THE ELECTRON MECHANISM OF SUPERCONDUCTIVITY

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INTEREST in superconductivity has noticeably increased recently because of the appearance of new possibilities for practical application of superconductors. These possibilities have come into play after the discovery of superconducting alloys with large critical magnetic fields, reaching $(1-3) \times 10^5$ Oe.[1] However, superconductivity has been attained so far only at very low temperatures, and this is the main obstacle to extensive use of superconductors in engineering. As is known, the maximum critical temperatures for the presently known superconductors approach only 20°K. This raises the question of the possibility of obtaining superconductors with much higher critical temperatures, on the order of room temperature.

According to the microscopic theory of superconductivity, which, as is well known, is based on the notion that the attraction forces between electrons, which give rise to the superconductivity, are the result of phonon exchange, the expression for the critical temperature is[2,3]

$$T_c = 1.14 \theta_D e^{-1/g}.$$

Here θ_D is the Debye temperature and g is the effective constant of the electron-phonon interaction between the electrons multiplied by the density of states on the Fermi surface. The condition for stability of the lattice leads to the inequality[4-6]

$$g < \frac{1}{2},$$

that is, T_c is approximately one order of magnitude lower than the Debye temperature. Thus, the possibility of increasing the critical temperature is limited primarily by the Debye temperature. If the attraction between the electrons is connected with spin-wave rather than phonon exchange, then a similar role is played not by the Debye temperature, but by the effective energy of the spin waves (magnons), which usually turns out to be of the same order or somewhat higher than the Debye temperature[7,8].

Little[9,10] has recently proposed for the interaction between electrons of molecular chains in polymers a new mechanism, which can lead to critical temperatures much higher than in the case of the phonon or magnon mechanism. In [9] he considers a special model of a polymer, consisting of a central molecular chain to which side chains are connected on both sides. It is assumed that the Ψ functions of the electrons in molecular chains have the form of modulated plane waves. It is easy to see that the Coulomb repulsion between the electrons of the central and side chains, in second-order perturbation-theory approximation, leads to attraction between electrons of the central chain (since the correction to the energy in the second approximation for the ground state is always negative). If these attraction forces exceed the Coulomb repulsion forces, then the electrons of the central chain can turn out to be superconducting. The matrix element of the attraction forces obviously differs from zero for energies of the two interacting electrons (reckoned from the Fermi surface)—of the order of the average energy of transition for the electrons of the side chains (the energy denominator in the expression for the correction to the energy in the second approximation). It is just this quantity—the scale of interaction in the energy space ΔE_e —which now enters in the expression for the critical temperature T_c in lieu of θ_D. The ratio of θ_D to the electron energy ΔE_e is obviously of the order of $(m/m_i)^{1/2}$ (m and m_i are the masses of the electron and ion, respectively). Therefore T_c will be larger for such a superconducting polymer than for superconductors in the case of the phonon interaction mechanism. According to Little's estimate for the polymer model considered by him, the critical temperature is of the order of 2×10^3 °K.

However, the possible existence of superconductivity in one-dimensional systems, such as molecular chains in polymers, meets with serious objections, as shown by Ferrell[11]. According to [11] the superconducting state of infinite one-dimensional systems is unstable against fluctuations. Ferrell's reasoning is physically very lucid but not fully rigorous. Therefore Ferrell's objection to the superconducting polymer model proposed by Little is argued against in a paper by Gor'kov, Dzyaloshinskiĭ, and Bychkov[12], where the calculations for the interaction of the superconducting polymer are carried out not by perturbation theory, as in [9], but exactly, on the basis of summation of all the diagrams which are significant in this case. The final answer to the question of the feasibility of superconductivity in one-dimensional systems will apparently require more detailed research. It should be noted that even if superconductivity of infinite molecular chains is possible, the macroscopic magnetic and electric properties of a real polymer, consisting of individual relatively short molecular chains, will differ

essentially from the properties of ordinary superconducting metals (absence of resistance in a constant electric field, etc.).

It can be shown, however, that a pure electronic mechanism, similar to the Little mechanism for polymers and leading to the same high critical temperatures, can exist in principle in the case of ordinary three-dimensional metals[13]. This eliminates all the difficulties indicated above. In [13] there was considered an electronic superconductivity mechanism connected with the presence of two groups of electrons, for two cases of three-dimensional systems: 1) a pure transition-group metal with two overlapping unfilled bands (s and d or s and f) or else an ordered alloy of a metal with a metal (compound) with comparable concentrations of the two components and an identical structure of the electronic spectrum; 2) an ordered alloy of a metal with a nonmetal, with comparable concentrations of the components, in the case when the electrons of the upper unfilled shell of the atom of the nonmetal are not "collectivized."

Of greatest interest is the first model. Just as in the case of the polymer considered by Little, the Coulomb repulsion between the electrons of the first and second bands leads in the second (and higher) approximation of perturbation theory to the appearance of attraction forces between each pair of electrons in the first band and each pair of electrons in the second band. It can be stated that these attraction forces result from the interaction between the electrons of the given band with the charge-density vibrations of the electrons of the other band.

The total effective interaction between the s-electrons and the d(f)-electrons, not limited to the second perturbation-theory approximation, can be obtained by summing the diagrams in the so-called high-density approximation. For a simple but close-to-reality model of weakly coupled s electrons and strongly coupled d(f)-electrons the calculations become much simpler, for in this case the attraction between the s-electrons exceeds the repulsion. In the general case, the investigation is more complicated but under certain conditions the attraction can exceed the repulsion for real metals, too. The critical temperature for the resultant superconducting state is of the order $10^2 - 10^3$ °K. In another model (alloy of a metal with a nonmetal) the attraction between the conduction electrons is the result of the Coulomb interaction with the electrons of the nonmetal. In this case conditions for the appearance of superconductivity turn out to be more stringent, and the critical temperature is lower.

We shall investigate here in greater detail the possibility of realizing superconductivity in these two models.

1. EFFECTIVE INTERACTION OF ELECTRONS IN THE MODEL OF TWO OVERLAPPING BANDS

We consider first the model of a metal with two overlapping bands. We assume that one of these bands, which we arbitrarily call the d-band (actually it can also be the f-band or some band with a different angular momentum) is noticeably narrower than the other (s-band) (Fig. 1). At first we disregard the phonon-exchange attraction forces between electrons, so that only Coulomb repulsion forces will act on each pair of electrons (two s-electrons, two d-electrons, and s- and d-electrons).

Let us obtain for this case the total interaction between the electrons in each band. To this end we consider first matrix elements of Coulomb interaction between s- and d-electrons. These matrix elements can be of different types. If two electrons interact and the first is in the s-band and has a quasimomentum p_1, and remains in the s-band after the interaction but acquires a quasimomentum p_3, while the second electron is in the d-band and has a quasimomentum p_2 before the interaction and remains in the d-band and acquires a quasimomentum p_4 after the interaction (Fig. 2), then the matrix element will be

$$V^{sd;\,sd}_{p_1 p_2;\,p_3 p_4} = \int \frac{e^2}{r_{12}} \Psi^s_{p_1}(r_1)\,\Psi^d_{p_2}(r_2)\,\Psi^{s*}_{p_3}(r_1)\,\Psi^{d*}_{p_4}(r_2)\,dr_1\,dr_2,$$

$$p_1 + p_2 = p_3 + p_4 + 2\pi l\,\mathbf{b} \qquad (1)$$

(we shall henceforth disregard umklapp processes, that is, we shall put $\mathbf{b} = 0$ (see the Appendix); $\mathbf{b}$ is the integer reciprocal-lattice vector). In the expression for the matrix element, the first two indices denote as usual the initial state of two interacting electrons, and the last two denote the final state. We shall henceforth write in lieu of $V^{sd;\,sd}_{p_1 p_2;\,p_3 p_4}$ simply $V_{sd;sd}$; Ψ^s_p and Ψ^d_p are single-particle functions of the s- and d-electrons, that is, the Bloch functions. In addition to $V_{sd;sd}$, there obviously exist the following matrix elements: $V_{ss;dd} = V^*_{dd;ss}$, $V_{sd;ds}$, $V_{sd;dd} = V^*_{dd;ds}$, and $V_{ds;ss} = V^*_{ss;sd}$. Let us estimate these matrix elements using the approximate expressions for the single-particle Ψ-functions. For the s-electrons we confine ourselves to a plane-wave approximation

$$\Psi^s_p = V^{-1/2}\,e^{i(k,r)},\ k = p/\hbar$$

(V is the volume of the crystal, which will henceforth be assumed equal to unity), and for the d-electrons we shall use the so-called strong-coupling approximation:

$$\Psi^d_p = N^{-1/2} \sum_n e^{i(k,R_n)}\Psi_0(r - R_n);$$

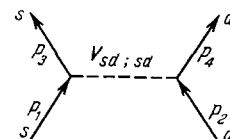$\Psi_0(r)$ is the function of the electron in the isolated atom, R_n the

FIG. 1

FIG. 2

integer radius vector of the lattice point, and N the number of particles. If we neglect the overlap of the Ψ_0-functions of the neighboring atoms in this case, then

$$V_{dd;\,dd}=e^2 \int \mid \Psi_0(r)\mid^2 \mid \Psi_0(r')\mid^2 \frac{dr\,dr'}{\mid r-r'\mid}+\frac{e^2}{n}\sum_{n\neq 0}\frac{1}{R_n}e^{i(k_3-k_1,\,R_n)};$$

n is the particle density. When $\mid k_3 - k_1 \mid d \ll 1$ (d is the lattice constant) the summation with respect to n can be replaced by integration; then

$$V_{dd;\,dd}\approx\frac{4\pi e^2}{\mid k_3-k_1\mid^2}\,,\qquad V_{ss;\,ss}=\frac{4\pi e^2}{\mid k_3-k_1\mid^2}\,. \tag{2}$$

Let us now find $V_{sd;sd}$ and $V_{dd;ss}$, likewise neglecting the overlap of the Ψ_0-functions of the neighboring atoms

$$V_{sd;\,sd}=\frac{4\pi e^2}{\mid k_3-k_1\mid^2}\int e^{i(k_3-k_1,\,r)}\mid\Psi_0(r)\mid^2 dr,$$

$$V_{dd;\,ss}=e^2\sum_n e^{i(k_3-k_1,\,R_n)}\int e^{-(ik_1,r)-(ik_2,r')}\Psi_0(r)\,\Psi_0(r')\frac{dr\,dr'}{\mid r-r'+R_n\mid}$$

$$\approx e^2\sum_n\frac{e^{i(k_3-k_1,\,R_n)}}{[\delta_{n,\,0}+R_n(1-\delta_{n,\,0})]}\int\frac{e^{(ik_1,r)-(ik_2,r')}}{[1-\delta_{n,\,0}+\delta_{n,\,0}\mid r-r'\mid]}$$

$$\times\Psi_0(r)\,\Psi_0(r')\,dr\,dr'. \tag{3}$$

$k_1 \sim k_0$ and $k_2 \sim k_0$ ($\hbar k_0$ is the momentum on the Fermi surface), so that the argument of the exponential in (3) is of the order $k_0 r_0$ (r_0 is the radius of the atom); $k_0 r_0 \ll 1$. In view of this, we can replace in the zeroth approximation the exponential by unity:

$$V_{dd;\,ss}\sim e^2\sum_{n\neq 0}\frac{1}{R_n}e^{i(k_3-k_1,\,R_n)}\int\Psi_0(r)\,dr\int\Psi_0(r')\,dr'.$$

Usually $\Psi_0(r)$ does not correspond to the s-state (in the case of d- and f-functions there can be only a small admixture of s-functions). Then

$$\int\Psi_0(r)\,dr=0 \text{ and } V_{dd;\,ss}=0.$$

On the other hand, if we take into account the difference between the exponential and unity, and expand this difference in powers of $(k_1\cdot r)+(k_2\cdot r')$, then we obtain for the internal electrons with angular momentum l ($l = 2$ for the d-electrons)

$$V_{dd;\,ss}\sim(k_0 r_0)^{2l}V_{dd;\,dd}.$$

Indeed, in the case of d-electrons $\Psi_0(r)$ contains the spherical function $Y_{lm}(\vartheta,\varphi)$; therefore, only the l-th order term yields a non-vanishing result in the series expansion of the exponential. We obtain in this manner

$$V_{dd;\,ds}\cong e^2 n^{-1/2}\sum_n e^{i(k_3-k_1,\,R_n)}R_n^{-1}$$

$$\times\int\Psi_0(r)\,\Psi_0^*(r')\,\Psi_0(r')\,e^{-i(k_1,r)}\,dr\,dr',$$

that is,

$$V_{dd;\,ds}\sim(k_0 r_0)^l V_{dd;\,dd},\; V_{ds;\,ss}\sim(k_0 r_0)^l V_{ss;\,ss},\; V_{sd;\,sd}\sim V_{dd;\,ss}. \tag{4}$$

From (2) and (3) we see that $V_{ss;ss}$, $V_{dd;dd}$, $V_{sd;sd}$ depend only on the momentum $k = k_3 - k_1$ transferred during the interaction.

Consequently, in the approximation under consideration, when $l \neq 0$ the only matrix element of the interaction of the s- and d-electrons to be retained is $V_{sd;sd}$. This gives rise in the second perturbation-theory approximation to an additional interaction for

each pair of s-electrons (owing to the interaction between the s-electrons and the d-electrons):

$$V'^{ss;\,ss}_{k_1k_2;\,k_3k_4}=\sum_{k,\,k'}V^{sd;\,sd}_{k_1k;\,k_3k'}V^{sd;\,sd}_{k'k_2;\,kk_1}n^d_{k'}(1-n^d_k)$$

$$\times[(\xi^s_{k_3}-\xi^s_{k_1}-\xi^d_k+\xi^d_{k'})^{-1}+(\xi^s_{k_1}-\xi^s_{k_3}-\xi^d_k+\xi^d_{k'})^{-1}] \tag{5}$$

(and an analogous interaction for the d-electrons).

Here n^d_k are the occupation numbers for the d-electrons ($n^d_k = a^{d+}_k a^d_k$), and ξ^s_k and ξ^d_k are the single-particle energies of the s- and d-electrons reckoned from the Fermi surface. Owing to the factor $n^d_{k'}(1-n^d_k)$ we set $\xi^d_k-\xi^d_{k'}>0$, and consequently $V'_{ss;ss}<0$ for small $\xi^s_{k_3}-\xi^s_{k_1}$, that is, $V'_{ss;ss}$ corresponds to attraction. No account is taken in the matrix elements $V_{sd;sd}$, $V_{ss;ss}$, and $V_{dd;dd}$ of the Debye screening, which plays a decisive role in systems of particles with Coulomb interaction whenever the particles can move through the entire volume. As is well known, the Debye screening causes the effective radius of the forces to become finite: in the case of electrons in metals it is of the order of $(r_B/n^{1/3})^{1/2}$ ($r_B = \hbar^2/me^2$ is the Bohr radius and n is the particle density). Therefore the screening can be taken approximately into account by substituting for $V_{ss;ss}$ the quantity

$$V^e_{ss;\,ss}=\frac{4\pi e^2}{\mid k_3-k_1\mid^2+\varkappa^2_{0D}},\qquad \varkappa_{0D}\sim(r_B/n^{1/3})^{-1/2}$$

and by introducing similar changes in $V_{sd;sd}$ and $V_{dd;dd}$. However, in a consistent approach, the screening effect and the effective interaction with the d-electrons must be taken into account simultaneously, since this screening is in part also determined by the interaction between the s- and d-electrons. Such a consistent calculation, which is furthermore accurate for the model in question and not limited to the second perturbation-theory approximation, can be carried out on the basis of the method of diagram summation (see the Appendix). We then obtain for the total matrix element of the resultant interaction (the so-called four-pole), for two s-electrons with initial quasimomenta p_1 and p_2 and final momenta p_3 and p_4, the expression (A.6)

$$\Gamma_{ss;\,ss}=[V_{ss;\,ss}+\Pi_{dd}(V^2_{sd;\,sd}-V_{ss;\,ss}V_{dd;\,dd})]/S, \left.\begin{array}{l}\\ \\ \\ \end{array}\right\}$$
$$S=1-V_{ss;\,ss}\Pi_{ss}-V_{dd;\,dd}\Pi_{dd}-\Pi_{ss}\Pi_{dd}(V^2_{sd;\,sd}-V_{ss;\,ss}V_{dd;\,dd}),$$
$$\Gamma_{dd;\,dd}=[V_{dd;\,dd}+\Pi_{ss}(V^2_{sd;\,sd}-V_{ss;\,ss}V_{dd;\,dd})]/S.$$
$$\tag{6}$$

The analogous expression for the four-pole $\Gamma_{sd;sd}$, which determines the effective interaction of the s- and d-electrons, is (see (A.6))

$$\Gamma_{sd;\,sd}=V_{sd;\,sd}/S; \tag{7}$$

here Π_{ss} and Π_{dd} are the so-called polarization operators (see (A.5) and (A.8)),

$$\Pi_{dd} = \frac{2}{(2\pi)^3} \int dq \, \frac{n_d(q) - n_d(q+k)}{\varepsilon - \xi^d(q+k) + \xi^d(q)} ; \qquad (8)$$

$k = k_3 - k_1$ and $\varepsilon = \xi_3 - \xi_1$ are the quasimomentum and the energy transferred during the interaction. It is easy to see that if $V_{ss;ss}\Pi_{ss} \ll 1$ and $V_{dd;dd}\Pi_{dd} \ll 1$ we obtain from (6) for $\Gamma_{ss;ss}$ an expression of the same type as the expression obtained in the second perturbation-theory approximation (see (5)):

$$\Gamma_{ss;\,ss} \simeq V_{ss;\,ss}(1 + V_{ss;\,ss}\Pi_{ss}) + \Pi_{dd}V_{sd;\,sd}^2.$$

From (6) and (8) we see that Π_{dd} depends little on ε (when $k \sim k_0$) if $\varepsilon \ll [\xi^d(q+k) - \xi^d(q)]_{av}$ and consequently also the second term in (6), tends to zero when $\varepsilon \gg [\xi^d(q+k) - \xi^d(q)]_{av}$. It is obvious that $[\xi^d(q+k) - \xi^d(q)]_{av} \sim \Delta E_d$, where ΔE_d is the distance from the Fermi surface to the top of the d-band.

Let us consider $\Gamma_{ss;ss}$ for small k. From (2) and (3) we see that when $k \to 0$ we have $V_{dd;dd} \to V_{ss;ss} = 4\pi e^2/k^2$ and $V_{sd;sd} \to V_{ss;ss}$. This is physically understandable, for at small values of k (i.e., at large wavelengths (kd $\ll$ 1)), the periodic potential of the lattice (i.e., the crystal structure) does not play any role, and consequently, $V_{sd;sd}$ and $V_{dd;dd}$ should have the same form as the matrix element $V_{ss;ss}$ for free electrons. From (2) we see that the ratio $V_{dd;dd}/4\pi e^2 k^{-2}$ which depends on k^2, begins to differ noticeably from unity when $kd \cong k/k_0 \sim 1$ and tends to zero when $k \gg k_0$, and from (3) we see that $V_{sd;sd}/4\pi e^2 k^{-2}$ begins to differ appreciably from unity when $kr_0 \sim 1$ and also tends to zero when $k_0 \gg r_0^{-1}$. Therefore near $k = 0$ (we disregard the anisotropy effect for non-cubic lattices):

$$V_{dd;\,dd} \simeq \frac{4\pi e^2}{k^2}(1 - \alpha_{dd}k^2/k_0^2 + \beta_{dd}k^4/k_0^4),$$

$$V_{sd;\,sd} \simeq \frac{4\pi e^2}{k^2}(1 - \alpha_{sd}k^2 r_0^2 + \beta_{sd}k^4 r_0^4), \qquad (9)$$

where $a_{dd} \sim 1$, $a_{sd} \sim 1$, $\beta_{dd} \sim 1$, $\beta_{sd} \sim 1$, $a_{dd} > 0$, and $a_{sd} > 0$. Let us determine the so-called static interaction between the s-electrons (neglecting retardation), i.e., the four-pole $\Gamma_{ss;ss}$ in the limit $\varepsilon/k \to 0$; $k \to 0$, $\Gamma^k_{ss;ss}$; we retain in the denominator only the term of first order in k^2. It will be shown below that $\Gamma^k_{ss;ss}$ plays the decisive role in the occurrence of pairing. We denote $\lim_{\varepsilon/k \to 0} \Pi$ by $(-\Pi^k)$; as will be shown below, $\Pi^k > 0$. Then we get from (6) and (9)

$$\Gamma^k_{ss;\,ss} = \frac{4\pi e^2}{\varepsilon_D}[1 - \Pi^k_{dd}4\pi e^2 k_0^{-2}(\alpha_{dd} - 2\alpha_{sd}k_0^2 r_0^2)]/(k^2 + \varkappa_D^2), \qquad (10)$$

where

$$\varepsilon_D = 1 - \Pi^k_{dd}4\pi e^2 k_0^{-2}[\alpha_{dd} + \Pi^k_{ss}4\pi e^2 k_0^{-2}(\beta_{dd} + \alpha_{sd}^2 k_0^4 r_0^4 + 2\beta_{sd}k_0^4 r_0^4)],$$

$$\varkappa_D^2 = \frac{4\pi e^2}{\varepsilon_D}[\Pi^k_{ss} + \Pi^k_{dd} - \Pi^k_{ss}\Pi^k_{dd}4\pi e^2 k_0^{-2}(\alpha_{dd} - 2\alpha_{sd}k_0^2 r_0^2)] > 0,$$

$$\Gamma^k_{sd;\,sd} = \frac{4\pi e^2}{\varepsilon_D} \Big/ (k^2 + \varkappa_D^2).$$

Since $k_0 r_0 \ll 1$, we can neglect the terms with $(k_0 r_0)^2$ and $(k_0 r_0)^4$. If $\xi \equiv (p^2 - p_0^2)/2m_{eff}$, i.e., in the so-called effective-mass approximation, we can use for the polarization operator an expression analogous to that for the free electrons (see (A.9)):

$$\Pi_{dd} = -\frac{p_{0d}m_d}{\pi^2 h^3}\left[1 - \frac{\varepsilon m_d}{2hkp_{0d}}\ln\left|\frac{\varepsilon + hkp_{0d}/m_d}{\varepsilon - hkp_{0d}/m_d}\right|\right.$$

$$\left. + \frac{i\pi|\varepsilon|m_d}{2hkp_{0d}}\theta\left(\frac{hkp_{0d}}{m_d} - |\varepsilon|\right)\right],$$

$$\theta(x) = \begin{cases} 1, & x > 0, \\ 0, & x < 0 \end{cases} \qquad (11)$$

(m_d is the effective mass of the d-electrons, $m_s \cong m$), then

$$\Pi^k_{dd} = \frac{k_0 m_d}{(\pi h)^2}, \qquad k_0 \equiv k_{0d}. \qquad (12)$$

Here

$$\Gamma^k_{ss;\,ss} \cong \frac{4\pi e^2}{\varepsilon_D}\left(1 - \frac{4m_d \alpha_{dd}}{\pi m k_0 r_B}\right)\Big/ (k^2 + \varkappa_D^2)$$

(in $\Gamma^k_{dd;dd}$ we use m_s in lieu of m_d)

$$\varepsilon_D = 1 - \frac{4m_d}{\pi m k_0 r_B}\left(\alpha_{dd} + \frac{4m_s \beta_{dd}}{\pi m k_0 r_B}\right),$$

$$\varkappa_D^2 = \frac{4m_s k_0}{\pi m r_B \varepsilon_D}\left(1 + \frac{m_d}{m_s} - \frac{4m_d \alpha_{dd}}{\pi m k_0 r_B}\right). \qquad (13)$$

We see that $\Gamma^k_{ss;ss}$ represents the screening interaction with a screening radius equal to $\varkappa_D^{-1}$, which differs somewhat from the ordinary screening radius $\varkappa_{0D}^{-1}$, but has the same order of magnitude. We assume further that $\varepsilon_D > 0$. Then the first term $4\pi e^2 \varepsilon_D^{-1}(k^2 + \varkappa_D^2)^{-1}$ gives the usual screened Coulomb repulsion, with ε_D playing the role of the dielectric constant, while the second term $16e^2 m_d \alpha_{dd}[\varepsilon_D m k_0 r_B(k^2 + \varkappa_D^2)]^{-1}$ gives attraction with the same screening radius. Although $k_0 r_B < 1$, both terms in $\Gamma^k_{ss;ss}$ are of the same order, since α_{dd} can be sufficiently small. In addition, greatest interest is attached to the mean value of $\Gamma^k_{ss;ss}$, that is, the value of $\Gamma^k_{ss;ss}$ when $k \sim \varkappa_D$. Then the expansions (9) will no longer be valid and the effective value of $\alpha_{dd}(k)$ for $k \sim \varkappa_D$ will be smaller than the constant α_{dd}. Analogous considerations make the case of $\varepsilon_D > 0$ more probable. In principle, however, the case when $\varepsilon_D < 0$, that is, the dielectric constant is negative, is also possible. In this case the first term in $\Gamma^k_{ss;ss}$ corresponds to attraction and the second to repulsion. In a more general sense we can assume that in any case when the attraction exceeds the repulsion, even when $\varepsilon_D > 0$, the generalized dielectric constant is negative, for in this case the resultant interaction between electrons has the character of attraction. It must be borne in mind here, however, that the sign of the resultant interaction is not determined by the sign of $\Gamma^k_{ss;ss}$, since the behavior of the first and second terms of $\Gamma_{ss;ss}$ as functions of the energy transferred ε, is essentially different. The second term tends to zero when $\varepsilon \gg \Delta E_d$ as a result of the factor Π_{dd}; when $\varepsilon \ll \Delta E_d$, the second term is practically constant.

It is easy to see that if the s- and d-electrons were to have identical Ψ-functions, particularly in the case of free s- and d-electrons, the difference $V_{sd;sd}^2 - V_{ss;ss}V_{dd;dd}$ and consequently also the second term in $\Gamma_{ss;ss}$ would be equal to zero.

We see that occurrence of attraction between s-electrons, as in the Little model for a polymer, is connected with the interaction between the electrons of the main group (s-electrons or electrons of a central chain in a polymer), and oscillations of the elec-

tron charge density of the auxiliary group (d-electrons or electrons of the side chains).

We see from (12) that Π_{dd} is approximately proportional to the effective mass m_d, that is, it is the larger the narrower the d-band. Therefore the conditions for attraction to exceed repulsion in $\Gamma_{dd;dd}$ even when $\epsilon_D > 0$ are less favorable ($\Pi_{ss}^k \ll \Pi_{dd}^k$; $\Pi_{sd}^k \sim \Pi_{ss}^k$), although both terms in $\Gamma_{ss;ss}$, $\Gamma_{dd;dd}$, $\Gamma_{sd;sd}$ are of the same order when $m_s \cong m$.

So far we have used the model of strongly bound d-electrons and free s-electrons. Real metals may noticeably deviate from this model. If, as before, $V_{ss;ss}$, $V_{dd;dd}$, and $V_{sd;sd}$ are noticeably larger than all the remaining matrix elements, then the expressions (6) and (7) for $\Gamma_{ss;ss}$, $\Gamma_{dd;dd}$, and $\Gamma_{sd;sd}$ remain in force. Since the general character of the dependence of Π_{dd} on k and ϵ (in particular, the negative sign of $\lim_{\epsilon/k \to 0} \Pi_{dd}$) does not depend essentially on the model, in order for the second term in $\Gamma_{ss;ss}$ to correspond to attraction in the case when $\epsilon_D > 0$, it is necessary that the difference $(V_{sd;sd}^2 - V_{ss;ss}V_{dd;dd})_{av}$ have a positive sign (in the model considered above, this condition was satisfied automatically, since $k_0 r_0 \ll 1$ and $\alpha_{dd} > 0$). If $\epsilon_D < 0$, then both terms correspond to attraction when $(V_{sd;sd}^2 - V_{ss;ss}V_{dd;dd})_{av} < 0$.

It must be noted that even if $V_{ss;sd}$, $V_{dd;ds}$, $V_{ss;dd}$, and $V_{sd;ds}$ are not very small compared with $V_{ss;ss}$, $V_{dd;dd}$, or $V_{sd;s}l$, the expression for the second term in $\Gamma_{ss;ss}$ in (9), describing attraction when $\epsilon_D > 0$, will be sufficiently accurate, since the discarded last two terms in the first two equations of Fig. 6 contain Π_{sd}, which is smaller than Π_{dd} by a factor $\sim m_s/m_d$.

We note that in the model in which the s- and d-electrons are described by strong-coupling Ψ-functions, the matrix elements $V_{dd;ss}$, $V_{dd;ds}$, $V_{ds;ss}$, and $V_{sd;ds}$ are even smaller than in the model considered above; for example,

$$V_{dd;ss} \approx \frac{e^2}{n} \sum_n e^{i\,(k_3 - k_1,\,R_n)} \int \frac{dr\,dr'}{|\,r - r' + R_n\,|}$$

$$\times \Psi_{0s}^*(r)\,\Psi_{0d}(r)\,\Psi_{0s}^*(r')\,\Psi_{0d}(r') \approx 0.$$

In this model, however, the difference $V_{sd;sd}^2 - V_{ss;ss}V_{dd;dd}$ differs from zero only in the case when the Ψ-functions overlap.

On the other hand, if both overlapping bands are sufficiently broad and their width is of the same order, and consequently also the coupling of the electrons in them, then obviously we cannot neglect all the matrix elements other than $V_{ss;ss}$, $V_{dd;dd}$, or $V_{sd;sd}$. In this case the expression for $\Gamma_{ss;ss}$ can likewise be determined in a sufficiently simple manner; as shown in the Appendix, it is necessary for this purpose to solve a system of four linear algebraic equations (see Fig. 6). This can be easily done if one knows the expressions for the Coulomb matrix elements. We do not present here the expression for $\Gamma_{ss;ss}$, nor do we investigate the criterion for the occurrence of at-

traction in this case. It will be shown below that if the matrix element $V_{dd;ss}$ is of the same order as $V_{ss;ss}$, $V_{dd;dd}$, or $V_{sd;sd}$, then an additional pairing mechanism arises, connected with the four-pole $\Gamma_{dd;ss}$.

We have assumed above that only Coulomb forces act between the electrons. Actually, there are always also attraction forces connected with phonon exchange. In this case the effective interaction will be sufficiently well approximated by expressions (6) and (7) for the four-poles, to which we add terms corresponding to the interaction via the phonons.

2. PAIRING AND CRITICAL TEMPERATURE IN THE MODEL OF TWO OVERLAPPING BANDS

If attraction exceeds repulsion for electrons of the s-bands, the latter form Cooper pairs and the system of s-electrons turns out to be superconducting (see [2]). We shall assume for simplicity that there is no pairing in the system of d-electrons, although a consideration of the case when pairing exists in both bands likewise entails no great difficulty (see the Appendix). In spite of the presence of superconductivity, absorption of radio waves will not have a threshold character in this case.

In the case of weak interaction, the energy spectrum of the excitations for the system of s-electrons can be obtained in simplest fashion with the aid of the well-known u, v transformation of Bogolyubov [5].

Let the Hamiltonian of the s-electrons have the form

$$\widetilde{H} = H - \mu N = \sum \xi_k a_{k\sigma}^+ a_{k\sigma}$$

$$+ \frac{1}{2} \sum V(\xi_k,\,\xi_{k'})\,a_{k,\sigma}^+\,a_{k',-\sigma}^+\,a_{k+q,\sigma}\,a_{k'-q,\,-\sigma},$$

$$\sigma = \frac{1}{2},\ -\frac{1}{2}\,;\qquad\qquad\qquad (14)$$

$a_{k\sigma}^+$ and $a_{k\sigma}^-$ are the second-quantization amplitudes satisfying the commutation relations

$$a_{k\sigma}a_{k'\sigma'}^+ + a_{k'\sigma'}^+ a_{k\sigma} = \delta_{\sigma\sigma'}\delta_{kk'},$$

$$a_{k\sigma}^+ a_{k'\sigma'}^+ + a_{k'\sigma'}^+ a_{k\sigma}^+ = a_{k\sigma}a_{k'\sigma'} + a_{k'\sigma'}a_{k\sigma} = 0.$$

We change over to new second-quantization amplitudes $a_{k\sigma}$ and $a_{k\sigma}^+$, which make it possible to take into account the rearrangement of the Fermi surface connected with the possible formation of Cooper pairs:

$$a_{k,\frac{1}{2}} = u_k \alpha_{k,\frac{1}{2}} + v_k \alpha_{-k,-\frac{1}{2}}^+,\quad a_{k,-\frac{1}{2}} = u_k \alpha_{k,-\frac{1}{2}} - v_k \alpha_{-k,\frac{1}{2}}^+,$$

where u_k and v_k satisfy the condition $u_k^2 + v_k^2 = 1$, which ensures conservation of the Fermi commutation conditions for $a_{k\sigma}$ and $a_{k\sigma}^+$. Let us find the mean value of $\widetilde{H}$ over the new occupation numbers $n_{k\sigma} = a_{k\sigma}^+ a_{k\sigma}$:

$$\langle \widetilde{H} \rangle = E = 2 \sum \xi_k v_k^2 + \sum \xi_k (u_k^2 - v_k^2)(n_{k,\frac{1}{2}} + n_{k,-\frac{1}{2}})$$

$$+ \sum V(\xi_k,\,\xi_{k'})\,u_k v_k (1 - n_{k,\frac{1}{2}} - n_{k,-\frac{1}{2}})$$

$$\times u_{k'} v_{k'} (1 - n_{k',\frac{1}{2}} - n_{k',-\frac{1}{2}}). \qquad (15)$$

Minimizing E with respect to u_k and v_k we obtain the condition

$$2\xi_k u_k v_k = -(u_k^2 - v_k^2) \sum V(\xi_k, \xi_{k'})(1 - n_{k', \frac{1}{2}} - n_{k', -\frac{1}{2}}). \quad (16)$$

We introduce the notation

$$\Delta_s(k) = \Delta(k) = \sum V(\xi_k, \xi_{k'}) u_{k'} v_{k'}(1 - n_{k', \frac{1}{2}} - n_{k', -\frac{1}{2}}).$$

We then obtain from (16) expressions for u_k and v_k

$$u_k^2 = \frac{1}{2}(1 + \xi_k/(\Delta^2 + \xi_k^2)^{1/2}),$$

$$v_k^2 = \frac{1}{2}(1 - \xi_k/(\Delta^2 + \xi_k^2)^{1/2}). \quad (17)$$

From the condition of the maximum entropy of the excitation gas

$$S = -\sum_{k\sigma}[n_{k\sigma}\ln n_{k\sigma} + (1 - n_{k\sigma})\ln(1 - n_{k\sigma})] \quad (k_B = 1),$$

as a function of $n_{k\sigma}$ for a specified energy E, we get
$n_{k\sigma} = (e^{\epsilon(k)/T} + 1)^{-1}$ where

$$\epsilon(k) = \frac{\delta E}{\delta n_k}.$$

From (15) we obtain

$$\epsilon(k) = \sqrt{\Delta(k)^2 + \xi_k^2}.$$

Substituting (17) and the expression for $n_{k\sigma}$ in (16), we obtain an expression for the energy gap Δ:

$$\Delta(k) = -\frac{1}{2}\sum \Delta(k')V(\xi_k, \xi_{k'})\,\text{th}(\epsilon(k')/2T)/\epsilon(k'). \quad (18)^*$$

At absolute zero $n_{k\sigma} = 0$ and we get from (18)

$$\Delta(k) = -\frac{1}{2}\sum \Delta(k')V(\xi_k, \xi_{k'})/\epsilon(k'). \quad (19)$$

It is shown in the Appendix that in the case when the interaction is not weak, Eqs. (18) and (19) retain their form (see (A.11) and (A.12)), but they contain in lieu of $V(\xi_k, \xi_{k'})$ the four-pole $\Gamma_{ss;ss}$. For an approximate estimate of Δ we assume, as in [2,5], that the different terms in ξ_k are constant in a definite region of $|\xi_k|$, and that outside this region the following quantities vanish: (a) the term connected with phonon exchange when $|\xi_k|$, $|\xi_{k'}| < h\omega_D$ (when $|\xi_k|$, $|\xi_{k'}| > h\omega_D$ the matrix element of the interaction between electrons via the phonons is, as is well known, very small[1]; ω_D is the Debye frequency); (b) the attraction connected with the second term in (6) (for $\epsilon_D > 0$) when $|\xi_k|$, $|\xi_{k'}| < \Delta E_d$ (see above) and the Coulomb repulsion when $|\xi_k|$, $|\xi_{k'}| < \epsilon_0$ (ϵ_0 is the Fermi energy for the s-electrons).

Going over in (19) (with $\Gamma_{ss;ss}$ replacing $V(\xi_k, \xi_{k'})$) from summation to integration with respect to k, and then by means of a change of variables to integration with respect to ξ_k, we calculate the integral with respect to ξ_k and obtain a system of equations (we disregard here the anisotropy of Δ)

$$\left.\begin{aligned}
\Delta_1 &= (g_1 + g_2 - g_3)\Delta_1\ln\frac{2\omega_a}{\Delta_1} + (g_2 - g_3)\Delta_2\ln\frac{\omega_2}{\omega_b} - g_3\Delta_3\ln\frac{\omega_3}{\omega_2}, \\
\Delta_2 &= (g_2 - g_3)\left[\Delta_1\ln\frac{2\omega_a}{\Delta_1} + \Delta_2\ln\frac{\omega_2}{\omega_b}\right] - g_3\Delta_3\ln\frac{\omega_3}{\omega_2}, \\
\Delta_3 &= -g_3\left[\Delta_1\ln\frac{2\omega_a}{\Delta_1} + \Delta_2\ln\frac{\omega_2}{\omega_b} + \Delta_3\ln\frac{\omega_2}{\omega_2}\right];
\end{aligned}\right\} \quad (20)$$

here

$$\omega_a = \frac{1}{2}(\omega_1 + \sqrt{\omega_1^2 + \Delta_1^2}), \quad \omega_b = \frac{1}{2}(\omega_1 + \sqrt{\omega_1^2 + \Delta_2^2}),$$

$$\omega_1 = h\omega_D, \quad \omega_2 = \Delta E_d, \quad \omega_3 = \epsilon_0, \quad \Delta_1 = \Delta(k) \text{ for } |\xi_k| < \omega_1,$$

$$\Delta_2 = \Delta(k) \text{ for } \omega_2 > |\xi_k| > \omega_1, \quad \Delta_3 = \Delta(k) \text{ for } |\xi_k| > \omega_2:$$

g_1, g_2, and g_3 are the products of a state density on the Fermi surface N_s (this factor appears on going over from integration with respect to k to integration with respect to ξ_k) and the absolute value of the corresponding term $\Gamma_{ss;ss}$ (their sign is taken into account in (20)), i.e., respectively, the phonon-proper term, the second term in (6), and the Coulomb repulsion.

A solution of (20) can be readily obtained when $\Delta_1 \ll \omega_1$ and $\Delta_2 \ll \omega_1$. The solution exists only under the condition

$$g_0 > 0, \quad g_0 = g_1 + (g_2 - \tilde{g}_3)\Big/\left[1 - (g_2 - \tilde{g}_3)\ln\frac{\omega_2}{\omega_1}\right];$$

$$\tilde{g}_3 = g_3\Big/\left(1 + g_3\ln\frac{\omega_3}{\omega_2}\right) \text{ and } \Delta_1 = 2\omega_1 e^{-1/g_0},$$

$$\Delta_2 = 2\omega_1 e^{-1/g_0}\Big/\left[1 + g_1\left(\frac{1}{g_2 - \tilde{g}_3} - \ln\frac{\omega_2}{\omega_1}\right)\right],$$

$$\Delta_3 = -\tilde{g}_3 2\omega_1 e^{-1/g_0}\Big/\left\{g_1\left[1 - (g_2 - \tilde{g}_3)\ln\frac{\omega_2}{\omega_1}\right] + g_2 - \tilde{g}_3\right\}. \quad (21)$$

Let us obtain now the critical temperature T_C at which the energy gap $\Delta(k)$ vanishes. To this end we put in (18) $T = T_C - 0$, assuming that $\Delta(k) = 0$ in the expression for $\epsilon(k)$; the integration with respect to ξ_k is easily carried out[2,6] and we get from (18)

$$\left.\begin{aligned}
\Delta_1 &= (g_1 + g_2 - g_3)\Delta_1\ln(1.14\omega_1/T_c) \\
&\quad + (g_2 - g_3)\Delta_2\ln\frac{\omega_2}{\omega_1} - g_3\Delta_3\ln\frac{\omega_3}{\omega_2}, \\
\Delta_2 &= (g_2 - g_3)\left[\Delta_1\ln(1.14\omega_1/T_c) + \Delta_2\ln\frac{\omega_2}{\omega_1}\right] - g_3\Delta_3\ln\frac{\omega_3}{\omega_2}, \\
\Delta_3 &= -g_3\left[\Delta_1\ln(1.14\omega_1/T_c) + \Delta_2\ln\frac{\omega_2}{\omega_1} + \Delta_3\ln\frac{\omega_3}{\omega_2}\right],
\end{aligned}\right\} \quad (22)^*$$

$$\Delta_1 \approx \Delta_2 \approx \Delta_3 \approx 0, \quad \int_0^\infty \frac{\ln x}{\text{ch}^2 x}dx = -\ln(4\gamma/\pi), \quad \ln\gamma = 0.577.$$

Equating to zero the determinant type system (22), we obtain

$$T_c = 1.14\omega_1 e^{-1/g_0} = T_c^e e^{g_1/g_0(g_0 - g_1)}, \quad (23)$$

where $T_c^e = 1.14\omega_2 e^{-1/(g_2 - \tilde{g}_3)}$. Since g_0 contains $\tilde{g}_3$, the effective Coulomb repulsion is weakened by a factor $1/(1 + g_3\ln\frac{\omega_3}{\omega_2})$ which can be noticeably smaller than unity if $\Delta E_d \ll \epsilon_0$ (see [5]).

Expression (23) can be written in a different form:

$$T_c = T_c^{ph}\exp\left\{g_2\left[(g^*)^2 + g_2 g^*(1 - g_1\ln\frac{\omega_2}{\omega_1})\right]^{-1}\right\}, \quad (24)$$

where

$$T_c^{ph} = 1.14\omega_1 e^{-1/(g_1 - \tilde{g}_3)}, \quad \tilde{\tilde{g}}_3 = g_3\Big/\left(1 + g_3\ln\frac{\omega_2}{\omega_1}\right),$$

$$g^* = g_1\left(1 + \tilde{g}_3\ln\frac{\omega_2}{\omega_1}\right) - \tilde{g}_3.$$

---

*th ≡ tanh.

*ch ≡ cosh.

Thus, when $g_2 \ll (g^*)^2 - g_2 g^*(1 - g_1 \ln \frac{\omega_2}{\omega_1})$ we set $T_c \approx T_c^{ph}$. A similar expression for T_c is obtained, as is well known, when the phonon mechanism is effective[2,5,6]. On the other hand, if $g_1 \ll g_0 (g_0 - g_1)$, then $T_c \cong T_c^e$, corresponding to predominance of the electronic mechanism. Since $\omega_2 \gg \omega_1$ ($\Delta E_d \gg \hbar\omega_D$) and $g_2 \sim g_1$, the critical temperature will in this case be considerably higher than in the case of the phonon mechanism. For example, when $\Delta E_d \sim 0.3-1$ eV we have $T_c \sim (10^2-10^3)$ °K. In the intermediate case when $g_1 \sim g_2$ the dependence of T_c on ω_1 and ω_2 will be very complicated, as we see from (23). A rapid growth of T_c should be observed when $g_2 - \tilde{g}_3 \approx 1/\ln(\omega_2/\omega_1)$.

We see that the attraction between the s-electrons due to their interaction with d-electrons can lead to superconductivity with a critical temperature much higher than the critical temperature in the case of the phonon mechanism.

There exists also one electronic mechanism, which is close in its character to that considered above and which, in principle, can lead to high critical temperatures. We have seen so far that one of the two overlapping bands is much narrower than the other. Let us assume now that the widths of both overlapping bands, and consequently also the coupling between the electrons in them, are of the same order. Then we can no longer neglect, as above, the matrix elements $V_{dd;ss}$, $V_{dd;ds}$, $V_{ds;ss}$, and $V_{sd;ds}$ compared with $V_{ss;ss}$, $V_{dd;dd}$, and $V_{sd;sd}$; by virtue of this (see the Appendix) we cannot neglect the four-poles $\Gamma_{dd;ss}$, $\Gamma_{dd;ds}$, $\Gamma_{ds;ss}$, and $\Gamma_{sd;ds}$ compared with $\Gamma_{ss;ss}$, $\Gamma_{dd;dd}$, and $\Gamma_{sd;sd}$.

The equations for the energy gaps of the s- and d-electrons Δ_s and Δ_d can be readily obtained in the case of weak interaction with the aid of a u,v transformation on the amplitudes a_k^s and a_k^d (see [14]). In the case of an arbitrary interaction, the equations for Δ_s and Δ_d are similar in form, but in lieu of the matrix elements the equations will contain the corresponding four-poles (see the Appendix); these equations are generalizations of (18):

$$\Delta_s = -\Delta_s N_s (\Gamma_{ss;ss})_{av} R_s - \Delta_d N_d (\Gamma_{dd;ss})_{av} R'_d,$$
$$\Delta_d = -\Delta_d N_d (\Gamma_{dd;dd})_{av} R_d - \Delta_s N_s (\Gamma_{ss;dd})_{av} R'_s,$$
$$R_s = \int_0^{\Delta E_d} d\xi_s \, \text{th} \, [(\Delta_s^2 + \xi_s^2)^{1/2}/2T]/(\Delta_s^2 + \xi_s^2)^{1/2}; \quad (25)$$

the indices s and d have been interchanged in R_d, and in R'_s and R'_d the upper limit of the integral is equal to ΔE_c. It is assumed here that there is no phonon mechanism and that $\Gamma_{ss;ss} = $ const when $|\xi_k|$, $|\xi_{k'}| < \Delta E_d$, $\Gamma_{ss;ss} = 0$ when $|\xi_k|$, $|\xi_{k'}| > \Delta E_d$, $\Gamma_{dd;dd} = $ const when $|\xi_k|$, $|\xi_{k'}| < \Delta E_s$, $\Gamma_{dd;dd} = 0$ when $|\xi_k|$, $|\xi_{k'}| > \Delta E_s$, $\Gamma_{ss;dd} = $ const when $|\xi_k|$, $|\xi_{k'}| < \Delta E_c$, and $\Gamma_{ss;dd} = 0$ when $|\xi_k|$, $|\xi_{k'}| > \Delta E_c$. It is easy to see that even when $\Gamma_{ss;ss} = \Gamma_{dd;dd} = 0$ the system (25) has a nonvanishing solution for Δ_s and Δ_d regardless of

the sign of $\Gamma_{ss;dd}$, i.e., even when $\Gamma_{ss;dd}$ corresponds to repulsion:

$$\Delta_{ss} = \Delta_{ss} N_s N_d (\Gamma_{ss;dd})_{av}(\Gamma_{dd;ss})_{av} R'_s R'_d. \quad (26)$$

This effect, which favors pairing, has the same nature as the occurrence of attraction in $V'_{ss;ss}$ in the second perturbation-theory approximation in accord with (5), but is connected with $V_{ss;dd}$ and not with $V_{sd;sd}$. However, the conditions for the occurrence of pairing in this case are apparently less favorable than in that considered above—with bands of essentially different widths—since the attraction effect described by (26), is no longer intensified by a large factor of the type of the polarization operator Π_{dd}, as in (6). Therefore the probability that the attraction will exceed the Coulomb repulsion is lower in the case of bands of equal width than in the case of bands with essentially different widths, but this possibility cannot be completely excluded. The pairing effect connected with $V_{ss;dd}$ was known even before Little's paper[15,16]. However, the papers of Kondo and Perretti did not attract much attention, for this effect was considered in them only for an explanation of properties of certain superconducting alloys with ordinary critical temperature (on the basis of the u,v transformation, i.e., assuming weak interaction) and sight was lost in this case of the possibility of obtaining high critical temperatures.

This raises the question of the extent to which the possibility of obtaining superconductors with high critical temperatures, such as room temperature and above, is indeed realistic. In the most favorable model with two overlapping bands of different widths, the necessary condition for pairing, as shown above, is the inequality

$$(V_{sd;sd}^2 - V_{ss;ss} V_{dd;dd})_{av} > 0;$$

in addition it is necessary that the attraction exceed the repulsion, i.e., $g_2 > \tilde{g}_3$. In order for the critical temperature to be sufficiently high, i.e., to be determined by the electronic mechanism, it is necessary to satisfy the condition $g_2 - \tilde{g}_3 \sim 1$ (when $\exp[g_1/g_0(g_0 - g_1)] \sim 1$). Thus, although in principle the production of superconducting metals with high critical temperatures is possible, this is a very complicated task. In the case of pure transition-group metals, the electronic mechanism of superconductivity is apparently either not realized or realized only in the form of a small admixture to the phonon mechanism. Superconductors with high critical temperatures, in which the electronic mechanism prevails, should be sought among the alloys. These searches are made very difficult by the fact that the electronic spectrum and the single-particle Ψ-functions of the electrons in the alloys, are unknown and are difficult to calculate. Of course, in the case when the electronic mechanism predominates, the isotropic effect is almost completely missing.

Further research is necessary also in connection with the question of stability of the superconducting state in the case of the electronic superconducting mechanism. It can be assumed, however, that the superconducting state is stable: although the energy gap Δ can now be of the same order as the Debye frequency, the pairing is connected not with the interaction between the electrons and the phonons, but with the interaction between the electrons themselves; therefore, the realignment of the ground state of the system of the electrons cannot apparently disturb the stability of the lattice. On the other hand, the stability of the superconducting state against collective excitations does not depend on the physical nature of the attraction forces between the electrons (see [17]).

3. ALLOY OF METAL WITH NONMETAL

We now consider the alloy of a metal with a nonmetal (for example, with C, N, Si, S, Se, Sb, etc.) with comparable concentrations of the two components. Such alloys are well known. We assume that the alloy is well ordered and that the upper shell of the nonmetal atoms, like the upper band of the metal electrons, is not filled and the electrons of the nonmetal are not collectivized. This is possible only in the case of strong coupling between the electrons of the nonmetal with their atoms, and in the case when the upper filled level of the nonmetal atom is lower than the Fermi surface of the metal electrons. It is difficult to say at present to what degree such an idealized model with non-collectivized electrons of the nonmetal atom can be realized. The electrons of the nonmetal will play in this case the role of auxiliary electrons, which induce attraction between electrons of the metal, i.e., the same role as the d-electrons in the model of the metal with overlapping bands. However, unlike the d-electrons, the nonmetal electrons will be described not by Bloch functions, but by atomic functions. The pairing for the electrons of the nonmetal is missing in this case, and therefore the calculations are greatly simplified. In the four-pole $\Gamma_{ss;ss}$, the term connected with the interaction between the electrons of the metal and the electrons of the nonmetal can be obtained by perturbation theory (or else, in the case of two close atomic levels, by perturbation theory with account of degeneracy). On the other hand, the screening of the conduction-electron potential will be determined only by the conduction electrons themselves, since the electrons of the nonmetal are localized. Then the four-pole $\Gamma_{ss;ss}$, if we disregard the phonon mechanism, will have the following form (see (5) and (6))

$$\Gamma_{ss;ss} = \Gamma'_{ss;ss} + \Gamma''_{ss;ss},$$
$$\Gamma'_{ss;ss} = V_{ss;ss}/(1 - \Pi_{ss}V_{ss;ss}),$$
$$\Gamma''_{ss;ss} = \sum_{n,\lambda,\lambda'} V^{sd;sd}_{k_1,n\lambda;\,k_3,n\lambda'}\, V^{sd;sd}_{n\lambda',k_2;\,n\lambda,k_4}\, n_{n\lambda'}\,(1-n_{n\lambda})$$
$$\times\,[(\xi^s_{k_3}-\xi^s_{k_1}-\xi^d_{n\lambda}+\xi^d_{n\lambda'})^{-1}+(\xi^s_{k_1}-\xi^s_{k_3}-\xi^d_{n\lambda}+\xi^d_{n\lambda'})^{-1}];\quad(27)$$

here the indices s and d correspond to the conduction electrons and to the nonmetal electrons, and λ is the aggregate of the quantum numbers of the electron of the nonmetal atom situated at the crystal lattice point with integer radius vector R_n. If, as before, we use for the conduction electrons the plane-wave approximation, then we get from (1)

$$V^{sd;\,sd}_{k_1,\,n\lambda;\,k_3,\,n\lambda'} \approx \frac{4\pi e^2 \exp[i\,(k_3-k_1,\,R_n)]}{|\,k_3-k_1\,|^2}$$

$$\times \int e^{i\,(k_3-k_1,\,r)}\,\Psi_{0\lambda}(r))\,\Psi^*_{0\lambda'}(r)\,dr.$$

The argument of the exponential under the integral sign is of the order of $k_0 r_0 \ll 1$. If we replace the exponential by unity, then the integral vanishes. Therefore, as shown above,

$$V_{k_1,\,n\lambda;\,k_3,\,n\lambda'} \sim k_0 r_0 V_{ss;\,ss},\ \text{i.e.,}\ \frac{\Gamma''}{\Gamma'} \sim \frac{(k_0 r_0)^2\,n e^2}{\Delta E_d \varkappa^2_{0D}}.\quad(28)$$

In order for the second term in (27), corresponding to attraction, to outweigh the repulsion it is obviously necessary to have

$$\Delta E_d \lesssim n k_0 r_0\,(V_{sd;\,sd})_{av}\ln(\varepsilon_0/\Delta E_d);\quad(29)$$

account was taken here of the logarithmic attenuation of the Coulomb repulsion (see (21)). At the same time, the condition of applicability of perturbation theory leads to the inequality $\Delta E_d \gtrsim n\,(V_{sd;sd})_{av}$, that is, it is necessary to have

$$\ln(\varepsilon_0/\Delta E_d) \gg (k_0 r_0)^{-1}.\quad(30)$$

The corresponding small values of ΔE_d are possible in the case of fine-structure levels or in the case of Stark-effect splitting of atomic levels in the electric field of the crystal. The critical temperature is determined as before by formula (23), but now ΔE_d is equal to the distance between the upper filled level in the nonmetal atom and the nearest unfilled level. Since ΔE_d is much smaller in this case than in (23), even when condition (30) is satisfied, the critical temperature in the case of an alloy of a metal with a nonmetal will be smaller than for a metal with two overlapping bands. The same considerations are applicable apparently in the case of a dielectric film which covers the surface of the metal; as indicated in [18], such a film can produce more favorable conditions for the occurrence of superconductivity surfaces.

Let us consider in conclusion a metal with impurities, that is, an alloy with low concentration of one of the components when the levels of the atom of even the metallic impurity have a local character. In this case it is possible to use for an estimate formula (27) but, the second term of (27) must be multiplied by the impurity concentration $c_{imp} \ll 1$, which greatly reduces the effect of attraction (in addition, the coordinates R_n will now be randomly distributed). It can be assumed that the increase of T_c in certain known alloys is connected with the additional attraction which is
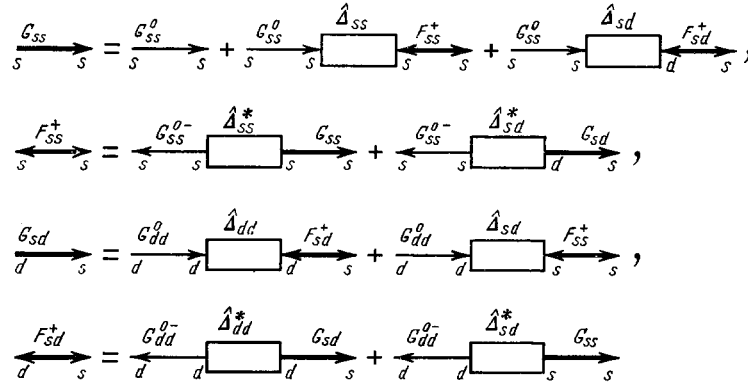
FIG. 3

caused by the presence of impurities. A similar effect in the case of ferromagnetic impurities was considered earlier in [19].

APPENDIX

Let us find the Green's function, and also the expression for the energy gap and for the four-poles for the system of s- and d-electrons without assuming that the interaction between electrons is small.

In this case we can introduce the following Green's functions and F-functions: G_{ss}, G_{dd}, G_{sd}, F_{ss}, F_{dd}, and F_{sd}, with

$$G_{sd} = -i \langle T (\Psi_d (x) \Psi_s^+ (x'))\rangle, \qquad F_{sd}^+ = -i \langle T (\Psi_s^+ (x) \Psi_d^+ (x'))\rangle,$$

and the remaining G and F or F$^+$ are defined in similar fashion. If we do not write out the terms containing the self-energy parts Σ_{ss}, Σ_{dd}, and Σ_{sd} with one incoming and one outgoing ends (these terms lead essentially only to renormalization of the chemical potential), then the system of equations for G_{ss}, G_{sd}, F_{ss}^+, and F_{sd}^+ has a graphic form indicated in Fig. 3. A similar form is possessed by the system of equations for G_{dd}, G_{ds}, F_{dd}, and F_{ds}. In analytic form, in the representation of the single-particle functions $\Psi_\lambda(r)$ ($\Psi_\lambda = e^{i(k, r)} u_{kj}(r)$), the equations for G_{ss}, G_{sd}, F_{ss}^+, and F_{sd}^+ (the Dyson equation) are written in the form

$$
\begin{aligned}
&(\varepsilon - \xi_\lambda^s)\, G_{ss\lambda} = a_s\,(1 + \hat{\Delta}_{ss\lambda} F_{ss\lambda}^+ + \hat{\Delta}_{sd\lambda} F_{sd\lambda}^+), \quad -(\varepsilon + \xi_\lambda^s)\, F_{ss\lambda}^+ \\
&= a_s\,(\hat{\Delta}_{ss\lambda}^* G_{ss\lambda} + \hat{\Delta}_{sd\lambda}^* G_{sd\lambda}), \quad (\varepsilon - \xi_\lambda^d)\, G_{sd\lambda} = a_d\,(\hat{\Delta}_{dd\lambda} F_{sd\lambda}^+ \\
&\quad + \hat{\Delta}_{sd\lambda} F_{ss\lambda}^+), \quad -(\varepsilon + \xi_\lambda^d)\, F_{sd\lambda}^+ = a_d\,(\hat{\Delta}_{dd\lambda}^* G_{sd\lambda} + \hat{\Delta}_{sd}^* G_{ss\lambda}), \\
&(G_{ss}^0)_{\lambda\lambda'} = \delta_{\lambda\lambda'} a_s\,(\varepsilon - \xi_\lambda^s + i\delta \operatorname{sgn}\xi_\lambda^s)^{-1}, \quad G_{\lambda\lambda'} = G_\lambda \delta_{\lambda\lambda'}, \\
&\hspace{3cm} F_{\lambda\lambda'}^+ = F_\lambda^+ \delta_{\lambda\lambda'};
\end{aligned}
\quad\quad (A.1)
$$

$a_s \leq 1$ and $a_d \leq 1$; the spin vectors $\hat{\Delta}$ have the form [20] $\hat{\Delta}_{\alpha\beta} = i\sigma_{\alpha\beta}^y \Delta$ (Δ is a number). We shall henceforth assume for simplicity that $a_s = a_d = 1$. We assume by the same token that not only Δ_{ss} and Δ_{dd} but also Δ_{sd} differ from zero. Since the values of $|k|$ on the Fermi surface differ for the s- and d-electrons, this is possible only when the umklapp processes are taken into account. Indeed, for a delta-function interaction in the second perturbation-theory approximation, with umklapp taken into account, the correction to the amplitude for the scattering of an s-electron by a d-electron is of the form [6]

$$f = \frac{g^2}{(2\pi)^3} \int [\xi^s (k_1) + \xi^d (k_2) - \xi^s (q) - \xi^d (k_1 + k_2 + 2\pi b - q)]^{-1}\, dq.$$

We assume that $|k_1 + k_2 + 2\pi b| \ll q$, and obtain in the usual fashion [6] an expression for f which diverges logarithmically when $|k_1 + k_2 + 2\pi b| \to 0$. Consequently, pairing of the s- and d-electrons is possible only if $|k_1 + k_2 + 2\pi b| = 0$ (such a pairing is possible

also in the case of two s- or two d-electrons). This condition can be realized (for both the electronic and phonon mechanisms) only when the occupation and structure of the two bands have a different character, and in definite regions of directions in k-space. We shall henceforth assume that $\Delta_{sd} = F_{sd}^+ = 0$. In this case G_{sd} will also be equal to zero if we take into account the Σ_{sd}, Σ_{ss}, and Σ_{dd} which were not written out in (A.1), since $k_s \neq k_d + 2\pi b$. Then the solution of (A.1) will take the form

$$
\begin{aligned}
G_{ss} &= (\varepsilon + \xi_s)/D_s, \quad F_{ss}^+ = -\Delta_s/D_s, \\
G_{dd} &= (\varepsilon + \xi_d)/D_d, \quad F_{dd}^+ = -\Delta_d/D_d;
\end{aligned}
\quad\quad (A.2)
$$

here

$$\varepsilon_1 = (\Delta_s^2 + \xi_s^2)^{1/2}, \quad \varepsilon_2 = (\Delta_d^2 + \xi_d^2)^{1/2},$$

$$\Delta_s \equiv \Delta_{ss}, \quad \Delta_d \equiv \Delta_{dd}, \quad \Delta_s = \Delta_s^*, \quad \Delta_d = \Delta_d^*. \quad\quad (A.3)$$

The poles of the Green's functions determine the energy spectrum of the excitations: $\epsilon = \epsilon_1$ and $\epsilon = \epsilon_2$. At nonzero temperature, the system of equations for the temperature functions G and F is similar to (A.2), except that $\epsilon + i\delta \operatorname{sgn}\xi$ must be replaced everywhere by $i\omega_n$ ($\omega_n = (2n + 1)\,\pi T$). We now find equations for the self-energy parts, i.e., the energy gaps Δ_s and Δ_d. These equations are shown graphically in Fig. 4, i.e., their mathematical form (with symbolic notation) is

$$\Delta_{ss} = \Gamma_{ss;\,ss} F_{ss}^+ + \Gamma_{dd;\,ss} F_{dd}^+, \qquad \Delta_{dd} = \Gamma_{dd;\,dd} F_{dd}^+ + \Gamma_{ss;\,dd} F_{ss}^+.$$

The four-poles Γ which enter in the equation cannot be cut into two parts joined only by two lines of identical direction, since F and F$^+$ already take into account the corresponding diagrams (see [20]). It was shown above (see (4)) that the matrix elements $V_{ss;dd}$, $V_{ss;sd}$, $V_{dd;ds}$, and $V_{sd;ds}$ can be neglected compared with $V_{ss;ss}$, $V_{dd;dd}$, and $V_{sd;sd}$. We shall show below that we also neglect in this case the four-poles $\Gamma_{ss;dd}$, $\Gamma_{ss;sd}$, $\Gamma_{dd;ds}$, and $\Gamma_{sd;ds}$, compared with $\Gamma_{ss;ss}$, $\Gamma_{dd;dd}$, and $\Gamma_{sd;sd}$. Then we can retain only the first terms in the equations of Fig. 4. In mathematical form they become (when T = 0)

$$
\begin{aligned}
\Delta_s\,(p) &= \frac{1}{i\,(2\pi)^4} \int dp' \Gamma_{ss;\,ss}\,(p',\, p';\, p,\, p)\, F_{ss}^+\,(p'), \\
\Delta_d\,(p) &= \frac{1}{i\,(2\pi)^4} \int dp' \Gamma_{dd;\,dd}\,(p',\, p';\, p,\, p)\, F_{dd}^+\,(p'); \\
\hbar &= 1, \quad \text{for}\quad T \neq 0 \quad (2\pi i)^{-1} \int d\varepsilon \to T \sum_{\omega_n},\ \varepsilon \to i\omega_n.
\end{aligned}
\quad\quad (A.4)
$$

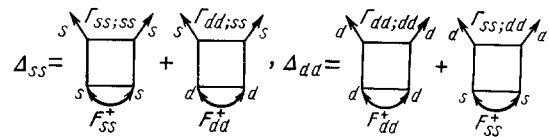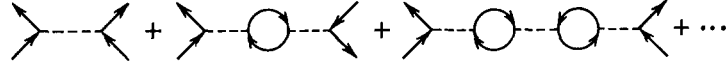When calculating the four-poles Γ in the case of Coulomb forces,
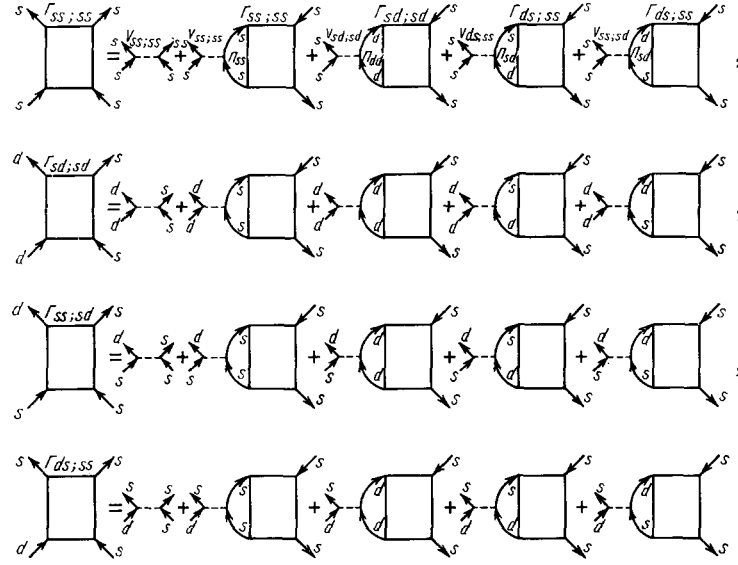

FIG. 4

FIG. 5

FIG. 6

the principal role is played, as is well known, by diagrams of the chain type (Fig. 5). For highly compact systems, the remaining diagrams make a negligibly small contribution. But even for such highly compact systems like metals, allowance for the chain diagrams only is a sufficiently good approximation, especially for small values of the momentum transfer k (see (10)). If we neglect the loops made up of the F- and F$^+$-functions, compared with the loops of the G-functions (the loops of the first type yield terms of order Δ^2/ϵ_0^2), then we obtain for the four-poles Γ the system of equations indicated in Fig. 6, which has an analytic form

$$\Gamma_{ss;\;ss} = V_{ss;\;ss} + V_{ss;\;ss}\Pi_{ss}\Gamma_{ss;\;ss} + V_{sd;\;sd}\Pi_{dd}\Gamma_{sd;\;sd}$$
$$+ V_{ds;\;ss}\Pi_{sd}\Gamma_{ss;\;sd} + V_{ss;\;sd}\Pi_{sd}\Gamma_{ds;\;ss},$$

$$\Gamma_{sd;\;sd} = V_{sd;\;sd} + V_{sd;\;sd}\Pi_{ss}\Gamma_{ss;\;ss} + V_{dd;\;dd}\Pi_{dd}\Gamma_{sd;\;sd}$$
$$+ V_{dd;ds}\Pi_{sd}\Gamma_{ss;\;sd} + V_{sd;\;dd}\Pi_{sd}\Gamma_{ds;\;ss},$$

$$\Gamma_{ss;\;sd} = V_{ss;\;sd} + V_{ss;\;sd}\Pi_{ss}\Gamma_{ss;\;ss} + V_{sd;\;dd}\Pi_{dd}\Gamma_{sd;\;sd}$$
$$+ V_{sd;\;ds}\Pi_{sd}\Gamma_{ss;\;sd} + V_{ss;\;dd}\Pi_{sd}\Gamma_{ds;\;ss},$$

$$\Gamma_{ds;\;ss} = V_{ds;\;ss} + V_{ds;\;ss}\Pi_{ss}\Gamma_{ss;\;ss} + V_{dd;\;ds}\Pi_{dd}\Gamma_{sd;\;sd}$$
$$+ V_{dd;\;ss}\Pi_{sd}\Gamma_{ss;\;sd} + V_{sd;\;ds}\Pi_{sd}\Gamma_{ds;\;ss},$$

and an analogous system for $\Gamma_{ss;dd}$ (which contains $\Gamma_{ss,dd}$, $\Gamma_{ss;sd}$, $\Gamma_{sd;dd}$, and $\Gamma_{sd;ds}$); $\Gamma_{dd;dd}$ is obtained from $\Gamma_{ss;ss}$ and $\Gamma_{dd;ss}$ from $\Gamma_{ss;dd}$ by permutation of the indices s and d. It was shown above (see (A.4)) that one can neglect all of the matrix elements except $V_{ss;ss}$, $V_{dd;dd}$, and $V_{sd;sd}$. We then see from the equations of Fig. 6 that the four-pole $\Gamma_{ss;sd}$ can be neglected (it is easy to show analogously that the remaining four-poles can also be neglected) compared with $\Gamma_{ss;ss}$, $\Gamma_{sd;sd}$, (and $\Gamma_{dd;dd}$). In mathematical form the system of equations for $\Gamma_{ss;ss}$ and $\Gamma_{sd;sd}$ is

$$\left.\begin{aligned}
\Gamma_{ss;\;ss} &= V_{ss;\;ss} + V_{ss;\;ss}\Pi_{ss}\Gamma_{ss;\;ss} + V_{sd;\;sd}\Pi_{dd}\Gamma_{sd;\;sd}, \\
\Gamma_{sd;\;sd} &= V_{sd;\;sd} + V_{sd;\;sd}\Pi_{ss}\Gamma_{ss;\;ss} + V_{dd;\;dd}\Pi_{dd}\Gamma_{sd;\;sd}, \\
\Pi_{ss}(k) &= \frac{2}{i(2\pi)^4} \int dp\, G_{ss}(p)\, G_{ss}(p+k).
\end{aligned}\right\} \quad \text{(A.5)}$$

For $\Gamma_{dd;dd}$ and $\Gamma_{sd;sd}$ we obtain an approximate system of two equations, similar to (A.5). The solution of the system (A.5) is

$$\Gamma_{ss;\;ss} = [V_{ss;\;ss} + \Pi_{dd}\,(V^2_{sd;\;sd} - V_{ss;\;ss}V_{dd;\;dd})]/S,$$

$$S = 1 - V_{ss;\;ss}\Pi_{ss} - V_{dd;\;dd}\Pi_{dd} - \Pi_{ss}\Pi_{dd}\,(V^2_{sd;\;sd} - V_{ss;\;ss}V_{dd;\;dd}), \quad \text{(A.6)}$$

that is, (see [13])

$$\Gamma_{ss;\;ss} = [V_{ss;\;ss} + V_{sd;\;sd}\Pi_{dd}\,(1 - V_{dd;\;dd}\Pi_{dd})^{-1}\,V_{sd;\;sd}]\,(1 + \Pi_{ss}\Gamma_{ss;\;ss}),$$

$$\Gamma_{sd;\;sd} = V_{sd;\;sd}/S.$$

Analogously we obtain

$$\Gamma_{dd;\;dd} = [V_{dd;\;dd} + \Pi_{ss}\,(V^2_{sd;\;sd} - V_{ss;\;ss}V_{dd;\;dd})]/S. \quad \text{(A.7)}$$

In calculating the polarization operators Π_{ss} and Π_{dd} we can use the Green's function in the absence of pairing, since in the integral with respect to p for Π an important role is played by the energy $\sim \epsilon_0$ and not by Δ. For estimating purposes we use G^0 in (A.1), which contains no regular parts (when $T \neq 0$ $\epsilon \to i\omega_n$):

$$\Pi_{dd}(k) = \frac{2}{(2\pi)^3} \int \frac{n_d(p) - n_d(p+k)}{\epsilon - \xi^d(p+k) + \xi^d(k)}\, dp. \quad \text{(A.8)}$$

Usually $|k| \ll k_0$; then the integrand in (A.8) can be expanded in powers of $|k|$:

$$\Pi_{dd}(k) = -\frac{2}{(2\pi)^3} \int \left(\left(\frac{\partial n_d}{\partial \mathbf{p}}\right)_{|p|=p_0}, \mathbf{k}\right)\frac{dp}{\epsilon - \left(\left(\frac{\partial\xi^d}{\partial\mathbf{p}}\right)_{|p|=p_0}, \mathbf{k}\right)}.$$

(A.9)

In the effective-mass approximation we obtain from (A.9) the expression (11)[21]. To obtain in explicit form expressions for Δ_s and Δ_d we substitute F^+_{ss} and F^+_{dd} from (A.2) and (A.4). In integrating with respect to ϵ' by means of the residue theorem, the principal role will be assumed by the poles of F^+_{ss} and F^+_{dd}. On the other hand, the poles of $\Gamma_{ss;ss}$ and $\Gamma_{dd;dd}$, corresponding to the frequency of the plasma oscillations [21]

$$\omega_p^2 = \frac{4e^2}{3\pi} \, (p_{0s}^3/m_s + p_{0d}^2/m_d), \qquad \text{(A.10)}$$

will make a very small contribution, since ω_p is much larger than Δ_s and Δ_d. This contribution can be neglected, and we can substitute in (A.4) the four-poles Γ for $\epsilon = \epsilon' = 0$, i.e., we can neglect retardation. Inasmuch as different terms in Γ, as shown above, can be approximately regarded as constant in a definite region of ξ when $k \sim \kappa_D$, and as equal to zero outside this region, we shall replace these terms by the constant terms which enter in Γ^k (Γ^k (ξ_k, $\xi_{k'}$) in the case of $k \sim \kappa_D$).

We assume for simplicity that $\Gamma_{dd;dd}$ exceeds the repulsion; then $\Delta_d = 0$, i.e., the pairing exists only in the s-band. For Δ_s we obtain the equation

$$\Delta_s(k) = -\frac{1}{2\,(2\pi)^3} \int dk' \Gamma_{ss;\,ss}^k (\xi_k, \, \xi_{k'}) \, \Delta_s(k')/\epsilon_1(k'). \quad \text{(A.11)}$$

When $T \neq 0$ the summation over ω_n' gives an extra factor $\tanh\,(\epsilon(k')/2T)$ (see[21]):

$$\Delta_s(k) = -\frac{1}{2\,(2\pi)^3} \int dk' \Gamma_{ss;\,ss}^k (\xi_k, \, \xi_{k'}) \, \Delta_s(k') \, \mathrm{th}\,(\epsilon_1(k')/2T)/\epsilon_1(k'). \quad \text{(A.12)}$$

If both $\Delta_s \neq 0$ and $\Delta_d \neq 0$, then we obtain for Δ_s and Δ_d the system of equations (25) (see Fig. 4).

For simplicity, we have considered above a model of free s-electrons and strongly bound d-electrons. If we know the expressions for all the Coulomb matrix elements, we obviously can readily obtain a solution of the equations of Fig. 6, and then of the equations of Fig. 4 in the general case.

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Translated by J. G. Adashko