

Charge-Transfer Excitations in the Model Superconductor $\text{HgBa}_2\text{CuO}_{4+\delta}$

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We report a Cu K -edge resonant inelastic x-ray scattering (RIXS) study of charge-transfer excitations in the 2–8 eV range in the structurally simple compound $\text{HgBa}_2\text{CuO}_{4+\delta}$ at optimal doping ($T_c = 96.5$ K). The spectra exhibit a significant dependence on the incident photon energy which we carefully utilize to resolve a multiplet of weakly dispersive (<0.5 eV) electron-hole excitations, including a mode at 2 eV. The observation of this 2 eV excitation suggests the existence of a remnant charge-transfer gap deep in the superconducting phase. Quite generally, our results, which include additional data for the Mott insulator La_2CuO_4 , demonstrate the importance of exploring the incident photon-energy dependence of the RIXS cross section.

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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 quasiparticle 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 [1], while electron energy loss spectroscopy (EELS) is surface sensitive and strongly affected by multiple scattering effects at large momentum transfers [2–5]. 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 [6].

Previous RIXS studies focused predominantly on the undoped insulators and revealed an excitation with an energy of ~ 2 eV [7–9], consistent with optical spectroscopy [1]. 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 La_2CuO_4 [9], the excitation was found to disperse strongly (~ 1 eV) along $[\pi, 0]$ and was quickly suppressed along $[\pi, \pi]$, while in $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ [8] it was observed to disperse by ~ 0.7 eV along $[\pi, 0]$, but by ~ 1.6 eV along $[\pi, \pi]$. Finally, in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, it was found to shift very weakly and to lose definition along $[2\pi, \pi]$ [7]. In each case, RIXS also revealed additional broad excitations at higher energy. The strongest such

feature, located at 6–7 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 CuO_4 plaquette [10]. An additional, weakly dispersing mode was observed near 4 eV in La_2CuO_4 [9]. 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 $[\pi, 0]$ and $[\pi, \pi]$. 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 CuO_2 planes, and the absence of structural features characteristic of other cuprates, such as superstructure modulations and Cu-O chains [11]. Through a careful analysis of the incident energy dependent RIXS spectra, we are able to identify a ~ 2 eV CT excitation and to determine an upper bound of 0.5 eV for its dispersion. The observation of this mode suggests the existence of a remnant CT gap in optimally doped Hg1201. In addition, we are able to resolve weakly dispersive excitations at $\sim 3, 4, 5, 6,$ and 7 eV. We also present new results for La_2CuO_4 which reveal that this multiplet structure is present already in the undoped Mott insulators. To account for this rich structure, we suggest that in addition to a ZRS contribution, it is necessary to consider CT processes that involve nonbonding O $2p$ bands with a small admixture of Cu $3d$ levels.

A large ($\sim 20 \text{ mm}^3$) Hg1201 single crystal was grown by the flux method at Stanford University [12]. It was heat treated in an oxygen atmosphere to achieve optimal doping, and magnetometry indicated $T_c = 96.5$ K (onset), as shown in Fig. 1(a). Initial characterization at the Stanford Synchrotron Radiation Laboratory, with 12 keV x rays at beam line 7-2, revealed a mosaic of 0.04° (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 $1s \rightarrow 4p_\sigma$ transitions responsible for the resonant enhancement present in the RIXS spectra. The La_2CuO_4 crystal had a Néel 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 \mathbf{q} and use units with lattice

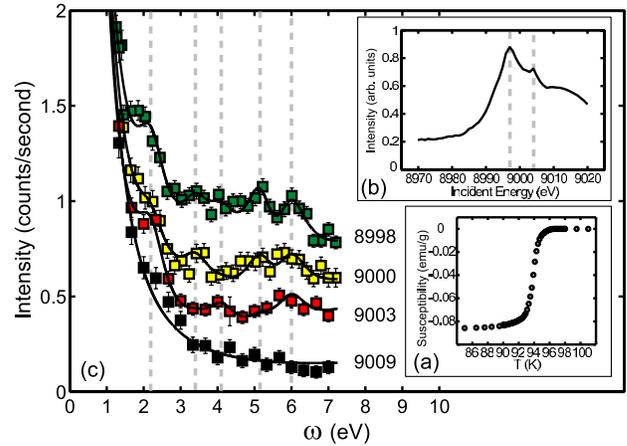


FIG. 1 (color online). Hg1201: (a) Magnetic susceptibility. (b) X-ray absorption spectrum monitored by fluorescence yield. (c) Zone-center RIXS spectra at four incident energies, shifted below 9009 eV by 0.2 counts/s relative to each other. Solid lines are fits described in the text. Vertical lines indicate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

constant $a \equiv 1$ and $\hbar \equiv 1$. The energy transfer is defined as $\omega = E_i - E_f$.

Figure 1(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 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 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 ω and E_i [6].

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_2CuO_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 and 3 eV features, which are not discernible at $(\pi, 0)$, and (π, π) , 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 ~ 7 eV and ~ 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 $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, for which separate bands with

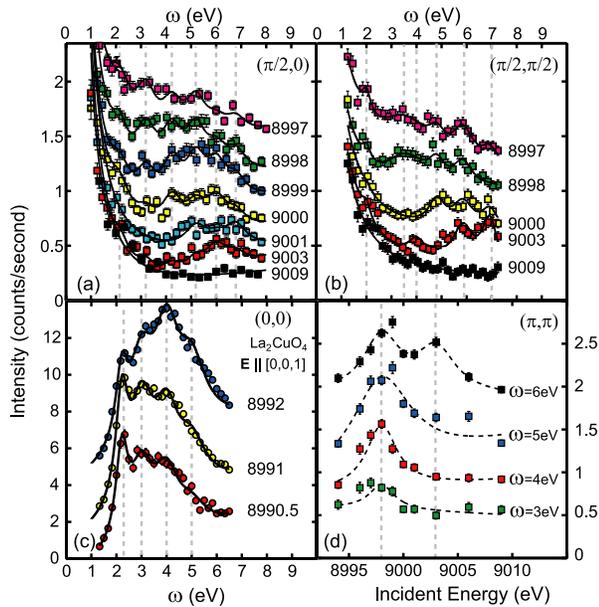


FIG. 2 (color online). Hg1201 RIXS spectra at (a) $(\pi/2, 0)$ and (b) $(\pi/2, \pi/2)$. The data are shifted below 9009 eV by 0.2 counts/s relative to each other. The solid lines are fits described in the text. (c) La_2CuO_4 zone-center spectra; 8991 and 8992 eV data are shifted vertically. (d) Hg1201 E_i dependence at (π, π) for several energy transfers.

rather different mixing between Cu $3d$ and O $2p$ orbitals have been associated with the significant intensity variations with momentum and energy [15,16].

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 wave vector 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 [17–19] 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 excitations, within 0.5 eV. Rather than observing a single highly dispersive mode below 4 eV, as found previously for the Mott insulators La_2CuO_4 [9] and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ [8,20], we discern two separate and much less dispersive branches. Because of the significant E_i dependence observed here for Hg1201, it appears possible that two weakly dispersive low-energy modes already are present in the undoped Mott insulators, which could unify the seemingly disparate behavior of different compounds [7–9]. To test this possibility, we performed a new measurement for La_2CuO_4 [at $(0, 0)$, shown in Fig. 2(c), and also at $(\pi/2, 0)$], and a reanalysis of the zone-center result

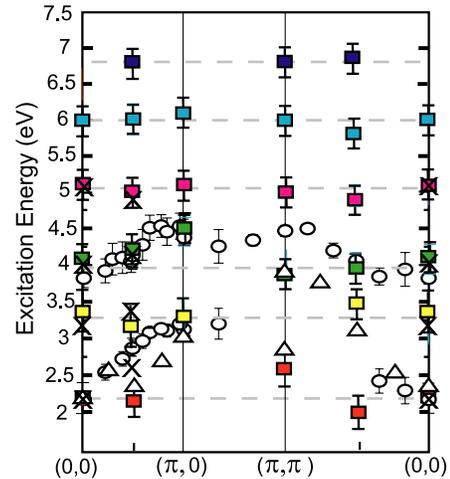


FIG. 3 (color online). Dispersion of CT excitations for optimally doped Hg1201 (squares), compared with previous results below 6 eV for $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ (triangles) [8,20] and La_2CuO_4 (circles) [9], and new data for La_2CuO_4 (crosses).

of Ref. [9] 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 excitations. 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 [21] and experiment [22].

Recent RIXS studies of doped cuprates suggest an interesting doping dependence of the spectral features [22–24]. A continuum of intensity was found to emerge below 2 eV with increasing doping for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [22,23], and the lowest-energy CT excitation (at ~ 2 eV) is completely suppressed for $x = 0.17$ [23]. Because of 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 $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, which appears to be consistent with optical spectroscopy [1], we clearly resolve a well-defined low-energy feature at ~ 2 eV. It rapidly decreases in strength away from the zone center, but can still be traced up to the zone boundary at (π, π) , with a net dispersion no greater than 0.5 eV. We note that this is not likely a $d-d$ type excitation. The latter lie below 2 eV [25,26] and are expected to be much weaker at the K edge than at the L [25] and M edges [26]. Furthermore, at the Cu K edge, one might expect such excitations to be significant at the pre-edge ($E_i = 8985$ eV, $1s-3d$ transition), but we did not observe a “2 eV” feature at this incident energy. Therefore, optimally doped Hg1201, the single-layer cuprate with the highest T_c , appears to exhibit a remnant CT gap. For comparison, it would be very valuable to extend initial results for the optical conductivity of Hg1201 [27].

The most significant feature for $E_i = 9003$ eV is the nondispersing 6 eV mode, which is very likely the (local) molecular orbital excitation from the bonding (predominantly $3d^9$) to the antibonding state (predominantly $3d^{10}\underline{L}$), consistent with a systematic study among cuprates of the bond-length dependence of the energy of this feature ($d_{\text{Cu-O}} = 1.9396$ Å at $T = 300$ K for our crystal) [10]. As further indication of its local character, we note that this excitation resonates at both $E_i = 8998$ and 9003 eV, as can be seen from Fig. 2(d). These two resonance energies are the final states in the x-ray absorption spectra of Fig. 1(b), and they correspond to different intermediate states in the RIXS process, one which is well screened (8998 eV; predominantly $1s3d^{10}\underline{L}4p$) and the other poorly screened (9003 eV; predominantly $1s3d^94p$). The double-resonance behavior has been captured using the Anderson impurity model of a single CuO_4 plaquette [18,19], 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 ($3d^{10}\underline{L}$) 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 [28–32]. In nonlocal screening, a hole residing on the surrounding oxygen ligand is Coulomb repelled by the $1s$ 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 nonbonding O $2p$ orbitals ($2p_\pi$, $2p_\sigma$, and $2p_z$). Because of 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 [18,19] reveal that the final state has nearly pure O $2p$ character due to the strong core hole potential 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 $2p$ orbitals ($2p_\sigma$, $2p_\pi$). Consequently, we arrive at five candidate modes for the four observed features below 6 eV. Because of the intrinsic broadening and the relatively high density of modes, we might not be able to discern all of them.

Initial EELS measurements of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ indicated a single CT gap excitation of ~ 2 eV with a large dispersion of 1.5 eV along $[\pi, \pi]$ [2]. However, a more recent high-resolution (115 meV) study revealed a multiplet structure in this Mott insulator [3,4], analogous to our present observations. By extending theoretical models to include a

complete set of Cu $3d$ and O $2p$ 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 multiband Hubbard model approach, show that at half filling a total of four transitions appear below 6 eV [33–35]. 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 Hg1201 and La_2CuO_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 $\text{HgBa}_2\text{CuO}_{4+\delta}$ 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 $(\text{La, Sr})_2\text{CuO}_4$. 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 $\text{HgBa}_2\text{CuO}_{4+\delta}$ is expected to have significant spectral weight at lower energies, our finding suggests the existence of a remnant charge-transfer gap. Now that sizable $\text{HgBa}_2\text{CuO}_{4+\delta}$ 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 reinvestigation of La_2CuO_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 multiband theoretical approach.

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