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Spin-Orbit Coupling Effects in Zinc Blende Structures*

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Character tables for the "group of the wave vector" at certain points of symmetry in the Brillouin zone are given. The additional degeneracies due to time reversal symmetry are indicated. The form of energy *vs* wave vector at these points of symmetry is derived. A possible reason for the complications which may make a simple effective mass concept invalid for some crystals of this type structure will be presented.

THE effect of symmetry on the energy band structures of crystals of the zinc blende type can be readily derived using the machinery developed by Bouckaert, Smoluchowski, and Wigner[1] and Elliott.[2] Recent extensive studies of the semiconductor properties[3] of InSb, which has the zinc blende structure, and preliminary cyclotron resonance investigations[4] have indicated a need for a more thorough understanding of the possible energy band structures of a zinc blende type crystal.

A zinc blende structure consists of two interpenetrating face centered cubic lattices; each f.c.c. may be considered a sublattice. The two sublattices are displaced by one quarter of a body diagonal and each consists entirely of one species of atom. If the two sublattices are identical, one has a diamond structure. The symmetry properties of diamond are fully discussed in reference 2.

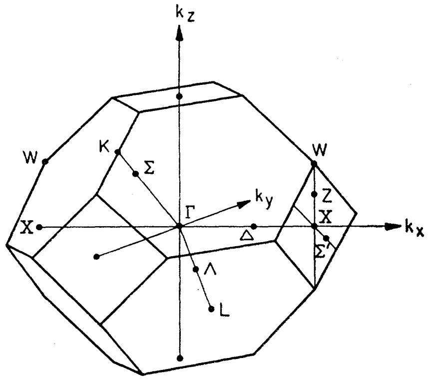

Fig. 1. The first Brillouin zone for a face centered cubic, diamond, and zinc blende structure. Points and lines of symmetry are indicated using the notation of reference 1.

The zinc blende structure has the space group symmetry $F\bar{4}3m$ or T_d^2. There are no glide planes or screw axes, so the group of any wave vector **k** has only simple operations. The first Brillouin zone is the well-known truncated octahedron shown in Fig. 1. The character tables for the group of the wave vector **k** for certain points of symmetry in the Brillouin zone are given in Tables I through VI. When the spin is included in the problem only the double representations occur (i.e., representations for which a 360° rotation, $\bar{E}$, changes the sign of the wave function). The effect of including spin in the problem is to form wave functions of a spatial function times a spin function which will transform[5] as $D_{\frac{1}{2}}$. The total wave function will then transform as the direct product of a single group representation with $D_{\frac{1}{2}}$. This direct product then can be decomposed in terms of representations of the double group. If more than one representation of the double group occurs in the decomposition of the direct product, a spin-orbit splitting of the level is indicated. A table of the direct products of the single group representations with $D_{\frac{1}{2}}$ is included with each character table. The compatibility relations for certain lines of symmetry are given in Table VII. These relations give the splitting of the degeneracies as one proceeds along the symmetry axes. The extra degeneracies due to time reversal symmetry can be found using the standard test due to Herring[6] and Eliott.[2] The extra degeneracies are indicated in each table.

The principal difference from the diamond structure is the lack of inversion symmetry for the point groups in the zinc blende structure. Without inversion symmetry one still has the result from Kramers' theorem[7] that $E(\mathbf{k})=E(-\mathbf{k})$, but now the periodic part of the Bloch functions no longer satisfies the condition $u_{-\mathbf{k}}(\mathbf{r})=u_{\mathbf{k}}(-\mathbf{r})$, and hence a twofold degeneracy throughout the Brillouin zone is not required.

The one electron Schrödinger equation for the

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[1] Bouckaert, Smoluchowski, and Wigner, Phys. Rev. **50**, 58 (1936).

[2] R. J. Elliott, Phys. Rev. **96**, 280 (1954).

[3] H. Welker, Z. Naturforsch. **7a**, 744 (1952); **8a**, 248 (1953); M. Tanenbaum and H. B. Briggs, Phys. Rev. **91**, 1561 (1953); G. L. Pearson and M. Tanenbaum, Phys. Rev. **90**, 153 (1953); M. Tanenbaum and J. P. Maita, Phys. Rev. **91**, 1009 (1953); H. Weiss, Z. Naturforsch. **8a**, 463 (1953); O. Madelung and H. Weiss, Z. Naturforsch. **9a**, 527 (1954).

[4] Dresselhaus, Kip, Kittel, and Wagoner, Phys. Rev. **98**, 556 (1955).

[5] E. Wigner, *Gruppentheorie* (J. W. Edwards, Michigan, 1944), p. 245.

[6] C. Herring, Phys. Rev. **52**, 361 (1937).

[7] This theorem states that in the absence of magnetic fields $\Psi_{\mathbf{k}}$ and $i\sigma_y\Psi_{\mathbf{k}}^*$ are solutions of the Hamiltonian for the same energy. The second solution belongs to wave vector $-\mathbf{k}$, and hence we have two solutions at **k** and $-\mathbf{k}$ with the same energy.

TABLE I. Character table of the double group of Γ; $\mathbf{k}=(000)$.

Γ	E	$\bar{E}$	$6C_4^2$	$8C_3$	$8\bar{C}_3$	$6I\times C_4$	$6I\times\bar{C}_4$	$12I\times C_2$
Γ_1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	-1	-1	-1
Γ_3	2	2	2	-1	-1	0	0	0
$\Gamma_4(x,y,z)$	3	3	-1	0	0	-1	-1	1
Γ_5	3	3	-1	0	0	1	1	-1
Γ_6	2	-2	0	1	-1	$\sqrt{2}$	$-\sqrt{2}$	0
Γ_7	2	-2	0	1	-1	$-\sqrt{2}$	$\sqrt{2}$	0
Γ_8	4	-4	0	-1	1	0	0	0

Γ_i	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5
$\Gamma_i\times D_{\frac{1}{2}}$	Γ_6	Γ_7	Γ_8	$\Gamma_7+\Gamma_8$	$\Gamma_6+\Gamma_8$

Selection rules

Γ_i	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8
$\Gamma_i\times\Gamma_4$	Γ_4	Γ_5	$\Gamma_4+\Gamma_5$	$\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5$	$\Gamma_2+\Gamma_3+\Gamma_4+\Gamma_5$	$\Gamma_7+\Gamma_8$	$\Gamma_6+\Gamma_8$	$\Gamma_6+\Gamma_7+2\Gamma_8$

problem with spin-orbit coupling is

$$\left[\frac{p^2}{2m}+V+\frac{\hbar}{4m^2c^2}(\nabla V\times\mathbf{p})\cdot\boldsymbol{\sigma}\right]\Psi_{\mathbf{k}}=E_{\mathbf{k}}\Psi_{\mathbf{k}}. \tag{1}$$

The translational symmetry of the lattice requires that the wave functions be of the Bloch form, i.e.,

$$\Psi_{\mathbf{k}}=u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}},$$

where $u(\mathbf{r})$ is periodic and satisfies the equation

$$\left[\frac{\mathbf{p}^2}{2m}+V+\frac{\hbar}{4m^2c^2}(\nabla V\times\mathbf{p})\cdot\boldsymbol{\sigma}\right]u_{\mathbf{k}} +\hbar\mathbf{k}\cdot\left(\frac{\mathbf{p}}{m}+\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\times\nabla V\right)u_{\mathbf{k}}=\left(E_{\mathbf{k}}-\frac{\hbar^2k^2}{2m}\right)u_{\mathbf{k}}. \tag{2}$$

The equation for $\mathbf{k}+\mathbf{K}$ is

$$\left[\frac{\mathbf{p}^2}{2m}+V+\frac{\hbar}{4m^2c^2}(\nabla V\times\mathbf{p})\cdot\boldsymbol{\sigma}\right]u_{\mathbf{k}+\mathbf{K}} +\hbar\mathbf{k}\cdot\left(\frac{\mathbf{p}}{m}+\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\times\nabla V\right)u_{\mathbf{k}+\mathbf{K}} +\hbar\mathbf{K}\cdot\left(\frac{\mathbf{p}}{m}+\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\times\nabla V\right)u_{\mathbf{k}+\mathbf{K}} =\left(E_{\mathbf{k}+\mathbf{K}}-\frac{\hbar^2(\mathbf{k}+\mathbf{K})^2}{2m}\right)u_{\mathbf{k}+\mathbf{K}}. \tag{3}$$

Treating the term

$$\mathcal{H}'=\hbar\mathbf{K}\cdot\left(\frac{\mathbf{p}}{m}+\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\times\nabla V\right)$$

as a perturbation, the energy at $\mathbf{k}+\mathbf{K}$ for a nondegenerate level is

$$E_{\mathbf{k}+\mathbf{K}}=E_{\mathbf{k}}+\frac{\hbar^2k^2}{2m}+(\Psi_{\mathbf{k}}|\,\mathcal{H}'\,|\Psi_{\mathbf{k}})+\cdots. \tag{4}$$

Degenerate levels are treated by solving the customary secular determinants.

In working out the matrix elements for perturbation theory, it is helpful to use group theoretical selection rules. Due to the scalar character of the Hamiltonian,

TABLE II. Character table of the double group of Δ; $\mathbf{k}=k[100]$.

Δ	E	$\bar{E}$	$2C_4^2$	$2I\times C_2$	$2I\times C_2'$
$\Delta_1(x)$	1	1	1	1	1
Δ_2	1	1	1	-1	-1
$\Delta_3(y+z)$	1	1	-1	-1	1
$\Delta_4(y-z)$	1	1	-1	1	-1
Δ_5	2	-2	0	0	0

$\Delta_i\times D_{\frac{1}{2}}=\Delta_5,\quad i=1,2,3,4$

Δ_3 and Δ_4 are degenerate by time reversal

Selection rules

Δ_i	Δ_1	Δ_2	Δ_3	Δ_4	Δ_5
$\Delta_i\times\Delta_1$	Δ_1	Δ_2	Δ_3	Δ_4	Δ_5
$\Delta_i\times\Delta_3$	Δ_3	Δ_4	Δ_1	Δ_2	Δ_5
$\Delta_i\times\Delta_4$	Δ_4	Δ_3	Δ_2	Δ_1	Δ_5

TABLE III. Character table of the double group of Λ or L; $\mathbf{k}=(k/\sqrt{3})[111]$ or $(\pi/a)(111)$.

Λ,L	E	$\bar{E}$	$2C_3$	$2\bar{C}_3$	$3I\times C_2$	$3I\times\bar{C}_2$
$\Lambda_1(x+y+z)$	1	1	1	1	1	1
Λ_2	1	1	1	1	-1	-1
$(x+\omega y+\omega^2z)$ $\Lambda_3(x+\omega^2y+\omega z)$ $(\omega^3=1)$	2	2	-1	-1	0	0
Λ_4	1	-1	-1	1	i	$-i$
Λ_5	1	-1	-1	1	$-i$	i
Λ_6	2	-2	1	-1	0	0

L_4 and L_5 are degenerate by time reversal
(Λ_4 and Λ_5 are nondegenerate)

Λ_i	Λ_1	Λ_2	Λ_3
$\Lambda_i\times D_{\frac{1}{2}}$	Λ_6	Λ_6	$\Lambda_4+\Lambda_5+\Lambda_6$

Selection rules

Λ_i	Λ_1	Λ_2	Λ_3	Λ_4	Λ_5	Λ_6
$\Lambda_i\times\Lambda_1$	Λ_1	Λ_2	Λ_3	Λ_4	Λ_5	Λ_6
$\Lambda_i\times\Lambda_3$	Λ_3	Λ_3	$\Lambda_1+\Lambda_2+\Lambda_3$	Λ_6	Λ_6	$\Lambda_4+\Lambda_5+\Lambda_6$

TABLE IV. Character table of the double group of Σ or K; $\mathbf{k}=(k/\sqrt{2})[110]$ or $(3\pi/2a)(110)$.

Σ,K	E	$\bar{E}$	$I\times C_2$	$I\times\bar{C}_2$
$\Sigma_1(z)(x+y)$	1	1	1	1
$\Sigma_2(x-y)$	1	1	-1	-1
Σ_3	1	-1	i	$-i$
Σ_4	1	-1	$-i$	i

$$\Sigma_i\times D_{\frac{1}{2}}=\Sigma_3+\Sigma_4,\quad i=1,2$$

Selection rules

Σ_i	Σ_1	Σ_2	Σ_3	Σ_4
$\Sigma_i\times\Sigma_1$	Σ_1	Σ_2	Σ_3	Σ_4
$\Sigma_i\times\Sigma_2$	Σ_2	Σ_1	Σ_4	Σ_3

TABLE V. Character table of the double group of X; $\mathbf{k}=(2\pi/a)(100)$.

X	E	$\bar{E}$	$4C_{4\perp}^2$	$2C_{4\parallel}^2$	$2I\times C_{4\parallel}$	$2I\times\bar{C}_{4\parallel}$	$4I\times C_2$
X_1	1	1	1	1	1	1	1
X_2	1	1	1	1	-1	-1	-1
$X_3(x)$	1	1	-1	1	-1	-1	1
X_4	1	1	-1	1	1	1	-1
$X_5(y,z)$	2	2	0	-2	0	0	0
X_6	2	-2	0	0	$\sqrt{2}$	$-\sqrt{2}$	0
X_7	2	-2	0	0	$-\sqrt{2}$	$\sqrt{2}$	0

X_i	X_1	X_2	X_3	X_4	X_5
$X_i\times D_{\frac{1}{2}}$	X_6	X_7	X_7	X_6	X_6+X_7

Selection rules

X_i	X_1	X_2	X_3	X_4	X_5	X_6	X_7
$X_i\times X_3$	X_3	X_4	X_1	X_2	X_5	X_7	X_6
$X_i\times X_5$	X_5	X_5	X_5	X_5	$X_1+X_2+X_3+X_4$	X_6+X_7	X_6+X_7

TABLE VI. Character table of the double group of W; $\mathbf{k}=(2\pi/a)(0\,\frac{1}{2}\,1)$.

W	E	$\bar{E}$	C_4^2	$\bar{C}_4^2$	$I\times C_4$	$I\times\bar{C}_4$	$I\times C_4'$	$I\times\bar{C}_4'$
W_1	1	1	1	1	1	1	1	1
$W_2(x)$	1	1	1	1	-1	-1	-1	-1
$W_3(y+iz)$	1	1	-1	-1	i	i	$-i$	$-i$
$W_4(y-iz)$	1	1	-1	-1	$-i$	$-i$	i	i
W_5	1	-1	$-i$	i	$i\sqrt{i}$	$-i\sqrt{i}$	$\sqrt{i}$	$-\sqrt{i}$
W_6	1	-1	i	$-i$	$\sqrt{i}$	$-\sqrt{i}$	$i\sqrt{i}$	$-i\sqrt{i}$
W_7	1	-1	$-i$	i	$-i\sqrt{i}$	$i\sqrt{i}$	$-\sqrt{i}$	$\sqrt{i}$
W_8	1	-1	i	$-i$	$-\sqrt{i}$	$\sqrt{i}$	$-i\sqrt{i}$	$i\sqrt{i}$

W_i	W_1	W_2	W_3	W_4
$W_i\times D_{\frac{1}{2}}$	W_5+W_6	W_7+W_8	W_6+W_7	W_5+W_8

Selection rules

W_i	W_1	W_2	W_3	W_4	W_5	W_6	W_7	W_8
$W_i\times W_2$	W_2	W_1	W_4	W_3	W_7	W_8	W_5	W_6
$W_i\times W_3$	W_3	W_4	W_2	W_1	W_8	W_5	W_6	W_7
$W_i\times W_4$	W_4	W_3	W_1	W_2	W_6	W_7	W_8	W_5

the term

$$\mathbf{R}=\frac{\hbar}{m}\left(\mathbf{p}+\frac{\hbar}{4mc^2}\boldsymbol{\sigma}\times\nabla V\right)$$

transforms as a vector. Matrix elements of the type $(\Psi_{\mathbf{k}}^i|R_x|\Psi_{\mathbf{k}}^j)$ will vanish unless the direct product $\Gamma_i\times\Gamma_R\times\Gamma_j$ contains the unit representation, where Γ_i is the irreducible representation of wave vector $\mathbf{k}$ according to which $\Psi_{\mathbf{k}}^i$ transforms and Γ_R is the representation according to which a vector transforms. Another way of viewing the selection rules is that the only representations that mix with Γ_i under the perturbation $\mathcal{H}'$ are those contained in the decomposition of the direct product $\Gamma_i\times\Gamma_R$. Tables I to VII also give the decomposition of these direct products for the points of symmetry in the Brillouin zone. For convenience the combinations of vector components which transform as a given irreducible representation are indicated in the character tables.

In order to give a more complete treatment of the point Γ, the bases shown in Table VIII may be selected for the irreducible representations.[8] In this notation the spin-orbit splittings at $\mathbf{k}=0$ are, for $\Gamma_4^{\frac{3}{2}}-\Gamma_4^{\frac{1}{2}}$,

$$\Delta E_{S0}=\frac{3\hbar}{4m^2c^2}i\left(\delta_1\left|\frac{\partial V}{\partial x}p_y-\frac{\partial V}{\partial y}p_x\right|\delta_2\right);\tag{5}$$

and for $\Gamma_5^{\frac{3}{2}}-\Gamma_5^{\frac{1}{2}}$,

$$\Delta E_{S0}=\frac{3\hbar}{4m^2c^2}i\left(\epsilon_1\left|\frac{\partial V}{\partial x}p_y-\frac{\partial V}{\partial y}p_x\right|\epsilon_2\right).\tag{6}$$

Selection rules suggest that the representations Γ_4 and Γ_5 have first-order matrix elements with $\mathcal{H}'$ and hence finite slopes. Actually all first-order matrix elements with $\mathbf{p}$ vanish due to time reversal symmetry. For example, $(\delta_1|p_y|\delta_3)=(\delta_3|p_y|\delta_1)$ by a reflection in the (101) plane, but by partial integration $(\delta_1|p_y|\delta_3)=-(\delta_3|p_y|\delta_1)$, as the δ_i's are real if the Hamiltonian has time-inversion symmetry; hence all such matrix elements vanish. This argument only holds if all δ_i's are from the same degenerate Γ_4 level.

When spin-orbit interaction is included in the perturbation (i.e., the $\boldsymbol{\sigma}\times\nabla V$ term is not neglected), the energy to first order in k for a Γ_8 level is given by the

TABLE VII. Compatibility relations.

$\Gamma_1\rightarrow\Delta_1$
$\Gamma_2\rightarrow\Delta_2$
$\Gamma_3\rightarrow\Delta_1+\Delta_2$
$\Gamma_4\rightarrow\Delta_1+(\Delta_3+\Delta_4)$
$\Gamma_5\rightarrow\Delta_2+(\Delta_3+\Delta_4)$
$\Gamma_6,\Gamma_7,\Gamma_8\rightarrow\Delta_5$

$X_1\rightarrow\Delta_1$
$X_2\rightarrow\Delta_2$
$X_3\rightarrow\Delta_1$
$X_4\rightarrow\Delta_2$
$X_5\rightarrow(\Delta_3+\Delta_4)$
$X_6,X_7\rightarrow\Delta_5$

$\Gamma_1\rightarrow\Lambda_1$
$\Gamma_2\rightarrow\Lambda_2$
$\Gamma_3\rightarrow\Lambda_3$
$\Gamma_4\rightarrow\Lambda_1+\Lambda_3$
$\Gamma_5\rightarrow\Lambda_2+\Lambda_3$
$\Gamma_6,\Gamma_7\rightarrow\Lambda_6$
$\Gamma_8\rightarrow\Lambda_4+\Lambda_5+\Lambda_6$

$(L_4+L_5)\rightarrow\Lambda_4+\Lambda_5$

Time reversal degenerate representations are indicated by parentheses.

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[8] See F. von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).

secular determinant

$$\begin{vmatrix} -\lambda & (i/2)Ck_+ & -Ck_z & -(i\sqrt{3}/2)Ck_- \\ -(i/2)Ck_- & -\lambda & -(i\sqrt{3}/2)Ck_+ & Ck_z \\ -Ck_z & (i\sqrt{3}/2)Ck_- & -\lambda & (i/2)Ck_+ \\ (i\sqrt{3}/2)Ck_+ & Ck_z & -(i/2)Ck_- & -\lambda \end{vmatrix} = 0, \tag{7}$$

where $\lambda = E_{\mathrm{k}} - (\hbar^2 k^2/2m)$, which has solutions

$$\begin{aligned} \lambda &= \pm C\{k^2 + [3(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)]^{\frac{1}{2}}\}^{\frac{1}{2}}, \\ \lambda &= \pm C\{k^2 - [3(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)]^{\frac{1}{2}}\}^{\frac{1}{2}}, \end{aligned} \tag{8}$$

where

$$\begin{aligned} C &= -\frac{1}{2\sqrt{3}}\frac{\hbar^2}{m^2c^2}\left(\delta_1\left|\frac{\partial V}{\partial y}\right|\delta_3\right), \quad \text{for } \Gamma_4^{\frac{3}{2}}, \\ C &= -\frac{1}{2\sqrt{3}}\frac{\hbar^2}{m^2c^2}\left(\epsilon_1\left|\frac{\partial V}{\partial y}\right|\epsilon_3\right), \quad \text{for } \Gamma_5^{\frac{3}{2}}, \\ C &= 0, \quad \text{for } \Gamma_3. \end{aligned} \tag{9}$$

The first-order energies are shown in Fig. 2 for the [100], [111], and [110] directions. In polar coordinates, $k_x = k\sin\theta\cos\phi$, $k_y = k\sin\theta\sin\phi$, $k_z = k\cos\theta$, Eqs. (8) become

$$\lambda = \pm Ck[1 \pm (3)^{\frac{1}{2}}\sin\theta(\cos^2\theta + \tfrac{1}{4}\sin^2\theta\sin^2 2\phi)^{\frac{1}{2}}]^{\frac{1}{2}}. \tag{10}$$

Figure 3 shows the four first-order energies given by Eq. (10) for constant k plotted against the angle θ for wave vectors in a (110) plane ($\phi = \pi/4$). It is interesting to note that the two-dimensional Λ_6 level is the intersection of surfaces which arise from two different representations in a [100] direction. Any large separation of the energy levels which transform as Γ_8 at the center of the zone, as one proceeds toward the edge of the zone, then would entail a rather complex band structure with highly deformed energy surfaces and accidental degeneracies.[9]

Second-order perturbation theory for the Γ_8 level is tractable on the approximation that only first-order terms in $\boldsymbol{\sigma} \times \nabla V$ and second-order terms in $\mathbf{p}$ be considered. The fourth-order equation which results from the 4×4 secular determinant is

$$\begin{aligned} y^4 - 2y^2\Bigg[&\left(\frac{L-M}{3}\right)^2 k^4 + \frac{N^2-(L-M)^2}{3} \\ &\times(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2) + C^2k^2\Bigg] \\ &+ 4yC^2N(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2) + \Bigg[\left(\frac{L-M}{3}\right)^2 k^4 \\ &+ \frac{N^2-(L-M)^2}{3}(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)\Bigg]^2 \\ &+ C^4[k^4 - 3(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)] \\ &+ 2\left(\frac{L-M}{3}\right)^2 C^2(k_x^6 + k_y^6 + k_z^6) \\ &- \left[3\left(\frac{L-M}{3}\right)^2 + \frac{2}{3}N^2\right]C^2k^2(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2) \\ &+ 21\left(\frac{L-M}{3}\right)^2 C^2k_x^2k_y^2k_z^2 = 0, \end{aligned} \tag{11}$$

where L, M, and N are real numbers and can be expressed in terms of sums over the squares of the

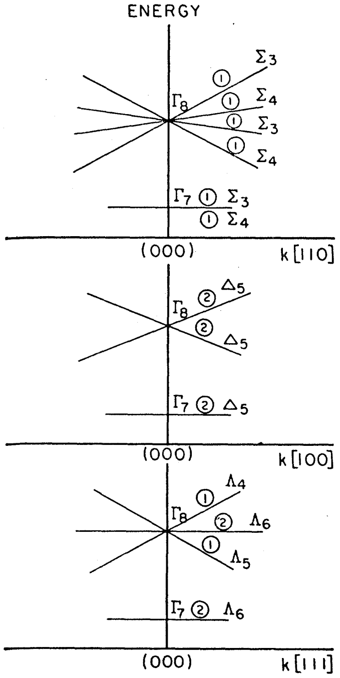

FIG. 2. Plot of energy *vs* wave vector showing the first-order energy for the spin-orbit split Γ_4 or Γ_5 level in [100], [110], and [111] directions. The circled numbers indicate the dimension of the representation.

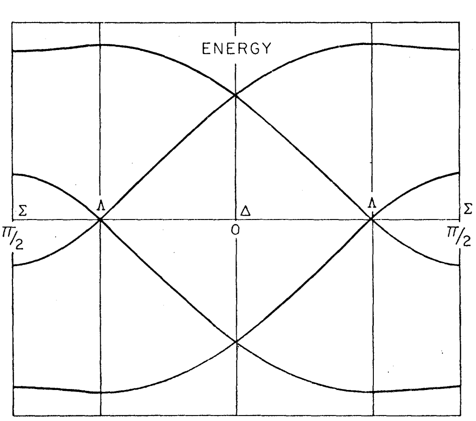

FIG. 3. Cylindrical cross section around the point Γ of a plot of energy *vs* wave vector for wave vectors in a (110) plane.

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[9] C. Herring, Phys. Rev. 52, 365 (1937).

TABLE VIII. Basis functions for the irreducible representations[8] of the double group for the point Γ.

$\Gamma_1,\ \alpha=1$	$\Gamma_6,\ \alpha\vert-\rangle$ $\alpha\vert+\rangle$
$\Gamma_2,\ \beta=[x^4(y^2-z^2)$ $+y^4(z^2-x^2)$ $+z^4(x^2-y^2)]$	$\Gamma_7,\ \beta\vert-\rangle$ $\beta\vert+\rangle$
$\Gamma_3,\ \gamma_1=x^2+\omega y^2+\omega^2z^2$ $\gamma_2=x^2+\omega^2y^2+\omega z^2$ $\omega^3=1$	$\Gamma_8(\Gamma_3),\ \frac{1}{\sqrt2}(\omega^2\gamma_2+\omega\gamma_1)\vert+\rangle$ $-\frac{i}{\sqrt2}(\omega^2\gamma_2-\omega\gamma_1)\vert-\rangle$ $\frac{i}{\sqrt2}(\omega^2\gamma_2-\omega\gamma_1)\vert+\rangle$ $-\frac{1}{\sqrt2}(\omega^2\gamma_2+\omega\gamma_1)\vert-\rangle$
	$\Gamma_7(\Gamma_4^{\frac12}),\ \frac{1}{\sqrt3}[-i(\delta_1-i\delta_2)\vert+\rangle+\delta_3\vert-\rangle]$ $\frac{1}{\sqrt3}[i(\delta_1+i\delta_2)\vert-\rangle-\delta_3\vert+\rangle]$
$\Gamma_4,\ \delta_1=x$ $\delta_2=y$ $\delta_3=z$	$\Gamma_8(\Gamma_4^{\frac32}),\ \frac{i}{\sqrt2}(\delta_1-i\delta_2)\vert-\rangle$ $\frac{1}{\sqrt6}[i(\delta_1-i\delta_2)\vert+\rangle+2\delta_3\vert-\rangle]$ $\frac{1}{\sqrt6}[i(\delta_1+i\delta_2)\vert-\rangle+2\delta_3\vert+\rangle]$ $\frac{i}{\sqrt2}(\delta_1+i\delta_2)\vert+\rangle$
	$\Gamma_6(\Gamma_5^{\frac12}),\ \frac{1}{\sqrt3}[-i(\epsilon_1-i\epsilon_2)\vert+\rangle+\epsilon_3\vert-\rangle]$ $\frac{1}{\sqrt3}[i(\epsilon_1+i\epsilon_2)\vert-\rangle-\epsilon_3\vert+>]$
$\Gamma_5,\ \epsilon_1=x(y^2-z^2)$ $\epsilon_2=y(z^2-x^2)$ $\epsilon_3=z(x^2-y^2)$	$\Gamma_8(\Gamma_5^{\frac32}),\ \frac{i}{\sqrt2}(\epsilon_1-i\epsilon_2)\vert-\rangle$ $\frac{1}{\sqrt6}[i(\epsilon_1-i\epsilon_2)\vert+\rangle+2\epsilon_3\vert->]$ $\frac{1}{\sqrt6}[i(\epsilon_1+i\epsilon_2)\vert-\rangle+2\epsilon_3\vert+\rangle]$ $\frac{i}{\sqrt2}(\epsilon_1+i\epsilon_2)\vert+\rangle$

absolute value of matrix elements,[10] and

$$E_{\mathbf{k}}=\frac{\hbar^2}{2m}k^2+\left(\frac{L+2M}{3}\right)k^2+y.$$

For a general $\mathbf{k}$, Eq. (11) has four real roots; for

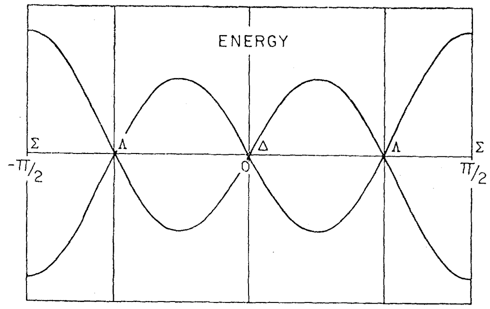

FIG. 4. A cylindrical cross section around the point Γ of a plot of energy *vs* wave vector for wave vectors in a (110) plane showing the third order splitting of the Γ_6 or Γ_7 surface.

$\mathbf{k}=k[100]$ the energy eigenvalues are

$$E_{k[100]}=\frac{\hbar^2}{2m}k^2+\left(\frac{L+2M}{3}\right)k^2\pm\left[\left(\frac{L-M}{3}\right)^2k^4+C^2k^2\right]^{\frac12} \tag{12}$$

where each root is double; and for $\mathbf{k}=(k/\sqrt3)[111]$

$$E_{[k/\sqrt3][111]}=\frac{\hbar^2}{2m}k^2+\left(\frac{L+2M}{3}\right)k^2+\begin{cases}\dfrac{|N|}{3}k^2 & \text{(double)}\\[2mm] -\dfrac{|N|}{3}k^2+\sqrt2Ck\\[2mm] -\dfrac{|N|}{3}k^2-\sqrt2Ck.\end{cases} \tag{13}$$

An estimate of the magnitude of the constant C may be obtained if one considers the zinc blende structure as a deformed diamond type structure.[11,12] Here we will consider $V'=V-V_i$ as a perturbation, where V_i is a diamond type potential with inversion symmetry and V is the actual zinc blende type potential. The correct first-order spatial wave functions for a zinc blende structure are then given by the following equations.

For Γ_1,

$$\alpha=\alpha^++\sum_{i=\Gamma_1^+}\frac{(\alpha_i^+|V'|\alpha^+)}{E_0-E_i}\alpha_i^++\sum_{i=\Gamma_2^-}\frac{(\beta_i^-|V'|\alpha^+)}{E_0-E_i}\beta_i^-,$$
$$\alpha=\beta^-+\sum_{i=\Gamma_1^+}\frac{(\alpha_i^+|V'|\beta^-)}{E_0-E_i}\alpha_i^++\sum_{i=\Gamma_2^-}\frac{(\beta_i^-|V'|\beta^-)}{E_0-E_i}\beta_i^-. \tag{14}$$

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[10] Dresselhaus, Kip, and Kittel, Phys. Rev. **98**, 368 (1955).

[11] For a more detailed treatment see the paper by F. Herman (to be published).

[12] R. H. Parmenter, Phys. Rev. **100**, 573 (1955).

For Γ_2,

$$\beta=\alpha^-+\sum_{i=\Gamma_1^-}\frac{(\alpha_i^-|V'|\alpha^-)}{E_0-E_i}\alpha_i^-+\sum_{i=\Gamma_2^+}\frac{(\beta_i^+|V'|\alpha^-)}{E_0-E_i}\beta_i^+,$$
$$\beta=\beta^++\sum_{i=\Gamma_1^-}\frac{(\alpha_i^-|V'|\beta^+)}{E_0-E_i}\alpha_i^-+\sum_{i=\Gamma_2^+}\frac{(\beta_i^+|V'|\beta^+)}{E_0-E_i}\beta_i^+. \tag{15}$$

For Γ_3,

$$\gamma_K=\gamma_K^++\sum_{i=\Gamma_{12}^+}\frac{(\gamma_{Ki}^+|V'|\gamma_K^+)}{E_0-E_i}\gamma_{Ki}^+ +\sum_{i=\Gamma_{12}^-}\frac{(\gamma_{Ki}^-|V'|\gamma_K^+)}{E_0-E_i}\gamma_{Ki}^-,$$
$$\gamma_K=\gamma_K^-+\sum_{i=\Gamma_{12}^+}\frac{(\gamma_{Ki}^+|V'|\gamma_K^-)}{E_0-E_i}\gamma_{Ki}^+ +\sum_{i=\Gamma_{12}^-}\frac{(\gamma_{Ki}^-|V'|\gamma_K^-)}{E_0-E_i}\gamma_{Ki}^-. \tag{16}$$

For Γ_4,

$$\delta_K=\delta_K^-+\sum_{i=\Gamma_{15}^-}\frac{(\delta_{Ki}^-|V'|\delta_K^-)}{E_0-E_i}\delta_{Ki}^- +\sum_{i=\Gamma_{25}^+}\frac{(\epsilon_{Ki}^+|V'|\delta_K^-)}{E_0-E_i}\epsilon_{Ki}^+,$$
$$\delta_K=\epsilon_K^++\sum_{i=\Gamma_{15}^-}\frac{(\delta_{Ki}^-|V'|\epsilon_K^+)}{E_0-E_i}\delta_{Ki}^- +\sum_{i=\Gamma_{25}^+}\frac{(\epsilon_{Ki}^+|V'|\epsilon_K^+)}{E_0-E_i}\epsilon_{Ki}^+. \tag{17}$$

For Γ_5,

$$\epsilon_K=\delta_K^++\sum_{i=\Gamma_{15}^+}\frac{(\delta_{Ki}^+|V'|\delta_K^+)}{E_0-E_i}\delta_{Ki}^+ +\sum_{i=\Gamma_{25}^-}\frac{(\epsilon_{Ki}^-|V'|\delta_K^+)}{E_0-E_i}\epsilon_{Ki}^-,$$
$$\epsilon_K=\epsilon_K^-+\sum_{i=\Gamma_{15}^+}\frac{(\delta_{Ki}^+|V'|\epsilon_K^-)}{E_0-E_i}\delta_{Ki}^+ +\sum_{i=\Gamma_{25}^-}\frac{(\epsilon_{Ki}^-|V'|\epsilon_K^-)}{E_0-E_i}\epsilon_{Ki}^-, \tag{18}$$

where the cubic harmonics are as defined in reference 8 except that $\gamma_1^+=\gamma_2^{+*}=x^2+\omega y^2+\omega^2z^2$, $(\omega^3=1)$, and the ± superscript is used to denote the parity of the functions.

For the Γ_4 level arising from a diamond type Γ_{25}^+ level

$$C=\frac{1}{\surd 3}\frac{\hbar^2}{m^2c^2}\sum_{i=\Gamma_{15}^-}\frac{(\epsilon_1^+|\partial V_i/\partial y|\delta_{3i}^-)(\delta_{1i}^-|V'|\epsilon_1^+)}{(E_0-E_i)}. \tag{19}$$

To a very rough approximation[10] $V'\sim V_i/Z$ where Z is the atomic number. $C\sim(1/Z)\Delta_{SO}a$, where a is the lattice constant and Δ_{SO} is the spin-orbit splitting at $\mathbf{k}=0$. The first-order energy at the zone edge in a [100] direction is

$$E\sim C\frac{2\pi}{a}\sim 2\pi\frac{\Delta_{SO}}{Z}\sim 0.02 \text{ ev (in InSb).}$$

Hence the splitting due to the first-order terms would be only of the order of 0.02 ev if the slope were linear all the way to the edge of the zone. Actually the second-order terms which should be large due to the small energy gap will turn the surfaces down very rapidly. Using this value for C and the values of L, M, and N from cyclotron resonance experiments on Ge,[10] it would seem from Eq. (11) that near the center of the Brillouin zone the removal of the twofold Kramers degeneracy is at most 10^{-4} ev for holes with thermal energies. Under these circumstances it seems quite likely that a perturbation expansion about the extremum should contain several orders of perturbation theory, and a simple energy surface with effective mass tensor components independent of wave vector would be a very poor approximation.

For the Γ_6 and Γ_7 level the energy to third order in k is given by

$$E=C_0k^2\pm C_1[k^2(k_x^2k_y^2+k_y^2k_z^2+k_z^2k_x^2)-9k_x^2k_y^2k_z^2]^{\frac{1}{2}}. \tag{20}$$

In third order the levels are split in all but the [100] and [111] directions. In polar coordinates Eq. (20) reads

$$E=C_0k^2\pm C_1k^3\sin\theta[1-\sin^2\theta(1+2\sin^2 2\phi) +(9/4)\sin^2 2\phi\sin^4\theta]^{\frac{1}{2}}. \tag{21}$$

Figure 4 shows a plot of energy *vs* θ for constant k and $\phi=\pi/4$ [i.e., $\mathbf{k}$ in a (110) plane]. The surfaces have their maximum separation along <110> axes. In the III–V class of semiconducting compounds like InSb, the high mobility electrons are presumably in a spherically symmetric Γ_6 state.[4] Higher orders in k should not enter until the thermal or Fermi energy for the electrons is of the order of the band splittings at $k=0$. In impure n-type InSb with electron concentrations $\sim 10^{18}/\text{cm}^3$ and a Fermi energy[13] of ~0.2 ev one may be entering into a region where the splitting of the degeneracy for the electrons should be considered.

Perturbation expansions for other points in the Brillouin zone are facilitated by writing the perturbation in a form such that the vector combinations indicated in the character tables appear; these combinations are, for the points Γ, (000), and X, $(2\pi/a)(100)$,

$$\mathcal{H}'=k_xR_x+k_yR_y+k_zR_z; \tag{22}$$

for the point W, $(2\pi/a)(0,\frac{1}{2},1)$,

$$\mathcal{H}'=K_xR_x+\tfrac{1}{2}[(K_y+iK_z)(R_y-iR_z) +(K_y-iK_z)(R_y+iR_z)]; \tag{23}$$

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[13] Hrostowski, Wheatley, and Flood, Phys. Rev. **95**, 1683 (1954).

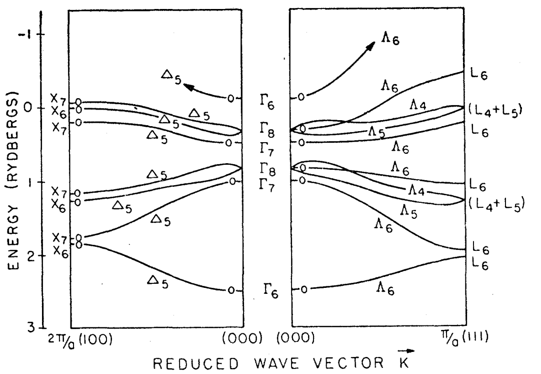

FIG. 5. A schematic drawing of the energy levels for a zinc blende type structure modification of boron nitride based on Herman's calculation for diamond [F. Herman, Phys. Rev. **88**, 1210 (1952); thesis, Columbia University, 1953 (unpublished)]. The spin-orbit splittings are highly exaggerated for the purpose of illustration. The levels marked with an 0 have zero slope along that axis. This figure should be compared with Elliott's Fig. 2. [R. J. Elliott, Phys. Rev. **96**, 266 (1954).]

for the points Λ, $(k/\sqrt{3})(111)$, and L, $(\pi/a)(111)$,

$$\begin{aligned}\mathcal{H}'=\tfrac{1}{3}[&(K_x+K_y+K_z)(R_x+R_y+R_z)\\&+(K_x+\omega K_y+\omega^2K_z)(R_x+\omega^2R_y+\omega R_z)\\&+(K_x+\omega^2K_y+\omega K_z)(R_x+\omega R_y+\omega^2R_z)],\end{aligned}\quad(24)$$

and for the points Σ, $(k/\sqrt{2})(110)$, and Δ, $k(001)$

$$\begin{aligned}\mathcal{H}'=K_zR_z+\tfrac{1}{2}[&(K_x+K_y)(R_x+R_y)\\&+(K_x-K_y)(R_x-R_y)].\end{aligned}\quad(25)$$

Using these perturbations the first-order energies can be written down at sight and are of the following form: for Δ_5, $k(100)$,

$$E=C_2K_x\pm C_3(K_y^2+K_z^2)^{\frac{1}{2}};\quad(26)$$

for Λ_4 and Λ_5, $(k/\sqrt{3})(111)$,

$$E=C_4(K_x+K_y+K_z);\quad(27)$$

for Λ_6,

$$\begin{aligned}E=C_5&(K_x+K_y+K_z)\\&\pm C_6[K^2-(K_xK_y+K_yK_z+K_zK_x)]^{\frac{1}{2}};\end{aligned}\quad(28)$$

for Σ_4 or Σ_5, $(k/\sqrt{2})(110)$,

$$E=C_7(K_x+K_y)+C_8K_z;\quad(29)$$

and for X_6 or X_7, $(2\pi/a)(100)$,

$$E=\pm C_9(K_y^2+K_z^2)^{\frac{1}{2}}.\quad(30)$$

The second-order energies for the point W, $(2\pi/a)(0,\tfrac{1}{2},1)$, are of the form

$$E=C_{10}K_x^2+C_{11}(K_y^2+K_z^2).\quad(31)$$

If the energy extremum is at the point W, the constant energy surfaces will be spheroids with $<100>$ axes.

The irreducible representations Λ_4 and Λ_5 only have slopes along a $<111>$ axis, hence if the constant C_4 is zero at some point along the axis as it presumably is near the center of the zone in InSb due to the perturbing influence of the lowest conduction states (see Fig. 5), then the constant energy surfaces at these extrema will be spheroids with $<111>$ axes. However, because of the smallness of the first-order terms compared to the second-order terms, it is not expected that these extrema will be of any significance in the band structure if they occur near the center of the zone.

TABLE IX. Possible energy extrema for the representations of the double group in zinc blende structures.

Extrema at		Representations of double group	Constant energy surfaces
(000)	Γ	Γ_6	sphere
		Γ_7	sphere
		Γ_8 (from Γ_3)	2 warped energy surfaces as for holes in Si and Ge
$(k/\sqrt{3})[111]$	Λ	Λ_4	8 spheroids; $<111>$ axes
		Λ_5	8 spheroids; $<111>$ axes
$(2\pi/a)(1,\tfrac{1}{2},0)$	W	W_5, W_6, W_7, W_8	6 spheroids; $<100>$ axes
General point		$\cdots$	48 general ellipsoids

The representation Γ_8 at the center of the zone can have zero slope if it arises from the two-dimensional representation Γ_3 of the single group. In this case the energy to second order in k is given by

$$E=C_{12}k^2\pm[C_{13}^2k^4+C_{14}^2(k_x^2k_y^2+k_y^2k_z^2+k_z^2k_x^2)]^{\frac{1}{2}},\quad(32)$$

in the limit that all spin-orbit splittings are negligible compared with the spacing between levels at $k=0$, then $C_{14}^2=-3C_{13}^2$. In atomic Sn it is known that the 4*d* levels overlap the 5*s* atomic levels, hence in grey Sn or InSb it is conceivable that a Γ_3 level, which can be represented in a tight binding approximation by *d*-orbitals, could be the uppermost valence band.

Table IX gives a tabulation of the types of energy surfaces which might be expected at certain points in the Brillouin zone. It should be emphasized in all these considerations that if the spin-orbit interaction is small or the difference in the crystal potential from the diamondlike potential is only slight, then the region of convergence of the energy expressions will be small compared to kT and one should then consider only the single group representations in the first case, or the diamond structure double group representations in the latter case. If the region of convergence of the perturbation expansion is $\sim kT$, then one is not justified in keeping only the lowest nonvanishing term and a simple effective mass approximation would seem unjustified. From the order of magnitude estimate of the spin-orbit splitting, it seems this might be the case for holes in InSb.

I should like to thank Professor C. Kittel for suggesting this problem and for guidance throughout the course of the investigation. I am indebted to Dr. F. Herman and Dr. R. Paramenter of R.C.A. Laboratories for communicating their results to me prior to publication. I also wish to thank Mr. R. E. Behringer for checking the manuscript.