Electronic Screening-Enhanced Hole Pairing in Two-Leg Spin Ladders Studied by High-Resolution Resonant Inelastic X-Ray Scattering at Cu $M$ Edges

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We study the electronic screening mechanisms of the effective Coulomb on-site repulsion in hole-doped Sr$_{14}$Cu$_{24}$O$_{41}$ compared to undoped La$_x$Ca$_{8-x}$Cu$_2$O$_{41}$ using polarization dependent high-resolution resonant inelastic x-ray scattering at Cu $M$ edges. By measuring the energy of the effective Coulomb on-site repulsion and the spin excitations, we estimate superexchange and hopping matrix element energies along rungs and legs, respectively. Interestingly, hole doping locally screens the Coulomb on-site repulsion reducing it by as much as 25%. We suggest that the increased ratio of the electronic kinetic to the electronic correlation energy contributes to the local superexchange mediated pairing between holes.

As pointed out by Hubbard, electronic screening in condensed matter systems is an example for a correlation effect [1]. Recent examples of the importance of electronic screening processes are the phase transitions in correlated materials such as in Ca$_{60}$ [2] and in the BaFe$_2$As$_2$ family [3].

Quasi-one-dimensional spin-ladder compounds (SLCs) such as (La, Sr)$_{14-}$(Ca, Sr)$_{8}$Cu$_{24}$O$_{41}$ are an ideal example to study electronic screening effects of correlations energies; i.e., correlation energies are lower when electronic screening of Coulomb interactions is present. The SLCs have as a key-structural element copper-oxygen bonds that form Cu$_2$O$_3$ ladders and CuO$_2$ chains [4]. They contain the basic physics given by the competition between the kinetic energy determined by the hopping matrix elements $t$, the electron-electron interaction (or electronic correlation) energies driven by on-site Coulomb repulsions, and super-exchange energies $J$. Indeed, SLCs show striking properties: superconductivity under high pressure [5], a gapped spin-liquid state [6], charge-density waves [7–11], as well as a paired-hole state [12,13]. This rich physics is a result of competing energy scales that foster a large number of nearly degenerate ground states [13–17].

In this Letter, we study in unprecedented detail the screening of electronic correlation energies, super-exchange, and kinetic energies in undoped La$_x$Ca$_8$Cu$_{24}$O$_{41}$ (LCCO) and hole-doped Sr$_{14}$Cu$_{24}$O$_{41}$ (SCO). We have developed and used a vacuum-ultraviolet (VUV) off-axis parabolic double-monochromator Raman spectrometer for high-resolution resonance inelastic x-ray scattering (RIXS) at the Free Electron Laser Hamburg (FLASH) of DESY. This allows us to measure and distinguish magnetic and phonon excitations with orbital selectivity at the Cu $M_3$ edges (Cu-$3p$ $\rightarrow$ 3$d$) and the Cu $M_1$ edge (Cu-$3s$ $\rightarrow$ 4$p$), and thus to reveal the electronic correlation and super-exchange energies, which are then used to determine the hopping matrix elements in LCCO and SCO. The energy resolution was set to $\sim$24 meV. We have used sandblasted Si as the reference to further define elastic, Stokes, and anti-Stokes lines for calibration purposes. All RIXS spectra were corrected to the FLASH intensity. The samples were characterized using resonant soft x-ray scattering, x-ray absorption [9,11,12], and UV-Raman spectroscopy [13]. More details on the RIXS measurements are shown in the Supplemental Material [18].

Figures 1(a) and 1(b) display x-ray absorption spectroscopy (XAS) and FLASH intensities at the Cu $M_3$ edge and Cu $M_1$ edge from SCO, respectively. Figure 1(c) shows a schematic diagram of the electronic band structure of LCCO and SCO. The bare electronic correlation can be described by the bare Coulomb on-site repulsion ($U_{dd}$ $\sim$ 10–12 eV for cuprates [2,23,24]) defined by the Cu-3$d$ orbitals. This splits Cu-3$d$ states exhibiting the bare lower Hubbard band (LHB) and the bare upper Hubbard band (UHB). However, a downfolding of the Hamiltonian,
i.e., representing electrons from high energy bands by effective electrons from low energy bands, would screen $U_{dd}$ yielding to a reduced effective Coulomb on-site repulsion [25]. In this scenario, the effective low energy band needs to be clearly separated and decoupled from high energy degrees of freedom and, very importantly, there is only one dominant effective correlation energy, and without involving O-$2p$ orbitals. On the other hand, in SLCs the $O-2p$ bands are closest to the Fermi level [9,12] and thus may strongly affect the effective low energy bands. Strong hybridizations between Cu-$3d$ and O-$2p$ orbitals [15,23] influence $U_{dd}$ and further modify the bare LHB and bare UHB, normalizing them to an effective LHB and effective UHB, respectively. We call this $U_{pd}$, an effective electronic correlation energy due to strong Cu-$3d$ and O-$2p$ hybridization. This view is further supported by the fact that in doped SCO the holes have more O-$2p$ character [9,12]. Theoretically, but yet to be proven experimentally, doping should, therefore, result in a significant change in $U_{pd}$ and this can, in principle, yield an anisotropic $U_{pd}$ [25]. Our $M$-edge RIXS measurement aims to reveal $U_{pd}$ and its anisotropy, if any, for undoped LCCO and doped SCO.

By tuning the incoming photon energy to the $M_3$ edge, effective electronic correlation energies can be studied through the so-called resonance effect. Hereby, we are accessing spin excitation via matrix elements outlined in Figs. 1(d)–1(g) as discussed later. Upon doping, the O-$2p$ orbitals host the holes [9,11]. Furthermore, because the Cu-$3d$ orbitals hybridize with the O-$2p$ orbitals close to the Fermi level [see Fig. 1(c)], they determine the properties of the low-energy electronic states [12,26]. In contrast, the Cu-$4p$ orbitals reside well above the Fermi level and hybridize with the O-$3p$ orbitals, thus allowing the coupling of photons to oxygen related phonons at the $M_1$ edge [see also Fig. 1(c)].

Figure 2(a) highlights the different nature of the excitations for the Cu $M_1$ and $M_3$ edge. Indeed, we observe strong phonon excitations for incident photon energies of $\sim 122$ eV and spin excitations for incident photon energies of $\sim 80$ eV. At $\sim 122$ eV strong two-phonon scattering can be seen at 120 meV in agreement with visible Raman scattering [13,27]. Figure 2(b) shows the high-resolution

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FIG. 2 (color online). (a) Raman spectra (Stokes side is denoted by negative energies) taken at 79.3 and 122.0 eV from the hole-doped Sr$_{14}$Cu$_{24}$O$_{41}$ (SCO) with the polarization along the rung (E $\parallel \hat{a}$) and the elastic line from sandblasted Si for reference. (b) Contour plot of the incident photon energy versus excitation energy (Raman shift) of SCO for E $\parallel \hat{a}$ showing the resonance behavior of the low-energy phonon excitations. The scale of contour plots is shown.
resonance profile at the Cu-M\(_1\) edge with a resonance energy of 122.5 eV. For increasing incident photon energies, we observe the development of one-phonon scattering from oxygen modes below 100 meV Raman shift also in agreement with Raman scattering [13,27]. As reference, for Si, we only observe elastic contributions. At \(\sim 80\) eV higher-energy inelastic scattering can be seen from double spin-flip-two-magnon excitation.

Our main observation relates to the dependence of the spin-flip excitation spectrum on the incident photon energy, polarization, and with doping as shown in Fig. 3. The resonance dependence of the excitation spectrum of LCCO can be seen in Figs. 3(a) and 3(b) as a contour plot for polarizations along the rung (\(E \parallel \hat{a}\)) and the leg (\(E \parallel \hat{c}\)), respectively. In Figs. 3(c) and 3(d) spectra at selected energies of 78, 79, and 80 eV are displayed for \(E \parallel \hat{a}\) and \(E \parallel \hat{c}\), respectively. For the lowest energy close to the XAS edge at 78 eV, a strong excitation is evident at around 90 meV Raman shift that corresponds to a one-magnon excitation [28–30] at the spin-gap energy with momentum transfer \((q) \approx 0\). The one-magnon excitation couples to photons by a finite spin-orbit coupling (\(\sim 280\) meV) of the Cu-3\(d\) orbitals [31,32]. Interestingly, the one-magnon excitation exhibits a strong anisotropy. For \(E \parallel \hat{a}\) magnetic bonds are broken along the \(\hat{c}\) direction, along the leg of the ladder, allowing the propagation of long distance, i.e., small \(q\), magnetic excitations [see Figs. 1(d) and 1(e)]. For \(E \parallel \hat{c}\), one-magnon excitations are suppressed due to the geometry of ladders. The one-magnon excitation for LCCO is about 6 times stronger as compared to the two-magnon peak. The inset of Fig. 3(a) displays the sharp resonance of the two-magnon peak \(\sim 4\) eV above the XAS edge. A strong two-magnon excitation spectrum develops in an energy range up to \(E_{\text{mag}}^{\text{max}} \approx 400\) meV with a resonance energy of about 79.3 eV as seen in Fig. 3(a) (see inset) and Fig. 3(c).

Based on the Fleury-Loudon Hamiltonian [33] a two-magnon process that considers explicitly a transition of an electron from Cu-3\(p\) states is shown in Figs. 1(d) and 1(e). In Fig. 1(d) we display the initial state. The Cu-3\(p\) orbitals are split by the spin-orbit coupling, while the Cu-3\(d\) orbitals are split by \(U_{pd}\). The initial state relies on the dipole allowed transition due to the \((\mathbf{P} \cdot \mathbf{A})\)-matrix element from the Cu-3\(p\) orbital to the unoccupied effective UHB. This results in a doubly occupied site and a hole in the Cu-3\(p\) state forming a Cu-3\(d\)\(^{10}\) and a Cu-3\(p\)\(^{5}\) in the intermediate state costing an energy of \(\Delta_{\text{Cu3p-Cu3d}} + U_{pd}\) being supplied by the incident photon as shown in Figs. 1(f) and 1(g). In the final step we have a transition from effective UHB back into the Cu-3\(p\)\(^{5}\) emitting via the \((\mathbf{P} \cdot \mathbf{A})\)-matrix element a Raman shifted photon. The energy loss or Raman shift is then given by the effective number of broken spin bonds [cf. Fig. 1(f)]. Within an Ising model each broken bond corresponds to \(J/2\). In two-dimensional antiferromagnetic cuprates this would correspond to \(3J\), i.e., the typical energy of a two-magnon excitation. In the SLCs the anisotropy of the kinetic energy needs to be considered. This leads for a hopping along the leg to an energy of \((J_{\parallel} + J_{\perp})\) or for hopping along the rungs to \(2 \times J_1\).

The effective scattering Hamiltonian can be projected onto spin states [33] and written as

\[
H_{\text{int}}(q, \omega) = \frac{(t_{\perp}/\|)^2}{\Delta_{\text{Cu3p-Cu3d}} + U_{pd} - \hbar \omega_{\text{nc}}} \times \sum_{k, q} P(k, q) \hat{S}_{k+q/2} \cdot \hat{S}_{k-q/2} 
\]

\[
\approx J \sum_{k, q} P(k, q) \hat{S}_{k+q/2} \cdot \hat{S}_{k-q/2}. \quad (1)
\]

As displayed in Fig. 1(c), \(\Delta_{\text{Cu3p-Cu3d}}\) is \(\sim 75\) eV. Accordingly, \(U_{pd}\) affects the resonance energy of the spin excitation relative to the XAS edge. In the momentum
transfer $q \to 0$ limit, we find for incident photon energies close to the energy difference between Cu-$3p$ and Cu-$3d$ states ($\Delta E_{mag} \approx 80 \pm 10$ meV) due to the anisotropic superexchange $J_{\parallel (\perp)} = 2t_{\parallel (\perp)}/U_{pd}$ between legs (rungs) (see discussion below). Based on $M$-edge RIXS, $U_{pd}$ is isotropic [see Figs. 2(a) and 2(b)].

Upon the doping of holes into the O-$2p$ state in SCO [7,24], which is the isostructural doped counterpart of LCCO [4], we find the following striking behavior as shown in Figs. 2(e) [7,24], which is the isostructural doped counterpart of the Fleury-Loudon Hamiltonian for $q \neq 0$ limit concluding that symmetry selection rules are still valid for $q \to 0$. The dispersion of the two-magnon excitation does not represent the single-particle dispersion, but rather the $q$ dependence of the magnon-magnon interactions through the vertex correction that results in an effective $q$-dependent vertex.

For LCCO, we find surprisingly large anisotropies in intensity and in the energy of the spin-flip excitations denoted by $\Delta E_{mag} \approx 80 \pm 10$ meV due to the anisotropic superexchange $J_{\parallel (\perp)} = 2t_{\parallel (\perp)}/U_{pd}$ between legs (rungs) (see discussion below). Based on $M$-edge RIXS, $U_{pd}$ is isotropic [see Figs. 2(a) and 2(b)].

The results are summarized in Table I. For LCCO, the superexchange energy is anisotropic with $J_{\parallel} = 140 \pm 10$ and $J_{\perp} = 80 \pm 10$ meV leading to a maximum two-magnon energy of about $360 \pm 10$ meV $= E_{mag}^{\max}$ (see Fig. 3 and also the Supplemental Material [18]). Whereas the effective correlation energy is isotropic with $U_{pd} = U_{pd} = 4.00 \pm 0.03$ eV, in good agreement with local-density approximation calculations [40]. In SCO, the magnetic peaks become more isotropic leading to $J_{\parallel} = 128 \pm 10$ and $J_{\perp} = 107 \pm 10$ meV. Noting that inelastic neutron scattering [41] and $^{17}$O NMR [6] measurements suggested that $J_{\parallel}$ and $J_{\perp}$ are about 72–80 and 130–160 meV, respectively, yielding a higher superexchange anisotropy as compared to the values measured by $M$-edge RIXS. While the $J_{\parallel}$ is close to the value given by inelastic neutron scattering, the $J_{\perp}$ is slightly larger, reducing the overall anisotropy. Another surprising result is the anisotropy of $U_{pd}$ in SCO (cf. Table I). This anisotropy is essentially embedded in the downfolding procedure that would lead to an effective $U$ [25], but is shown here experimentally to be relevant. Since $U_{pd}$ and $t_{\parallel}$ vary as a function of doping, $t_{\parallel}$ change to $486 \pm 40$ and $400 \pm 40$ meV, respectively, also in good agreement with model calculations [40]. Thus, the enhancement of $J_{\perp, SCO}$ is equivalent with the reduction of $U_{pd,SCO}$ along the $\tilde{a}$ direction of about 1 eV. This is indeed confirmed by the changes in $U_{pd}$ [compare Figs. 3(a) and 3(e)]. In undoped LCCO $U_{pd}$ is isotropic, whereas in doped SCO the redistribution of holes in the rungs and legs lead to the anisotropic $U_{pd}$ [12,13]. A screening contribution of $U_{pd}$ develops predominantly along the rungs, where the holes reside in the O-$p$ orbitals and along which they pair accordingly. This effect is negligible along the legs [compare Figs. 3(e) with 3(f)]. Thus, we argue that the anisotropic screening of $U_{pd}$ along the rung triggers the formation of the paired hole state. The observed asymmetry of $U_{pd}$ upon hole doping will have strong consequences for other more isotropic cuprate systems as well.

<table>
<thead>
<tr>
<th>$J_{\parallel}$</th>
<th>140 ± 10 meV</th>
<th>128 ± 10 meV</th>
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<tr>
<td>$J_{\perp}$</td>
<td>80 ± 10 meV</td>
<td>107 ± 10 meV</td>
</tr>
<tr>
<td>$t_{\parallel}$</td>
<td>529 ± 40 meV</td>
<td>486 ± 40 meV</td>
</tr>
<tr>
<td>$t_{\perp}$</td>
<td>400 ± 40 meV</td>
<td>400 ± 40 meV</td>
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<tr>
<td>$U_{pd}$</td>
<td>4.00 ± 0.03 eV</td>
<td>3.70 ± 0.03 eV</td>
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<tr>
<td>$U_{pd,SCO}$</td>
<td>4.00 ± 0.03 eV</td>
<td>3.00 ± 0.03 eV</td>
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In conclusion, from the polarization dependent RIXS measurements, we obtain for doped and undoped SLCs the effective Coulomb on-site repulsion energy \( U_{pd} \), super-exchange energies \( J \), and estimate anisotropic hopping matrix elements \( t \) along the leg and the rung of the ladder. We find that the local pairing of holes is promoted by a local screening of the correlation energy \( U_{pd} \). Upon doping holes into the O-2p states, local screening of \( U_{pd} \) leads to a local enhancement of the superexchange and triggers the formation of the paired hole state along the rung. Our result shows the potency of high-resolution RIXS at the Cu M edges to determine competing energy scales in correlated electron systems.

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