Superconducting properties of systems with local pairs

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An analysis is made of the superconducting properties of systems with a strong electron attraction at one center, in the limit when such attraction is strong compared with the energy band width. This model describes superconductors with local pairs. Expressions are derived for the critical magnetic fields \( H_{c1} \) and \( H_{c2} \) and it is shown that the field \( H_{c2} \) is much higher than the paramagnetic Ginzburg limit \( 1.25T_c/\mu_B \). The fluctuation region in superconductors with local pairs is as large as in magnetic systems and in superfluid helium, so that the critical behavior and the dynamic properties of these systems resemble the properties of He II. The feasibility of realization of a state of this kind is considered.

1. INTRODUCTION

Real semiconductors are usually described on the basis of the BCS model in which it is assumed that the width of the conduction band and, consequently, the Fermi energy of electrons are much greater than the energy corresponding to the phonon Debye frequency \( \omega_p \) or the binding energy \( \Delta \) of Cooper pairs. However, a model in which this respect is opposite to the BCS theory has been used in several investigations: it is a model with a strong static binding of electrons at localized centers and a very weak motion between the centers. The first to use this model were Schafroth, Butler, and Blatt.1 Anderson1 then proposed to describe this situation (applicable specifically to amorphous semiconductors) by a Hubbard Hamiltonian with an effective attraction of electrons at one site. Subsequently, the establishment of a superconducting long-range order in a model with local pairs, and also the competition between the superconducting and insulator transitions of the charge ordering type had been investigated by Abrahams and Kulik,2 Kulik and PeDan,3 and by Alexandrov and Ranninger.4 The effective attraction of electrons at a localized center may occur because of their interaction with phonons if this interaction predominates over the Coulomb repulsion (this approach is known as the bipolaron model). It is not yet known whether such a situation is feasible in practice. Some authors are of the opinion that in certain semiconductors the electron pairing mechanism can be described adequately by the local pair model and by the BCS model (see Ref. 4 and the literature cited there). The suitability of a given model for the description of real superconductors can be judged only by comparing the superconducting properties predicted by different (BCS and local pair) models and then identifying the differences so as to be able to distinguish between the models on the basis of the experimental data. We shall consider the magnetic and critical properties of the local pair model and we shall discuss the behavior predicted by the local pair model occurring in real compounds.

2. SPIN HAMILTONIAN FOR THE DESCRIPTION OF THE SUPERCONDUCTIVITY IN THE LOCAL PAIR MODEL

It is shown in Refs. 2 and 5 that the Hamiltonian of a system of electrons and phonons under the conditions of a strong local polaron effect reduces to the Hubbard Hamiltonian with an effective attraction:

\[
\mathcal{H} = \sum_{\mathbf{r} \mathbf{m}} \epsilon_{\mathbf{m}} n_{\mathbf{m}, \uparrow} n_{\mathbf{m}, \downarrow} - \frac{\Delta}{2} \sum_{\mathbf{m}} n_{\mathbf{m}, \uparrow} n_{\mathbf{m}, \downarrow} - \frac{\Delta}{2} \sum_{\mathbf{m}} n_{\mathbf{m}, \uparrow} n_{\mathbf{m}, \downarrow} + \frac{\Delta}{2} \sum_{\mathbf{m}} n_{\mathbf{m}, \uparrow} n_{\mathbf{m}, \downarrow},
\]

where \( \mathbf{m} \) are the lattice sites (we shall consider a simple cubic lattice); summation over \( \mathbf{m} \) is applied to the nearest-neighbor sites; \( a^\dagger \) and \( a \) are the creation and annihilation operators for electrons at sites; \( \Delta \) is the effective attraction parameter; \( t \) is the effective resonance integral of a transition; it is assumed that \( \Delta > 0 \) and \( \Delta > t \). In the bipolaron model the parameter \( \Delta \) and the effective resonance integral \( t \) are expressed in terms of the initial parameters of the electron-phonon Hamiltonian using the relationships

\[
\Delta = \sum_{\mathbf{m}} \left( \frac{\epsilon^0_{\mathbf{m}, \uparrow} + \epsilon^0_{\mathbf{m}, \downarrow}}{2} \right) V, \quad t = \frac{\epsilon^0_{\mathbf{m}, \uparrow} - \epsilon^0_{\mathbf{m}, \downarrow}}{4 |\epsilon^0_{\mathbf{m}, \uparrow} + \epsilon^0_{\mathbf{m}, \downarrow}|},
\]

where \( V \) is the Coulomb repulsion between electrons at a center; \( g \) is the parameter representing the interaction of electrons with local phonons of type \( i \), whose frequency is \( \omega_i \);
t_{N}$ is the "bare" (unrenormalized resonance integral) for electron transitions between the centers $m$ and $m'$. The polaron effect results in narrowing of the electron energy bands and also in the appearance of a net attraction when $\Delta > 0$. The expressions in Eq. (2) are valid if $t_{N} \ll \Delta^{2}/\epsilon_{0}$ (and this condition is essential to ensure that the local pair model applies. It should be pointed out that the delay effects are ignored in the derivation of the expressions in Eq. (2). This is justified if $t_{N} \ll \Delta^{2}/\epsilon_{0}$. We shall later (see Sec. 6) show that the model in question may be realized in practice when this condition is satisfied. It therefore follows that the local pair model represents the case opposite to the BCS model not only in respect of the parameter $t/\Delta$, but also in respect of $t/\epsilon_{0}$.

Equation (1) ignores the interaction between electrons at different centers; we shall now for this interaction within the framework of the effective spin Hamiltonian.

The Hamiltonian of Eq. (1) applies to a system in zero magnetic field. The field can be included in Eq. (1) in the usual way. Its influence on the electron spins reduces to the introduction of an additional term $-\mu_{0}H\sum_{m} n_{m}$, whereas an allowance for the orbital effect of the field is made in the second order with respect to $t$, we should allow only for the attraction of electrons at lattice sites. The ground state of a system of $N_{e}$ electrons at lattice sites corresponds to a distribution of $N_{e}$ electron pairs in the lattice. Such a state has an energy $-\Delta N_{e}/2$ and it is degenerate in respect of the distribution of pairs. Since at each center the number of pairs can only have two values ($0$ or $1$), a system of degenerate levels can be described by an effective spin Hamiltonian for $N_{e}$ spins each of value $1/2$. All the other levels of the system (which correspond to dissociated pairs) are separated from the ground state by an energy $\Delta$ and in the range $\Delta \Delta$ the thermodynamic properties are governed only by those levels which are described by the effective spin Hamiltonian. The degeneracy in respect of the pair distribution is lifted in the second order with respect to $t$ and the adoption of spin operators in a space of $2^{N_{e}}$ states involves the substitution (see Ref. 5).

$$S_{m} = n_{m} - n_{m},$$

$$S_{N} = -t_{N} \sum_{m} n_{m} n_{m},$$

$$S_{N} = \frac{1}{2} \left(1 - \sum_{m} n_{m} n_{m}\right).$$

The spin Hamiltonian is in the form of the anisotropic Heisenberg Hamiltonian:

$$H = \frac{2t_{N}}{\Delta} \sum_{m} \left[ S_{m} S_{m+1} + S_{m} S_{m-1} \exp(i\phi_{m}) - S_{m} S_{m} \exp(-i\phi_{m}) \right],$$

where

$$\phi_{m} = \frac{2\pi}{\Delta} \sum_{m} \mu_{m},$$

and the corresponding Schrödinger equation with this Hamiltonian is a secular equation for the degenerate levels of the Hamiltonian.

If we split the lattice into two sublattices and if for one of them we substitute $S_{m}^{z} \rightarrow -S_{m}^{z}$ and $S_{m}^{x} \rightarrow -S_{m}^{x}$, i.e., $S_{m}^{+} \rightarrow -S_{m}^{+}$, we find that the Hamiltonian (4) can be converted into one which is completely antiferromagnetic, i.e., in the absence of a magnetic field if $\phi_{m} = 0$, we obtain the isotropic Heisenberg model of an antiferromagnet. A minimum of the energy of the system can be found subject to the additional condition

$$\sum_{m} S_{m} = \frac{1}{2}(N-N_{e}),$$

which corresponds to fixing the number of electrons in the system under consideration. An allowance for the Coulomb interaction between pairs at different sites reduces to an addition of the term

$$\sum_{m} \mu_{m} S_{m}^{z} S_{m}'^{z}.$$
(we are considering a simple cubic lattice). The functional for the entropy $\mathcal{S}()$ can be deduced from the usual expression for the entropy of a spin system

$$\mathcal{S}(\mu) = \left[\frac{1}{2} - \frac{S}{2}\right] \ln \left(\frac{1}{2} + \frac{S}{2}\right) + \left(\frac{1}{2} + \frac{S}{2}\right) \ln \left(\frac{1}{2} + \frac{S}{2}\right),$$

where $S$ is the average spin, i.e.,

$$\mathcal{S}(\mu) = (S_z^2 + S_m^2 + S_m^2) \ln \left[\frac{1}{2} + |\mu|\right].$$

Using Eqs. (5) and (6), we obtain the following functional of the Ginzburg-Landau type:

$$\mathcal{F}(\psi) = \mathcal{S}(\mu) - \frac{1}{2} \sum_{n=1}^{N} \left[\frac{1}{2} - S_m\right] \ln \left(\frac{1}{2} + S_m\right) + \left(\frac{1}{2} + S_m\right) \ln \left(\frac{1}{2} + S_m\right),$$

where

$$S_m = S(\mu) = \left[\left(\frac{1}{2} + \mu\right)^2 + |\mu|\right].$$

Variation of Eq. (7) with respect to the vector potential gives the following expression for the superconducting current density:

$$j = \frac{2e}{h} \sum_{n=1}^{N} \left[\psi_n \psi_m \exp(i\Phi_m) - \psi_n \psi_m \exp(-i\Phi_m)\right] (n_m - m),$$

where $d$ is the distance between the sites. The functional (7) and the expression for the current (8) provide a complete description of the superconductivity by the local pair model at all temperatures in the self-consistent field approximation. It is clear from Eqs. (7) and (8) that the Ginzburg-Landau functional for the local pair model is of the difference type and it describes the Josephson interaction between the neighboring centers. The difference nature of the functional leads to unique superconducting properties of the local pair model: they are analogous to the properties of the Josephson systems.

3. UPPER CRITICAL MAGNETIC FIELD

The condition for the appearance of an infinitely small superconducting nucleus can be found simply from the quadratic terms of the expansion of $\mathcal{F}(\psi)$ as a function of $\psi$. The resultant quadratic functional is

$$\mathcal{F}(\psi) = \frac{2e^2}{\hbar} \sum_{n=1}^{N} \left[\psi_n \psi_m \exp(i\Phi_m) \right]$$

$$+ \frac{\psi_n \psi_m \exp(-i\Phi_m)}{\mathcal{S}(-\Phi_m)} + \frac{\psi_n \psi_m \exp(i\Phi_m)}{\mathcal{S}(\Phi_m)}$$

$$+ \frac{\psi_n \psi_m \exp(-i\Phi_m)}{\mathcal{S}(-\Phi_m)} + \frac{\psi_n \psi_m \exp(i\Phi_m)}{\mathcal{S}(\Phi_m)},$$

where $\Phi_0$ is a flux quantum; the coordinate is $x = dm$ and the integer $m$ labels the lattice sites in the $x$ direction. Then, Eq. (9) yields the following difference equation for the order parameter:

$$\frac{1}{\Lambda} \left[\frac{\psi_{n+1} + \psi_{n-1}}{2} + 2\psi_n \cos \frac{2\pi H d}{\Phi_0} \right] - \psi_n = 0,$$

which gives the upper critical field near $T_c = T_{c,0}$, we can transform Eq. (10) into a differential equation

$$\frac{1}{6} \frac{d^2 \psi}{dt^2} = \frac{2\pi H d}{3\Phi_0} \psi + \psi = 0.$$

This expression is conventional for the case when the correlation length $\xi(T) = \Lambda d$ is.

At lower temperatures Eq. (10) can be solved only numerically and the dependence of $H_{c2}$ on $T$ has the form shown in Fig. 1, plotted on the basis of the results of Ref. 6.

It is clear from Eq. (10) and Fig. 1 that:

(a) the effects of the fields $H$ and $H + \Phi_0/d^2$ on the system are equivalent, because the field $\Phi_0/d^2$ gives precisely the flux quantum across the closed path of a pair with the smallest area.

We shall assume that the magnetic field is directed along the $z$ axis and that the vector potential component $A_z = -Hx$ differs from zero. Then, in accordance with Eq. (6), the value of $\Phi_{m,n}$ differs from zero for the $m$, $n$ pairs along the $y$ axis and is given by

$$\Phi_{m,n} = \frac{2\pi H d}{\Phi_0} \sum_{n=1}^{N} m d \psi_n \Phi_0.$$

The eigenvalue solution of Eq. (10) was obtained by Turkevich and Klemm. For $H = 0$, it is found that $T_c = T_{c,0}$, we can transform Eq. (10) into a differential equation

$$\frac{1}{6} \frac{d^2 \psi}{dt^2} = \frac{2\pi H d}{3\Phi_0} \psi + \psi = 0.$$
below $T^* \approx 0.88$ $T_c$, the magnetic field does not destroy the Cooper pairs, but they become localized in the region of the Josephson effect. This range of temperatures corresponds to the Josephson regime when the currents through a contact cannot destroy the superconductivity at the “banks” of the contact. In fact, below $T^*$ the superconductivity is destroyed only by the paramagnetic effect and the corresponding critical field is $H_{c2}$. This field exceeds the Clogston limit (of the order of $T_c/\mu_B$) by a factor $(\Delta / \Gamma)^2$.

This behavior of $H_{c2}(T)$ is predicted on the basis of the self-consistent field approximation. An allowance for the fluctuations can alter this behavior. A similar situation was considered in layer superconductors by Efetov and he concluded that three-dimensional correlations were suppressed by an increase in the magnetic field. The system under consideration can also exhibit a change in the detailed nature of the behavior of the field $H_{c2}(T)$ under the influence of fluctuations, but—as indicated also by the results of Ref. 7—the scale of the change in the critical field remains unaffected by the presence of fluctuations: $H_{c2} \approx \Phi_0 / d^2$. Moreover, in contrast to layer semiconductors, the dependence on $H$ obtained in our case is periodic already in the initial free-energy functional (7) and, therefore, the periodicity should be retained by the dependence $T_c(H)$ also when an allowance is made for the fluctuations.

We may therefore see that the characteristic feature of the superconductivity in the local pair model is its stability in the presence of a magnetic field. In the BCS model the upper critical field does not exceed a value approximately amounting to $T_c / \mu_B$ (in the presence of a strong spin-orbit scattering), whereas in the local pair model the limiting field exceeds the Clogston limit by a factor $(\Delta / \Gamma)^2$. Superconductors which exceed by so much the Clogston limit are not known. Therefore, we are of the opinion that none of the compounds known at present is a superconductor of the local pair type.

Another interesting property of superconductors with local pairs is their “reverse” behavior, compared with the BCS case, in the presence of impurities. It follows from the results of the present section that such superconductors should be practically insensitive to magnetic impurities since their influence would have to be compared with the large parameter $\Delta$. On the other hand, these superconductors should be very sensitive to the influence of ordinary impurities (see also Ref. 4). The potential of these impurities, such as the local potential $\Sigma \mu_j a_j \bar{a}_j$, gives rise to additional terms in the spin Hamiltonian (4) and these are in the form of a random magnetic field along the $z$ axis: $\Sigma \mu_j a_j \bar{a}_j$, so that it is clear that the field in question is comparable with $T_c$, and it can destroy completely the order in the $xy$ plane, i.e., it can suppress the superconducting coherence. The local pairs are not broken up, but they become localized in the region of the impurity potential minimum.

4. DEPTH OF SCREENING OF THE MAGNETIC FIELD, GINZBURG-LANDAU PARAMETER, AND LOWER CRITICAL FIELD

It follows from the expression for the current given by Eq. (8) that the screening of the magnetic field is governed by the following relationship between the current and the vector potential:

$$I = \frac{2\mu e}{\hbar} \frac{\Delta}{d^2} \left| \psi \right|^2 \sin \left[ \frac{2\pi d}{\hbar} \left( \frac{\Delta}{\lambda} \right) \right],$$

where $\left| \psi \right|^2 = \pi \mu_0 \sin \left( r r \right)$ for $r < 1$ and $\left| \psi \right|^2 = \pi \mu_0$ for $r > 1$. It follows from Eq. (12) that the penetration depth of a weak field is

$$\lambda = \left( \frac{\pi e^2}{\hbar} \right) \left( \frac{\Delta}{\lambda} \right),$$

and we shall assume that the field is weak if it obeys the inequality $H < H_{c1} = \left| \psi \right| d^{-1} d^{-1}$, when $\sin x < x$ in Eq. (12) can be replaced with $x$ defined by $x = 2\pi d d / \hbar c$. Knowing $\lambda$, we can write down the expression for the lower critical field:

$$H_{c2} = \frac{\Phi_0}{\lambda^2} \frac{\lambda}{\hbar} \frac{\Delta}{d} \delta \phi = \frac{\Phi_0}{\lambda^2} \frac{\lambda}{\hbar} \frac{\Delta}{d} \delta \phi,$$

where $H_{c2}$. The thermodynamic critical field $H_1$ is of the order of $(T d^{-1} \left| \psi \right| d^{-1})$ near $T_c$, whereas in the limit $T \rightarrow 0$ we have to replace $\left| \psi \right|^2$ with $\left| \psi \right|^2$. The Ginzburg-Landau parameter $\kappa = \lambda / \Phi_0 = \lambda / d$ considered in the local pair model is

$$\kappa = \frac{\Phi_0}{\epsilon (d) \left( \frac{\Delta}{\lambda} \frac{\lambda}{\hbar} \right)}.$$

When the numerical values of the relevant parameters are substituted in Eqs. (13) and (14), it is found that the depth of penetration $\lambda$ is one or two orders of magnitude greater than typical values of this quantity for an ordinary superconductor and the field $H_{c2}$ is then three or four orders of magnitude less than for known superconducting systems.

The large values of $\lambda$ (compared with those for ordinary superconductors) in combination with a short coherence length $\lambda \sim d$ make the properties of the systems under consideration similar to those of an uncharged Bose liquid in the form of superfluid helium II. The similarity of the two types of systems was already pointed out in Ref. 5. We shall make the following additional comments.

In contrast to ordinary superconductors, the systems with local pairs should exhibit—in direct analogy with the $\lambda$ transition in helium—a wide critical fluctuation region. This follows already from the fact that the model under consideration is close to the Heisenberg model and the corresponding superconducting transition is equivalent to a phase transition in what is known as the XY (or planar rotator) model, which—as is well known—the Ginzburg-Levyukov parameter is $\omega > 1$ and the average field approximation is not valid under any conditions. This circumstance gives rise to several specific phenomena in local pair systems and we shall deal with them in the next section.

All that we have said so far is summarized in Table I where a comparison is made of the orders of magnitude of the principal characteristics of the superconducting states predicted by the BCS and local pair models. It is clear from Table I that local pair systems are characterized by an anomalously high critical field, an anomalously low lower critical field, and a wide fluctuation region.
5. COLLECTIVE OSCILLATIONS AND CRITICAL BEHAVIOR

It follows from the above discussion that in the case of a strong interaction characterized by $\Delta \equiv \pi$ our local pair system is described by the effective spin Hamiltonian of Eq. (4), and the superconducting state corresponds to the ordering of "spins" in the $xy$ plane. In view of this equivalence, we can expect the critical behavior to be very different from that in the BCS model and, in general, a different spectrum of collective excitations.

It follows directly from the Hamiltonian of Eq. (4), which is the Hamiltonian for the anisotropic Heisenberg model with an easy-plane anisotropy, that there is a zero-gap branch of collective oscillations ("spin waves") with a spectrum $\omega \sim t^2/k^2/\Delta$. In this case the specific heat at low temperatures $T \ll T_c$ is not an exponential function but behaves in accordance with a power law. However, it is known that in the BCS model there is a also a collective mode with a spectrum of the acoustic type, but an allowance for the long-range part of the Coulomb repulsion of electrons increases its frequency to the plasma value. We can expect the situation to be similar in the local pair model.

This is indeed confirmed by a direct calculation of the spin wave spectrum when an allowance is made for the Coulomb interaction between pairs. This interaction reduces to addition, to the Hamiltonian [6], of a term

$$V_{ac} S_x S_y, \quad V_{ac} = -e^2 |R_x - R_y|^{-1}.$$

Conventional calculations yield the frequency of spin waves which differs from zero in the limit $k \to 0$ and is given by

$$\omega_0 = \frac{\hbar}{\Delta} \frac{e^2}{|R_x - R_y|},$$

where $\lambda$ is defined by Eq. (13). The expression (15) agrees with the familiar dispersion law of acollective ("acoustic") mode:

$$\omega = \nu \lambda k$$

which follows from the magnetohydrodynamics of superconductors (see, for example, Ref. 9).

It is a requirement of the local pair model that $\omega_0 \leq T_c$, because otherwise there would be no superconducting state but a state with a charge density wave. Therefore, the low-temperature specific heat deduced in the local pair model obeys the exponential function $C_s \propto \exp(-\omega_0/T)$, but the activation energy is $\alpha_0 \Delta \propto \gamma / \Delta^2$, i.e., this energy is considerably less than the gap $\Delta$ in the electron spectrum.

The difference between the local pair and BCS superconductors should be also manifested in the critical behavior. It is obvious that a local pair system is equivalent in respect of its symmetry to the XY model or superfluid He II; the presence of a gap in the low-temperature spectrum does not affect the critical behavior.

It follows from the Ginzburg-Levanyuk criterion that the width of the critical (fluctuation) region is $\Delta\omega$ (for $T < T_c$) and it is found from the condition

$$\langle |\psi|^2 \rangle / |\psi|^2 = T / 2 \alpha / \Delta > 1.$$  \hspace{1cm} (16)

Here, $\langle |\psi|^2 \rangle$ is the temperature-dependent part of the rms value of the fluctuations $\psi$, $a$ and $b$ are coefficients in the expansion of the volume part of the density of the free Ginzburg-Landau energy, $\gamma$ is the coefficient in front of the gradient term; $\gamma = (\gamma / 2 \alpha / \Delta)^{-1 / 2}$ is the coherence length. In the model under discussion (corresponding to $\gamma < 1$) these coefficients are as follows:

$$a = \frac{\gamma}{b}, \quad b = \frac{2 \gamma}{\alpha / \Delta} > 1.$$  \hspace{1cm} (16')

Using the above values of the coefficients and $T = (\gamma / 2 \alpha / \Delta)^{-1 / 2}$ [see Eq. (11)], we find from Eq. (16) that

$$t_0 = \frac{27}{\Delta^2}, \quad \alpha = \frac{\Delta^2}{\Delta^2} > 1.$$  \hspace{1cm} (17)

Therefore, in the local pair model the fluctuations are large practically throughout the range of existence of the superconducting phase.

Inside the fluctuation region the temperature dependences of the various physical quantities should be different from the corresponding dependences calculated in the average field approximation (and applicable to ordinary superconductors). We can expect that, on the basis of the principle of universality of critical phenomena, these dependences are of the same nature for the local pair systems as those near the $\lambda$ transition in helium. The specific expressions for these dependences can be found employing the ordinary functional of the free Ginzburg-Landau energy, but with the temperature dependences of the coefficients modified in the spirit of the theory of the scaling invariance of analogies with the phenomenological theory of superfluid helium II near the $\lambda$ point:

$$\omega = \omega_0 \gamma / \Delta^2, \quad b = \omega_0 / \Delta^2, \quad f = \omega_0 / \Delta^2,$$

where $\Delta \leq 10^{-3}$. (see Ref. 11).

Similarly, in the case of the dynamic phenomena at temperatures $T > T_c$ we should assume that the temperature dependence of the damping constant is $\gamma \sim T^{-1 / 2}$ (Ref. 11) in the frequently used—in such cases—time-dependent Ginzburg-Landau equation. Table II gives the temperature-de-
pendences of the following physical quantities: the specific heat, the density of superconducting electrons \( n_s \), the quantities \( \xi, \lambda \propto n_s^{-1/2} \), and also possibly by triple chalcogenides of the A15 type. Among the currently available superconductors the A15 structure and compounds with the A15 structure\(^{14},\) however, for all of them the ratio in question is still \( \geq 10^2 \).

It would be very interesting to continue the search for such systems and to study them.

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### TABLE II

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It follows from Eq. (2) that the effective attraction between electrons at centers occurs if the attraction of electrons via phonons predominates over the Coulomb repulsion. On the other hand, the exponential narrowing of the polaron energy band and the corresponding reduction in \( T_c \rightarrow \lambda / \Delta \) can be avoided provided the phonon frequency \( \omega_0 \) is of the order of the electron-phonon interaction \( g \). Consequently, it should be possible to observe the local pair behavior predicted on the basis of the bipolaron model if \( \omega_0 \gg \omega - V \), i.e., if the phonon frequencies approach the electron frequencies. Clearly, the pairing centers should be sufficiently large to reduce the Coulomb repulsion \( V \) between electrons, i.e., in other words, they should be fairly large molecules. It seems to us that the situation under consideration may be realized in crystals composed of large organic molecules provided it is realizable at all. These molecules \( M \) should have a unique property: the energy of a system composed of a doubly charged molecule \( M^{2+} \) and a neutral molecule \( M^{-} \) should be less than the energy of a system of two homogeneously charged molecules \( M^{+} \) because of the interaction of electrons with the internal molecular vibrations. Molecules with such characteristics are not known at present.

On the other hand, certain experimental evidence of the conductivity (but not yet superconductivity) due to bipolarons has been found for systems such as trans-polyacetylene or polyphenylenes.\(^{12,13}\) However, bipolarons are present in such systems only as excitations with a low concentration.

The situation in \( T_1 \Omega_0 \), (Ref. 14) is closer to the one under consideration: it is postulated that a high concentration of bipolarons exists in this compound at temperatures in the range \( 130K < T < 140K \). However, the low-temperature transition in this compound is not a superconducting state but to an insulator state with a spatial ordering of bipolarons.

We can summarize this discussion by saying that the superconducting properties of local pair systems are in many respects very different from the properties of ordinary superconductors of the BCS type. Although none of the presently known superconductors can be described by the local pair model, an investigation of this model is still very illuminating. In a certain sense the local pair model is the opposite limiting case to the BCS model. If we compare the results obtained for both models, we can gain a general idea of the nature of changes in the principal superconducting characteristic on increase in the interaction and on reduction in the energy band width. Such a comparison is made in Tables I and II and it is illustrated in Fig. 2. Although, as pointed out already, there are no real superconductors which would manifest the local pair case in its pure form with \( \Gamma < \Delta \), the results mentioned above may help in a qualitative interpretation of the intermediate cases.

Among the currently available superconductors the lowest value of the ratio \( \Gamma / \Delta \) is exhibited by systems with heavy fermions [CeCu,Se,\( \alpha=0 \) to the electron interaction strength \( \Delta \).
We shall denote the attraction between two electrons at one site by $A$ instead of the usual $U$, because in the $A>t$ case considered below it is this quantity that acts as the binding energy of electrons in a local (''Cooper'') pair.

In Table II and below we shall mark some of the usual symbols for critical indices by a tilde (\(\tilde{\eta}\)) so as to distinguish them from the other quantities used by us.


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