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ELECTRONIC STRUCTURE OF HIGH-T_c SUPERCONDUCTORS

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ABSTRACT

The band structure of doped high-T_c superconductors ($La_{2-x}Sr_xCuO_4$, etc.) is considered. Strong electron-electron Coulomb interaction as well as strong coupling with the excitons play an important role in the band formation. The charged quasi-particle in x^2-y^2 band has spin $S=0$ with small admixture of $S=1$ state. Close to the lowest x^2-y^2 band there is z^2 band ($\Delta E \leqslant 1$ eV) with $S=1/2$ quasi-particle. Dependence of frequency of Cu nuclear quadrupole resonance (NQR) on x is considered.

RESULTS OF CALCULATION

Transfer integrals for $t-t'-J$ model which describes the motion of a hole in the background of spins are determined. Here t is the effective transfer integral for hopping to nearest cell, t' is the transfer integral for hopping to next nearest cell (diagonal hopping). Structure of quasi-particle is characterized by the following probabilities: $P(\bar{d}^2)=P(d^8)$ — two holes on Cu, $P(\bar{d}\bar{p})=P(d^9)$ — one hole on Cu and one hole on O, $P(\bar{p}\bar{p})=P(d^{10})$ — two oxygen holes.

x^2-y^2 band: $t=0.18$ eV, $t'=-0.06$ eV, $m \simeq m_e$,

$$P(d^8)=27\%,\ P(d^9)=65\%,\ P(d^{10})=8\%.$$

z^2 band: $t=0.10$ eV, $t'=0.025$ eV, $m \simeq 5m_e$,

$$P(d^8)=P(\bar{x}^2-\bar{y}^2,\bar{z}^2)=57\%,$$

$$P(d^9)=P(\bar{z}^2)+P(\bar{x}^2-\bar{y}^2)=30+10=40\%,\ P(d^{10})=3\%.$$

X-dependence of NQR-frequency for Cu in $La_{2-x}Sr_xCuO_4$.

If we suppose that concentration of holes in CuO_2 plane equals to x then

$$x^2-y^2: \frac{d\nu}{dx}=40 \text{ MHz},$$

$$z^2: \frac{d\nu}{dx}=-87 \text{ MHz}.$$

For $\nu(x=0.12)-\nu(x=0)$ experiment gives 5 MHz in agreement with x^2-y^2 band result. At $x>0.12$ $d\nu/dx$ is essentially smaller. Probably it means that number of holes in CuO_2 plane very slowly increases with x at $x>0.12$. The other possible explanation of the small value of $d\nu/dx$ is the crossing with the oxygen π band.

INTRODUCTION

Since the discovery of the high-T_c superconductors a number of band structure calculations have been published [1]. The main part of this works are local density band structure calculations. This approach fails to explain the fact that pure La_2CuO_4 is insulator. The situation is better in local spin density approach, but still there are the problems with localized magnetic moment in antiferromagnetic state, noncentral Coulomb interaction and strong electron-exciton coupling.

We think that it is evident now that one should consider the undoped materials (e. g. La_2CuO_4) as Mott-Habbard insulators. More exactly, these materials are charge transfer insulators in Zaanen—Savatzky—Allen scheme [2]. In this approach there is no problems with the value of the localized magnetic moment. The very important test is the calculation of the frequencies of nuclear magnetic and nuclear quadrupole resonances for Cu [3].

In this situation it is natural to calculate the band structure of doped system (e. g. $La_{2-x}Sr_xCuO_4$) considering the holes in charge—transfer insulator in tight-binding approximation. In previous paper [4] we did such an attempt, but there we strongly overestimated the oxygen $2p$-orbitals splitting (see discussion in the Ref. [3]) and did not take into account the oxygen-oxygen hopping matrix element t_{pp}. Therefore we got the wrong order of bands in Ref. [4] and had the problems with the explanation of melting of magnetic order.

In the present paper we calculate the band structure of the hole doped CuO_2 plane basing on the parameters checked in the calculation of the frequencies of nuclear resonances. The strong interaction with the exciton and noncentral Coulomb interaction are taken into account in the variational wave function. The weights of configurations d^8p^6, d^9p^5, $d^{10}p^5p^5$ are estimated. The lowest hole bands are x^2-y^2 and z^2. The dynamics in the x^2-y^2 band turns to be close to that in the Hubbard model as well as to $t-t'-J$ model for singlet pair motion [5, 6]. The difference from the simple Hubbard model arises due to the close z^2 band.

CALCULATION OF THE HOLE BANDS

It is well established that for undoped case CuO_2 sheet is insulator with electronic configuration d^9p^6 ($d=3d$ copper orbital,

$p=2p$ oxygen orbital). The $3d$-hole is in the state x^2-y^2 (x and y axes lie in the CuO_2 plane). It should be noted that there is 17% admixture of the configuration $d^{10}p^5$ [3]. It is virtual admixture of charge transfer excitation. The energy of this excitation equals [7, 3]:

$$\Delta=E(d^{10}p^5)-E(d^9p^6)=5\text{ eV}. \tag{1}$$

The excitation $d^9p^6d^9\to d^{10}p^6d^8$ has the energy $U_{dd}=6$ eV [7]. The value of Δ is slightly larger than that excepted in Ref. [8]: $\Delta\simeq 3$ eV. We should note that precise value of Δ is not very important. It is essential only that Δ is larger than hopping matrix element to provide undoped system being insulator.

In the calculation we use tight binding approximation and include in the basis set the $3d$ state of Cu ion and $2p$-state of oxygen ion.

$$3d: |x^2-y^2\rangle,\ |z^2\rangle,\ |xy\rangle,\ |xz\rangle, |yz\rangle,$$
$$2p: |x\rangle,\ |y\rangle,\ |z\rangle. \tag{2}$$

Let us list all the parameters we will use. The hopping transfer integrals of the hole are as follow.

1) Cu-O hopping. Link directed along x axis:

$$t_{x^2-y^2,x}=-\frac{\sqrt{3}}{2}(pd\sigma),\quad t_{z^2,x}=\frac{1}{2}(pd\sigma),$$
$$(pd\sigma)=1.6\text{ eV},\quad (pd\pi)=-0.8\text{ eV}. \tag{3}$$

2) O-O hopping

$$t_{pp}=(pp\sigma)\simeq -1\text{ eV},\quad (pp\pi)=0. \tag{4}$$

Let us stress that (3), (4) describe the hole hopping. For the electron the transfer integrals are of opposite sign. The values of transfer integrals (3), (4) are close to generally excepted (see e. g. Ref. [1]). We have checked this values by calculating the constant of superexchange $J\overline{ss_2}$ [7] and the frequencies of Cu nuclear quadrupole and magnetic dipole resonances [3].

The Coulomb integrals of the second and forth multipolarities for the $3d$ electrons can be found from the Cu ion spectrum [9]:

$$F_2=0.245\text{ eV},\quad F_4=0.017\text{ eV}. \tag{5}$$

According to the photoemission data (see e. g. Ref. [10]) the energy of separation of $3d$ electron from Cu^{2+} in the compounds under discussion is equal to the energy of separation of $2p$ electron from O^{2-}. Thus

$$E(d^8p^6)=E(d^9p^5)\,. \tag{6}$$

We should stress that here $E(d^8p^6)$ is the center of configuration, i. e. the value averaged over all possible LS-states of d^2-pair.

The electronic band structure problem is closely connected with the problem of magnetic structure. The melting of the antiferromagnetic order at the doping is due to the strong interaction of moving hole with magnetic system. To avoid this problem at the first step let us consider the hole band structure in the ferromagnetic state, similar to Refs [11, 4].

In this case without doping all the $3d$ holes are in the state $|x^2-y^2\rangle_\uparrow$. Let us add one additional hole of the symmetry $|x^2-y^2\rangle$. Due to the Pouli principle it has spin down: $|x^2-y^2\rangle_\downarrow$. If we choose the average energy of $3\bar{d}^2$ configuration to be zero

$$\langle E(3d^8)\rangle=0\,. \tag{7}$$

then due to the Coulomb interaction of the second and fourth multipolarities (5) the energy of the state $|1\rangle=|x^2-y^2\rangle_\uparrow|x^2-y^2\rangle_\downarrow$ equals

The next point is the exciton contribution [4]: the $|x^2-y^2\rangle_\uparrow$ hole can virtually hope to the nearest oxygen. It can not move further to the following copper due to the Pouli blocking. Let us denote by a_σ the creation operator of function $|x^2-y^2\rangle_\sigma$ hole and by b_σ the creation operator of $2p_\sigma$ oxygen hole. Then the exciton-like mixing is

$$|1\rangle=a_\uparrow a_\downarrow\to|\tilde{1}\rangle=\sqrt{1-4\xi^2}\;a_\uparrow a_\downarrow-\xi(b_{2\uparrow}-b_{3\uparrow}-b_{4\uparrow}+b_{4\uparrow})\,a_\downarrow\,. \tag{9}$$

The oxygen ions denoted by *2*, *3*, *4*, *5* are pointed at Fig. 1. The signs $\pm$ before b_i in (9) are due to the signs of $2p_\sigma$-functions with respect to x^2-y^2 Cu function in the point of their overlapping.

The energy of the state $|\tilde{1}\rangle$ equals

$$\tilde{\varepsilon}_1=\varepsilon_1(1-4\xi^2)+4\xi^2\varepsilon_p-4\sqrt{3}\,\xi\sqrt{1-4\xi^2}\,(pd\sigma)+\frac{1}{2}\,\xi^2t_{pp}\,. \tag{10}$$

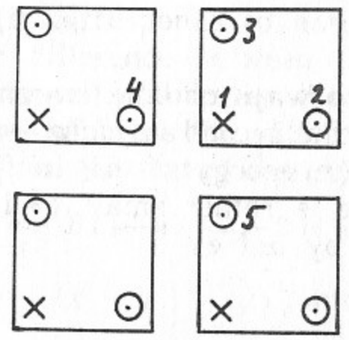

Fig. 1. CuO_2 plane split into the elementary cells. The cross corresponds to the Cu ion and the circle corresponds to the oxygen.

Here ε_p is the single-particle energy of $2p$-hole at oxygen. According to the Eqs (6), (7) $\varepsilon_p=0$. The ξ in Eqs (9), (10) is the variational parameter and we should find it at the final step.

Consider now the motion of a spin down hole. It is not blocked by Pouli principle and the Bloch wave arises. It consists of the states $|\tilde{1}\rangle$ and $|x^2-y^2\rangle_\uparrow|p_\sigma\rangle_\downarrow$

$$\psi_k=\frac{1}{\sqrt{N}}\sum_n\{\alpha\,|\tilde{1}\rangle+a_\uparrow(\beta b_{2\downarrow}+\gamma b_{3\downarrow})\}\exp\{i\vec{k}\,\vec{r}_n\}\,. \tag{11}$$

If we neglect the t_{pp} the dispersion is

$$\varepsilon_k(\xi)=\frac{\tilde{\varepsilon}_1+\varepsilon_p}{2}-\left\{\left(\frac{\varepsilon_p-\tilde{\varepsilon}_1}{2}\right)^2+4t_\xi^2\left(\sin^2\left(\frac{k_xa}{2}\right)+\sin^2\left(\frac{k_ya}{2}\right)\right\}^{1/2}. \tag{12}$$

Here $t_\xi=-\frac{\sqrt{3}}{2}(pd\sigma)\sqrt{1-4\xi^2}$, $a=3.81\text{Å}=7.2a$ is the lattice period. To take into account t_{pp} and mixing with other configurations (z^2, xy, p_π etc.) we have carried out numerical calculations. It makes deeper the bands bottom. The lowest energy corresponds to k_x, $k_y=\pm\pi/a$ (let us remind that we discuss the hole band but not the electron band).

The Eq. (11) takes into account the hybridization of the states $\bar{d}^2$ and $\bar{d}\bar{p}$. The other types of configurations are $\bar{p}^2$ and $\bar{p}\bar{p}$. We neglect the contribution of high state $\bar{p}^2$. As far as $\bar{p}\bar{p}$ is concerned it can be added easily to the Bloch wave (11):

$$\psi_k = \frac{1}{\sqrt{N}} \sum_n \left\{ \alpha |\tilde{1}\rangle + a_\uparrow (\beta b_{2\downarrow} + \gamma b_{3\downarrow}) + \sum_{\substack{i \neq j = \\ 1,2,3,4}} \Phi_{ij}\, b_{i\uparrow}\, b_{j\downarrow} \right\} \exp\{i\vec{k}\vec{r}_n\} . \quad (13)$$

Note that there are two ways of hole movement here. The first is $d^8p^6d^9 \to d^9p^5d^9 \to d^9p^6d^8$, the second is $p^5d^9p^6 \to p^5d^{10}p^5 \to p^6d^9p^5$. According to the Eq. (1) the energy of $\bar{p}\bar{p}$ configuration is $\Delta \simeq 5$ eV. Therefore its admixture is rather small ($\sim 10\%$). It pushes down the bottom of the band by $\simeq 1$ eV.

Fig. 2. Position of the bottom of the x^2-y^2, z^2, and xy bands as a function of the $(pd\sigma)$.

The lowest energy of the x^2-y^2 band as a function of hopping parameter $(pd\sigma)$ is plotted at Fig. 2 (solid line). Other hopping parameters are scaled proportionally to $(pd\sigma)$, e. g.

$$t_{pp} = -\frac{1 \text{ eV}}{1.6 \text{ eV}} (pd\sigma) .$$

The weights of configurations P_i, effective mass m^* and amplitude of exciton admixture ξ near the bottom of the band are as follow:

$$\begin{aligned} x^2-y^2 &: m^* = 0.8 m_e , \quad \xi = 0.31 ; \\ & P(\bar{d}^2) = \alpha^2(1-4\xi^2) = 0.27 ; \\ & P(\bar{d}\bar{p}) = 4\alpha^2\xi^2 + |\beta|^2 + |\gamma|^2 = 0.65 ; \\ & P(\bar{p}\bar{p}) = \sum_{i \neq j} |\Phi_{ij}|^2 = 0.08 . \end{aligned} \quad (14)$$

The calculation of z^2, xy, xz, yz bands is very similar to that for x^2-y^2 band. The only difference is that the spin of the band hole can be parallel or antiparallel with respect to the localized x^2-y^2

hole. According to Hund rule the configuration with parallel spins has lower energy and we consider this case. It is possible to consider averaged case (it corresponds to antiferromagnetic order of x^2-y^2 spins) but the difference between these two cases is not large (0.35 eV for z^2 band). Moreover the estimation shows that higher order correlations suppress this difference to ~ 0.1 eV.

The Coulomb energy of the state $|x^2-y^2\rangle_\uparrow |z^2\rangle_\uparrow$ equals

$$\varepsilon_1 = -8F_2 - 9F_4 = -2.11 \text{ eV} . \quad (15)$$

For the xy band we have $|x^2-y^2\rangle_\uparrow |xy\rangle_\uparrow$ and

$$\varepsilon_1 = 4F_2 - 69F_4 = -0.19 \text{ eV} . \quad (16)$$

Similar to x^2-y^2 band calculation, the hopping of the $|x^2-y^2\rangle_\uparrow$ hole to the nearest oxygen gives coupling with exciton (compare with Eq. (9)) and motion of $|z^2\rangle$ or $|xy\rangle$ hole leads to the band. We use all the configurations $\bar{d}^2$, $\bar{d}\bar{p}$, $\bar{p}\bar{p}$ as the basis for numerical diagonalization of Hamiltonian matrix. The lowest energy for z^2 and xy bands corresponds to k_x, $k_y = \pm\pi/a$. This lowest energy as a function of $(pd\sigma)$ is plotted at Fig. 2. (We suppose that $(pd\pi) = (-1/2)(pd\sigma)$, $t_{pp} = -\frac{1 \text{ eV}}{1.6 \text{ eV}}(pd\sigma)$.) The effective masses, amplitudes of exciton admixture ξ and the weights of configurations are as follows:

$$\begin{aligned} z^2 \text{ band} &: m^* = 5m_e , \quad \xi = 0.29 ; \\ & P(\bar{d}^2) = \alpha^2(1-4\xi^2) = 0.57 ; \\ & P(\bar{d}\bar{p}) = P(\bar{z}^2) + P(\bar{x}^2-\bar{y}^2) = 0.4 ; \\ & P(\bar{z}^2) = 4\alpha^2\xi^2 = 0.30 , \quad P(\bar{x}^2-\bar{y}^2) = |\beta|^2 + |\gamma|^2 = 0.10 ; \\ & P(\bar{p}\bar{p}) = \sum_{i \neq j} |\Phi_{ij}|^2 \simeq 0.03 ; \end{aligned} \quad (17)$$

$$\begin{aligned} xy \text{ band} &: m^* = 8.8\, m_e , \quad \xi = 0.35 ; \\ & P(\bar{d}^2) = 0.46 ; \\ & P(\bar{d}\bar{p}) = P(\bar{x}\bar{y}) + P(\bar{x}^2-\bar{y}^2) = 0.45 + 0.07 = 0.52 ; \\ & P(\bar{p}\bar{p}) = 0.02 . \end{aligned} \quad (18)$$

We would like to remind that $P(\bar{d}^2)$ consists of $P(\bar{x}-\bar{y})$ which is

due to exciton and $P(\bar{z}^2)$ or $P(\bar{x}\bar{y})$ which are due to the Bloch wave. The both contributions are presented at Eqs (17, 18).

Note that at k_x, $k_y=\pm\pi/a$ the mixing between the bands x^2-y^2, z^2, xy, xz, yz is forbidden due to symmetry selection rule. If k deviates from this points the mixing matrix elements are proportional to δk^2, and they are small in interesting region of δk. Therefore the mixing could be important only in the vicinity of the crossing of different bands. Moreover, this mixing is sensitive to spin structure and ferromagnetic model probably overestimates it.

The calculation of xz, yz bands shows that they are close to xy band. Thus the lowest band is the x^2-y^2 band (see Fig. 1). The splitting between x^2-y^2 and z^2 is about 1 eV. It should be noted that we do not know exactly the matrix element t_{pp} (the superexchange and nuclear resonance frequency are not sensitive to it). If we set $t_{pp}=0$ the bottoms of these two bands become practically degenerate.

Stress that noncentral Coulomb interaction of $3d$ holes is important here. Just this interaction pushes down z^2 band and reduces the interval between x^2-y^2 and z^2 bands.

Thus our calculation shows that at small doping hole states at Fermi surface are of x^2-y^2 type. However it is possible that at some finite doping the Fermi level crosses the bottom of the z^2 band. In this case the states at Fermi surface became mainly of z^2 type due to large effective mass in this band (Eq. (17)).

From the photoemission data [10] we know that the distance between the center of $3d$-peak and Fermi level is about 4—4.5 eV.

The position of $3d$-peak center is shifted from zero (Eq. (7)) by -1 eV due to correlation in the initial state $|p^6d^9p^6\rangle=|\bar{x}^2-\bar{y}^2\rangle$ (Ref. [3]). Let us suppose that Fermi level is about 1 eV above the bottom. Then we see from Fig. 2 that at $(pd\sigma)=1.6$ eV our calculation agrees with the experimental distance between the center of $3d$ peak and Fermi level.

It is necessary to say a few words about oxygen π-orbital band (for CuO link directed along x axis, $|\sigma\rangle=|p_x\rangle$, $|\pi\rangle=|p_y\rangle$). Energy of the bottom of this band and effective mass are approximately equal to

$$p_\pi \text{ band: } E(k_x, k_y=\pm\pi/a)\simeq\varepsilon_\pi-2|t_{pp}|+\Delta E_{pp},$$
$$m^*\simeq m_e, \tag{19}$$

Here $\Delta E_{pp}\simeq -1$ eV is the shift of the band bottom due to mixing

with two oxygen hole states (excitation $p^\nu d^9 p^6\to p^5 d^{10} p^5$), ε_π is the splitting of σ and π $2p$-hole energies (we set $\varepsilon_\sigma=0$). This splitting probably $\leqslant 1$ eV, however the value $\varepsilon_\pi\simeq -2$ eV is not excluded (e. g., splitting between σ- and π-orbitals in CuO molecule is just 2 eV). If we take $\varepsilon_\pi=-2$ eV and $t_{pp}=-1$ eV, we get $E_\pi=-5$ eV. It is very close to the energies of x^2-y^2 and z^2 bands.

THE FREQUENCY OF NUCLEAR QUADRUPOLE RESONANCE FOR Cu

We calculated the frequencies of NQR and NMR for undoped CuO_2 plane in the Ref. [3]. In the doped system the NMR-frequency practically vanishes [12]. As far as we understand this is the consequence of spin liquid type of magnetic structure. The frequency of NQR does not change drastically but slightly depends on the doping. The calculation of this dependence can elucidate the question of electronic structure.

x^2-y^2 band

It has been shown in the Ref. [3] that the contribution of x^2-y^2-hole to the NQR-frequency equals (all numerical values are presented for ^{65}Cu nucleus)

$$\frac{2}{7}b_{3\bar{d}}=89 \text{ MHz}. \tag{20}$$

With no doping this hole is at the Cu ion with the probability $1-4\alpha^2=0.835$ [3]. In the doped compound additional band holes arise (see Eq. (14)). The total contribution of $3d$-holes to the NQR-frequency equals

$$\frac{2}{7}b_{3\bar{d}}\{(1-\delta)(1-4\alpha^2)+\delta[2P(\bar{d}^2)+P(\bar{d})]\}=74 \text{ MHz}+\delta\cdot 32 \text{ MHz}. \tag{21}$$

Here δ is the concentration of additional holes per cell ($\delta=1$ corresponds to one additional hole in every cell). The contribution of oxygen electrons to the NQR-frequency is of the form [3]:

$$\frac{8}{5}b_{4p}\{\beta_\sigma^2(2p,4p)+\beta_\sigma^2(2s,4p)-\beta_\pi^2(2p,4p)-$$
$$-\tilde{\beta}_\sigma^2(2p,4p)-\tilde{\beta}_\sigma^2(2s,4p)+\tilde{\beta}_\sigma^2(2p,4p)\}=-42 \text{ MHz}. \tag{22}$$

Here $b_{4p}=-65$ MHz is the quadrupole constant of Cu $4p$-electron and β_i are the decomposition coefficients of oxygen wave functions in terms of copper wave functions. The details of calculations and numerical values of β_i are presented in Ref. [3]. Due to the doping the holes at $2p_\sigma$-state of oxygen arise. The corresponding contribution to the NQR-frequency equals

$$-\frac{2}{3}\delta P(\bar{d})\, b_{4p}\, \beta_\sigma^2(2p, 4p) = \delta \cdot 8 \text{ MHz}. \tag{23}$$

The NQR-frequency is the sum of contributions (21) — (23). Thus we obtain for x^2-y^2 band

$$\frac{d\nu}{d\delta} = 40 \text{ MHz}. \tag{24}$$

z^2 band

Simple calculation shows that the contribution of localized z^2-hole is just opposite to that of x^2-y^2-hole. Therefore using the Eqs (17), (21) we obtain for the case when doping leads to the z^2 band holes

$$\frac{d\nu}{d\delta} = \frac{2}{7} b_{3\bar{d}} \{-(1-4\alpha^2) + |P(\bar{x}^2-\bar{y}^2) - P(\bar{z}^2)|\} -$$

$$-\frac{2}{5} P(\bar{d})\, b_{4p}\, \beta_\sigma^2(2p, 4p) = -87 \text{ MHz}. \tag{25}$$

xy band

The calculation similar to that for x^2-y^2 bands gives

$$\frac{d\nu}{d\delta} = \frac{2}{7} b_{3\bar{d}} \{-(1-4\alpha^2) + |2P(\bar{d}^2) + P(\bar{d})|\} -$$

$$-\frac{2}{5} b_{4\bar{p}} \{P(xy)\, \beta_\sigma^2(2p, 4p) - P(\bar{x}^2-\bar{y}^2)\, \beta_\pi^2(2p, 4p)\} = 59 \text{ MHz}. \tag{26}$$

Now we can compare our calculations with experiment. The dependence of NQR-frequency on x for $La_{2-x}Sr_xCuO_4$ was observed in Ref. [12]. The measurements have been done for $0.12<x<0.4$. For small x certainly $\delta=x$. Therefore from Eq. (24) for x^2-y^2 band we get

$$\nu(x=0.12) - \nu(x=0.\ ) = 5 \text{ MHz}. \tag{27}$$

This value agrees very well with experimental one [12, 13]. However at $x>0.12$ the experimental slope is smaller [12]:

$$\frac{d\nu}{dx} \simeq 10 \text{ MHz}. \tag{28}$$

We can try to explain this fact following the statement by Shafer et al. [14] that for $x>0.1\div0.15$ the concentration of the holes in CuO_2 plane δ very slowly increases with x. From experimental data [12] and our calculations we estimate the maximal concentration of the holes in CuO_2 plane: $\delta_{max} \simeq 0.15\div0.2$.

There is no hint in the experimental data for the crossing of z^2 band by Fermi level. This crossing would be evident in x-dependence of NQR-frequency due to large negative derivative for z^2 band (see Eq. 25)). However according to our calculation Fermi level should be close to the bottom of z^2 band (see Fig. 2). It could give another explanation of small derivative (28).There is strong mixing of z^2 and x^2-y^2 band near crossing point. If the Fermi level is very close to the crossing point the negative contribution of z^2 band admixture decreases the derivative (24). But in this case we would not have linear dependence of NQR-frequency on x. Therefore the first explanation seems more reasonable.

Of course one can say that we use incomplete basis set ($3d$ copper and $2p$ oxygen orbitals refined near copper ion) and overestimate the density of holes on copper which leads to strong x-dependence of NQR-frequency. However, this basis set allows us to get correct value of NQRand NMR-frequencies without doping. It is the very sensitive test of hole density. Another good test is a frequency gap between $x=0.12$ and $x=0$.

It is not excluded also that close to x^2-y^2 band there is oxygen p_π band (see (19)). In this band $d\nu/d\delta$ is very small (~-2 MHz). If x^2-y^2 band and p_π band are populated simultaneously for $x>0.12$, we get $d\nu/dx=17$ MHz. It is not too far from experimental value (28).

Regretably we do not know the detailed data for the dependence of plane Cu NQR-frequency on x in other high-T_c superconductors. It would be very interesting to compare this dependence with the formulae (24), (25).

SPIN SINGLET BEHAVIOUR FOR x^2-y^2 BAND AND SPIN 1/2 FOR z^2 BAND

In the above calculation we have used the model of ferromagnetic background. This model allows us to calculate the position of the bands, effective masses, distribution of the hole between the oxygen and copper. To discuss the spin structure of the system one needs the model which includes the spin degrees of freedom of the background. At the same time we can simplify the band problem considering the hole near the bottom of the band. Let us divide the CuO_2-plane into the overlapping cells containing one copper ion and four oxygen ions (see Fig. 3). According to our calculation the motion of the hole in x^2-y^2 band looks like a motion of spin singlet via the lattice of cells. This conclusion agrees with the result by Zhang and Rice [5]. Their arguments were based on large AF superexchange interaction between O- and Cu-holes.

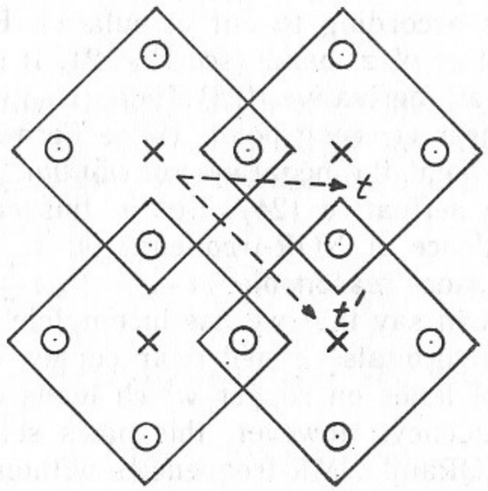

Fig. 3. CuO_2 plane split into the effective elementary cells. The cross corresponds to the Cu ion and the circle corresponds to the oxygen. The effective intercell transfer integrals t, t' are pointed out.

To confirm this statement let us expand the wave function of a cell in the states with definite spin. According to Eqs (9), (13) at the bottom of the band (k_x, $k_x=\pm\pi/a$) the cell wave function is of the form

$$\psi_{cell}=\alpha\{\sqrt{1-4\xi^2}\,a_\uparrow a_\downarrow-\xi(b_{2\uparrow}-b_{3\uparrow}-b_{4\uparrow}+b_{5\uparrow})\,a_\downarrow\}$$

$$+\beta a_\uparrow(b_{2\downarrow}-b_{3\downarrow}-b_{4\downarrow}+b_{5\downarrow})+\sum_{\substack{i\neq j=\\2,3,4,5}}\Phi_{ij}\,b_{i\uparrow}\,b_{j\downarrow}. \qquad (29)$$

We take into account that at k_x, $k_y=\pm\pi/a$ $\gamma=-\beta$. This wave function is not normalized due to overlapping of the cells (see Fig. 3). Using the values (14) we find $\langle\psi_{cell}|\psi_{cell}\rangle=1.48$. It is easy to verify that $\Phi_{ij}=\Phi_{ji}$ and therefore $\bar{p}\bar{p}$ as well as $\bar{d}\bar{d}$ does not contribute to $|S=1\rangle$ component. Using values (14) we get

$$\frac{\psi_{cell}}{\sqrt{\langle\psi_{cell}|\psi_{cell}\rangle}}=0.94\,|S=0\rangle+0.33\,|S=1,S_z=0\rangle. \qquad (30)$$

Thus the weight of $|S=1\rangle$ in ψ_{cell} is small $(0.33)^2=11\%$), and this confirms the picture of scalar quasi-particle (spin singlet).

It is easy to understand the origin if $S=1$ component in (29), (30). It appears due to ferromagnetic background which suppresses the motion of the spin up hole. The admixture of $S=1$ component is proportional to the asymmetry of spin up and spin down amplitudes. In symmetrical case $\beta=-\alpha\xi$ there is only $S=0$ component in (29), (30).

Using the Eqs (9), (13), (14) one can easy calculate the average spin of Cu $3d$-hole and O $2p_\sigma$-hole in x^2-y^2 band

$$\langle\sigma_z\rangle_{3d}=|\beta|^2+|\gamma|^2-4\alpha^2\xi^2=0.314,$$

$$\langle\sigma_z\rangle_{2p}=2\alpha^2\xi^2-\frac{1}{2}(|\beta|^2+|\gamma|^2)=-\frac{1}{2}\langle\sigma_z\rangle_{3d}=-0.157. \qquad (31)$$

Emery and Reiter solved the model for hole motion in ferromagnetic background [11]. Similar to (31) they got the $\langle\sigma_z\rangle_{2p}\neq0$ and basing on this fact they argued against the picture of spin singlet. We do not agree with their conclusion. It is true that $\langle\sigma_z\rangle_{2p}\neq0$ means that there is admixture of $S=1$ component to singlet. But for singlet picture it is only necessary that this admixture is small (and it is $\sim11\%$). Moreover it can not exactly vanish in ferromagnetic background. Let us consider simple model elucidating this statement. Let $\vec{s}$ be the spins of the particle localized at linear lattice and $\vec{j}$ be the spin of the particle which can hop between the nearest points of the lattice with the transfer integral t ($s=j=1/2$). The exchange interaction between the localized and delocalized particle is large

$$H=J\,\vec{s}_n\vec{j}, \quad J>0, \quad J\gg t, \qquad (32)$$

and therefore we have hopping of spin singlet.

$$\psi_k = \frac{1}{\sqrt{N}} \sum_n |S=0\rangle_n \exp(i\,kr_n)\,. \tag{33}$$

One can easy verify that the transfer integral for singlet in ferromagnetic background equals $t/2$. Hence the dispersion is

$$\varepsilon_k = -\frac{3}{4}J + t\cos ka\,. \tag{34}$$

The band with $S=1$ lies higher $(\Delta E = J)$

$$\psi_k = \frac{1}{\sqrt{N}} \sum_n |S=1\rangle_n \exp(i\,kr_n)\,. \tag{35}$$

Due to hopping the bands are mixed. The lower band $S=0$ gets admixture of higher band $S=1$:

$$\psi_k = \frac{1}{\sqrt{N}} \sum_n \Big\{ |S=0\rangle_n + \\ + \frac{t}{J}\cos ka\,|S=1, S_z=0\rangle - \frac{t}{J}|S=1,\ S_z=1\rangle \Big\} \exp(i\,kr_n)\,,$$

$$|S=0\rangle_n = \frac{1}{\sqrt{2}}(b^+_{n\uparrow}a^+_{n\downarrow} - b^+_{n\downarrow}a^+_{n\uparrow})\,a_{n\uparrow}\,|\psi_0\rangle,$$

$$|S=1, S_z=0\rangle_n = \frac{1}{\sqrt{2}}(b^+_{n\uparrow}a^+_{n\downarrow} + b^+_{n\downarrow}a^+_{n\uparrow})\,a_{n\uparrow}\,|\psi_0\rangle, \tag{36}$$

$$|S=1, S_z=1\rangle_n = \frac{1}{\sqrt{2}}b^+_{n\uparrow}(e^{-i\,ka}a^+_{n-1\downarrow}\,a_{n-1\uparrow} + e^{i\,ka}a^+_{n+1\downarrow}\,a_{n+1\uparrow})\,,$$

$$|\psi_0\rangle = \prod_m a^+_{m\uparrow}\,|0\rangle.$$

However it is still a singlet in the sense of number of states.

In the case of x^2-y^2 band this high $S=1$ band is oxygen band. And we really can calculate its admixture by perturbation theory if we start from $S=0$ state ($\beta = -\alpha\xi$ in Eq. (29)). Thus spin dynamics is described mostly by spin singlet motion and the mixing with $S=1$ band slightly perturbed spin structure only. Note that in our variational wave function for x^2-y^2 band state $|S=1, S_z=1\rangle$ is absent (see Eq. (36)). It is possible to take it into account by means of perturbation theory but its admixture is small.

Let us discuss briefly z^2 band. This case is not so complicated. The interaction of moving hole spin with magnetic background is not very large here (exchange interaction between moving and localized hole is 0.7 eV and it is suppressed few times by higher order correlations — see above). In any case it can be taken into account by means of perturbation theory. Therefore we can consider the hole in z^2 band as a usual spin 1/2 quasi-particle.

THE EFFECTIVE INTERCELL TRANSFER INTEGRALS

For the model description we consider the overlapping cells presented at Fig. 3 as elementary units. To calculate magnetic structure and its influence on charge motion we need the transfer integrals between these units. Let t be the nearest neighbour transfer integral and t' be diagonal transfer integral (see Fig. 3). Then the model hole dispersion in the ferromagnetic background is of the form

$$E = E_0 + 2t(\cos k_x a + \cos k_y a) + 4t'\cos k_x a \cos k_y a \simeq \\ \simeq E_0 - 4t + 4t' + (\delta k_x^2 + \delta k_y^2)(t - 2t')\,. \tag{37}$$

The lower line in Eq. (37) is the expansion near the bottom $(k_x\ k_y = \pm\pi/a)$. We would like to stress that the description in terms of elementary units and effective transfer integrals is valid only at $\delta ka \leqslant 1$ where the internal degrees of freedom of the unit are not important (i. e. coefficients of expansion in basis states for the internal state of the cell do not change essentially). This is just the region of physical interest. The value $(t-2t')$ is found from the value of effective mass (14), (17), (18). We can estimate t and t' separately. The nondiagonal hopping t' is mainly due to oxygen-oxygen hopping t_{pp} (see Fig. 3), i. e. t' is proportional to t_{pp}. In the same time t is roughly independent of t_{pp} (since internal state of cell very slightly depend on t_{pp}). Using this arguments and calculations of effective mass for different t_{pp} we have obtained:

$$x^2-y^2 \text{ band}: t = 0.18 \text{ eV}, \quad t' = -0.06 \text{ eV};$$
$$z^2 \text{ band}: t = 0.10 \text{ eV}, \quad t' = -0.025 \text{ eV}. \tag{38}$$

For spin singlet (x^2-y^2 band) t, t' have been calculated in Ref. [15] using cluster approach. Our estimate (38) is about two times smaller.

CONCLUSION

In the present paper we have calculated the band structure of hole doped CuO_2 plane. It is shown that x^2-y^2 band is the lowest and z^2 band is very close to it.

We have calculated the dependence of the frequency of Cu nuclear quadrupole resonance on the holes concentration. Comparison with experimental data for $La_{2-x}Sr_xCuO_4$ supports the statement that doping leads to holes in the x^2-y^2 band. We do not know such a detailed data for $YBa_2Cu_3O_{6.5+x}$. It would be very interesting to measure it.

Concerning the x^2-y^2 band spin dynamics we confirmed the spin singlet picture suggested in Ref. [5]. Small admixture of $S=1$ state to $S=0$ state of quasi-particle is not very essential. The one-hole dynamics is nearly the same as in single-band Hubbard model in the large-U limit. This quasi-particle is like a holon [16]. The doping leads to the melting of antiferromagnetic order and formation of droplets of spin liquid (RVB) [17].

As far as hole-hole interaction is concerned the essential difference from Hubbard model dynamics could appear due to close z^2 band. There is the possibility of virtual hopping to z^2 band due to hole-hole interaction. It is not excluded also that z^2 band is populated in the case of large doping. One can speculate that the variation of T_c from 60 K to 90 K is due to z^2 band.

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