

Spin-Resolved Photoemission on *Anti-Ferromagnets*: Direct Observation of Zhang-Rice Singlets in CuO

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(Received 10 September 1996)

We demonstrate that it is possible to obtain spin-resolved valence band spectra with a very high degree of spin polarization from antiferromagnetic transition metal materials if the excitation light is circularly polarized and has an energy close to the cation $2p_{3/2}$ (L_3) white line. We are able to unravel the different spin states in the single-particle excitation spectrum of CuO and show that the top of the valence band is of pure singlet character, which provides strong support for the existence and stability of Zhang-Rice singlets in high- T_c superconductors. [S0031-9007(97)02343-0]

PACS numbers: 74.25.Jb, 74.72.-h, 75.25.+z, 79.60.-i

To determine the nature and behavior of quasiparticles in strongly correlated transition metal oxides, including high- T_c superconductors, it is highly desirable to have experimental information about the energies and band widths of the different spin and multiplet states in the single-particle excitation spectrum. Identification of these states, which have their meaning within the Anderson impurity model, could facilitate the modeling of the low-energy excitations of the lattice in terms of those of the impurity. Knowledge of the character of the first ionization states is important for a better understanding of the behavior of the charge carriers in the doped materials, which could be quite intricate, especially when bound states occur with a compensated local spin contrary to that expected from Hund's first rule. There is a tendency for such to occur in charge transfer insulators, with perhaps the high- T_c cuprates as the most famous of them. In fact, the basic assumption in main stream theories concerning high- T_c superconductivity, like the single band Hubbard model [1] and the t - J model [2], is that the relevant states in the CuO₂ planes are of local singlet character, based on theoretical estimates [3–7]. Up to now, however, no direct experimental observation of such spin compensated states have been reported, mainly because spin-resolved photoemission [8–11], which is the obvious spectroscopic tool to use, cannot be applied due to the fact that most of the oxide materials, including the high- T_c cuprates, are macroscopically not magnetic, so that all the spin-resolved signals from the magnetically opposite cation sites cancel each other. For the same reason, magnetic circular dichroism experiments [12–14] at the cation $2p$ and O $1s$ photoabsorption edges of hole doped oxides [15] and cuprates [16,17] would provide no information about the magnetic coupling between the cation and oxygen holes.

In this paper we report the combined use of circularly polarized light and electron spin detection in our resonant photoemission study on CuO. Of all strongly correlated transition materials, CuO has the simplest atomic multiplet structure, and may therefore serve as a first test for this new type of spin-resolved photoemission technique applied to antiferromagnets. CuO may also serve as a model compound for high- T_c cuprates, since in comparing it with the insulating parent compounds of the superconductors, the magnitude of the insulating gap, the antiferromagnetic superexchange interactions, the basic structural unit (CuO₄), the Cu-O distances, as well as the Cu valence appear to be quite similar. Therefore, the characteristics of the first ionization states in CuO may be representative for the behavior of the doped holes in cuprates. Our results demonstrate that it is possible to obtain spin-resolved valence band spectra from macroscopically nonmagnetic transition metal materials. The spectra have a very high degree of spin polarization, for which the use of the resonance condition, i.e., using light with energies around the cation $2p_{3/2}$ (L_3) photoabsorption edge, proves to be essential. We are able to unravel the different spin states in the single-particle excitation spectrum of CuO. We show, in particular, that the top of the valence band is of pure singlet character, which provides strong support for a meaningful identification of the so-called Zhang-Rice singlets [5] in high- T_c cuprates.

The experiments were performed using the helical undulator [18] Dragon beam line BL26/ID12 [19] at the European Synchrotron Radiation Facility (ESRF) at Grenoble, together with the New York University (NYU) spin-resolved spectrometer specifically designed for soft-x-ray photoemission experiments [20]. The overall monochromator and electron analyzer resolution was set at 1.5 eV. The degree of the circular polarization

at the Cu $2p_{3/2}$ (L_3) photoabsorption white line ($h\nu = 931.5$ eV) was 0.85, and the detector's spin sensitivity (Sherman function) was 0.07. The angle between the electron emission direction and the light beam was set at 90° , and the spin detector was set to measure the degree of the electron spin polarization in the direction along the light beam in order to obtain complete parallel and antiparallel alignment of the photon spin and electron spin. The spectra were recorded with the four possible combinations of light helicity (σ^+/σ^-) and spin detector channels (e^\uparrow/e^\downarrow , measured simultaneously), in order to exclude any systematic errors. The CuO sample was prepared *in situ* by high-pressure (2–10 torr O_2) and high-temperature (400 °C) oxidation of polycrystalline Cu as described in earlier studies [21–23], yielding unpolarized spectra identical to those measured previously. The measurements were carried out at room temperature, which is above the Neel temperature of 230 K.

The top panel of Fig. 1 shows the valence band photoemission spectra of CuO with photon energy tuned at the Cu $2p_{3/2}$ (L_3) white line. The thick solid line is the sum of the spectra taken with parallel ($\sigma^+e^\uparrow + \sigma^-e^\downarrow$) and antiparallel ($\sigma^+e^\downarrow + \sigma^-e^\uparrow$) alignment of the photon

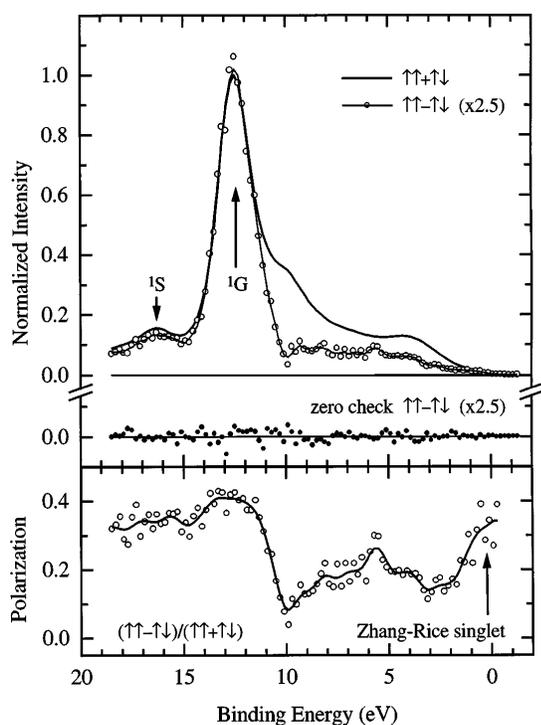


FIG. 1. Spin-resolved circularly polarized $2p_{3/2}$ (L_3) resonant valence band photoemission spectrum of CuO. The thick solid line in the top panel is the sum of two spectra, one taken with parallel and the other with antiparallel alignment of the photon spin and electron spin. The thin line with open circles is the difference spectrum. The bottom panel shows the degree of spin polarization, calculated as the ratio between the difference and sum spectrum. The zero check measurement as described in the text verifies a correct experimental setup.

spin and electron spin. Aside from a slightly poorer energy resolution, it is identical to the unpolarized $2p$ resonant photoemission spectrum in an earlier work [23]. The spectrum reveals primarily the Cu $3d^8$ final states, and the peaks at 16.2 and 12.5 eV binding energy are states derived from the typical atomiclike 1S and 1G states, respectively, as explained before [21–23]. The thin line with open circles is the difference between the spectra taken with parallel and antiparallel alignment of the photon and electron spins. After taking into account the spin detector's sensitivity and degree of circular polarization, we notice that this difference is very large, up to 41% of the sum spectrum, which is quite remarkable since we are studying a polycrystalline system with randomly oriented local moments. To verify that this observation is not flawed by instrumental errors, we have performed a zero check experiment. We repeated the measurements under identical conditions with a carbon target replacing *in situ* the gold target of the spin detector. Since the carbon target is not sensitive to the spin of the electron being analyzed, any difference signal detected can be ascribed to instrumental asymmetries. As shown in Fig. 1, we measured a difference spectrum which is zero, proving that the experiment has been set up correctly and that the above mentioned spin-resolved signals are real.

Figure 1 also shows that the difference spectrum has a different line shape than the sum spectrum. For further analysis, we represent in the bottom panel of Fig. 1 the data in terms of the degree of spin polarization defined as the ratio between the difference and the sum spectrum. The states assigned as 1S and 1G have a polarization of about +35% and +41%, respectively, and this compares very well with an analysis of the selection rules in which the polarization for a $3d^9$ ion, neglecting the small $3d$ spin-orbit interaction, is found to be $+\frac{5}{12}$ (+42%) for the singlet and $-\frac{1}{3} \times \frac{5}{12}$ (-14%) for the triplet final states. While for 12 eV and higher binding energies only singlet states are present, between 1 and 12 eV the polarization is much reduced but not negative, indicating the presence of both singlet and triplet states as proposed in earlier studies [21–23]. Quite remarkable is that the polarization is high again for states located at the top of the valence band, suggesting strongly that they are singlets, i.e., the Zhang-Rice singlets in cuprates. With a value of +35%, one is tempted to make a comparison with the polarization of the high-energy 1S state (also +35%) and suggest a common origin. In fact, model calculations [6,22] showed that both the first ionization state and the high-energy 1S state belong to the 1A_1 irreducible representation of the D_{4h} point group, and that the first ionization state, which is mainly $3d^9\bar{L}$ -like, acquires some ($\pm 7\%$) $3d^8$ character which is now being probed in this resonant photoemission experiment (\bar{L} denotes an oxygen ligand hole). The calculations [6,22] also showed that it is the large $3d$ Coulomb interaction together with the strongly noncubic environment, present in all cuprates, that makes

the first ionization state to be a singlet. In CuO, the stability of this singlet with respect to other states can be estimated from the width of the high polarization region, which is about 1 eV.

Figure 2 shows a breakdown of the $3d^8$ final states in terms of singlets and triplets, using the above-mentioned selection rules. The results demonstrate clearly that this type of experiment can unravel the different spin states of the valence band of transition metal materials. A quantitative analysis which includes Auger matrix elements could provide a much more accurate modeling of the complicated electronic structure of such strongly correlated systems. In our case, a qualitative analysis is more than sufficient to establish that the first 1 eV of the valence band consists of singlets only, as can be seen from the inset of Fig. 2. While much theoretical work has been carried out in the past [5–7], our study provides the direct experimental support for a meaningful identification of Zhang-Rice singlets in cuprates.

In this photoemission work on CuO we make use of the $2p_{3/2}$ (L_3) resonance condition: when the photon energy is near the Cu $2p$ ($L_{2,3}$) absorption edges, the photoemission consists not only of the direct channel ($3d^9 + h\nu \rightarrow 3d^8 + e$) but also, and, in fact, overwhelmingly, of the deexcitation channel in which a photoabsorption process is followed by a nonradiative Auger decay ($2p^6 3d^9 + h\nu \rightarrow 2p^5 3d^{10} \rightarrow 2p^6 3d^8 + e$). In principle, to observe spin signal one needs only the use of a spin detector and circularly polarized light. It is important to realize, however, that circularly polarized light can only be very effective if a strong spin-orbit splitting is present in the atomic subshell under study, because then angular momenta will govern the selection rules [24]. Conse-

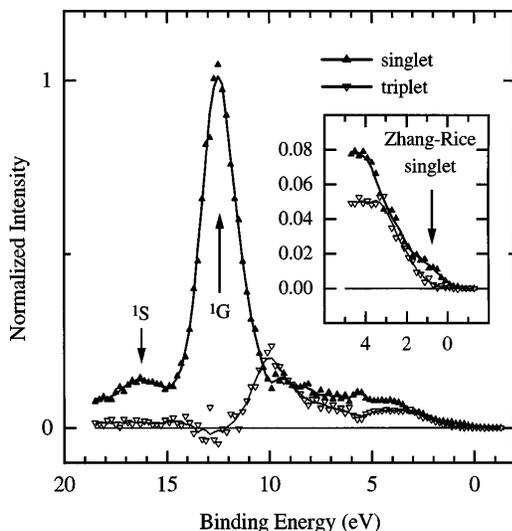


FIG. 2. A breakdown of the spin-resolved circularly polarized $2p_{3/2}$ (L_3) resonant valence band photoemission spectrum of CuO in terms of singlets and triplets. The inset shows that the top of the valence band consists of singlets only.

quently, direct (nonresonant) photoemission on $3d$ transition metal materials would produce little spin signal, because the spin-orbit interaction (of order 0.1 eV) is negligible compared to other interactions like crystal fields and hybridizations (of order 1 eV). By making use of the $2p$ core level as an intermediate state in the deexcitation channel of the $2p$ resonant photoemission process, we now can take advantage of the large $2p$ spin-orbit splitting (of order 20 eV) and the well known strong $L_{2,3}$ magnetic circular dichroism [13]. This forms the main principle of our technique: tuning into one of the two well separated spin-orbit split $2p$ white lines, circular polarized light produces a spin polarized $2p$ core hole, allowing the subsequent Auger decay to produce photoelectrons which are also spin polarized (with a polarization depending on the final state). Essential is the fact that the core hole state is a bound state so that the Auger decay is a participator process and reaches a *photoemission* final state. Figure 3 depicts in detail the deexcitation channel for a $3d^9$ initial state. Starting with a valence shell hole which is spin up or spin down, the photoabsorption process will produce a $2p$ core hole which is spin up and spin down. This process is therefore determined by four different cross sections: A^+, A^- for creating core holes with the same spin as the valence shell hole, and B^+, B^- with opposite spin, where the $+/-$ signs refer to an antiparallel/parallel alignment, respectively, of the valence shell hole and photon spin. Of further consideration is that the strength of the subsequent Auger decay of the core hole state depends on the final state reached: C_s for singlets, C_t for triplets with $M_S = \pm 1$, and $\frac{1}{2}C_t$ for triplets with $M_S = 0$, where the factor $\frac{1}{2}$ takes into account that an $M_S = 0$ state is only for 50% a triplet. Using Fig. 3 as a guide, one can find that a measurement of the intensity difference ($\sigma^+ e^{\uparrow} - \sigma^+ e^{\downarrow}$) for an antiferromagnet containing equal numbers of spin-up and spin-down $3d^9$ ions yields $[(A^+ - B^+) - (A^- - B^-)]C_s$ for singlets and $-\frac{1}{2}[(A^+ - B^+) - (A^- - B^-)]C_t$ for triplets, with analogous expressions for σ^- light. One can also find that the polarization, defined as the intensity difference divided by the sum, is $[(A^+ - B^+) - (A^- - B^-)]/[(A^+ + B^+) + (A^- + B^-)]$ for singlets and $-\frac{1}{3}$ of this value for triplets. We now arrive at the striking result that the polarization is essentially determined by the photoabsorption process. We note that the polarization in this type of experiment is different from that in a photoabsorption experiment (supposing that the sample can be made ferromagnetic), because the latter is given by $[(A^+ + B^+) - (A^- + B^-)]/[(A^+ + B^+) + (A^- + B^-)]$. The difference could be substantial: for the $3d^9$ ion, neglecting the small $3d$ spin-orbit interaction, the polarization in resonant photoemission is $\frac{5}{12}$ while in absorption it is only $\frac{1}{4}$ (from $A^+ = 14, A^- = 6, B^+ = 1, B^- = 3$). It is also important to realize that the observed polarization in our experiment does not depend on the *orientation* of the local moment. This is because each $3d(m_l)$ state with

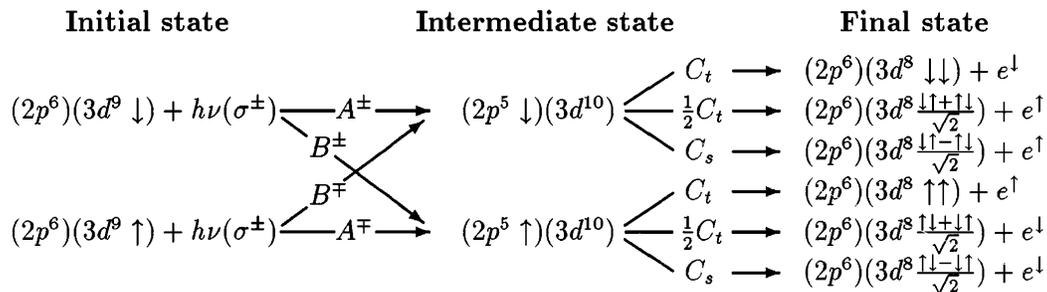


FIG. 3. Deexcitation channel in spin-resolved circularly polarized $2p$ resonant photoemission. Up and down arrows between parentheses label the spin of the holes in the $3d^9$, $2p^5$, and $3d^8$ configurations, σ^+ , σ^- the helicity of the light, and e^\uparrow , e^\downarrow the spin polarized photoelectrons. A^+ , A^- , B^+ , B^- are photoabsorption cross sections, and C_s , C_t are the squares of the Auger matrix elements for singlets and triplets, respectively.

a spin oriented perpendicularly to the quantization axis can be expressed as a linear combination of $3d(m_l, \uparrow)$ and $3d(m_l, \downarrow)$ states with the spins (\uparrow, \downarrow) along the quantization axis, and because photoabsorption matrix elements do not couple a core level state $2p(j, m_j)$ with the $3d(m_l, \uparrow)$ and $3d(m_l, \downarrow)$ states simultaneously. The result is that any perpendicular oriented local moment will be seen as a local antiferromagnet along the quantization axis, indistinguishable from a real antiferromagnet. Its insensitivity to the spin orientation makes this type of experiment an ideal tool for studying local moments in itinerant ferromagnets above the Curie temperature [25].

In summary, we demonstrate the feasibility of spin-resolved valence band photoemission on macroscopically nonmagnetic transition metal materials, i.e., antiferromagnets, paramagnets, and materials with disordered magnetic structure, and show that a very high degree of spin polarization can be obtained. The combined use of circularly polarized light, electron spin detection, and $2p_{3/2}$ (L_3) resonance condition is essential. We are able to unravel the different spin states in the single-particle excitation spectrum of antiferromagnetic CuO and show that the top of the valence band is of pure singlet character, which provides strong support for the existence and stability of Zhang-Rice singlets in high- T_c cuprates.

It is a pleasure to acknowledge the technical assistance of J.C. Kappenburg, L. Huisman, and J.F.M. Wieland. We are grateful to the ESRF staff for their support, in particular, R. Mason and J. Klora. We thank C.T. Chen, J.-H. Park, and V. Chakarjian for making testing facilities available at the AT&T Bell Laboratories Dragon beam line. This investigation was supported by the Netherlands Foundation for Chemical Research (SON), the Netherlands Foundation for Fundamental Research on Matter (FOM) with financial support from the Netherlands Organization for the Advancement of Pure Research (NWO), the Committee for the European Development of Science and Technology (CODEST), the New York University Research Challenge Grant No. 5-201-396, and the

National Science Foundation Grant No. DMR-9625340. The research of L.H.T. and F.M.F.dG. has been made possible by fellowships of the Royal Netherlands Academy of Arts and Sciences.

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