Magnetic Energy Levels in the Bismuth Conduction Band

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(Received 2 September 1964)

The effect of other bands on the structure of the conduction band of bismuth is examined by means of perturbation theory. The unperturbed Hamiltonian is that of the Cohen-Blount two-band model as used by Lax and Mavroides and investigated more fully by Wolff. The new terms appearing in the effective-mass Hamiltonian are those already studied by Cohen in the absence of a magnetic field plus those which arise in the presence of a field because the various components of the quasimomentum do not commute. Formulas are presented for the Landau levels at $p_z=0$ which can be compared with the expressions of Cohen and Blount and of Smith, Baraff, and Rowell.

I. INTRODUCTION

THE electronic structure of the conduction band of bismuth is both understandable and interesting. For this reason, the material has been the object of much experimental and theoretical study. The adjective "understandable" applies because a simple model of the band structure seems to describe the gross electronic properties very closely, and the adjective "interesting" applies because the electrons populating the conduction band have such low masses and are so few in number that a variety of quantum effects can be observed under conditions of moderately strong fields and moderately low temperatures.[1]

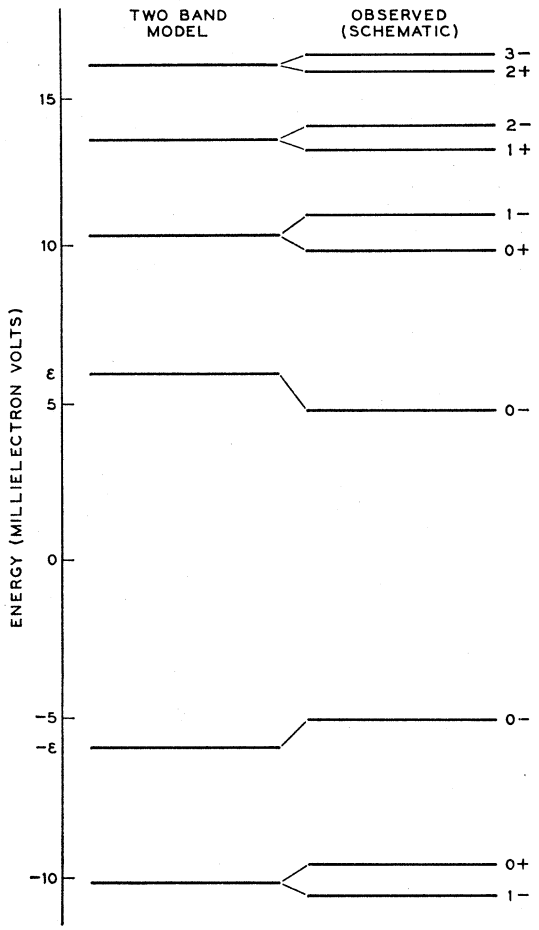

FIG. 1. Comparison between the magnetic energies as predicted by the two-band nonparabolic model and the sort of magnetic energies actually observed.

The simple model which has been successful in describing the conduction band is the so-called two-band model, in which the properties of the conduction band are determined by the presence of a valence band separated from it by a very small energy gap. As was first shown by Cohen and Blount,[2] this situation leads to a spin mass which is equal to the cyclotron mass. Thus, the energy levels, labeled by orbital quantum number $n=0, 1, 2, \cdots$ and spin quantum number $s=\pm 1$ have the characteristic degeneracy

$$E(n+1, s=-1)=E(n, s=+1). \tag{1.1}$$

The observed levels in bismuth are approximately degenerate as given by (1.1), with fractional deviations $\delta(n)$

$$\delta(n)=\frac{E(n+1, s=-1)-E(n, s=+1)}{E(n+1, s=-1)-E(n, s=-1)} \tag{1.2}$$

ranging from about 10 to 30% depending on the direction of the magnetic field.[3] Figure 1 represents schematically the levels in one of the conduction-band minima for a fixed magnetic field.

It is clear that the nonzero values of δ arise from the presence of bands other than the two considered in the two-band model. Our purpose in this paper is to calculate the effect of these other bands on the energy levels $E(n,s)$ by using a perturbation theory in which the two-band model plays the role of the unperturbed Hamiltonian. We shall find reasonably simple forms for the dependence of $E(n,s)$ on the strength and orientation of the magnetic field. These forms contain parameters which will have to be evaluated experimentally, but at least the forms given provide the framework by which future experiments may be interpreted.

[1] L. C. Hebel, Symposium on Plasma Effects in Solids, International Conference on the Physics of Semiconductors, Paris, 1964 (unpublished).
[2] M. H. Cohen and E. I. Blount, Phil. Mag. **5**, 115 (1960).
[3] G. E. Smith, G. A. Baraff and J. M. Rowell, Phys. Rev. **135**, A1118 (1964).

In Sec. II, we use standard Luttinger–Kohn[4] techniques to obtain an effective two-band Hamiltonian which includes the effects of other bands to lowest order. The same program has been carried out by Cohen[5] in the absence of a magnetic field. Although Cohen was able to solve his equations exactly so as to obtain an analytic $E(\mathbf{p})$ energy momentum relationship, his $E(\mathbf{p})$ is not the proper starting point for studying the magnetic energy levels because his treatment discards the antisymmetric part of the effective mass tensor which gives rise to the spin energy.[6]

Our effective two-band Hamiltonian may be expressed as a sum of two parts. One part is the two-band Hamiltonian proposed by Lax and Mavroides[7] and studied in greater detail by Wolff.[8] The other part includes the effect of the other bands. The successes of the Lax and Mavroides form of the two-band model in fitting magnetoreflection experiments[9,10] suggests that the "other band" part of our Hamiltonian will be small, at least in the light-mass directions. It is then natural to use perturbation theory with Wolff's eigenfunctions as the unperturbed states. This we do, relegating the details to the three appendices A, B, C and stating the results in Sec. III. Section IV describes the energy-level structure resulting and discusses what should be seen experimentally. In that section, we compare the formulas to those of Cohen and Blount. Finally, Appendix D makes contact between our results and those formulas used by Smith, Baraff, and Rowell[3] (SBR) in the interpretation of the magnetoresistance measurements.

This first-order perturbation approach probably loses its validity in the heavy mass direction. First of all, the heavy mass itself cannot be understood within the context of a pure two-band model.[2,5] Secondly, the parameter $\delta(n)$ becomes almost $\frac{1}{3}$ in this direction,[3] indicating large deviations from the two-band model, i.e., indicating a perturbation which is no longer small.

The principal conclusions of this work are twofold; first that the motion of the two $n=0$, $s=-1$ levels with magnetic field is, for a fixed field direction, either linear or hyperbolic, as shown in Fig. 2. If the levels approach and repel each other, as in the lower figure, then the optical activity as seen in cyclotron resonance experiments, etc., will transfer from one level to the other at the field of closest approach. The second conclusion is that the motion of the other levels is given by formulas similar to that used by SBR, but modified by allowing the orbital inverse mass tensor and spin inverse mass tensor to be linear functions of energy.

II. THE EFFECTIVE HAMILTONIAN

The method we shall use to study the magnetic spectrum of the conduction band is similar to the standard one for studying cyclotron resonance in semiconductors at a point of degeneracy. The difference is that in bismuth, the conduction-band minimum (which is twofold degenerate because of spin) has an energy only slightly greater than the valence band (also doubly degenerate) lying just beneath it. The energy gap E_G between the conduction-band minimum and the valence-band maximum is smaller than the magnetic energies and thus must be treated as though valence and conduction bands were degenerate. The situation is similar to that in InSb where the energy gap is comparable to the kinetic energies of interest. Kane's[11] treatment of the InSb band structure provides the generalization of the field-free Kohn–Luttinger method to the situation of near degeneracy, and the Bowers and Yafet[12] treatment of the magnetic susceptibility of InSb provides the generalization of the Kohn–Luttinger method to the case of small gap and large magnetic field. We must apply this method to the conduction band of bismuth by specifying the parameters to be used in the equations. More to the point, we must specify the relations *between* these parameters which exist because of the symmetry

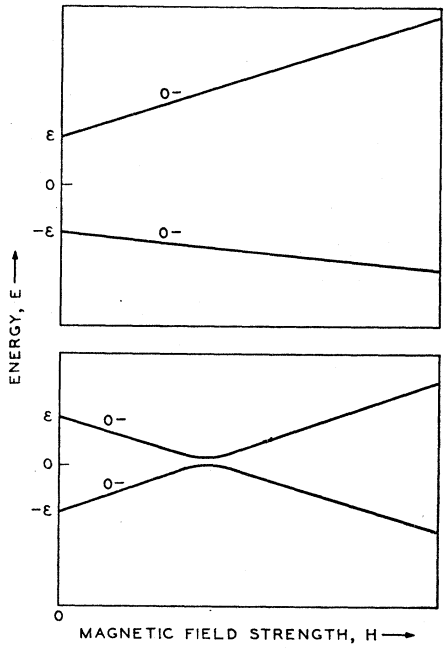

FIG. 2. Energy of the two 0^- Landau levels as a function of magnetic field. The levels may either approach each other and repel or else may repel each other initially, depending on the direction of the magnetic field.

[4] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).
[5] M. H. Cohen, Phys. Rev. **121**, 387 (1961).
[6] J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).
[7] B. Lax, Bull Am. Phys. Soc. **5**, 167 (1960); and B. Lax and J. G. Mavroides, in *Advances in Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 11.
[8] P. A. Wolff, Phys. Chem. Solids (to be published).
[9] R. N. Brown, J. G. Mavroides, and B. Lax, Phys. Rev. **129**, 2055 (1963).
[10] L. C. Hebel and P. A. Wolff, Phys. Rev. Letters **11**, 368 (1963).
[11] E. O. Kane, Phys. Chem. Solids **1**, 249 (1957).
[12] R. Bowers and Y. Yafet, Phys. Rev. **115**, 1165 (1959).

of the bismuth crystal. Some of the work has already been done for us by Cohen and Blount[2] and by Cohen.[5] All that remains is for us to study the form of the "other band" contributions to the effective Hamiltonian. Our notations will follow that of Ref. 2 where possible; but before starting, let us review briefly the ideas on which the calculation rests.

Suppose that one has a Hamiltonian H and a Schrödinger equation

$$H=H_0+V, \tag{2.1a}$$

$$H\psi=E\psi, \tag{2.1b}$$

for which the eigenstates and energies of the unperturbed Hamiltonian H_0 are known:

$$H_0\varphi_n=\epsilon_n\varphi_n. \tag{2.2}$$

Among the energies ϵ_n are some which are very close to E. These will be called the degenerate energies and will be labeled by a subscript i or $j=1, 2, \cdots, r$. The other energies far from E will be labeled by a subscript $p=r+1, r+2, \cdots$. To solve (2.1), one expands ψ in eigenstates of H_0, $\psi=\sum A_n\varphi_n$, and arrives in the usual way[13] at

$$\sum_{j=1}^{r}\left(\epsilon_j\delta_{ij}+V_{ij}-\sum_{p=r+1}^{\infty}\frac{V_{ip}V_{pj}}{\epsilon_p}\right)A_j=EA_i \tag{2.3}$$

as the equation determining the energy and that portion of the wave function within the degeneracy set. The zero of energy has been taken at the average energy of the degeneracy set.

The motion of the electron in a perfect crystal under the influence of a magnetic field is assumed to be governed by the Pauli Hamiltonian,

$$H=(\mathbf{p}-e\mathbf{A}/c)^2/2m+U(r)+(\hbar/4m^2c^2)(\mathbf{p}-e\mathbf{A}/c)\cdot\boldsymbol{\sigma}\times\boldsymbol{\nabla}U(r), \tag{2.4}$$

where $U(r)$ is the periodic crystal potential, $\mathbf{p}$ is the actual momentum, $\mathbf{A}(\mathbf{r})$ is the vector potential giving rise to the magnetic field $\mathfrak{K}=\boldsymbol{\nabla}\times\mathbf{A}$, and $\boldsymbol{\sigma}$ are the three Pauli matrices, the last term representing the spin-orbit coupling. Luttinger and Kohn[4] introduced a useful set of states $\varphi_n(\mathbf{k},\mathbf{r})$ for expanding the wave function. If their expansion is written as

$$\psi(\mathbf{r})=\sum\int d\mathbf{k}A_n(\mathbf{k})\varphi_n(\mathbf{k},\mathbf{r}) \tag{2.5}$$

then their equation analogous to (2.3) is

$$\sum_j\left\{\left(\epsilon_j+\frac{1}{2m}\boldsymbol{\pi}\cdot\boldsymbol{\pi}\right)\delta_{ij}+\mathbf{v}_{ij}\cdot\boldsymbol{\pi}-\sum_p\frac{\boldsymbol{\pi}\cdot\mathbf{v}_{ip}\mathbf{v}_{pj}\cdot\boldsymbol{\pi}}{\epsilon_p}\right\}A_j(k)=EA_i(k), \tag{2.6}$$

where $\mathbf{v}_{ij}$ are matrix elements of the velocity operator evaluated at a fixed k_0, the ϵ_j are band energies at k_0 and the $\boldsymbol{\pi}$ are differential operators

$$\boldsymbol{\pi}=\hbar(\mathbf{k}-\mathbf{k}_0)-\frac{e}{c}\mathbf{A}(i(\partial/\partial\mathbf{k})). \tag{2.7}$$

Equation (2.6) is general and must be specialized to describe bismuth by assigning the energies ϵ_n and the matrix elements $\mathbf{v}_{ij}$ in accord with what is known about the bismuth band structure and symmetry. Time reversal and a center of inversion in the bismuth crystal results in a degeneracy such that there are two states $\varphi_{01}(k_0,r)$ and $\varphi_{02}(k_0,r)$ with the same energy ϵ_0 at k_0 the minimum of the conduction band. These two states are time-reversal conjugates of each other, that is,

$$\varphi_{02}(k_0,r)=\hat{U}\varphi_{01}(k_0,r), \tag{2.8a}$$

$$\hat{U}=(i\sigma_y)CI, \tag{2.8b}$$

$$\hat{U}^2=-1. \tag{2.8c}$$

I denotes spatial inversion and C denotes complex conjugation. The operator $i\sigma_yC$ is the time-reversal operator in the presence of spin. The operator $\hat{U}$ plays an important role in restricting the form of the velocity matrix elements.

There are also two states $\varphi_{a1}(k_0,r)$ and $\varphi_{a2}(k_0,r)=\hat{U}\varphi_{a1}(k_0,r)$ with the same energy ϵ_a at the top of the valence band. These four states and these two energies will be our degeneracy set j to be used in Eq. (2.6). This split into a degeneracy set and other states far removed is a basic assumption of the model. The evidence for the remoteness of the other states is again the validity of the *simple* two-band model in which the other states are, in effect, infinitely removed in energy.

Since energies are to be measured from the average energy of the degeneracy set,

$$\epsilon_0=-\epsilon_a=\tfrac{1}{2}E_G\equiv\epsilon.$$

The operator $\hat{U}$ which causes the degeneracy also leads to the relations between the velocity matrix elements[2]

$$\begin{aligned}(01|\,\mathbf{v}\,|a1)&=\mathbf{t}=(a2|\,\mathbf{v}\,|02),\\(01|\,\mathbf{v}\,|a2)&=\mathbf{u}=-(a1|\,\mathbf{v}\,|02).\end{aligned} \tag{2.9}$$

If at this point we were to ignore the second and fourth terms on the left of (2.6), we would have exactly the equations of the two-band model as studied by Wolff.[8] Our main interest, however, is in just those two terms in Eq. (2.6) which augment the standard two-band model.

The last term on the left of (2.6) may be regarded as composed of the matrix elements of the tensor operator

$$S_{\alpha\beta}=V_\alpha PH_0^{-1}V_\beta,$$

where P is the projection operator out of the degeneracy set, i.e., it acts to restrict the sum over intermediate

[13] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison Wesley Publishing Company, Reading, Massachusetts, 1958), p. 137.

states to states p outside the degeneracy set. From the definition, Hermiticity, and the fact that velocity but not energy changes sign under time reversal, it follows that $S_{\alpha\beta}^{\dagger}=S_{\beta\alpha}$, $US_{\alpha\beta}U^{-1}=S_{\alpha\beta}$. These relations and the time-reversal conjugacy relations between the two states in each band lead to the following restrictions on the matrix elements of $\mathbf{S}$:

$$(0\cdot|S_{\alpha\beta}|0\cdot)=\begin{pmatrix} V_{\alpha\beta} & W_{\alpha\beta} \\ W_{\beta\alpha}^{*}=-W_{\alpha\beta}^{*} & V_{\beta\alpha}=V_{\alpha\beta}^{*}\end{pmatrix}, \quad (2.10a)$$

$$(a\cdot|S_{\alpha\beta}|a\cdot)=\begin{pmatrix} X_{\alpha\beta} & Y_{\alpha\beta} \\ Y_{\beta\alpha}^{*}=-Y_{\alpha\beta}^{*} & X_{\beta\alpha}=X_{\alpha\beta}^{*}\end{pmatrix}. \quad (2.10b)$$

There is some evidence that the electrons occupy three rather than six ellipsoids.[14] In this event, the vector k_0 must be at a point of high symmetry in the Brillouin zone such that the states have definite parity, with both states of a given band having the same parity. The strong curvature of the conduction band means that it interacts strongly via the velocity operator (odd parity) with the valence band. Hence, conduction band and valence band are of opposite parity. It follows that the operator $\mathbf{S}$ (even parity) cannot connect valence and conduction states, and therefore that all elements of $\mathbf{v}$ and $\mathbf{S}$ other than those given in (2.9) and (2.10) vanish. This establishes that the effective Hamiltonian, the operator on the left of (2.6), is a 4×4 matrix of the form

$$\begin{pmatrix} \epsilon+\pi\cdot\left(\frac{1}{2m}+V\right)\cdot\pi & \pi\cdot W\cdot\pi & t\cdot\pi & u\cdot\pi \\ -\pi\cdot W^{*}\cdot\pi & \epsilon+\pi\cdot\left(\frac{1}{2m}+V^{*}\right)\cdot\pi & -u^{*}\cdot\pi & t^{*}\cdot\pi \\ t^{*}\cdot\pi & -u\cdot\pi & -\epsilon+\pi\cdot\left(\frac{1}{2m}+X\right)\cdot\pi & \pi\cdot Y\cdot\pi \\ u^{*}\cdot\pi & t\cdot\pi & -\pi\cdot Y^{*}\cdot\pi & -\epsilon+\pi\cdot\left(\frac{1}{2m}+X^{*}\right)\cdot\pi \end{pmatrix}. \quad (2.11)$$

It is convenient to regard this operator as a 2×2 matrix, each of whose elements is, in turn, a 2×2 matrix,

$$H=\begin{pmatrix} \epsilon+H_u & H_1 \\ H_1^{\dagger} & -\epsilon+H_l\end{pmatrix}. \quad (2.12)$$

The entries in (2.12) are conveniently regarded as linear combinations of the four Pauli matrices, with vector or tensor coefficients, dotted into the π operators. For example,

$$H_u=\pi\cdot\begin{pmatrix} \frac{1}{2m}+\mathbf{V} & \mathbf{W} \\ -\mathbf{W}^{*} & \frac{1}{2m}+\mathbf{V}^{*}\end{pmatrix}\cdot\pi \quad (2.13a)$$

$$=\pi\cdot\Big[\mathbf{D}(0)+i\sum_{r=1}^{3}\mathbf{D}(r)\sigma_r\Big]\cdot\pi, \quad (2.13b)$$

with

$$\mathbf{D}(0)=\frac{1}{2m}\mathbf{1}+\mathrm{Re}\mathbf{V},$$
$$\mathbf{D}(1)=\mathrm{Im}\mathbf{W}, \quad (2.13c)$$
$$\mathbf{D}(2)=\mathrm{Re}\mathbf{W},$$
$$\mathbf{D}(3)=\mathrm{Im}\mathbf{V}.$$

The Pauli matrices in (2.13) have nothing to do with the spin of the electron; they are introduced only to facilitate the considerable amount of manipulation yet to come.

A comparison of (2.13c) and (2.10) reveals that $\mathbf{D}(0)$ is a symmetric tensor while the other three are antisymmetric. Therefore in the product $\pi\cdot\mathbf{D}(0)\cdot\pi$, only the symmetrized product of $\pi\pi$ will appear:

$$\pi\cdot\mathbf{D}(0)\cdot\pi=\sum\pi_\alpha D_{\alpha\beta}(0)\pi_\beta=\sum D_{\alpha\beta}(0)\Delta_{\alpha\beta}, \quad (2.14a)$$

$$\Delta_{\alpha\beta}=\tfrac{1}{2}(\pi_\alpha\pi_\beta+\pi_\beta\pi_\alpha). \quad (2.14b)$$

Similarly, in the product $\pi\cdot\mathbf{D}(r)\cdot\pi$ only the antisymmetric product of $\pi\pi$ will appear. This antisymmetrized product is evaluated using the definition of π in Eq. (2.7) in the well-known way:

$$(\pi_\alpha\pi_\beta)_{as}\equiv\tfrac{1}{2}(\pi_\alpha\pi_\beta-\pi_\beta\pi_\alpha)=\frac{ie\hbar}{2c}\sum\epsilon_{\alpha\beta\gamma}\mathfrak{H}_\gamma, \quad (2.15)$$

where $\epsilon_{\alpha\beta\gamma}$ is the completely antisymmetric tensor[15] and where $\mathfrak{H}$ is the magnetic field arising from the vector potential $\mathbf{A}$. Thus

$$\pi\cdot\mathbf{D}(r)\cdot\pi=(ie\hbar/2c)\sum D_{\alpha\beta}(r)\epsilon_{\alpha\beta\gamma}\mathfrak{H}_\gamma.$$

[14] A. L. Jain and S. H. Koenig, Phys. Rev. **127**, 442 (1962); S. Mase, J. Phys. Soc. Japan **13**, 434 (1958); **14**, 584 (1958); M. H. Cohen, L. M. Falicov and S. Golin, IBM J. Res. Develop. **8**, 215 (1964).

[15] A useful form of the definition of $\epsilon_{\alpha\beta\gamma}$ is that $\mathbf{A}\times\mathbf{B}=\mathbf{C}$ is, in component form, $C_\alpha=\epsilon_{\alpha\beta\gamma}A_\beta B_\gamma$.

We may define a symmetric real tensor β^u and three real axial vectors $\mathbf{L}^u(r)$ by

$$\beta_{\alpha\beta}{}^u = 2mD_{\alpha\beta}(0),$$
$$L_\gamma{}^u(r) = m\sum_{\alpha\beta} D_{\alpha\beta}(r)\epsilon_{\alpha\beta\gamma},$$

so that the operator H_u in Eq. (2.13) takes the simple form

$$H_u = \frac{1}{2m}\beta^u : \mathbf{\Delta} - \frac{1}{2}\frac{e\hbar}{mc}\sum_r \mathfrak{K}\cdot\mathbf{L}^u(r)\sigma_r. \quad (2.16)$$

By the same steps, we also find

$$H_l = (1/2m)\beta^l : \mathbf{\Delta} - \tfrac{1}{2}(e\hbar/mc)\textstyle\sum_r \mathfrak{K}\cdot\mathbf{L}^l(r)\sigma_r. \quad (2.17)$$

Finally, comparison of (2.11) and (2.12) gives

$$H_1 = \begin{pmatrix} \mathbf{t} & \mathbf{u} \\ -\mathbf{u}^* & \mathbf{t}^* \end{pmatrix}\cdot\boldsymbol{\pi} \quad (2.18a)$$

$$= [W(0) + i\sum \mathbf{W}(r)\sigma_r]\cdot\boldsymbol{\pi}, \quad (2.18b)$$

where

$$\begin{aligned} \mathbf{W}(0) &= \mathrm{Re}\mathbf{t}, \\ \mathbf{W}(1) &= \mathrm{Im}\mathbf{u}, \\ \mathbf{W}(2) &= \mathrm{Re}\mathbf{u}, \\ \mathbf{W}(3) &= \mathrm{Im}\mathbf{t}. \end{aligned} \quad (2.18c)$$

Equation (2.18) is of a form used by Wolff to study the two-band model. He showed that linear combinations of the two conduction states and linear combinations of the two valence states can be found which will cause all three components of $\mathbf{W}(0)$ to vanish. A study of his proof reveals that the time-reversal conjugacy is maintained and therefore that $\mathbf{S}$ retains the form (2.10) even after $\mathbf{W}(0)$ is eliminated. Hence, H^u and H_l retain the forms (2.16) and (2.17) while H_1 and $H_1{}^\dagger$ become

$$H_1 = i\sum_r \mathbf{W}(r)\sigma_r\cdot\boldsymbol{\pi} = -H_1{}^\dagger. \quad (2.19)$$

III. MATRIX ELEMENTS OF THE PERTURBATION

We now wish to regard the effective Hamiltonian H of (2.12) as an unperturbed part H_0 which is large and exactly solvable and a perturbation U which is small. We take for H_0 the Hamiltonian of the usual two-band model.

$$H = H_0 + U, \quad (3.1a)$$

$$H_0 = \begin{pmatrix} \epsilon & H_1 \\ H_1{}^\dagger & -\epsilon \end{pmatrix} \quad U = \begin{pmatrix} H_u & 0 \\ 0 & H_l \end{pmatrix}. \quad (3.1b)$$

Wolff has studied the solutions to the unperturbed Schrödinger equation

$$H_0\chi = E_0\chi$$

by considering the four-component function χ to be written as a two-component φ_u and a two-component φ_l:

$$\chi = \begin{pmatrix} \varphi_u \\ \varphi_l \end{pmatrix}. \quad (3.2)$$

Written in this partitioned form (3.1b) and (3.2), the matrix elements of U take the form

$$\langle\chi|U|\chi'\rangle = (\varphi_u|H_u|\varphi_u') + (\varphi_l|H_l|\varphi_l'), \quad (3.3)$$

where the round bras and kets are matrix elements taken with respect to the two-component functions.

Much algebra is required for the general evaluation of these two component matrix elements. The amount of work may be reduced materially by restricting attention to those states for which there is zero momentum in the direction of the field. Fortunately, the level structure at $P_z = 0$ where the density of states becomes infinite is the determining factor in interpreting both the Lincoln Laboratory data[9] and that of SBR.[3] The bare minimum of work required to evaluate those terms necessary for the $P_z = 0$ lowest order calculation will be found in appendices A, B, and C. It turns out that only the excitation values of U are needed. If the states χ are labeled by n and s, the orbital and spin quantum numbers of φ_u, then the results of these appendices may be summarized in the form

$$\begin{aligned} \langle ns|U|ns\rangle &= \tfrac{1}{2}(1+\epsilon/E_0)(ns|H_u|ns) \\ &\quad + \tfrac{1}{2}(1-\epsilon/E_0)(n+s,-s|H_l|n+s,-s) \\ &\qquad\qquad \text{if} \quad E_0 \neq -\epsilon, \\ &= (0,-1|H_l|0,-1) \qquad \text{if} \quad E_0 = -\epsilon, \end{aligned} \quad (3.4)$$

where

$$E_0 = \pm[\epsilon^2 + 2\epsilon(n+\tfrac{1}{2}+\tfrac{1}{2}s)e\hbar\mathfrak{K}/m^*c]^{1/2} \quad (3.5)$$

and where

$$\begin{aligned} (ns|H_i|ns) &= (n+\tfrac{1}{2})(m^*/m)\boldsymbol{\lambda}\cdot\mathfrak{B}_i\cdot\boldsymbol{\lambda}\mathfrak{K} \\ &\quad + s(m^*/m)\boldsymbol{\lambda}\cdot\mathfrak{F}_i\cdot\boldsymbol{\lambda}\mathfrak{K}, \end{aligned} \quad (3.6a)$$

$$i = u \quad \text{or} \quad l, \quad (3.6b)$$

$$s = \pm 1. \quad (3.6c)$$

The first term on the right of (3.6a) amounts to a change in the cyclotron mass and the second term on the right of (3.6a) amounts to a change in the g factor, or in the spin mass. E_0 is the unperturbed energy of the two-band model and m^* is the cyclotron mass of the two-band model,[2] namely,

$$(m/m^*) = [\det(\boldsymbol{\alpha})\boldsymbol{\lambda}\cdot\boldsymbol{\alpha}^{-1}\cdot\boldsymbol{\lambda}]^{1/2}. \quad (3.7)$$

The unit vectors $\boldsymbol{\lambda}$ are in the direction of the magnetic field. The real, symmetric tensors $\boldsymbol{\alpha}$, $\mathfrak{B}$ and $\mathfrak{F}$ have the same form, each being determined by the symmetry of the bismuth structure. The tensor $\boldsymbol{\alpha}$ is the inverse effective mass tensor which would be found in the absence of "other band" contributions, and the other four tensors ($\mathfrak{B}_u, \mathfrak{B}_l, \mathfrak{F}_u, \mathfrak{F}_l$) are complicated combinations of components of $\boldsymbol{\alpha}$ and matrix elements arising from other

bands. Each of the tensors has four independent components so there are 16 new parameters in all which are brought in by the other bands. The reader is referred to the appendices for further detail.

IV. LANDAU LEVELS AT $P_z=0$

The simple two-band model predicts that the two levels $E_0(n,s)$ and $E_0(n+s,-s)$ will be degenerate. The experiments indicate that the degeneracy between these states is lifted slightly, their separation being of the order $\frac{1}{10}$ to $\frac{1}{3}$ the spacing between the degenerate pair and the next degenerate pair.[3] To solve for the wave functions and energies of H (3.1a) using an expansion in terms of the eigenfunctions χ of H_0 (3.1b), we write

$$(H_0+U)\psi=E\psi,$$
$$\psi=\sum_{n's'}A(n',s')\chi(n',s'),$$
$$H_0\chi(n',s')=E_0(n',s')\chi(n',s').$$

Then, choosing the two states $\chi_1=\chi(n,+)$ and $\chi_2=\chi(n+1,-)$ as the degeneracy set leads to an equation analogous to (2.3), namely,

$$\sum_{j=1,2}\left(U_{ij}-\sum_p\frac{U_{ip}U_{pj}}{E_0(p)-E_0}\right)A_j=(E-E_0)A_i, \quad (4.1)$$

where $i=1, 2$ and where p runs over all n' and s' other than those in the degeneracy set. The energy E is thus given by solving a 2×2 secular determinant. Note that each of the terms on the left of (4.1) is proportional to the strength of the magnetic field and therefore the level shift $(E-E_0)$ is linear in $\mathfrak{IC}$, while the coefficients A_j are $\mathfrak{IC}$ independent.

For the $n=0$, $s=-1$ level (which is not degenerate) it would be natural to take the level shift equal to the expectation value of the perturbation in that state, as conventional first-order perturbation theory prescribes. There is some evidence that the $n=0$, $s=-1$ state of positive energy ϵ (the lowest conduction-band Landau level) drops in energy as the magnetic field is increased, at least for some orientations of the field. If the $n=0$, $s=-1$ state of negative energy $-\epsilon$ (the highest valence band Landau level) rises in energy, then there is the possibility that these two states will approach each other, giving rise to a new degeneracy. To treat this possibility, we set up the 2×2 determinant between the two $n=0$, $s=-1$ states of energy $\pm\epsilon$.

Now, we let χ_1 be the state of energy ϵ and χ_2 be the state of energy $-\epsilon$. The equations analogous to (2.3) are

$$\left(\epsilon+U_{11}-\sum\frac{U_{1p}U_{p1}}{E(p)}\right)A_1+\left(U_{12}-\sum\frac{U_{1p}U_{p2}}{E(p)}\right)A_2=EA_1,$$
$$\left(U_{21}-\sum\frac{U_{2p}U_{p1}}{E(p)}\right)A_1+\left(-\epsilon+U_{22}-\sum\frac{U_{2p}U_{p2}}{E(p)}\right)A_2=EA_2, \quad (4.2)$$

and again, the energy is determined by annulling a 2×2 secular determinant.

We will not have to carry out in detail the program just outlined for reasons which will soon be evident, but it is useful nevertheless to consider the sort of results which might emerge if we did. In particular, we want to think about the energies of the two $n=0$, $s=-1$ levels as the field magnitude is changed without altering its direction. We find, in the notation of (B1),[16] that

$$\chi_1=\begin{pmatrix}u_0\xi(-1)\\0\end{pmatrix}\quad\chi_2=\begin{pmatrix}0\\u_0\xi(-1)\end{pmatrix},$$

where u_0 is the $n=0$ harmonic oscillator wave function and $\xi(-1)$ is the $s=-1$ two-component spin function. Hence, the perturbation U has elements

$$U_{11}=(\tfrac{1}{2}A-B)\mathfrak{IC},\quad U_{12}=0,$$
$$U_{21}=0,\quad U_{22}=(\tfrac{1}{2}C-D)\mathfrak{IC},$$

where

$$A=(m^*/m)\mathfrak{A}\cdot\mathfrak{B}^u\cdot\mathfrak{A},\quad C=(m^*/m)\mathfrak{A}\cdot\mathfrak{B}^l\cdot\mathfrak{A},$$
$$B=(m^*/m)\mathfrak{A}\cdot\mathfrak{F}^u\cdot\mathfrak{A},\quad D=(m^*/m)\mathfrak{A}\cdot\mathfrak{F}^l\cdot\mathfrak{A}. \quad (4.3)$$

The 12 and 21 elements of U vanish, and hence, any off diagonal elements in (4.2) arise from the UU/E terms. These terms are smaller than the diagonal terms of (4.2) by roughly the factor $U_{ii}/\hbar\omega_c$ which is about the amount by which the degeneracy is lifted, and therefore, quite small. Because of their smallness, there is no reason to include the out-of-degeneracy set contributions to the diagonal terms, and the secular equation takes the form

$$\begin{vmatrix}\epsilon+a\mathfrak{IC}-E & b\mathfrak{IC}\\ b^*\mathfrak{IC} & -\epsilon+c\mathfrak{IC}-E\end{vmatrix}=0, \quad (4.4)$$

where $a=(\frac{1}{2}A-B)$, and $c=(\frac{1}{2}C-D)$, and $b\mathfrak{IC}$ represents the small UU/E terms. The energies resulting are

$$E=\tfrac{1}{2}(a+c)\mathfrak{IC}\pm\{[\epsilon+\tfrac{1}{2}(a-c)\mathfrak{IC}]^2+bb^*\mathfrak{IC}^2\}^{1/2}, \quad (4.5)$$

which, considering the smallness of b, is approximately

$$E_1=\epsilon+(\tfrac{1}{2}A-B)\mathfrak{IC}\equiv\epsilon+\Delta E(+),$$
$$E_2=-\epsilon+(\tfrac{1}{2}C-D)\mathfrak{IC}\equiv-\epsilon+\Delta E(-). \quad (4.6)$$

The effect of b becomes important only if a and c are such that the two energies E_1 and E_2 approach each other. At that field $\mathfrak{IC}$ for which (4.6) indicates that the two levels would cross, the term in b in (4.5) pushes the levels apart. As the field is increased the levels repel

[16] Appendix B, Eq. (B1).

each other, E_2 becoming asymptotic to the linear dependence established by E_1 at low fields, and vice versa.

If the motion, of say, level E_i is being followed by some optical transition technique such as cyclotron resonance or interband transitions, then this repulsion may not be observed. Instead, the optically active level will appear to move (nearly) linearly with field, as given by (4.6). This happens because the selection rules which determine the optical activity are determined by the wave functions χ_1 and χ_2, of which state E_1 is a linear combination. The state E_i which, at low fields, was predominantly χ_1 becomes predominantly χ_2 at high fields, and thus, the optical activity switches gradually from one state to the other if they approach and repel each other. If the region of closest approach is not observed, the optically active state will appear to have moved linearly with field. If the region of closest approach is observed, there will be deviations from linearity, doubling (simultaneous activity of both levels) and a change of intensity as the activity of one of the levels is transferred to the other. If the levels approach, then the transition region (range of field where this may be seen) will be largest for those orientations of magnetic field for which b is largest relative to a and c, i.e., where $U_{ii}/\hbar\omega_c$ is largest. This is where the lifting of the degeneracy is most pronounced.

Now let us consider the lifting of the degeneracy of the two levels $E_0(n,s)$ and $E_0(n+s,-s)$. A study of Appendix B indicates that here too, the off-diagonal elements of U vanish and that the out-of-degeneracy-set contribution to the off-diagonal terms of the secular equation may be neglected except if an apparent level crossing is indicated. Thus, as in (4.6), the energy shift is given by the expectation value of U in the state. From (3.4) and (3.6), using the notation (4.3), we have

$$\Delta E(n,s)=\tfrac{1}{2}(1+\epsilon/E_0)[(n+\tfrac{1}{2})A+sB]\mathfrak{IC} +\tfrac{1}{2}(1-\epsilon/E_0)[(n+s+\tfrac{1}{2})C-sD]\mathfrak{IC}. \quad (4.7)$$

The splitting of the degeneracy is the energy difference between the two formerly degenerate states:

$$\Delta\mathcal{E}_s\equiv E(n+1,\,s=-1)-E(n,\,s=+1) =(1+\epsilon/E_0)(\tfrac{1}{2}A-B)\mathfrak{IC}-(1-\epsilon/E_0)(\tfrac{1}{2}C-D)\mathfrak{IC}, \quad (4.8)$$

and is closely related to the energy shifts of the two $n=0$, $s=-1$ Landau levels (4.6)

$$\Delta\mathcal{E}_s=(1+\epsilon/E_0)\Delta E(+)-(1-\epsilon/E_0)\Delta E(-). \quad (4.9)$$

It is interesting to see how our expression for the energy levels is related to the formulas given by Cohen and Blount. If we let the gap become large with respect to the magnetic energy, then $E_0\approx\epsilon$ and the nonparabolicity of the conduction band will not be important as may be seen by expanding the square root in (3.5). Combining this expression with (4.7) gives an expression for the Landau levels of the conduction band similar in form to that of Cohen and Blount:

$$\mathcal{E}(n,s)=\epsilon+(n+\tfrac{1}{2})(\hbar\omega_c+A\mathfrak{IC})+s/2(\hbar\omega_c+B\mathfrak{IC}) =\epsilon+(n+\tfrac{1}{2})\hbar\Omega_c+\tfrac{1}{2}s\hbar\Omega_s. \quad (4.10)$$

Cohen and Blount give explicit formulas for evaluating what we have here called Ω_c and Ω_s. If, in their formulas, the contribution of valence band is treated as large compared to the contribution of the other bands, then a power series expansion of their results is possible. The first two terms of that power series reproduce exactly our Eq. (4.10) and those equations needed to relate A and B to the "other band" velocity matrix elements.

It is interesting to see how our expression for the energy of the Landau levels compares with the empirical form used by Smith, Baraff, and Rowell for the analysis of the magnetoresistance data. The SBR expression was essentially

$$\mathcal{E}(n,s)=\{\epsilon^2+2\epsilon[\hbar\omega_o(n+\tfrac{1}{2})+\tfrac{1}{2}s\hbar\omega_s]\}^{1/2}, \quad (4.11a)$$

$$\hbar\omega_o=(e\hbar\mathfrak{IC}/mc)[(\det\boldsymbol{\alpha}_o)\boldsymbol{\lambda}\cdot\boldsymbol{\alpha}_o^{-1}\cdot\boldsymbol{\lambda}]^{1/2}, \quad (4.11b)$$

$$\hbar\omega_s=(e\hbar\mathfrak{IC}/mc)[(\det\boldsymbol{\alpha}_s)\boldsymbol{\lambda}\cdot\boldsymbol{\alpha}_s^{-1}\cdot\boldsymbol{\lambda}]^{1/2}, \quad (4.11c)$$

where $\boldsymbol{\alpha}_o$ and $\boldsymbol{\alpha}_s$ were tensors whose components were adjusted to fit the data. Although this does provide a useful way of describing the magnetoresistance data, it has no firm theoretical basis.

In Appendix D, we show that for $E_0^2\neq\epsilon^2$, the SBR energies are the same as ours provided that the inverse spin mass tensor and inverse orbital mass tensor are regarded as being energy-dependent with the form

$$\alpha_o=\alpha+\alpha_o^{(1)}+(E_o/\epsilon)\alpha_o^{(2)}, \qquad \alpha_s=\alpha+\alpha_s^{(1)}+(E_o/\epsilon)\alpha_s^{(2)}. \quad (4.12)$$

This energy dependence is a new feature, not included in (4.11) as used by SBR.

These remarks do *not* apply to the energy of the $n=0$, $s=-1$ level. For this level, the SBR formula (4.11), with its parabola-like field dependence, is just not right. The motion of this level is, as we have seen, either linear or hyperbola-like.

It may be easier to use (4.7) and (4.3) directly to interpret experiments, rather than go to the intermediary of an energy-dependent shift of α. In such case, it is useful to know that an analysis of the transformation property of the wave functions leads to the result that the real symmetric tensors $\mathfrak{B}$ and $\mathfrak{F}$ have the forms

$$\begin{pmatrix} b_1 & 0 & 0 \\ 0 & b_2 & b_4 \\ 0 & b_4 & b_2 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} g_1 & 0 & 0 \\ 0 & g_2 & g_4 \\ 0 & g_4 & g_3 \end{pmatrix}$$

for one of the three electron ellipsoids. The other two ellipsoids may be obtained by rotation of the above tensors by $\pm 120°$ about the 3 axis.

ACKNOWLEDGMENTS

The most important event in a study is often the question which initiates the work. In this case, Dr. L. C. Hebel, Jr., asked the question. I should like to acknowledge his continuing interest and his comments on the manuscript. I should also like to thank Dr. P. A. Wolff and Dr. A. G. Chynoweth for helpful remarks on the presentation.

APPENDIX A

In this Appendix, we wish to restate results first obtained by Wolff and to establish the notation which we shall need in the subsequent appendices. Consider the unperturbed partitioned form (3.1) and (3.2) as a pair of coupled equations:

$$\epsilon\varphi_u+H_1\varphi_l=E_0\varphi_u, \tag{A.1}$$

$$H_1^\dagger\varphi_u-\epsilon\varphi_l=E_0\varphi_l. \tag{A.2}$$

From the second of these, one obtains

$$\varphi_l=(E_0+\epsilon)^{-1}H_1^\dagger\varphi_u, \tag{A.3}$$

which, inserted into the first, gives

$$H_1H_1^\dagger\varphi_u=(E_0^2-\epsilon^2)\varphi_u. \tag{A.4}$$

Had we chosen to eliminate φ_u, the equation for φ_l would have been

$$H_1^\dagger H_1\varphi_l=(E_0^2-\epsilon^2)\varphi_l. \tag{A.5}$$

If φ_u is normalized to unity, then the normalized four-component χ is

$$\chi=[\tfrac{1}{2}(1+\epsilon/E_0)]^{1/2}\begin{pmatrix}\varphi_u\\(E_0+\epsilon)^{-1}H_1^\dagger\varphi_u\end{pmatrix}. \tag{A.6}$$

The operator in (A.4) or (A.5) is readily evaluated using (2.19) and the multiplication rule for the Pauli matrices

$$\sigma_\alpha\sigma_\beta=\delta_{\alpha\beta}+i\sum_\gamma\epsilon_{\alpha\beta\gamma}\sigma_\gamma, \tag{A.7}$$

with the result

$$H_1H_1^\dagger=\boldsymbol{\pi}\cdot[\mathbf{C}(0)+i\sum_r\mathbf{C}(r)\sigma_r]\cdot\boldsymbol{\pi}, \tag{A.8a}$$

$$C_{ij}(0)=\sum_p W_i(p)W_j(p), \tag{A.8b}$$

$$C_{ij}(r)=\sum_{pq}W_i(p)W_j(q)\epsilon_{pqr}. \tag{A.8c}$$

Again, the symmetry of $\mathbf{C}(0)$ and the antisymmetry of $\mathbf{C}(r)$ may be used to set

$$\frac{H_1H_1^\dagger}{2\epsilon}\equiv H^*\equiv\frac{1}{2m}\boldsymbol{\alpha}:\boldsymbol{\Delta}-\frac{1}{2}\frac{e\hbar}{mc}\sum\mathfrak{K}\cdot\mathbf{G}(r)\sigma_r, \tag{A.9a}$$

$$\boldsymbol{\alpha}=(m/\epsilon)\,\mathbf{C}(0), \tag{A.9b}$$

$$G_k(r)=(m/2\epsilon)\textstyle\sum_{ij}C_{ij}(r)\epsilon_{ijk}. \tag{A.9c}$$

The operator H^* is the effective mass Hamiltonian of the two-band model, as studied by Cohen and Blount. Its eigenfunctions are the well-known products of harmonic oscillator states u_n for the transverse motion, plane waves for motion parallel to the field, and two component spin functions $\xi(s)$, $s=\pm1$, which diagonalize the spin operator in (A.9a). The eigenvalues $E^*(n,s)$ are degenerate, with

$$E^*(n+s,-s)=E^*(n,s). \tag{A.10}$$

From this degeneracy, it follows that if

$$\varphi_u=u_n\xi(s) \tag{A.11a}$$

then

$$\varphi_l=\alpha u_n\xi(s)+\beta u_{n+s}\xi(-s), \tag{A.11b}$$

where α and β must be chosen to satisfy (A.3). In writing (A.10) and (A.11), the plane waves for the motion parallel to the field have not been written, nor has the dependence of E^*, φ_u or φ_l on P (the momentum parallel to the field) been shown. The dependence of E^* on P, however, is[2]

$$E^*(n,s,P)=\hbar\omega_c(n+\tfrac{1}{2}+\tfrac{1}{2}s)+P^2/2m_z, \tag{A.12a}$$

$$\hbar\omega_c=e\mathfrak{K}\hbar/m^*c, \tag{A.12b}$$

$$(m/m^*)=[(\det\boldsymbol{\alpha})\boldsymbol{\lambda}\cdot\boldsymbol{\alpha}^{-1}\cdot\boldsymbol{\lambda}]^{1/2}, \tag{A.12c}$$

$$\boldsymbol{\lambda}=\mathfrak{K}/\mathfrak{K}, \tag{A.12d}$$

$$m_z=\boldsymbol{\lambda}\cdot\boldsymbol{\alpha}^{-1}\cdot\boldsymbol{\lambda}. \tag{A.12e}$$

APPENDIX B: MATRIX ELEMENTS OF THE PERTURBATION

This Appendix contains the evaluation of those matrix elements (3.3) which are actually needed for the lowest-order $P=0$ calculation. From (A.3), (A.6), and (A.11), we have

$$\chi(n,s)=\tfrac{1}{2}(1+\epsilon/E_0)^{1/2}\begin{pmatrix}u_n\xi(s)\\\alpha u_n\xi(s)+\beta u_{n+s}\xi(-s)\end{pmatrix}, \tag{B.1}$$

and therefore, the matrix elements of U are

$$\begin{aligned}\langle ns|U|n's'\rangle=[\tfrac{1}{4}(1+\epsilon/E_0)(1+\epsilon/E_0')]^{1/2}&\\\times\{(ns|H_u|n's')+\alpha^*\alpha'(ns|H_l|n's')&\\+\alpha^*\beta'(ns|H_l|n's',-s')&\\+\beta^*\alpha'(n+s,-s|H_l|n's')&\\+\beta^*\beta'(n+s,-s|H_l|n'+s',-s')\}.&\end{aligned} \tag{B.2}$$

The round bras and kets on the right denote matrix elements calculated with respect to the two component functions $u_n\xi(s)$. To evaluate these, we must first evaluate the matrix elements of the operators Δ_{ij} and σ_r which appear in (2.16), and the coefficients α and β.

Consider first the spinor operator. It cannot change the orbital quantum number, and we have

$$\begin{aligned}(ns|\sigma_r|n's')&=\delta_{nn'}(\xi^\dagger(s),\sigma_r\xi(s'))\\&=\delta_{nn'}\langle s|\sigma_r|s'\rangle.\end{aligned} \tag{B.3}$$

To evaluate the spin matrix element here, we use the fact that the states $\xi(s)$ diagonalize the spin operator in (A.9a). By dividing that operator by the magnitude of the eigenvalue we obtain

$$s\sum_r \mu_r\sigma_r\xi(s)=\xi(s)\,, \tag{B.4a}$$

where

$$\mu_r=\mathfrak{K}\cdot\mathbf{G}(r)/\{\sum_p[\mathfrak{K}\cdot\mathbf{G}(p)]^2\}^{1/2}. \tag{B.4b}$$

Then using (B.4a) and the multiplication rule (A.7) to evaluate the $s'=s$ element gives

$$\langle s|\sigma_p|s\rangle=\langle s|\sigma_p s\sum\mu_q\sigma_q|s\rangle=s\mu_p+i\sum\epsilon_{pqr}\mu_q\langle s|\sigma_r|s\rangle.$$

Since the expectation value of Hermitian operators must be real, the sum which is pure imaginary must vanish, leaving

$$\langle s|\sigma_p|s\rangle=s\mu_p. \tag{B.5}$$

Note that from (A.9a), the eigenvalue of the spin part of H^* is

$$\mp\tfrac{1}{2}(e\hbar/mc)\{\sum[\mathfrak{K}\cdot G(r)]^2\}^{1/2}.$$

Setting this equal to $\mp\frac{1}{2}\hbar\omega_c$, the known spin energy in the two-band model gives, using (A.12)

$$\{\sum[\mathfrak{K}\cdot G(r)]^2\}^{1/2}=\mathfrak{K}(m/m^*). \tag{B.6}$$

Thus in terms of $\mathfrak{\lambda}$, the unit vector parallel to the magnetic field,

$$\langle s|\sigma_p|s\rangle=s(m^*/m)\mathfrak{\lambda}\cdot\mathbf{G}(p) \tag{B.7}$$

and the expectation value of the spin part of the perturbation is

$$\langle s|\tfrac{1}{2}(e\hbar/mc)\sum\mathfrak{K}\cdot\mathbf{L}(r)\sigma_r|s\rangle = -s\mathfrak{K}(m^*/m)\mathfrak{\lambda}\cdot\mathfrak{F}\cdot\mathfrak{\lambda}, \tag{B.8a}$$

where

$$\mathfrak{F}\equiv-(e\hbar/2mc)\tfrac{1}{2}\sum_r[\mathbf{L}(r)\mathbf{G}(r)+\mathbf{G}(r)\mathbf{L}(r)]. \tag{B.8b}$$

Now consider the orbital part of perturbation. Since it cannot change the spin quantum number, we have

$$(ns|\Delta_{ij}|n's')=\delta_{ss'}(u_n{}^\dagger,\Delta_{ij}u_{n'}). \tag{B.9}$$

Let us recall, for a moment, one of the methods used to obtain the eigenfunctions and eigenvalues of the orbital operator in H^*. The method involves finding a coordinate transformation which reduces the inverse mass tensor to the unit tensor by appropriate stretchings of the coordinate axes, then rotating the transformed coordinate system so that the transformed magnetic field lies along the 3′ direction. When this is done, only the primed momenta π_1' and π_2' fail to commute. Linear combinations a and $a^\dagger$ can be formed from π_1' and π_2' such that

$$[a,a^\dagger]=1 \quad\text{and}\quad [a,P]=0, \tag{B.10}$$

where P is the notation for π_3', the component of π' parallel to the transformed field. The result of these stretchings and rotations is that the operators π_i can be regarded as linear combinations of a, $a^\dagger$ and P:

$$\pi_i=S_ia+S_i{}^*a^\dagger+r_iP. \tag{B.11}$$

These linear combinations will be such, that when (B.11) is substituted into the orbital part of H^*, the result is

$$(1/2m)\boldsymbol{\alpha}\colon\boldsymbol{\Delta}\equiv(1/2m)\boldsymbol{\pi}\cdot\boldsymbol{\alpha}\cdot\boldsymbol{\pi} =\hbar\omega_c(a^\dagger a+\tfrac{1}{2})+P^2/2m_z\,, \tag{B.12}$$

while when the commutator of the π is evaluated using (B.10), the result is

$$[\pi_i,\pi_j]=(ie\hbar/c)\sum\epsilon_{ijk}\mathfrak{K}_k. \tag{B.13}$$

It is clear from these equations, even without a detailed calculation of the coefficients, that S_i is proportional to $\mathfrak{K}^{1/2}$, and that r_i is real and independent of the strength of $\mathfrak{K}$. It is also known that the functions u_n which diagonalize (B.12) satisfy

$$\begin{aligned} a^\dagger au_n&=nu_n\,,\\ a^\dagger u_n&=(n+1)^{1/2}u_{n+1}\,,\\ au_n&=n^{1/2}u_{n-1}\,. \end{aligned} \tag{B.14}$$

Using (B.11), the operator Δ_{ij} becomes

$$\Delta_{ij}=K_{ij}aa+\text{H.c.}+N_{ij}Pa+\text{H.c.} +L_{ij}P^2+M_{ij}(a^\dagger a+\tfrac{1}{2})\,, \tag{B.15a}$$

$$\begin{aligned} K_{ij}&=S_iS_j\,,\quad M_{ij}=S_iS_j{}^*+S_jS_i{}^*,\\ L_{ij}&=r_ir_j\,,\quad N_{ij}=\tfrac{1}{2}(r_iS_j+r_jS_i)\,. \end{aligned} \tag{B.15b}$$

The most direct, but rather cumbersome way to evaluate the quantities defined in (B.15b) is to study in detail the stretchings and rotations which finally reduce the orbital Hamiltonian to the form given in (B.12). For our purposes here, however, only M_{ij} is needed and this can be obtained quite simply as follows:

Inserting (B.11) into the left of (B.12) and comparing the coefficients of $(a^\dagger a+\frac{1}{2})$ on both sides of the resulting equation shows that

$$(1/2m)\sum\alpha_{ij}M_{ij}=\hbar\omega_c\,,$$

or, using (A.12b),

$$\sum\alpha_{ij}M_{ij}=(2e\hbar\mathfrak{K}/c)(m/m^*).$$

This may be differentiated with respect to $\alpha_{\mu\nu}$

$$\sum M_{ij}(\partial\alpha_{ij}/\partial_{\mu\nu})=(2e\hbar\mathfrak{K}/c)\partial(m/m^*)/\partial\alpha_{\mu\nu}. \tag{B.16}$$

Using (A.12c)

$$(m/m^*)=[\tfrac{1}{2}\sum\lambda_i\lambda_j\alpha_{kl}\alpha_{mn}\epsilon_{ikm}\epsilon_{jln}]^{1/2}$$

we have

$$\partial(m/m^*)/\partial\alpha_{\mu\nu}=(m^*/2m)\sum\lambda_i\lambda_j(\partial\alpha_{kl}/\partial\alpha_{\mu\nu})\alpha_{mn}\epsilon_{ikm}\epsilon_{jln}\,.$$

Inserting this into (B.16) gives

$$M_{\mu\nu}=(e\hbar\mathfrak{K}m^*/mc)\sum\lambda_i\lambda_j\alpha_{mn}\epsilon_{i\mu m}\epsilon_{j\nu n}\,, \tag{B.17}$$

a result which may be verified with considerable labor by studying the transformations directly.

Using (B.14), (B.15), and (B.17), we have

$$\left(ns\left|\frac{1}{2m}\beta^u:\Delta\right|ns\right)=\frac{1}{2m}(n+\tfrac{1}{2})\sum_{ij}\beta_{ij}{}^uM_{ij}$$

$$=(n+\tfrac{1}{2})(m^*/m)\mathfrak{A}\cdot\mathfrak{B}^u\cdot\mathfrak{A}\mathfrak{K}\,, \tag{B.18a}$$

where

$$\mathfrak{B}_{ij}{}^u=(e\hbar/2mc)\sum\epsilon_{ikm}\epsilon_{jln}\alpha_{kl}\beta_{mn}{}^u\,. \tag{B.18b}$$

Now, we must choose the coefficients α and β of (A.11) so that (A.3) is satisfied. Using (2.19) for $H_1{}^\dagger$ gives

$$\alpha u_n\xi(s)+\beta u_{n+s}\xi(-s)$$

$$=-i(E_0+\epsilon)^{-1}\sum_r\mathbf{W}(r)\cdot\boldsymbol{\pi}\sigma_r u_n\xi(s)\,. \tag{B.19}$$

The effect of π on the orbital function follows from (B.11) and (B.14)

$$\pi_i u_n=S_i n^{1/2}u_{n-1}+S_i{}^*(n+1)^{1/2}u_{n+1}+r_iPu_n\,,$$

while the effect of σ_r on the spin function, using (B.5), may be written

$$\begin{aligned}\sigma_r\xi(+1)&=\mu_r(+1)+\theta_r\xi(-1)\,,\\ \sigma_r\xi(-1)&=\theta_r{}^*\xi(+1)-\mu_r\xi(-1)\,,\end{aligned} \tag{B.20}$$

$$\theta_r\equiv\langle+|\sigma_r|-\rangle\,. \tag{B.21}$$

These results, used in (B.19) give

$$\alpha=-i(E_0+\epsilon)^{-1}sP\sum_q r_iW_i(q)\mu_q\,, \tag{B.22a}$$

$$\beta=-i(E_0+\epsilon)^{-1}[(n+1)]^{1/2}\sum S_i{}^*W_i(q)\theta_q\,,\quad\text{if}\quad s=+1\,,$$

$$=-i(E_0+\epsilon)^{-1}n^{1/2}\sum S_i{}^*W_i(q)\theta_q{}^*\,,\quad\text{if}\quad s=-1\,. \tag{B.22b}$$

Now observe that the normalization of φ_l implied by (A.3) and (A.4), namely,

$$(\varphi_l,\varphi_l)=(E_0{}^2-\epsilon^2)/(E_0+\epsilon)^2=2\epsilon E^*/(E_0+\epsilon)^2$$

requires, via (A.11b), that

$$(E_0+\epsilon)^2(\alpha\alpha^*+\beta\beta^*)=2\epsilon E^*.$$

Inserting (B.22) here gives

$$2\epsilon E^*=|\sum S_iW_i(q)\theta_q{}^*|^2$$

$$\times[(n+1)\text{ or }n]+P^2|\sum r_iW_i(q)\mu_q|^2.$$

Comparing this with (A.12a) indicates that

$$\begin{aligned}|\sum S_iW_i(q)\theta_q{}^*|^2&=2\epsilon\hbar\omega_c\,,\\ |\sum r_iW_i(q)\mu_q|^2&=\epsilon/m_z\,,\end{aligned} \tag{B.23}$$

and therefore, that

$$\alpha\alpha^*=(2\epsilon P^2/2m_z)/(E_0+\epsilon)^2\,, \tag{B.24a}$$

$$\begin{aligned}\beta\beta^*&=[2\epsilon\hbar\omega_c(n+\tfrac{1}{2}+\tfrac{1}{2}s)]/(E_0+\epsilon)^2\\ &=(E_0-\epsilon)/(E_0+\epsilon)\,.\end{aligned} \tag{B.24b}$$

Evidently, in the limit $P\to 0$, $\alpha\alpha^*$ approaches zero unless $(E_0+\epsilon)=0$. For this special case, $n=0$ and $s=-1$ so that β is zero and $\alpha\alpha^*=2\epsilon E^*/(E+\epsilon)^2$. Although this diverges as $P=0$, the divergence is exactly canceled by the coefficient in front of (B.2). Putting all of these results together gives, for the expectation value of U at $P=0$, the expressions

$$\langle ns|U|ns\rangle=\tfrac{1}{2}(1+\epsilon/E_0)(ns|H_u|ns)$$

$$+\tfrac{1}{2}(1-\epsilon/E_0)(n+s,-s|H_l|n+s,-s)$$

$$\text{if}\quad E_0\neq-\epsilon \tag{B.25}$$

$$=(0,-1|H_l|0,-1)\,,\quad\text{if}\quad E_0=-\epsilon \tag{B.26}$$

while, deleting the subscript or superscript u or l,

$$(ns|H|ns)=(n+\tfrac{1}{2})(m^*/m)\mathfrak{A}\cdot\mathfrak{B}\cdot\mathfrak{A}\mathfrak{K}$$

$$+s(m^*/m)\mathfrak{A}\cdot\mathfrak{F}\cdot\mathfrak{A}\mathfrak{K}\,. \tag{B.27}$$

APPENDIX C: LANDAU LEVELS AT $P=0$, DEPENDENCE ON FIELD DIRECTION

We must consider how the four constants A, B, C, D of Eq. (4.3) depend on the direction of the magnetic field. This means, in effect, a detailed study of the tensors $\mathfrak{B}$ and $\mathfrak{F}$ appearing in (4.3). The form of these tensors is determined ultimately by the transformation properties of the four states on which our effective Hamiltonian (2.11) is based.

Our assumption of three electron ellipsoids means that the conduction band minimum is at a point of twofold rotational symmetry in the Brillouin zone.[17] The Bloch wave states in the presence of spin transform according to the double group representation, for which $(C_2)^2=-1$, C_2 being the symbol for the twofold rotation. Hence, it is possible to choose a linear combination $|01)$ of the two states $\varphi_{01}(k_0,\tau)$ and $\varphi_{02}(k_0,\tau)$ such that

$$C_2|01)=-i|01)\,. \tag{C.1}$$

If we apply the time reversal operator $\hat{U}$ to this equation, we obtain

$$C_2\hat{U}|01)=i\hat{U}|01)\,,$$

so that we are at liberty to take another linear combination $|02)$ of the states $\varphi_{01}(k_0,r)$ and $\varphi_{02}(k_0,r)$ such that

$$|02)=\hat{U}|01)\,, \tag{C.2}$$

$$C_2|02)=+i|02)\,. \tag{C.3}$$

Similarly, the two valence band states can be combined

[17] Reference 5, Table I.

such that

$$C_2|a1) = -i|a1), \tag{C.4a}$$

$$C_2|a2) = +i|a2), \tag{C.4b}$$

$$|a2) = \hat{U}|a1). \tag{C.4c}$$

The time-reversal conjugacy (C.2) and (C.4c) guarantees that all steps from (2.9) through (2.18) remain valid, while the transformation properties (C.1), (C.3), and (C.4) place additional restrictions on the elements of the vectors and tensors **t**, **u**, **V**, etc., of Sec. II. We take the C_2 axis in the x direction: then

$$\begin{aligned} C_2 v_\alpha C_2^{-1} &= (-1)^\lambda v_\alpha, \\ C_2 S_{\alpha\beta} C_2^{-1} &= (-1)^\lambda S_{\alpha\beta}, \end{aligned} \tag{C.5}$$

where λ is the number of times y and z appear in the subscripts on the left. Matrix elements of **v** and **S** between states $(\cdot\rho|$ and $|\cdot\rho)$ vanish for λ odd, elements between states $(\cdot 1|$ and $|\cdot 2)$ vanish for λ even. Thus, in the notation of (2.19) and (2.10), our operators have the form

$$\begin{vmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & V_{yz} \\ 0 & V_{zy} & V_{zz} \end{vmatrix} \begin{vmatrix} 0 & W_{xy} & W_{xz} \\ W_{yx} & 0 & 0 \\ W_{zx} & 0 & 0 \end{vmatrix} \begin{vmatrix} t_x \\ 0 \\ 0 \end{vmatrix} \begin{vmatrix} 0 \\ u_y \\ u_z \end{vmatrix}, \tag{C.6}$$

with **X** being similar in form to **V** and **Y** being similar in form to **W**.

The only question which arises is whether the linear combinations $|n\rho)$ of states φ_{n1} and φ_{n2} which resulted in these forms is compatible with the linear combination Wolff would have had us take in order that **t** be purely imaginary. The answer is clearly that they are compatible: by choosing states so that $C_2|n\rho) = \pm i|n\rho)$ as we have done, the vector **t** is reduced to one nonzero component whose phase (reality) can be adjusted by adjusting the phase of the valence band function $|a1)$. This can be done without further linear combination, and can give Re**t**$=0$. Thus, Eq. (2.19) is also valid, as are all following equations. We may therefore thread our way back through the string of equations defining $\mathfrak{B}$ and $\mathfrak{F}$ in terms of the vectors $\mathbf{W}(r)$, (2.18) and tensors $\mathbf{D}(r)$, (2.13), and obtain useful information about the elements of $\mathfrak{B}$ and $\mathfrak{F}$.

From (C.6), (2.18), (2.13), and the equations just preceding (2.16), we have

$$\mathfrak{z} = \begin{vmatrix} x & 0 & 0 \\ 0 & y & \omega \\ 0 & \omega & z \end{vmatrix},$$

$$\mathbf{L}(1) = \begin{vmatrix} 0 \\ a \\ b \end{vmatrix}, \quad \mathbf{L}(2) = \begin{vmatrix} 0 \\ c \\ d \end{vmatrix}, \quad \mathbf{L}(3) = \begin{vmatrix} e \\ 0 \\ 0 \end{vmatrix}, \tag{C.7}$$

$$\mathbf{W}(1) = \begin{vmatrix} 0 \\ \alpha \\ \beta \end{vmatrix}, \quad \mathbf{W}(2) = \begin{vmatrix} 0 \\ \gamma \\ \delta \end{vmatrix}, \quad \mathbf{W}(3) = \begin{vmatrix} \eta \\ 0 \\ 0 \end{vmatrix},$$

the entries on the right being independent real quantities. Using these in (A.8b, c), (A.9b, c) and (B.8b) give (to within constant multipliers)

$$\alpha = \begin{vmatrix} \eta^2 & 0 & 0 \\ 0 & \alpha^2+\gamma^2 & \alpha\beta+\gamma\delta \\ 0 & \alpha\beta+\gamma\delta & \beta^2+\delta^2 \end{vmatrix}, \tag{C.8}$$

$$\mathfrak{F} = \begin{vmatrix} e(\alpha\delta-\beta\gamma) & 0 & 0 \\ 0 & \eta(a\delta-c\beta) & \eta\theta \\ 0 & \eta\theta & \eta(d\alpha-b\gamma) \end{vmatrix}, \tag{C.9}$$

$$\theta = \tfrac{1}{2}(b\delta - d\beta + c\alpha - a\gamma).$$

Now consider a rotation in the yz plane such that α is diagonal in the new $xy'z'$ coordinate system. Evaluated in the new system, we would have found

$$\begin{aligned} \alpha_1 &= \eta^2, \\ \alpha_2 &= \alpha^2+\gamma^2, \\ \alpha_3 &= \beta^2+\delta^2, \\ 0 &= \alpha\beta+\gamma\delta. \end{aligned} \tag{C.10}$$

Evaluating $\mathfrak{B}$ (B.18) in this new coordinate system gives, again to within constants,

$$\mathfrak{B} = \begin{vmatrix} \alpha_2\beta_{33}+\alpha_3\beta_{22} & 0 & 0 \\ 0 & \alpha_3\beta_{11}+\alpha_1\beta_{33} & -\alpha_1\beta_{23} \\ 0 & -\alpha_1\beta_{23} & \alpha_1\beta_{22}+\alpha_2\beta_{11} \end{vmatrix}. \tag{C.11}$$

APPENDIX D

Consider the tensors α_o and α_s as having the form

$$\begin{aligned} \alpha_o &= \alpha + \delta\alpha_o(E), \\ \alpha_s &= \alpha + \delta\alpha_s(E), \end{aligned} \tag{D.1}$$

that is, they differ from the α of the two-band model by a small, energy-dependent term. This energy dependence is a new feature, not included in (4.11) as used by SBR. If we expand ω_o and ω_s to first order, we obtain

$$\begin{aligned} \hbar\omega_o &= (e\hbar\mathfrak{K}/mc)[\tfrac{1}{2}\textstyle\sum \lambda_i\lambda_j(\alpha+\delta\alpha_o)_{kl}(\alpha+\delta\alpha_o)_{mn}\epsilon_{ikm}\epsilon_{jln}]^{1/2} \\ &\approx (e\hbar\mathfrak{K}/mc)[\tfrac{1}{2}\textstyle\sum \lambda_i\lambda_j\alpha_{kl}\alpha_{mn}\epsilon_{ikm}\epsilon_{jln} \\ &\qquad + \textstyle\sum \lambda_i\lambda_j\alpha_{kl}(\delta\alpha_o)_{mn}\epsilon_{ikm}\epsilon_{jln}]^{1/2} \\ &= (e\hbar\mathfrak{K}/mc)[(m/m^*)^2 + \textstyle\sum \lambda_i\cdots\epsilon_{jln}]^{1/2} \\ &\approx (e\hbar\mathfrak{K}/m^*c) + \theta_o(E)\mathfrak{K}, \end{aligned} \tag{D.2a}$$

where

$$\theta_o(E) \equiv (e\hbar/2mc)(m^*/m)\textstyle\sum \lambda_i\lambda_j\alpha_{kl}(\delta\alpha_o)_{mn}\epsilon_{ikm}\epsilon_{jln}. \tag{D.2b}$$

A similar expansion is used on $\hbar\omega_s$. Using these expressions in (4.11a) gives

$$\begin{aligned} \mathcal{E}(n,s) &= \{\epsilon^2 + 2\epsilon[\hbar\omega_c(n+\tfrac{1}{2}+\tfrac{1}{2}s) + (n+\tfrac{1}{2})\theta_o + \tfrac{1}{2}s\theta_s]\}^{1/2} \\ &= \{E_0^2(n,s) + 2\epsilon[(n+\tfrac{1}{2})\theta_o + \tfrac{1}{2}s\theta_s]\mathfrak{K}\}^{1/2}. \end{aligned} \tag{D.3}$$

For all levels except $n=0$, $s=-1$, E_0^2 will be large enough so that we may expand the radical, and, to

lowest order,

$$\mathcal{E}(n,s)=\pm\{E_0(n,s)+(\epsilon/E_0)[(n+\tfrac{1}{2})\theta_o+\tfrac{1}{2}s\theta_s]\mathcal{H}\}. \quad \text{(D.4)}$$

Comparing this with (4.7) shows that the energy shifts for the conduction band levels will agree provided that the energy dependence of θ_o and θ_s satisfies

$$\begin{aligned}\theta_o&=\tfrac{1}{2}[(A-C)+(E_0/\epsilon)(A+C)],\\ \theta_s&=[(B-C+D)+(E_0/\epsilon)(B+C-D)].\end{aligned} \quad \text{(D.5)}$$

Returning to (4.3), we see that the right side of (D.5) has a directional dependence of exactly the form required by (D.2b), and hence establishes that $\delta\alpha$ is a linear function of (E_0/ϵ). Thus, the (SBR) formula (4.11) will provide a satisfactory account of all Landau levels except the $n=0$, $s=-1$ level provided that we understand that

$$\begin{aligned}\alpha_o&=\alpha+\delta\alpha_o{}^0+(E_0/\epsilon)\delta\alpha_o',\\ \alpha_s&=\alpha+\alpha_s{}^0+(E_0/\epsilon)\delta\alpha_s'.\end{aligned} \quad \text{(D.6)}$$

The experimentally determined values of α in bismuth (and the extreme smallness of α_2 in particular) must now be regarded as a feature of α_o and α_s, that is, of the complete expression (D.6), rather than of the single α contribution to it.

PHYSICAL REVIEW VOLUME 137, NUMBER 3A 1 FEBRUARY 1965

Behavior of First- and Second-Kind Superconducting Films Near Their Critical Fields*

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(Received 2 September 1964)

The upper critical magnetic field of thin superconducting films has been studied as a function of its orientation with respect to the surface of the sample and as a function of the film thickness compared with $\lambda(T)$ and $\xi(T)$, for second-kind (**Sn**-In, **In**-Pb, **Pb**-Bi) and first-kind (Sn) materials. The results have been obtained by resistivity, dynamic-susceptibility, penetration-depth, and tunneling measurements.

I. INTRODUCTION

IN first- and second-kind superconductors, it has appeared that the upper critical field, defined as when the first trace of superconductivity appears in decreasing field, depends on the orientation of the field with respect to the sample as well as on the sample size compared with $\lambda(T)$ and $\xi(T)$,[1,2] where $\lambda(T)$ is the penetration depth and $\xi(T)$ is the temperature-dependent correlation length. To study these effects, we choose the simple geometry of a thin film of thickness d. The domain of length of $\lambda(T=0)$ and $\xi(T=0)$ extends from 300 to 2000 Å in the alloys which we have studied, but both $\lambda(T)$ and $\xi(T)$ increase drastically near T_c: Thus with films of thickness 500 Å$<d<$10 000 Å and with $t=T/T_c$ varying from $t=0.99$ to $t\ll1$, a wide range of ratios $d/\lambda(T)$ and $d/\xi(T)$ can be explored. The upper critical field, $H_{cr}(\theta)$, is a function of the angle θ between the field and the surface, but in most of the experiments to be discussed here we studied only the critical fields $H_{\parallel}(\theta=0)$ and $H_{\perp}(\theta=\pi/2)$.

These results can be interpreted in terms of the Ginsburg-Landau theory[3] and some extensions of it to lower temperatures, in dirty superconductors.[4,5]

Section II is devoted to the experimental technology. In Sec. III we present and discuss the results obtained for second-kind superconductors. Section IV gives a brief review of the experimental data on pure metal films (first kind). This will contrast the behavior of the two types of superconductors.

II. EXPERIMENTAL

a. Preparation of the Samples

Our work has been devoted mainly to the study of Sn and **Sn**-In alloys in thin films, up to the limit of solubility of In in Sn(~6 at.%). Alloys of In and Bi in Pb have also been studied.

The materials were evaporated by Joule effect in a conventional evaporator where the use of a booster diffusion pump, a liquid N_2 trap, and a Meismer trap in the evaporation room allowed us to work in a static

* Research supported in part by the General Electric Company, the Cie des Machines Bull, the Commissariat à l'Energie Atomique, and the Direction des Recherches et Moyens d'Essais.

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