

THE PROBLEM OF HIGH-TEMPERATURE SUPERCONDUCTIVITY. II

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IS it possible to create superconductors with a "high" critical temperature  $T_c \gtrsim 80$  to  $300^\circ\text{K}$ ? To obtain an answer to this question is not only exceptionally important for technology, but it is also very interesting from a physical point of view. The state of the problem of high-temperature superconductivity up to the beginning of the year 1968 has already been elucidated in the article<sup>[1]</sup>. During the two years which have elapsed since then no decisive events have occurred—the possibility of the existence of high-temperature superconductors has not been proved, and it has not been disproved. At the same time the approach to this problem and its discussion has lately become more serious and careful. In particular, in the fall of 1969 the question of high-temperature superconductivity was discussed at two international conferences held in the USA. Thus, at a conference on superconductivity at Stanford (August 26-29) one plenary session was entirely devoted to high-temperature superconductivity. Then there was a symposium in Honolulu from the 5-th to the 9-th of September which was devoted to physical and chemical problems of "organic superconductors" (here high-temperature superconductivity was actually considered). Participation in these conferences (the corresponding Proceedings will be published<sup>[2,3]</sup>) and also acquaintance with new work have stimulated the author to write the present article. One can hope that the special timeliness of the theme justifies the appearance of this article, in spite of the fact that we cannot answer many questions, and the discussion is basically qualitative in nature.

1. This is not the place to review the theory of superconductivity (see<sup>[4-7]</sup>), but nevertheless let us begin with several general remarks pertaining to the nature of the superconducting state and the dependence of the critical temperature  $T_c$  on different parameters.

For the occurrence of superconductivity of electrons in a metal it is necessary that near the Fermi surface the conduction electrons must attract one another. As a result of such an attraction the Fermi distribution for particles (quasiparticles) existing in the normal state turns out to be unstable. The point is that in the presence of an attractive interaction, it is "more favorable" for the particles near the Fermi surface to be bound in pairs, which undergo a process somewhat analogous to Bose-Einstein condensation. In other words, a gap appears in the energy spectrum of the system whose width depends on the temperature and is a maximum for  $T = 0$ . In order to break a pair with the creation of two quasiparticles, it is necessary to expend an amount of energy not less than  $2\Delta(T)$ , where  $\Delta(T)$  is the minimum energy of a single quasiparticle. The critical temperature  $T_c$  is determined from the condition  $\Delta(T_c) = 0$ , and in the cases\* discussed below it is proportional to the maximum width of the gap,  $\Delta(0)$ .

\*In particular, we shall not be concerned with gapless superconductivity (see [6], Chapter VIII).

Within the framework of the expounded ideas about the nature of superconductivity which are well-known at the present time, one can already conclude that the value of  $T_c$  is determined by the form of a certain dimensionless "interaction function"  $U(\xi, \xi')$ . This function, which in the simplest case only depends on the difference  $\xi - \xi'$ , is a measure of the interaction energy between the electrons, where attraction corresponds to a minus sign. The arguments  $\xi$  and  $\xi'$  are the energies of the interacting electrons reckoned from the Fermi surface, which is assumed to be spherical (the isotropic case); as is well known  $\xi = v_F(p - p_F)$  where  $v_F$  and  $p_F = \hbar q_F = mv_F$  are, respectively, the velocity and momentum at the Fermi boundary (it is assumed that  $\xi \ll E_F = p_F^2/2m$ ). As has been stated, for the appearance of superconductivity it is necessary that near the Fermi surface, i.e., in the appropriate range of values of the variable  $\hbar\omega = \xi - \xi'$  the condition  $U(\omega) < 0$  should be satisfied (see below for a more precise condition; here and in what follows we usually assume that  $U = U(\xi - \xi')$ ).

In order to obtain a specific expression for  $T_c$  it is necessary, of course, to specify the form of the function  $U(\omega)$ . In the original version of the Bardeen-Cooper-Schrieffer theory (BCS) it was assumed that (see below for more details—especially the passage from Eq. (15) to Eq. (16))

$$U(\omega) = U(0) = -N(0)V = \text{const}, \quad -\omega_c < \omega < \omega_c, \\ U(\omega) = 0, \quad |\omega| > \omega_c. \tag{1}$$

In this case (provided that  $N(0)V \ll 1$ )

$$T_c = (\gamma/\pi k) \Delta(0) = (2\gamma/\pi) (\hbar\omega_c/k) e^{-1/N(0)V} = 1.14 (\hbar\omega_c/k) e^{-1.718/N(0)V}. \tag{2}$$

where  $\gamma = e^C = 1.781 \dots$  ( $C = 0.577$  is Euler's constant) and  $k$  is the Boltzmann constant; the exact meaning of the function  $U(\omega)$  and the advisability of writing it in the form  $U = -N(0)V$  will be clear from what follows.

The approximation of the function  $U(\omega)$  by a rectangular potential "well" (see Eq. (1) and Fig. 1a) can be justified only provided that a similar result is obtained for an analogous "well" but with rounded edges (see Fig. 1b). The latter actually holds—for the well shown in Fig. 1b one obtains a formula of the BCS type

$$T_c = 0.625 \omega_c, \tag{3}$$

where here the approximation of weak coupling is being

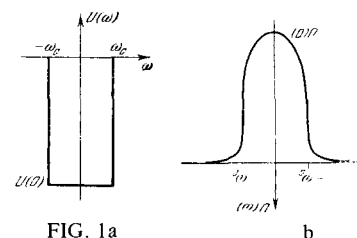


FIG. 1a b

used

$$g \ll 1. \quad (4)$$

In formula (3) the parameter  $\Theta$  characterizes the width of the "well", i.e., the region of attraction for particles near the Fermi surface; the parameter  $g$  is a measure of the strength of the attraction or, in other words, it corresponds to the depth of the well (in the model described by Eqs. (1) it is obvious that  $\Theta = 1.14 \hbar \omega_c / k$  and  $g = N(0)V$ ).

First of all, one can formulate the problem of high-temperature superconductivity (and it appears to us to be convenient to do so) within the framework of the ideas of the BCS theory and formula (3) corresponding to it. Such an approach was used in article<sup>[1]</sup>, and for convenience the corresponding considerations will now be briefly repeated.

Under conditions when the attraction between the electrons is due to their interaction with the lattice vibrations (i.e., with the phonons), the frequency  $\omega_c$  in Eq. (1) is of the order of the highest phonon frequency  $\omega_{ph} \sim k\Theta_D/\hbar$ , where  $\Theta_D$  is the Debye temperature. By the same token it is clear that for the phonon mechanism of superconductivity (the attraction between the electrons is due to their interaction with phonons or, more specifically, is a result of an exchange of phonons) in the BCS formula (3)

$$\Theta \sim \Theta_D \quad (\text{phonon mechanism of superconductivity}). \quad (5)$$

The Debye temperature  $\Theta_D$  usually does not exceed a few hundred degrees. By the same token it becomes clear that for phonon superconductivity, especially in the weak-coupling approximation (4), the values of  $T_c$  should not exceed a few tens of degrees (at present the known values of  $T_c$  do not exceed 21°K). In order to obtain more accurate estimates of  $T_c$  it is necessary to go outside the framework of the original BCS theory, to take into consideration the specific nature of the spectrum, to reject the limitation (4) of weak coupling, etc. All of this has recently been done (although also involving the use of a series of approximations)<sup>[2,8-10]</sup>, and it confirms the conclusion that for the phonon mechanism of superconductivity in general

$$T_c \lesssim 40^\circ\text{K} \quad (\text{phonon mechanism of superconductivity}). \quad (6)$$

To be sure, the estimate (6) remains somewhat conditional, since it is based on an examination of metals with known parameters and cannot be applied directly to all hypothetical cases. The latter is already clear in the example of the calculations for metallic hydrogen, leading to values  $T_c \sim 30$  to  $300^\circ\text{K}$  (see below, and also<sup>[11]</sup> and the literature cited there; we note that for metallic hydrogen  $\Theta_D \approx 3.5 \times 10^3^\circ\text{K}$  and, consequently, in this case one also has  $T_c \ll \Theta_D$ ). Nevertheless, in accordance with what has been said one can regard the existence of restrictions of the type (6) as sufficiently reliably established since metallic hydrogen and its possible alloys possessing conjectured high values of  $T_c$  are a well-known exception; in addition, it is probable that they exist in a stable state only under very high pressures.

Comparing the estimate (6) with the maximal value  $T_c \approx 21^\circ\text{K}$  which has been achieved, one can assume that the possibilities of the phonon mechanism have

still not been exhausted. At the same time, even the development of materials having a critical temperature  $T_c \approx 25$  to  $30^\circ\text{K}$  would probably be of great practical value—it would permit one to widely use liquid hydrogen in place of the more expensive and less-available liquid helium (stockpiles of hydrogen are practically unlimited; helium, however, is far from being available everywhere).\* By the same token there is no doubt of the appropriateness of a further search for superconductors with higher values of  $T_c$  along the traditional path of obtaining new compounds and alloys.<sup>[12]</sup> But, on the other hand, in this way and moreover within the framework of using only a phonon mechanism besides, it is rather difficult to expect to actually create high-temperature superconductors with  $T_c \gtrsim 80^\circ\text{K}$ .

If we confine our attention to a very general formulation, then in order to create high-temperature superconductors at the present time we can indicate only one path—the use of an exciton mechanism of superconductivity. Here and in what follows, by excitons we mean excitons of the electron type, i.e., excitations (waves, quasiparticles) which are basically associated with the motion of electrons (for more details see<sup>[1,13-15]</sup>). Energies  $\hbar\Omega_e \sim 1$  to  $10$  eV are characteristic for such excitons, which correspond to a temperature  $\Theta_e = \hbar\Omega_e/k \sim 10^4$  to  $10^5^\circ\text{K}$ . If the attraction between the conduction electrons is due to an exchange of excitons (instead of phonon exchange), then within the framework of the BCS theory (see (1)) the maximum frequency  $\omega \sim \Omega_e$  and in formula (3)

$$\Theta \sim \Theta_e = \hbar\Omega_e/k \quad (\text{exciton mechanism of super conductivity}). \quad (7)$$

From here one can arrive at a high critical temperature even under the weak-coupling conditions (4). For example, for  $\Theta_e = 10^4$  and  $g = 1/4$  (such values of  $g$  are quite reasonable for a phonon mechanism) according to formula (3)  $T_c = 180^\circ\text{K}$ .

Thus, a high critical temperature can be reached within the framework of the BCS model provided that a selection of parameters of the following type can be realized:

$$\Theta_e = \hbar\Omega_e/k \sim 10^4^\circ\text{K}, \quad g \gtrsim 1/5 \text{---} 1/4. \quad (8)$$

To answer the question about the admissibility of values of the type (8) is more difficult since the BCS model itself, being based on the approximation (1) or even on a somewhat more general approximation (see Fig. 1b and formula (3)), is extremely schematic and incomplete in two respects. In the first place, within its framework the dependence of  $T_c$  on the form of the function  $U(\omega)$  remains an open question, and also the exact meaning of this function remains an open question. In the second place the relation between the function  $U(\omega)$  and the characteristics of the metal such as the phonon or exciton spectra, electron concentration, etc. remain unexplained. Specifically, in the case of an exciton mechanism the use of the BCS approximation (1) is equivalent to an assumption about the presence of an effective attrac-

\*Under atmospheric pressure liquid hydrogen boils at  $T_b = 20.3^\circ\text{K}$  and melts at  $T_m = 14.0^\circ\text{K}$ . It is not convenient to use liquid hydrogen as a coolant for  $T < T_b$ , owing to the need to operate under reduced pressure and the associated increased danger of the formation of a detonating mixture.

tion between the electrons within all of an extremely wide band near the Fermi boundary (the width of the band,  $2\hbar\omega_c \sim 2\hbar\Omega_e$ , is of the order of one or even several electron volts). Is such an assumption permissible? Such a question is more urgent since in article<sup>[16]</sup> a conclusion was reached about the non-effective nature of the exciton mechanism just as a result of a more detailed, one would think, consideration of the interaction between electrons for all frequencies  $\omega \lesssim \Omega_e$ .

In order to clarify the dependence of  $T_c$  on the nature of the interaction between electrons it is necessary to dwell in more detail on certain aspects of the theory of superconductivity. In this connection, on the one hand even a very concise account, not containing any proofs, turns out to be cumbersome and possibly difficult to understand for a number of readers. On the other hand, in general the results are simple and for an extremely broad number of cases reduce in considerable measure to establishing the feasibility of using the BCS approximation for a series of qualitative discussions and for estimates of  $T_c$ .

Taking what has been said into account, the following discussion is constructed in such a way that the reader may, according to his wishes, only skim or even omit Secs. 2 and 3 of the article which follow below. Moreover, a recapitulation is given at the beginning of Sec. 4—this briefly states the basic conclusions which we have reached in Secs. 2 and 3.

2.\* Let us consider two electrons with momenta  $\mathbf{p}$  and  $-\mathbf{p}$ , respectively, which are found near the Fermi surface. As a result of the interaction (collisions) the momenta of the electrons change and take certain values  $\mathbf{p}' = \mathbf{p} - \hbar\mathbf{q}$  and  $-\mathbf{p}' = -\mathbf{p} + \hbar\mathbf{q}$ . The matrix element of the interaction energy  $V(\mathbf{p}, \mathbf{p}')$  is a measure of the interaction (collision probability). In the case of the Coulomb interaction of electrons in vacuum  $V(\mathbf{p}, \mathbf{p}') = 4\pi e^2/q^2$ . The presence of other electrons and a lattice modifies the interaction, and it generally becomes anisotropic and inelastic. Assuming, nevertheless, the interaction to be isotropic, independent of the position of the electrons (homogeneity), and effective only near the Fermi surface, one can set

$$V(\mathbf{p}, \mathbf{p}') = V(\omega, q), \quad \hbar\mathbf{q} = \mathbf{p} - \mathbf{p}', \quad \hbar\omega = \xi - \xi', \quad \xi = v_F(p - p_F).$$

Under such conditions it is convenient to write  $V$  in the form

$$V(\omega, q) = 4\pi e^2/q^2 \epsilon_{\text{eff}}(\omega, q). \tag{9}$$

As long as the meaning of the function  $\epsilon_{\text{eff}}(\omega, q)$  is not disclosed, expression (9) only represents a convenient form of notation since the interaction of electrons in vacuum corresponds to the value  $\epsilon_{\text{eff}} = 1$ . Further, the potential  $\varphi$  of the electric field created by charges with a density  $\rho$  in a medium with a dielectric constant  $\epsilon(\omega)$  obeys the equation  $\nabla^2\varphi = -4\pi\rho(\omega)/\epsilon(\omega)$ . However, if spatial dispersion also exists then for the Fourier com-

ponents  $\varphi(\omega, \mathbf{q})$  and  $\rho(\omega, \mathbf{q})$  we have the relation  $\varphi(\omega, \mathbf{q})$  and  $\rho(\omega, \mathbf{q})$  have the relation  $\varphi(\omega, \mathbf{q}) = 4\pi\rho(\omega, \mathbf{q})/q^2\epsilon(\omega, \mathbf{q})$ ; here  $\epsilon(\omega, \mathbf{q})$  is the dielectric constant connecting the electric displacement  $\mathbf{D} = \epsilon\mathbf{E}$  in the medium and the longitudinal electric field of the type  $\mathbf{E} = \mathbf{E}_0 \exp i(\mathbf{q} \cdot \mathbf{r} - \omega t)$ ,  $\mathbf{E}_0 = \mathbf{E}_0\mathbf{q}/q$ . If the difference between the macroscopic field and the actual (effective) field is neglected (see, for example,<sup>[17]</sup> Sec. 28), and also if the influence of the static periodic field on the motion of the electrons in a metal<sup>[18]</sup> is not taken into account, then the interaction energy between two electrons is given by expression (9) with  $\epsilon_{\text{eff}} = \epsilon(\omega, \mathbf{q})$ . Thus, the dielectric constant  $\epsilon(\omega, \mathbf{q})$  appears in a certain approximation in (9), and this makes the meaning of the quantity  $V(\omega, q)$  clearer and more familiar.

In what follows the fundamental problem of calculating the dielectric constant  $\epsilon_{\text{eff}}(\omega, \mathbf{q})$  on the basis of data concerning the structure of a metal, the composition of the atoms forming it, etc. will not actually be discussed. Instead of this, only simple model expressions for  $\epsilon_{\text{eff}}(\omega, \mathbf{q})$  will be used for the purpose of establishing the dependence of the temperature  $T_c$  on the form of the function  $\epsilon_{\text{eff}}(\omega, \mathbf{q})$ . Within the framework of such a treatment (it is obvious that this treatment is, by its very nature, extremely limited) the question of the distinction between  $\epsilon_{\text{eff}}$  and  $\epsilon$  does not have any particular significance, and below for simplicity we shall write expression (9) in the form

$$V(\omega, q) = 4\pi e^2/q^2 \epsilon(\omega, q). \tag{9a}$$

The quantity described by expressions (9) and (9a) is, so to speak, the initial interaction. The interaction function  $U$  appearing above is obtained from  $V$  as the result of a series of operations and, in particular, as a result of averaging over the Fermi surface. In the simplest case, which is widely used in the literature,<sup>[4-6,16,19,20]</sup> the function  $U$  is simply the averaged value\*  $\bar{V}(\omega, \mathbf{q}) \equiv \bar{V}$  multiplied by the density of states  $N(0)$  at the Fermi surface, where

$$N(0) = (1/2)(dn/dE)_{E_F} = m q_F / 2\pi^2 \hbar^2, \tag{10}$$

$$n = q_F^3 / 3\pi^2, \quad E_F = \hbar^2 q_F^2 / 2m, \quad p_F = \hbar q_F = mv_F.$$

Thus, in the approximation being discussed just now

$$U = U_0(\omega) = N(0) \bar{V} = \alpha \int_{\omega/v_F}^{2q_F} \frac{dq}{q\epsilon(\omega, q)}, \tag{11}$$

where  $\hbar\omega = \xi - \xi'$  and the parameter  $\alpha$  for a free electron gas (see Eq. (10)) can be expressed in terms of the electron concentration  $n$ :

$$\alpha = e^2/\pi\hbar v_F = e^2 m / \pi \hbar^2 q_F = e^2 m / (3\pi^2)^{1/3} \pi \hbar^2 n^{1/3}. \tag{12}$$

The parameter  $\alpha$  has the meaning of the ratio (to within a small numerical factor) of the average energy  $e^2/\bar{r} = e^2 n^{-1/3}$  of the Coulomb interaction between the electrons to their kinetic energy at the Fermi surface,  $E_F = \hbar^2 q_F^2 / 2m = (3\pi^2)^{2/3} \hbar^2 n^{2/3} / 2m$ . In ordinary metals  $\alpha \sim 1$ , and in strongly compressed matter  $\alpha \ll 1$ .

\*In writing Secs. 2 and 3, the author has extensively made use of advice from D. A. Kirzhnits and the results of his article<sup>[20]</sup>, and also the results of the article by D. A. Kirzhnits, E. G. Maksimov, and D. I. Khomskii.<sup>[22]</sup> I wish to take this opportunity to express my gratitude to D. A. Kirzhnits, E. G. Maksimov, and D. I. Khomskii for discussions and to L. V. Keldysh for comments made upon reading the manuscript.

\*The topic of discussion is the average value

$$\bar{V} = \frac{1}{2} \int_{-1}^{+1} \frac{4\pi e^2 d \cos \theta}{q^2 \epsilon(\omega, \eta)} \approx \frac{\int_{\frac{p-p'}{\hbar}}^{\frac{p+p'}{\hbar}} \frac{4\pi e^2 dq^2}{4q_F^2 q^2 \epsilon(\omega, \eta)}}{\int_{\frac{p-p'}{\hbar}}^{\frac{p+p'}{\hbar}} \frac{dq}{q_F}} = \frac{2\pi e^2}{q_F^2} \int_{\omega/v_F}^{2q_F} \frac{dq}{q\epsilon(\omega, q)},$$

$$\hbar^2 q^2 = p^2 + p'^2 - 2pp' \cos \theta, \quad q_{\min} = (p - p')/\hbar = \omega/v_F, \quad q_{\max} = 2q_F$$

With the appearance of superconductivity, a gap  $\Delta$  appears in the spectrum of the electrons (of their excitations), where the energy of an electron is given by

$$\epsilon = \sqrt{\Delta^2(\xi, T) + \xi^2}, \quad \xi = v_F(p - p_F). \quad (13)$$

The equation which determines the gap  $\Delta(\xi, T)$  is fundamental in the microscopic theory of superconductivity. In case (11) this equation has the form<sup>[19,20]</sup>

$$\Delta(\xi, T) = -\frac{1}{2} \int_{-\infty}^{+\infty} U_0(\xi - \xi') \Delta(\xi', T) \frac{\text{th} \left[ \frac{\sqrt{\Delta^2(\xi', T) + (\xi')^2} / 2kT}{\sqrt{\Delta^2(\xi', T) + (\xi')^2}} \right]}{\sqrt{\Delta^2(\xi', T) + (\xi')^2}} d\xi'. \quad (14)$$

The critical temperature  $T_C$  is determined from (14) as the condition for the appearance of a nontrivial solution for  $\Delta$ . Since  $\Delta(\xi, T_C) = 0$  the equation

$$\Delta(\xi, T) = -\frac{1}{2} \int_{-\infty}^{+\infty} U_0(\xi - \xi') \Delta(\xi', T) \frac{\text{th}(\xi' / 2kT_C)}{\xi'} d\xi'. \quad (15)$$

serves for the determination of  $T_C$ . In order to obtain the BCS formula (2), in Eqs. (14) and (15) it is necessary to use the BCS approximation (1) for the function  $U_0$ . In this approximation the gap  $\Delta$  for  $\xi, \xi' < \hbar \omega_C$  turns out to be independent of  $\xi$  (this is confirmed by the result), and therefore the widely known equations for  $\Delta(0) = \Delta(\xi, T = 0) = \Delta(\xi = 0, T = 0)$  and for the temperature  $T_C$  at which  $\Delta(T_C) = 0$  are immediately obtained from Eqs. (14) and (15):

$$\Delta(0) = \frac{1}{2} N(0) V \int_{-\hbar\omega_C}^{\hbar\omega_C} \Delta(0) \frac{d\xi'}{\sqrt{\Delta^2(0) + (\xi')^2}}; \quad N(0) V \int_0^{\hbar\omega_C} \frac{d\xi'}{\xi'} \text{th} \left( \frac{\xi'}{2kT_C} \right) = 1. \quad (16)$$

Formula (2) is obtained from (16) by elementary methods (more precisely, a somewhat more general result is obtained which goes over into (2) in the weak-coupling approximation,  $N(0)V \ll 1$ ; see<sup>[4-7]</sup>).

If certain plausible expressions are given for the dielectric constant  $\epsilon(\omega, q)$  and then the function  $U_0(\omega)$  is calculated, then dependences are obtained which are, on the whole, quite different from the BCS approximation (1). What has been said will be illustrated below (it is sufficient to compare Fig. 1 with Figs. 4 and 6). It is precisely with this property that apprehension is connected—apprehension that the BCS approximation may not bear any relation to reality, especially in connection with the transition to the case of high-temperature superconductivity when the BCS “well” (see Fig. 1) must be regarded as very broad.

Such apprehension, however, is not warranted or at any rate the BCS approximation is much better than it may appear to be at first glance. This conclusion is not new and is first of all associated with a fact that has been known for a long time—the “suppression” of the role of Coulomb repulsion in the theory of superconductivity (see<sup>[19]</sup> and also, for example,<sup>[6]</sup>, p. 128).

The point is that the interaction  $V$ , and as a consequence also  $U$ , usually may be regarded as the sum of two terms corresponding to a screened Coulomb repulsion (the term  $V_C$ ) and a phonon or exciton attraction (the term  $V_A$ ). To a rather good approximation

$$V_c(\omega, q) = 4\pi e^2 / (q^2 + \kappa^2), \quad \omega \ll \omega_F = E_F / \hbar; \quad (17)$$

here  $\kappa$  is the screening parameter and is defined more precisely below. The independence of  $V_C$  on  $\omega$  (actually the question concerns a weak dependence so long as  $\omega < \omega_F$ ) is associated with the instantaneous nature of the Coulomb interaction and at the same time with the

rapid response of the screening for frequencies  $\omega < \omega_F$  (the screening is associated with the motion of the electrons, which traverse the average distance  $n^{-1/3} \sim q_F^{-1}$  between them during a time  $\tau_F \sim 1/v_F q_F \sim \hbar/E_F = 1/\omega_F$ ; therefore, for frequencies  $\omega \ll \omega_F$  the screening can take place during a time appreciably smaller than the period  $\tau = 2\pi/\omega$ ). As to the part  $V_A(\omega, q)$ , it corresponds to an attraction (i.e.,  $V_A < 0$ ) within a certain range of frequencies  $\omega_C \ll \omega_F$ ; at the same time the role of the interaction  $V_A$  is unimportant for  $\omega > \omega_C$ . By the same token the term  $V_A$  is qualitatively given by the BCS approximation (see Eq. (1) and Fig. 1).

By virtue of what has been said, the total interaction  $V = V_C + V_A$  corresponds to a function  $U_0$  which, to a very rough approximation, has the form (Fig. 2a)

$$\left. \begin{aligned} U_0 &= U_c + U_a = N(0) \bar{V}_c + N(0) \bar{V}_a; \\ \bar{V}_c &= C_1 > 0, \quad \omega < \omega_F; \quad \bar{V}_c = 0, \quad \omega > \omega_F; \\ \bar{V}_a &= C_2 < 0, \quad \omega < \omega_c \ll \omega_F; \quad \bar{V}_a = 0, \quad \omega > \omega_c. \end{aligned} \right\} \quad (18)$$

For  $C_1 \sim |C_2|$  the difference between the function (18) and the function (1) is radical and, for example, for  $C_1 > |C_2|$  there is no attraction at any single frequency. But in the integral equation (15) the contributions from  $U_C$  and  $U_A$  under the condition  $\omega_C \ll \omega_F$  turn out to be quite different due to the nonidentical frequency dependences of these terms (for the corresponding contributions, see<sup>[6]</sup>, pp. 128—131). Namely, the role of the Coulomb term is suppressed, and it is necessary to compare not  $U_A$  with  $U_C$ , but  $U_A$  with

$$\tilde{U}_c = U_c / [1 + U_c \ln(\omega_F/\omega_c)]. \quad (19)$$

It is obvious that for  $U_C \ln(\omega_F/\omega_C) \gg 1$  the quantity  $\tilde{U}_C \approx 1/\ln(\omega_F/\omega_C) \ll 1$ . The total effective interaction is given by

$$\left. \begin{aligned} \tilde{U}_0 &= U_a + U_c / [1 + U_c \ln(\omega_F/\omega_c)], \quad \omega < \omega_c, \\ \tilde{U}_0 &= 0, \quad \omega > \omega_c, \end{aligned} \right\} \quad (20)$$

and it may be close to  $U_a$  even for  $U_C \sim |U_A|$ , as is illustrated by Fig. 2b.

The obtained result, which above has been rather arbitrarily called the effect of the suppression of the Coulomb interaction, indicates that in the region of large frequencies (far from the Fermi surface) even a positive interaction ( $U_0(\omega) > 0$ ) is not dangerous. And what is more, superconductivity may occur even in that case when the function  $U_0(\omega)$  is everywhere positive but close to zero near the Fermi boundary (Fig. 3). Such a result<sup>[20]</sup>—the independence of  $T_C$  on the sign of the interaction function  $U_0(\omega)$  far away from the Fermi boundary—at first glance appears to be paradoxical. In fact the inequality  $V(\omega, q) > 0$  which leads to the inequality  $U_0(\omega) > 0$  means that the corresponding Fourier component of the interaction energy of two electrons corresponds to a repulsion; superconductiv-

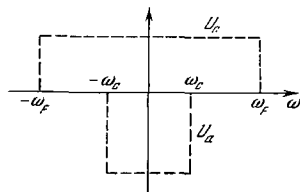


FIG. 2a

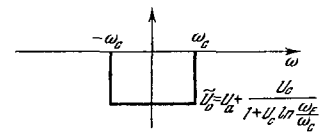


FIG. 2b

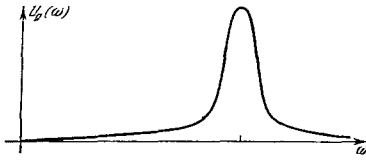


FIG. 3

ity, however, is due to an attraction between the electrons. The paradox is resolved if it is taken into consideration that in the case being discussed (Fig. 3) the electrons are attracted but not repelled. The point is that the assumption concerning the absence of any interaction at the Fermi boundary itself and in its immediate neighborhood leads to the appearance of an interaction only in the second-order approximation of perturbation theory. Under such conditions the perturbation energy for the ground state is always negative (attraction) quite independently of the sign of the perturbation  $V$  (we recall the standard formula of quantum-mechanical perturbation theory,

$$E_n^{(2)} = \sum_m \frac{|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}},$$

from which we always obtain  $E_n^{(2)} < 0$  for the ground state  $E_n^{(0)} = 0$ ). In terms of the physics one can say that for  $U(\omega = (\xi - \xi')/\hbar = 0) = 0$  in order for their interactions to appear the particles must first be virtually displaced from the Fermi boundary by a certain distance to a place where an interaction exists; only after this do the particles interact among themselves, where the interaction energy turns out to now be proportional to  $|V|^2$  and to always be negative.

Equation (15) not only correctly takes account of the effect of "suppression" of the Coulomb interaction, but a general analysis of this equation also turns out to be very fruitful. At the same time the utilization of Eqs. (14)–(15) is not always possible: for a wide class of functions  $U_0(\omega)$  it is inconsistent, and in certain other cases it leads to erroneous results. Thus, according to a general theorem for an equilibrium system  $\epsilon(\omega = 0, q) \geq 0$  (see, for example,<sup>118</sup>). But this means that the function  $U_0(\omega)$ , defined according to Eq. (11), cannot be negative at  $\omega = 0$ ; meanwhile for the BCS approximation (1) one has just  $U_0(0) < 0$ . On the other hand for functions  $U_0(\omega)$  of a more complicated type, for example, having a resonance character (see Fig. 4 and Fig. 6), the utilization of Eq. (15) not only turns out to be inconsistent but it may also lead to incorrect results. This is indicated by a detailed derivation<sup>17,21,22</sup> of the equation for the superconducting gap  $\Delta(\xi, T)$ , taking into consideration the frequency and spatial dispersion (i.e., the dependence of  $\epsilon$  on  $\omega$  and  $q$ ), and also taking damping into account (the presence of an imaginary part in  $\epsilon$ ).

At the present stage the most exact theory of superconductivity, which is expounded and used in the articles<sup>18-10,21,22</sup> and in the book<sup>17</sup>, is extremely complicated and cumbersome. Here there is not any possibility to dwell on this theory in any amount of detail, and we shall limit ourselves to only a few remarks.

One can see the main result of the theory in the fact that the superconducting gap  $\Delta(\xi, T)$  and the temperature  $T_C$  are not determined by the quantity

$V = 4\pi e^2/q^2 \epsilon(\omega, q)$  (or, what is the same thing, by the dielectric constant  $\epsilon(\omega, q)$ ), but by some other function  $V_{\text{eff}}(\omega, q)$ . What has been said holds in spite of the fact that the question involves the isotropic and homogeneous approximation, when the scattering of electrons on one another is exactly described by the matrix element  $V(\omega, q)$ .

With the aid of dispersion relations (see, for example,<sup>17,14,18</sup>) the real and imaginary parts of  $\epsilon$  or  $1/\epsilon$  can be expressed one in terms of the other. In particular,

$$\text{Re} \left[ \frac{1}{\epsilon(\omega, q)} \right] = 1 + \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} \frac{\text{Im} [1/\epsilon(\omega', q)] d\omega'}{\omega' - \omega} = 1 + \frac{2}{\pi} \mathcal{P} \int_0^{\infty} \frac{\omega' \text{Im} [1/\epsilon(\omega', q)] d\omega'}{\omega'^2 - \omega^2}, \quad (21)$$

where the symbol  $\mathcal{P}$  means that the integral is to be evaluated in the sense of a principal value, and the conversion to an integration from 0 to  $\infty$  is possible by virtue of an assumption about the validity of the condition  $\epsilon(\omega, q) = \epsilon^*(-\omega, q)$ . As it turns out the quantity  $V_{\text{eff}}$  which appears in the theory in place of  $V$  has the form\*

$$V_{\text{eff}}(\omega, q) = \frac{4\pi e^2}{q^2} \left( 1 - 2 \int_0^{\infty} \frac{\rho(\omega', q) d\omega'}{\omega + \omega'} \right), \quad \rho(\omega, q) = -\frac{1}{\pi} \text{Im} \left[ \frac{1}{\epsilon(\omega, q)} \right]. \quad (22)$$

For an equilibrium system the function  $\rho \geq 0$  (the function  $\rho$  is proportional to the electrical conductivity or to a quantity equivalent to it). Taking into consideration the fact that

$$\frac{1}{\omega'^2 - \omega^2} = \frac{1}{2\omega'} \left( \frac{1}{\omega - \omega'} - \frac{1}{\omega + \omega'} \right),$$

from (21) and (22) we arrive at the following conclusion: not  $\text{Re}(1/\epsilon)$  and not  $1/\epsilon$  but the nonresonant quantity

$$\text{Re} \left( \frac{1}{\epsilon} \right) - \int \frac{\rho d\omega'}{\omega - \omega'} - \int \frac{\rho d\omega'}{\omega + \omega'} = 1 - 2 \int \frac{\rho d\omega'}{\omega + \omega'}$$

enters into  $V_{\text{eff}}$ .

The replacement of  $V$  by  $V_{\text{eff}}$  in the equations of the theory of superconductivity is associated with the fact that superconductivity does not reduce to the scattering of two electrons on each other with the exchange of excitations (it is precisely this last process which is described by the matrix element  $V = 4\pi e^2/q^2 \epsilon$ ). The following equation now serves for the determination of the critical temperature  $T_C$ :

$$\Phi(\xi) = -\frac{1}{2} \int_{-\infty}^{+\infty} U_{\text{eff}}(\xi, \xi') \Phi(\xi') \frac{\text{th}(\xi'/2kT_C)}{\xi'} d\xi', \quad (23)$$

which agrees in form with Eq. (15) but is written for the function  $\Phi$  which differs from the gap  $\Delta$  (this property is not essential for the determination of  $T_C$ ), and instead of  $U_0(\xi - \xi')$  it contains a function  $U_{\text{eff}}(\xi, \xi')$  of the two variables  $\xi$  and  $\xi'$ . In this connection

\*Formally one might say that (22) reduces to the quantity (9) with a certain value  $\epsilon_{\text{eff}}(\omega, q)$ . However, in case (9) one had in mind a change from  $\epsilon$  to  $\epsilon_{\text{eff}}$  at the expense of, for example, taking account of the difference between the effective field and the average field. Now it is assumed that the scattering of electrons is determined by the quantities (9) and (9a) where  $\epsilon$  has the usual meaning, but the superconducting gap turns out to depend on the function (22) but not on the function described by Eqs. (9) or (9a).

$$U_{\text{eff}}(\xi, \xi') = N(0) \bar{V}_{\text{eff}} = u(\xi, \xi') - 2 \int_0^{\infty} \frac{v(\xi, \xi', \omega') d\omega'}{|\xi/\hbar| + |\xi'/\hbar| + \omega'},$$

$$u(\xi, \xi') = \alpha \int_{|\xi - \xi'|/\hbar v_F}^{2q_F} \frac{dq}{q}, \quad v(\xi, \xi') = \alpha \int_{|\xi - \xi'|/\hbar v_F}^{2q_F} \rho(\omega', q) \frac{dq}{q}. \quad (24)$$

In virtue of the nearness (and in a certain sense even the identity) of Eqs. (15) and (23) the conclusion about the "suppression" of the Coulomb interaction (an interaction with a broad frequency spectrum) is also completely preserved in the exact theory. The replacement of the interaction function  $U_0(\xi - \xi')$ , which is capable of having resonances (see the following Section), by the smoothed-out function  $\tilde{U}_{\text{eff}}(\xi, \xi')$  is new. Here the function  $U_{\text{eff}}$  may be negative for  $\xi = \xi' = 0$  without violating the condition  $\epsilon(\omega, q) \geq 0$ . Any consistent calculation or even an estimate of  $T_c$  for a given dielectric constant  $\epsilon(\omega, q)$  is possible only on the basis of expressions (22)–(24).

In concluding the present section, in order to avoid confusion let us compare some of the functions introduced above in the form of a Table (the function  $\tilde{U}_{\text{eff}}$ , which is used below, is also cited):

Function	Formula	Explanation
$V(\omega, q) = \frac{4\pi e^2}{q^2 \epsilon(\omega, q)}$	(9a), (9)	Determines the scattering of two electrons exchanging momentum $\hbar q$ and energy $\hbar \omega = \xi - \xi'$ .
$U_0(\omega) = N(0) \bar{V}$	(11)	This quantity is equal to the product of the density of states $N(0)$ times the average (with respect to $q$ ) value $\bar{V}$ of the function $V(\omega, q)$ . It appears in Eqs. (14) and (15).
$\tilde{U}_0(\omega)$	(20)	An approximation of the function $U_0(\omega)$ , taking into account the effect of suppression of the Coulomb interaction.
$V_{\text{eff}}(\omega, q)$	(22)	The effective interaction appearing in a consistent theory of superconductivity.
$U_{\text{eff}}(\xi, \xi') = N(0) \bar{V}_{\text{eff}}$	(24)	The interaction function appearing in the integral equation (23), which serves for the determination of $T_c$ . It is the analog of the function $U_0(\omega)$ .
$\tilde{U}_{\text{eff}}(\xi, \xi')$	(31)	An approximation of the function $U_{\text{eff}}(\xi, \xi')$ . It is an analog of the function $\tilde{U}_0(\omega)$ appearing in the approximate theory.

All of the interaction functions  $U_0$ ,  $\tilde{U}_0$ ,  $U_{\text{eff}}$ , and  $\tilde{U}_{\text{eff}}$  determine the critical temperature  $T_c$  with the aid, in fact, of one and the same integral equation (see Eqs. (15), (23), and (31)). The transition from  $U_0$  to  $\tilde{U}_0$  or from  $U_{\text{eff}}$  to  $\tilde{U}_{\text{eff}}$  corresponds to taking account of the effect of suppression of the Coulomb interaction by means of replacing the integration up to the frequency  $\omega_F$  by an integration up to a certain frequency  $\omega_c \ll \omega_F$  (see Eqs. (20) and (31) and the explanations given for these formulas). Finally, the difference between  $U_0$  and  $U_{\text{eff}}$  consists in the fact that they are expressed in a different way in terms of the longitudinal dielectric constant  $\epsilon(\omega, q)$  which, in the approximation discussed by us (isotropy, homogeneity) determines the initial interaction between the electrons. In those cases when the interaction function  $U(\omega)$  is given "by hand", as was done in the original BCS theory and in a whole number of subsequent articles, it is obvious that the question of the difference between  $U_0$  and  $U_{\text{eff}}$  does not arise.

3. In the theory of superconductivity, the "jellium" model is quite often used in the form of an example;<sup>[16, 18, 20, 22]</sup> in this model

$$\epsilon(\omega, q) = 1 + (\kappa^2/q^2) - (\omega_i^2/\omega^2); \quad (25)$$

here  $\omega_i = \sqrt{4\pi e^2 Z^2 n_i/M} \approx \sqrt{4\pi e^2 Z n/M}$  is the plasma frequency for the ions (the charge of an ion is  $eZ$ , the ion mass is  $M$ , the concentration of ions  $n_i$ , and the concentration of electrons  $n = Zn_i$ ) and  $\kappa^2 = 6\pi e^2 n/E_F = 4e^2 m q_F / \pi \hbar^2$  ( $1/\kappa$  denotes the screening radius).

Expression (25) is valid only for  $\omega \ll qv_F$  and upon neglect of damping (for a more general expression, see<sup>[18, 22]</sup>). For the "jellium" model described by Eq. (25) one has

$$V(\omega, q) = \frac{4\pi e^2}{q^2 \epsilon(\omega, q)} = \frac{4\pi e^2}{q^2 + \kappa^2} \left( 1 + \frac{\omega_q^2}{\omega^2 - \omega_q^2} \right), \quad (26)$$

where  $\omega_q$  denotes the frequency of the longitudinal waves which can be propagated in a medium with dielectric constant (25); as is well known the frequency of the longitudinal waves satisfies the condition  $\epsilon(\omega_q, q) = 0$ , and therefore

$$\omega_q^2 = \omega_i^2 q^2 / (q^2 + \kappa^2), \quad \epsilon(\omega_q, q) = 0. \quad (27)$$

Substituting (26) into (11) we obtain the "interaction function"

$$U_0(v) = \frac{\alpha}{2(1-v^2)^2} \ln \left| 1 + \frac{1}{\alpha} \left( 1 - \frac{1}{v^2} \right) \right|,$$

$$v^2 = \frac{\omega^2}{\omega_q^2}, \quad \alpha = \frac{r^2}{\pi \hbar v_F}. \quad (28)$$

A graph of the function (28) is shown in Fig. 4. For the "jellium" model it is obvious that  $U_0(0) = 0$ . In the case of weak coupling,  $\alpha \ll 1$ , a calculation based on Eq. (15) leads to the result<sup>[20]</sup>

$$T_c = \frac{\gamma}{\pi} \alpha \frac{\hbar \omega_i}{k} \exp \left( -\frac{8}{\pi^2 \alpha} + \frac{3}{2} - \frac{\pi^2}{6} \right) \sim \alpha \frac{\hbar \omega_i}{k} \exp \left( -\frac{8}{\pi^2 \alpha} \right). \quad (29)$$

The function  $U_{\text{eff}}(\xi, \xi')$ , determined according to Eq. (24) for the "jellium" model, has the form

$$U_{\text{eff}}(\xi, \xi') = \frac{\alpha}{2} \ln \left( \frac{1}{\alpha} \right) \frac{v + v'}{1 + v + v'}, \quad v = \frac{|\xi|}{\hbar \omega_i}, \quad v' = \frac{|\xi'|}{\hbar \omega_i}. \quad (30)$$

It is characteristic that whereas the function  $U_0(\omega)$  possesses a resonance (see Fig. 4) the function  $U_{\text{eff}}(\xi, \xi')$  smoothly depends on its arguments. It is obvious that this fact is a consequence of the already noted property—expressions (22) and (24) only depend on the nonresonant part of the function  $1/\epsilon$ . Investigation of Eq. (23) reveals the effect of suppression of the interaction for large values of  $\xi$  (this would also be expected in connection with the relationship between Eqs. (15) and (23)). Formally this "suppression" reduces to the fact that Eq. (23) is replaced by the following:

$$\Phi(\xi) = -\frac{1}{2} \int_0^{\xi_0} \tilde{U}_{\text{eff}}(\xi, \xi') \Phi(\xi') \frac{\text{th}(\xi'/2kT_c)}{\xi'} d\xi', \quad (31)$$

where

$$\tilde{U}_{\text{eff}}(\xi, \xi') = U_{\text{eff}}^{(s)}(\xi, \xi') - \frac{U_{\text{eff}}^{(s)}(\xi, \xi_0) U_{\text{eff}}^{(s)}(\xi_0, \xi') \ln(E_F/\xi_0)}{1 + U_{\text{eff}}^{(s)}(\xi_0, \xi_0) \ln(E_F/\xi_0)},$$

$$U_{\text{eff}}^{(s)}(\xi, \xi') = \frac{U_{\text{eff}}(\xi, \xi') + U_{\text{eff}}(\xi, -\xi')}{2}.$$

In connection with the change from (23) to (31) it is assumed that the rapidly changing part  $U_{\text{eff}}$  (if it exists) is concentrated in the range of values  $\xi \leq \xi_0$ , but then  $U_{\text{eff}}$  changes slowly in the region between  $\xi_0$  and the Fermi energy  $E_F \gg \xi_0$  (more precisely, an energy  $\xi \sim E_F$  occurs instead of  $E_F$ , but within the framework

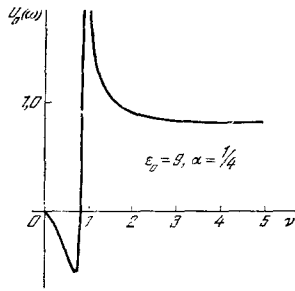


FIG. 4

of the accuracy being used this is not important). It is obvious that the function  $\tilde{U}_{\text{eff}}$  plays the role of the function  $\tilde{U}_0$  used in Sec. 2 (see Eq. (20)); in accordance with what was asserted in (31) the integration is carried out up to  $\xi_0$ , which is equivalent to an integration up to  $\infty$  with  $\tilde{U}_{\text{eff}} = 0$  for  $\xi' > \xi_0$ .

For "jellium"  $\xi_0 \sim \hbar\omega_i$  and the function  $\tilde{U}_{\text{eff}}$  has the form

$$\tilde{U}_{\text{eff}}(v, v') = -\frac{\alpha}{2} \ln\left(\frac{1}{\alpha}\right) \frac{1}{1-v-v'}, \quad (32)$$

$$v = \frac{|\xi|}{\hbar\omega_i}, \quad v' = \frac{|\xi'|}{\hbar\omega_i}.$$

The functions  $U_{\text{eff}}(v, v')$  and  $\tilde{U}_{\text{eff}}(v, v')$  for "jellium" (formulas (30) and (32)) are shown in Fig. 5 for  $v = v'$  and for  $\alpha = 1/4$ . Both the difference between  $U_{\text{eff}}$  and  $\tilde{U}_{\text{eff}}$ , as well as their difference from the function  $U_0(v)$ , are striking for the same "jellium" model (see Eq. (28)). It is natural, therefore, that according to Eqs. (31) and (32) an expression is obtained for  $T_c$  which in general differs substantially from (29). Namely, for the "jellium" model characterized by Eq. (25) we finally obtain<sup>[22]</sup>

$$T_c \sim \frac{\hbar\omega_i}{k} e^{-1/g}, \quad g = \frac{[(\alpha/2) \ln(1/\alpha)]^2 \ln(E_F/\hbar\omega_i)}{1 + (\alpha/2) \ln(1/\alpha) \ln(E_F/\hbar\omega_i)}. \quad (33)$$

If

$$(\alpha/2) \ln(1/\alpha) \ln(E_F/\hbar\omega_i) = \alpha \ln(1/\alpha) \ln(M/mZ\alpha) \gg 1, \quad (34)$$

then

$$T_c \sim (\hbar\omega_i/k) e^{-2/\alpha \ln(1/\alpha)}. \quad (35)$$

Assuming  $M/mZ \sim 10^4$  we see that condition (34) may in practice be assumed to be fulfilled for  $\alpha > 1/10$  to  $1/5$ , i.e., in the region which is of most interest from the point of view of any applications (in the opposite case the temperature  $T_c$  is very small). Formula (25) is used in article<sup>[11]</sup> in order to estimate  $T_c$  for strongly compressed, completely ionized matter. According to (35) for this case

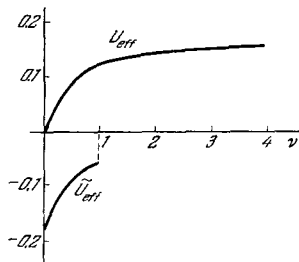


FIG. 5

$$T_c \sim 10^4 \left(\frac{Z}{A}\right) \rho^{1/2} \exp\left\{-\frac{8.7(Z/A)^{1/3} \rho^{1/3}}{\ln[4.35(Z/A)^{1/3} \rho^{1/3}]}\right\}, \quad (36)$$

where  $\rho \approx AM_p n_i$  is the density of matter in  $\text{g/cm}^3$  ( $A$  denotes the atomic weight,  $M_p$  is the proton mass) and

$$\alpha = \frac{e^2 m}{(3\pi^2)^{1/3} \pi \hbar^2 n^{1/3}} = \frac{e^2 m M_p^{1/3}}{(3\pi^2)^{1/3} \pi \hbar^2} \left(\frac{A}{Z}\right)^{1/3} \rho^{-1/3} = 0.23 \left(\frac{A}{Z}\right)^{1/3} \rho^{-1/3}.$$

For metallic hydrogen at a density of  $\rho = 1.1 \text{ g/cm}^3$ , when this phase becomes stable (see<sup>[11]</sup> and the literature cited there),  $\alpha \approx 0.23$ ,  $\omega_i \approx 10^{15}$ , and according to Eq. (36)  $T_c \sim 25^\circ \text{K}$ . However, if the calculation is based on formula (29) then for  $\rho = 1.1$  the temperature  $T_c \sim 80^\circ \text{K}$ . The feasibility of using formula (36) in order to estimate  $T_c$  in the case of metallic hydrogen for  $\rho \sim 1$  remains, of course, unclear. Probably the estimate  $T_c \sim 300^\circ \text{K}$  cited in article<sup>[65]</sup> is more reliable.

Expression (35) is found to be in agreement with the BCS formulas (2) and (3) if one sets  $\omega_c \sim \omega_i$  or  $\omega_c \sim \hbar\omega_i/k$ , and also if the value of  $\tilde{U}_{\text{eff}}$  is estimated on the basis of expression (26) with neglect of that part of it which corresponds to Coulomb repulsion (in connection with such an estimate, as we saw earlier  $\tilde{U}_{\text{eff}} \sim (-4\pi e^2/q_F^2)N(0) \sim -\alpha$ ).

Now let us turn our attention to a model which we shall call a generalized model of "jellium". In this model, which was used earlier in article<sup>[16]</sup>, the dielectric constant is given by

$$\epsilon(\omega, q) = 1 - \frac{\alpha^2}{q^2} - \frac{\omega_i^2}{\omega^2} + \frac{\Omega^2(\epsilon_0 - 1)}{\Omega^2 - \omega^2}. \quad (37)$$

Expression (37) corresponds to a situation when oscillators with an eigenfrequency  $\Omega$  are also present in the medium described by the usual "jellium" model (25); if the medium only consisted of these oscillators then its dielectric constant would be equal to

$$\epsilon_{\text{osc}}(\omega) = 1 + \frac{\Omega^2(\epsilon_0 - 1)}{\Omega^2 - \omega^2},$$

where  $\epsilon_{\text{osc}}(0) = \epsilon_0$ . It is important to emphasize that by choosing in (37) a sufficiently high electronic frequency  $\Omega \gg \omega_i$  as the quantity  $\Omega$ , we obtain exactly the model of a medium for which one can expect the appearance of high values of  $T_c$ .

In article<sup>[16]</sup> the model (37) was considered within the framework of the approximation (14) and (15), and in this connection the unfavorable conclusion was reached that for large values of  $\Omega$  one always has  $T_c < \hbar\omega_i/k$ , i.e., a high critical temperature is not attained. Such a conclusion, however, is erroneous even if we remain within the limits of the approximation (14), (15).

Substituting (37) into (11) we obtain

$$U_0(v) = \frac{\alpha \ln\left|1 + \frac{1}{\alpha} \left(1 - \frac{\omega_i^2}{\Omega^2 v^2} + \frac{\epsilon_0 - 1}{1 - v^2}\right)\right|}{2 \left(1 - \frac{\omega_i^2}{\Omega^2 v^2} + \frac{\epsilon_0 - 1}{1 - v^2}\right)}, \quad v^2 = \frac{\omega^2}{\Omega^2}. \quad (38)$$

In connection with the transition to (38), an assumption was made which amounts to using the condition  $\epsilon \Omega^2 \ll \omega_e^2$ , where  $\omega_e = \sqrt{4\pi e^2 n/m} = \sqrt{4e^2 q_F^3/3\pi m} = \sqrt{16\alpha/3} (EF/\hbar) = 5.6 \times 10^4 \sqrt{n} \text{ sec}^{-1}$  is the electron plasma frequency. In addition, we are only interested in the case when

$$\Omega^2 \gg \omega_i^2. \quad (39)$$

Upon fulfillment of the last condition one can hope to obtain a better approximation by setting  $\omega_i = 0$  in Eq. (38), i.e., by using the expression

$$U_0(\nu) \sim \frac{\alpha(1-\nu^2)}{2(\epsilon_0-\nu^2)} \ln \left| 1 + \frac{\epsilon_0-\nu^2}{\alpha(1-\nu^2)} \right|. \quad (40)$$

A graph of the function (40) is shown in Fig. 6. Provided that

$$\epsilon_0 \gg 1, \quad \alpha \ll 1, \quad (41)$$

the functions (28) and (40) practically coincide if one only replaces  $\nu$  in (38) by  $\nu' = \sqrt{\epsilon_0}\nu$ . One can see, both from this remark and also directly, that for the generalized model of "jellium" under conditions (41) the following estimate is obtained from formula (29):

$$T_c \sim \alpha \sqrt{\epsilon_0} (\hbar\Omega/k) e^{-8/\pi^2\alpha}, \quad (42)$$

$$\epsilon_0 \gg 1, \quad \alpha \ll 1.$$

A more accurate calculation, performed by D. A. Kirzhnits by starting directly from expression (38) under the condition (41) leads to formula (29) with the replacement of  $\omega_i$  by  $\sqrt{\epsilon_0}\Omega$ . By the same token, of course, the estimate (42) is verified. According to Eqs. (42), for  $\alpha\sqrt{\epsilon_0} \sim 1$  the temperature  $T_c \sim (\hbar\Omega/k)e^{-8\pi^2\alpha}$  and may be large for a sufficiently large (electronic) frequency  $\Omega$ . Therefore, the assertion made in<sup>116</sup> is disproved. It was a consequence of an incorrect solution of the integral equation (15) for the case (37).

At the same time, for the generalized model of "jellium" (37), as for the usual model of "jellium" (25), Eq. (15) with the utilization of the function  $U_0$  defined according to (11) in general cannot serve for the determination of  $T_c$  or even for an estimate of  $T_c$ . The reason for this has already been indicated—it lies in the resonant nature of the function  $U_0$  for the "jellium" model (see Eqs. (28) and (38)), which must be replaced by the "smoothed" interaction function  $U_{\text{eff}}$  (see Eq. (24)). As a result the estimate (35) is valid for the "jellium" model instead of (29), but for the generalized model of "jellium" the more exact formula

$$T_c \sim (\hbar\sqrt{\epsilon_0}\Omega/k) e^{-a/\alpha}, \quad a \sim 1. \quad (43)$$

is valid instead of (42).

Let us discuss the derivation of this formula (with a more precise definition of the constant  $a$ ) and the generalized model of "jellium" itself in somewhat more detail. First of all let us determine the spectrum of the longitudinal waves which can be propagated in a medium

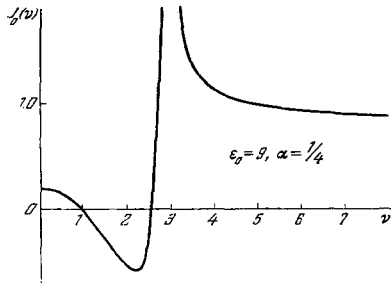


FIG. 6

with dielectric constant (37). The frequencies  $\omega_q$  of these waves are determined from the condition

$$\epsilon(\omega_q, q) = 1 + \frac{\kappa^2}{q^2} - \frac{\omega_q^2}{\omega_q^2} + \frac{\Omega^2(\epsilon_0-1)}{\Omega^2-\omega_q^2} = 0. \quad (44)$$

The solution of the dispersion equation (44) is as follows:

$$\omega_q^2 = \frac{(\epsilon_0 q^2 + \kappa^2)\Omega^2 + \omega_i^2 q^2 \pm \sqrt{[(\epsilon_0 q^2 + \kappa^2)\Omega^2 - \omega_i^2 q^2]^2 + 4(\epsilon_0-1)\omega_i^2 \Omega^2 q^4}}{2(q^2 + \kappa^2)}. \quad (45)$$

Provided that  $\Omega^2 \gg \omega_i^2$  (see Eq. (39)) we obtain two approximate solutions:

$$\omega_{q-}^2 \approx \omega_{q, ph}^2 - \frac{\omega_i^2 q^2}{\epsilon_0 q^2 + \kappa^2}, \quad (46)$$

$$\omega_{q+}^2 \approx \Omega_e^2(q) = (\epsilon_0 q^2 + \kappa^2)\Omega^2/(q^2 + \kappa^2). \quad (47)$$

Of course, the solutions (46) and (47) are obtained immediately from (44) if one seeks the frequencies  $\omega_q^2$  which are, respectively, much smaller than  $\Omega^2$  or much larger than  $\omega_i^2$ . The solution (46) represents the phonon branch of the excitation spectrum; it differs from the spectrum (27) due to the fact that for the generalized model of "jellium" at small frequencies

$$\epsilon = \epsilon_0 + (\kappa^2/q^2) - (\omega_i^2/\omega^2)$$

in contrast to expression (25). The spectrum (47) represents the spectrum of longitudinal excitons, where the values of  $q$  of interest to us lie between  $q \approx 0$  and  $q = 2q_F$  (see Eq. (24)). It is obvious that

$$\Omega_e(0) = \Omega, \quad \Omega_e(2q_F) = \sqrt{(\epsilon_0 + \alpha)/(1 + \alpha)}\Omega, \quad (48)$$

where the relation  $\kappa^2 = \alpha(2q_F)^2$  has been taken into account.

In the case (41)

$$\Omega_e(2q_F) \approx \sqrt{\epsilon_0}\Omega, \quad \epsilon_0 \gg 1, \quad \alpha \ll 1. \quad (49)$$

It is precisely the frequency  $\Omega_e(2q_F)$  of the short wavelength excitons which determines the exciton contribution to the interaction between the electrons and, specifically, the value of  $T_c$  depends on this frequency. In order to estimate  $T_c$  let us write down the interaction  $V$  for the model (37):

$$V(\omega, q) = \frac{4\pi e^2}{q^2 \epsilon} \approx \frac{4\pi e^2}{q^2 + \kappa^2} \left\{ 1 + \frac{\omega_i^2 q^2 (q^2 + \kappa^2) (\epsilon_0 q^2 + \kappa^2)^{-1}}{\omega^2 - \omega_{q, ph}^2} + \frac{(\epsilon_0 - 1)\Omega^2 q^2 (q^2 + \kappa^2)^{-1}}{\omega^2 - \Omega_e^2(q)} \right\}. \quad (50)$$

Upon averaging over angles, in order of magnitude  $\bar{V}(\omega) \sim V(\omega, 2q_F)$ ; then  $\alpha(2q_F)^2 = \kappa^2$ , and therefore for  $\alpha \ll 1$  one can replace  $(2q_F)^2 + \kappa^2$  by  $(2q_F)^2$ , which in order of magnitude is permissible even for  $\alpha < 1$ . Taking what has been said into account, one can set (see Eqs. (46) and (47))

$$\omega_{q, ph} = \omega_i / \sqrt{\epsilon_0}, \quad \Omega_e = \Omega_e(2q_F) = \sqrt{\epsilon_0}\Omega. \quad (51)$$

in the expression for  $\bar{V}$ . As a result

$$\bar{V} = \bar{V}_c \left\{ 1 + \frac{\omega_i^2/\epsilon_0^2}{\omega^2 - (\omega_i^2/\epsilon_0)} + \frac{(\epsilon_0 - 1)\Omega^2}{\omega^2 - \epsilon_0\Omega^2} \right\}; \quad (52)$$

here  $\bar{V}_c$  is the value of the Coulomb interaction  $\bar{V}_c = 4\pi/(q^2 + \kappa^2)$  averaged with respect to  $q$  (of course,  $\bar{V}_c \sim 4\pi e^2/q_F^2$  but since the quantity  $\bar{V}_c$  appears as a common factor, it is more convenient and more accurate to introduce  $\bar{V}_c$  as a parameter). According to the results of the theory of superconductivity indicated



earlier, one can estimate  $T_c$  by using an interaction function  $U_0$  or  $U_{\text{eff}}$  of the following form (also see Fig. 7):

$$\left. \begin{aligned} U &= U_c + U_{ph} + U_e, \quad U_c = N(0) \bar{V}_c, \quad U_{ph} = N(0) \bar{V}_{ph}, \quad U_e = N(0) \bar{V}_e; \\ \bar{V}_c &> 0 \text{ for } \omega < \omega_F; \quad \bar{V}_c = 0 \text{ for } \omega > \omega_F; \\ \bar{V}_{ph} &= -\bar{V}_c/\epsilon_0 \text{ for } \omega < \omega_{ph} = \omega_i/\sqrt{\epsilon_0}; \quad \bar{V}_{ph} = 0 \text{ for } \omega > \omega_{ph}; \\ \bar{V}_e &= -\bar{V}_c(\epsilon_0 - 1)/\epsilon_0 \text{ for } \omega < \Omega_e = \sqrt{\epsilon_0} \Omega; \quad \bar{V}_e = 0 \text{ for } \omega > \Omega_e. \end{aligned} \right\} (53)$$

These estimates turn out to be valid when  $\omega_{ph} \ll \Omega_e \ll \omega_F$ , making it possible to reach a conclusion about the "suppression" of the Coulomb interaction (see Eqs. (20) and (31)). Specifically, the solution of Eqs. (15) or (23) with the functions (53) leads to the following estimate<sup>[22]</sup>

$$\left. \begin{aligned} T_c &\sim (\hbar\omega_{ph}/k) e^{-1/g} \approx \frac{\hbar}{k} \omega_{ph} (\Omega_e/\omega_{ph})^{g_e/(g'_{ph}+g_e)} e^{-1/(g'_{ph}+g_e)}, \\ g &= |U_{ph}| + \frac{|U_c|}{1 - |U_c| \ln(\Omega_e/\omega_{ph})} - \frac{U_c}{1 + U_c \ln(\omega_F/\omega_{ph})}, \\ g'_{ph} &= g_{ph} + g_e = |U_{ph}| - \frac{U_c}{1 + U_c \ln(\omega_F/\omega_{ph})}, \quad g_e = |U_e|. \end{aligned} \right\} (54)$$

Here the last expression for  $T_c$  is obtained under the assumption that  $g'_{ph} g_e \ln(\Omega_e/\omega_{ph}) \ll g'_{ph} + g_e$ , in virtue of which

$$\frac{1}{g} = \frac{1 - g_e \ln(\Omega_e/\omega_{ph})}{g_{ph} + g_e - g_{ph} g_e \ln(\Omega_e/\omega_{ph})} \approx \frac{1 - g_e \ln(\Omega_e/\omega_{ph})}{g_{ph} + g_e}.$$

It is obvious that  $g'_{ph}$  corresponds to an effective parameter  $g$  in the BCS formula (3) for the case when the exciton interaction does not play a role. Provided that

$$g_e = \frac{\epsilon_0 - 1}{\epsilon_0} U_c \gg g'_{ph} = \left| \frac{U_c}{\epsilon_0} \right| - \frac{U_c}{1 + U_c \ln(\omega_F/\omega_{ph})} \quad (55)$$

we obtain formula (43) from (54) because  $\Omega = \sqrt{\epsilon_0} \Omega$  and  $U_c \sim N(0) \cdot 4\pi e^2/q_F^2 = 2/\alpha$ . At the same time formula (55) coincides with the estimate obtained with the aid of the BCS formula (3) for  $\Theta = \Theta_e = \hbar \Omega_e/k = \hbar \sqrt{\epsilon_0} \Omega/k$  and  $g = \alpha/a$ ,  $a \sim 1$ .

4. The result of the discussion carried out in Sections 2 and 3 first of all reduces to a justification of the simple approach to the problem of high-temperature superconductivity, which is used in<sup>[11]</sup> and in Sec. 1 of the present article, and which is based on the BCS formulas (2)–(3). Specifically, for the appearance of high-temperature superconductivity it is sufficient, in the first place, that in the matrix element of the interaction energy between electrons  $V(\omega, q) = 4\pi e^2/q^2 \epsilon(\omega, q)$  there exists an appropriate attractive (i.e., negative) contribution over a sufficiently wide range of frequencies  $\omega \sim \Omega_e = k\Theta_e/\hbar \gg \omega_{ph} = k\Theta_D/\hbar$  (above we assumed  $\Theta_e \sim 10^4$  whereas  $\Theta_D \sim 100$  to  $300^\circ\text{K}$ ). In the second place, the attraction must be sufficiently strong ( $g \gtrsim 1/5$  to  $1/4$ ; see (8)) in the frequency range  $\omega \leq \Omega_e$ .

In the generalized "jellium" model described by the

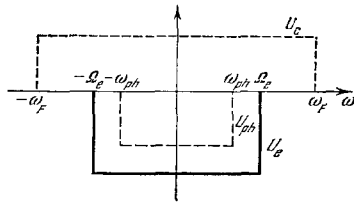


FIG. 7

longitudinal dielectric constant (37), both of these conditions are satisfied provided the frequency  $\Omega_e \sim \sqrt{\epsilon_0} \Omega$  is sufficiently large and at the same time (see Eqs. (54) and (55))

$$\frac{\epsilon_0 - 1}{\epsilon_0 \alpha} \gtrsim \frac{1}{5} - \frac{1}{4}, \quad g_e \gtrsim g'_{ph}. \quad (56)$$

For  $\epsilon_0 \gg 1$  this condition will be satisfied if the parameter  $\alpha$  is not too small, which is quite attainable for ordinary metals.

However, if the language of the theory of excitons is used, then one can say that the characteristic feature of the "jellium" model (37) is the existence of a band of longitudinal excitons—longitudinal waves with a frequency (see Eq. (47))

$$\Omega_e(q) = \sqrt{\frac{\epsilon_0 q^2 + \alpha^2}{q^2 + \alpha^2}} \Omega.$$

For the maximum value possible at the Fermi surface,  $q = 2q_F$ , the frequency  $\Omega_e(2q_F) = \sqrt{(\epsilon_0 + \alpha)/(1 + \alpha)} \Omega \approx \sqrt{\epsilon_0} \Omega$  (see expressions (48) and (49)). It is precisely this latter frequency  $\Omega_e$  which determines the characteristic temperature  $\Theta \sim \Theta_e = \hbar \Omega_e/k$  in the BCS formula (3), i.e., in the formula  $T_c = \Theta_e e^{-1/g}$  for the exciton mechanism of superconductivity. Thus, for the appearance of high-temperature superconductivity in a metal a suitable exciton band must exist. Specifically, the width of the band  $\Delta\omega \approx (\sqrt{\epsilon_0} - 1)\Omega$  must be sufficiently large; the same, of course, also pertains to the frequency  $\Omega_e = \sqrt{\epsilon_0} \Omega$  itself.

Some of the remarks and estimates which have been cited may appear to be overly technical in nature. In fact, the situation is quite the opposite—the period of general discussions about high-temperature superconductivity has already passed; now a more realistic analysis of the problem is required. At the same time, above only one step was made in this direction—it was shown that high values of  $T_c$  are possible not only for the BCS model but also for more general models of a medium which possesses a sufficiently large electronic resonance frequency  $\Omega$ . It is also advantageous if the static value of the electronic part of the dielectric constant,  $\epsilon_0 - 1$ , is as large as possible (this conclusion is physically quite clear because a large value of  $\epsilon_0 - 1$  corresponds to large oscillator strengths). The basic unsolved problem remains the choice of the conditions and the realizable parameters of the medium or system (sandwiches, etc.) under which an exciton mechanism can actually lead to high values of  $T_c$ . As has already been discussed in<sup>[11]</sup>, for the achievement of this goal three objects of investigation have been contemplated (we do not explicitly deal with nonequilibrium systems, which are obtained as a result of irradiation, the passage of current, etc.):

a) A homogeneous (three-dimensional) metal in which a sufficiently strong exciton attraction is guaranteed due to the polarization of bound electrons in impurities or in the atoms (ions) of the lattice, and also due to the interaction of s-electrons with d- or f-electrons.<sup>[23–26]</sup>

b) Long molecules with side "branches" playing the role of polarizers.<sup>[27]</sup> Here thread-like chemical compounds<sup>[28]</sup> and different polymer structures are joined together.

c) Systems of the "sandwich" type—a metallic film

between plates of dielectric, semiconductor, or even a poor metal.<sup>[1,29,30]</sup> Layered chemical compounds with the neighboring layers having markedly different conductivities may be regarded as a stack of sandwiches and, in any case, are related to sandwiches.<sup>[1,31]</sup>

Below we shall dwell on the merits and deficiencies of each of these versions, where at any given stage the question can basically involve only qualitative considerations.

Method a) would appear to be very simple in concept, but actually it may encounter the greatest difficulties. If the generalized model of "jellium" is used, then in order to obtain high values of  $T_c$  it is necessary to require the existence in the metal of an exciton band with frequencies within the limits from  $\Omega$  to  $\sqrt{\epsilon_0}\Omega$ . In other words, the dielectric constant  $\epsilon(\omega, q)$  should vanish in the indicated region. In this connection the frequency  $\sqrt{\epsilon_0}\Omega$  must be appreciably below the frequency  $\omega_F = E_F/\hbar$  (in certain approximate calculations the plasma frequency  $\omega_e = \sqrt{4\pi e^2 n/m} = \sqrt{16\alpha/3}\omega_F$  appears instead of  $\omega_F$ , but in the cases of interest to us it is always of the order of  $\omega_F$ ).

The condition  $\sqrt{\epsilon_0}\Omega \ll \omega_F$  was used above in order to obtain a number of expressions and the main region of frequencies comparable and larger than  $\omega_F$  does not introduce a contribution to the part of the energy of interaction between the electrons which is of interest to us; consequently, it is evidently in no way possible to give up the requirement  $\sqrt{\epsilon_0}\Omega < \omega_F$  or even  $\sqrt{\epsilon_0}\Omega \ll \omega_F$ . At the same time neither the experimental data nor the different estimates give any indications concerning the possibility of the appearance of such a shallow, but at the same time possessing large oscillator strengths, exciton band in a metal. The point here is primarily the fact that the very same factors which lead to the appearance of a conduction band with width  $E_F = \hbar\omega_F$  will, in general, cause the collectivization of the electrons belonging to atoms having resonance levels with energies  $\hbar\Omega < E_F$ . In other words, in a metal it is extremely difficult to maintain (as a result of introducing impurity atoms, let us say) levels of bound electrons with excitation energies appreciably smaller than  $E_F$ . Moreover, in order for the quantity  $\epsilon_0 - 1$  in (37) to be of any significance, the number of impurities or, if you please, the number of atoms with non-collectivized electrons entering into the composition of the metal (alloy) must be very large. Under such conditions it is especially difficult to maintain a resonance or, more formally, to guarantee an appreciable contribution of the type  $\Omega^2(\epsilon_0 - 1)/(\Omega^2 - \omega^2)$  to the permittivity (see Eq. (37)). Furthermore, in a metal the excitons must be rather strongly damped, which has not been taken into consideration above. One might think that the strong damping of the excitons is an unfavorable factor (unfortunately, the question of the role of attenuation remains insufficiently clear\*).

It is also necessary to note the unfavorable role of

\*Let us emphasize the arbitrary nature of the terminology being used. In the first place, even in a sandwich a semiconductor or even a poor metal (semimetal, doped semiconductor) may play the role of the dielectric. In filamentary and layered amalgamations the division into conducting (metallic) and poorly conducting (dielectric) filaments or layers almost inevitably is of an approximate nature.

electron exchange.<sup>[32]</sup> Actually the conduction electrons and the polarizable electrons, which guarantee the appearance of the appropriate contribution to  $\epsilon$ , are identical and in general can be exchanged with each other. But taking account of exchange, as is well known, for example, from the theory of molecules and as is clear from general considerations leads to a decrease of the interaction between the electrons (exchange is associated with the identity of the electrons, but this identity leads to a certain "kinematical" repulsion between fermions). Under the conditions for an "ordinary" metal or alloy (here the term "ordinary" indicates the absence of ordering occurring in filamentary or layered metallic systems), the wave functions of the conduction electrons and of the polarizable atoms generally overlap, which also leads to exchange and to a corresponding weakening of the attraction between the conduction electrons (we start from the assumption that such an attraction exists, since this is necessary for the appearance of superconductivity). The remarks which have been made about the role of exchange apparently do not directly pertain to models of a metal with overlapping s- and d- (or f-) bands. But even in this case the interaction leading to superconductivity vanishes in the presence of a large number of impurities which "intermingle" the states in different bands.<sup>[23]</sup> In general it appears to be extremely probable that if high-temperature superconductivity can be achieved in three-dimensional structures of the "ordinary" type, it can only be achieved under some kind of far reaching additional conditions (ordering, absence of exchange, etc.). Such a conclusion is in agreement with and is strongly supported by considerations of an empirical nature. In fact, an enormous number of metallic compounds and alloys have already been investigated, but temperatures  $T_c > 21^\circ$  have still not been achieved.

On the basis of what has been said, it is, of course, still not possible to reach a conclusion about the unattainability of large values of  $T_c$  in "ordinary" metals (homogeneous metallic compounds or alloys). Nevertheless, it is quite natural to turn out attention primarily to "unusual" metallic systems.

The general idea (and the only one known to us) indicating a way for the creation of the cited "unusual" metallic systems consists in a spatial separation of the region of conductivity (superconductivity) and the dielectric region responsible for the electronic polarization or, using the other language, responsible for the propagation of electronic excitons. The systems of types b) and c) enumerated above are precisely such, i.e., long conducting molecules with side "branches", conducting filamentary compounds, dielectric-metal-dielectric sandwiches, and layered compounds.

As long as the discussion is about only the qualitative aspects of the problem, such inhomogeneous systems undoubtedly appear to have advantages, because weakly-damped excitons can exist in a dielectric with frequencies  $\omega$  smaller than the electronic plasma frequency and the frequency  $\omega_F = E_F/\hbar$  corresponding to the metallic part of the system.\* The absence of any apprecia-

\*Above we had in mind the influence of the non-collective levels (in particular, levels in impurity atoms) on  $\epsilon$ . However, the frequencies  $\Omega < \omega_F$  and  $\Omega \ll \omega_F$  may also correspond to interband transitions

ble overlap between the wave functions of the electrons in the metal and in the dielectric guarantees the absence of exchange. Finally, sandwiches and other inhomogeneous systems with the necessary parameters (see<sup>[1]</sup> and below) still have not been created and investigated, so that here there are also in practice no objections based on experimental data. It is necessary, however, to note that already at the level of similar very general discussions the negative aspects of inhomogeneous systems are also evident. It is sufficient to make the metallic film in the sandwich (or the analogous "metallic" part of the other objects being considered) thick enough so that there is no hope of obtaining large values of  $T_C$ , owing to the presence of the dielectric. Such a conclusion is clear from general considerations, but it finds its own more concrete quantitative expression in the results of article<sup>[33]</sup>. In<sup>[33]</sup> it is shown that, in the case of an interaction which is inhomogeneous with respect to the film thickness, the value of  $T_C$  for the film is determined by the average value of this interaction

$$\bar{V} = \frac{1}{d} \int_{-d/2}^{d/2} V(z) dz.$$

From here it follows that even the presence of an extremely strong attraction between electrons in the immediate neighborhood of a dielectric is not sufficient for the achievement of high values of  $T_C$  provided  $\bar{V}$  corresponds to a small temperature  $T_C$ . Physically such a result is associated with the fact that the electrons in a metallic film move throughout the whole of its volume and spend only a small fraction of the time in the region with a strong attraction.

Thus, in order to achieve large values of  $T_C$ , a metallic film must have a thickness  $d$  of the order of the "radius of action" of the dielectric for electrons in metal. But, for a good metal this "radius of action" is a quantity of the order of an atomic distance. Therefore, a priori it is still not clear whether an inhomogeneous system (a sandwich, let us say) will prove to be substantially more favorable in comparison with an "ordinary" metal or alloy, which is also obviously inhomogeneous at an "atomic level." From this point of view the search for a system with a high critical temperature  $T_C$  represents an attempt to find certain optimal and, at the same time, compromise conditions (the existence of a suitable exciton band, and its effective utilization in order to guarantee attraction between the conduction electrons).

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of the electrons in a metal in the absence of impurities. In the cases known to us, as a result of insufficiently large oscillator strengths for such transitions, their large spectral widths, and the influence of attenuation, interband transitions do not lead to the appearance of an expressed low-frequency exciton band (frequencies  $\Omega \ll \omega_F$ ) although they have a substantial effect on the plasma frequency  $\omega_e$  and on the entire frequency behavior of  $\epsilon(\omega, q)$ . In other words, the interband transitions usually do not lead to the appearance of regions with negative values of  $\text{Re } \epsilon$  (see [18, 63, 64]). Independently of the nature of the exciton band, in a plan of search for high-temperature superconductivity it is necessary to investigate metals (or metallic systems—sandwiches, etc.) for which transitions of a resonant type exist and there is a corresponding band with frequencies  $\Omega \ll \omega_F$  (actually the frequency  $\Omega$  may be smaller than  $\omega_F$  all together by a factor of several times).

Let us proceed to a more specific discussion of inhomogeneous systems of the type of long molecules (case b)) and of the sandwich type (case c)).

5. The conjecture about possible superconductivity of long molecules<sup>[27]</sup> and of related structures has attracted a great deal of attention, but at the same time it has given rise to a whole series of objections:

1) In one-dimensional and two-dimensional systems a superconducting phase transition associated with the appearance of "long range order" is impossible<sup>[34, 35]</sup> as a result of the presence of overly strong fluctuations. Here a system is one- or two-dimensional, not only if the question involves infinitely thin filaments or planes, but also for systems with one- and two-dimensional momentum spaces. Therefore, long range order also does not arise in that case when the question involves superconductors which are bounded in one or two dimensions—for example, in a wire or in a plate. Thus, in a long (formally an infinitely long) molecule a superconducting state of exactly the same type as for three-dimensional systems (i.e., with long-range order) cannot arise.

2) A one-dimensional metal generally is unstable in the sense that the period of the lattice may double with a transformation of the chain into a dielectric state (a gap appears in the spectrum, analogous to the forbidden band in dielectrics).

3) In a one-dimensional conducting chain (filament) the Coulomb field is not screened, and consequently the Coulomb repulsion will always prevail.

4) Even if superconducting molecules turn out to exist, it will still be unclear how to use them to prepare superconducting materials, in virtue of the difficulties involved in order to realize appropriate contacts between the molecules and metallic electrodes.

These objections, especially the first of them, to a considerable extent have discredited the concept of the creation of superconductors of a molecular type. Meanwhile, in actual fact not one of the cited critical remarks can apparently be regarded as "cutting off" macromolecular superconductivity. Thus, the absence of long-range order,\* as already mentioned, holds not only for a molecular chain (filament) but also for ordinary superconducting wires and, in general, for arbitrary superconductors with one or two finite dimensions. Nevertheless, such superconductors even in the case of a wire or of a film with a thickness amounting to a hundred angstroms, and sometimes even less, do not differ at all from bulk superconductors (we have in mind general properties, but not possible changes of one or the other parameters which, for a bulk metal, depend on the method of preparation, processing, and so forth).

Long-range order is not present in a one-dimensional filament because thermal fluctuations destroy

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\*The superconducting state is characterized by a certain complex "order parameter"  $\Psi = |\Psi|e^{i\varphi}$  (unless we consider gapless superconductivity, the modulus  $|\Psi|$  is proportional to the width  $\Delta$  of the superconducting gap). The presence of longrange order means that the values of  $\Psi$  are correlated for any two arbitrarily separated points in the superconductor. This means that upon neglect of the fluctuations (which must be sufficiently small) both  $|\Psi|$  as well as the phase  $\varphi$  vary along the superconductor in a quite regular manner so that, for example,  $|\Psi| = \text{const}$  and  $\varphi = kz$ .

this ordering (if, let us say, it existed at a certain instant of time). Here the one-dimensional nature is essential in this respect, that in order to violate the long-range order it is sufficient to "disrupt" the ordering even if only at one place (in the two-dimensional case, in order to violate the long-range order it is necessary to destroy the ordering on a certain curve, and in the three-dimensional case—now over an entire surface). For a wire of arbitrary diameter, in principle a fluctuation which destroys the superconducting circuit is also always possible. Therefore, in a state of total thermodynamic equilibrium long-range order is not present in the wire. But it is quite obvious that for a sufficiently fine wire the probability of a fluctuation which converts it into the normal state over its entire cross section is insignificantly small, especially if the question does not involve the region of temperatures immediately adjacent to  $T_c$ . As a result, now for a wire of thickness up to one hundred angstroms the fluctuational breaking of the circuit is practically impossible, and the superconducting current will not be attenuated. For still finer wires near  $T_c$  the fluctuations now turn out to be appreciable, and they lead to a reduction of the effective critical temperature  $T_{c,eff}$ , which is somewhat arbitrarily defined as the highest temperature with a negligibly small resistance. As to the thermodynamic properties of the system, here long-range order (coherence over arbitrarily large distances) is not required—the thermodynamic properties can be practically the same independently of the presence of long-range order, but provided that the dimensions of the system are sufficiently large.

We are unable (but we also do not see any special reasons) to develop these considerations here (see<sup>[36,42]</sup>). In our opinion they testify with complete assurance to the feasibility of passing a practically unattenuated current along a very fine wire, and in principle also along certain macromolecules. To be sure, with a reduction of the diameter of the wire (system) the temperature  $T_{c,eff}$  is lowered, and for molecular dimensions  $d \sim 3 \times 10^{-8}$  to  $3 \times 10^{-7}$  cm it may turn out to be small in comparison with the value of  $T_c$  for the same material but in bulk form. Also one cannot exclude the possibility that  $T_{c,eff} = 0$  for a "wire" of molecular dimensions, owing to some kind of still obscure reason. But this is already another problem—just now we wish to emphasize only one fact: the absence of superconducting long-range order (the first objection) still does not at all cut off the possibility of the existence of macromolecules of the superconducting type, i.e., able to carry a practically unattenuated current (if you like, such a superconducting state without long-range order can be called quasi-superconductivity<sup>[11]</sup>).

The second of the objections mentioned above—the instability of a one-dimensional "metal"—also is not categorical and generally pertains only to a "metal" in the normal state. Impossibility of the appearance of a superconducting gap in the energy spectrum does not follow from here. The third objection—the absence of screening—only pertains to a strictly one-dimensional system. In coordinate space a molecule is by no means one-dimensional—it has dimensions that are different from zero. Therefore, some screening of the Coulomb field in molecules must, of course, occur, as follows

from calculations and from their comparison with spectroscopic results.<sup>[32,43,44]</sup> Finally, the fourth objection, which is connected with the difficulty of realizing contact with a macromolecule, is not a fundamental difficulty. In any case the creation of polymer superconducting materials is still far away, and if one were able to synthesize or observe just even individual superconducting macromolecules, this would be a prominent achievement.

Thus, in principle the superconductivity (or more precisely the quasi-superconductivity) of long macromolecules is possible. By the same token, efforts which have as their goal the synthesis or observation of such molecules, a study of their properties, the performance of appropriate calculations, etc. are completely justified. Unfortunately, there is still nothing to say about real progress in this direction. The author of the present article is not competent in questions of structure and polymer chemistry and therefore, unfortunately, cannot dwell here on the difficulties which were encountered in the attempts to synthesize superconducting macromolecules. The conclusion of the corresponding discussion,<sup>[3]</sup> however, is quite definite: as yet no one has succeeded in synthesizing not only superconducting molecules but not even any kind of prototypes of them (long chains with the number of links greater than 10 to 15, and with a corresponding large number of  $\pi$ -electrons), and no new ideas for accomplishing such a synthesis were reported. Nevertheless, the synthesis work is being continued because there are no completely convincing reasons to exclude the possibility of its successful development.

An extremely elegant and original approach to the problem consists in a hunt for the superconductivity of bacteria.<sup>[45]</sup> If superconductivity or something of its nature plays a role in biology, then during the course of evolution certain bacteria might acquire a large diamagnetic susceptibility or (and) a large conductivity. For the detection and selection of such bacteria, it is assumed that they pass through a diamagnetic separator (the analog of a Stern-Gerlach apparatus in which the bacteria move in a strongly inhomogeneous magnetic field) and through a separator which separates bacteria having different conductivities (if the conducting "particles"—bacteria—are in a liquid medium with a different conductivity, then during the passage of current and in the presence of a current perpendicular to the magnetic field the motion of the "particles" depends on their electrical conductivity). Selecting bacteria with "favorable" indices with the aid of two separators, and also subjecting them to multiple mutagenesis effects, one can hope to obtain a superconducting "species" of bacteria.

Numerous other experimental and theoretical investigations of macromolecules, polymers, etc.<sup>[3,44,46]</sup> also pertain to the problem of high-temperature superconductivity. In this direction one immediately touches the investigation of three-dimensional polymer "networks" and filamentary compounds.<sup>[36,28]</sup> In a qualitative sense it is immediately clear that a transition from individual macromolecules to a system of such interacting molecules, filamentary structures, and so forth leads to a decrease of the fluctuations (in this connection it is essential that the long-wavelength fluctuations repre-

sent the fundamental danger from the point of view of destruction of long-range order). And what is more, if conducting filaments which are parallel to each other not only interact (the question is the Coulomb interaction, let us say, associated with the formation of fluctuations of the charge density in the filaments) but also overlap (in the sense of an overlap of the wave functions of the electrons in different filaments),<sup>[28]</sup> then in point of fact a three-dimensional system is formed, capable of long-range superconducting order. For filamentary compounds the other difficulties mentioned above, which exist on the way to the creation and utilization of individual superconducting macromolecules, generally speaking vanish or become less serious.

Thus, searches for high-temperature superconductivity by way of the investigation of appropriate macromolecules and filamentary compounds remain quite deserving of attention and completely justified.

6. The last conclusion does not at all prevent the author from assuming, just as previously,<sup>[1]</sup> that for the creation of high-temperature superconductors the use of a system having "plane geometry" is more favorable and promising, i.e., sandwiches and layered compounds. The point is that although all known objections against the possibility of the existence of molecular superconductivity are not conclusive, but nevertheless they are supportive. The fluctuations in one-dimensional and quasi-one-dimensional systems are undoubtedly larger than in two- and three-dimensional cases, and "other conditions being the same" they lead to a reduction of  $T_C$ . The screening for macromolecules is also weaker than in two- or three-dimensional systems. At the same time for sandwiches and layered compounds these disadvantageous features are not present; for sandwiches there is also no real danger of the appearance of an instability of the conducting state, and no special difficulties of any kind arise in the question of contacts. To be sure, in the two-dimensional case just as in the one-dimensional case, long-range superconducting order is not present,<sup>[34,35]</sup> but it vanishes, so to speak, in a logarithmic fashion. This means that the critical temperature, for example, for an extremely thin film of dimension  $L$  varies according to a law of the type  $T_C \sim \text{const}/\ln(L/a)$ , where  $a$  is a certain atomic size (here we are extrapolating the calculations for a boson gas; for more details see<sup>[1,30,42]</sup>). From here it follows that superconductivity might, in general, be observed even for strictly two-dimensional films of macroscopic dimensions (such a situation holds for two-dimensional crystals; see<sup>[47]</sup>, Sec. 147). Another property is essential—in the case of a sandwich (without even talking about layered structures) the question does not at all involve two-dimensional structures. In a film of thickness  $d$ , if it is ideal and "filled" with noninteracting electrons, the energy of the latter is given by  $E = (\hbar^2/2m)(q_x^2 + q_y^2) + E_{\perp,l}$ . One can regard such a film as two-dimensional if, near the Fermi energy  $E_F$ , the energy of the electrons only depends on  $q_x$  and  $q_y$  ( $x$  and  $y$  denote the coordinates in the plane of the film), and the levels  $E_{\perp,l} \sim \hbar^2 l^2/2md^2$  ( $l = 0, 1, 2, \dots$ ) corresponding to transverse motion are sufficiently far apart from each other. It is obvious that near the Fermi boundary the smallest distance between the levels of the transverse motion is given by  $\Delta E \sim E_{\perp,1} \sim \hbar^2/2md^2$ .

One can believe that the presence of these levels does not violate the two-dimensional nature of the distribution provided  $\Delta E \sim \hbar^2/2md^2 > \Delta(0) \sim kT_C$ , i.e., provided  $d < \hbar/\sqrt{2mkT_C}$ . Hence for  $T_C \sim 10^\circ\text{K}$  we arrive at the inequality  $d < 5 \times 10^{-7}$  cm. But in fact films of thicknesses  $d \sim 20$  to  $30 \text{ \AA}$  are still superconducting, they generally behave like three-dimensional superconductors, and have a similar value of  $T_C$  (see<sup>[48,49]</sup>). Therefore one can believe that even for a thickness  $d \sim 10$  to  $20 \text{ \AA}$  the film can still be regarded as three-dimensional. The probable explanation for the incompatibility of this conclusion with the estimate cited above is connected with the non-ideal nature of the film and with the inter-electron interaction, by virtue of which the motion of the electrons cannot be separated into longitudinal and transverse. As a consequence, it is probable that a film becomes authentically two-dimensional (in the sense of the two-dimensional nature of momentum space) only for  $d \sim a \sim 3 \text{ \AA}$ .

What has been said enables us to believe that for a sandwich with a metallic center of thickness  $d \sim 10$  to  $15 \text{ \AA}$ , the superconductivity of this center (film) will be close to three-dimensional. But then the transition to the two-dimensional case ( $d \sim 3$  to  $10 \text{ \AA}$ ) also is obviously not dangerous since under such conditions a practically undamped current can flow along the film (quasi-superconductivity; see above).

Regarding the question of screening then, in the first place, for the two-dimensional case in contrast to the one-dimensional case the Coulomb field is already screened and, in the second place, in the case of interest to us of films with  $d \geq 10 \text{ \AA}$  the screening is certainly stronger than in a two-dimensional film and is close to that corresponding to a three-dimensional metal.

Among the number of advantages which a sandwich has belongs the feasibility to create sandwiches with different parameters, and also to control these parameters. It is easiest of all to make a sandwich as the result of the deposition of metal on a dielectric substrate and dielectric on metal, but other methods are conceivable: cleavage of a crystal in vacuum with subsequent deposition of the film and a joining together of the cleaved parts of the crystal, a thinning of the film inside the sandwich by means of the treatment of thicker layers under pressure, the creation of narrow layers of heavily doped semiconductor in such an undoped semiconductor, and finally chemical methods.<sup>[50]</sup>

It would be advisable to dwell in a little more detail on the last method, in connection with a discussion of the fundamental question concerning the deficiencies of sandwiches. Properly speaking, we can only indicate one such potential deficiency—the interaction between the metallic and dielectric parts of the system is weaker in a sandwich than it is for filaments. Here we have in mind simple geometrical considerations—a conducting filament (a conducting chain in a macromolecule) is surrounded by dielectric on all sides, in connection with which, all other conditions being equal the electrons in the filament interact more strongly with this dielectric than in the case of a metallic layer which is located between dielectric sheets. In order to somehow decrease or compensate for this "weakness" feature of sandwiches, it is necessary to make the metallic film in them

as thin as possible, but still retaining high conductivity. Thus, one is forced to deal with another somewhat related property (the question is the rapid decrease of the interaction energy with separation from the surface of the dielectric; see above). It is also clear that the dielectric must be joined to the metallic film as closely as possible. Here then the possible advantages of deposition of the dielectric by chemical means emerge on the scene, i.e., as the result of a chemical reaction on the surface. Namely, for chemical binding the contact of the dielectric with the metal will probably be especially tight and favorable from the point of view of achieving the strongest possible interaction.

Thus, incidentally, there is no basis to set off physical methods against chemical methods, as may prove to be natural if one confines his attention to only a consideration of the synthesis of long macromolecules and layered compounds, on the one hand, and sandwiches created without using chemical reactions on the other hand.

Let us add one more comment to what has been said.<sup>[50]</sup> Attempts to synthesize superconducting macromolecules are associated with the simultaneous solution of two problems—the creation of very long conducting (or superconducting) chains and the surrounding of this chain by strongly-polarizable molecular side branches. The situation is more or less analogous to the case of the synthesis of layered compounds possessing a metallic conductivity. Meanwhile, each of the mentioned problems is sufficiently complicated individually (it is possible that both problems cannot be solved one without the other, but this changes the situation very little). However, in the case of sandwiches, from the very beginning we can actually separate both problems: a metallic film is created by well-known methods, and one can easily control its conductivity; therefore it is only necessary to solve the second problem—to select a suitable dielectric and to join it with the metallic film, for the accomplishment of which a chemical reaction may turn out to be fruitful (what has been said also pertains to granulated metal-dielectric systems which are discussed in Section 8).

One can suppose that further attempts to convince one of the merits of sandwiches are not very fruitful and are unnecessary, at least in this respect, that real progress forward is possible only by means of the appropriate experiments and calculations.

At present there are methods whereby,<sup>[48,49,51a]</sup> operating in a high vacuum ( $p \lesssim 10^{-10}$  torr), one can deposit films having thicknesses down to a few atomic layers ( $d \sim 10$  to  $15 \text{ \AA}$ ) on a substrate. The diffraction

of slow electrons on such a film makes it possible to monitor its structure. Obtaining the Auger spectra of inelastically scattered electrons opens up the possibility of verifying that the film is continuous (in the opposite case lines will be detected which correspond to the material of the substratum). This same method makes it possible to detect the presence in the film or on it of any kind of impurity (also see<sup>[51b]</sup>). There are also methods to determine the thickness of the film without even saying anything about its conductivity. At the present time the most complicated part of the program of investigation of sandwiches consists in the selection of a dielectric, the preparation of its surface, and the deposition of dielectric on both sides of the metallic film. There is no doubt that only the accomplishment of numerous and diverse experiments with sandwiches (or for well-known orientations with very thin metallic films deposited on dielectrics) makes it possible to estimate the extent of the truth in the stated assumptions concerning the feasibility to substantially increase the superconducting critical temperature in such a way.

7. Emphasis on the decisive role of experiment at the present stage, of course, does not mean any negation of the timeliness of the various estimates and calculations aimed at facilitating the choice of the parameters and materials to be used in sandwiches. Certain general considerations on this account were already presented in<sup>[11]</sup>; let us just now regard the parameters indicated there as correct, but they are not sufficiently concrete. Unfortunately, a more complete theory of sandwiches has not yet been developed, not even for simple models. Therefore, below we are forced to confine our attention to only several remarks.

In order to find  $T_c$  for a sandwich it is first of all necessary to find the interaction energy of two electrons existing in the metallic film of the sandwich. In virtue of the presence of spatial dispersion this problem is no longer simple, but upon neglect of spatial dispersion it is elementary to solve. In fact, we shall describe the three media entering into the composition of the sandwich (Fig. 8) by dielectric constants  $\epsilon_1(\omega)$ ,  $\epsilon_2(\omega)$ , and  $\epsilon_3(\omega)$ . Let us position a charge (electron) at the origin of coordinates, and let us find the potential  $\varphi$  created by it. In medium 1, where the charge is located, the potential satisfies the equation  $\nabla^2 \varphi_1 = -4\pi e\delta(\mathbf{r})/\epsilon_1(\omega)$ , and in media 2 and 3 it is obvious that  $\nabla^2 \varphi_{2,3} = 0$ . The conditions  $\varphi_i = \varphi_k$  and  $\epsilon_i(\partial\varphi/\partial z) = \epsilon_k(\partial\varphi/\partial z)$  for  $i, k = 1, 2, 3$  must be satisfied at the boundaries of the media  $i$  and  $k$ . The solution of such an electrostatic problem can easily be found by the method of images and has the form

$$\left. \begin{aligned} \varphi_1 &= \frac{e}{\epsilon_1} \left\{ \frac{1}{\sqrt{r^2+z^2}} + \left( \frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2} \right) \frac{1}{\sqrt{r^2+(z-d)^2}} + \left( \frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2} \right) \frac{1}{\sqrt{r^2+(z+d)^2}} \right. \\ &\quad \left. + \left( \frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2} \right) \left( \frac{\epsilon_1-\epsilon_3}{\epsilon_1+\epsilon_3} \right) \left( \frac{1}{\sqrt{r^2+(z-2d)^2}} + \frac{1}{\sqrt{r^2+(z+2d)^2}} \right) + \right. \\ &\quad \left. + \left( \frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2} \right)^2 \left( \frac{\epsilon_1-\epsilon_3}{\epsilon_1+\epsilon_3} \right) \frac{1}{\sqrt{r^2+(z-3d)^2}} + \left( \frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2} \right) \left( \frac{\epsilon_1-\epsilon_3}{\epsilon_1+\epsilon_3} \right)^2 \frac{1}{\sqrt{r^2+(z+3d)^2}} \dots \right\}; \\ \varphi_2 &= \frac{2e}{\epsilon_1+\epsilon_3} \left\{ \frac{1}{\sqrt{r^2+z^2}} + \left( \frac{\epsilon_1-\epsilon_3}{\epsilon_1+\epsilon_3} \right) \frac{1}{\sqrt{r^2+(z+d)^2}} + \right. \\ &\quad \left. + \left( \frac{\epsilon_1-\epsilon_3}{\epsilon_1+\epsilon_3} \right) \left( \frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2} \right) \frac{1}{\sqrt{r^2+(z+2d)^2}} + \dots \right\}; \\ \varphi_3 &= \frac{2e}{\epsilon_1+\epsilon_2} \left\{ \frac{1}{\sqrt{r^2+z^2}} + \left( \frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2} \right) \frac{1}{\sqrt{r^2+(z-d)^2}} + \right. \\ &\quad \left. + \left( \frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2} \right) \left( \frac{\epsilon_1-\epsilon_3}{\epsilon_1+\epsilon_3} \right) \frac{1}{\sqrt{r^2+(z-2d)^2}} + \dots \right\}. \end{aligned} \right\} \quad (57)$$

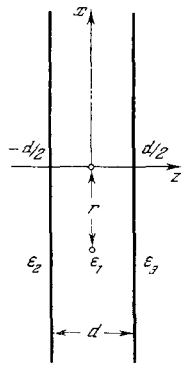


FIG. 8

The interaction energy between the given electron and another located at the point  $r = \sqrt{x^2 + y^2}$ ,  $z$  is equal to  $e\varphi_1$ . For simplicity let us locate the second electron symmetrically, i.e., let us set  $z = 0$ . Then for a symmetric sandwich, when  $\epsilon_2 = \epsilon_3$  we obtain

$$V = \frac{e^2}{\epsilon_1} \left\{ \frac{1}{r} + \left( \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right) \frac{2}{\sqrt{r^2 + d^2}} + \left( \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right)^2 \frac{2}{\sqrt{r^2 + (2d)^2}} + \left( \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right)^3 \frac{2}{\sqrt{r^2 + (3d)^2}} + \dots \right\}. \quad (58)$$

For an asymmetric sandwich and, specifically, for a metal film (of permittivity  $\epsilon_1$ ) on a dielectric substratum (of permittivity  $\epsilon_2$ ) in the absence of medium 3 (i.e., for  $\epsilon_3 = 1$ ) a formula analogous to (58) follows directly from (57). In view of its simplicity, let us write an expression for  $V$  in the case of two electrons existing at a distance  $d/2$  from the interface between media 1 and 2 in the absence of medium 3 (for this, in (57) it is necessary to set  $\epsilon_3 = \epsilon_1$ ):

$$V = \frac{e^2}{\epsilon_1} \left[ \frac{1}{r} + \left( \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right) \frac{1}{\sqrt{r^2 + d^2}} \right]. \quad (59)$$

The interaction (59) to some extent also characterizes the situation in sandwiches for the electrons located close to one of its boundaries with the dielectric.

From the expressions cited, it is obvious that even for  $d \rightarrow 0$  the interaction of electrons in sandwiches does not at all reduce to the interaction in a continuous medium but, let us say, with permittivity  $\epsilon_1 + \epsilon_2$ . In an unbounded medium the longitudinal waves (excitons) may propagate only under the cited condition  $\epsilon(\omega) = 0$  (let us confine our attention to the case of an isotropic medium in the absence of spatial dispersion; for more details see<sup>[14]</sup>). As is well known, in connection with the presence of interfaces the appearance of surface exciton states is possible (in these states the field in the waves is localized only near the interface). On the interface between two media with dielectric constants  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  the frequencies of the surface excitons satisfy the condition (see<sup>[14,15,18]</sup>)

$$\epsilon_1(\omega) + \epsilon_2(\omega) = 0. \quad (60)$$

It is obvious that the interaction (58) or (59) is especially large both in the region of the existence of volume excitons for medium 1 (the condition  $\epsilon_1(\omega) = 0$ ) in which the interacting particles are found, and in the region of the existence of surface excitons (condition (60)). Upon taking account of retardation, spatial dis-

persion, and anisotropy (of the crystal)<sup>[14,15,52,53]</sup> and also certain other factors (thus, in<sup>[54]</sup> the influence of quantization of the energy of the transverse motion in the film is investigated), the spectrum of the surface plasmons may differ in a very substantial way from that obtained on the basis of the simplest condition (60).

In order to put together some kind of idea about the nature of the surface exciton band in sandwiches, we shall assume that in the metal  $\epsilon_1$  corresponds to the "jellium" model, where for simplicity we immediately neglect the term  $-\omega_1^2/\omega^2$  in Eq. (25); we shall assume medium 2 to be a dielectric possessing a resonance frequency  $\Omega$ . In other words, we set

$$\epsilon_1(\omega, q) = 1 + \frac{\kappa^2}{q^2}, \quad \epsilon_2(\omega, q) = 1 + \frac{\Omega^2(\epsilon_0 - 1)}{1\Omega^2 - \omega^2}. \quad (61)$$

From condition (60), where now even if it is not completely consistent still spatial dispersion is taken into account, we obtain a dispersion equation for the surface excitons (the solution of Eq. (60) is denoted by  $\Omega_{e,s}$ )

$$\Omega_{e,s}^2 = \frac{(\epsilon_0 + 1)q^2 + \kappa^2}{2q^2 + \kappa^2} \Omega^2,$$

$$\Omega_{e,s}(0) = \Omega, \quad \Omega_{e,s}(2q_F) = \sqrt{(\epsilon_0 + 1 + \alpha)/(2 + \alpha)} \Omega. \quad (62)$$

The frequencies  $\Omega_{e,s}$  are of the same order as the frequencies  $\Omega_e$  for volume excitons (see Eq. (42)), as one would be led to expect in the present case in virtue of the similarity of expression (37) for  $\epsilon$  and the sum  $\epsilon_1 + \epsilon_2$  (see (61)). The difference between the interaction functions  $U(\omega)$  in both cases is also probably small, although it may turn out to be more appreciable than for the case of the frequencies  $\Omega_e$  and  $\Omega_{e,s}$ . Since for sandwiches the equations determining the gap  $\Delta$  and the temperature  $T_c$  have still not been obtained, we cannot indicate the corresponding expression for  $U_0(\omega)$ ,  $U_{eff}$ , or for an analogous function. For a known orientation one can probably treat the problem in the following way: we compare the interaction energy  $V = e^2/\epsilon r$  in the bulk case with expressions (58) and (59). Under conditions when the term containing the factor  $(\epsilon_1 - \epsilon_2)/(\epsilon_1 + \epsilon_2)$  is the major term in Eqs. (58) and (59), one might believe that for an estimate the same expression for  $U_{eff}$  would be valid as for the volume case, but with the replacement of  $1/\epsilon$  by

$$\frac{1}{\epsilon_s} = \frac{1}{\epsilon_1} \left( \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right).$$

Let us proceed in precisely this fashion, using expression (61). Then

$$V = \frac{4\pi e^2}{q^2 \epsilon_s(\omega, q)} = \frac{4\pi e^2}{q^2 + \kappa^2} \left\{ 1 + \frac{[2q^2/(2q^2 + \kappa^2)](\epsilon_0 \Omega^2 - \omega^2)}{\omega^2 - \Omega_{e,s}^2(q)} \right\}, \quad (63)$$

where the frequency  $\Omega_{e,s}(q)$  is determined by the expression (62).

Now proceeding in the same way as for the transition from (50) to (52), we have

$$\bar{V} \approx \bar{V}_c \left\{ 1 + \frac{\epsilon_0 \Omega^2 - \omega^2}{\omega^2 - [(\epsilon_0 + 1)\Omega^2/2]} \right\}. \quad (64)$$

One can think that in order to estimate  $T_c$  one should proceed just as in the case (50)–(53), by assuming

$$\bar{V}_{ph} = -\frac{2f_0}{\epsilon_0 - 1} \bar{V}_c \quad \text{for } \omega < \Omega_{e,s} = \sqrt{\frac{(\epsilon_0 - 1)}{2}} \Omega \quad \text{and } \bar{V}_{ph} = 0$$

for  $\omega > \Omega_{e,s}$ . Then we obtain

$$T_c \sim \frac{\hbar}{k} \sqrt{\frac{\epsilon_0 + 1}{2}} \Omega e^{-1/\alpha_e}, \quad g_e = |U_e| = N(0) \bar{V}_c \sim \frac{1}{\alpha}. \quad (65)$$

This estimate agrees in practice with the estimate (43) for the bulk case—it is not necessary to talk about the difference here in connection with the approximate nature of the calculation, and due to the tentative nature of the initial expression (63). At the same time the conclusion about the desirability of the selection of large values of  $\epsilon_0$  (large oscillator strengths; see (61)), not too small values of  $\alpha$ , and large resonance frequencies  $\Omega$  (but upon fulfillment of the condition  $\sqrt{\epsilon_0} \Omega \ll \omega_F = E_F/\hbar$ ) is quite plausible and probable. From here one can conclude that it is reasonable to make the dielectric layers of the sandwich out of a dielectric having a strong absorption band in the range of values  $\hbar \Omega \sim 0.1$  to 1 eV (for light  $q \ll q_F$ , and therefore absorption takes place near the resonance frequency  $\Omega$ , but not at the frequencies  $\omega \sim \Omega_{e,s}(2q_F) \sim \Omega_e(2q_F) \approx \sqrt{\epsilon_0} \Omega$ ).

Above we assumed the conducting film in the sandwich to be made out of a good metal ( $E_F \sim 10$  eV). In the same way it should be emphasized (see also<sup>[53,54]</sup>) that sandwiches of the semiconducting type also deserve attention (the question involves heavily doped semiconductors possessing a metallic conductivity). In<sup>[55]</sup> it is proposed to investigate sandwiches with semiconducting centers and granulated metallic coverings. The utilization of ferromagnetics (ferrites), antiferromagnetics, and ferroelectrics as dielectric layers in sandwiches may turn out to be useful, and it may also turn out to be useful to investigate the influence of external magnetic and electric fields on  $T_c$ . We have in mind the influence of fields (internal and external) on the electrical spectrum of the system (in particular, the dielectric constants  $\epsilon_1$  and  $\epsilon_2$  are changed as a consequence), the change of the electron concentration, and exchange effects. For example, in the case of sandwiches with ferrite layers, both from the theory<sup>[56,57]</sup> and from experiment<sup>[58]</sup> it is known that  $T_c$  depends on the mutual orientation of the magnetization vectors in both coatings. As a result one can control the value of  $T_c$  within well-known limits by changing the direction of magnetization in the coating. One also cannot exclude the possibility that for sandwiches with a very thin conducting layer the effect of the cited factors may turn out to be favorable from the point of view of achieving the highest possible values for  $T_c$ . Thus, it is clear that there is a very broad circle of possibilities associated with the preparation and investigation of sandwiches. However, the fundamental and decisive difference between sandwiches and a homogeneous metal is the significantly greater case of creation of a system with metallic conductivity and, at the same time, with a clearly expressed exciton spectrum.

8. The creation of a sandwich with a high critical temperature would immediately place in our hands the appropriate superconducting element of a current-carrying circuit. In order to obtain such a sandwich, however, it is not only necessary to find the appropriate combination of materials with a high value of  $T_c$ . In order to do this it is obviously necessary also to create a conducting film of macroscopic dimensions. Meanwhile it is quite possible that at first it is easier to obtain only a microscopic combination of metal and dielec-

tric (in the form of a metallic lamella or droplet, which is surrounded on all sides by an appropriate dielectric), possessing a high value of  $T_c$ .\* One can observe the appearance of superconductivity and measure  $T_c$  for such lamellas or droplets by using the tunnel effect (see, for example,<sup>[59]</sup>) or with the aid of diamagnetic measurements (in the latter case the concentration of superconducting particles in the dielectric matrix must be relatively larger). Dispersed (granulated) superconductors, which the question is just now about, can be prepared by different methods, for example, by sputtering or by imbedding the metal in a porous, poorly conducting material (in the last case, to be sure, the metallic particles and filaments usually turn out to be relatively large;<sup>[60]</sup> but in such a way that the possibility of obtaining particles with the required dimensions of the order of 10 to 30 Å is not excluded).

Under pressure or as a result of diffusion one can evidently also obtain systems with a subdivided surface and materials with a layered structure. However, it is natural to first study layered chemical compounds possessing metallic conductivity (a review of the properties of a number of such compounds of the type  $TX_2$  is contained in article<sup>[61]</sup>). Solutions of metals in non-metals are also of interest. Cooled solutions of sodium in ammonia are an example. It is of interest that as long ago as 1946 a report<sup>[62]</sup> appeared about the observation of high-temperature superconductivity in such solutions. This report was not confirmed by other authors. However, as Little<sup>[63]</sup> has correctly emphasized, it is advisable to repeat similar experiments. The point is that in article<sup>[62]</sup> † the effect was only observed in a few cases and perhaps it was caused by impurities which were not present in the other experiments. Therefore, there are reasons to clarify the role of various impurities, which are knowingly-introduced, on the conductivity of solutions of sodium in ammonia and on other similar solutions with metallic conductivity.

We have enumerated all of these alternatives and potential possibilities first of all in order to emphasize the major thesis: there is no reason to approach the problem of high-temperature superconductivity with preconceived ideas, and the preference which the author gives to sandwiches does not in any way bear the character of a denial of the advisability to also conduct searches in other directions.

In the article<sup>[1]</sup> we were obliged to state that the problem of high-temperature superconductivity was not being given sufficient consideration. By February 1970, when the present article was completed, the situation had improved—an ever larger number of physicists and chemists have accepted the challenge and are endeavoring to create high-temperature superconductors. The

\*We note that just such a case is discussed in article [16]. According to an opinion expressed by A. I. Shal'nikov during a discussion of one of the author's reports at the end of 1969, to seek high-temperature superconductivity via the investigation of dispersed (granulated) superconductors may prove to be an appreciably easier task than as the result of an investigation of sandwiches.

†It is interesting to note that already in this article an hypothesis was expressed about the possibility of the occurrence of superconductivity associated with a "pairing" of fermions with their subsequent Bose-Einstein condensation.



author would not be overly surprised if the first successes on one of the paths leading toward this goal were achieved even before the appearance of this article in print. But as long as this has not taken place, it is still necessary to specifically see to it that searches for high-temperature superconductors are carried out intensively and over a broad front. It is precisely this circumstance which explains and, so one can hope, justifies the inclusion in the present article of certain remarks which by their nature would usually be regarded as suitable only in the case of the popular scientific literature, lectures, and so forth.

Note Added in Proof. In [66] it is reported that organic molecules were introduced between metallic layers and layered compounds of transition metals (dichalcogenides). The most thorough study was made on tantalum disulfide, in which pyridine ( $C_5H_5N$ ) was introduced. As much as one molecule of pyridine per two tantalum atoms was introduced. In this case the distance between the planes formed by the tantalum atoms amounted to 12Å. Such a material has  $T_C \sim 3.5^\circ K$ , whereas  $T_C$  of the initial compound ( $TaS_2$ ) is  $\sim 0.7^\circ K$ . The observed new class of layered organometallic compounds [66] is of great interest from the point of view of the study of quasi-two-dimensional superconductors and the exciton mechanism of the superconductivity.

<sup>1</sup>V. L. Ginzburg, *Usp. Fiz. Nauk* 95, 91 (1968); *Contemp. Phys.* 9, 355 (1968).

<sup>2</sup>Proceedings of International Conference on the Science of Superconductivity, *Physica* (in press).

<sup>3</sup>Proceedings of International Symposium on the Physical and Chemical Problems of Organic Superconductors (in press).

<sup>4</sup>E. A. Lynton, *Superconductivity*, Methuen and Co., Ltd., 1962, 3rd ed. (Russ. Transl., Mir, 1968).

<sup>5</sup>J. Bardeen and J. R. Schrieffer, *Recent Developments in Superconductivity*, *Progress in Low Temp. Physics*, Vol. III, Ch. VII, North Holland, 1961.

<sup>6</sup>P. G. de Gennes, *Superconductivity of Metals and Alloys*, W. A. Benjamin, Inc., 1966 (Russ. Transl., Mir, M. 1968).

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<sup>8</sup>W. L. McMillan, *Phys. Rev.* 167, 331 (1968).

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<sup>10</sup>B. T. Geilikman, *Fiz. Tverd. Tela* 12, (1970) [*Sov. Phys.-Solid State* 12, (1970)].

<sup>11</sup>V. L. Ginzburg, *Usp. Fiz. Nauk* 97, 601 (1969) [*Sov. Phys.-Uspekhi* 12, 241 (1969)]; *J. Statistical Physics* 1, 3 (1969).

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