PHYSICAL REVIEW B VOLUME 39, NUMBER 10 1 APRIL 1989

# Possibility of a resonating-valence-bond state in the high-$T_c$ superconductor $Bi_4Ca_3Sr_3Cu_4O_{16+x}$

Y. Chang, Ming Tang, Y. Hwu, M. Onellion, D. L. Huber, and G. Margaritondo
*Department of Physics and Synchrotron Radiation Center, University of Wisconsin, Madison, Wisconsin 53706*

P. A. Morris, W. A. Bonner, J. M. Tarascon, and N. G. Stoffel
*Bellcore, 331 Newman Springs Road, Red Bank, New Jersey 07701*

(Received 8 December 1988)

We compared the photoemission edge line shape of $Bi_4Ca_3Sr_3Cu_4O_{16+x}$ with those of the Au and Al Fermi edges. Specifically, we searched for the intensity decrease in the neighborhood of the Fermi level, predicted in the case of photoemission from a resonating-valence-bond (RVB) state. We found no positive evidence for this decrease and we estimated that, if the RVB state exists, then the upper limit for the maximum spinon energy is 65 meV. Our data analysis also indicates that the mere observation of an apparent spectral edge is not sufficient per se to rule out a RVB state.

The discovery of high-temperature superconductivity has generated a fundamental question: Can this new phenomenon be explained within the conceptual framework of a Fermi liquid, with fermion pairing in the superconducting phase? In 1986, Anderson proposed a revolutionary departure from such a framework, based on the hypothesis of a resonating-valence-bond (RVB) state for the $CuO_2$ planes.[1,2] The basic feature of the RVB state is that electrons are described in terms of spin-singlet pairs. In the excited states, two important quasiparticles must be considered. The first are chargeless, spin-$\frac{1}{2}$ fermions called spinons, and the second are positively charged, spinless bosons called holons, which are paired below $T_c$. The interest generated by Anderson's revolutionary approach justifies a major effort in proving or disproving its factual implications by experimental tests. Unfortunately, these tests have been very scarce.[3,4]

Recently, one of us (D.L.H.) proposed[5] that photoemission spectra in the region of the Fermi level, taken in the normal phase, can be used to test the existence of a RVB state. The conceptual background of such a test is similar to that of tunneling experiments with injection of electron holes from a normal metal into a RVB system.[3,4] The emission of a photoelectron from a Fermi liquid corresponds to the creation of a hole. On the contrary, when the photoelectron is emitted from a RVB system, *two* quasiparticles are created, a holon and a spinon.[3] The energy corresponding to that of the hole in the Fermi liquid must be shared between the holon and the spinon. Because of phase-space restrictions, this can be done in a number of ways that decreases as the magnitude of the shared energy decreases. As a consequence, the photoemission intensity for a RVB state is smaller than that of a Fermi liquid in the spectral region near the Fermi-liquid edge.

We report the first results of experimental tests of this prediction. The test was performed by measuring the edge line shape of the high-temperature superconductor $Bi_4Ca_3Sr_3Cu_4O_{16+x}$. Then, this line shape was compared to those of thick Au or Al films deposited *in situ* on top of the $Bi_4Ca_3Sr_3Cu_4O_{16+x}$ specimens. The experiments were performed both on sintered pellets scraped under ultrahigh vacuum, and on single crystals cleaved *in situ*. The comparison of the metal and $Bi_4Ca_3Sr_3Cu_4O_{16+x}$ line shapes did not reveal a measurable decrease.

In order to make the analysis quantitative, we use an expression for the near-edge line shape derived in Ref. 5 in an approximation in which the holon and spinon densities of states and the matrix element governing the photoemission process are taken to be constant. One has

$$I(\varepsilon) \propto \frac{Te^{y}}{\cosh y}\left[\ln\left(\frac{\cosh y-1-\sinh y}{\cosh y+1-\sinh y}\right)-\ln\left(\frac{\cosh y-1+\sinh y\tanh[(\alpha-y)/2]}{\cosh y+1-\sinh y\tanh[(\alpha-y)/2]}\right)\right], \quad (1)$$

where $T$ is the temperature, $y=(\varepsilon-\mu)/2k_BT$, and $\alpha=-\mu/k_BT$. Here $\varepsilon$ is the difference between the photon energy and the photoelectron energy (measured from the Fermi level), and $\mu$ is the chemical potential of the holons. This theoretical line shape is valid for $\varepsilon \ll \hbar\omega_c$, where $\hbar\omega_c$ is the maximum spinon energy. In the opposite limit, $\varepsilon > \hbar\omega_c$, the line shape becomes a constant.

The behavior of the calculated line shape can be better understood in the limit $\varepsilon \gg k_BT, -\mu$. In such a limit, for $\varepsilon \ll \hbar\omega_c$ the above expression becomes $I(\varepsilon) \approx A\varepsilon$, where $A$ is a constant. For $\varepsilon > \hbar\omega_c$, we have $I \approx A\hbar\omega_c$. Thus, the line shape increases, in first approximation linearly, with $\varepsilon$ near the edge. Then it reaches a plateau, for $\varepsilon \approx \hbar\omega_c$, and stays constant thereafter.

The behavior of the calculated RVB line shape is visible in Fig. 1. The figure compares the Fermi-edge line shape of an ordinary Fermi liquid and the RVB line shape for $\hbar\omega_c=200$ meV. We have assumed room temperature for both curves, $T=300$ K, and $\alpha \approx 1.1$.[6] We have also used linear extrapolation from the outside regions to estimate

 

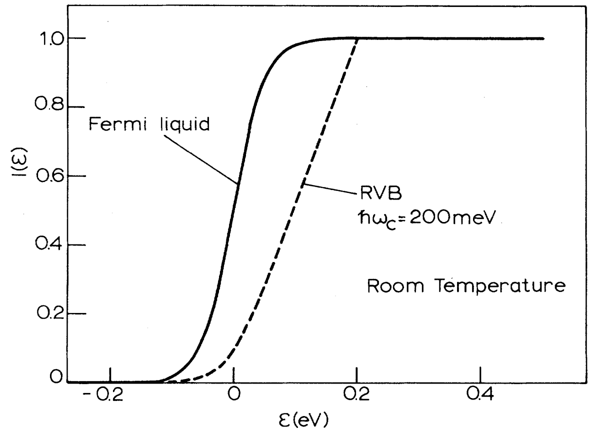


FIG. 1. Calculated photoemission edge line shapes for a Fermi liquid at room temperature and for a system with a RVB state, also at room temperature. The zero of the energy scale is the Fermi level.

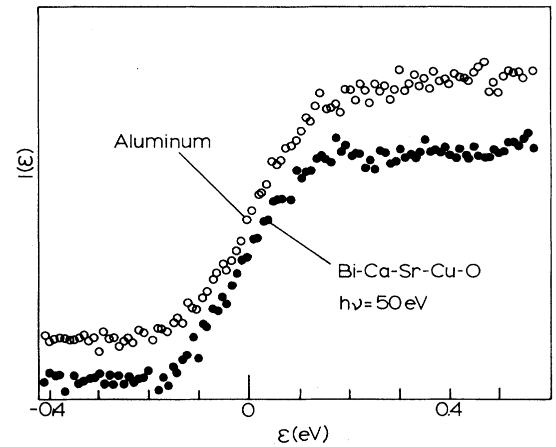


FIG. 3. Experimental photoemission edge spectra of a thick Al film and of a sintered pellet of $Bi_4Ca_3Sr_3Cu_4O_{16+x}$. The spectra were normalized to the midpoint of the metal edge. The estimated instrumental broadening (Gaussian FWHM) was 220 meV.

the RVB line shape near $\omega_c$, since no analytical line shape is available for this region.

Note the strong difference between the two curves in the region $\varepsilon < \hbar\omega_c$. Since $\hbar\omega_c$ is expected, in general, to be of the order of hundreds of meV, the deviations from the Fermi-liquid line shape should be observable with the typical resolution of photoelectron spectroscopy.

In order to understand the practical problems in detecting such deviations, we convoluted the RVB and Fermi-liquid line shapes with a Gaussian instrumental response function. We performed the convolution for different values of the Gaussian full width at half maximum (FWHM), and of the parameter $\hbar\omega_c$. The most important results can be derived directly from Fig. 2, which shows the results in the case of FWHM equal to 220 meV. In essence, the broadened RVB line shape is quite similar to a broadened Fermi-liquid line shape—*except for an apparent shift of the leading edge.*

Thus, the fingerprint of the presence of a RVB state is the apparent shift of the Fermi edge. Note that the commonly used procedure to extract the Fermi-edge position directly from the experimental edge can be misleading in the case of a RVB state. It is always recommended, therefore, to directly compare the near-edge line shape of a high-temperature superconductor with that of a metal, taken in the same experimental run.

We performed the comparison using room-temperature $Bi_4Ca_3Sr_3Cu_4O_{16+x}$ specimens and gold and aluminum overlayers deposited *in situ* on the same specimens. Some of the first results of these tests are shown in Fig. 3. In order to emphasize possible deviations of the $Bi_4Ca_3Sr_3Cu_4O_{16+x}$ edge line shape from that of a Fermi liquid,

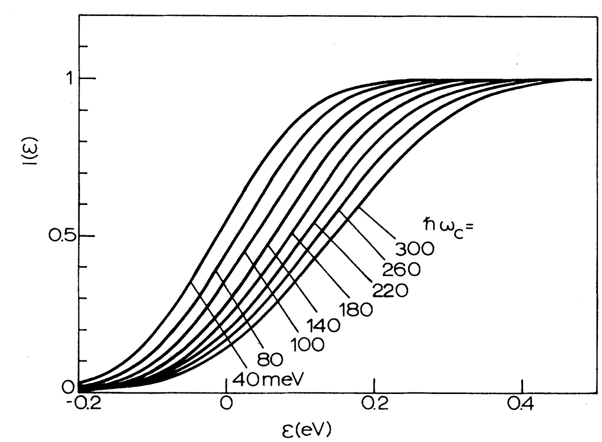


FIG. 2. Broadened RVB line shapes for different values of the maximum spinon energy, $\hbar\omega_c$. The broadening function was a Gaussian with FWHM of 220 meV.

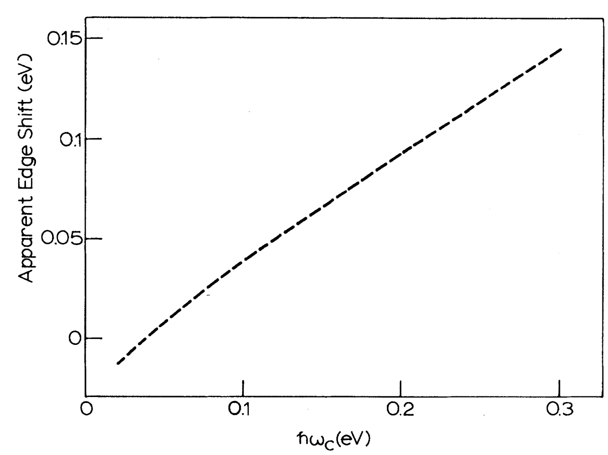


FIG. 4. Apparent edge shift of the broadened RVB line shape with respect to the broadened Fermi-liquid line shape, as a function of the parameter $\hbar\omega_c$. The curve was derived from calculated line shape with a broadening (Gaussian FWHM) of 220 meV.

the two curves were normalized to the midpoint of the metallic edge. It is quite clear from the figure that no dramatic differences are visible between the two curves.

This experimental finding does not necessarily rule out a RVB state for $Bi_4Ca_3Sr_3Cu_4O_{16+x}$ at room temperature, but it does set an approximate upper limit for the spinon energy of such a state, if it exists. The upper limit can be derived from the data by using the curve of Fig. 4, which shows the apparent shift in energy of the edge of the broadened RVB line shape with respect to the Fermi-liquid edge, as a function of $\hbar\omega_c$. The curve was derived from the data in the case of a Gaussian FWHM of 220 meV. We found, however, that this is "empirical" curve does not change much when the broadening FWHM varies from 100–300 meV. Note that the curve becomes unphysical for small values of $\hbar\omega_c$, for which the assumption $\varepsilon \ll \hbar\omega_c$ is no longer valid.

Data such as those of Fig. 3 rule out apparent shifts of magnitude larger than 20 meV. With use of Fig. 4, this corresponds to an upper limit for $\hbar\omega_c$ of the order of 65 meV. Thus, the search for evidence of a hypothetical RVB state must be continued with better resolution and signal-to-noise level. This may not be compatible with possible changes in the surface chemical composition occurring over a period of hours or days. We are, nevertheless, performing extensive tests to push the search as far as it is feasible.

In summary, our analysis predicts measurable differences between the photoemission spectrum of a Fermi liquid and that of a system in a RVB state. We also predict that the broadened RVB edge line shape could be *mistaken for a Fermi-liquid edge,* as seen in Fig. 2. Thus, the mere observation of an edge that appears similar to a Fermi edge is not sufficient to rule against a RVB state and in favor of a Fermi liquid. A stringent test requires a direct comparison with the Fermi-edge line shape of a clean metal. In fact, several different metals should be used, since the edge of each metal can deviate from that of a pure Fermi liquid due to structure in the local density of states. The test could also be influenced by features in the superconductor one-electron density of states, by matrix element effects, and by other approximations used in deriving Eq. (1).[5] With these *caveats,* in the case of $Bi_4Ca_3Sr_3Cu_4O_{16+x}$ our first results rule out a RVB state with maximum spinon energy larger than $\approx 65$ meV.

This work was supported by the National Science Foundation (NSF), by the Office of Naval Research, and by the Wisconsin Alumni Research Foundation. We are grateful to G. W. Hull, M. Giroud, and P. Barboux for their contributions to the experiments. The photoemission work was performed at the University of Wisconsin Synchrotron Radiation Center, a national facility supported by the NSF.

[1] P. W. Anderson, Science **235**, 1196 (1987).
[2] R. B. Laughlin, Science **242**, 525 (1988).
[3] P. W. Anderson and Z. Zou, Phys. Rev. Lett. **60**, 132 (1988).
[4] See K. Flensberg, P. Hedegård, and M. Brix, Phys. Rev. B **38**, 841 (1988), and the tunneling experiments quoted therein.
[5] D. L. Huber, Solid State Commun. **68**, 459 (1988).

[6] In the ideal Bose gas approximation, where $\alpha = -\ln[1 - \exp(-T_0/T)]$, the value $\alpha \approx 1.1$ corresponds to a degeneracy temperature $T_0 \approx 120$ K. The choice of $\alpha$ affects $I(\varepsilon)$ in the immediate vicinity of the Fermi energy, where it is no longer a linear function of $\varepsilon$. Its effects on the broadened line shape are marginal, and irrelevant to our conclusions.