

Eq. (35a), we obtain finally

$$I_{kh} = \frac{\pi^2}{\sqrt{2}} L \left\{ - (3\alpha_{1k}\alpha_{1h} - \delta_{kh}) \frac{1}{2\zeta} \frac{d}{d\zeta} (\operatorname{erf}\zeta/\zeta) + (\delta_{kh} - \alpha_{1k}\alpha_{1h}) \operatorname{erf}\zeta/\zeta \right\}.$$

This result is used in Eq. (43b). As a partial check of the correctness of this result, we may verify the following relation:

$$I_k = p_{ah} I_{kh},$$

since  $I_k$  was calculated in Eq. (35b).

## Stark Effect for Cyclotron Resonance in Degenerate Bands

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A calculation of the motion is given for an electron in a simple band subjected to perpendicular magnetic and electric fields. It is shown that the cyclotron resonance frequency is unaffected by the presence of the electric field. For degenerate bands, however, there is a Stark shift of the cyclotron transitions between the low-lying "quantum" states. Calculations using second-order perturbation theory indicate that fractional line shifts of  $\Delta\nu/\nu_0 \sim 10\%$  may be obtained under reasonable experimental conditions. This effect may be useful in the study of the valence bands of germanium and silicon.

### I. INTRODUCTION

IN the presence of a magnetic field  $\mathcal{H}$  the continuum of energy levels for a band coalesces into discrete sub-bands, the so-called Landau levels. An electric field applied perpendicular to  $\mathcal{H}$  perturbs the motion of the carriers in the crystal giving rise to "Stark" energy shifts of these Landau levels. For simple bands, however, an appropriate translation of the coordinate axes can transform the Schrödinger equation to a form free of the electric field. Although this transformation displaces the Landau levels, it will be shown that the selection rules allow transitions only between levels which have undergone equal energy shifts. Consequently, there is no observable effect on the cyclotron resonance lines corresponding to these transitions.

An example where this is not the case is provided by degenerate bands such as the valence bands in germanium and silicon. In the framework of the effective-mass formalism, Luttinger<sup>1</sup> has determined in detail the energy level schemes for these bands in the presence of a magnetic field. Here the situation is described by a system of coupled Schrödinger equations. These calculations predict that the spacing of low-lying energy levels will deviate considerably from the classical cyclotron frequencies. These anomalous "quantum" effects have been observed in germanium by Fletcher, Yager, and Merritt<sup>2</sup> in cyclotron resonance and by Zwerdling, Lax, and Roth<sup>3</sup> in the oscillatory magneto-absorption effect.

If the above system is perturbed by a uniform electric field, the coupled Schrödinger equations no longer admit

the simple transformation of the classical case; and, consequently, the low-lying quantum levels may experience a Stark shift. That the energy differences do indeed undergo a shift will be shown in Sec. III using second-order perturbation theory for the approximate "isotropic" case described by Luttinger.<sup>1</sup> In this model the energy surfaces of the valence band are assumed spherical rather than fluted so that the energy levels are independent of the direction of the magnetic field. For a more realistic comparison with experiment the calculations in principle can be extended to an anisotropic case.

Numerical results indicate that the Stark shift may be large enough to aid in the identification and measurement of many of the cyclotron transitions in germanium involving the low-lying anomalous magnetic states.

### II. SIMPLE BANDS

Let us consider first the motion of an electron or hole in a simple band subjected to a uniform magnetic field  $\mathcal{H}$  and a uniform electric field  $\mathcal{E}$  perpendicular to  $\mathcal{H}$ . We shall assume this band to have ellipsoidal energy surfaces similar to those for the conduction bands of silicon and germanium but centered in the Brillouin zone at  $\mathbf{k}=0$ :

$$\epsilon(\mathbf{k}) = \hbar^2 \left( \frac{k_x^2 + k_y^2}{2m_1} + \frac{k_z^2}{2m_2} \right), \quad (1)$$

where  $\mathbf{k}$  is the usual band wave number that varies over the Brillouin zone. In (1)  $m_1$  and  $m_2$  are the effective masses, respectively, along the transverse and principal axes of the energy ellipsoids. It is not difficult to extend the results to bands having displaced minima at  $\mathbf{k}=\mathbf{k}_0$ .

<sup>1</sup> J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).

<sup>2</sup> Fletcher, Yager, and Merritt, Phys. Rev. **100**, 747 (1955).

<sup>3</sup> Zwerdling, Roth, and Lax, Phys. Rev. **109**, 2207 (1958).

The symmetry of the energy ellipsoid about the principal axis allows us to orient the  $x$  and  $y$  coordinate axes so that an arbitrary external magnetic field will lie along a direction in the  $xz$  plane. If we assign new coordinates  $x_1, x_2$ , and  $x_3$  with  $\mathfrak{H}\mathcal{C}$  in the  $x_3$  direction, then  $x_3$  will lie in the  $xz$  plane at an angle  $\theta$  with respect to  $z$ . The  $x_2$  axis is taken along  $\mathfrak{E}$  which is chosen perpendicular to the  $xz$  plane for all orientations of  $\mathfrak{H}\mathcal{C}$ . In the new coordinate system the energy ellipsoids are described by

$$\epsilon(\mathbf{k}) = \hbar^2 \left\{ \frac{1}{2m_1} [k_2^2 + (k_1 \cos\theta + k_3 \sin\theta)^2] + \frac{1}{2m_2} (k_1 \sin\theta - k_3 \cos\theta)^2 \right\}. \quad (2)$$

With  $\mathfrak{H}\mathcal{C}$  along the  $x_3$  axis it is convenient to work in the "Landau" gauge<sup>4</sup> for the magnetic vector potential

$$\mathbf{A} = (-\mathfrak{H}\mathcal{C}x_2, 0, 0). \quad (3)$$

Furthermore, the electric potential is

$$V = -e\mathcal{E}x_2. \quad (4)$$

The effects of the electron spin are not essential here and will be neglected.

The motion of an electron in a band with external fields applied is described (in the effective mass theory) by a zero-order wave function<sup>5</sup>

$$\psi(\mathbf{r}) = \varphi_0(\mathbf{r})f(\mathbf{r}), \quad (5)$$

where  $\varphi_0(\mathbf{r})$  is the Bloch function for the band at  $\mathbf{k}=0$ , and  $f(\mathbf{r})$  is obtained from a Schrödinger equation

$$\left[ \epsilon \left( \mathbf{p} - \frac{e}{c} \mathbf{A} \right) + V \right] f(\mathbf{r}) = \epsilon f(\mathbf{r}). \quad (6)$$

Here,  $\mathbf{p} = (\hbar/i)\nabla$  is the momentum operator. The potential  $V$  derives in the present case from the external electric field given in (4).

Taking  $\epsilon(\mathbf{k})$  from (2) and the potentials from (3) and (4) we obtain

$$\left\{ \frac{1}{2m_1} \left[ p_2^2 + \left( \left( p_1 + \frac{e\mathfrak{H}\mathcal{C}}{c} x_2 \right) \cos\theta + p_3 \sin\theta \right)^2 \right] + \frac{1}{2m_2} \left[ \left( p_1 + \frac{e\mathfrak{H}\mathcal{C}}{c} x_2 \right) \sin\theta - p_3 \cos\theta \right]^2 - e\mathcal{E}x_2 - \epsilon \right\} f(\mathbf{r}) = 0. \quad (7)$$

<sup>4</sup> L. Landau, *Z. Physik* **64**, 629 (1930).

<sup>5</sup> This procedure is based on a theorem due G. H. Wannier, *Phys. Rev.* **52**, 191 (1937). See also J. C. Slater, *Phys. Rev.* **76**, 1592 (1949); J. M. Luttinger, *Phys. Rev.* **84**, 814 (1951); E. N. Adams, II, *Phys. Rev.* **85**, 41 (1952); *J. Chem. Phys.* **21**, 2013 (1953); and J. M. Luttinger and W. Kohn, *Phys. Rev.* **97**, 869 (1954).

In (7) the coordinates  $x_1$  and  $x_3$  are cyclic, so that we obtain the well-known solution<sup>4</sup>

$$f_n(\mathbf{r}) = \frac{1}{L} \exp \left[ \frac{i}{\hbar} (p_1' x_1 + p_3' x_3) \right] u_n(x_2 + \xi). \quad (8)$$

The normalization of the plane waves is assumed for a cube of length  $L$  on a side. Using periodic boundary conditions, the momenta  $p_1'$  and  $p_3'$  are

$$p_1' = 2\pi\hbar n_1/L, \quad n_1 = 0, \pm 1, \pm 2, \dots, \\ p_3' = 2\pi\hbar n_3/L, \quad n_3 = 0, \pm 1, \pm 2, \dots. \quad (9)$$

The functions  $u_n(x_2 + \xi)$  in (8) are one-dimensional harmonic oscillator functions displaced from the origin by an amount

$$\xi = \frac{c}{e\mathfrak{H}\mathcal{C}} p_1' + p_3' \frac{\mu c}{\lambda e\mathfrak{H}\mathcal{C}} - \frac{\mu c^2 \mathcal{E}}{e\mathfrak{H}\mathcal{C}^2}, \quad (10)$$

where

$$\frac{1}{\lambda} = \left( \frac{1}{m_1} - \frac{1}{m_2} \right) \sin\theta \cos\theta, \\ \frac{1}{\mu} = \frac{\cos^2\theta}{m_1} + \frac{\sin^2\theta}{m_2}. \quad (11)$$

The eigenvalues of (7) are

$$\epsilon(n) = \hbar\omega \left( n + \frac{1}{2} \right) + \frac{1}{2\mu} (p_1'^2 + p_3'^2) + \frac{p_1' p_3'}{\lambda} - \frac{e^2 \mathfrak{H}\mathcal{C}^2}{2\mu c^2} \xi^2, \quad (12)$$

where  $\omega = e\mathfrak{H}\mathcal{C}/m^*c$  is the cyclotron frequency in terms of  $m^*$ , the effective mass associated with the cyclotron resonance, defined by

$$\frac{1}{m^*} = \left( \frac{\cos^2\theta}{m_1^2} + \frac{\sin^2\theta}{m_1 m_2} \right)^{\frac{1}{2}}. \quad (13)$$

If we set  $m_1 = m_2 = m$ , then (12) reduces to the energy for a free electron of mass  $m$  moving in the given electric and magnetic fields:

$$\epsilon_0(n) = \hbar\omega_0 \left( n + \frac{1}{2} \right) + \frac{p_3'^2}{2m} + \frac{c p_1'}{\mathfrak{H}\mathcal{C}} \mathcal{E} - \frac{m c^2}{2} \left( \frac{\mathcal{E}}{\mathfrak{H}\mathcal{C}} \right)^2, \quad (14)$$

and  $\omega_0 = e\mathfrak{H}\mathcal{C}/mc$ .

Although the levels in (12) and (14) are clearly shifted by the application of the electric field, we shall show that no Stark effect results owing to operation of the selection rules for electric dipole transitions. The probability for the absorption of electromagnetic radiation is proportional to the square of the matrix element for electric dipole transitions:

$$M_{i \rightarrow f} = -\frac{e}{mc} \left( f \left| \mathbf{A}' \cdot \left( \mathbf{p} - \frac{e}{c} \mathbf{A} \right) \right| i \right), \quad (15)$$

where  $\mathbf{A}'$  is the vector potential describing the incident em radiation. By making the dipole approximation we are assuming essentially that the spatial variation of  $\mathbf{A}'$  can be neglected over the extent of an oscillator system. Using the zero-order wave functions in (5) we write the matrix elements

$$M_{m,n} = -\frac{e}{mc} \int_{\text{crystal}} \varphi_0^*(\mathbf{r}) f_m^*(\mathbf{r}) \times \left[ \mathbf{A}' \cdot \left( \mathbf{p} - \frac{e}{c} \mathbf{A} \right) \right] \varphi_0(\mathbf{r}) f_n(\mathbf{r}) d\mathbf{r}, \quad (16)$$

for intraband transitions from oscillator state  $m$  to state  $n$ . It should be born in mind that in addition to the Landau principal quantum number  $n$ , the quantum numbers  $n_1$  and  $n_3$  also are necessary to specify the eigenfunctions  $f(\mathbf{r})$ .

The Bloch functions  $\varphi_0(\mathbf{r})$  are rapidly varying with the lattice periodicity  $a$ , while  $f(\mathbf{r})$  are slowly varying functions having a "range"

$$r_0 = (\hbar c / e\mathcal{H})^{1/2} \sim 10^{-5} \text{ cm}$$

essentially equal to the cyclotron radius. Under these conditions it is possible to split the matrix elements (16) to allow integration separately over rapidly and slowly varying parts. The error incurred in breaking up the integral in this way will be of the order  $(a/r_0)^2 \sim 10^{-6}$  for ordinary microwave experiments. In this approximation the matrix element (16) becomes

$$M_{m,n} = -\frac{e}{mc} \frac{(2\pi)^3}{\Omega} \int_{\text{cell}} \varphi_0^*(\mathbf{r}) \varphi_0(\mathbf{r}) d\mathbf{r} \int_{\text{crystal}} f_m^*(\mathbf{r}) \times \left[ \mathbf{A}' \cdot \left( \mathbf{p} - \frac{e}{c} \mathbf{A} \right) \right] f_n(\mathbf{r}) d\mathbf{r} - \frac{e}{mc} \frac{(2\pi)^3}{\Omega} \times \int_{\text{cell}} \varphi_0^*(\mathbf{r}) \mathbf{A}' \cdot \mathbf{p} \varphi_0(\mathbf{r}) d\mathbf{r} \times \int_{\text{crystal}} f_m^*(\mathbf{r}) f_n(\mathbf{r}) d\mathbf{r}, \quad (17)$$

with  $\Omega$  the unit cell volume. The integral which contains the Bloch functions is zero because the matrix element of  $\mathbf{A}' \cdot \mathbf{p}$  between Bloch states contributes only for interband transitions connecting states of different parity.

Using the vector potential  $\mathbf{A}$  from (3) and the eigenfunctions  $f(\mathbf{r})$  from (8), we obtain the off-diagonal matrix elements

$$M_{m,n} = -\frac{e}{mc} \delta_{n_1, n_1'} \delta_{n_3, n_3'} \mathbf{A}_2' \times \int_{\text{crystal}} u_m(x_2) \left( p_2 + \frac{e\mathcal{H}}{c} x_2 \right) u_n(x_2) dx_2, \quad (18)$$

which contribute to cyclotron transitions. The integral in (18) is a well-known matrix element between harmonic-oscillator states. Clearly transitions will occur only when the following selection rules are obeyed:

$$\begin{aligned} \Delta n_1 &= 0, \\ \Delta n_3 &= 0, \\ \Delta n &= \pm 1. \end{aligned}$$

Since the principal quantum number  $n$  appears in the energy eigenvalues (12) as  $\hbar\omega(n + \frac{1}{2})$ , we conclude that the allowed transitions give rise to absorption only at the conventional cyclotron frequency  $\omega$ . In other words, an electric field perpendicular to  $\mathcal{H}$  has no observable effect upon the cyclotron resonance.

### III. DEGENERATE BANDS

#### A. The Cyclotron Resonance

The cyclotron resonance in degenerate bands differs markedly from the nondegenerate situation. For germanium and silicon degeneracy occurs for the valence bands at  $\mathbf{k}=0$  where, in the absence of spin-orbit coupling, there are three degenerate space wave functions belonging to the representation  $\Gamma_{25'}$  of the crystal point group. Each of these space functions is, in turn, twofold degenerate due to spin. The spin-orbit coupling partially lifts the sixfold degeneracy by separating the states into fourfold and twofold states which correspond, respectively, to  $p_{3/2}$  and  $p_{1/2}$  multiplets in the limit of tight binding. In germanium, for instance, this splitting amounts to roughly 0.3 eV which is much larger than the energies involved in ordinary microwave cyclotron resonance, so we need be concerned here only with the upper fourfold degenerate band. When the magnetic field is applied, the remaining degeneracy at  $\mathbf{k}=0$  is removed and the band is separated, thereby, into four sets of Landau levels, one pair corresponding to the "heavy" holes and the other pair to the "light" holes.

Luttinger and Kohn<sup>5</sup> have applied the effective-mass approximation to the cyclotron resonance for such degenerate bands. Their results give the zeroth-order wave function

$$\psi = \sum_j f_j(\mathbf{r}) \varphi_{j,0}(\mathbf{r}), \quad (19)$$

where  $\varphi_{j,0}$  are the four degenerate Bloch wave functions of the unperturbed system at  $\mathbf{k}=0$ . The functions  $f_j(\mathbf{r})$  satisfy a set of coupled equations,

$$\sum_{j'} \{ D_{jj'}^{\alpha\beta} k_\alpha k_\beta - \delta_{jj'} \epsilon \} f_{j'}(\mathbf{r}) = 0, \quad (20)$$

where

$$\mathbf{k} = (\hbar/i) \nabla - (e/c) \mathbf{A}. \quad (21)$$

The constants  $D_{jj'}^{\alpha\beta}$ , analogous to the effective masses for a nondegenerate band, are given by

$$D_{jj'}^{\alpha\beta} = \frac{1}{2m} \delta_{jj'} \delta_{\alpha\beta} + \frac{1}{m^2} \sum_i \frac{\pi_{ji}^\alpha \pi_{ij'}^\beta}{\epsilon_0 - \epsilon_i}, \quad (22)$$

in which the summation index  $i$  extends over all states of the unperturbed system excluding the four degenerate states.  $\epsilon_0$  is the energy of the degenerate set  $j$ , and  $\epsilon_i$  is the energy of each state  $i$  not in the degenerate set. The quantities  $\pi_{ij}$  are momentum matrix elements between states  $i$  and  $j$  at  $\mathbf{k}=0$ .

If a matrix  $D$  is defined by its elements (using summation convention for  $\alpha$  and  $\beta$ )

$$D_{jj'} = D_{jj'}^{\alpha\beta} k_\alpha k_\beta, \quad (23)$$

then the Schrödinger equation (20) is rewritten

$$(D-E)f=0. \quad (24)$$

Since the quantities  $D_{jj'}^{\alpha\beta}$  are to be determined experimentally, Luttinger<sup>1</sup> has constructed the explicit representation of the Hamiltonian  $D$  in terms of five parameters  $\gamma_1, \gamma_2, \gamma_3, \kappa$ , and  $q$  taking into account the symmetry of the diamond lattice. The  $\gamma_1, \gamma_2$ , and  $\gamma_3$  are related to the band parameters  $A, B$ , and  $C$  of Dresselhaus, Kip, and Kittel<sup>6</sup> by

$$\begin{aligned} (\hbar^2/2m)\gamma_1 &= A, \\ (\hbar^2/2m)\gamma_2 &= \frac{1}{2}B, \\ (\hbar^2/2m)\gamma_3 &= \frac{1}{2}(B^2 + \frac{1}{3}C^2)^{\frac{1}{2}}. \end{aligned} \quad (25)$$

The constant  $\kappa$  arises from the noncommutivity of  $k_1$  and  $k_2$  and does not appear in the classical cyclotron resonance. Theoretical estimates by Kohn<sup>7</sup> indicate that  $q$  is negligibly small for germanium and silicon.

A particularly simple solution obtains for the Schrödinger equation (24) when the energy surfaces are spherical rather than fluted. In this "isotropic" case  $\gamma_2 = \gamma_3 = \bar{\gamma}$ , Luttinger<sup>1</sup> finds that the  $4 \times 4$  matrix  $D$  decouples into a pair of  $2 \times 2$  matrices which can be diagonalized exactly (see Appendix A). The resulting zero-order wave functions (19) are

$$\begin{aligned} \psi_{1\pm}(n) &= [\varphi_{1,0}(\mathbf{r})a_{1\pm}u_{n-2}(x_2) \\ &\quad + \varphi_{2,0}(\mathbf{r})b_{1\pm}u_n(x_2)] \exp\left(\frac{i}{\hbar}p_1'x_1\right), \\ \psi_{2\pm}(n) &= [\varphi_{3,0}(\mathbf{r})a_{2\pm}u_{n-2}(x_2) \\ &\quad + \varphi_{4,0}(\mathbf{r})b_{2\pm}u_n(x_2)] \exp\left(\frac{i}{\hbar}p_1'x_1\right), \end{aligned} \quad (26)$$

corresponding to four "ladders" of energy eigenvalues  $\epsilon_{1\pm}(n)$  and  $\epsilon_{2\pm}(n)$ . In this notation the "1" and "2" label the decoupled systems and the (+) and (-), which distinguish between the two eigensolutions of each system, refer in the limit of high quantum numbers to the light and heavy holes, respectively. The  $u_n$  are the ordinary one-dimensional harmonic oscillator functions, and the  $a$ 's and  $b$ 's are constants depending upon  $\gamma_1, \bar{\gamma}$ , and  $\kappa$ .

<sup>6</sup> Dresselhaus, Kip, and Kittel, Phys. Rev. **98**, 368 (1955).

<sup>7</sup> W. Kohn (private communication to R. K. Goodman).

## B. The Stark Shift

An electric field  $\mathcal{E}$  applied to the system perpendicular to the magnetic field  $\mathcal{H}$  perturbs the original energy levels  $\epsilon_{1\pm}(n)$  and  $\epsilon_{2\pm}(n)$ , giving a Stark line shift for the cyclotron electric dipole transitions. The Hamiltonian for the electric field is

$$H' = -e\mathcal{E}x_2, \quad (27)$$

with energies measured in usual units. Second-order perturbation theory gives for the weak-field case the level shifts in each of the decoupled systems "1" and "2" designated generically by "i":

$$\begin{aligned} \Delta E_{i\pm}(n) &= \frac{1}{\hbar\omega_0} \sum_m \left[ \frac{|(m, i+ | H' | n, i\pm)|^2}{\epsilon_{i\pm}(n) - \epsilon_{i+}(m)} \right. \\ &\quad \left. + \frac{|(m, i- | H' | n, i\pm)|^2}{\epsilon_{i\pm}(n) - \epsilon_{i-}(m)} \right], \end{aligned} \quad (28)$$

with the summation extending over all states  $m$  except  $m=n$ . The energy denominator contains the cyclotron frequency  $\omega_0 = e\mathcal{H}/mc$  for a free electron.

A typical matrix element in (28)

$$(m, i\pm | H' | n, j\pm) = \int_{\text{crystal}} \psi_{i\pm}^*(m) H' \psi_{j\pm}(n) d\mathbf{r} \quad (29)$$

involves integrals of the form

$$M_{m,n}^{\alpha,\beta} = \int_{\text{crystal}} \varphi_{\alpha,0}^*(\mathbf{r}) u_m(x_2) H' \varphi_{\beta,0} u_n(x_2) d\mathbf{r}. \quad (30)$$

The integrand of (30) contains both rapidly varying Bloch functions  $\varphi_{\alpha,0}(\mathbf{r})$  as well as the slowly varying harmonic oscillator functions  $u_n$ . Following the procedure in Sec. II, we can integrate each part separately:

$$\begin{aligned} M_{m,n}^{\alpha,\beta} &= \frac{(2\pi)^3}{\Omega} \int_{\text{cell}} \varphi_{\alpha,0}^* \varphi_{\beta,0} d\mathbf{r} \\ &\quad \times \int_{\text{crystal}} u_m(x_2) H' u_n(x_2) dx_2, \end{aligned} \quad (31)$$

with an error of order  $(a/r_0)^2$ . We are thus left with reduced matrix elements containing only the  $u_n$ :

$$\begin{aligned} (m, i\pm | H' | n, j\pm) &= a_{i\pm} a_{j\pm} (m-2 | H' | n-2) \\ &\quad + b_{i\pm} b_{j\pm} (m | H' | n). \end{aligned} \quad (32)$$

Bearing in mind that the argument of the  $u_n$  is  $(c/e\hbar\mathcal{H})^{\frac{1}{2}} \times [p_1' + (e\mathcal{H}/c)x_2]$ , we can compute these reduced matrix elements in a straightforward manner:

$$\begin{aligned} (m | H' | n) &= -e\mathcal{E} \left( \frac{c\hbar}{e\mathcal{H}} \right)^{\frac{1}{2}} \left[ \left( \frac{n}{2} \right)^{\frac{1}{2}} \delta_{m,n-1} \right. \\ &\quad \left. + \left( \frac{n+1}{2} \right)^{\frac{1}{2}} \delta_{m,n+1} \right] + \frac{c\mathcal{E}}{\mathcal{H}} p_1' \delta_{m,n}. \end{aligned} \quad (33)$$

Clearly the diagonal term  $(c\mathcal{E}/3\mathcal{C})p_1'$  does not imply a first-order Stark shift of the resonance, since it contributes an identical energy shift to all levels. The first-order term, incidentally, has appeared previously in (14).

Using Eqs. (28), (32), and (33) we obtain the final expression for the energy shifts:

$$\Delta E_{i\pm}(n) = K_{i\pm}(n)mc^2(\mathcal{E}/3\mathcal{C})^2, \quad (34)$$

where the dimensionless Stark coefficient  $K_{i\pm}$  is

$$K_{i\pm}(n) = \left[ \frac{|A_{i+}(n-1)B_{i\pm}(n)|^2}{\epsilon_{i\pm}(n) - \epsilon_{i+}(n-1)} + \frac{|A_{i\pm}(n)B_{i+}(n+1)|^2}{\epsilon_{i\pm}(n) - \epsilon_{i+}(n+1)} + \frac{|A_{i-}(n-1)B_{i\pm}(n)|^2}{\epsilon_{i\pm}(n) - \epsilon_{i-}(n-1)} + \frac{|A_{i\pm}(n)B_{i-}(n+1)|^2}{\epsilon_{i\pm}(n) - \epsilon_{i-}(n+1)} \right]. \quad (35)$$

For conciseness we have introduced in (35) the matrices

$$A_{i\pm}(n) = [(n-1)^{\frac{1}{2}}a_{i\pm}(n); (n+1)^{\frac{1}{2}}b_{i\pm}(n)],$$

$$B_{i\pm}(n) = \begin{pmatrix} a_{i\pm}(n) \\ b_{i\pm}(n) \end{pmatrix}. \quad (36)$$

In the isotropic case, four matrix elements contribute to (35). In general, however, when the Hamiltonian  $D$  does not decouple,  $K_{i\pm}(n)$  contains up to eight nonvanishing matrix elements.

Since the isotropic approximation  $\gamma_2 = \gamma_3 = \bar{\gamma}$  applies best to germanium where the actual values of  $\gamma_2$  and  $\gamma_3$  differ by about 15% from the mean  $\bar{\gamma}$ , the coefficients  $K_{i\pm}(n)$  are evaluated for a "germanium-like" crystal using the constants

$$\gamma_1 = 13.2, \quad \bar{\gamma} = 5.0, \quad \kappa = 4.0.$$

This value of  $\bar{\gamma}$  was selected as being approximately the mean of the best presently known values<sup>8</sup>

$$\gamma_2 = 4.1, \quad \gamma_3 = 5.6.$$

TABLE I. The Stark-shift coefficients  $K$ . The limiting value as  $n \rightarrow \infty$  is  $K = -m^*/2m$ . The column headings label the ladders in the notation of Luttinger.<sup>a</sup>

$n$	1 <sup>+</sup>	1 <sup>-</sup>	2 <sup>+</sup>	2 <sup>-</sup>
0	-0.0610	...	-0.0275	...
1	+0.1044	...	-0.0082	...
2	-0.0029	-0.2979	-0.0170	-0.1699
3	-0.0161	-0.2244	-0.0193	-0.1710
4	-0.0190	-0.1886	-0.0202	-0.1667
5	-0.0201	-0.1746	-0.0208	-0.1639
6	-0.0207	-0.1685	-0.0210	-0.1621
$n \rightarrow \infty$	-0.0216	-0.1553	-0.0216	-0.1553

<sup>a</sup> See reference 1.

<sup>8</sup> R. R. Goodman, thesis, University of Michigan, 1958 (unpublished).

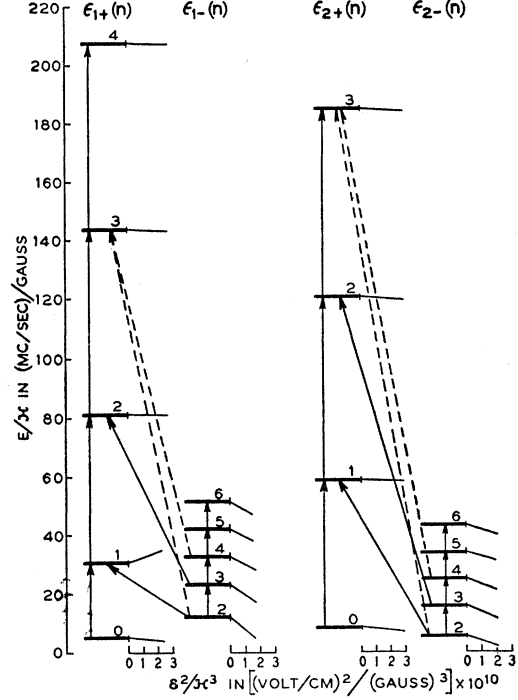


Fig. 1. The low-lying energy levels for cyclotron resonance in spherical degenerate bands calculated for the values  $\gamma_1 = 13.2$ , and  $\bar{\gamma} = 5.0$ , and  $\kappa = 4.0$ . To the right of each unperturbed level the Stark shift is shown as a function of  $\mathcal{E}^2/3\mathcal{C}^3$ . The solid arrows indicate the allowed absorption transitions between unperturbed levels, while the dotted arrows represent the first-forbidden transitions.

For silicon this approximation is probably unsatisfactory. The results of the calculations are tabulated in Table I up to and including the levels  $n = 6$ . In the classical limit of high quantum numbers, the constant in the Stark level shift approaches

$$K = -m^*/2m, \quad (37)$$

where  $m^*$  is the effective mass associated with the transitions in a particular ladder. The limiting values of  $K$  are also included in Table I.

When the level shifts  $\Delta E$  are added to the original energy levels, the energy states of the perturbed system are

$$E_{i\pm}(n) = \hbar(e3\mathcal{C}/mc)\epsilon_{i\pm}(n) + K_{i\pm}(n)mc^2(\mathcal{E}/3\mathcal{C})^2 \quad (38)$$

expressed in the dimensionless cyclotron energies  $\epsilon$  and Stark shift coefficients  $K$ . A plot of the energy levels obtained in this way is shown in Fig. 1. It has been convenient to divide (38) by  $3\mathcal{C}$  to give a universal energy scale independent of the magnetic field at a zero electric field strength. Arrows drawn in Fig. 1 indicate the absorption transitions between the low-lying states. The selection rule,  $\Delta n = \pm 1$ , derived in Sec. II, applies here.

For the lowest quantum transitions involving "light"

holes, the Stark effect gives a line shift of

$$\Delta\nu = mc^2 \left( \frac{\mathcal{E}}{\mathcal{H}} \right)^2 \times \frac{6\bar{\gamma}^2}{(\gamma_1 - \bar{\gamma})(8\bar{\gamma}^2 + \gamma_1^2 - 3\gamma_1\bar{\gamma} + 2\kappa\bar{\gamma} - 2\kappa\gamma_1)}, \quad (39)$$

for the transition  $(1^+, 0) \rightarrow (1^+, 1)$  and

$$\Delta\nu = mc^2 \left( \frac{\mathcal{E}}{\mathcal{H}} \right)^2 \times \frac{6\bar{\gamma}^2}{(\gamma_1 + \bar{\gamma})(8\bar{\gamma}^2 + \gamma_1^2 + 3\gamma_1\bar{\gamma} - 2\kappa\bar{\gamma} - 2\kappa\gamma_1)}, \quad (40)$$

for the transition  $(2^+, 0) \rightarrow (2^+, 1)$ . Analogous expressions for the higher transitions are considerably more complex.

#### IV. DISCUSSION

As shown in Fig. 1, the theory predicts marked shifts for the Landau levels of the degenerate valence bands of germanium when an electric field is applied, especially for the low-lying anomalous states. Because of the nonuniform displacement, we can expect a large Stark line shift for the cyclotron resonances. A typical case with  $\mathcal{E} = 0.3$  volt/cm and  $\mathcal{H} = 1000$  gauss gives  $\mathcal{E}^2/H^2 \sim 1 \times 10^{-10}$  which produces a fractional line shift of  $\Delta\nu/\nu_0 \sim 10\%$  for some transitions. While this effect should be directly observable, detection of even much smaller shifts could be achieved by application of an electrical square-wave modulation of a fraction of a volt/cm amplitude and a few kilocycles per second in frequency to the sample. The subsequent coherent demodulation of the resonance absorption signal would allow identification and measurement of these levels in spite of the presence of strong electron transitions.

In the region of high quantum numbers  $n$ , the levels within a "ladder" undergo identical shifts and the Stark effect vanishes. On the other hand, for transitions between ladders a considerable line shift will still occur because the level displacements for light and heavy holes do not approach the same limit as  $n \rightarrow \infty$ . Such transitions, however, become highly forbidden as  $n \rightarrow \infty$ ; so, in short, there are no Stark shifts in the "classical" limit of large  $n$ . Although they are first forbidden, the lower transitions between ladders should give especially large energy shifts—a property which should be helpful in their detection.

The experimental feasibility of observing Stark shifts rests strongly upon limitations set by the magnitude of the electric field that can be applied to silicon or germanium. Although fields up to approximately 5 volts/cm can be usually reached before breakdown, there is evidence that "heating" of the carriers occurs considerably below this limit. A current estimate<sup>9</sup> indi-

<sup>9</sup> S. Koenig (private communication).

cates the holes will reach a temperature of approximately  $10^\circ$ – $20^\circ$ K for a field of 1 volt/cm. In order to observe the cyclotron quantum effects, however, the lowest possible temperature should be maintained in order to encourage preferential population of the lower states. If this end is to be achieved it seems clear that the upper limit of  $\mathcal{E}$  will be several tenths of a volt/cm. If one is willing to sacrifice line intensity in the anomalous transitions, the limit may be raised possibly to 1 volt/cm.

A quantitative comparison with experimental results will undoubtedly require further calculations when the values of  $\gamma_2$  and  $\gamma_3$  are determined with more certainty from microwave cyclotron resonance. The isotropic case used here was chosen for its simplicity and does not exactly describe the valence band in either germanium or silicon. It is believed, however, that the second-order perturbation calculations can be readily extended to the anisotropic cases discussed by Luttinger<sup>1</sup> and Goodman.<sup>8</sup>

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#### APPENDIX A. CYCLOTRON RESONANCE FOR DEGENERATE BANDS WITH SPHERICAL ENERGY SURFACES

By assuming spherical energy surfaces  $\gamma_2 = \gamma_3 = \bar{\gamma}$  (also setting  $k_3 = 0$ ), Luttinger<sup>1</sup> finds that the matrix  $D$  (23) decouples into a pair of  $2 \times 2$  matrices designated  $D_1$  and  $D_2$ :

$$D_1 = \begin{bmatrix} (\gamma_1 + \bar{\gamma})(a^\dagger a + \frac{1}{2}) + \frac{3}{2}\kappa & -\sqrt{3}\bar{\gamma}a^2 \\ -\sqrt{3}\bar{\gamma}a^{\dagger 2} & (\gamma_1 - \bar{\gamma})(a^\dagger a + \frac{1}{2}) - \frac{1}{2}\kappa \end{bmatrix}, \quad (A.1)$$

$$D_2 = \begin{bmatrix} (\gamma_1 - \bar{\gamma})(a^\dagger a + \frac{1}{2}) + \frac{1}{2}\kappa & -\sqrt{3}\bar{\gamma}a^2 \\ -\sqrt{3}\bar{\gamma}a^{\dagger 2} & (\gamma_1 + \bar{\gamma})(a^\dagger a + \frac{1}{2}) - \frac{3}{2}\kappa \end{bmatrix}.$$

The quantities  $a^\dagger$  and  $a$  are creation and annihilation operators:

$$a^\dagger = (c/2e\mathcal{H}\hbar)^{\frac{1}{2}}(k_1 + ik_2), \quad (A.2)$$

$$a = (c/2e\mathcal{H}\hbar)^{\frac{1}{2}}(k_1 - ik_2).$$

The Landau gauge (3) for the magnetic field has been employed here. Since we are dealing with holes, it has been convenient to replace  $D$  by  $-D$  in writing (A.1), so that the energy level scheme will be arranged so that the energy increases with ascending order of excited states.

The Schrödinger equations for the two decoupled systems are

$$(D_1 - \epsilon_1)f_1 = 0, \quad (A.3)$$

$$(D_2 - \epsilon_2)f_2 = 0,$$

with the energies  $\epsilon_1$  and  $\epsilon_2$  measured in units of  $\hbar(e\mathcal{H}/mc)$ .

Since (A.3) is cyclic in  $x_1$ , we write

$$\begin{aligned} f_1 &= \exp[(i/\hbar)p_1'x_1]g_{n,1}(x_2), \\ f_2 &= \exp[(i/\hbar)p_1'x_1]g_{n,2}(x_2), \end{aligned} \quad (\text{A.4})$$

which is equivalent to a canonical transformation of variables  $k_1 \rightarrow x_2$ . By this transformation (A.1), (A.2), and (A.3) retain the same form but undergo the replacements

$$\begin{aligned} p_1 + (e\mathcal{H}c/c)x_2 &\rightarrow p_1' + (e\mathcal{H}c/c)x_2, \\ f_1 &\rightarrow g_{n,1}, \\ f_2 &\rightarrow g_{n,2}. \end{aligned}$$

The properties of  $a^\dagger$  and  $a$ ,

$$\begin{aligned} au_n &= n^{\frac{1}{2}}u_{n-1}, \\ a^\dagger u_n &= (n+1)^{\frac{1}{2}}u_{n+1}, \end{aligned} \quad (\text{A.5})$$

allow solutions to (A.3) (transformed) to be written at once:

$$\begin{aligned} g_{n,1\pm} &= \begin{bmatrix} a_{1\pm}(n)u_{n-2} \\ b_{1\pm}(n)u_n \end{bmatrix}, \\ g_{n,2\pm} &= \begin{bmatrix} a_{2\pm}(n)u_{n-2} \\ b_{2\pm}(n)u_n \end{bmatrix}, \end{aligned} \quad (\text{A.6})$$

where the  $u_n$  are the ordinary one-dimensional harmonic oscillator functions of the argument

$$(c/e\hbar\mathcal{H})^{\frac{1}{2}}[p_1' + (e\mathcal{H}c/c)x_2].$$

For  $n < 2$ ,  $a_{1\pm}$  and  $a_{2\pm}$  are to be taken equal to zero. The notation ( $\pm$ ) labels the two eigensolutions of the determinantal equations for the  $a$ 's and  $b$ 's.

The eigenvalues of the determinantal equations are

$$\begin{aligned} \epsilon_{1+}(n) &= (\gamma_1 - \bar{\gamma})(n + \frac{1}{2}) - \frac{1}{2}\kappa, \\ \epsilon_{2+}(n) &= (\gamma_1 + \bar{\gamma})(n + \frac{1}{2}) - \frac{3}{2}\kappa \end{aligned} \quad (\text{A.7})$$

for  $n < 2$  and

$$\begin{aligned} \epsilon_{1\pm}(n) &= \gamma_1 n - (\frac{1}{2}\gamma_1 + \bar{\gamma} - \frac{1}{2}\kappa) \\ &\quad \pm \{[\bar{\gamma}n - (\gamma_1 - \kappa + \frac{1}{2}\bar{\gamma})]^2 + 3\bar{\gamma}^2 n(n-1)\}^{\frac{1}{2}}, \end{aligned} \quad (\text{A.8})$$

$$\begin{aligned} \epsilon_{2\pm}(n) &= \gamma_1 n - (\frac{1}{2}\gamma_1 - \bar{\gamma} + \frac{1}{2}\kappa) \\ &\quad \pm \{[\bar{\gamma}n + (\gamma_1 - \kappa - \frac{1}{2}\bar{\gamma})]^2 + 3\bar{\gamma}^2 n(n-1)\}^{\frac{1}{2}} \end{aligned}$$

for  $n \geq 2$ . The energy levels are thus grouped into four "ladders" designated by (+) for the light holes and (-) for the heavy holes.

Finally, with the aid of the eigenvalues  $\epsilon_{1\pm}(n)$  and  $\epsilon_{2\pm}(n)$  the determinantal equations are solved for the coefficients  $a_{i\pm}(n)$  and  $b_{i\pm}(n)$  which are normalized according to

$$a_{i\pm}^2(n) + b_{i\pm}^2(n) = 1. \quad (\text{A.9})$$

For  $n < 2$ , we have

$$\begin{aligned} a_{1+}(n) &= a_{2+}(n) = 0, \\ b_{1+}(n) &= b_{2+}(n) = 1. \end{aligned} \quad (\text{A.10})$$

Calling

$$\begin{aligned} p_1 &= \sqrt{3}\bar{\gamma}[n(n-1)]^{\frac{1}{2}}, & p_2 &= p_1, \\ q_1 &= \bar{\gamma}n - (\gamma_1 - \kappa + \frac{1}{2}\bar{\gamma}), & q_2 &= \bar{\gamma}n + (\gamma_1 - \kappa - \frac{1}{2}\bar{\gamma}), \end{aligned} \quad (\text{A.11})$$

we obtain for  $n \geq 2$

$$\begin{aligned} a_{1\pm}(n) &= -N_{1\pm}(n)p_1, \\ b_{1\pm}(n) &= N_{1\pm}(n)[-q_1 \pm (p_1^2 + q_1^2)^{\frac{1}{2}}], \\ N_{1\pm}(n) &= [2p_1^2 + 2q_1^2 \mp 2q_1(p_1^2 + q_1^2)^{\frac{1}{2}}]^{-\frac{1}{2}}, \end{aligned} \quad (\text{A.12})$$

and

$$\begin{aligned} a_{2\pm}(n) &= -N_{2\pm}(n)p_2, \\ b_{2\pm}(n) &= N_{2\pm}(n)[q_2 \pm (p_2^2 + q_2^2)^{\frac{1}{2}}], \\ N_{2\pm}(n) &= [2p_2^2 + 2q_2^2 \pm 2q_2(p_2^2 + q_2^2)^{\frac{1}{2}}]^{-\frac{1}{2}}. \end{aligned} \quad (\text{A.13})$$