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PHOTOEMISSION SPECTROSCOPY OF SINGLE CRYSTAL HTSC MATERIALS: A FERMIL LIQUID ELECTRONIC STRUCTURE

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ABSTRACT

Photoemission spectra from HTSC materials (primarily 123 -type) , cleaved and measured at 20K, reveal a rich DOS structure which compares favorably with a calculated band structure, except for a residual 0.5 eV shift which may reflect some correlation effects. Band dispersion is observed throughout the valence bands, with clear evidence for a 0.2 eV wide band dispersing through E_F . The orbital character at E_F is a mix of Cu-3d and O-2p. There is unambiguous evidence for a large BCS-like gap ($2\Delta \geq 4kT_C$).

INTRODUCTION

Photoemission spectroscopy, normally a powerful tool for probing the electronic structure of materials¹ has proven inconsistent in the study of high- T_c superconductors (HTSC's). Its main drawback is its extreme surface sensitivity since the escape depth of photoexcited electrons is at most 20 Å from below the surface¹, and is usually no more than 5-10 Å. In the 123- type HTSC's the problem is severe since it is well known² that the chain oxygens are particularly unstable. If oxygen loss occurs in vacuum, it is obvious that the near-surface region of a specimen will be the first to suffer such losses.

We believe that it is just such a mechanism which was responsible for the inconsistencies in the early photoemission work. This work, primarily on sintered powders, has been reviewed by Wendin³ and shows a notable lack of a Fermi edge in the 123 materials, and a very weak Fermi edge in the 214 compounds⁴. These observations were a contributing factor to the general perception that a novel, unconventional normal state conductivity⁵ was responsible for the bulk properties. The one-electron model⁶ was believed inapplicable because of the above absence of a Fermi edge, as well as the existence of satellites in the photoemission spectra, and the inability to predict a magnetic transition or an insulating state in the undoped parent compounds.

Recently, however, we have shown⁷⁻¹⁰ that the surface of a 123- type HTSC material can be stabilized against deterioration if the sample is kept at low temperatures, $T < 50$ K. If a fresh surface is exposed by cleaving a single crystal in situ at $T < 50$ K, we find that a very distinct, large, stable Fermi edge is observed. Indeed the surface remains very stable while cold, but deteriorates rapidly upon warming above 50 K. Reports of temperature-dependence¹¹ very possibly had their basis in a deteriorating surface. Work on sintered powders at room temperature is particularly suspect, even with the deeper sampling depth of an XPS probe, since it was

shown¹² that the core-level lineshape is a strong function of the sample preparation method. Not only a modified surface, but also varying grain boundary composition contributes to the inconsistent signal.

The absence of the -9 eV oxygen related feature, which we now know to be due to surface contamination, is not sufficient evidence for claiming an unmodified surface. We have found¹³ in 123 materials that the Fermi edge disappears even before the -9 eV peak becomes measurable. It is the absence of a Fermi edge that is most telling.

In this paper, then, we review photoemission data, particularly that taken on single crystals at low temperatures, and re-examine what the data tell us regarding the electronic structure. Experimental details have been reported elsewhere.¹³ We will show that for $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ a large intensity is obtained at E_F and that the valence bands are fairly consistent with a previously calculated band structure. Indeed, a band dispersing through E_F , together with a resolution limited Fermi edge even for $\Delta E = 30$ meV, appear to be consistent with conventional Fermi liquid behavior. This is the same conclusion reached by Takahashi et al.¹⁴

RESULTS AND DISCUSSION

A) Core Levels

The most extensively studied core levels are the Cu-2p_{3/2} and the O-1s levels in the cuprates. Most studies concluded that, based on a comparison to CuO spectra, there is no evidence for a Cu^{3+} configuration. All the Cu is in the Cu^{2+} state. As the surface deteriorates, some Cu^{1+} begins to build up with oxygen loss. The conflicting reports^{11,12,15-17} may possibly be traced to sample variations in sintered materials. We withhold judgement on the presence of Cu^{3+} as well as any reported temperature-dependence of the Cu-2p_{3/2} line until such a measurement is done on single crystals at low-T, and is shown to be reversible in the same sample and the same surface. The uncontested feature of the Cu-2p_{3/2} lineshape, however, is the similarity among all cuprates, and particularly to the CuO spectra where only Cu^{2+} is present. For this reason it has been assumed that the Anderson model is applicable^{4,18} and the data have been extensively analyzed for the relevant parameters. The ground state in all the cuprates is assumed to consist of $3d^9$ and $3d^{10}\underline{L}$ states which yield the two peaks in the 2p_{3/2} core level spectra.

Some controversy also exists regarding the O-1s core level. Weaver et al.¹² showed that, by comparing to CuO spectra, the O-1s line can be decomposed into an in-plane $3d^9$ ($\text{O-}2p^6$) component (at -528 eV), an out-of-plane component (at -529 eV), as well as the $3d^{10}\underline{L}$ ($\text{O-}2p^5$) satellite at -531 eV, as in CuO. It is with respect to this latter that some question exists, since a contamination peak tends to form at this same binding energy. Single crystal data¹⁹ on Bi-2212 yield no component at -531 eV. Our own 2212 data, shown as curve "a" in Fig.1, show the same result as Ref. 19. Curves "b" and "c" in Fig. 1 are for Y-123. Curve "b" was taken at 20 K several hours after cleaving, and already shows some evidence for a -531 eV line. However, a warmup to 300 K even for 10 minutes (curve "c") results in a dramatic irreversible increase in its intensity. Based on this, and the comparison to curve "a", we, like Shen et al.¹⁹, would conclude that the -531 eV line (i.e., the so-called $3d^{10}\underline{L}$ O-1s satellite) does not exist in the pure cuprates. Thus the direct comparison to CuO should be re-examined.

B) Valence Bands

Our primary focus, since our discovery of the surface stabilization technique, has been a study of the valence bands, since these have a direct bearing on the nature of the normal and the superconducting states of HTSC's. We have already mentioned in the introduction that a relatively large Fermi edge is found in the 123 materials, which would indicate a conventional metallic normal state. This edge is resolution limited even for an instrument resolution $\Delta E \approx 30$ meV, and displays the normal Fermi function broadening as T increases. We point out that Fermi function broadening yields an effective width of the Fermi edge of $3 kT$ so that a 30 meV instrument resolution compares to thermal broadening of the Fermi edge of ≈ 100 K. Down to this temperature, then, these materials are indistinguishable from ordinary metals; or, more correctly, Fermi liquids.

In Fig.2 we show four angle integrated energy distribution curves (EDC's) for

Fig.1 O-1s core level spectra. a) Bi₂CaSr₂Cu₂O₈-fresh cleave at 20K. b) YBa₂Cu₃O_{6.9}-T=20K, 12 hrs after cleave. c) YBa₂Cu₃O_{6.9}- after 10 min at room temp.

Fig 2 Valence band EDC's for YBa₂Cu₃O_{6.9} with background subtracted. Dotted curves are calculated spectra from Ref. 20.

Y-123 taken at photon energies ranging from 20 eV to 70 eV. We have subtracted the secondary electron background from the EDC's in order to better compare these experimental spectra to calculated²⁰ spectra (dashed lines) obtained by a convolution of the calculated partial densities of states (PDOS) with appropriate photo-absorption cross sections, $\sigma(h\nu)$, as well as lifetime and instrument broadening functions. The features A through F can be identified in both experimental and theoretical EDC's (they are not necessarily obvious in every EDC), but it was necessary to shift the calculated spectra by 0.5 eV to higher binding energy to line up the well-defined features A and B. Having done that, however, we get good alignment of all features. A very important point is that not only peak positions, but also spectral shapes seem to agree with calculations. Since the change in the spectral shape with $h\nu$ is a consequence of relative variations in $\sigma(h\nu)$ between p- and d-like orbitals²¹, it follows that a correct prediction

of the shape implies a correct mix of p- and d-orbitals in the DOS. Thus irrespective of which model eventually proves to correctly predict the HTSC properties, it will have to reproduce the one-electron DOS.

The intensity at E_F actually exhibits large non-monotonic variations in amplitude with $h\nu$ which can only be interpreted as resulting from van Hove singularities in the empty states. These van Hove singularities are, in fact, seen in the secondary electron spectrum at low $h\nu$. Space restrictions do not permit showing a figure. Suffice it to say that the observation of these final state effects is in keeping with the concept of well-defined dispersive bands²².

D) The Orbital Character of States at E_F

Although the observation²⁴ of electron doped HTSC's demonstrates the symmetry of electrons and holes, many models still rely on hole hopping either purely on O or Cu sites. Thus it is important to the understanding of HTSC phenomena to experimentally determine the orbital character states at E_F . The usual photoemission technique for this determination is that of resonant photoemission whereby the photon energy is tuned through a core absorption edge (2s edge at $h\nu = 22$ eV for O, and 3p edge at $h\nu = 74$ eV for Cu) and observing any enhancement in the amplitudes of the valence band features at these photon energies. One would expect O-2p enhancement at $h\nu = 22$ eV and Cu-3d enhancement at $h\nu = 74$ eV. However, there are complications. The previously-mentioned van Hove singularities preclude a clear identification of the O-2p enhancement at E_F at $h\nu = 22$ eV, while the entire valence band with its 27 3d electrons per formula unit (in the 123's) shows little or no resonance at $h\nu = 74$ eV. All the 3d resonant spectral weight is in the -12 eV satellite. If one concludes the absence of 3d character at E_F , then the same conclusion is necessitated for the entire valence band. In other words, there is no reason to expect a resonance at E_F at the 3p edge.

Fig. 3 Photon energy variation of calculated atomic Cu 3d and O 2p cross sections and the experimental Bi 2-2-1-2 Fermi edge intensities normalized by integrated valence band cross sections. Open circles point to either resonant or final state enhancements not modelled by the calculations. The best fit to the solid circles is 35% Cu 3d and 65% O 2p character

One can still determine the orbital character at E_F by a careful study of the intensity at E_F as a function of photon energy (i.e., a cross section study). Figure 3 shows the intensity at E_F for the 2212 compound as a function of photon energy (open circles indicate either van Hove singularity or resonant enhancements and are not included in the analysis). The expected variation for pure Cu 3d and pure O 2p character is also shown. We assumed a Cu 3d⁹ and O 2p⁶ configuration. The spectra

were normalized to equal integrated valence band intensities scaled by the calculated²¹ cross-sections ($18 \sigma_d(h\nu) + 48 \sigma_p(h\nu)$). Clearly the amplitude at E_F is neither purely Cu-3d nor purely O-2p. A simple linear combination of Cu-3d and O-2p intensities needed to reproduce the observed intensity variation at E_F yields approximately a 35-65 mix of d and p orbitals.

C) Angle-resolved Photoemission

The best method for measuring band dispersion is, of course, angle-resolved photoemission or ARPES, where one determines not only the energy of the photoemitted electron, but also its direction θ with respect to the sample surface. Takahashi et al.¹⁴ were first to measure dispersion in an HTSC material ($\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$). However, their relatively low signal-to-noise, as well as only moderate resolution left some room for skepticism. We have reproduced their data on the 2212's, but have observed a substantially larger Fermi edge as well as some differences in actual peak positions²³. In Fig. 4 we show these ARPES data, for the 2212's. Very similar results were obtained in $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ at $T \approx 20$ K. Thus the band crossing of E_F appears universal in HTSC systems. In the figure we see unambiguously a peak in the spectrum dispersing through E_F with the analyzer at $\theta = 180^\circ$ from the sample normal, which corresponds to $\approx 0.7 \text{ \AA}^{-1}$ relative to the Γ -point in the Brillouin zone. The minimum of this band is at the Γ -point (i.e., at normal emission, $\theta = 0$) where the band is ≈ 0.2 eV below E_F . In Y-123 the band minimum is likewise at the Γ -point, 0.2 eV below E_F . Along the Γ -M direction it crosses E_F at $\approx 110^\circ$, or $0.45 \text{ \AA}^{-1}$ from Γ .

While band calculations⁶ for 123 materials actually predict a dispersion very similar to that observed (i.e., an 0.2 eV wide band due to chains), it appears that the very similar band observed¹⁴ in 2212's near E_F is somewhat narrower than band structure predictions⁶. Such narrowing of bands may be a consequence of correlation effects¹⁸. If this observation survives further measurements, it may be that we have obtained accidental agreement in the 123 compounds near E_F . More work will be done, but these initial results nonetheless clearly show the band-like nature of these materials with a bandwidth similar to predictions. Moreover, we again stress that the overall agreement with DOS is excellent.

That these materials show effects of correlation has been, of course, obvious from the beginning from the various core level and valence band satellites and the nearby magnetic phases. Correlation effects may also be responsible for the 0.5 eV shift of the calculated DOS relative to the measurements (except for the band at E_F), although larger shifts have been observed in well-behaved systems¹⁸ such as Cu_2O . What we don't know is if correlations play the dominant role in the HTSC superconducting properties. Certainly the deviations from a one-electron DOS appear to be minor - possibly smaller than in Ni metal. The surprising observation is that the agreement is as good as it is. At a minimum it reinforces the concept of the Fermi liquid nature of these materials.

E) The Superconducting Gap

The greatly improved resolution of photoemission apparatus combined with the large superconducting gap of the HTSC's has enabled at long last a direct measurement of the gap via photoemission. Imer et al.²⁵ were first to observe this effect in their

angle-integrated measurement at a resolution $\Delta E \approx 20$ meV. In the angle-integrated mode, however, the finite resolution of the instrument (even at $\Delta E = 20$ meV) will measure all those states just below E_F which are within the resolution window, but which do not contribute to the gap. Thus the effect of the gap will appear to be smaller than in actuality. By making the measurement in the angle-resolved mode one can avoid most band features just below E_F by measuring at an angle where the band just crosses E_F . In Fig. 5 we show our results²³ for the 2212 compounds ($T_C = 85$ K) with the analyzer set to accept electrons at $\theta = 15^\circ$ relative to the c-axis, where the band is just at E_F . The sharply peaked spectrum is taken at $T = 20$ K (far below T_C) while the less pronounced spectrum is taken at the very same angle, and on the same unaltered surface, at $T = 90$ K (just above T_C). The spectra are normalized to photon flux. The effect is completely reversible. To show that the effect is indeed due to the gap, we also made a measurement at $\theta = 11^\circ$ where the band is still 0.1 eV below E_F . There we find (not shown due to space limitations) that the 90 K and 20 K spectra coincide (i.e., no shifting of E_F or pile-up of the DOS).

Fig. 4 Angle-resolved EDC's within the first 300 meV of E_F for $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$; $T=90$ K.

Fig. 5 EDC's, normalized to photon flux, for $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$ above and below T_C for the analyzer at 15° . Note the pile-up of states at E_F at $T=20$ K due to the opening of the gap.

In Fig. 5 we see a clear shift of E_F to higher binding energies at 20 K as the gap opens up, together with a pile-up of states just below the gap, which results in the sharp peaking effect. This is very much as expected on the basis of the BCS theory. A determination of the exact value of the gap will require substantial modeling (the data are very recent) including such subtle effects as a decrease in lifetime broadening of the features near E_F . We can with confidence, however, already place a lower limit on the gap; i.e. $2\Delta \geq 4 kT_C$, larger than the weak-coupling BCS value.

CONCLUSIONS

There can be little room for argument about the Fermi liquid nature of the cuprate HTSC's. The reasonably good agreement with band calculations even lends support to the one-electron model although the effects of correlation are clearly evident in the form of satellites. The states at E_F are strongly-hybridized 3d 2p bands.

The surprisingly large effect caused by the opening of the gap appears to be BCS-like (although the gap is larger than 3.5 kTc) but requires additional modeling.

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