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Electrons, holes, and spin in $Nd_{2-x}Ce_xCuO_{4-\delta}$

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The spin nature of the states at the top of the valence band in Nd_2CuO_4 and $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ has been investigated with spin polarized resonant photoemission. A clear Zhang-Rice singlet state is observed at the top of the valence band in the undoped compound showing that the parent compound of this electron doped superconductor is similar to the parent compounds of hole doped cuprate superconductors. Upon doping, the stability of the singlet is destroyed and the optimum doped compound $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ does not display any well-separated singlet state. These results indicate that hole contribution to the superconductivity in this system is not important in contrast to what has previously been suggested on the bases of transport measurements.

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In the decade and a half that have passed since the discovery of high temperature superconductivity in cuprates,[1] an overwhelming amount of experimental information has been obtained. The majority of this information concerns the hole doped family of cuprates. The properties of the electron doped family of cuprates have been studied to a lesser extent, and it was, for example, not until recently that the symmetry of the order parameter in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ (NCCO) was measured by photoemission.[2] As a matter of fact, the denomination of NCCO as an electron doped cuprate might be misleading. Even though Ce doping seems to introduce extra electrons,[3,4] transport measurements indicate that both electronlike and holelike carriers contribute to the transport properties, with the Hall coefficient being positive for optimally doped samples below 80 K.[5,6] These findings have led to propositions of two-band theories with both hole- and electron-type charge carriers. Furthermore, the superconductivity in NCCO only occurs when the samples are subjected to an oxygen reducing procedure, and cannot be obtained by doping alone.[7] For the understanding of superconductivity in cuprates it is important to be able to put constraints on possible underlying mechanisms. One such possible constraint is the electron-hole symmetry. As mentioned above, the symmetry of the order parameter seems to be the same for both electron and hole doped cuprates, but other measurements indicate differences. The electron doped compounds show a T^2 dependence of the resistivity in contrast to the linear T dependence in the hole doped counterparts.[8] Angle resolved photoemission data also pointed to differences in the electronic structure of hole and electron doped cuprates.[9] Because of this mixed picture of the symmetry between hole and electron doped high-T_c superconductors, further comparative studies of the respective electronic structures are important. It is also important to establish the nature of a possible hole-type contribution to superconductivity in NCCO.

An important topic in the discussion of hole states in cuprate superconductors is the Zhang-Rice singlet (ZRS).[10] The ZRS is the two hole singlet state formed by pairing of a hole in a Cu $3d$ orbital with a hole distributed over the O ligands. Recently, the existence and stability of the ZRS in hole doped cuprates were experimentally verified for the first time by use of spin resolved resonant photoemission.[11,12] This technique permits a determination of the spin polarization of the photoemission final state and is an ideal tool in the study of cuprate systems because of the very simple intermediate state. In this paper, we present the results of spin resolved resonant photoemission on the electron doped high temperature superconductor $Nd_{2-x}Ce_xCuO_{4-\delta}$. It is found that in the case of the undoped and thus insulating compound a singlet final state corresponding to the ZRS is present at the top of the valence band very much in the same way as in the case of hole doped compounds. In the case of optimum doping, the near Fermi edge intensity is lower, but there is still a hole contribution at the Fermi level. In contrast to the hole doped compounds there is, however, no well separated singlet state at the Fermi level. This difference in the nature of the hole states put severe constraints on any hole type contribution to the superconductivity.

The experiments were carried out at the helical undulator based beam line ID12B of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.[13] The electron monochromatization and detection was done with an 140-mm mean radius hemispherical analyzer equipped with a mini-Mott spin detector.[14] The analyzer is mounted at a 60° angle relative to the incident light, and has an angular acceptance of $\pm 20°$. The mini-Mott detector has a Sherman function of 0.17 at 25-keV electron energy, and the total energy resolution including monochromator and analyzer was set to 0.75 eV. Single crystals of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ (NCCO) and Nd_2CuO_4 (NCO) were grown by the traveling solvent floating zone method.[15,16] The superconducting sample had a

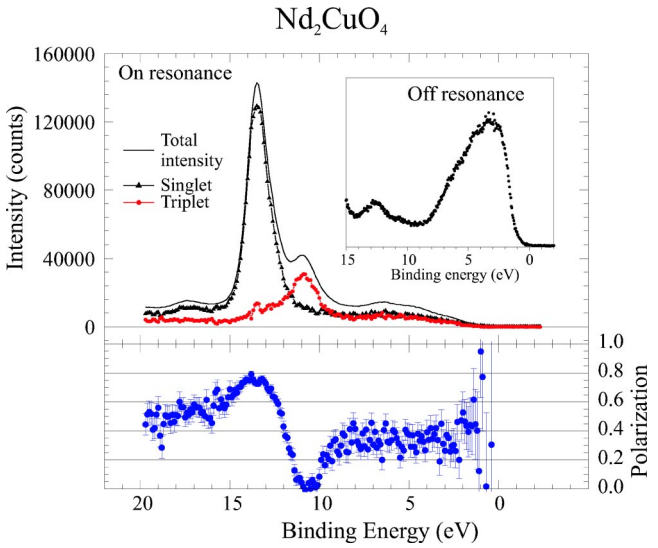

FIG. 1. (Color online) Spin polarized photoelectron spectra from Nd_2CuO_4 recorded with the photon energy tuned the Cu L_3 absorption threshold. The upper part of the figure shows the spin integrated spectrum together with a separation of singlet and triplet contributions (see the text). In the lower part of the figure, the corresponding spin polarization is shown. The inset in the upper part of the figure shows the valence band spectrum measured off resonance.

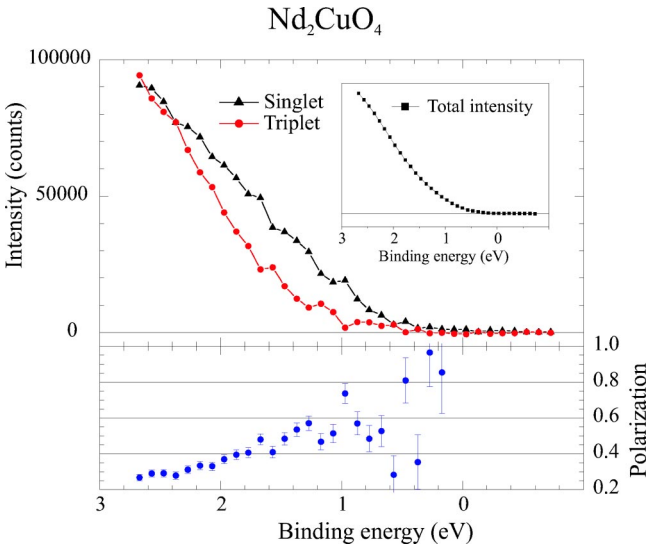

FIG. 2. (Color online) Near Fermi edge spectrum of Nd_2CuO_4. The lower part of the figure shows the spin polarization and the upper part the singlet/triplet intensity together with the total intensity (inset).

critical transition temperature $T_c = 21K$ after reduction in flowing N_2 at 900 °C for 30 h. All samples were cleaved and measured at a temperature of $\approx 25K$. The pressure in the experimental chamber was below 5×10^{-11} mbar during the measurements and the samples showed no signs of degradation during the 36-h measurement period. In order to avoid asymmetry problems and drift in the experimental setup, the spectra were collected with both light helicities and in alternating order. By doing this, any difference in detection efficiency between the two spin channels is eliminated.

In Fig. 1, we show the NCO valence band measured with the photon energy tuned to the Cu L_3 absorption maximum at $h\nu = 931.5$ eV. The zero of the binding energy scale was determined by measuring the Fermi edge of a silver foil mounted in electrical contact with the sample. With the photon energy tuned to the Cu L_3 white line, the final state of the absorption process is dominated by the $2p^5 3d^{10}$ state.[17,18] As a result, the main contribution to the spectrum in the top part of Fig. 1 comes from the $3d^8$ final state, with the ^1S, ^1G, and ^3F states clearly visible. The total intensity spectrum, which is simply the sum of the two spin channels, shows the same features as has been reported previously.[17] The inset in Fig. 1 shows the off resonance valence band spectrum recorded with a photon energy of 927.5 eV i.e., 5 eV below the Cu L_3 absorption maximum. The Cu $^1G + {}^3F$ states can still be seen off resonance, but the intensity ratio to the lower binding energy part of the valence band is quite different since there is no enhancement of Cu $3d^8$ states in this case. Furthermore, the low binding energy part of the valence band has a different shape due to a non-negligible Nd $4f$ contribution.[4] In the lower part of Fig. 1 the spin polarization of the on resonance spectrum is shown. This is the difference between the two spin channels divided by the total intensity. The polarization has been compensated for the Sherman function and the degree of circular polarization of the light (92%). The error bars indicate the statistical uncertainty in the polarization, but do not take into account systematic errors due to uncertainties in the polarization rate and Sherman function. These latter errors are estimated to $\leqslant \pm 6\%$ of the measured polarization. It is seen that there is a strong variation in the measured polarization throughout the valence band. The peak at ≈ 13.5 eV which can be assigned to a ^1G atomiclike state has a rate of polarization close to 80%, whereas the feature at 11-eV binding energy which is of ^3F character shows a 0% polarization. Assuming a $3d^9$ ion, with an initial hole in a x^2-y^2 orbital and the E vector of the light in the x-y plane, a straightforward calculation of the expected polarization for a pure singlet or triplet state gives 83.3% and -27.8%, respectively.[19,20] These values can be used to decompose the total intensity spectrum into its singlet and triplet contributions, since $Pol_{TOT} = 0.833 Int_S - 0.278(1 - Int_S)$ with the sum of singlet and triplet intensity $Int_S + Int_T = 1$. Such a decomposition is shown in the upper part of Fig. 1. As expected, the features at ≈ 17.5 and ≈ 13.5 eV are almost of pure singlet character, while the 11 eV feature is almost of pure triplet character. Approaching the top of the valence band, the uncertainty in the measured polarization diverges due to decreasing count rate and no conclusions about the spin nature of these states can be drawn.

In order to study the polarization of the part of the valence band closest to the Fermi level, a more detailed and well-counted spectrum of the upper part of the valence band was collected. This spectrum is displayed in Fig. 2. Apart from the energy range and step, the spectrum was measured under the same conditions as the one in Fig. 1. Here it can be seen that there is an increase in polarization as the valence band top is approached from a higher binding energy, indicating an increasing singlet contribution to the spectrum. Decomposing the spectrum as before, we see, in the upper part of

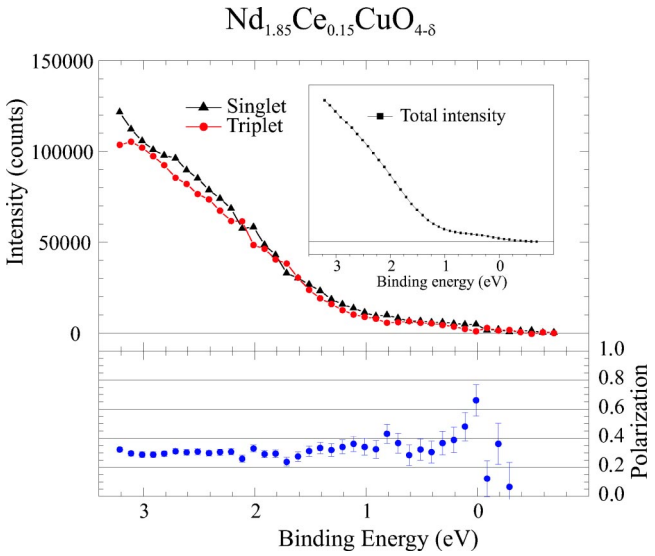

FIG. 3. (Color online) Near Fermi edge spectrum of optimum doped $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. The lower part of the figure shows the spin polarization and the upper part the singlet/triplet intensity together with the total intensity (inset).

Fig. 2, that the top of the NCO valence band is dominated by a singlet state. Since the photoemission process ejects an electron, the final state thus has an added hole, and as such is similar to what happens when holes are introduced through doping. In the upper part of the valence band, however, the extra hole is not located on the copper site but distributed on the surrounding oxygens $3d^9\underline{L}$.[10,21] These states are probed in our experiment through the hybridization between the $3d^8$ and $3d^9\underline{L}$ states. Even though this hybridization is rather weak, the $3d^9\underline{L}$ contribution can still be measured because of the very strong resonant enhancement at the Cu L_3 edge. The singlet state at the top of the NCO valence band is thus a $3d^9\underline{L}$ singlet, and can therefore be identified as the ZRS. This is similar to what has been previously observed in CuO, $Sr_2CuO_2Cl_2$, $Bi_2Sr_2CaCu_2O_{8+\delta}$, and $La_{2-x}Sr_xCuO_4$.[11,12,19,20] The undoped parent compound to NCCO is thus similar to other cuprates in this respect. This establishes the important fact that the parent compound for the electron doped high-T_c superconductor has the same type if spin states at the top of the valence band as do the parent compounds of the hole doped cuprates.

Having established the common starting point for hole as well as electron doped cuprates, it is now possible to consider the case of optimum doping. As mentioned earlier, transport measurements[5,6] indicate the presence of hole type carriers even in the optimum doped compound. It is therefore of quite some interest to determine whether the holes still present in the optimum doped NCCO behave in a similar manner to those in the hole doped compounds.

In Fig. 3, near Fermi level data on optimum doped NCCO are presented. The on resonance intensity near the Fermi level is very low, making the measurement rather difficult. This low but nonzero intensity is of course an indication of a weak but existing two hole contribution to the photoemission final state at the Fermi level. Because of the low intensity it is important to consider the influence of nonresonant contributions to the measured spectrum. Due to the nature of the resonance in the present case as well as the choice of photon energy, the nonresonant contribution can be shown to be very small.[22,23] The on resonance emission can therefore be considered as being dominantly of autoionization origin and no correction of the data has therefore been performed. This means that the polarization measured close to the Fermi level is representative of a two hole final state. As seen from Fig. 3, the polarization is more or less constant across the spectrum. Very close to the Fermi level, there are a few points that show a deviation in the polarization that is larger than indicated by the error bars. Again using the polarization values to separate the spectrum into singlet and triplet contributions it is, however, clear that there is no well separated singlet state at the Fermi level in stark contrast to the undoped case. The one or two points that seem to indicate an increase in polarization right at the Fermi level are most likely due to the same type of divergence because of low countrate as seen in Fig. 2.[24] The important fact is that the singlet/triplet spectra show no sign of any clear ZRS. In other words, the doping destroys the stability of the two hole singlet state. In many theoretical treatments such as the single band Hubbard model[25] or the t-J model,[26–29] the basic quasiparticle state is implicitly assumed to be the ZRS. If the hole contribution in NCCO plays a crucial role in the occurrence of superconductivity, as has been suggested,[5] then the relevant quasiparticle states are no longer the ZRSs. The existence of a well defined singlet state in several undoped and hole doped compounds[11,19,20] seems to indicate that the existence of the ZRS is intimately related to the occurrence of hole type superconductivity and that any hole type contribution in NCCO would be of a different nature. Since this scenario seems rather unlikely in our view, the most likely conclusion is that the hole contribution to the superconductivtiy in NCCO is not important. On the other hand, if the states relevant for the superconductivity are considered to be of mostly $3d^{10}$ character then there is a natural hole-electron symmetry in the sense that the $3d^{10}$ state is of course also a singlet.

In conclusion, we have shown that Nd_2CuO_4, the parent compound of the high temperature supeconductor $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, shows a clear Zhang-Rice state at the upper part of the valence band. This establishes an important similarity in the electronic structure of the parent compounds for hole and electron doped superconductors. Upon doping with electrons, the similarity is destroyed in the sense that no clear Zhang-Rice singlet can be observed in the optimally doped compound in contrast to the hole doped compounds. This indicates that the remaining holes in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ do not play a role in the occurrence of superconductivity in contrast to what has previously been suggested on the bases of transport measurements.

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[24] When the total number of counts is sufficiently low i.e. right at the Fermi level, the statistical error bars will no longer give a proper value for the uncertainty in the measured polarization.
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