The phenomenon of exciton-fermion condensation

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Conditions are investigated under which a finite density of excitons can arise spontaneously, which then mediate BCS-type pairing of free electrons through virtual excitonic transitions involving higher state (excited) excitonic levels. This cooperative exciton-fermion condensation, which takes place primarily via a first-order phase transition that is close to second order, is characterized by large values of the ratio of the superconducting gap to the transition temperature, even when the coupling constant is small. In the limit of small free-electron densities and high temperatures, polaron effects give rise to a discontinuity in the exciton concentration, leading to a considerable relaxation of the conditions for subsequent appearance of the superconducting condensate. It is shown that the maximum transition temperatures for a given position of the Fermi level correspond to a line of critical points. Near this critical line, the nature of the exciton transition turns out to be irrelevant, which eliminates any direct or indirect influence of the isotopic shift on the transition temperature. The applicability of the model to layered superconducting oxides is discussed.

1. INTRODUCTION

The discovery of the phenomenon of high-temperature superconductivity (HTSC) has led to further development of exciton models of superconductivity (see Ref. 1). However, use of these models to describe HTSC compounds is hindered by the difficulty of suppressing the bare Coulomb contribution[1] μ_C (see, e.g., Refs. 2–4); in addition, nonadiabatic vertex corrections have been found to be important, which decrease the effectiveness of the exciton mechanism.[5] Both of these facts are consequences of the small value of the Fermi energy $E_F \approx 0.1$ eV, which is obtained from band-structure calculations.[6] This in turn implies that nonphonon pairing is possible only if we postulate the existence of an electric-dipole active soft mode with characteristic energies $\omega_0 < 0.1$ eV.

A mode of this sort should undergo strong longitudinal-transverse splitting, so that its longitudinal frequency ω_L will be bounded from below by the characteristic plasma frequency[1)]

$$\omega_p = (8\pi e^2/\varepsilon_\infty m_{ex}\Omega)^{1/2}, \qquad (1)$$

where e is the electron charge, m_{ex} is the reduced mass of the exciton, ε_∞ is the high-frequency dielectric permittivity, and Ω is a quantity on the order of the effective volume of the exciton. It is easy to see that condition (1) sharply restricts the possible exciton pairing mechanism in the limit of small E_F, even if umklapp processes, which include interactions with the transverse branch, turn out to be important for some reason or other.

However, virtual creation of excitons is not the only way to increase the superconducting transition temperature T_c: under suitable conditions, T_c can be increased by a partial metal-insulator transition which increases the density of states D_0 at the Fermi surface.[7] Recently, a number of HTSC models[8–10] have been proposed that are based on this effect and the possibility of enhancing the polarizability of a medium in the presence of an excitonically anomalous background.[9] These models are also successful in explaining several features of the normal phase of HTSC materials.[11]

It is noteworthy that an increase of T_c within the framework of the models proposed in Refs. 7–10 occurs only in the presence of an excitonic order parameter. In this paper we investigate the possibility of a novel mutual coupling of the exciton system to the Fermi liquid of free carriers which can lead to high T_c without necessarily requiring coherence of the exciton ensemble. Let us discuss this possibility in detail.

Suppose that for some reason a finite density of excitons N_1 appears in the system, and that each exciton is in its lowest state E_1 with respect to the motion of the electrons and holes. If the virtual transition $E_1 \rightleftarrows E_2$ to the next internal exciton state is characterized by a large oscillator strength, then a considerable polaron shift in the Fermi energy of free carriers is possible even for small values of N_1; this also holds for the enhancement of BCS pairing. Formation of heavy strong-coupling polarons and their Wigner crystallization is also not ruled out. Under certain conditions, the corresponding gain in energy F^* can exceed the bare energy $F_0 = E_1 N_1$ per unit volume of the exciton collective system, leading to stabilization of a state with a finite exciton density N_1 that is considerably higher than the thermal density. This state will nominally be referred to as an exciton-fermion condensate (EFC). It is clear that coherence of excitons in the EFC is not a necessary condition for its existence, and that a situation is possible where at finite temperatures T the excitons form a gas accompanied by a superconducting condensate of fermions, which are bound in Cooper pairs.

The possibility of nonequilibrium excitons mediating superconducting pairing was investigated in Ref. 12. In this paper it was assumed that the exciton spectrum was hydrogenic, and therefore could be characterized by a universal value $f \lesssim 1$ of the strength of a non-ground-state transition. It will be clear from the analysis that follows that it is difficult to attain high T_c in the EFC phase in this case, although an exciton-polaron EFC phase may exist. In this same paper[12] the authors noted a possibly fundamental role for anisotropy

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in enhancing the influence of nonequilibrium excitons on T_c. It will be shown here that in a quasi-two-dimensional system there is no such universality for the oscillator strengths f of non-ground-state transitions, and that high values of $f \gg 1$ are attainable, which can lead to a high T_c.

In what follows, starting from a simplified physical picture of EFC formation a very simple model of the phenomenon is investigated and the possibility of its realization in real systems, including the HTSC materials, is discussed. Specific properties of the EFC phase are identified which, when known, may make it possible to observe the phase experimentally. It is proved that the fundamental outlines of the superconducting transition in an EFC at least do not contradict the important features of the HTSC system.

2. OSCILLATOR STRENGTHS OF THE EXCITON TRANSITION

As we mentioned above, large oscillator strengths favor the formation of a superconducting exciton-fermion condensate

$$f=\omega_p^2/\omega_0^2 \gg 1, \quad \omega_0 \equiv E_2-E_1, \quad \hbar=1 \tag{2}$$

for the non-ground-state exciton transition $E_1 \rightleftarrows E_2$. Here ω_p has the meaning of a maximum plasma frequency for this transition, which is attained at a maximum exciton concentration $N_{\max} \approx 1/\Omega$. For $N_1 < N_{\max}$, the frequency of the longitudinal branch

$$\omega_L=(\omega_0^2+\omega_p^2 N_1/N_{max})^{1/2} \tag{3}$$

turns out to be a function that depends strongly on the number of excitons if condition (2) is fulfilled. If, however, the following additional requirement is also fulfilled

$$\omega_0 \ll E_F, \quad \omega_p \gtrsim E_F, \tag{4}$$

then it turns out to be possible for the system to tune itself to that value of N_1 [the frequency ω_L Eq. (3)] at which the maximum possible T_c is ensured.[1] Thus, it is advantageous to discuss in detail whether relations (2) and (4) can be realized.

First of all, let us note that the excitons that can provide effective pairing are those whose size a_{ex} satisfies the condition[1]

$$a_{ex} \lesssim k_F^{-1}, \tag{5}$$

where k_F is the Fermi momentum. Thus, if we introduce the reduced mass of the exciton m_{ex}, the following estimate for ω_0 can be derived:

$$\omega_0 \approx 1/2m_{ex}a_{ex}^2 \gtrsim k_F^2/2m_{ex}. \tag{6}$$

Consequently, the first term in (4) is not allowed if the exciton is formed out of free-carrier wave functions. Therefore, in what follows, we will not specify the origin of the exciton, assuming only that it does not involve the free carriers. Then in principle we can choose a value of m_{ex} large enough to satisfy (4) and (6).

For the case of an isotropic medium, the volume of the exciton satisfies $\Omega \approx a_{ex}^3$. The value of a_{ex} can be identified by requiring that the Coulomb energy $U_C \approx e^2/\varepsilon_\infty a_{ex}$ associated with the electron-hole interaction be comparable to the kinetic energy (6) of their relative motion. By taking (1) into account, we immediately obtain the universal estimate $f \lesssim 1$ for non-ground-state transitions of a hydrogenic exciton.

For a strongly anisotropic layered medium the situation is fundamentally different. In fact, using the simplest dimensional estimate of the parameters of a $2D$ hydrogenic exciton, and introducing the interlayer distance c into the expression for the volume $\Omega \approx a_{ex}^2 c$ of such an exciton (where e_{ex} is its size along the layer), we obtain

$$f \approx \varepsilon_\infty a_{ex}/c \lesssim \varepsilon_\infty/k_F c, \tag{7}$$

where (1), (2), and (5) are taken into account. Thus, when k_F is sufficiently small, values $f > 1$ are possible.

Screening effects weaken the Coulomb interaction U_C and makes it short-range. In a $3D$ isotropic medium this circumstance can lead to the disappearance of bound states. However, for the case of $2D$ anisotropy the size of the bound state a_{ex} can significantly exceed the range of the weak potential.[13] Using the result of Ref. 13 for the energy of a shallow $2D$ level and relations (1), (2), and (5), we find

$$f \approx a_{ex}^2/ca^* \lesssim (k_F^2 a^* c)^{-1}, \quad a^* \equiv \varepsilon_\infty/e^2 m_{ex}. \tag{8}$$

Thus, for the case of a strong $2D$ anisotropy it is possible to fulfill conditions (2), (4), and (5) simultaneously.

At this point it is useful to consider the experimental situation. First of all, something should be said about the concept of charged phonons[14] used previously to explain large oscillator strengths observed in certain organic materials.[14] In a recent paper[15] this concept was invoked to interpret the giant oscillator strengths[16,17] of certain phonon modes of the HTSC oxides. The model of Ref. 14 was based on the assumption that large changes in the effective charge of an ion are possible for small ionic displacements. In this case the frequency of the longitudinal "charged" phonon can exceed the Fermi energy $E_F \approx 0.1$ eV (Ref. 6), i.e., such phonons cannot mediate pairing of the carriers. However, once the existence of a mechanism[14] for non-ground-state oscillator transitions is established, the conditions discussed above can be fulfilled. The quantity N_1 now characterizes the number of ions in new equilibrium positions (or in higher oscillator states), which includes the mechanism of Ref. 14.

It is relevant at this point to discuss the phenomenon of giant two-photon absorption[18] in the excitonic portion of the spectrum of CuCl, which is due to the anomalously large strength of the exciton-excitonic molecule transition. As was shown in Ref. 18, absorption at this transition is comparable in intensity to single-photon absorption even for photo-induced exciton densities of only $\sim 10^{15}$ to 10^{16} cm^{-3}. Consequently, the appearance of an EFC may be expected in systems like CuCl, in which the formation of polaron or superconducting states is accompanied by the appearance of a finite density of excitonic molecules, which decay virtually into pairs of excitons and thereby ensure the strong polarizability of the medium.

3. A MODEL OF EFC

Assume the energy E_1 of the ground-state transition $0 \rightarrow E_1$ is large compared to E_F. Then this transition serves only to redefine ε_∞. For finite small densities N_1, N_2 of excitons with levels E_1 and E_2 occupied, respectively, the $E_1 \rightleftarrows E_2$ transition "switches on," giving a contribution

$$\varepsilon_{ex}=A/(\omega_0^2-\omega^2), \quad A\equiv\varepsilon_\infty\omega_p^2(N_1-N_2)/N_{max} \qquad (9)$$

to the overall dielectric constant $\varepsilon(\omega,\mathbf{k})$. In Eq. (9) the quantity $\Omega\omega_p^2$ is given by the squared matrix element of the dipole moment of the transition $E_1\rightleftarrows E_2$, and naturally does not depend on the volume of the exciton. In what follows, for the sake of definiteness we will use the estimate (1) for ω_p^2.

Now we must discuss the question of the admissibility of using expression (9), first in the region of wave vectors $k\sim k_F$, and secondly for $\varepsilon_{ex}\sim\varepsilon_\infty$. First of all, it is clear that (9) is an additive sum of the polarizabilities of the individual excitons in the dipole approximation; therefore, the applicability of (9) for calculating the intensity of non-ground-state excitonic absorption is only limited by the admissibility of neglecting spatial dispersion of the quantity ω_p^2. This limitation requires that the exciton size a_{ex} be small compared to the wavelength, as in fact condition (5) implies. A nondispersive transition energy ω_0 is possible if the internal degrees of freedom of the exciton are decoupled from the motion of its center of mass, which we will assume holds here.

For large exciton numbers corrections to the effective field, which decrease the bare value of ω_0^2 and lead to a global ferroelectric transition, may turn out to be important. This possibility can be ignored here if we assume that the quantity ω_0^2 is not a "bare" quantity, but rather is the observed value and is fixed. Then Eq. (9) can still function as a model expression in the region of momenta (5) for exciton densities up to the maximum value $1/\Omega$.

The total function $\varepsilon(\omega,\mathbf{k})$ should include the screening contribution of the free carriers, which in a range of momenta $\approx k_F$ is comparable to ε_∞. Taking into account that this is in fact the region in which we will need an expression for $\varepsilon(\omega,\mathbf{k})$ in what follows, let us ignore screening as $k\to 0$ and use the expression

$$\varepsilon(\omega,2k_F)\approx\varepsilon_\infty\left[1+\frac{\omega_p^2\Omega}{\omega_0^2-\omega^2}(N_1-N_2)\right]. \qquad (10)$$

Then we can use the dielectric permittivity formalism[1] to derive a coupling constant $\lambda\sim 1/\varepsilon-1/\varepsilon_\infty$, $0<\omega<\omega_L$, of the form

$$\lambda\approx\frac{\omega_p^2 n^*}{\omega_L^2}\mu_C,$$

$$\omega_L^2=\omega_0^2+\omega_p^2 n^*, \qquad (11)$$

$$n^*\equiv(N_1-N_2)\Omega,$$

where

$$\mu_C\approx\frac{2\pi e^2}{\varepsilon_\infty k_F^2}D_0 \qquad (12)$$

is the average value of the Coulomb repulsion.[1]

The quantity λ in (11) determines that contribution F^* to the total energy density

$$F=E_1N_1+E_2N_2+F^*(N_1-N_2), \qquad (13)$$

which is capable of compensating the "activation" energy E_1 of the excitons. Note that F^* depends on the difference N_1-N_2. It is easy to see that this assertion can be justified on a deeper level than the approximation used to obtain it. Actually, for a two-level system (the isolated transition $E_1\rightleftarrows E_2$ is an example of this) it is the difference in occupation numbers that enters into the expression for the effective Hamiltonian of the interaction.

In what follows we specify the nature of the "compensating" mechanism. First, however, it is useful to derive a certain consequence of (13) which is independent of this mechanism and therefore reflects the specifics of the EFC state, and which corresponds (for $T=0$) to the equilibrium condition[2)]

$$N_2=0, \quad \partial F/\partial N_1=0. \qquad (14)$$

The renormalized value of the transition energy ω_0 can be defined as follows:

$$\omega_0^*=\partial F/\partial N_2-\partial F/\partial N_1=E_1+E_2\approx 2E_1\gg\omega_0, \qquad (15)$$

where the latter relation is obtained by taking into account (13) and (14). Thus, in the EFC state there is a strong increase in the frequency ω_0. This fact should manifest itself in the following way: in the absence of equilibrium excitons ($N_1=0$ for $T=0$) the non-ground-state optical transition appears as an absorption line that is photo-induced near ω_0. However, in the EFC state ($N_1\neq 0$ and $T=0$) this line appears without additional irradiation, but only to the extent that the absorption is nonadiabatic due to subsequent relaxation of the system, which changes the value of the transition energy from ω_0 to ω_0^* (Ref. 15). Consequently, we should observe a band of optical absorption in the EFC state that is rather strong in proportion to ω_p^2, extending over a large energy region

$$\omega_0<\omega<\omega_0^* \qquad (16)$$

4. SUPERCONDUCTIVITY IN THE EFC STATE

The quantity F^* in (13) can be represented in the form of a sum

$$F^*=F_p+F_s, \qquad (17)$$

where F_p is a term by the polaron shift of the Fermi energy, and F_s is the Cooper-pair energy density. In order to calculate the latter we can use the results of BCS theory (see Ref. 19) and write F_s in the form

$$F_s=-{}^1/_2 D_0\Delta(T,\ n^*)^2[1-T/T_c(n^*)], \qquad (18)$$

where for the sake of argument we make explicit the dependence on n^* through the coupling constant (11) and the renormalization of the Coulomb pseudopotential[19]

$$\mu^*=\frac{\mu_C}{1+\mu_C\ln(E_F/\omega_L)}, \qquad (19)$$

and also the temperature dependence of the energy, which is taken into account phenomenologically, and the superconducting gap

$$\Delta(T,n^*)=2\omega_L\exp\left[-\frac{1+\lambda}{\lambda-\mu^*}\right]\left[1-\frac{T}{T_c(n^*)}\right]^{1/2}. \qquad (20)$$

In (18) and (20) the BCS relation must be used for the temperature of the superconducting transition $T_c(n^*)$ as a function of n^*:

$$T_c(n^*)=(2/\gamma)\Delta(0,\ n^*),\ \gamma\approx 3{,}5. \qquad (21)$$

The partitioning (17) of the quantity F^* implies that the

renormalization of the quantity D_0 is small. However, situations[7] can arise in which both D_0 and the pre-exponential factor in (20) are strongly renormalized by the effect of a partial metal-insulator transition on the spectrum.[7] These effects are not taken into account here because they are fundamentally uninteresting within the framework of the model we are using, which involves only the averaged N_1 and Δ. Their incorporation into the model would require inclusion of the entropy of the exciton ensemble in (13), e.g., in the ideal gas approximation. However, it is clear that for $E_1/T_c \gg 1$ the thermal concentration of excitons will be exponentially small, which shows that it is legitimate to neglect the entropy contribution.

The simplest way to include the polaron shift F_p of the system energy is to do so within the framework of the Fermi liquid theory[20] for small coupling constants $\lambda \lesssim 1$. In the opposite case, $\lambda \gg 1$, it is necessary to consider the possiblity of forming strong-coupling polarons,[21] which can lead to a metal–insulator transition of the system along the lines of the Wigner crystallization of polarons. We will postpone discussion of this situation and treat the case $\lambda \lesssim 1$, taking into account the renormalization of the effective mass $m^* \to (1+\lambda)m^*$ of the carriers at the Fermi surface (see Ref. 1). Then the corresponding shift of the total energy can be found by integrating the relation between the chemical potential (see Ref. 20) and the quasiparticle spectrum, which gives

$$F_p \approx -\int_0^{N_e} E_F(N)\lambda(N)\,dN, \tag{22}$$

where N_e is the density of free electrons (holes); as a variable of integration we use the N_e dependence of the Fermi energy E_F and the coupling constant λ [through the Coulomb potential (12)].

Assembling the resulting expressions in (13), and solving the equilibrium equation (14), we can construct a phase diagram in the space of parameters E_1, T, ω_p, N_e, and ω_0, which is a rather complicated task. Therefore, some simple cases will be investigated here.

From the requirement $\lambda - \mu^* > 0$, taking into account (11), (12), and (19), we find the following bound

$$\omega_0 < \omega_s,$$
$$\omega_s = \frac{E_F}{(1+y_s)^{1/2}} \exp\left(-\frac{1}{\mu_C y_s}\right), \quad y_s \equiv \mu_C^{-1} + (\mu_C^{-2}+2\mu_C^{-2})^{1/2} \tag{23}$$

on the quantity ω_0 which allows superconductivity to exist. For $\omega_0 > \omega_s$ only the polaron phase of the EFC ($F_s = 0$) can exist. The critical point where it appears is determined by solving (13) and (14), and taking (11) and (22) into account in the form

$$E_1 = E_p, \quad E_p = (\omega_p/\omega_0)^2 \Omega g(N_e),$$
$$g(N_e) \equiv \int_0^{N_e} E_F(N)\mu_C(N)\,dN. \tag{24}$$

Below the critical point a finite exciton density appears:

$$N_1 = \frac{\omega_0^2}{\Omega\omega_p^2}\left[\left(\frac{E_p}{E_1}\right)^{1/2} - 1\right], \quad E_1 < E_p. \tag{25}$$

It is important that in the limit (2) of large oscillator strengths f condition (24) is certainly fulfilled for any value of E_1. However, the number of spontaneous excitons turns out to be small, on the order of $f^{-1/2}$ as $f \to 0$.

When condition (23) is fulfilled, it is possible to have a transition from the normal polaron phase of the EFC to the superconducting state. In general, this should be a first-order transition. It is simplest to discuss its specifics in the limit $f \to \infty$, in which, as we have noted above, the normal EFC phase is characterized by disappearance of the small density of excitons. Then we may assume that the formation of the EFC is accompanied simultaneously by the appearance of a superconducting gap and by a discontinuity in the quantity N_1.

In the limit we have chosen, the quantities λ and ω_L from (11) have the form

$$\lambda \approx \mu_C, \quad \omega_L \approx \omega_p (n^*)^{1/2} \tag{26}$$

while expressions (13) and (18) for the energy F simplify considerably because we now can ignore (22). In the dimensionless variables x, Θ, and Γ,

$$n^* = (E_F/\omega_p)^2 \exp(-2x), \quad x > 0,$$
$$T = \frac{4E_F}{\gamma}\Theta \exp\left(-\frac{1+\mu_C}{\mu_C}\right), \quad \Gamma = \frac{E_1}{2D_0\omega_p^2\Omega}\exp\left(2\frac{1+\mu_C}{\mu_C}\right), \tag{27}$$

we find the superconducting gap (20):

$$\Delta(0, n^*) = 2\tilde{E}_F \exp(-x-\beta/x),$$
$$\beta \equiv \frac{1+\mu_C}{\mu_C^2}, \quad \tilde{E}_F \equiv E_F \exp\left(-\frac{1+\mu_C}{\mu_C}\right), \tag{28}$$

and the energy density:

$$F = 2D_0\tilde{E}_F^2 w,$$
$$w \equiv \Gamma\exp(-2x) - [\exp(-x-\beta/x)-\Theta]^2\eta(\exp(-x-\beta/x)-\Theta), \tag{29}$$

where $\eta(z) = 1$ for $z > 0$ and $\eta(z) = 0$ for $z \leqslant 0$.

The equilibrium solution (14), $N_1 = 0$, appears when

$$\Gamma \leqslant 1 \to E_1 < E_c, \quad E_c = 2D_0\omega_p^2\Omega\exp\left(-2\frac{1+\mu_C}{\mu_C}\right). \tag{30}$$

It is useful to turn our attention to the fact that (30) is necessarily fulfilled in the limit of infinite values of ω_p, which corresponds in some sense to the longitudinal frequency ω_L in Eq. (11) having its maximum possible value when $N_1 = 1/\Omega$.

For $\Gamma \to 1 - 0$ the density of excitons and the superconducting gap rapidly go to zero:

$$N_1 = \frac{n^*}{\Omega}, \quad n^* \approx \left(\frac{E_F}{\omega_p}\right)^2 \exp\left(-\frac{4\beta}{1-\Gamma}\right) \to 0,$$
$$\Delta(0, n^*(0)) = \Delta(0), \quad \Delta(0) \approx 2\tilde{E}_F \exp\left(-\frac{2\beta}{1-\Gamma}\right) \to 0. \tag{31}$$

In this range the values of Γ of the dimensionless transition temperature Θ_c are small:

$$\Theta_c \approx \frac{3}{8}\frac{(1-\Gamma)^2}{\beta}\exp\left(-\frac{2\beta}{1-\Gamma}\right)\to 0. \tag{32}$$

For the temperature Θ_m of absolute instability we find

$$\Theta_m \approx {}^4/_3\Theta_c,\ \Theta_c\to 0. \tag{33}$$

Because the superconducting transition under discussion here turns out to be a first-order transition, the observed value of the ratio

$$\gamma^* = 2\Delta(0)/T_c, \tag{34}$$

can differ considerably from the value $\gamma = 3.5$ implied by Eq. (21). Combining (31) and (32) and taking (27) into account, we obtain

$$\gamma^* \approx \frac{8}{3}\frac{\beta}{(1-\Gamma)^2}\gamma \gg 3{,}5. \tag{35}$$

In the limit $\omega_p \to \infty$ (or $\Gamma\to 0$) equilibrium is attained for those exciton concentrations where

$$N_1 = N_0,\ N_0\Omega = (E_F/\omega_p)^2\exp(-2\beta^{1/2}) < 1, \tag{36}$$

which corresponds to the optimum value of the frequency ω_L given by Eq. (11) in (20) and (19), implying a maximum transition temperature:[1]

$$\Theta_c = \Theta_{max},\quad \Theta_{max} = \exp(-2\beta),$$
$$T_{max} \simeq 1{,}14E_F\exp\left(-\frac{1+\mu_c+2(1+\mu_c)^{1/2}}{\mu_c}\right). \tag{37}$$

It is easy to see that (37) determines the transition point for a second-order transition. Accordingly, the ratio (34) is found to equal the value from the BCS theory.

For small finite values of Γ we can obtain an equation for the line of absolute instability:

$$\Theta_m = \Theta_{max}[1-3\cdot 2^{-4/3}\beta^{1/6}\exp({}^4/_3\beta^{1/2})\Gamma^{3/2}], \tag{38}$$

and an equation for the first-order phase transitions, which are close to second-order:

$$\Theta_c = \Theta_{max}[1-\Gamma^{1/2}\exp(\beta^{1/2})], \tag{39}$$

as well as the value of γ^* from Eq. (34):

$$\gamma^* \approx \frac{\gamma}{1-\Gamma^{1/2}\exp(\beta^{1/2})} > 3{,}5. \tag{40}$$

5. LINE OF CRITICAL POINTS IN THE EFC PHASE

The maximum superconducting transition temperatures for fixed values of E_F are attained along a line of critical points in the multi-dimensional parameter space. Within the framework of the approximation that we used, i.e., BCS theory, the maximum transition temperature corresponds to an extremum of the gap as a function (20) of the number of excitons at $T = 0$. Consequently, in order to obtain the line of critical points it is sufficient to solve the equation

$$N_2 = 0,\quad \partial\Delta(0)/\partial n^* = 0 \tag{41}$$

taking into account relations (11) and (19), and then setting the solution so obtained equal to the exciton density Eq. (25) in the normal EFC polaron phase. Unfortunately, it is not possible to solve Eq. (41) for arbitrary values of the parameters. However, for system parameters such that the inequalities (4) hold, the solution (36) satisfies Eq. (41). Therefore, comparing (36) with (25) leads to an equation for the line of critical points:

$$E_1 = E^*,\quad E^* = \left(\frac{\omega_0\omega_p}{E_F^2}\right)^2\Omega g(N_e)\exp(4\beta^{1/2}), \tag{42}$$

close to which the maximum T_c are attained, i.e., from Eq. (37). It is easy to see that such a region of values of ω_0 does exist, and lies within the interval (23). Equation (42) is a weaker condition than (30), especially in the limit $\Gamma\to 0$, which determines the critical points without taking into account the polaron contribution (22) to (17). Physically the existence of such a region is understandable from the following considerations: because of the polaron effect, an exciton density can be "prepared" in the normal phase of the FEC such that a discontinuity in the number of excitons is not required for the appearance of a superconducting gap at a decreased temperature; for large oscillator strength (2) it is necessary to prepare a small number of excitons, i.e., the energy cost is small for their activation, which permits the value of the parameter E_1 to be quite large. Thus, e.g., we can obtain the bound

$$E^* \lesssim (\omega_p/E_F)^2\Omega g(N_e)\exp(2\beta^{1/2}), \tag{43}$$

which can lead to values of $E_1 \sim 1$ eV when (2) is fulfilled and E_F is small.

Near the line of critical points (42) the transition temperature T_c is given by the universal relation (37), independent of the parameters ω_0 and ω_p ($\omega_p \gg \omega_0$). In the case of a Fermi surface of cylindrical shape, which represents the real form of the Fermi surface in the HTSC materials rather well,[22] we have $E_F \sim N_e$. Accordingly, from (37) we find $T_c \sim N_e$ as $N_e \to 0$ and an exponential decrease for large values of N_e. The qualitative description of this behavior can be obtained by making use of quasi-two-dimensional estimates.

$$E_F \approx e^2/2\varepsilon_\infty c\mu_c,\quad N_e \approx 2D_0E_F. \tag{44}$$

Substitution of (44) into (37) gives

$$T_{max} \approx 0{,}23\frac{N_e}{D_0}\exp\left\{-\left[1+2\left(1+\frac{1}{\varkappa N_e}\right)^{1/2}\right]\varkappa N_e\right\},$$
$$\varkappa \equiv \varepsilon_\infty c/D_0e^2. \tag{45}$$

The optimum T_{max} is attained for

$$N_e = N_{opt},\ N_{opt} \approx 0{,}28/\varkappa \tag{46}$$

and lies with the range $\lesssim$ 100–300 K (Ref. 1) for reasonable values of $\varkappa$. In the optimum condition (46) there appears the universal relation

$$N_{opt} \approx 18{,}9D_0T_{max}. \tag{47}$$

Using the published data for the density of states in HTSC materials $D_0 \approx 1\ \text{eV}^{-1}$ (see Refs. 6, 22) we obtain a value of $N_{opt} \approx (2\text{–}6)\cdot 10^{21}\ \text{cm}^{-3}$. For these values of D_0 and N_{opt},

Eqs. (44) give $E_F \approx 0.1$–0.2 eV (Ref. 6). Thus, the dependence (45) agrees rather well with the experimental data of Ref. 22 for such a simple model (see also Ref. 23).

The universality of Eq. (37) and the behavior of T_c near the critical line imply certain things about the weakening of the isotopic shift as we approach this line (42), independent of the nature of the exciton. In fact, the parameters of the latter are contained only in the quantity that characterizes the deviation ($E_1 \neq E^*$) from the critical point $T_{\max}$, i.e., the parameter Γ of Eq. (27), where in place of E_1 we substitute the difference $|E_1 - E^*|$ [see (42)]. If for some reason or another this parameter undergoes an isotopic shift, e.g., in the form $\Gamma \sim M^{2\nu}$, $\nu > 0$, where M is the ionic mass, then from (39) we can obtain the value

$$\alpha = \nu(\Theta_{max} - \Theta_c) \to 0 \tag{48}$$

of the isotopic exponent ($\delta T_c / T_c = -\alpha \delta M / M$). As $\Gamma \to 1$, i.e., in the vicinity of low T_c (32), the value of α formally becomes arbitrarily large:

$$\alpha = \nu/(1-\Gamma)^2 \to \infty. \tag{49}$$

Let us note that decreasing α with increasing $T_c \to T_{\max}$ agrees qualitatively with the empirically observed rule (see Ref. 24). Also noteworthy is the recently observed anomalously large isotopic shift[25] which accompanies the decrease in T_c.

In concluding this section let us discuss the possibility of a spontaneous population inversion of the excitonic level $E_2 > E_1$. As we have already remarked, when the bound (23) is violated a superconducting state in the EFC phase with $N_1 \neq 0$ and $N_2 = 0$ is impossible. However, the formal transition in (11) from the condition $N_1 > N_2$ to

$$N_2 - N_1 > N_c, \quad \Omega N_c = \omega_0^2/\omega_p^2 < 1, \tag{50}$$

in which the smallness in (23) of the frequency ω_0 is no longer implied, leads to a coupling constant

$$\lambda \approx \mu_c \frac{N_c}{N_2 - N_1 - N_c} > \mu_c, \tag{51}$$

which ensures the existence of the superconduting gap (20), at least in the region $N_2 - N_1 \to N_c + 0$. However, it is clear that N_c given by Eq. (50) is that critical value of the population of the level $E_2 (N_1 = 0)$ at which the longitudinal frequency ω_L given in (11) reduces to zero; this implies that a charge-density wave appears near the Fermi surface and accompanies the exciton polarization wave. Thus, a superconducting state in the EFC phase with a population inversion of excitonic levels should be accompanied by the appearance of a nonuniform superstructure of this kind,[3)] and the large coupling constant (51) is a consequence of the strong overscreening in a state with the charge-density wave (see Ref. 1).

6. DISCUSSION OF RESULTS

It is usually assumed that the role of excited states that lie considerably above the Fermi energy reduces only to a redefinition of the high-frequency susceptibility of the system, which suggests that their influence on the dynamic behavior of low-energy processes at the Fermi surface can be neglected. However, as was noted first in Ref. 26, such states are fundamentally important for metal-insulator transitions, which in essence are interpreted[26] as the spontaneous population of high-energy but delocalized states by electrons, where the cost in energy is compensated by the effect of screening of the Coulomb interaction. In fact, analogous considerations applied to a classical system of Frenkel defects are invoked to describe the superionic transition in Ref. 27.

The primary intent of the discussion of the EFC model given here is to draw attention to the fundamental role which non-ground-state excitations possessing large oscillator strengths can play in a metal. It has been shown that under certain entirely realistic conditions it is energetically favorable for a metal to undergo a transformation in such a way that a certain quantity of excitons are spontaneously created, which are generally speaking high-energy and thus easily polarized. The compensating mechanism can be the polaron shift of the Fermi energy (up to the transition from the metallic state to a Wigner insulator) as well as the appearance of superconductivity.

It is significant that the formation of a superconducting state in the EFC phase is clearly possible in the limit of large plasma frequency ω_p of the non-ground-state exciton transition given by (1), whereas for the ground-state exciton this is the very limit in which the superconductivity of the metal disappears due to the absence of suppression of the Coulomb repulsion. We also note that for large ω_p the effect of EFC formation makes possible a self-consistent readjustment of the system so that the values of the parameters[1] that determine the maximum superconducting transition temperature are optimized.

The requirement of large values of ω_p does not presuppose that the exciton binding energy be comparable to the width of the forbidden gap. On the other hand, the energy of the ground-state exciton E_1, as is clear for (30) and (42), can be rather large. Consequently, the appearance of the EFC does not lead directly to the formation of a state of excitonic-insulator type.[28] However, as was noted by B. A. Volkov and Yu. V. Kopaev, the condition for spontaneous appearance of excitons can be described in terms of strong renormalization of the energy E_1 of the ground-state exciton down to zero. Thus, the question of the role played by insulator formation of the type discussed in Ref. 28 becomes important. Nevertheless, the discussion given here shows that coherence of the excitonic ensemble is not a necessary condition for formation of an EFC. Therefore, we can hope that the subsequent inclusion of collective intrinsic exciton effects will not change the fundamental results of the model.

In connection with the HTSC problem, it is useful to note some fundamental characteristics of the effect discussed here. The formation of a superconducting EFC state takes place through a first-order phase transition which is close to second order, i.e., it is accompanied by a discontinuity in the gap, which agrees with the experimental data (see Ref. 22).

The maximum temperatures (37) are attained on a line of critical points of the normal-superconducting phase transition for the EFC, near which the isotope effect has neither a direct nor indirect influence on T_c. This latter circumstance is correct no matter what sort of exciton transition is involved, and agrees with the empirical rule that the isotopic

shift of T_c is small in HTSC oxides which exhibit high values of T_c (Ref. 24).

Within the model discussed here, it is possible to obtain a linear dependence of T_c on the carrier density when the latter is small without making the assumption of Ref. 23, i.e., treating the superconducting transition as a process involving Bose condensation of quasi-two-dimensional localized pairs.

One problem posed by HTSC is that it is difficult to reconcile the large value of the ratio $\gamma^* \approx 8$ [Eq. (34)] with the absence of an optical Holstein structure.[29] In the EFC model the deviation of γ^* from the value given by BCS theory is due not so much to the strength of interaction as to proximity to the line of critical points. Accordingly, a large γ^* is possible even in the weak-coupling limit, in which the Holstein structure does not appear.

A characteristic feature of the EFC is the presence of a wide optical absorption band [see (16) and (15)] which extends from the small energy ω_0 (on the order of the exciton binding energy) of the non-ground-state transition up to double the energy of the ground-state exciton $2E_1$. The intensity of this band is practically independent of temperature. As is well-known, the optical spectra of HTSC materials exhibits an extensive background with similar properties,[22] which is interpreted[30] to be a manifestation of the presence of strong-coupling polarons. However, realization of a strong-coupling polaron regime in the oxides is problematic because the resistive measurements in the normal phase give values of $\lambda < 1$ (Ref. 22). Furthermore, there is evidence for the existence of a well-defined edge to the Fermi surface,[22] which also argues against large coupling constants.[30] It is easy to see that in the model presented here the appearance of a wide absorption band induced by spontaneous excitons is permitted even for small λ, i.e., in the region of applicability of Fermi liquid theory, as shown by Eq. (11). Furthermore, unlike the optical effects of Ref. 30 caused by strong-coupling polarons, the appearance of this band appears to have a threshold with regard to the concentration N_e of free carriers [see Eqs. (24) and (25)] near which we should observe features which are characteristic of phase transitions.

Thus, it is worthwhile to investigate photo-induced IR absorption lines experimentally in the insulating phase of HTSC materials for differing degrees of doping. One indication of a phase transition into the EFC state is suggested by the appearance at a certain concentration N_e of a wide band which extends from the low energy ω_0 up to large energies E_1, where ω_0 determines the position of the photo-induced resonance while E_1 corresponds to that frequency of the external pump signal for which this resonance is a maximum. Similar experiments should also be carried out on the material CuCl, which demonstrates a gigantic two-photon absorption.[18] In this case a wide band of single-photon absorptions should appear at a certain degree of doping (donors or acceptors), starting near the bi-exciton binding energy.

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[1)]Estimate (1) is violated when the system is close to a transition point into a state with a charge-density wave, where it is possible for soft longitudinal excitations to exist (see Ref. 1).

[2)]The situation in which a spontaneous population inversion $N_2 > N_1$ is possible, which requires a separate discussion, will be addressed partially in what follows.

[3)]Starting from other considerations, the authors of Ref. 10 suggested earlier that there was an interrelation between the superconducting transition and the appearance of a crystalline superstructure in HTSC compounds.

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