EFFECT OF DEFORMATION ON THE ELECTRON SPECTRUM OF BISMUTH

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The effect of deformation on the electron spectrum of bismuth is considered. Simple results are obtained in the small deformation limit, when in a first approximation the electron and hole Fermi surfaces vary similarly to themselves. If the deformation does not change the symmetry of the lattice, then the change of the hole spectrum can be described by two parameters, one of which depends only on the displacement of the sublattices.

IT is known that the number of carriers in bismuth decreases[1] under pressure. New information was published recently[2] [1)]. It turned out, for example, that the Fermi surface of the holes decreases and exhibits a certain tendency to spherization. The transformation into a dielectric should apparently occur at a pressure on the order of 25 kbar (at helium temperature). At higher pressure, approximately 40 kbar, bismuth becomes a substance possessing the properties of a good metal, for example, superconductivity. Unfortunately, the lattice parameters of the bismuth were measured only at atmospheric pressure. The most interesting parameter is u, which determines the position of the two atoms in the unit cell - their rhombohedral coordinates (u, u, u) and ($\bar{u}$, $\bar{u}$, $\bar{u}$). Under ordinary conditions, $u_i = 0.234$, and a lattice with a single atom per cell is produced when $\bar{u}_i^0 = 0.25$. In the latter case, the bismuth should be a good metal. If the vector $\tau = u - u^0$ changes by an amount of the order of its own magnitude, then the deformation should be regarded as large. However, with respect to a lattice with a single atom per cell, such a deformation is small if the doubling of the cell volume is suitably taken into account.

Abrikosov and the present author proposed earlier for the energy spectrum a theory[3] in which the starting point was the small deviation between the space lattice of the bismuth from primitive cubic. If the elementary vectors of the primitive cubic lattice are denoted by a_i^0, then the elementary vectors of the bismuth-type lattice can be written in the form $a_i' = (\delta_{ik} + u_{ik})a_k$, where $a_1 = a_2^0 + a_3^0$, $a_2 = a_3^0 + a_1^0$, and $a_3 = a_1^0 + a_2^0$. The position of any atom is determined by the vector $R_n^j = (n_i + ju_i)a_i'$; here $j = \pm 1$ for two atoms per cell, and n_i are integers. The vector u behaves like an axial vector under those symmetry transformations (for example, inversions) which interchange the locations of the two atoms in the cell. In the undeformed bismuth lattice all three components u_i (in terms of the axes a_i') are equal and the tensor u_{ik} has two independent components which can be determined if the values of the vectors a_i' and the angle between them are known. We are left with the quantity a_i^0. It can be chosen, for example, in such a way that for undeformed bismuth $u_i = 0$. The smallness of u_{ik} is insured by the fact that the angle between the pair of vectors a_i' in the bismuth lattice amounts to 57°14′, and in the primitive cubic lattice it is equal to 60°.

The spectrum $\epsilon(p)$ was determined in[3] by considering the vicinity of the points of intersection of the threefold symmetry axes of the cube with the boundaries of the Brillouin zone of bismuth. To find the spectrum it was necessary, in analogy of the procedure used in semiconductor theory, to diagonalize a certain matrix. This entire procedure can be transferred to the case of deformed bismuth. The only difference is that u_{ik} and τ_i no longer have, generally speaking, the symmetry of the undeformed lattice. For holes we obtain the following equation

$$\begin{vmatrix} \varkappa_z+\Delta+f-\varepsilon & \varkappa_++\beta_+ & \gamma & \delta_+ \\ \varkappa_-+\beta_- & \varkappa_z-\Delta+f-\varepsilon & \delta_- & \gamma \\ \gamma & \delta_+ & -\varkappa_z+\Delta+f-\varepsilon & -\varkappa_++\beta_+ \\ \delta_- & \gamma & -\varkappa_-+\beta_- & -\varkappa_z-\Delta+f-\varepsilon \end{vmatrix} = 0, \quad (1)$$

where

$$\varkappa_z = ap_z,\ \varkappa_\pm = b(p_y \pm ip_x),\ \beta_\pm = \beta_1(\tau_y \pm i\tau_x) + \beta_2(u_{yz} \pm iu_{xz}),$$
$$\delta_\pm = \delta_1(\tau_y \pm i\tau_x),\ \gamma = \gamma_1\tau_z,\ f = f_1\tau_z + f_2u_{zz} + f_3u_{ii},$$

and the proportionality coefficients are certain real numbers. We use here a rectangular coordinate system with the z axis along a threefold axis of the undeformed crystal. On the left are indicated the basis functions, which transform in accordance with the two-dimensional representation of the group C_{3v} - the small group of the point T in the cube. The points T and −T become equivalent as a result of the displacement of the sublattice, and the corresponding nondiagonal elements are proportional to τ_i. The equation corresponding to the second projection of the spin is obtained from (1) by replacing the sign in front of the constant Δ that takes into account the spin-orbit interaction and does not depend on the deformation. It leads to the same eigenvalues as (1). Equation (1) is very similar to the equation that determines the spectrum of the electrons in undeformed bismuth[3]. In (1), however, besides inversion of the space coordinates and of the time, there are no symmetry elements, whereas for electrons in undeformed bismuth there is still a twofold axis (and consequently a symmetry plane).

The electron spectrum can be obtained from (1) by

1)I take the opportunity to thank E. S. Itskevich, L. M. Fisher and V. V. Kechin for reporting their experimental results prior to publication.

a rotation that transforms the point T in the cube into the point L, near which the electrons are located. This yields an equation of the same type as in (1), and certain parameters of the electron spectrum can be expressed in terms of the hole parameters [3].

In view of the complicated character of (1), we shall consider two limiting cases.

1. Deformation that does not change the lattice symmetry; holes. In this case the only nonzero components of u_{ik} and τ_i are those which do not change under lattice symmetry transformations, i.e., τ_z, u_{zz}, and u_{ii}. Therefore $\beta_\pm = \delta_\pm = 0$ and the hole spectrum is

$$\varepsilon = f - \{\Delta^2 + \gamma^2 + (ap_z)^2 + (bp_\perp)^2 - 2[(\gamma\Delta)^2 + (abp_zp_\perp)^2 + (a\Delta p_z)^2]^{1/2}\}^{1/2}, \quad (2)$$

where $p_\perp^2 = p_x^2 + p_y^2$. The top of the band ($p = 0$) corresponds to $\epsilon^0 = f - \gamma + \Delta$ (here and below we assume $\gamma, \Delta > 0$, since their squares are contained in (2). The experimentally measured quantities will change under pressure both as a consequence of the displacement of the top of the band and as a result of the change in the Fermi level. The latter is determined by the condition that the numbers of electrons and holes be equal, and thus depend also on the deformation of the electron spectrum. It is therefore convenient to use the Fermi energy $\tilde{\epsilon}$ reckoned from ϵ^0 (in the undeformed crystal the Fermi energy $\tilde{\epsilon} < 0$), as well as the parameter γ. We emphasize that γ is determined only by the displacement of the sublattices τ. The general expressions for the experimentally measured extremal sections of the surface (2) and of the cyclotron masses are given in [4]. We present the expansions in γ and $\tilde{\epsilon}$ for the sections of S_z and S_x by the planes $p_z = 0$ and $p_x = 0$, and also for the extremal cyclotron mass ($p_z = 0$);

$$\frac{dS}{S} = \frac{d\tilde{\varepsilon}}{\tilde{\varepsilon}} + \frac{d\gamma}{\gamma} \quad (3a)$$

$$\frac{dS_x}{S_x} - \frac{dS_z}{S_z} = -\frac{d\tilde{\varepsilon}}{4\Delta} - \Delta\frac{d\gamma}{2\gamma^2}, \quad (3b)$$

$$\frac{dm_z}{m_z} = -\frac{d\tilde{\varepsilon} - d\gamma}{\gamma - \Delta}. \quad (3c)$$

In calculating the derivatives we have retained here only the principal terms of the expansion in $\tilde{\epsilon}/\Delta$ and $\Delta/2\gamma$, inasmuch a comparison of the theory [3] with the experimental data on undeformed bismuth has revealed that these quantities are of the order of 0.1 [4]. Therefore the areas S_z and S_x change essentially in a similar manner (3a) (they decrease when $d\tilde{\epsilon} > 0$), and the difference appears only in the next higher approximation (3b). For the same reason, expressions (3a) and (3b) are determined essentially by the variation of $\tilde{\epsilon}$, whereas in (3c) $d\tilde{\epsilon}$ and $d\gamma$ are on par.

2. Electrons, two-band approximation. In a comparison [4] of the experimental data with the theory [3], it turned out that only two out of the four bands taken into account in (1) are particularly close at the point L, and the distance between them $\epsilon_g \equiv \epsilon_3^0 - \epsilon_2^0$ is smaller than the Fermi energy $\tilde{\epsilon}$, which is now reckoned from the bottom of the conduction band ϵ_3^0. Therefore the free term in the equation (see (9) of [4]) that determines the electron spectrum in undeformed bismuth can now be represented in the form

$$C - AB = -(\varepsilon - \varepsilon_1^0)(\varepsilon - \varepsilon_2^0)(\varepsilon - \varepsilon_3^0)(\varepsilon - \varepsilon_4^0) \approx \approx -\varepsilon_1^0\varepsilon_4^0\varepsilon_g\tilde{\varepsilon}(1 + \tilde{\varepsilon}/\varepsilon_g).$$

If we are interested in small values of p, we can neglect the dependence of the coefficients A, B, and D on $\tilde{\epsilon}$, after which we arrive at the nonquadratic ellipsoidal model

$$\alpha_{ik}p_ip_k = \varepsilon_g\tilde{\varepsilon}(1 + \tilde{\varepsilon}/\varepsilon_g), \quad (4)$$

where $\alpha_{xy} = \alpha_{xz} = 0$, if the x axis is chosen along the twofold axis of the small group of the point L. We have departed here from the traditional notation, separating the gap ϵ_g in explicit form.

In order to take into account the influence of the deformation, it is convenient to return to the matrix notation (see, for example, [5]):

$$\begin{vmatrix} \psi_2^+ & -\varepsilon_g - \tilde{\varepsilon} & 0 & t & u \\ \psi_2^- & 0 & -\varepsilon_g - \tilde{\varepsilon} & -u^* & t \\ \psi_3^+ & t & -u & -\tilde{\varepsilon} & 0 \\ \psi_3^- & u^* & t & 0 & -\tilde{\varepsilon} \end{vmatrix} = 0, \quad (5)$$

where $t = v_xp_x$ and $u = v_yp_y + v_zp_z$; v_x is a real constant and v_y and v_z are complex constants. On the left are indicated the basis functions, which transform in accordance with the double-valued representations of the small group C_{2h} of the point L (the spin-orbit interaction cannot be regarded as small in this case, since it plays the same role as the deviation from the primitive cube).

The two-valued representations of the group C_{2h} are one-dimensional, and the functions ψ_α^+ and ψ_α^- with identical α transform in accordance with complex-conjugate representations, while ψ_3 and ψ_2 have different parities with respect to inversion. From the components u'_{ik} of the deformation tensor and the τ'_i of the displacement tensor, which are now taken with respect to the lattice of the undeformed bismuth and not the cubic lattice, we can make up two types of quantities, depending on the parity upon reflection in a plane perpendicular to the twofold axis (the x axis). To abbreviate the notation, we shall write down only one representation of each of the even components (which are conveniently taken in the form u'_{zz}, u'_{ii}, u'_{yz}, $u'_{yy} - u'_{xx}$, τ'_z and τ'_y, the z axis being a threefold axis of the crystal) and of the odd components (u'_{xy}, u'_{xz}, and τ'_x). Taking into account the requirement of invariance to time inversion, we see that in the approximation that is linear in the deformation it is necessary to make the following substitutions in (5):

$$\begin{aligned} t \to t' &= p_x(v_x + c_1u_{zz}') + c_2u'_{xy}p_y + c_3u_{xy}'p_z, \\ u \to u' &= p_y(v_y + d_1u_{zz}') + p_z(v_z + d_2u_{zz}') + d_3u_{xy}'p_x, \\ \varepsilon_g &\to \varepsilon_g' = \varepsilon_g + eu_{zz}', \end{aligned} \quad (6)$$

where c and e are real constants and d are complex constants. The latter statement, besides the one made earlier that v_x is real and v_y and v_z are complex, can be verified with the aid of the formulas given in [6]. To this end it is sufficient to combine the representations according to which ψ_2^+ and ψ_3^- transform, and determine how many times the representation according to which the sought-for component p_i, u'_{ik}, or $p_iu'_{jk}$ is contained in the corresponding product (symmetrical, antisymmetrical, or the product of two complex-conjugates).

We again reckon the energy from the bottom of the conduction band, whose displacement as a result of

the deformation is of the same form as ϵ_g'. We note that this shift depends both on the components u_{zz}', u_{ii}', and τ_i, which do not change on going from one point L to another by rotation around a threefold axis, as well as on u_{yz}', $u_{yy}' - u_{xx}'$, and τ_y', which are changed by this rotation. If the deformation changes the symmetry of the lattice, the latter differ from zero, and the extrema of the bands at different points L are not displaced in the same manner.

Substituting (6) in (5), we arrive at an equation of the same type as (4), but now all the α_{ik} are different from zero. Since the components p_i corresponding to the Fermi level in the undeformed bismuth are small, the crossing terms of the type $u_{ik}p_j$ in (6) are also small, and the principal result of the deformation is a change of the gap and of the Fermi level.

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