Resonant Inelastic X-Ray Scattering Study of Charge Excitations in La_2CuO_4

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We report a resonant inelastic x-ray scattering study of the dispersion relations of charge-transfer excitations in insulating La_2CuO_4. These data reveal two peaks, both of which show two-dimensional characteristics. The lowest energy excitation has a gap energy of $\sim$2.2 eV at the zone enter, and a dispersion of $\sim$1 eV. The spectral weight of this mode becomes dramatically smaller around (π, π). The second peak shows a smaller dispersion ($\sim$ 0.5 eV) with a zone-center energy of $\sim$3.9 eV. We argue that these are both highly dispersive exciton modes damped by the presence of the electron-hole continuum.

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Understanding strongly correlated electron systems, such as the cuprate superconductors, remains at the heart of much of the current condensed matter research. As a first step toward elucidating electron correlation effects in these systems, it is important to study the behavior of elementary excitations using various spectroscopic tools. For example, angle-resolved photoemission has become an indispensable probe for studying the excitation spectrum of a single quasiparticle [1,2], while inelastic neutron scattering has been invaluable in the investigation of low-energy collective modes (1 $\sim$ 100 meV), such as phonons and magnons [3]. However, until now, only limited information has been available on collective excitations at an energy scale on the order of $\sim$1 eV. This is unfortunate, since in this energy range, the electron dynamics are governed directly by the various hopping integrals and by the Coulomb interaction. Thus, an investigation of the dispersion relations of such collective charge excitations would yield invaluable information for any microscopic theory of charge dynamics in the copper oxides.

In this Letter, we present a detailed study of the momentum dependence of the charge excitations in La_2CuO_4, utilizing resonant inelastic x-ray scattering (RIXS). In the simplest picture of this insulating cuprate, the ground state consists of one hole per copper ion (Cu^{2+}), and the low-lying electronic excitations include excitons formed via a charge-transfer (CT) process, in which charge is moved from the oxygen onto the copper [4–6]. Specifically, an electron-hole pair, created by exciting an electron from the valence band—the Zhang-Rice (ZR) band [7]—to the conduction band across the CT gap, can form a bound exciton state as a result of the Coulomb interaction. This CT exciton is expected to have a large dispersion, since it has zero spin and can move without disturbing the antiferromagnetic order of the copper oxide plane. Consistent with this, our high-resolution measurements have enabled us to identify an excitonlike feature at 2.2 eV with a dispersion of 1 eV. In addition, a second peak at slightly higher energy is also observed. This has a zone-center energy of 3.9 eV and a dispersion of 0.5 eV. Finally, we also discuss a dramatic reduction in spectral weight of the CT exciton observed near the $(\pi\,\pi)$ position.

The RIXS technique in the hard x-ray regime is a powerful new experimental method to probe momentum-dependent collective excitations in condensed matter systems. As first observed in NiO [8], a large enhancement of the inelastic x-ray scattering signal is obtained when the incident x-ray energy is tuned near the transition metal K edge. Until now, a number of insulating cuprates have been studied [9–12]. While these previous studies provided detailed information on the local resonance processes, they provided only qualitative information on the momentum ($\mathbf{Q}$) dependence of the CT excitations, mainly due to a poor signal-to-noise ratio. In the present work, we rectify this, studying in detail the $\mathbf{Q}$ dependence of the RIXS spectrum in La_2CuO_4.

This work was carried out at the Advanced Photon Source on the undulator beam line 9IDB. A double-bounce Si(111) monochromator and a Si(333) channel-cut secondary monochromator was utilized. A spherical, diced, Ge(733) analyzer was used to obtain an overall energy resolution of 0.2 eV (HWHM). The scattering plane was vertical and the polarization of the incident x-ray was kept fixed along the $\mathbf{c}$ direction for all data reported here. The single crystal sample of La_2CuO_4 was grown using the traveling solvent floating zone method, and annealed to remove excess oxygen. The crystal was cut along the (100) plane and mounted on an aluminum sample holder at room temperature. Throughout this

paper, we use the tetragonal notation ($a \approx b \approx 3.85$ Å along the Cu-O-Cu bond direction).

In Fig. 1(a), we plot the incident energy (E_i) dependence of the scattered intensity as a function of energy transfer (ω) at a fixed momentum transfer of $\mathbf{Q} = (3\,0\,0)$, which corresponds to the Brillouin zone (BZ) center. A resonant feature is observed between 2 and 4 eV for $E_i = 8991$ eV, becoming weaker as the incident energy is tuned away from resonance. This feature consists of two peaks, labeled A and B, which show slightly different resonance behavior. In addition, there is another feature (C) at 7.2 eV, which resonates around $E_i \approx 8998$ eV. To show the resonance profile of these peaks, we plot the scattered intensity as a function of E_i, with the energy transfer, ω, fixed at each excitation: $\omega_A = 2.2$ eV, $\omega_B = 4$ eV, and $\omega_C = 7.2$ eV, in Fig. 1(b). Also shown is the measured x-ray absorption spectrum (solid line). The final states of this latter process are the intermediate states of the RIXS process. For example, the broad peaks around 8991 and 8998 eV in the absorption spectrum have been associated with the well-screened ($1\underline{s}3d^{10}\underline{L}4p$) and poorly screened ($1\underline{s}3d^{9}4p$) core hole final states, respectively, where $\underline{L}$ denotes the hole in oxygen ligand [13]. With this assignment, the intermediate states responsible for the resonant enhancement of the low-energy features (i.e., A and B) are the well-screened states and those for the higher-energy feature (C), the poorly screened states.

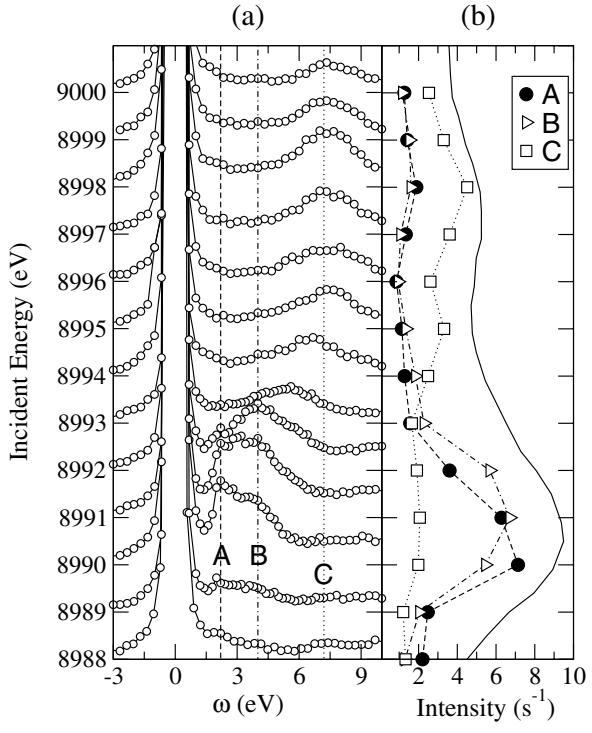

FIG. 1. (a) Scattered intensity at the zone center, $\mathbf{Q} = (3\,0\,0)$, plotted as a function of energy transfer, ω. The incident energy for each scan can be read off from the vertical axis. (b) Scattered intensity at the three energy transfers, labeled A, B, and C in (a), as a function of E_i. Also plotted is the x-ray absorption (in arbitrary units) as measured by monitoring the fluorescence yield (solid line).

The low-energy excitations A and B have relatively sharp resonance profiles. As a result, one can see that the incident energies for which A and B exhibit maxima differ slightly, by about 1 eV. It should be noted in Fig. 1(a) that, due to matrix element effects, which depend strongly on E_i, the spectral line shape exhibits a strong E_i dependence. However, the peak positions of A and B are largely independent of E_i. In the rest of this paper, we focus on the $\mathbf{Q}$ dependence of these two excitations, obtained with the incident photon energy fixed at $E_i = 8991$ eV. A detailed analysis of the polarization and the incident energy dependence will be presented elsewhere. We note, however, that, when the incident x-ray polarization is perpendicular to the $\mathbf{c}$ direction, the behavior is qualitatively similar to that observed here, except for an upward shift in the resonance energy by about 4 eV.

We have measured the energy spectra along the high-symmetry directions (0 0)-(π 0) and (0 0)-(π π), as well as the L dependence of the two-dimensional (2D) BZ center spectrum. Representative scans at the high-symmetry positions, shown in Fig. 2, exhibit several characteristics of the excitations: (i) The excitations A and B show clear dispersion as $\mathbf{q}$ is varied within the Cu-O plane, where $\mathbf{q}$ is the reduced wave vector, defined as $\mathbf{q} \equiv \mathbf{Q} - \mathbf{G}$, with $\mathbf{G}$ denoting a reciprocal lattice vector [14]. (ii) They exhibit dispersionless behavior along the L direction, as shown in the top two scans in Fig. 2, and therefore can be regarded as effectively two dimensional. (iii) There is a dramatic change in the line shape and/or width at the (π π) position. The double peak (A and B) feature is still present at (π 0), while only one peak is evident at (π π). One can fit the (π π) data with a single Lorentzian with 0.8(1) eV width.

Away from the anomalous (π π) position, we were able to analyze our data by fitting to two Lorentzians. Our fitting results suggest that it is peak A that becomes weaker and disappears at the (π π) position. The results of these fits are shown as solid lines in Fig. 2, and the fitted peak position is plotted as a function of $\mathbf{q}$ in Fig. 3. We note that it is very difficult to extract reliable peak widths from fitting two overlapping peaks. In addition, the peak intensity is strongly dependent on E_i. Thus, we focus on the peak position as the most meaningful quantity to be extracted. Since both peaks are much broader than our resolution, these results are insensitive to any resolution effects, nor do they depend on the particular line shape chosen. Furthermore, we emphasize that the resolution is independent of the momentum transfer, so that the unusual behavior around (π π) cannot be a resolution effect.

As shown in Fig. 3, excitation A has a gap of 2.2 eV and a dispersion of 1.0 eV, and it disappears near the (π π) position. The peak position of 2.2 eV at the zone center agrees well with that observed in optical conductivity studies [15,16]. In contrast, excitation B has a zone-center

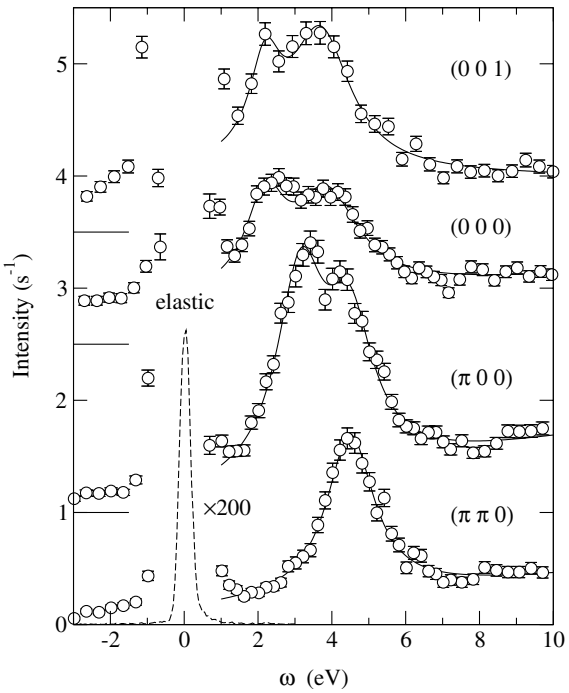

FIG. 2. RIXS spectra with $E_i = 8991$ eV for a fixed reduced wave vector (**q**) as noted. Absolute momentum transfers (**Q**), respectively, correspond to (1 0 1), (1 0 0), (2.5 0 0), and (2.5 0.5 0), from top to bottom. A representative scan through the elastic line is plotted to show the instrumental energy resolution. Solid lines are fits to a double Lorentzian line shape as described in the text. The horizontal bars denote the baselines for each spectrum, which are offset vertically for clarity.

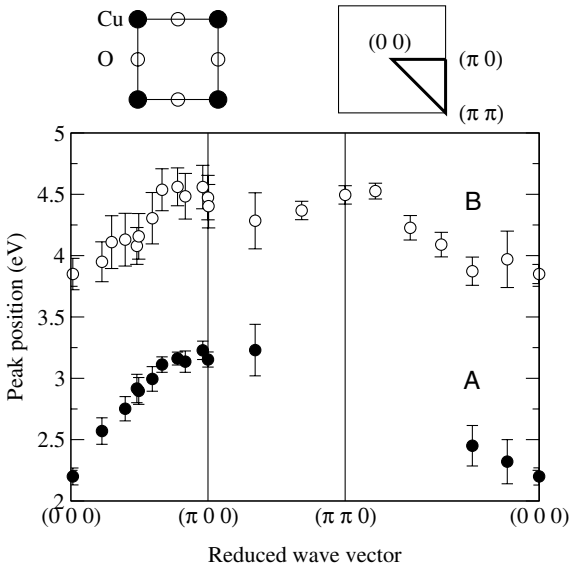

FIG. 3. The peak positions of the double peak feature (*A* and *B*) obtained from the fitting are plotted along the high symmetry directions. The 2D unit cell of the copper oxide plane and the 2D BZ are shown at the top.

energy of 3.9 eV and a dispersion of 0.5 eV, and does not exhibit a strong momentum dependence to its intensity. Note that both excitations have a direct gap, that is, a minimum energy at the zone center. This observation of **q**-dependent excitations in the $2 \sim 4$ eV range is broadly consistent with the recent RIXS studies of $Ca_2CuO_2Cl_2$ [11] and of $Sr_2CuO_2Cl_2$ [10], although, in these experiments, the low statistics prevented the authors from being able to resolve any double peak features. In addition, the amount of dispersion observed here along the Cu-O bond direction (~ 1.0 eV) is almost twice that observed for $Ca_2CuO_2Cl_2$ and, in fact, is close to that observed in the quasi-one-dimensional cuprate Sr_2CuO_3 [12]. The data in Fig. 3 also show some similarities to the electron-energy-loss spectroscopy (EELS) results of Wang *et al.* on $Sr_2CuO_2Cl_2$ [17], for which they observed two excitations with zone-center energies of 2.5 and 4.1 eV, which disperse with large intensity changes as the momentum is varied. Wang and co-workers identified the 2.5 eV mode as a CT exciton mode with *p*-wave symmetry.

This assignment of the 2.5 eV feature as an exciton is consistent with a number of optical conductivity studies of layered copper oxides, which have associated a sharp peak near the optical gap (~ 2.2 eV for La_2CuO_4) with a bound exciton mode [15,18]. However, this is not without controversy; Falck and co-workers have argued that the sharp feature in the optical data arises from the short-range interaction between an *unbound* electron and hole pair created by the CT process [16,19]. The present data, and, in particular, the **q** dependence of Fig. 3, provide new insight into this question, and, as discussed below, place stringent constraints on any quantitative theories of the CT excitation spectrum.

First, the minimum of the excitation energy spectrum is located at the 2D BZ center. This immediately highlights the importance of the strong electron correlations in determining the excitation gap, since in the absence of such correlations simple interband transitions would be expected to have a minimum excitation energy at $(\pi/2\ \pi/2)$. This is a result of the fact that the ZR band maximum is located at $(\pi/2\ \pi/2)$ [1], while the upper Hubbard band minimum is at $(\pi\ 0)$ [20]. Calculations of two-particle excitations which include the effect of correlations—in the context of the so-called t-t'-t''-U model [20]—predict that such excitations, in fact, have a minimum at $(\pi/2\ 0)$, in disagreement with our observations. Second, as pointed out in Ref. [17], the dispersion of excitation *A* (~ 1 eV) is much larger than the bandwidth of a single hole in the ZR band [1], which suggests that electrons and holes form a composite (i.e., bound) object that disperses more easily [5,17]. Third, the strong **q** dependence of the intensity suggests that the symmetry—of a bound exciton—may play an important role. Specifically, for $\mathbf{q} \neq 0$, the symmetry of any exciton eigenstate does not remain pure, but becomes mixed with states of other symmetries, for which different selection rules apply [5,21]. Taken together, the above arguments suggest that the behavior of the 2.2 eV feature is consistent with a bound exciton state.

Turning to the origin of excitation B, we first note that this excitation also shows a strong resonance behavior and that therefore excitations involving the La bands can be ruled out. One possibility then is that this excitation is, in fact, the broad continuum arising from interband transitions creating electron-hole pairs. This continuum is known to begin around 2 eV from photoconductivity data [19]. In this scenario, the observed **q**-dependent line shape changes would reflect changes in the band structure.

However, it is more likely that excitation B is, in fact, an additional exciton mode. First, in common with the 2.2 eV feature, the excitation has a minimum at the zone center, exhibits dispersion larger than that of a single hole and has a Lorentzian line shape—the latter suggestive of a finite lifetime excitation. In addition, the RIXS cross section emphasizes local excitations over delocalized ones, since the intermediate state of the resonance process is itself spatially compact and therefore has a much larger overlap with a localized final state. Specifically, the $\underline{1s}3d^{10}\underline{L}4p$ intermediate state involved here will have a large overlap with a CT exciton [22] and therefore strongly enhance the inelastic scattering from such objects, relative to that from the continuum of delocalized electrons and holes. In optical measurements, Lövenich *et al.* estimated that the spectral weight of the exciton was approximately twice that of the continuum [18]. If this ratio is indeed significantly enhanced for RIXS then—based on the count rates of the 2.2 eV feature—the continuum would be expected to be at the limit of detection. Based on this and the above physical arguments, we conclude that excitation B is also a CT exciton.

There are at least two possibilities for the nature of this higher-energy exciton mode. One is that the hole again resides in the ZR band, but has a different symmetry to that of the 2.2 eV feature. For example, Wang *et al.* have argued that the 4.1 eV feature observed in EELS work on $Sr_2CuO_2Cl_2$ is the same CT exciton but with s-wave symmetry [17]. Another possibility is that the hole is in fact in the nonbonding oxygen p_π orbitals on the same CuO_4 plaquette as the electron [2,23]. Unfortunately, our data do not distinguish between these two possibilities and detailed theoretical calculations will be required to resolve this question.

The picture our data present then is of two distinct, highly dispersive exciton modes in La_2CuO_4, both residing *in* the electron-hole continuum. The presence of the continuum provides numerous decay channels and as a result the excitons are highly damped and the observed peaks are broader than the resolution. These excitons are quite different from conventional excitons, observed in semiconductors, for example, and our data point to the need for detailed theoretical calculations to explain their properties, in particular, the dispersion relations and momentum-dependent intensities. In turn, such calculations will shed light on the charge dynamics of the copper oxide layers.

In summary, we have carried out a RIXS study of the CT excitation spectra as a function of **q** along the high-symmetry directions in insulating La_2CuO_4. We have observed two highly dispersive and highly damped excitonlike CT excitations, both of which show 2D characteristics. The low-energy mode has a gap of 2.2 eV and bandwidth of 1.0 eV, and shows a strong **q**-dependent intensity variation. The second peak shows a smaller dispersion (~ 0.5 eV) with a zone-center energy of ~ 3.9 eV.

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