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Single Hole Dynamics in the CuO_2 Plane at Half Filling

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We present a **k**-dependent study of the single hole states in $Sr_2CuO_2Cl_2$. We demonstrate that the controversial "1 eV peaks" in the high T_c's are quasiparticles derived from the same O $2p$ states as the Zhang-Rice (ZR) singlets, but of different symmetry and intensity in those regions of the Brillouin zone where the hybridization with the correlated Cu $3d$ states vanishes by symmetry. We use this new source of information to estimate the quasiparticle weight of the ZR singlets, discuss the quasiparticle line shape, and suggest a strong **k** dependence of the self-energy. [S0031-9007(96)02271-5]

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The spectral properties and propagation of a single hole in a strongly correlated antiferromagnetically ordered quasi-two-dimensional lattice have been the topic of much debate, mainly because this problem is believed by many to be at the heart of a basic understanding of high-T_c superconductors. One of the most direct ways of obtaining information on this is photoelectron spectroscopy (PES) of the insulating materials, since PES does exactly that, namely create one hole. Wells *et al.* [1] have recently done a pioneering study of the lowest energy electron removal states in $Sr_2CuO_2Cl_2$, in which the CuO_2 planes are very similar [2] to those in the high-T_c superconductors. The results of this study have raised as many questions as they have answered. The states closest to the chemical potential, which are widely believed to be Zhang-Rice (ZR) singlets [3], exhibit a very wide energy distribution, which is quite strongly angle (momentum) dependent as far as the intensity, the shape, and the energy are concerned. Qualitatively, the behavior resembles that predicted by the *t-J* model, but there are also strong differences. One example is the very strong momentum ($\mathbf{k}$) dependence of the spectral weight of the ZR singlet going from $(0,0)$ to $(1,1)$, mapped in the CuO_2 Brillouin zone (BZ) in units of π/a. The asymmetry of the intensity around the highest intensity point $(1/2,1/2)$, is not consistent with the *t-J* model, although the more general Hubbard model gives results closer to experimental findings [4]. Also, the dispersion along $(0,0)$ to $(1,0)$ is a problem since experiment finds little, if any, dispersion contradictory to the simple *t-J* model. In recent studies [5] it has been shown that this can be improved by including longer range hopping integrals. In the optimally doped high T_c's, however, the dispersion along $(0,0)$ to $(1,0)$ is very strong, except for a region around $(1,0)$, exhibiting the much discussed extended van Hove singularity at energies close to the Fermi energy [6]. To explain all this within the same model, one would have to invoke very strongly doping-dependent parameters or invent a model with very strong doping- and **k**-dependent quasiparticle shapes.

For comparison with the photoemission spectral distribution of strongly correlated states, it is interesting to look for other oxygen $2p$ derived states, which have little or no communication with the Cu $3d_{x^2-y^2}$ states. The spectral function in angular resolved ultraviolet photoemission spectroscopy (ARUPS) is related to the one-electron Green's function which for strongly correlated systems may be thought of as consisting of two parts, namely, a rather broad so-called incoherent part and a peaky coherent quasiparticle part. For states in which correlation effects dominate, most of the total intensity will reside in the structureless incoherent part and little in the peaky quasiparticle part, in contrast to states which are one-electron-like and have most of the intensity in the peaky part. The intensity in the peaky part is a direct measure of the single-electron character of the quasiparticle. In this Letter we confirm this picture and contrast the ZR singlet behavior with that of higher energy features composed of different combinations of the same O $2p$ orbitals, which do not hybridize with the strongly correlated d states at certain high symmetry points in the BZ. These states at these special **k** vectors have all of their intensity in the peaky part and that also explains their very high intensity. We give strong evidence that the so-called "1 eV peaks" observed in the high T_c's have this characteristic. We will use them to estimate the quasiparticle weight of the ZR singlets, to suggest a strong **k** dependence of the self-energy, and to imply the importance of other degrees of freedom than spin fluctuations on the quasiparticle line shape.

Our ARUPS experiments on $Sr_2CuO_2Cl_2$ are performed in a mu-metal chamber with a Vacuum Generators hemispherical electron analyzer installed on a two-axis goniometer. The analyzer acceptance angle was 2° and the energy resolution 30 meV. The ultimate aperture and resolution are 0.5° and 14 meV. The crystals were grown by means of the floating zone technique, using an elliptical furnace [7]. The samples were cleaved *in situ* and measured at a base pressure of 1×10^{-10} mbar. After the ARUPS measurements the surfaces were checked by using low energy electron diffraction (LEED).

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Figure 1 displays a small portion of the spectra taken at 300 K along the high symmetry directions of the two-dimensional Brillouin zone, with the in-plane component of the Poynting vector of the ultraviolet radiation within a few degrees along the $(1,1)$ direction. Aside from the ZR singletlike structure visible in a magnified view close to $(1/2,1/2)$, we see very intense features above 2 eV binding energy with strongly **k**-dependent intensities and energies. A similar intense and sharp peak, called the "1 eV peak," exhibiting a comparable **k**-dependent intensity has been observed by Tobin *et al.* [8] at the $\bar{X}$-point on untwinned $YBa_2Cu_3O_{6.9}$. Olson and coworkers [9] have seen similar features at the high symmetry points in a wide range of high T_c's and related compounds, which limits the origin to an intrinsic property of the electronic structure of the CuO_2 plane. In our spectra a second peak is observed at higher binding energy in other regions of the BZ. From incident angle dependent normal emission studies we found that in grazing excited spectra the 3.96 eV feature is more pronounced relative to the 2.85 eV feature, suggesting that the 3.96 eV feature at $(0,0)$ originates from orbitals with an out-of-plane character. In the low energy region of the spectra we see the ZR singlet state with an appreciable intensity in those regions of the BZ where the higher energy features are weak. The energy dispersion and intensity variation of this state are close to that reported by Wells *et al.* [1] at a somewhat higher temperature (350 K).

Figure 1(b) shows that the behavior along $(0,0)$ to $(1,0)$ is quite different from the $(0,0)$-$(1,1)$ direction. The most pronounced peak is present around 4 eV and has a dispersion of 250 meV going along $(0,0)$ to $(1,0)$. The peak at 2.85 eV contributes near $(0,0)$ as in panel (a). The low energy quasiparticle as observed halfway in the $(1,1)$ direction does not develop to a peak along $(0,0)$ to $(1,0)$. From the data it becomes clear that the higher energy peaks are intense and sharp only at the high symmetry points, and their quasiparticle weight strongly reduces when moving away from these points.

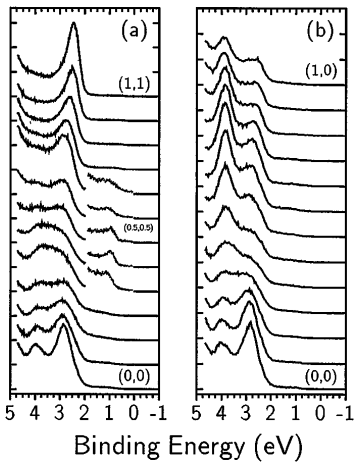

FIG. 1. ARUPS spectra of $Sr_2CuO_2Cl_2$. (a) The spectra from $(0,0)$ to $(1,1)$ in equidistant parallel momentum steps. Near $(1/2,1/2)$ the ZR singlet region is multiplied by a factor of 5. (b) The spectra from $(0,0)$ to $(1,0)$.

This leads us to propose that the intense features seen above 2 eV binding energy originate from the same O $2p$ orbitals as those contributing to the ZR singlets. Whereas the O $2p$ orbitals in the ZR singlet are combined to hybridize maximally with the Cu $3d$ orbitals, it is also possible to form linear combinations of O $2p$ orbitals which do not mix with the Cu $3d$ orbitals at all. A photoelectron hole created in such a specific O $2p$ state therefore does not communicate with the Cu spin system and will have all its spectral weight concentrated in the quasiparticle peak. The most important justification of this interpretation is the intensity variation with **k**, namely, a very high intensity at high symmetry points of the BZ, where the mixing with $d_{x^2-y^2}$ is zero, and a strong decrease in intensity in the quasiparticle peaks as one moves away from these regions. The experimental fact, that the "1 eV peaks" are so intense at certain high symmetry points, points to states which are not or only weakly coupled to the strongly correlated Cu $3d$ states. To identify such nonmixing oxygen states, we performed tight binding band calculations for the CuO_2 plane using a basis of five Cu $3d$ and three O $2p$ orbitals. Although the one-electron-like tight binding framework is not suitable for quantitatively describing this correlated system, it is suitable to identify those O $2p$ derived states which have little or no communication with the strongly correlated Cu $3d$ states due to symmetry. The results of the tight binding band calculation are given in the lower part of

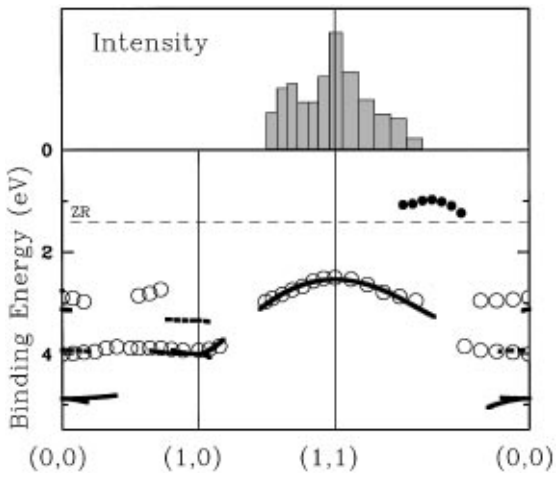

FIG. 2. Comparison of tight binding calculation with experiment. Thick solid and dashed lines show the O $2p$ derived band dispersion limited to those regions of the BZ where they have less than 5% Cu $3d$ character. Open circles represent the experimental data in regions with appreciable intensity for the higher energy features, solid points for the lower energy ZR singlet feature. A theoretical estimate for the binding energy of the ZR singlet relative to the oxygen bands is indicated by a thin dashed line. The peaked intensity of the oxygen band at $(1,1)$ is indicated in the top part of the figure.

Fig. 2. We show only those portions of the calculated bands which have less than 5% Cu $3d$ character. The bands with an in-plane character are marked with solid lines, while the out-of-plane character bands are indicated with dashed lines. Also shown are the experimentally observed peak positions of well defined peaks. We have found that the strong dispersive peak at 2.45 eV near $(1, 1)$ is very well described by one of the portions of the 5% electron bands. This in-plane O $2p\pi$ derived band at the $(1, 1)$ point of the BZ has zero Cu $3d$ character by symmetry, and its Cu d character only increases as $|\Delta k|^2$ on moving away from this point. The strongly peaked intensity of this state at $(1, 1)$ is indicated in the upper part of the figure. The large reduction in intensity, with only a small increase of mixing, stresses the importance of correlation effects. The symmetry of this band at $(1, 1)$, the other lowest energy nonmixed in-plane bands and the Zhang-Rice singlet are shown in Fig. 3. From this it is obvious why these oxygen bands do not mix with Cu $3d$ states. The characters of the bands as found by our calculations are consistent with the incoming angle dependence found at $(0, 0)$ and $(1, 1)$ in our experiments. From our data set we selected the regions in the BZ in which each of the features has its highest intensity, as is shown in the center of Fig. 3. Region ZR of the Zhang-Rice singlet derived feature demonstrates that this is a part of the BZ where all other features are weak. Note its asymmetry around $(1/2, 1/2)$. A theoretical first order estimate [10] of the binding energy of the strongly hybridized ZR singlet feature relative to the oxygen bands is indicated by a horizontal dashed line in Fig. 2.

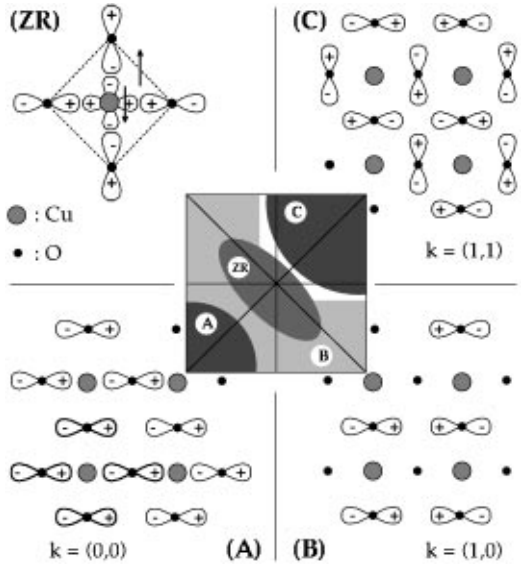

FIG. 3. Symmetry of the lowest energy in-plane O $2p$ derived electron bands at the indicated high symmetry points and the symmetry of the Zhang-Rice singlet. The center part is a gray scale plot indicating the regions of the BZ in which the various features have appreciable intensity. Region B shows where we have found a feature near 4 eV, regions A and C show the strong dispersive peaks near 2.45 and 2.85 eV, respectively. Region ZR shows that the ZR singlet is observed in a region hardly covered by the higher energy quasiparticles.

By fitting the tight binding calculation to the experimentally determined dispersion relations close to the high symmetry points, we could obtain an accurate value for the O $2p$ hopping integral (t_{pp}), an important microscopic parameter in various theories. According to the tight binding model the energy difference between the in-plane bands at $(1, 0)$ and $(1, 1)$ is equal to $4t_{pp}$. The dispersion near $(1, 1)$ and the energy difference between the minima at $(0, 0)$ and $(1, 1)$ are also determined by t_{pp} only. The fact that these relations are fulfilled by a single t_{pp} value strongly supports the credibility of our interpretation. The value obtained here, $t_{pp} = -0.37$ eV, is close to those found previously [10,11].

We can now make use of the fact that both the higher energy structures, which do not hybridize with the d bands, and the lowest energy feature originate from the same O $2p$ states to establish an internal calibration for the quasiparticle weight. If our interpretation is correct, the spectral distribution of the high energy feature will be entirely concentrated in the quasiparticle part ($Z_k = 1$) at those points in the BZ where the hybridization with d bands vanishes. We can thus compare this spectral distribution with that of the ZR singlet quasiparticle part to get an experimental value for the quasiparticle weight of the Zhang-Rice singlet. In Fig. 4 we show the "1 eV" feature at $(1, 1)$, together with the ZR singlet feature at $(1/2, 1/2)$, shifted by 1.54 eV for two different temperatures. Both features appear at the top of their respective bands and therefore cannot easily decay via electron-hole channels. Because the coherent and incoherent part of the features are inseparable [12], as they both are part of the one-particle Green's function, we did not perform a step subtracted peak fitting. As the widths of the peaks are comparable, we decided to rescale the spectra in intensity and not in weight. To obtain the same intensity, the ZR singlet part had to be multiplied by 34 for the

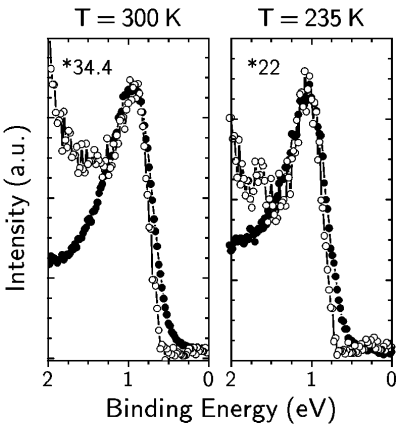

FIG. 4. Direct comparison of ZR singlet (∘) and "1 eV peak" (•) taken at $(1/2, 1/2)$, $(1, 1)$, respectively, at two different temperatures.

spectra taken at 300 K, and 22 at 235 K. To compare this with the quasiparticle weight as found by the t-J model at $(1/2, 1/2)$, $Z_k = 0.175$, for $t/J = 3.3$ [13], we must first correct for the larger number of channels available for ionizing the higher energy hole (i.e., both singlets and triplets may be reached), which results in an extra factor of 2. The fact that the hole created in any given plaquette has a 50% chance to form a singlet with the Cu hole of a neighboring plaquette results in another factor of 2. The t-J model prediction would then result in an intensity ratio of $4/0.175 \approx 23$. The close agreement with experiment is probably fortuitous. Another interesting aspect is that the widths and line shapes of both features are comparable. As the nonmixed oxygen feature has no communication with the spin carrying Cu $3d$ orbitals, its width indicates strong contributions from other mechanisms than those involving spin fluctuations, such as phonons, which then suggests that the large width at the top of the ZR singlet band is also due to this other mechanism.

If we adopt the explanation of the "1 eV peaks" as being the fingerprints of isolated regions of otherwise mixed electron bands, this will lead to a reconsideration of a generally used assumption. This observation of strong **k** dependence of the character of electron bands, in this case the oxygen bands, claims the necessity of including both ω and **k** dependence of the self-energy in theoretical models. The generally accepted assumption of a local or **k**-independent self-energy is proven by our data to be nontrivial. Although a **k**-independent self-energy may be a reasonable starting point in a single band system of strongly correlated states, we are dealing with a multiband system here. If we attempt to reduce it to a single band system, we will have to use strongly **k**-dependent wave functions, because the hybridizations are so strongly **k** dependent. This is obviously demonstrated in the study presented here. Such a strong **k** dependence of the effective wave functions will manifest itself in the necessity of strong **k**-dependent self-energies, if we insist on an effective single band approach as in the t-J or Hubbard-like approaches to the high T_c's.

In conclusion, we have presented experimental and theoretical arguments on the interpretation of strong features seen in photoemission at particular regions in **k** space in high T_c's and related compounds as O $2p$ derived states which, because of symmetry, have little or no hybridization with the strongly correlated Cu $3d$ states. We showed that the intensity at the special points in the BZ can be used to obtain an experimental estimate of the quasiparticle weight of the ZR singlet, and found reasonable agreement with a t-J model prediction at $(1/2, 1/2)$. The comparable and large widths of the two features point to the importance of other degrees of freedom than spin fluctuations on the quasiparticle line shape. We then used the strong **k**-dependent shape and intensity of the structures to argue that, if we would want to resort to a single band model, we would be required to have a strong **k**-dependent self-energy because the actual wave function is so strongly **k** dependent in such a model. So we are left with a choice between the lesser of two evils: single band models and **k**-dependent self-energies or multiband models for which the self-energies could possibly be **k** independent. Unfortunately, neither of the two is exactly solvable.

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