then using formula (4), we obtain the value 7.5×10^{-5} for $\Delta r/r$. For the Dy^{161} deformed nucleus, the isomeric shift is probably due to the difference in deformation between the 26-keV level and the ground state, and the nuclear factor $\Delta r/r$ in Eq. (4) should be replaced by $\alpha\Delta\alpha$[24] ($\alpha=\frac{2}{3}\delta$, where δ is the deformation factor[20]). The quadrupole moment of the ground level of Dy^{161}(2.6 b) corresponds to a value of 0.20 for $\alpha=\frac{2}{3}\delta$. We therefore obtain for $\Delta Q/Q=\Delta\alpha/\alpha$ the value 2×10^{-3}. This value is not in disagreement with the direct Mössbauer effect measurements of Q_1/Q_0 (Table II).

The fact that no isomeric shifts were found between Dy_2O_3 and the intermetallic compounds of Dy implies that $|\psi_{6s}(0)|^2$ is at least a factor of 3 smaller in $DyAl_2$ and in $DyFe_2$ than in Dy metal.

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Band Structure of Platinum Antimonide

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The band structure of $PtSb_2$ is calculated in a tight-binding approximation, assuming that the conduction and valence bands are formed primarily from an incomplete set of 5*d* electrons on ionized Pt, the band gap arising from spin-orbit splitting; the interaction with the 6*s* orbitals is included. Interactions with the Sb atoms have been largely ignored, apart from certain geometrical effects. The calculated bands show the observed symmetries and approximately the observed effective masses, but are very shallow; the full effect of this shallowness on the transport properties has not yet been determined.

I. INTRODUCTION

PLATINUM antimonide ($PtSb_2$) forms a cubic crystal with the pyrite structure (see Fig. 1); i.e., the Pt atoms constitute a face-centered cubic lattice, while the Sb pairs have their centers either on one of the cube edges or at the body center of the Pt lattice. The axes of the four nonequivalent Sb_2 pairs point along the four (111) directions. The cell parameter is 6.43 Å, the separation of the antimony atoms in each pair is 2.67 Å.

There are four nonequivalent Pt sites in the unit cell; the surroundings of one of these sites has been sketched in Fig. 1. It will be seen that the nearest neighbors are a nearly regular octahedron of six Sb atoms, the axes of the octahedron being tilted at an angle of 24° from the cubic axes. The angles between the axes of the octahedron are $90°\pm5\frac{1}{4}°$; we shall presume that this small departure from orthogonality is unimportant in comparison with the large tilt of the octahedron.

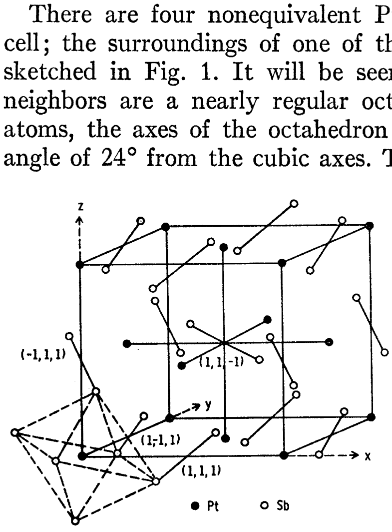

FIG. 1. Crystal structure of $PtSb_2$, the nearest neighbors to a corner Pt atom being shown. Cell parameter 6.43 Å, separation of Sb_2 pairs 2.67 Å.

Platinum antimonide is a low-band-gap semiconductor—data taken from the rate of change of conductivity with temperature give a band gap of 0.08 eV. The behavior of the magnetoresistance and the piezoresistance indicate that the maxima of the valence band are on the (1,0,0) axes, while the minima of the conduction band are on the (1,1,1) axes.[1] The crystal is hard, and has a melting point of 1230°C. The conjunction of a high-melting point with a small band gap suggests that the electrons involved in the formation of the conduction and valence bands are not primarily involved in the cohesion of the crystal. Unfortunately, it is not possible to be certain *a priori* which of the electrons are not involved in bonding, but a plausibility argument suggests that there is an unfilled shell of nonbonding *d* electrons around each Pt atom, and that we are therefore most likely to find the conduction bands associated with this shell. The structure of atomic Pt is $5s^2p^6d^{10}$; the formation of octahedral bonds with the surrounding Sb atoms will take up the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ electrons, as well as all the *s* and *p* electrons in the outer shell; we are now left with six *d* electrons not involved in bonding. Either two or four of these will

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[1] D. H. Damon, R. C. Miller, and A. Sagar (to be published).

be removed by each Sb$_2$ pair to complete the Sb-Sb bond, the precise number depending on the Sb-valence state. It will appear that the only band gap that can exist when states are formed from the available d orbitals occurs when only two out of the six states are filled, so that the subsequent calculation will involve bands formed from the d_{xy}, d_{yz}, and d_{xz} states in quadruply ionized platinum. In view of the high degree of ionization, a tight-binding calculation has been judged appropriate.

II. THE INTERACTION MATRIX

Since there are four nonequivalent sites, the Hamiltonian must involve the interaction of each sublattice with the other three. Three d orbitals are involved, so that the resulting Hamiltonian will be a 12×12 matrix—or 24×24 when spin is included. Fortunately, the 12×12 matrix can be simplified readily in such a way that only one 3×3 block need be considered in detail, the remainder being merely a perturbation on the basic solutions.

The starting point of the calculation is the presumption that the nonbonding orbitals on each Pt site can be expressed in terms of the axes defined by the Sb octahedron surrounding it. If θ is the angle between one of the octahedral axes and the nearest cubic axis, then it turns out that a convenient parameter to use is $\tan\theta$.

$$\alpha=\tan\theta=[b/\sqrt{3}/(a-b/\sqrt{3})], \tag{1}$$

where a is the lattice parameter, b the separation of an Sb pair. For PtSb$_2$, we find $\alpha=0.316$.

The coordinates (x',y',z') defined by the octahedron surrounding the Pt atom in the site $\frac{1}{2}a(i,j,k)$ are then $\mathbf{r}'=\mathbf{A}_{(i,j,k)}\cdot\mathbf{r}$, where (for the case of Fig. 1)

$$\mathbf{A}_{(000)}=(1+2\alpha^2)^{-1/2}\begin{bmatrix}1&-\alpha&-\alpha\\ \alpha&1&\alpha\\ \alpha&-\alpha&1\end{bmatrix} \quad \mathbf{A}_{(110)}=(1+2\alpha^2)^{-1/2}\begin{bmatrix}1&\alpha&-\alpha\\ -\alpha&1&-\alpha\\ \alpha&\alpha&1\end{bmatrix},$$

$$\mathbf{A}_{(101)}=(1+2\alpha^2)^{-1/2}\begin{bmatrix}1&\alpha&\alpha\\ -\alpha&1&\alpha\\ -\alpha&-\alpha&1\end{bmatrix} \quad \mathbf{A}_{(011)}=(1+2\alpha^2)^{-1/2}\begin{bmatrix}1&-\alpha&\alpha\\ \alpha&1&-\alpha\\ -\alpha&\alpha&1\end{bmatrix}. \tag{2}$$

The angular dependence of the wave function around each atom can then be written in terms of the crystal coordinates through the appropriate transformation, terms of order α^2 being ignored except in the major term. As was remarked in the Introduction, the $d_{x'^2-y'^2}$ and $d_{3z'^2-r^2}$ orbitals are considered to be removed from the calculation, since they are involved in bonding, and should therefore be of much lower energy than the remaining d orbitals. The basis states are then the $d_{x'y'}$, $d_{x'z'}$, and $d_{y'z'}$ orbitals. The radial dependences are all the same, the angular dependences must be expressed in terms of crystal coordinates; for example, the angular dependence of the $d_{x'y'}$ orbital on the corner atom is

$$\begin{aligned}(x'y')_{(000)}&=(x-\alpha y-\alpha z)(\alpha x+y+\alpha z)/(1+2\alpha^2)\\ &=\frac{1-\alpha^2}{1+2\alpha^2}(xy)-\alpha(yz)+\alpha(xz)+\alpha(x^2-y^2).\end{aligned} \tag{3}$$

This function is normalized to order α, it being understood that the (x^2-y^2) orbital is not properly normalized, but has the same constant multiplying the angular dependence as have the $(xy)\cdots$ set of orbitals. The remaining wave functions are listed in Part A of the Appendix.

The determination of the interaction matrix follows the usual course for a tight-binding calculation, though somewhat complicated by the presence of four sublattices. Denoting the ith orbital on a site in the μth sublattice by $\phi_\mu{}^i$, the basis functions take the form

$$\psi_\mu{}^i(\kappa)=\frac{1}{\sqrt{N}}\sum\nolimits_n \phi_\mu{}^i(\mathbf{r}-\mathbf{r}_\mu{}^n)e^{i\kappa\cdot\mathbf{r}_\mu{}^n},$$

where N is the number of cells in the crystal, n stands for the nth cell, $\mathbf{r}_\mu{}^n$ is the position of the member of sublattice μ in the nth cell, and κ is the wave number.

If the actual potential in the crystal is $V(\mathbf{r})$, while the potential due to a single Pt ion at $\mathbf{r}_\mu{}^n$ is $U(\mathbf{r}-\mathbf{r}_\mu{}^n)$, then the matrix element connecting the states $\psi_\mu{}^i$, $\psi_{\mu'}{}^{i'}$ is

$$\begin{aligned}H_{ii'}{}^{\mu\mu'}=\sum_n\int d^3\mathbf{r}\phi_\mu{}^i(\mathbf{r}-\mathbf{r}_\mu{}^0)[V(\mathbf{r})-U(\mathbf{r}-\mathbf{r}_\mu{}^0)]&\\ \times\phi_{\mu'}{}^{i'}(\mathbf{r}-\mathbf{r}_{\mu'}{}^n)\exp[i\kappa\cdot(\mathbf{r}_{\mu'}{}^n-\mathbf{r}_\mu{}^0)],&\end{aligned} \tag{4}$$

where the sum over n is now taken to be a sum over nearest neighbors only.

Provided that the interaction is between nearest neighbors only, only four interaction energies appear in the final form of the calculation, and it can be shown[2] that only three of these are independent, provided that only two-center integrals are involved. These four are

$$\begin{aligned}\langle(xy)_{(000)}|V-U|(xy)_{(110)}\rangle&=-\tfrac{1}{4}A,\\ \langle(xy)_{(000)}|V-U|(xy)_{(011)}\rangle&=\tfrac{1}{4}B,\\ \langle(xy)_{(000)}|V-U|(yz)_{(110)}\rangle&=-\tfrac{1}{4}C,\\ \langle(yz)_{(000)}|V-U|(x^2-y^2)_{(011)}\rangle&=\tfrac{1}{4}D=\tfrac{1}{2}(B+C).\end{aligned} \tag{5}$$

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[2] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

The factor $\frac{1}{4}$ has been inserted because a sum over four atoms is always involved; A, B, and C are all positive, with A greater than the others. Various other interaction energies—reducible to sums of A, B, and C—do appear in the calculation, but can be eliminated later. The elements of the interaction matrix can now be written down, being derived from (4), using basis functions of the same type as (3). For the most part, terms of only zero and first order in α will be included, apart from one systematic exception—the factor $(1-\alpha^2)/(1+2\alpha^2)$ that appears in the principle term of (3) will be retained wherever it appears multiplying another principal term; the reason for omitting other terms of order α^2 will be given later.

The total interaction matrix can be written as a 4×4 supermatrix in which the rows and columns correspond to the sublattices, taken in the order (000), (110), (011), (101); each element is then a 3×3 matrix in which the rows and columns correspond to the wave functions taken in the order d_{xy}, d_{xz}, and d_{yz}. The result is

$$H=\begin{bmatrix} 0 & E_1+a_1+b_1 & E_2+a_2+b_2 & E_3+a_3+b_3 \\ E_1+\tilde{a}_1-b_1 & 0 & E_3-a_3+b_3 & E_2-\tilde{a}_2-b_2 \\ E_2+\tilde{a}_2+b_2 & E_3-\tilde{a}_3-b_3 & 0 & E_1-a_1+b_1 \\ E_3+\tilde{a}_3-b_3 & E_2-a_2+b_2 & E_1-\tilde{a}_1-b_1 & 0 \end{bmatrix}, \tag{6}$$

where $\tilde{a}_1$ is the transpose of a_1, etc., and

$$E_1=\begin{bmatrix} -A_rc_1c_2 & \cdot & \cdot \\ \cdot & B_rc_1c_2 & -C_rs_1s_2 \\ \cdot & -C_rs_1s_2 & B_rc_1c_2 \end{bmatrix} \quad E_2=\begin{bmatrix} B_rc_2c_3 & -C_rs_2s_3 & \cdot \\ -C_rs_2s_3 & B_rc_2c_3 & \cdot \\ \cdot & \cdot & -A_rc_2c_3 \end{bmatrix},$$
$$E_3=\begin{bmatrix} B_rc_1c_3 & \cdot & -C_rs_1s_3 \\ \cdot & -A_rc_1c_3 & \cdot \\ -C_rs_1s_3 & \cdot & B_rc_1c_3 \end{bmatrix}, \tag{7}$$

and the matrices a_μ, b_μ are linear in α; their explicit forms are given in Part B of the Appendix.

In the above the following abbreviations have been introduced:

$$A_r=\left(\frac{1-\alpha^2}{1+2\alpha^2}\right)^2 A, \text{ and similarly for } B_r, C_r. \tag{8}$$

$$\cos k_i=c_i \quad \sin k_i=s_i, \tag{9}$$

where $k_i=\kappa_i a/2$. The reduced wave number $\mathbf{k}$ will be used throughout the rest of the calculation. The interaction matrix (6) can be simplified greatly by a similarity transformation with the unitary matrix

$$S=\tfrac{1}{2}\begin{bmatrix} I & I & I & I \\ I & -I & I & -I \\ I & -I & -I & I \\ I & I & -I & -I \end{bmatrix},$$

where I is the unit 3×3 matrix. Then

$$S^{-1}HS=\begin{bmatrix} H_0 & d_1 & d_2 & d_3 \\ \tilde{d}_1 & H_1 & d_4 & d_5 \\ \tilde{d}_2 & \tilde{d}_4 & H_2 & d_6 \\ \tilde{d}_3 & \tilde{d}_5 & \tilde{d}_6 & H_3 \end{bmatrix}, \tag{10}$$

where

$$H_0=E_1+E_2+E_3 \quad H_1=-E_1-E_2+E_3$$
$$H_2=E_1-E_2-E_3 \quad H_3=-E_1+E_2-E_3, \tag{11}$$

and

$$d_1=\tfrac{1}{2}(\tilde{a}_1-a_1)+\tfrac{1}{2}(\tilde{a}_3+a_3)-b_2 \quad d_2=\tfrac{1}{2}(\tilde{a}_2-a_2)+\tfrac{1}{2}(\tilde{a}_1+a_1)-b_3$$
$$d_3=\tfrac{1}{2}(\tilde{a}_3-a_3)+\tfrac{1}{2}(\tilde{a}_2+a_2)-b_1 \quad d_4=-\tfrac{1}{2}(\tilde{a}_3-a_3)-\tfrac{1}{2}(\tilde{a}_2+a_2)+b_1 \tag{12}$$
$$d_5=-\tfrac{1}{2}(\tilde{a}_2-a_2)-\tfrac{1}{2}(\tilde{a}_1+a_1)-b_3 \quad d_6=\tfrac{1}{2}(\tilde{a}_1-a_1)-\tfrac{1}{2}(\tilde{a}_3+a_3)+b_2.$$

All terms of order α have been shifted off the diagonals, and are now simply a perturbation on the bands formed by H_0, H_1, etc. It is for this reason that most terms of order α^2 were omitted from the interaction matrix, for they too are removed to the off-diagonals by the transformation S.

H_0 is the principal part of the Hamiltonian, H_1, H_2, and H_3 being derived from it. The explicit forms of H_0 and H_1 are

$$\begin{aligned}
H_0&=\begin{bmatrix} -A_rc_1c_2+B_r(c_2c_3+c_1c_3) & -C_rs_2s_3 & -C_rs_1s_3 \\ -C_rs_2s_3 & -A_rc_1c_3+B_r(c_1c_2+c_2c_3) & -C_rs_1s_2 \\ -C_rs_1s_3 & -C_rs_1s_2 & -A_rc_2c_3+B_r(c_1c_2+c_1c_3) \end{bmatrix}, \\
H_1&=\begin{bmatrix} A_rc_1c_2+B_r(c_1c_3-c_2c_3) & C_rs_2s_3 & -C_rs_1s_3 \\ C_rs_2s_3 & -A_rc_1c_3-B_r(c_1c_2+c_2c_3) & C_rs_1s_2 \\ -C_rs_1s_3 & C_rs_1s_2 & A_rc_2c_3-B_r(c_1c_2-c_1c_3) \end{bmatrix}.
\end{aligned}\tag{13}$$

It will be seen that H_1 can be derived from H_0 by replacing k_2 by $\pi+k_2$ in H_0; in fact, H_1, H_2, and H_3 are translations of H_0 over one reciprocal lattice vector along the axes of y, z, and x, respectively. The presence of four matrices on the diagonal with nonvanishing matrix elements connecting them corresponds to the fact that the four Pt sites are nonequivalent, so that the basic zone is now the simple cubic zone rather than the zone for the face-centered cubic structure. Thus the principal effect that the tilt of the octahedra has had is to reduce the interaction energies by the factor $[(1-\alpha^2)/(1+2\alpha^2)]^2$, and to introduce a connection between the matrices on the diagonal; a more subtle effect is that the nature of the off-diagonal matrices is such as to reduce the symmetry of the bands from full cubic (O^h) to T^h, which is the symmetry of the crystal. However, as will be shown later, the interaction of the d bands with the s bands is far stronger than the interaction between the d bands, so that the only part of the Hamiltonian with which we shall be concerned is H_0.

Figure 2 sketches the bands resulting from H_0 for the (100) and (111) directions, the bands are triply degenerate at the origin of k space, with energy $-A_r+2B_r$. The upper band is doubly degenerate, the lower band is single. The bands are shown as reflected back towards the origin at $k_1=\pi/2$ rather than continuing out to $k_1=\pi$, which is the zone boundary for the face-centered cubic structure; one would normally expect that the interband degeneracy at $k_i=\pi/2$ would be lifted either by the matrices d_i, or by a combination of spin-orbit splitting and the d_i, resulting in the formation of a band gap at the zone boundary. This is the case over most of the surface of the zone, but it is shown in Part C of the Appendix that there are some particular combinations of functions such that the degeneracy at the intersection of the principal axes with the zone surface cannot be lifted. The only band gap possible for this combination of d orbitals must then come from the effect of spin-orbit coupling acting on the triple degeneracy at the origin.

III. THE BAND STRUCTURE

A. Preliminary

Before introducing the spin-orbit coupling the interaction energies, A, B, and C will be determined, since it is necessary to know their relative magnitudes in order to keep track of the behavior of the results. The integrals were found using wave functions of the type introduced by Slater, i.e.,

$$\psi\sim r^{n^*-1}e^{-Z^*r/n^*a_0}f(\theta,\phi),$$

where n^* is the effective quantum number, Z^* the effective nuclear charge, and a_0 the first Bohr radius. Following Slater's rules, $n^*=4$ for the shell with quantum number 5, and $Z^*=10-Ns$ for an electron in the d shell, where N is the number of other electrons in the shell and s is a screening constant. Slater's value for the screening constant (0.35) cannot be expected to hold for electrons of such high quantum number; s was therefore calculated from the second ionization energy of Pt, since this involves the ionization of a $5d$ electron (the first ionization energy is the removal of a $6s$ electron). This energy[3] is 18.35 eV; on using the rule $W=W_H(Z^*/n^*)^2$, where W_H is the ionization energy of hydrogen, we find $Z^*=4.67$ for Pt$^+$, and hence $Z^*=6.67$ for quadruply ionized Pt; the value of s is 0.666.

The contribution of one of the nearest Pt neighbors to the difference between the crystal potential and the atomic potential for an atom at the origin was taken to be

$$(V-U)_{\text{one atom}}=Z^*e^2[1/r_2-(1+\lambda)/r_0],$$

where r_0 is the separation of nearest neighbors, and r_2

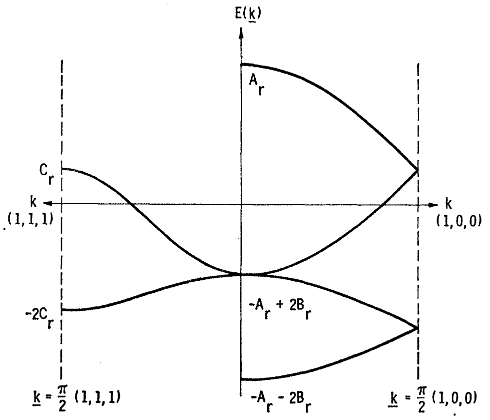

FIG. 2. Sketch of the complete d orbital band structure within the first cubic zone. The upper band ($E>-A_r+2B_r$) is doubly degenerate, the lower band is single.

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[3] *American Institute of Physics Handbook* (McGraw-Hill Book Company Inc., New York, 1957).

is measured from the neighboring site; λ is a small constant such that $\int\psi^*(r_1)(V-U)\psi(r_1)d\tau=0$.[4] On evaluating the integrals, one finds

$$\begin{array}{cccccc} A & B & C & A_r & B_r & C_r \\ 3.54 & 0.741 & 0.878 & 2.0 & 0.42 & 0.50, \end{array} \qquad (14)$$

all values being expressed in eV.

A couple of changes will be made before the spin-orbit coupling is introduced. An effect of Sec. II has been to show that the Hamiltonian H_0 involves states that are unambiguously the simple d orbitals; it is now convenient to relabel these in the order

$$d_{xy}=|1\rangle,\quad d_{xz}=|2\rangle,\quad d_{yz}=|3\rangle. \qquad (15)$$

Further, it will appear later that all effects with which we shall be concerned occur fairly close to the origin of $\mathbf{k}$ space; the Hamiltonian (13) will therefore be expanded as far as order k^2:

$$H_0\rightarrow\begin{bmatrix} \frac{1}{2}(A_r-B_r)k^2-\frac{1}{2}(A_r+B_r)k_3{}^2 & -C_rk_2k_3 & -C_rk_1k_3 \\ -C_rk_2k_3 & \frac{1}{2}(A_r-B_r)k^2-\frac{1}{2}(A_r+B_r)k_2{}^2 & -C_rk_1k_2 \\ -C_rk_1k_3 & -C_rk_1k_2 & \frac{1}{2}(A_r-B_r)k^2-\frac{1}{2}(A_r+B_r)k_1{}^2 \end{bmatrix}, \qquad (16)$$

where the zero of energy has been shifted to $-A_r+2B_r$.

The spin-orbit interaction can be taken as

$$H_{s0}=-2\mu l\cdot s, \qquad (17)$$

where l is the orbital angular momentum, s the spin, and $5\mu=\Delta$, Δ being the spin-orbit splitting. The constant μ should be positive (corresponding to inversion of levels), since the d band is more than half filled. The usual procedure of setting up the total Hamiltonian in terms of eigenfunctions of J will be followed, but it should be remarked that eigenfunctions of both J and m_J cannot be formed—since only three of the five d orbitals are being used. The matrix of H_{s0} is shown in Part B of the Appendix, the eigenfunctions and associated eigenvalues are

$$\left.\begin{array}{l} (\surd 2)^{-1}[|\beta 1\rangle-i|\alpha 2\rangle] \\ (\surd 6)^{-1}[2|\alpha 3\rangle+i|\alpha 2\rangle+|\beta 1\rangle] \\ (\surd 6)^{-1}[2|\beta 3\rangle-i|\beta 2\rangle-|\alpha 1\rangle] \\ (\surd 2)^{-1}[|\alpha 1\rangle-i|\beta 2\rangle] \end{array}\right\} E=\mu,\ J=\tfrac{3}{2},$$
$$\left.\begin{array}{l} (\surd 3)^{-1}[|\beta 1\rangle+i|\alpha 2\rangle-|\alpha 3\rangle] \\ (\surd 3)^{-1}[|\alpha 1\rangle+i|\beta 2\rangle+|\beta 3\rangle] \end{array}\right\} E=-2\mu,\ J=\tfrac{5}{2}, \qquad (18)$$

where $|\alpha\rangle$, $|\beta\rangle$ are the states with electron spin up and spin down, respectively.

The total Hamiltonian is most conveniently written out with the group of terms for which $J=\frac{3}{2}$ separated from those for which $J=\frac{5}{2}$, as follows:

$$\mathcal{H}=\begin{bmatrix} \mathcal{H}_i & \mathcal{H}_{i\sigma} \\ \mathcal{H}_{i\sigma}{}^{\dagger} & \mathcal{H}_\sigma \end{bmatrix}, \qquad (19)$$

where $i=1\cdots 4$, $\sigma=5, 6$, the states being numbered in the order in which they appear in (18). In terms of the matrix elements H_{ij} of H_0 we find

$$\left.\begin{array}{l} \mathcal{H}_i=\begin{bmatrix} \frac{1}{2}(H_{11}+H_{22}) & (2\surd 3)^{-1}(H_{11}-H_{22}+2iH_{23}) & (\surd 3)^{-1}(H_{13}-iH_{12}) & 0 \\ (2\surd 3)^{-1}(H_{11}-H_{22}-2iH_{23}) & \frac{1}{6}(H_{11}+H_{22}+4H_{33}) & 0 & (\surd 3)^{-1}(H_{13}-iH_{12}) \\ (\surd 3)^{-1}(H_{13}+iH_{12}) & 0 & \frac{1}{6}(H_{11}+H_{22}+4H_{33}) & -(2\surd 3)^{-1}(H_{11}-H_{22}+2iH_{23}) \\ 0 & (\surd 3)^{-1}(H_{13}+iH_{12}) & -(2\surd 3)^{-1}(H_{11}-H_{22}-2iH_{23}) & \frac{1}{2}(H_{11}+H_{22}) \end{bmatrix} \\ \mathcal{H}_\sigma=\begin{bmatrix} \frac{1}{3}(H_{11}+H_{22}+H_{33})-\delta & 0 \\ 0 & \frac{1}{3}(H_{11}+H_{22}+H_{33})-\delta \end{bmatrix} \\ \mathcal{H}_{i\sigma}{}^{\dagger}=\begin{bmatrix} (\surd 6)^{-1}(H_{11}-H_{22}+iH_{23}) & (3\surd 2)^{-1}(H_{11}+H_{22}-2H_{33}-3iH_{23}) & (\surd 2)^{-1}H_{13} & (\surd 6)^{-1}(H_{13}+2iH_{12}) \\ (\surd 6)^{-1}(H_{13}-2iH_{12}) & (\surd 2)^{-1}H_{13} & -(3\surd 2)^{-1}(H_{11}+H_{22}-2H_{33}+3iH_{23}) & (\surd 6)^{-1}(H_{11}-H_{22}-iH_{23}) \end{bmatrix} \end{array}\right\}, \qquad (20)$$

where $\delta=3\mu=0.6\Delta$, and the zero of energy is now $-A_r+2B_r+\mu$.

The Hamiltonian defined by (19) and (20) is identical in form with that found in the valence bands of Si and Ge.[5] $\mathcal{H}_i$, which corresponds to the valence band in

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[4] Although $V-U$ is not constant within the cell surrounding the first atom, yet the d orbitals on this atom are not connected to each other through $V-U$, nor is their energy changed. The requirement that the basic orbitals be locally eigenfunctions of the crystal potential is therefore sufficiently well satisfied—a too perfect adherence to this principle would appear to prohibit the formation of bands. Exception can be taken to the use of Z^* as being literally the charge that the electron on one site sees on its neighbor, this choice is intuitive, based on the usual argument that the greatest part of the integral comes when the electron is close to the neighbor. A justification can be given, since the value of Z^* for $6s$ and $6p$ electrons is 6.1, not far different from the value for d electrons; thus if one decomposes the $5d$ state on one atom into a set of states based on the neighbor, the principal contributors will move in fields corresponding to values of Z^* between 6.1 and 6.67.

[5] G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. 95, 568 (1954).

these compounds, has been much investigated, while $\mathcal{H}_\sigma$, which corresponds to the split-off band, is already diagonal. There are two distinct solutions of $\mathcal{H}_i$, each doubly degenerate; the solutions of the upper and lower bands will first be considered separately, before going on to consider their interactions through $\mathcal{H}_{i\sigma}$. From $\mathcal{H}_i$ we find

$$E_i=\tfrac{1}{3}(A_r-2B_r)k^2\pm\tfrac{1}{2}\{\tfrac{1}{9}(A_r+B_r)^2k^4 +\tfrac{1}{3}[4C_r^2-(A_r+B_r)^2](k_1^2k_2^2+k_2^2k_3^2+k_1^2k_3^2)\}^{1/2}.$$

These solutions can be greatly simplified by making the "spherical" approximation

$$C_r=\tfrac{1}{2}(A_r+B_r)\,. \tag{21}$$

The two bands are then

$$\left.\begin{aligned}E_1&=\tfrac{1}{2}(A_r-B_r)k^2,\\ E_2&=\tfrac{1}{6}(A_r-5B_r)k^2.\end{aligned}\right\} \tag{22}$$

$\mathcal{H}_\sigma$ gives, for the split-off band,

$$E_\sigma=-\delta+\tfrac{1}{3}(A_r-2B_r)k^2. \tag{23}$$

The numerical values of A_r, B_r given in (14) yield: $E_1=0.79k^2$, $E_2=-0.017k^2$, $E_\sigma=-\delta+0.39k^2$, all energies being in eV. It is obviously not certain whether E_2 goes up or down with increase of k, but it is clear that E_2 and E_σ intersect, so that the effect of $\mathcal{H}_{i\sigma}$ must be considered in detail. It is to the interaction of these two bands that we must look for the formation of the valence and conduction bands.

B. Interaction of the *d* Bands

The matrix which diagonalizes $\mathcal{H}_i$ has been given by Ehrenreich and Overhauser[6] as follows: If we write

$$\mathcal{H}_i=\begin{bmatrix} a & ce^{i\theta} & de^{i\phi} & 0\\ ce^{-i\theta} & b & 0 & de^{i\phi}\\ de^{-i\phi} & 0 & b & -ce^{i\theta}\\ 0 & de^{-i\phi} & -ce^{-i\theta} & a\end{bmatrix}\text{ and define } U \text{ such that } U^{-1}\mathcal{H}_iU=\begin{bmatrix}E_1 & & & \\ & E_1 & & \\ & & E_2 & \\ & & & E_2\end{bmatrix},$$

then

$$U=(\Delta\sqrt{2})^{-1}\begin{bmatrix}(c-id)e^{i\theta} & -i(c+id)e^{i\phi} & -(E_1-a) & -i(E_1-a)e^{i(\theta+\phi)}\\ (E_1-a) & -i(E_1-a)e^{i(\phi-\theta)} & (c+id)e^{-i\theta} & i(c-id)e^{i\phi}\\ -i(E_1-a)e^{-i(\phi-\theta)} & (E_1-a) & -i(c+id)e^{-i\phi} & -(c-id)e^{i\theta}\\ i(c-id)e^{-i\phi} & -(c+id)e^{-i\theta} & -i(E_1-a)e^{-i(\theta+\phi)} & -(E_1-a)\end{bmatrix}, \tag{24}$$

where $\Delta^2=(E_1-a)^2+c^2+d^2$.

$\mathcal{H}$ can now be reduced as follows:

$$\begin{bmatrix}U^{-1} & 0\\ 0 & I\end{bmatrix}\begin{bmatrix}\mathcal{H}_i & \mathcal{H}_{i\sigma}\\ \mathcal{H}_{i\sigma}^\dagger & \mathcal{H}_\sigma\end{bmatrix}\begin{bmatrix}U & 0\\ 0 & I\end{bmatrix}=\begin{bmatrix}E_i & U^{-1}\mathcal{H}_{i\sigma}\\ \mathcal{H}_{i\sigma}^\dagger U & \mathcal{H}_\sigma\end{bmatrix}, \tag{25}$$

where I is the unit 2×2 matrix, and E_i is the diagonal form of $\mathcal{H}_i$. Since $\mathcal{H}_\sigma$ is already diagonal, the blocks $U^{-1}\mathcal{H}_{i\sigma}$ represent interactions between diagonal forms. It is still impossible to obtain the eigenvalues of this matrix exactly; however, it is only that part which involves the interaction of the bands E_2 and E_σ that need be treated exactly, for E_1 is a sufficiently rapidly increasing function of k that the interaction between it and the other bands can be considered to be no more than a perturbation. We therefore strike out from (24) those rows and columns in which E_1 is on the diagonal, being left with the 4×4 matrix

$$\begin{bmatrix}E_2 & 0 & T_{35} & T_{36}\\ 0 & E_2 & T_{45} & T_{46}\\ T_{35}^* & T_{45}^* & E_\sigma & 0\\ T_{36}^* & T_{46}^* & 0 & E_\sigma\end{bmatrix}, \tag{26}$$

where $T_{ij}=\sum_k U_{ik}^{-1}\mathcal{H}_{kj}$.

It is quite easy to show from the forms given in (24) and (20) for U and $\mathcal{H}_{i\sigma}$ that the following relationships hold:

$$T_{46}=T_{35}^*,\quad T_{45}=-T_{36}^*.$$

The matrix (26) is therefore formally identical with $\mathcal{H}_i$, apart from a reordering of rows and columns. The eigenvalues are the roots of the secular equation

$$(E-E_2)(E-E_\sigma)=|T_{35}|^2+|T_{36}|^2.$$

The right-hand side of the above equation can be found analytically without approximation, though the job is extremely tedious. The calculation is, however, greatly simplified by the use of the spherical approximation, Eq. (21). This approximation gives E_1 and E_2 fairly well, but is quite evidently unjustified for the calculation of the interaction between E_2 and E_σ, for on taking the explicit forms of the matrix elements it is seen that $\mathcal{H}_{i\sigma}$ depends only on $\frac{1}{2}(A_r+B_r)$ in the (100) directions, and only on C_r in the (111) directions. The coupling between the bands therefore appears to be much stronger along the principal axes then it is along the body diagonals, since $\frac{1}{2}(A_r+B_r)$ is more than twice as great as C_r. However, it will be shown in the next section that the interaction of the *d* bands with the *s* band is such that the effective value of C_r is doubled, with the result that Eq. (20) is nearly satisfied. We therefore write

$$\tfrac{1}{2}(A_r+B_r)\to\bar{C},\quad C_r\to\bar{C}.$$

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[6] H. Ehrenreich and A. W. Overhauser, Phys. Rev. **104**, 331 (1956).

These substitutions being made, the calculation becomes straightforward, though tedious. An outline is given in part (D) of the Appendix; the result is

$$(E-E_2)(E-E_\sigma)=(2/9)\bar{C}^2k^4. \tag{27}$$

C. Interaction with the *s* Bands

As is to be expected where a transition metal is involved the origin of the s band formed from $6s$ wave functions centered on Pt sites is close to the center of the d bands, and the action of the s bands on the d bands is an important part of the Hamiltonian, though it has been omitted from the discussion in the interests of clarity.

The various matrix elements needed to describe the generation of the s band and its interactions with the d band are:

$$\begin{aligned}\langle s_{(000)}|V-U|s_{(110)}\rangle&=-\tfrac{1}{4}S,\\ \langle s_{(000)}|V-U|(xy)_{(110)}\rangle&=-\tfrac{1}{4}P,\\ \langle s_{(000)}|V-U|(x^2-y^2)_{(101)}\rangle&=-\tfrac{1}{4}Q,\end{aligned} \tag{28}$$

the notation being similar to that used in (5).

Of these constants, only S is needed to describe the generation of the s band, which, because of its symmetry, is not affected by the nonequivalence of the Pt sites. P is the major contributor to the interaction with the d bands, since no interaction involving Q could appear if α were zero.

First the interaction energies will be calculated and an attempt made to find the relative positions of the d and s bands, before going on to find their contribution to the interaction matrix. Slater's rules give the ionization energy of a $6s$ electron from Pt sufficiently well (for this case the rules are $n^*=4.2$, $Z^*=18-0.85N$, N being the number of electrons in the fifth shell); for the $6s$ electron when four of the $5d$ states are not filled, we have $Z^*=6.1$. Then, following the same procedure as before, we find

$$\begin{array}{cccc} S & P & P_r & \\ 4.01 & 3.54 & 2.65 & \text{and}\quad Q\simeq P,\end{array} \tag{29}$$

where $P_r=(1-\alpha^2)/(1+2\alpha^2)P$, and all values are in eV; Q has not been calculated accurately because there is no need for an exact value. There is a slight inconsistency in the notation, since the ratio P_r/P is not equal to the ratios A_r/A, etc.; the difference comes about through the fact that the s orbitals are not affected by the tilt of the octahedra, so that the product of an s orbital with the principal part of one of the d orbitals contains the factor $(1-\alpha^2)/(1+2\alpha)^2$ once only.

The energy of the s band measured from s level *in vacuo* is

$$E_s=-S(c_1c_2+c_2c_3+c_1c_3)=-3S+Sk^2$$

for small values of k.

The difference in energy between the s band and the principal d bands at $k=0$ is therefore

$$E_{ds}=W_d-W_s+A_r-2B_r-3S-\delta_d+\delta_s, \tag{30}$$

where W_d, W_s are the ionization energies for the $5d$ and $6s$ states *in vacuo*, and δ_d, δ_s are perturbations on the energies of the d and s bands due to other bands. The ionization energies can be calculated from the rule $W=W_H(Z^*/n^*)^2$, where W_H is the ionization energy for hydrogen; then, neglecting δ_d, δ_s, one finds $E_{ds}=-1.8$ eV. A correction for the interaction with the rather small number of bands that we already know about can be made,[7] reducing E_{ds} to -1.0 eV. This calculation indicates that the origin of the s band is somewhat below the origin of the d band—a feature which would altogether destroy any possibility of finding a finite band gap. Fortunately, the result should not be taken too literally, since it involves the difference of large quantities (e.g., $W_d=37.8$ eV); all that has been shown is that $5d$ and $6s$ bands are in fact close—it will be assumed that E_{ds} is small and positive.

The interaction of the d bands with the s bands can be treated by the methods of Sec. II, resulting in the formation of four s bands (a single band of energy E_{ds} at $k=0$, and three others derivable from it, of energy $E_{ds}+4S$ at $k=0$), and of a set of interactions between these and the d bands (there are no interactions between the s bands). The three upper bands are of no particular interest, but will be used in a later section to illustrate a point; they are therefore listed here. The interaction matrix for the principal d bands and all of the s bands has the form

$$\begin{bmatrix} H_0 & H_{ds}\\ \tilde{H}_{ds} & H_s\end{bmatrix},$$

where

$$H_s=\begin{bmatrix} E_{ds}+Sk^2 & & & \\ & E_{ds}+4S-Sk_2^2 & & \\ & & E_{ds}+4S-Sk_3^2 & \\ & & & E_{ds}+4S-Sk_1^2\end{bmatrix}, \tag{31a}$$

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[7] The energy of the d band at $k=0$ is perturbed both by the other d bands through the matrices d_i defined in (12) and by the upper part of the s bands through the perturbations listed in (31b). The effect can be determined by second-order perturbation theory, with the result

$$\delta_d=-2\alpha^2\left[\frac{1+2\alpha^2}{1-\alpha^2}\right]^2(A-3B)-\alpha^2Q^2/S.$$

The energy of the s band at $k=0$ is not affected by this set of bands, the numerical results are then $\delta_d=-0.8$ eV, $\delta_s=0$.

and

$$H_{ds}=\begin{pmatrix} P_rk_1k_2 & \alpha Pk_1k_3 & \alpha Pk_2k_3 & \alpha Q[2+\frac{1}{2}(k^2+k_3^2)] \\ P_rk_1k_3 & \alpha Pk_1k_2 & \alpha Q[2+\frac{1}{2}(k^2+k_2^2)] & \alpha Pk_2k_3 \\ P_rk_2k_3 & \alpha Q[2+\frac{1}{2}(k^2+k_1^2)] & \alpha Pk_1k_2 & \alpha Pk_1k_3 \end{pmatrix}, \tag{31b}$$

and H_0 is defined in (16).

Only the principal s band need be considered now; this is the first term in H_s and the interactions related to it are the first column in H_{ds}. On writing out H_0 as a matrix, and denoting the elements of the first column of H_{ds} by H_{is} $(i=1,2,3)$, the interaction matrix becomes

$$\begin{pmatrix} H_{11} & H_{12} & H_{13} & H_{1s} \\ H_{12} & H_{22} & H_{23} & H_{2s} \\ H_{13} & H_{23} & H_{33} & H_{3s} \\ H_{1s} & H_{2s} & H_{3s} & E_s(k) \end{pmatrix},$$

where $E_s(k)=E_{ds}+Sk^2$.

The most convenient way to take account of the s band is to use second-order perturbation theory on all the elements of H_0 before diagonalization, by means of the following stratagem: $E_s(k)$ is a much more rapidly increasing function of k than are any of the diagonal elements of H_0, so that $E_s(k)-H_{ii}$ is always much greater than are the differences between the various H_{ii}. Therefore, despite the fact that the valence and conduction bands are formed some distance away from the origin of k space, one can set all the diagonal elements of H_0 equal to their average, which is $\frac{1}{3}(A_r-2B_r)k^2$, when dealing with the perturbation from the s band. Second-order perturbation theory then gives

$$\delta H_{ij}=\frac{H_{is}H_{sj}}{\bar{H}_{ii}-E_s(k)}\to\frac{H_{is}H_{sj}}{Rk^2}, \tag{32}$$

where $R=S-\frac{1}{3}(A_r-2B_r)$.

In the last step it has been supposed that $E_{ds}\ll Sk^2$ for those values of k which are involved in the formation of the valence and conduction bands; E_{ds} has, in effect, been kept as an adjustable parameter up to this point, and has now been set virtually equal to zero—a choice which has the advantages of both analytic simplicity and of providing the best fit to the available data.

The above procedure reduces the effective part of the interaction matrix back down to a 3×3 block, so that spin-orbit splitting can be incorporated and the energy levels determined as before[8] using matrix elements $H_{ij}+\delta H_{ij}$. The energy of the heavy mass band is now

$$E_2'=\frac{1}{6}(A_r-5B_r)k^2-\frac{P_r^2}{Rk^2}\left\{\frac{1}{6}(k_1^2k_2^2+k_2^2k_3^2+k_1^2k_3^2)+\left(\frac{3}{2}+\frac{6C}{A+B}\right)k_1^2k_2^2k_3^2/k^2\right\}, \tag{33a}$$

and the energy of the split-off band is

$$E_\sigma'=-\delta+\frac{1}{3}(A_r-2B_r)k^2-\frac{1}{3}\frac{P_r^2}{Rk^2}(k_1^2k_2^2+k_2^2k_3^2+k_1^2k_3^2). \tag{33b}$$

It now remains to determine the interaction of E_2' with E_σ' through $\mathcal{H}_{i\sigma}$; in this interaction the off-diagonal terms of H_0 are peculiarly important, and will be treated in a different manner from the remainder. For example, consider H_{12}

$$H_{12}=-C_rk_2k_3,\quad \delta H_{12}=-(P_r^2/Rk^2)k_1^2k_2k_3.$$

The form of δH_{12} is the same as the form of H_{12}, apart from the factor k_1^2/k^2. On replacing this factor by its angular average of $\frac{1}{3}$ the effect of the perturbation is just to increase the effective value of C_r to

$$C_{\text{eff}}=C_r+\tfrac{1}{3}P_r^2/R. \tag{34}$$

The numerical value of C_{eff} is 1.15 eV, from the values given in (14) and (29). But $\frac{1}{2}(A_r+B_r)=1.2$ eV, so that the spherical approximation is now sufficiently good for the calculation of the matrix elements T_{ij} defined in (26). The procedure followed is to use the unperturbed values of the diagonal elements of H_0 together with C_{eff} in place of C_r on the off-diagonal elements—it being considered that the use of E_2', E_σ' in place of E_2 and E_σ will take sufficiently good account of the variation of the diagonal elements.[9] The secular equation for the energy E is then

$$(E-E_2')(E-E_\sigma')=(2/9)\bar{C}^2k^4, \tag{35}$$

where $\bar{C}=\frac{1}{2}[\frac{1}{2}(A_r+B_r)+C_{\text{eff}}]=1.17$ eV, and E_2', E_σ' are given in Eqs. (33).

D. Numerical Evaluation of the Band Structure

Equation (35) determines the band structure; the positions of the valence and conduction band's maxima

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[8] This reduction to a 3×3 interaction matrix necessarily implies the use of mixed d and s orbitals as basis functions; the elements of the spin-orbit coupling matrix are therefore changed in magnitude as a result of the decrease in amplitude of the d orbitals, though the matrix is not changed in form since $l=0$ for the s orbitals. The effect is greatest on the (111) axes since each basic d state is here mixed with a fraction $\frac{1}{3}P_r/R$ of the s state, this fraction is 0.24, from which the square of the amplitude of the d orbitals is found to be 0.94. This change is small enough to be ignored.

[9] This method is better than might be supposed, after taking all perturbations into account, the value of the effective coupling constant $\bar{C}$ remains exactly $\frac{1}{2}(A_r+B_r)$ on the principal axes, and is exactly C_{eff} in the (111) directions. Since the approximation described was made only for the purpose of determining the coupling matrix T, and since the coupling constant changes by only 5% between the major symmetry axes, the assumption that it is constant is reasonable.

and minima, together with the values of the effective masses, can be found from it analytically. However, before proceeding with the calculation, some qualitative remarks on the origin of the band structure will be made, since the complexity of the argument has been such as to hide the simplicity of the effects involved.

The band structure arises primarily from the d_{xy}, d_{xz}, and d_{yz} subset of the $5d$ orbitals, though these are defined in coordinates that differ for each Pt site. Nevertheless, the main part of the interaction matrix is precisely that which would be found if the orbitals were defined in terms of the crystal coordinates, except that the magnitudes of their interactions are decreased. This set of d orbitals has cubic symmetry, so it is not very surprising that their Hamiltonian in a face-centered cubic lattice has precisely the same form as that derived for p orbitals in the valence bands of Si and Ge; any resemblance to these materials ends at this point, for it turns out that the split-off band has a positive effective mass, while the heavy-mass band has a negative effective mass. A rather strong interaction prevents the two bands from crossing, with the result that the maximum of the valence band and the minimum of the conduction band are removed from the origin of k space.

If d bands alone were involved, then, in the spherical approximation, the same maxima and minima of energy would be found at all orientations in $\mathbf{k}$ space—though the breakdown of the spherical approximation would prevent so peculiar a structure, and both valence and conduction bands would be located on the (111) axes, where the magnitude of the interaction between them is least. However, the $6s$ band interacts strongly with the $5d$ bands, depressing the energies of both split-off and heavy mass bands downward in the (111) directions while leaving them unchanged in the (100) directions. A more subtle—and less comprehensible—effect of the $6s$ band is that it alters the interaction between the valence and conduction bands in such a way that the magnitude of the interaction is virtually independent of orientation; it is therefore only necessary to find where the split-off and heavy mass bands go up or down most steeply in order to locate the orientations of the various maxima and minima. Since both bands are depressed in the (111) directions by their interaction with the s band, the maxima of the valence band must fall on the principal axes of the crystal, while the minima of the conduction band must lie on the (111) axes.

The magnitudes of E_2' and E_σ' are

$$E_2' = -0.02k^2 - 0.32(k_1^2k_2^2 + k_2^2k_3^2 + k_1^2k_3^2)/k^2 - 5.32k_1^2k_2^2k_3^2/k^4,$$

$$E_\sigma' = -\delta + 0.39k^2 - 0.65(k_1^2k_2^2 + k_2^2k_3^2 + k_1^2k_3^2)/k^2.$$

The axes on which the principal maxima and minima of E fall are known; to find the appropriate values of k it is sufficient to use the magnitudes of E_2', E_σ' on these axes alone. But since all the effective masses are required, not just the effective mass parallel to the axis on which the band is formed, E_2' and E_σ' will be expanded to order k_t^2, where k_t is a small component of wave-number normal to the axis in question. Measuring k along an appropriate symmetry axis, E_2' and E_σ' must have the forms

$$E_2' = -\lambda k^2 + lk_t^2, \quad E_\sigma' = -\delta + \nu k^2 + nk_t^2. \tag{36}$$

When $\mathbf{k}$ is on one of the (111) axes, we use the relationship

$$(k_1^2k_2^2 + k_2^2k_3^2 + k_1^2k_3^2)/k^2 \longrightarrow \tfrac{1}{3}k^2 - \tfrac{1}{3}k_t^2 + \cdots$$

$$k_1^2k_2^2k_3^2/k^4 \longrightarrow \frac{1}{27}k^2 - \frac{5}{27}k_t^2 + \cdots.$$

The values of the constants in (36) are then found to be

	λ	l	ν	n	
(100) axis	0.02	-0.32	0.39	-0.65	(37)
(111) axis	0.33	1.09	0.17	0.22.	

The positions of the maxima and minima of E can be derived from (35) and (36), setting $k_t = 0$. The energy eigenvalues are

$$E = \tfrac{1}{2}[-\delta + (\nu - \lambda)k^2] \pm \tfrac{1}{2}\{[\delta - (\nu + \lambda)k^2]^2 + 4Ik^4\}^{1/2}, \tag{38}$$

where $I = (2/9)\bar{C}^2 = 0.30$ (eV)^2.

The values $k = k_0$ for which $\partial E/\partial k = 0$ satisfy the relationship

$$\lambda - \nu = \pm\{(\lambda + \nu)[\delta - (\lambda + \nu)k_0^2] + 4Ik_0^2\}/\{[\delta - (\lambda + \nu)k_0^2]^2 + 4Ik_0^4\}^{1/2}. \tag{39}$$

The solutions of (39) are

$$k_0^2 = \delta[(\lambda + \nu) \pm (\lambda - \nu)I^{1/2}(\lambda\nu + I)^{-1/2}]/[(\lambda + \nu)^2 + 4I]. \tag{40}$$

The ± sign in (40) comes from the solution of another quadratic; values of k_0 must be substituted back into (39) to determine whether they belong to the valence or conduction bands.

The curvature of the band at k_0 is

$$\frac{\partial^2 E}{\partial k^2} = [-2\delta\lambda + 2(\lambda - \gamma)E_0 + 12k_0^2(\lambda\nu + I)]/[\delta + 2E_0 + (\lambda - \nu)k_0^2]. \tag{41}$$

The effective masses normal to the symmetry axis involved can be found from the change in E when k_t is nonzero. This change is

$$\delta E = \tfrac{1}{2}(1 \pm f)lk_t^2 + \tfrac{1}{2}(1 \mp f)nk_t^2, \tag{42}$$

where

$$f = [\delta - (\lambda + \nu)k_0^2]/\{[\delta - (\lambda + \nu)k_0^2]^2 + 4Ik_0^4\}^{1/2}.$$

Since k is the reduced wave number defined in (9), the effective mass is given by

$$\frac{m^*}{m} = \frac{4\hbar^2}{ma^2} \bigg/ \frac{\partial^2 E}{\partial k^2} = 0.733 \bigg/ \frac{\partial^2 E}{\partial k^2} \text{ (E being in eV)}. \tag{43}$$

Using the relationship (38) to (43), together with the table of values listed in (37), the effective masses and other quantities are found to be

	m_1/m	m_2/m	m_N/m	σ_i	E_0	E_g	k_0
Valence band	0.52	0.60	0.57	1.0	-0.89δ	0.81δ	0.24
Conduction band	0.53	0.37	0.42	1.15	-0.08δ		0.22

where m_1= effective mass parallel to symmetry axis, m_2= effective mass normal to symmetry axis, m_N = density-of-states effective mass, $m_N=(m_1m_2^2)^{1/3}$, σ_i = conductivity of band when material is intrinsic, (normalized to 1.0 for the valence band), E_0= value of E at which the band is formed, E_g= band gap, and k_0 = value of k at which the band is formed.

The first four columns listed above do not depend on δ; using the experimental value of E_g (0.08 eV), δ was found to be 0.10 eV. The value of k_0 was derived from this value. The conductivities σ_i are estimated by making the (probably correct) assumption that the scattering mechanisms for both bands are the same, so that the conductivities will be proportional to $nm_N^{3/2}(1/m_1+2/m_2)$, n being the number of bands.

The bands are drawn in Fig. 3. Further comment on the results is reserved for the final section of this paper.

E. Inequality of the Transverse Masses in the Valence Bands

This calculation has proceeded so far as though the only relevant part of the lattice were a face-centered cubic lattice of Pt ions, a substantial number of interactions that have the symmetry T^h rather than O^h having been ignored. The most important result of the author's disregard of the true symmetry of the crystal has been that both valence and conduction bands appear as ellipsoids of revolution about the appropriate axes. However, it is possible without violating the symmetry for a band located on one of the (100) axes to have three distinct effective masses rather than two—though this is not possible when the band is on one of the (111) axes. This effect is observed in the magnetoresistance of p-type samples; the data can be fitted by supposing the surfaces of constant energy in the valence band to be ellipsoids centered on the (100) axes, the principal axes of the ellipsoids being in the ratio 0.7:1.0:1.3.

The author has not been able to calculate the magnitude of this effect, and must therefore be content with a demonstration that it exists. This demonstration could, presumably, be given in terms of a sum of the interactions of the d bands with all other bands, but such a procedure would both be cumbersome and would still fail to give quantitative results; for this reason only interactions that are already known will be used. Such interactions are those between the principal d bands and the other d bands, and also those with the s bands; the latter are far simpler in form, so they alone will be considered.

If the moduli of the matrix elements connecting some band μ of energy $E_\mu(\mathbf{k})$ with the basic d states $|i\rangle$ are $H_{i\mu}$, then the changes in energy of the split-off band and the heavy mass band are

$$\delta E_\sigma=\tfrac{1}{3}[H_{1\mu}^2+H_{2\mu}^2+H_{3\mu}^2]/(E_\sigma-E_\mu),$$

$$\delta E_2=\frac{1}{k^2}[\tfrac{1}{6}(k^2+3k_3^2)H_{1\mu}^2+\tfrac{1}{6}(k^2+3k_2^2)H_{2\mu}^2+\tfrac{1}{6}(k^2+3k_1^2)H_{3\mu}^2+k_2k_3H_{1\mu}H_{2\mu}+k_1k_3H_{1\mu}H_{3\mu}+k_1k_2H_{2\mu}H_{3\mu}]/(E_2-E_\mu).$$

(the latter formula is quite readily proved in the spherical approximation by the same means that are used in the Appendix in deriving the interaction between the bands E_2, E_σ).

The low-energy s band produces no effects that are of any consequence in the present discussion; it is the upper three which involve the crystal symmetry. The energies are listed in (31a), the interaction matrix elements $H_{i\mu}$ are the last three columns of (31b). Both energies and matrix elements will be used in the form in which they are shown (but with $E_{ds}=0$), and the perturbations written out to order k^4; terms of fourth order in $\mathbf{k}$ that should appear in both the E_μ and $H_{i\mu}$ will be neglected—they add only to the complexity of the results without altering their form. On setting $Q=P$ one finds

$$\delta E_\sigma=-\alpha^2\frac{P^2}{S}\left[1+\frac{9}{4}k^2+\frac{11}{48}k^4\right],$$

$$\begin{aligned}\delta E_2=-\alpha^2\frac{P^2}{S}-\frac{5}{8}\alpha^2\frac{P^2}{S}\{k^2+(k_1^2k_2^2+k_2^2k_3^2+k_1^2k_3^2)/k^2\}\\ -\frac{\alpha^2}{48}\frac{P^2}{S}\{9k^4-9\tfrac{2}{3}(k_1^2k_2^2+k_2^2k_3^2+k_1^2k_3^2)+11k_1^2k_2^2k_3^2/k^2+\tfrac{3}{2}(k_1^6+k_2^6+k_3^6)/k^2\}\\ +\frac{3}{64}\alpha^2\frac{P^2}{S}\{k_1^4(k_2^2-k_3^2)+k_2^4(k_3^2-k_1^2)+k_3^4(k_1^2-k_2^2)\}/k^2. \quad (44)\end{aligned}$$

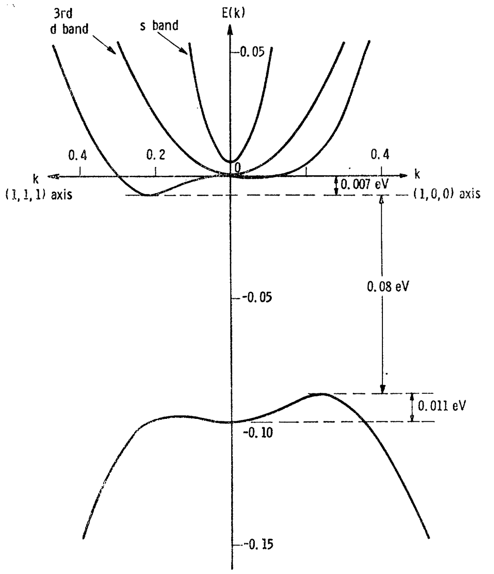

FIG. 3. Band structure near $k=0$. The position of the s band is undetermined; it need not come as close to the d bands as is indicated.

The only term of interest here is the last term in δE_2, for it is the only term that does not involve full cubic symmetry. The method which will be followed is to add this term into the secular equation (35), neglecting any changes in the coupling of the valence and conduction bands. This procedure is adequate for demonstration purposes, though not sufficient for a full evaluation of the effect.

If the maximum of the valence band on the x axis is at $\mathbf{k}=(k_0,0,0)$, then the last term in (44) is proportional to $k_0^2(k_2^2-k_3^2)$ in the neighborhood of this maximum. Adding this term into the secular equation, the alteration in the valence band becomes

$$\delta E_{v(100)}=\tfrac{1}{2}(1-f)\frac{3}{64}\alpha^2\frac{P^2}{S}k_0^2(k_2^2-k_3^2),$$

f being defined in (42). The nature of this change is clear: it represents an increase in the effective mass parallel to the y axis, and a decrease in the effective mass parallel to the z axis; the symmetry of the corresponding changes for bands on the y and z axes can be read off from (44). It is readily verified that terms such as the above do not affect the equality of the transverse masses in the conduction band.

The actual magnitude of this contribution to the mass difference is only 10^{-3} electron masses, or about 0.5% of the total difference; it is, however, typical in form of other contributions, particularly in the absence of any effect from E_σ. The magnitude of $\tfrac{1}{2}(1-f)$ is 0.12, so that only 12% of any change in E_2 appears in E_v; this would imply a rather gross distortion of E_2 if it alone were to provide the observed mass difference. It therefore seems likely that the greater part of the effect is derived from a change in the interband coupling.

IV. CONCLUSION

The above model of the band structure of $PtSb_2$ has eight conduction band minima on the (111) axes, and six valence band maxima on the (100) axes. Piezoresistance and magnetoresistance data suggest that the symmetry assignments are correct. The most striking feature of the calculated bands is the extreme compression of the structure around the origin of **k** space, resulting in very shallow maxima and minima—the barrier between the maxima of the valence band is 0.011 eV, that between the minima of the conduction band is 0.007 eV. For energies of excitation greater than the barrier height the original six or eight surfaces of equal energy fuse into a single surface; cross sections of this surface are shown in Fig. 4 for the valence band in the case when $E=-\delta$. The surface contains 3×10^{19} states; it may be possible to detect this effect through the abrupt decrease in frequency of de Haas–van Alphen oscillations that would result when the doping exceeded this level, provided that the mobility were not too low.

There are few methods which could detect the suggested compression of the band structure, but infrared absorption could provide a check on the calculation if sufficiently pure samples were available. The first absorption edge corresponds to an indirect electronic transition, since the conduction band is not above the valence band; the least band gap for direct transitions is 0.91δ. Direct transitions should therefore start at photon energies only 0.01 eV above the first absorption edge.

The only check that can be made on this calculation is through the transport data of Damon *et al.*[10] At low

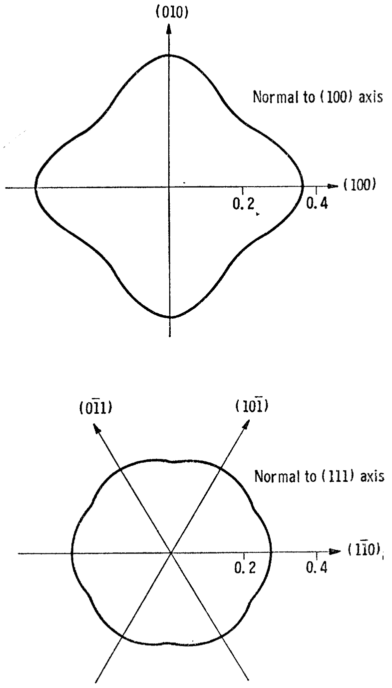

FIG. 4. Valence band; cross sections of the surface of constant energy for $E=-\delta$. The volume contained is equivalent to 2.9×10^{19} electron states.

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[10] D. H. Damon, R. C. Miller, and A. Sagar (to be published).

temperatures and impurity levels the calculated values of the effective masses are given as the simple values at the stationary points, as in Sec. IIID. At high temperatures and impurity levels the majority of the holes or electrons move in a single deformed band rather than in several degenerate bands; an estimate of the effective masses at high temperature was made by finding the angular average of the effective mass at mean excitation energies corresponding to 700°K in the valence band, and to 1100°K in the conduction band.[11] The calculated ratios of masses at high temperatures are presented as though the bands were ellipsoids of revolution about the appropriate symmetry axes, with mass m_1 parallel to the axis and m_2 normal to it; m_1 is found from $\partial^2E/\partial k^2$ when $\mathbf{k}$ is on the axis, and m_2 then obtained from the relation

$$\frac{1}{\bar{m}}=\frac{1}{3}\left(\frac{1}{m_1}+\frac{2}{m_2}\right),$$

$\bar{m}$ being the mean effective mass. This scheme was followed since it is the way in which experimental results are usually interpreted, and since it gives a convenient estimate of the warping of the band.

The comparison with experiment is shown at the top of the next column. The first figure given for each calculated quantity is for low temperature, the second for high temperature. The measured values are given under the appropriate calculated values.

	$(m_N)_v$	$(m_N)_c$	$(m_1/m_2)_v$	$(m_1/m_2)_c$	$(\sigma_i)_c/(\sigma_i)_v$
Calc.	0.57–0.72	0.42–0.54	0.87–0.67	1.43–1.36	1.15–1.6
Obs.	0.21–0.7	0.5	0.61	$2\pm\frac{1}{2}$	1.3

Subscripts c and v refer to the conduction and valence bands, respectively.

The total density-of-states effective mass for the valence band—i.e., $n^{2/3}m_N$, where n is the number of bands—was determined from the variation of Seebeck coefficient with carrier concentration at 77°K; the value found, 0.7, also fitted the high-temperature data, which were used to find the ratio of densities of states in the conduction and valence bands. The mass ratio in the valence band is derived from the magnetoresistive effect; the value given refers to the mean transverse mass, since the two transverse masses are not in fact equal (Sec. IIIE). The mass ratio in the conduction band is a rough estimate from the piezoresistivity.

ACKNOWLEDGMENTS

The author wishes to thank Dr. R. C. Miller for first drawing his attention to this subject and for subsequent useful information, and also Dr. D. H. Damon, most particularly for pointing out the importance of the s bands.

APPENDIX A: THE BASIS STATES

The angular dependences of the various basic d states, derived in the same way as (3), are

$$\begin{aligned}
(x'y')_{(000)}&=f(xy)-\alpha(yz)+\alpha(xz)+\alpha(x^2-y^2)\\
(x'z')_{(000)}&=-\alpha(xy)-\alpha(yz)+f(xz)+\tfrac{1}{2}\alpha(x^2-y^2)-\tfrac{1}{2}\alpha(3z^2-r^2)\\
(y'z')_{(000)}&=\alpha(xy)+\alpha(xz)+f(yz)+\tfrac{1}{2}\alpha(x^2-y^2)+\tfrac{1}{2}\alpha(3z^2-r^2)\\
(x'y')_{(110)}&=f(xy)-\alpha(xz)-\alpha(yz)-\alpha(x^2-y^2)\\
(x'z')_{(110)}&=\alpha(xy)+f(xz)+\alpha(yz)+\tfrac{1}{2}\alpha(x^2-y^2)-\tfrac{1}{2}\alpha(3z^2-r^2)\\
(y'z')_{(110)}&=\alpha(xy)-\alpha(xz)+f(yz)-\tfrac{1}{2}\alpha(x^2-y^2)-\tfrac{1}{2}\alpha(3z^2-r^2)\\
(x'y')_{(011)}&=f(xy)-\alpha(xz)+\alpha(yz)+\alpha(x^2-y^2)\\
(x'z')_{(011)}&=\alpha(xy)+f(xz)-\alpha(yz)-\tfrac{1}{2}\alpha(x^2-y^2)+\tfrac{1}{2}\alpha(3z^2-r^2)\\
(y'z')_{(011)}&=-\alpha(xy)+\alpha(xz)+f(yz)-\tfrac{1}{2}\alpha(x^2-y^2)-\tfrac{1}{2}\alpha(3z^2-r^2)\\
(x'y')_{(101)}&=f(xy)+\alpha(xz)+\alpha(yz)-\alpha(x^2-y^2)\\
(x'z')_{(101)}&=-\alpha(xy)+f(xz)+\alpha(yz)-\tfrac{1}{2}\alpha(x^2-y^2)+\tfrac{1}{2}\alpha(3z^2-r^2)\\
(y'z')_{(101)}&=-\alpha(xy)-\alpha(xz)+f(yz)+\tfrac{1}{2}\alpha(x^2-y^2)+\tfrac{1}{2}\alpha(3z^2-r^2),
\end{aligned}$$

where $f=(1-\alpha^2)^2/(1+2\alpha^2)^2$.

APPENDIX B: MISCELLANEOUS MATRICES

The various matrices a_μ, b_μ defined in (6) are

$$a_1=\alpha\begin{pmatrix} \cdot & -(A-B)c_1c_2+(C+D)s_1s_2 & -(A+B)c_1c_2-(C-D)s_1s_2 \\ (A-B)c_1c_2+(C+D)s_1s_2 & \cdot & \cdot \\ -(A+B)c_1c_2+(C-D)s_1s_2 & \cdot & \cdot \end{pmatrix},$$

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[11] The latter temperature is the calculated degeneracy temperature in the only n-type sample used, with 6×10^{19} electrons/cm^3; the former an estimate of the region which was most important in finding the high-temperature results in p-type samples. The temperature chosen is not very critical, the mean effective mass in the conduction band only changes from 0.40 to 0.56 as the excitation increases from 300°K to infinity, most of the change occurs at low energies.

$$a_2=\alpha\begin{bmatrix} \cdot & \cdot & (A-B)c_2c_3-(C+D)s_2s_3 \\ \cdot & \cdot & -(A+B)c_2c_3+(C-D)s_2s_3 \\ -(A-B)c_2c_3-(C+D)s_2s_3 & (A+B)c_2c_3+(C-D)s_2s_3 & \cdot \end{bmatrix},$$

$$a_3=\alpha\begin{bmatrix} \cdot & -(A+B)c_1c_3-(C-D)s_1s_3 & \cdot \\ -(A+B)c_1c_3+(C-D)s_1s_3 & \cdot & (A-B)c_1c_3+(C+D)s_1s_3 \\ \cdot & -(A-B)c_1c_3+(C+D)s_1s_3 & \cdot \end{bmatrix},$$

$$b_1=\alpha\begin{bmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & -2Bc_1c_2 \\ \cdot & 2Bc_1c_2 & \cdot \end{bmatrix}\quad b_2=\alpha\begin{bmatrix} \cdot & 2Bc_2c_3 & \cdot \\ -2Bc_2c_3 & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{bmatrix}\quad b_3=\alpha\begin{bmatrix} \cdot & \cdot & -2Bc_1c_3 \\ \cdot & \cdot & \cdot \\ 2Bc_1c_3 & \cdot & \cdot \end{bmatrix}.$$

The matrices d_i can be derived from the above from their definition in Eq. (12). One of them, d_3, will be used in the next section of the Appendix; its explicit form is

$$d_3=\alpha\begin{bmatrix} \cdot & -(C-D)s_1s_3 & (C+D)s_2s_3 \\ (C-D)s_1s_3 & \cdot & -(A+B)c_2c_3+(A-B)c_1c_3-2Bc_1c_2 \\ (C+D)s_2s_3 & -(A+B)c_2c_3-(A-B)c_1c_3+2Bc_1c_2 & \cdot \end{bmatrix}.$$

The matrix of the spin-orbit coupling Hamiltonian (17) is

$$\begin{bmatrix} \cdot & i\mu & -\mu & & & \\ -i\mu & \cdot & i\mu & & 0 & \\ -\mu & -i\mu & \cdot & & & \\ & & & \cdot & -i\mu & \mu \\ & 0 & & i\mu & \cdot & i\mu \\ & & & \mu & -i\mu & \cdot \end{bmatrix},$$

the states being written in the order $|\alpha 3\rangle$, $|\alpha 2\rangle$, $|\beta 1\rangle$, $|\beta 3\rangle$, $|\beta 2\rangle$, $|\alpha 1\rangle$.

APPENDIX C: INTERACTIONS BETWEEN THE BANDS AT THE CUBIC ZONE BOUNDARY

It was stated at the end of Sec. II that the d orbitals could not give rise to a band gap at the first cubic zone boundary; the proof will now be given though it should be noticed that even if such a gap did exist a filled valence band could still not be formed from doubly ionized Pt since the s band would now be partially filled.

Consider the behavior of the bands near the intersection of the x axis with the zone boundary; at $\mathbf{k}=(\pi/2,0,0)$ both H_0 and H_3 are equal and diagonal, the diagonal elements being B_r, B_r, $-A_r$. The energies, B_r are those which correspond to doubly ionized Pt, being approached from below by H_0 and from above by H_3 as the wave vector increases toward the zone boundary; since these eigenvalues are those of the states $|1\rangle$ and $|2\rangle$, it is at first expected that a band gap will arise from the interactions of these states through d_3, which links H_0 and H_3. However, for values of $\mathbf{k}$ close to $(\pi/2,0,0)$, the relevant part of d_3 is

$$\begin{bmatrix} 0 & -\alpha(C-D)k_3 \\ \alpha(C-D)k_3 & 0 \end{bmatrix},$$

which is zero along the line $k_1=\pi/2$, $k_3=0$. A finite interaction on this line must come from a mixing of the state $|3\rangle$ with the states $|1\rangle$ and $|2\rangle$, since the elements of d_3 involving the interaction between $|2\rangle$ and $|3\rangle$ are finite over the whole zone boundary. Such a mixture of states occurs everywhere except at the point $\mathbf{k}=(\pi/2,0,0)$, since H_0 and H_3 are nondiagonal elsewhere; it then remains to see whether the introduction of spin-orbit coupling will lift the degeneracy at this point.

At $\mathbf{k}=(\pi/2,0,0)$ the sum of H_0, or H_3, and the spin-orbit coupling Hamiltonian is

$$M=\begin{bmatrix} B_r & -i\mu & & & -\mu & \\ i\mu & B_r & & & -i\mu & \\ & & B_r & -i\mu & & \mu \\ & & i\mu & B_r & & i\mu \\ -\mu & i\mu & & & A_r & \\ & & \mu & -i\mu & & A_r \end{bmatrix},$$

unmarked elements being zero, and the states being written in the order $|\beta 1\rangle$, $|\alpha 2\rangle$, $|\alpha 1\rangle$, $|\beta 2\rangle$, $|\alpha 3\rangle$, $|\beta 3\rangle$.

M can be simplified by a similarity transformation with the matrix S

$$S=\begin{bmatrix} V & & \\ & V & \\ & & I \end{bmatrix},\quad \text{where}\quad V=\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & i \\ i & 1 \end{pmatrix}$$

and I is the 2×2 unit matrix. We then find

$$S^{-1}MS=\begin{bmatrix} B_r+\mu & & & & -\sqrt{2}\mu & \\ & B_r-\mu & & & & \\ & & B_r+\mu & & & \sqrt{2}\mu \\ & & & B_r-\mu & & \\ -\sqrt{2}\mu & & & & A_r & \\ & & \sqrt{2}\mu & & & A_r \end{bmatrix}.$$

The eigenvalues $B_r-\mu$ are exact; the degeneracy at the zone edge cannot be split by any interaction that has so far been invoked. The eigenfunctions corresponding to the energies $B_r-\mu$ are

$$\frac{1}{\sqrt{2}}[\alpha 1|\rangle+i|\beta 2\rangle],\quad \frac{1}{\sqrt{2}}[-i|\beta 1\rangle+|\alpha 2\rangle].$$

Corresponding eigenfunctions can be found on the other zone boundaries; they are

$$\text{at}\quad \mathbf{k}=(0,\pi/2,0);\ \frac{1}{\sqrt{2}}[|\alpha 1\rangle-|\beta 3\rangle],\quad \frac{1}{\sqrt{2}}[|\beta 1\rangle+|\alpha 3\rangle].$$

$$\text{at}\quad \mathbf{k}=(0,0,\pi/2);\ \frac{1}{\sqrt{2}}[i|\alpha 2\rangle+|\alpha 3\rangle],\quad \frac{1}{\sqrt{2}}[|\beta 2\rangle+i|\beta 3\rangle].$$

The functions in this set are both eigenfunctions of the spin-orbit coupling and are invariant under the symmetry operations of the crystal. There is, therefore, no way in which the crystal potential can remove the degeneracy at the zone boundary.

APPENDIX D: INTERACTION BETWEEN THE VALENCE AND CONDUCTION BANDS

We here find the term $|T_{35}|^2+|T_{36}|^2$, the elements T_{ij} being defined in (26); the spherical approximation [preceding Eq. (26)] will be assumed valid.

The quantities needed to determine the matrix U defined in (24) are:

$$E_1-a=\tfrac{1}{2}\bar{C}(k_2^2+k_3^2),\qquad ce^{i\theta}=\frac{1}{2\sqrt{3}}\bar{C}[(k_2^2-k_3^2)-2ik_1k_2],$$

$$de^{i\phi}=-\frac{1}{\sqrt{3}}\bar{C}k_3(k_1-ik_2),\qquad \Delta^2=\tfrac{1}{3}\bar{C}^2k^2(k_2^2+k_3^2).$$

The elements of $\mathcal{H}_{i\sigma}$, defined in (20), are:

$$\mathcal{H}_{15}=-\frac{1}{\sqrt{6}}\bar{C}[(k_3^2-k_2^2)-ik_1k_2],\qquad \mathcal{H}_{25}=\frac{1}{3\sqrt{2}}\bar{C}[3k_1^2-k^2-3ik_1k_2],$$

$$\mathcal{H}_{16}=-\frac{1}{\sqrt{6}}\bar{C}k_3[k_1+2ik_2],\qquad \mathcal{H}_{26}=-\frac{1}{\sqrt{2}}\bar{C}k_1k_3,$$

$$\mathcal{H}_{35}=\mathcal{H}_{26}\qquad \mathcal{H}_{36}=-\mathcal{H}_{25}^*,\qquad \mathcal{H}_{45}=-\mathcal{H}_{16}^*\qquad \mathcal{H}_{46}=\mathcal{H}_{16}^*.$$

Only T_{35} and T_{36} are needed; their evaluation proceeds most readily by first using the form for U given in (24) and the above relationships between the $\mathcal{H}_{i\alpha}$ before substituting the explicit forms of the matrix elements. One then finds

$$T_{35}=\sum_\alpha U_{\alpha 3}^*\mathcal{H}_{\alpha 5}=\frac{1}{\Delta\sqrt{2}}[X+iYe^{-i(\theta+\phi)}],$$

$$T_{36}=\sum_\alpha U_{\alpha 3}^*\mathcal{H}_{\alpha 6}=\frac{1}{\Delta\sqrt{2}}[-Y^*+iX^*e^{-i(\theta+\phi)}],$$

where

$$X=-(E_1-a)\mathcal{H}_{15}-ce^{i\theta}\mathcal{H}_{26}+de^{i\phi}\mathcal{H}_{25}$$

$$=-\frac{2}{3\sqrt{6}}\bar{C}^2k^2[(k_2^2+k_3^2)-ik_1k_2],$$

and

$$Y=(E_1-a)\mathcal{H}_{16}^*-ce^{i\theta}\mathcal{H}_{26}+de^{i\phi}\mathcal{H}_{25}$$

$$=-\frac{2}{3\sqrt{6}}\bar{C}^2k^2k_3[k_1-2ik_2].$$

Then

$$|T_{35}|^2+|T_{36}|^2=\frac{1}{\Delta^2}(XX^*+YY^*)$$

$$=(2/9)\bar{C}^2k^4.$$