Superconducting properties of a nonideal bipolaron gas

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Abstract

The properties of a Bose gas of translation-invariant (TI) bipolarons analogous to Cooper pairs are considered. As in the BCS theory, the description of a TI-bipolaron gas is based on the electron-phonon interaction and Froehlich Hamiltonian. As distinct from the BCS theory, when the correlation length greatly exceeds the mean distance between the pairs, here we deal with the opposite case when the correlation length is much less than the distance between the pairs. We calculate the critical temperature of the transition of a TI-bipolaron Bose-gas into the superconducting state, its energy, heat capacity and heat of the transition. The results obtained are used to explain the experiments on high-temperature superconductors. Possible ways of raising the critical temperature of high-temperature superconductors are discussed.

Keywords: high-temperature superconductors, translation-invariant (TI) bipolarons

1. Introduction

In this paper a translation-invariant (TI) bipolaron gas is considered as a gas of Bose particles capable of forming a Bose condensate. As is shown in \cite{1-3}, a TI bipolaron is a state of two electrons coupled by electron-phonon interaction (EPI) which remains delocalized for any value of the EPI constant. According to \cite{1-3}, this state of electrons is energetically more advantageous than a self-trapped localized two-electron state or a Pekar bipolaron.

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Since a TI-bipolaron gas is a gas of charged bosons, its Bose condensate corresponds to a superconducting (SC) state. This fact is of interest since nowadays numerous experimental and theoretical papers on high-temperature superconductivity (HTSC) rely on the idea of bipolarons [4]-[8].

It is important that the TI-bipolaron theory relies on the same initial Froehlich Hamiltonian that the BCS theory does [9]. The only difference is that in the BCS theory electrons interact with acoustical phonons, while in the TI-bipolaron theory - with optical ones, because the properties of HTSC are better explained in terms of this interaction. As for the difference in the theoretical approaches, the BCS theory is based on the exclusion of phonon variables from the Hamiltonian and investigation of the resultant Hamiltonian containing only electron variables. In the TI-bipolaron gas theory, on the contrary, the electron variables are excluded from the Hamiltonian which results in the Hamiltonian depending only on phonon variables. The spectrum of eigen values of such a Hamiltonian determines the spectrum of bipolaron states excitations. The latter is just used to describe the statistic properties of an ideal bipolaron gas.

This approach, however, raises some important questions. Being charged, a TI-bipolaron gas cannot be ideal since there must be a Coulomb interaction between the bipolarons. According to the theory of a nonideal gas, consideration of an interaction between particles leads to qualitative changes in the spectral properties of the gas. According to [10], even in the case of a short-range interaction, consideration of the latter results in the emergence of a gap in the gas spectrum which is absent in the ideal gas. Still greater changes would be expected in the case of a long-range Coulomb interaction. Discussion of these problems is just the aim of this paper.

The logical scheme of our approach is as follows: a) first we consider a special case of two electrons interacting with a phonon field. This is the classical problem of a bipolaron [11].

b) then we deal with a many-electron problem which leads to the concept of Fermi liquid. For this many-electron problem we analyze the case of two additional electrons occurring over the Fermi surface (near it) coupled by the
c) then we believe that almost all the electrons occurring in the \([E_F+E_{pol}, E_F]\)
energy layer, where \(E_F\) is the Fermi energy, \(E_{pol}\) is the polaron energy, are in
the TI-polaron state \([12]\); accordingly all electrons are in the TI-bipolaron states
in narrow energy layer \([E_F + E_{bp}/2 - \delta E, E_F + E_{bp}/2 + \delta E]\), \(\delta E \to 0\), where
\(E_{bp}\) is the energy of TI-bipolaron. Condensed bipolaron gas leads to the infinite
density of electronic states in this layer.

d) bipolarons are considered to be charged bosons placed in the electron
Fermi liquid (polaron gas) which screens the interaction between the bipolarons;
in this case the problem is reduced to that of a nonideal charged Bose gas.

e) the spectrum obtained upon solving this problem is used to calculate the
statistic properties of a TI-bipolaron gas.

As was noted above, the superconductivity theory is developed as a theory of
a bipolaron Bose gas where the superconducting state is a bipolaron condensate.
As distinct from an ordinary ideal Bose gas where superfluidity is absent, an
ideal TI-bipolaron gas demonstrates this phenomenon. Hence, in the theory
under consideration, superconductivity is a superfluidity of an ideal bipolaron
gas. In an ordinary Bose gas, superfluidity is possible only if bosons interact with
one another and usually takes place only at low temperatures. Being superfluid,
an ideal bipolaron gas retains this property even in the case of its nonideality.

The considered theory of a bipolaron gas can be used as the basis for the
theory of high-temperature superconductivity. The latter, however, has some
limitations, if for no other reason than because it, like the BCS theory, deals
with the case of a continuous medium. It is important, however, that being
delocalized, a TI bipolaron does not feel discreteness of the lattice, nor the
presence of impurities or defects, if the interaction with them is not strong.

If the interaction of electrons with the lattice is strong or, what is the same,
an electron occurring at an atom of the lattice weakly interacts with neighbor-
boring atoms, then the TI bipolaron whose interaction is based on Froehlich
Hamiltonian, breaks. In this case the state of the electrons is described by dis-
crete models. The most popular superconductivity theories developed within
this approach are the model of resonating valence bonds (RVB) and t-J model [13]. They are based on Hubbard Hamiltonian and its generalization Hubbard-Holstein Hamiltonian. In the continuum approximation the latter is transformed to Froehlich Hamiltonian which is basic for the TI-bipolaron theory.

The problems of developing the theory of superconductivity as a theory of Bose condensation with the use of discrete models can be illustrated by the use of the small-radius bipolaron theory for description of HTSC [4], [5]. This theory relies on the idea that a stable bound bipolaron state is formed at one site of the lattice. The small-radius bipolarons thus formed are considered as a gas of charged bosons. However, really this approach can hardly be applied to HTSC since, on the one hand, for small-radius bipolarons to be formed the electron-phonon interaction (EPI) constant should be large, but on the other hand, for high value of Bose condensation temperature we need a small mass, i.e. a small EPI constant [14]-[19]. It is clear that the HTSC theory based on the concept of a small-radius bipolaron which uses any other (non-phonon) mechanisms of interaction would encounter the same problems.

The theory developed below will be shown to be free of this drawback.

The paper is arranged as follows. In §2 we consider a problem of a nonideal gas of TI-bipolarons which is reduced to the well-known problem of a charged Bose gas. It is shown that due to screening in the system under consideration no gap caused by interaction of Bose particles arises and actually the problem is reduced to that of an ideal gas of TI-bipolarons having a gap in the spectrum.

In §3 we deal with the thermodynamic properties of a TI-bipolaron gas. For various values of the parameters which are the phonon frequencies, we calculate the values of the critical temperatures of Bose condensation, the heat of the transition to the condensate state, the heat capacity and jumps in the heat capacity at the transition point.

In §4 the results are compared with experimental data.

In §5 we sum up the results obtained and discuss possible ways of raising the critical temperature of high-temperature superconductors.
2. Nonideal TI-bipolaron gas

To develop a theory of a nonideal TI-bipolaron gas we should know the spectrum of the states of an individual TI bipolaron in a polar medium. This problem was thoroughly discussed in \[11\]. As is shown in \[12\], this spectrum of the states will be the same as that of TI bipolarons arising in the vicinity of the Fermi surface. Hence TI bipolarons in the \([E_F + E_{bp}/2, E_F]\) layer can be considered as a TI-bipolaron Bose gas occurring in the polaron gas \[20\]. If we believe that TI bipolarons do not interact with one another, then the gas can be considered to be ideal. Its properties will be fully determined if the spectrum of an individual TI bipolaron is known.

When considering the theory of an ideal gas and the theory of superconductivity on the basis of Bose particles of TI bipolarons, Coulomb interaction between the electrons is taken into account only for electron pairs, i.e. only for the problem of an individual bipolaron. Hamiltonian of such a system, according to \[11\], has the form:

\[
H_0 = \sum_k \epsilon_k \alpha_k^+ \alpha_k
\]  

(1)

\[
\epsilon_k = E_{bp} \Delta_{k,0} + (\omega_0 + E_{bp} + k^2/2M_e) (1 - \Delta_{k,0})
\]  

(2)

where \(\alpha_k^+, \alpha_k\), -are operators of the birth and annihilation of TI bipolarons; \(\epsilon_k\) is the spectrum of TI bipolarons obtained in \[11\]; \(E_{bp}\) is the energy of a TI bipolaron; \(M_e = 2m^*\), \(m^*\) is the electron effective mass; \(\omega_0 = \omega_0(\vec{k})\) is the energy of an optical phonon; \(\Delta_{k,0} = 1\) for \(k = 0\) and \(\Delta_{k,0} = 0\) for \(k \neq 0\). Expression (1), (2) can be rewritten as:

\[
H_0 = E_{bp} \alpha_0^+ \alpha_0 + \sum_k (\omega_0 + E_{bp} + k^2/2M_e) \alpha_k^+ \alpha_k
\]  

(3)
where the prime in the sum in the right-hand side of (3) means that the term with \( k = 0 \) is lacking in the summation. Extraction of the term with \( k = 0 \) corresponds to the formation of a Bose condensate, where:

\[
\alpha_0 = \sqrt{N_0}
\]

(4)

\( N_0 \) is the number of TI bipolarons in the condensed state. Thus, in the theory of an ideal TI bipolaron gas, the first term is merely \( E_{bp} N_0 \).

In developing the theory of a nonideal TI-bipolaron Bose gas we will proceed from the Hamiltonian:

\[
H = E_{bp} N_0 + \sum_k' (\omega_0 + E_{bp}) \alpha_k^+ \alpha_k + \sum_k t_k \alpha_k^+ \alpha_k + 1/2 V \sum_{k,k',k''} V_{k-k',k''} \alpha_k^+ \alpha_{k'} \alpha_{k''}, \quad t_k = k^2 / 2M_c,
\]

(5)

This is Hamiltonian \( H_0 \) (3) plus the term responsible for bipolaron interaction; \( V_k \) is the matrix element of the bipolaron interaction. The last two terms in (5) exactly correspond to the Hamiltonian of a charged Bose-gas [21]. Following the standard procedure of the Bose condensate resolving, we get from (5):

\[
H = E_{bp} N_0 + \sum_k' (\omega_0 + E_{bp}) \alpha_k^+ \alpha_k + \sum_k \left[ (t_k + n_0 V_k) \alpha_k^+ \alpha_k + 1/2 n_0 V_k (\alpha_k \alpha_{-k} + \alpha_k^+ \alpha_{-k}^+) \right],
\]

(6)

where \( n_0 = N_0 / V \) is the density of the particles in a Bose-condensate. Then, using Bogolyubov transformation:

\[
\alpha_k = u_k b_k - v_k b_k^+, \quad u_k = \left[ (t_k + n_0 V_k + \epsilon_k) / 2\epsilon_k \right]^{1/2}, \quad v_k = \left[ (t_k + n_0 V_k - \epsilon_k) / 2\epsilon_k \right]^{1/2}
\]

(7)
we get the Hamiltonian:

\[ H = E_{bp}N_0 + U_0 + \sum_k' \left( \omega_0 + E_{bp} + \epsilon_k \right) b_k^* b_k, \]

\[ U_0 = \sum_k' \left( \epsilon_k - t_k - n_0 V_k \right), \]  

(8)

where \( U_0 \) is the ground state energy of a charged Bose gas with no regard for its interaction with the crystals polarization. Hence, the spectrum of excitations of a nonideal TI-bipolaron gas has the form:

\[ E_k = E_{bp} + u_0 + \left( \omega_0(\tilde{k}) + \sqrt{k^4/4M_e^2 + k^2V_kn_0/M_e} \right) \]

\[ (1 - \Delta_{k,0}), \]

(9)

where \( u_0 = U_0/N, \) \( N \) is the total number of particles. If we reckon the energy of excitations from the ground state energy of a bipolaron in a nonideal gas, on the assumption that \( \Delta_k = E_k - (E_{bp} + u_0), \) then \( \Delta_k \) for \( k \neq 0 \) will be:

\[ \Delta_k = \omega_0(\tilde{k}) + \sqrt{k^4/4M_e^2 + k^2V_kn_0/M_e} \]

(10)

The spectrum obtained suggests that a TI-bipolaron gas has a spectrum gap \( \Delta_k \) between the ground and the excited states, i.e. it is superfluid. Being charged, such a gas will be superconducting. To determine the particular form of the spectrum we should know the value of \( V_k. \) If we considered only a charged Bose gas with positive homogeneous background induced by rigid ion backbone, then the value of \( V_k \) in (9) would be equal to \( V_k = 4\pi e_B^2/k^2 \) in the absence of screening. Accordingly the second term in the radical expression in (9) would be equal to \( \omega_p^2 = 4\pi n_0 e_B^2/M_e, \) where \( \omega_p \) is the plasma frequency of the boson gas, \( e_B \) is the boson charge (2e for a TI bipolaron). Actually, if we take account of screening, then \( V_k \) will take the form of \( V_k = 4\pi e^2/k^2\epsilon_B(k), \) where \( \epsilon_B(k) \) is the dielectric permittivity of a charged Bose gas which was calculated in [22, 23]. The expression obtained for \( \epsilon_B(k) \) in [22, 23] is too lengthy and is not given here. In the case of a TI-bipolaron Boson gas under consideration this modification of \( V_k \) is not sufficient. As was shown in [12], bipolarons are
just few charged particles in the system. Most of the charged particles occur in the electron gas where the bipolarons reside. It is just the electron gas that makes the main contribution into the screening of the interaction between the bipolarons. To take account of this screening $V_k$ should be expressed as 

$$V_k = \frac{4\pi e^2}{k^2} \epsilon_e(k)$$

where $\epsilon_e(k)$ is the dielectric permittivity of the electron gas. Finally, if we consider the mobility of the ion backbone, $V_k$ will take the form 

$$V_k = \frac{4\pi e^2}{k^2} \epsilon_e(k) \epsilon_\infty \epsilon_0$$

where $\epsilon_\infty$, $\epsilon_0$ are the high-frequency and static dielectric permittivities.

As a result, $\Delta_k$ is written as:

$$\Delta_k = \omega_0(\vec{k}) + k^2/2Me \sqrt{1 + \chi(k)}$$  \hspace{1cm} (11)

$$\chi(k) = \frac{\omega_F^2}{k^4} \epsilon_B(k) \epsilon_e(k) \epsilon_\infty \epsilon_0$$  \hspace{1cm} (12)

To estimate the value of $\chi(k)$ in (11) let us consider the long-wave limit. In this limit $\epsilon_e(k)$ has Thomas-Fermi form: $\epsilon_e(k) = 1 + \kappa^2/k^2$, where $\kappa = 0.815 k_F (r_s/a_B)^{1/2}$, $a_B = \hbar/Me e^2 B$, $r_s = (3/4\pi n_0)^{1/3}$, therefore, according to \[22, 23\], the value of $\epsilon_B(k)$ is equal to $\epsilon_B(k) = 1 + q_s^4/k^4$, $q_s = \sqrt{2M e \omega_p}$.

Bearing in mind that in calculations of thermodynamic quantities the main contribution is made the values of $k$: $k^2/2Me \approx T$, (where $T$ is the temperature), the value of $\chi(k)$ will be estimated to be $\chi \sim T/\epsilon_F \epsilon_\infty \epsilon_0$, where $\epsilon_F$ is the Fermi energy. Hence the spectrum of the screened TI-bipolaron gas differs from the spectrum of an ideal TI-bipolaron gas (2) only slightly.

Notice that due to screening the value of the correlation energy $u_0$ in (10) turns out to be much less than the energy calculated in \[21\] without regard for screening, and for real values of the parameters, much less than the bipolaron energy $|E_{bp}|$. Notice also that in view of screening a TI-bipolaron gas does not form the Wigner crystal for arbitrarily small bipolaron density.
3. Statistical thermodynamics of a low-density TI-bipolaron gas

As was shown in §2, a nonideal Bose gas of TI bipolarons differs from an ideal one only slightly.

Let us consider an ideal Bose gas of TI bipolarons as a system of \( N \) particles occurring in a volume \( V \). Let us write \( N_0 \) for the number of particles in the lower one-particle state, and \( N' \) for the number of particles in the higher states. Then:

\[
N = \sum_{n=0,1,2,...} \bar{m}_n = \sum_n \frac{1}{e^{(E_n - \mu)/T} - 1},
\]

\[
N_0 = \frac{1}{e^{(E_{bp} - \mu)/T} - 1},
\]

\[
N' = \sum_{n_i \neq 0} \frac{1}{e^{(E_n - \mu)/T} - 1}.
\]

In this section we will consider \( \omega_0 \) as independent of \( k \).

In the expression for \( N' \), we will perform integration over quasicontinuous spectrum (instead of summation) and assume \( \mu = E_{bp} \). As a result from (13), (14) we get an equation for the critical temperature of Bose condensation \( T_c \):

\[
C_{bp} = f_{\bar{\omega}} \left( \bar{T}_c \right),
\]

\[
f_{\bar{\omega}} \left( \bar{T}_c \right) = \bar{T}_c^{3/2} F_{3/2} \left( \bar{\omega}/\bar{T}_c \right),
\]

\[
F_{3/2}(\alpha) = \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} \frac{x^{1/2}dx}{e^{x+\alpha} - 1},
\]

\[
C_{bp} = \left( \frac{n^2/3\pi \hbar^2}{M_{e\omega^*}} \right)^{3/2},
\]

\[
\bar{\omega} = \frac{\omega_0}{\omega^*}, \quad \bar{T}_c = \frac{T_c}{\omega^*},
\]

where \( n = N/V \). Relation of the notation \( F_{3/2} \) with other notations is given in the Appendix.

Fig. 1 shows a graphical solution of equation (15) for the values of the parameters \( M_c = 2m^* = 2m_0 \), where \( m_0 \) is the mass of a free electron in vacuum,
Figure 1: Solutions of equation (15) with $C_{bp} = 331, 3$ and $\hat{\omega}_i = \{0, 2, 1; 2, 10, 15; 20\}$, which correspond to $\hat{T}_{ci}$: $\hat{T}_{c1} = 27, 3; \hat{T}_{c2} = 30; \hat{T}_{c3} = 32; \hat{T}_{c4} = 42; \hat{T}_{c5} = 46, 2; \hat{T}_{c6} = 50$. 
\( \omega^* = 5 \text{ meV (}\approx 58 K\), \( n = 10^{21} \text{ cm}^{-3} \) and the values: \( \tilde{\omega}_1 = 0, 2; \tilde{\omega}_2 = 1; \tilde{\omega}_3 = 2; \tilde{\omega}_4 = 10, \tilde{\omega}_5 = 15, \tilde{\omega}_6 = 20. \)

It is evident from Fig. 1 that the critical temperature grows as the phonon frequency \( \omega_0 \) increases. The relations of the critical temperatures \( T_{ci}/\omega_{oi} \) corresponding to the parameter values chosen are listed in Table 1.

| i | \( \tilde{\omega}_i \) | 0   | 0.2 | 1   | 2   | 10  | 15  | 20  |
|---|-----------------|-----|-----|-----|-----|-----|-----|-----|
| \( T_{ci}/\omega_{oi} \) | \( \infty \) | 136.6 | 30  | 16  | 4.2 | 3   | 2.5 |
| \( q_i/T_{ci} \) | 1.3  | 1.44 | 1.64 | 1.8 | 2.5 | 2.8 | 3   |
| \(-\Delta(\partial C_{v,i}/\partial T)\) | 0.11 | 0.12 | 0.12 | 0.13 | 0.14 | 0.15 | 0.15 |
| \( C_{v,i}(T_c - 0) \) | 1.9  | 2.16 | 2.46 | 2.7 | 3.74 | 4.2 | 1.6 |
| \( (C_s - C_n)/C_n \) | 0    | 0.16 | 0.36 | 0.52 | 1.23 | 1.53 | 1.8 |
| \( n_{bp_i} \text{ cm}^{-3} \) | \( 16\cdot10^{19} \) | \( 9.4\cdot10^{18} \) | \( 4.2\cdot10^{18} \) | \( 2.0\cdot10^{18} \) | \( 1.2\cdot10^{17} \) | \( 5.2\cdot10^{14} \) | \( 2.3\cdot10^{13} \) |

Table 1: Calculated characteristics of Bose-gas of TI-bipolarons with concentration \( n = 10^{21} \text{ cm}^{-3} \).

Table 1 suggests that the critical temperature of a TI-bipolaron gas is always higher than that of an ideal Bose gas (IBG). It is also evident from Fig. 1 that an increase in the concentration of TI bipolarons \( n \) will lead to an increase in the critical temperature, while a gain in the electron mass \( m^* \) to its decrease. For \( \tilde{\omega} = 0 \), the results go over into the well-known IBG limit. In particular, (15) for \( \tilde{\omega} = 0 \) yields the expression for the critical temperature of IBG:

\[
T_c = 3.31\hbar^2n^{2/3}/M_e
\]  

(16)

It should be stressed however that (16) involves \( M_e = 2m^* \), rather than the bipolaron mass. This resolves the problem of the low temperature of condensation which arises both in the small-radius polaron theory and in the large-radius polaron theory where expression (16) involves the bipolaron mass \( \square \). Another important result is that the critical temperature \( T_c \) for the parameter values calculated considerably exceeds the energy of the gap \( \omega_0 \).
From (13), (14) it follows that:
\[
\frac{N'(\tilde{\omega})}{N} = \frac{\tilde{T}^{3/2} C_{bp}}{F_{3/2}} \left( \frac{\tilde{\omega}}{T} \right)
\]  
(17)

\[
\frac{N_0(\tilde{\omega})}{N} = 1 - \frac{N'(\tilde{\omega})}{N}
\]  
(18)

Fig. 2 shows the temperature dependencies of the number of supracondensate particles \(N'\) and the number of particles in the condensate \(N_0\) for the above-listed parameter values \(\tilde{\omega}_i\).

Fig. 2 suggests that, as would be expected, the number of particles in the condensate grows as the gap increases \(\omega_i\).

The energy of a TI-bipolaron gas \(E\) is determined by the expression:
\[
E = \sum_{n=0,1,2,...} \bar{m}_n E_n = E_{bp} N_0 + \sum_{n \neq 0} \bar{m}_n E_n
\]  
(19)

With the use of (14), (15) and (19) the specific energy (i.e. the energy per one TI bipolaron) \(\tilde{E}(\tilde{T}) = E/N\omega^*\), \(\tilde{E}_{bp} = E_{bp}/\omega^*\) will be:
\[
\tilde{E}(\tilde{T}) = \tilde{E}_{bp} + \frac{\tilde{T}^{5/2} C_{bp}}{F_{3/2}} \left( \frac{\tilde{\omega} - \tilde{\mu}}{T} \right) \left[ \tilde{\omega} + \frac{F_{5/2} \left( \frac{\tilde{\omega} - \tilde{\mu}}{T} \right)}{F_{3/2} \left( \frac{\tilde{\omega} - \tilde{\mu}}{T} \right)} \right],
\]  
(20)

where \(\tilde{\mu}\) is determined by the equation:
\[
\tilde{T}^{3/2} F_{3/2} \left( \frac{\tilde{\omega} - \tilde{\mu}}{T} \right) = C_{bp}
\]  
(21)

Relation of \(\tilde{\mu}\) with the chemical potential of the system \(\mu\) is written as: \(\tilde{\mu} = (\mu - E_{bp})/\omega^*\). From (20)-(21) we can also get the expressions for the free energy:
\[
\Delta F = -\frac{\tilde{\mu}}{\tilde{T}^1} \Delta E, \quad \Delta F = F - E_{bp} N, \quad \Delta E = E - E_{bp} N \quad \text{and entropy} \quad S = -\partial F/\partial T.
\]

Fig. 3 illustrates the temperature dependencies of \(\Delta \tilde{E} = \tilde{E} - \tilde{E}_{bp}\) for the above-listed parameter values \(\omega_i\). The salient points on the curves \(\Delta \tilde{E}_i(\tilde{T})\) correspond to the values of critical temperatures \(T_{ci}\).
Figure 2: Temperature dependencies of the relative number of supracondensate particles $N'/N$ and the particles occurring in the condensate $N_0/N = 1 - N'/N$ for the parameter values $\tilde{\omega}_i$, given in Fig. [I].
Figure 3: Temperature dependencies $\Delta E(\tilde{T}) = \tilde{E}(\tilde{T}) - \tilde{E}_{bp}$ for the parameter values $\tilde{\omega}_i$ presented in Fig. [1][2]
The dependencies obtained enable us to find the heat capacity of a TI bipolaron gas: \( C_v(\tilde{T}) = d\tilde{E}/d\tilde{T} \). With the use of (20) \( C_v(\tilde{T}) \) for \( \tilde{T} \leq \tilde{T}_c \) is expressed as:

\[
C_v(\tilde{T}) = \frac{\tilde{T}^{3/2}}{2C_{bp}} \left[ \tilde{\omega}^2 F_{1/2} \left( \frac{\tilde{\omega}}{\tilde{T}} \right) + 6 \left( \frac{\tilde{\omega}}{\tilde{T}} \right)^2 F_{3/2} \left( \frac{\tilde{\omega}}{\tilde{T}} \right) + 5F_{5/2} \left( \frac{\tilde{\omega}}{\tilde{T}} \right) \right],
\]

(22)

\[
F_{1/2}(\alpha) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{1}{\sqrt{x}} \frac{dx}{e^{x+\alpha} - 1}
\]

Expression (22) yields a well-known exponential dependence of the heat capacity at low temperatures \( C_v \sim \exp(-\omega_0/T) \), caused by the availability of the energy gap \( \omega_0 \).

Fig. 4 shows the temperature dependencies of the heat capacity \( C_v(\tilde{T}) \) for the above-listed values of the parameters \( \tilde{\omega}_i \). Table 1 lists the values of jumps in the heat capacity \( \tilde{\omega}_i \) for the same parameter values:

\[
\Delta \frac{\partial C_v(\tilde{T})}{\partial \tilde{T}} = \left. \frac{\partial C_v(\tilde{T})}{\partial \tilde{T}} \right|_{\tilde{T}=\tilde{T}_c+0} - \left. \frac{\partial C_v(\tilde{T})}{\partial \tilde{T}} \right|_{\tilde{T}=\tilde{T}_c-0}
\]

at the transition points.

The dependencies obtained enable us to find the latent heat of the transition \( q = TS \), where \( S \) is the entropy of the supracondensate particles. At the point of transition this value is equal to: \( q = 2T_c C_v(T_c-0)/3 \), where \( C_v(T) \) is determined by formula (22) and for the above-listed values of \( \omega_i \) is given in Table 1.

The results obtained can be generalized to the case of a nonideal charged Bose gas if we replace \( E_{bp} \) by \( E_{bp} + u_0 \) and \( M \) by \( M\sqrt{1+\chi} \) in formulas of this section. The results can also be generalized to the case when the dispersion of \( \omega_0(k) \) takes the form \( \omega_0(k) = \omega_0(0) + \beta k^2 \). In this instance \( \omega_0 \) is replaced by \( \omega_0(0) \) and \( 1/(2M_c) \) is replaced by \( \beta + 1/(2M_c) \).

4. Comparison with the experiment

Success of the BCS theory is related to the fact that it has managed to explain some experiments in ordinary metal superconductors where EPI is not
Figure 4: Temperature dependencies of the heat capacity for various values of the parameters

\[ \omega_i: \omega_0 = 0; T_C_0 = 25, 2; C_v(T_{C1} - 0) = 2, 16; C_v(T_{C1} + 0) = 1, 9; \omega_1 = 1; T_C_1 = 27, 3; C_v(T_{C1} - 0) = 2, 16; C_v(T_{C1} + 0) = 1, 9; \omega_2 = 1; T_C_2 = 30; C_v(T_{C2} - 0) = 2, 46; C_v(T_{C2} + 0) = 1, 8; \omega_3 = 2; T_C_3 = 32, 1; C_v(T_{C3} - 0) = 2, 7; C_v(T_{C3} + 0) = 1, 78; \omega_4 = 10; T_C_4 = 41, 9; C_v(T_{C4} - 0) = 3, 7; C_v(T_{C4} + 0) = 1, 7; \omega_5 = 15; T_C_5 = 46, 2; C_v(T_{C5} - 0) = 4, 2; C_v(T_{C5} + 0) = 1, 65; \omega_6 = 20; T_C_6 = 50; C_v(T_{C6} - 0) = 4, 6; C_v(T_{C6} + 0) = 1, 6. \]
strong. There are grounds to believe that EPI in high-temperature ceramic superconductors is rather strong \cite{24, 26} and the BCS theory is hardly applicable to them. In this case the bipolaron theory can suit. As is known, Eliashberg theory \cite{27} which was developed especially to describe superconductors with strong EPI fails to describe bipolaron states \cite{4}, \cite{5}.

Let us cite some experiments on HTSC which are in agreement with the TI-bipolaron theory.

According to the main SC theories available thus far (BCS, RVB, t-J theories \cite{9}, \cite{13}), at low temperatures all the current carriers should be paired (i.e. the density of superconducting electrons coincides with superfluid density). In recent experiments on overdoped SC \cite{28} it has been shown that this is not the case: only a small part of current carriers appeared to be paired. Analysis of this situation made in \cite{29} shows that the results obtained in \cite{28} do not fit in with the theoretical constructions available. The TI-bipolaron theory of SC developed in this paper gives an answer to the question of the paper \cite{29}, namely where most of the electrons disappear in the superconductors analyzed. It lies in the fact that only a small part of electrons $n_{bp}$: $n_{bp} \ll n_{bp}/\epsilon_F \ll n$ occurring near the Fermi surface are paired and determine the superconducting properties of HTSC materials.

In fact, the theory of strong EPI developed here is not applicable to overdoped SC where weak EPI coupling is expected and can hardly be used for explaining experiments on overdoped samples used in \cite{28}. Particularly, in the underdoped samples we cannot expect a linear dependence of the critical temperature $T_c$ on the density of SC electrons observed in \cite{28}. Rather this dependence would be nonlinear as it follows from equation (15). For the overdoped regime, recently a theory \cite{30} has been developed on the basis of the Fermi condensation idea \cite{31}, which is a generalization of the BCS theory where the number of SC carriers was shown to be only a small part of their total number and which is in agreement with other observations of \cite{28}. Thus we can conclude that the phenomenon obtained in \cite{28} is rather general and takes place both in overdoped and underdoped regimes (see also \cite{32}). We can also expect a linear dependence
of the resistivity on $T$ if $T > T_c$ both in the overdoped and underdoped regimes since the number of bipolarons is small as compared with the total number of electrons and if EPI dominates in the homogeneous crystal.

On the contrary to [30] it was shown in recent work [33] that the linear dependence of $T_c$ on the number of Cooper pairs observed in [28] in the overdoped $La_{2-x}Sr_xCu_2O$ crystals can be described by BCS model for plasmon mechanism of SC. It seems nevertheless that the special case considered in [30] can not explain the general character of results obtained in [28].

The problem of inconsistency of BCS with [28] was also considered in recent work [34] where a simple bipolaron SC model was introduced and was shown that the number of bipolarons should be much less then the total number of carriers. The result obtained in [34] confirms our results that only a small part of carriers are paired in the limit of low temperatures.

Fig. 3 shows typical dependencies of $E(\tilde{T})$. They suggest that at the point of transition the energy is a continuous function of $E(\tilde{T})$. This means that the transition per se occurs without energy expenditure being a phase transition of the 2-kind in complete agreement with the experiment. At the same time transition of Bose particles from a condensate state to a supercondensate one occurs with consumption of energy which is determined by the value of $q$ (§3, Table 1), determining the latent heat of the transition of a Bose gas which makes it a phase transition of the 1-st kind.

By way of example let us consider HTSC $YBa_2Cu_3O_7$ (YBCO) with the temperature of transition $90 \div 93$K, volume of the unit cell $0.1794 \cdot 10^{-21}$cm$^{-3}$, concentration of holes $n \approx 10^{21}$cm$^{-3}$. According to estimates [35], the Fermi energy is equal to $\epsilon_F = 0.37$ eV. The concentration of TI-bipolarons in $YBa_2Cu_3O_7$ is found from equation (15):

$$\frac{n_{bp}}{n} C_{bp} = f_{\tilde{\omega}} \left( \tilde{T}_c \right)$$ (24)

with $\tilde{T}_c = 1.6$. Table 1 lists the values of $n_{bp,i}$ for the values of parameters $\tilde{\omega}_i$ given in §2. It follows from Table 1 that $n_{bp,i} << n$. Hence, only a small part of charge carriers is in a bipolaron state. It follows that in complete agreement
with the results of the previous section, the Coulomb interaction will be screened by nonpaired electrons which justifies the approximation of a noninteracting TI-bipolaron gas used by us.

According to our approach, superconductivity arises when coupled states are formed. The condition for the formation of such states near the Fermi surface, by \[20\], has the form: \( E_{bp} < 0 \). The value of the pseudogap, according to §2, will be:

\[
\Delta_1 = |E_{bp} + u_0|
\]

Naturally, this value is independent of the vector \( \vec{k} \), but depends on the concentration of current carriers, i.e. the level of doping.

In the simplest variant of the superconductivity theory presented here, the gap \( \omega_0 \) does not change as the system passes on from the condensed state to the uncondensed one, i.e. from the superconducting state to the nonsuperconducting one, therefore \( \omega_0 \) has also the meaning of a pseudogap:

\[
\Delta_2 = \omega_0(\vec{k})
\]

which depends on the wave vector \( \vec{k} \).

Numerous discussions of the problem of a gap and a pseudogap rely on the statement that the energy gap in HTSC is determined by the coupling energy of Cooper pairs which leads to insoluble contradictions (see reviews \[36\]-\[40\]).

Actually, the value of the superconducting gap \( \Delta_2 \) (26) has no concern with the energy of paired states which is determined by \( E_{bp} \). As is shown in \[12\], the energy of a TI bipolaron is \( |E_{bp}| \sim \alpha^2 \omega_0 \) for both small and large values of \( \alpha \) i.e. \( |E_{bp}| \) does not depend on \( \omega_0 \) at all.

Thus, within our concept an answer to the question of why the pseudogap \( (\Delta_2) \) has the same anisotropy as the superconducting gap is made clear – this is one and the same gap. It also becomes evident why the gap and the pseudogap depend on temperature only slightly. In particular, it becomes clear why under a superconducting transition a gap arises immediately and does not vanish as \( T = T_c \) (which is not typical for the BCS). The oft-debated question of what order
As it is seen from Fig. 6, the heat capacity jump calculated theoretically (4) coincides with the experimental value in $YBaCu[44]$ for $\omega = 1.5$, i.e. for $\omega = 7.5$ meV. This corresponds to the concentration of TI-bipolarons equal to $n_{bp} = 2.1 \cdot 10^{18} \text{cm}^{-3}$. Hence, in contrast to the widespread notion that in oxide ceramics superconductivity is determined by high-energy phonons (with energy 70–80 meV [45]) actually, the superconductivity in HTSC materials should be determined by soft phonon modes.

Notice that in calculations of the temperature of transition it was believed that the effective mass in equation (22) is independent of the direction of the wave vector, i.e. isotropic case was dealt with. In the anisotropic case, choosing principal axes of vector $\mathbf{v}$ as coordinate axes, we will get the quantity $\left(\begin{array}{ccc} e_x & e_y & e_z \end{array}\right)$ instead of the effective mass. In complex HTSC materials the values of effective masses lying in the plane of layers $e_x e_y$ are close in value. Assuming in this case $e_x e_y e_z$, we will get instead of $n_{bp}$ determined by (22), the value $n_{bp} n_{bp}/\gamma/M$ is the parameter of anisotropy. Hence anisotropy of effective masses gives for the concentration $n_{bp}$ the value $\tilde{n}_{bp} \gamma n_{bp}$. Therefore taking account of anisotropy can an order of magnitude and greater enhance the estimate of the concentration of TI-bipolarons. If for $YBaCu[44]$ we take the estimate $\gamma = 30$ [45], then for the concentration of TI-bipolarons we will get: $\tilde{n}_{bp} = 1.1 \cdot 10^{19} \text{cm}^{-3}$, which holds valid the general conclusion: in the case under consideration only a small number of charge carriers are in TI-bipolaron state. The situation can change if the anisotropy parameter is very large. Thus, for example, in layered HTSC Bi-Sr-Ca-Cu-O the anisotropy parameter is $\gamma > 100$, accordingly, the concentration of TI-bipolarons in these compounds can have the same order of magnitude.

At present there are many methods for measuring the gap: angle-resolved photoelectron spectroscopy (ARPES), Raman (combination) spectroscopy, scanning tunnel spectroscopy, neutron magnetic scattering, etc. According to [40], the maximum value of the gap $YBCO$ (6.6) (in antinodal direction in ab-plane) was found to be $\Delta_1/T_\text{c} \approx 16$. This gives $|E_{bp}| \approx 80$ meV.

Now let us find a characteristic energy of phonons responsible for formation of TI bipolarons and determining the superconducting properties of oxide ceramics, i.e. the value of the superconducting gap $\Delta_2$. For this purpose we will compare the calculated values of the heat capacity jumps with the experimental data (Fig. 5).

As is evident from Fig. 5 the theoretically calculated jump in the heat capacity (§3) coincides with the experimental values in $YBa_2Cu_3O_7$ [41], for $\tilde{\omega} = 1, 5$ i.e. for $\omega = 7.5$ meV. This corresponds to the concentration of TI bipolarons equal to $n_{bp} = 2.6 \cdot 10^{18} \text{cm}^{-3}$. Taking into account that $|E_{bp}| \approx 0.44 \alpha^2 \omega$ [11],

![Figure 5: Comparison of the theoretical (solid line) and experimental (broken line) dependencies in the region of the heat capacity jump.](image)
\[ |E_{bp}| = 80 \text{meV}, \omega = 7,5 \text{meV} \] the EPI constant \( \alpha \) will be: \( \alpha \approx 5 \), and lies beyond the range of applicability of the BCS theory.

The availability of a gap \( \omega_0 \) in HTSC ceramics is proved by numerous spectroscopy experiments (ARPES) on angular dependence of \( \omega_0 \) on \( \vec{k} \) for small \( |\vec{k}| \). The availability of d-symmetry in the angular dependence of \( \omega_0(\vec{k}) \) is probably concerned with arising of a pseudogap and rearrangement of Fermi system into the system of Fermi arcs possessing d-symmetry. In experiments on tunnel spectroscopy \( \omega_0 \) can manifest itself as an occurrence of a pseudogap structure superimposed on a pseudogap \( \Delta_1(\Delta_1 >> \omega_0) \). In optimally doped \( YBa_2Cu_3O_7 \) and \( Bi_2Sr_2CaCu_2O_8 \) (BCCO) such a structure was observed many times in the region of \( 5 \div 10 \text{meV} \) which coincides with the above-cited estimation of \( \omega_0 \).

Many experimenters measure the dependence of the value of a gap and pseudogap on the level of doping \( x \). Even early experiments on magnetic responsibility and Knight shift demonstrated the availability of a pseudogap which arises for \( T^* > T_c \). Numerous subsequent experiments revealed peculiarities of \( T - x \) phase diagram: \( T^* \) increases while \( T_c \) decreases as doping grows smaller. As is shown in [20], this behavior can be explained by peculiarities of the existence of bipolarons in a polaron gas [20]. In [20] mention is also made of possibly general character of 1/8 anomaly in HTSC systems.

In conclusion it should be noted that a longstanding discussion of the nature of the gap and pseudogap in HTSC materials is in many respects associated with the problem of measurement, when different measurement methods in fact measure quite different quantities, rather than similar ones. In the case under consideration, ARPES measures \( \omega_0(\vec{k}) \), while tunnel spectroscopy measures \( |E_{bp}| \). In this field unfortunately there are a lot of unsolved problems which offer a challenge for both the theory and the experiment.
5. Discussion of results

The above considered theory of TI-bipolaron superconductivity as well as the BCS theory rely on Froehlich Hamiltonian. These theories, however, have different domains of applicability. In the BCS theory EPI is considered to be weak, accordingly, the correlation length, or the characteristic size of the pair is $l_{corr} \gg n_{bp}^{-1/3}$. The concentration of bipolarons (i.e. Cooper pairs) $n_{bp}$ in the BCS is very large and for $T = 0$ coincides with the concentration of charge carriers in metals.

In the above considered theory EPI is considered to be strong, therefore the correlation length is $l_{corr} \ll n_{bp}^{-1/3}$. At the same time even at $T = 0$ bipolarons are only a small part of charge carriers. This situation is realized in oxide ceramics. The notion of a pair in the TI-bipolaron theory under these conditions is well determined. Thus, according to [2], the value of the correlation length for a TI bipolaron is $l_{corr} = \hbar^2 c x(\eta)/e^2 M_e$, where $x(\eta)(\eta = \epsilon_\infty/\epsilon_0)$ varies within $6 \div 10$ in the area of stability of bipolaron states. For the values of parameters corresponding to YBCO, it makes up $l_{corr} \approx 10^{-7}$ cm while $n_{bp}^{-1/3} \approx 10^{-6}$ cm. Thus: $n_{bp} l_{corr}^3 \sim 10^{-3} \ll 1$, that is, individual pairs practically do not overlap.

The results obtained suggest that in order to raise the critical temperature $T_c$ one should either decrease the effective mass of charge carriers or increase the phonon frequency $\omega_0$, or else enhance the concentration of bipolarons $n_{bp}$. Hence, the problem of raising $T_c$ is related to the search for crystals with optimal parameter values. Notice that an increase in $\omega_0$ will not necessarily lead to an increase in $T_c$, since an increase in $\omega_0$ leads to a decrease in the EPI constant $\alpha$.

For small $\alpha$ we find ourselves in the field of applicability of the BCS which yields small $T_c$. This situation is probably realized in the anticorrelation dependence of $T_c$ on $\omega_0$ [45].

The most effective way to change the concentration of $n_{bp}$ is to change the level of doping. In this case both the concentration of charge carriers $n$ and the concentration of $n_{bp}$ alter. The dependence of $n_{bp}(n)$ can be rather complicated.
In particular, an increase in $n$ does not necessarily lead to an increase in $n_{bp}$.

To enhance the transition temperature one can apply external pressure. Enhanced pressure leads to a decrease in the crystal volume and, accordingly an increase in the concentration of $n_{bp}$, a decrease in the effective mass of charge carriers and a rise in the phonon frequency $\omega_0$.

An effective way to raise $T_c$ can be the use of unhomogeneous doping. Thus, in a wire with cylindrical symmetry, doping as a result of which the concentration of acceptors is maximal on the cylinder axis, will lead to an increased concentration of bipolarons along the crystals axis since a Bose gas will concentrate in the regions with minimal potential energy.

Such conclusions do not account at all for many important factors. Consideration of EPI alone is not adequate since in HTSC materials of importance is the availability of a magnetic order. Thus, for example, in many papers the occurrence of a pseudogap is associated not with EPI, but with magnetic fluctuations [46]. Consideration of other interactions such as electron-plasmon interaction can also compete with EPI.

The theory of TI-bipolaron superconductivity as well as the BCS is based on isotropic 3D model. Actually most cuprates are layered structures possessing high anisotropy. Generalization of the theory to this case seems to be rather actual. The situation is complicated by the fact that in real HTSC materials of great importance are imperfections such as stripes and clusters. In particular, the availability of stripes suggests a 1D scenario of superconductivity in oxide ceramics. TI-bipolaron mechanism leads in this case to possible existence of a Bose condensate in 1D systems and, as a consequence, to new opportunities obtaining of HTSC in materials with long stripes [47].

Let us specify the main conclusions emerging from consistent translation-invariant consideration of EPI. Electron pairing (for any coupling constant) based on such consideration leads to a concept of TI polarons and TI bipolarons. Being bosons, TI bipolarons can experience Bose condensation leading to superconductivity. Let us point out the main consequences of this approach.
First of all, the theory under consideration resolves the problem of the great value of the bipolaron effective mass (§3). As a consequence, formal restrictions on the value of the critical temperature of the transition are removed. The theory quantitatively explains some thermodynamic properties of HTSC such as the availability (§3) and value (§4) of the jump in the heat capacity which is lacking in the theory of Bose condensation of an ideal gas. It accounts for a large ratio of the pseudogap width to $T_c$ (§4). The small value of the correlation length $\xi$ is clarified. The theory explains the occurrence of a gap and a pseudogap (§3, §4) in HTSC materials. The angular dependence of a gap and pseudogap (§4) is also clarified.

Accordingly, an isotropic effect straightforwardly follows from expression (13) where phonon frequency $\omega_0$ plays the role of a gap. Application of the theory to 1D and 2D systems yields qualitatively new results since the availability of a gap in the TI bipolaron spectrum eliminates divergencies which are observed for small impulses in the theory of an ideal Bose gas [47].

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**Appendix. Remarks on the notation**

Function $F_3/2(\alpha)$ is called a polylogarithm = $Li_{3/2}(e^{-\alpha})$, in mathematics this is the function $\text{PolyLog}$, therefore the function $\tilde{f}_{\omega}$ in (15) will be: $\tilde{f}_{\omega} = \tilde{T}^{3/2}\text{PolyLog} \left[\frac{3}{2}, e^{-\omega/\tilde{T}}\right]$. 

In the general case, function $\text{PolyLog}$ of the order of $s$ is determined as:

$$\text{PolyLog} \left[s, e^{-\alpha}\right] = \frac{1}{\Gamma(s)} \int_{0}^{\infty} \frac{t^{s-1}}{e^{t + \alpha} - 1} \, dt$$

where $\Gamma(s)$ is a gamma function: $\Gamma(1/2) = \sqrt{\pi}$, $\Gamma(3/2) = \sqrt{\pi}/2$, $\Gamma(5/2) = 3\sqrt{\pi}/4$. 24
Accordingly, the functions $F_{1/2}$, $F_{3/2}$, $F_{5/2}$ occurring in the text will be:

\[
F_{1/2} = 2\text{PolyLog}\left[1/2, e^{-\tilde{\omega}/\tilde{T}}\right];
\]
\[
F_{3/2} = \text{PolyLog}\left[3/2, e^{-\tilde{\omega}/\tilde{T}}\right];
\]
\[
F_{5/2} = 3/2\text{PolyLog}\left[5/2, e^{-\tilde{\omega}/\tilde{T}}\right].
\]

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