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Charge-transfer exciton in La_2CuO_4 probed with resonant inelastic x-ray scattering

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We report a high-resolution resonant inelastic x-ray scattering study of La_2CuO_4. A number of spectral features are identified that were not clearly visible in earlier lower-resolution data. The momentum dependence of the spectral weight and the dispersion of the lowest-energy excitation across the insulating gap have been measured in detail. The temperature dependence of the spectral features was also examined. The observed charge-transfer edge shift, along with the low dispersion of the first charge-transfer excitation, are attributed to the lattice motion being coupled to the electronic system. In addition, we observe a dispersionless feature at 1.8 eV, which is associated with a *d-d* crystal field excitation.

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As the prototypical parent insulating compound, La_2CuO_4 has drawn much attention as a starting point for the study of high-temperature superconductors. La_2CuO_4 is well described as an antiferromagnetic insulator with a $d_{x^2-y^2}$ hole localized at the Cu site due to the strong electron correlations. In particular, this material is classified as a charge-transfer (CT) insulator, since the lowest-energy charge excitation across the insulating gap corresponds to transferring an electron from oxygen to a neighboring copper. This CT excitation creates a Cu^{1+} ion and an oxygen $2p$ hole that forms a Zhang-Rice singlet (ZRS) with the neighboring copper spin, the two copper sites forming a bound state.[1] Over the years, exciton formation of these electron-hole pairs has been considered by several authors as a possible low-energy elementary excitation in this half-filled copper oxide plane.[2–8] The strong magnetic interaction in this system has been pointed to as the origin of the exciton binding energy[2] as well as the large dispersion of the excitation.[4] Indeed the apparently large dispersion observed in $Sr_2CuO_2Cl_2$ using electron-energy-loss spectroscopy was attributed to a CT exciton with a small effective mass.[9]

Experimentally, optical spectroscopy and Raman scattering studies have been carried out to address the nature of the excitation spectrum near this CT gap.[10–13] Ohana *et al.*[10] directly observed the coupling of the electronic excitations to the lattice system in the resonance of phonon Raman lines at laser energies around the CT energy (2.14 eV) and a low-energy shoulder at 1.9 eV. Falck *et al.*[11] found that a polaron model was able to reproduce their reflectivity data very well for a wide temperature range. However, despite extensive experimental and theoretical studies to date, the nature of the CT exciton is still controversial. Outstanding questions include whether the electron-hole pair actually form a bound exciton state, or if they remain as a resonance state within the particle-hole continuum. Another question relates to the relative role played by magnetic interactions and/or phonons in the exciton formation and dispersion. For each of these questions, valuable information can be gained by studying the momentum dependence of the charge-transfer excitations. In recent years, resonant inelastic x-ray scattering (RIXS) has drawn considerable interest as a valuable spectroscopic tool for studying the momentum dependence of various electronic excitations in insulating cuprates such as these excitons.[14–21] However, these earlier studies have been hampered by relatively poor instrumental energy resolution.

Here we report detailed studies of electronic excitations near the CT gap in the prototypical cuprate compound, La_2CuO_4, using the highest-energy resolution to date for RIXS, 130 meV [full width at half maximum (FWHM)]. We observe several features that were previously not as clearly visible. We find that (1) the RIXS spectra are composed of multiple spectral features which exhibit complex dispersion and spectral weight change as a function of momentum transfer; (2) the two lowest-energy features observed correspond to a dispersionless *dd* excitation at 1.8 eV and a CT exciton at 2.2 eV; (3) the latter disperses with a bandwidth of $\sim$0.3 eV in the $(\pi,0)$ direction and of at least that much along (π,π), where its intensity decreases rapidly as one goes from the zone center toward (π,π); and (4) the edge of the CT excitation shifts to lower energy for increased temperatures in accordance with previous optical studies.[11] We argue that these results are consistent with a picture of a bound exciton state in the presence of strong electron-phonon (*e*-ph) coupling.

The RIXS experiments were carried out at the Advanced Photon Source on the undulator beamline 9IDB. A detailed description of the experimental setup was reported by Hill *et al.*.[22] The floating-zone-grown La_2CuO_4 sample was cooled to 27 K by a closed cycle refrigerator to reduce the phonon contribution to the background. We used the same scattering geometry as that used by Kim *et al.*[18]

The improvement in energy resolution is clearly visible in Fig. 1, in which we compare the RIXS spectra of La_2CuO_4 obtained with two different resolutions. The open square symbols represent data taken from Kim *et al.*,[18] obtained with 400 meV resolution, while the filled circles represent the data obtained in the current experiment with 130 meV resolution. Both spectra were measured with the same inci-

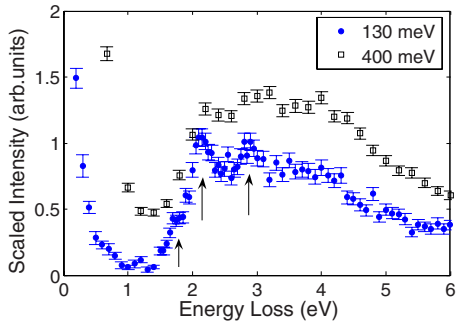

FIG. 1. (Color online) Comparison of RIXS spectra obtained using 400 meV resolution [squares, from Kim *et al.* (Ref. 18)] and 130 meV resolution (circles) used in the present work. The 400 meV spectrum has been scaled by a factor of 1/5 to display comparable inelastic intensity with the 130 meV spectra.

dent energy[23] (E_i=8992 eV) and momentum transfer $\mathbf{Q}$ =(3 0 0) in tetragonal notation. Note that the tail of the elastic line is drastically reduced in the energy range below 2 eV. Although the overall shapes of the spectral features are almost identical, the improved energy resolution allows us to see several sharp features in the spectrum. Specifically, one can identify a sharp peak at the energy corresponding to the CT gap of this material at 2.2 eV, and several spectral features at higher energies, including a prominent peak at 2.9 eV. These features have been observed in a recent study by Lu *et al.*,[20] where the incident energy was varied to elucidate the different peaks. In addition, a low-energy shoulder of the main peak at zone center is resolved at around 1.8 eV (this feature has been recently observed near the zone boundary[21]). Since the overall incident energy dependence of the spectral features at zero momentum transfer was found to be consistent with earlier studies,[18] we focus our attention on the momentum dependence at fixed incident energy in the following.

To investigate the momentum dependence, energy-loss scans were taken with the fixed incident energy at various reciprocal space points in the two high-symmetry directions: $(\pi,0)$ along the Cu-O bond, and (π,π) at a 45° angle. Each scan was normalized by the intensity of the elastic peak. Figure 2 shows the development of the spectra as the reduced wavevector $\mathbf{q}$ increases away from zone center. The zone boundary scans at $(\pi,0)$ and (π,π) look similar to earlier low-resolution data; that is, there exist two well-defined peaks at $(\pi,0)$, while only one prominent peak appears at (π,π). The progression of the spectral features as a function of momentum transfer involves both actual shifts of the peak positions as well as intensity changes in the respective peaks. In order to analyze the dispersion quantitatively, the spectra were fitted to multiple Lorentzian peaks (solid lines in Fig. 2).

The results of the fits for the two lowest-energy features are shown in Fig. 3. The salient feature of the 1.8 eV peak is its lack of energy dispersion, which suggests that this excitation is spatially localized. The most likely candidate for this excitation is a crystalline field *dd* excitation. We note that charge transfer with the surrounding O 2*p* states of the same symmetry would also be involved.[8,13] This peak assignment is consistent with earlier studies using different experimental techniques, such as large-shift Raman scattering,[13] Cu *M*-edge RIXS,[24] and *L*-edge RIXS.[25] In addition, the 1.8 eV shoulder was also observed near the zone boundary in a recent *K*-edge RIXS study by Collart *et al.*,[21] and likewise attributed to a crystal field excitation. It is interesting to note that the *dd* excitation is much stronger than the CT excitation (at 2.2 eV) in the *L*-edge spectra, and vice versa in our *K*-edge spectra. Since the intermediate state of the *L*-edge RIXS directly involves Cu *d* orbitals, it would have large overlap with the final state of the *dd* excitation, and generate

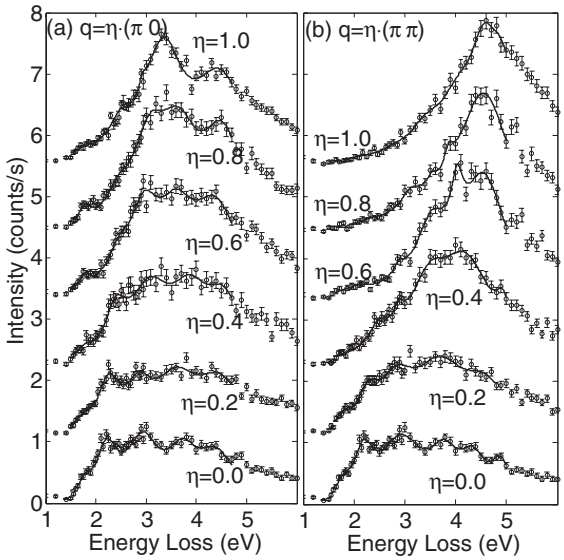

FIG. 2. Momentum dependence of the RIXS spectrum along the (a) $(\pi,0)$ and (b) (π,π) directions. The incident energy is 8992.5 eV. All curves are normalized by the elastic peak intensity during each scan, and shifted along the intensity axis for clarity.

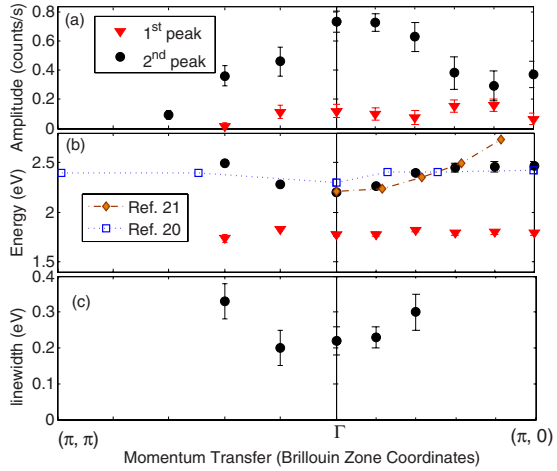

FIG. 3. (Color online) Momentum dependence of fitting parameters: (a) amplitudes, (b) center positions, and (c) Lorentzian widths (FWHM). Due to the vanishing spectral weights, the energies and widths were only reliably determined until about halfway across the Brillouin zone in the (π,π) direction. Included in the energy dispersion plot is a comparison with the results from other recent studies (Refs. 20 and 21).

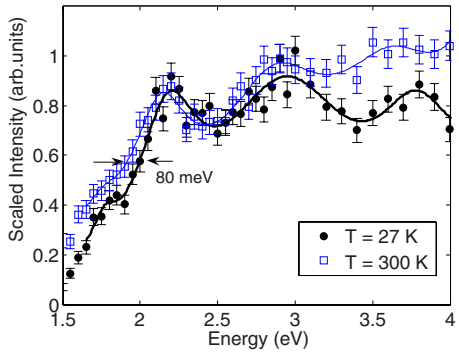

FIG. 4. (Color online) Comparison of the zone center spectra at $T=27$ and 300 K. The two spectra were scaled to match their intensities at 10 eV energy loss.

large *dd* intensity as predicted by Tanaka *et al.*[26]

The next peak, corresponding to the main sharp feature at $\omega \sim 2.2$ eV in Fig. 1, was seen in previous RIXS and optical conductivity studies and widely associated with the excitation across the CT gap.[27] The dispersion of the CT excitation is shown in Fig. 3(b). A direct gap is exhibited, with a total bandwidth along the $(\pi,0)$ direction of around 0.3 eV. This observation of a small bandwidth is in contrast to the earlier report of ~1 eV bandwidth observed with a lower-resolution setup,[18] but is consistent with the small bandwidth ($\leq$0.5 eV) observed in more recent RIXS studies[19–21] as shown in Fig. 3(b). We note that our energies near $(\pi,0)$ seem to match well with those of Lu *et al.*[20] In contrast, the dispersion we observe matches very well with that of Collart *et al.*[21] from low q's up to two-thirds of the way toward the zone boundary, but then the two studies disagree for the last point. This is not entirely surprising, since the 2.2 eV peak loses intensity near the zone boundary and becomes a shoulder of the higher-energy peaks, making energy determination more uncertain, especially in the case of lower resolution.

The observed bandwidth is in fact very close to that of the ZRS band of the insulating cuprates.[28] Along the (π,π) direction, the intensity of the 2.2 eV peak decreases, and the peaks eventually becomes unobservable around the halfway point across the zone. Similar dramatic momentum dependencies of the spectral weight have been predicted for certain CT excitons.[4,8] We also note that the peak width is not limited by resolution, and broadens as q increases, as shown in Fig. 3(c), suggesting that the excitation becomes less well defined at larger momentum transfers. Such a result would be expected if there are more decay channels available at higher q.

We have also obtained the zone center spectrum at 300 K which is compared to the 27 K scan in Fig. 4. Since the elastic intensities vary at different temperatures, the two spectra were in this case scaled to match the intensities of their Cu $K\beta_5$ emission lines, which are at 10 eV. Note that the CT peak intensity also happens to match when this normalization scheme is used, which is appropriate for comparing shifts in the CT gap edge. A redshift of ~80 meV is seen in the CT gap edge, measured at $\omega=2$ eV as shown in the figure. Sources of error in this shift determination include uncertainty in the energy-loss scale, and possible incident energy variations between the two scans. The effect of the latter was found to be negligible; even for relatively large changes in the incident energy (500 meV), the fitted edge of the CT peak did not shift by more than 5 meV. One contribution to the error in energy-loss scale between the two scans is the zero-loss reference, determined by fitting the elastic line, and is accurate to within 10 meV. Thus, we conclude that the observed shift is mostly due to the temperature change, and agrees with the ~100 meV shift observed in optical reflectivity measurements.[11] We would like to point out that, although the RIXS spectrum has often been compared with the corresponding optical spectrum, it has been difficult to draw direct correlation between the features observed in the two spectroscopies. The same thermal behavior of the 2.2 eV peak from the RIXS and the reflectivity measurement[11] implies that these peaks have the same origin.

One of the outstanding questions is whether or not the 2.2 eV peak seen in these data indeed corresponds to a two-copper-site, bound exciton as described by a Zhang-Ng-type model.[4] One might use the nonzero peak width, indicative of a relatively short lifetime, to argue against a bound-exciton-type picture. However, we argue that in fact a bound exciton is a good description of the data. As possible explanations for the finite peak width, we point to the possibility of multiple excitations within the instrumental resolution, or alternatively intrinsic broadening mechanisms associated with the antiferromagnetic lattice.[29] A third possibility is that the observed broadening of the RIXS peak as q is increased could result from the unbinding of the exciton. In this proposed scenario, the exciton energy lies just below the upper Hubbard band. Increasing q causes the bound exciton to disperse into the electron-hole continuum, decreasing the lifetime of the exciton and broadening the associated peak. This picture is somewhat similar to the situation in the one-dimensional system Sr_2CuO_3 [Fig. 2(b) of Neudert *et al.*[30]], but the bound exciton exists near the zone center in La_2CuO_4. Note that the binding energy of this exciton must be very small, since a large increase of the photoconductivity was observed just above the gap.[31] With these possible explanations for the observed nonzero peak width, it is reasonable to suppose that the 2.2 eV peak is indeed the lowest-energy CT exciton.

The relatively small overall magnitude of the observed dispersion would be expected if the excitations are strongly coupled to phonons, which will give them a high effective mass. On the other hand, a purely electronic model with only magnetic degrees of freedom (such as the Zhang-Ng model[4]) predicts much larger dispersion than that observed, since singlet exciton propagation does not disturb a magnetically ordered spin background. Thus, our results support a picture in which the e-ph interaction plays an important role in the exciton dispersion. This is also consistent with the optical reflectivity study.[11] Presumably the same mechanism, namely, a temperature-dependent e-ph interaction is also responsible for the observed redshift of the RIXS peak.[32,33]

Finally, the higher-energy excitations are somewhat more difficult to interpret, given the large overlap with each other and uncertainties in the fitting, and we can provide at most speculations about them. However, there is a clear peak in Fig. 2 at 2.9 eV which shows little or no energy dispersion, and whose amplitude decreases along the (π,π) direction

but not along $(\pi,0)$, where it can be seen as a shoulder to the main peak at the zone boundary. This could be the dispersionless $b_{1g}e_u(\pi)$ two-center exciton discussed by Moskvin *et al.*[8] At the zone boundaries, there are strong peaks at 4.5 eV for $\mathbf{q}=(\pi,\pi)$ and 3.3 eV for $\mathbf{q}=(\pi,0)$. The narrowing of the latter feature gives the appearance of neighboring modes drawing together as q approaches the zone boundary, likely involving strong interaction between the modes.[8]

In summary, we have studied the electronic excitations near the charge-transfer gap of La_2CuO_4 using high-resolution resonant inelastic x-ray scattering, observing a dispersionless *dd* excitation at 1.8 eV, and a weakly dispersive CT exciton at 2.2 eV at the Brillouin zone center, as well as higher-energy peaks. Away from the zone center, the CT exciton peak broadens and disperses to higher energy, while losing its spectral weight. Its observed bandwidth is similar to that of the ZRS,[28] and is much smaller than previously reported values, but in accordance with recent studies.[20,21] This small bandwidth of the exciton dispersion, as well as the observed temperature dependence, underscores the importance of the e-ph interaction in insulating cuprates. It is clear that further theoretical study of exciton behavior in the presence of strong e-ph interactions would be useful for quantitative understanding of the electron correlations in cuprates.

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