. Phys. Chem. Solids 1, 137 (1956).

binding energy. At greater concentrations, there will be no bound states.

Thus a magnetic field increases the binding energy while screening by conduction-band electrons decreases it. At any value of the field, we can expect that there is a critical concentration of conduction-band electrons such that there are no bound states. Clearly, this critical concentration increases as the field increases.

Now consider a degenerately doped semiconductor at 0°K. In this case, as in a metal, screening of impurity-ion potentials by quasi-free electrons is sufficient to prevent binding of conduction-band electrons to impurity ions. If a magnetic field is applied and continuously increased from zero, a point is reached at which the concentration of conduction-band electrons is the critical concentration required to prevent binding of electrons to impurity ions. An infinitesimal increase of the field beyond this point introduces a bound state. Electrons which become bound to impurity ions reduce the number of electrons in the conduction band, which in turn increases the binding energy due to decreased screening. The process is regenerative and at 0°K, the number of electrons in the conduction band as a function of magnetic field changes discontinuously. This then is a Mott transition[2] introduced by increasing the magnetic field. If the temperature is not 0°K, a discontinuity in the number of conduction-band electrons does not occur, because thermal excitation maintains some electrons in the conduction band at fields where the binding energy is small. Nevertheless, a very rapid change of carrier density with magnetic field may be expected even at finite temperatures under suitable conditions.

In the following sections the energy of the lowest impurity level is calculated as a function both of magnetic field strength and the number of electrons in the conduction band. Dependence of the number of electrons in the conduction band on the magnetic field is discussed.

I. ENERGY LEVELS

A Coulomb potential screened by free electrons is approximately described by[3]

$$V(R)=-(Ze^2/KR)\exp(-R/\Lambda)\,, \qquad (1)$$

where K is the dielectric constant discussed previously and Λ is the screening length.

In the transverse gauge, the Hamiltonian for an electron in the screened Coulomb potential of an impurity ion and in a magnetic field H is

$$\mathcal{H}=\frac{P^2}{2m^*}+\tfrac{1}{2}\hbar\omega_c L_z+\tfrac{1}{8}m^*\omega_c^2(X^2+Y^2)-\frac{Ze^2}{KR}\exp\left(-\frac{R}{\Lambda}\right). \qquad (2)$$

Since we are interested in calculating the energy levels relative to the bottom of the conduction band, the Zeeman spin-splitting term does not enter. The magnetic field is along the Z axis, and L_z is a dimensionless operator for the Z component of orbital angular momentum. For the ground state the eigenvalue of L_z is zero. If we use the effective Rydberg $m^*Z^2e^4/2K^2\hbar^2$ as a unit of energy, and the effective Bohr radius $K\hbar^2/m^*e^2$ as a unit of length, the Hamiltonian may be expressed as

$$\mathcal{H}=-\nabla^2+\gamma L_z+\tfrac{1}{4}\gamma^2(x^2+y^2)-(2/r)\exp(-r/\lambda)\,, \qquad (3)$$

where

$$x=X/a_0^*\,,\quad y=Y/a_0^*\,,\quad r=R/a_0^*\,,\quad \text{and}\quad \lambda=\Lambda/a_0^*\,.$$

In a weak magnetic field $\gamma\ll 1$ the magnetic terms can be treated as a perturbation. The ground-state eigenfunction when $\gamma=0$ and $\lambda=\infty$ is

$$\Psi_0(\lambda=\infty)=Ae^{-r}\,, \qquad (4)$$

where A is a constant. No exact analytic form can be obtained when $\lambda\neq\infty$, that is when the effects of screening are considered. To second order in γ, the perturbation result for the ground-state energy is

$$E=E(\lambda)=E_0(\lambda)+\tfrac{1}{6}\gamma^2\langle r^2(\gamma=0)\rangle\,, \qquad (5)$$

where E_0 is the energy of the lowest bound state when $\gamma=0$. The second term of Eq. (5) is the usual diamagnetic energy shift (although in this case it is a function of the screening length) and arises entirely from the γ^2 term in the Hamiltonian. When $\lambda=\infty$, $E_0=-1$ and $\langle r^2\rangle=6$. When $\lambda\neq\infty$, solutions can only be obtained by numerical methods. (For a δ-function potential, $\langle r^2\rangle=1$ with $E_0=-1$.[4])

When $\gamma\ll 1$ the binding energy increases when a magnetic field is applied. If γ is infinitesimal, the binding energy must always increase for any binding energy such that $\langle r^2\rangle$ is finite, or for $E_0<0$. When $E_0\geqslant 0$ no simple perturbation result can be obtained. However, by a continuity argument we can see that when no bound state occurs at zero field, bound states will not be introduced until the magnetic field has exceeded some critical value.

Next consider a strong magnetic field, $\gamma\gg 1$. When the screened Coulomb term is neglected, the eigenfunctions are

$$\Psi_{NMk}=\Phi_{NM}(x,y)e^{ikz}\,. \qquad (6)$$

N is the principal quantum number, M is the eigenvalue of L_z, and the Φ_{N0} are the harmonic oscillator functions.[5]

$$\Phi_{N0}=H_N(a\rho)e^{-a^2\rho^2/2}\,. \qquad (7)$$

Here $\rho=(x^2+y^2)^{1/2}$ and a is a parameter which depends on γ.

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[2] J. M. Ziman, *Theory of Solids* (Cambridge University Press, Cambridge, England, 1964).

[3] J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960).

[4] Yu. N. Demkov and G. F. Drukarev, Zh. Eksperim. i Teor Fiz. **49**, 257 (1965) [English transl.: Soviet Phys.—JETP **22** 182 (1965)].

[5] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949).

With the screened Coulomb term introduced as a perturbation, the eigenfunctions near the limit $\gamma \to \infty$ have the form

$$\Psi_{NM\xi} = \Phi_{NM}(x,y) Z_{NM\xi}(z) , \tag{8}$$

where $Z_{NM\xi}(z)$ satisfies the equation

$$\left\{ -\frac{d^2}{dz^2} - 2 \int \Phi_{NM}{}^* \Phi_{NM} e^{-r/\lambda} \frac{1}{r} dxdy \right\} Z_{NM\xi}(z) = \epsilon_{NM\xi} Z_{NM\xi}(z) . \tag{9}$$

Equation (9) can only be solved by numerical methods. The energy eigenvalues, neglecting terms of order $1/\gamma$ and higher, are

$$E_{NM\xi} = (2N+1)\gamma + \epsilon_{NM\xi} . \tag{10}$$

For the states with $N=0$, the first term is equal to the lowest energy of the conduction band. The ground state is given by $N=M=\xi=0$. Since $\epsilon_{000}<0$ for all values of λ, a bound state occurs for any screening length in the limit $\gamma \to \infty$.

To summarize, the low- and high-field limits show that when λ is sufficiently small so that there are no bound states with $\gamma=0$, at least one bound state is introduced at some noninfinitesimal magnetic field ($E_0>0$ and noninfinitesimal). This supports the remarks in the Introduction.

Both high- and low-field approximations can only be obtained by numerical methods. For this reason and particularly because we are interested in the intermediate fields where we expect bound states to be introduced, the ground state energy will be determined by a variational calculation. A normalized trial function of the correct symmetry, which is mathematically tractable, is given by

$$\Psi = [\pi^{1/2} a_\perp a_\parallel{}^{1/2}]^{-1} \exp\left\{ -\left[\frac{x^2+y^2}{a_\perp{}^2} + \frac{z^2}{a_\parallel{}^2} \right]^{1/2} \right\} . \tag{11}$$

$a_\perp$ and $a_\parallel$ are variational parameters. When $\gamma=0$, this expression reduces to the exact wave function for $\lambda=\infty$ given by Eq. (4).

An expression for the trial value of the energy as a function of the screening length is obtained:

$$E(\lambda,\gamma) = \frac{1}{a_\perp{}^2}\left(1-\frac{\epsilon}{3}\right) + \frac{\gamma^2 a_\perp{}^2}{2} - \frac{(1-\epsilon)^{1/2}}{a_\perp} \cdot \left\{ \frac{1}{\epsilon^{1/2}\alpha^{3/2}} \ln\left[\frac{\alpha^{1/2}+\epsilon^{1/2}}{\alpha^{1/2}-\epsilon^{1/2}}\right] - \frac{1}{\epsilon^{1/2}\alpha^{3/2}} \ln\left[\frac{\alpha^{1/2}+\epsilon^{1/2}[(1-\alpha)/(1-\epsilon)]^{1/2}}{\alpha^{1/2}-\epsilon^{1/2}[(1-\alpha)/(1-\epsilon)]^{1/2}}\right] - \frac{2(1-\alpha)^{1/2}}{\alpha(\alpha-\epsilon)}[(1-\alpha)^{1/2}-(1-\epsilon)^{1/2}] \right\} . \tag{12}$$

In this expression $\epsilon=1-a_\perp{}^2/a_\parallel{}^2$ is the eccentricity of the wave function, and $\alpha=1-a_\perp{}^2/\lambda^2$ is a dimensionless parameter. It is noteworthy that the energy depends on screening length entirely through the ratio $a_\perp/\lambda$.

An expression has been obtained for the trial value of the energy by Yafet, Keyes, and Adams,[1] neglecting screening, with the trial function

$$\exp -\left(\frac{x^2+y^2}{4a_\perp{}^2} + \frac{z^2}{4a_\parallel{}^2}\right) .$$

With $\lambda=\infty$, their energy is given by

$$E_{\mathrm{YKA}} = \frac{3}{4a_\perp{}^2}\left(1-\frac{\epsilon}{3}\right) + \frac{\gamma^2 a_\perp{}^2}{2} - \frac{(1-\epsilon)^{1/2}}{a_\perp \epsilon_\perp{}^{1/2}} \left(\frac{\pi}{2}\right)^{1/2} \ln\left[\frac{1+\epsilon^{1/2}}{1-\epsilon^{1/2}}\right] . \tag{13}$$

If we let $\lambda=\infty$ in Eq. (12), an expression identical in form with Eq. (13) is obtained, although numerical coefficients of the first and third terms are slightly different.

When Eq. (12) is minimized with respect to ϵ and $a_\perp$, two equations are obtained:

$$-\frac{1}{3a_\perp{}^2} + \frac{1}{2(1-\epsilon)^{1/2}a_\perp} \left\{ \frac{1}{\epsilon^{3/2}\alpha^{3/2}} \ln\left[\frac{\alpha^{1/2}+\epsilon^{1/2}}{\alpha^{1/2}-\epsilon^{1/2}}\right] - \frac{1}{\epsilon^{3/2}\alpha^{3/2}} \ln\left[\frac{\alpha^{1/2}+\epsilon^{1/2}[(1-\alpha)/(1-\epsilon)]^{1/2}}{\alpha^{1/2}-\epsilon^{1/2}[(1-\alpha)/(1-\epsilon)]^{1/2}}\right] - \frac{2(1-\alpha)^{1/2}}{\alpha(\alpha-\epsilon)^2}[(1-\alpha)+(1-\epsilon)][(1-\alpha)^{1/2}-(1-\epsilon)^{1/2}] - \frac{2(1-\alpha)}{\epsilon\alpha(\alpha-\epsilon)}[1-(1-\alpha)^{1/2}(1-\epsilon)^{1/2}] \right\} = 0, \tag{14}$$

and

$$\frac{1}{a_\perp{}^2}\left(1-\frac{\epsilon}{3}\right) + 2\gamma^2 - \frac{(1-\epsilon)^{1/2}}{a_\perp} \left\{ \frac{(3-4\alpha)}{2\epsilon^{1/2}\alpha^{5/2}} \ln\left[\frac{\alpha^{1/2}+\epsilon^{1/2}}{\alpha^{1/2}-\epsilon^{1/2}}\right] - \frac{(3-4\alpha)}{2\epsilon^{1/2}\alpha^{5/2}} \ln\left[\frac{\alpha^{1/2}+\epsilon^{1/2}[(1-\alpha)/(1-\epsilon)]^{1/2}}{\alpha^{1/2}-\epsilon^{1/2}[(1-\alpha)/(1-\epsilon)]^{1/2}}\right] + \frac{(1-\alpha)}{\alpha(\alpha-\epsilon)} + \frac{(1-\alpha)^{1/2}}{\alpha^2(\alpha-\epsilon)^2}[(3-4\alpha)(\alpha-\epsilon)+2\alpha(1-\epsilon)][(1-\alpha)^{1/2}-(1-\epsilon)^{1/2}] \right\} = 0. \tag{15}$$

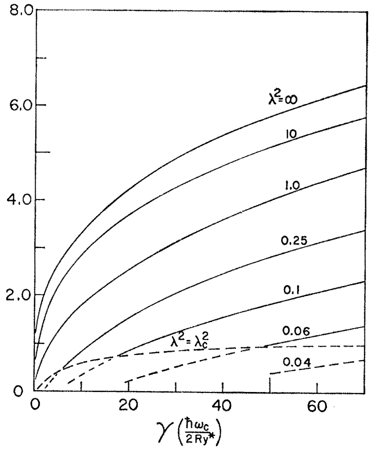

FIG. 1. Field dependence of the binding energy with screening length as a parameter. The $\lambda^2=\lambda_c^2$ curve bounds the region above in which real solutions of Eqs. (14) and (15) exist for both $a_\perp$ and $a_\parallel$.

These equations can be solved numerically for ϵ and $a_\perp$ in terms of γ and λ, and an upper bound established for the energy using Eq. (12). With $\gamma=0$ and $\lambda=\infty$, the exact value 1 effective Rydberg is obtained for the binding energy, and $a_\perp=a_\parallel=1$, the effective Bohr radius. With $\gamma=0$, Yafet *et al.* obtained a trial value of 0.85 Ry for the binding energy (the trial value of the energy is approximately 15% higher than the exact value) using Eq. (13). The trial wave function used by Yafet *et al.* (which is not mathematically tractable when $\lambda\neq\infty$) is more appropriate at high fields, and in fact describes exactly the ground-state wave function in the plane perpendicular to H when $\gamma=\infty$. Thus the binding energies obtained by Yafet *et al.* (with $\lambda=\infty$) are much more accurate than 15% at high fields.

When $\gamma\lesssim 2$, the energies obtained from Eq. (12) with $\lambda=\infty$ are lower than those from Eq. (13), and when $\gamma>2$, they are higher. When $\gamma\to\infty$, the trial value obtained from Eq. (12) is approximately 15% higher than the value obtained from Eq. (13), which in this regime is very accurate. At lower fields the values obtained from Eq. (12) are more accurate than 15% since the trial wave function used to obtain Eq. (12) is exact when $\gamma=0$ and $\lambda=\infty$.

The best estimate of the energy for a finite screening length at fields higher than $\gamma\sim 2$ can be obtained by calculating the upper bound for the difference $E(\infty)-E(\lambda)$ using Eq. (12), and subtracting this value from the upper bound $E_{\text{YKA}}(\infty)$ obtained from Eq. (13). Although this procedure does not yield an upper bound for the energy, the departure of E_{YKA} and of $E(\infty)-E(\lambda)$ from the corresponding true values are opposed and will at least partially cancel.

The binding energy is the difference between the energy of the lowest bound state and the energy of the lowest conduction-band state, $E=\gamma$. Then the trial value for the binding energy is

$$\gamma\lesssim 2:\quad E_B=\gamma-E(\lambda), \tag{16}$$

$$\gamma\gtrsim 2:\quad E_B=[\gamma-E_{\text{YKA}}(\infty)]+[E(\infty)-E(\lambda)]. \tag{17}$$

As we have discussed above, $E(\infty)$ is within 15% of the true value. Since at high fields calculation of $E(\lambda)$ for some value of γ is similar to a calculation of an $E(\infty)$ which applies to some higher value of γ, the difference $E(\infty)-E(\lambda)$ is accurate to $\sim$15% when $\gamma>2$. At low fields, $E(\infty)$ is nearly exact, and judging from numerical results for the Yukawa potential in the literature,[6] $E(\lambda)$ is accurate to 5%. Thus an error of 15% or less occurs in $E(\infty)-E(\lambda)$ at any field, which is in the opposite sense to an error of less than 15% in $\gamma-E_{\text{YKA}}(\infty)$. When E_B is close to zero, a great deal of the error in the calculation is self-cancelling and the total error is much less than 15% of $\gamma-E_{\text{YKA}}(\infty)$ or $E(\infty)-E(\lambda)$.

Figure 1 shows a graph of binding energy as a function of γ for several values of λ.

II. SCREENING LENGTH WHEN THE BINDING ENERGY BECOMES ZERO

If λ is decreased from infinity with γ constant, the energy of the impurity level increases and the binding energy decreases. At some critical screening length, the binding energy vanishes. A rough estimate of this critical length as a function of γ can be obtained from the screening lengths which yield zero for the trial value of the binding energy. This estimate is denoted by λ_c' in Fig. 2. A second estimate of the critical screening length which is an upper bound may be obtained from the variational calculation. This estimate is the value of λ, which will be denoted by λ_c, at which real solutions for both ϵ and $a_\perp$ can no longer be obtained from Eqs. (14)

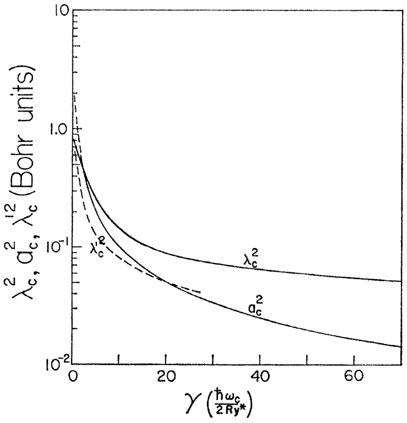

FIG. 2. Field dependence of the critical screening length below which there are no bound impurity states. λ_c is obtained from the screening length below which there are no real solutions of Eqs. (14) and (15) for both a_c and $a_\parallel$ and λ_c' from the projected intersections of the curves of Fig. 1. a_c is the cyclotron radius.

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[6] G. F. Chew, Phys. Rev. 74, 809 (1948).

and (15). In this case, for $\lambda < \lambda_c$, $a_\perp$ is real but $a_\parallel$ is not. The trial wave function no longer describes a bound state. This situation is similar to the example of a square well potential, a case where an exact solution can be obtained. A trial wave function similar in form to the one given by Eq. (11) yields real solutions of the variational parameter only when the well depth is greater than a critical value, which is greater than the exact value where the binding energy vanishes. The trial value for the energy vanishes for a well depth greater than either of these values.

Figure 2 shows a graph of λ_c, λ_c' and the cyclotron radius $a_c = \gamma^{-1/2}$ as a function of magnetic-field strength.

III. DENSITY OF CONDUCTION-BAND ELECTRONS

In this section, discussion will be confined to an idealized semiconductor which is dominated by uncompensated monovalent donor impurities. Only the ground-state impurity levels will be considered and it will be assumed that valence and conduction bands are well separated.

For a degenerate semiconductor, the relationship between density of quasi-free electrons in the conduction band and the screening length of Eq. (11) is given by the Thomas-Fermi expression[3]

$$\lambda^2 = \tfrac{1}{4}(\pi/3)^{1/3} n^{-1/3}. \tag{18}$$

λ is in units of the effective Bohr radius, a_0^*, and n is the number of free electrons in a volume a_0^{*3}. For a nondegenerate semiconductor in which $n \, \alpha \exp(-E_B/kT)$, the screening length is given by the Debye-Huckel expression

$$\lambda^2 = \frac{1}{8\pi}\left(\frac{kT/(1\ \mathrm{Ry}^*)}{n}\right). \tag{19}$$

Now consider the density of states of a nondegenerate semiconductor in the conduction band and at the impurity level (ignoring spin degeneracy). When $\gamma = 0$, the effective density of free-electron states in the conduction band is

$$N_F(0) = \frac{1}{4\pi^{3/2}}\left(\frac{kT}{1\ \mathrm{Ry}^*}\right)^{3/2} \tag{20}$$

(number of states in a volume a_0^{*3}). At high fields the density of states thermally accessible with $kT < 1$ Ry* is

$$N_F(\gamma) = \frac{\gamma}{4\pi^{3/2}}\left(\frac{kT}{1\ \mathrm{Ry}^*}\right)^{1/2}. \tag{21}$$

This expression neglects all Landau levels above the first and is accurate when $\gamma > 1$. In the range $0 < \gamma < 1$ in which higher Landau levels must be considered, N_F is described by a more complicated expression.

In order to calculate the influence of magnetic fields on the free-carrier concentration, one must solve for the free-carrier density n and for the binding energy E_B self-consistently. Two limiting regimes may be identified for a nondegenerate semiconductor.[7] Denoting the density of impurity levels by N_I (per volume a_0^{*3}) we have the following:

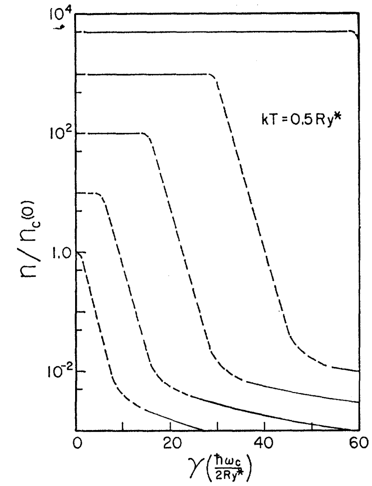

FIG. 3. Field dependence of the number of electrons in the conduction band with $N_I \geq n_c(0) kT = 0.5$ Ry*. The impurity concentration is equal to the number of free electrons at zero field.

1. $N_I N_F^{-1} \exp(E_B/kT) \ll 1$. In this case, the free-carrier density n is essentially equal to N_I and is therefore independent of E_B.
2. $N_I N_F^{-1} \exp(E_B/kT) \gg 1$. In this limit, the free-carrier density is approximately given by

$$n \sim (N_I N_F)^{1/2} \exp(-E_B/2kT). \tag{22}$$

For intermediate regimes, the relationship between free-carrier density and binding energy is more complicated.

As can be seen from Fig. 2, at zero field the critical screening length for the existence of bound states is $\lambda_c(0) = [0.95]^{1/2}$. This corresponds to a critical free-electron density $n_c(0) = (\pi/3)[0.25/0.95]^3$. The influence of magnetic field on the number of conduction-band electrons has been calculated approximately for $kT = 0.5$ Ry* and $kT = 0.2$ Ry* as shown in Figs. 3 and 4. For intermediate values of $N_I N_F^{-1} \exp(E_B/kT)$ the dashed curves of Figs. 3 and 4 are schematic. The regenerative or feedback effects of screening cause rapid changes in the carrier density when $kT = 0.2$ Ry* and somewhat slower changes when $kT = 0.5$ Ry*. The range of impurity concentrations extends from $n_c(0)$ to $10^4 n_c(0)$ in Fig. 3. For concentrations greater than $5 \times 10^3 n_c(0)$, no freeze out of carriers occurs throughout the range of fields shown.

The results shown in Figs. 3 and 4 can be related to actual semiconductors at the same temperatures if departure from the idealized model is small and if the

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[7] J. S. Blakemore, *Semiconductor Statistics* (Pergamon Press, Inc., New York, 1962).

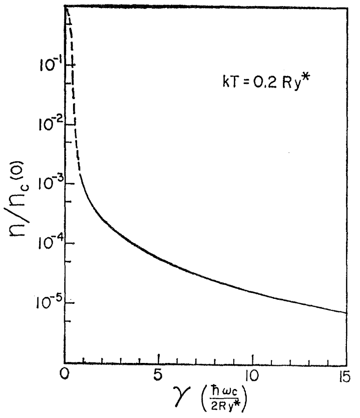

FIG. 4. Field dependence of the number of electrons in the conduction band with $N_I=n_c(0)$ and $kT=0.2$ Ry*.

effective Rydberg, Bohr radius, and magnetic field at which $\gamma=1$ are known. Table I lists these values for four semiconductors on which meaningful experiments are feasible.[8]

IV. COMPARISON WITH EXPERIMENT

The reduction of binding energy in a magnetic field due to screening of the impurity potential can be measured by either optical or electrical methods. In either case the temperature must be in the range $kT<\text{Ry}^*$ and the concentration of impurities near $N_I\sim n_c(0)$. Since the binding energy becomes small when the effects of screening increase, measurements of optical absorption for this purpose become more difficult in the regimes of greatest interest. Measurements of the Hall constant are possibly more satisfactory for comparison with the theory.

Although there are published measurements of the Hall constants of many semiconductors in a large range of fields, the temperature and impurity concentration are seldom in the regime of interest here (for semiconductors which have low effective mass and high dielectric constant). Frederikse and Hosler[9] have measured the Hall constant of InSb at 4.2°K which is slightly higher than 0.5 Ry* (see Table I), with a concentration of $\sim 20n_c(0)$ monovalent donor impurities (10^{15} cm^{-3}). The Hall constant increases rapidly beyond 11 kG ($\gamma\sim 9$), indicating carrier freeze-out. (Unfortunately the measurements extend only to 22 kG). The zero-field screening length at this impurity concentration is $\Lambda(0)\sim 0.25a_0^*$ corresponding to a critical field $\gamma_c\sim 5$ for appearance of the impurity level. The field at which the transition commences must be such that the binding energy has become comparable to kT, and from Figs. 1 and 2, $\gamma\sim 10$ when the binding energy $\sim 0.5kT$. Small errors in the true binding energy may introduce large errors in this value, and the agreement here is fortuitious.

TABLE I. Characteristics of four semiconductors with low effective mass and high dielectric constant.

Semi-conductor	m_e^*/m_e	K (dielectric constant)	$H_{\gamma=1}$ (kG)	1 Ry* (°K)	$n_c(0)$ (cm^{-3})
InSb	0.013	16.8	1.20	7.27	5.7×10^{13}
InAs	0.019	11.5	5.46	22.7	5.5×10^{14}
GaSb	0.047	15.2	19.1	32.1	3.6×10^{15}
GaAs	0.072	13.5	56.8	62.3	1.87×10^{16}

Keyes and Sladek[10] measured the Hall constant of InSb at 4.2°K (~ 0.58 Ry*) with concentrations of 4×10^{14} cm^{-3} and 2×10^{16} cm^{-3} monovalent donor impurities. These concentrations correspond to $\sim 8n_c(0)$ and $\sim 400n_c(0)$. The number of conduction-band electrons in the former case decreases with magnetic field in a manner similar to the decrease shown in Fig. 3. With $N_I\sim 400n_c(0)$, the number of conduction-band electrons remains constant to the maximum field, $\gamma\sim 60$. From the results of our calculations, a transition from degenerate to nondegenerate regimes would be expected to commence with $\gamma\sim 25$. A concentration of approximately $5.5\times 10^3 n_c(0)$ is required if the semiconductor is to remain degenerate beyond $\gamma=60$.

Sladek[11] has conducted a detailed study of the Hall coefficient of InSb as a function of magnetic field and temperature in the liquid-helium range. Free-carrier concentrations at zero field are comparable to or only slightly greater than $n_c(0)$. Data are all at magnetic fields where the Mott transition has already commenced. Although the data are difficult to interpret due to the fact that electrons at the impurity level have appreciable mobility, increases of the Hall coefficient at low fields seem to be more rapid than would be expected for unscreened impurity potentials. This is in agreement with the rapid decrease of free-carrier concentrations (due to regenerative or feedback effects) which are indicated in Figs. 3 and 4. Binding energies are appreciably smaller than the results of Yafet, Keyes, and Adams,[1] in agreement with the decrease due to screening by free carriers shown in Fig. 1. (The number of free carriers as a function of magnetic field at constant temperature is not shown in Ref. 11, and quantitative comparison is difficult.)

V. DISCUSSION

Aside from the obvious limitations of a variational calculation of the energy when small errors can be important, the validity of the effective mass approximation for impurity ions must be considered. It is well known that the approximation is most representative when the dimensions of the wave function of the electron are

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much larger than the unit cell of the crystal.[12–14] At large magnetic fields the dimensions of the wave function perpendicular to the field are reduced, but remain greater than $0.1a_0^*$ when $\gamma<100$. Thus for semiconductors with low effective mass ($m^*\sim 0.01m$), the approximation can be regarded as representative when the field is less than $\gamma\sim 100$.

Demkov and Drukarev[4] have considered particles in a δ-function potential and magnetic field. They conclude that for an arbitrarily weak potential which yields no bound state and is characterized by a negative scattering length, an arbitrarily weak magnetic field is sufficient to introduce a bound state. This of course is directly contradictory to our results. Demkov and Drukarev use a procedure in which the $r\rightarrow 0$ limit of the wave function in the presence of the magnetic field is equated with the zero field form, a procedure which we have not been able to justify. Indeed, if the scattering method of Demkov and Drukarev is applied to a problem which is solvable by other methods (i.e., square-well potential, no magnetic field), it does not yield a criterion for the existence of a bound state. This method merely expresses consistency of the sign of the scattering length with the sign of the energy.

The experimental results of Frederikse and Hosler and of Keyes and Sladek are in good agreement with the results of our calculations when $N_I\sim 10n_c(0)$, but not $N_I\sim 400n_c(0)$. As well as inaccuracy in our calculations (or limitations of the screening length theory), a possible explanation would be that the electric field in this case was sufficiently high to increase the number of free carriers by impact ionization. Experimentally, the applied electric field must be increased at high concentrations of free carriers to maintain Hall voltages comparable to when the concentration is much less.

Although our calculation shows the essential features of the model, clearly an accurate numerical solution of the Schrödinger equation Eq. (2) would be a considerable improvement on the variational calculation. In addition, a more satisfactory comparison of theory with experiment could be made if measurements of the Hall constant were conducted at a temperature of ~1°K, at fields up to 100 kG or higher, and with a number of impurity concentrations in the range $n_c(0)<N_I<10^4n_c(0)$.

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Lattice Dynamics of Diamond

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The lattice dynamics of diamond has been investigated on the basis of the Cochran version of the dipole-approximation model. Results have been presented for the dispersion curves, and effective calorimetric and x-ray Debye temperatures of diamond. The effective calorimetric and x-ray Debye temperatures of germanium have also been obtained.

INTRODUCTION

EXPERIMENTAL studies of the inelastic scattering of slow neutrons by crystals have recently made it possible to determine directly the relation between frequency and wave number of the normal modes of a crystal. Germanium was one of the first substances to be investigated by this technique by Brockhouse and Iyengar[1] and by Ghose *et al.*[2]

A detailed analysis of these results by Herman[3] and by Pope[4] showed that to fit all the data concerned it was necessary to include interactions out to fifth neighbors in the general force model. The theory then involves numerous parameters which have no clear physical signficance. Cole and Kineke[5] calculated the vibrational spectrum of Ge using the force constants of Herman.[3]

Lax[6] proposed to fit the data to a force model involving one parameter to represent electrostatic interaction between quadrupoles generated by the lattice vibrations, and as many near-neighbor parameters as proves necessary.

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