EFFECT OF A METAL-DIELECTRIC PHASE TRANSITION ON THE SUPERCONDUCTING TRANSITION TEMPERATURE

Yu. V. KOPAEV and R. Kh. TIMEROV

P. N. Lebedev Physics Institute, USSR Academy of Sciences

Submitted December 31, 1971

Zh. Eksp. Teor. Fiz. 63, 290–307 (July, 1972)

A model of a metal with narrow allowed bands is investigated. For certain crystal structures an instability appears at a higher temperature than the instability in the electron system. As a result a distortion of the crystal structure occurs. The distortion is of the type which doubles the period, and leads to a metal-dielectric transition. The conditions which the parameters of the electron spectrum must satisfy in order to achieve a change of the crystal structure with the simultaneous formation of dielectric and superconducting gaps on the Fermi surface are determined. It is established that the superconducting transition temperature T_S may be much higher than the corresponding temperature in the absence of the dielectric transition; this is due to the increased density of states near the edge of the allowed bands of the dielectric phase. The main changes in the phonon spectrum caused by the structural distortion result in the appearance of an optical phonon branch which is separated from the acoustic branch by a gap.

1. INTRODUCTION

IT is known that the highest-temperature superconducting compounds undergo a structural transformation at temperatures T_C lying somewhat above the superconducting transition temperature T_S.[1] The point of view has been expressed[2] that the proximity of T_C to T_S guarantees high values of the latter, since near the temperature of the structural transformation one of the optical phonon modes becomes sufficiently low-frequency. Therefore, the effective coupling constant λ for the interaction of the electrons with this mode, which is inversely proportional to the average value $\langle\omega^2\rangle^{1/2}$ of the phonon frequency, must increase in this connection. On the other hand, the expression for the superconducting transition temperature[3]

$$T_s = 1.14\langle\omega^2\rangle^{1/2}\exp(-1/\lambda N(0)) \qquad (1)$$

contains the average value of the phonon frequency in the factor in front of the exponential (N(0) denotes the density of electron states near the Fermi level). The investigation of the possibility of increasing T_S by means of an exciton mechanism of superconductivity[4] is connected with precisely this fact. As is clear from Eq. (1), T_S must have a maximum as a function of $\langle\omega^2\rangle$. In the article by Anderson and Blount[2] it is conjectured that, as a consequence of the structural transformation, a state near this maximum is realized.

There is an opposite point of view concerning the effect of the structural transformation on T_S which asserts that, due to the large value of the constant λ in the high-temperature phase, the latter becomes unstable upon lowering the temperature to T_K, and the new phase existing below T_K possesses a smaller electron-phonon coupling constant T, which thus ensures its stability. Therefore, it is asserted that in the absence of a structural transformation T_S would be above the observed value.

Up to now the topic of discussion has been the changes of the phonon characteristics associated with a structural transformation. We note that the value of T_S given by Eq. (1) is very sensitive to the density N(0) of electron states near the Fermi level, which may vary in connection with the structural transformation. An appreciable change of the density of states N(0), accompanying the structural transformation, was observed by Chu et al.[5] for V-Ru alloys undergoing a structural transition near T_S. One can deduce the formation of a dielectric gap on part of the Fermi surface from the temperature dependences of the resistivity and of the magnetic susceptibility near T_K. It has been shown that the density of states N(0) increases sharply near the dielectric gap as a result of the formation of a dielectric gap near the Fermi level; this is shown for the case of a semimetal having unequal concentrations of electrons and holes in the authors' articles[6] and in the article by Mattis and Langer[7] for the case of a metal with a narrow, not precisely half-filled band. As a result the expression for T_S has the form

$$T_s = 1.14\langle\omega^2\rangle^{1/2}\frac{\mu}{d}\exp\left(-\frac{\mu}{\lambda N(0)d}\right),$$

where μ is the energy of degeneracy of the "excess" electrons and d is the dielectric gap.

The density of states $N(0)d/\mu$ effectively increases for $\mu/d \ll 1$, a result which is related to the "expulsion" of states from the region of the dielectric gap. For the same reason the energy region near the Fermi level where an attractive interelectron interaction exists is decreased, a fact which is reflected by the presence of the factor μ/d in front of the exponential. Thus, the superconducting transition temperature T_S must have a maximum as the impurity concentration determining the value of μ is varied, just as it has a maximum associated with variation of the average phonon frequency.

The model of a one-dimensional metal[8,9] is another example of the effect of dielectric pairing on super-

conductivity. Here quartets of particles are formed near the Fermi surface instead of electron-electron or electron-hole pairs. Since without taking Umklapp processes[8] into account the effective coupling constant in a dielectric (electron-hole) pair is half as large as in a Cooper (electron-electron) pair, it follows that when quartets of particles are taken into account the superconducting transition temperature coincides with the usual expression for T_S.[3] It was shown in[10] by one of the authors that the formation of similar quartets of particles is possible for a transition metal or for a semimetal with almost identical carrier concentrations in two bands having markedly different effective masses. Since the binding energies of the Cooper and dielectric pairs are identical in the present case, the superconducting transition temperature T_S due to the Bose condensation of quartets of particles may be much higher than the Bose-condensation temperature for Cooper pairs.[3] The qualitative explanation of such mutual influence between the dielectric and superconducting pairings lies in the fact that, as a result of each pairing separately, the density of states near the gap being formed (dielectric or superconducting) is increased, and the other type of pairing occurs against the background of this enhanced density of states. However, if the dielectric gap is exponentially small (in the absence of Cooper pairing) in comparison with the superconducting gap Δ, as happens in the one-dimensional case, then the variation of the density of states in a very narrow (in comparison with Δ) energy interval (of order d) essentially does not have any effect on Δ. On the other hand, in this case the influence of the superconducting pairing on the dielectric pairing is very important for the analogous reason. As a result the dielectric gap d appears at the same temperature as the superconducting gap.

In the present article we shall investigate the transition into the dielectric state, due to the change of crystalline structure which occurs as a result of the electron-phonon interaction, using a model of a metal having rather narrow allowed bands (see below). It turns out that for a certain type of crystalline structure the metallic state is unstable at $T < T_c$ in the nearest-neighbor approximation (the transition integral w is considered only between nearest-neighbor atoms). In the presence of an interaction u with non-nearest atoms (the integral corresponding to the transition of an electron from a given atom to the next-nearest neighbor atom is considered) which is larger than a certain critical value, the initial metallic state is stable at any arbitrary temperature. In the present case the effect of u on the metal-dielectric phase transition is analogous to the influence of the magnetization M on the superconductivity of a ferromagnetic substance:[11] when $\mu_B M$ (here μ_B denotes the Bohr magneton) is smaller than the width Δ of the superconducting gap, the position of the Fermi level is shifted (for one direction of the spin), by an amount $\mu_B M$, from the middle of the superconducting gap toward the upper band; for the other spin direction it is shifted by the same amount toward the lower band. In the case which we are considering, the coordinate of the point on the edge of the Brillouin zone, which is rearranged as a result of the metal-dielectric transition, plays the role of the spin, that is, on a certain part of the boundary of the new Brillouin zone the conduction band comes closer to the Fermi level, which lies in the forbidden band, and on the other part of the boundary the valence band comes closer to the Fermi level. Thus, the minimum distance 2δ between the valence band and the conduction band (the so-called indirect forbidden band) may be much smaller than the quantity d (the so-called direct forbidden band). On the other hand, the increase in the density of states in comparison with the density of states in the initial metallic phase takes place in an interval of order d. Such a dielectric state with $\delta \ll d$ may turn out to be unstable with respect to the formation of Cooper pairs.

In fact, let us excite two electrons into the conduction band, expending thereby an energy 2δ. If their binding energy in a Cooper pair turns out to be greater than 2δ, then such a process is energetically favorable, and the system must be rearranged, that is, a changeover of the covalent pairs, which are responsible for the dielectric state, into Cooper pairs seems to occur. Moreover, since the density of states in the allowed bands increases in an interval of the order of d, the binding energy of the Cooper pairs can be much greater than in the initial metallic state. A similar situation occurs in the model of the so-called exciton insulator.[12] If the dielectric gap is smaller than the binding energy of the electron and the hole in an exciton, then the amount of energy expended in the excitation of the electron and hole is smaller than the amount gained as a result of exciton formation. Therefore, a rearrangement of the initial state occurs. To be sure, in this case the initial and final (exciton dielectric) states do not differ qualitatively. As will be clear from what follows (see Fig. 1 below), the dependence of the superconducting gap or T_S on δ has a form which is analogous to the dependence of the order parameter Δ_i for an exciton insulator on the width of the initial forbidden band. Namely, just as in the case considered earlier,[12] there exists a certain positive value of δ, above which superconductivity is impossible. In the model of an exciton insulator this value corresponds to the width of the forbidden band,

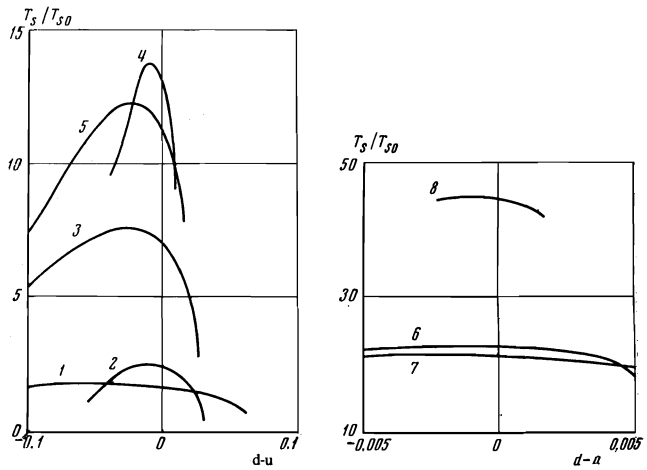

FIG. 1. The dependence of T_S/T_{S0} on d-u for the following values of the varied parameters λ'_s/λ'_d and ω_D/w: curve 1—0.8 and 0.1; curve 2—0.8 and 0.025; curve 3—0.5 and 0.1; curve 4—0.5 and 0.025; curve 5—0.45 and 0.1; curve 6—0.45 and 0.025; curve 7—0.4 and 0.1; curve 8—0.4 and 0.025.

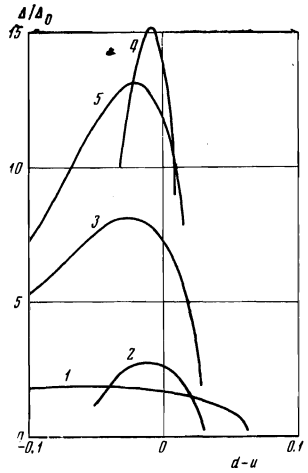

FIG. 2. The dependence of Δ/Δ_0 on d–u for several pairs of values of the parameters λ'_s/λ'_d and ω_D/w, the labelling of the curves being the same as in Fig. 1.

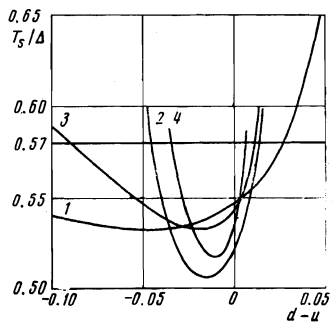

FIG. 3. The dependence of T_s/Δ on d–u for several pairs of values of the parameters λ'_s/λ'_d and ω_D/w, the labelling of the curves being the same as in Fig. 1.

which is equal to the exciton's binding energy. Just as in[12], a maximum of Δ or T_s corresponds to the region $\delta \sim 0$. The difference between the present case and the model of an exciton insulator lies in the fact that in the latter case the solution for Δ_i tended to zero for large negative values of the forbidden band. In the present case the solutions for Δ and T_s tend to the solution given by Eq. (1)[3] for values of δ which are large in comparison with d.

As is clear from Fig. 3 (see below), the ratio T_s/Δ can be larger than 0.57.[3] This effect is associated with the fact that in the simultaneous presence of dielectric and superconducting gaps near the Fermi level, the number of thermally broken superconducting pairs is determined by both the superconducting and by the dielectric (d) gaps. Therefore, the effectiveness of thermal breaking of superconducting pairs may be substantially suppressed, as indicated by the value $T_s/\Delta > 0.57$ under certain conditions. On the other hand, there is also an opposite tendency associated with the effect of the dielectric gap on the superconducting transition temperature. Namely, the high density of states near the edge of the allowed band leads to an increase in the role of the entropy factor, which characterizes the distribution of the electrons excited through the gap with respect to the states in the allowed band. This explains the value $T_s/\Delta < 0.57$ at the maximum value of the ratio T_s/T_{s_0} (see Fig. 3).

2. THE METAL-DIELECTRIC PHASE TRANSITION UNDER THE INFLUENCE OF THE ELECTRON-PHONON INTERACTION

Let us consider a metallic system with the dependence of the electron energy spectrum on the quasi-momentum having the property

$$\varepsilon_{p+q} = -\varepsilon_p,$$

for selected values of the vector q. Simple cubic and body-centered cubic lattices in the tight-binding limit and only taking z nearest neighbors into account, when $q = (\pi/a)(\pm 1, \pm 1, \pm 1)$, may serve as a typical example to which we shall constantly turn. Let us show that in this case the crystal lattice becomes unstable for an arbitrarily weak electron-phonon interaction at T = 0. This type of instability was investigated by Afanas'ev and Kagan[13] for the special case of Fermi surfaces containing flat regions. The nature of the instability can be investigated with the aid of the Dyson equation for the phonon Green's function:

$$D(\mathbf{k}, \omega) = D_0(\mathbf{k}, \omega) / [1 - \Pi(\mathbf{k}, \omega) D_0(\mathbf{k}, \omega)] \qquad (2)$$

with the polarization operator given by

$$\Pi(\mathbf{k}, \omega) = -ig^2 \sum_\sigma \sum_{\mathbf{p}} \int \frac{d\omega}{2\pi} G^{\sigma\sigma}(\mathbf{p}+\mathbf{k}) G^{\sigma\sigma}(\mathbf{p}), \qquad (3)$$

where g is the electron-phonon coupling constant, and $G^{\sigma\sigma}(1)$ is the Green's function of the electrons.

Under condition (1) the evaluation of the polarization operator for $\mathbf{k} = \mathbf{q}$ gives the following result (without taking Umklapp processes into account)

$$\Pi(\mathbf{k}, \omega) = 2\frac{g^2}{8} N(0) \left[\ln\left(e \left| \frac{w}{\omega} \right| \right) + i\frac{\pi}{2} - i\varphi \right], \qquad (4)$$

where N(0) = 1/2w is the average density of states in the allowed band of width 2w. The factor 1/8 in (4) reflects the reduction of the volume participating in the integration over dp in Eq. (3) for normal scattering processes, when states with quasimomenta $\mathbf{p} + \mathbf{q}$ and $\mathbf{p}$ must belong to states in the first Brillouin zone. Taking the Umklapp processes into account amounts to making the substitution

$$^1/_8 g_N^2 \to g^2 = {}^1/_8 (g_N^2 + 3g_{U1}^2 + 3g_{U2}^2 + g_{U3}^2), \qquad (5)$$

where g_N corresponds to normal processes, and g_{U_1}, g_{U_2}, and g_{U_3} correspond to Umklapp processes involving reciprocal lattice vectors of modulus $2\pi/a$, $2\pi\sqrt{2}/a$, and $2\pi\sqrt{3}/a$, corresponding to the edge, the diagonal across the face, and the space diagonal of the cubic Brillouin zone.

Substituting the calculated value (4) of the polarization operator Π (having made the substitution indicated in (5)) into Eq. (2), we find that the phonon function D has a pure imaginary pole

$$|\omega| = 2w \exp(-1/2g^2 N(0)), \qquad (6)$$

which reflects the instability of the lattice due to the interaction with electrons involving a momentum transfer q. The difference between expression (6) and the analogous expression in the theory of superconductivity (which describes there the instability in the electron system) consists, in the first place, in the fact that the energy of the states participating in the integration in (3) is limited only to the region of allowed states $\pm w$ instead of being restricted to a narrow layer $\pm\omega_D$ near the Fermi level and, in the second place, the summation over the spin index in (3) leads to an effective doubling of the square of the electron-phonon coupling constant. The introduction into the investigation of a certain order

parameter for the new phase with the help of the so-called "anomalous" averages can lead to a general method for the elimination of such instabilities. In the present case we introduce into consideration the anomalous average $\langle \Phi_q \rangle = \langle b_q + b^+_{-q} \rangle$, which characterizes (in accord with the definition of the phonon creation and annihilation operators b^+_q and b_q) the macroscopic deformation of the lattice. It will be shown below that the expression for the dielectric gap d in the electron spectrum coincides with expression (6), and the magnitude of the distortion $\langle b_q + b^+_{-q} \rangle$ of the crystal lattice is proportional to the gap

$$\langle \Phi_q \rangle = \langle b_q + b_{-q}{}^+ \rangle = d/g. \tag{7}$$

The Coulomb interaction was not taken into consideration in the work by Mattis and Langer,[7] since it was assumed to be smaller than the electron-phonon interaction. However, no quantitative relationship between these interactions can justify the neglect of the Coulomb effects, since from considerations of the stability of the system as a whole it follows that in the static limit $\omega = 0$ the Coulomb repulsion must exceed the attraction due to the electron-phonon interaction. However, Cooper pairing of the electrons becomes possible thanks to the well-known effect of the suppression of the Coulomb repulsion by the factor $\ln(\epsilon_F/\omega_D)$. We note that the Coulomb vertex part in the annihilation channel,

$$\Gamma(\mathbf{k}, \omega) = \frac{4\pi e^2}{k^2} \Big/ \left[1 - \frac{4\pi e^2}{k^2} \Pi(\mathbf{k}, \omega)\right] \tag{8}$$

contains the same polarization operator $\Pi(\mathbf{k}, \omega)$ as appears in expression (2) for the phonon Green's function D. However, the function $D_0 = \omega_0^2(q)/(\omega^2 - \omega_0^2(q)$ appearing in Eq. (2) is negative for $\omega^2 < \omega_0^2(q)$, whereas only the positive factor $4\pi e^2/k^2$ plays an essential role in expression (8) for the vertex part. This indicates that the Coulomb vertex $\Gamma(\mathbf{k}, \omega)$ in (8) does not have a pole at $\mathbf{k} = \mathbf{q}$ and $\omega = 0$, but instead it vanishes. This means that the screening of the Coulomb interaction turns out to be very strong in the neighborhood of the point $\mathbf{k} = \mathbf{q}$, owing to the property $\epsilon_{\mathbf{p}+\mathbf{q}} = -\epsilon_{\mathbf{p}}$ of the electron spectrum; at the same time the nature of the screening at large distances (corresponding to small values of $|\mathbf{k}|$) remains the same as usual. The vertex parts have opposite signs in the annihilation and scattering channels. Therefore the Coulomb vertex has a purely imaginary pole, reflecting the instability of the system with respect to electron-hole pairing, only in the channel associated with particle-hole scattering with total momentum $\mathbf{k} = \mathbf{q}$ (see Eq. (15′) below). Finally, in the channel for electron-electron scattering with small total momentum there is the Cooper-type singularity, whose nature is not related to the special form (1) of the electron spectrum.[3]

The cited analysis of the singularities of the vertex parts in the annihilation and scattering channels can serve as a basis for the use of the "parquet" approximation.[8] However, the effect mentioned above concerning the effective doubling of the electron-phonon interaction in expression (6) for the pole, together with the condition $w \gg \omega_D$, permits us to confine our attention to only taking the singularities of the phonon Green's function into account, since the instability in the phonon system appears sooner when the temperature is lowered.

Thus, we take the distortion of the crystal lattice due to the electron-phonon interaction to be the mechanism which governs the metal-dielectric phase transition. In our scheme the distortion of the lattice, which is described by the above-mentioned anomalous averages $\langle b_q + b^+_{-q} \rangle$, must necessarily lead in turn to the inclusion of anomalous averages $\langle a_{\mathbf{p}-\mathbf{q},\sigma} a^+_{\mathbf{p}\sigma} \rangle$ of the electron annihilation and creation operators in the investigation. The quantity $\langle a_{\mathbf{p}-\mathbf{q},\sigma} a^+_{\mathbf{p}\sigma} \rangle$ characterizes the rearrangement of the electron spectrum, since after multiplication by the effective interaction constant this quantity determines the energy gap in the electron spectrum.

Now let us turn to an investigation of the thermodynamics of the transition within the framework of the approach outlined above. In order to do this, let us consider the system of electrons and phonons in the crystal:

$$\mathcal{H} = \sum_{\mathbf{p},\sigma} [\varepsilon(\mathbf{p}) - \delta\mu] a_{\mathbf{p}\sigma}{}^+ a_{\mathbf{p}\sigma} + \sum_{\mathbf{k}} \omega_0(\mathbf{k}) (b_{\mathbf{k}}{}^+ b_{\mathbf{k}} + {}^1/_2)$$
$$+ \sum_{\mathbf{p},\sigma} \sum_{\mathbf{k}} g(\mathbf{k}) a^+_{\mathbf{p}+\mathbf{k},\sigma} a_{\mathbf{p}\sigma} (b_{\mathbf{k}} + b_{-\mathbf{k}}{}^+) + {}^1/_2 \sum_{\mathbf{p},\sigma} \sum_{\mathbf{p}',\sigma'} \sum_{\mathbf{k}} U(\mathbf{k}) a^+_{\mathbf{p}+\mathbf{k},\sigma} a^+_{\mathbf{p}'-\mathbf{k},\sigma'} a_{\mathbf{p}'\sigma'} a_{\mathbf{p}\sigma}, \tag{9}$$

where the first and second terms describe the energies of the free electrons and free phonons, and the third and fourth terms allow for the electron-phonon interaction and the Coulomb interaction between the electrons. Let us represent the dependence of the kinetic energy of the electrons on their quasimomentum, $\epsilon(\mathbf{p})$, measured with respect to the middle of the allowed band, in the form

$$\varepsilon(\mathbf{p}) = \varepsilon_{\mathbf{p}} + \varepsilon_1(\mathbf{p}), \qquad \varepsilon_{\mathbf{p}+\mathbf{q}} = -\varepsilon_{\mathbf{p}}, \tag{10}$$

where the correction $\epsilon_1(\mathbf{p})$ takes the influence of non-nearest neighbors into account in the tight-binding limit, their effect being to produce some additional modulation (in momentum space) of the equal-energy surfaces $\epsilon_{\mathbf{p}} = \text{const}$. For example, for the case of a simple cubic lattice we have

$$\varepsilon_p = {}^1/_3 w (\cos ap_x + \cos ap_y + \cos ap_z), \tag{11}$$

and in the approximation taking only next-nearest atoms into account the expression for $\epsilon_1(p)$ has the following form:

$$\varepsilon_1(p) = u(\cos ap_x \cos ap_y + \cos ap_x \cos ap_z + \cos ap_y \cos ap_z) \tag{12}$$

By virtue of our choice of the origin for the energy reference system (namely, the middle of the allowed band), a shift $\delta\mu$ of the chemical potential is introduced in order to allow for the deviation $\delta n = n - n_0$ of the electron concentration from the value n_0, which corresponds to occupation up to the middle of the allowed band with $\delta\mu = 0$.

For the following calculations, in which we shall make extensive use of the smallness of $u \ll w$ and $\delta n \ll n_0$, it is convenient to introduce the notation

$$\varepsilon(p) - \delta\mu = \varepsilon_p - \nu_p, \qquad \nu_p = -\varepsilon_1(p) + \delta\mu. \tag{13}$$

Besides the condition $u \ll w$ we shall also assume that the interaction of two electrons on a single center is smaller than the width w of the allowed band, and therefore the Hubbard metal-dielectric transition is absent.[14]

We introduce furthermore the operators of the electron and phonon fields in the "Heisenberg" representation:

$$c_p(\tau)=e^{\tau\mathcal{H}}\,c_p e^{-\tau\mathcal{H}},\qquad \bar{c}_p(\tau)=e^{\tau\mathcal{H}}\,c_p^{+}e^{-\tau\mathcal{H}},$$

where c = a, b, and we determine the Green's functions of the electrons in the temperature technique:[3]

$$G_{pp}^{\sigma\sigma}(\tau)=-\langle\hat{T}a_{p\sigma}(\tau)\bar{a}_{p\sigma}(0)\rangle,$$
$$G_{p-q,p}^{-}(\tau)=\langle\hat{T}a_{p-q,\sigma}(\tau)\bar{a}_{p\sigma}(0)\rangle, \tag{14}$$

where $\langle\ldots\rangle$ denotes averaging according to Gibbs, and $\hat{T}$ is the operator of chronological ordering with regard to the "time" τ. The equations of motion for the Green's functions (14) are obtained in the usual way:[3]

$$\left(-\frac{\partial}{\partial\tau}-\varepsilon_k+\nu_k\right)G_{kk}^{\sigma\sigma}(\tau)+[d_q]_\tau G_{k-q,k}^{\sigma\sigma}(\tau)=\delta(\tau),$$
$$\left(\frac{\partial}{\partial\tau}-\varepsilon_k-\nu_k\right)G_{k-q,k}^{\sigma\sigma}(\tau)-[d_q]_\tau G_{kk}^{\sigma\sigma}(\tau)=0, \tag{15}$$

where

$$[d_q]_\tau=\sum_h g(q+h)\langle\Phi_{q+h}(\tau)\rangle+\sum_h U(q+h)\sum_{p,\sigma}G_{p-q-h,p}^{\sigma\sigma}(+0)$$
$$-\sum_h\sum_p U(p-q-h)G_{p-q-h,p}^{\sigma\sigma}(+0). \tag{15'}$$

Here we have used the fact that the vector 2q belongs to the space of the reciprocal lattice vectors h, that is

$$c_{k+h}=c_k,\quad \bar{c}_{k+h}=\bar{c}_k,\quad c=a,\ b,$$

and the summation over h takes Umklapp processes in the system into account. With the screening effects which were established in the investigation of the corresponding vertex part (8) taken into account, one finds that the term containing U(q + h) in (15'), corresponding to the annihilation channel, vanishes. In turn one can write down equations of motion of the following form for the average values of the phonon-field operators appearing in (15'):

$$\left(-\frac{\partial}{\partial\tau}-\omega_0(q)\right)\langle b_{q+h}(\tau)\rangle=-g(q+h)\sum_{h'}\sum_{p,\sigma}(G_{p-q-h-h',p}^{\sigma\sigma}(+0))^{*},$$
$$\left(-\frac{\partial}{\partial\tau}+\omega_0(q)\right)\langle\bar{b}_{-q-h}(\tau)\rangle=g(q+h)\sum_{h'}\sum_{p,\sigma}(G_{p-q-h-h',p}^{\sigma\sigma}(+0))^{*}. \tag{16}$$

Equations (15) together with Eqs. (16) for the determination of the unknown coefficients $\langle b_q(\tau)\rangle$ and $\langle b_{-q}(\tau)\rangle$ form a closed system of equations permitting us to determine the unknown functions $G_{kk}^{ss}(\tau)$ and $G_{k-q,k}^{ss}(\tau)$ in a self-consistent way (thanks to the relation (15')). Actually it is easier to solve the system of algebraic equations which arise from Eqs. (15) and (16) after making the transition to a Fourier series expansion of all τ-dependent quantities in the interval (0, 1/T). To sum up, after eliminating the quantities $\langle\Phi_q(\tau)\rangle$ with the aid of the relations

$$\langle\Phi_{q+h}(\tau)\rangle_{\omega_n}=\langle b_{q+h}(\tau)+\bar{b}_{-q-h}(\tau)\rangle_{\omega_n}$$
$$=g(q+h)\frac{2\omega_0(q)}{-\omega_n^2-\omega_0^2(q)}\delta_{0n}T^{-1}\sum_{p,\sigma}G_{p-q,p}^{\sigma\sigma}(+0) \tag{17}$$

(the presence of the factor δ_{0n} reflects the static nature of the distortion of the crystal structure), we obtain the following equations, which are familiar from the theory of superconductivity:[3]

$$(i\omega_n+\nu_k-\varepsilon_k)G_{kk}^{\sigma\sigma}(\omega_n)+d_qG_{k-q,k}^{\sigma\sigma}(\omega_n)=1,$$
$$d_qG_{kk}^{\sigma\sigma}(\omega_n)+(i\omega_n+\nu_k+\varepsilon_k)G_{k-q,k}^{\sigma\sigma}(\omega_n)=0; \tag{18}$$

$$d_q=\lambda_d\sum_{p,\sigma}T\sum_{\omega_n}G_{p-q,p}^{\sigma\sigma}(\omega_n), \tag{19}$$

$$\lambda_d=\left[2g^2+g_c^2\left(1-2g^2\ln\frac{w}{\tilde{\omega}}\right)\right]\Big/\left[1+g_c^2\ln\frac{w}{\tilde{\omega}}\left(1-2g^2\ln\frac{w}{\tilde{\omega}}\right)\right], \tag{19'}$$

where $g_c^2=(2\pi^2e^2/\epsilon p_F)\ln(4p_F^2/\kappa_D^2)$ is the effective coupling constant of the Coulomb interaction,[15] $\tilde{\omega}$ is a quantity of the order of the plasma frequency, and $p_F\approx q/2$. The effective coupling constant λ_d of the electron-hole interaction, given by Eq. (19'), is obtained from Eq. (15') in which the integration is defined in a region of width 2w for the electron-phonon interaction and in a region of width $2\tilde{\omega}$ for the Coulomb interaction.

The functions

$$G_{kk}^{\sigma\sigma}(\omega_n)=(i\omega_n+\nu_k+\varepsilon_k)/D,\qquad G_{k-q,k}^{\sigma\sigma}(\omega_n)=d_q/D,$$
$$D=(i\omega_n+\nu_k)^2-\varepsilon_k^2-d_q^2. \tag{20}$$

satisfy the system of equations (18). Returning to the self-consistency condition (19), we obtain the following equation after summing over ω_n:

$$1=\lambda_d\sum_k\frac{1}{(\varepsilon_k^2+d_q^2)^{1/2}}\frac{1}{2}\left\{\mathrm{th}\frac{\nu_k+(\varepsilon_k^2+d_q^2)^{1/2}}{2T}\right.$$
$$\left.+\mathrm{th}\frac{-\nu_k+(\varepsilon_k^2+d_q^2)^{1/2}}{2T}\right\}; \tag{21}$$

which determines the order parameter d_q as a function of the temperature T, the electron-phonon coupling constant g, and the effective Coulomb interaction constant g_c. Let us determine the chemical potential $\delta\mu$ from the other equation:

$$\delta n=T\sum_{k,\sigma}\sum_{\omega_n}G_{kk}^{\sigma\sigma}(\omega_n)-n_0$$
$$=\sum_k\frac{1}{2}\left[\mathrm{th}\frac{-\varepsilon_1(k)+\delta\mu+(\varepsilon_k^2+d_q^2)^{1/2}}{2T}\right. \tag{22}$$
$$\left.+\mathrm{th}\frac{-\varepsilon_1(k)+\delta\mu-(\varepsilon_k^2+d_q^2)^{1/2}}{2T}\right].$$

Equations (21) and (22) are well-known in the theory of a semimetal-semiconductor phase transition,[15,16] the only difference being that the summation over the quasimomentum k in Eq. (21) goes over all states in the Brillouin zone, but not in a layer of the order of ω_{pl} near the Fermi surface (here ω_{pl} denotes the plasma frequency). As an example we present the solution of Eq. (21) in the simplest case $\delta n = 0$ (i.e. $\delta\mu = 0$). Equation (22) is identically satisfied by virtue of the specific dependence of ϵ_1 on k. In the subsequent discussions it is important to realize that, because of the chosen origin of our energy reference system (energy is measured from the middle of the allowed band), the Fermi surface is, by definition, the surface where

$$\varepsilon_k+\varepsilon_1(k)=0. \tag{23}$$

In order to simplify the subsequent calculations, we replace the true Fermi surface (23) by the surface

$$\varepsilon_k+u=0 \tag{24}$$

in one-half of the solid angle of each octant in momentum space, and we replace it by the surface

$$\varepsilon_k-u=0 \tag{24'}$$

in the other half. The substitution (24), (24') corresponds to a change from a smooth modulation of the Fermi surface to a step-like modulation. If we further change

from a summation over **k** to an integration over **dk**, and then to an integration over the energy, that is, after making the changes $\sum_{\mathbf{k}} \to \int d\mathbf{k} \to N(0)\int d\epsilon$, then instead of Eq. (21) we obtain

$$\frac{1}{\lambda_d'} = \int_0^w \frac{d\varepsilon}{(\varepsilon^2+d^2)^{1/2}} \frac{1}{2}\left(\mathrm{th}\frac{u+(\varepsilon^2+d^2)^{1/2}}{2T} + \mathrm{th}\frac{-u+(\varepsilon^2+d^2)^{1/2}}{2T}\right), \tag{25}$$

where $\lambda_d' = \lambda_d N(0)$ and $N(0) = 1/2w$ denotes the average density of states.

It is clear from Eq. (25) that at T = 0 the modulation of the Fermi surface does not have any effect on the dielectric gap d as long as the amplitude u is smaller than the gap itself, u < d, since in this case

$$d = w/\mathrm{sh}(-1/\lambda_d') = d_0. \tag{26}$$

In the region u > d we have

$$\frac{1}{\lambda_d'} = \int_{(u^2-d^2)^{1/2}}^{w} \frac{d\varepsilon}{(\varepsilon^2+d^2)^{1/2}},$$

that is,

$$d = [d_0(2u-d_0)]^{1/2}.$$

Thus, when the amplitude u of the modulation exceeds the maximum value d_0 of the dielectric gap, then the metallic phase is stable with respect to a metal-dielectric transition right down to the temperature of absolute zero. This, of course, does not exclude a transition into the superconducting state, a point which will be investigated below. Finally, we note that the maximum critical temperature T_c of the dielectric transition is attained when $u = \delta\mu = 0$ and amounts to $T_c = 0.57\ d_0$.

3. THE DIELECTRIC-SUPERCONDUCTOR PHASE TRANSITION

The transition into the superconducting state might be a competing phase transition in the system under consideration if the fact that the very same electron-phonon interaction is responsible for the electron-electron attraction is taken into consideration. The expression for the gap Δ_0 (superconducting in the present case) in the spectrum has the following form (at T = 0):

$$\Delta_0 = 2\omega_D \exp[-1/(\lambda' - \lambda_c')];$$
$$\lambda' = g_N^2 N(0), \quad \lambda_c' = g_c^2 N(0)/[1 + g_c^2 N(0)\ln(w/\omega_D)]. \tag{27}$$

Since the dependence of the free energy of the superconducting and dielectric phases on the order parameters Δ and d is identical,[7] a comparison of the dielectric d and superconducting Δ gaps enables us to establish which phase is actually realized. For example, from Eqs. (26) and (27) we obtain the following result for the ground state associated with δn = 0 and u = 0:

$$\frac{d}{\Delta} = \frac{w}{\omega_D}\exp\left(\frac{1}{\lambda_s'} - \frac{1}{\lambda_d'}\right), \qquad \lambda_s = \lambda' - \lambda_c'. \tag{28}$$

In the case when the electron-phonon coupling constants g_{U1}, g_{U2}, and g_{U3} in (5) are small in comparison with g_N, the ratio d/Δ given by (28) may become smaller than unity, and the ground state then turns out to be superconducting. However, if it is assumed that $g_N^2 = g_{U1}^2 = g_{U2}^2 = g_{U3}^2$, then the conclusion of Mattis and Langer[7] about the impossibility of a superconducting transition turns out to be correct.

Everywhere below we shall assume the condition d/Δ > 1 to be satisfied, but it will be shown that upon taking account of the interaction with non-nearest neighbors (0 < u < $d_0/2$) the coexistence of dielectric and superconducting phases is possible in the sense that compatible nontrivial solutions exist for Δ and d. In this connection, depending on the relation between T_s and T_c a sequence of metal-superconductor (if $T_c < T_s$) or metal-dielectric-superconductor (if $T_c > T_s$) transitions may be realized as the temperature is lowered. In the present article we shall only investigate this latter possibility without taking the parquet diagrams into account, having in mind that the superconducting transition temperature T_s (allowing for the lattice distortion $\langle \Phi_q \rangle$) is higher than the temperature T_c at which the singularity in the parquet diagrams first appears.

One can carry out a combined calculation of the dielectric and superconducting pairings in a system of electrons having the energy spectrum (1) on the basis of the initial Hamiltonian (9). However, in order to shorten the calculations it is convenient to change (with the aid of the usual procedure for the elimination of the phonon variables) to the following effective Hamiltonian $\mathcal{H}_e$:

$$\mathcal{H}_e = \sum_{\mathbf{k},\sigma}(\varepsilon_{\mathbf{k}} - \nu_{\mathbf{k}})a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma} + \sum_{\mathbf{p}}\omega_0(\mathbf{p})(b_{\mathbf{p}}^+ b_{\mathbf{p}} + 1/2) + g(\mathbf{q})\sum_{\mathbf{p},\sigma} a_{\mathbf{p}+\mathbf{q},\sigma}^+ a_{\mathbf{p}\sigma}$$
$$\times (b_{\mathbf{q}} + b_{-\mathbf{q}}^+) + 1/2 \sum_{\mathbf{p},\sigma}\sum_{\mathbf{p}',\sigma'} U(\mathbf{q}) a_{\mathbf{p}+\mathbf{q},\sigma}^+ a_{\mathbf{p}'-\mathbf{q},\sigma'}^+ a_{\mathbf{p}'\sigma'} a_{\mathbf{p}\sigma} -$$
$$- 1/2 g_N^2 \sum_{\mathbf{p}}\sum_{\mathbf{p}'}\sum_{\sigma} a_{\mathbf{p}\sigma}^+ a_{-\mathbf{p},-\sigma}^+ a_{-\mathbf{p}',-\sigma} a_{\mathbf{p}'\sigma}, \tag{29}$$

in which only those terms of the electron-phonon interaction remain which correspond to momentum transfers **q** selected according to condition (1). Further, together with the Green's functions $G_{\mathbf{kk}}$ and $G_{\mathbf{k}-\mathbf{q},\mathbf{k}}$ defined by Eqs. (14) we also introduce the anomalous Gor'kov functions into the treatment:

$$F_{\mathbf{kk}}^+ = \langle T\bar{a}_{-\mathbf{k},-\sigma}(\tau)\bar{a}_{\mathbf{k}\sigma}\rangle, \qquad F_{\mathbf{k}-\mathbf{q},\mathbf{k}}^+ = \langle T\bar{a}_{-\mathbf{k}+\mathbf{q},-\sigma}(\tau)\bar{a}_{\mathbf{k},\sigma}\rangle,$$
$$F_{\mathbf{kk}} = \langle Ta_{-\mathbf{k},-\sigma}(\tau)a_{\mathbf{k}\sigma}\rangle, \qquad F_{\mathbf{k}-\mathbf{q},\mathbf{k}} = \langle Ta_{-\mathbf{k}+\mathbf{q},-\sigma}(\tau)a_{\mathbf{k},\sigma}\rangle. \tag{30}$$

The following calculations follow the scheme discussed in Sec. 2. The equations of motion for the Green's functions G and F (defined by Eqs. (14) and (30)) with the Hamiltonian (29) turn out to be rather complicated in comparison with (18). We shall write them down (after expanding the functions (14) and (30) in Fourier series) in the form of a system of equations for the unknown Fourier coefficients $G_{\mathbf{kk}}(\omega_n)$, $G_{\mathbf{k}-\mathbf{q},\mathbf{k}}(\omega_n)$, $F_{\mathbf{kk}}^+(\omega_n)$, and $F_{\mathbf{k}-\mathbf{q},\mathbf{k}}^+(\omega_n)$:

$$(i\omega_n + \nu - \varepsilon)G_{\mathbf{kk}} + d^* G_{\mathbf{k}-\mathbf{q},\mathbf{k}} - \Delta^{+*}F_{\mathbf{kk}}^+ = 1,$$
$$dG_{\mathbf{kk}} + (i\omega_n + \nu + \varepsilon)G_{\mathbf{k}-\mathbf{q},\mathbf{k}} - \Delta^{+*}F_{\mathbf{k}-\mathbf{q},\mathbf{k}}^+ = 0,$$
$$-\Delta^+ G_{\mathbf{kk}} + (i\omega_n - \nu - \varepsilon)F_{\mathbf{kk}}^+ + dF_{\mathbf{k}-\mathbf{q},\mathbf{k}}^+ = 0, \tag{31}$$
$$-\Delta^+ G_{\mathbf{k}-\mathbf{q},\mathbf{k}} + d^* F_{\mathbf{kk}}^+ + (i\omega_n - \nu + \varepsilon)F_{\mathbf{k}-\mathbf{q},\mathbf{k}} = 0,$$

where the commutation properties of the electron field operators upon averaging their products in expressions of the type

$$d = \lambda_d \sum_{\mathbf{p},\sigma}\langle a_{\mathbf{p}-\mathbf{q},\sigma}(\tau)\bar{a}_{\mathbf{p}\sigma}(\tau)\rangle = \lambda_d \sum_{\mathbf{p},\sigma} T\sum_{\omega_n} G_{\mathbf{p}-\mathbf{q},\mathbf{p}}^{\sigma\sigma}(\omega_n),$$
$$\Delta^+ = \lambda_s \sum_{\mathbf{p}}\langle \bar{a}_{-\mathbf{p}}(\tau)\bar{a}_{\mathbf{p}}(\tau)\rangle = \lambda_s \sum_{\mathbf{p}} T\sum_{\omega_n} F_{\mathbf{pp}}^+(\omega_n). \tag{32}$$

have already been taken into consideration.

The solution of the system (31) can be obtained without any difficulty. Substituting the found functions $G_{k-q,k}$ and F^{+}_{kk} into the self-consistency condition (32), we obtain the following equations after performing the summation indicated in (32) over the frequencies $\omega_n = \pi T(2n+1)$:

$$\frac{1}{\lambda_d'}=\int_0^{w}d\varepsilon\,\frac{1}{4}\left\{\left(1+\frac{v_1}{(\varepsilon^2+d^2)^{1/2}}\right)\mathrm{fh}(A_1^{+})+\left(1-\frac{v_1}{(\varepsilon^2+d^2)^{1/2}}\right)\mathrm{fh}(A_1^{-})+\left(1+\frac{v_2}{(\varepsilon^2+d^2)^{1/2}}\right)\mathrm{fh}(A_2^{+})+\left(1-\frac{v_2}{(\varepsilon^2+d^2)^{1/2}}\right)\mathrm{fh}(A_2^{-})\right\},$$

$$\frac{1}{\lambda_s'}=\int_0^{\omega_D}d\varepsilon\,{}^1\!/_4\{\mathrm{fh}(A_1^{+})+\mathrm{fh}(A_1^{-})+\mathrm{fh}(A_2^{+})+\mathrm{fh}(A_2^{-})\},$$

$$\mathrm{fh}(A)=\mathrm{th}(A/2T)/A,\quad A^{\pm}_{1,2}=[((\varepsilon^2+d^2)^{1/2}\pm v_{1,2})^2+\Delta^2]^{1/2},\quad (33)$$

$$v_{1,2}=\pm u+\delta\mu,\qquad \lambda'_{s,d}=N(0)\lambda_{s,d}. \quad (34)$$

In Eqs. (33) and (34) the usual transition

$$\text{fo}\ \sum_k \to N(0)\int d\varepsilon,$$

has already been completed, and the function $\epsilon_1(\mathbf{k})$ has been replaced by a step-function (see Eqs. (24) and (24′)), just as was done in Sec. 2.

Equations (33) and (34) together with the equation

$$\delta n=2\int_{-w}^{w}d\varepsilon\,{}^1\!/_4\{((\varepsilon^2+d^2)^{1/2}+v_1)\mathrm{fh}(A_1^{+})-((\varepsilon^2+d^2)^{1/2}-v_1)\mathrm{fh}(A_1^{-})+((\varepsilon^2+d^2)^{1/2}+v_2)\mathrm{fh}(A_2^{+})-((\varepsilon^2+d^2)^{1/2}-v_2)\mathrm{fh}(A_2^{-})\} \quad (35)$$

form a system which in principle allows us to determine the order parameters d, Δ and the chemical potential $\delta\mu$ as functions of the temperature T, the coupling constants λ_s and λ_d, and so forth. The existence of a simultaneous solution of Eqs. (33)—(35) with nonzero values of d and Δ would imply the existence of a superconducting state of the system. Let us consider, for example, the case of a half-filled allowed band ($\delta n = 0$) at the temperature of absolute zero. Then instead of Eqs. (33) and (34) one can write down

$$\frac{1}{\lambda_d'}=\int_0^{w}d\varepsilon\,\frac{1}{2}\left\{\frac{1+u/(\varepsilon^2+d^2)^{1/2}}{[((\varepsilon^2+d^2)^{1/2}+u)^2+\Delta^2]^{1/2}}+\frac{1-u/(\varepsilon^2+d^2)^{1/2}}{[((\varepsilon^2+d^2)^{1/2}-u)^2+\Delta^2]^{1/2}}\right\} \quad (36)$$

$$\frac{1}{\lambda_s'}=\int_0^{\omega_D}d\varepsilon\,\frac{1}{2}\left\{\frac{1}{[((\varepsilon^2+d^2)^{1/2}+u)^2+\Delta_2]^{1/2}}+\frac{1}{[((\varepsilon^2+d^2)^{1/2}-u)^2+\Delta^2]^{1/2}}\right\} \quad (37)$$

Let us clarify the nature of the conditions to be imposed on the parameters λ_d, λ_s, w, ω_D, and u such that an infinitesimal, nontrivial solution first arises for the superconducting gap. In order to do this, let us set $\Delta = +0$ in Eqs. (36) and (37). In this limit Eq. (36) has the solution for the dielectric gap d which was derived earlier; for example, for $u < d$ the solution is given by (see Eq. (26)):

$$d=w/\mathrm{sh}(-1/\lambda_d'). \quad (26')$$

When taken in the same limit $\Delta = +0$, Eq. (37) has the form

$$\frac{1}{\lambda_s'}=\mathrm{Arsh}\frac{\omega_D}{d}+\frac{u}{(u^2-d^2)^{1/2}}\frac{1}{2}\left\{\arcsin\frac{d+u(\omega_D^2+d^2)^{1/2}/d}{u+(\omega_D^2+d^2)^{1/2}}-\arcsin\frac{d-u(\omega_D^2+d^2)^{1/2}/d}{-u+(\omega_D^2+d^2)^{1/2}}\right\} \quad (38)$$

and with the value of d obtained from (26) substituted into this expression it is exactly the condition imposed on λ'_d, λ'_s, etc. This condition becomes particularly transparent if $(d-u)/u \ll 1$

$$\frac{1}{\lambda_s'}=\mathrm{Arsh}\frac{\omega_D}{d}+\frac{\pi}{2\sqrt{2}}\left(\frac{u}{d-u}\right)^{1/2} \quad (39)$$

when condition (39) is satisfied for an arbitrarily weak attraction λ'_s.

Nonzero solutions for d and Δ do not imply anything other than the coexistence of dielectric and superconducting phases with order parameters d and Δ, respectively, and reflect the condensation of boson-like formations in the system in the form of electron-hole and electron-electron pairs. The nature of the coexistence of dielectric and superconducting condensates is evident from a comparison of the amount of energy, $2(d-\epsilon_1(\mathbf{k})) \sim 2(d-u)$, needed to excite a pair of electrons from the dielectric condensate, with their "binding" energy in superconducting pairs. If the gain in energy of the superconducting pairing exceeds the energy $2(d-u)$, which is expended in exciting an electron pair through the thermal dielectric gap, then the superconducting state of the system becomes energetically advantageous. In the theory of an exciton insulator, a similar relationship between the width of the forbidden semiconductor band and the exciton binding energy is necessary for the existence of the exciton-insulator phase.[12]

We note, incidentally, that virtually excited electrons fall into a region having a high density of states in the allowed band. Condition (39) essentially illustrates this concept. Now let us turn to the investigation of the superconducting transition temperature T_s. For this purpose we set $\Delta = +0$ in Eqs. (33) and (34) (as before $\delta\mu = \delta n = 0$):

$$\frac{1}{\lambda_d'}=\int_0^{w}d\varepsilon\,\frac{1}{(\varepsilon^2+d^2)^{1/2}}\frac{1}{2}\left\{\mathrm{th}\frac{(\varepsilon^2+d^2)^{1/2}+u}{2T_s}+\mathrm{th}\frac{(\varepsilon^2+d^2)^{1/2}-u}{2T_s}\right\} \quad (40)$$

$$\frac{1}{\lambda_s'}=\int_0^{\omega_D}d\varepsilon\,\frac{1}{2}\left\{\frac{1}{(\varepsilon^2+d^2)^{1/2}+u}\mathrm{th}\frac{(\varepsilon^2+d^2)^{1/2}+u}{2T_s}+\frac{1}{(\varepsilon^2+d^2)^{1/2}-u}\mathrm{th}\frac{(\varepsilon^2+d^2)^{1/2}-u}{2T_s}\right\}. \quad (41)$$

The assumption that the dielectric transition temperature T_c, associated with the phonon instability, is higher than the critical temperature T_s of the superconducting transition has been used in these equations, that is, the dielectric gap d(T) retains a finite value at $T = T_s$. Therefore in the present case our treatment pertains to systems possessing the following sequence of transitions: metal—dielectric (at $T = T_c$)—superconductor (at $T = T_s$). For an arbitrary relation between the occupation δn of the band and the parameter u (which describes the effect of non-nearest neighbors), the intermediate phase may turn out to not be dielectric, but instead it may be either a doped semiconductor ($\delta n \neq 0$) or a semimetal ($d - u < 0$). Therefore, in the general case T_c denotes the critical temperature of the structural transformation, which precedes (as the temperature is lowered) the superconducting transition. The effectiveness of the superconductivity mechanism considered here is most easily traced by making a compar-

ison of the critical temperature T_S, determined from Eqs. (40) and (41), with the value $T_{S0} = (0.57) \times 2\omega_D \exp(-1/\lambda'_S)$ which applies in the absence of a dielectric transition.

The dependence of the ratio T_S/T_{S0} on the difference $d - u$ (in units of d_0), obtained from the simultaneous solution of Eqs. (40) and (41) with regard to d and T_S, is shown in Fig. 1 for several values of the variational parameters u, λ'_S/λ'_d, and ω_D/w. Let us illustrate that positive values of the difference $d - u$ on Figs. 1–3 correspond to the position of the chemical potential inside the forbidden band of the dielectric phase, and in the case $\delta n = 0$ under consideration they correspond to the states in the allowed band of the initial metallic phase being half-filled. It is quite clear that with a reduction of the excitation energy $d - u$ from the level of the chemical potential to the nearest allowed state above the dielectric gap, the ratio T_S/T_{S0} increases. The increase of T_S/T_{S0} becomes especially clearly defined for small values of λ'_S/λ'_d. (All of the numerical examples are cited for the value $\lambda'_d = 1/3$.) We note that in all of the examples cited in Fig. 1 the maximum value of the ratio T_S/T_{S0} is reached at negative (but comparatively small in absolute magnitude) values of $d - u$. With increasing values of $|d - u|$ the Fermi level is shifted away from the edge of the allowed band, and for $|d - u| \gtrsim d$ it is found in the energy region where the structural transformation has little effect on the density of states. Therefore T_S tends to T_{S0}. It is clear from Fig. 1 that the maximum values of T_S/T_{S0} increase with decreasing values of the parameters λ'_S/λ'_d and ω_d/w. The largest of the cited values of T_S/T_{S0} amounts to 44.7, which occurs when $\lambda'_S/\lambda'_d = 0.4$ and $\omega_D/w = 0.025$.

Now let us turn our attention to the case when, in connection with the equality of the electron-phonon coupling constant g_N for normal processes and the constant g_U for Umklapp processes, the ratio λ'_S/λ'_d is equal to 0.5. Taking account of the Coulomb interaction decreases the value of the ratio λ'_S/λ'_d, since the Coulomb interaction leads to a decrease of λ'_S (which is defined in (28)) associated with a simultaneous increase of λ'_d (given by expression (19′)). However, if $g_N > g_U$ then the ratio λ'_S/λ'_d may become even larger than 0.5. It is particularly worth noting that the increase in the maximum values of the ratio T_S/T_{S0} associated with a reduction of the values of λ'_S/λ'_d and ω_D/w, which can be traced in Fig. 1, is accompanied by an abrupt contraction of the range of values of the parameter $d - u$ in which $T_S/T_{S0} > 1$ is generally achieved.

From the dependence of the ratio of the superconducting gap Δ at $T = 0$ (determined from the solution of Eqs. (36) and (37)) to the value of the superconducting gap $\Delta_0 = \omega_D/\sinh(-1/\lambda'_S)$ in the absence of the dielectric transition, which is shown in Fig. 2, it is clear that the ratio Δ/Δ_0 behaves like T_S/T_{S0}. However, Fig. 3 indicates that the ratio T_S/Δ is smaller than 0.57 in the region of maximum values of the ratio T_S/T_{S0}. The range of values of $d - u$, where $T_S/\Delta > 0.57$, widens in connection with a decrease in the values of λ'_S/λ'_d and ω_D/w.

Finally let us consider the case when the band is not exactly half-full, that is, $\delta n \neq 0$. It is clear that in this case the first transition to be encountered (upon decreasing the temperature) corresponds to the transition of the metal into a doped (up to the level δn) semiconductor. A further reduction of the temperature leads to a semiconductor-superconductor transition. In order to investigate this case it is necessary to consider the solution of a system of equations of the general form (33), (34), and (35). We obtain the following result for the magnitude of the superconducting gap at the temperature of absolute zero, $T = 0$ (if, in addition, we assume that $\nu_1 = u + \delta\mu \gtrsim d$ and $\nu_2 = -u + \delta\mu < d$):

$$\left(\frac{1}{\lambda_s'} - \frac{1}{\lambda_d'} - \ln\frac{\omega_D}{w} + \frac{1}{2}\right) = \frac{1}{2}\frac{\nu_1}{(\nu_1^2 - d^2)^{1/2}} \ln\frac{4d(\nu_1^2 - d^2)^{1/2}}{\Delta^2}. \quad (42)$$

Equation (42) can be treated as a certain equation of the BCS type with an effective coupling constant λ_e (an attractive interaction if $\lambda_e > 0$)

$$1/\lambda_e = 1/\lambda_s' - 1/\lambda_d' - \ln(\omega_D/w) + 1/2,$$

where the effective density of states is $\nu_1 N(0)/(\nu_1^2 - d^2)^{1/2}$ and the effective cutoff energy for this attractive interaction is $2[d^2(\nu_1^2 - d^2)]^{1/4}$. It is clear that Eq. (42) can certainly have solutions which appreciably exceed the usual value Δ_0 (given by Eq. (27)) for reasonable values of ω_D, w, λ_d, λ_S, and u.

4. THE PHONON SPECTRUM

The order parameter d in the electron system, determined from the equation of self-consistency (15), is related to the order parameter $\langle \Phi_q \rangle$ in the phonon system by the relation $d = g\langle \Phi_q \rangle$. By the same token the equilibrium density of the Bose condensate of phonons is uniquely determined, although the total number of phonons is not conserved. We note that in the classical problem concerning the condensation of a Bose gas with repulsion,[3] the density of the condensate is determined from the condition for conservation of the total number of particles. The formation of a finite, longitudinal displacement proportional to $\langle b_q + b^+_{-q}\rangle/(2\omega_0(q))^{1/2}$ should be regarded, according to definition, as the physical manifestation of a macroscopic filling of the phonon states with momentum q. In order to explain the changes in the phonon spectrum due to the effect of Bose condensation in the state with $q = (\pi/a)(\pm 1, \pm 1, \pm 1)$ let us include the term

$$\tfrac{1}{2}\sum_{p_1}\sum_{p_2} B(p_1, p_2)\Phi_{p_1}\Phi_{p_2}\Phi_{-p_1-p_2},$$

in the Hamiltonian (9), where this term corresponds to a phonon-phonon interaction due to the anharmonic nature of the lattice vibrations.

Just as in the investigation of the electron spectrum, the introduction of the anomalous averages $\langle \Phi_q \rangle$ inevitably involves the anomalous phonon Green's function $\hat{D}_k(t - t') = -i\langle \hat{T}\Phi_{k-q}(t)\Phi_{-k}(t')\rangle$ in the treatment, together with the usual phonon Green's function $D_k(t - t') = -i\langle T\Phi_k(t)\Phi_{-k}(t')\rangle$. The equations of motion for $D_k(t - t')$ and $\hat{D}_k(t - t')$ (after Fourier transformation with respect to the difference $t - t'$) have the form[3]

$$\begin{aligned}[\omega^2 - \omega_0^2(p)]D_p(\omega) - \Sigma_{20}(p)\hat{D}_p(\omega) &= 1,\\ [\omega^2 - \omega_0^2(p+q)]\hat{D}_p(\omega) - \Sigma_{02}(p)D_p(\omega) &= 0,\end{aligned} \quad (43)$$

where we have the following expressions for the self-energy parts Σ_{02} and Σ_{20} in the case of a weak phonon-

phonon interaction:

$$\Sigma_{02}(\mathbf{p}) = 8\langle\Phi_{\mathbf{q}}\rangle_{\omega}[B(\mathbf{p}, -\mathbf{q}) + B(\mathbf{p}, \mathbf{p}+\mathbf{q})],$$
$$\Sigma_{20}(\mathbf{p}) = 8\langle\Phi_{\mathbf{q}}\rangle_{\omega}[B(\mathbf{p}+\mathbf{q}, \mathbf{q}) + B(\mathbf{p}+\mathbf{q}, \mathbf{p})]. \quad (44)$$

If it is impossible to regard the interaction of the phonons as weak (see, for example,[3]), then for the case of a rarefied Bose gas it is necessary to replace the Fourier components B(p) of the potential in formulae (44) by the total scattering amplitude. From Eqs. (43) we obtain the following results for the phonon functions:

$$D_{\mathbf{p}}(\omega) = [\omega^2 - \omega_0^2(\mathbf{p}+\mathbf{q})]/\det, \quad \tilde{D}_{\mathbf{p}}(\omega) = \Sigma_{02}(\mathbf{p})/\det,$$
$$\det = [\omega^2 - \omega_0^2(\mathbf{p})][\omega^2 - \omega_0^2(\mathbf{p}+\mathbf{q})] - \Sigma_{20}^2(\mathbf{p}).$$

Hence, from the meaning of the poles of the Green's function we obtain the following result for the excitation spectrum:

$$[\omega^{\pm}(\mathbf{p})]^2 = {}^1/_2\{\omega_0^2(\mathbf{p}) + \omega_0^2(\mathbf{p}+\mathbf{q}) \pm [(\omega_0^2(\mathbf{p}) - \omega_0^2(\mathbf{p}+\mathbf{q}))^2 + 4\Sigma_{20}^2]^{1/2}\}. \quad (45)$$

Let us assume that in the normal phase, prior to distortion of the lattice, the system only has an acoustic branch $\omega_0(\mathbf{p})$ with period $2\pi/a$. The poles (of the Green's function) $\omega^+(\mathbf{p})$ and $\omega^-(\mathbf{p})$ (given by Eq. (45)) characterize the spectrum of the optical and acoustic branches in the rearranged lattice. It is clear from Eq. (45) that, by virtue of relations (44), the gap in the phonon spectrum is determined by the anharmonicity constants B and the electron-phonon coupling constant g. The oxides, chalcogenides, and dichalcogenides of the transition metals appear to be the most suitable materials, in which it might be possible to realize the superconductivity mechanism considered above. It is well-known that the behavior of the s-electrons in solids can be described rather well in the approximation of almost free electrons. On the other hand, due to the stronger localization of d-electrons near the atoms, their behavior can be described better in the tight-binding approximation. But in the transition metals the energy levels of the d-electrons overlap with the levels of the s-electrons. In this connection an additional delocalization of the d-electron states occurs due to the s – d interaction, and in this case the tight-binding approximation, which has been used in the present work, turns out to be unjustified. However, in many transition metal compounds the overlap of the s- and d-electron energy levels is removed, and the one-electron, tight-binding approximation turns out to be adequate for the d-electrons.

On the other hand, it may turn out that the correlation effects, which are omitted in the one-electron approximation, will play a decisive role. Namely, if the interaction U between two electrons with opposite spins on a single atom is larger than the width w of the allowed band, then the electrons turn out to be completely localized on the center, and a band description is not suitable. Such a situation occurs for f-electrons due to their very weak overlap on neighboring atoms, which leads to a very small value of w. For d-electrons the ratio between U and w may vary over wide limits. For example, the value of U in compounds containing the same atom, but compounds in which the atom manifests a difference valence, decreases in connection with an increase of the number of d-electrons remaining on the atom, as a consequence of their mutual screening. However, the value of w is directly proportional to the number of nearest neighbors and therefore depends on the type of crystal structure. A wide class of transition metal compounds exist in which the role of correlation effects is not decisive and which undergo a metal-semiconductor phase transition with a change in the symmetry of the crystal lattice. For example, VO_2 undergoes such a transition at a temperature of 340°K, V_2O_3 at 150°K, and NiS at 290°K. The model of a metal-semiconductor phase transition considered in the present article may have a relation to some of these.

As was indicated above (see Fig. 1), the appearance of superconductivity in the dielectric phase is very sensitive to the parameters characterizing the initial metallic spectrum, namely it is very sensitive to the relationship between the magnitude d of the dielectric gap resulting from the structural transformation and the value of the integral u characterizing the overlap with non-nearest neighbors. As is clear from Fig. 1, it is necessary to investigate compounds in which the indirect forbidden band d – u in the semiconducting phase is much smaller than the direct forbidden band d. In this connection, after rearrangement of the crystal lattice the state may turn out to be semimetallic ($d - u < 0$). Realization of these conditions may be achieved by varying the density of the system by pressure or by an isomorphic partial replacement of the transition metal atoms (e.g., changing the concentration of Cr in Cr-doped V_2O_3).[17] Similar changes in the electron spectrum occur in the V-Ru system[5] in connection with a structural transformation near the superconducting transition temperature. The change in the temperature dependence of the conductivity and the magnetic susceptibility associated with the structural transformation indicates the appearance of a dielectric gap on part of the Fermi surface. It is possible that similar changes of the electronic characteristics occur in connection with structural transformations in systems having the lattice structure of β – W.

[1] B. W. Batterman and C. S. Barrett, Phys. Rev. Letters 13, 390 (1964); Phys. Rev. 145, 296 (1966).

[2] P. W. Anderson and E. I. Blount, Phys. Rev. Letters 14, 217 (1965).

[3] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, Metody kvantovoĭ teorii polya v statisticheskoĭ fizike (Methods of Quantum Field Theory in Statistical Physics), Fizmatgiz, 1962 (English Transl., Prentice-Hall, 1963).

[4] V. L. Ginzburg, Usp. Fiz. Nauk 101, 185 (1970) [Sov. Phys.-Uspekhi 13, 335 (1970)].

[5] C. W. Chu, E. Bucher, A. S. Cooper, and J. P. Maita, Phys. Rev. B4, 320 (1971).

[6] Yu. V. Kopaev, Zh. Eksp. Teor. Fiz. 58, 1012 (1970) [Sov. Phys.-JETP 31, 544 (1970)]; Yu. V. Kopaev and R. Kh. Timerov, Fiz. Tverd. Tela 14, 86 (1972) [Sov. Phys.-Solid State 14, 69 (1972)].

[7] D. C. Mattis and W. D. Langer, Phys. Rev. Letters 25, 376 (1970).

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

[9] I. E. Dzyaloshinskiĭ and A. I. Larkin, Zh. Eksp.

Teor. Fiz. 61, 791 (1971) [Sov. Phys.-JETP 34, 422 (1972)].
[10] Yu. V. Kopaev, Zh. Eksp. Teor. Fiz. 61, 1591 (1971) [Sov. Phys.-JETP 34, 848 (1972)].
[11] G. Sarma, J. Phys. Chem. Solids 24, 1029 (1963).
[12] A. N. Kozlov and L. A. Maksimov, Zh. Eksp. Teor. Fiz. 48, 1184 (1965) [Sov. Phys.-JETP 21, 790 (1965)].
[13] A. M. Afanas'ev and Yu. Kagan, Zh. Eksp. Teor. Fiz. 43, 1456 (1962) [Sov. Phys.-JETP 16, 1030 (1963)].
[14] Laurent G. Caron and G. Kemeny, Phys. Rev. B3, 3007 (1971).
[15] L. V. Keldysh and Yu. V. Kopaev, Fiz. Tverd. Tela 6, 2791 (1964) [Sov. Phys.-Solid State 6, 2219 (1965)].
[16] Yu. V. Kopaev, Fiz. Tverd. Tela 12, 3 (1970) [Sov. Phys.-Solid State 12, 1 (1970)].
[17] D. B. McWhan, T. M. Rice, and J. P. Remeika, Phys. Rev. Letters 23, 1384 (1969).

Translated by H. H. Nickle
31