

ORIGIN OF THE ELECTRON SPECTRUM IN METALS OF THE BISMUTH GROUP

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An attempt is made to ascribe some peculiarities of the bismuth spectrum to smallness of the number of carriers. It is pointed out that the phenomenon may be due to the Keldysh-Kopaev dielectric transition effect. The results are compared to those of the Abrikosov-Fal'kovskii phenomenological model^[4]. It is demonstrated that the spectrum which follows from their assumption^[4] corresponds to a dielectric gap. The influence of Fermi-fluid effects on Brillouin-zone filling rules is discussed.

1. INTRODUCTION

IN spite of the great brilliance of the model proposed first by Keldysh and Kopaev^[1] for the "metal-dielectric" transition (see also the paper of Kozlov and Maksimov^[2] for the case of a strong band overlap), we still do not know whether there exist accessible objects in which such a transition can be realized. Since it is very important in the initial picture^[1,2] that in the metallic state the electron and hole Fermi surface are close in shape, there is apparently no hope of observing this transition in metals of group V, where the carrier-spectrum anisotropy is strong. Mnatsakanov and one of the authors^[3] have already advanced the idea that the Keldysh-Kopaev mechanism^[1] may itself be the cause of the formation of small carrier groups. Therefore in the case of bismuth it would be possible to attempt to pose the inverse question, namely that of explaining the singularities of the bismuth spectrum by starting with a model of two coinciding Fermi surfaces.

This problem seems all the more timely because the most likely phenomenological picture of the bismuth spectrum, proposed by Abrikosov and Fal'kovskii^[4], is based on a group analysis of the splitting of the degenerate electron term in the vicinities of points L and T of the Brillouin zone, and the initial state is chosen to be precisely a state in which the electron-hole surfaces coincide. This picture seems at first glance to be highly artificial and was assumed^[4] because in the opposite case an arbitrarily small deformation is incapable of "closing" the diverging sections of the Fermi surfaces. In addition, this initial state, called the "dielectric phase" by Abrikosov and Fal'kovskii^[4], is in general unstable, in accordance with the results of^[1,2]. Therefore the group-theoretical calculation of the term splitting^[4], performed in the manner used in semiconductor theory^[5,6], must be replaced by a microscopic analysis of the picture of the electron interaction with one another and with the phonons.

In Sec. 2 we attempt to show that the possible existence of states in which the electronic spectrum is close to the Keldysh-Kopaev model follows quite naturally from the concepts of the band theory with respect to the spectrum in a dielectric, if these concepts are supplemented with allowance for the interaction between the electrons.

In Sec. 3 we investigate the role of different interac-

tions in the dielectric transition. In particular, we shall show that, depending on the ratio of the electron-electron and electron-phonon interaction constants, the dielectric transition can be due to the instability of either the electron spectrum alone or the phonon spectrum alone. It is shown in the Appendix that this result does not depend on any assumptions concerning the anisotropy of the crystal.

Finally, in Sec. 4 we apply the results to bismuth. The equations obtained for the spectrum are analogous, in the main, to those of Abrikosov and Fal'kovskii^[4], except that there are no matrix elements responsible for the band overlap at the points L and T. Thus, the assumptions of Abrikosov and Fal'kovskii^[4] actually lead to the dielectric spectrum of this method.

In the conclusion we list additional possibilities that might lead to band overlap and to the production of electrons and holes.

2. INITIAL ELECTRONIC STATE OF UNDEFORMED LATTICE

The bismuth lattice is close to primitive-cubic and can be constructed of two cubic face-centered sublattices by a small shift ($\sim 10\%$) of the latter relative to each other along the body diagonal, and a small rhombohedral deformation (see, for example,^[7]). Thus, a unit cell contains two atoms, and from the point of view of the usual concepts, bismuth could be a dielectric. Abrikosov and Fal'kovskii^[4] have assumed that the dielectric state is preserved down to such small deformations that the bismuth lattice becomes a primitive-cubic one, and the "dielectric" and metallic phases cannot be obtained from one another by a continuous transition. It should be noted that these concepts are not easy to reconcile with the usual ones, since bismuth in a primitive-cubic lattice should always be a metal.

Let us analyze this situation. We consider a dielectric with two identical atoms per cell, each atom having an odd number of electrons. We shall show that there is a possible deformation that must lead continuously to a picture of coinciding Fermi surfaces in the dependence of the electron energy on the lattice coordinates.

Figure 1 shows a dielectric with an indirect gap; a decrease of the gap and further overlap would give

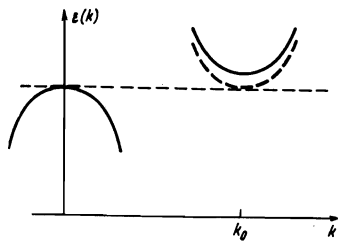


FIG. 1

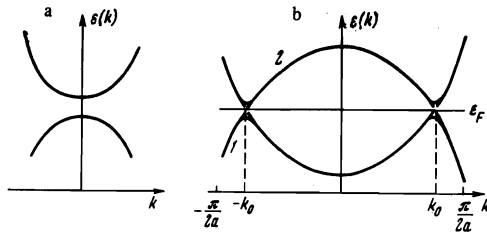


FIG. 2

rise to a metallic phase. It is important, however, that in this case there is a structure transition caused by Coulomb interactions, which occurs at the instant when the edge of the exciton band, shown dashed in Fig. 1, touches the valence band. The resultant structure is characterized by a vector q_0 (see the review^[8]), so that the transition is accompanied by an increase in the number of atoms per unit cell. Let us consider a deformation that gives rise to a small direct gap (Fig. 2a). It is possible, of course, for the gap to start increasing again with further deformation, but a more probable picture is that of "quasi-penetration" of the two branches, as shown in Fig. 2b.

We do not consider the region in which this penetration barely begins, for this is a region where Coulomb interactions play an essential role. We note, however, that the assumption that the gap in Fig. 2a is small denotes strong screening of the Coulomb interactions by the short-range forces that determine the course of the branches of the spectrum $\epsilon(k)$ at large k . Nor do the effective interactions increase in the situation of Fig. 2b, since screening by free carriers comes into play.

The arguments advanced offer qualitative evidence that it is possible to obtain the picture of the electronic levels of the model of^[1] from the dielectric state by means of symmetry-conserving deformation, if one excludes the structure transitions made inevitable by the specifics of the Coulomb interaction. We recall that when speaking of deformation we had in mind the dependence of the electron energy on the lattice displacements, and not a real deformation due to external uniform stresses. Therefore the state of Fig. 2b need not necessarily correspond to a stable equilibrium. This is hardly ever the case with respect to small perturbations, as we shall show in Sec. 3, regardless of the signs of the interactions in the dielectric-pairing effect. Nor is it obvious that this corresponds to a primitive lattice in our case of a dielectric made up of identical atoms. In real bismuth the rhombohedral deformation is very small, and we therefore assume, as do Abrikosov and Fal'kovskii^[4], that, neglecting the

interactions, the state of Fig. 2b corresponds to a primitive-cubic lattice with one atom per cell. Then the instability of the described state leads in turn to a slightly deformed lattice.

Let us examine in greater detail Fig. 2b from the point of view of this picture. The wave functions of the system, with allowance for the invariance of the spectrum $\epsilon(k) = \epsilon(-k)$ in both the dielectric and the metallic phase, can be unified into bands 1 and 2. At arbitrary k , the functions ψ_{1k} and ψ_{2k} are transformed by a translation through a period $2a$ in the usual manner:

$$\hat{C}(2a)\psi_k = e^{i2\pi}\psi_k.$$

In a lattice with half the period, invariance against translations $C(a)$ sets in: This means that far from the band intersection we have

$$\hat{C}(a)\psi_k = \sqrt{C(2a)}\psi_k = \pm e^{i\pi}\psi_k. \quad (1)$$

Since the number of states does not change on going over to a classification of states in a primitive lattice, we can have in the new lattice, instead of Fig. 2b, the two variants shown in Fig. 3a (the signs in (1) are the same for both bands) and 3b (opposite signs). Thus, the discontinuities in the energy branches and in the occupation of the states (the shaded regions) vanish only if the points of tangency of the bands in Fig. 2b (k_0 and $-k_0$) coincide with the boundary $(-\pi/2a, \pi/2a)$. In the three-dimensional case this would mean that the tangency occurs on the boundaries of the Brillouin zone, i.e., we would have to assume that in the zero-deformation limit the dielectric phase^[4] has flat sections of the Fermi surface. This also seems quite artificial, and in fact, it would be necessary to stipulate in Abrikosov and Fal'kovskii's paper^[4] that the coefficient b in the matrix Z_{SS} , should vanish^[4].

Thus, we encounter here a case when the occupation-number concepts of band theory are not applicable. Of course, the interactions between the electrons themselves cause the actual distribution $n(k)$ to become closed (Fig. 3c), leaving discontinuities only on the Fermi surface; as to the energy spectrum, it is likewise meaningful in the Fermi-liquid theory only near

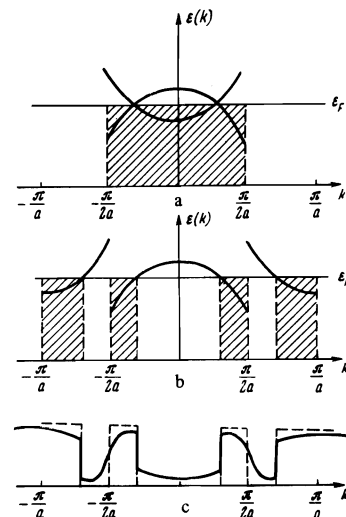


FIG. 3

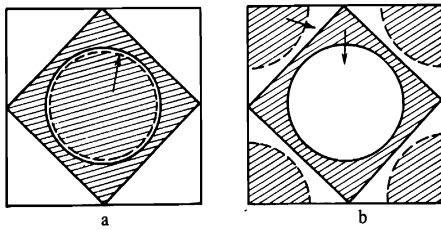


FIG. 4

the Fermi surface. It remains to see how this state can be reconciled with Luttinger's theorem^[9] (see^[10]), which is usually formulated as

$$n = 2(2\pi)^{-3}(pV + V_F), \quad (2)$$

where n is the electron density, V is the volume of the reciprocal cell, p is an integer, and V_F is the volume of the Fermi surface within the limits of the reciprocal cell. The latter is determined by the sum of the volumes lying between all the Fermi surfaces (on the side opposite to the normal vector $\nabla_{\mathbf{p}}\epsilon(\mathbf{p})$) and the boundaries of the unit cell.

Figures 4a and 4b illustrate, using a two-dimensional model, the situation of Figs. 3a and 3b. The internal square corresponds to Fig. 2b, i.e., it represents the reciprocal cell with two electrons. To obtain the previous number of electrons (in accordance with (2)) after constructing a reciprocal cell that is twice as large (a lattice with one electron per cell), it is necessary to change the definition of V_F , i.e., to take into account the regions shown shaded in Figs. 4a and 4b. Following Luttinger^[9], we define $G_{\omega}(\mathbf{r}, \mathbf{r}')$, the Green's function in the quasimomentum representation over an arbitrary set of Bloch waves $\psi_{\mathbf{j}\mathbf{k}}(\mathbf{r})$ (at a fixed form of the unit cell of the direct and reciprocal lattices):

$$G(\mathbf{r}, \mathbf{r}'; t - t') = \int \sum_{\mathbf{j}, \mathbf{l}} G_{\mathbf{j}\mathbf{l}}(\mathbf{k}, \omega) \psi_{\mathbf{j}\mathbf{k}}(\mathbf{r}) \psi_{\mathbf{l}\mathbf{k}}^*(\mathbf{r}') e^{-i\omega(t-t')} \frac{d\omega}{2\pi}. \quad (3)$$

In (3), $G_{\mathbf{j}\mathbf{l}}$ is an operator that is non-diagonal in the band indices. Determination of the particle-number density leads to the expression

$$n = \int \frac{d\omega}{2\pi} \int \frac{d^3k}{(2\pi)^3} \text{Sp}[\hat{G}(\mathbf{k}, \omega)] e^{i\omega 0}. \quad (4)$$

This leads (see^[10]) to Eq. (2) in the form

$$n = V \int_{\Omega} \frac{d^3k}{(2\pi)^3}, \quad (4')$$

where Ω is bounded by the cell and by the condition $G_{\mathbf{i}}(\omega = 0, \mathbf{k}) > 0$ ($G_{\mathbf{i}}$ are the eigenvalues of the operator \hat{G}).

It is usually assumed that $G_{\mathbf{i}}(\omega = 0, \mathbf{k})$ becomes infinite as a pole on the Fermi surface (properly speaking, this is indeed the definition of the spectrum and of the Fermi surface). Expression (4), at first glance, is invariant relative to the representation of the Bloch functions. It is clear, however, that it should also be invariant to the choice of the unit cell and to admit of an invariant continuation to infinite \mathbf{k} space. It follows therefore that in a crystal, unlike in an ordinary Fermi liquid, it is necessary to use in (4') the definition of Ω as the region where $G_{\mathbf{i}}(\omega = 0, \mathbf{k}) \geq 0$. In other words, a distinguishing feature of periodic structures is the possibility that $G_{\mathbf{i}}(\omega = 0, \mathbf{k})$ not only can become infinite, but can also vanish on

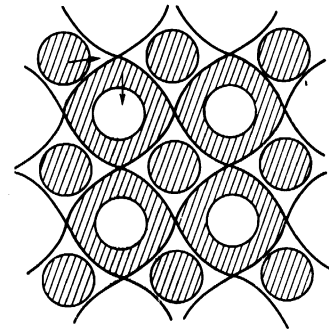


FIG. 5

entire surfaces. The surfaces $G_{\mathbf{i}}(\omega = 0, \mathbf{k}) = 0$ are determined by the structure and by the real interactions. Therefore, while preserving symmetry of the lattice, they need not necessarily be flat. The only limitation on them is imposed by the ratio of the volumes enclosed between them and the Fermi surface (4').

Unlike the poles, the vanishing of $G_{\mathbf{i}}(\omega = 0, \mathbf{k})$ introduces no discontinuities whatever in the occupation. Figure 5 shows a generalization of Fig. 4b, with the circles representing the two types of Fermi surfaces and the wavy lines corresponding to the vanishing of $G_{\mathbf{i}}(\omega = 0, \mathbf{k})$. The introduction of the assumption in the general case enables us to formulate the picture of the metallic state for a monovalent metal with one atom per cell and with a number of electrons equal to the number of holes.

3. ROLE OF THE ELECTRON-ELECTRON AND ELECTRON-PHONON INTERACTIONS¹⁾

For simplicity we choose an electronic model in which the interactions are of the "contact" type, i.e., the interaction parameters are assumed to be independent of the magnitude and direction of the quasimomentum. It is shown in the Appendix that the conclusions of the present section remain in force in the general anisotropic case. We introduce the following vertices $V_{\mathbf{i}\mathbf{j}\mathbf{l}\mathbf{m}}(\mathbf{p}_1, \mathbf{p}_2; \mathbf{p}_3, \mathbf{p}_4)$ for the scattering of two electrons from the states (\mathbf{p}_1) , (\mathbf{p}_2) into the states (\mathbf{p}_3) , (\mathbf{p}_4) . Here $\mathbf{i}, \mathbf{j}, \mathbf{l}, \mathbf{m} = 1, 2$ are the Fermi-surface indices, $\Sigma \mathbf{p}_{\alpha} = \mathbf{K}$,

$$V_{1212} = \lambda_1, V_{1221} = \lambda_2. \quad (5)$$

Analogously, in the scattering of an electron from the state (\mathbf{p}_i) into the state $(\mathbf{p} - \mathbf{k}_j)$, owing to interaction with a phonon from among all the vertices $\gamma_{\mathbf{i}\mathbf{j}}(\mathbf{p}, \mathbf{p} - \mathbf{k})$, we are left only with²⁾

$$(5')$$

It is assumed that the electrons interact with one of the branches of the phonon spectrum.

¹⁾This question was considered already in Kopaev's article^[11], where instabilities due to the interactions with phonons and only those due to the dielectric pairing were considered separately. We present later on formulas in which the competition of all the possible mechanisms is taken into account.

²⁾ λ and g in (5) and (5') are generally speaking dimensional quantities. The final equations contain dimensionless combinations of these quantities with the parameters of the electron spectrum. We do not discuss this question.

We have shown earlier that, as a consequence of (1), the electron and hole Fermi surfaces are located in the undeformed lattice either one under the other (Fig. 4a), or else are shifted by the vector q_0 , which equals half the period in the reciprocal cell (Fig. 4b). Therefore the integrals for the vertex parts, Γ_{ijlm} , which contain the cross sections

$$\int G_1(p)G_2(p-q)d^4p,$$

acquire logarithmic singularities either at $q = q_0$ or at $q = 0$, leading in final analysis to instability of the lattice with respect to a shift of the sublattices, or to elastic deformation of the unit cell, respectively. The latter case will sometimes be referred to as "acoustic" deformation. It is clear from general considerations that, for example in the first case, the shift of the sublattices also causes a certain acoustic deformation, at least on account of the anharmonicities. It is very important in what follows, however, that since the instability is determined by the logarithmic singularities of the vertex parts^[1,2], the type of the instability is determined by the initial arrangement of the Fermi surfaces.

Let us consider the case $q = q_0$. In connection with the analysis of the paper by Kozlov and Maksimov^[2] we wish to add here the remark^[11,12] (see also^[13]) that logarithmic singularities occur not only in the vertex parts corresponding to the scattering of electrons on account of the vertices (5), but also in the polarization operator $\Pi(k)$ for the phonon Green's function $D(k)$:

$$D^{-1}(k) = D_0^{-1}(k) - \Pi(k), \quad (6)$$

where $\Pi(k)$ at $k = q_0$ contains, in particular, logarithmic integrals of the type

$$g_{12} \int G_1(p)G_2(p-q_0)d^4p. \quad (7)$$

We assume subsequently that all the constants are small: $g, \lambda \ll 1$. Following the usual ideas of phase transitions, we investigate the onset of singularities in the thermodynamic quantities. In the logarithmic situation, the properties of the ground state at $T = 0$, as is well known (see^[10]), are determined completely by the introduction of the so-called "anomalous" Green's functions. Of course, for example in the case of bismuth, the singularities of the electron spectrum have an energy scale 10^{-2} eV, i.e., they correspond to the melting temperatures.

We introduce the thermodynamic Green's functions of the electrons and phonons:

$$G_\alpha(p, \epsilon_n) = \frac{1}{i\epsilon_n + (-1)^\alpha |v_\alpha| t}, \quad D(k, \omega_n) = -\frac{\omega^2(k)}{\omega_n^2 + \omega^2(k)}, \quad (8)$$

where $\epsilon_n = (2n + 1)\pi T$, $|v_\alpha| = |\nabla_p \epsilon_\alpha(p)|$, and t is the distance in momentum space along normals to the Fermi surface. Analogously, $\omega_M = 2n\pi T$, and $\omega(k)$ is the unrenormalized dispersion law of the phonon branch with which the electrons interact. In this notation, the function D corresponds to the average of the arbitrary Fourier components of the displacement vectors in the acoustic wave.

Let us study the singularities of the vertex parts for scattering of electrons by electrons. The diagrams containing on the left and on the right one entering end (electron) and one outgoing one (hole) are subdivided

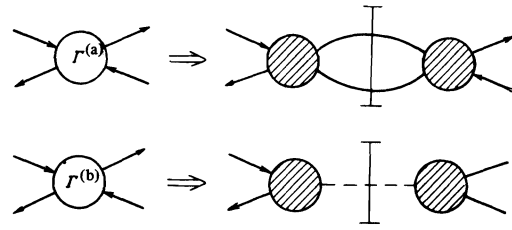


FIG. 6

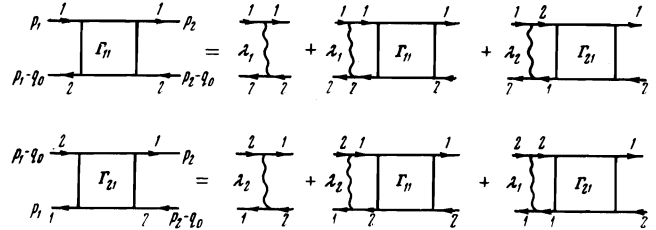


FIG. 7

topologically into two classes, namely $\Gamma^{(a)}$, where a vertical line can cross only two G-functions, and $\Gamma^{(b)}$ where the vertical sections contain also D functions (Fig. 6). The sum of diagrams of the ladder type, leading to logarithmic terms

$$\sum_n \int \frac{d^4p}{(2\pi)^4} G_1(\epsilon_n, p)G_2(\epsilon_n, p - q_0) \propto \ln \frac{c\epsilon_F}{T} = N(\epsilon_F)L, \quad (9)$$

is shown in Fig. 7 in the form of an integral equation for the two quantities Γ_{11} and Γ_{21} (and, symmetrically, Γ_{22} and Γ_{12}). Allowance for the transverse phonon lines and the contribution from corrections of the non-ladder type changes the definition of the constant c which appears when the logarithmic integrals (9) are cut off at energies $\sim \epsilon_F$. Hence (leaving out the spin indices), we obtain

$$\Gamma_{11} = \frac{\lambda_1(1 - \lambda_1 L) + \lambda_2^2 L}{[1 - (\lambda_1 + \lambda_2)L][1 - (\lambda_1 - \lambda_2)L]}, \quad (10)$$

$$\Gamma_{21} = \frac{\lambda_2}{[1 - (\lambda_1 + \lambda_2)L][1 - (\lambda_1 - \lambda_2)L]}$$

The density of states on the Fermi surface $N(\epsilon_F)$ is contained in the definition of the dimensionless constant (5). The singularity in Γ_{11} and Γ_{21} with respect to temperature is determined by the larger positive quantity $\lambda_1 + \lambda_2$ or $\lambda_1 - \lambda_2$ and may be missing if the relations between the interaction constants are not of the right type.

Let us turn to diagrams of the type $\Gamma^{(b)}$. The expression for the block of the diagram $\Gamma^{(b)}$ is shown in Fig. 8a. The polarization operator $\Pi(q_0)$ and the equation for the "screened" interaction are shown in Fig. 8b. Finally, the triangular vertex T_{12} ($= T_{21}$) satisfies the equation of Fig. 8c. Leaving out the cumbersome albeit elementary calculations, we present the final result for the "renormalized" phonon spectrum $\tilde{\omega}^2(q)$ at the point q_0 :

$$\tilde{\omega}^2(q_0) = \omega^2(q_0) \frac{1 - (\lambda_1 - 3\lambda_2 + 3g_{12}^2)L}{1 - (\lambda_1 - 3\lambda_2 - g_{12}^2)L}. \quad (11)$$

Let us discuss the results. The constants in (10) and (11) and their signs are generally speaking arbitrary. The definition is such that $\lambda_1 > 0$ corresponds

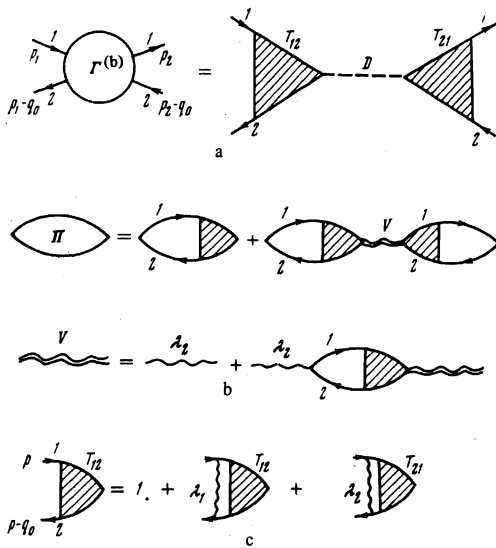


FIG. 8

to electron-hole attraction. Therefore (with all the stipulations with respect to the role of the Fermi-liquid effects), we assume nevertheless $\lambda_1 > 0$ for the electron-hole interaction. Let the singularity in (10) correspond to $\lambda_1 + \lambda_2$, i.e., $\lambda_2 > 0$. In (11), ω^2 can become negative later than the appearance of a pole in Γ if $\lambda_2 > g_{12}^2$, and earlier (i.e., at higher temperatures) if the inverse is true. In the latter case, an instability of the phonon spectrum with the corresponding deformation (displacement of the sublattices) sets in prior to the dielectric pairing. In the opposite case ($\lambda_2 < 0$) it follows directly from (11) that in this case the phonon spectrum is unstable at any ratio of g_{12} to λ_2 , and the Keldysh-Kopaev effect does not have time to develop.

The method of determining the equilibrium values of the resultant deformation is well known, for example, from the theory of ferroelectric transitions of the displacement type^[14]. In essence, the matter reduces to a minimization of the sum of the energies of the elastic deformations (the lattice term) and of the electron thermodynamic potential calculated as a function of the positions of the ion nuclei. We have already mentioned that allowance for the anisotropy, together with high transition temperatures comparable with the melting point, makes the question somewhat methodological. We note here only the following qualitative consideration. After the restructuring (doubling of the period in this case), three branches of optical vibrations appear in the new cell. In this case, two frequencies retain the same order of magnitude as before, whereas the frequency of the branch interacting with the electron-hole pairs turns out to be lower, owing to the cancellation of the logarithmic terms in (11) with unity. The smallness of this gap, $\tilde{\omega}^2 \sim g_{12}^2 \omega^2(q_0)$, is determined of course by the actual weakness of the interactions g_{12}^2 and λ_2 . On the other hand, if the instability is due to the effect of^[1,2] (the case $\lambda_2 > g_{12}^2$), then there is no cancellation in (11) and $\tilde{\omega}^2 \sim \omega^2(q_0)$. On the basis of the foregoing it seems, in general, that the effect of the dielectric pairing is less probable than the lattice instability.

The case $q = 0$ (the Fermi surfaces coincide) leads

to analogous instabilities in the acoustic region, i.e., to incorrect signs of the elastic constants.

In concluding this section, we point out one curious physical possibility that is admitted by the model under consideration. The initial state referred to in the first section and in which the presence of the investigated nontrivial electron spectrum was assumed (by virtue of its symmetry), makes the electron energy extremal, but is not necessarily stable. It is therefore reasonable to consider also the case when the non-renormalized phonon spectrum is unstable, i.e., $\omega^2(q) < 0$. We then see from (11) that the inverse situation is possible, namely stability of the metallic state at low temperatures and a transition into a dielectric at higher ones.

4. ELECTRON SPECTRUM AT LOW TEMPERATURES. BISMUTH

Returning to bismuth, we recall in greater detail the assumptions made by Abrikosov and Fal'kovskii^[4] concerning the spectrum of the initial primitive-cubic lattice. Since, according to experiment, the Fermi surfaces of the electrons and holes in bismuth lie at the points L and T of the Brillouin zone, respectively, four pairs of points, located at the quarter-points of the body diagonals of the cube, were considered in the reciprocal cell of the primitive cubic lattice. Indeed, following the rhombohedral deformation and the doubling of the period, one pair in the reduced band forms the points T, and the three others form the points L. In the primitive-cubic lattice the symmetry of the points on the three-dimensional diagonal (C_{3v}) admits of a two-dimensional representation (we have in mind throughout single-valued representations, unless otherwise stipulated). Abrikosov and Fal'kovskii have proposed^[4] that it is precisely this double degeneracy of the electron spectrum which is realized at the point k_1 , and furthermore exactly on the Fermi surface. The two branches of the spectrum $\epsilon(\kappa)$ in the vicinity of small $\kappa = k - k_1$ are given by

$$\epsilon_{1,2} = a\kappa_x + b|\kappa_\perp| \quad (12)$$

with conical Fermi surfaces about the threefold axis. Figure 9 shows these surfaces in the intersection of the cube with a plane passing through one of the body

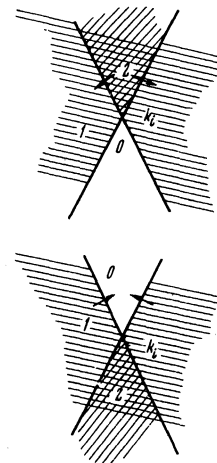


FIG. 9

diagonals, and show the "occupation numbers" for the spectrum (12). The encountered difficulties were already discussed in Sec. 2. Abrikosov and Fal'kovskii's principal assumption^[4] is that the sections of the energy surface labeled by the index 2 are congruent, i.e., the Fermi surface coincides with itself when displaced by the vector $q_1 = 2k_1$. Their arguments reduced to the fact that in the opposite case open Fermi surfaces would be left following a small deformation. The rhombohedral deformation unifies the points $(k_1, -k_1)$, imparting a symmetry D_{3d} (holes in bismuth) to one pair of points, and a symmetry C_{2h} (electrons) to the other three pairs.

The secular equation in^[4] was obtained in the usual manner on the basis of the symmetry relations for the matrix elements, with allowance for the spin-orbit splitting. For a better understanding of the situation, the latter can be omitted. We note, first, that a certain error was incurred in^[4], namely, the series of the elements of the matrix D_{SS} ^[4] contained the sublattice displacement vector u for functions belonging to the representation of one of the k_1 , whereas the representation of the space group for u corresponds to the vector q_0 (doubling of the period). Therefore β in D_{SS} is equal to zero, and f' depends only on the acoustic deformation:

$$w = \frac{1}{3}(u_{x1} + u_{y1} + u_{z1}).$$

The band overlap occurs if $f \neq 0$. Yet we have seen in Sec. 3 that if the overlap of the Fermi surfaces occurs following a displacement by a certain vector q_0 , then the acoustic deformation occurs only as a secondary effect after the anharmonic terms are taken into account. We shall discuss below the magnitude of the acoustic deformation, but getting ahead of ourselves we note that it turns out to be of lower order than the sublattice displacement.

Let us see how the equations for the electron spectrum are obtained in general in dielectric pairing. Following Kozlov and Maksimov^[2], we write down the equations for the Green's functions of the two bands, $G_{11}(p, p)$ and $G_{22}(p + q_0, p + q_0)$, introducing the non-diagonal function $G_{12}(p, p + q_0)$:

$$\begin{aligned} G_{11}(p, p) &= G_{11}^0(p) [1 + \Sigma_{12}(p, p + q_0) G_{21}(p + q_0, p)], \\ G_{21}(p + q_0, p) &= G_{22}(p + q_0) \Sigma_{21}(p + q_0, p) G_{11}(p, p), \end{aligned} \quad (13)$$

where $\Sigma_{12}(p + q_0, p) = \sigma(T) \chi_{q_0}(p)$, and a function $\chi_{q_0}(p)$ is determined in the logarithmic approximation by the same integral equation

$$\chi_{q_0}(p) = \lambda_1 \ln \frac{c\varepsilon_F}{T} \int K(p, p') \chi_{q_0}(p') \frac{d\sigma'}{|v_{F'}|}, \quad (14)$$

from which the critical temperature is determined^[3,15].

If the spectrum is given by $\epsilon_\alpha = \pm |v|t$, where t is the normal to the Fermi surface, then we obtain from (13) the spectrum of the dielectric:

$$\epsilon(p) = \pm (v^2 t^2 + \sigma^2(T) |\chi_{q_0}(p)|^2)^{1/2}. \quad (15)$$

To obtain actually the spectrum with allowance for the symmetry and periodicity properties of the real crystal, it is necessary, in the case of degeneracy, to formulate (13) and (14) in a more invariant manner. Indeed, for example, if we seek the electron spectrum in the vicinity of the points k_1 (Fig. 9) then, by virtue of the

interaction (5) and the double degeneracy of the levels, it becomes necessary to take into account at each point the off-diagonal proper parts $\Sigma_{11}(p, p + q_0)$ and $\Sigma_{22}(p, p + q_0)$ and the nondiagonal Green's functions³⁾ $G_{\alpha\alpha}(p, p + q_0)$ and $G_{12}(p, p)$. As a result we would obtain in place of the system of two equations (13) a system of four equations corresponding to allowance for fourfold degeneracy of the unified representations of the point $(k_1, -k_1)$.

The determinant of this system governs, as usual, the electron-level behavior of interest to us near these points. Naturally, the symmetry conditions simplify the problem, so that $\Sigma(p, p + q_0)$ and $\Sigma(p + q_0, p)$ should be contained in (13) in the form of matrices unifying the representations of the points k_1 and $-k_1$. To find the possible matrix elements, we formulate the symmetry properties of the operators $\hat{\Sigma}(p, p + q_0)$. First, at the temperature T_c there occurs in the crystal a transition in which the long-range order and the lattice symmetry are altered. We shall bear in mind, for concreteness, the case $q_0 \neq 0$. The resultant state is such that the Green's function $G(r, r'; t - t') = -i \langle T(\tilde{\psi}(x)\tilde{\psi}^*(x')) \rangle$ is transformed in accordance with one of the nontrivial representations upon transformation of the complete space group. In the case $q_0 = 0$, all the possibilities are exhausted by listing the nontrivial irreducible representations of the point group O_h . At $q \neq 0$, the representations are determined by specifying the vector q_0 and the small group of the vector.

Thus, the nontrivial parts of $g(x, x')$ and $\Sigma(x, x')$ are expanded in accordance with the representations

$$G(x, x') = \sum_{n, q_{0j}} C_{n, q_{0j}} A_{n, q_{0j}}(x, x') \exp\left(iq_{0j} \frac{r + r'}{2}\right), \quad (16)$$

where $A_{n, q_{0j}}(x, x')$ realize the representations of the point group of the vector q_{0j} . Since the vectors q_{0j} form a star in a primitive cubic lattice, it follows that $C_{n, q_{0j}} A_{n, q_{0j}}(x, x')$ will realize point-group representations. The three-dimensional representation of the vector F_1 ^[16] was used in^[4]. We did not investigate other possibilities since, at any rate according to (15), there are no matrix elements responsible for the relative displacement of the levels at the points L and T of the Brillouin zone (in first approximation), inasmuch as the type of instability in Fig. 9 corresponds to $q_0 \neq 0$.

5. CONCLUSIONS

We discuss in conclusion the resultant situation with the bismuth spectrum. It is known that the acoustic deformation (rhombohedral compression of the cube) in bismuth is of the same order as the sublattice shift. In addition, the splitting of the acoustic and optic branches at the point T is also of the usual order of magnitude^[7]. Yet, if there is no interaction between the new optic and acoustic branches, then there is also no splitting. As to the anharmonic interactions, disregarding the magnitude of this interaction, we see that

³⁾ $\Sigma_{11}(p, p + q_0)$ is proportional to the constant λ_3 , which is equal to $V_{11,12}$ in the notation of (5).

it is possible to construct third-order terms of the type $S_{ij}u_i(q_0)u_j(-q_0)$, where S_{ij} is the elastic-deformation tensor and $u_i(q_0)$ is the amplitude of the sublattice displacement; the mean value $\langle S_{ij} \rangle$ is obviously proportional to $\langle u_i^2 \rangle$ and is therefore small.

It would be simplest to assume, in addition to the picture of^[4] (Fig. 9), the presence of one more pair of electron-hole surfaces lying one under the other. In this case, of course, the acoustic deformations are "coupled" with the optic ones in a unified scheme. We consider, however, this picture to be unnatural, at least from the point of view of the genesis of the intersecting bands, which was discussed in Sec. 2.

On the other hand, if we introduce a deformation potential describing the interaction of the electrons with acoustic phonons $S_{\alpha\beta}g_{\alpha\beta}(p)$, then the mean value $\langle S_{\alpha\beta} \rangle$ takes the form

$$\langle S_{\alpha\beta} \rangle = L_{\alpha\beta\gamma\delta} T \sum_n \int \text{Sp} D(\omega_n = 0, k) \hat{g}(p) G(\epsilon_n, p) \frac{d^3 p}{(2\pi)^3}, \quad k \rightarrow 0,$$

where $L_{\alpha\beta\gamma\delta}$ is a certain tensor of the order of unity and g has matrix elements for the interaction of different acoustic branches with the electrons. Far from the spectrum degeneracy points, this expression can be written, disregarding the tensor indices, in the form

$$\langle S \rangle \propto \sum_i g_i T \sum_n G_i(\epsilon_n, p) d^3 p. \quad (17)$$

In the initial primitive-cubic lattice, expression (17) vanishes because of the aforementioned symmetry of the configuration, i.e., the energy has by assumption no terms that are linear in the ion displacements. The right-hand sides of (17) are equal to zero and, as can be readily shown^[3] by solving the system (13), also in the dielectric phase. Actually the right-hand side of (16) or (17) is of the order of the electron-phonon interaction constant multiplied by the number of electrons or holes in the bands. From this we see again that by assuming the presence of acoustic deformation (i.e., the already mentioned $f \neq 0$ in the paper of Abrikosov and Fal'kovskii^[4]) it is impossible to obtain self-consistency in (17), since in accordance with their model^[4] the volumes of the electrons and holes are proportional to the cube of the deformation. We see therefore that in order for the lattice distortion to be different from zero it is necessary to assume, in accordance with (17), that the Fermi surfaces do not coincide in the initial state, and the resultant volumes between the surfaces are of the order of the optical deformation. The authors are unable as yet to propose a clear picture that explains the nature of such a phenomenon.

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APPENDIX

In an anisotropic region, both the complete and the bare vertex parts of the electron-electron interactions depend on the initial and final momenta. Assuming, as before, a contact interaction, we have

$$\lambda_{11}(p_1, p_2) = \lambda_1 \int \psi_{1p_1}^*(r) \psi_{1p_2}(r) \psi_{2p_1-q_0}(r) \psi_{2p_2-q_0}(r) d^3 r = \lambda_1 K_{11}(p_1, p_2),$$

$$\lambda_{12}(p_1, p_2) = \lambda_2 \int \psi_{1p_1}^*(r) \psi_{1p_2}(r) \psi_{2p_1-q_0}(r) \psi_{2p_2-q_0}(r) d^3 r = \lambda_2 K_{12}(p_1, p_2),$$

$$\lambda_{21}(p_1, p_2) = \lambda_2 \int \psi_{1p_1}^*(r) \psi_{1p_2}(r) \psi_{2p_1-q_0}(r) \psi_{2p_2-q_0}(r) d^3 r = \lambda_2 K_{21}(p_2, p_1),$$

$$\lambda_{22}(p_1, p_2) = \lambda_1 \int \psi_{1p_1}(r) \psi_{1p_2}^*(r) \psi_{2p_1-q_0}(r) \psi_{2p_2-q_0}(r) d^3 r = \lambda_1 K_{22}(p_1, p_2). \quad (A.1)$$

Representing $d^3 p$ in the form $d^3 p = d\xi d\sigma / |v_F|$, integrating in the equations of Fig. 7 with respect to ξ , and assuming that $K_{\alpha\beta}$ depends essentially only on the directions of p_1 and p_2 , we obtain the following system of equations for the determination of $\Gamma_{\alpha\beta}(p_1, p_2)$ (p_1 and p_2 on the Fermi surface):

$$\begin{aligned} \Gamma_{11}(p_1, p_2) &= \lambda_1 K_{11}(p_1, p_2) + \lambda_1 L \int K_{11}(p_1, p') \Gamma_{11}(p', p_2) \frac{d\sigma'}{|v_{F'}|} \\ &\quad + \lambda_2 L \int K_{12}(p_1, p') \Gamma_{21}(p', p_2) \frac{d\sigma'}{|v_{F'}|}; \\ \Gamma_{21}(p_1, p_2) &= \lambda_2 K_{21}(p_1, p_2) + \lambda_2 L \int K_{21}(p_1, p') \Gamma_{11}(p', p_2) \frac{d\sigma'}{|v_{F'}|} \\ &\quad + \lambda_2 L \int K_{22}(p_1, p') \Gamma_{21}(p', p_2) \frac{d\sigma'}{|v_{F'}|}; \end{aligned} \quad (A.2)$$

and a symmetrical system for the pairs Γ_{22} and Γ_{12} .

Let us consider the homogeneous system

$$\xi^\alpha(p) = \mu \int K_{\alpha\beta}(p, p') \xi^\beta(p') \frac{d\sigma'}{|v_{F'}|}, \quad \alpha, \beta = 1, 2. \quad (A.3)$$

It is proposed from now on that integration with respect to repeated indices be carried out from one to two. According to (A.1), $K_{\alpha\beta}(p_1, p_2) = K_{\beta\alpha}^*(p_2, p_1)$, i.e., the kernel of the system (3) is Hermitian. As usual, we represent $K_{\alpha\beta}(p_1, p_2)$ in the form

$$K_{\alpha\beta}(p_1, p_2) = \sum_j \frac{\xi_j^\alpha(p_1) \xi_j^{\beta*}(p_2)}{\mu_j}, \quad (A.4)$$

where μ_j are real eigenvalues of the system (A.3), and $\xi_j^\alpha(p)$ are the corresponding two sets of orthonormalized functions:

$$(\xi_j^\alpha, \xi_k^\alpha) = \int \xi_j^\alpha(p) \xi_k^{\alpha*}(p) \frac{d\sigma}{|v_F|} = \delta_{jk}.$$

Since, in addition, $K_{11}(p_1, p_2) = K_{22}(p_2, p_1)$, it follows that $\xi_j^1 = \xi_j^{2*} = \xi_j(p)$, and there exists in fact only one set of eigenfunctions normalized to $1/2$.

Substituting (A.4) in (A.2) and putting

$$\begin{aligned} \int \xi_j^*(p') \Gamma_{11}(p', p) \frac{d\sigma'}{|v_{F'}|} &= a_j^{11}(p), \\ \int \xi_j^*(p') \Gamma_{21}(p', p) \frac{d\sigma'}{|v_{F'}|} &= a_j^{21}(p), \end{aligned}$$

we obtain, after multiplying the first equation in (A.4) by $\xi_j^*(p)$, the second by $\xi_j(p)$, and integrating, a simple system with respect to a_j^{11} and a_j^{21} . Using its solutions, we obtain

$$\begin{aligned} \Gamma_{11}(p_1, p_2) &= 2 \sum_j \xi_j(p_1) \xi_j^*(p_2) \left[\frac{\lambda_1}{2\mu_j} \left(1 - \frac{\lambda_1}{2\mu_j} \right) \right. \\ &\quad \left. + \left(\frac{\lambda_2}{2\mu_j} \right)^2 L \right] / \left[\left(1 - \frac{\lambda_1}{2\mu_j} L \right)^2 - \left(\frac{\lambda_2}{2\mu_j} L \right)^2 \right], \\ \Gamma_{21}(p_1, p_2) &= 2 \sum_j \xi_j^*(p_1) \xi_j^*(p_2) \frac{\lambda_2}{2\mu_j} / \left[\left(1 - \frac{\lambda_1}{2\mu_j} L \right)^2 - \left(\frac{\lambda_2}{2\mu_j} L \right)^2 \right], \\ \Gamma_{12}(p_1, p_2) &= \Gamma_{21}^*(p_2, p_1), \quad \Gamma_{22}(p_1, p_2) = \Gamma_{11}(p_2, p_1). \end{aligned} \quad (A.5)$$

We are interested only in that pole of Γ which is obtained at the smallest value of $L \sim \ln(\epsilon_F/P)$, i.e., corresponding to the eigenvalue with the smallest modulus. Thus, there are two possibilities, depending

on the sign of λ_2 . The equations for $\Pi(\mathbf{q})$ are written in terms of $\Gamma_{\alpha\beta}$ and the vertices of $V_{\alpha\beta}$ satisfying the equation of Fig. 8b:

$$V_{\alpha\beta}(\mathbf{p}_1, \mathbf{p}_2) = \lambda_2 K_{\alpha\beta}(\mathbf{p}_1, \mathbf{p}_2) + \lambda_2 L \int K_{\alpha\gamma}(\mathbf{p}_1, \mathbf{p}') V_{\gamma\beta}(\mathbf{p}', \mathbf{p}_2) \frac{d\sigma'}{|\mathbf{v}_{\mathbf{p}'}|} + \lambda_2 L^2 \int K_{\alpha\gamma}(\mathbf{p}_1, \mathbf{p}') \Gamma_{\gamma\delta}(\mathbf{p}', \mathbf{p}'') V_{\delta\beta}(\mathbf{p}'', \mathbf{p}_2) \frac{d\sigma' d\sigma''}{|\mathbf{v}_{\mathbf{p}'}| |\mathbf{v}_{\mathbf{p}''}|}. \quad (\text{A.6})$$

Using the obtained expressions for $K_{\alpha\beta}$ and $\Gamma_{\alpha\beta}$ we get, after simple calculations similar to those used in the solution of (A.2),

$$V_{11}(\mathbf{p}_1, \mathbf{p}_2) = \lambda_2 \sum_j \xi_j(\mathbf{p}_1) \xi_j^*(\mathbf{p}_2) / \mu_j \left(1 + \frac{4\lambda_2 L}{2\mu_j - (\lambda_1 + \lambda_2)L} \right),$$

$$V_{21}(\mathbf{p}_1, \mathbf{p}_2) = \lambda_2 \sum_j \xi_j(\mathbf{p}_1) \xi_j^*(\mathbf{p}_2) / \mu_j \left(1 + \frac{4\lambda_2 L}{2\mu_j - (\lambda_1 + \lambda_2)L} \right), \quad (\text{A.7})$$

$$V_{21}(\mathbf{p}_1, \mathbf{p}_2) = V_{12}^*(\mathbf{p}_2, \mathbf{p}_1), \quad V_{22}(\mathbf{p}_1, \mathbf{p}_2) = V_{11}(\mathbf{p}_2, \mathbf{p}_1).$$

Using (A.7) and (A.6) we obtain after some transformations the final result:

$$\Pi(\mathbf{q}_0, \omega_n = 0) = -4L(g, g) - 2L^2 \sum_j ((g\xi_j) + (\xi_j g))^2 \frac{\lambda_1 - 3\lambda_2}{2\mu_j - (\lambda_1 - 3\lambda_2)L} + 2L^2 \sum_j ((g\xi_j) - (\xi_j g))^2 \frac{\lambda_1 - \lambda_2}{2\mu_j - (\lambda_1 - \lambda_2)L}. \quad (\text{A.8})$$

Here $g \equiv g_{12}(\mathbf{p})$ is the matrix element of the electron-phonon interaction.

It is easy to see the following facts. If $\lambda_2 < 0$ and the transition in the electron spectrum occurs with $\lambda_1 - \lambda_2$, as in the isotropic case, then the phonon instability sets in first, and if $\lambda_2 > 0$ and the constant $\lambda_1 + \lambda_2$ is responsible for the electronic transition, then it is possible that at sufficiently small g the electronic transition assumes the primary role in this case, since $\Pi(\mathbf{q}_0)$ has no pole term corresponding to the constant $\lambda_1 + \lambda_2$. We note also that if there are negative values among the μ_j , then the system will not be stable at any ratio of the constants.

¹L. V. Keldysh and Yu. V. Kopaev, *Fiz. Tverd. Tela* **6**, 2791 (1964) [*Sov. Phys.-Solid State* **6**, 2219 (1965)].

²A. N. Kozlov and L. P. Maksimov, *Zh. Eksp. Teor. Fiz.* **48**, 1184 (1965) [*Sov. Phys.-JETP* **21**, 790 (1965)].

³L. P. Gor'kov and T. Mnatsakanov, *ibid.* **63**, 684 (1972) [**36**, 361 (1973)].

⁴A. A. Abrikosov and L. A. Fal'kovskii, *ibid.* **43**, 1089 (1962) [**16**, 769 (1963)].

⁵G. E. Pikus, *ibid.* **41**, 1258 (1961) [**14**, 898 (1962)].

⁶A. A. Abrikosov, *ibid.* **43**, 1083 (1962) [**16**, 765 (1963)].

⁷L. A. Fal'kovskii, *Usp. Fiz. Nauk* **94**, 3 (1968) [*Sov. Phys.-USP.* **11**, 1 (1968)].

⁸B. I. Halperin and T. M. Rice, *Solid St. Phys.*, **21**, 116 (1968).

⁹S. M. Luttinger, *Phys. Rev.*, **119**, 1153 (1960).

¹⁰A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, *Metody kvantovoi teorii polya v statisticheskoi fizike* (Quantum Field Theoretical Methods in Statistical Physics), Fizmatgiz, 1962, [Pergamon, 1965].

¹¹Yu. V. Kopaev, *Fiz. Tverd. Tela* **8**, 2730 (1966) [*Sov. Phys.-Solid State* **8**, 2177 (1967)].

¹²Yu. A. Bychkov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, *Zh. Eksp. Teor. Fiz.* **50**, 738 (1966) [*Sov. Phys.-JETP* **23**, 489 (1966)].

¹³Yu. V. Kopaev and R. Kh. Timerov, *ibid.* **63**, 290 (1972) [**36**, 153 (1973)].

¹⁴V. G. Vaks, *ibid.* **54**, 910 (1968) [**27**, 486 (1968)].

¹⁵L. V. Pokrovskii, *ibid.* **40**, 641 (1961) [**13**, 447 (1962)].

¹⁶L. D. Landau and E. M. Lifshitz, *Kvantovaya mekhanika* (Quantum Mechanics), Fizmatgiz, 1963 [Addison-Wesley, 1965].

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212