THEORY OF ELECTRON SPECTRA OF BISMUTH TYPE METALS IN A MAGNETIC FIELD

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The "hole" and "electron" spectrum in a magnetic field is considered for metals of the bismuth type. The paramagnetic energy increment is calculated on the basis of a quasi-classical approximation. It is characterized by a g-factor which depends on the quasi-momentum. Calculation of the diamagnetic levels is carried out completely only for "holes" in the case in which the magnetic field is directed along the trigonal axis of the crystal.

1. The spectrum of bismuth in a magnetic field has been the subject of a large number of experimental investigations and one theoretical paper.[1] In the latter, the paramagnetic increment to the energy of the electron had been computed by starting out from model assumptions on the existence of the near zone.

The electron energy spectrum of a bismuth type metal in the absence of a magnetic field has been determined by Abrikosov and the author [2] (this work is cited below as I). It was shown that the small deformation which transforms the simple cubic lattice into a lattice of the bismuth type leads to the appearance of a small number of "holes" and "electrons" close to certain points of the reciprocal lattice space. The "holes" and "electrons" arise in a mutually-dependent fashion, and their spectrum (with account of the equality of the number of "holes" and of "electrons") is entirely determined by seven constants (the same number as in the universally adopted ellipsoidal model).

In the present work, beginning with the results obtained by us previously,[2,3] we consider the energy spectrum (of "holes" and "electrons") of Bi in the presence of a magnetic field. Fundamentally, we shall be interested in the g-factor, and we shall not be concerned with the de Haas–van Alphen effect in not-too-large magnetic fields (where the quasi-classical quantization is valid) and in cyclotron resonance, inasmuch as the frequencies of the corresponding oscillations are connected with the extremal cross sections and the masses of the Fermi surface, i.e., they are determined by the parameters of the spectrum in the absence of the magnetic field.

The experimental investigation of paramagnetic resonance reveals a difference in the g-factor from two (by 10—100 times) and its large anisotropy.[4] This means that the g-factor in metals of the bismuth type depends essentially on the quasi-momentum. From the calculation given below, it is evident that the dependence arises because of the appreciable spin-orbit coupling, which plays an important role also in considering the spectrum in the absence of the magnetic field.

2. The energy spectrum of Bi must be known in the vicinities of the points

$$\mathbf{k}_0 = \tfrac{1}{4}(\mathbf{b}_1^0 + \mathbf{b}_2^0 + \mathbf{b}_3^0), \quad \mathbf{k}_1 = \tfrac{1}{4}(-\mathbf{b}_1^0 + \mathbf{b}_2^0 + \mathbf{b}_3^0),$$
$$\mathbf{k}_2 = \tfrac{1}{4}(\mathbf{b}_1^0 - \mathbf{b}_2^0 + \mathbf{b}_3^0), \quad \mathbf{k}_3 = \tfrac{1}{4}(\mathbf{b}_1^0 + \mathbf{b}_2^0 - \mathbf{b}_3^0)$$

in the reciprocal lattice space ($\mathbf{b}_i^0$ is the lattice spacing). Close to the first point there are "holes," close to the other three, "electrons." Prior to the deformation which transforms the cubic lattice into a lattice of the Bi type, each of these points has the symmetry C_{3v}. For the same reasons as given in I, we consider only two-dimensional representations of the groups C_{3v}, such that for determination of the spectrum from the deformation it is necessary to compute the principal values of the second-rank matrix D. We expand the matrix D in a complete set of linearly independent matrices of second rank. These four matrices are chosen in the following fashion: E is the unit matrix, and

$$J_z = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}, \quad J_+ = \begin{vmatrix} 0 & 0 \\ i & 0 \end{vmatrix}, \quad J_- = \begin{vmatrix} 0 & -i \\ 0 & 0 \end{vmatrix}.$$

The coefficients J_i of expansion of the matrix D in E are functions of $\kappa = \mathbf{k} - \mathbf{k}_i$ and H. Inasmuch as we are interested in small values of κ, we can limit ourselves to the first terms in the expansion of these functions in κ and H.

In the discussions given here, electron spin has not been taken into account. For account of the effect of spin it would generally be necessary to

use the double-value representation group. Assuming, as in I, the energy of the spin-orbit coupling Δ to be small in comparison with the characteristic electron energy in the cubic lattice, we can take the spin into account by assuming the expansion coefficients J_i of D in E to be dependent on the operators σ_i of the projection of the spin, and limit ourselves to the first order in Δ. The procedure set forth coincides formally with the technique developed primarily for semiconductors by Pikus.[5]

Under these assumptions, and with account of the requirement of spatial symmetry, time inversion and hermiticity, we get

$$D = E\,[a\varkappa_z + \mu_1(\sigma\mathbf{H})] + J_z\,[\Delta\sigma_z + \mu_2 H_z] + ib\,[\varkappa_+ J_- - \varkappa_- J_+], \qquad \varkappa_\pm = \varkappa_y \pm i\varkappa_x, \tag{1}$$

where μ_1 is the Bohr magneton, while a, b, Δ, and μ_2 are real constants. The z axis is directed along the C_3 axis and the x axis is perpendicular to one of the symmetry planes of the small group. The components κ_i are operators connected by the well-known commutation relations:

$$\{\varkappa_x, \varkappa_y\} = ie\hbar H_z/c \quad \text{etc.} \tag{2}$$

In the construction of D, it is taken into account that in transformations of the group C_{3v} the matrices J_i are transformed as components of an axial vector. In order to find out what invariant combination is permitted in D, one must make use of formulas developed in [5].

Going over to the matrix elements J_i, we get

$$D = \begin{vmatrix} a\varkappa_z + \mu_1(\sigma\mathbf{H}) + \Delta\sigma_z + \mu_2 H_z & b\varkappa_+ \\ b\varkappa_- & a\varkappa_z + \mu_1(\sigma\mathbf{H}) - \Delta\sigma_z - \mu_2 H_z \end{vmatrix}.$$

We describe D in terms of the spin matrices:

$$D = \begin{vmatrix} D_{11} & b\varkappa_+ & -i\mu_1 H_+ & 0 \\ b\varkappa_- & D_{22} & 0 & -i\mu_1 H_+ \\ i\mu_1 H_- & 0 & D_{33} & b\varkappa_+ \\ 0 & i\mu_1 H_- & b\varkappa_- & D_{44} \end{vmatrix}$$

Here

$$D_{11} = a\varkappa_z + \Delta + (\mu_1 + \mu_2) H_z,$$

$$D_{22} = a\varkappa_z - \Delta + (\mu_1 - \mu_2) H_z,$$

$$D_{33} = a\varkappa_z - \Delta - (\mu_1 - \mu_2) H_z,$$

$$D_{44} = a\varkappa_z + \Delta - (\mu_1 + \mu_2) H_z.$$

The spectrum before deformation is found by diagonalization of the matrix D.

For the determination of the spectrum after deformation, the matrix D′ is diagonalized, for the construction of which it is necessary to take it into account that the deformation, although small, nevertheless doubles the volume of the elementary cell. New elementary vectors appear, and the points $\mathbf{k}_0$ and $-\mathbf{k}_0$, $\mathbf{k}_i$ and $-\mathbf{k}_i$ become pairwise equivalent. Now it is necessary to combine two two-dimensional representations, corresponding to the points $\mathbf{k}_0$ and $-\mathbf{k}_0$ (and similarly also for the points $\mathbf{k}_i$). Thus, in order to obtain D′, it is necessary to combine D with the matrix obtained from D by means of inversion (inasmuch as $-\mathbf{k}_0$ is obtained from $\mathbf{k}_0$ by inversion). Moreover, terms proportional to the deformation appear explicitly in the elements of the matrix D′. After the permutation of several columns and rows, D′ can be written in the form

$$D' = \begin{vmatrix} A & \mathcal{H} \\ \mathcal{H}^* & A' \end{vmatrix},$$

$$A = \begin{vmatrix} A_{11} & b\varkappa_+ + \beta & \gamma & \delta \\ b\varkappa_- + \beta & A_{22} & \delta & \gamma \\ \gamma & \delta & A_{33} & -b\varkappa_+ + \beta \\ \delta & \gamma & -b\varkappa_- + \beta & A_{44} \end{vmatrix}. \tag{3}$$

Here $A_{11} = D_{11}$; $A_{22} = D_{22}$; $A_{33} = -a\kappa_z + \Delta + (\mu_1 + \mu_2)H_z$; $A_{44} = -a\kappa_z - \Delta + (\mu_1 - \mu_2)H_z$. The matrix A′ is obtained from A by the substitution $\mu_1 \to -\mu_1$, $\Delta \to -\Delta$; $\mathcal{H} = -i\mu_1 H_+ E$, E is a unit matrix. The notation is the same as in I. The terms appearing on the main diagonal, which are proportional to the deformation, can be added to the energy ω. Here they are omitted.

The energy spectrum is found from the equation

$$\mathrm{Det}\,|D' - E\omega| = 0. \tag{4}$$

Equation (4) calls for an explanation, because D′ depends on the operators κ_i. As was shown by Abrikosov,[3] the spectrum is determined by the poles of the matrix G_{ik} satisfying the equation

$$(D' - E\omega)_{ij} G_{jk} = \delta_{ik}. \tag{5}$$

However, for estimating the poles G_{ik}, it is sufficient to find in place of the solution (5), the non-trivial solution of the system

$$(D' - E\omega)_{ij}\psi_j = 0. \tag{6}$$

Thus Eq. (4) must be understood to be the condition for the existence of a non-trivial solution of the set (6).

3. The solution of (4) with account of the commutation relation (2) is a difficult problem. However, it is materially simplified for holes ($\beta = \delta = 0$) and for a magnetic field along the C_3 axis. In this case,

$$\{\varkappa_+, \varkappa_z\} = \{\varkappa_-, \varkappa_z\} = 0, \ \{\varkappa_-, \varkappa_+\} = 2e\hbar H/c. \qquad (7)$$

The matrix elements of the operator satisfying the relations (7) are known:

$$(\varkappa_+)_{n+1,\,n} = \sqrt{2e\hbar H\,(n+1)/c}, \qquad (\varkappa_-)_{n-1,\,n} = \sqrt{2e\hbar Hn/c}.$$

Inasmuch as the magnetic field is directed along the z axis, the matrix $\mathcal{H} = 0$. The equation (4) divides into two. The first part takes the form (for $n = 1, 2, \ldots$);

$$\mathrm{Det}\begin{vmatrix} A_{11}-\omega & b\sqrt{2e\hbar Hn/c} & \gamma & 0 \\ b\sqrt{2e\hbar Hn/c} & A_{22}-\omega & 0 & \gamma \\ \gamma & 0 & A_{33}-\omega & b\sqrt{2e\hbar Hn/c} \\ 0 & \gamma & b\sqrt{2e\hbar Hn/c} & A_{44}-\omega \end{vmatrix} = 0, \qquad (8)$$

and (for $n = 0$)

$$\mathrm{Det}\begin{vmatrix} A_{11}-\omega & \gamma \\ \gamma & A_{33}-\omega \end{vmatrix} = 0.$$

Here the function ψ_i is sought in the form

$$\psi_i = \begin{vmatrix} c_1\psi_n \\ c_2\psi_{n-1} \\ c_3\psi_n \\ c_4\psi_{n-1} \end{vmatrix}.$$

Equation (8) reduces to the following substitutions (see I) in the expression for the spectrum $\omega = \omega_0(\kappa_z, \kappa_\perp)$:

$$\omega \to \omega - \mu_1 H_z, \qquad \Delta \to \Delta + \mu_2 H_z,$$

$$\varkappa_\perp^2 = \varkappa_x^2 + \varkappa_y^2 \to 2e\hbar Hn/c, \qquad n = 1, 2, \ldots, \qquad (9)$$

The solution of the second equation, which is separated from (4), is obtained from (9) by the substitution $\mu_1 \to -\mu_1$, $\Delta \to -\Delta$. We see that in this case the exact condition for quantization is identical with the quasi-classical one. This leads to the result that the oscillations of the magnetic susceptibility (for **H** along C_3) on the "hole" part of the Fermi surface are periodic in 1/H also for large magnetic fields, for which $n \sim 1$ is important. For $n = 0$, we have

$$\omega = \pm(\Delta + \mu_1 H_z) + \mu_2 H_z \pm \sqrt{\gamma^2 + a^2\varkappa_z^2}.$$

4. Inasmuch as it is not possible to solve Eq. (4) in the arbitrary case, we shall limit ourselves to the region of not-too-large values of the magnetic field $\mu H \ll \epsilon$; μ, ϵ are of the order of the magneton and of the Fermi energy in bismuth (for Bi this corresponds to $H \ll 10^4$ G). Then one can regard the operators κ_i as numbers, and take the explicit dependence of D′ on the magnetic field into account by perturbation theory.

The spectrum in zero order in the magnetic field was obtained in I. In the subsequent linear approximation it is possible to consider H_z and H_+ in turn. First we set $H_+ = 0$. Then Eq. (4) splits into two parts, reducing to the part already solved in I by the substitution $\omega \to \omega - \mu_1 H_z$, $\Delta \to \Delta + \mu_2 H_z$ in the first and $\omega \to \omega + \mu_1 H_z$, $\Delta \to -\Delta + \mu_2 H_z$ in the second equation. Assuming $\mu_1 H_z \ll \omega$, $\mu_2 H_z \ll \Delta$, and taking it into account that ω_0 if even in Δ, we get

$$\omega(\varkappa, H_z) = \omega_0(\varkappa) \pm (\mu_1 + \mu_2\,\partial\omega_0/\partial\Delta)\,H_z. \qquad (10)$$

We now set $H_z = 0$ and use the well-known identity from matrix theory[6]

$$\mathrm{Det}\begin{vmatrix} A & B \\ C & D \end{vmatrix} = \mathrm{Det}\,|\,AD - ACA^{-1}B\,|.$$

Here A, B, C, and D are matrices. Then

$$\mathrm{Det}\,|D' - E\omega\,| = \mathrm{Det}\,|(A^0 - E\omega)(A^{0\prime} - E\omega) - \mu_1^2 H_\perp^2 E\,|$$
$$= \mathrm{Det}\,|(A^0 - E\omega)(A^{0\prime} - E\omega)\,| - \mu_2^2 H_\perp^2 a_{ii} = 0,$$

where a_{ik} are the co-factors of the element $[(A^0 - E\omega)(A^{0\prime} - E\omega)]_{ik}$;

$$A^0 = A\,(H_z = 0), \qquad A^{0\prime} = A'\,(H_z = 0).$$

We set $\omega = \omega_0 + \delta\omega$, where ω_0 satisfies the equation

$$\mathrm{Det}\,|(A^0 - E\omega_0)(A^{0\prime} - E\omega_0)\,| = [\mathrm{Det}\,(A^0 - E\omega_0)]^2 = 0.$$

We then find

$$\delta\omega = \pm\mu_1 H_\perp \sqrt{a_{ii}}\Big/\frac{\partial}{\partial\omega_0}\mathrm{Det}\,(A^0 - E\omega_0). \qquad (11)$$

It is easy to compute the derivative in (11) by using the value of $\mathrm{Det}\,(A^0 - E\omega_0)$ computed in I. We have

$$\frac{\partial}{\partial\omega_0}\mathrm{Det}\,(A^0 - E\omega_0) = 4\omega_0(\omega_0^2 - \gamma^2 - \delta^2 - \beta^2 - \Delta^2 - b^2\varkappa_\perp^2$$
$$- a^2\varkappa_z^2) - 8\beta(\gamma\delta + ab\varkappa_y\varkappa_z) \equiv 4\varphi.$$

It is not difficult also to compute the sum a_{ii}:

$$a_{ii} = 16\{\varphi^2 - 4\Delta^2[(a\varkappa_z\omega_0 + b\varkappa_y\beta)^2 + (\gamma\omega_0 + \beta\delta)^2$$
$$+ b^2\varkappa_x^2\delta^2]\}.$$

Combining (10) and (11), we get the following expression for the paramagnetic increment to the energy of the "electrons":

$$\mu(\varkappa) = \pm [\mu_\perp^2(\varkappa) H_\perp^2 + \mu_z^2(\varkappa) H_z^2]^{1/2},$$
$$\mu_z = \mu_1 + \mu_2\Delta(\omega_0^2 - \delta^2 - \beta^2 + \gamma^2 - \Delta^2 - b^2\varkappa_\perp^2 + a^2\varkappa_z^2)/\varphi,$$
$$\mu_\perp = \mu_1\sqrt{a_{ii}}/4\varphi, \qquad \omega_0 = \omega - f^{(1)}. \tag{12}$$

For the "holes," Eqs. (12) lead to

$$\mu_z = \mu_1 + \mu_2\frac{\Delta}{\omega_g}\frac{\omega_g^2 + 9\gamma^2 - \Delta^2 - b^2\varkappa_\perp^2 - a^2\varkappa_z^2}{\omega_g^2 - 9\gamma^2 - \Delta^2 - b^2\varkappa_\perp^2 - a^2\varkappa_z^2},$$
$$\mu_\perp = \mu_1 ab\varkappa_z\varkappa_\perp [a^2b^2\varkappa_z^2\varkappa_\perp^2 + \Delta^2(9\gamma^2 + a^2\varkappa_z^2)]^{-1/2},$$
$$\omega_g = \omega - f^{(0)}; \tag{13}$$

for the expressions for $f^{(1)}$ and $f^{(0)}$, see I.

As expected, $\mu_Z = \mu_\perp = \mu_1$ for $\Delta = 0$. Thus, in the absence of spin-orbit coupling, the g-factor does not depend on the quasi-momentum and does not differ from the g-factor of the free electron. For a spin-orbit coupling energy different from zero, the g-factor depends upon κ in a rather complicated way. In this case the symmetry of the g-factor corresponds to the symmetry of the Fermi surface. These considerations are confirmed by experiments.[4]

A detailed comparison of Eqs. (12) and (13) with experimental data cannot be given here for the following reason. It follows from (12) and (13) that the paramagnetic increment to the energy is determined both by the seven constants of the spectrum in the absence of the magnetic field and also by two new ones: μ_1 and μ_2. From data on the de Haas–van Alphen effect and cyclotron resonance, it is possible to derive the seven constants mentioned and to establish the spectrum completely in the absence of the magnetic field. Turning then to paramagnetic resonance, one can also determine the constant μ_2. However, in bismuth, the ratio of the minimum to the maximum mass (and also the ratio of the cross sections) is $m_{min}/m_{max} \approx 1/15$. This requires that the accuracy of measurement of the absolute value of say m_{max} be known to exceed the value of m_{min}. Even in very sensitive experiments,[7] such an accuracy has not yet been achieved. The situation is much worse with the accuracy of experiments on paramagnetic resonance.

After achievement of the desired experimental accuracy, the finding of all constants of the spectrum reduces only to a solution of seven algebraic equations; that is, it is completely solvable with a computer. It will then be possible to make a quantitative comparison of Eqs. (12) and (13) with experimental data.

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