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Doping dependent charge transfer gap and realistic electronic model of n-type cuprate superconductors

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Based on the analysis of the measurement data of angle-resolved photoemission spectroscopy (ARPES) and optics, we show that the charge transfer gap is significantly smaller than the optical one and is reduced by doping in electron doped cuprate superconductors. This leads to a strong charge fluctuation between the Zhang-Rice singlet and the upper Hubbard bands. The basic model for describing this system is a hybridized two-band t-J model. In the symmetric limit where the corresponding intra- and inter-band hopping integrals are equal to each other, this two-band model is equivalent to the Hubbard model with an antiferromagnetic exchange interaction (i.e. the t-U-J model). The mean-field result of the t-U-J model gives a good account for the doping evolution of the Fermi surface and the staggered magnetization.

The evolution of the Fermi surface and the Mott insulating gap with hole or electron doping is a central issue in elucidating the mechanism of high-T_c superconductivity. In the hole doped case, a small Fermi surface arc appears first near $(\pi/2, \pi/2)$ and then extends towards $(\pi, 0)$ and $(0, \pi)$ with increasing doping. In contrast, in the electron dope case, electrons are first doped into the upper Hubbard band (Cu $3d^{10}$ band) near (π ,0) and equivalent points. With further doping but still in the antiferromagnetic phase, in-gap spectral weight develops below the Fermi level. These in-gap states move upwards and eventually form a hole-like Fermi surface pocket around ($\pi/2$, $\pi/2$)[1]. In the heavily overdoped sample, these two Fermi pockets merge together and form a large Fermi surface with a volume satisfying the Luttinger theorem.

The peculiar doping dependence of the Fermi surface topology in electron-doped cuprates is a manifestation of correlation effects. To understand the physics behind, much of the theoretical study has been carried out with the one-band Hubbard model[2, 3, 4]. In this model, a metallic band is split into two effective bands, namely the upper and lower Hubbard bands, by a correlation energy U that represents the energy cost for a site to be doubly occupied. Under the mean-field approximation, this model gives a good account for the experimental data if U is assumed to fall strongly with doping. However, this strong reduction of U by doping is not usually expected[5]. The nominal Hubbard U-term could arise either from the on-site Coulomb repulsion between two electrons in a Cu $3d_{x^2-y^2}$ orbital or from the charge transfer (CT) gap between O $2p$ and Cu $3d^{10}$ bands. The on-site Coulomb repulsion in a Cu $3d_{x^2-y^2}$ states in high-T_c cuprates is generally larger than 5 eV. The CT gap in electron doped cuprates quoted from the optical data is also quite large ($\sim$ 1.5 eV)[6, 7]. It seems that in neither case U can be dramatically suppressed by only 15% doping.

An alternative interpretation to the two Fermi pockets is based on the notion of band folding induced by the antiferromagnetic interaction[5, 8]. This interpretation is consistent with the measurement data in the overdoped regime ($x > 0.15$). However, in the low doping antiferromagnetic phase, it breaks down. The band folding assumes implicitly a band with large Fermi surface exists and it is the antiferromagnetic interactions between the hot spots split this band into a conduction electron and a shadow hole band. However, in the antiferromagnetic phase at low doping, these bands with the folding gap at the hot spots were not observed and the band near $(\pi/2, \pi/2)$ is well below $(\pi, 0)$.[1] Furthermore, the antiferromagnetic interaction is too small to account for the energy splitting between the lower and upper CT bands at least in the low doping limit.

To resolve the above problems, it is important to understand correctly how the hole-like Fermi pockets develop with doping. In a nominally undoped Nd_2CuO_4, a dispersive band structure is observed by ARPES at roughly 1.2 eV below the chemical potential. As shown in Ref. [1], the energy-momentum dispersion of this spectral peak behaves almost the same as the lower CT band observed in $Ca_2CuO_2Cl_2$, except in the latter case the band lies at only $\sim$ 0.7 eV below the chemical potential. This suggests that these two bands have the same physical origin. The difference is probably due to the intrinsic doping and the Fermi energy is pinned near the bottom of conduction band (i.e. Cu $3d^{10}$ band) in Nd_2CuO_4 and near the top of the valence band (*i.e.* Zhang-Rice singlet band[11]) in $Ca_2CuO_2Cl_2$.

Doping electrons into Nd_2CuO_4 results in a spectral weight transfer from the main spectral peak at $\sim$ 1.2eV to a "in-gap" state. This in-gap state first appears as a week low energy "foot" at $\sim$ 0.5 eV below the Fermi level ε_F along the zone diagonal in the undoped Nd_2CuO_4 (Fig. 1). It moves towards the Fermi level with doping

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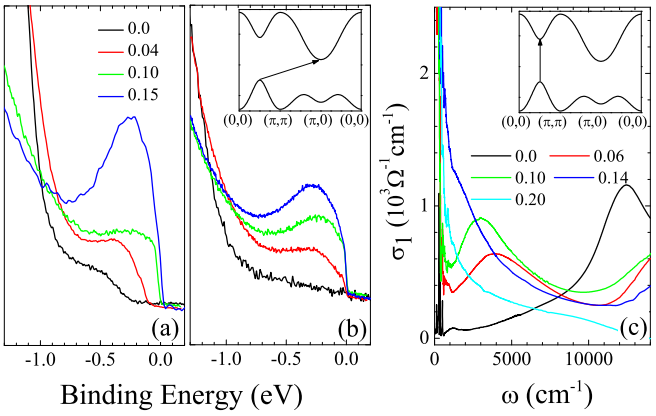

Figure 1: ARPES spectra near (a) the nodal and (b) antinodal regions, reproduced from the data published in Ref. [1]. (c) The infrared conductivity reproduced from the data published in Ref. [7]. The insets of (b) and (c) illustrate the indirect and direct CT gaps.

and becomes a broad hump just below the Fermi level at optimal doping. The hole Fermi pockets observed at high doping originate from these in-gap states. In contrast, the states near $(\pi, 0)$ resides at ε_F as they are derived from the bottom of the upper Hubbard band. The fact that the broad maximum is slightly below ε_F is caused by the Frank-Condon broadening as discussed below.

It should be pointed out that, same as for the dispersive high energy band, the in-gap states behave similarly as the low energy coherent states observed in hole-doped $Ca_2CuO_2Cl_2$[9]. Near half filling, the in-gap state in Nd_2CuO_4 lies also at $\sim$ 0.7 eV above the high energy spectral peak. This suggests that, similar as in hole doped materials, the high energy hump structure in the spectra results from the Franck-Condon broadening and the in-gap states are the true quasiparticle excitations located at the top of the lower CT band[9]. At half filling, the in-gap state is not observed because its quasiparticle weight is vanishingly small[10].

The spectral weight transfer induced by doping has also been observed in the optical measurements (Fig. 1). At zero doping, the optical CT gap appears at $\sim$ 1.5 eV. Upon doping, a mid-infrared conductivity peak develops. This mid-infrared peak appears at $\sim$ 0.5 eV at low doping[6, 7], and then moves towards zero energy with increasing doping. The doping dependence of the mid-infrared peak is consistent with the doping evolution of the "in-gap" states observed by ARPES. It suggests that the mid-infrared peak results mainly from the optical transition between the "in-gap" states and the upper Hubbard band. The polaron effect may also have some contribution to these mid-infrared peaks.[12]

The above discussion indicates that the true CT gap, measured as the minimum excitation energy between the lower and upper Hubbard bands, is only 0.5 eV at half filling, much lower than the optically measured CT gap, which is usually believed to be about 1.5 eV. This difference between the true quasiparticle gap that determines the transport and thermodynamics and optically measured CT gaps has also been found in hole doped materials. For La_2CuO_4, Ono *et al.*[13] found recently that the CT gap obtained from the high temperature behavior of the Hall coefficient is only 0.89 eV, while the corresponding optical CT gap is about 2 eV. This means that the optical CT gap, which is generally determined from the peak energy of the optical absorption, does not correspond to the true gap between the two bands in high-T_c oxides. The indirect nature of the gap (insets of Fig. 1) and the Frank-Condon effect lead to the overestimate of the gap by optics. It also means that the charge fluctuation in high-T_c materials is much stronger than usually believed and should be fully considered in the construction of the basic model of high-T_c superconductivity [14, 15, 16].

The doping dependence of low energy peaks observed by both APRES and optics indicates that there is a gap closing with doping. This gap closing may result from the Coulomb repulsion between O $2p$ and Cu $3d$ electrons. Doping electrons will increase the occupation number of Cu $3d$ states, which in turn will add an effective potential to the O $2p$ states and raise their energy level. If U_{pd} is the energy of the Coulomb interaction between neighboring O and Cu ions, then the change in the O $2p$ energy level will be $\delta\varepsilon_p \approx +2xU_{pd}$, where x is the doping concentration and the factor 2 appears since each O has two Cu neighbors. U_{pd} is generally estimated to be of order 1-2 eV. Thus a 15% doping of electrons would reduce the CT gap by 0.3-0.6 eV, within the range of experimentally observed gap reduction. Furthermore, the electrostatic screening induced by doping can reduce the on-site Coulomb interaction of Cu $3d_{x^2-y^2}$ electrons. This can also reduce the gap between the O $2p$ and the upper Hubbard bands.

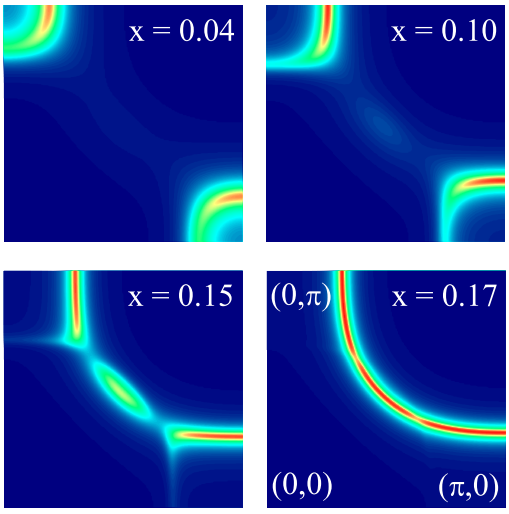

Figure 2: Fermi surface density map at different dopings x, obtained by integrating the spectral function from -40 to 20 meV around the Fermi level, for the t-U-J model.

Now let us consider how to characterize the low energy charge and spin dynamics of the system. For simplicity, we focus on the electronic structure and leave the additional electron-phonon interaction effect for future study. The lower CT band behaves similarly as the Zhang-Rice singlet band. Thus if its charge fluctuation with the upper Hubbard band is ignored, this band should be described by an effective one-band t-J model[11]. Similarly, the upper Hubbard band should also be described by an effective one-band t-J model if there is no charge fluctuation. However, in the case the hybridization or charge transfer between these bands is important, it can be shown from a three-band model that these two t-J models should be combined together and replaced by the following hybridized two-band t-J model[17]

$$\begin{aligned} H &= \sum_{ij\sigma} t^e_{ij} e^\dagger_i d_{i\sigma} d^\dagger_{j\sigma} e_j + \sum_{ij\sigma} t^h_{ij} h^\dagger_i d_{i\sigma} d^\dagger_{j\sigma} h_j \\ &+ \sum_{ij\sigma} t_{ij} \left(\sigma d^\dagger_{i\sigma} d^\dagger_{j\overline{\sigma}} e_i h_j + h.c. \right) + J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \\ &+ \sum_i \left(\varepsilon_e e^\dagger_i e_i + \varepsilon_h h^\dagger_i h_i \right) - V_{pd} \sum_{\langle ij \rangle} e^\dagger_i e_i h^\dagger_j h_j, \quad (1) \end{aligned}$$

where h_i, e_i and $d_{i\sigma}$ are the annihilation operators of a Zhang-Rice singlet hole, a doubly occupied $d_{x^2-y^2}$ state (doublon), and a pure Cu^{2+} spin, respectively. At each site, these three states cannot coexist and the corresponding number operators should satisfy the constraint

$$e^\dagger_i e_i + h^\dagger_i h_i + \sum_\sigma d^\dagger_{i\sigma} d_{i\sigma} = 1. \quad (2)$$

The difference between the number of doubly occupied $d_{x^2-y^2}$ states and Zhang-Rice singlet holes is the doping concentration of electrons, $\langle e^\dagger_i e_i - h^\dagger_i h_i \rangle = x$.

In Eq. (1), $\mathbf{S}_i = d^\dagger_i \sigma d_i/2$ is the spin operator and σ is the Pauli matrix. ε_e and ε_h are the excitation energies of a doublon and a Zhang-Rice singlet, respectively. t^e_{ij} and t^h_{ij} are the hopping integrals of the upper Hubbard and Zhang-Rice singlet bands. In Eq. (1), if $\varepsilon_h \gg \varepsilon_e > 0$, then $\langle h^\dagger_i h_i \rangle \approx 0$ and H simply reduces to the one-band t-J model of doubly occupied electrons in the doublon-spinon representation. On the other hand, if $\varepsilon_e \gg \varepsilon_h > 0$, then $\langle e^\dagger_i e_i \rangle \approx 0$ and H becomes simply the one-band t-J model of Zhang-Rice singlets in the holon-spinon representation. The t_{ij} term describes the hybridization between the upper Hubbard and Zhang-Rice singlets. The last term results from the Coulomb repulsion between a Cu $3d_{x^2-y^2}$ and its neighboring O $2p_{x,y}$ electrons. V_{pd} is proportional to the Coulomb repulsion between Cu and O ions U_{pd}.

The above Hamiltonian can be simplified if $t^e_{ij} = t^h_{ij} = t_{ij}$. In this case, by using the holon-doublon representation of an electron operator $c_{i\sigma} = \sigma h^\dagger_i d_{i\sigma} + e_i d^\dagger_{i\overline{\sigma}}$, and taking a mean-field approximation for the V_{pd}-term, $e^\dagger_i e_i h^\dagger_j h_j \approx \langle e^\dagger_i e_i \rangle h^\dagger_j h_j + e^\dagger_i e_i \langle h^\dagger_j h_j \rangle - \langle e^\dagger_i e_i \rangle \langle h^\dagger_j h_j \rangle$, one can then express H as

$$H = \sum_{ij\sigma} t_{ij} c^\dagger_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + J \sum_{\langle ij \rangle} S_i \cdot S_j, \quad (3)$$

where $n_{i\sigma} = c^\dagger_{i\sigma} c_{i\sigma}$ and $U = \varepsilon_e + \varepsilon_h - 4V_{pd}(\langle e^\dagger_i e_i \rangle + \langle h^\dagger_i h_i \rangle)$. In electron doped materials, as the induced hole concentration is very small, $\langle h^\dagger_i h_i \rangle \ll \langle e^\dagger_i e_i \rangle \approx x$, we have $U \approx \varepsilon_e + \varepsilon_h - 4xV_{pd}$. It should be emphasized that the spin exchange term in Eq. (3) is not a derivative of the one-band Hubbard model in the strong coupling limit. It actually arises from the antiferromagnetic superexchange interaction between two undoped Cu^{2+} spins via an O $2p$ orbital. This term, as shown in Ref. [18], can enhance strongly the superconducting pairing potential.

The t-U-J model defined by Eq. (3) is obtained by assuming $t^e_{ij} = t^h_{ij} = t_{ij}$. This is a strong approximation which may not be fully satisfied in real materials. Nevertheless, we believe that this simplified model still catches qualitatively the low energy physics of high-T_c cuprates. It has already been used, as an extension of either the Hubbard or the t-J model, to explore physical properties of strongly correlated systems, such as the gossamer superconductivity.[19]

The above Hamiltonian reveals two features about the effective Hubbard interaction. First, U is determined by the CT gap[14], not the Coulomb interaction between two electrons in a Cu $3d_{x^2-y^2}$ orbital. It is in the intermediate or even weak coupling regime, rather than the strong coupling limit as usually believed. Second, U is doping dependent. It drops with doping. These are in fact the two key features that are needed in order to explain the experimental results with the Hubbard model [2, 3, 4].

We have calculated the single-particle spectral function and the staggered magnetization for the t-U-J model using the mean-field approximation. In the calculation, t_{ij} are parameterized by the first, second and third nearest neighbor hopping integrals (t, t', t''). The parameters used are $t = 0.326$ eV, $t' = -0.25t$, $t'' = 0.15t$, $J = 0.3t$ eV, $\varepsilon_e + \varepsilon_h = 4t$ and $V_{pd} = 2.7t$.

Fig. 2 shows the intensity plot of the spectral function at the Fermi level. The doping evolution of the Fermi surface agrees with the ARPES measurements.[1] It is also consistent with the mean-field calculation of the Hubbard model by Kusko et al., while our calculation has the same shortcoming of the mean field calculation in providing too large band width.[2] The difference is that, in our calculation, the Hubbard interaction U is not an adjustable parameter of doping. It decreases almost linearly with doping. For the parameters given above, $U \approx 4t - 10.8xt$. Whereas in the calculation of Kusko et al.[2], U is determined by assuming the mean-field energy gap to be equal to the experimentally observed value of the "pseudogap".

Fig. 3 shows the theoretical result of the staggered magnetization $m = (\langle n_{i\uparrow} - n_{i\downarrow} \rangle)/2$. The simple mean-field result agrees well with the experimental data[20, 21, 22, 23], especially in the low doping range. It is also consistent qualitatively with other theoretical

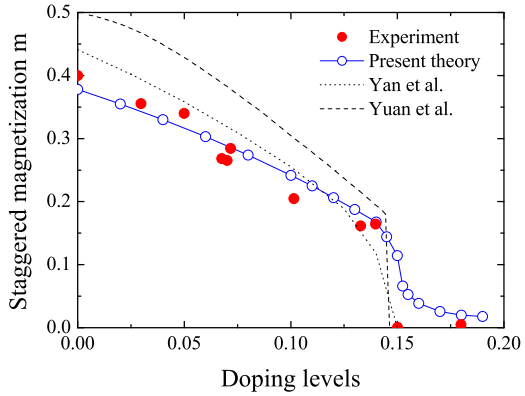

Figure 3: Comparison of the mean field result (open circles) of the staggered magnetization m as a function of doping with the experimental data (solid circles)[23]. The theoretical data obtained by Yan *et al.*[24] and by Yuan *et al.*[5] are also shown for comparison.

calculations[5, 24]. m decreases almost linearly at low doping. However, it shows a fast drop above ~ 0.14, when the lower Zhang-Rice singlet holes begin to emerge above the Fermi surface. This abrupt change of m is an indication of a significant renormalization of the Fermi surface. It may result from the quantum critical fluctuation as suggested in Ref. [25]. m does not vanish above the optimal doping, this is probably due to the mean-field approximation.

In conclusion, we have shown that the minimal CT gap is much smaller than the optical gap and the charge fluctuation between the Zhang-Rice singlet and the upper Hubbard bands is strong in electron doped copper oxides. The low-lying excitations of the system are governed by the hybridized two-band t-J model defined by Eq. (1) or approximately by the t-U-J model defined by Eq. (3). This conclusion is drawn based on the analysis of electron doped materials. However, we believe it can be also applied to hole doped cuprate superconductors. Our mean-field calculation for the t-U-J model gives a good account for the doping evolution of the Fermi surface as well as the staggered magnetization. It sheds light on the further understanding of high-T_c superconductivity.

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