Effect of temperature on the energy gap in a superconductivity model using U-centers.

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Abstract. According to the theory of U-centers, a strong electron-lattice interaction can lead to the fact that the binding energy of two electrons at certain temperatures is higher than the energy of their Coulomb repulsion and, therefore, the possibility of the formation of Cooper pairs appears. If these pairs move coherently without falling apart, then superconductivity occurs. In this work using the Hubbard Hamiltonian and applying the secondary quantization method, we calculate the temperature dependence of the superconducting gap $\Delta = \Delta(T)$. A temperature dependence of the HTSC resistance in the normal state demonstrates the features of both semiconductor and metallic behavior. It is known that high-temperature superconductors exhibit such properties only in the normal state. In the work presented now, using mathematical calculations, we discuss the presence of four regions of the HTSC phase diagram $T = T(\nu)$, where $\nu$ is the relative concentration of U-centers. The formation mechanisms of negative U-centers are not considered here. We only assume that they are present in HTSC.

1. Introduction
It is known that high-temperature superconductors (HTSC) exhibit a number of unusual properties in both normal and superconducting states. By this reason the phase diagram of HTSC contains a large number of characteristic regions. The aim of this study is to demonstrate that a change in the relative positions of $E_F$ (Fermi level) and $E_F$ is determined by the properties of the Negative-U Centers for Superconductivity (NUCS) model itself. We consider the statistical properties of the system of negative-U centers and construct the phase diagram of HTSC on the basis of the obtained results. The same quantity determines the variation of relative positions of levels related to negative-U centers and to ordinary electrons from the valence band, which makes it possible to describe the presence of all regions of the normal state in the phase diagram.

This communication is aimed to explain the properties of four regions: PG, SC, NFL, and FL. Nowadays, there exist numerous approaches accounting as the properties of these regions as transitions between them. For example, surveys [1,2,3] summarized the results for the optimal doping region, obtained via a slightly modified classical approach based on the BCS theory. However, the optimal-doping region was considered in this case. The difference between the properties of HTSC and those of the classical superconductors has led to a wide use of non-phonon mechanisms of electron pairing, which were discussed in detail in the papers [4,5,6]. It should be stated that at the moment there is no unified

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explanation of the whole phase diagram both in terms of the classical approach [7,8] and from the standpoint on non-phonon mechanisms.

![Figure 1](image)

**Figure 1** A typical phase diagram of HTSC in the "temperature-doping level" coordinates. Here \( x \) is the real content of the oxygen for \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x \).

The concept of negative-U centers was introduced by Anderson in 1975 for describing some properties of chalcogenide glassy semiconductors [3,8] and was further developed in [5,9,10,11]. It was assumed that centers with a specific property exist in the atomic lattice of a material. The strong electron-lattice interaction ensures that the binding energy of two electrons exceeds their Coulomb repulsion. Such an effect is also observed under normal conditions, i.e., electrons coupled into a pair exist even at room and higher temperatures. For the appearance of superconductivity, it suffices that the pairs can move, and the nondegenerate Bose gas become degenerate, i.e., all the moving pairs pass into the coherent state. The possibility of superconductivity in such a system was noted even before developing of the BCS theory. This idea was first suggested by Ogg in 1946; later, such a possibility was analyzed in detail by Shafroth in 1955. Models based on this concept became widely accepted after Bednorz and Muller discovered the first HTSC based on cuprates [12].

2. Theory. The superconducting gap in the model of U-centers

The model of negative-U centers for superconductivity (NUCS model) [1] is based on the results of theoretical studies [1,2,3,4], where superconducting properties of pairs moving over the system of negative-U centers were considered. In the one-electron energy band diagram, the energies of the first and second ionization of an isolated negative-U center are \( E_1 \) and \( E_2 \), respectively. These energies are commonly denoted by the arrows connecting the \( D^- \) and \( D^+ \) levels of the negative-U center and the conduction band.

The system of interacting negative-U centers can be described by the Hubbard Hamiltonian with a negative effective correlation energy, whose absolute value is equal to the difference of the energies of the \( D^- \) and \( D^+ \) levels.

To do this, we use the creation and annihilation operators of the electron at \( k^{th} \) site, which we denote by \( c_{\sigma}^+ \) and \( c_{\sigma} \), respectively. Denoting by \( t_{kk'} \) the matrix elements of a one-electron transition between the nearest negative-U centers, we obtain the Hubbard Hamiltonian in the following form [13]:

\[
H_{\text{eff}} = \sum_k (E_k - U - \mu) c_{\sigma}^+ c_{\sigma} - \frac{1}{2} \sum_{k,k'} t_{kk'}^2 c_{\sigma}^+ c_{\sigma}^+ c_{\sigma} c_{\sigma}'\]

(1)

Since the energy difference \( U \) is positive (see fig. 2(a)), we see that \( -U \) is negative. The latter implies the attraction of electrons with opposite spins at a site. The binding energy of such a coupling can exceed
the usual Hubbard Coulomb correlation energy. Moreover, if a concentration of negative-U centers is high enough, the $D^-$ and $D^+$ levels turn into corresponding $W^-$ and $W^+$ bands with a total width $2zJ = 2W$ for a simple cubic lattice.

\[
\Delta \text{ into account the } w \text{ which determine }
\]

Using the Bogolyubov transformations and retaining only the diagonal matrix elements in (1)

Transformation coefficients must satisfy the normalization condition:

\[
\Delta \text{ into account the restructuring of the energy spectrum, new operators the 'birth' and 'annihilation' pairs are introduced using the Bogolyubov transformation formulas [13].}
\]

\[
\text{Note that the Bogolyubov operators are the unite operators of pairs on neighboring nodes } (k \text{ and } k'),
\]

\[
b_k = u_k A_k + v_k A_k^\dagger, \quad b_k^\dagger = u_k A_k - v_k A_k^\dagger,
\]

where $A_{k'} = c_{k'}^\dagger c_{k'}$, $A_k = c_k c_{k'}$ and obey the Fermi commutation rules: $b_k b_k^\dagger + b_k^\dagger b_k = 1$.

Transformation coefficients must satisfy the normalization condition:

\[
u_k^2 + v_k^2 = 1.
\]

Using the Bogolyubov transformations and retaining only the diagonal matrix elements in (1)

\[
b_k^\dagger b_k \dagger = n_k \quad \text{and} \quad b_k^\dagger b_k \dagger = 1 - n_k,
\]

which determine an average energy, we get

\[
\varepsilon = E - (\mu + U)N = \langle H - (\mu + U)N \rangle >
\]

\[
= 2 \sum_k \varepsilon_k v_k^2 + 2 \sum_k \varepsilon_k (u_k^2 - v_k^2)n_k - \frac{1}{2} \left[ \sum_{kk'} \frac{2t_{kk'}}{U} u_k u_{k'} v_k v_{k'} (1 - n_k) \right]^2,
\]

where $n_k = b_k^\dagger b_k$. The coefficients $u_k$ and $v_k$ are found from the condition of minimum energy. Taking into account the normalization condition, we have $\frac{\delta \varepsilon_k}{\delta u_k} = 0$. From here we find the equation: $2\varepsilon_k u_k = \Delta(u_k^2 - v_k^2)$, where

\[
\Delta_k = \sum_{k'} \frac{2t_{kk'}}{U} u_k u_{k'} v_k v_{k'} (1 - n_{k'}).
\]

Setting

\[
\Delta = \frac{t^2}{U} \sum_k \frac{n_k}{\sqrt{\Delta_k^2 + \varepsilon_k^2}}
\]

and replacing summation by integration we arrive at
where $\Delta$ stands for the state density. An elementary calculation shows that
$$I = \ln \frac{2W(1-\nu)}{\Delta} - \ln \frac{2\nu W}{\Delta_0},$$
where $\Delta_0$ denotes the magnitude of the energy gap at $T = 0$ K.

In the region of low temperatures ($T \ll U$) we get
$$\Delta = 2\nu W \left(1 - \sqrt{\frac{T}{\Delta_0}} e^{-\frac{\Delta_0}{T}}\right).$$ (3)

According to [3,9,10,11,14], the model of negative-U centers has the following special features:

1. A concentration of negative-U centers is sufficiently high, and a binding energy $U$ is essentially larger as the single-electron matrix elements $t$ responsible for the transition of electrons between the centers: $t \ll U$. Hence, pre-formed electron pairs can move inside the system of negative-U centers.
2. There exist also "ordinary" band electrons weakly interacting with the lattice and statistically interacting with electrons belonging to the negative-U system.

These two main points of the model allow to understand all the features of HTSC, that is, the entire phase diagram of HTSC without additional assumptions.

The description of superconducting properties is close to the bi-polaron approach [6]. However, a significant difference of the model is the presence there both the bi-polaron bands and bands of "ordinary" electrons. The statistical properties of the system of negative-U centers are determined by mutual arrangement of the position of $E_F$ and $E_\nu$. Hence, the magnitude of the energy gap $\Delta$ is given by formula (3).

3. Discussion
In the region $1/2 < \nu < 1$, the middle level between $W^-$ and $W^+$ zones, i.e., the Fermi level at zero temperature, is placed above $E_\nu$. At low temperatures, the resistance of the sample has a typical semiconductor temperature dependence with an activation energy equal to $E_F - E_\nu$.

If temperature increases up to the magnitude $T_p = E_F - E_\nu$, the activation law of hole production in the valence band actually ceases. In this case, the temperature dependence of the resistance is determined mainly by mobility.

Thus, in our interpretation, the points of the curve $T_p(x)$ are the temperatures of crossover from the semiconductor temperature dependence of the resistance in pseudo-gap region (PG-region) to a metallic dependence in non-Fermi-liquid region (NFL-region) [15]. Therefore, PG-region in the phase diagram could be called the semiconductor region, where the conductivity is determined by the holes of the valence band, and the position of the Fermi-level located at zero temperature in the band gap is determined by negative-U centers. However, the metallic conductivity in NFL-region should also have features that we generally call non-Fermi-liquid, since for $T > T_p$ a direct quantum-mechanical mixing of the states of negative-U centers and the "ordinary" valence band electrons remains strong.

As temperature decreases, we move from PG-region to the superconductivity region (SC-region) (fig.1). At $T = T_c$ (see (2)), the sample passes into the superconducting state providing to the Bose condensation of pairs belonging to $W^-$ zone. According to our papers [1] and [4,13], the dependence of $E_F$ on $x$ is described in this case by the line shown on fig. 2(c).

In fig.1, the upper boundary of the valence band $E_\nu$ is the edge of the mobility band; the tail of the density of localized states is not shown. Thus, in our interpretation, the underdoped HTSCs from PG-region are Fermi glasses with a Fermi level located on a background of localized states. The density of the latter is responsible for the signal intensity in photoemission experiments.
For temperatures above $T_p(x)$ and $1/2 < v < 1$, we pass from PG-region to NFL-region of non-Fermi-liquid behaviour (see fig.1). In the discussed model, the main reason for non-Fermi-liquid behavior is a strong resonant quantum-mechanical interaction of electrons from negative-U centers with electrons from the valence band. For considered $v$, this interaction becomes significant provided the temperature exceeds the difference $E_F - E_v$.

In the case $0 < v < 1/2$, the Fermi level at zero temperature lies below $E_v$ (see fig.1) and belongs to the valence band. The energy diagram of HTSC normal state looks similar to a diagram of a classical metal with a valence band filled with electrons (shaded region) up to $E_F$. We emphasize that this normal state is not the state of an ordinary metal, since $0 < v < 1/2$. Indeed, the Fermi-level in this state is pinned at mid-distance between the top $E_W^-$ of $W^-$ band and the bottom $E_c^+$ of $W^+$ band. For this range of $v$, only the electrons with the left band states lying above the Fermi level participate in formation of the negative-U centers bands and they do not determine the position of $E_F$. However, the Bose condensation of holes from the $W^+$ band in the considered range of $v$ gives superconductivity. At $T > T_c$, a transition to NFL-region occurs caused the strongest nature of the quantum-mechanical interaction between the electrons of the valence band and the electrons of negative-U centers.

The region of the Fermi-liquid behavior in the normal state (FL) lies to the right of the value $v = 0$. In this case, the width of $W^-$ band vanishes since all negative-U centers are in $D^+$ states. With a further change in doping, a position of the Fermi level comes off the middle between the edges of $W^-$ and $W^+$ bands and follows the decreasing number of electrons in the valence band. In other words, we arrive at the situation of the classical Fermi-liquid metal. This situation is preserved only at low temperatures $T \ll [E_W^-(v = 0) - E_c^+(v = 1)]/2 - E_F = T_L$, when thermal electrons located near the Fermi level do not interact with electrons of negative-U centers.

For temperatures exceeding $T_L$, an effective quantum-mechanical interaction begins between ordinary electrons of the valence band and electrons of negative-U centers, and a transition from FL-region to NFL-region occurs.

4. Conclusions
Assuming the existence of negative-U centers in HTSCs, we have justified the presence of four regions PG, SC, NFL and FL in the phase diagram and explained all transitions between them. The main parameter determining the properties of HTSCs in the negative-U centers model is the relative concentration of electrons belonging to negative-U centers. In our previous publications [1,4,5], the mutual position of the Fermi level and the top of the valence band were postulated. In the present paper we have shown that a change in the mutual arrangement of $E_F$ and $E_v$ is determined by the properties of the negative-U centers model itself.

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