

# Problems of high-temperature superconductivity in three-dimensional systems

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Usp. Fiz. Nauk 109, 65-90 (January 1973)

The article describes theoretical work on the electron (exciton) mechanism of superconductivity in three-dimensional systems, which leads to high critical temperatures. Two models are considered: 1) systems with collective electrons of one group and localized electrons of another group (compounds of metals with dielectrics, organic substances, semiconductors or molecular crystals); 2) systems with two (or more) groups of collective electrons (metals with overlapping bands and multi-domain semiconductors). In the first case, uniform and granulated systems are considered. The effect of the critical fluctuations impeding the superconductivity is discussed in the case of granulated systems. Experimental work on the superconductivity of compounds of metals with dielectrics, organic substances, semiconductors and semimetals is described and discussed.

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## 1. INTRODUCTION

The problem of high-temperature superconductivity has recently excited widespread interest, although the possibility of creating superconductors with a critical temperature approaching or even exceeding room temperature is, as yet, only theoretical. This interest is entirely understandable, since, in addition to the wide prospects of very important technical applications, high-temperature superconductivity is in itself an extremely interesting physical phenomenon.

The problems of high-temperature superconductivity have been the subject of two very full reviews<sup>[1,2]</sup>. However, even since the publication of the review<sup>[2]</sup>, a large number of interesting, and mainly experimental, papers has appeared. These papers (published by the time of writing of the present review, February, 1972) will be discussed below, since, from the point of view of choosing directions for future investigations, it may turn out to be very useful to analyze them. In the reviews<sup>[1,2]</sup>, attention was concentrated principally on two-dimensional and approximately two-dimensional systems (sandwiches with dielectric layers). Below, the possibilities of creating high-temperature superconductivity in three-dimensional systems will be considered.

A new mechanism of superconductivity, which in principle can lead to considerably higher critical temperatures than the usual phonon mechanism (and the less studied magnon mechanism) was proposed by Little in a paper<sup>[3]</sup> devoted to superconductivity of polymer molecules. In<sup>[3,4]</sup>, a special model of a polymer was considered, consisting of a central polymer chain, to which side-chains are attached on both sides. It is assumed that there are collective  $\pi$ -electrons in the central and side-chains. It is easy to show that the Coulomb repulsion between the electrons of the central and side chains leads, in second order of perturbation theory, to the appearance of attraction between the electrons of the cen-

tral chain (and between the electrons of the side chains). This attraction is connected with the fact that the second-order correction  $E_0''$  to the energy of the ground state is always negative:

$$E_0'' = \sum_m |V_{0m}|^2 (E_0^{(0)} - E_m^{(0)})^{-1};$$

$V_{0m}$  is a matrix element of the interaction between the electrons of the central and side chains.

The physical nature of the interaction arising in this way between the electrons of the central chain consists in the fact that they exchange quanta of the oscillations of the electron density of the side chains, i.e., they exchange electron excitons, (and the interaction between the electrons of the side chains is connected correspondingly with the fact that they exchange virtual quanta of the oscillations of the electron density of the central chain). Thus, the nature of the attractive forces in Little's model is the same as in the phonon mechanism: in the latter case, the attraction arises as a result of the fact that the electrons exchange virtual phonons, i.e., quanta of oscillations of the ion density. If the attractive forces between the electrons of the central chain exceed the Coulomb repulsive forces between them, these electrons can become superconducting. A characteristic of the attractive forces, in addition to the interaction constant, is the virtual energy  $\Delta E$  transferred in the interaction. Whereas in the phonon mechanism  $\Delta E$  is equal to the energy of a phonon, i.e., will be of the order of the Debye frequency  $\hbar\omega_D$ , in the mechanism under consideration, which we shall call the electron or exciton mechanism,  $\Delta E$  will be of the order of the mean transition energy for the electrons of the auxiliary system, i.e., of the side chain. But since  $\Delta E$  is now of the order of the electron energy, the ratio  $\Delta E/\hbar\omega_D$  will be of the order of  $(M/m)^{1/2} \sim 10^2$  ( $m$  is the electron mass and  $M$  the ion mass). It follows from the microscopic theory of superconductivity<sup>[5]</sup> that the critical temperature  $T_c$  is given by the expression

$$T_c \approx \Delta E e^{-1/g} \quad (1)$$

where  $g$  is the dimensionless interaction constant. A simple estimate shows that the order of magnitude of  $g$  is the same in the phonon and electron mechanisms (a scaling estimate gives for the constant  $g$  the quantity  $e^2/\hbar v$ , although  $g$  can also have a factor containing the ratio of the electron and ion concentrations to some power and depending on the specific characteristics of the metal;  $v$  is the electron velocity at the Fermi surface). Then it can be seen from (1) that we may expect critical temperatures a factor of  $(M/m)^{1/2}$ , i.e.,  $\sim 10^2$  times, greater in the electron mechanism than in the phonon mechanism. Subsequently, a calculation within the framework of Little's model was performed in<sup>[6]</sup>, not by perturbation theory but exactly using a diagram technique; this calculation confirmed the basic conclusions of<sup>[3]</sup>.

In<sup>[7]</sup>, a model of superconducting sandwiches with dielectric layers was put forward. As a result of virtual transitions of electrons in the atoms of the dielectric, attraction of the same order of magnitude as in<sup>[3]</sup> should arise between the electrons of the metallic film, i.e., the dielectric layers play the same role as the polymer side chains in<sup>[3]</sup>. Since the  $\psi$ -functions of the electrons of the dielectric and the metal overlap only over distances on the atomic scale, additional attraction will arise between the electrons of the metal in a surface layer with thickness of the same scale (cf. <sup>[1,2]</sup>). According to to<sup>[8]</sup> (cf. also<sup>[9]</sup>), in a non-uniform medium the critical temperature is determined by an interaction constant equal to the mean of the interaction constants of the different parts,  $g = (g_1 d_1 + g_2 d_2) / (d_1 + d_2)^{-1}$ ;  $g_1$  and  $d_1$  are the interaction constant and thickness of the surface layer, and  $g_2$  and  $d_2$  are the interaction constant and thickness of the other film. Therefore, in order that the effect of the dielectric layers be substantial, it is obviously necessary, as was observed in<sup>[1,2]</sup>, that the thickness of the whole metallic film be of the same order as the thickness  $\Delta R$  of the surface layer, i.e., 10–20 Å (see also<sup>[10a]</sup>).<sup>1)</sup> Thus, the sandwich must approximate to a two-dimensional system. Even before the publication of<sup>[3]</sup>, in which the problem of high-temperature superconductivity was brought forward, the possibility of superconductivity with ordinary critical temperatures in purely two-dimensional systems (surface electrons) was investigated in<sup>[11]</sup>.

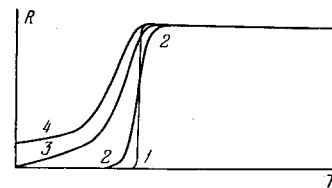
The possibility of an electron mechanism of superconductivity with high critical temperatures in purely three-dimensional systems was investigated in<sup>[12]</sup>. Two three-dimensional models were considered: 1) a pure metal or an ordered alloy (with comparable concentrations of the components) with overlapping unfilled bands ( $s$  and  $d$  or  $s$  and  $f$ ), 2) an ordered compound of a metal and a non-metal possessing localized electrons (with comparable concentrations of the components). As in<sup>[3]</sup>, the Coulomb repulsion between the electrons of the first and second bands in the first model, and between the collective conduction electrons and the localized electrons of the nonmetallic atoms in the second model, leads in the second and higher orders of perturbation theory to the appearance of attraction between the electrons of each of the bands (in the first model) and between the conduction electrons (in the second model).

Thus, in the first model the electrons of the two groups (the interaction between which leads to the appearance of attraction between the electrons in each

group) are collective electrons, and in the second model the electrons of one group are collective while those of the second group, playing the auxiliary role, are localized.

Soon after the appearance of<sup>[3]</sup>, papers were published<sup>[13]</sup> in which it was shown that electron fluctuations should destroy the superconducting order (and order of a different nature) in one-dimensional and two-dimensional systems. It was rigorously in<sup>[14]</sup> proved that in infinite purely one-dimensional and purely two-dimensional systems superconducting order is impossible, i.e., the critical temperature goes to zero. However, for a two-dimensional Bose gas (and a lattice of plane rotators equivalent to it), "approximate" long-range order is apparently possible, corresponding to a power-law rather than an exponential falling off of the correlation function at infinity<sup>[15]</sup> (in the presence of strict long-range order, the correlation function tends to a constant at infinity). According to<sup>[14]</sup>, in one-dimensional systems the divergence of the fluctuations has a power-law character and in two-dimensional systems is logarithmic, so that, in the latter case, for systems with finite dimensions, the critical temperature will be only decreased (compared with three-dimensional systems) as a result of the fluctuations, but will not go to zero.

In order to avoid the effect of fluctuations, a system with a stack of such chains was proposed in<sup>[16]</sup> in place of the model with one central polymer chain. To conserve the quasi-one-dimensional nature of the model it is assumed that the conductivity in the direction perpendicular to the chains is considerably lower than in the longitudinal direction, although, for substantial suppression of the fluctuations it is necessary that the ratio of these conductivities be nevertheless not very small. Thus, in this case, a one-dimensional system is effectively converted into a three-dimensional system. Clearly, fluctuations will also impede the establishment of superconducting order in systems approximating to one-dimensional or two-dimensional systems. It was shown in the paper<sup>[17]</sup> on the basis of the solution of the Ginzburg-Landau equations that for a superconducting wire ring of macroscopic dimensions the phase transition becomes more and more smeared out as the cross-section diameter of the conductor decreases, and for a sufficiently small diameter  $d$  the transition region can extend down to zero (see the figure, in which  $R$  is the resistance and  $T$  the temperature). As can be seen from the figure, this blurring leads to a lowering of the criti-



cal temperature from  $T_{c0}$  to  $T_{ci}$ . The Ginzburg-Landau theory, as is well known, has no region of applicability in the case of one-dimensional systems. Therefore calculations for very small values of  $d$  could not be performed in<sup>[17]</sup>; however, it may be supposed that for sufficiently small  $d$  we should observe the curve 3 for which  $T_c$  is found to be equal to zero. In<sup>[18]</sup>, also on the basis of the Ginzburg-Landau expression for the free energy, similar (but in certain respects also slightly different) results were obtained for the resistance of a cylindrical conductor. According to<sup>[18]</sup>,

$$R/R_n = \exp[\gamma - (\tau/\tau_{c1})^{3/2}]; \quad (2)$$

here,  $\gamma = \ln[k_F d^4 (\epsilon_F/T_c)] \approx 44$ ,  $\tau = 1 - (T/T_c)$ ,  $\tau_{c1} = (\epsilon_F/T_c)^{2/3} (k_F \xi(0) d^2)^{-2/3}$ ,  $R_n$  is the resistance in the normal state,  $d$  is the diameter of the conductor,  $\xi(T)$  is the correlation length of the superconducting state (see below), and  $\epsilon_F$  and  $\hbar k_F = p_F$  are the energy and momentum of the electrons at the Fermi surface ( $T$  is measured in energy units).

As in<sup>[17]</sup>, the transition in the resistance is found to be more blurred the smaller is  $d$ , but, in contrast to<sup>[17]</sup>, although the resistance  $R$  falls exponentially below  $T_c$ , it is nonzero at all temperatures, even for conductors with macroscopic values of  $d$ . For large  $d$ , the resistance is negligibly small below  $T_c$ , but nevertheless non-zero, i.e., the concept of a critical temperature at which  $R$  goes to zero exactly loses its meaning, strictly speaking. Thus, the formula (2) corresponds not to exact but to so-called approximate superconductivity, even for bodies of macroscopic dimensions (i.e., strict long-range order is absent).

It is known, however, that the Ginzburg-Landau theory, on the basis of which the calculations in<sup>[17,18]</sup> were performed, is applicable in only a small region about the transition point, i.e., for the condition  $|\tau| \lesssim 1$ . Therefore, outside this region ( $|\tau| \gg 1$ ), the Ginzburg-Landau theory can be used only to make qualitative estimates, but cannot be used to draw conclusions on the details of the behavior of superconductors corresponding to formula (2) with  $\tau > 1$ , or, in particular, to reach conclusions about the approximate superconductivity of macroscopic superconductors.

Thus, in the range in which the Ginzburg-Landau theory is accurate, a lowering of  $T_c$  with decreasing diameter of the conductor, owing to the growth of critical fluctuations, is predicted in<sup>[17,18]</sup>. Qualitatively, the same pattern should apparently also be observed for a film as its thickness is decreased (see Sec. 2 for more detail).

In experiments with films, as is well known, on decrease of the thickness an increase of the critical temperature is often first observed, associated, apparently, with size quantization<sup>[19]</sup> or, in some cases, with a change of the form of the phonon spectrum. However, at a certain thickness, which is different for different superconductors (from 30 to 100 Å), the critical temperature reaches a maximum and, on further decrease of the thickness of the film, begins to fall. In certain cases,  $T_c$  begins to decrease at a sufficiently small thickness without any preliminary increase<sup>[20-22]</sup>. Most probably, this lowering of  $T_c$  is associated, as is indeed assumed in<sup>[22]</sup>, with growth of fluctuations as the system approximates more closely to a two-dimensional system. In this case, for sandwiches with dielectric layers, it would be very important that the optimal thickness, of the order of one or two tens of Angstroms (see above), turn out to be greater than the thickness at which fluctuations are already decreasing the critical temperature substantially. We note that, as will be shown below, the theoretical estimates for the critical thickness at which the fluctuations destroy the superconductivity turn out to be more favorable for a film than for a filament or spherule.

If the superconductivity is true for macroscopic bodies and not approximate it would be interesting to realize

for quasi-one-dimensional and quasi-two-dimensional systems the approximate superconductivity discussed in<sup>[2,18,23,24]</sup>, corresponding to the curve 4 in the figure for the resistance, i.e., to realize a system with a resistance that is non-zero but sufficiently low at temperatures considerably below  $T_c$ . Also of interest is the possibility of realizing metastable superconductivity for quasi-one-dimensional and quasi-two-dimensional systems, i.e., a superconducting state that does not correspond to the absolute minimum free energy and is therefore thermodynamically unstable (cf.<sup>[2]</sup>). However, it is at present difficult to say whether the lifetime of such a metastable state could be sufficiently long. These considerations also apply to a type of three-dimensional system such as metallic hydrogen, whose superconducting state is stable, according to theoretical estimates, only under pressures greater than  $\sim 10^6$  bar, and is metastable under ordinary pressures.

We proceed to analyze the possibilities of high-temperature superconductivity in three-dimensional systems. First we shall consider the second model, which can be analyzed in more detail at present: compounds of metals with non-metallic substances, i.e., three-dimensional systems (uniform and non-uniform) in which there are conduction electrons and electrons localized in atoms. Interaction between the electrons of these two groups leads to attraction between the conduction electrons.

## 2. SYSTEMS WITH COLLECTIVE ELECTRONS OF ONE GROUP AND LOCALIZED ELECTRONS OF ANOTHER GROUP (COMPOUNDS OF METALS WITH NON-METALS—DIELECTRICS, ORGANIC SUBSTANCES, UNDOPED SEMICONDUCTORS, AND MOLECULAR CRYSTALS)

Ordered (or non-ordered) compounds of a metal with a non-metal, with comparable concentrations of the components, were investigated in<sup>[12]</sup>. It is assumed that the electrons of the non-metal atoms remain localized in such a compound, although their  $\psi$ -functions undergo change. Of course, this condition (small impurity-bandwidth) can be fulfilled for compounds of this type only in certain cases.

Because of the interaction of the conduction electrons with the electrons in the non-metal atoms, there appears, along with the screened Coulomb repulsion between the conduction electrons, an interaction which, for clarity, we shall write only to second order of perturbation theory<sup>[12b,c]</sup> (a more exact calculation will be performed elsewhere):

$$\begin{aligned} \Gamma_{p_1 p_2; p_3 p_4} &\approx \Gamma_{p_1 p_2; p_3 p_4}^* + \Gamma_{p_1 p_2; p_3 p_4}^{\prime\prime} \\ \Gamma_{p_1 p_2; p_3 p_4}^* &\approx V_q / [1 - \Pi(\mathbf{q}, \omega)], \\ \Gamma_{p_1 p_2; p_3 p_4}^{\prime\prime} &\approx \sum_{n, \lambda, \lambda'} V_{p_1, n\lambda; p_3, n\lambda'} V_{n\lambda'; p_2, n\lambda, p_4} \Pi_{\lambda\lambda'}, \\ V_q &= 4\pi e^2 / q^2, \quad \Pi_{\lambda\lambda'} = (n_\lambda - n_{\lambda'}) / (E_\lambda - E_{\lambda'} + \hbar\omega), \\ \hbar\mathbf{q} &= \mathbf{p}_3 - \mathbf{p}_1, \quad \hbar\omega = \xi_3 - \xi_1. \end{aligned} \quad (3)$$

The  $\psi$ -functions of the conduction electrons are taken in the form of plane waves.  $p_1$  and  $p_2$  are the momenta of the two conduction electrons before collision and  $p_3$  and  $p_4$  are their momenta after collision. The first term in (3) corresponds, for  $\omega/q \rightarrow 0$ , to the usual screened Coulomb repulsion, and the second term to the attraction.  $V_{p_1, n\lambda; p_3, n\lambda'}$  is a matrix element of the interaction between the conduction electrons and the localized electrons;  $\lambda$  is the set of quantum numbers of an electron in the non-metal atom at the lattice site with coordinates

$n$ ;  $\xi(\mathbf{p})$  is the conduction-electron energy reckoned from the Fermi surface;  $E_\lambda$  is the energy of the electron in the non-metal atom;  $\Pi(\mathbf{q}, \omega)$  and  $\Pi_{\lambda\lambda'}$  are the polarization operators for the conduction electrons and the non-metal electrons respectively; for  $\Pi(\mathbf{q}, \omega)$ , see formula (11) below;  $n_\lambda$  is the occupation number of the electrons. Because of the summation over  $n$ ,  $\Gamma'' \sim n_a$  ( $n_a$  is the concentration of non-metal atoms);

$$V_{p_1, n\lambda; p_3, n\lambda'} \approx (4\pi e^2 e^{iqn}/q^2) \int e^{iqr} \psi_\lambda(r) \psi_{\lambda'}^*(r) dr.$$

If  $|l - l'|$  is odd, then  $V_{p_1, \lambda; p_3, \lambda'} q \rightarrow 0$   $1/q$ . In [4] it was pointed out that allowance for exchange produces a marked decrease in the attraction in three-dimensional systems. However, the exchange graph in  $\Gamma''$ , corresponding to the replacement of  $p_3$  by  $p_4$ , will clearly be smaller by the factor  $\hbar q/p_F$  than the non-exchange graph that we have written out, and therefore will play no role for small  $q$  ( $p_F$  is the Fermi momentum).

We see that the additional interaction between the conduction electrons caused by the localized electrons is attractive. Superconducting pairing can arise if the attraction outweighs the Coulomb repulsion; for this, as can be seen from (3), it is necessary that the energy denominator in  $\Gamma''$  (3), i.e., the spacing  $\Delta E_a = E_1 - E_0$  between the lowest level (which possesses finite width) of the electron in the non-metal atom and the nearest excited level (the exciton energy, in the language of excitons) be sufficiently small. Of course, as  $\Delta E_a$  decreases so too does  $T_c$  (see formula (1)). Therefore, the optimum value of  $\Delta E_a$  should be chosen: it is sufficient that it should be small enough for the attraction (associated with the exchange of excitons) between the conduction electrons to outweigh the Coulomb repulsion between them (in any case,  $\Delta E_a \ll \epsilon_F$ ). Apparently,  $\Delta E_a$  should be of the order of 0.1–0.5 eV. Such small values are possible in the case of fine-structure levels and in the splitting of degenerate levels due to the Stark effect in the electrostatic field of a crystal. In this case, large molecular sizes are, generally speaking, not essential (cf. [25]).

Thus, in the model considered, sufficiently low values of the exciton energy (low values of the exciton-bandwidth) are entirely possible, and the exciton attenuation, which is determined by the imaginary part of the polarization operator  $\Pi_{\lambda\lambda'}$ , can be neglected.

An expression for the critical temperature in the case when there is simultaneous attraction due to the electron and phonon mechanisms (and, of course, the Coulomb repulsion) can be obtained easily by means of the so-called step method [12b, c]:

$$T_c = 1.14 \hbar \omega_D e^{-1/g_0} \equiv T_{ce} e^{g_{ph}/[g_0(g_0 - g_{ph})]} \\ \equiv T_{cph} \exp \{g_c [(g^*)^2 + g_c g^* (1 - g_{ph} \ln(\Delta E_a/\hbar \omega_D))]^{-1}\},$$

where

$$\left. \begin{aligned} T_{ce} &= 1.14 \Delta E_a e^{-1/(g_e - \tilde{g}_c)}, & T_{cph} &= 1.14 \hbar \omega_D e^{-1/(g_{ph} - \tilde{g}_c)}, \\ g_0 &= g_{ph} + (g_e - \tilde{g}_c) / [1 - (g_e - \tilde{g}_c) \ln(\Delta E_a/\hbar \omega_D)], \\ \tilde{g}_c &= g_c / [1 + g_c \ln(\epsilon_F/\Delta E_a)], & \tilde{g}_c &= g_c / [1 + g_c \ln(\epsilon_F/\hbar \omega_D)], \\ g^* &= g_{ph} [1 + g_c \ln(\Delta E_a/\hbar \omega_D)] - \tilde{g}_c. \end{aligned} \right\} \quad (5)$$

$g_p$ ,  $g_e$  and  $g_c$  are products of the density of states at the Fermi surface  $N(0)$  with the absolute value of the effective interaction (vertex part) (for the phonon mechanism, the electron mechanism and the Coulomb repulsion respectively) and with the renormalization factor

$1/(1 + b)$ , which defines the ratio of the mass of the free electron to its mass when the interaction is taken into account. As is well known,  $b$  is equal to the coefficient of  $-\omega$  in the expansion of the usual self-energy part  $\Sigma_1(\mathbf{p}, \omega)$  in powers of  $\omega$ ;  $b \rightarrow 0$  as  $g_p \rightarrow 0$ ,  $g_e \rightarrow 0$  and  $g_c \rightarrow 0$ , and so  $1/(1 + b) \sim 1$  in the case of weak coupling. It can be seen from (4) that  $T_c = T_{cp}$  when  $g_e = 0$  and  $T_c = T_{ce}$  when  $g_p = 0$ , and to obtain a high critical temperature it is necessary that  $g_e > \tilde{g}_c$  and  $g_e - \tilde{g}_c \gtrsim (1/6) - (1/5)$ . If in this case we still have  $g_p < g_e$ , the role of the phonon mechanism is small. The step method and formula (4) are inapplicable for  $g_0 \approx 0$ . We note that in the electron mechanism the Coulomb repulsion is not weakened as much as in the phonon mechanism, since  $\ln(\epsilon_F/\hbar \omega_D) > \ln(\epsilon_F/\Delta E_a)$  and  $\tilde{g}_c > \tilde{g}_c$ , which makes it more difficult to realize the condition  $g_e > \tilde{g}_c$ .

In the search for high-temperature superconductivity one can also use metals which are good conductors, e.g., noble metals with small  $g_p$ . As is well known, in the case of the phonon mechanism of superconductivity only poor metals with large values of  $g_p$  possess high critical temperatures for a given Debye temperature.

It can be seen from (3) that the effect of the attraction is proportional to the concentration of the non-metal atoms, i.e., in order that the second term in (3) be sufficiently large it is necessary that the concentrations of the metal and non-metal be comparable.

If, however, the concentration of non-metal atoms is small,  $c \ll 1$ , the virtual transitions in the non-metal atoms (at low concentrations even metallic impurities, as is well known, give local levels) also lead to attraction, which will, however, be only a small correction to the attraction via the phonons. This additional attractive effect is not usually considered in the investigation of the effect of impurities on the properties of superconductors. For the case of ferromagnetic impurities, such an effect has been considered earlier in the paper [26]. There it was shown that, owing to virtual transitions between the singlet and triplet levels in the ferromagnetic atom, the attraction between the conduction electrons increases. This attraction, supplementing the phonon mechanism, can explain the raising of  $T_c$  observed experimentally in certain cases when magnetic impurities are introduced. The usual theory of superconductors with magnetic impurities leads only to a lowering of  $T_c$  as a result of the breakup of the Cooper pairs in the magnetic field of the impurity atom.

In the uniform model, considered above, of a compound of a metal with a non-metal with comparable concentrations of the components, any substance with more or less localized electrons, i.e., semiconductors and dielectrics, can be taken as the non-metallic component. It is essential, however, that the metal form a sufficiently stable compound with the non-metal, i.e., with the substance possessing the localized electrons, with the condition that a well-defined number of localized electrons be conserved. Examples of such systems are known: compounds of noble metals and aluminum with germanium, and compounds of various metals with  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  (cf. [27–30] and other experimental papers cited in Sec. 3). True, in certain cases these compounds apparently have a granular structure.

Another example of a system with collective and localized electrons is provided by certain molecular

crystals<sup>[31]</sup>. As is well known, molecular crystals exist which possess high conductivity, in particular, salts of tetracyanoquinodimethan (TCNQ). In this case, the electrons in TCNQ form a degenerate Fermi system. Of course, it may be hoped in the case of molecular crystals too that the attraction between the collective electrons, associated with their Coulomb interaction with the localized electrons in the molecules, will be able to outweigh the Coulomb repulsion only if the spacing between the ground level of the atomic electron and the nearest excited level is sufficiently small—of the order of a few tenths of an electron volt.

It is obvious that the above considerations are also completely applicable to non-uniform systems with collective and localized electrons, i.e., to granular compounds of a metal with organic substances, dielectrics and semiconductors<sup>[10c,32,33]</sup>. Although such a system is three-dimensional, in many respects it is similar to an aggregate of sandwiches with dielectric layers<sup>[7]</sup>, owing, in particular, to the presence of an interface between the metal and the non-metal.

In addition to the requirement that  $\Delta E$  be sufficiently small for non-uniform systems too, it is necessary that the condition  $g_e > \tilde{g}_c$  be fulfilled. A system of metallic granules in a dielectric matrix was specifically considered in<sup>[34]</sup>. The appearance, examined in<sup>[34]</sup>, of additional attraction between the electrons of the metal as a result of the exchange of polarization waves is completely equivalent to the exchange of excitons and correctly describes the mechanism of the electron interaction. However, the model applied in<sup>[34]</sup>, with a definite dependence of the dielectric permittivity  $\epsilon(q, \omega)$  on  $q$  and  $\omega$  (the so-called generalized "jellium" model), is limited by the fact that the form of the function  $\epsilon(q, \omega)$  is, to a considerable degree, arbitrary and cannot be found from a consistent study of the problem. Therefore, the results obtained on the basis of this model can have only a qualitative rather than a quantitative character (cf. also the comments in<sup>[2,10c]</sup> concerning the incorrectness of the calculation in<sup>[34]</sup>).

We note that, in other cases too, quantitative results and, in particular, estimates of the magnitude of the interaction constant (or, in the language of dielectric permittivities, of the oscillator strength) on the basis of different models that use a simple, but to a certain extent arbitrary, dependence of the dielectric permittivity on  $q$  and  $\omega$  to describe the interaction of the electrons (e.g., in the ordinary "jellium" model) must be approached with a certain caution, since, in view of the absence of a regular expansion in a small parameter, it is difficult to estimate the error made. In addition, we must bear in mind that, if the total matrix element of the interaction (the so-called vertex part  $\Gamma$ ) is represented in the form  $\Gamma = 4\pi e^2 / (q^2 \epsilon_e)$ , then, generally speaking, the factor  $\epsilon_e$  is not the usual dielectric permittivity  $\epsilon$  relating the macroscopic induction to the macroscopic field strength. This is clear if only from the fact that  $\Gamma$ , and therefore  $\epsilon_e$  too, can depend on both the total ( $p_1 + p_2$ ) and the relative ( $p_1 - p_2$ ) momenta and the energies of the two particles, i.e., not only on the transferred momentum  $\hbar q = p_3 - p_1$  and transferred energy  $\hbar \omega = \epsilon_3 - \epsilon_1$  as  $\epsilon(q, \omega)$  does. The difference between  $\epsilon_e$  and  $\epsilon$  can be seen especially clearly in the case of a metal with several overlapping bands, when, for both the interaction via the phonons (cf.<sup>[35]</sup>) and for the Coulomb interaction<sup>[12b,c]</sup> (see formula (10)), there is not one vertex part, but several:  $\Gamma_{aa;aa}$ ,  $\Gamma_{bb;bb}$ ,  $\Gamma_{aa;bb}$ ,  $\Gamma_{ab;ab}$ ,

$\Gamma_{aa;ab}$  and  $\Gamma_{ab;bb}$ , and, consequently, there are as many coefficients  $\epsilon_e$  in place of the one  $\epsilon$ . The situation is the same in the case we have considered of two groups of electrons—collective and localized ( $a$  and  $b$  are the indices of the band or group of electrons). In (3), only the vertex part  $\Gamma_{aa;aa}$  has been written out, and  $\Gamma_{ab;ab}$  corresponds to the matrix element  $V_{p_1, n\lambda; p_3, n\lambda'}$ , i.e.,  $V_{ab;ab}$  (cf.<sup>[12b,c]</sup>). As was correctly observed in<sup>[2]</sup>, attempts to identify  $\epsilon_e$  with  $\epsilon$  can lead to ambiguities: the interaction via the phonons, as an attraction, corresponds to  $\epsilon_e < 0$ , whereas for  $\epsilon$  the inequality  $\epsilon(q, 0) \geq 0$  should be fulfilled. Nevertheless, in the paper<sup>[36]</sup>, the difference between  $\epsilon$  and  $\epsilon_e$  is practically ignored, since it is assumed that  $\epsilon_e(q, 0) \geq 0$ . In<sup>[36]</sup>, the maximum of  $T_c$  as a function of  $\Delta E(\hbar\omega_D)$  is found; a weak logarithmic dependence of  $g$  on  $\omega_D$  through  $\tilde{g}_c$  was taken into account, and not the stronger dependence ( $g_p \sim \langle \omega^2 \rangle^{-1}$  given in<sup>[37]</sup> (cf. (9)) or, in the case of the electron mechanism, given by the formulas (3) and (10)). Then, from the inequality  $\epsilon(q, 0) \geq 0$ , one first derives the impossibility of large values of  $g$  ( $g_p \leq g_c$ ) and, consequently, of high  $T_c$ ;  $T_{c \max}$  is found to be  $\sim 10^\circ \text{K}$ . In<sup>[36]</sup> it is assumed that  $g_p$ , or another constant associated with the attraction, cannot exceed  $1/2$ . However, according to<sup>[37]</sup>, for large  $T_c$  we have  $g_p > \tilde{g}_c$ , and even  $g_p > g_c$ , and values of  $g_p$  appreciably greater than  $1/2$  follow from the experimental data: 1.3 (Pb), 1.6 (Hg), 0.91 (MoTe);  $g_c \approx 0.1-0.15$ ; according to<sup>[38]</sup>,  $g_p = 2.46$  for Bi and 2.25 for Ga. The disagreement with experiment is removed in the paper<sup>[36]</sup> by taking into account Umklapp processes, which also lead to a difference between the local and macroscopic fields, i.e., to the non-coincidence of  $\epsilon$  and  $\epsilon_e$ . In this case, the condition  $\epsilon_e(q, 0) \geq 0$  is no longer essential (cf. also<sup>[39]</sup>).

We note that, even if  $\epsilon$  were equal to  $\epsilon_e$ , then in the case when the superconductivity is associated with retarded interaction (attraction for  $\omega \neq 0$ ), as in the case considered in<sup>[33]</sup> (see p. 46), the arguments limiting the magnitude of  $T_c$  on the basis of the condition  $\epsilon(q, 0) \geq 0$  naturally lose their force.<sup>2)</sup>

In the case of non-uniform systems, systems of granules of an organic substance, dielectric or semiconductor in a metallic matrix, and of metallic granules in a matrix of a semiconductor, organic substance or (the case considered above) dielectric substance, are possible. Apparently, such non-uniform systems can be prepared for the most diverse metallic and non-metallic components.

However, non-uniform systems have two drawbacks compared with uniform systems. First, since the localized electrons and the conduction electrons are on different sides of the granule surface, because of a purely geometrical factor their interaction (oscillator strength) is somewhat weakened, other conditions being equal, compared with that in a uniform system, in which the conduction electrons and localized electrons permeate through each other, as it were. In addition, since the interaction occurs through the surface, for reasons based on Cooper's theorem<sup>[8]</sup> it is necessary that the volume of any metallic region be not much greater than the volume of the active surface layer, whose scale is of atomic dimensions (cf. above). Therefore, in the case of non-metallic (organic, dielectric and semiconducting) granules in a metallic matrix, the concentration of the non-metal should be comparable with the metal concentration

(the effect is proportional to the non-metal concentration; cf. above) and the compound should be sufficiently finely dispersed, i.e., the dimensions of the non-metallic granules should be not much greater than atomic dimensions<sup>[33]</sup>. In the case of metallic granules in a non-metallic matrix, the latter condition for the dimensions of the granules is again necessary, but the metal concentration can also be appreciably lower than the non-metal concentration. True, in this case, a current flowing through the whole sample is impossible (because of the non-conducting regions between the metallic granules), but the superconductivity of the granules can be detected, e.g., by means of magnetic measurements or heat-capacity measurements.

The second drawback is associated with the role of fluctuations, destroying the superconducting order. As has already been pointed out in the case of films, to avoid the effect of fluctuations the film thicknesses and, in the present case, the dimensions of the granules should be chosen sufficiently large. On the other hand, to obtain a sufficiently large attractive effect these dimensions, according to Cooper's theorem, should be small—on the atomic scale.

The effect of fluctuations on the critical temperature can be estimated in the following way. In<sup>[41]</sup> (cf. also the more recent<sup>[17,18,23,42]</sup>), it was shown (on the basis of the Ginzburg-Landau theory) that the width  $\Delta T$ , due to fluctuations, of the superconducting transition for bodies of small dimensions will be of the order of

$$\left. \begin{aligned} \Delta T_0 &\equiv \Delta T_0/T_c \approx (\epsilon_F/T_c)^{1/2} (k_F d)^{-3/2} \\ \text{for a spherule of diameter } d, \\ \Delta T_1 &\equiv \Delta T_1/T_c \approx (\epsilon_F/T_c)^{2/3} (k_F^3 \xi(0) d^2)^{-2/3} \\ \text{for an infinite filament of diameter } d, \text{ and} \\ \Delta T_2 &\equiv \Delta T_2/T_c \approx (\epsilon_F/T_c) (k_F^3 \xi^2(0) d)^{-1} \\ \text{for a film of thickness } d; \end{aligned} \right\} (6)$$

here  $\xi(0)$  is the correlation length at  $T = 0$ .

Clearly, for a qualitative estimate of the critical dimensions  $d_c$  at which the critical temperature vanishes, we must put  $\Delta T$  equal to  $T_c$ . Then from (6) we find

$$d_{0c} \approx (\epsilon_F/T_c)^{1/3}/k_F, \quad d_{1c} \approx (\epsilon_F/T_c)^{1/2}/k_F^{3/2} \xi^{1/2}(0), \quad d_{2c} \approx (\epsilon_F/T_c)/k_F^3 \xi^2(0). \quad (7)$$

$(\epsilon_F/T_c)^{1/3} \sim 20$  for  $T_c \sim 5-10^\circ \text{K}$ . If for  $\Delta T_1$  and  $\Delta T_2$  we take the correlation length to be the same as in the case of a clean superconductor:

$$\xi_0 \equiv \xi_0(0) \approx 0.2 \hbar v_F/T_c \quad (v_F = p_F/m),$$

then for  $d_{1c}$  and  $d_{2c}$  we obtain values considerably smaller than  $\xi_0$  (and, moreover, meaninglessly small). But it is well known that superconductors with dimensions  $d$  less than  $\xi_0$  and with diffusional scattering at the boundaries are equivalent to "dirty" superconductors with mean free path  $l$  for scattering by impurities equal to  $d$ . The correlation length  $\xi$  for "dirty" superconductors is of order  $(\xi_0 l)^{1/2}$ , i.e., in the present case,  $\xi \sim (\xi_0 d)^{1/2}$ . Substituting into (7) this expression for  $\xi(0)$  and  $\xi_0 = 0.2 \hbar v_F/T_c$ , we find from (7)

$$d_{0c} \approx (\epsilon_F/T_c)^{1/3}/k_F, \quad d_{1c} \approx (\epsilon_F/T_c)^{1/3}/k_F, \quad d_{2c} \approx 1/k_F. \quad (8)$$

Again in the framework of the Ginzburg-Landau

theory, it was shown in<sup>[18]</sup> that in a more exact calculation for a filament the quantity  $\Delta T_1$  is multiplied by  $\gamma^{2/3}$  (cf. formula (2)). For a film and a spherule, the corresponding refined calculations have not been performed (cf. <sup>[43,44]</sup>), but if we assume that the numerical factors for  $\Delta T$  differ little for a film and a filament, the expression for  $d_{1c}$  must be multiplied by  $\gamma^{2/5} \approx 4-5$ , and the expression for  $d_{2c}$  by  $\gamma^{1/3} \approx 3-4$ . However, as was noted above, the Ginzburg-Landau theory is applicable only for  $\Delta T \ll T_c$ , and to estimate the critical values  $d_c$  the case  $\Delta T \sim T_c$  is considered. Therefore, the estimates (7) and (8) are highly qualitative and approximate.

As we should expect, the least favorable case from the point of view of fluctuations is that of the spherule, bounded in all three dimensions, and the most favorable is the case of the film, which is bounded only in one dimension.

If we assume that the lowering of  $T_c$  observed in very thin films<sup>[20-22]</sup> is connected with fluctuations (cf. above), then in the formula for  $d_{2c}$  there should be a factor of order 5, which is perfectly possible, if we take into account the above-mentioned tentative nature of the estimate (8). Here we must bear in mind that, for  $d \sim 50-100 \text{ \AA}$ ,  $T_c$  is only just beginning to decrease, while  $d_{2c}$  correspond to the actual vanishing of  $T_c$ .

We note that there exists another way of estimating the critical dimensions of a spherule. Clearly, in a system with discrete levels, pairing is energetically unfavorable and, consequently, will not occur if the gap  $\Delta$  ( $\Delta \sim T_c$ ) is of the order of the spacing between the levels. For a gas with zero boundary conditions or periodicity conditions at the boundary, the spacing  $\Delta \epsilon$  between the levels will be of the order of: a)  $p_F \Delta p/m$  at the Fermi surface, and b)  $(\Delta p)^2/m$  for the lower levels, with  $\Delta p \sim \hbar/d$ . From the condition  $\Delta \epsilon \sim T_c$  we find in the case a), which, it would seem, should actually occur,  $d_{0c} \sim (\epsilon_F/T_c)/k_F$ , and in the case b),  $d_{0c} \sim (\epsilon_F/T_c)^{1/2}/k_F$ . Such unreasonably high values are explained, apparently, by the fact that the model of a gas with ideal boundary conditions is completely inapplicable for real superconductors of small dimensions (cf. <sup>[2]</sup>).

Thus, in granulated compounds of metals with non-metallic substances, there are certain extra difficulties, compared with the analogous uniform systems, in the realization of high-temperature superconductivity. However, these difficulties are not completely irremovable and, in view of this, the search for high-temperature superconductivity in non-uniform systems is entirely justified, the more so since it is evidently an easier task to obtain stable compounds of metals with dielectrics and organic substances in the case of granulated systems than in the case of uniform systems.

In metals with molecular impurities, there is one further possibility of raising  $T_c$ <sup>[45]</sup>, associated with a change of form of the phonon mechanism: the exchange of virtual molecular phonons in place of exchange of phonons of the metal lattice.

Since the frequencies of the molecular phonons are usually somewhat higher than the frequencies of phonons in the metal, we may expect a certain increase of  $T_c$  because of the pre-exponential factor in (1), if the interaction constant is not appreciably decreased because of the high phonon frequency.

### 3. EXPERIMENTAL INVESTIGATIONS OF SUPERCONDUCTING COMPOUNDS OF METALS WITH ORGANIC SUBSTANCES, DIELECTRICS, SEMICONDUCTORS AND SEMIMETALS

There is at the present time an already fairly large number of experimental papers devoted to the investigation of the superconductivity of compounds of metals with non-metallic substances (dielectrics, semiconductors, organic substances and semimetals).

We shall not discuss here the earlier papers on thin films, which are of interest chiefly from the point of view of quasi-two-dimensional superconductivity, inasmuch as the subject of our review is three-dimensional systems, and we shall discuss only the experimental studies with fairly thick films (from several hundred to a few thousand angstroms). In the absence of a magnetic field, such films are equivalent to bulk samples.

It is well known that, even in the first experiments with films of clean superconductors (Zn, Al, Sn, In, Pb), formed by means of condensation on to a cold substrate (at liquid helium temperatures), critical temperatures higher (by a factor of 1.2–2.3) than for the equilibrium phase of the bulk samples were obtained<sup>[46]</sup>.

The largest effect—the raising of  $T_c$  by a factor of 2.3—was obtained for Al, and a zero effect for Pb.

We note that the experimentally observed “resistance” of Pb (and Hg) to different attempts to raise their  $T_c$  (cf. also<sup>[47,48]</sup>) can be explained in the framework of the phonon mechanism by the closeness of the effective interaction constant  $g_{\text{eff}}$  for the equilibrium phase of pure Pb and Hg to the maximum possible value—unity<sup>[37,49]</sup>. It is well known that the upper limit, equal to 1/2, for the interaction constant, obtained earlier on the basis of considerations of lattice stability, is connected with the fact that the constant  $g^0$  appearing in the Fröhlich model does not coincide with the real constant  $g$ . Calculations on the basis of consistent adiabatic perturbation theory give for the phonon frequency (in the case of an acoustic dispersion law) not the previous expression  $\omega = \omega_0(1 - 2g)^{1/2}$ , but the expression  $\omega = \omega_0/(1 + 2g)^{1/2}$  (where  $\omega_0$  does not depend on  $g$ ), and thus a value of  $g$  equal to 1/2 is not the critical value<sup>[50a]</sup>. The limiting value for  $g$  is not determined by considerations of lattice stability, but is connected with the renormalization of the electron velocity at the Fermi surface and at the energy gap, which leads also to a renormalization of the interaction constant:  $g_{\text{eff}} = g/(1 + g)$ ; therefore,  $\lim_{g \rightarrow \infty} g_{\text{eff}} = 1$ ; this can also be seen from formula (9) (cf.<sup>[37,49]</sup>).

Results analogous to those of Buckel and Hilsch<sup>[46a]</sup> were later obtained with other films of the pure metals Bi, Ga, Pb, In and granulated Al<sup>[38,51]</sup>. After warming (at room temperature),  $T_c$  was usually lowered somewhat, but remained above the  $T_c$  of the bulk sample. This tells us that, in the condensation on to the cold substrate (at liquid-helium or liquid-nitrogen temperatures), a non-equilibrium modification of the superconductor is formed, with comparatively small crystallite dimensions (after warming, the crystallite dimensions increase) and, apparently, with different parameters of the phonon spectrum. In<sup>[38,51]</sup>, the phonon spectrum of films was measured by means of tunneling experiments; it was found in<sup>[38,51a]</sup> that the mean phonon frequency  $\langle \omega \rangle$  is markedly lower than in the bulk samples. In<sup>[51b]</sup>, the

increase of  $T_c$  for Al (up to 2–3°K) was not accompanied by an appreciable lowering of  $\langle \omega \rangle$ .

According to<sup>[37]</sup> (cf. also<sup>[50,52]</sup>), in the case of strong electron-phonon interaction the critical temperature (for a phonon spectrum similar to that of Nb) is given by the expression

$$T_c = \frac{\hbar \omega_D}{1.45} \exp \left[ -\frac{1.04(1+\lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right], \quad \lambda \equiv g_{\text{ph}}, \quad (9)$$

$$\mu \equiv g_c \text{ (see (5)), } \mu^* = \mu / [1 + \mu \ln(\epsilon_F / \hbar \omega_D)];$$

Here  $\mu$  is a parameter characterizing the magnitude of the Coulomb repulsion, and the interaction constant  $\lambda$  is inversely proportional to the mean square phonon frequency  $\langle \omega^2 \rangle$ . Usually, the increase of  $\lambda$  in the exponent on decrease of  $\langle \omega \rangle$  is more important than the decrease of  $\omega_D$  in the pre-exponential factor. Therefore, according to (9), decrease of  $\langle \omega \rangle$  should lead to an increase of  $T_c$ . In<sup>[38,51a]</sup>, the lowering of  $\langle \omega \rangle$  is apparently associated with the formation of a non-equilibrium phase. However, for a final solution of the question of the effect on  $T_c$  of change of the phonon spectrum, it is desirable to measure the phonon-spectrum parameters by other methods, in addition to the tunneling experiments (cf. below). Thus, a raising of  $T_c$  can also be achieved in films of clean superconductors.

In the experiments of<sup>[53]</sup>,  $T_c$  was measured for films obtained by vaporization of metals (Al, Ga, Sn, In, Pb) together with a small quantity of oxygen, with condensation on to a cold substrate. The oxygen, apparently, only assisted the formation of amorphous metal. The greatest effect was obtained for Ga and Al, and zero effect for Pb. After warming,  $T_c$  was lowered, as in the preceding experiments.

We now consider experiments with compounds of metals and nonmetallic substances. The papers<sup>[54,55]</sup> on the investigation of compounds of metals with organic substances are of great interest. In<sup>[54]</sup>, thick films obtained by concurrent vaporization of Al and TCNQ, deposited on a substrate at temperature 4°K, were studied. The critical temperature was found to be 5.24°K (after warming at 273°K,  $T_c$  was lowered by 30%). The residual resistance (after warming) increased linearly with the concentration of TCNQ. The value of  $T_c$  was found to be close to the  $T_c$  in experiments with Al + 10% Cu ( $T_c \sim 5.5^\circ\text{K}$ ) and in experiments with alternating layers of Al and other metals or a dielectric<sup>[56]</sup> ( $T_c \sim 5.7^\circ\text{K}$ ), but appreciably greater than in the first experiments<sup>[46a]</sup> with pure Al (2.7°K). In the paper<sup>[55]</sup>, films of Al, Zn and In obtained in the same way by concurrent vaporization of these metals with anthraquinone were studied. For In,  $T_c = 4.6^\circ\text{K}$  when the temperature of the substrate is  $T_s = 4.2^\circ\text{K}$  (for pure In with the same  $T_s$  we have  $T_c \sim 3.8\text{--}4.2^\circ\text{K}$ ); on increase of  $T_s$ , the value of  $T_c$  was lowered (for  $T_s = 150^\circ\text{K}$ ,  $T_c = 3.84^\circ\text{K}$ ). After warming at 350°K,  $T_c = 4.15\text{--}4.3^\circ\text{K}$  in the first case, and 3.84°K in the second case. An analogous, but weaker, effect was observed in the case of Zn. In the case of Al, anthraquinone did not lead to an increase of  $T_c$  ( $T_c \sim 3^\circ\text{K}$ ). The dimensions of the organic granules and of the final concentration of the organic compound were not made determined exactly in<sup>[54,55]</sup>. In<sup>[54]</sup>, the TCNQ content is estimated as 3% of the whole volume. The ratio of the resistances of films at the temperature of the substrate and at room temperature is  $\rho_{T_s} / \rho_{300^\circ\text{K}} = 1.4$  for  $T_s = 4.2^\circ\text{K}$  and  $\rho_{T_s} / \rho_{300^\circ\text{K}} = 0.7$  for  $T_s = 150^\circ\text{K}$ . This is evidence of

TABLE I

	$T_C$ of the pure bulk metal, °K	$T_C$ (°K) of the compounds:				
		As	Sb	Bi	Ge	Si
Zn	0.9°	—	< 3.3°	5–5.2°	—	—
Al	1.2°	—	5.2°	5.8°	6.45°	—
In	3.4°	4.8–5.5°	5.2°	5.9°	6.2°	6.05°

the non-metallic (semiconducting) nature of the conductivity of the compounds obtained at  $T_S = 4.2^\circ\text{K}$ , and of the almost metallic character at  $T_S = 150^\circ\text{K}$ .

Similar results were obtained in<sup>[57]</sup> with films of alternating metal-organic layers.

It is difficult to say whether the observed increase of  $T_C$  is connected with some new mechanism of superconductivity or with change of the parameters of the phonon mechanism on formation of a new phase, in particular, with change of the phonon spectrum of the metal (cf. above). The phonon spectrum was not investigated in these experiments.

In<sup>[58]</sup>, films were investigated of compounds of metals (Zn, Al, In—90 at.%) with semimetals (As, Sb, Bi—10 at.%) in the case of InSb, the compound with 40% Sb was also investigated,  $T_C$  being found to be the same) and with semiconductors (Ge, Si—10 at.%).

The condensation on to the substrate was performed at  $T_S = 4^\circ\text{K}$ . The results given in Table I were obtained. After warming InSb to  $300^\circ\text{K}$ ,  $T_C$  was found to be  $\sim 3.4^\circ\text{K}$ .

In<sup>[56]</sup>, an increase of  $T_C$  was observed for films of alternating layers of Al and Cu, and Al and Sn, and in<sup>[59]</sup> for disordered films of Sn with a 10% admixture of Cu. In neither case was the phonon spectrum measured.

In<sup>[60]</sup>, films of Pb, Sn and Bi with a 10% admixture of Cu or a small quantity of  $\text{SiO}_2$  were investigated and an increase of  $T_C$  was also observed. By means of tunneling measurements, the phonon spectra of the Pb and Sn films were obtained. It was found that the frequency of the phonon peak in the case of Pb with 10% Cu content is unchanged compared with pure Pb, and is decreased in the case of Sn with 10% Cu content. The phonon spectrum for the Pb and Sn films was practically unchanged after warming.

In<sup>[29]</sup>, compounds of Mo and La with  $\text{SiO}_2$  were observed. For different concentrations of  $\text{SiO}_2$  (with a substrate temperature of  $77^\circ\text{K}$ ), in the case of Mo a broad maximum of  $T_C$ , equal to  $\sim 6.4^\circ\text{K}$  (for pure Mo,  $T_C = 2^\circ\text{K}$ ) was observed for 10–30% Si concentration (by volume); in the case of La,  $T_C$  is lowered monotonically as the concentration of  $\text{SiO}_2$  increases. In both cases, the resistance at  $300^\circ\text{K}$  increases with increase of the concentration  $c_{\text{SiO}_2}$ —it first increases slowly, and then begins to grow sharply at the  $c_{\text{SiO}_2}$  corresponding to the fall of  $T_C$ . The electron-diffraction pattern showed that, for low  $c_{\text{SiO}_2}$ , the lattice parameters are the same as for the pure bulk metals. According to the electron-diffraction data, the dimensions of the granules are  $\sim 30 \text{ \AA}$  (in pure La films,  $100 \text{ \AA}$ , and in pure Mo films,  $200 \text{ \AA}$ ). On increase of  $c_{\text{SiO}_2}$ , the diffraction rings are broadened, indicating a decrease of the granule dimensions. As a control, films of compounds of Mo and La with other metals were investigated. In the case of Mo, the normal metal Y was chosen, and in the case of La, Nb was chosen. In the first case, the dependence of  $T_C$  on  $c_Y$

was similar to the curve for Mo— $\text{SiO}_2$ . In the second case,  $T_C$  was also lowered (for 18% Nb by volume,  $T_C = 3.3^\circ\text{K}$ , instead of  $4.9^\circ\text{K}$  for pure La). Therefore, the authors assume that the behavior of Mo and La is characteristic of the transition metals themselves and is unconnected with the nature of the partners in the compounds. The raising of  $T_C$  in the case of Mo is ascribed to the change in the dimensions of the granules and to the softening of the phonon spectrum, which, however, was not measured. In<sup>[29]</sup>, an increase of  $T_C$  is also observed for the systems W— $\text{SiO}_2$  and Be— $\text{SiO}_2$ .

In<sup>[61]</sup>, films obtained by concurrent laminar vaporization of Mo and C and condensation on to a substrate at the temperature of liquid nitrogen were investigated.  $T_C$ , as a function of the atomic concentration  $c_C$  of the carbon, has a broad maximum (plateau) for  $0.2 \leq c_C \leq 0.5$ ;  $T_C \text{ max} \approx 8^\circ\text{K}$  for a film thickness  $d = 200 \text{ \AA}$ . For pure Mo,  $\rho_{300^\circ\text{K}}/\rho_0 \approx 1.2$ ; for  $0.2 \leq c_C \leq 0.5$ ,  $\rho_{300^\circ\text{K}}/\rho_0 \approx 1$ ; for  $c_C = 0.9$ ,  $\rho_{300^\circ\text{K}}/\rho_0 \approx 0.6$ . On deposition of a layer of carbon with  $d_C = 5\text{--}10 \text{ \AA}$  on to a film of Mo and C with  $d = 60\text{--}100 \text{ \AA}$ ,  $T_C$ , as a function of  $d_C$ , goes through a maximum ( $\delta T_C \sim 1^\circ\text{K}$ ), then through a minimum, and then remains constant. This effect disappears as the film thickness increases. It is possible that it is connected with phonons of the membrane modes of the thin carbon coating (cf. p. 27 and<sup>[62]</sup>).

In<sup>[63]</sup>, films of Al and  $\text{SiO}_2$  with a substrate at the temperature of liquid nitrogen were studied.  $T_C$ , as a function of  $c_{\text{SiO}_2}$ , has a broad maximum when  $c_{\text{SiO}_2} = 0.2\text{--}0.3$ ; for  $c_{\text{SiO}_2} = 0.4$ ,  $T_C$  vanishes. The curve for  $\rho_{300^\circ\text{K}}$  has the same form as in<sup>[29]</sup>. The dimensions a of the metallic granules are estimated from electron micrograms: for  $c_{\text{SiO}_2} = 0.1$ ,  $a \sim 100 \text{ \AA}$ ; for  $c_{\text{SiO}_2} = 0.4$ ,  $a \sim 30 \text{ \AA}$ . It is assumed that the sharp (nonlinear) increase of  $\rho_{300^\circ\text{K}}$  at sufficiently large  $c_{\text{SiO}_2}$  ( $c_{\text{SiO}_2} \geq 0.4$ ) is evidence of a structure of a metallic-granule type in the  $\text{SiO}_2$  matrix. The authors ascribe the vanishing of  $T_C$  to the growth of critical fluctuations for small a. The probability of fluctuations is estimated from the usual formula  $W \sim \exp(-\Delta F/T)$ , where  $\Delta F = F_N - F_S$  but, in view of the small granule dimensions, it is assumed that the principal contribution to  $\Delta F$  is made not by the volume term, but by the free energy of the Josephson junctions between the metal granules, which is equal to  $\hbar I(T)/2e$ , where the maximum Josephson current  $I(T) = \pi \Delta(T)/2eR$  and the junction resistance  $R = \rho_N/a$ . Clearly,  $T_C = 0$  if  $W \sim 1$ , i.e., if  $\Delta F \sim T_C$ , whence (for 6 neighboring granules)  $\rho_{N,C} = 3\pi \hbar a / (2T_C e^2) \sim 2.6 \times 10^2 \text{ ohm-cm}$  for  $30 \text{ \AA}$ , which agrees with experiment (cf. also<sup>[29]</sup>). In<sup>[43a]</sup>, the role of fluctuations is investigated in more detail. The general case of a granulated metal in a non-conducting matrix is considered:  $F_S \approx F_N - (1/2)N(0)\Delta^2 a^3 - (\pi \hbar \Delta a / 4e^2 \rho_N)$ .

For small a and small  $\rho_N$ , the second term plays the main role.  $T_C$  vanishes when  $(1/2)N(0)\Delta^2 a^3 + \pi \hbar \Delta a / 4e^2 \rho_N \sim T_C \sim \Delta$ . In<sup>[63]</sup> the main role is played by the second term, while in the article<sup>[30]</sup> it is played by the first, in view of the large values of  $\rho_N \sim 10^2 \text{ ohm-cm}$ .

Films of Al and  $\text{Al}_2\text{O}_3$  and Al and Ge were investigated in<sup>[30]</sup>. In the case of Al— $\text{Al}_2\text{O}_3$ , the substrate was at room temperature, and in the case of Al—Ge, at  $77^\circ\text{K}$ . The dependence of  $T_C$  on the residual resistance, which was measured with varying concentrations of  $\text{Al}_2\text{O}_3$  and Ge, was found. In both cases, the maximum  $T_C$  corresponded



to 10% Al<sub>2</sub>O<sub>3</sub> or Ge by weight (3.6°K for Ge, and 2.5°K for Al<sub>2</sub>O<sub>3</sub>). In the case of Al<sub>2</sub>O<sub>3</sub>,  $\rho_{300^\circ\text{K}}/\rho_0 < 1$  (semi-conducting behavior), and  $\rho_{0\text{max}} \sim 54$  ohm-cm for 40% Al<sub>2</sub>O<sub>3</sub> by weight. In the case of Ge,  $\rho_{300^\circ\text{K}}/\rho_0 > 1$  (metallic behavior) and  $\rho_{0\text{max}} \sim 4 \times 10^{-3}$  ohm-cm for 20% Ge by weight. The author assumes that the dependence of  $T_c$  on  $\rho_0$  is the same for Al-Al<sub>2</sub>O<sub>3</sub>, Al-O<sub>2</sub><sup>[53]</sup> and also Al-SiO<sub>2</sub><sup>[64a]</sup> when the substrate is at room temperature. However, in each of the latter two cases, there is only one point corresponding to maximum  $T_c$ , and these two points lie on the curve for Al-Al<sub>2</sub>O<sub>3</sub>. In the case of Al-Ge, the curve for  $T_c$  goes higher and has a sharper maximum;  $T_c$  in these three cases corresponds to 10% dielectric by weight, which contradicts<sup>[58]</sup>. Measurements of the phonon spectrum did not display an appreciable shift of  $\langle\omega\rangle$  ( $\langle\omega\rangle$  is a little lower). In the case of Al + 10% Ge by weight and Al + 10% Al<sub>2</sub>O<sub>3</sub> by weight, a 5.5% decrease in density compared with pure Al was found by direct measurements. From the diffuseness of the electron-diffraction rings, the granule size is estimated as 50 Å (Al + 10% Ge by weight and Al + 10% Al<sub>2</sub>O<sub>3</sub> by weight). On increase of the Al<sub>2</sub>O<sub>3</sub> concentration to 40% the diffuseness increases, corresponding to the fact that the sample has become completely amorphous. By electron diffraction, an increase of lattice constant was detected, corresponding to a 10.5% decrease of density. It is assumed that this density decrease, leading to a decrease of  $\langle\omega\rangle$ , explains the increase of  $T_c$ .

In the experiments of<sup>[64b]</sup> with films of Al + 10–20% Ge, the phonon spectrum was plotted in tunneling experiments. It was found that, whereas for pure bulk Al  $\langle\omega^2\rangle = 868$  meV<sup>2</sup> ( $T_c = 1.3^\circ\text{K}$ ) and for granulated Al<sup>[51b]</sup>  $\langle\omega^2\rangle = 702$  meV<sup>2</sup> ( $T_c = 3.75^\circ\text{K}$ ), for Al + Ge with  $T_s = 77^\circ\text{K}$   $\langle\omega^2\rangle = 1150$  meV<sup>2</sup> ( $T_c = 5.5^\circ\text{K}$ ) and for Al + Ge after warming  $\langle\omega^2\rangle = 1175$  meV<sup>2</sup>. Thus, although  $T_c$  has increased, the mean frequency  $\langle\omega\rangle$  has risen. A calculation using formula (9) (with small changes in accordance with<sup>[65]</sup>) gives for  $N(0)\langle J^2\rangle$ , with  $\mu^* = 0, 1$  ( $\lambda = N(0)\langle J^2\rangle/M\langle\omega^2\rangle$ ), a 70% increase compared with pure Al.

It must be remarked, however, that if the investigation of the phonon spectrum is performed by means of tunneling measurements, we must approach such conclusions with caution<sup>[66]</sup>. Indeed, for tunneling measurements, the phonon spectrum is set up from the Eliashberg equation for the frequency-dependent energy gap, with the electron-phonon interaction taken into account exactly. But, in the kernel of this equation, only the interaction of the electrons via the phonons and the Coulomb repulsion is taken into account. Therefore, if in reality there is also an additional attraction, associated with a new mechanism, then for  $g_e < g_p$  it could be perceived only as an apparent increase of the electron-phonon interaction constant and an apparent decrease of  $\langle\omega^2\rangle$ . An increase of  $T_c$  will then be ascribed to the decrease of  $\langle\omega^2\rangle$ . Thus, in order to decide the question of the existence of a new mechanism of attraction, control measurements of the phonon spectrum by means of neutrons are necessary.

Films of Al + Ge were investigated in<sup>[28]</sup>. It was found that  $4 < T_c < 6.4^\circ\text{K}$  for  $c_{\text{Al}} > 0.8$ ,  $6.3 < T_c < 6.6^\circ\text{K}$  for  $0.8 > c_{\text{Al}} > 0.4$ ,  $5.8 < T_c < 6.6^\circ\text{K}$  for  $0.4 > c_{\text{Al}} > 0.2$ , and  $T_c = 0$  and  $c_{\text{Al}} < 0.2$ . The authors investigate two hypotheses: 1) one amorphous phase, 2) granules of Al in a matrix of Ge (for sufficiently high

$c_{\text{Ge}}$ ).  $\rho_{300^\circ\text{K}} \sim 200$  mohm-cm for  $c_{\text{Al}} = 0.6-1$ , and  $0.25 < \rho_{300^\circ\text{K}} < 1$  ohm-cm for  $c_{\text{Al}} < 0.5$ ;  $\rho_{4^\circ\text{K}}/\rho_{300^\circ\text{K}} > 1$ . A calculation assuming equal radii for the Al granules and the same distances between them leads to the conclusion that the Al granules will not come into contact with each other for  $c_{\text{Al}} < 0.74$ . The resistance of the granulated system is made up of the resistance  $\rho_s$  of the granules and the resistance  $\rho_j$  of the barriers between them (the tunneling resistance),  $\rho_n = \rho_j + \rho_s$ . For low  $c_{\text{Al}}$ ,  $\rho_n \sim \rho_j$ , and for high  $c_{\text{Al}}$ ,  $\rho_n \sim \rho_s$ . The behavior of  $\rho_n$  for  $c_{\text{Al}} < 0.6$  confirms the second hypothesis, in the authors' opinion. Assuming that  $T_c$  vanishes owing to the critical fluctuations, one can find from<sup>[63]</sup>  $a_c = 30$  Å for the case of small  $a$ . Hence one can find  $j_c$ , which agrees with the experimental values. The authors assume that the increase of  $T_c$  is connected with polarization effects of the Ge matrix<sup>[34]</sup>, as also in<sup>[55]</sup>.

In the experiments of<sup>[67]</sup>, films obtained by vaporization, and condensation on to a cold substrate, of beryllium together with an organic dielectric (zinc aetio-porphyrin) and Zn with zinc aetio-porphyrin were investigated. In the first case it was found that  $T_c \approx 10-11^\circ\text{K}$  (irrespective of the film thickness), and in the second case,  $1.4^\circ\text{K}$  (for pure Be, the maximum  $T_c = 8.2^\circ\text{K}$  for a film of thickness  $60$  Å<sup>[22]</sup>). On warming,  $T_c$  was not lowered to zero. Also in<sup>[67]</sup>,  $T_c \approx 9^\circ\text{K}$  was obtained for films of Ga and KCl.

Of great interest is the superconductivity, investigated in<sup>[68]</sup> and later in<sup>[27]</sup>, of compounds of the noble metals (Cu, Ag, Au), which, as is well known, are non-superconducting in the pure form, with Ge. The superconductivity of Au-Ge films (with  $c_{\text{Ge}} \sim 0.3-0.66$ ) was first detected in<sup>[69]</sup>, but with a lower  $T_c \approx 1.63^\circ\text{K}$ .

In<sup>[68]</sup>, the maximum  $T_c = 2.7^\circ\text{K}$  for Au-Ge,  $1.5^\circ\text{K}$  for Ag-Ge, and  $1.9^\circ\text{K}$  for Cu-Ge; in<sup>[27]</sup>, the maximum  $T_c = 3.6^\circ\text{K}$  for Au-Ge,  $1.2^\circ\text{K}$  for Ag-Ge, and  $3.3^\circ\text{K}$  for Cu-Ge. The somewhat higher  $T_c$  in the article<sup>[27]</sup> are explained by the lower temperature ( $4.2^\circ\text{K}$ ) of the substrate; in the first case, the vaporization was effected by a laser, on to a support at liquid-nitrogen and liquid-helium temperatures. After warming to room temperature,  $T_c$  was lowered by  $0.5-1^\circ\text{K}$ <sup>[68]</sup>, and even to zero for Cu in<sup>[27]</sup>. In both papers, the dependence of  $T_c$  on the concentration of Ge was found.  $T_c$  has a fairly broad maximum, e.g., for 60% Cu and 60% Au in the paper<sup>[27]</sup>, and for 50% Cu, Ag and Au in<sup>[68]</sup>. On the basis of tunneling measurements and the fact that the resistance is independent of the strength of current, it is concluded in<sup>[27]</sup> that the films form a uniform amorphous phase. It is assumed that not very large quantities of Au, Ag and Cu convert Ge into a metallic superconducting phase, while large quantities give  $T_c = 0$ , as for the pure noble metals.

Stacks of alternating films of thickness  $10-20$  Å (ten Cu films and ten Ge films) were investigated in<sup>[27]</sup>;  $T_c$  for such sandwiches was found to be equal to zero. Deposition of a copper film of thickness  $20-160$  Å on to the Cu-Ge film gives the usual proximity effect.

In neither experiment was the phonon spectrum measured. Meanwhile, it is difficult to say whether the appearance of superconductivity in the systems Cu-Ge, Ag-Ge and Au-Ge is connected entirely with the phonon mechanism, or whether the electron mechanism of superconductivity plays some role here.

TABLE II

Crystal	$\delta$ , Å	$T_{\Delta C}$ , °K
(TaS <sub>2</sub> ) <sub>1</sub> (2, 6-dimethylpyridine) <sup>1/53</sup>	3.55	2.8
(TaS <sub>2</sub> ) <sub>1</sub> (pyridine) <sup>1/2</sup>	5.8 and 6	3.7
(TaS <sub>2</sub> ) <sub>1</sub> (3-ethylpyridine) <sub>0.29</sub>	5.3	3.2
(TaS <sub>2</sub> ) <sub>1</sub> (aniline) <sub>0.75</sub>	12.1	3.06
(TaS <sub>2</sub> ) <sub>1</sub> (octadecylamine) <sub>0.58</sub>	29 and 45	3.05

We note that the disappearance of the superconductivity at sufficiently high concentrations of the non-metallic component is usually explained, in the framework of the granular model, by the growth of critical fluctuations for small metallic-granule sizes<sup>[430,63]</sup>. However, even in the case of a granulated structure, on increase of the concentration it is also possible that the granule size does not decrease but that only an increase of the distance between the granules occurs. The vanishing of  $T_C$  can be explained, as also in the paper<sup>[27]</sup>, in the framework of a model of a non-granulated uniform phase by the fact that the film loses its metallic properties at high non-metal concentrations. It would be interesting to measure the anomaly in the specific heat and susceptibility at those concentrations of the non-metallic component at which  $T_C$ , from the resistance, approaches zero (cf. below).

Of great interest is the study of the superconductivity of layer crystals consisting of alternating metallic layers (TaS<sub>2</sub>, NbS<sub>2</sub>, PdTe<sub>2</sub>) and organic layers (pyridine and other organic substances)<sup>[70,71]</sup>. Such crystals are obtained by "wedging" (intercalating) the organic compound into the layer crystals TaS<sub>2</sub>, NbS<sub>2</sub>, PdTe<sub>2</sub>, in which the bonds between the layers are very weak (the layer crystal NbSe<sub>2</sub> was investigated earlier in<sup>[72]</sup>). In the case of pyridine,  $T_C = 4-6^\circ\text{K}$  was obtained for NbS<sub>2</sub>, and a temperature of 1.45–1.65°K for PdTe<sub>2</sub>. A particularly detailed study has been made of crystals with TaS<sub>2</sub> (for pure TaS<sub>2</sub>,  $T_C = 0.8^\circ\text{K}$ ) with  $\sim 10^6$  layers. The thickness of a metallic layer of TaS<sub>2</sub> is equal to 6 Å. To elucidate the influence of the organic-layer thickness, various organic substances were used. The following results were obtained (Table II;  $\delta$  is the thickness of an organic layer).

Attempts to detect the transition using the vanishing of the resistance and to detect the Meissner effect proved unsuccessful.  $T_{\Delta C}$  is the temperature at which the specific heat falls to the previous curve after the anomaly (a smeared-out discontinuity). The transition was also detected in the behavior of the magnetic susceptibility  $\chi$  in a weak alternating field ( $\omega \sim 18$  Hz) in the presence of a strong constant field ( $10^2-3 \times 10^3$  gauss); in a stronger constant field,  $T_\chi$  is somewhat lower.  $T_\chi$  differs somewhat from  $T_{\Delta C}$  (by 1°K when  $\delta = 5.3$  Å). The magnitude of the discontinuity  $\Delta C/C_n \sim 0.65-0.8$ , in contrast to the BCS-theory value of 1.43; the discontinuity is strongly smeared out, and is simply a specific-heat anomaly.

In<sup>[71]</sup>, it was observed that the magnetic susceptibility  $\chi_\perp$  in the direction perpendicular to the plane of the layers remains (unlike  $\chi_\parallel$ ) less than the paramagnetic susceptibility in the normal state up to 40–50°K. Thus, from both the specific heat and the susceptibility, the transition is strongly smeared out, and this is obviously associated with the large magnitude of the fluctuations, due to the small thickness of the metallic layer. In<sup>[41]</sup>, a smeared specific-heat discontinuity of a similar form

was found theoretically for superconductors of small dimensions. It would be interesting to measure the resistance directly. It is possible that it is non-zero even at zero temperature (cf. Sec. 2). The properties of the crystals are strongly anisotropic; e.g., in the case of pyridine,  $H_{C2\parallel}/H_{C2\perp} > 80$  and  $\rho_\perp/\rho_\parallel \sim 10^4$  (the resistance measurements are very difficult); apparently, for  $\delta \sim 3.55$  Å,  $\rho_\perp$  and  $\rho_\parallel$  are still of the same order. Thus, we can assume that the tunneling conductivity is still non-zero in a small layer of the organic compound, and then falls practically to zero, i.e., the effective thickness of the metallic layer is somewhat greater than 6 Å—of the order of 10 Å. After  $\rho_\parallel$  has become much lower than  $\rho_\perp$ , further increase of the organic-layer thickness does not change the properties of the crystal; this is completely understandable. As in the case of metallic granules, increasing the dielectric layers between them plays no role after the connection between them has ceased to exist (the metallic layers are equivalent to plane granules). Naturally, therefore,  $T_C$  depends weakly on  $\delta$ . Thus, if the resistance is equal to zero, we are dealing with quasi-two-dimensional superconductivity. The authors consider that the superconductivity is a property of the bulk metal, since the conductivity in the perpendicular direction plays an important role (cf. also<sup>[25]</sup>), while the entropy has a two-dimensional character, since the form of the specific-heat discontinuity does not depend on  $\delta$ . Evidently, the raising of  $T_C$  is connected with the increase of the density of states on introduction of the organic compound, because of the transfer of a part of the electrons from the organic substance to the metal.

It would be interesting, if it were possible, to increase the thickness of the metallic layer, rather than that of the organic layer. We should then observe a decrease of the fluctuations and a narrowing of the transition region (of the width of the specific-heat discontinuity and of the width of the anomaly in  $\chi$ ). Meanwhile, it is difficult to say whether there is a contradiction between the data on the decrease of  $T_C$  in thin films (60–100 Å) and the properties of crystals of TaS<sub>2</sub> with an organic compound, inasmuch as the dependence of the resistance on  $T$  has not been measured in the latter case.

Crystals with alternating layers of MoS and Na or K and  $M_x\text{MoS}_2$  ( $0 < x < 0.5$ ) were investigated in<sup>[73]</sup>. For pure MoS<sub>2</sub>,  $T_C = 0$ . In the case of intercalation by sodium,  $T_C \approx 1.3^\circ\text{K}$ , and in the case of intercalation by potassium,  $T_C \approx 4.5^\circ\text{K}$ . It is assumed that Na and K give up a small fraction of their electrons to the unfilled d-bands of MoS<sub>2</sub>.

Thin films of NbSe<sub>2</sub> were studied in<sup>[74]</sup>. On decrease of their thickness  $d$  from 40 to 13–15 Å,  $T_C$  was lowered from 7 to  $\sim 4.2^\circ\text{K}$ ; this makes it possible to predict that  $T_C = 3.8^\circ\text{K}$  for a film of one elementary layer ( $d = 6.3$  Å). However, the apparent width of the transition, by the author's estimates, increased by a small amount—from 0.2 to 0.3°K, in contrast to the results of<sup>[71]</sup>. Apparently, the lowering of  $T_C$  is nevertheless connected with the growth of fluctuations, in accordance with the formulas (6) and (8).

In the analysis of the experiments with superconducting compounds of metals and non-metallic substances considered above, the question arises as to whether the experimentally observed increase of the critical temperature is connected with some new mechanism of superconductivity, in addition to the phonon (and, perhaps,

magnon) mechanism, or whether this increase is completely explicable within the framework of the phonon mechanism.

Since the values of  $T_C$  obtained up to now are not high, it is natural to assume that we are concerned only with a change of the parameters of the phonon mechanism. In this case, it is most often assumed that compounds of metals with dielectrics, semiconductors and organic substances have a granulated structure and the raising of  $T_C$  is brought about by a lowering of the mean phonon frequency  $\langle\omega\rangle$ , due, in particular, to the appearance of surface modes of vibration (the so-called membrane modes), according to [62]. Indeed, for a granulated structure, the bulk properties of the metal (in a granule) should evidently remain unchanged, and only the surface properties, associated with the presence of a boundary interface between the metallic and non-metallic components, can change. But then, for sufficiently large metallic-granule sizes ( $a \sim 100 \text{ \AA}$ ), at which, according to [28, 43b, 63], the maximum values of  $T_C$  are observed (for smaller granule sizes  $\sim 50-30 \text{ \AA}$ ,  $T_C$  falls to zero because of the critical fluctuations), even for the phonon degrees of freedom surface effects should be still very small compared with volume effects ( $\sim k_F a$ )<sup>-1</sup>  $\ll 1$ ) and can hardly explain even the small experimentally observed increase of  $T_C$ . These arguments in favor of a uniform rather than a granulated structure are particularly applicable to compounds of noble metals with germanium [27, 68, 69], inasmuch as the pure noble metals are non-superconducting and, consequently, the superconductivity of their compounds with Ge should, in the case of a granulated structure, be completely determined by surface phonon modes (or by surface polarization effects in the electron-exciton mechanism; see Sec. 2 above).

On the basis of the experimental data available at the present time, it is still difficult to say whether the electron mechanism plays any role, along with the phonon mechanism, in the experiments considered above. Although the absolute values of  $T_C$  in these experiments are still not large, the relative increase of  $T_C$  is not so small. For example, whereas an increase of  $T_C$  from 1.2 to 2.7°K was observed in experiments with condensation of pure Al on to a cold substrate [48a],  $T_C$  has been raised to 6.6°K for compounds of Al and Ge [28]. But if  $g_e < \tilde{g}_C$ , we cannot expect high absolute values of  $T_C$ , since in this case the electron mechanism plays a secondary role alongside the phonon mechanism. It is apparently very difficult to realize the condition  $g_e > \tilde{g}_C$  for which the electron mechanism would play the principal role. From this point of view, it may not be completely ruled out that, in the compound  $Nb_3Al_{0.8}Ge_{0.2}$ , which has the highest critical temperature at the present time (20.7–21°K), there is a small admixture of the electron mechanism, due to the presence of the Ge.

We have already seen that, along with cases in which a raising of  $T_C$  is accompanied by a lowering of the phonon frequency  $\langle\omega\rangle$  (according to tunneling measurements), there is also a case with a raising of  $\langle\omega\rangle$  [64b], which is more difficult to explain in the framework of the phonon mechanism. To elucidate this question, it would be worthwhile to perform measurements of the phonon spectrum by means of neutrons (see above).

To elucidate the role of non-phonon mechanisms, it would also be worthwhile to perform measurements of the isotope effect for those compounds of metals with non-metals which give an increase of  $T_C$ , since in the

electron mechanism the isotope effect should be equal to zero (cf. [12b, c, 75]). However, the measurement of the isotope effect for alloys and compounds is an extremely difficult experimental problem.

#### 4. SYSTEMS WITH TWO (OR MORE) GROUPS OF COLLECTIVE ELECTRONS

An example of such a system is a pure transition-group metal or an ordered metallic alloy with overlapping unfilled bands (e.g., s- and d-bands).

In [12b, c], the effective interaction (vertex part  $\Gamma$ ) was found for s- and d-electrons with allowance for the interaction between these two groups of electrons when  $q \ll k_F$  ( $\hbar q$  is the transferred momentum). In the case of a narrow d-band and a broad s-band, if we use the tight-binding approximation for the  $\psi$ -functions of the d-electrons, the expressions for  $\Gamma$  have the simple form:

$$\left. \begin{aligned} \Gamma_{p_s, p_s; p_s, p_s} &\equiv \Gamma_{ss} = (V_{ss} + \Pi_{dd} R_{sd})/S, \\ \Gamma_{dd; dd} &= (V_{dd} + \Pi_{ss} R_{sd})/S, \\ R_{sd} &= V_{sd}^2 - V_{ss} V_{dd}; \quad S = 1 - V_{ss} \Pi_{ss} - V_{dd} \Pi_{dd} - \\ &\quad - \Pi_{ss} \Pi_{dd} R_{sd}, \quad \Gamma_{sd; sd} = V_{sd}/S; \end{aligned} \right\}$$

here  $V$  are the matrix elements:

$$V_{ss} = 4\pi e^2/q^2, \quad V_{dd} \approx \frac{4\pi e^2/q^2}{q \rightarrow 0} [1 - (\alpha_d q^2/k_d^2) + (\beta_d q^4/k_d^4)],$$

$$V_{sd} \approx \frac{4\pi e^2/q^2}{q \rightarrow 0} (1 - \alpha_s \alpha_d q^2 r_0^2), \quad \hbar q = p_s - p_d,$$

$\hbar\omega = \epsilon_s - \epsilon_d$  and  $p_d \equiv \hbar k_d$  and  $p_s \equiv \hbar k_s$  are the Fermi momenta for the d- and s-electrons;  $r_0$  is the d-orbital radius in an isolated atom; in the case of a narrow d-band,  $k_d r_0 \ll 1$  and the corresponding terms can be neglected.  $\Pi_{ss}$  and  $\Pi_{dd}$  are polarization operators. If  $\epsilon_d \approx p^2/2m_d$ , then

$$\Pi_{dd}(q, \omega) \approx -\frac{p_d m_d}{\pi^2 \hbar^3} \left[ 1 - \frac{\omega m_d}{2q p_d} \ln \left| \frac{\omega + (q p_d / m_d)}{\omega - (q p_d / m_d)} \right| + \frac{i\pi |\omega| m_d}{2q p_d} \theta \left( \frac{q p_d}{m_d} - |\omega| \right) \right], \quad \theta(x) = \begin{cases} 1, & x > 0, \\ 0, & x < 0. \end{cases} \quad (11)$$

$\Pi_{ss}$  has the same form—with  $p_d$  and  $m_d$  replaced by  $p_s$  and  $m_s$ . In the static limit, when the retardation of the interaction can be neglected (i.e., when we can put  $\omega/q = 0$ ,  $q \rightarrow 0$ ),

$$\begin{aligned} \Gamma_{ss}^k &= \frac{4\pi e^2}{(\kappa^2 + q^2)} \left( 1 - \frac{\delta}{\delta - \gamma^2} \right), \quad \gamma = \frac{4\alpha_d m_d}{\pi m k_d r_B} - 1, \\ \delta &= \frac{16\beta_d m_d^2}{\pi^2 k_d^2 r_B^2 m^2}, \quad r_B = \frac{\hbar^2}{m e^2}, \quad r_d = \frac{m}{m_d} r_B, \quad r_s = \frac{m}{m_s} r_B, \\ \kappa^2 &= \frac{4k_d m_d}{\pi r_B m} \left( \gamma - \frac{k_s m_s}{k_d m_d} \gamma^2 \right) \frac{1}{\delta - \gamma^2}. \end{aligned}$$

We see that the first term corresponds to the usual screened Coulomb repulsion, and the second, for  $\delta/(\delta - \gamma^2) > 0$ , to attraction with the same screening length  $\kappa^{-1}$ . For  $\delta > \gamma^2$ , the attraction outweighs the repulsion. In order that the interaction potential have an exponentially decreasing rather than an oscillating dependence on  $r$ , the fulfillment of the condition  $\gamma - (k_s m_s \gamma^2 / k_d m_d) > 0$ , i.e.,  $\gamma \rightarrow 0$ ,  $\alpha_d > 0$ , is also necessary (cf. [75]).

In the high-density approximation ( $r_s, r_d \gg n^{-1/3}$ ), only the case  $q \ll p_F$  plays an important role, and the expressions (10) may be considered exact. For ordinary metal densities  $r_B \sim n^{-1/3}$ , these expressions are still qualitatively applicable. As is well known, a quantitative treatment of the Coulomb interaction for the case of intermediate density is not possible at the present time.

It was shown in [75] that, in the tight-binding approximation for the  $\psi$ -functions of the d-electrons,  $\alpha_d > 0$  under certain conditions for  $r_0$ , and a value of  $\alpha_d$  for a

simple cubic lattice was found. From the calculations of<sup>[75]</sup> it is easily established that, usually,  $\beta_d > 0$  and, consequently,  $\delta > 0$ . However, the condition  $\delta > \gamma^2$  can be fulfilled only when there are special relations between the lattice constant  $d$ , the radius  $r_0$  of the d-orbital, and the Fermi momentum  $p_d$ .

$\Gamma_{SS;SS}$  becomes infinite at frequencies  $\omega$  corresponding to the frequencies of the collective oscillations of the electrons.

Putting  $S = 0$ , we find the frequencies of the two branches of the acoustic plasmon oscillations<sup>[33]</sup>:

$$\omega_1^2 = v_1^2 k^2, \quad (12)$$

$$v_1^2 \approx p_d^2 \left[ 1 - \frac{4\alpha_d p_s m_s}{\pi p_d k d^2 r_B^2 m} \right] (3p_s m_s m_d)^{-1},$$

and of the usual Langmuir plasmon oscillations:

$$\omega_s^2 = \omega_0^2 + v_2^2 k^2,$$

$$\omega_0^2 = \frac{4e^2}{3\pi} \left( \frac{k_s^3}{m_s} + \frac{k_d^3}{m_d} \right),$$

$$v_2^2 = \frac{4e^2 \hbar^2}{5\pi \omega_0^2} \left( \frac{k_s^3}{m_s^2} + \frac{k_d^3}{m_d^2} \right) + \frac{4p_s^3 p_d e^2 \alpha_d}{3\pi m_s m_d [(p_s^2/m_s) + (p_d^2/m_d)] \hbar}.$$

Such acoustic plasmon oscillations had already been treated previously in the case of a semiconductor with electron and hole bands<sup>[76]</sup>. Indirect evidence in favor of the existence of acoustic plasmons, based on experimental data on the specific heat, magnetic susceptibility and other properties of certain transition metals, is given in<sup>[77]</sup> (where only the case of small values of the velocity  $v_1$  is considered).

It is not difficult to see that, for  $\delta > \gamma^2$ , the interaction, as a function of  $\omega$ , remains attractive in character from  $\omega = 0$  to  $\omega \sim v_1 k_{\max}$ . Therefore, for  $T_c$ , we obtain the formula (1) with  $\Delta E = v_1 p_{\max}$ . If we neglect pairing in the d-band, the corresponding function with allowance for the attraction via the phonons has the form (4).

If  $\delta < \gamma^2$  and  $\alpha_d < 0$ , pairing is nevertheless possible, since for  $0 < \omega^2 < \omega_1^2$  and  $\omega^2 > \omega_4^2$ ,  $\Gamma_{SS;SS}$  is repulsive in character, but for  $\omega_4^2 < \omega^2 < \omega_1^2$  it is attractive<sup>[33]</sup>, where

$$\omega_4^2 = -4\alpha_d e^2 p_d k^2 / 3\pi m_d \hbar > 0 \text{ for } \alpha_d < 0.$$

This case is less favorable for pairing, since the constant  $g_0$  in (5) will be logarithmically weakened<sup>[33]</sup>.

In<sup>[12b,c]</sup>, the case  $\delta > \gamma^2$ ,  $\alpha_d > 0$  was investigated, when it is possible to confine oneself to the static expression for  $\Gamma^k$  and not introduce the collective oscillations (acoustic plasmons) explicitly, just as, in the case of the phonon mechanism in the Bardeen model, the phonons are not introduced in explicit form (and only the energy integrals are cut off at the Debye frequency). Thus, the role of the excitons transmitting the attraction is played by plasmons in the case of a metal with overlapping bands. Pairing and attractive interaction between the electrons due to exchange of plasmons was treated in<sup>[78]</sup>, and for a degenerate semiconductor with electron and hole bands in<sup>[79]</sup>. Qualitative arguments about the appearance of additional attraction between the s-electrons due to their interaction with d-electrons, which can lead to negative values of the dielectric permittivity  $\epsilon(q, \omega)$  for large  $\omega$  and, in view of this, to a certain raising of  $T_c$  in the ordinary phonon mechanism, were given in an earlier paper<sup>[80]</sup>.

As in the case of a system with localized electrons, it can be seen from (10) that on replacing  $q = p_3 - p_1$  by  $p_4 - p_1 = p_4 - p_3 + q$ , i.e., on going over from the ordinary

interaction to an exchange interaction, we obtain for  $\Gamma$  a quantity smaller by a factor of  $q^2/k_F^2$ . Therefore, for small  $q$  (and this case makes a large contribution to  $\Gamma$ ) for arbitrary densities, and in all cases for high densities ( $n^{1/3} r_B > 1$ ), the exchange graphs (and also all those other than the ladder graphs) can be neglected.

As was shown above, the width  $\Delta E_{\text{ex}}$  of the exciton band plays an important role. It can be seen from (12) that, for  $p_d \sim p_s$ ,

$$\Delta E_{\text{ex}} \approx v_1 p_{\max} \approx (m_s/m_d)^{1/2} p_s^2 / 2m_s = (m_s/m_d)^{1/2} \epsilon_{FS}.$$

Thus, in the case of a narrow d-band and a broad s-band ( $p_d \sim p_s$ ,  $m_s \gg m_d$ ), the exciton-band width is considerably smaller than the Fermi energy for the s-band.

The damping for the acoustic plasmon branch is also easily calculated; for this, to find the  $\omega$  at which  $S$  vanishes, we must take account of the imaginary parts in the expressions for  $\Pi_{SS}$  and  $\Pi_{dd}$ . Then (by the estimate of Galitskiĭ),

$$\text{Im } \omega_1 / \text{Re } \omega_1 \approx (m_s/m_d)^{1/2} \ll 1 \text{ (for } p_s \sim p_d).$$

Analogous expressions for  $\text{Im } \omega_{\text{ac}}$  in the case of a semiconductor with electron and hole bands were obtained in the paper<sup>[76b]</sup>. Thus, the damping of the excitons is small in the model considered.

In order that superconducting pairing become possible in a system with overlapping bands, all the conditions indicated above must be fulfilled:  $\Delta E_{\text{ex}}$  must be sufficiently small and  $\tilde{g}_c < g_e$ .

In the case of large values of  $g_e$ , the phonon frequency and, consequently, the lattice stability are apparently lowered, as in the case of large values of  $g_p$  in the phonon mechanism (cf. p. 23). However, there are no reasons to suppose that this lowering of the stability for three-dimensional uniform systems, both in the case of a metal with overlapping bands and in the case of compounds of metals with non-metallic components (cf. Sec. 2), is more important than for quasi-two-dimensional and quasi-one-dimensional systems (the difficulties of obtaining uniform compounds of metals with non-metals is not connected with the large value of  $g_e$ ).

It is well known that, up to the present time, a large number of superconducting alloys has been investigated, and an alloy with high  $T_c$  has not yet been found. This argument is usually regarded as a purely empirical argument against three-dimensional systems with two collective groups of electrons. However, in the investigation of different metallic alloys up to the present time, one necessary condition has not been fulfilled. Such alloys should necessarily be ordered, with a small concentration of random impurities. Actually, as can be seen from (10), in order that the second term, corresponding to attraction, exist, it is necessary that two groups of electrons with  $\psi$ -functions of different form exist close to the Fermi surface. As is well known, the scattering of electrons by random impurities (unlike scattering by phonons) hybridizes the  $\psi$ -functions of electrons from different bands and a single  $\psi$ -function for all the bands arises<sup>[81]</sup>. It was shown in<sup>[81]</sup> that, if  $l \ll \xi_0$ , then, in place of the different gaps for each band, a common gap appears. The condition that  $l \gg \xi_0$  for the  $\psi$ -functions to remain distinct is evidently too strong. Meanwhile, it is difficult to give exact conditions for the length  $l$ , but it is obvious that  $l$  must be sufficiently large<sup>[33,75,81]</sup>. Thus, the removal of random im-

purities, which was not carried out in the earlier experiments, is a necessary condition for the appearance of attraction. This condition is not so easily fulfilled.

Clearly, in addition to ordered metallic alloys with overlapping bands, one can use many-valley semiconductors with a sufficiently large number of carriers (degenerate semiconductors) and semimetals<sup>[31]</sup>, degenerate electron-hole semiconductors<sup>[31,79,82]</sup>, and semiconducting films in the presence of size quantization<sup>[82]</sup>.

In the first case, the removal of impurities is also necessary, while in the second and third cases, impurities are not harmful, since the energy gap between the valence band and the conduction band impedes the hybridization of the  $\psi$ -functions of the different bands.

In the case of semiconductors and semimetals, along with electron-electron pairing electron-hole pairing is also possible (in this case, the Coulomb forces are attractive). Such pairing is possible if the Fermi surface has the same form for the electrons and the holes.

Electron-hole pairing, leading to a number of interesting effects, was considered in<sup>[83]</sup> (cf. also<sup>[84]</sup>). In this case, electron-electron pairing should also be taken into account<sup>[31]</sup>. A simultaneous treatment of the two types of pairing (in the particle-hole channel and in the particle-particle channel) was performed in<sup>[85]</sup>. It is found that, in certain special cases, it is possible to obtain appreciably higher critical temperatures than in the absence of the metal-dielectric transition<sup>[86]</sup>. Obviously, in the usual case of a metal with two unfilled bands, rather than the case of one band almost filled and a second band almost empty (semiconductor, semimetal), only electron-electron pairing is important, and electron-hole pairing can be neglected.

<sup>1</sup>) An estimate made in [10b] on the basis of experiments on the raising of  $T_C$  in finely dispersed tin, with the use of a theoretical formula obtained in [10c], gives for  $\Delta R$  a value  $\sim 1.5\text{\AA}$ .

<sup>2</sup>) After this review was written, an interesting paper [40] appeared in which calculations were performed for a metal-semiconductor sandwich. It was shown that a marked increase of  $T_C$  can be obtained in the case of sufficiently thin metallic films ( $\sim 10\text{\AA}$ ).

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Translated by P. J. Shepherd