Pseudogap state of underdoped cuprate HTSC  
as a display of the Jahn-Teller pseudoeffect

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Abstract:

For underdoped cuprate HTSC within the framework of the two-component model of charge carries (holes and Zhang-Rice polarons) it is considered near degenerate states of hole molecular orbitals of one-site cluster \(Cu^{2+}O_2^{2-}\) and two-site cluster \(Cu^{2+}O_2^{2-} + Cu^{2+}O_2^{2-}\) in \(CuO_2\) planes. It is shown that the vibronic mixing of two near-degenerate electronic states with near energies, separated by the energy barrier \(\Delta\varepsilon\), and mixed by Jahn-Teller \(Q_2\) normal mode of oxygen ions leads to the two-site Jahn-Teller polaron. The supposition that the pseudogap state is a consequence of the Jahn-Teller pseudoeffect and that the energy barrier \(\Delta\varepsilon\) is stipulated by magnetic interaction is discussed. It is shown that existence of two-site Jahn-Teller polarons is consistent with a recent observation of broken time-reversal symmetry in the pseudogap state.

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The Jahn-Teller pseudoeffect at first was predicted by U. Opic and M.H.L. Pryce in 1957 \[1\]. In \[2\] it was shown that a degeneracy between different electronic states leads to the Jahn-Teller effect \[2\] and so the vibronic mixing of near-degenerate electronic states leads to the dynamical Jahn-Teller (JT) effect. At a later date the consequences of this vibronic mixing of near-degenerate electronic states were named as the JT pseudoeffect \[1, 3, 4\]. Actually, let us consider two non-degenerate electronic states with near energies \(\varepsilon_\alpha, \varepsilon_i\), separated by the gap \(\Delta\varepsilon = \varepsilon_\alpha - \varepsilon_i < \varepsilon_j, j = \alpha, i\), and being mixed by vibronic (i.e. combined electron-vibration) interaction. At describing the ground state the degeneracy \(\Delta\varepsilon \to 0\) occurs only in the vicinity of Fermi surface, that leads to vibronic instability and to double-valued chemical potential function.

The first theoretical attempt to connect low-temperature superconductivity with the
JT pseudoeffect was made in 1961 by R.K. Nesbet [5] who calculated corrections to the Born-Oppenheimer approximation for near-degenerate electronic states in the presence of strong enough electron-phonon interaction. Obtained in [5] electron configurations differ qualitatively from Fermi-distribution of the normal metal, and in the chemical potential function there are relative maximum inside the Fermi surface and relative minimum just outside.

This work was published at the time of a triumph of the BCS theory and didn’t attract marked interest. It should be noted the work [6] containing critical remarks to [5] that cannot be accepted. Firstly, in [6] the electron and nuclear Hamiltonians are treated independently, whereas a considering of nuclear motion in systems with strong electron-phonon interaction, having low-lying electronic states (active electrons) close to degeneracy, results in a transformation of the two independent Hamiltonians of nuclei and active electrons to the combined electron-nuclear Hamiltonian. That just as in the JT effect leads to a splitting of energy levels of electrons on near degenerate orbitals, i.e. to the dynamical JT effect. Secondly, in [6] the conclusion that an interaction between the phonon and electron subsystems brings to a considerable phonon contribution to the energy correction was obtained within the Frohlich theory [7]. But it is known that within the framework of the Frohlich theory it is impossible to describe the phonon spectrum correctly [8, 9].

Though at present, 40 years later, we may say that in [5] it was predicted the pseudogap state (a dynamical analog of charge ordering) which is observed in doped antiferromagnets (AFs) whose Fermi surface consists of electron and hole regions almost coinciding under the translation over the wave vector of an antiferromagnetic cell (dispersion laws with nesting). Pseudogap (PG) state in doped antiferromagnets is a state with the two types of excitations: the holes are light carriers and heavy carriers are Zhang-Rice (ZR) polarons [10, 11, 12, 13]. For cuprate HTSC the PG state precedes a transition to the superconducting state: with decreasing temperature at $T_c < T \leq T^*$ a maximum and a minimum are observed in the density of states near Fermi level at $\varepsilon \sim \varepsilon_F$, which are characteristic for the JT pseudoeffect [1, 5].

In the present paper for underdoped cuprate HTSC within the framework of the two-component model of charge carries [11] (which are holes and ZR polarons) it is considered near degenerate states of hole molecular orbitals of one-site and two-site clusters in $CuO_2$ planes. The first is an occupied by a hole molecular orbital $\phi_i$ of ZR polaron which is
a hole localized on a square \( \text{Cu}^{2+}\text{O}_4^{2-} \) with JT distortions by \( Q_2 \) normal mode of oxygen ions. Another molecular orbital is an unoccupied hole molecular orbital \( \phi_\alpha \) around the two-site cluster \( \text{Cu}^{2+}\text{O}_4^{2-} + \text{Cu}^{2+}\text{O}_4^{2-} \) with common oxygen ion and with antiferromagnetic spin ordered JT \( \text{Cu}^{2+} \) ions \[14\]. JT distortions that lead to two-site clusters come to an agreement with evidences of dynamical lattice distortions on time scales \( 10^{-13} \) – \( 10^{-15} \) s. \[15, 16, 17\].

Taking into account that the vibronic mixing of these near-degenerate electronic states leads to the dynamical JT effect in this paper the model of pseudogap state as a consequence of the Jahn-Teller pseudoeffect is discussed.

In the absence of the Jahn-Teller pseudoeffect (i.e. in the absence of near degenerate electronic levels) the Born-Oppenheimer approximation is valid for eigen-functions of the electron-nuclear Hamiltonian:

\[
\Psi = \psi_n(q, Q) \varphi(n, Q), \tag{1}
\]

where \( \psi_n(q, Q) \) and \( \varphi(n, Q) \) are electronic and nuclear wave functions. In \( \Psi \) \( \psi_n(q, Q) \) is a solution of the Schredinger equation for electrons at nuclei of the site \( \text{Cu}^{3+}\text{O}_4^{2-} \) being in a fixed position, and \( \varphi(n, Q) \) is a solution of the Schredinger equation for nuclei with electron energy \( E_n(Q) \).

For JT \( \text{Cu}^{2+} \) ions near-degenerate electronic states \( \psi_n(q, Q) \) depend on \( Q_2 \) JT normal mode, which leads to JT distortion of squares \( \text{Cu}^{2+}\text{O}_4^{2-} \). Let us consider sixteen one-site clusters from which there are nine \( \text{Cu}^{2+}\text{O}_4^{2-} \) clusters (see Fig. 1). The occupied by a hole molecular orbital \( \phi_i \) is localized on one-site cluster \( m_{ij} \) and forms the ZR polaron (here the label \( i \) is a number of horizontal \( \text{Cu} - \text{O} \) row, the label \( j \) is a number of vertical \( \text{Cu} - \text{O} \) row). Taking into account the JT distortions for twelve \( \text{O}^{2-} \) ions of four nearest one-site clusters \( m_{i+1,j}, m_{i-1,j}, m_{i,j+1}, m_{i,j-1} \) we can suppose that a hole can be excited from the one-site molecular orbital \( \phi_i \) of \( \text{Cu}^{2+}\text{O}_4^{2-} \) cluster with energy \( \varepsilon_i \) to the unoccupied two-site molecular orbital \( \phi_\alpha \) of \( \text{Cu}^{2+}\text{O}_4^{2-} + \text{Cu}^{2+}\text{O}_4^{2-} \) cluster with energy \( \varepsilon_\alpha \) and with antiferromagnetic spin ordering JT \( \text{Cu}^{2+} \) ions. The hole excitation can be described as a scattering of a charge carrier with absorption of the phonon \( \varepsilon_\alpha - \varepsilon_i = \hbar \omega_k \), where \( \omega_k \) is the frequency of \( Q_2 \) normal mode. At that rate the electronic wave function \( \psi_n(q, Q) \) is equal to

\[
\psi_n(q, Q) = \Phi_0 + \sum_{Q_k, i, \alpha} \Phi_i^\alpha (iss_{\alpha i}Q_k)
\]

\[
s_{\alpha i} = i(F_i^\alpha)_k / (\varepsilon_\alpha - \varepsilon_i); \quad (F_i^\alpha)_k = \langle \alpha | \partial V / \partial Q_k | i \rangle.
\tag{2}
\]
where $\Phi_0$ is the Hartree-Fock many-electron ground state wave function, and $\Phi^\alpha_i$ is the Slater determinant obtained from $\Phi_0$ by replacing an occupied hole molecular orbital $\phi_i$ by an unoccupied hole molecular orbital $\phi^\alpha_i$.

Let us consider that after transition the occupied two-site molecular orbital $\phi^\alpha_i$ belongs to two-site cluster $m_{ij} + m_{i,j+1}$ (Fig. 1). The excited state of a hole which occupies the two-site molecular orbital $\phi^\alpha_i$ can be considered as a quasilocal state of a hole, i.e. the two-site Jahn-Teller (TSJT) polaron [14]. TSJT polaron moves with low damping in $CuO_2$ plane from two-site cluster $m_{ij} + m_{i,j+1}$ with two JT $Cu^{2+}$ ions to nearest two-site clusters with antiferromagnetic spin ordered JT $Cu^{2+}$ ions. As we see in Fig. 1, any of unoccupied molecular orbitals of two-site clusters with two JT $Cu^{2+}$ ions can be occupied by a hole, for example $m_{ij} + m_{i+1,j} , m_{i,j+1} + m_{i+1,j+1}, m_{i,j} + m_{i,j-1} , m_{i,j} + m_{i-1,j} , m_{i+1,j} + m_{i+1,j+1}$. But the molecular orbital of two-site cluster $m_{i+1,j} + m_{i,j-1}$ cannot be occupied by a hole because it has only one JT $Cu^{2+}$ ion. It should be noted that TSJT polaron cannot move along the diagonal direction of squares formed by four $Cu^{2+}$ ions because there is no oxygen ion on the diagonal between two $Cu^{2+}$ ions. For example, TSJT from cluster $m_{ij} + m_{i,j+1}$ cannot be transferred on two-site cluster $m_{i,j+1} + m_{i+1,j}$ (Fig. 1).

In this model it is easy to illustrate the formation of the three spin polaron [15, 18]. For $Cu^{3+}$ ion (site $m_{i-1,j+1}$), which is surrounded by four $Cu^{2+}$ ions, positions of all nearest oxygen ions are distorted by JT normal modes. It was shown by E.L. Nagaev [19] that in layered AF charged impurity (here it is $Cu^{3+}$ ion) leads to an almost spherical ferromagnetic cluster with the localized state of a hole. So, in site $m_{i-1,j+1}$ the transition $Cu^{3+} \rightarrow Cu^{2+}_4 + h^{\uparrow}_t$ (with zero total spin) generates the three spin polaron on two-site cluster with the localized state of a hole (spin up) and parallel spins (down) of ions $Cu^{2+}$, and with three dimensional JT distortions by $Q_4$ and $Q_5$ normal modes of seven in-plane and four apex oxygen ions. This three spin polaron can be localized by one of three two-site clusters around site $m_{i-1,j+1}$, for example by cluster $m_{i-1,j+1} + m_{i-2,j+1}$. The chains of three spin polarons form in $CuO_2$ planes narrow stripes with distorted low temperature tetragonal-like lattice [18]. But the transition $Cu^{3+} \rightarrow Cu^{2+}_4 + h^{\uparrow}_t$ can generate the TSJT polaron with the quasilocal state of a hole (spin down) and conserves antiferromagnetic order in two-site cluster $m_{i-1,j+1} + m_{i-2,j+1}$.

For the ground state such near degeneracy only occurs at Fermi energy. In [5] it was obtained a relation for the transition matrix element between an occupied orbital $\phi_i$ and an
unoccupied orbital $\phi_\alpha$ accompanied with absorption of the phonon with energy $\varepsilon_\alpha - \varepsilon_i = \hbar \omega_k$. For processes of phonon absorption which occur between non-degenerate, but close to degeneracy Born-Oppenheimer states the transition probability is proportion to the quantity

$$\lim_{\delta_i \rightarrow 0} \frac{\delta_i}{(\varepsilon_\alpha - \varepsilon_i)^2 + \delta_i^2} = \pi \delta(\varepsilon_\alpha - \varepsilon_i),$$

that brings to modification of stationary states on the different sides of Fermi surface. Here $\delta_i = (s/v)\varepsilon_i$, where $s$ is the velocity of longitudinal acoustic waves, $v$ is the velocity of electrons on the Fermi surface. In consideration of (3) and finiteness of the quantity $\delta_i$ the correction $\varepsilon'(\sigma_i) = \mu(\sigma_i) - \varepsilon(\sigma_i)$ to the Hartree-Fock energy of a single-electron state $\sigma_i$ has opposite signs on the different sides of Fermi surface and is of the order

$$\varepsilon'(\sigma_F) \approx \pm (s/v)\varepsilon_F, \quad (s/v) \cong (Zm/3M)^{1/2}, \quad \text{(4)}$$

where $m$ is the electron mass, $M$ is the ion mass, $Z$ is the ion charge, $\mu(\sigma_i)$ is the electron chemical potential function. As seen from (4), there always exists a state whose energy doesn’t shift, and if value of $\varepsilon'(\sigma_F)$ is large enough, $\mu(\sigma_i)$ may have maximum on the inner side of Fermi surface and minimum on the outside. Existence of such succession of maximum and minimum for the electron chemical potential, as Frohlich pointed out [7], implies presence of qualitative change in the ground state of the electron system and can be a sign of the superconducting state.

The series of optical measurements [12, 13] have great importance for studying the excitation of polaron into delocalized states. At introducing doping into $CuO_2$ plane the optical conductivity $\sigma(\omega)$ shows two peaks at $0.07 - 0.1$ eV and at $0.8 - 1$ eV [12], and in [13] was proposed that this structure of $\sigma(\omega)$ corresponds to the transition of a polaron into delocalized states with energy barrier of the order of the Frank-Condon shift. Some of the first results which give evidence for existence of the energy barrier for the polaron transport in 2D case were received in [20], where it was shown that this barrier is attributed to the finite charge carriers bandwidth.

The first conclusive proof of existence of TSJT polarons in pseudogap and superconducting states was the observation at $T < T^*$ in YBCO films of the double bimagnon-assisted absorption band with maxima at $E_1 = 2.15$ eV and $E_2 = 2.28$ eV in metallic films [21]. The first component peaked at $E_1$ arises from the interband transition of ZR polaron at the absorption of magnons for AF dielectric films. The observation at $T < T^*$ of two components
for metallic films evidences about two-site nature of heavy charge carriers with the antiferromagnetic core and the exchange energy $E_2 - E_1 = J \approx 0.13$ eV. This allows us to suppose that the energy barrier $\Delta \varepsilon = \varepsilon_\alpha - \varepsilon_i \simeq J$ for the hole excitation from the orbital $\phi_i$ of ZR polaron to the unoccupied hole molecular orbital $\phi_\alpha$ around a two-site cluster is stipulated by magnetic interaction between the hole spin and the $Cu^{2+}$ spin: this magnetic interaction tries to conserve antiparallel direction of these spins in each site of TSJT polaron.

Recently T.D. Stanesku and P. Phillips [22] showed that origin of the pseudogap in all 2D doped Mott insulators is caused by local correlations, and the energy barrier for the hole transport is $\sim t^2/U$, where $t$ is the nearest-neighbour hopping and $U$ is on-site Coulomb repulsion. In the dynamic 2D Hubbard model they computed the density of states and found that near Fermi level at $\varepsilon < \varepsilon_F$ maximum is observed and minimum is observed at $\varepsilon > \varepsilon_F$. This means that the pseudogap reflects the restricted phase space where strongly correlated excitations on neighbouring sites in are taken into account. It should be noted that received in [22] estimation coincides with measurement [21] of the energy barrier $\Delta \varepsilon \simeq J \sim t^2/U$.

Thus, in $CuO_2$ plane two near-degenerate electronic states with near energies $\varepsilon_\alpha, \varepsilon_i$, separated by the gap $\Delta \varepsilon$ and mixed by JT $Q_2$ normal mode of oxygen ions, lead to transition of the system to the excited state with new quasi-particles — ”heavy holes” with two-site antiferromagnetic core which may be considered as two-site Jahn-Teller polarons [14, 16, 17].

It is discussed the supposition that the pseudogap state is a consequence of the Jahn-Teller pseudo effect, and the energy barrier $\Delta \varepsilon$ is stipulated by magnetic interaction. Two-site JT polarons move in $CuO_2$ plane along the $(\pi, 0)$ and $(0, \pi)$ directions and not along $(\pi, \pi)$. Recent circular dichroism experiments [23] point to time-reversal as the relevant symmetry that is broken in PG state along the $(\pi, 0)$ and $(0, \pi)$ directions and not along $(\pi, \pi)$. In the context of this paper we can consider the movement of two site JT polarons (which cannot move along $(\pi, \pi)$ direction) as local currents that lead to breaking of time-reversal symmetry in PG state. This symmetry must be broken as well in the superconducting state because there are observations of pseudogap at $T < T_c$.

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FIGURE CAPTIONS

FIG. 1: Transition from the one-site Zhang-Rice polaron to the two-site Jahn-Teller polaron in CuO$_2$ plane. The label $i$ is a number of horizontal Cu – O row, $j$ is a number of vertical Cu – O row. Black circles denote Cu$^{3+}$ ions, black circles with arrows denote Cu$^{2+}$ ions (where arrows specify the direction of spin of these ions), open circles denote O$^{2-}$ ions, the small open circle with an arrow denotes a hole $h^+$. Small shading inside one-site cluster $m_{ij}$ denotes the occupied one-site hole molecular orbital $\phi_i$ of the Zhang-Rice polaron. Big shading outside two-site cluster $m_{ij} + m_{i,j+1}$ denotes the occupied two-site hole molecular orbital $\phi_\alpha$ of the Jahn-Teller polaron.