Detection of Zhang-Rice Singlets Using Spin-Polarized Photoemission

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From a spin-resolved photoemission study on the $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconductor, we show experimentally that the first ionization state is of nearly pure singlet character. This is true both above and below the superconducting transition and in the presence of doping and band formation. This provides direct support for the existence and stability of Zhang-Rice singlets in high-temperature superconductors, justifying the ansatz of single-band models. Moreover, we establish this technique as an important probe for a wide range of cuprates and strongly correlated materials.

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Since the discovery of high-temperature (high-T_c) superconductors [1], over a decade ago, there is a continuing intense research effort to understand this phenomenon. In the search for the pairing mechanism, numerous models have been proposed to explain the normal state properties. In many mainstream theories, such as the single-band Hubbard model [2] and the *t*-*J* model [3–6], the relevant states in the $(CuO_2)^{2-}$ planes which are responsible for the superconductivity in the high-T_c cuprates, are assumed to be built up of states with a singlet character, often referred to as Zhang-Rice singlets [7]. However, this assumption is mostly based on electronic structure calculations [7–9], rather than on experimental evidence. Consequently, having a direct probe to test whether single-band approaches are able to capture the essential low energy physics [10–13] in these materials is very important. In this context, it should be remembered that the concept of the singlet states does not exist in a local density approximation approach and that which approximation is the best is still an open question [14].

It is generally thought that the copper-oxygen planes are the essential element of these materials, so much attention has been focused on them. However, the electronic structure of these hole-doped $(CuO_2)^{2-}$ planes are still quite complex due to the presence of strong electron-electron interactions involving several different bands [10]. In an effort to reduce the problem to a simpler model, Zhang and Rice [7] and Eskes and Sawatzky [8] considered the energetics of holes in the vicinity of a copper site. The undoped state has a single hole residing mainly in the $3d_{x^2-y^2}$ orbital of the copper site ($3d^9$) and less on the oxygen sites. On doping, the additional hole is primarily on the oxygen sites (Cu $3d^9$ O $2p^5$) and much less on the copper site (Cu $3d^8$) due to the strong Coulomb repulsion within the Cu $3d$ shell. This has been confirmed experimentally [15–17]. The additional hole forms a coherent state distributed over the oxygen ligands (L, ligand hole) with $(x^2 - y^2)$ symmetry due to the strong hybridization of the O $2p$ orbitals with the Cu $3d$ orbitals and also due to the hybridization between neighboring O $2p$ orbitals. The central idea is that the spins of the two holes in this cluster are expected to be aligned antiparallel for typical parameters calculated for high-T_c cuprates [9]. The formation of such a singlet state is somewhat unusual since normally one would expect the triplet states (the spins of the two holes are parallel) to be the lowest in energy based on Hund's first rule for a Cu $3d^8$ configuration. The singlet nature is therefore the result of the unusual properties of these materials, namely, that the Cu $3d$ Coulomb energy is much higher than the Cu $3d$ to O $2p$ charge transfer energy. This classifies the undoped cuprates as charge transfer insulators within the Zaanen-Sawatzky-Allen phase diagram [18].

The main issue is whether the results of such a single cluster analysis can be applied to the two-dimensional CuO_2 planes. In these planes band formation and finite doping, essential ingredients for the (super)conducting properties, could destroy the stability of the local singlet state in favor of other spin states. If so, the currently widely used approaches, such as the single-band Hubbard model [2] or the *t*-*J* model [3–6], which are entirely based on the assumption that local singlets are the only relevant building blocks, may no longer be sufficient to describe the low energy scale physics of high-T_c superconductors. Since a variety of different theoretical approaches are used to explain experimental results [3,14], a direct experimental probe is highly desirable. From experiments on the superconducting cuprates using angle resolved photoemission, which is a powerful tool to determine the energetics of the valence band states, it is difficult to evaluate whether there is a clear split-off state that could be identified as the low lying local singlet states. In some nonsuperconducting undoped cuprates ($Sr_2CuO_2Cl_2$), weak structures have been observed near the Fermi level [19–22]. In this case, there has been some success in fitting the dispersion with an extended *t-J* model. However, even then there is an incoherent background which leaves doubt as to whether there is a split-off *singlet* state, particularly, since the spin character is not known. Similar features are seen in $Bi_2Sr_2CaCu_2O_{8+\delta}$ [14,23]. Confirming that these features have a local singlet character is very important in order to understand the best approach for interpreting the spectra [14]. This is a general problem for the cuprates, but even more true for the superconductors, where there is band formation and the local singlet states could be destroyed by doping. An experimental confirmation for the fundaments of these single band approaches is highly desirable in view of the large amount of theoretical effort that is still being made today to understand high-T_c superconductivity using these approaches. For instance, the problem of the striped phases in the cuprates [24] is a current example of the application of this approach. In this Letter, we show that we have an important probe for the local spin state, which allows us to address directly these questions.

Recently, an important step was made in experimentally determining the nature of the electronic states closest to the Fermi level in the cuprates. This was the development of a new technique that enables the measurement of the spin character of valence band electrons in materials that macroscopically have no net magnetization [25,26]. It was shown that the photoemission spectra of transition metal materials could have a very high degree of spin polarization. This occurs if the incident light is circularly polarized and if the light is tuned into the transition metal L_3 ($2p \rightarrow 3d$) absorption white line giving a strong resonant enhancement of the valence band spectrum. In the present case, the direct photoemission channel is $3d^9 + h\nu \rightarrow 3d^8 + e$ but, at the L_3 resonance, this is totally dominated by the process $2p^6 3d^9 + h\nu \rightarrow 2p^5 3d^{10} \rightarrow 2p^6 3d^8 + e$. The large $2p$ spin-orbit splitting ($\sim$20 eV) gives us spin selectivity in the absorption process and then, by measuring the spin of the outgoing electron and by using the selection rules, one can unravel completely the spin character of the valence band. This can be, for instance, in terms of singlet and triplet $3d^8$ final states, if the initial state is $3d^9$ [25]. It is also important to remember that, in this type of experiment, it is the photoemission process that introduces the hole.

In the current experiments, optimally doped $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples ($T_c = 91$ K) [27], were cleaved *in situ* in an ultrahigh vacuum chamber with a base pressure of 4×10^{-11} mbar. The photoemission experiments were performed using the helical undulator [28] based beam line, ID12B at the ESRF [29], which provides soft x-rays with a degree of circular polarization of $\sim$92%. The spectra were recorded at room temperature using a 140 mm mean radius hemispherical analyzer with a $\pm 20°$ angular acceptance and coupled to a mini-Mott 25 kV spin polarimeter [30]. The combined energy resolution for the measurements was 0.75 eV and the spin detector had an efficiency (Sherman function) of 17%. The high sensitivity of this new detector was essential for the success of these measurements. The x-rays were tuned to the peak of the Cu $2p_{3/2}$ (L_3) photoabsorption white line ($h\nu = 931.5$ eV). The photon beam was at normal incidence to the sample (i.e., along the c-axis of the crystal) and the analyzer/spin detector was at 60° to the incident beam. The spin-resolved spectra ($e^\uparrow$ and $e^\downarrow$ measured simultaneously) were measured for both light helicities (σ^+ and σ^-) to eliminate systematic errors. The experiments were reproduced several times from different cleaves of the same sample.

In the top panel of Fig. 1, we show the spin-integrated resonant photoemission spectrum and, in the lower panel, we show the spin polarization given by the spin difference (using both helicities) normalized to the spin-integrated spectrum. The Fermi level position was determined from a silver foil in electrical contact with the superconductor sample. The spin-integrated spectrum is as reported previously [31]. The spectrum results principally from Cu $3d^8$ final states and the peak at $\sim$12 eV binding energy can be assigned to an atomiclike ^1G state [31]. (This is still essentially true even in the doped case, due to the choice of photon energy as discussed below.) The spin polarization of this peak is very large, namely, $\sim$80%. This value is consistent with an analysis of the selection rules [32]. For a $3d^9$ ion, with an initial state with a hole in the ($x^2 - y^2$) orbital and with the E vector of the light in the $x - y$ plane, this gives a polarization of $5/6$ (83.3%) for pure singlet states and $-1/3 * 5/6$ (-27.8%) for triplet states. The strong dip in the polarization at $\sim$9 eV binding energy indicates a significant triplet contribution to the spectrum

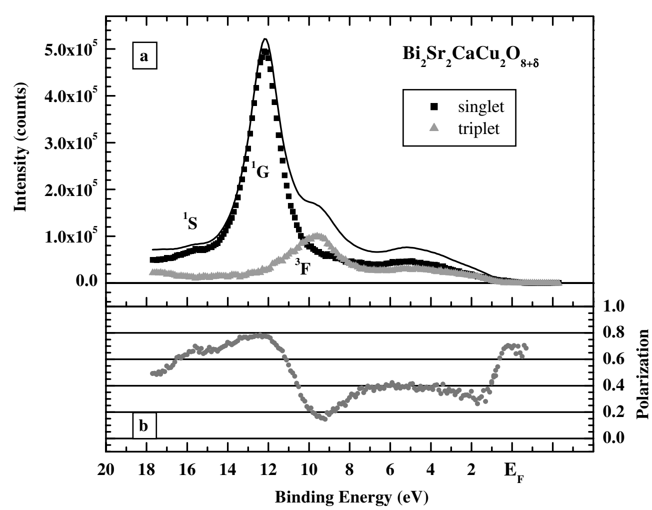

FIG. 1. Spin-polarized photoemission spectra from $Bi_2Sr_2CaCu_2O_{8+\delta}$. (a) The spin-integrated resonant photoemission spectra taken at the Cu L_3 absorption edge (full line). The symbols show the integrated spectra separated into its singlet (■) and triplet (▲) components. (b) The measured spin polarization corresponding to the spectra in panel (a).

at this energy. It should be noted that, for a polycrystalline sample, such as CuO in previous work [25], the $(x^2 - y^2)$ orbital is randomly aligned with the E vector of the light and the expected spin polarization is reduced to $5/12$ $(-5/36)$ for pure singlet (triplet) states.

Using the selection rules [25,32], we can separate the singlet and triplet contributions to the spectrum [33], and the results are shown in the top panel of Fig. 1. We are principally interested in the electronic states closest to the Fermi level. Although the intensity is very low, the spin polarization increases dramatically in the last few eV up to the Fermi level, as can be seen from the lower panel of Fig. 1. This is a strong indication that the states close to the Fermi level have a significant singlet character. These singlet states are mostly of $3d^9\underline{L}$ character [7,8] (additional hole on the oxygen sites), and it is important to remember that in the experiment we probe these states through the hybridization with the $3d^8$ final states that make up only about 7% [34] of this singlet peak. However, due to the very strong resonance [31] (100 times) the small $3d^8$ weight is more than sufficient to clearly observe the features.

In contrast to the previous work on CuO, we are studying the electron-removal excitation from the hole-doped ground state. As an ansatz for this ground state, one could think of a coherent superposition of local $3d^9$ and $3d^9\underline{L}$ configurations, where the $3d^9$ represents the ground state of an undoped local cluster and the $3d^9\underline{L}$ of a hole-doped one. In this experiment, the photon energy is tuned into the absorption peak, which is essentially a local $2p^53d^{10}$ state [31,35], so that effectively the experiment projects out the local $3d^9$ character of the initial state and, consequently, measures the $3d^8$ electron removal spectrum, for which the lowest energy state is determined to be of singlet character [36]. The main effect of doping on the absorption spectra is to broaden the absorption peak on the high energy side, 1.5–2.0 eV above the peak [31,35].

A breakdown of the low energy part of the spectrum in terms of singlets and triplets is shown in Fig. 2 [33]. It can now be clearly seen that not only are the singlets lower in energy than the triplets, but also that the energy separation is as large as 1 eV. The results shown here are for measurements at room temperature. We have also carried out the measurements below the superconducting transition temperature T_c, and, within our experimental resolution, the results are essentially identical. These results show that we can detect the singlet states even when band formation is important. This in turn means that we have a technique of wide interest for studies of cuprates and other highly correlated materials.

It is somewhat surprising that the stability of the singlets in the high-T_c superconductors is about the same as that found in CuO [25]. The crystal structure of CuO is such that inter-Cu band formation (via the oxygens) is strongly suppressed, quite unlike in the high-T_c cuprates. It is precisely this band formation that caused the debate about the stability of the singlets in the superconductors [10–12]. In addition, there is another important difference, namely,

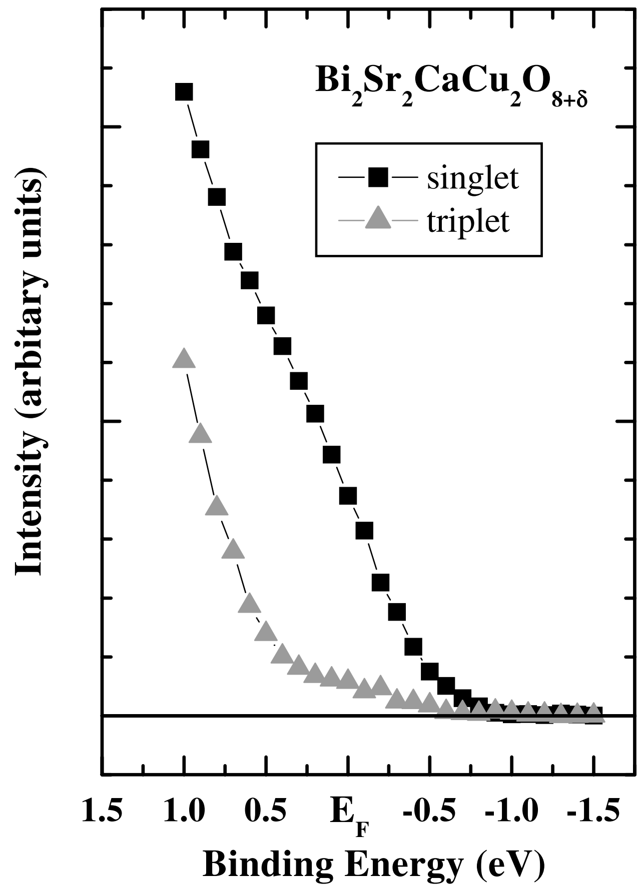

FIG. 2. Spin-polarized photoemission spectra close to the Fermi level separated into singlet and triplet components.

the fact that CuO is an insulator while the superconductors have an appreciable amount of doped charge carriers. If one compares the resonant photoemission spectra of the high-T_c superconductor with that of CuO (see Fig. 3), one can clearly see that the features, such as the ^1S peak at $\sim$16 eV binding energy and the foot near the Fermi level (0–2 eV binding energy), are appreciably broader for the superconductor than for CuO. This indicates the strong influence of band formation and the presence of charge carriers. Nevertheless, this broadening appears not to substantially affect the stability of the singlets. In addition, the observed dispersion [23] of $\sim$0.3 eV is much less than the triplet-singlet separation, thereby validating the assumptions made when working with models within the t-J framework.

We would also like to point out that due to the large angular acceptance of the electron energy analyzer several Brillouin zones are probed, hence, the spectrum is essentially a Brillouin zone average. This in turn implies that the singlets are lower in energy than the triplets over the entire Brillouin zone, although the energy separation between them may vary with the location within the Brillouin zone and may be smaller at certain points than the average of $\sim$1 eV. Nevertheless, these results provide strong experimental support that the low energy physics of high-T_c superconductors is mostly determined by the propagation of

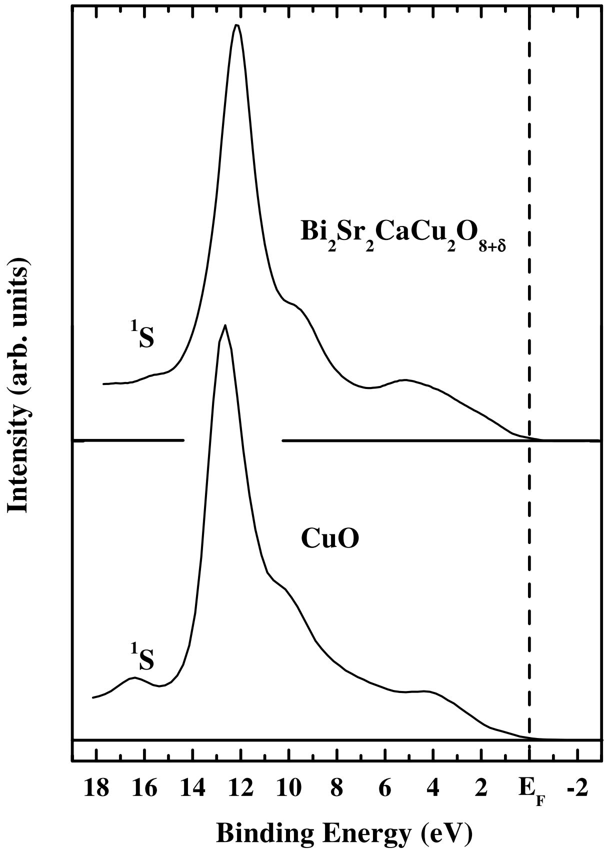

FIG. 3. A comparison of the spin-integrated resonant photoemission spectra for $Bi_2Sr_2CaCu_2O_{8+\delta}$ and CuO. The spectra have been scaled to the same peak height and shifted vertically for clarity.

these singlets. This in turn supports the idea that one can project out all other states, except the lowest energy singlet state and use a single-band model such as the t-J model.

Consequently, this work confirms the idea that the lowest lying states in high-T_c superconductors are of singlet character and shows that these states are more stable than the triplet states by about 1 eV. This justifies the basic assumptions of one of the most important classes of theoretical models for high-T_c superconductivity. Moreover, this work shows the robustness of the singlet character against hole doping, which in turn could provide new insight into the anomalous metallic phase and the phase separation issue in the doped Mott insulators and high-T_c superconductors [37].

The success of this experimental method in the doped cuprates opens up the prospects of systematic studies. For instance, one should study the purity and stability of the singlet states close to the Fermi level as the doping is changed. Similarly, it will be interesting to compare the different families of high-T_c superconductors, for example, $La_{2-x}Sr_xCuO_4$, $Bi_2Sr_2CaCu_2O_8$, and $YBa_2Cu_3O_7$. The method, of course, is not restricted to the cuprates and can be applied to other strongly correlated materials.

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