## SUPERCONDUCTING TRANSITION TEMPERATURE OF A THIN FILM

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It is shown that the usual electron-phonon interaction leads to a growth of the critical temperature with decrease of the film thickness L. This is due to the special nature of electron pairing. The growth of  $T_c$  is especially great for  $L \sim 10^{-6}$  cm; with further decrease of L  $(L \leq 10^{-7} \text{ cm})$  the dependence becomes exponential. The results describe the experimental data. The correctness of this interpretation can be confirmed by measurements of the isotopic effect. The possibility of an electron mechanism, due to the presence of different electron groups in the film, is also considered.

HE superconducting state of thin films has many characteristic singularities. In particular, experiments<sup>[1-3]</sup> have disclosed a change in the critical temperature  $T_c$  with decreasing thickness. Thus, a monotonic increase of  $T_c$  was observed<sup>[2]</sup> in a stress-relieved aluminum film. The rate of change of  $T_c$  increased in this case with decreasing L.

In this connection, a theoretical analysis of the possible causes of the variation of  $T_c$  in films becomes important. One of them may be the realignment of the crystal lattice on going over from the bulk metal to the film. However, the indicated change in the modification cannot lead to a monotonic dependence of  $T_c$  on the film thickness L, as observed, at any rate, in aluminum films.

The superconducting state of a film may change appreciably if its surface is coated in some manner. The phononless mechanism connected with the interaction between the electrons and such a coating was first considered by Ginzburg<sup>[4]</sup>. The increase in  $T_c$  connected with this mechanism was quantitatively investigated by Kirzhnits and Maksimov<sup>[5]</sup>. From the point of view of the indicated mechanism, the increase of  $T_c$  of Al films can be attributed to the interaction between the electrons and the oxide on the surface<sup>[2]</sup>. In this case  $T_c$  should depend on the thickness and on the composition of the coating, as can be verified experimentally.

Another phononless mechanism leading to an increase of  $T_C$  was proposed by us earlier<sup>[6]</sup> and, in particular, will be analyzed in detail in the present paper.

An essential feature of phononless mechanisms is the absence of the isotopic effect, and in the presence of a phonon mechanism—a dependence of the isotopic effect on the film thickness. In the present paper we consider not a surface but a volume effect, due to ordinary electronphonon interaction in the film. We show that quantization of the transverse motion of the electron in the film leads to an increase of  $T_c$  with decreasing film thickness. We also consider in detail an electronic mechanism, due to the existence of different groups of electrons in the film.

The observation of superconducting semiconductors (GeTe,  $T_C \approx 0.08^\circ$ ; SrTiO<sub>3</sub>,  $T_C \approx 0.3^\circ$ ; PbTe,  $T_C \approx 5.3^\circ$ )<sup>[7]</sup> makes consideration of semiconductor films important. It was shown earlier by Demikhovskiĭ, Kogan, and one of the authors<sup>[8,9]</sup> that the usual electron-phonon interaction leads to a growth of  $T_C$  with decreasing L. Therefore we do not confine ourselves in this paper to metallic films, but discuss also the question of the critical temperature in films made of semiconductors and semimetals.

## 1. SINGULARITIES OF COOPER PAIRING IN THIN FILMS

Owing to the finite character of transverse electron motion in a film, the state and energy  $\epsilon(\mathbf{k}, \mathbf{n})$  of the electron are determined by the longitudinal component of the quasimomentum  $\mathbf{k}$  ( $\mathbf{k}$  is a two-dimensional vector) and by the discrete number n. The quasimomentum  $\mathbf{k}$  takes on continuously values lying in a two-dimensional Brillouin zone. To each given n there corresponds a region of continuous spectrum—a sub-band. These sub-bands constitute a system of overlapping bands that are shifted relative to one another. In the degenerate case, each is populated up to a certain value of the two-dimensional quasimomentum  $\kappa_{\rm Fn}$ , which decreases with increasing n.

For estimates we can assume that n determines the quantized value of  $|k_{\rm Z}|$ , with  $k_{\rm Zn} = \pi n/L$ , n = 1, 2, ... In the effective mass approximation this gives for the shift of the first sub-bands  $\delta \epsilon$  $\sim \pi^2 \hbar^2/mL^2$ . For  $L \sim 10^{-6}$  cm we obtain  $\delta \epsilon$  $\sim 10^2 \,{\rm ^oK}$ .

In semiconductors and semimetals, owing to the small carrier density, only one sub-band with n = 1 f can be populated. In momentum space, problems spertaining to such films become two-dimensional, finalthough in coordinate space the films remain three-dimensional formations, since  $L \gg a$  (a is the lattice constant). The conditions that lead to population of only one sub-band were investigated in <sup>[8]</sup>. For example, for  $L \sim 10^{-6}$  cm the required density is  $N < 10^{19}$  cm<sup>-3</sup>. Since  $\delta \epsilon \sim 10^2$  °K at such thicknesses, the thermal scatter is of no importance  $\Delta$  at temperatures corresponding to the superconducting state. However, when  $L \gtrsim 10^{-5}$  cm, it cannot be neglected, since the mixed sub-band become populated.

When the film goes over into the superconducting state, Cooper pairs are produced, consisting of electrons with opposite  $\kappa$ . Inasmuch as at the Fermi level the electrons from different sub-bands have unequal values of  $|\kappa_{\rm Fn}|$ , pairing of such electrons can be neglected. This neglect, of course, is valid so long as  $\delta \epsilon \gg T_c$  (this corresponds to L  $\leq 10^{-5}$  cm). Thus, electrons with opposite  $\kappa$  and identical n will be paired in a thin superconducting film. The described picture is analogous to the twoband model of a bulk superconductor<sup>[10]</sup>, in which one neglects the pairing of electrons belonging to different bands. The condensate of pairs in the given sub-band can be produced, first, because of the attraction of the electrons in the same subband, and, second, because of transitions of particles initially situated in other sub-bands to the bound state.

## 2. INCREASE OF T<sub>c</sub> IN A SUPERCONDUCTING FILM

We proceed to calculate the critical temperature in a thin film whose superconductivity is due to the usual electron-phonon interaction.

In the case when only one sub-band is populated (semimetal or semiconductor), the Cooper equation, as shown in [8], is of the form\*

$$1 = \frac{g}{2V} \sum_{\kappa} \frac{\operatorname{th} (\varepsilon/2T)}{\varepsilon};$$

where the summation is over a two-dimensional region. For a semimetal or a degenerate semiconductor, this leads to an exponential dependence of  $T_c$  on L:

$$T_{\rm c} = 1.14\hbar\omega_D \exp\left(-\frac{2\pi L\hbar^2}{m^*g}\right).$$
(1)

In a metallic film, which is characterized by the filling of many sub-bands, it is necessary to consider in place of one equation a system of equations for the self-energy parts  $\Delta_i$ :



$$\Delta_{i}(\mathbf{k},\omega_{n}) = -\sum_{\mathbf{k}',\omega_{n'}} C_{il}D(\mathbf{k}-\mathbf{k}_{l}',\omega_{n}-\omega_{n'})$$

$$\times \frac{\Delta_{l}(\mathbf{k}_{l}',\omega_{n'})}{\omega_{n'}^{2}+\xi t^{2}(\mathbf{k}_{l}')+\Delta t^{2}(\omega_{n'},\mathbf{k}_{l}')}, \qquad (2b)$$

where  $F_{ii}^{\dagger} = -i \langle T(\psi_i^{\dagger} \psi_i^{\dagger}) \rangle^{[11]}$ .

The nondiagonal terms reflect the possibility of the transition of the electron pair from one subband into another as a result of interaction with phonons. As seen from the system (2), all the  $\Delta_n$  vanish at one temperature  $T_c$ . We rewrite Eq. (2a) in the weak-coupling approximation in analytic form:

$$\Delta_{1} = \frac{g_{1l}}{2V} \sum_{\varkappa_{l}} \frac{\Delta_{l} \operatorname{th} \left( \varepsilon_{l} / 2T \right)}{\varepsilon_{l}}; \qquad (3)$$

Here  $\epsilon_l = (\xi_l^2 + \Delta_l^2)^{1/2}$ ;  $\xi_l$  is the energy of the normal electron, reckoned from the Fermi level; the summation is over the values of the two-dimensional vector  $\kappa_l$ , and also over the different subbands l.

Going over in (3) to integration with respect to  $\xi_l$ , we obtain

$$\mathbf{1} = g_{1l} N_l \lambda_l \int_0^{\omega_l} d\xi_l \frac{\operatorname{th} \left(\varepsilon_l/2T\right)}{\varepsilon_l}, \qquad (4)$$

where  $\omega_l \sim \omega_D$ ,  $\lambda_l = \Delta_l / \Delta_1$  ( $\omega_D$  = Debye frequency), and N<sub>l</sub> is the two-dimensional state density per unit volume:

$$N_l = \frac{1}{4\pi} \frac{2m^*}{\hbar^2} \frac{1}{L}.$$
 (5)

In going over to (4), a quadratic dependence of  $\epsilon$  on  $\kappa$  is assumed.

From (4) we obtain the following expression for  $T_c$ :

$$T_{\rm c} = 1.14 \,\widetilde{\omega} \exp\left(-2\pi \hbar^2 L \,\Big|\, m \, \sum_l g_l \lambda_{lc}\,\right), \qquad (6)$$

<sup>\*</sup>th ≡ tanh.

where  $\tilde{\omega}$  is the effective phonon frequency,  $\tilde{\omega} \sim \omega_{\rm D}$ , and  $\lambda_{lc} = \lambda_l |_{\rm T=T_c}$ . The summation in (6) is over all sub-bands. Since their number is  $\sim k_{\rm F}L$ , the value of T<sub>c</sub> does not depend on L when all the g<sub>l</sub> are equal (when all  $\lambda_l = 1$ ). At the same time, differences in g<sub>l</sub> lead, as can be seen from (6), to a dependence of the critical temperature on the film thickness.

The manifestation of this dependence is observed most clearly when limiting cases are considered. At thickness  $L \leq 10^{-7}$  cm the displacement of the sub-bands is  $\delta \epsilon \sim \epsilon_{\rm F}$ . Consequently only one subband will essentially be populated, corresponding to  $g_l = 0$  with  $l \neq 1$ . This results in an exponential dependence of T<sub>c</sub> on L, in analogy with the case of thin superconducting or semimetal films<sup>[8]</sup>. For sufficiently thick films ( $L \gtrsim 10^{-5}$  cm) the critical temperature, naturally, tends to  $T_{c}$  of the bulk sample and ceases to depend on L. By virtue of the large number of sub-bands, the differences between the values of  $g_l$  become insignificant in this case. In films of thickness  $L \sim 10^{-6}$  cm, we get an intermediate dependence which, apparently, is indeed observed in experiment<sup>[1,2]</sup>.

The coupling constants  $g_l$ , as seen from (2), are connected with the integral over the momenta of the virtual phonons. (In formula (2b) it is necessary, as usual, to go over (see, for example, <sup>[12]</sup>) to integration with respect to  $dq^2$ , where q is the phonon momentum.) We see that  $g_l$  decreases with increasing l, since the transition of electrons to higher sub-bands cannot be realized by phonons with small momenta q. An approximate relation characterizing this decrease is

$$\frac{\overline{g_i - g_{i+1}}}{g_i} \sim \frac{q_i^2_{min} - q_{(i+1)min}^2}{q_D^2} \sim \frac{a}{L}$$

 $(q_D \text{ is the Debye momentum, a the lattice period, and <math>q_{i \min}$  the minimum phonon momentum that transfers the electron from the first to the i-th sub band). Thus, the values of  $g_l$  are not equal to each other and form a monotonically decreasing sequence, leading to an increase of  $T_c$  with decreasing L. We see that the rate of growth increases here with decreasing film thickness in agreement with the experimental data<sup>[1,2]</sup>.

It was observed in experiment<sup>[2]</sup> that the critical temperature increases from 1.6 to 1.9° when the film thickness is reduced by one-half in the region L ~ 100Å. To explain this 20% growth of T<sub>c</sub> it is necessary that the relative decrease of the sum in (6), when L is reduced by one-half, amount to ~ 3% ( $\omega_D$  ~ 400° for aluminum). This will take place if g<sub>l</sub> for neighboring sub-bands decreases on the average in the same ratio. Within the limits of accuracy, this coincides with the estimate presented (in the case under consideration  $a \sim 3$ Å).

The presence of anisotropy leads to a difference in the effective masses  $m_l$  for different sub-bands. Then formula (6) for  $T_c$  will contain the sum  $\Sigma_{lglml\lambda_l}$ , which leads, when allowance is made for the monotonic decrease of  $\lambda_l$ , to nonequivalence of the individual terms, and by the same token to a dependence of  $T_c$  on L.

The influence of quantization of transverse motion on  $T_c$  was considered by Singh<sup>[13]</sup>. His results, however, seem incorrect to us, primarily because he did not take into account the differences in  $g_l$ . The variation of  $T_c$  with L is attributed by him to a decrease in the total density of the states  $N_f$  with change in L. This quantity, however, is a steplike function<sup>[14]</sup>.

Indeed, assume that s sub-bands are populated, but the (s+1)-st sub-band is not populated. Then the density is

$$N = \sum_{l} 2(\varepsilon_{s+1} - \varepsilon_l) N_l,$$

where  $N_l$  is the density of states in one sub-band. After simple calculations we obtain, for a quadratic dispersion law with allowance for quantization of  $k_z$ ,

$$s(s+1)(s+1/2) = (3/8\pi)NL^3$$

The total density of the states in the film is N<sub>f</sub> =  $2 \text{sN}_l$ ; the factor 2 is connected with the fact that in the approximation employed both the state with  $k_z = (2l-1)\pi/L$  and the state with  $-k_z$  belong to the given sub-band. In the limit of large s (see (5)) we have

$$N_f pprox 2\left(rac{3}{8\pi}NL^3
ight)^{\prime h}rac{1}{4\pi}rac{2m}{\hbar^2}rac{1}{L}\equiv N_{
m bulk}.$$

For finite s we get N<sub>f</sub> < N<sub>bulk</sub>.

We now assume that L has increased somewhat, so that the (s+1)-st sub-band begin to be populated. The number of sub-bands S = s+1 satisfies the equation

$$S(S-4)(S-4/2) = (3/8\pi)NL^3$$
,

which leads to  $N_f > N_{bulk}$ . Thus, with increasing L and at a constant volume concentration,  $N_f$  oscillates about the value of  $N_{bulk}$ .

## 3. ELECTRONIC MECHANISMS IN FILMS

We now consider a phononless superconductivity mechanism, which can lead to essential changes on going over from the bulk sample to a thin film. Several recent papers<sup>[15]</sup> have proposed new superconductivity mechanisms. In the electronic mechanism, the Cooper pairing is the result of the Coulomb interaction of the electrons from different groups. Such a mechanism, which is connected with the presence of overlapping the bands, was considered for a bulk crystal by Geĭlikman<sup>[16]</sup>. In thin films, different electron groups are overlapping sub-bands (see Sec. 1). In addition, in a crystalline semiconducting film, owing to the decrease in the symmetry, the degeneracy is lifted<sup>[17]</sup>, and this also leads to formation of two or more groups of electrons differing in their effective masses and in their wave functions.

<u>Semiconductors</u>. We consider first the electronic mechanism in a thin semiconducting film. This case was briefly analyzed in a paper by the authors <sup>[5]</sup>. We assume the following model, corresponding to the possible band structure of such a film. There are two groups of electronic states, and the minimum electron energy  $\epsilon_{1 \text{ min}}$  lies below  $\epsilon_{2 \text{ min}}$ . We denote by  $\mu$  the chemical potential, which in this case depends on the temperature, reckoned from  $\epsilon_{1 \text{ min}}$  and  $\epsilon_{2 \text{ min}}$  respectively. We assume further that  $\mu_2 < 0$  and consequently the electrons of the second group are described by a Boltzmann distribution.

A unique additional interaction, due to the Coulomb interaction of the electrons of the first and second groups, occurs between the electrons of the first group. This can be visualized intuitively in the following manner. As a result of the Coulomb scattering by certain electrons of the first group, an electron from the second sub-band experiences a virtual transition to an excited state; its inverse transition is accompanied by a change in the state of the second electron from the first sub-band.

The self-energy part  $\Delta_{11}$  describing the Cooper pairing of the electrons in the first group, satisfies the equation

$$\Delta_{ii}(\mathbf{p},\omega_n) = \frac{T}{(2\pi)^3} \sum_{\omega_n'} \int d\mathbf{p}' \\ \times \Gamma_{ii,\,ii}(\mathbf{p}',\omega_n';\mathbf{p}',\omega_n';\mathbf{p},\omega_n;\mathbf{p},\omega_n) F_{ii}^+(\mathbf{p}',\omega_n'), \quad (7)$$

where  $\omega_n = (2n+1)\pi T$  and  $\Gamma_{11,11}$  is a complete four-pole. It has been calculated in general form by Geĭlikman<sup>[16]</sup>. It is determined from the system of equations

$$\Gamma_{11,11} = V_{11,11} + V_{11,11}\Pi_{11}\Gamma_{11,11} + V_{12,12}\Pi_{22}\Gamma_{12,12},$$
  

$$\Gamma_{12,12} = V_{12,12} + V_{12,12}\Pi_{11}\Gamma_{11,11} + V_{22,22}\Pi_{22}\Gamma_{12,12}$$
(8)

and is equal to

$$\Gamma_{11,11} = (V_{11,11} + \Pi_{22}R) / S, \tag{9}$$

where  $R = V_{12,12}^2 - V_{11,11}V_{22,22}$ ;  $V_{11,11}$ ,  $V_{22,22}$ , and  $V_{12,12}$  are the matrix elements of scattering in which the electrons remain in their groups;

$$S = 1 - V_{11,11} \Pi_{11} - V_{22,22} \Pi_{22} - \Pi_{11} \Pi_{22} R;$$

the polarization operator  $\Pi_{22}$  describes virtual transitions in the second sub-band, with  $\Pi_{22} < 0$ .

Unlike the usual case, the constant describing the effective interelectron interaction is a function of the temperature. This is connected with the temperature dependence of the polarization operator  $\Pi_{22}$  which enters in (9).

It follows from (9) that attraction occurs under two conditions: first, if R > 0, and second if  $\Pi_{22}R$ is sufficiently large compared with the renormalized Coulomb repulsion. When the sample becomes thicker, the difference in the matrix elements vanishes ( $R \rightarrow 0$ ), and this leads to a vanishing of the effect, which thus turns out to be possible only in thin films.

In our case, when Boltzmann's statistics are applicable for the electrons of the second group,  $\Pi_{22}$  takes the form

$$\Pi_{22}(\varkappa, T) = -2 \exp\left(-\frac{|\mu_2|}{T}\right) \\ \times \sum_{\mathbf{p}} \frac{\exp\left(-\varepsilon_{\mathbf{p}}/T\right) - \exp\left(-\varepsilon_{\mathbf{p}+\mathbf{x}}/T\right)}{i\omega - \varepsilon_{\mathbf{p}} - \varepsilon_{\mathbf{p}+\mathbf{x}}}, \qquad (10)$$

where  $\kappa$  is the momentum transfer. For small  $\kappa$  ( $\kappa^2 \ll m_2 T$ ) the operator  $\Pi_{22}$  is a constant quantity, equal to  $m_2 V \exp(-|\mu_2|/T)\hbar^2/L$ , and for  $\kappa^2 \gg m_2 T$  we have  $\Pi_{22} \sim \kappa^{-2}$ , that is, it approaches zero quite rapidly. Therefore we can assume that the attraction is constant in an energy region of the order of T and is equal to zero outside this region. The situation here is analogous to the usual theory of superconductivity, in which the interaction is assumed constant up to energies of the order of  $\hbar\omega_D$ , and assumed equal to zero for larger energies. In this case, however, a different cutoff parameter arises.

Carrying out further the summation in (7), we obtain

$$1 = \frac{g(T)N}{2} \int d\xi \frac{\operatorname{th}\left[(\xi^2 + \Delta^2)^{\frac{1}{2}}/2T\right]}{(\xi^2 + \Delta^2)^{\frac{1}{2}}}, \quad (11)$$

where  $\xi = \epsilon - \mu_1(T)$ , N is the state density (see (5)),  $g = 2\Gamma V = g_{attr} - \tilde{g}$ , where  $\tilde{g}$  is the renormalized Coulomb repulsion;  $\omega_c \gg T$ , where  $\omega_c$  is the plasma frequency.

The temperature of the transition is determined from (4) by putting  $\Delta = 0$ . In the nondegenerate case (tanh ( $\xi/2T_c$ ) = 1) we obtain the equation  $\hbar^4 L^2 \varkappa_D^4 \exp(|\mu_2| / T_c) / m_1 m_2 e^4$ 

$$= \ln |[T_{\rm c} - \mu(T_{\rm c})] / \mu(T_{\rm c})|.$$
(12)

In a semiconducting film we have <sup>[18]</sup>

 $2\mu = -E_D + T \ln \left( N_D L \pi \hbar^2 / mT \right).$ 

The solution of (12) can be obtained graphically. In the figure, the f and u curves correspond to the left and right sides of (11) at the parameters indicated below; for T < 1° the curves have been calculated from Eq. (12). We see that the effect can arise only at a finite temperature, and if the superconductivity criterion is satisfied, then the effect exists in the temperature interval  $T_{C.u} \ge T \ge T_{c.l}$ . An estimate for  $L \approx 5 \times 10^{-6}$ ,  $\kappa_D \approx 5 \times 10^{5}$ ,  $E_D \approx 5^{\circ}$ , and  $N \approx 5 \times 10^{18}$  yields for the lower limit, for example, a value  $T_{c.l} \approx 0.5^{\circ}$ .



The existence of a  $T_{c.l}$  below which there is no superconductivity is due to the temperature dependence of the populations of the first and second sub-bands. At absolute zero g = 0, since there are no electrons in the second sub-band, and when  $\mu_1 < 0$  there are likewise no carriers in the first sub-band. When  $0 < T < T_{c.l}$  the electrons of the first group, with Boltzmann statistics, interact weakly with one another and do not form a bound state.

For nondegenerate superconducting semiconductors, the lower critical temperature  $T_{c.l}$  remains different from zero even for ordinary electron-phonon interaction. In films in which the conditions for the occurrence of superconductivity are more favorable, the appearance of  $T_{c.l}$  is discussed in <sup>[9]</sup>. In the case when  $\mu_1 > 0$ , the lower critical temperature remains different from zero so long as  $\mu_2 < 0$ . At temperatures lower than  $T_{c.l}$  normal conductivity will be observed.

We assumed above that there is no pairing in the higher sub-band. At a certain temperature it may turn out that the superconductivity criterion is satisfied even for this band, too, but this does not change our results in principle.

A phononless superconductivity mechanism is possible in principle also in a bulk superconductor in which there are carriers (holes or electrons) that differ in their effective masses and in their wave functions. They form different groups that interact with one another, and this can lead to an effective attraction described by formulas analogous to (7)-(11), in which the density of states must be taken for the bulk sample.

Semimetal or degenerate semiconductor. We now proceed to consider the case when the electron system is degenerate in both sub-bands. We write the equations for the self-energy parts  $\Delta_1$ and  $\Delta_2$ 



Unlike the semiconducting film considered above, terms containing  $\Gamma_{11,22}$  and  $\Gamma_{22,11}$  are added, describing transition of pairs from one sub-band to another.

Introducing, as usual, the effective coupling constants and carrying out in the (2) summation over  $\omega$ , we obtain

$$\Delta_{1} = g_{11}N_{1}\int_{0}^{\Delta E_{1}} \frac{\Delta_{1} \operatorname{th}\left(\varepsilon_{1}/2T\right)}{\varepsilon_{1}} d\xi + g_{12}N_{2}\int_{0}^{\Delta E_{2}} \frac{\Delta_{2} \operatorname{th}\left(\varepsilon_{2}/2T\right)}{\varepsilon_{2}} d\xi,$$
  
$$\Delta_{2} = g_{21}N_{1}\int_{0}^{\Delta E_{1}} \frac{\Delta_{1} \operatorname{th}\left(\varepsilon_{1}/2T\right)}{\varepsilon_{1}} d\xi + g_{22}N_{2}\int_{0}^{\Delta E_{2}} \frac{\Delta_{2} \operatorname{th}\left(\varepsilon_{2}/2T\right)}{\varepsilon_{2}} d\xi,$$
  
(14)

where  $N_1 N_2 = m/2\pi\hbar^2 L$ . Attraction, as in the usual model, is constant in the intervals  $\Delta E_{1,2}$  and vanishes outside them.

For the critical temperature we obtain from (14) an expression similar to the corresponding formula obtained in the two-band model of a superconductor:

$$T_{\rm c} \approx \Delta E \exp\left(-\frac{2\pi L\hbar^2}{m(g_{11}+g_{12}\lambda)}\right), \quad \lambda = \frac{\Delta_2}{\Delta_1}\Big|_{T=T_{\rm c}}.$$
 (15)

To estimate the value of the constants g we write out equations for the four-poles contained in (12):



and similarly for  $\Gamma_{22,22}$ . In (16) we neglect small terms containing matrix elements of the type V<sub>11,12</sub>

and  $V_{12,22}$  which describe the scattering of two electrons with resultant transition of one of the electrons to a second sub-band. Their smallness is connected with the approximate satisfaction of the quasimomentum conservation law.

The system (16) is easy to solve. In the expressions obtained for the four-poles, the attractions described by terms containing polarization operators. An estimate of the effective attraction leads to the following expression for the coupling constants

$$g_{\text{attr}} \sim V^2 \Pi \sim \frac{e^4}{\kappa_D^4} \frac{\kappa_F^2}{\Delta E} \frac{1}{L}$$
 (17)

 $(\kappa_D^{-1}$  —Debye radius,  $\Delta E$  —average value of the energy interval describing the virtual electron transitions). The coupling constant, as usual, is equal to  $g = g_{attr} - \tilde{g}$ , where  $\tilde{g}$  is the renormalized Coulomb repulsion.

In our case, as seen from (15),  $T_c$  increases with decreasing film thickness. This is connected, on the one hand, with the dependence of the state density on L. In addition, as already noted above, the interelectron attraction vanishes on going to the bulk sample. Thus, the constants contained in (15) depend themselves on the thickness of the film, which also leads to an increase of  $T_c$  with decreasing L.

<u>Metallic films</u>. The electronic mechanism considered above is possible in principle also in a metallic film. A distinguishing feature of this case is the population of many sub-bands, with the inequality  $\mu_l > 0$  satisfied for any *l*-th group of electrons. The system of equations for the self-energy parts is of the form

$$\Delta_{i} = \frac{T}{(2\pi)^{3}} \sum_{\omega'} \int \Gamma_{iill}(\varkappa_{l}', \omega'; \varkappa_{l}', \omega'; \varkappa, \omega; \varkappa, \omega) F_{ll}(\varkappa_{l}', \omega') d\varkappa_{l}'$$
(18)

(i = 1, 2, ..., l, ...). The summation in (18) over identical indices corresponds to summation over all sub-bands.

The four-poles  $\Gamma_{iiII}$  are described by system of equations which generalizes the system (16) to the case of many sub-bands. Thus, for example, the equation for  $\Gamma_{11,11}$  is

$$\Gamma_{11,11} = V_{11,11} + \sum_{n} V_{1n,1n} \Pi_{nn} \Gamma_{n1,n1}$$
(19)

that is,

$$\Gamma_{11,11} = \left( V_{11,11} + \sum_{l} V_{1l} \Pi_{ll} \Gamma_{l1,l1} \right) / (1 - V_{11,11} \Pi_{11}). \quad (20)$$

The four-poles  $\Gamma_{l_1,l_1}$ , which describes scattering, satisfy equations analogous to (16). These will not be written out here. After introducing in (18) the effective quantities  $g_{1l}$  corresponding to  $\Gamma_{11,ll}$ , we arrive at a system of equations analogous to (3), with different constants. It is seen from (20) that in view of the presence of many planes, the constants, generally speaking, are larger than in the case of the semimetal.

For  $T_c$  we obtain the expression

$$T_{\rm c} \approx \Delta E \exp\left(-2\pi L\hbar^2 \left| m \sum_i g_i \lambda_i \right| \right).$$
 (21)

The number of terms in the sum is  $\sim k_F L$ , and if all the  $g_{11}$  are identical, then the dependence on L, connected with the state density, vanishes. However,  $T_C$  does not cease to depend on L. This is connected with the essential dependence of the coupling constants themselves on the thickness in the case of the electronic mechanism.

It may turn out that pairing of the electrons occurs not in all the sub-bands. Then the film may turn out to be a gapless superconductor, that is, a thresholdless absorption of waves can be observed in it besides the absence of electric resistance.

We have disregarded above the additional electron scattering due to the presence of surface defects. For small  $k_z$ , however (lower sub-bands), this scattering can be neglected, inasmuch as  $\lambda \sim L \gg a$ . Therefore allowance for scattering by the surface defects cannot alter the results greatly. In semiconducting films, owing to the large electron wavelength, the scattering by surface defects plays no role. Quantization in aluminum and bismuth films was found experimentally<sup>[19]</sup>.

Thus, in the usual phonon mechanism, the transition from the bulk sample to the film leads, generally speaking, to a monotonic growth of the critical temperature. The existence of an electronic mechanism also leads to a rise in  $T_c$ . At the same time, a case is also possible when a substance which is not superconducting in bulk displays superconductivity as a film. The electronic mechanism leads to the absence of an isotopic effect, and in conjunction with the phonon mechanism it leads to the dependence of the isotopic effect on the film thickness.

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