Transition temperature of strong-coupling superconductors

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The possible existence of superconductors with high transition temperatures is analyzed for both the ordinary electron-phonon interaction and nonphonon superconductivity mechanisms. The existence of such systems depends on a negative static dielectric permittivity. The possible occurrence of this situation for an electronion system is analyzed. It is shown that negative values of the static dielectric permittivity are possible in the case of strong local-field effects, i. e., in the case of exchange-correlation interactions in the electron subsystem or the localization of point ions for an electron-phonon system. Equations for the transition temperature of strong-coupling superconductors are analyzed. Restrictions imposed on the transition temperature by the equations themselves and by the conditions for stability of the material are examined.

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1. INTRODUCTION

The search for superconductors with high transition temperatures is one of the most urgent and interesting problems in solid state physics. The successful resolution of this problem promises huge practical benefits which completely justify not only the many original papers on the problem but also the appearance of yet another review. The really active research on the problem of high-temperature super-conductivity, however (and unfortunately), has been mostly theoretical, beginning in 1964 after Little's¹ and Ginzburg's² suggestions regarding the possibility of nonphonon superconductivity mechanisms. There is a detailed review in Ref. 3 of the history of the problem and its state in 1977. In the present review we wish to discuss some new results which have appeared since then. Of particular interest is the determination of the role played by local-field and strong-coupling effects in the problem of high-temperature superconductivity, including the cases of nonphonon superconductivity mechanisms (see, in particular, Refs. 3-5).

Section 2 of this review is a discussion of the condition for the efficacy of superconductivity mechanisms. This is not a new question nor the first discussion of it, so we attempt to deal with it as briefly as possible.

Section 3 is a detailed discussion of the question of negative values of the static dielectric permittivity and, in particular, the interrelationship between the existence of values $\varepsilon(q, 0) < 0$, on the one hand, and magnetic and structural instabilities of the system, on the other. In Section 4 we derive superconductivity equations for

strong-coupling systems. Section 5 is devoted to superconductors with a strong electron-phonon interaction. Some possible restrictions on T_c which exist within the framework of the Éliashberg equations are discussed. There is a detailed analysis of the microscopic determination of the spectral density function for the electron-phonon interaction. We adopt a system of units with \hbar , $k_B = 1$.

2. CONDITION FOR SUPERCONDUCTIVITY IN WEAK-COUPLING SYSTEMS

We begin our examination of the problem of hightemperature superconductivity with a brief review of what is known about systems exhibiting a weak coupling.³ We will then be in a position to formulate clearly several basic questions which will remain important in a more rigorous discussion of the problem. Furthermore, the subject is of interest in its own right, since many of the theoretical papers on the problem of hightemperature superconductivity have in fact been devoted to weak-coupling systems.

We first note that if we write the effective electronelectron interaction in a quasi-isotropic system in the

form

$$V_{\text{eff}}(\mathbf{q}, \omega) = \frac{4\pi e^2}{q^2 e\left(\mathbf{q}, \omega\right)}, \qquad (1)$$

where $\varepsilon(\mathbf{q}, \omega)$ is the total dielectric permittivity of the system, we can express the critical temperature for the superconducting transition, (or simply "transition

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temperature") T_c , as a function of $\varepsilon(\mathbf{q}, \omega)$ as follows³:

$$T_{\rm c} = \frac{\bar{\omega}}{1.45} \exp\left(-\frac{1}{\lambda - \mu^*}\right), \qquad (2)$$

where

$$\mu^* = \frac{\mu}{1 + \mu \ln \left(e_F / \widetilde{\omega} \right)}, \qquad (3)$$

and λ and μ are the constants of the attractive electronphonon (exciton) and repulsive Coulomb interactions. The quantities $\overline{\omega}$, λ , and μ can be expressed in terms of integrals of the spectral density of the dielectric permittivity, $\text{Im } \varepsilon^{-1}(\mathbf{q}, \omega)$. We will omit these expressions (which are given in Ref. 3) and simply write a relation between the constants λ and μ which is very important for the discussion below:

$$\mu - \lambda = N(0) \left\langle \frac{4\pi e^2}{a^2} e^{-1}(\mathbf{q}, 0) \right\rangle.$$
(4)

Here N(0) is the electron state density at the Fermi surface, and the angle brackets on the right side of (4) indicate the average over the momentum q.

As was first noted by Cohen and Anderson⁶ (see also Ref. 7), Eqs. (2)-(4) yield some rather stringent limitations on the maximum transition temperature T_c^{max} . For example, if we assume that λ and μ satisfy

$$\lambda \leqslant \mu$$
, (5)

then $T_{\rm c}$, thought of as a function of the average phonon frequency $\overline{\omega}$, is bounded and has a maximum $T_{\rm c}^{\rm max}$ at some frequency $\omega_{\rm op}$. In the most favorable case ($\lambda = \mu$), $T_{\rm c}^{\rm max}$ is

$$T_{\rm c}^{\rm max} = \frac{\varepsilon_{\rm F}}{1.45} e^{-3/\lambda},\tag{6}$$

where $\varepsilon_{\rm F}$ is the electron Fermi energy. If strong-coupling effects are taken into account in a simple way, the coupling constant λ is renormalized and replaced by $\lambda/(1+\lambda)$, and we find an even more stringent limitation on $T_{\rm c}^{\rm max}$:

$$T_{\rm c}^{\rm max} = \frac{\varepsilon_{\rm F}}{1.45} \, e^{-3 - (3/\lambda)}. \tag{7}$$

Adopting the values¹⁾ $\varepsilon_{\rm F} \approx 1$ eV and $\lambda = \mu = 1/2$, we find $T_{\rm c}^{\rm max}$ to be of the order of 1 K. We wish to emphasize that this restriction applies in equal measure to any superconductivity mechanism, either phonon or non-phonon. Furthermore, it follows from (2)–(7) that the optimum average frequencies $\omega_{\rm op}$, which correspond to $T_{\rm c}^{\rm max}$, in fact lie in the region of phonon frequencies of the crystal. This circumstance shows that in systems in which inequality (5) holds any nonphonon superconductivity mechanism would be completely ineffective. Consequently, the inequality converse to (5),

$$\lambda > \mu$$
, (8)

may be regarded as a condition for the existence of an effective superconductivity mechanism with high values of $T_{\rm c}$.

A more careful analysis of the superconductivity equations reveals yet another factor which tends to lower T_c , which was not considered above. The equations describing superconductivity in weak-coupling systems,⁷ of which expression (2) for T_c is a solution, ignore the possibility of spin fluctuations. These effects can be taken into account through a generalized random-phase approximation which incorporates, in addition to the direct Coulomb repulsion, the exchange interaction between electrons. The expression for T_c in this approximation can be written⁸

$$T_{\rm c} = \frac{\overline{\omega}}{1.45} \exp\left[-\left(\lambda - \mu^* - \alpha \mu \ln \frac{1}{1 - \mu}\right)^{-1}\right], \qquad (9)$$

where α is a numerical coefficient of the order of unity. The condition for superconductivity in this approximation is

$$\lambda > \mu^* + \alpha \mu \ln \frac{1}{1-\mu}$$
 (10)

It can be seen from this inequality that at large values of μ the spin fluctuations lower T_c greatly. Berk and Schrieffer⁹ were the first to point out the destructive effect of spin fluctuations on superconductivity. This effect is often cited as responsible for the absence of superconductivity in such metals as palladium.

It thus follows from this discussion that in systems with a positive static dielectric permittivity [i.e., with $\varepsilon(\mathbf{q}, 0) > 0$] superconductivity, if possible at all, is so only at very low temperatures, under the conditions $\lambda \le \mu \le 1$ [see (9)]. Unfortunately, very low temperatures are not of much practical interest. It follows that a question of fundamental importance to the entire problem of high-temperature superconductivity is whether the static dielectric permittivity can take on negative values, and we must determine just how $\varepsilon(\mathbf{q}, 0)$ might become negative.

3. THE DIELECTRIC PERMITTIVITY AND THE PROBLEM OF HIGH-TEMPERATURE SUPERCONDUCTIVITY

a) Possibility of negative values of the static dielectric permittivity

The permissible values of the static dielectric permittivity have been discussed previously in several places.^{3-6,10-13} Kirzhnits analyzed the problem in detail.¹³ He showed that the assertions in the literature that $\varepsilon(q, 0)$ can take on only positive values are in fact valid only if spatial dispersion is ignored, i.e., only for $\varepsilon(\mathbf{q}, 0)$ with a wave vector $\mathbf{q} \equiv 0$. This is the case dealt with, for example, in Landau and Lifshitz' book.¹⁰ Generally speaking, it is not correct to extend this assertion to systems having a spatial dispersion [i.e., to the dielectric permittivity $\varepsilon(\mathbf{q}, 0)$ with $\mathbf{q} \neq 0$, as has been done by Pines and Nozières¹¹ and Cohen and Anderson.⁶ Kirzhnits¹³ showed that negative values of the static dielectric permittivity do not contradict causality and are consistent with stability of the system. However, the question of whether systems with $\varepsilon(\mathbf{q}, \mathbf{0}) < \mathbf{0}$ actually exist was essentially not taken up in Ref. 13. Some related questions had been discussed in an earlier paper by Martin.¹² That paper dealt with the existence of the Kramers-Kronig relations for the function $\varepsilon(\mathbf{q}, \omega)$ and the possible violation of these relations. The problem of negative values of $\varepsilon(\mathbf{q}, \mathbf{0})$ was not taken up, although violation of the Kramers-Kronig relations for the function $\varepsilon(\mathbf{q}, \omega)$ may in fact mean that the inequality $\varepsilon(\mathbf{q}, 0)$ <0 can hold. The actual existence of either isotropic or crystalline systems with a negative static dielectric

 $^{^{1)}}$ The value μ = 1/2 is the largest value of the Coulomb constant in the weak-coupling limit. 3

permittivity was studied in detail in Refs. 4, 5, and 14. The physical nature of the effects which give rise to a negative $\varepsilon(\mathbf{q}, \mathbf{0})$ was determined, as were the conditions required for the actual occurrence of these effects in several systems. It was shown that the inequality $\varepsilon(\mathbf{q}, \mathbf{0}) < \mathbf{0}$ can arise only from local-field effects, i.e., from a difference between the effective field acting on the particles of the medium and the average field in the system, with respect to which the dielectric permittivity is determined. Local-field effects are by no means fundamentally new effects in the theory of condensed systems; they have been under study, albeit for other purposes, for a rather long time now, in both classical electrodynamics¹⁵⁻¹⁷ and classical¹⁸ and quantum¹⁹ plasmas. In this section we briefly review some results derived in Refs. 4, 5, 14, and 20, and we discuss some implications of these results for the problem of hightemperature superconductivity.

b) Homogeneous electron gas

We begin with the very simple model of a homogeneous, interacting electron gas on a neutralizing substrate in which there are no phonon excitations of any sort. We may therefore study the possibility in principle of the nonphonon superconductivity mechanisms proposed by Little¹ and Ginzburg,² and we can reach an understanding of the factors which make it extremely complicated to produce real materials in which such mechanisms operate.

We begin by formulating the basic questions which we will discuss for a homogeneous electron gas. First, we must show that it is possible in principle for the inequality $\varepsilon(\mathbf{q}, 0) < 0$ to hold. Second, we must determine which instabilities can occur in an interacting electron gas and to what extent these instabilities may prevent the appearance of negative values of the static dielectric permittivity.

The properties of an interacting electron gas can be characterized completely by the single dimensionless parameter r_s , which is related to the electron density nby

$$\frac{1}{n} = \frac{4\pi}{3} (a_{\rm B} r_{\rm s})^3.$$
(11)

The parameter r_s gives (in units of the first Bohr radius, $a_{\rm B} = 1/me^2$) the radius of the sphere whose volume is equal to the average volume per electron. This parameter is the same in order of magnitude as the ratio of the potential energy of electrons with a Coulomb interaction to their average kinetic energy.

It is a well-known fact (see the reviews in Refs. 5 and 19, for example) that at small values of r_s ($r_s \ll 1$) the properties of an interacting electron gas are similar to those of an ideal gas of noninteracting particles, and the static dielectric permittivity in this case is definitely a positive quantity $[\varepsilon(\mathbf{q}, 0) > 1]$. Also, no instabilities of any sort occur in the electron gas under these conditions. As the parameter r_s in the electron gas increases or, equivalently, as the density decreases, the static dielectric permittivity may turn negative. At the same time, as the parameter r_s increases the electron gas may become unstable with respect to the formation of states with a space-charge wave or spin-density wave. To find those values of r_s at which the static dielectric permittivity becomes negative in an electron gas, and at which instabilities with respect to transitions to states with a space-charge wave or a spin-density wave occur, we write expressions for the dielectric permittivity for the charge susceptibility $\chi(\mathbf{q}, 0)$, and the spin susceptibility $\chi(\mathbf{q}, 0)$. These expressions are^{5,20}

$$\varepsilon (\mathbf{q}, 0) = 1 + \frac{V(\mathbf{q}) \chi_{0} (\mathbf{q}, 0)}{1 - V(\mathbf{q}) G(\mathbf{q}, 0) \chi_{0} (\mathbf{q}, 0)},$$
(12)

$$\chi(\mathbf{q}, 0) = \frac{\chi_0(\mathbf{q}, 0)}{1 + V(\mathbf{q}) \left[1 - G(\mathbf{q}, 0)\right] \chi_0(\mathbf{q}, 0)},$$
(13)

$$\chi_{s}(\mathbf{q}, 0) = \frac{\mu_{B}\chi_{0}(\mathbf{q}, 0)}{1 - V(\mathbf{q})\,\widetilde{G}(\mathbf{q}, 0)\,\chi_{0}(\mathbf{q}, 0)};$$
(14)

here $V(\mathbf{q}) = 4\pi e^2/\mathbf{q}^2$, $G(\mathbf{q}, 0)$ is the charge local-field correction function, $\tilde{G}(\mathbf{q}, 0)$ is the spin local-field correction function, $\mu_{\rm B}$ is the Bohr magneton, and $\chi_0(\mathbf{q}, 0)$ is the ordinary Lindhard function,

$$\chi_{0}(\mathbf{q}, 0) = \frac{mk_{\rm F}}{2\pi^{2}} \Big[1 + \frac{(2k_{\rm F})^{2} - q^{2}}{4k_{\rm F}q} \ln \Big| \frac{2k_{\rm F} + q}{2k_{\rm F} - q} \Big| \Big], \tag{15}$$

where $k_{\rm F}$ is the Fermi momentum.

We first note that expressions (12) and (13) yield

$$V(\mathbf{q}) G(\mathbf{q}, 0) \geqslant \frac{1}{\chi_0(\mathbf{q}, 0)}$$
(16)

as the condition for the occurrence of negative values of the static dielectric permittivity; as the condition for an instability with respect to the appearance of a spacecharge wave $(\chi = \infty)$ they give

$$V(\mathbf{q}) G(\mathbf{q}, 0) \geqslant V(\mathbf{q}) + \frac{1}{\chi_0(\mathbf{q}, 0)}.$$
(17)

Since G(q, 0) and $\chi_0(q, 0)$ are monotonically increasing functions of the parameter r_s , it follows from (16) and (17) that the static dielectric permittivity becomes negative at values of r_s smaller than those which correspond to the spontaneous appearance of a space-charge wave in the system.

The appearance of space-charge waves or, equivalently, crystallization usually occurs as a first-order phase transition, i.e., at values of r_s smaller than those which follow from condition (17). This circumstance, however, by no means rules out the existence of negative values of the static dielectric permittivity. First, as we will show below, the static dielectric permittivity $\varepsilon(\mathbf{q}, \mathbf{0})$ is negative for an interacting electron gas in a state with a space-charge wave. Second, the value $r_s^{(1)}$, at which $\varepsilon(\mathbf{q}, \mathbf{0})$ becomes negative, and the value $r_s^{(2)}$, at which the electron gas crystallizes, are markedly different in order of magnitude $(r_s^{(1)} \ll r_s^{(2)})$. The static dielectric permittivity of the electron gas becomes negative at²⁰ $r_{s} \leq 6.02$. In contrast, the crystallization of an electron gas occurs at $r_s \approx 70-100$ according to Monte Carlo calculations and calculations based on various approximations.²³

A far more complicated question is that of the relationship between the negative static dielectric permittivity and an instability of the system with respect to the spontaneous appearance of a spin-density wave. In the already mentioned random phase approximation (which takes into account the exchange interaction on the electrons in addition to the direct Coulomb interaction) the charge and spin functions of corrections for the local field are equal to each other¹⁹:

$$G(\mathbf{q}, 0) = \widetilde{G}(\mathbf{q}, 0) = \frac{1}{4} \frac{q^2}{k_{\rm P}^2}.$$
 (18)

This means that the negative value of the quantity $\epsilon(\mathbf{q}, 0)$ appears at the same values $r_s = 6.02$ for which the system becomes absolutely unstable with respect to the spontaneous appearance of spin-density wave.

It can be shown,²⁰ however, that the transition to the ferromagnetic state of an interacting electron gas is always a first-order phase transition; it is a transition to a state of complete magnetization, with the spins of all the electrons aligned in the same direction. In the generalized random-phase approximation this transition occurs at^{20,24} $\gamma_{\rm s} = (2\pi/5\alpha)(2^{1/3}+1) \simeq 5.45$. In the ferromagnetic phase, the static dielectric permittivity becomes negative at $r_s = 7.61$. It is clear, however, that in this case, even with negative $\varepsilon(\mathbf{q}, \mathbf{0})$, there can be no question of the existence of an ordinary superconducting state, with a pairing of electrons with antiparallel spins. In the ferromagnetic state of a homogeneous electron gas with a negative static dielectric permittivity we might expect the existence of a superconductivity with a triplet pairing of electrons, somewhat similar to the superfluidity of liquid ³He. However, a homogeneous electron gas does not exist in nature. The best approximation of the model assumed here is the electron fluid in a simple metal, in particular, cesium, where $r_s = 5.64$. This value of r_s is larger than the value $r_s = 5.45$ which corresponds to a transition of a homogeneous electron gas to a ferromagnetic state in the generalized random-phase approximation. Experiments with cesium, however, reveal no magnetic anomalies of any sort. This fact alone shows that this simple model fails to describe the properties of an interacting electron gas.

Let us consider the relationship between negative values of $\varepsilon(\mathbf{q}, 0)$ and an instability of the system with respect to the spontaneous appearance of spin-density waves, taking both exchange and correlation effects into account. The charge and spin local-field correction functions, $G(\mathbf{q}, 0)$ and $\tilde{G}(\mathbf{q}, 0)$, can be written^{5,25}

$$G(\mathbf{q}, 0) = \frac{1}{2} [G_p(\mathbf{q}, 0) + G_a(\mathbf{q}, 0)], \qquad (19)$$

$$\widetilde{G}(\mathbf{q}, 0) = \frac{1}{2} [G_p(\mathbf{q}, 0) - G_a(\mathbf{q}, 0)].$$
(20)

Here, $G_{\rho}(\mathbf{q}, 0)$ is the local-field correction function for electrons with parallel spin, and $G_{a}(\mathbf{q}, 0)$ is the equivalent for electrons with antiparallel spins. All these functions, as well as $G(\mathbf{q}, 0)$ and $\tilde{G}(\mathbf{q}, 0)$, are positive definite.⁵ To take only exchange interaction into account is to ignore the correlations between electrons with opposite spins. As mentioned earlier, in this case we would have $G(\mathbf{q}, 0) = \tilde{G}(\mathbf{q}, 0)$. When correlation effects are taken into account, as can be seen from Eqs. (12) and (14) with (19) and (20), the static dielectric permittivity becomes negative for values of r_s below those corresponding to the occurrence of a spin instability:

$$V(\mathbf{q}) G(\mathbf{q}, 0) = \frac{1}{\chi_0(\mathbf{q}, 0)}.$$
(21)

To determine the specific values of r_s we must in some way calculate the local-field correction functions. The solution of this problem has attracted a huge number of papers²⁶⁻²⁸ (see also the reviews in Refs. 19 and 29). This problem has been analyzed in detail²⁰ by the density-functional method. The most common approach to calculating correlation effects in this method is to use a local approximation for the exchange-correlation energy functional:

$$E_{\rm XC} \{n (\mathbf{r})\} = \int d\mathbf{r} \varepsilon_{\rm XC} (n (\mathbf{r})), \ s (\mathbf{r}), \ n (\mathbf{r}). \tag{22}$$

In this approximation the functions $G(\mathbf{q}, 0)$ and $\tilde{G}(\mathbf{q}, 0)$ are²⁰

$$G(\mathbf{q}, 0) = -\frac{q^2}{4\pi\epsilon^2} \frac{\partial^2}{\partial n^2} \left[e_{\mathrm{XC}}(n, s) n \right]$$
(23)
and

$$\widetilde{G}(\mathbf{q}, 0) = -\frac{q^2}{4\pi e^2} \frac{1}{n} \frac{\partial^2}{\partial s^2} [e_{\mathrm{XC}}(n, s)].$$
(24)

Using the expressions which follow from the microscopic calculations of Ref. 30-33 for the exchangecorrelation energy $\varepsilon_{xc}(n,s)$, which use various approximations to incorporate correlation effects, Rashkeev²⁰ calculated the functions $G(\mathbf{q}, \mathbf{0})$ and $\tilde{G}(\mathbf{q}, \mathbf{0})$ in the limit of small q. As a result, he calculated the ground-state energy of the system; the quantity $\lim_{q \to 0} [q^2 \varepsilon(q, 0)]^{-1}$, which determines the sign of the static dielectric permittivity at small momenta q; and the magnetic susceptibility for various values of parameter r_s . Table I, from Ref. 20, shows the values of $r_s^{(1)}$, at which the static dielectric permittivity becomes negative; $r_{a}^{(2)}$, at which a phase transition to a ferromagnetic state occurs; and also $r_s^{(3)}$, the point of the absolute instability of the paramagnetic state, in which the spin magnetic susceptibility diverges in various approximations.³⁰⁻³³

It can be seen from Table I that all four approximations which were used lead to roughly the same values for $r_s^{(1)}$. We also see that correlation effects lead to $r_{\rm s}^{(1)}$ values smaller than the value $r_{\rm s}^{(1)}$ = 6.02 which is found in the generalized random-phase approximation. As for the transition to the ferromagnetic state, we note that the values of $r_s^{(2)}$ in the case with correlation effects are higher than those in the purely exchange case. Correlation effects thus reduce both the tendency of the homogeneous electron gas to switch to a ferromagnetic state and the importance of spin fluctuations. Expression (9) for the superconducting transition temperature, derived in the generalized random-phase approximation, thus clearly exaggerates the effect of spin fluctuations on $T_{\rm e}$. Perdew and Datta³⁴ recently derived some similar results regarding the calculation of $r_s^{(3)}$. They did not discuss the possibility of a first-order phase transition or the possibility of negative values of the static dielectric permittivity.

The values found for $r_s^{(2)}$ (corresponding to the ferromagnetic transition) in all these methods, which are the most common in the recent literature, are clearly unrealistic. As Vosko *et al.* have recently shown,³⁵ the approximations used in Refs. 36–39 for the dependence of the function $\varepsilon_{\rm XC}(n,s)$ on the spin density *s* are unsatisfactory at densities in the metallic range ($1 \le r_s \le 6$). Vosko *et al.* derived an interpolation expression for $\varepsilon_{\rm XC}(n,s)$ from a comparison with numerical data obtained by the Monte Carlo method.^{21,22} This expression TABLE I.

	Ref. 33	R ef. 30	R ef. 31	Re f. 32
$r_{s}^{(1)}$	5.145	5.109	5.06	5.225
r _s ⁽²⁾	1 6.33	10.25	8.82	7.72
$r_{z}^{(3)}$	18.10	11.16	9.82	8.46

was used by Rashkeev,²⁰ who found the following values: $r_s^{(1)} = 5.28$, $r_s^{(2)} = 79.7$, and $r_s^{(3)} = 99.1$.

The results obtained on $r_s^{(2)}$ and $r_s^{(3)}$ through the use of the approximation of $\varepsilon_{\rm XC}(n,s)$ proposed by Vosko et al.35 are thus quite different from the results found previously. In particular, these new results show that at densities corresponding to real metals a homogeneous electron gas is very far from a transition to a ferromagnetic state. Spin fluctuations also have a negligible effect on the physical characteristics of such a gas at $r_s \ll 80$. The maximum values of r_s found in metals are 5.18 for Rb and 5.64 for Cs. There are, it is true, some indications³⁶ that the static dielectric permittivity at small momenta q is in fact negative in cesium. Even if this is the case, however, this circumstance could be of no real importance for hightemperature superconductivity. Returning to the condition for the existence of negative values of the static dielectric permittivity, (16), we see that since the function $\chi_0(\mathbf{q}, \mathbf{0})$ decreases with increasing momentum q the corresponding minimum value of r_s , which we are defining as $r_s^{(1)}$, corresponds to the appearance of negative values of the static dielectric permittivity as q - 0. As the momentum q increases, progressively larger values of r_s are required for negative $\varepsilon(q, 0)$. Even in cesium, therefore, with $r_s = 5.64$, the static dielectric permittivity, if negative at all, is so only in a very small region of momentum space. The corresponding interaction constant is thus generally positive (i.e., $\mu \ge \lambda$), since it is determined by an integral over the entire momentum space. An effective superconductivity with a nonphonon mechanism might operate in a homogeneous electron gas only at the rather large values $80 \gg r_s \gg 6$. Unfortunately, we are unaware of the existence of any corresponding systems in nature. The question might be posed more pointedly: Could such systems exist at all?

Up to this point, the entire discussion has been of the model of a homogeneous interacting gas on a rigid, incompressible substrate. In this model, as has already been emphasized repeatedly, negative values of the static dielectric permittivity are completely permissible, and they do not contradict any general conditions of causality or the stability of the system. What happens if we alter the model slightly to take into account a possible compression of the substrate? This question can be treated most simply in the jellium model, quite popular in the theory of metals, in which the ions are treated as a continuous, homogeneous charged medium. The phonon oscillations in this system are expressed in the following way in terms of the dielectric permittivity of the electrons, $\varepsilon_{el}(q, 0)$:

$$\omega^{2}\left(\mathbf{q}\right) = \frac{\Omega_{\mathrm{pl}}^{2}}{\varepsilon_{\mathrm{el}}\left(\mathbf{q},0\right)},\tag{25}$$

where $\Omega_{pl} = \sqrt{4\pi Nz^2 e^2/M}$ is the ion plasma frequency. We have also introduced the subscript "el" on the dielectric permittivity to emphasize that this is the dielectric permittivity of the electron gas, not of the entire system (the electron gas plus the homogeneous ion fluid). It can be seen from (25) that in this system it would be impossible in principle for the static dielectric permittivity of the electron gas to take on negative values, so that there could be no effective nonphonon superconductivity mechanisms. The appearance of negative values of $\varepsilon_{el}(\mathbf{q}, 0)$ in this system would quickly lead to an instability of the phonon spectrum $[\omega^2(\mathbf{q}) < 0]$. This is the only model to which it is valid to apply Pines and Nozières' proof¹¹ that the static dielectric permittivity cannot have negative values. We might note that there is complete screening in this model because of the ion oscillations: $\varepsilon_{tot}^{-1}(\mathbf{q}, 0) = 0$, (i.e., $\lambda = \mu$).

c) Dielectric permittivity of a crystal

In the homogeneous and isotropic models which we have been considering up to this point the dielectric permittivity is a function of only the momentum (aside from the frequency). In crystals, all the dielectric-response functions become matrices in the space of reciprocal lattice vectors. The condition for the stability of the system in this case must be formulated as a requirement that the sign of appropriate quadratic forms of these functions must remain constant. In particular, the condition for the stability of the system with respect to charge perturbations is that the susceptibility matrix^{5,37} χ (**q** + **K**, **q** + **K**', 0) be negative definite, where **K** and **K'** are reciprocal lattice vectors. This matrix is related to the dielectric-permittivity matrix:

$$\chi (\mathbf{q} + \mathbf{K}, \ \mathbf{q} + \mathbf{K}', \ \omega) = \frac{|\mathbf{q} + \mathbf{K}|^2}{4\pi e^2} [e^{-i} (\mathbf{q} + \mathbf{K}, \ \mathbf{q} + \mathbf{K}', \ \omega) - \delta_{\mathbf{K}\mathbf{K}'}].$$
(26)

In turn, the condition for the effectiveness of the superconductivity mechanisms is that the matrix $\varepsilon^{-1}(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', 0)$ be negative definite; this case would correspond to an electron-electron attraction.

It can be shown³⁷ that a necessary condition for the satisfaction of this criterion is that the macroscopic static dielectric permittivity $\varepsilon_{m}(\mathbf{q}, 0)$, defined by

$$\varepsilon_{\mathbf{m}}(\mathbf{q}, 0) = \frac{1}{\varepsilon^{-1}(\mathbf{q}+0, \mathbf{q}+0, 0)} \,. \tag{27}$$

must be negative. To avoid complicating the discussion with secondary details, we will discuss in this section the possible existence of negative values of this macroscopic dielectric function in crystals.

In simple metals, where the off-diagonal matrix elements of the dielectric matrix $\varepsilon(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', 0)$ with $\mathbf{K} \neq \mathbf{K}'$ are small, of the order of the small electron-ion pseudopotential $V_{ie}(\mathbf{K} - \mathbf{K}')$, we can write the macroscopic dielectric permittivity in the following form

$$\varepsilon_{\mathbf{m}}(\mathbf{q}, 0) = \varepsilon (\mathbf{q} + 0, \mathbf{q} + 0, 0) - \sum_{\mathbf{K} \neq 0} \frac{\varepsilon (\mathbf{q} + 0, \mathbf{q} + \mathbf{K}, 0) \varepsilon (\mathbf{q} + \mathbf{K}, \mathbf{q} + 0, 0)}{\varepsilon (\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K})}.$$
(28)

Expression (28) shows that the macroscopic dielectric permittivity is always smaller than the diagonal element of the dielectric matrix, $\varepsilon(\mathbf{q} + 0, \mathbf{q} + 0, 0)$. It does not follow at this point that $\varepsilon_m(\mathbf{q}, 0)$ is smaller than the dielectric permittivity of a homogeneous electron gas of the same density, since the diagonal matrix element $\varepsilon(\mathbf{q} + 0, \mathbf{q} + 0, 0)$ is also changed by the electron-ion pseudopotential. Nevertheless, it can be proved rigorously that in a perturbation theory in the pseudopotential the macroscopic dielectric permittivity of an electron gas in a simple metal is in fact always smaller than $\varepsilon(\mathbf{q}, 0)$ for a homogeneous electron gas of the same density. This conclusion means that in simple metals the condition for the existence of nonphonon superconductivity mechanisms is worse than in the case of a homogeneous electron gas.

This conclusion does not apply to all metals by any means. Even if a weak pseudopotential exists we cannot use perturbation theory to calculate $\varepsilon_m(\mathbf{q}, 0)$ if there are reciprocal-lattice vectors $\mathbf{K} \approx 2k_F$ in the metal. The situation is even more complicated in the transition metals and semimetals, where perturbation theory in the crystal potential is immediately ruled out. In these systems, however, the situation may be more favorable for the existence of negative values of the static dielectric permittivity than in a homogeneous electron gas or a simple metal; the possibility is aided by the presence of congruent parts of the Fermi surface in the electron band spectrum. We know from the theory of exciton dielectrics³⁸ that the diagonal matrix element of the susceptibility of the band electrons,

$$\chi_0 (\mathbf{q} + \mathbf{0}, \ \mathbf{q} + \mathbf{0}, \ \mathbf{0}) = -\frac{1}{\Omega} \sum_{\mathbf{K}} \frac{n_{\mathbf{K}} - n_{\mathbf{K}} + \mathbf{q}}{E_{\mathbf{K}} - E_{\mathbf{K}} + \mathbf{q}}$$
(29)

diverges in this case at a momentum q_e which connects congruent parts of the Fermi surface. For the macroscopic dielectric permittivity $\varepsilon_m(q, 0)$, an expression similar to Eq. (28) can be written⁵ for momenta qnear q_e :

Here, in contrast with (28), the summation is over all the vectors K, including K=0. The quantity $\Delta \varepsilon (\mathbf{q} + 0, \mathbf{q} + \mathbf{K}, 0)$ is that part of the dielectric matrix which does not have singularities at $\mathbf{q} = \mathbf{q}_c$. Unfortunately, specific calculations of the local-field correction functions $G(\mathbf{q}, 0)$ for Bloch electrons present formidable difficulties and have not been carried out in practice. For systems with congruent parts of the Fermi surface³⁸ the quantity $(4\pi e^2/q^2)G(\mathbf{q}, 0)$ is usually assumed equal to some constant g^2 . Under the assumption $\chi_0(\mathbf{q} + 0, \mathbf{q} + 0, 0) > 0$ it follows from (30) that the electron macroscopic dielectric permittivity of such systems becomes negative under the condition

$$\frac{4\pi e^2}{q^2} G(\mathbf{q}, 0) \ge \frac{1}{\chi_0 (\mathbf{q} + 0, \mathbf{q} + 0, 0)}.$$
(31)

Let us compare this condition with (16), which is the condition for the existence of negative values of $\varepsilon(\mathbf{q}, 0)$ in a homogeneous electron gas. The two conditions are formally of the same type, but actually there is a very important difference, which stems from the properties of the function $\chi_0(\mathbf{q}+0,\mathbf{q}+0,0)$. In a homogeneous electron gas, $\chi_0(\mathbf{q}, 0)$ remains finite at any momentum \mathbf{q} , so that condition (16) can hold only at large values of the exchange-correlation interaction constant. In the case of systems having congruent parts of the Fermi surface, in contrast, condition (31) can be satisfied at any values of the exchange-correlation interaction constants, including arbitrarily small values, because of the divergence of the function $\chi_0(\mathbf{q}+0,\mathbf{q}+0,\mathbf{q})$.

However, some further explanation is necessary. As

we have already seen, in a homogeneous electron gas with a strong exchange-correlation interaction there is the possibility not only that the static dielectric permittivity will take on negative values but also that there may be a phase transition to a state with a spin-density wave or a space-charge wave. For a homogeneous electron gas we were able to show that instabilities associated with these waves occur at values of the interaction constants larger than those at which values $\varepsilon(q, 0) < 0$ appear. There has been no corresponding analysis of the situation for systems with congruent regions of the Fermi surface, but it is doubtful that an instability associated with a spin-density wave will generally occur at values of the interaction constants other than those which satisfy condition (31), as in the case of a homogeneous electron gas. Whether these constants are larger or smaller than those corresponding to condition (31) is a question for which we do not yet have an exact answer. As for instabilities associated with the appearance of electron space-charge waves, we note that they cannot occur at all in a crystal. In this case, electrons will cause structural transitions in the crystal even at far smaller values of the exchange-correlation constants. We have already discussed the simplest case of this instability, in the example of the jellium model. It is thus clear that the problem of nonphonon mechanisms for superconductivity is only now coming under serious study. The solution of this problem will require, first and foremost, the development of exact microscopic calculation methods for dealing with strongly interacting inhomogeneous electron systems.

Turning to the sign of the total dielectric permittivity of the system and the contribution of the electron-phonon interaction to this function, we see a much clearer picture. The local-field effects in the ion subsystem of the metal play a governing role. Generally speaking, the local-field effects are greatest in a system of localized point charges.^{4,5} The localization itself is, in a sense, a consequence of nothing other than the localfield effects. In metals, at least in simple metals, the ion subsystem may be treated very accurately as a system of point charges. Fortunately, a system of localized charges which are oscillating with a small amplitude around their equilibrium positions may be treated exactly with full account of the exchange-correlation interaction. For simplicity we shall explain the situation for the particular case of a Wigner crystal of classical point charges in which, of course, there is no exchange interaction between charges, and correlation effects can be taken into account exactly. The dielectric permittivity of such a crystal is⁵

$$\varepsilon_{\rm m}^{-1}(\mathbf{q}, \omega) = 1 \pm \frac{\Omega_{\rm pl}^2}{q^2} \sum_{\boldsymbol{\lambda}} \frac{(\mathbf{q} \cdot \mathbf{q}_{\boldsymbol{\lambda}})^2}{\omega^2 - \omega_{\boldsymbol{\lambda}}^2(\mathbf{q})}, \qquad (32)$$

where $\Omega_{pl}^2 = 4\pi Z^2 e^2 N/M$ is the square of the plasma frequency of the charges, $\omega_{\lambda}(\mathbf{q})$ is the oscillation frequency of the crystal, and $\mathbf{e}_{q\lambda}$ is the polarization vector of these oscillations. As mentioned earlier, in the jellium model, which ignores the localization of the ions and thus correlations between ions, there is only a single collective oscillation, specifically, longitudinal plasma oscillations with the frequency

$$\omega = \Omega_{pl}$$
 (33)

The inhomogeneity of the system or, equivalently, the local-field effects in a system of point charges split this excitation into three oscillation modes: a longi-tudinal mode $\omega_{\mu}(\mathbf{q})$ and two transverse modes $\omega_{\mu}(\mathbf{q})$. The frequencies of these oscillations obey a strict sum rule³⁹:

$$\sum_{\mathbf{i}} \omega_{\mathbf{i}}^{\mathbf{z}} (\mathbf{q}) = \Omega_{\mathrm{pl}}^{\mathbf{z}}.$$
(34)

It is easy to see from (32) and (34) that this fact—the splitting of the single collective oscillation of the jellium model into three modes—causes the static dielectric permittivity of a Wigner crystal to become negative at arbitrary vectors **q**. In particular, for vectors **q** in a high-symmetry direction we have

$$\varepsilon(\mathbf{q}, 0) = 1 - \frac{\Omega_{\text{pl}}^2}{\omega_{\perp}^2(\mathbf{q})} < 0. \tag{35}$$

The total dielectric permittivity of simple metals has been analyzed in detail¹⁴; both the ion and electron systems have been taken into account. It was shown that the part of $\varepsilon_{tot}(q, 0)$ which is due to the electron-phonon interaction can give rise to negative values of this function. The physical nature of this phenomenon is absolutely the same as in a case of a Wigner crystal: localfield effects in the ion subsystem and a splitting of the ion plasma oscillations into longitudinal and transverse phonons. The coupling of the electron-phonon interaction constant λ and the Coulomb constant μ can be described by

$$\lambda \approx \mu \left\langle \frac{\Omega_{p_1}^2}{\mathfrak{r}_{e_1}(q, 0) \, \omega_{\mathbb{I}}^*(q)} \right\rangle \left\langle \frac{V_{\frac{s}{4}e}^*(q)}{V_e^*(q)} \right\rangle; \tag{36}$$

where $V_{ie}(q)$ is the pseudopotential of the electron-ion interaction, and

$$V_{\rm c} (q) = \frac{4\pi Z e^2}{q^2}$$
(37)

is the ion Coulomb potential. In simple metals we can write sum rules for the phonon frequencies which are similar to (34), and we can demonstrate the inequality

$$\omega_{\parallel}^{2}(\mathbf{q}) < \frac{\Omega_{\mathbf{p}1}}{\varepsilon_{\mathbf{e}1}(\mathbf{q}, 0)}.$$
(38)

It is this inequality which makes it possible for the electron-phonon coupling constant λ to exceed the Coulomb constant μ in metals. The second factor, $\langle V_{1e}^2(\mathbf{q})/V_c^2(\mathbf{q})\rangle$, is usually less than one, and the final relationship between the constants λ and μ is determined by the mutual effects of the two quantities, i.e.,

$$\Big\langle \frac{\Omega_{\mathrm{pl}}^{2}}{\epsilon_{\mathrm{el}}\left(\mathbf{q}, \ \mathbf{0}\right) \omega_{\parallel}^{2}\left(\mathbf{q}\right)} \Big\rangle, \quad \Big\langle \frac{V_{\mathrm{le}}^{2}\left(\mathbf{q}\right)}{V_{\mathrm{c}}^{2}\left(\mathbf{q}\right)} \Big\rangle.$$

In particular, we find $\lambda \leq \mu$ for the alkali metals. In polyvalent simple metals (lead and aluminum, for example), on the other hand, λ is larger than μ .

An expression for the relationship between λ and μ similar to (36) was also derived in the paper⁶ by Cohen and Anderson which we mentioned earlier. Their interpretation of the results, however, was clearly incorrect. For example, it was assumed in Ref. 6 that the static dielectric permittivity cannot ever be negative $[\epsilon(\mathbf{q}, 0) > 1]$. The existence of an expression like (35) was regarded as a manifestation of scattering processes in the electron-phonon interaction. Actually, as we have already seen, expression (36) and the inequality (8) which follows from it,

 $\lambda > \mu$

are in fact consequences of a negative total dielectric permittivity of the system. Generally speaking, (36) is written without consideration of scattering processes. The incorporation of these processes, however, adds no new information to the fact that the inequality $\lambda > \mu$ actually does or does not hold. All that is required is to replace the longitudinal phonon frequency $\omega_{\parallel}^2(\mathbf{q})$ by the average phonon frequency $\langle \omega^2(\mathbf{q}) \rangle$. In the simplest case this replacement takes the form

$$\frac{1}{\omega_{\parallel}^{\mathfrak{q}}(\mathfrak{q})} \rightarrow \frac{1}{3} \left(\frac{1}{\omega_{\parallel}^{\mathfrak{q}}(\mathfrak{q})} + \frac{2}{\omega_{\perp}^{\mathfrak{q}}(\mathfrak{q})} \right).$$
(39)

To conclude this section we take a brief look at the meaning of inequality (38), which may be thought of in a sense as the condition for the existence of an ordinary phonon mechanism for superconductivity. If we write the longitudinal-phonon frequency at small q as

$$\omega_{\parallel}(\mathbf{q}) = cq, \tag{40}$$

where c is the longitudinal sound velocity, then inequality (38) can be rewritten in the form

$$c < c_j;$$
 (41)

where c_j is the longitudinal sound velocity in the jellium model, given by

$$c_{j}^{2} = \frac{1}{3} \frac{m}{M} v_{F}^{k}, \qquad (42)$$

and $v_{\rm F}$ is the electron Fermi velocity. We should point out that Kulik⁴⁰ derived a condition for superconductivity back in 1964 which is actually the same as (41). The derivation in Ref. 40 made use of the method developed by Silin et al.^{41,42} and Kantorovich⁴³ for describing electron-phonon systems. This method is based on singling out the macroscopic electric field in the interaction of ions and electrons. By its very nature, this approach is valid only for describing phenomena characterized by small momenta, while for superconductivity it is large momentum transfers which are important. The limited applicability of this condition can also be seen clearly from the derivation above. Curiously, however, condition (41) does a fairly good job of separating metals into superconductors and nonsuperconductors, according to Ref. 40.

4. SUPERCONDUCTIVITY EQUATIONS FOR STRONG-COUPLING SYSTEMS

a) General analysis of strong-coupling effects

As was shown in the preceding section, a necessary condition for the existence of an effective mechanism for high-temperature superconductivity is a negative static dielectric permittivity $[\varepsilon(\mathbf{q}, 0) < 0]$ (for isotropic systems) or a negative definite matrix for the static dielectric permittivity for crystals. In most theoretical papers on the problem, however, this circumstance has not been fully heeded, since the specific calculations have usually been carried out in the random-phase approximation. That the dielectric permittivity is positive in an isotropic, single-component plasma in the





random-phase approximation can be seen directly from Eqs. (12) and (15) above. In the more general case of a multiband metal or semiconductor it can also be shown rigorously^{4,5} that the matrix for the static dielectric permittivity is positive definite in the random-phase approximation. It is clear that the many attempts to find effective nonphonon mechanisms for a high-temperature superconductivity in multiband metals and semiconductors in the random-phase approximation (see, for example, Refs. 44-46 and the more detailed review in Ref. 3) have not been justified, for precisely this reason.

As we showed in the preceding section, the static dielectric permittivity could have negative values only because of local-field effects, i.e., in systems with a strong interaction or an anomalously high polarizability. In Feynman-diagram terms, the dielectric permittivity could have a negative sign only by virtue of the socalled vertex functions in a calculation of the total polarizability of the system:

$$\Pi (\mathbf{q}, 0) = -2i \int d\mathbf{p} d\omega G (\mathbf{p}, \omega) G (\mathbf{p} - \mathbf{q}, -\omega) \Gamma (\mathbf{p}, \omega; \mathbf{p} - \mathbf{q}, -\omega; \mathbf{q}, 0),$$

(43)

where $\Gamma(p, \omega; p-q, -\omega; q, 0)$ is the vertex function. Unfortunately, it is not possible to write anything in the way of a closed equation for the vertex function in its general form. Figure 1 shows the set of diagrams of lowest order in the effective interaction $V_{eff}(\mathbf{q}, \omega)$ = $4\pi e^2/q^2 \varepsilon(\mathbf{q}, \omega)$. A wavy line corresponds to $V_{eff}(\mathbf{q}, \omega)$. The fact that the vertex functions must be incorporated in a calculation of the polarizability of the system in order to obtain negative values of $\varepsilon(\mathbf{q}, 0)$ means that these functions must also be taken into account in a calculation of the effective electron-electron interaction. The simplest diagrams for the effective electron-electron interaction are shown in Fig. 2. The calculations from (2) for T_c and the derivation of condition (8) ($\lambda > \mu$) for the effectiveness of the superconductivity mechanism in Refs. 6 and 7 actually used an approximation for the electron-electron interaction which corresponds to only the diagram in Fig. 2(a). This approach is clearly inadequate for strong-coupling systems; the vertex functions must be taken into account more accurately. The corrections to the bare interaction $V_{eff}(\mathbf{q}, \omega)$ of the types in Figs. 2(b) and 2(c) can be taken into account quite simply. The electron-electron interaction can be written as the skeletal diagram in Fig. 3, where the dark triangle represents the complete vertex function



FIG. 2.

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 Γ . A diagram of the type in Fig. 2(d) on the other hand, does not reduce to this form but may still prove to be important, especially for a correct analysis of the spin structure of the electron-electron interaction and for a calculation of the anomalous Green's functions.

Kirzhnits³ has carried out a detailed perturbationtheory analysis of the corrections of second order in $V_{eff}(\mathbf{q}, \omega)$ and of their effect on the critical temperature of the superconducting transition for weak-coupling systems. For strong-coupling systems, e.g., for a single-component plasma with $r_s > 1$, all the perturbation-theory diagrams must be taken into account. The problem thus becomes essentially unsolvable by perturbation theory and must be approached in a different way, e.g., through the use of some sort of variational principle. For systems with congruent regions on the Fermi surface it is possible to identify certain diagrams as the most important. These diagrams are shown in Fig. 4 for the vertex function Γ in the quasi-isotropic approximation. It should be noted, however, that this problem has yet to be analyzed systematically.

b) Derivation of superconductivity equations for strong-coupling systems

An exact equation for the single-particle Green's functions for the electrons of a normal metal was derived in Ref. 47. The results can easily be generalized to the case of a superconducting metal by introducing a Nambu representation for the electron operators in the usual manner $[x = (\mathbf{r}, t)]$,

$$\mathbf{\psi}\left(x\right) = \begin{vmatrix} \varphi_{\uparrow}^{*}\left(x\right) \\ \varphi_{\downarrow}^{*}\left(x\right) \end{vmatrix}, \quad \mathbf{\psi}^{*}\left(x\right) = \left|\varphi_{\uparrow}^{*}\left(x\right), \varphi_{\downarrow}\left(x\right)\right|$$
(44)

and examining the matrix Green's function

$$\mathbf{G}(x, x') = -i \langle T_{t} \psi(x) \psi^{+}(x') \rangle.$$
(45)

The following expression is found for the function G(x,x'):

$$G^{-1}(x, x') = i \frac{\partial}{\partial t} 1 + \left(\frac{\nabla^2}{2m} + \mu\right) \tau_3 - U_{eff}(x) \tau_3 - \Sigma(x, x'), \quad (46)$$

where I and τ_i are the ordinary Pauli matrices,

 $\mathbf{1} = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}, \quad \mathbf{\tau}_1 = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}, \quad \mathbf{\tau}_2 = \begin{vmatrix} 0 & t \\ -i & 0 \end{vmatrix}, \quad \mathbf{\tau}_3 = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix},$

 $U_{\rm eff}(\mathbf{x})$ is the effective Hartree potential acting on the electrons, given by

$$U_{\text{eff}}(x) = e^2 \int d\mathbf{r}' \frac{\langle \rho_{\text{e}}(\mathbf{r}', t) \rangle}{|\mathbf{r}' - \mathbf{r}|} + \sum_n V_{1\text{e}}(\mathbf{r} - \mathbf{R}_n^0), \qquad (47)$$

 $\langle \rho_{e}(\mathbf{r},t) \rangle$ is the expectation value of the electron density, given by

 $\langle \rho_e (\mathbf{r}, t) \rangle = -i \operatorname{Sp} (\boldsymbol{\tau}_3 \mathbf{G} (x, x)),$



FIG. 4.

and $V_{ie}(\mathbf{r} - \mathbf{R}_n^0)$ is the unscreened electron-ion potential. Also, $\Sigma(x,x')$, the eigenenergy part and a matrix in the space of Pauli matrices, is given by

$$\Sigma(x, x') = -i \int dx_1 dx_2 \int d\mathbf{r}'' \frac{e^2}{|\mathbf{r} - \mathbf{r}''|} \times e_{10}^{-i} (x_1; \mathbf{r}'', t) \tau_3 G(x, x_2) \tau_3 \Gamma(x_2, x', x_1),$$
(48)

where $\Gamma(x_2, x', x_1)$ is the matrix vertex function defined by

$$\Gamma(x_2, x', x_1) = \tau_3 \frac{\delta G^{-1}(x_2, x')}{\delta U_{eff}(x_1)}.$$
(49)

The function $\varepsilon_{tot}^{-1}(x,x')$, the inverse dielectric permittivity of the system, can be written

$$\varepsilon_{10t}^{-1}(x, x') = \varepsilon_{e1}^{-1}(x, x') + \sum_{n, n'} \int dx_1 dx_2 \varepsilon_{e1}^{-1}(x, x_1) \times \nabla_{\alpha} V_{1e}(\mathbf{r}_1 - \mathbf{R}_n^{\alpha}) D_{nn'}^{\alpha\beta}(t_1 - t_2) \nabla_{\beta} V_{1e}(\mathbf{r}_2 - \mathbf{R}_{n'}^{\alpha}) \frac{\nabla_{\mathbf{r}_1}^{\alpha}}{4\pi} \varepsilon_{e1}^{-1}(x_2, x');$$
(50)

here $D_{nn}^{\alpha\beta}(t)$ is the phonon Green's function, and $\varepsilon_{el}^{-1}(x, x')$ is the inverse matrix for the dielectric permittivity of the crystal electrons. The function $\varepsilon_{el}^{-1}(x, x')$ is determined by

$$e_{ei}^{-1}(x, x') = \delta(x - x') + \int dx_1 dr'' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \Pi(\mathbf{r}'', t; x_1) e_{ei}^{-1}(x_1, x'), \quad (51)$$

where $\Pi(x, x')$ is the total electron polarization operator, given by

$$\Pi(x, x') = \frac{\delta(\rho_{e}(x))}{\delta U_{eff}(x')}.$$
(52)

The matrix $\Sigma(x, x')$ can be expanded in Pauli matrices and written in the form

$$\Sigma(x, x') = i \left[\delta(x - x') - Z(x, x') \right] \frac{\partial}{\partial t} \mathbf{1} + \xi(x, x') \tau_3 + \varphi(x, x') \tau_1.$$
 (53)

The functions Z(x, x') and $\xi(x, x')$ determine the band structure and the renormalization of the spectrum of perturbations of the metal; they are nonvanishing in the case of a normal metal also. The function $\varphi(x, x')$, on the other hand, is the anomalous eigenenergy part, which determines the superconducting order parameter. Garland⁴⁸ has derived some equations which are actually the same as (46) and (48).

For quasi-isotropic weak-coupling systems, for which the random-phase approximation is valid, we may ignore $\xi(x,x')$ and assume $Z(x,x') = \delta(x-x')$, thereby retaining only the anomalous eigenenergy part, $\varphi(x,x')$, in (48). The vertex function $\Gamma(x_2,x',x_1)$ can be replaced in this approximation by the simple expression

$$\Gamma (x_2, x', x_1) = 1\delta (x_1 - x') \delta (x_2 - x_1).$$

In this case the problem simplifies substantially, and it becomes a simple matter to calculate, for example, the critical temperature for the superconducting transition, $T_{\rm e}$; the answer is given by (2).

For strong-coupling systems, in contrast, to solve Eqs. (48) is an exceedingly difficult problem. In the first place, these equations are extremely difficult to solve even for a normal metal. Only a very few attempts have been made to develop a systematic approach to the problem of calculating the single-particle properties of normal metals on the basis of the solution of Eqs. (48). The customary band-structure calculations for metals adopt at the outset a single-particle model in the density-functional method. The interrelationship between these two approaches has received essentially no attention.

It might be possible to simplify the calculations of the superconductivity characteristics of metals by rewriting the equation for the anomalous eigenenergy part, $\varphi(x,x')$, in such a way that the exact Green's functions of a normal metal appear in this equation. Unfortunately, this cannot be done in a general form, but it is possible to write a corresponding equation for T_c in the case $T_c < \varepsilon_F$. For this purpose we write the total Green's function G(x,x') as

$$\mathbf{G}(x, x') = \mathbf{G}_{N}(x, x') - \int dx_{1} dx_{2} \mathbf{G}_{N}(x, x_{1}) \notin (x_{1}, x_{2}) \tau_{1} \mathbf{G}_{N}(x_{2}, x'),$$
(54)

where $G_{N}(x, x')$ is the matrix Green's function for the electrons of a normal metal, given by

$$\mathbf{G}_{\mathrm{N}}(\boldsymbol{x}, \, \boldsymbol{x}') = \begin{vmatrix} G_{\mathrm{N}}(\boldsymbol{x}, \, \boldsymbol{x}') & 0 \\ 0 & G_{\mathrm{N}}^{\dagger\dagger}(\boldsymbol{x}', \, \boldsymbol{x}) \end{vmatrix}.$$

Substituting (54) into expression (48) for $\Sigma(x, x')$, we find

$$\begin{split} \Sigma\left(x, \ x'\right) &= -i \int \mathrm{d}x_1 \,\mathrm{d}x_2 \int \mathrm{d}\mathbf{r}'' \frac{e^2}{|\mathbf{r} - \mathbf{r}''|} \\ &\times e^{-i}_{\mathrm{tot}}\left(x_1, \ \mathbf{r}''t\right) \tau_3 G_N\left(x_1 \ x_2\right) \tau_3 \Gamma\left(x_2, \ x', \ x_1\right) \\ &- i \int \mathrm{d}x_1 \,\mathrm{d}x_2 \,\mathrm{d}x_3 \,\mathrm{d}x_4 \int \mathrm{d}\mathbf{r}'' \frac{e^2}{|\mathbf{r} - \mathbf{r}''|} e^{-i}_{\mathrm{tot}}\left(x_1, \ \mathbf{r}'', \ t\right) \\ &\times \tau_3 G_N\left(x, \ x_3\right) \varphi\left(x_3, \ x_4\right) \tau_1 G_N\left(x_4, \ x_2\right) \Gamma\left(x_2, \ x', \ x_1\right). \end{split}$$

We now write the eigenenergy part, $\Sigma(x,x')$, in a form analogous to (53):

$$\Sigma (x, x') = \Sigma_N (x, x') + \varphi (x, x') \tau_1,$$

where

$$\mathbf{\Sigma}_{\mathbf{N}} = \begin{vmatrix} \Sigma_{\mathbf{N}} & 0 \\ 0 & \Sigma_{\mathbf{N}}^{\star} \end{vmatrix}$$

is the eigenenergy part of the Green's function of a normal metal, which satisfies the equation

$$\Sigma_{\mathrm{N}} = -i \int \mathrm{d}x_1 \,\mathrm{d}x_2 \int \mathrm{d}\mathbf{r}' \,\frac{\epsilon^3}{|\mathbf{r} - \mathbf{r}^*|} \,\varepsilon_{\mathrm{tot}}^{-1}(x, \mathbf{r}^*t) \,G_{\mathrm{N}}(x, x_2) \,\Gamma(x_2, x', x_4),$$
(55)

where $\Gamma_{N}(x_{2}, x', x_{1})$ is the vertex part, which does not contain anomalous Green's functions.

In the derivation of the equation for $\varphi(x, x')$ we cannot ignore the anomalous vertices, but at $T = T_c$ it is sufficient to consider only those anomalous vertices in which the anomalous Green's function appears only once. The situation regarding these vertices is very reminiscent of that regarding Coulomb vertices in the electron-phonon system of a normal metal. In that case, the need to take into account the phonon corrections in the vertex function in the term in Σ_{ν} due to the Coulomb interaction gives rise to an asymmetry in the number of Coulomb vertices in the terms associated with the Coulomb and electron-phonon interaction. The Coulomb vertices appear quadratically in the contribution to the eigenenergy part due to the electron-phonon interaction. There is a corresponding situation in the equation for the anomalous eigenenergy part $\varphi(x, x')$. The vertex Green's functions of the normal metal, Γ_N , also appear quadratically in this equation, in contrast with (55) for the normal part, Σ_N . Finally, the equation for the function $\varphi(x, x')$ can be written in the symbolic form⁴

$$\varphi = -i \int \Gamma_{\rm N} V_{\rm c} \varepsilon_{\rm tot}^{-1} G_{\rm N} G_{\rm N}^* \Gamma_{\rm N} \varphi, \qquad (56)$$

where we have suppressed some of the indices on the functions to save space.

Comparison of (55) and (56) shows that the processes which give rise to the pairing of electrons and to the appearance of an order parameter, on the one hand, and to a renormalization of the properties of the normal metal, on the other, correspond to completely different interactions. Pairing corresponds to the interaction

 $V_{eff}^{n} = \int \mathbf{\Gamma}_{N} V_{e} \varepsilon_{eff}^{-1} \mathbf{\Gamma}_{N},$

while renormalization corresponds to

 $V_{et}^{n} = \int V_{e} \varepsilon_{tot}^{-1} \Gamma_{N}$.

An important point here is that the interaction V_{ett}^n is repulsive even if the static dielectric permittivity is negative, while the sign of the pairing interaction is determined by the sign of the static dielectric permittivity. However, nothing approaching a detailed analysis of these equations has been carried out for systems with nonphonon superconductivity mechanisms.

The situation is far more settled in systems with an electron-phonon superconductivity mechanism. For such metals, Eqs. (48) have been analyzed in detail in the review by Scalapino⁴⁹ and in a couple of books,^{3,8} and we will not dwell on these equations here. We simply note that for pure metals it is necessary to take into account the anisotropy of the superconductivity order parameter, and the calculations accordingly become much more complicated.⁵⁰ Actually, this anisotropy is quite small in most metals. Furthermore, in dirty metals, with impurities, the anisotropy disappears at a rather low impurity concentration, so that it is sufficient to examine the order parameter averaged over the Fermi surface. For this quantity we have the wellknown superconductivity equations which are usually called the "Eliashberg equations" after the researcher who derived them back in 1960 (Refs. 51 and 52). We move on now to a study of those equations.

5. TRANSITION TEMPERATURE OF SUPERCONDUCTORS WITH A STRONG ELECTRON-PHOTON INTERACTION

a) Calculation of the transition temperature

We write the Éliashberg equations for $T = T_c$ in the customary form^{3,8,49,50,52}:

$$Z(i\omega_n) \Delta(i\omega_n) = \pi T_c \sum_{\omega_m} \lambda(i\omega_m - i\omega_n) \frac{\Delta(i\omega_m)}{|\omega_m|} - \mu \sum_{\omega_m} \frac{\Delta(i\omega_m)}{|\omega_m|}, \quad (57)$$

$$1 - Z(i\omega_n) i\omega_n = -\pi T_c \sum_{\omega_m} \operatorname{sign} \omega_m \lambda(i\omega_m - i\omega_n); \quad (58)$$

here $\Delta(i\omega_n)$ is the superconductivity order parameter, $Z(i\omega_n)$ is the renormalization of the Green's function of the normal metal, $\omega_n = (2n+1)\pi T_c$, and $\lambda(i\omega_m - i\omega_n)$ is defined by

$$\lambda \left(i\omega_m - i\omega_n \right) = 2 \int_0^\infty d\omega \alpha^2 \left(\omega \right) g \left(\omega \right) \frac{\omega}{\omega^2 + (\omega_m - \omega_n)^2}.$$
 (59)

The function $\alpha^2(\omega)g(\omega)$ is the spectral density of the electron-phonon interaction; $g(\omega)$ is the phonon state density, and $\alpha(\omega)$ is the interaction constant of electrons and phonons with a given energy ω .

We first note that the contribution of the direct Coulomb repulsion [the second term on the right side of (57)] is written in a very simplified model form. Such a simple expression can be used for the following reasons: First, as was explained in the preceding sections of this review, local-field effects in the ion subsystem in a system with a strong electron-phonon interaction allow the electron-phonon interaction constant λ to be significantly larger than the Coulomb interaction constant µ, and this is the actual situation in all real superconducting metals. The coupling constant λ in superconductors ranges from $\lambda = 0.4$ in aluminum to $\lambda = 2.6$ in lead-bismuth alloys. In none of these metals does μ exceed 0.2 or 0.3 (Ref. 53). Because of the large difference between the average phonon frequencies and the Fermi energy, there is a further decrease in the contribution of the direct Coulomb interaction, due to a rescattering of electrons and a transition to the Coulomb pseudopotential $\mu^* = \mu / [1 + \mu \ln(\varepsilon_F / \overline{\omega})]$. As Batyev has shown,⁵⁴ the transition from μ to μ^* occurs not only in the weak-coupling case but also in a more accurate study of strong-coupling effects. The direct Coulomb repulsion in most real superconductors thus has a very small effect on T_c , and it can be described completely by the simple model used in (57).

This discussion does not, of course, mean that the Coulomb interaction between electrons is totally unimportant in such metals. It is extremely important in shaping the phonon frequencies of metals, in the screening of the electron-ion interaction, etc. The spectral density of the electron-phonon interaction, $\alpha^2(\omega)g(\omega)$, must of course be found by a method which correctly incorporates both the electron-ion and electron-electron Coulomb interactions. We will take up the microscopic definition of this function and methods for calculating it a bit further on; at this particular point we simply wish to point out that well-developed methods are available for finding the function $\alpha^2(\omega)g(\omega)$ from tunneling measurements in superconducting⁵⁵⁻⁵ and even normal^{59,60} metals. The function $\alpha^{2}(\omega)g(\omega)$ is thus known quite well for a very large number of metals and alloys.

Moving on to a calculation of T_c , we first rewrite Eqs. (57)-(58) as a single linear equation for the function $\Delta(i\omega_{\eta})$. The critical temperature T_c is then determined by finding the eigenvalues of this equation:

$$\sum_{n \ge 0}^{n \max} K(n, n', T_c) \Delta_{n'} = 0, \qquad (60)$$

where

$$K(n, n', T_c) = \lambda(n-n') + \lambda(n+n'+1) - \delta_{nn'} [2n+1+\lambda(0) + 2\sum_{m=1}^{n} \lambda(m)].$$
(61)

In this equation we introduced

$$\Delta_n = \frac{\Delta(i\omega_n)}{|\omega_n|}$$

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and on the right side of (57) we ignored the direct Coulomb repulsion. Where necessary, the contribution of this term, which is quite unimportant for our purposes, can easily be restored in the final results.

A major effort has been devoted to solving Eq. (60) and to deriving an analytic expression for $T_{\rm c}$ (Refs. 61– 63), starting with the work by McMillan.⁶⁴ It is perhaps worth noting that in all these studies it was not Eq. (60) which was solved but instead Eqs. (57)-(58), analytically continued to continuous values of the energy ω . Before we take up the specific solutions of these equations we would like to answer another, completely pertinent question: Is it possible in principle to derive an analytic expression for T_c from Eq. (60)? Actually, as can be seen from (57)-(61), the transition temperature is a functional of the function $\alpha^2(\omega)g(\omega)$. When we talk about deriving an analytic expression for T_c , we are implying, in view of the very nature of the problem and the results of Refs. 61-64, that it is possible to express T_c in terms of several moments of the function $\alpha^2(\omega)g(\omega)$. Clearly, this problem cannot be solved for an arbitrary function $\alpha^2(\omega)g(\omega)$, and the results derived for T_c will unavoidably be approximate.

For systems with weak and intermediate coupling, the problem has been studied in detail.⁶³ A method based on iterations in the parameter $\lambda/(1 + \lambda)$ has yielded the following analytic expression for T_c :

$$T_{\rm c} = 1.14 \,\omega_{\rm log} \, e^{-K} \exp\left[-\frac{1+\lambda}{\lambda-\mu^* \left(1+\left[\lambda K/(1+\lambda)\right]\right)}\right],\tag{62}$$

where λ is the electron-phonon coupling constant, given by

$$\lambda = 2 \int_{0}^{\infty} \frac{d\omega}{\omega} \alpha^{2}(\omega) g(\omega); \qquad (63)$$

and the other quantities in (62) are defined by

$$\omega_{1 \circ g} = \frac{2}{\lambda} \int_{0}^{\infty} \frac{d\omega}{\omega} \ln \omega \alpha^{2}(\omega) g(\omega), \qquad (64)$$

$$C = \frac{4}{\lambda^{2}} \int_{0}^{\infty} d\omega_{1} \alpha^{2}(\omega_{1}) g(\omega_{1}) \ln \frac{\omega_{1}}{\omega_{1 \circ g}} \int_{0}^{\infty} d\omega_{2} \alpha^{2}(\omega_{2}) g(\omega_{2}) \left(\frac{1}{\omega_{2} + \omega_{1}} - \frac{1}{\omega_{2} - \omega_{1}}\right)$$

(65)
and
$$\mu^*$$
 is the Coulomb pseudopotential. For a suffi-
ciently narrow peak in the phonon state density, or in
the absence of phonon modes of greatly different fre-
quency, K becomes 1/2. In this case, expression (62)
for T_c is actually the same as the McMillan expression

for $T_{\rm c}$ is actually the same as the McMillan expression with the one modification that the Debye energy of the phonons is replaced by ω_{\log} :

$$T_{c} = \frac{\omega_{\log}}{1.45} \exp\left[-\frac{1+\lambda}{\lambda-\mu^{*}(1+0.5[\lambda/(1+\lambda)])}\right].$$
 (66)

If we consider a situation in which the function $\alpha^2(\omega)g(\omega)$ can be represented as several isolated peaks,

$$\alpha^{2}(\omega) g(\omega) = \sum_{i} \frac{\lambda_{i} \omega_{i}}{2} \delta(\omega - \omega_{i}), \qquad (67)$$

the logarithmic-average frequency ω_{\log} becomes

$$\omega_{\log} = \frac{\prod_{i} \omega_{i} \lambda_{i}}{\lambda}; \qquad (68)$$

where λ is the total coupling constant. It follows, in particular, from (68) that as some one of the frequencies ω_i tends toward zero the transition temperature

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should do so also. This result is obviously wrong, however, if only for the simple reason that Eqs. (62) and (66) themselves were derived under the assumption that all the frequencies ω_i satisfy the inequality $\omega_i > T_c$.

If the system contains low-frequency oscillation modes with $\omega_i \lesssim T_c$, these modes must be taken into account more carefully than in the derivation of (62) and (66). With this goal in mind, we write $\lambda(i\omega_n)$ as the sum of the two terms $\lambda_1(i\omega_n)$ and $\lambda_2(i\omega_n)$, where $\lambda_1(i\omega_n)$ is the contribution of the low-frequency modes. The following representation can be written for $\lambda_1(i\omega_n)$ in the case in which the corresponding frequencies ω_1 satisfy the inequality $\omega_1 \ll T_c$:

$$\lambda_{1}(i\omega_{n}) = \begin{cases} \frac{M(1)}{(2\pi T_{c}n)^{2}}, & n \neq 0, \\ \lambda_{1}, & n = 0. \end{cases}$$

Here we have introduced coupling constants for the coupling of the electrons with the low-frequency modes, λ_1 , defined in accordance with (63) by

$$\lambda_{1} = 2 \int_{0}^{\infty} \frac{d\omega_{1}}{\omega_{1}} \alpha^{2}(\omega_{1}) g(\omega_{1}),$$

and M(1) is the first moment of the function $\omega^2(\omega_1)g(\omega_1)$,

$$M(1) = 2 \int_{0}^{\infty} d\omega_{1} \omega_{1} \alpha^{2}(\omega_{1}) g(\omega_{1}).$$
 (69)

If we now substitute expressions for $\lambda_1(i\omega_n)$ into (60) and (61), which determine T_c , we easily see that the contribution from $\lambda_1(i\omega_n)$ cancels out completely for n = 0. The low-frequency modes have an effect in this case only through the quantity $M(1)/(2\pi T_c n)^2$. If we use representation (67) for $\alpha^2(\omega_1)g(\omega_1)$, we find the following for $\lambda_1(i\omega_n)$ for $n \neq 0$:

$$\lambda_1(i\omega_n) = \lambda_1 \frac{\omega_1^2}{(2\pi T_0 n)^2}.$$
 (70)

It can be seen from this expression that if the electronphonon coupling constant λ_1 remains constant or decreases as ω_1 tends toward zero then the low-frequency phonons will have no direct effect of any sort on T_c . If, on the other hand, λ_1 increases in accordance with $\lambda \approx 1/\omega_1^2$ as ω_1 tends toward zero, then M(1) remains finite, and the low-frequency phonons contribute to T_c even at $\omega_1 = 0$. This possibility has been pointed out elsewhere.⁶⁵ The behavior $\lambda \sim 1/\omega_1^2$ at small ω_1 , however, could hardly be given any physical meaning.

A more interesting possibility is the existence of solutions for the Éliashberg equations which have T_c above the typical phonon frequencies. This possibility was first pointed out by Allen and Dynes⁶⁶ and results from the existence at large λ of a finite ratio $M(1)/((2\pi T_c)^2 \approx 1)$. Here T_c is expressed in terms of M(1) as follows:

$$T_{\rm c} \approx \sqrt{\frac{M(1)}{(2\pi)^2}} = 0.159 \sqrt{M(1)}.$$

A more accurate calculation yields

$$T_{\rm c} = 0.1827 \sqrt{M(1)}.$$
 (71)

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TABLE II. Dependence of the coefficients in (74) on the Coulomb interaction. $^{67-69}$

μ*	α ₀		α1	a ₂₁		a22
$\mu^* = 0$ $\mu^* \neq 0$	*=0 0.12273 $-\frac{\alpha_0^9}{V_1+2.45\mu^*}$ $\alpha_1^9(1)$		$\begin{array}{c c c c c c c c c c c c c c c c c c c $		μ*)²	-0.2915 $\alpha_{22}^{0} (1+2.7 \ \mu^{*})^{2}$
μ •	μ • α ₃₁		a32			a ³³
μ* = 0 μ• ≠ 0	$-0.196 \\ \alpha_{31}^{0} (1+2.7 \mu^{*})^{3}$		$\begin{bmatrix} 0.615 \\ \alpha_{32}^{0} (1 + 2.7 \mu^{*})^{3} \end{bmatrix}$		0.420 α ₃₈ (1+2.7 μ*) ³	

Allen and Dynes⁶⁶ suggested combining Eqs. (66) and (71) in the $form^{2}$

$$\Gamma_{\rm e} = \frac{\omega_{\rm log}}{1.2} f_1 f_2 \exp\left[-\frac{1.0^{4} (1+\lambda)}{\lambda - \mu^{*} (1+0.62\lambda)}\right], \qquad (72)$$

where f_1 and f_2 are some empirically selected functions,

$$\begin{split} f_1 &= \left[1 \div \left(\frac{\lambda}{2.46 + 9.35 \mathrm{tr}^3} \right)^{3/2} \right]^{1/3} \,, \\ f_2 &= 1 \div \frac{\left[(\omega(1)/\omega_{\log}) - 1 \right] \lambda^2}{\lambda^2 + (1.82 \pm 11.5 \mathrm{tr}^3)^2 \, (\omega(1)/\omega_{\log})^2} \,. \end{split}$$

Here

 $\omega(1) = \frac{1}{\lambda} M(0),$ (73)

where M(0) is the zeroth moment of the function $\alpha^2(\omega)g(\omega)$.

A more systematic effort to derive an analytic expression for $T_{\rm c}$ for coupling constants $\lambda \approx 1$ was undertaken in Refs. 67-69, where it was suggested that $T_{\rm c}$ be written as a power series in $1/\lambda$:

$$T_{c} = A_{0} \left(1 + \frac{A_{1}}{\lambda} + \frac{A_{2}}{\lambda^{2}} + \frac{A_{3}}{\lambda^{3}} + \dots \right) = \alpha_{0} \left[M(1) \right]^{1/2} \left\{ 1 - \alpha_{1} \left(\frac{\omega(4)}{\omega(2)} \right)^{2} + \frac{1}{\lambda} + \left[\alpha_{21} \left(\frac{\omega(6)}{\omega(2)} \right)^{2} + \alpha_{22} \left(\frac{\omega(4)}{\omega(2)} \right)^{8} \right] \frac{1}{\lambda^{2}} + \alpha_{31} \left(\frac{\omega(8)}{\omega(2)} \right)^{8} + \alpha_{32} \frac{\omega^{4}(4) \omega^{4}(6)}{(6)^{10} (2)} + \alpha_{33} \left(\frac{\omega(4)}{\omega(2)} \right)^{12} \right] \frac{1}{\lambda^{3}} + \dots \right\}.$$
(74)

This expression can be derived in a straightforward way by substituting expansion (59), in powers of $\omega^2/(2\pi T_c)^2$, into (61). As a result, T_c depends on only the quantities λ and the average phonon frequencies $\omega(n)$, defined in terms of moments of the function $\alpha^2(\omega)g(\omega)M(n+1)$:

$$\omega(n) = \frac{1}{2} \left[M(n+1) \right]^{1/(n+1)}.$$
(75)

The moments themselves are defined as follows, by analogy with (63):

$$M(\omega) = 2 \int_{0}^{\infty} d\omega \, \omega^{n} \alpha^{2}(\omega) \, g(\omega) \,. \tag{76}$$

The coefficients α_{ij} are the same for all superconductors and are listed in Table II.

Calculations of T_c for real superconductors, through the use of the functions $\alpha^2(\omega)g(\omega)$ from Refs. 55 and 56, lead to good agreement with the experimental data (Table III). For metals with large values of λ , however, the convergence radius for this series depends strongly on the shape of the spectrum; for mercury ($\lambda = 1.62$),

TABLE III.

Material	λ:	7 (McM)	7(62) c	$\gamma_{c}^{(72)}$	T _c ⁽⁷¹⁾	T _c ⁽⁷⁷⁾	T _s expt
$\begin{array}{c} Hg \\ in \\ Pb \\ Sn \\ Ta \\ Tl_{n,5}Bi_{0,1} \\ Pb_{0,45}Bi_{0,55} \\ Pb_{n,45}Bi_{0,55} \\ Pb_{n,45}Bi_{0,55} \end{array}$	$\begin{array}{c} 1.62\\ 0.804\\ 1.55\\ 0.716\\ 0.692\\ 0.795\\ 0.78\\ 2.03\\ 2.13\\ 2.58\end{array}$	3.53 3.27 6.48 3.81 4.58 2.21 2.16 6.85 6.80 4.66	2.91 2.97 5.99 3.55 4.39 2.11 1.99 6.09 5.97 3.81	$\begin{array}{c} 4.14\\ 3.44\\ 7.26\\ 3.98\\ 4.75\\ 2.32\\ 2.26\\ 8.20\\ 8.20\\ 8.28\\ 6.18\end{array}$	<pre>< 0 6.78 7.47 4.84 3.78 2.95 2.99 8.52 8.72 7.03</pre>	5 32 3.60 7.43 3.07 3.45 2.40 2.29 8.50 8.69 6.89	4.19 3.40 7.23 3.72 4.47 2.39 2.30 8.45 8.95 7 00

for example, the value calculated for T_c from (74) becomes negative. The method of the Pade approximant can be used to improve the convergence of this series; as a result we find⁷⁰

$$T_{c} = A_{0} \frac{1 + \frac{1}{\lambda} \left(A_{1} + \frac{A_{3} - A_{1}A_{2}}{A_{1}^{2} - A_{2}} \right)}{1 + \frac{1}{\lambda} \frac{A_{3} - A_{1}A_{2}}{A_{1}^{2} - A_{2}} + \frac{1}{\lambda^{2}} \frac{A_{1}^{2} - A_{1}A_{3}}{A_{1}^{2} - A_{2}}},$$
(77)

where the coefficients A_i are given by (74). Results calculated from (74) and (77) with the help of the functions $\alpha^2(\omega)g(\omega)$ constructed from the tunneling characteristics^{55,56} are shown in Table III; we see from these results that expression (77) is in good agreement with experiment over a broad range of λ ($\lambda > 0.7$). Shown for comparison here are some results calculated from (72) and (62) and from the McMillan expression ("McM").

It can be seen from this analysis and the numerical calculations that the effort to derive an analytic expression for T_c which holds over the entire λ range and for any function $\alpha^2(\omega)g(\omega)$ has not been successful. At best it is possible to write expressions like (62), (74), or (77). In general, if the function $\alpha^2(\omega)g(\omega)$ is known there is no particular need to derive analytic expressions for T_c ; modern computers can easily find T_c directly from Eqs. (60) and (61). On the other hand, analytic expressions are more convenient for analyzing the dependence of T_c on the properties of the normal metal, especially when certain moments of the function $\alpha^2(\omega)g(\omega)$ are known experimentally but not the function itself.

Working from the expressions derived for $T_{\rm e}$, we can attempt to answer the following questions:

1) Are there any internal restrictions on the possible values of T_c^{max} embodied in the Éliashberg equations?

2) Which types of functions $\alpha^2(\omega)g(\omega)$ are preferable for the existence of high values of T_c ?

It would be more systematic, however, to seek answers to these questions by the method developed by Bergman and Rainer.⁷¹ They calculated⁷¹ the functional derivative $\delta T_c/\delta \alpha^2(\omega)g(\omega)$, which shows which frequencies are the most effective for increasing T_c . This function tends toward zero as $\omega \rightarrow 0$, indicating that phonons with very low energies are ineffective. At higher frequencies the function $\delta T_c/\delta \alpha^2(\omega)g(\omega)$ falls off as $1/\omega$ and has a maximum at $\omega \approx 2\pi T_c$. It follows, in particular, that the most preferable function $\alpha^2(\omega)g(\omega)$ from the standpoint of high values of T_c would be of the form

$$\alpha^{2}(\omega) g(\omega) = A\delta(\omega - \omega_{0}),$$

where $\omega_0 \approx 2\pi T_c$. Whether the function $\alpha^2(\omega)g(\omega)$ in a

²⁷Allen and Dynes⁸⁶ used numerical coefficients slightly different from those in Eq. (66), which was derived analytically by Karakozov *et al.*⁶³

real metal could actually be of this form or one close to it is a question which can, of course, be resolved only by studying the particular properties of the metal in question.

Bergman and Rainer's method⁷¹ can also be applied to the problem of identifying possible restrictions on the value of T_c which arise in the Éliashberg equations. Leavens⁷² has shown that for the values of T_c given by Eqs. (60) and (61) there is an upper limit

$$T_c^{\max} < a(n) \omega(n), \tag{78}$$

where the a(n) are certain constants, and the $\omega(n)$ are determined by (75) and (76). To calculate the constants a(n) we need an expression for the functional derivatives $\delta/T_c/\delta G(n, \omega)$ where $G(n, \omega) = \omega^n \alpha^2(\omega)g(\omega)$. This expression can easily be derived by the method of Bergman and Rainer.⁷¹ A specific calculation carried out by Leavens⁷² shows that a(n) is finite for only the zeroth and first moments. For $n \ge 2$, Leavens found $a(n) = \infty$, so that condition (78) leads to no restrictions on T_c . For the first two moments, on the other hand, the following inequalities arise:

$$T_{c}^{\max} \leqslant T_{c}^{0} = 0.231 \int_{0}^{\infty} d\omega \alpha^{2} (\omega) g(\omega)$$

$$T_{c}^{\max} \leqslant T_{c}^{1} = 0.258 \sqrt{\int_{0}^{\infty} d\omega \omega \alpha^{2} (\omega) g(\omega)}$$
(79)

As Leavens has shown, the first of these limitations is the more stringent if λ is not very large:

$$\frac{T_{\rm c}^{\rm o}}{T_{\rm c}^{\rm l}} \leqslant 0,633 \sqrt{\lambda}.$$

Table IV shows experimental values of T_c , along with the values of T_c^0 and T_c^1 calculated for several superconductors. We see from this table that for the most real superconductors the experimental values of T_c are not greatly different from their maximum possible values. To learn whether these maximum values can be attained in some way or other, and to determine whether it is possible in general to produce superconducting metals with T_c significantly higher than 22.4 K (T_c^1 for tantalum), we will need a microscopic study of the function $\alpha^2(\omega)g(\omega)$ and of its relationship with the properties of the metal.

b) Spectral density of the electron-phonon interaction; dependence of T_c on the properties of the normal metal

To derive an exact microscopic expression for the function $\alpha^2(\omega)g(\omega)$ will require a systematic analysis of superconductivity equations (46) and (48) with a thorough account of the electron-electron Coulomb interaction. Unfortunately, this problem has not yet been

TABLE IV.

Material	λ	T _c ^{expt}	r_c^0	T_{c}^{1}
Hg In Ph Ta T1 Pb _{0.7} Bi _{0.7} Pb _{0.43} Bi _{0.43} Pb _{0.43} Bi _{0.65}	1.6 0.805 1.55 0.72 0.69 0.795 2.01 2.12 2.59	4.19 3.40 4.23 3.72 4.47 2.36 8.45 8.45 8.95 7.0	7.1 7.35 10.8 9.17 11.1 5.36 12.0 12.3 11.4	-11.3 11.6 14.6 18.8 22.4 10.43 14.5 14.7 13.8

solved—for superconductors or even normal metals. Working in second-order perturbation theory in the weak electron-ion pseudopotential, Scalapino⁴⁹ derived the following microscopic expression for the function $\alpha^2(\omega)g(\omega)$:

$$\alpha^{2}(\omega) g(\omega) = \left(\int \frac{d^{2}\mathbf{p}}{v_{\mathrm{P}}}\right)^{-1} \int \frac{d^{2}\mathbf{p}}{v_{\mathrm{P}}} \int \frac{d^{2}\mathbf{p}'}{v_{\mathrm{F}}'} \sum_{\lambda} |g_{\mathbf{p},\mathbf{p}',\lambda}|^{2} \delta(\omega - \omega_{\mathbf{p}-\mathbf{p}',\lambda}).$$
(80)

The integration here is over the Fermi surface, v_F is the electron velocity on this surface, $\omega_{p-p',\lambda}$ is the frequency of phonons with momentum p-p', and $g_{p,p',\lambda}$ is the matrix element of the electron-phonon interaction. For simple metals $g_{p,p',\lambda}$ can be written in the form

$$g_{\mathbf{p},\mathbf{p}',\lambda} = i \sqrt{\frac{N}{2M\omega_{\mathbf{p}-\mathbf{p}',\lambda}}} \mathbf{e}_{\mathbf{p}-\mathbf{p}',\lambda}(\mathbf{p}-\mathbf{p}') \widetilde{V}_{1e}(\mathbf{p},\mathbf{p}').$$
(81)

Here $e_{p^-p',\lambda}$ is the phonon polarization, and $V_{i*}(\mathbf{p},\mathbf{p}')$ is the screened electron-ion pseudopotential, given by

$$\widetilde{V}_{ie}(\mathbf{p}, \mathbf{p}') = \frac{\Gamma_{\mathbf{p}\mathbf{p}}(\mathbf{p} - \mathbf{p}') \, V_{ie}(\mathbf{p} - \mathbf{p}')}{Z_{C} \varepsilon_{e1}(\mathbf{p} - \mathbf{p}', 0)}, \qquad (82)$$

where $\Gamma_{pF}(p-p')$ is the vertex function of the Coulomb interaction, Z_C is the renormalization of the electron Green's function due to the Coulomb interaction, $\varepsilon_{el}(p-p', 0)$ is the dielectric permittivity of the electrons, and $V_{ie}(p-p')$ is the bare electron-ion pseudopotential. At small momentum transfers we have the following important relation:

$$\lim_{q \to 0} \frac{\Gamma_{pF}(q) V_{le}(q)}{Z_{C} \varepsilon_{e1}(q, 0)} = \frac{V_{le}(q)}{\varepsilon_{e1}(q, 0)} = -\frac{Z}{N(0)} , \qquad (83)$$

where Z is the valence of the ion and N(0) is the electron state density on the Fermi surface. Equation (83) shows that at small momentum transfers the renormalizations of the screened pseudopotential due to the vertex function and Z_c cancel out completely. This circumstance means that a calculation of the function $\alpha^2(\omega)g(\omega)$ must systematically incorporate both these functions $[\Gamma_{pF}(q)$ and $Z_{c}]$. Such calculations, however, are extremely complicated, even when we take into account the fact that $\Gamma_{pF}(\mathbf{q})$, $\varepsilon_{el}(\mathbf{q}, 0)$ and Z_{c} are determined by the properties of a homogeneous electron gas. For the transition metals one can derive for the function $\alpha^2(\omega)g(\omega)$ expressions which are formally very similar to expressions (80)-(82). In this case, however, the functions $\Gamma_{pF}(\mathbf{p},\mathbf{p}')$, $\varepsilon_{el}(\mathbf{p},\mathbf{p}',0)$ and $Z_{C}(\mathbf{p},\mathbf{p}')$ must be determined not only for a homogeneous electron gas but also for a system of interacting Block electrons; the problem of calculating the function $\alpha^2(\omega)g(\omega)$ becomes even more complicated.

All the existing calculations of the function $\alpha^2(\omega)g(\omega)$ have actually been based on the simple single-particle approach to a system of Bloch electrons, rather than a systematic analysis of the interacting electrons. A Schrödinger equation with a periodic potential $V(\mathbf{r})$ is used to determine the electron band structure. The electron-phonon interaction matrix element $g_{\mathbf{p},\mathbf{p}',\mathbf{\lambda}}$ is determined from the gradient of this crystal potential:

$$g_{\mathbf{p}_{\mathbf{p}_{\mathbf{p}_{\mathbf{p}_{\mathbf{p}_{\mathbf{p}_{\mathbf{p}_{\mathbf{p}_{\mathbf{p}_{\mathbf{p}_{\mathbf{j}_{\mathbf{\lambda}}}}}}}}=-i\sqrt{\frac{N}{2M\omega_{\mathbf{p}-\mathbf{p}_{\mathbf{j}_{\mathbf{\lambda}}}\lambda}}}e_{\mathbf{p}-\mathbf{p}_{\mathbf{j}_{\mathbf{\lambda}}}\lambda}\langle\psi_{\mathbf{p}}^{*}|\nabla V(r)|\psi_{\mathbf{p}_{\mathbf{j}_{\mathbf{\lambda}}}}\rangle.$$
(84)

For simple metals the parameters of the crystal potential or, more precisely, pseudopotential, are usually chosen by fitting the theoretical calculations of the shape of the Fermi surface to experimental data. Either a single plane wave^{73,74} or a sum of several plane waves,^{75,76} is used for the electron wave functions which appear in the expression for the matrix element $g_{\mathbf{p},\mathbf{p}',\lambda}$. The phonon frequencies are calculated by a force-constant method. The functions $\alpha^2(\omega)g(\omega)$ calculated in this manner agree fairly well with the experimental data at a qualitative level. Quantitatively, the agreement of the calculated and experimental curves of $\alpha^2(\omega)g(\omega)$ is not very good.

For transition metals, Gaspari and Gyorffy⁷⁷ have developed a procedure for calculating M(1), which is the first moment of the function $\alpha^2(\omega)g(\omega)$ and which is usually denoted by $N(0)\langle I^2 \rangle / M$, where M is the ion mass. Gaspari and Gyorffy showed that this quantity can be expressed in terms of the phase shifts in the scattering of an electron by the crystal potential and in terms of the electron state density on the Fermi surface, N(0). The phase shifts and N(0) can be calculated by any standard method for band-structure calculations.^{3,8,32} This procedure was subsequently generalized to calculate not only M(1) but also the function $u^2(\omega)g(\omega)$ itself.⁷⁷⁻⁸⁰ As for simple metals, the calculated functions $\alpha^2(\omega)g(\omega)$ are in a reasonable qualitative agreement with the experimental data, while the quantitative agreement leaves something to be desired. A detailed analysis of the nature of the discrepancies between the calculated and experimental values of $\alpha^2(\omega)g(\omega)$ has been carried out for simple metals⁷⁶ and also for transition metals.⁸⁰ It follows from the results that the available methods for calculating $\alpha^2(\omega)g(\omega)$ cannot be expected to reveal the superconductivity properties of metals more accurately than in order of magnitude.

Glotzl *et al.*⁸⁰ believe that the primary reason for the inaccuracy of the calculations in the pseudopotential approach to simple metals is the definition of the pseudopotential $V_i(\mathbf{p}, \mathbf{p'})$: Band-structure calculations can give this quantity only at p - p' = K, where K is a reciprocal-lattice vector. To calculate $\alpha^2(\omega)g(\omega)$, on the other hand, requires knowledge of the function $V_{is}(\mathbf{p}, \mathbf{p'})$ for arbitrary differences $\mathbf{p} - \mathbf{p'}$. This will require making assumptions of some sort regarding the nature of this function, since it cannot be calculated analytically from (82). We should add that there is yet another fundamental reason for inaccuracies in the existing calculations of the function $\alpha^2(\omega)g(\omega)$ for simple metals: Expression (81) for the matrix element $g_{p,p',\lambda}$ is correct in second order in the bare pseudopotential $V_{ie}(\mathbf{p},\mathbf{p'})$, and only in this order is it a matrix element of the gradient of the screened pseudopotential $\tilde{V}_{i,\mathbf{r}}(\mathbf{r})$ in (82), which determines the band structure of the metal. In general, on the other hand, in the many-particle approach and in an interacting system of electrons and ions, the electron-phonon interaction matrix element cannot be represented as the gradient of some potential.

To prove this assertion we write the electron-phonon interaction matrix element for Bloch electrons in the form^{81,84}

$$g_{\mathbf{p}, \mathbf{p}', \lambda} = -i \sqrt{\frac{N}{2M\omega_{\mathbf{q}, \lambda}}} A_{\mathbf{p}, \mathbf{p}'} (\mathbf{q} + \mathbf{K}) e_{\mathbf{q}, \lambda}$$

$$\propto \sum_{\mathbf{K}'} \tilde{e}_{el}^{-1} (\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', 0) (\mathbf{q} + \mathbf{K}') V_{le} (\mathbf{q} + \mathbf{K}'),$$
(85)

$$A_{\mathbf{p},\mathbf{p}'}\left(\mathbf{q}+\mathbf{K}\right) = \int \mathrm{d}\mathbf{r} \, u_{\mathbf{p}'}^{*}\left(\mathbf{r}\right) e^{-i(\mathbf{q}+\mathbf{K})\mathbf{r}} u_{\mathbf{p}}\left(\mathbf{r}\right) \tag{86}$$

is the scattering form factor for the Bloch electrons, and $u_n(\mathbf{r})$ is the Bloch part of the wave function,

$$\Psi_{\mathbf{p}}(\mathbf{r}) = u_{\mathbf{p}}(\mathbf{r}) e^{i\mathbf{p}\mathbf{r}}.$$

The quantity $\tilde{\varepsilon}_{\mathbf{e}\mathbf{l}}^{-1}(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', 0)$ is the effective dielectric permittivity of the Bloch electrons; it incorporates the effects of the renormalization due to the vertex function. It is an extremely complicated matter to find $\tilde{\varepsilon}_{\mathbf{e}\mathbf{l}}^{-1}(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', 0)$ explicitly, but the result is not very important for our purposes. The only important thing is the following circumstance: For Bloch electrons, $\tilde{\varepsilon}_{\mathbf{e}\mathbf{l}}^{-1}(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', 0)$ is a matrix in the space of the reciprocal-lattice vectors **K** and **K'**. For a homogeneous electron gas, on the other hand, we would have $\tilde{\varepsilon}^{-1}(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', 0) = \delta_{\mathbf{K}\mathbf{K}} \tilde{\varepsilon}^{-1}(\mathbf{q} + \mathbf{K})$. It is then easy to see that for free electrons the expression for $g_{\mathbf{p},\mathbf{p}',\lambda}$ can be rewritten in the form of (84), where $\nabla V(r)$ is

$$\nabla V(\mathbf{r}) = \sum_{\mathbf{K}} \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} e^{-i(\mathbf{q}+\mathbf{K})\mathbf{r}} (\mathbf{q}+\mathbf{K}) \widetilde{\epsilon_{\mathrm{e}1}} (\mathbf{q}+\mathbf{K}, 0) V_{\mathrm{le}} (\mathbf{q}+\mathbf{K}). \tag{87}$$

In the general case of Bloch electrons, we denote the vector within the summation over \mathbf{K}' as $\mathbf{W}(\mathbf{q} + \mathbf{K})$,

$$W(\mathbf{q} + \mathbf{K}) = \sum_{\mathbf{K}'} \tilde{\varepsilon}_{el}^{-1} (\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', \mathbf{0}) (\mathbf{q} + \mathbf{K}') V_{1e} (\mathbf{q} + \mathbf{K}'), \quad (88)$$

and we resolve it into its components parallel and perpendicular to the vector (q + K). The expression for $g_{\mathbf{p},\mathbf{p}',\lambda}$ can then be rewritten as

$$g_{\mathbf{p},\mathbf{p}',\lambda} = -i \sqrt{\frac{N}{2M\omega_{\mathbf{q},\lambda}}} \mathbf{e}_{\mathbf{q},\lambda} [\langle \psi_{\mathbf{p}'}^{\bullet} | \nabla V(\mathbf{r}) \psi_{\mathbf{p}} \rangle + \langle \psi_{\mathbf{p}'}^{\bullet} | \operatorname{rot} M(\mathbf{r}) | \psi_{\mathbf{p}} \rangle.$$
(89)

The first term in square brackets here derives from the component of W(q + K) parallel to q + K and is given by

$$\boldsymbol{\nabla} V(\mathbf{r}) = \sum_{\mathbf{K}} \int \frac{\mathrm{d}\mathbf{q}}{(2\pi)^3} \, \mathbf{e}^{-i(\mathbf{q}+\mathbf{K})\mathbf{r}} \left(\mathbf{q}+\mathbf{K}\right) \widetilde{\widetilde{\varepsilon}_{e1}}^{-1} \left(\mathbf{q}+\mathbf{K}, \ 0\right) V_{1e} \left(\mathbf{q}+\mathbf{K}\right), \left(\mathbf{90}\right)$$

where

$$\widetilde{\widetilde{\varepsilon}}_{e1}^{-1}(\mathbf{q}+\mathbf{K},\ \mathbf{0}) = \sum_{\mathbf{K}'} \widetilde{\varepsilon}^{-1}(\mathbf{q}+\mathbf{K},\ \mathbf{q}+\mathbf{K}',\ \mathbf{0}) \frac{(\mathbf{q}+\mathbf{K})(\mathbf{q}+\mathbf{K}')}{|\mathbf{q}+\mathbf{K}|^2} \frac{V_{1e}(\mathbf{q}+\mathbf{K}')}{V_{1e}(\mathbf{q}+\mathbf{K})}.$$
(91)

Correspondingly, the second term can be written

$$\operatorname{rot} \mathbf{M} (\mathbf{r}) = \sum_{\mathbf{K}} \int \frac{d\mathbf{q}}{(2\pi)^3} e^{-i(\mathbf{q}+\mathbf{K})\mathbf{r}} \\ \times \left[\mathbf{W} (\mathbf{q}+\mathbf{K}) - (\mathbf{q}+\mathbf{K}) \widetilde{\widetilde{\mathbf{e}}}_{\mathbf{c}1}^* (\mathbf{q}+\mathbf{K}, 0) \, \mathcal{V}_{1\mathbf{c}} (\mathbf{q}+\mathbf{K}) \right].$$
(92)

We note that the first term in (89) corresponds to the rigid-ion approximation, which is the one customarily used to calculate the function $\alpha^2(\omega)g(\omega)$. The total crystal potential is used as the function $V(\mathbf{r})$. Glötzl *et al.*⁸⁰ have pointed out that it is most likely this circumstance which is responsible for the difference between the theoretical and experimental values of $\alpha^2(\omega)g(\omega)$. It can be seen from (89)–(92) that the rigid-ion approximation is indeed completely unjustified. The existence of terms of the type rot $\mathbf{M}(\mathbf{r})$ in the change in the crystal potential due to phonons has been mentioned in several cases.⁸²⁻⁸⁴ Unfortunately, nothing approaching a detailed quantitative analysis of rot $\mathbf{M}(\mathbf{r})$ and of its contribution to the electron-phonon interaction has so far been carried out.

The conclusion that the rigid-ion approximation is inadequate does not, of course, mean that all the microscopic calculations of the function $\alpha^2(\omega)g(\omega)$ and also of the electron-phonon coupling constants λ which have been carried out must be discarded as worthless. On the contrary, several of these calculations have revealed some extremely interesting qualitative results, e.g., on the nature of the differences between the constant λ in superconducting and nonsuperconducting carbides and nitrides of transition metals⁸⁵ and the tendencies in the behavior of T_c in the series of 4d transition metals⁸⁶ (see Refs. 3, 8, and 50 for more details). It is clear, however, that it will not be possible to construct a rigorous quantitative theory for the electronphonon interaction without a systematic analysis of the role played by the transverse effects associated with the function rotM.

Returning to possible restrictions on T_c imposed by the solution of the Éliashberg equations, we note that the only restrictions which are important in this theory are those associated with inequalities (79). Since there are no restrictions of any sort on the function $\alpha^2(\omega)g(\omega)$ or its moments in the Éliashberg equations themselves, these equations actually impose no restrictions on T_c either. On the other hand, it follows from the microscopic definition of the function $\alpha^2(\omega)g(\omega)$ that the moments of the function cannot be arbitrarily large for any metal. In particular, an expression for the first moment M(1) for simple metals can be derived in second order in V_{ie} in the rigid-ion approximation:

$$M(\mathbf{1}) = \frac{N(\mathbf{0})\langle I^2 \rangle}{M} = \frac{\mathbf{1}.5\mathbf{1}}{r_{\rm s}} \overline{\widetilde{V}_{\rm 1e}^2(\mathbf{q})} \,\Omega_{\rm p1}^2. \tag{93}$$

Here r_s is the compressibility of the electron gas, Ω_{pl} is the ion plasma frequency, and $\overline{\tilde{V}_{is}^2(\mathbf{q})}$ is the mean square screened pseudopotential, given by

$$\overline{\widetilde{V}_{1e}^{2}(\mathbf{q})} = \frac{1}{\widetilde{V}_{1e}^{2}(0)} \int_{0}^{2k_{\mathrm{F}}} \frac{dqq^{3}}{(2k_{\mathrm{F}})^{2}} \widetilde{V}_{1e}^{2}(\mathbf{q}).$$
(94)

In simple metals, $\overline{\tilde{V}_{ie}^2(\mathbf{q})}$ is quite small ($\approx 0.01-0.05$), so that M(1) is also small in comparison with the square of the ion plasma frequency. Yin et al.⁸⁹ derived corresponding restrictions on $N(0)\langle I^2 \rangle$ for the case of transition metals also, using a technique developed by Pettifor^{87,88} for evaluating the matrix elements of the electron-phonon interaction. Unfortunately, by themselves these restrictions are not much help for producing superconducting metals and alloys with the highest possible values of T_c . Returning to (93) we see that the primary restriction on M(1) is imposed by the small values of $\overline{V}_{ie}^2(\mathbf{q})$, but in the approximations used in deriving (93) the quantity $\overline{\tilde{V}_{ie}^2(\mathbf{q})}$ is determined primarily by the value of the bare pseudopotential $V_{i,e}(\mathbf{q})$, which is a property of the particular atom and cannot be arbitrarily changed. Furthermore, the quantities r_s and Ω_{nl} are determined by the valence and the equilibrium volume of the metal. The equilibrium volume depends in turn on the properties of the pseudopotential. It is thus clear that in order to reach an understanding of the factors which restrict the values of M(1) and thus $T_{\rm c}$ we need a self-consistent solution of the overall problem of calculating the electron and phonon properties of metals.

by posed by a note that in this theory 5d transition metals. The results derived in the singleparticle approximation cannot, of course, be relied upon completely, especially since the quantity $\langle \Omega^2 \rangle_0$ remains completely undetermined in this approach, but it can be shown rigorously⁵⁰ in the adjubatic many-partic

mains completely undetermined in this approach, but it can be shown rigorously⁵⁰ in the adiabatic many-particle approximation that an expression analogous to (95) actually exists for the average phonon frequencies. It is also possible to derive for $\left< \Omega^2 \right>_0$ an exact expression in terms of the matrix of the inverse dielectric permittivity of the Bloch electrons. Unfortunately, no specific calculations of $\langle \Omega^2 \rangle_0$ have so far been carried out. The so-called band contribution to the phonon frequencies, on the other hand, which is related to the contribution of the function $\alpha^2(\omega)g(\omega)$, has been calculated in the rigid-ion model for several transition metals and alloys.^{91,92} These studies have shown that it is the term caused by the electron-phonon interaction which can explain the various anomalies in the phonon spectra of the transition metals and alloys studied in Refs. 91 and 92. It follows from (95), even without reference to the exact definition of $\langle \Omega^2 \rangle_0$, that the values of M(1) for any metal are restricted by

$$M(1) \leqslant \frac{\langle \Omega^2 \rangle_{\theta}}{(4/5) \epsilon_{\rm F} N(0)} , \qquad (96)$$

for otherwise a lattice instability would occur in the system. It is of course clear that condition (96) is in a sense excessive. In a real system we could hardly have the mean square phonon frequencies vanishing. A lattice instability usually occurs upon the softening of some particular wave branch $\omega_{\lambda}(\mathbf{q})$ and in a small region of the wave vectors q. This circumstance—the interrelationship between the phonon frequencies and the matrix element of the electron-phonon interaction—thus cannot give us any general restrictions on T_c . All it can do is reemphasize the need for specific, exact calculations of all the properties of metals.

6. CONCLUSION

Let us briefly summarize the results of this review.

1. It has been shown that a necessary condition for the effectiveness of a superconductivity mechanism, i.e., for the existence of reasonably high values of T_c (at least $T_c > 1$ K), is that the total static dielectric permittivity of the system be negative. It has also been shown that this condition can be fully satisfied in real metallic systems, and no contradiction of any sort

A far more helpful factor restricting the values of M(1) in metals was pointed out by Gomersall and Gyorffy.⁹⁰ Taking the single-particle approach to the theory of the electron-phonon interaction, they showed that M(1) determines the renormalization of the average phonon frequencies of the metal due to the electron-phonon interaction:

$$\langle \omega^2 \rangle = \langle \Omega^2 \rangle_0 - \frac{4}{5} \epsilon_F N (0) M (1), \qquad (95)$$

where $\varepsilon_{\rm F}$ is the Fermi energy, and N(0) is the electron

state density on the Fermi surface. Using this expres-

Gyorffy⁹⁰ reached the conclusion that the mean square

frequency for 5d metals having a bcc structure vanishes

at n = 4.7 and 6.8 electrons per atom—corresponding to

the actual boundary between bcc and hcp lattices in the

sion for the 5d transition metals, Gomersall and

arises with either causality or the stability of the system.

2. Furthermore, this condition clearly holds in all real superconductors because of the ion contribution (or, equivalently, because of the electron-phonon interaction) to the total dielectric permittivity of the crystal. The physical reasons for a negative sign of the total static dielectric permittivity in electron-ion systems are the strong local-field effects in the system of point ions, because of which the electron-phonon interaction is stronger in absolute value than the direct Coulomb repulsion of electrons in such systems. In the simplest case of a quasi-isotropic system, the condition under which the total static dielectric permittivity is negative is the same as the superconductivity condition derived some time ago by Kulik⁴⁰:

 $C_{ac} < C_{jellium}$;

where C_{ac} is the actual sound velocity in the metal, and $C_{jellium}$ is the sound velocity in the jellium model.

3. For nonphonon superconductivity mechanisms to be effective, the electron part of the static dielectric permittivity must take on negative values $[\varepsilon_{e_1}(\mathbf{q}, 0) < 0]$. We have shown here, for the particular case of a onecomponent electron plasma on an incompressible substrate, that such a situation is also completely possible. In particular, the inequality $\varepsilon_{el}(q, 0) < 0$ holds in this model over a very broad range of electron-gas densities, $6 < r_s < 75$, and no instabilities of any sort occur in the electron gas itself up to $r_s \approx 75$. In metallic systems, however, because of the coupling of the electrons with the phonon system of the crystal, negative values of $\varepsilon_{ei}(\mathbf{q}, \mathbf{0})$ may cause a phonon-frequency instability. In particular, the phonon frequencies are expressed in terms of ε_{el} as follows in the jellium model, which treats the ions as a homogeneous, continuous medium:

$$\omega^2 \left(\mathbf{q} \right) = \frac{\Omega_{\mathrm{pl}}^2}{\varepsilon_{\mathrm{el}} \left(\mathbf{q}, 0 \right)} \,.$$

It can be seen from this expression that negative values of $\varepsilon_{el}(\mathbf{q}, 0)$ in such a system unavoidably lead to a phonon instability. In real crystals, in which the phonon frequencies are more complicated functions of the static electron dielectric permittivity, it is quite possible that the inequality $\varepsilon_{el}(\mathbf{q}, 0) < 0$ may hold. In this case, the question of the coexistence of a nonphonon superconductivity mechanism $[\varepsilon_{el}(\mathbf{q}, 0) < 0]$ and a stable phonon spectrum must be resolved through a specific, exact calculation of the properties of the system.

4. The static electron dielectric permittivity can have negative values only in systems with a strong exchangecorrelation interaction. It then follows, in particular, that we must go beyond the scope of the weak-coupling approximation to deal with the problem of high-temperature superconductivity. An equation derived for determining T_c with allowance for strong-coupling effects shows that the condition for the effectiveness of a superconductivity mechanism $[\varepsilon_{tot}(\mathbf{q}, 0) < 0]$ which had been derived earlier in the weak-coupling approximation is also a necessary condition in the strong-coupling case. To determine whether this is also a sufficient condition, i.e., whether $T_{\rm c}$ is actually high in a system with a negative static dielectric permittivity, will require finding an exact solution of this equation. Unfortunately, no systematic theory of this type is presently available.

5. In the superconductivity theory based on the Eliashberg equations there are no restrictions of any sort on the possible values of $T_{\rm c}$. A joint analysis of the superconductivity equations and the dynamic equations of the lattice, however, shows that such restrictions actually do exist and result from the effect of the electron-phonon interaction (more precisely, the adiabatic electronion interaction) on the phonon frequencies. Unfortunately, again in this case we lack a systematic theory at present which would yield anything approaching rigorous estimates of the maximum possible values of T_c or which would predict practical measures for developing materials with high values of T_c . On the other hand, the outlook here is quite good because of the development of methods for microscopic calculations of the electron and phonon properties of metals.

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- ¹W. A. Little, Phys. Rev. Ser. A 134, 1416 (1964).
- ²V. L. Ginzburg, Zh. Eksp. Teor. Fiz. 47, 2318 (1964) [Sov. Phys. JETP 20, 1549 (1964)]; Phys. Lett. 13, 101 (1964).
- ³V. L. Ginzburg and D. A. Kirzhnits (editors), Problema vysokotemperaturnol sverkhprovodimosti (The Problem of High-Temperature Superconductivity), Nauka, Moscow, 1977.
- ⁴O. V. Dolgov, D. A. Kirzhnitz, and E. G. Maksimov, Rev. Mod. Phys. 53, 81 (1981).
- ⁵O. V. Dolgov and E. G. Maksimov, Usp. Fiz. Nauk 135, 441 (1981) [Rev. Mod. Phys. 53, 81 (1981)].
- ⁶M. L. Cohen and P. W. Anderson, in: AIP Conference on d-and f-Band Superconductivity (AIP Conf. Proc.), New York, 1972, p. 17.
- ⁷D. A. Kirzhnits, E. G. Maksimov, and D. I. Khomskil, J. Low Temp. Phys. 10, 79 (1973).
- ⁸S. V. Vonsovskil, Yu. A. Izyumov, and É. É. Kurmaev, Sverkhprovodimost' perekhodnykh metallov, ikh splavov i soedinenil (Superconductivity of the Transition Metals, Their Alloys, and Their Compounds), Nauka, Moscow, 1977.
- ⁹N. F. Berk and J. R. Schrieffer, Phys. Rev. Lett. 17, 433 (1966).
- ¹⁰L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred, Fizmatlit, Moscow, 1959 (Electrodynamics of Continuous Media, Addison-Wesley, Reading, Mass., 1960).
- ¹¹D. Pines and P. Nozières, The Theory of Quantum Liquids, Benjamin, New York, 1966 (Russ. transl. Mir, Moscow, 1967).
- ¹²P. Martin, Phys. Rev. 161, 143 (1967).
- ¹³D. A. Kirzhnits, Usp. Fiz. Nauk **119**, 357 (1976) [Sov. Phys. Usp. **19**, 530 (1976)].
- ¹⁴O. V. Dolgov and E. G. Maksimov, Pis'ma Zh. Eksp. Teor. Fiz. 28, 3 (1978) [JETP Lett. 28, 1 (1978)].
- ¹⁵G. I. Skanavi, Fizika diélektrikov (Physics of Dielectrics), Gostekhizdat, Moscow-Leningrad, 1947.
- ¹⁶I. E. Tamm, Osnovy teorii élektrichestva (Basic Theory of Electricity), Nauka, Moscow, 1977.

- ¹⁷J. C. Slater, Quantum Theory of Molecules and Solids, Vol. 3. Insulators, Semiconductors, and Metals, McGraw-Hill, New York, 1967 (Russ. transl. Mir, Moscow, 1969).
- ¹⁸M. Baus and J. P. Hansen, Phys. Rep. 59, 1 (1980).
- ¹⁹V. D. Gorobchenko and E. G. Maksimov, Usp. Fiz. Nauk 130, 65 (1980) [Sov. Phys. Usp. 23, 35 (1980)].
- ²⁰S. N. Rashkeev, Diplomnaya rabota (Thesis), MFTI, Moscow, 1981.
- ²¹D. Ceperley, Phys. Rev. **B18**, 3126 (1978).
- ²²D. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).
- ²³C. M. Care and N. H. March, Adv. Phys. 24, 101 (1975).
- ²⁴F. Bloch, Z. Phys. 61, 206 (1930).
- ²⁵J. C. Kimball, Phys. Rev. A7, 1648 (1973).
- ²⁶A. A. Kugler, J. Stat. Phys. **12**, 35 (1975).
- ²⁷J. T. Devrecse, F. Brosens, and L. F. Lemmens, Phys. Rev. **B21**, 1363 (1980).
- ²⁸V. D. Gorobchenko and V. Kon, Zh. Eksp. Teor. Fiz. 80, 754 (1981) [Sov. Phys. JETP 53, 381 (1981)].
- ²⁹A. K. Rajagopal, Adv. Chem. Phys. 41, 59 (1980).
- ³⁰H. L. Von Barth, J. Phys. C 5, 1625 (1972).
- ³¹O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).
- ³²Y. I. Moruczzi, J. F. Janak, and A. K. Williams, in: Calculated Electronic Properties of Metals, Pergamon, New York, 1978.
- ³³A. K. Rajagopal, S. P. Singhal, M. Benerjee, and J. C. Kimball, Phys. Rev. B **17**, 2262 (1978).
- ³⁴J. P. Perdew and T. Datta, Phys. Status Solidi **B102**, 283 (1980).
- ³⁵H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. 58, 1200 (1980).
- ³⁶C. A. Kukkonen and A. W. Overhauser, Phys. Rev. **B20**, 550 (1979).
- ³⁷O. V. Dolgov, Avtoreferat kandidatskoĭ dissertatsii (Author's Abstract, Candidate's Dissertation), MFTI, Moscow, 1978.
- ³⁸Yu. V. Kopaev, Tr. FIAN SSSR 86, 3 (1975).
- ³⁹D. Pines, Elementary Excitations in Solids, Benjamin, 1963 (Russ. transl. Mir, Moscow, 1965).
- ⁴⁰I. O. Kulik, Zh. Eksp. Teor. Fiz. **47**, 2159 (1964) [Sov. Phys. JETP **20**, 1450 (1964)].
- ⁴¹V. P. Silin, Zh. Eksp. Teor. Fiz. 38, 977 (1960) [Sov. Phys. JETP 11, 703 (1960)].
- ⁴²P. S. Zyryanov, V. I. Okulov, and V. P. Silin, Zh. Eksp. Teor. Fiz. 58, 1295 (1970) [Sov. Phys. JETP 31, 696 (1970)].
- ⁴³V. M. Kantorovich, Zh. Eksp. Teor. Fiz. 45, 1638 (1963)
 [Sov. Phys. JETP 18, 1125 (1964)].
- ⁴⁴B. T. Geilikman, Usp. Fiz. Nauk 88, 327 (1966) [Sov. Phys. Usp. 9, 142 (1966)].
- ⁴⁵É. A. Pashitskii, Zh. Eksp. Teor. Fiz. 54, 2387 (1968) [sic].
- ⁴⁶J. Ihm, M. L. Cohen, and S. G. Tuan, Phys. Rev. **B23**, 3258 (1981).
- ⁴⁷E. G. Maksimov, Zh. Eksp. Teor. Fiz. **69**, 2236 (1975) [Sov. Phys. JETP **42**, 1138 (1975)].
- ⁴⁸J. W. Garland, Phys. Rev. 153, 460 (1966).
- ⁴⁹D. J. Scalapino, in: Superconductivity (ed. R. D. Parks), Vol. 1, M. Dekker, New York, 1969, p. 449.
- ⁵⁰P. B. Allen, in: Dynamical Properties for Solids (eds. G. K. Norton and A. A. Maradudin), Vol. 3, North-Holland, Amsterdam, 1980.
- ⁵¹G. M. Éliashberg, Zh. Eksp. Teor. Fiz. 38, 966 (1960) [Sov. Phys. JETP 11, 696 (1960)].
- ⁵²G. M. Éliashberg, Zh. Eksp. Teor. Fiz. **39**, 1437 (1960) [Sov. Phys. JETP **12**, 1000 (1960)].
- ⁵³G. Grimvall, Phys. Scripta 4, 63 (1976).
- ⁵⁴É. G. Batyev, Fiz. Tverd. Tela (Leningrad) 6, 3554 (1964)
 [Sov. Phys. Solid State 6, 2846 (1965)].
- ⁵⁵J. M. Rowell, W. L. McMillan, and R. C. Dynes, Preprint Bell Lab., Pt. I, 1971; Preprint Bell Lab., Pt. II, 1977.
- ⁵⁶W. L. McMillan and J. M. Roweel, cited in Ref. 49.

- ⁵⁷S. I. Vedeneev, Preprint No. 193, P. N. Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow, 1977.
- ⁵⁸A. A. Galkin, A. I. D'yachenko, and V. M. Svistunov, Zh. Eksp. Teor. Fiz. **66**, 2262 (1974) [Sov. Phys. JETP **39**, 1115 (1974)].
- ⁵⁹I. K. Yanson, Zh. Eksp. Teor. Fiz. 66, 1035 (1974) [Sov. Phys. JETP 39, 506 (1974)].
- ⁶⁰A. N. Omel'yanchuk, I. O. Kulik, and R. I. Shekhter, Fiz. Nizk. Temp. 3, 1543 (1977) [Sov. J. Low Temp. Phys. 3, 740 (1977)].
- ⁶¹C. R. Leavens and I. P. Carbotte, Can. J. Phys. **49**, 724 (1971).
- ⁶²M. V. Medvedev, É. A. Pashitskiĭ, and Yu. S. Pyatiletov, Zh. Eksp. Teor. Fiz. 65, 1186 (1973) [Sov. Phys. JETP 38, 587 (1974)].
- ⁶³A. E. Karakozov, E. G. Maksimov, and S. A. Mashkov, Zh. Eksp. Teor. Fiz. 68, 1937 (1975) [Sov. Phys. JETP 41, 971 (1975)].
- ⁶⁴W. L. McMillan, Phys. Rev. 167, 331 (1968).
- ⁶⁵L. B. Dubovskil and A. N. Kozlov, Zh. Eksp. Teor. Fiz.
 68, 2224 (1975) [Sov. Phys. JETP 41, 1113 (1975)].
- ⁶⁶P. B. Allen and R. C. Dynes, Phys. Rev. B12, 905 (1975).
- ⁶⁷Wu Hang-Sheng and Ji Guang-da, Acta Phys. Sinica 27, 746 (1978).
- ⁶⁸Ji Guang-da and Cai Jun-dao, Acta Phys. Sinica 28, 571 (1979).
- ⁶⁹Ji Guang-da and Cai Jun-dao, Acta Phys. Sinica 28, 853 (1979).
- ⁷⁰O. V. Dolgov, V. S. Karakhtanov, and E. G. Maksimov, in: XXI Vsesoyuznoe soveshchanie po fizike nizkikh temperatur: Tezisy dokladov (Abstracts, Twenty-First All-Union Conference on Low-Temperature Physics), Part 1, Khar'kov, 1980, p. 4.
- ⁷¹G. Bergman and D. Rainer, Z. Phys. 263, 59 (1973).
- ⁷²C. R. Leavens, J. Phys. F 7, 1911 (1977).
- ⁷³J. P. Carbotte and R. C. Dynes, Phys. Rev. **172**, 476 (1968).
- ⁷⁴B. Haymann and J. P. Carbotte, Phys. Status Solidi 656, 439 (1974).
- ⁷⁵ P. G. Tomlinson and J. P. Carbotte, Phys. Rev. B 13, 4739 (1976).
- ⁷⁶P. G. Tomlinson and J. C. Swihart, Phys. Rev. B 18, 1867 (1979).
- ⁷⁷G. D. Gaspari and B. L. Gyorffy, Phys. Rev. Lett. 28, 801 (1974).
- ⁷⁸B. L. Harmon and S. K. Sinha, Phys. Rev. B 16, 3919 (1977).
- ⁷⁹W. H. Butler, H. G. Smith, and Q. Wakabayashi, Phys. Rev. Lett. **33**, 1004 (1977).
- ⁸⁰O. Glötzl, D. Rainer, and H. R. Schober, Z. Phys. B35, 317 (1979).
- ⁸¹A. E. Karakozov and E. G. Maksimov, Zh. Eksp. Teor.
- Fiz. 74, 681 (1978) [Sov. Phys. JETP 47, 358 (1978)].
- ⁸²A. J. Pindor, Solid State Commun. 12, 153 (1973).
- ⁸³M. A. Ball, J. Phys. C 10, 4921 (1977).
- ⁸⁴W. E. Pickett, J. Phys. C 12, 1491 (1979).
- ⁸⁵B. M. Klein and D. A. Papaconstantopoulos, Phys. Rev. 32, 1193 (1974).
- ⁸⁶W. H. Butler, Phys. Rev. B 15, 5267 (1977).
- ⁸⁷D. G. Pettifor, J. Phys. F 7, 613 (1977).
- ⁸⁸D. G. Pettifor, J. Phys. 7, 1009 (1977).
- ⁸⁹Yin Dao-lo, Zhang Li-Yuan, and Dai Yauandong, Acta. Phys. Sinica 28, 841 (1979).
- ⁹⁰I. R. Gomersall and B. L. Gyorffy, Phys. Rev. Lett. 33, 1286 (1974).
- ⁹¹C. M. Varma and W. Weber, Phys. Rev. B19, 6142 (1979).
- ⁹²K. Terakura, J. Phys. C 11, 469 (1978).

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