Nonphonon mechanism for superconductivity and static screening in paramagnetic metals

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The static screened Coulomb interaction in metals is investigated in connection with the problem of high temperature superconductivity. The density functional method is used to show that this interaction is weakly attractive in strongly paramagnetic metals. Analysis of the conditions for the stability of a solid against electron- and spin-density fluctuations and for the stability of the crystal lattice shows that none of the instabilities rules out the existence of materials in which the static electron–electron force is attractive.

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INTRODUCTION

A nonphonon mechanism for superconductivity was proposed in 1964 by Little[1] and Ginzburg[2] as a means for radically raising the critical temperature (T_c).[1)] During the subsequent years serious attempts were made to realize such a mechanism in specific form, but no reliable practical results have yet been achieved. This is largely due to the difficulty of producing the required materials, such as systems of ultrathin films or easily polarizable quasi-one-dimensional substances. Theoretical studies, too, are made difficult by the complexity of the objects, and their results depend to a great extent on the physical model chosen to represent the selected material and sometimes turn out to be contradictory (see, e.g., Refs. 6–9). Moreover, there is no clarity even in the fundamental questions of the problem: a) whether attraction between the electrons can be assured by a nonphonon mechanism alone, and b) whether a system with such an interaction would be stable. The present work was undertaken in an attempt to analyze these questions in the weak coupling approximation without resorting to specific models but taking the spatial nonuniformity of the systems into account.

1. CONDITIONS FOR THE EXISTENCE OF A NONPHONON SUPERCONDUCTIVITY MECHANISM

In analyzing the possibility of an exciton superconductivity mechanism it is useful to disregard the effect of the electron-phonon interaction on T_c, taking the polarization of the electron subsystem alone into account in the electron-electron interaction. Then in the weak coupling approximation, or more accurately, to the lowest order in the screened Coulomb interaction V_{scr}, the equation for T_c will have the form[5]

$$\begin{aligned}
&\Phi_n = -\sum_{n'} \mathrm{th}(\xi_{n'}/2T_c)\, U_{nn'}\Phi_{n'}/2\xi_{n'},\\
&U_{nn'} = \sum_{\mathbf{G},\mathbf{G}'} \rho^{*}_{nn'}(\mathbf{k}+\mathbf{G})\rho_{nn'}(\mathbf{k}+\mathbf{G}')\Big\{V_0(\mathbf{k}+\mathbf{G})\delta_{\mathbf{G},\mathbf{G}'}\\
&+\frac{2}{\pi}\int_0^{\infty} d\omega\, \mathrm{Im}[V_{scr}(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}',\omega)]/(\omega+|\xi_n|+|\xi_{n'}|)\Big\},\\
&\rho_{nn'}(\mathbf{k}+\mathbf{G}) = \langle n|e^{i(\mathbf{k}+\mathbf{G})r}|n'\rangle,\ V_0(\mathbf{k}+\mathbf{G}) = 4\pi e^2/|\mathbf{k}+\mathbf{G}|^2,
\end{aligned} \tag{1}$$

where ξ_n is the energy of the one-electron state $|n\rangle$ reckoned from the Fermi level, $\mathbf{k}$ is the wave vector in the first Brillouin zone, and $\mathbf{G}$ is a reciprocal lattice vector. We assume for simplicity that the ions from a regular crystal lattice, but this limitation has no fundamental significance. To simplify Eq. (1) one usually averages its kernel over the equal-energy surfaces. The solution to the averaged equation is known[5]:

$$T_c = 1.14\omega_0 \exp\{1/\chi(0)\}\theta(-\chi(0)), \tag{2}$$

$$\chi(\xi) = \overline{U}(\xi,0) + \frac{1}{2}\int_{-\infty}^{\infty} d\xi' \ln\frac{|\xi'|}{\omega_0}\frac{d}{d|\xi'|}[\overline{U}(\xi,\xi')\chi(\xi')]. \tag{2a}$$

For the systems under consideration, in which the electron-phonon interaction is turned off, it is natural to assume that the kernel $\overline{U}(\xi,\xi')$ will vary appreciably from $\xi,\xi' \sim \bar{\xi} \sim 1$ eV. Other energy scales differing substantially from $\bar{\xi}$ can manifest themselves only in the case of a material having a very specific band structure (see, e.g., Ref. 5). Setting $\omega_0 = \bar{\xi}$ and solving Eq. (2a) by successive approximations, we easily find the solution to the lowest order in $\overline{U}$:

$$\begin{aligned}
\chi(0) \approx \overline{U}(0,0) = \sum_{\substack{n,n'\\ \mathbf{G},\mathbf{G}'}} &\delta(\xi_n)\delta(\xi_{n'})\rho^{*}_{nn'}(\mathbf{k}+\mathbf{G})\rho_{nn'}(\mathbf{k}+\mathbf{G}')\\
&\times V_{scr}(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}',\omega=0)\Big/\sum_n \delta(\xi_n).
\end{aligned} \tag{3}$$

In obtaining the last equation we used the spectral representation of the screened Coulomb interaction:

$$V_{scr}(\omega=0) = V_0 + \frac{2}{\pi}\int_0^{\infty} d\omega'\, \mathrm{Im}\{V_{scr}(\omega')/\omega'\}.$$

It follows from Eq. (3) that if the static screened interaction $V_{scr}(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}') \equiv V_{scr}(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}',\omega=0)$ is a positive definite matrix in $\mathbf{G}$ and $\mathbf{G}'$ for all $\mathbf{k}$, then the coupling constant $\overline{U}(0,0)$ will be positive for arbitrary $\rho_{nn'}$. Thus, for the exciton superconductivity mechanism to work the matrix must have negative eigenvalues. This condition is somewhat approximate. The exact condition for exciton superconductivity is that the kernel of Eq. (1), or if we go beyond the weak coupling approximation, the kernel of the analogous equation for T_c, have at least one negative eigenvalue. In most cases the two conditions are virtually equivalent. However, in the case of strong anisotropy or if several energy scales are significant in $\overline{U}(\xi,\bar{\xi})$, when the approximate condition is inapplicable, exciton superconductivity may arise, in principle, even if the matrix V_{scr} is positive definite (a detailed discussion of this question will be found in Refs. 5 and 10). These factors alone, however, are hardly

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sufficient for the achievment of high critical temperatures, and it is desirable to have a static electron-electron attraction.

2. IS A STATIC SCREENED ELECTRON-ELECTRON INTERACTION ALWAYS REPULSIVE?

It is convenient to use the density functional method in investigating static screening in metals. Since the temperature dependence of the electron-electron interaction is very weak we need consider only the case $T = 0$ °K. It has been shown[11-13] that the energy of an electron gas in a fixed external field (in our case this is the field of the nuclei) is uniquely determined by the electron- and spin-density distributions $n(\mathbf{r})$ and $\tilde{n}(\mathbf{r})$, respectively. For a nonmagnetic material the energy is minimum for the equilibrium values $n = n_0$ and $\tilde{n} = 0$ of the densities, and for small deviations from equilibrium we have[11-13]

$$E[n,\tilde{n}] = E[n_0,0] + \frac{1}{2}\sum_{\mathbf{G},\mathbf{G}'}\int d\mathbf{k}[-\delta n(\mathbf{k}+\mathbf{G})\delta n(\mathbf{k}+\mathbf{G}')\chi^{-1}(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}') + \tilde{n}(\mathbf{k}+\mathbf{G})\tilde{n}(\mathbf{k}+\mathbf{G}')\chi_m^{-1}(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}')] \quad \ldots \quad (4)$$

Here $\delta n = n - n_0$ and $\tilde{n} = n_\uparrow - n_\downarrow$, while $\chi \equiv \delta n/\delta U_{ext}$ and χ_m are the electron and spin susceptibilities, respectively, calculated at $n = n_0$ and $\tilde{n} = 0$ (U_{ext} is the external field). To simplify the calculations we assume that the system has cubic symmetry and neglect the spin-orbit interaction.

It is usual to separate the total electron energy into the energy E_0 of the noninteracting electrons, the Hartree energy

$$E_H = \frac{1}{2}\int d\mathbf{k}\sum_{\mathbf{G}} n^2(\mathbf{k}+\mathbf{G})V_0(\mathbf{k}+\mathbf{G})$$

and the exchange-correlation energy E_{xc}. It follows immediately from (4) that

$$\chi^{-1}(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}') = -\delta^2 E/\delta n(\mathbf{k}+\mathbf{G})\delta n(\mathbf{k}+\mathbf{G}') = -\delta^2(E_0+E_H+E_{xc})/\delta n\delta n = -(\pi_0^{-1}+V_0-I_e),$$
$$\chi_m^{-1} = -\delta^2 E/\delta\tilde{n}\delta\tilde{n} = \pi_0^{-1} - I_m, \quad (5)$$

where we have introduced the polarization operator

$$\pi_0(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}') = [\delta^2 E_0/\delta n(\mathbf{k}+\mathbf{G})\delta n(\mathbf{k}+\mathbf{G}')]^{-1} = [\delta E_0/\delta\tilde{n}\delta\tilde{n}]^{-1}$$
$$= \sum_{n_1 n_2} V^{-1}\langle n_1|e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}|n_2\rangle\langle n_2|e^{-i(\mathbf{k}+\mathbf{G}')\mathbf{r}'}|n_1\rangle\theta(\xi_{n_1})\theta(-\xi_{n_2})/(\xi_{n_1}-\xi_{n_2}) \quad (5a)$$

and the exchange-correlation interactions

$$I_e(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}') = -\delta^2 E_{xc}/\delta n(\mathbf{k}+\mathbf{G})\delta n(\mathbf{k}+\mathbf{G}'), \quad I_m = -\delta^2 E_{xc}/\delta\tilde{n}\delta\tilde{n}. \quad (5b)$$

Using (5), we can express the static screened Coulomb interaction directly in terms of π_0, V_0, and I_e:

$$V_{scr} = V_0 + V_0\chi V_0 = (\pi_0^{-1}-I_e)(\pi_0^{-1}-I_e+V_0)^{-1}V_0. \quad (6)$$

If we neglect exchange and correlation effects in (6), putting $I_e = 0$, we obtain the well known equation for V_{scr} in the random phase approximation (RPA):

$$V_{scr}^{RPA} = (V_0^{-1}+\pi_0)^{-1}.$$

It is not difficult to see that V_{scr}^{RPA} is a positive definite matrix. In fact, the polarization operator π_0 is a nonnegative definite matrix, since for an arbitrary function φ we have

$$\sum_{\mathbf{G}\mathbf{G}'}\varphi^*(\mathbf{k}+\mathbf{G})\pi_0(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}')\varphi(\mathbf{k}+\mathbf{G}') = V^{-1}\sum_{n_1,n_2}\theta(\xi_{n_1})\theta(-\xi_{n_2})\cdot\left|\sum_{\mathbf{G}}\varphi(\mathbf{k}+\mathbf{G})\langle n_1|e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}|n_2\rangle\right|^2/(\xi_{n_1}-\xi_{n_2}) \geqslant 0.$$

The unscreened Coulomb interaction

$$V_0(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}') = \delta_{\mathbf{G},\mathbf{G}'}\cdot 4\pi e^2/|\mathbf{k}+\mathbf{G}|^2$$

is also a nonnegative definite matrix ($V_0 \to 0$ as $|\mathbf{G}| \to \infty$). For exciton superconductivity, however, the region $|\mathbf{G}| \to \infty$ is of no interest, it being quite sufficient to consider only a region $|\mathbf{G}| < G_0$, where G_0 is an arbitrarily large but finite positive number. With this limitation the matrix V_0 will be positive definite. Of course the sum of a positive definite matrix (V_0^{-1}) and a nonnegative definite matrix (π_0) is a positive definite matrix, and the reciprocal of a positive definite matrix is also positive definite. Hence V_{scr}^{RPA} is a positive definite matrix, and within the limitations of the RPA, exciton superconductivity is impossible or very weak (the RPA is exact for a high-density electron gas).

Taking account of the exchange and correlation effects, which are not present in the RPA, complicates the situation. From the condition that the electron energy be minimum at $n = n_0$ and $\tilde{n} = 0$ it follows that the matrices

$$\delta^2 E/\delta n\delta n = -\chi^{-1} = \pi_0^{-1} + V_0 - I_e \text{ and } \delta^2 E/\delta\tilde{n}\delta\tilde{n} = \chi_m^{-1} = \pi_0^{-1} - I_m$$

must be positive definite. Hence, as is evident from (6), V_{scr} can have negative eigenvalues only if the matrix $\pi_0^{-1} - I_e$ has them. To clarify the sign of this matrix we express the matrix in terms of χ_m^{-1}.

Let us introduce the matrix Δ:

$$\Delta(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}') \equiv I_e - I_m = -\delta^2 E_{xc}/\delta n_\uparrow\delta n_\downarrow = -\delta^2 E_c/\delta n_\uparrow(\mathbf{k}+\mathbf{G})\delta n_\downarrow(\mathbf{k}+\mathbf{G}'), \quad (7)$$

which depends only on the correlation energy E_c, since for the exchange energy, which is due to the interaction of electrons with parallel spins, we have $\delta^2 E_x/\delta n\,\delta n = 0$. Then

$$\pi_0^{-1} - I_e = \chi_m^{-1} - \Delta.$$

Let us consider a paramagnetic material that is close to the transition to the magnetic state, i.e., which is nearly unstable against spin density fluctuations. In this case at least one eigenvalue of χ_m^{-1}, say the s-th one, must be close to zero. Choosing a basis in which the matrices χ_m^{-1} and Δ are both diagonal,[2)] we find

$$(\pi_0^{-1}-I_e)_s = (\chi_m^{-1}-\Delta)_s \approx -\Delta_s. \quad (8)$$

It is evident from (8) that the matrix $\pi_0^{-1} - I_e$ for an almost magnetic material that has a positive definite matrix Δ must have at least one negative eigenvalue. Now by diagonalizing $\pi_0^{-1} - I_e$ and χ simultaneously, we easily see that the matrix V_{scr} must have the same number of negative eigenvalues as $\pi_0^{-1} - I_e$. The fact that V_{scr} can have negative eigenvalues in the paramagnetic phase even when Δ is positive definite is very important for nonphonon superconductivity, since, as a rule, superconductivity and magnetism exclude each other.

It is evident from definition (7) that in the Hartree-Fock approximation, in which $E_c = 0$, the matrix Δ is also identically zero; within the limitations of this approx-

imation, therefore, V_{scr} can have negative eigenvalues only in the magnetic state. This fact has been discussed in Refs. 15 and 16.

For a more detailed study of Δ with the effect of antiparallel correlations taken into account it is expedient to begin with the case of a uniform electron gas, since that is the model that has now been most thoroughly investigated. In this case all the matrices are diagonal in the momentum representation, because of the spatial uniformity. For example, $\Delta(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}')=\Delta(Q)\delta_{G,G'}$, where $Q=|\mathbf{k}+\mathbf{G}|$. In the long-wavelength limit $Q\to 0$ in the region $r_s \leq 9.0$ of metallic densities we have[17]

$$\Delta(Q=0)=(2/3\pi^2)^{1/3}n[0.036+1.36/(1+10r_s)+0.621/(r_s+11.4)], \quad (9)$$

where $n=(4\pi r_s^3/3)^{-1}$ is the density of the electron gas. Similar expressions have been obtained in Refs. 12 and 18.[3)] Using the method of Ref. 20 for the short-wavelength limit $Q\to\infty$, we obtain

$$\Delta(Q\to\infty)\to 2[1-g_{\uparrow\downarrow}(0)]V_0(Q\to\infty)/3. \quad (10)$$

Here $g_{\uparrow\downarrow}(0)$ is the pair distribution function for electrons with antiparallel spins located at one point in coordinate space. As a distribution function, $g_{\uparrow\downarrow}(0)$ is less than unity, so we have $\Delta(Q)>0$ in the limit of large wave vectors. The Geldart-Taylor interpolation formula[21] can be used to find Δ in the intermediate region, and it turns out to be greater than zero for all Q (Fig. 1). The same result was obtained in Ref. 22 by the density functional method. Thus, for a uniform electron gas, Δ is a positive definite matrix.

The exchange-correlation interactions for a nonuniform electron gas unfortunately still remain poorly investigated. In the simplest local-density approximation,[12,17] I_e, I_m, and Δ represent point interactions. For example:

$$\Delta(\mathbf{r},\mathbf{r}')=\int d\mathbf{k}\sum_{G,G'}\Delta(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}')e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}e^{-i(\mathbf{k}+\mathbf{G}')\mathbf{r}'}$$
$$=\delta(\mathbf{r}-\mathbf{r}')\Delta(r_s(\mathbf{r})), \quad (11)$$

where $\Delta[r_s(\mathbf{r})]$ is given by Eq. (9) with $r_s(\mathbf{r})=[4\pi n(\mathbf{r})/3]^{-1/3}$. This approximation is exact for a nonuniform electron gas in the long-wavelength limit, and it may be expected to give I_e, I_m, and Δ correctly for $Q\leq k_F$. Despite its simplicity, the local-denstiy approximation can be used for fairly accurate calculations of many elastic and magnetic properties of metals,[23,24] as well as of the spectra of isolated atoms.[17] It is easy to see that in this approximation Δ is diagonal in the coordinate representation and has only positive eigenvalues.

The fact that Δ is a positive definite matrix in the electron-gas theories under consideration is hardly accidental. The matrix $\delta^2E_c/\delta n_\uparrow(\mathbf{r})\delta n_\downarrow(\mathbf{r}')\equiv -\Delta(\mathbf{r},\mathbf{r}')$ represents the interaction of a spin-up electron at $\mathbf{r}$ with the spin-down correlation hole (electron deficiency) produced by it at $\mathbf{r}'$. By its physical nature, the interaction of an electron with a hole is attractive, i.e., Δ should be positive definite. In view of the lack of more complete information on the exchange-correlation effects, we shall assume in what follows that Δ is always positive definite.

It was shown above that if Δ is positive definite, then for materials close to the transition to the spin-ordered state V_{scr} must have negative eigenvalues. It is easy to estimate the influence of this effect on the superconductivity, since in the region of interest to us near the magnetic transition we have $\chi_m^{-1} \ll V_0$, while $\Delta \ll V_0$ according to (9). Then

$$V_{scr}=(\chi_m^{-1}-\Delta)(\chi_m^{-1}-\Delta+V_0)^{-1}V_0\approx\chi_m^{-1}-\Delta. \quad (12)$$

To obtain a numerical estimate of the coupling constant, we use the expressions for χ_m^{-1} and Δ in the long-wavelength limit:

$$\bar{U}(0,0)=N(E_F)\langle\langle V_{scr}\rangle\rangle\approx N(E_F)[\pi_0^{-1}(0,0)-I_m(\bar{r}_s)-\Delta(\bar{r}_s)], \quad (13)$$

where I_m and Δ are taken in the local-density approximation (11) and $\bar{r}_s$ is the effective distance between electrons. Introducing the gain factor $\alpha_m=[1-I_m(\bar{r}_s)N(E_F)]^{-1}$ i.e., the factor by which exchange and correlation increase the spin susceptibility, and noting that $\pi_0(0,0)=N(E_F)$, we rewrite (13) in the following more convenient form:

$$\bar{U}(0,0)\approx 1-N(E_F)I_m(\bar{r}_s)(1+\Delta/I_m)=\alpha_m^{-1}[1-\Delta(\bar{r}_s)(\alpha_m-1)/I_m(\bar{r}_s)]. \quad (14)$$

The results of calculating $\bar{U}(0,0)$ with formula (14) for several strongly paramagnetic transition metals are given in Table I where, because of the nonuniform distribution of d electrons, we have used $r_0/2$ or r_0 for $\bar{r}_s$ (r_0 is the average distance between valence electrons in the metal). The greatest possible negative value of the coupling constant $\bar{U}(0,0)=-\Delta/I_m$, which is reached in the limit $\alpha_m\to+\infty$, is shown in Fig. 2 as a function of $\bar{r}_s$. The data show that appreciable electron-electron attraction is possible only when $\bar{r}_s \gtrsim 1.5$ and $\alpha_m \gtrsim 10$, the attraction certainly being small in other cases.

It is important to emphasize that according to the above investigation of the screening process in a nonuniform electron gas, there can be electron-electron attraction in a paramagnetic material only if the material is close to the magnetic transition point. The above estimates thus not only demonstrate the possibility of electron-electron attraction, but also indicate the existence of a definite limit to the magnitude of the coupling constant in the exciton superconductivity mechanism.

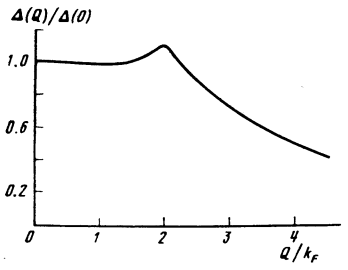

FIG. 1. Δ as a function of Q for $r_s=4$ according to the Geldart-Taylor interpolation formula.

TABLE I.

Metal	r_0, a_B	α_m	$\bar{U}(0,0)$ $(\bar{r}_s=r_0)$	$\bar{U}(0,0)$ $(\bar{r}_s=r_0/2)$
Pd	1.34	5 [25] 10 [24]	−0.028 −0.156	+0.037 −0.084
V	1.64	5 [25] 10 [25]	−0.061 −0.193	+0.024 −0.098
Sc	2.32	4 [26]	−0.052	+0.047

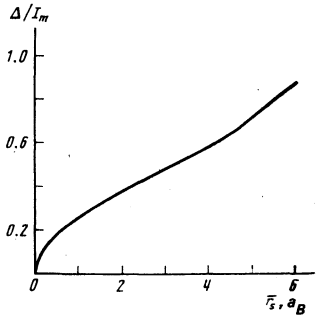

FIG. 2. Δ/I_m as a function of the average distance between electrons $\bar{r}_s$ according to Ref. 17.

3. THE POSSIBILITY OF A STATIC ELECTRON-ELECTRON ATTRACTION FROM THE POINT OF VIEW OF THE STABILITY OF SOLIDS

In the preceding section it was shown that for almost magnetic materials V_{scr} has negative eigenvalues. For such a material actually to exist, it must be stable. However, it has been stated[27] that a solid body must be unstable if $V_{tot.scr} < 0$, and the more so if $V_{scr} < 0$ ($V_{tot.scr}$ is the total screened Coulomb interaction, which includes not only the screening due to polarization of the electron subsystem, but also that due to polarization of the ion subsystem). This question generated lively discussion.[28-30] In particular, it was shown[29] that exchange of transverse phonons leads to negative values of $V_{tot.scr}$ for a number of nontransition metals. A consistent treatment of the stability of uniform systems against electron-density fluctuations[30] revealed that this sort of stability is not determined by the sign of $V_{tot.scr}$ or V_{scr}, but by the sign of the electron susceptibility. In this section we shall generalize the approach of Ref. 30 to spatially nonuniform systems, and shall use this approach to show that, while the stability of a solid against electron- and spin-density fluctuations and the stability of the crystal lattice do impose certain limitations on the strength of the electron-electron attraction, these stabilities are by no means determined by the sign of V_{scr}.

In analyzing the stability conditions we shall start with the fact that a system will be stable or metastable in a given state provided that state corresponds to an absolute or relative minimum of the energy. The energy will be minimum with respect to electron-density variations provided $\delta E(n)/\delta n|_{n=n_0} = 0$ and matrix $\delta^2 E(n)/\delta n \delta n|_{n=n_0} = -\chi^{-1}$ is positive definite. The first of these relations is the condition that the energy have an extremum and determines the possible equilibrium density n_0; the second is the condition that the energy extremum be a minimum. It is easy to trace the relation between V_{scr} and χ^{-1} is we rewrite Eq. (6) in the form $V_{scr} = (-\chi^{-1} - V_0)(-\chi)V_0$. Making use of the fact that V_0 is positive definite, we choose a basis in which both V_0 and χ are diagonal. Then for the s-th eigenvalue we have

$$V_{scr\,s} = (-\chi_s^{-1} - V_{0s})(-\chi_s)V_{0s}.$$

It is immediately evident from this relation that $V_{scr\,s} < 0$ when $-\chi_s^{-1} < V_{0s}$, and that at an instability point $V_{scr\,s} \to -\infty$ as $-\chi_s^{-1} \to +0$. Thus, instability of the system against electron-density fluctuations imposes no limitations on the strength of the electron-electron attraction.

The analogous conditions for the energy of a paramagnet to be minimum with respect to spin-density fluctuations are that $\delta E/\delta\tilde{n}|_{\tilde{n}=0}$ vanish and that the matrix

$$\delta^2 E/\delta\tilde{n}\delta\tilde{n}|_{\tilde{n}=0} = \chi_m^{-1}$$

be positive definite.

The relation between spin instability and the sign of the eigenvalues of V_{scr} has already been thoroughly discussed in Sec. 2. Here there remains only to note that the sign of the eigenvalues of V_{scr} changes in the paramagnetic phase before the appearance of spin instability and that the electron-electron attraction in the paramagnetic state is limited since for an arbitrary eigenvalue (say the s-th) we have $V_{scr\,s} > -(\Delta(V_0 - \Delta)^{-1}V_0)_s \approx -\Delta_s$.

The lattice instability is the most complicated to treat. The energy of the system has a minimum for given positions of the ions provided $\delta E/\delta u_i^\alpha|_{u_i=0} = 0$ and the force matrix

$$A^{\alpha\beta}(R_i - R_j) = \delta^2 E/\delta u_i^\alpha \delta u_j^\beta|_{u_i - u_j = 0}$$

is positive definite ($\mathbf{u}_i$ is the displacement vector of the i-th ion from its equilibrium position). It follows from the last condition that the squares of the lattice vibrational frequencies, the $\omega_\lambda^2(\mathbf{k})$, which are the eigenvalues of the dynamical matrix, i.e., of the Fourier transform of the force matrix, must be positive, and the frequencies themselves must be real. If any of the eigenvalues were negative the corresponding phonon frequencies would be imaginary, and the crystal lattice would be destroyed by the exponential growth of the amplitude of these vibrations.

There is a direct relation[31] between the dynamical matrix and the ion-ion interaction v (for simplicity we consider only the case of a Bravais lattice):

$$D^{\alpha\beta}(\mathbf{k}) = \frac{1}{\Omega}\sum_{\mathbf{G},\mathbf{G}'}[(\mathbf{k}+\mathbf{G})^\alpha(\mathbf{k}+\mathbf{G}')^\beta v(\mathbf{k}+\mathbf{G}, \mathbf{k}+\mathbf{G}') - G^\alpha G'^\beta v(\mathbf{G}, \mathbf{G}')],$$

$$v(\mathbf{k}+\mathbf{G}, \mathbf{k}+\mathbf{G}') = Z^2 V_0(\mathbf{k}+\mathbf{G})\delta_{\mathbf{G},\mathbf{G}'} + V_{ei}(\mathbf{k}+\mathbf{G})\chi(\mathbf{k}+\mathbf{G}, \mathbf{k}+\mathbf{G}')V_{ei}(\mathbf{k}+\mathbf{G}').$$

The ion-ion interaction will be equal to $Z^2 V_{scr}$ only if we have $V_{ei} = -ZV_0$ for the electron-ion interaction V_{ei} (Z is the valence of the ions and Ω is the atomic volume). For ions having filled electron shells, v is more repulsive since $V_{ei} > -ZV_0$ on account of the orthogonalization repulsion of the valence electrons from the region of the ion core. We note that the lattice stability depends not only on the ion-ion interaction, but also on the relative positions of the ions. If we expand v in eigenfunctions:

$$v(\mathbf{k}+\mathbf{G}, \mathbf{k}+\mathbf{G}') = \sum_s \varphi_s^*(\mathbf{k}+\mathbf{G})\varphi_s(\mathbf{k}+\mathbf{G}')v_s(\mathbf{k}),$$

it is directly evident from the expression

$$\omega_\lambda^2(\mathbf{k}) = \frac{1}{M\Omega}\sum_s\left[\left|\sum_{\alpha,\mathbf{G}} e_\lambda^\alpha(\mathbf{k})(\mathbf{k}+\mathbf{G})^\alpha\varphi_s(\mathbf{k}+\mathbf{G})\right|^2 v_s(\mathbf{k}) - \left|\sum_{\alpha,\mathbf{G}} e_\lambda^\alpha(\mathbf{k})G^\alpha\varphi_s(\mathbf{G})\right|^2 v_s(0)\right] \quad (15)$$

for the squared frequency of the λ-th vibrational mode that the stability of the lattice is determined not only by the sign of v_s, but also by the vectors $\mathbf{G}$ [$\mathbf{e}_\lambda \mathbf{k}$) is the polarization vector and M is the ion mass]. It is clear

from what has been said that there can be no direct relation between the sign of the eigenvalues of V_{scr} and the stability of the lattice, since the ion-ion interaction almost always differs from Z^2V_{scr} and the phonon frequencies also depend on the structure of the lattice. To make this discussion specific we shall examine two simple special cases.

In the "jellium" model the ions are replaced by a uniform positively charged medium in which only longitudinal vibrations with $\mathbf{e}(\mathbf{k})\|\mathbf{k}$ are possible. Since in this case only the term with $\mathbf{G}=0$ remains in the sum over $\mathbf{G}$ and the interaction v is diagonal in the momentum representation, we can easily find the vibrational frequency from Eq. (15):

$$\omega^2(Q)=Q^2v(Q)/\Omega M. \tag{16}$$

If we assume that $V_{ei}=-ZV_0$, we have $v=Z^2V_{scr}$ and states with $V_{scr}(Q)<0$ turn out to be unstable. If $V_{ei}>-ZV_0$, however, instability arises when $V_{scr}<(V_0\chi V_0-V_{ei}\chi V_{ei})<0$, i.e., an electron-electron attraction not exceeding a certain strength turns out to be possible.

Another interesting case is that of the instability of the lattice against spontaneous collapse, which arises when the bulk modulus $B=\Omega\delta^2E/\delta\Omega^2$ is negative. In the jellium model, in which $V_{ei}=-ZV_0$, the bulk modulus is related to V_{scr} by the well known sum rule[27]:

$$B_{jell}/B_0=V_{scr}(Q=0)\pi_0(Q=0), \tag{17}$$

which is a special case of relation (16) (B_0 is the bulk modulus of a noninteracting electron gas). In this model, states with $V_{scr}(0)<0$ are obviously unstable against spontaneous collapse.

On passing to real metals, the situation changes basically. The relation between $V_{scr}(0)$ and B can be most easily traced for the nontransition metals, in which the valence electrons are almost uniformly distributed in space and the bulk modulus can be calculated by the pseudopotential method. The energy per atom of a nontransition metal can be expressed as a series in powers of the pseudopotential[32]:

$$E=E_{jell}+E_{Ew}+E^{(1)}+E^{(2)}+\dots \tag{18}$$

Here E_{jell} is the energy of the system according to the jellium model, E_{Ew} is the Ewald energy, which is due to the point character of the ion, the energy

$$E^{(1)}=Z[V_{ei}(Q)+ZV_0(Q)]|_{Q\to 0}\Omega^{-1}$$

is related to the difference between V_{ei} and $ZV_0(-1)$, and the term $E^{(2)}$ takes account of the correction to the energy due to the weak nonuniformity of the electron gas. The terms $E^{(n)}\sim V_{ei}^n$ with $n\geq 3$ are small and are usually dropped. On differentiating Eq. (18) twice with respect to Ω, we obtain

$$B=B_{jell}+B_{Ew}+B^{(1)}+B^{(2)}+\dots. \tag{19}$$

It is quite clear that the bulk modulus of a metal differs from B_{jell}. The relative importance of the various terms in (19) can be judged from Table II, in which calculation results[33] and experimental data are listed for the alkali metals. The term $B^{(2)}$ is usually considerably smaller in magnitude than the other terms in (19), and

TABLE II.

Metals	$B_{Ew}/\lvert B_{Ew}\rvert$	$B_{jell}/\lvert B_{Ew}\rvert$	$B^{(1)}/\lvert B_{Ew}\rvert$	$B^{(2)}/\lvert B_{Ew}\rvert$	$B_{theor}/\lvert B_{Ew}\rvert$	$B_{exp}/\lvert B_{Ew}\rvert$
Li	−1.00	0.40	1.27	−0.14	0.53	0.51±1
Na	−1.00	0.22	1.57	−0.15	0.64	0.67±3
K	−1.00	0.06	1.77	−0.08	0.75	0.75±2
Rb	−1.00	0.01	1.82	−0.06	0.77	0.80±5
Cs	−1.00	−0.04	1.86	−0.03	0.80	0.83±3

we may neglect it in the first approximation.[4)] We easily find, using Eq. (17), that for such a "zeroth order model"[32] spontaneous collapse sets in when

$$V_{scr}(0)<-(B_{Ew}+B^{(1)})/B_0\pi_0(0). \tag{20}$$

Depnding on the magnitude of B_{Ew}, and especially on that of $B^{(1)}$ ($B_{Ew}\approx -0.4(4\pi/3)^{1/3}Z^2e^2\Omega^{-4/3}$ for close packed structures), the right-hand side of (20) may be negative or positive. As is evident from Table II, it is negative for the alkali metals, i.e., attractive electron-electron forces are entirely possible as far as stability is concerned. For cesium, for example, according to (17) we have $V_{scr}(0)<0$, although $B>0$. Thus, the nonCoulomb electron-ion interaction ($V_{ei}=-ZV_0$) and the pointlike character of the ions substantially alter the lattice stability conditions from those given by the jellium model. As a consequence of this, the lattice instability does not set in precisely when V_{scr} changes sign, and an attractive electron-electron force not exceeding a certain magnitude may exist in real materials.

CONCLUSION

Study of static screening in a nonuniform electron gas shows that for paramagnetic materials close enough to the transition to the spin-ordered state theinteraction V_{scr} must have negative eigenvalues. This electron-electron attraction does not exceed $-\Delta$ in magnitude, and the coupling constant is of the order of 0.1–0.2. Instability of the crystal lattice probably also leads to the same limitations, but the necessary numerical calculations have not yet been successfully performed. On the basis of a theoretical treatment in the lowest order in V_{scr}, therefore, it would seem to be entirely possible to produce superconductors with comparatively small coupling constants on the basis of the exciton mechanism.

Serious difficulties are encountered in the theory of nonphonon superconductivity on going beyond the limitations of the weak coupling approximation. The corresponding generalization of the equation for T_c is obtained by replacing the screened Coulomb interaction in Eq. (1) by a quadrupole that cannot be reduced to two electron lines. Since the higher order terms in V_{scr} are not particularly smaller than in the screened Coulomb interaction, they can not only produce a quantitative change in the result of the calculation, but can alter the character of the effective interaction from weakly attractive to repulsive. An indirect indication of this possibility may be found in the strong effective electron-electron repulsion obtained for almost magnetic materials on summing "paramagnon exchange" diagrams.[34] It should be noted that the summation carried through in Ref. 34 encompasses only part of the divergent diagrams occurring in the quadrupole. Two questions that are important for high-temperature superconductivity—whether the result of Ref. 34 will remain valid in a more rigorous treatment,

and whether it is possible to obtain an effective electron-electron attraction by taking higher order terms in V_{scr} into account— are still difficut to answer.

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[1)]Detailed discussions of possible ways of realizing the non-phonon or, as it is frequently called, the exciton mechanism of superconductivity will be found in Refs. 3–5.

[2)]It is well known[14] that there always exists a basis in which two given matrices, of which one (χ_n^{-1}) is positive definite, are both diagonal. The diagonalizing basis need not be orthogonal, so χ_n^{-1} and Δ will not necessarily commute (a necessary and sufficient condition that two matrices commute is that there exist an orthogonal basis in which both are diagonal).

[3)]The widely cited expression for I_m obtained by Brueckner and Sawada[19] contains a numerical error.[18]

[4)]The term B_{Jell} is also small in the alkali metals, which have a low electron density.

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