A pivotal challenge in the study of correlated electron systems is to understand the nature of their electronic excitations. Compared to our knowledge of magnetic and single quasi-particle excitations, remarkably little is known about the hierarchy and momentum dependence of elementary collective charge excitations in doped Mott insulators such as the cuprate superconductors. The reason for this limitation has been the lack of a suitable spectroscopic technique. Optical spectroscopy probes the dipole-allowed electron-hole pair excitations, but is limited to zero momentum transfer \[\not \rightarrow\], while electron energy loss spectroscopy (EELS) is surface sensitive and strongly affected by multiple scattering effects at large momentum transfers \[\not \rightarrow\] \[\not \rightarrow\]. The relatively new technique of resonant inelastic x-ray scattering (RIXS), on the other hand, has the potential both to probe such excitations with bulk sensitivity and to yield momentum-resolved information throughout the Brillouin zone \[\not \rightarrow\].

Previous RIXS studies focused predominantly on the undoped insulators and revealed an excitation with an energy of \[\sim 2\ \text{eV} \not \rightarrow\] \[\not \rightarrow\]. \[\not \rightarrow\]. \[\not \rightarrow\]. \[\not \rightarrow\]. \[\not \rightarrow\]. \[\not \rightarrow\]. \[\not \rightarrow\]. \[\not \rightarrow\] \[\not \rightarrow\] \[\not \rightarrow\]. \[\not \rightarrow\]. Consistent with optical spectroscopy \[\not \rightarrow\], this charge-transfer (CT) excitation is associated with dipole transitions from the top of the valence, or Zhang-Rice singlet (ZRS) band to the unoccupied conduction band. In \[\text{La}_2\text{CuO}_4\] \[\not \rightarrow\], the excitation was found to disperse strongly (\[\sim 1\ \text{eV}\] along \[\not \rightarrow\] \[\not \rightarrow\] \[\not \rightarrow\] \[\not \rightarrow\], while in \[\text{Ca}_2\text{CuO}_2\text{Cl}_2\] \[\not \rightarrow\] \[\not \rightarrow\], it was observed to disperse by \[\sim 0.7\ \text{eV}\] along \[\not \rightarrow\]. Finally, in \[\text{Sr}_2\text{CuO}_2\text{Cl}_2\] \[\not \rightarrow\], it was found to shift very weakly and to lose definition along \[\not \rightarrow\] \[\not \rightarrow\] \[\not \rightarrow\]. In each case, RIXS also revealed additional broad excitations at higher energy. The strongest such feature, located at \[6-7\ \text{eV}\], is commonly accepted to be a local molecular orbital excitation, where an electron is excited from a bonding to an antibonding state on a single \[\text{Cu}_4\] plaquette \[\not \rightarrow\]. An additional, weakly dispersing mode was observed near \[4\ \text{eV}\] in \[\text{La}_2\text{CuO}_4\] \[\not \rightarrow\]. Two important issues that remain to be resolved are the apparent material dependent differences and the evolution with doping of the low-energy CT excitations.

We present RIXS measurements for optimally-doped \[\text{HgBa}_2\text{CuO}_{4+\delta}\] (Hg1201) at high-symmetry positions along \[\not \rightarrow\] and \[\not \rightarrow\]. Hg1201 is a model superconductor due to its high value of \[T_c\] (highest among all single-layer cuprates), simple tetragonal structure, relatively large spacing between \[\text{Cu}_2\] planes, and the absence of structural features characteristic of other cuprates, such as superstructure modulations and \[\text{Cu}-\text{O}\] chains \[\not \rightarrow\]. Through a careful analysis of the incident energy dependent RIXS spectra, we are able to identify a \[\sim 2\ \text{eV}\] CT excitation and to determine an upper bound of \[0.5\ \text{eV}\] for its dispersion. The observation of this mode suggests the existence of a remnant CT gap deep in the superconducting phase. Quite generally, our data demonstrate the importance of exploring the incident photon energy dependence of the RIXS cross section.
(FWHM). RIXS was performed on the undulator beam line 9IDB at the Advanced Photon Source, with incident photon energy ($E_i$) set to values near the Cu $K$-edge using a Si(333) double monochromator. A spherical, diced Ge(733) analyzer was used, and the overall energy resolution was 300 meV (FWHM). The experiment was performed around the weak (2,0,1) and (3,0,0) reflections. The incident photon polarization was perpendicular to the vertical scattering plane and within the CuO$_2$ planes.

Figure 1(b) shows the x-ray absorption spectrum for our crystal. The main edge (8998 eV) and satellite peak (9003 eV) correspond to the two distinct 1s → $4p_a$ transitions responsible for the resonant enhancement present in the RIXS spectra. The La$_2$CuO$_4$ crystal had a Neél temperature of $T_N = 320$ K [13] and was measured with polarization perpendicular to the CuO$_2$ planes, consistent with previous work [9]. All measurements were carried out at room temperature. In this Letter, we specify the in-plane component of the reduced wave vector $q$ and use units with lattice constant $a = 1$ and $h = 1$. The energy transfer is defined as $\omega = E_i - E_f$.

Figure 2(c) shows Hg1201 zone-center spectra at four values of $E_i$. For $E_i = 8998$ eV, we observe a peak at $\omega = 2.2$ eV together with two less intense, but clearly resolvable features at 5.2 eV and 6.0 eV, and a spectral weight enhancement at intermediate energy transfers. By gradually tuning $E_i$ to higher energies, two additional features, centered at 3.4 eV and 4.1 eV, sequentially stand out when compared to the featureless “background” spectrum at $E_i = 9009$ eV. We will refer to these features as “2 eV,” “3 eV,” “4 eV,” “5 eV,” and “6 eV,” according to their approximate peak positions. We emphasize that, when viewed as a second-order process, the RIXS cross section, as in the case of resonant Raman scattering [14], depends on both $\omega$ and $E_i$ [6].

FIG. 1: Hg1201: (a) Magnetic susceptibility. (b) X-ray absorption spectrum monitored by fluorescence yield. (c) Zone-center RIXS spectra at four incident energies, shifted below 9009 eV by 0.2 counts/s relative to each other. Solid lines are fits described in the text. Vertical lines indicate (b) the two intermediate states where a resonant enhancement is observed in RIXS and (c) distinct electron-hole excitations.

FIG. 2: Hg1201 RIXS spectra at (a) ($\pi/2, 0$) and (b) ($\pi/2, \pi/2$). The data are shifted below 9009 eV by 0.2 counts/s relative to each other. The solid lines are fits described in the text. (c) La$_2$CuO$_4$ zone-center spectra; 8991 and 8992 eV data are shifted vertically. (d) Hg1201 $E_i$-dependence at ($\pi, \pi$) for several energy transfers.

The relative strength of the excitations also is a function of wave vector. Figure 2 contains results for (a) ($\pi/2, 0$) and (b) ($\pi/2, \pi/2$). The 2 eV mode rapidly decreases in strength toward the zone boundary, similar to previous results for La$_2$CuO$_4$ [9]. On the other hand, the higher-energy modes gain in intensity toward the zone boundary and the multiplet structure becomes more pronounced. Apart from the 2 eV and 3 eV features, which are not discernible at ($\pi, 0$), and ($\pi, \pi$), respectively, the multiplet structure in the 2-6 eV range is similar to the zone center result [Fig. 1(c)]. We focus on the five lowest-lying features, but note that some spectra exhibit additional features at $\sim 7$ eV and $\sim 9$ eV (not shown).

Although RIXS measures the electron-hole pair dynamics rather than the properties of a single hole quasiparticle, the multiplet structure resembles valence band photoemission results for Sr$_2$CuO$_2$Cl$_2$, for which separate bands with rather different mixing between Cu 3$d$ and O 2$p$ orbitals have been associated with the significant intensity variations with momentum and energy [13, 18].

A reasonable estimate of the peak positions can be obtained already by visual inspection of the data. To arrive at a more precise estimate, at each wavevector we first fit the $E_i = 9009$ eV data to a Lorentzian centered at $\omega = 0$, and then used this as “background” in a simultaneous fit of all the other spectra to a set of Lorentzians with $E_i$-independent peak positions and $E_i$-dependent amplitudes. The description of some of the spectra required an additional linear contribution. The peaks are broader
than our resolution of 0.3 eV, and in the fits of Figs. 1 and 2 the peak widths were fixed at a value of 0.8 eV based on their apparent widths.

As can be seen from Fig. 3, the difference between the excitation energies at (0,0) and the zone boundary is relatively small for all modes, within 0.5 eV. Rather than observing a single highly dispersive mode below 4 eV, as found previously for the Mott insulators La$_2$CuO$_4$ and Ca$_2$CuO$_2$Cl$_2$, we discern two separate and much less dispersive branches. Because of the significant $E_f$-dependence observed here for Hg1201, it appears possible that two weakly dispersive low-energy modes already present in the undoped Mott insulators, which could unify the seemingly disparate behavior of different compounds. To test this possibility, we performed a new measurement for La$_2$CuO$_4$ at (0,0), shown in Fig. 2 (c), and also at ($\pi$/2, 0)], and a reanalysis of the zone-center result of Ref. [8] along the lines discussed above, which suggests that this is indeed the case. The data indicate four features below 6 eV at energies very similar to those for Hg1201 (see Fig. 3). It therefore seems very likely that the strong dispersion observed in Refs. [8, 9] stems from an effective admixture of the two lowest-lying modes. Nevertheless, from our result at ($\pi$/2, 0) it appears that the 2 eV mode in the Mott insulator has a larger dispersion than in superconducting Hg1201, consistent with recent theory and experiment.

Recent RIXS studies of doped cuprates suggest an interesting doping dependence of the spectral features. A continuum of intensity was found to emerge below 2 eV with increasing doping for La$_{2-x}$Sr$_x$CuO$_4$ and the lowest-energy CT excitation (at $\sim$ 2 eV) is completely suppressed for $x = 0.17$. Due to the relatively strong "elastic tail" we were not able to probe the region well below 2 eV in Hg1201 with the present energy resolution. However, in contrast to the observation for La$_{2-x}$Sr$_x$CuO$_4$, which appears to be consistent with optical spectroscopy, we clearly resolve a well-defined low-energy feature at $\sim$ 2 eV. It rapidly decreases in strength away from the zone center, but can still be traced up to the zone boundary, with a net dispersion no greater than 0.5 eV. We note that it is unlikely to be a $d - d$ type excitations. The latter lie below 2 eV and are expected to be much weaker at the $K$-edge than at the $L$ and $M$ edges. Furthermore, at the Cu $K$-edge, one might expect such excitations to be significant at the pre-edge ($E_i = 8985$ eV, $1s \rightarrow 3d$ transition), but we did not observe a "2eV" feature at this incident energy. Therefore, optimally doped Hg1201, the single-layer cuprate with the highest $T_c$, exhibits a remnant CT gap. It would be very valuable to extend initial results for the optical conductivity of Hg1201.

The most significant feature for $E_i = 9003$ eV is the non-dispersing 6 eV mode, which is very likely the (local) molecular orbital excitation from the bonding (predominantly 3$d^9$) to the antibonding state (predominantly $3d^{10}4p$), consistent with a systematic study among cuprates of the bond-length dependence of the energy of this feature ($\partial c_{Cu-O} = 1.9396$ Å at $T = 300$ K for our crystal). As further indication of its local character, we note that this excitation resonates at both $E_i = 8998$ eV and 9003 eV, as can be seen from Fig. 2(d). These two resonance energies are the final states in the RIXS process, one which is well-screened ($\sim$ 9000 eV; predominantly $1s^{3}3d^{10}4p$) and the other poorly-screened ($\sim$ 9000 eV; predominantly $1s^{2}3d^{10}4p$). The double-resonance behavior has been captured using the Anderson impurity model of a single CuO$_4$ plaquette, thus enforcing the conclusion that these excitations are local.

With the exception of the 2 eV feature, the Hg1201 spectra for $\omega < 6$ eV exhibit a different resonant behavior as they are much stronger at $E_i = 8998$ eV than at 9003 eV [Fig. 2(d)]. This suggests that the corresponding excitations have a more significant overlap with the well-screened ($3d^{10}4p$) than with the poorly-screened ($3d^9$) intermediate states. In this scenario, the resultant screening can have both local and nonlocal contributions, as first suggested in the context of Cu $2p$ core-level photoemission. In nonlocal screening, a hole residing on the surrounding oxygen ligand is Coulomb-repelled by the 1$s$ core hole on the central Cu site and delocalizes to a neighboring CuO$_4$ plaquette. The delocalized hole can either form a ZRS with a neighboring Cu, or move to non-bonding O 2$p$ orbitals ($2p_z$, $2p_x$, and $2p_y$). Due to the planar polarization in our experiment, CT transitions to purely $2p_z$ orbitals are suppressed. Therefore, there are three nonlocal modes that may contribute to the observed spectra. In local screening, on the other hand, the single-Cu site Anderson impurity model calculations reveal that the final state has nearly pure O 2$p$ character due to the strong core hole potential.

FIG. 3: Dispersion of CT excitations for optimally-doped Hg1201 (squares), compared with previous results below 6 eV for Ca$_2$CuO$_2$Cl$_2$ (triangles) and La$_2$CuO$_4$ (circles), and new data for La$_2$CuO$_4$ (crosses).
on the same plaquette. Unlike for the nonlocal modes, the ligand hole does not migrate to a neighboring CuO$_4$ plaquette. For in-plane polarization, there should be two local modes that correspond to CT transitions to the two local in-plane O 2$p$ orbitals ($2p_x, 2p_y$). Consequently, we arrive at five candidate modes for the four observed features below 6 eV. Due to the intrinsic broadening and the relatively high density of modes, we might not be able to discern all of them.

Initial EELS measurements of Sr$_2$CuO$_2$Cl$_2$ indicated a single CT gap excitation of ~ 2 eV with a large dispersion of 1.5 eV along $[\pi, \pi]$. However, a more recent high-resolution (115 meV) study revealed a multiplet structure in this Mott insulator $[\pi, \pi]$, analogous to our present observations. By extending theoretical models to include a complete set of Cu 3$d$ and O 2$p$ states, the multiplet structure was found to be consistent with a prediction of multiple charge-transfer type excitations, originating either locally or nonlocally. Recent models of the Cu $K$-edge RIXS processes, based on a multi-band Hubbard model approach, show that at half-filling a total of four transitions appear below 6 eV $[32, 34, 35]$. In principle, the addition of holes permits additional transitions into the ZRS band which may not be easily discernible. At optimal (hole) doping, the theoretical prediction for the RIXS spectra is remarkably similar to the result at half-filling for a reasonably large choice of Cu onsite repulsion $[35]$. This is consistent with our experimental findings for HgI$_2$O$_4$ and La$_2$CuO$_4$.

In conclusion, we have measured electron-hole pair excitations in the 2-8 eV range along $[\pi, 0]$ and $[\pi, \pi]$ in optimally-doped HgBa$_2$CuO$_{4+\delta}$ using resonant inelastic X-ray scattering. By carefully utilizing the incident photon-energy dependence of the cross section, we discern a multiplet of excitations, and we establish an upper bound of 0.5 eV for the dispersion of all excitations. Our observation of an excitation at ~ 2 eV in this very-high-$T_c$ material is in surprising contrast with previous findings for (La, Sr)$_2$CuO$_4$. One possible reason for this difference may be the presence of significant quenched disorder in close proximity to the Cu-O sheets in the latter material $[11]$. While superconducting HgBa$_2$CuO$_{4+\delta}$ is expected to have significant spectral weight at lower energies, our finding suggests the existence of a remnant charge-transfer gap. Now that sizable HgBa$_2$CuO$_{4+\delta}$ crystals have become available, we plan to complement the present work on this model superconductor using other experimental techniques in order to fully elucidate materials specific differences among the cuprate superconductors. Our partial re-investigation of La$_2$CuO$_4$ revealed the multiplet structure already present in the Mott insulating parent compounds, and it indicates that the dispersion of the 2 eV mode is smaller than previous estimates. Importantly, our work establishes that the incident energy dependence of RIXS spectra of correlated materials is critical information that needs to be carefully considered in future experiments and theory, and it calls for the use of a multi-band theoretical approach.

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