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Angle resolved photoemission spectroscopy study of the spin-charge separation in the strongly correlated cuprates $SrCuO_2$ and Sr_2CuO_3 with S = 0 impurities

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ABSTRACT

We present the results of an Angle-Resolved Photoemission Spectroscopy study on the pristine and doped quasi-one dimensional spin chains cuprates: $SrCuO_2$, $SrCu_{0.99}M_{0.01}O_2$ with ($M = Mg^{2+}$ or Zn^{2+}), Sr_2CuO_3 and $Sr_2Cu_{(1-x)}Ni_xO_3$ with ($x = 0.01$ or 0.02), where the dopant is a non-magnetic impurity. Both systems are quantum critical and obey the Tomonaga-Luttinger spin liquid theory. Due to low dimensionality, the separation of the degrees of freedom of the collective excitation modes of spin and charge occurs, resulting in two distinct band dispersions ascribed to spinon and holon quasi-particles, at a binding energy of about 1.2 eV. Several experimental probes show that the finite size effect, in these strongly correlated electron compounds, resulting from chains breaking by the non-magnetic impurities, has a strong impact on the ground state of their quasi-particles excitations. On the other hand, our Angle Resolved Photoemission Spectroscopy data do not show any evolution of the spinon branch upon doping, in terms of energy position at Γ. We also extract the antiferromagnetic superexchange coupling and inter-site hopping constants J_{AF} and t.

1. Introduction

The combination of strong electronic correlations and low dimensionality in quantum critical systems results in exotic effects [1], such as modifying the ground state and propagation of the related quasi-particle excitations. Among the family of cuprates, the quasi-one-dimensional (1D) $SrCuO_2$ and Sr_2CuO_3 are found to be well described within this picture [2,3]. Both systems are Mott insulators and carry half-integer spin chains of Cu^{2+}, along the c and b-crystallographic directions, respectively. This arrangement of Cu^{2+} results in half-filled Cu $3d_{x^2-y^2}$ orbitals, which trigger strong inter-site electronic repulsions.

While Sr_2CuO_3 is a linear chain compound, $SrCuO_2$ carries a zigzag chain of Cu-ions, and both cuprates behave as quasi-1D Tomonaga-Luttinger spin liquids. Evidence for the existence of elementary half-integer spin excitations, or spinons, has been revealed in both systems, by Inelastic Neutron Scattering (INS), Raman scattering, and heat transport measurements [4–9]. Spinon quasi-particles propagate one-dimensionally along the spin chains direction, and their magnetic excitations spectrum consists in a two-spinon continuum [7].

The effect of low-dimensionality has also been reported to "deconfine" the spin, charge and orbital degrees of freedom of the electron, just as predicted from the Tomonaga-Luttinger theory. This results in the emergence of distinct dispersive bands for the corresponding collective excitation modes, namely: spinon and holon, probed by Angle-Resolved Photoemission Spectroscopy (ARPES) [10–16] in $SrCuO_2$ and Sr_2CuO_3, and spinon and orbiton, probed by Resonant Inelastic X-Ray Scattering (RIXS) [17] in Sr_2CuO_3.

Even if the spin-charge separation has been predicted to occur in these systems [12], it has only been evidenced later by ARPES

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[10,14], thanks to technological improvements of the technique. Kim et al. [14] reported the direct observation of the two distinct bands ascribed to spinon and holon dispersion in $SrCuO_2$, while Fujisawa et al. reported the same observation in Sr_2CuO_3 [10].

On the other hand, spinon quasi-particles have been reported to be highly sensitive to the finite size-effect in both low-dimensional systems [18–23]. Indeed, substitution by fractional amounts of non-magnetic impurities (1–2 %), on the copper site, has been proven to unexpectedly open a spin pseudo-gap in the low energy region of the magnetic excitations spectra of the corresponding compounds. The magnitude of the spin pseudo-gaps is shown to lie in the range of ∼6–8 meV. The pseudo-gap scales with the amount of dopant as Δ, the gap value, is directly proportional to x, the amount of substitution.

The first observation of the pseudo-gap opening has been made by F.Hammerath et al [23]. in the Ca-doped $SrCuO_2$ compound, with 10% Ca substitution on the Sr site. Simutis et al. [18] reported the same behaviour in the Ni-doped $SrCuO_2$, with only 1% Ni doping on the copper site. Nuclear Magnetic Resonance (NMR) and INS studies have then been extended to series of S = 0 doped materials including Mg, Pd, and Zn-doped $SrCuO_2$ and Ni-doped Sr_2CuO_3. The measurements revealed the same systematic response to the finite size effect, namely, spin pseudo-gaps opening in the low energy region of the, basically, gapless two spinons-continuum [19–21]. What is interesting is that the effect of the pseudo-gap in the 1%Ni-doped $SrCuO_2$, by means of the depletion of the density of states at low energies, is shown to remain up to 250 K. At 250 K, the size of the gap, which is convoluted to an envelope function, is decreased by only half in amplitude [18]. It is worth mentioning here that square planar coordinated Ni ions in $SrCuO_2$ are non-magnetic (S = 0), as demonstrated by NMR, X-ray Absorption Spectroscopy (XAS) and magnetic susceptibility measurements [21,24,25].

Thus, as the spinon propagation can be probed by ARPES, as well, the spin gap issue motivated our current work. We investigate the finite size effect on the spin-charge separation in the S = 0 substituted systems. We study the evolution of the spinon band in terms of energy as a function of doping in the 1% and 2% Ni-doped Sr_2CuO_3 and 1% Mg or Zn-doped $SrCuO_2$, where Ni, Mg, and Zn substitute the copper site, with, each time, S = 0.

2. Experimental

Our APRES measurements were carried out on the CASSIOPEE beamline of Synchrotron SOLEIL. High quality single crystals of $SrCuO_2$, $SrCu_{0.99}M_{0.01}O_2$ with (M = Mg or Zn), Sr_2CuO_3 and $Sr_2Cu_{(1-x)}$ NixO3 with (x = 0.01 or 0.02) were used. The crystals were grown by the traveling solvent floating zone method as described in [20]. In order to ensure electrical grounding, the insulating samples were in electrical contact with the sample holder, by means of colloidal graphite. The samples were then cleaved *in-situ*, under ultra-high vacuum at 10^{-11} mbar. The cleavage planes correspond to the [h, 0, l] and [0, k, l] planes for $SrCuO_2$ and Sr_2CuO_3, respectively, as determined from Laue diffraction. All the crystals were aligned with the spin chains parallel to the vertical slits of the detector. The measurements were performed at 300 K (Sr_2CuO_3, $Sr_2Cu_{0.99}Ni_{0.01}O_3$) and 200 K (pristine and doped $SrCuO_2$, Sr_2CuO_3, $Sr_2Cu_{0.99}Ni_{0.02}O_3$), in order to avoid charging effects. The incident photons energy was 57 eV and the data were collected using light with linear-horizontal polarization, perpendicular to the spin chains.

3. Results

In order to evaluate the doping impact on the spin-charge separation, we, first, determined the energy position of the spinon band at the high symmetry Γ point. Indeed, the spin- charge separation occurs in the range $k_{//}$= [- $\frac{\pi}{2}$, $\frac{\pi}{2}$] [10,14], where the center of the spinon band is at Γ. Therefore, as the spinon propagation is a direct consequence of the spin-charge separation, any changes in the energy position of the former should have an impact on the latter.

However, as the samples are insulating in nature, a procedure was established for data acquisition in order to avoid misinterpretations due to charging problems and allow comparisons between different scans. We followed the following steps:

- We measured the valence band dispersion, down to 7 eV binding energy, over one entire Brillouin Zone (by performing a θ scan, perpendicular to the analyser slits) in order to obtain constant-energy maps including the spinon and holon branches, and determine precisely the Γ point.
- We performed a wide energy E-k scan, at Γ, in order to determine the positions of the Sr 4p core level.
- We used the Sr 4p level, at 18.5 eV binding, energy as reported from X-ray photoelectron spectroscopy for Sr_2CuO_3 [26], to determine the Fermi level, defined as the zero of binding energy from the previously known binding energy of the Sr core-level.
- We scaled the whole scans to the deduced Fermi level, and then extracted the corresponding spinon band binding energy.

Fig. 1a. Shows the E-k map around Γ, with a large energy window, collected on the Mg- doped $SrCuO_2$ at 200 K. k_y corresponds to the direction of the spin chains. The map evidences the Sr 4p core level, along with the valence band and the holon quasi-particle dispersion, at an electron binding energy of about [0–1.8] eV.

Fig. 1b. shows a zoom on the valence band including the highly dispersive V-shaped holon band, along with the less dispersive spinon band lying in between, as evidenced on Fig. 1c. This last E-k map has been obtained by taking the second derivative of Fig. 1b. The valence band at Γ reproduces quite well the theoretical calculations made by Z. V. Popovic *et al.* and Ngasako et al. for $SrCuO_2$ [27,28]. The valence band shows three main dispersive bands down to 6 eV binding energy. The calculated band dispersion at Γ for Sr_2CuO_3, as reported by Rosner et al. [29], and the ones measured during this work are also in qualitative good agreement.

The authors in [27,29] show that the main contribution to the density of sates (DOS) in the valence band arises from both O_{2p} and 3d orbitals of Cu which are strongly hybridized within the CuO_4 plaquettes of the spin chains. Furthermore, the constant-energy map in Fig.1d., taken at the top of the holon band, shows two quasi-one-dimensional parallel sheets attesting for the quasi-one-dimensionality of the system.

The collected E-k maps for the pristine and doped samples are similar. All of the compounds exhibit the same number of bands with no additional feature upon doping. The spin-charge separation also remained present for all the crystals with the different compositions.

Now, using the aforementioned procedure, the electron binding energies of the spinons bands at Γ were determined by Gaussian fits to the Energy Distribution Curves (EDCs). The resulting values are listed in Table 1. The EDCs for the pristine and doped $SrCuO_2$ compounds used for this analysis, after renormalization to the energy position and intensity of the Sr 4p level, are also given in Fig. 2. The EDCs look all similar.

The differences between peak positions in the EDCs, and their relative intensities come from slight mis-orientations of the samples, shifting the recorded maps slightly away from Γ. This misalignements could not be corrected during the experiment as the experimental setup does not allow the in-plane rotation of the sample. However, as the spinon dispersion occurs only along the