E versus k Relations and Many Body Effects in the Model Insulating Copper Oxide $Sr_2CuO_2Cl_2$

B. O. Wells,[1] Z.-X. Shen,[2] A. Matsuura,[2] D. M. King,[2] M. A. Kastner,[1] M. Greven,[1] and R. J. Birgeneau[1]

[1]*Physics Department, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

[2]*Applied Physics Department, Stanford University, Stanford, California 94305*

(Received 4 May 1994)

We report angle resolved photoemission measurements on $Sr_2CuO_2Cl_2$, an insulating layered copper oxide. We find that the overall width of the highest occupied band and the position of the band maximum at $(\pi/2, \pi/2)$ agree with predictions of the t-J model and other calculations based on the Hubbard model. However, in many regions of the Brillouin zone, the shape of the band differs from these predictions. A comparison of our data with spectra previously reported on metallic samples leads to new suggestions for the phenomenology of doping.

PACS numbers: 71.20.Cf, 74.72.Hs, 79.60.Bm

During the past several years there has been an extensive effort to understand the properties of the layered copper oxides. When undoped, with one hole per copper site, these materials are antiferromagnetic Mott insulators. When doped with sufficient carriers they are superconductors with very high transition temperatures. This behavior cannot be explained by one-electron band calculations which predict even the undoped compounds to be metals. It is generally accepted that the one-electron description breaks down in the insulators due to the large Coulomb repulsion U between the conduction electrons. These materials thus present two basic physics challenges. The first is to create a theory that describes the correlated insulator and the second is to understand what happens when the correlated insulator is doped with carriers. There are competing views as to the best description of the doped system in the normal state. One picture is that the normal state is a doped Mott insulator, for which correlations among the electrons are still centrally important. The opposite view is that a phase transition occurs with doping and a one-electron description is appropriate.

Many of the results from photoelectron spectroscopy (PES) have been interpreted as favoring a one-electron approach to the doped compounds. The heavily doped copper oxides appear to have large Fermi surfaces consistent with local density approximation (LDA) band calculations [1,2]. Some previous results apparently showed that the act of doping creates new states which lie in the gap of the insulator with the Fermi level in these new states [3], although this point has been controversial [4]. These results have been used to claim that the optimally doped superconductors exhibit fundamentally different physics from the insulators [5]. However, there is strong evidence from transport [6] and neutron scattering [7] that no sharp phase transition occurs. The evolution of the conductivity and magnetic correlation length appears to be continuous over dopant concentrations spanning the insulator to metal transition. In addition, the photoemission spectra of both doped and undoped materials show satellite peaks caused by the Coulomb interaction, an indication that correlations are important to the electronic structure for both materials [8]. Furthermore, the large Fermi surfaces determined from PES, which should shrink with doping, seem inconsistent with transport measurements that indicate the number of carriers grows linearly with doping.

Most of the PES experiments to date have been on the metals and there has been little work on the undoped compounds [9]. We report angle resolved photoemission results on $Sr_2CuO_2Cl_2$, a carrier free layered copper oxide. This is a measurement of the dispersion of a single hole in an antiferromagnetic background, a problem that has been heavily investigated theoretically. We find that the highest occupied band has a similar dispersion and position with respect to the rest of the valence spectrum as the band that crosses E_F in the metallic copper oxides. This is evidence that hole doping causes the Fermi level to drop into the insulator valence band, although doping apparently leads to significant changes in the shape of the band. The measured bandwidth is close to the value $W = 2.2J$ predicted by calculations based on the t-J model. However, the shape of this band is not well described by this model or any other of which we are aware. We find a sudden drop in the spectral weight of this band as a function of wave vector that reflects the antiferromagnetic periodicity. Combining the results for the bandwidth, band shape, and spectral weight variation we arrive at a complete description of the lowest energy quasiparticle spectrum which must be described by any model appropriate for the insulating copper oxides.

Single crystals of $Sr_2CuO_2Cl_2$ were grown following the procedure used by Miller *et al.* [10]. $Sr_2CuO_2Cl_2$ has the K_2NiF_4 structure with CuO_2 layers separated by double layers of SrCl. The material is tetragonal down to at least 10 K. Crystals grown by the identical method have a Néel temperature of 256.5 ± 1.5 K as determined by neutron scattering. Neutron scattering studies have shown that at the temperature of our experiment, 350 K, the magnetic correlation length is about 250 Å [11].

 0031-9007/95/74(6)/964(4)$06.00

Thus PES, a very fast local probe, should still see the effects of antiferromagnetic order. Two magnon Raman scattering measurements of Tokura *et al.* imply a nearest neighbor exchange $J = 125 \pm 6$ meV [11,12]. Doping $Sr_2CuO_2Cl_2$ with carriers has been difficult, giving us confidence that we are really studying undoped material. However, there has been a recent report of the synthesis of a closely analogous compound, $Sr_2CuO_2F_{2+\delta}$, which for large enough δ is a superconductor with $T_c = 46$ K [13].

Our experiment was performed at the undulator beam line 5 at the Stanford Synchrotron Radiation Laboratory. The spectra shown here were taken with an overall system energy resolution of 75 meV and angular resolution of the emitted electrons of $\pm 1°$, or $\pm(1/20)\pi$ in k_x and k_y. In this Letter we use the notation of the two-dimensional Brillouin zone for the square-planar copper oxygen sheet with a lattice parameter equal to one which has edges at $(\pm\pi, k_y)$ and $(k_x, \pm\pi)$ and corners at $(\pm\pi, \pm\pi)$. We deduced the peak position for each spectrum using a simple fit by a Lorentzian added to a background and convolved with the experimental resolution function. The data were taken at 350 K because at this temperature the conductivity was high enough to insure that there was no charging of the sample.

The full valence band spectrum of $Sr_2CuO_2Cl_2$ is very similar to the spectra for the metallic copper oxides [1,2]. The spectrum is approximately 7 eV wide with several intense peaks. There is a foot with small intensity extending over the highest eV of the valence band. All of the spectra presented in this Letter show only this foot region. Figure 1(a) shows a set of scans taken at different **k** positions along the direction from the zone center $(0,0)$ to (π,π). As **k** is increased, a peak appears and shifts towards higher energies as **k** approaches $(\pi/2, \pi/2)$. At larger **k** values there is a sudden drop in the intensity of the peak and it appears to move back to lower energies. The $(\pi/2, \pi/2)$ point is the global valence band maximum (VBM). The closest that the peak approaches to the Fermi energy is approximately -0.8 eV. We measure a total dispersion of 280 ± 60 meV. For parallel cuts, the peak intensity always drops at **k** locations forming a line connecting $(\pi, 0)$ and $(0, \pi)$.

Figure 1(b) shows similar data along the same direction in the square lattice Brillouin zone for the metallic copper oxide $Bi_2Sr_2CaCu_2O_{8+\delta}$ from Dessau *et al.* [2]. The peaks in the metal are sharper and disappear after crossing the Fermi level near $(0.45\pi, 0.45\pi)$. The spectra are quite similar and suggest that doping has moved the Fermi level into the valence band of the insulator. For comparison, the measured dispersion in $Bi_2Sr_2CaCu_2O_{8+\delta}$ is 270 ± 30 meV over a **k** range from $(0.27\pi, 0.27\pi)$ to $(0.45\pi, 0.45\pi)$. Over the same **k** region we see dispersion of 240 ± 30 meV in $Sr_2CuO_2Cl_2$, which is the same within the errors.

The peak intensity drops along a line connecting $(\pi, 0)$ to $(0, \pi)$, the boundary of the antiferromagnetic Brillouin zone. The weak part of the band results from a folding of the zone due to antiferromagnetic order. This drop in spectral weight is analogous to that expected for a weak coupling spin density wave model [14,15] and is also evident in Monte Carlo calculations of the spectral weight function for the Hubbard model at intermediate coupling strengths [15]. For strong coupling we expect that the original and folded sections of the band would have nearly equal weight. Thus the variation in spectral weight could indicate that $Sr_2CuO_2Cl_2$ is in an intermediate coupling regime.

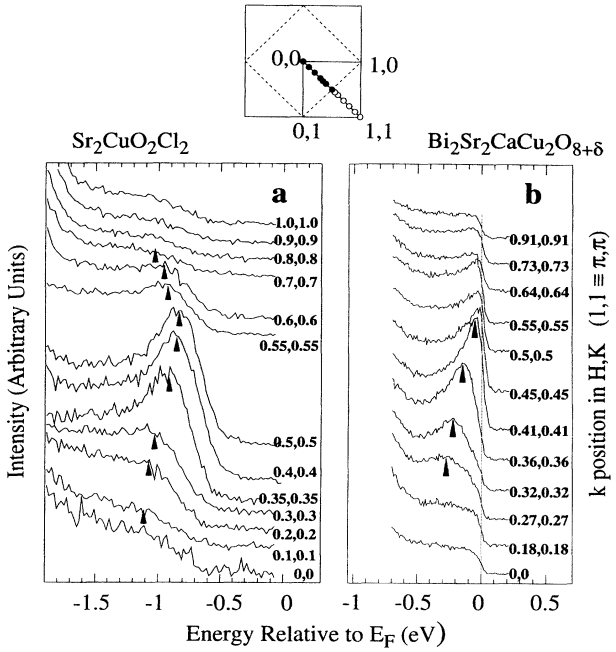

FIG. 1. PES data showing the peak dispersion along the $(0,0)$ to (π,π) direction for insulating $Sr_2CuO_2Cl_2$ (a) and for metallic $Bi_2Sr_2CaCu_2O_{8+\delta}$(b). The daggers beneath each spectrum are guides to the eye. The legend at the top has circles indicating the points in the two-dimensional Brillouin zone where the data were taken and is labeled with $(1,1) = (\pi,\pi)$. The dark circles in the legend are on the side of the zone where the peak is strong in the insulator and the open circles where the peak is weak. The size of the circles indicates the **k** resolution.

Figure 2(a) shows the data taken from $(0,0)$ to $(\pi,0)$. There is an overall intensity modulation along this direction but no evidence for band dispersion. We have attempted to determine if there might be a higher energy peak in this direction that is hidden by a weak optical matrix element. Experiments using different photon energies as well as turning the sample to change the light polarization direction gave data consistent with Fig. 2(a). Figure 2(b) shows the peak dispersion along a line from $(0, \pi)$ through $(\pi/2, \pi/2)$ to $(\pi, 0)$. From a maximum at $(\pi/2, \pi/2)$ the peak disperses to lower energy in either direction to a lowest energy near both $(\pi, 0)$ and $(0, \pi)$. Thus the lack of a dispersing peak in Fig. 2(a) indicates a band that remains

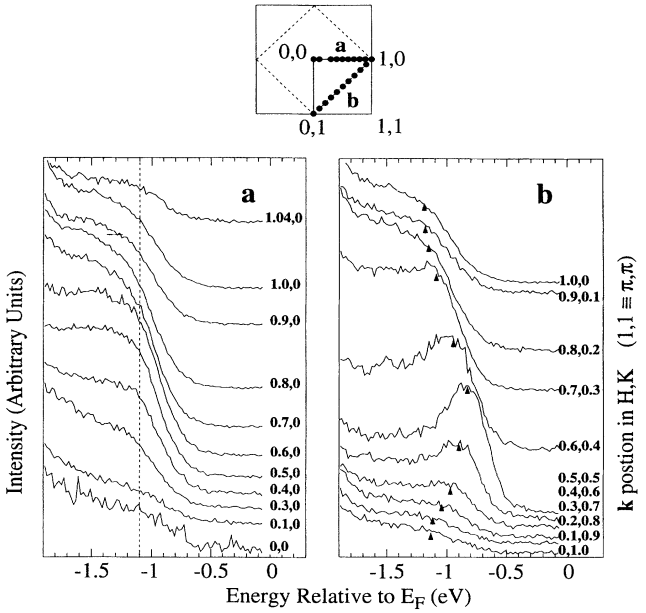

FIG. 2. PES data along the $(0,0)$ to $(\pi,0)$ direction in (a) and along $(0,\pi)$-$(\pi/2,\pi/2)$-$(\pi,0)$ in (b). The dashed line in (a) is the maximum energy for any peak in this direction. The legend is the same as in Fig. 1.

at least 1.1 eV below E_F, as indicated by the dashed line. This is in contrast to the hole doped copper oxides which have a flat band close to E_F in the vicinity of $(\pi,0)$, as is discussed further below.

In Fig. 3 the experimentally determined E vs $\mathbf{k}$ relation is compared with that found for a numerical solution of one hole in a t-J model [16]. For the region from $(0,0)$ to (π,π) the t-J model provides a good description of the experimental results. However, near $(\pi,0)$ the calculation does not describe the data and we see much greater dispersion from $(\pi,0)$ to $(0,\pi)$ than the calculation predicts. The bandwidth (W) determined by fitting the peaks over the entire region from $(0,0)$ to $(\pi/2,\pi/2)$ is 280 ± 60 meV. The t-J model calculation that gives the curve in Fig. 3 predicts the quasiparticle bandwidth to be $2.2J$ for a wide range of t/J [16]. There are other t-J model calculations that give a comparable bandwidth [17]. Calculations on small clusters of the Hubbard model with intermediate U show a similarly narrow quasiparticle bandwidth [18]. We find $W/J = 2.2 \pm 0.5$, with $J = 125 \pm 6$ meV for $Sr_2CuO_2Cl_2$ [11,12]. This is in contrast to the prediction of one-electron calculations which find a total occupied bandwidth of about 1 eV at half filling, and a total bandwidth of about 3.25 eV [19]. As stated above, the doped samples show similar dispersion to $Sr_2CuO_2Cl_2$, although we cannot be certain of the location of the band maximum in the metals. Still, even for the metals, the LDA calculations predict a bandwidth much too large.

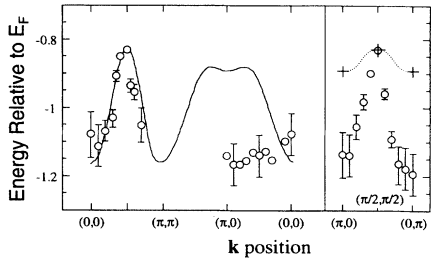

FIG. 3. A comparison of the experimentally determined E vs $\mathbf{k}$ relation (circles) with a calculation for the t-J model [15]. All error bars are shown when larger than the symbol size except for the region from $(0,0)$ to $(\pi,0)$, where for clarity only some representative error bars are shown. The far right panel shows the direction along the antiferromagnetic zone edge from $(0,\pi)$ to $(\pi,0)$. Here only the points marked by a + are calculated in Ref. [16] and the dotted line is our interpolation between these points.

Our results lead us to speculate about the evolution of the electronic structure with doping. A rigid band doping model would account for the evolution of the data seen from $(0,0)$ to (π,π), but is not sufficient to account for the changes near $(\pi,0)$. The overall shape of the band in $Sr_2CuO_2Cl_2$ is that of a peak centered at $(\pi/2,\pi/2)$. The effective mass we find at the top of the band is isotropic and equal to 1.5 ± 0.75, consistent with transport and optical measurements [6]. Current models for the insulating state predict that this band should form a ridge extended in the direction from $(\pi,0)$ to $(0,\pi)$. The photoemission data from the metals are consistent with such a ridge, since the metallic compounds show a band near E_F over a wide region of $\mathbf{k}$ space near $(\pi,0)$. This has been described as an extended saddle point and there has been speculation that it is important to the physics of the superconductors [2,20]. There are no states near the top of the band in $Sr_2CuO_2Cl_2$ at $(\pi,0)$. The states forming the extended saddle point must be created or move up in energy as a result of doping. Such states strongly affect the shape of the Fermi surface, since they serve to pin E_F near the top of this band at the high doping levels of the superconductors. Nevertheless, there is a strong correspondence between the highest occupied band in $Sr_2CuO_2Cl_2$ and the band crossing E_F in the metallic copper oxides. It appears that while no new band is created by doping, the highest energy band is greatly modified.

If the spectral weight variation that we observe in $Sr_2CuO_2Cl_2$ is still present in the metallic copper oxides, then this would affect the measured Fermi surfaces. Lowering the Fermi level into the top of the valence band should produce a small hole pocket Fermi surface centered at $(\pi/2,\pi/2)$. However, photoemission would not easily detect the band dispersing back down below E_F from $(\pi/2,\pi/2)$ to (π,π). We expect that for very low doping levels the copper oxides must have small pocket Fermi surfaces. The picture may be more complicated

for the heavily doped samples used in most previous PES experiments. The pockets may merge together to form large Fermi surfaces and the low spectral weight band Fermi surface sections may be too faint to detect. Nevertheless, we do not expect the carrier concentration to decrease with hole doping as we would for a large one-electron Fermi surface with rigid band doping.

There are other recent experiments which our data may help explain. Liu *et al.* reported PES data on insulating, but not carrier free, $YBa_2Cu_3O_{6.35}$ [9]. They did not see any well-defined peaks but a strong shoulder that appeared to disperse along the $(0,0)$ to (π,π) direction, reach a maximum at E_F near $(\pi/2,\pi/2)$, and then disappear. This was interpreted as a Fermi level crossing. Since they saw an apparent band at E_F only near $(\pi/2,\pi/2)$, they interpreted this as evidence for a small pocket Fermi surface even though they did not see the peak reappear at the other side of the pocket. Although no well-defined peak was detected, the $YBa_2Cu_3O_{6.35}$ data are consistent with our results. The variation in spectral weight makes it impossible to detect a peak for $\mathbf{k}$ greater than $(\pi/2,\pi/2)$, thus they would not see the peak reappear. However, without well-defined peaks, this spectral weight drop makes it difficult to distinguish between a small pocket Fermi surface and a model where the small density of holes serves to pin the Fermi level near the VBM. The major change needed to evolve from these data to the large Fermi surfaces apparently seen in the metallic copper oxides is an evolution of the flat band states near $(\pi,0)$.

Aebi *et al.* have recently reported a mapping of the Fermi surface in $Bi_2Sr_2CaCu_2O_{8+\delta}$ using PES in a mode that scans across $\mathbf{k}$ space at a fixed energy [21]. They found a two part Fermi surface. One piece had strong spectral weight and was close to that expected from the LDA calculation. The other piece had little spectral weight and was derived from the strong, LDA-like Fermi surface by adding a translation of (π,π). The Fermi surface they reported might be predicted from the results of this work. The weak section could be derived from regions where we found a weak band in $Sr_2CuO_2Cl_2$.

In summary, we have measured the $\mathbf{k}$ dependent single-particle excitation spectra of the highest energy band in the model insulating copper oxide $Sr_2CuO_2Cl_2$. This band has a strong correspondence to the band crossing E_F in the metallic copper oxides. It is well described by a t-J model calculation along $(0,0)$ to (π,π) but not near $(\pi,0)$. There is a strong variation in spectral weight as a function of $\mathbf{k}$ which reflects the antiferromagnetic order. Clearly, further experimental and theoretical work is necessary to explain the results and explore further the speculations we report in this Letter.

We would like to acknowledge helpful conversations with P. W. Anderson, V. Emery, E. Dagotto, R. B. Laughlin, P. A. Lee, and D. J. Scalapino. We thank O. Jepsen for producing an LDA calculation for $Sr_2CuO_2Cl_2$, D. S. Dessau for help with the experimental setup, and P. Blakeslee for characterizing the crystals. SSRL is operated by the DOE Office of Basic Energy Science, Division of Chemical Sciences. The work at Stanford was supported by DOE materials science, NSF Grant No. DMR9357057, and the Stanford Center for Materials Research. The work at M.I.T. was supported by NSF Grants No. DMR90-22933 and No. DMR93-15715.

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