one ionization state.[14] The particular state of ionization of each defect is determined by the position of the Fermi level. This is sensitive to the total number and type of impurities in the crystal and hence varies greatly from crystal to crystal. The time required for the establishment of steady state conditions is often rather long, for example the slow rise in photoconductivity in CdS observed by Bube.[17] Quasi steady-state conditions might be expected to exist during and following the periods of heavy ionization caused by electron bombardment which can cause a change in the distribution of the electrons over the existing defects. Temperature cycling or long decay times or both may be required before a return to equilibrium is accomplished. This is evidenced by the decrease in intensity of the 7200 A band under bombardment at low temperature followed by the partial recovery of this fluorescence by warming to 20°C then cooling again. The initial increase in intensity of the 1.03 μ band during bombardment at 275 kev, below the threshold, and its decrease following warming and cooling is an example of a similar phenomenon with opposite effect. Much work remains to be done before any real understanding about the character of the defect levels in CdS can be accomplished. Electron bombardment near the thresholds for displacement of the cadmium and sulfur atoms offers a new approach to the problem; however, the results obtained are complicated.

ACKNOWLEDGMENTS

The author wishes to thank Captain Raymond H. Kelley for his assistance in the Cd overlay experiments and R. G. Schulze and R. G. Peacock for aiding in the other experiments. The crystals were grown by L. C. Greene and D. C. Reynolds of this laboratory.

PHYSICAL REVIEW VOLUME 125, NUMBER 6 MARCH 15, 1962

Valence Bands of Germanium and Silicon in an External Magnetic Field*

VIKTOR EVTUHOV†
California Institute of Technology, Pasadena, California
(Received July 17, 1961; revised manuscript received October 23, 1961)

The problem of the valence band structure of germanium and silicon in the presence of an external magnetic field is considered from a quantum-mechanical point of view. The analysis is carried out using first- and second-order perturbation theory. The approach is an extension of methods of Shockley and Kane to include the effects of the magnetic field. The usual approximation of the decoupling of the V_1 and V_2 bands from the V_3 band is not made, thus making the analysis applicable to Si as well as Ge. Spherical energy bands are not assumed in this calculation and the case of $k_H \neq 0$ is considered. Detailed analysis is carried out for the magnetic field H in the [001] direction. The analytical results obtained are more general than those of Luttinger but reduce to the latter if certain approximations are introduced.

Numerical calculations of the Landau energy levels are carried out for certain special cases. The results predict an increase of the hole effective mass with the magnetic field. They also indicate mixing of the Landau levels even at $k_H=0$, which leads to a prediction of new transitions some of which are of "negative mass" type. The mixing is more pronounced in Si than in Ge. Calculations for $k_H \neq 0$ show that the ϵ_1^- levels possess negative curvatures near $k_H=0$. Gradual "crossing" or reordering of the heavy hole levels is found at relatively high k_H.

I. INTRODUCTION

THE quantum-mechanical effective mass formalism for treating problems of magnetic energy levels (Landau levels) in semiconductors has been developed by Luttinger and Kohn.[1] The method has been extended by Luttinger[2] who used it to analyze the valence band of germanium. Since in the valence band of Ge the spin-orbit splitting is rather large, Luttinger has been able to consider the V_1 and V_2 bands separately from the V_3 band. He has written down a 4×4 matrix, a diagonalization of which should yield the energy levels for electrons in a Ge crystal which is subjected to a magnetic field in the [111] direction. In deriving this, Luttinger assumed that the momentum of the electrons in the direction of the magnetic field (k_H) is zero. He has then simplified the problem further by assuming the energy bands to be isotropic. This reduced the problem to the solution of two 2×2 determinants which Luttinger has carried out. He also formulated a perturbation approach to the anisotropic problem. The numerical results for Ge have been given by Goodman.[3] One of the most interesting results obtained by Luttinger and Goodman is the unevenness in the spacing of the Landau levels at low quantum numbers, an effect which has been experimentally observed.[4–6]

* This work was performed while the author was a recipient of the Howard Hughes Fellowship in Science and Engineering, and was supported in part by the Office of Naval Research.
† Present address: Hughes Research Laboratories, Malibu, California.
[1] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).
[2] J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).
[3] R. R. Goodman, doctoral dissertation, University of Michigan, 1958; Phys. Rev. **122**, 397 (1961).
[4] R. C. Fletcher, W. A. Yager, and R. F. Merritt, Phys. Rev. **100**, 747 (1955).
[5] J. C. Hensel, Bull. Am. Phys. Soc. **6**, 115 (1961).
[6] J. J. Stickler *et al.*, Bull. Am. Phys. Soc. **6**, 115 (1961).

Calculations on the behavior of the Landau levels in the valence band of Ge at values of $k_H \neq 0$ have recently been performed by Wallis and Bowlden.[7] However, in their calculations they assume isotropic energy bands which prevents them from predicting possible reordering of the Landau levels at high k_H. They also do not concern themselves with the wave functions corresponding to the various Landau levels and thus cannot discuss transition probabilities or the possible existence of new allowed transitions.

No calculations of the sort described above have been made for silicon. In the case of Si the analysis is complicated by the small spin-orbit splitting. It appears to be necessary to consider all three valence bands together, which leads to the formulation of the general problem in terms of 6×6 matrices. It may be expected that in this case the unevenness in the Landau level spacings, mixing between the Landau levels, the nonparabolic effects, and the anisotropy effects will be even more pronounced than in the case of Ge.

The problem of energy band structure of Ge and Si in the presence of a magnetic field, which relates to the problems of cyclotron resonance[8] and interband magnetoabsorption,[9,10] is considered here from a quantum-mechanical point of view. For the sake of clarity and completeness, some of the results of Luttinger and Kohn[1] and Luttinger[2] are rederived in Sec. II using a slightly different approach to the problem. Also, the analysis given makes use of a smaller number of approximations than previously so as to enable one to study Si as well as Ge. Thus we do not make the assumption of decoupling of the V_1 and V_2 bands from the V_3 band which results in a 6×6 matrix operator. Spherically symmetric energy bands are not assumed, although approximations must, of course, be used in dealing with the resulting infinite secular determinants.

In Sec. III the Landau energy levels in Ge and Si are found at $k_H=0$ for the case of a magnetic field in the [001] direction. No approximations other than those involved in the use of the second-order perturbation theory are made in that section. In Sec. IV the approximation of the decoupling of the V_1 and V_2 bands from the V_3 band mentioned above is introduced. The validity of this approximation is numerically checked for both Ge and Si. The behavior of the energy levels for $k_H \neq 0$ is then considered.

II. PERTURBATION MATRIX

To analyze the energy-level structure of a Ge or Si crystal in a magnetic field, one must solve the following Schrödinger equation:

$$\frac{1}{2m}\left(\mathbf{p}+\frac{|e|\mathbf{A}}{c}\right)^2\psi+\frac{\hbar}{4m^2c^2}\left[\nabla V\times\left(\mathbf{p}+\frac{|e|\mathbf{A}}{c}\right)\right]\cdot\boldsymbol{\sigma}\psi + \frac{|e|}{2mc}\boldsymbol{\sigma}\cdot\mathbf{H}\psi+V(r)\psi=E\psi, \quad (1)$$

where standard symbolism is employed.

The corresponding equation for the case of no magnetic field has been solved quite accurately for Ge and Si in the region of the Brillouin zone near $\mathbf{k}=0$ with the help of the perturbation theory. The method has been suggested by Shockley[11] and has been carried out in detail by Dresselhaus, Kip, and Kittel[12] and by Kane.[13]

To solve (1), we use an approach similar in principle to that of Kane[14] but introduce modifications required by the presence of the magnetic field. The solutions to (1) are obviously not of the Bloch type, as are the solutions to the no-magnetic-field problem. However, choosing a coordinate system x_1, x_2, x_3 such that the magnetic field lies along x_3 and selecting the Landau gauge $A_1=Hx_2$, $A_2=A_3=0$ we find by arguments exactly analogous to Bloch's[15]

$$\psi=e^{i(k_1x_1+k_3x_3)}\mathfrak{U}_{k_1k_3}(\mathbf{r}), \quad (2)$$

where $\mathfrak{U}_{k_1k_3}(\mathbf{r})$ has the periodicity of the lattice in the x_1 and x_3 directions and k_1 and k_3 are the wave vectors in the x_1 and x_3 directions, respectively.

In view of the form of the solution to the Schrödinger equation for an electron in a magnetic field and otherwise free, given by Landau,[16] it is convenient to write $\mathfrak{U}_{k_1k_3}$ in the following way:

$$\mathfrak{U}_{k_1k_3}(\mathbf{r})=\sum_{i=1}^{6}\sum_{n=0}^{\infty}\alpha_{in}f_n(x_2)\phi_i, \quad (3)$$

where the f_n are the harmonic oscillator wave functions and the ϕ_i are the six zero-order wave functions of Kane which are written in terms of the coordinates x, y, z, and the spins. The x, y, z axes are along the [100], [010], [001] directions of the crystal, respectively. $\mathfrak{U}_{k_1k_3}(\mathbf{r})$ given by Eq. (3) is seen to have the required periodicity in the x_1 and x_3 directions, and is expressed in terms of a complete set of functions of x_2. Eqs. (2) and (3) may now be substituted into (1). Performing the necessary algebraic operations, defining the operators

$$k_1'=k_1-|e|Hx_2/c\hbar, \quad (4)$$
$$k_2'=(1/i)\partial/\partial x_2, \qquad k_3'=k_3,$$

[7] R. F. Wallis and H. J. Bowlden, Phys. Rev. **118**, 456 (1960).
[8] For a review see B. Lax, Revs. Modern Phys. **30**, 122 (1958) and B. Lax and J. G. Mavroides, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Vol. 11, p. 261.
[9] E. Burstein, G. S. Picus, R. F. Wallis, and F. Blatt, Phys. Rev. **113**, 15 (1959).
[10] S. Zwerdling, B. Lax, L. M. Roth, and K. J. Button, Phys. Rev. **114**, 80 (1959) and L. M. Roth, B. Lax, S. Zwerdling, *ibid.* **114**, 90 (1959).
[11] W. Shockley, Phys. Rev. **78**, 173 (1950).
[12] G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. **98**, 368 (1955).
[13] E. O. Kane, J. Phys. Chem. Solids **1**, 82 (1956).
[14] Here, as well as below, we refer to Kane's article (reference 13) rather than the others since the former generally gives a more complete treatment.
[15] F. Bloch, Z. Physik **52**, 555 (1928).
[16] L. D. Landau, Z. Physik **84**, 629 (1930).

which operate only on the harmonic oscillator wave functions, and transforming to the x, y, z coordinate system, the following is obtained

$$\sum_{i=1}^{6}\sum_{n=0}^{\infty}\alpha_{in}f_n\left[-\frac{\hbar^2}{2m}\nabla^2\phi_i+V(r)\phi_i\right]$$
$$+\sum_{i=1}^{6}\sum_{n=0}^{\infty}\alpha_{in}\phi_i\frac{\hbar^2}{2m}k'^2f_n-\sum_{i=1}^{6}\sum_{n=0}^{\infty}\alpha_{in}\frac{i\hbar^2}{m}(\mathbf{k}'f_n)\cdot\boldsymbol{\nabla}\phi_i$$
$$+\sum_{i=1}^{6}\sum_{n=0}^{\infty}\alpha_{in}f_n\frac{\hbar}{4m^2c^2}[\nabla V\times\mathbf{p}']\cdot\boldsymbol{\sigma}\phi_i$$
$$+\sum_{i=1}^{6}\sum_{n=0}^{\infty}\alpha_{in}\frac{\hbar^2}{4m^2c^2}[\nabla V\times\mathbf{k}'f_n]\cdot\boldsymbol{\sigma}\phi_i$$
$$+\sum_{i=1}^{6}\sum_{n=0}^{\infty}\alpha_{in}\frac{|e|}{2mc}\boldsymbol{\sigma}\cdot\mathbf{H}\phi_if_n=E\sum_{i=1}^{6}\sum_{n=0}^{\infty}\alpha_{in}f_n\phi_i. \quad (5)$$

This equation is analogous to Kane's Eqs. (2) and (8). Following Kane one may neglect the term involving $[\nabla V\times\mathbf{k}']\cdot\boldsymbol{\sigma}$, and treat the first term as the zero-order equation with all other terms as perturbations. This restricts the calculation to the region close to the center of the Brillouin zone and to relatively low Landau level quantum numbers. The zero-order equation is thus given by

$$\sum_{i=1}^{6}\alpha_{in}{}^0\left[-\frac{\hbar^2}{2m}\nabla^2\phi_i+V(r)\phi_i\right]=E^0\sum_{i=1}^{6}\alpha_{in}{}^0\phi_i, \quad (6)$$

for each n since all f_n are linearly independent. This is essentially the zero-order equation of Kane, and therefore the solutions and the zero-order energy levels are as indicated in Kane's paper.

In calculating the effects of the perturbation terms we restrict our attention to the case with the external magnetic field applied in the [001] direction, i.e., along the z axis. We thus have $x_1=x$, $x_2=y$, $x_3=z$, etc. Since $\mathbf{k}'$ operates only on f_n, one can carry out the second-order $\mathbf{k}\cdot\mathbf{p}$ and the first-order spin-orbit perturbation analysis exactly as in the no-magnetic-field case, substituting k_α' for k_α in the final result and operating with the resulting matrix on some linear combination of functions f_n. There will be only one modification which arises from the noncommutivity of k_α' whereas the k_α do commute.[2] Thus all off-diagonal terms $H_{ij}{}^{kp}(i\neq j)$ in Kane's Eq. (6) must be replaced by

$$H_{ij}{}^{kp}(i\neq j)=N\{k_\alpha'k_\beta'\}+\tfrac{1}{2}K(k_\alpha'k_\beta'), \quad (7)$$

where $\{k_\alpha'k_\beta'\}$ is the symmetrized product of k_α' and k_β' and $(k_\alpha',k_\beta')$is the commutator of k_α' and k_β'. K is the antisymmetric constant introduced by Luttinger.[2]

The transformation U given by Kane which diagonalizes the spin-orbit interaction can also be used in our case which will transform the problem to the Jm_J representation in which the basis functions are the angular momentum functions $\phi_{m_J}{}^{(J)}$. Note, however, that relations (21) and (22) of Kane are not applicable in view of (7). Performing the transformation the matrix $\|V_{ij}{}^{kp\ so}\|$ may be explicitly written. We use the definitions (following the form of Luttinger and Kohn,[1] although L, M, N constants[12,13] used here are different numerically from their A, B, C constants)

$$\begin{aligned}&P=(L+M)(k_x'^2+k_y'^2)+2Mk_z^2;\\&Q=M(k_x'^2+k_y'^2)+Lk_z^2;\\&\mathfrak{L}=-(iN/\sqrt{3})(k_x'-ik_y')k_z;\\&\mathfrak{M}=[1/(12)^{\frac{1}{2}}][(L-M)(k_x'^2-k_y'^2)-2iN\{k_x'k_y'\}].\end{aligned} \quad (8)$$

Ordering the matrix elements so as to conform with Luttinger and Kohn, one gets

$$\|v_{ij}{}^{kp\ so}\|=\left\|\begin{array}{cccccc}
\frac{1}{2}P+\frac{Ks}{2} & -i\mathfrak{L} & -\mathfrak{M} & 0 & \frac{i}{\sqrt{2}}\mathfrak{L} & -\sqrt{2}M \\
i\mathfrak{L}^* & \frac{1}{6}P+\frac{2}{3}Q+\frac{Ks}{6} & 0 & \mathfrak{M} & \frac{1}{3\sqrt{2}}(P-2Q+Ks) & \frac{\sqrt{3}}{\sqrt{2}}i\mathfrak{L} \\
-\mathfrak{M}^* & 0 & \frac{1}{6}P+\frac{2}{3}Q-\frac{Ks}{6} & -i\mathfrak{L} & \frac{\sqrt{3}}{\sqrt{2}}i\mathfrak{L}^* & \frac{1}{3\sqrt{2}}(P-2Q-Ks) \\
0 & \mathfrak{M}^* & i\mathfrak{L}^* & \frac{1}{2}P-\frac{Ks}{2} & \sqrt{2}M^* & -\frac{i}{\sqrt{2}}\mathfrak{L}^* \\
-\frac{i}{\sqrt{2}}\mathfrak{L}^* & \frac{1}{3\sqrt{2}}(P-2Q+Ks) & -\frac{\sqrt{3}}{\sqrt{2}}i\mathfrak{L} & \sqrt{2}\mathfrak{M} & \frac{1}{2}(P+Q)+\frac{Ks}{3}-\Delta & 0 \\
-\sqrt{2}\mathfrak{M}^* & -\frac{\sqrt{3}}{\sqrt{2}}i\mathfrak{L}^* & \frac{1}{3\sqrt{2}}(P-2Q-Ks) & \frac{1}{\sqrt{2}}\mathfrak{L} & 0 & \frac{1}{3}(P+Q)-\frac{Ks}{3}-\Delta
\end{array}\right\|, \quad (9)$$

$$\begin{array}{c}(\frac{3}{2})\frac{3}{2}\\(\frac{3}{2})\frac{1}{2}\\(\frac{3}{2})-\frac{1}{2}\\(\frac{3}{2})-\frac{3}{2}\\(\frac{1}{2})\frac{1}{2}\\(\frac{1}{2})-\frac{1}{2}\end{array}$$

where

$$s=|e|H/c\hbar. \tag{10}$$

Now if $\|V_{ij}{}^{kp\ so}\|$ is transformed using an appropriate unitary transformation[17] and K is set equal to zero, a matrix is obtained which is identical in form with the final result of Luttinger and Kohn.

Now the terms $(\hbar^2/2m)k'^2$ and $(|e|/2mc)\boldsymbol{\sigma}\cdot\mathbf{H}$ which appear in (5) must be introduced. Since the operator k' is simply a multiplier as far as the wave functions ϕ_i are concerned, $\|H_{ij}{}^{k^2}\|=\|(\hbar^2/2m)k'^2\delta_{ij}\|$. The contribution of the $(|e|/2mc)\boldsymbol{\sigma}\cdot\mathbf{H}$ term in the ϕ_i representation is a matrix $\|H_{ij}{}^{\sigma\cdot H}\|$ which is diagonal with values $(1, 1, 1, -1, -1, -1)$ times $\hbar|e|H/mc$.

One may now write the complete perturbation Hamiltonian $\|V_{ij}\|$ by transforming both $\|H_{ij}{}^{k^2}\|$ and $\|H_{ij}{}^{\sigma\cdot H}\|$ to the Jm_J representation and adding the results to (9). The resulting matrix must then be allowed to operate on linear combinations of the harmonic oscillator wave functions f_n. This is most conveniently done by writing the operators k_x' and k_y' in terms of the raising and lowering operators defined by

$$a^*=-(2s)^{-\frac{1}{2}}(k_x'+ik_y'); \quad a=-(2s)^{-\frac{1}{2}}(k_x'-ik_y'). \tag{11}$$

Using the definitions

$$\begin{aligned} &(\hbar^2/2m)(l-1)=L; \quad &&-(\hbar^2/m)(3\kappa+1)=K;\\ &(\hbar^2/2m)(\mu-1)=M; \quad &&s^{\frac{1}{2}}d=k_z; \\ &(\hbar^2/2m)\nu=N; \quad &&(\hbar^2/m)s\Delta'=\Delta; \end{aligned} \tag{12}$$

reordering the terms in $\|V_{ij}\|$ in a manner which will be found convenient, and changing its sign so as to deal with holes instead of electrons one gets ⟶

$$\|v_{ij}\|=\frac{\hbar^2 s}{m}\begin{array}{|cccccc|}
\hline
\alpha(a^*a+\frac{1}{2})-\frac{\mu}{2}d^2+\frac{3}{2}\kappa & -(\beta a^{*2}+\delta a^2) & -\frac{1}{\sqrt{6}}\nu a d & 0 & \frac{1}{2\sqrt{3}}\nu a d & -\sqrt{2}(\beta a^2+\delta a^{*2}) \\
-(\beta a^{*2}+\delta a^2) & \zeta(a^*a+\frac{1}{2})+\eta d^2-\frac{1}{2}\kappa & 0 & -\frac{1}{\sqrt{6}}\nu a d & -\frac{1}{2}\nu a^* d & \rho(a^*a+\frac{1}{2}-d^2)-\frac{\kappa+1}{\sqrt{2}} \\
-\frac{1}{\sqrt{6}}\nu a^* d & 0 & \zeta(a^*a+\frac{1}{2})+\eta d^2+\frac{1}{2}\kappa & \beta a^{*2}+\delta a^2 & \rho(a^*a+\frac{1}{2}-d^2)+\frac{\kappa+1}{\sqrt{2}} & \frac{1}{2}\nu a d \\
0 & -\frac{1}{\sqrt{6}}\nu a^* d & \beta a^{*2}+\delta a^2 & \alpha(a^*a+\frac{1}{2})-\frac{\mu}{2}d^2-\frac{3}{2}\kappa & \sqrt{2}(\beta a^{*2}+\delta a^2) & \frac{1}{2\sqrt{3}}\nu a^* d \\
\frac{1}{2\sqrt{3}}\nu a^* d & -\frac{1}{2}\nu a d & \rho(a^*a+\frac{1}{2}-d^2)+\frac{\kappa+1}{\sqrt{2}} & \sqrt{2}(\beta a^2+\delta a^{*2}) & \lambda(a^*a+\frac{1}{2}+\frac{1}{2}d^2)+\frac{2\kappa+1}{2}+\Delta' & 0 \\
-\sqrt{2}(\beta a^{*2}+\delta a^2) & \rho(a^*a+\frac{1}{2}-d^2)-\frac{\kappa+1}{\sqrt{2}} & \frac{1}{2}\nu a^* d & \frac{1}{2\sqrt{3}}\nu a d & 0 & \lambda(a^*a+\frac{1}{2}+\frac{1}{2}d^2)-\frac{2\kappa+1}{2}+\Delta' \\
\hline
(\frac{3}{2})\frac{3}{2} & (\frac{3}{2})-\frac{1}{2} & (\frac{3}{2})\frac{1}{2} & (\frac{3}{2})-\frac{3}{2} & (\frac{1}{2})\frac{1}{2} & (\frac{1}{2})-\frac{1}{2}
\end{array}, \tag{13}$$

where

$$\begin{aligned} &\alpha=-(l+\mu)/2, \quad &&\beta=-(l-\mu+\nu)/4\sqrt{3},\\ &\delta=-(l-\mu-\nu)/4\sqrt{3}, \quad &&\zeta=-(l+5\mu)/6,\\ &\eta=-(\mu+2l)/6, \quad &&\rho=-(l-\mu)/3\sqrt{2},\\ &\lambda=-(l+2\mu)/3. \end{aligned}$$

To compare this result with Luttinger's[2] the following approximations are introduced: (1) The 4×4 matrix in the upper left-hand corner may be decoupled from the 2×2 matrix in the lower right-hand corner. The validity of this approximation is discussed in Sec. IV. (2) $d=0$ (i.e., $k_z=k_H=0$). (3) $l-\mu-\nu=0$ which implies spherically symmetric energy bands. Luttinger makes this approximation in all cases except that of the magnetic field in the [111] direction, and then treats $l-\mu-\nu\neq0$ case by perturbation theory. This procedure seems to be applicable to Ge where $l-\mu-\nu$ is small, but is questionable in case of Si, as Luttinger

[17] V. Evtuhov, doctoral dissertation, California Institute of Technology (1961) (unpublished). Also available as California Institute of Technology Electron Tube and Microwave Laboratory Technical Report No. 16 from the Office of Naval Research.

himself points out. We also define $\gamma_1=-\frac{1}{3}(l+2\mu)$, $\gamma_2=-\frac{1}{6}(l-\mu)$, $\gamma_3=-\frac{1}{6}\nu$, $\gamma_1, \gamma_2, \gamma_3$ being the constants used by Luttinger. Assumption (3) implies $\gamma_2=\gamma_3=\bar{\gamma}$. The resulting 4×4 matrix is identical with Luttinger's Eq. (71) with the exception of some signs. It is easily shown, however, that these signs do not affect the solutions.

III. LANDAU LEVELS IN Ge AND Si AT $k_H=0$ FOR H IN THE [001] DIRECTION

We now calculate the energy levels in the valence bands of Ge and Si as functions of the external magnetic field H for a special case of H in the [001] direction and $k_H=0$. This special case is analogous to the case of $k_z=0$, but k_x and k_y finite in the no-magnetic-field problem. The resulting energy levels are the ones involved in the interband magneto-optical transitions and probably in most of the cyclotron resonance transitions. They are thus of primary importance in the interpretation of the experimental data.

Since no approximations, aside from the basic ones which have already been discussed, are being made in this calculation, it will serve as a basis of comparison for other calculations.

Upon setting $d=0$ (i.e., $k_H=k_z=0$) it is found that the matrix of (13) decouples into two 3×3 matrices. Using these the following eigenvalue problem must be solved:

$$\|V_{ij}{}^{3\times3}\|F=E\|I\|F, \tag{14}$$

where $\|I\|$ is the unit matrix and F can be taken to be of the form

$$F=\left\|\begin{array}{c}\sum_i a_i f_i\\ \sum_j b_j f_j\\ \sum_k c_k f_k\end{array}\right\|. \tag{15}$$

Performing the operations indicated in (14) using the first (one involving $(\frac{3}{2})\frac{3}{2}$, $(\frac{3}{2})-\frac{1}{2}$, $(\frac{1}{2})-\frac{1}{2}$ zero-order functions) of the two 3×3 operator matrices one obtains an infinite set of linear equations involving coefficients a, b, and c and the harmonic oscillator functions f.

Now if the energy bands are assumed to be spherically symmetric, i.e., $l-\mu-\nu=0$, one may write $j=i+2$, $k=i+2$. Then for each i a set of three simultaneous equations is obtained, the solution of which will involve simply a diagonalization of a 3×3 matrix.

If the assumption of spherical symmetry is not made ($l-\mu-\nu\neq0$), one must use the orthogonality properties of the f_n's to obtain algebraic equations for the coefficients a_i, b_j, and c_k. This yields an infinite number of coupled algebraic equations which may be arranged in such a way that the system determinant has the following form [the symbolism employed should be obvious—see Eq. (13)]:

	b_0	c_0	b_1	c_1	a_0	b_2	c_2	a_1	b_3	c_3	a_2	b_4	c_4	a_3	b_5	c_5	a_4	b_6	c_6	a_5	b_7	⋯
II f_0	ϵ	ρ		A							δ											
III f_0	ρ	ϵ									$\sqrt{2}\delta$											
II f_1			ϵ	ρ	B									δ								
III f_1			ρ	ϵ										$\sqrt{2}\delta$								
I f_0					ϵ	β	$\sqrt{2}\beta$															
II f_2					β	ϵ	ρ	C									δ					
III f_2					$\sqrt{2}\beta$	ρ	ϵ										$\sqrt{2}\delta$					
I f_1								ϵ	β	$\sqrt{2}\beta$												
II f_3								β	ϵ	ρ	D									δ		
III f_3								$\sqrt{2}\beta$	ρ	ϵ										$\sqrt{2}\delta$		
I f_2	δ	$\sqrt{2}\delta$									ϵ	β	$\sqrt{2}\beta$									
II f_4											β	ϵ	ρ	A								
III f_4											$\sqrt{2}\beta$	ρ	ϵ									
I f_3			δ	$\sqrt{2}\delta$										ϵ	β	$\sqrt{2}\beta$						
II f_5														β	ϵ	ρ	B					
III f_5														$\sqrt{2}\beta$	ρ	ϵ						
I f_4						δ	$\sqrt{2}\delta$										ϵ	β	$\sqrt{2}\beta$			
II f_6																	β	ϵ	ρ	C		
III f_6																	$\sqrt{2}\beta$	ρ	ϵ			
I f_5									δ	$\sqrt{2}\delta$										ϵ	β	
II f_7																				β	ϵ	
III f_7																				$\sqrt{2}\beta$	ρ	
⋮																						⋯

(16)

It will be observed that the infinite set of equations can be decoupled into four independent sets (labeled A, B, C, D) which reduces the problem to the solution of four independent infinite determinants, each of which can be quite accurately solved by truncating it sufficiently far from the 3×3 block which gives rise to the eigenvalue of interest. This is possible because the terms involving δ are smaller than those in the main blocks. In this process one must avoid the "decoupling" of levels close to each other in energy.

The second of the two 3×3 matrices (the one involving $(\frac{3}{2})\frac{1}{2}$, $(\frac{3}{2})-\frac{3}{2}$, $(\frac{1}{2})\frac{1}{2}$ zero-order functions) may be treated in a similar fashion.

Again, if $\delta=0$, one may set $j=i+2$, $k=i$, and obtain for each i a set of three simultaneous equations. If, on the other hand, $\delta\neq0$ as is actually the case, one proceeds as indicated in the previous case obtaining an infinite determinant of the form similar to (16). This also decouples into four infinite determinants which are solved by the same methods as (16).

For the constants l, μ, ν, and κ which appear in the above analysis one must rely on the experimentally determined values. The determinations based on experimental data have been made by Dresselhaus, Kip, and Kittel,[12] Dexter, Zeiger, and Lax,[18] Dexter and Lax,[19] and Goodman.[3] The first three estimates have been based on the "semiclassical" model of cyclotron resonance, while the one by Goodman is based on fitting the quantum-mechanical energy-level calculation (for Ge at $k_H=0$) to the data obtained by Fletcher, Yager, and Merritt.[4]

Due to the difficulty of obtaining the data for Si with sufficient degree of precision,[20] there arise certain ambiguities in the determination of the LMN constants[13] for Si. Here we used the constants preferred by Kane. All the above constants, as well as the antisymmetric constant can be related to the constants (sums of matrix elements) F, G, H_1, and H_2 defined by Dresselhaus, Kip, and Kittel. If H_2 is taken to be zero, which is the value quoted by Dresselhaus, Kip, and Kittel, the constant κ can be easily evaluated. The following are the constants used in the subsequent calculations: for Ge $l=-31.0$, $\mu=-4.3$, $\nu=-32.4$, $\kappa=3.3$, $\Delta=0.29$ ev[13]; for Si $l=-6.2$, $\mu=-2.9$, $\nu=-7.7$, $\kappa=-0.016$, $\Delta=0.0441$ ev.[21]

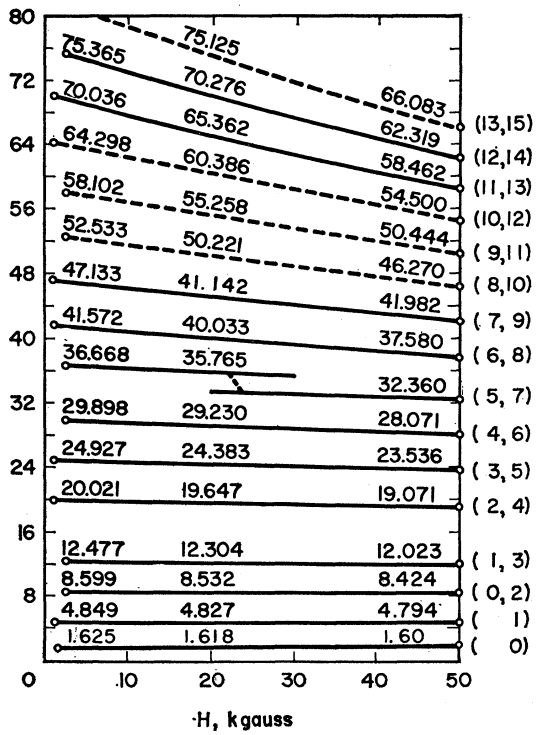

FIG. 1. Landau levels belonging to the ϵ_1^+ ladder in Si as functions of the magnetic field. The dotted lines indicate levels whose energies have not been as accurately computed as those of the others.

TABLE I. Eigenvalues belonging to the V_1 and V_2 bands in Ge.

	H (kgauss)	(0)	(1)	(0,2)	(1,3)	(2,4)	
ϵ_1^+	1	2.661[a]	11.18	29.60	51.12	73.39	
	50	2.659	11.09	28.78	48.76	68.00	
ϵ_2^+	1	3.691	21.88	43.30	65.58	88.11	
	50	3.679	21.89	42.73	63.66	83.97	
		(0,2)	(1,3)	(2,4)	(3,5)	(4,6)	(5,7)
ϵ_1^-	1	4.428	9.07	13.05	16.94	20.14	23.85
	50	4.357	9.06	13.01	16.87	20.06	23.75
ϵ_2^-	1	2.058	6.05	9.97	13.04	16.80	20.40
	50	2.054	5.98	9.89	12.91	16.63	20.19

[a] All eigenvalues are normalized so that the actual energy of a given level above the band edge is given by $E=(\hbar|e|H/mc)\epsilon$.

A. Numerical Results for Ge

The energy eivenvalues as well as the coefficients in the corresponding wave function expansions, are determined by solving the eight eigenvalue problems discussed above. The four problems arising from (16) result in eigenvalues which correspond to the two ϵ_1 ladders of Luttinger,[2] since they involve only the $\phi_{\frac{3}{2}}^{(\frac{3}{2})}$, $\phi_{-\frac{1}{2}}^{(\frac{3}{2})}$ and $\phi_{-\frac{1}{2}}^{(\frac{1}{2})}$ angular momentum functions. The eigenvalues arising from the other four problems correspond to the ϵ_2 ladders of Luttinger and involve the $\phi_{\frac{1}{2}}^{(\frac{3}{2})}$, $\phi_{-\frac{3}{2}}^{(\frac{3}{2})}$ and $\phi_{\frac{1}{2}}^{(\frac{1}{2})}$ functions.

By examining the results obtained by solving determinants of various orders[17] it is found that in general for Ge in order to find the first n eigenvalues with 1% or less error a determinant of the order of $n+3$ must be solved. Errors larger than ordinary may result if close-lying energy levels arising from different basic 3×3 blocks of the same determinant are decoupled during the truncating process. However, this effect becomes smaller as the basic blocks which given rise to the close-lying levels become farther separated. Thus for Ge there seem to be few if any cases where the above must be seriously considered.

The eigenvalues for Ge for $H=1$ kgauss and $H=50$ kgauss are given in Table I. It will be observed that the energy levels for the heavy holes (ϵ_1^- and ϵ_2^- ladders)

[18] R. N. Dexter, H. J. Zeiger, and B. Lax, Phys. Rev. **104**, 637 (1956).

[19] R. N. Dexter and B. Lax, Phys. Rev. **96**, 223 (1954).

[20] The most recent and accurate determination of these constants was made by Hansel and Feher [Phys. Rev. Letters **5**, 307 (1960)], but was, unfortunately, published after our calculations were completed.

[21] S. Zwerdling, K. J. Button, B. Lax, and L. M. Roth, Phys. Rev. Letters **4**, 173 (1960).

TABLE II. Eigenvalues belonging to the V_1 and V_2 bands in Si.

	H (k gauss)	(0)	(1)	(0,2)	(1,3)	(2,4)	(3,5)	(4,6)	(5,7)	(6,8)	(7,9)	(8,10)
ϵ_1^+	1	1.63[a]	4.85	8.60	12.48	20.02	24.93	29.90	36.67	41.57	47.13	52.53
	50	1.60	4.79	8.42	12.02	19.07	23.54	28.07	32.36	37.58	41.98	46.27
ϵ_2^+	1	2.13	6.08	13.30	18.03	23.00	29.68	34.82	40.26	45.71	51.32	56.75
	50	2.10	5.96	13.10	17.48	22.08	28.42	32.66	37.06	41.17	45.43	49.54
		(0,2)	(1,3)	(2,4)	(3,5)	(4,6)	(5,7)	(6,8)	(7,9)	(8,10)	(9,11)	
ϵ_1^-	1	1.51	4.61	7.38	10.00	12.66	15.78	15.73	18.38	20.08	23.16	
	50	1.44	4.46	7.10	9.57	12.07	15.04	14.96	17.35	19.57	21.73	
ϵ_2^-	1	1.20	3.84	6.47	9.42	9.49	12.20	14.68	17.04	19.35	21.75	
	50	1.18	3.79	6.38	9.30	9.16	11.67	14.00	16.18	18.35	20.63	

[a] All eigenvalues are normalized as in Table I.

depend very little on the magnetic field. This is to be expected since the energy levels shown lie quite close to the band edge (thus the ϵ_1^- (5,7) level is $\sim$0.014 ev above the band edge at $H=50$ kgauss) and therefore the interaction of these levels with the V_3 valence band is small. This interaction is, of course, the one responsible for the dependence of the energy eigenvalues on the magnetic field. The light hole energy levels, on the other hand, show a more marked dependence on the magnetic field. The dependence of the normalized energy on the magnetic field is for practical purposes linear.

Values of the coefficients in the eigenfunction expansions corresponding to various levels have also been computed. It was found that although the leading coefficients for a given level are in most cases appreciably larger than the others, significant mixing does occur in some instances. In general if the leading coefficients are a_n and b_{n+2} the coefficients a_{n-4}, a_{n+4}, b_{n-2}, b_{n+6} are on the average about 10% and sometimes as large as 30% of the value of the leading one. In these cases transitions of relatively high probability may occur between the $\epsilon(n, n+2)$ level and the $\epsilon(n+3, n+5)$ or $\epsilon(n+5, n+7)$ levels. The $\epsilon(n, n+2)$ to $\epsilon(n+3, n+5)$ transition will be a "negative mass" transition, i.e., it will be caused by a circularly polarized photon with the sense of polarization opposite to that causing the normal cyclotron resonance transitions.[9,22]

B. Numerical Results for Si

The calculations for this case are very similar to the ones just described. However, because the δ terms for Si are relatively larger than for Ge, it was found[17] that determinants of the order of $n+6$ must be solved to obtain the first n eigenvalues. Also, the difficulties due to the proximity in energy of the heavy and light hole levels arise somewhat more frequently here than in the case of Ge. An example of very strong coupling is provided by the ϵ_1^+ (5,7) and the ϵ_1^- (13,15) levels (see Fig. 1).

[22] G. C. Dousmanis, Phys. Rev. Letters 1, 55 (1958).

The energy levels can be identified and classified in the same way as for Ge, but in the present instance the task is somewhat more difficult since in many cases mixing is quite strong.

As may be seen from Table II the effect of the magnetic field on the energy levels is in this case appreciably more pronounced than in the case of Ge. For example, for the ϵ_2^+ ladder, the approximate changes in the effective masses are by factors of 1.08 to 1.5. This is due to the small spin-orbit splitting in Si. The dependence of the normalized energy on the magnetic field is in this case not quite linear especially for the deeper lying levels as is illustrated in Fig. 1 for the ϵ_1^+ ladder.

Since, in Si, mixing between the Landau levels is

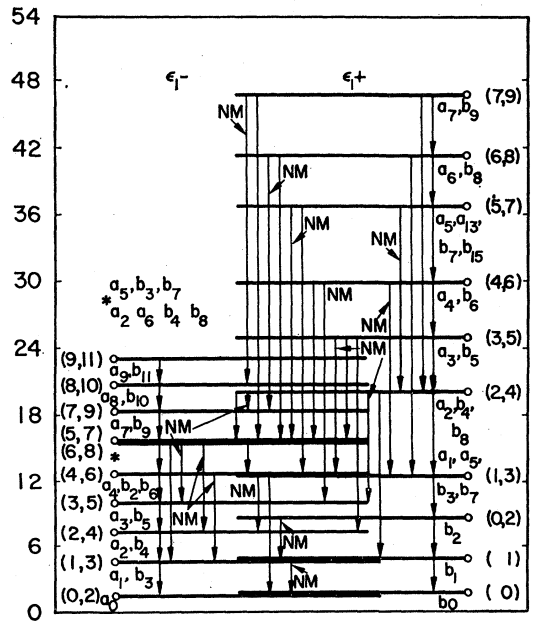

FIG. 2. Transitions between the Landau levels belonging to the ϵ_1 ladders in Si at $H=5$ kgauss. Expansion coefficients indicated are approximately equal to or greater than 0.50. Transitions marked *NM* are of the "negative mass" type.

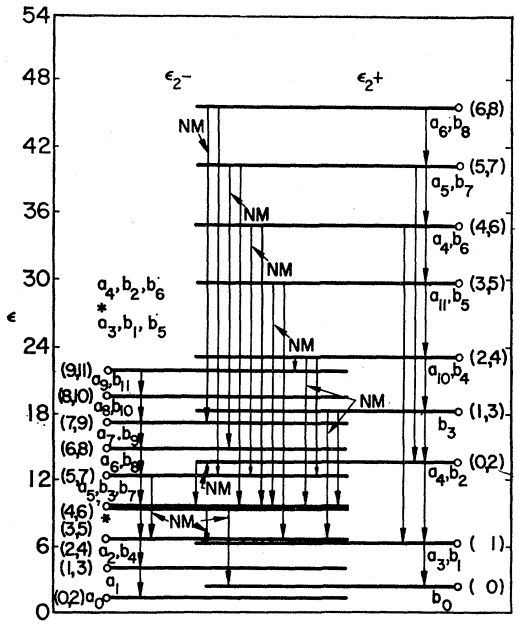

FIG. 3. Transitions between the Landau levels belonging to the ϵ_2 ladders in Si at $H=5$ kgauss. Expansion coefficients indicated are approximately equal to or greater than 0.50. Transitions marked *NM* are of the "negative mass" type.

quite strong, many interesting transitions should be possible. Some of these are shown in Figs. 2 and 3 at $H=5$ kgauss. It will be observed that some of the transitions are "negative mass" (NM) transitions in the sense mentioned above. No transitions between the ϵ_1 and ϵ_2 ladders are possible at $k_H=0$.

The expansion coefficients for different values of the external magnetic field have been computed.[17] Few qualitative changes in the coefficients with the change in the magnetic field were found except for stronger coupling to the V_3 band. However, some levels do change the mixing pattern sufficiently so that the absorption spectrum must be expected to be somewhat different at different values of the magnetic field.

As one may estimate from Kane's calculations, the "nonparabolic" effects in the V_2 band of Si appear at about 0.015 ev below the valence band edge. The deepest light hole energy level computed here is the ϵ_2^+ (12,14) level which lies about 0.017 ev away from the band edge at $H=20$ kgauss. Thus the "nonparabolic" effects should start manifesting themselves. However, in order to see them clearly, a few additional deep-lying levels would have to be calculated.

IV. VALENCE BAND LANDAU LEVELS AS FUNCTIONS OF k_H FOR H IN THE [001] DIRECTION

A. Check on the Validity of an Approximation Involving the Decoupling of the V_1 and V_2 Bands from the V_3 Band

Because of the complicated nature of Eq. (13), it is desirable to introduce some approximations before proceeding with further numerical computations. The approximation that has been extensively used so far is that of the decoupling of V_1 and V_2 bands from the V_3 band. According to Dresselhaus, Kip, and Kittel, who used the assumption in computing the band structure of Ge and Si without the magnetic field, the error involved is of the order of k^4/Δ where Δ is the spin-orbit splitting. Thus the assumption is good near the center of the Brillouin zone and should be much better for Ge than for Si. For the problem of a crystal in a magnetic field, this assumption is expected to be reasonably good for small k_H and for energy levels lying close to the band edge.

To check the extent of the validity of the approximation the solutions to the exact and the approximate problems for the special case considered in Sec. III, i.e., the case of $k_H=0$ and H in the [001] direction were compared.

The assumption in question reduces (13) to two matrices, one 4×4 and involving the $(\frac{3}{2})\frac{3}{2}$, $(\frac{3}{2})-\frac{1}{2}$, $(\frac{3}{2})\frac{1}{2}$, and $(\frac{3}{2})-\frac{3}{2}$ zero-order wave functions and the other 2×2 and involving $(\frac{1}{2})\frac{1}{2}$ and $(\frac{1}{2})-\frac{1}{2}$ wave functions. The 4×4 matrix (V_1 and V_2 bands) is of primary interest.

As in Sec. III the problem to be solved in the following:

$$\|V_{ij}^{4\times4}\|F=E\|I\|F, \tag{17}$$

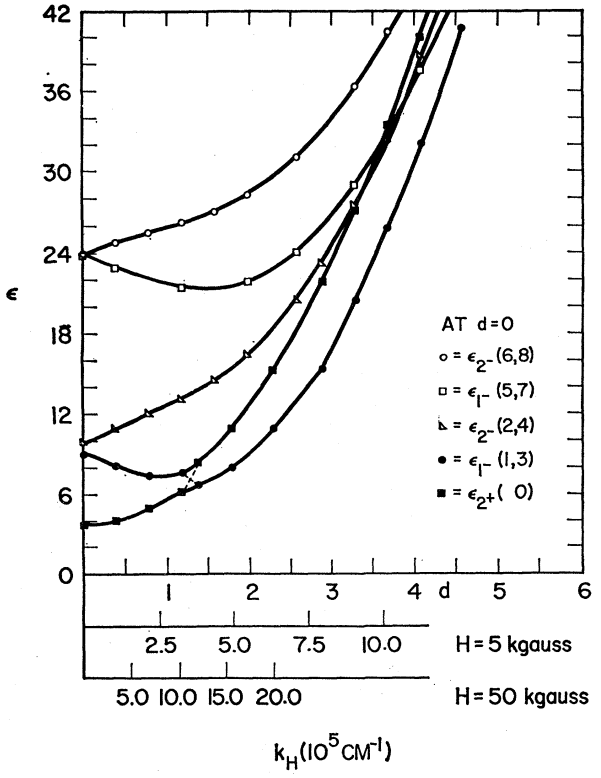

FIG. 4. Energy sub-bands resulting from the solution of a 13×13 determinant for Ge.

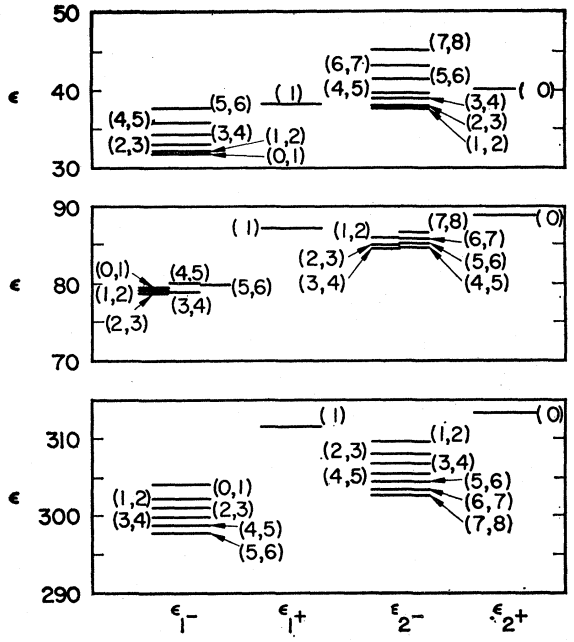

FIG. 5. Landau levels in Ge at $d=4.1$, 6.3 and 12.0 for H in the [001] direction.

where F is assumed to be

$$F=\begin{Vmatrix} \sum_i a_i f_i \\ \sum_j b_j f_j \\ \sum_k c_k f_k \\ \sum_l g_l f_l \end{Vmatrix}. \tag{18}$$

The assumption of $\delta=0$ leads to the substitutions $j=i+2$, $k=i+1$, $l=i+3$, which results in sets of four equations for each i. In the case of $\delta\neq 0$ one has a system determinant similar in character to (16) which also decouples into four independent determinants but with 4×4 basic blocks.

The solutions for Ge are obtained by solving determinants of the order of $n+4$ if the first n energy eigenvalues are required. The eigenvalues for Ge thus computed were compared to the "correct" ones given in Sec. III at $H=20$ kgauss. The deviations ranged from 0.05% to 3.8% and increased with the energy of the eigenvalue. However, for the levels considered, the errors introduced by decoupling the 4×4 and the 2×2 matrices seem to be sufficiently small to make the approximation an excellent one. The wave function expansion coefficients have also been computed in this case[17] and were found to agree quite closely with the values obtained by methods of Sec. III.

Calculations were also performed using Goodman's parameters. The results were found to agree very well (within 1% or better) with Goodman's results even though he used the first-order perturbation theory to introduce the δ terms. The only levels to show marked disagreement ($\sim 10\%$) with Goodman's values were the $\epsilon_1{}^+(\ 0)$ and the $\epsilon_2{}^+(\ 0)$ levels. This may be due to the fact that the low-lying levels couple rather strongly to the other levels, making the perturbation treatment inadequate.

Similar calculations have been performed for Si. Here the deviations from the eigenvalues given in Sec. III range from $\sim 0.15\%$ to $\sim 3.0\%$ at 10 kgauss and from $\sim 1.2\%$ to $\sim 15\%$ at 50 kgauss. The eigenfunctions were found to be quite appreciably in error compared with the correct ones at 50 kgauss, but were not as bad when compared to the 5 kgauss eigenfunctions. The decoupling approximation may therefore be assumed to be satisfactory for low magnetic fields (below ~ 10 kgauss). For purposes of the present computation it is especially well justified, since the l, μ, ν, and κ parameters for Si are not very accurately known at the present time. However, a more accurate calculation for Si involving careful quantitative comparisons with experiments should probably use the 6×6 matrix operator given by (13).

B. Landau Levels as Function of k_H in the Valence Band of Ge

To illustrate the general behavior of the Landau levels the solutions of one of the four determinants discussed above are plotted in Fig. 4. The following important features should be observed. The heavy hole

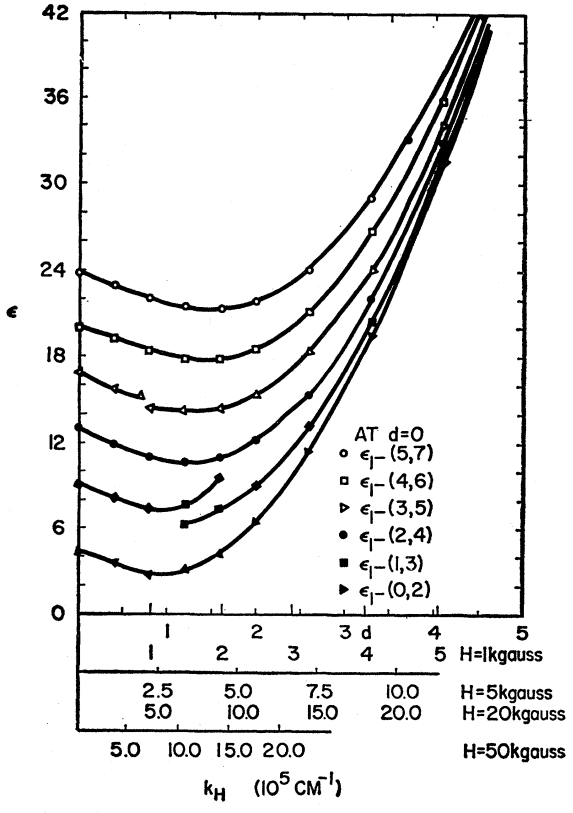

FIG. 6. Energy sub-bands belonging to the $\epsilon_1{}^-$ ladder in Ge for H in the [001] direction.

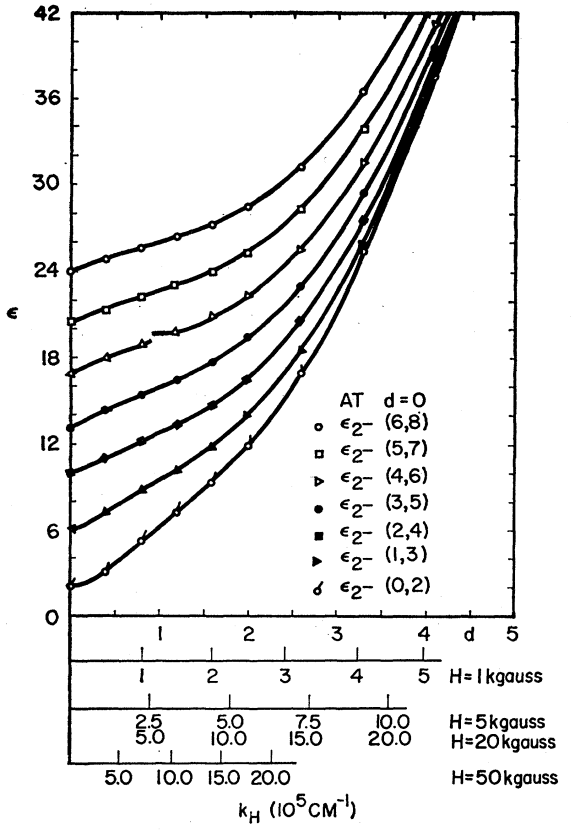

FIG. 7. Energy sub-bands belonging to the ϵ_2^- ladder in Ge for H in the [001] direction.

levels seem to occur in pairs consisting of an ϵ_1^- $(n, n+2)$ level and an ϵ_2^- $(n+1, n+3)$ level. The separation between these levels at $d=0$ decreases as n increases. One of the levels, the ϵ_1^- level, has a curvature corresponding to negative mass in the k_H direction near $d=0$, reaches a minimum at some finite value of d, and soon acquires the same curvature as the ϵ_2^- member of the pair. The higher pairs seem to have smaller average curvatures than the lower ones and thus crossing of the levels occurs. Beyond the crossover, the cyclotron resonance effective mass is "negative." The crossing over, however, is very gradual and occurs at relatively high values of d (see Fig. 5). Duncan and Rosenblum[23] deduced from semiclassical arguments the possible existence of such "crossing over" while attempting to explain the experimental results of Dousmanis *et al.*[24]

The presence of the δ terms causes appreciable interaction between the levels in some cases as is illustrated by the $\epsilon_2^+(0)$ and the $\epsilon_1^-(1,3)$ levels in Fig. 4. In general, coupling between the heavy and the light hole levels seems to decrease as d increases and as the quantum numbers associated with them increase.

The character of the energy levels changes as d increases. The main change is in the leading coefficients in the eigenfunction expansions according to the following rule:

	Leading coefficients $d=0$		d large	
ϵ_1 levels	a_i	b_{i+2}	a_i	c_{i+1}
ϵ_2 levels	c_i	g_{i+2}	b_{i+1}	g_{i+2}

It should be noted that mixing occurs rather rapidly as a function of d.

Although when $d\neq 0$ transitions can occur between all four ladders with relatively high dgree of probability in some cases, it is still convenient to classify the various levels and plot them according to the ladders. This has been done for the heavy holes in Figs. 6 and 7. In general, it can be said that the first-order transitions take place between the adjoining levels.

It should be noted that, judging by the curvatures of the $\epsilon_1^+(0)$ and the $\epsilon_2^+(0)$ levels, their effective mass is much larger than that of the light holes, although they are assigned to the light hole ladders by Luttinger.[2]

C. Landau Levels as Functions of k_H in the Valence Band of Si

Qualitatively, the behavior of the Landau levels in the valence band of Si is similar to that in Ge. However, the couplings between levels are much stronger and therefore the levels are so strongly mixed—especially

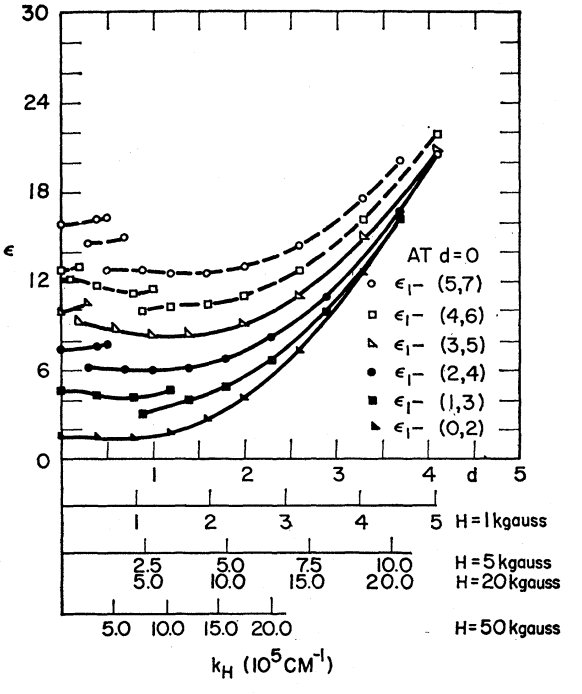

FIG. 8. Energy sub-bands belonging to the ϵ_1^- ladder in Si for H in the [001] direction.

[23] R. C. Duncan, Jr. and B. Rosenblum, Bull. Am. Phys. Soc. 5, 177 (1960). B. Rosenblum and R. C. Duncan, Jr., in the Proceedings of the Prague International Conference on Semiconductor Physics (Czechoslovakian Academy of Science, Prague, 1961).

[24] G. C. Dousmanis, R. C. Duncan, Jr., J. J. Thomas, and R. C. Williams, Phys. Rev. Letters 1, 404 (1958).

at low values of d and low quantum numbers, that the general pattern discussed in the preceding section is not always easily recognizable. This accounts for the rather confused appearance of the heavy hole ladder plots in Figs. 8 and 9. Here the levels at finite values of d were identified as belonging to a certain ladder defined by the levels of ($d=0$) by inspecting the coefficients in the eigenfunction expansions. As is evident from the plots, the levels assume a more or less "normal" character as d increases.

Characteristic determinants for the case of magnetic field in the [101] and the [111] directions have also been derived.[17] They were found to have the same general nature as the determinants already considered although the coupling terms were found to depend on d, the normalized momentum in the direction of the magnetic field. For the [111] case the nature of the determinant indicated allowed transition between levels in all four "ladders" even at $d=0$.

V. SUMMARY

The following are considered to be some of the most important results of the present calculations:

(1) The hole effective mass is found to increase with the magnetic field. Although this effect is fairly small in Ge, it is quite considerable in Si. It must be noted that the change in the eigenfunctions and the level spacings are not the same for all levels and thus a variation in the magnetic field will not only shift the spectrum but may alter it considerably.

(2) Mixing between the Landau levels even at $k_H=0$ is considerable, especially in Si. This leads to a prediction of new transitions among them some of "negative mass" type.

(3) ϵ_1^- levels in both Si and Ge are found to have negative curvatures near $k_H=0$.

(4) The character of the eigenfunctions corresponding to various levels changes as k_H increases.

(5) At relatively high k_H gradual "crossing" or reordering of the heavy hole Landau levels takes place. The transitions past the "crossing" point have "negative mass" character.

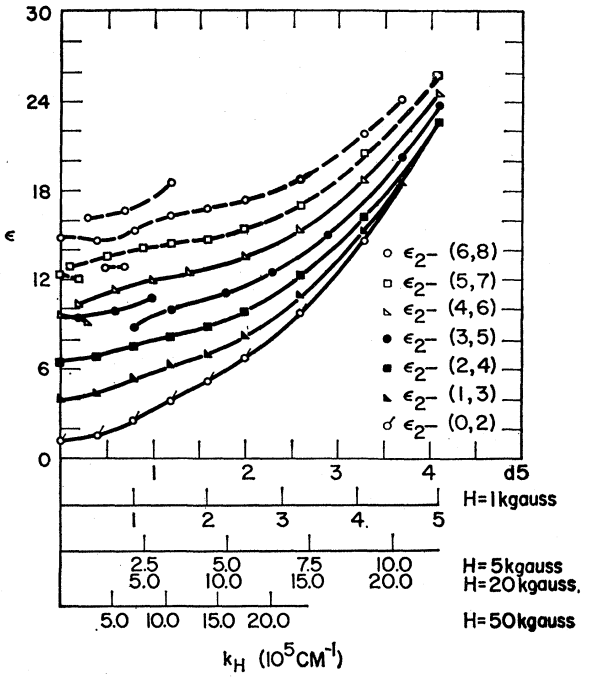

FIG. 9. Energy sub-bands belonging to the ϵ_2^- ladder in Si for H in the [001] direction.

Several of these results are pertinent to some of the proposals made in recent years[22,25] for practical utilization of the Landau levels in semiconductors.[17]

ACKNOWLEDGMENTS

The author would like to thank Professor R. W. Gould for his encouragement and help in the course of this work. He is indebted to Dr. George Birnbaum, Dr. E. O. Kane, Dr. B. Lax, Dr. H. Krömer, and Dr. H. J. Zeiger for stimulating discussions. Thanks are extended to Hughes Aircraft Company for performing the machine computations.

---

[25] B. Lax, *Quantum Electronics—A Symposium*, edited C. H. Townes (Columbia University Press, New York, 1960), p. 428.