Possible nature of ground state of HTSC

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Abstract. A qualitative model describing the ground state and the mechanism of superconducting pairing in Cu- and Fe-based high-temperature superconductors (HTSCs) is suggested. In this model, doping by localized charges is supposed to be responsible for the closing of the gap between the occupied anionic band and unoccupied states of the cation band and for the formation of the electron-excitonic band of unusual nature.

1. Introduction
It is commonly agreed that strong electron correlations at the cations, which determine the band structure of cuprates, are absent in Fe-based HTSCs. However, in spite of these differences, it looks like in both cases there exists some general and fairly “coarse” mechanism independent of fine details of the band structure and responsible for superconductive pairing in these materials.

Both Cu- and Fe-based undoped HTSCs have approximately equal interband gap $\Delta_{ib} \sim 2 \text{ eV}$ between the occupied anionic band and unoccupied states of the cation band in the electronic spectra of these materials. In the case of cuprates (Fig. 1a), it is thought that $\Delta_{ib}$ is related to the Coulomb correlation of electrons at Cu ions; in the case of Fe-based HTSCs (Fig. 1b), $\Delta_{ib}$ is the band gap.

However, it is another, exciton-like excitation $3d^{n+1}(L^{-})$, which has the lowest energy $\Delta_{ct} < \Delta_{ib}$. This excitation corresponds to the transfer of an electron from an anion (O, As) to the nearest 3d cation (Cu, Fe) with the formation of an $L^{-}$ hole localized at the neighboring anions (Fig. 1c). Thus, as $\Delta_{ib}$ are gradually reduced, one expects that a state with $\Delta_{ct} = 0$ be attained first. What is important is that in both cases it is possible to control the value of $\Delta_{ib}$ by by doping (i.e. decreasing the Madelung energy).

2. Model of HTSC ground state
Suppose that a state with $\Delta_{ct} = 0$ for the entire anion–cation plane is attained with no extra carriers added to the plane. Then, under the conditions of hybridization of $3d^{n+1}(L^{-})$ and band $p$-states, we obtain a system with one half-occupied band for cuprates (Fig. 1d) and two overlapping bands for Fe-based HTSC (Fig. 1e). In such a system, transitions of electrons between nearest and next-nearest ions are possible (Fig. 2). Accordingly, this system possesses a gapless Fermi surface (FS), whose shape can be determined in the tight-binding approximation using the appropriate hopping integrals. At the same time, the transition of an electron to a cation is possible only in the presence of a hole on one of the nearest anions (Fig. 2a,b). Therefore, an electron and hole can only move around each other or together (as exciton). This means that incoherent electronic transport cannot occur in this system.

However, despite the fact that incoherent electronic transport in such a system cannot take place, the existence of a FS leads to the possibility of coherent transport, when the entire electron system moves as a whole (a condensate). Besides, incoherent hole transport is possible in this system if there were a mechanism of free-hole generation.
Figure 1. Modification of the electronic structure of Cu- and Fe-based HTSCs upon a decrease in the interband gap $\Delta_{ib}$. a, b – the electronic structures of undoped Cu- and Fe-HTSC, correspondingly; c – the minimal energy for the interband excitation in undoped Cu- and Fe-based superconductors is the energy of the exciton-like excitation $\Delta_{ct}$, which corresponds to the transfer of an electron from an anion to a neighboring cation with the formation of a localized hole; d,e – modifications of the electronic spectrum “a” and “b” for vanishing $\Delta_{ct}$ for Cu- and Fe-HTSC, correspondingly.

Within the simplest ionic model, the gap value $\Delta$ for the transfer of an electron from an anion to the nearest cation is given by the following formula [1]:

$$\Delta \sim \Delta E_M + A_p - I_d$$

Here $I_d$ is the ionization potential of cation, $A_p$ is the electronegativity of anion, and $\Delta E_M$ is the difference in the electrostatic Madelung energies between two configurations, in which the charges of neighboring cation and anion are changed on $\pm 1$. It is possible to control the local value of $\Delta$ by local electron or hole doping changing the Madelung energy. The change of $\Delta E_M$ (and $\Delta$) under doping is determined by the total result of interaction of electron with both dopant ion and distributed doped charge. We will suppose that charges (both holes and electrons) introduced by doping into HTSC parent phases are localized in the nearest vicinity of the dopant ions. We speculate that localization is the result of self-trapping of doped charges in the area limited by an arising barrier layer with $\Delta_{ct} = 0$.

3. Mechanisms of doping
Taking into account the localization of doped carriers we will divide all Cu- and Fe-based HTSCs into two classes: “noble” HTSCs, where doped charges are localized outside the anion–cation planes, and “ignoble” HTSCs, where doped charges are localized in the anion–cation planes.

The first class includes YBCO, BSCCO, Fe-1111 and some others. The role of doped charges in these HTSCs consists in the closing of $\Delta_{ct}$ gap in their nearest vicinity. As an example, Fig. 3 shows the mechanism of doping in YBCO. A doped holes from the excess oxygen ions in the CuO$_2$ chain are...
distributed in the vertical copper-oxygen plaquettes of CuO$_3$ chain and induce a positive charges on the apical oxygens which have determining influence on $\Delta E_M$. This charge redistribution results in reduction of $\Delta E_M$ and $\Delta ib$ (by $\sim$0.5-0.9 eV in dependence on doping) for electron transition to nearest Cu ion from neighboring oxygen in CuO$_2$ plane. Let's consider this is enough to close the gap $\Delta ct$. If all oxygen sites in the chains are occupied, $\Delta ct=0$ for all CuO$_2$ plane. At the same time, it is insufficient to close $\Delta ib\approx1.5-2$ eV.

**Figure 3.** The mechanism of doping in YBCO. Doped holes from the three oxygen ions in the CuO$_3$ chain are distributed among seven oxygen ions (circles with plusses), including two pairs of oxygen ions nearest to the two CuO$_2$ planes. These ions close the $\Delta ct$ for the two pairs of Cu ions (circles with crosses) in the two CuO$_2$ planes. Oxygen ions in CuO$_2$ planes are not shown.

**Figure 4.** The principle of doping in “ignoble” hole-doped HTSC. For the hole doping a doped charge ($-e$) closes the $\Delta ib$ gap in the region where it is localized (green). For the electron doping a doped charge ($+e$) preserves the $\Delta ib$ gap in the region where it is localized (green). In both cases under the influence of the localized charges, a layer (yellow) is formed, around “overdoped” localization area, where $\Delta ct=0$.

The second class includes all HTSCs where charges ($+e$ or $-e$) are introduced directly into anion–cation planes. In particular, this class includes LSCO, NCCO, and some other Cu- and Fe-based HTSCs. The principle of doping in “ignoble” hole-doped HTSC is shown on Fig.4. Here 2 different situations when the dopant ion is out of or in the anion-cation plane are possible.

For example, for hole doping (dopant ion out of the plane, as in LSCO), an extra doped hole is distributed by symmetry over 4 anions around a central cation in CuO$_2$ plane. The total value of such charge ($+e$) is enough for closing of the $\Delta ib$ gap for electron transitions to the central cation from neighboring anions. This area inside this anion square represents a metallic (or overdoped) nano-islet (Fig. 4). At the same time the value of charges of bordering anions ($+e/4$) is enough to close the gap $\Delta ct$ for electron transitions to nearest cations from neighboring anions. As a result, a one-cell belt with $\Delta ct=0$ is formed around such an overdoped islet.

Another example (dopant ion in the plane) is Co-doped “122”-pnictides. Here the extra doped electron ($-e$) is distributed by symmetry over 5 cations around a central dopant cation, i.e. occupy cation orbitals. This area of localization represents a metallic (or overdoped) nano-islet with $\Delta ib>\Delta ct>0$ just as in undoped phase (Fig. 4). The border of the electron localization area is defined by the
condition that the charge of boundary cations is sufficient for closing $\Delta_c$ in one-cell anion-cationic belt formed in the plane around the electron localization area.

Therefore, around metallic nano-islets with $\Delta_b>0$ in the anion-cation plane, there forms a layer with $\Delta_c=0$. As the doping level increases (near the threshold of percolation through metallic nano-islets), extended clusters with $\Delta_c=0$ are formed (Fig. 4).

Let us now examine a possible mechanism whereby a coherent superconducting state may be established. We will show that the systems under consideration are inherently predisposed to superconductive pairing because each pair of nearest cations acts as a two-atom negative-U center (NUC) [2].

It will be recalled that in these systems the transition of an electron to a cation is possible only in the presence of a hole on one of the nearest anions. At the same time the energy of two such excitations is lower if two electrons are located on neighboring cations because in this case the repulsion energy of these cations is less (by 3.5 eV). This is sufficient to reduces $\Delta_{EM}$ to such size to close $\Delta_b$ between and $p$-state of neighboring anion and $3d$-state of adjacent cation. In this way, in the presence of two electrons on neighboring cations, the ion triplet (cation$_1$-anion–cation$_2$) is “metallized” ($\Delta_b=0$) and two holes become free band holes.

Thus, each pair of adjacent cations in such a system may be considered as a two-atom negative-U center (NUC). Owing to virtual transitions of electron pairs to these NUCs, states ($\vec{k}, \uparrow \downarrow$) in the vicinity of the FS are pairwise coupled, which leads to superconducting pairing in the system.

In the normal state of the system, the electron transport is impossible. At the same time, because each pair of cations represents a NUC, there is pair hybridization on NUC’s orbitals with band states [3,4]. The magnitude of the pair hybridization $\Gamma \propto T$. This results in a dynamic process of transitions of real electron pairs to NUCs and back into the band. The transition of an electron pair to a NUC creates two free holes. It is these holes that are responsible for the current flow in such system irrespective of the sign of doping.

Thus, the carriers in normal state are always holes. At the same time, the carriers in superconducting state are electron pairs. Therefore, the carrier sign in the Hall experiments should be changed at the transition temperature $T_c$.

4. Conclusion
We have suggested a qualitative model describing the ground state and the mechanism of superconductive pairing in Cu- and Fe-based HTSCs. In this model, doping by localized charges is supposed to be responsible for the closing of the gap between the occupied anionic band and unoccupied states of the cation band and for the formation of the electron-excitonic band of unusual nature. The resulting HTSC ground state is strongly correlated insulator with Fermi surface, where the electron transfer between the nearest and next-nearest ions is only permitted. The incoherent electron transport is impossible in this system but coherent superconducting transport is possible because the band is not fully occupied. It is shown that such electronic system is inherently predisposed to superconductive pairing because each pair of nearest cations acts as a two-atom negative-U center.

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