Dispersion Relation of Charge Gap Excitations in quasi-1D Mott Insulators Studied by Resonant Inelastic X-ray Scattering

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Introduction

The discovery of unusual electronic, magnetic and optical properties such as high temperature superconductivity, colossal magnetoresistance and highly nonlinear optical responses in doped transition metal oxides has led to the extensive research interests in their parent compounds – the Mott insulators. The parent compounds of such oxides are half-filled systems where a large onsite Coulomb interaction dominates the physics and these systems exhibit a low-temperature insulating state characterized by a charge-excitation gap known as the Mott-gap. The existence of those exotic properties is believed to be related to the strong electron-electron Coulomb correlations in these systems[1-4]. Inelastic x-ray scattering is a powerful tool to probe electron dynamics in correlated electron systems. This relatively new *momentum-resolved* and *bulk* (unlike photoemission spectroscopy (ARPES)) spectroscopy of electronic structure of matter is becoming possible due to the recent advancements in synchrotron radiation facilities and crystal optics[5-9]. The advantage of resonant inelastic x-ray scattering is that one can selectively and highly enhance certain excitations depending on the resonance unlike electron energy loss spectroscopies (EELS)[5-13]. We make use of this aspect of the technique combined with its unique and fairly large momentum space accessibility to study the momentum structure of the Mott gap in several model correlated systems. The momentum dependence of the effective Mott gap has been reported recently in a quasi-two dimensional cuprate using some novel aspects of inelastic x-ray scattering[6,7,9]. Here we report high resolution inelastic x-ray scattering study of two edge sharing 1D insulators Li_2CuO_2 (Li-cuprate), $GeCuO_3$ (Ge-cuprate) and compare it with the corner sharing 1D $SrCuO_2$ (Sr-cuprate) system. We studied the momentum dependence of the charge excitation spectrum up to the third Brillouin zone. We find that the particle-hole pair excitation at the Mott gap edge are only weakly dispersive in the Li and Ge-cuprate but largely dispersive in Sr-cuprate system, which is consistent with the theoretical results. Unlike earlier reports[10] the lowest energy charge excitations in Li_2CuO_2 (around 2 eV) can be interpreted in the charge-transfer framework.

Methods and Materials

The experiments were performed using the high flux undulator beamline 12-ID (BESSRC-CAT) and 9-ID (CMC-CAT) at the Advanced Photon Source of Argonne National Lab and the BL X-21 at the National Synchrotron Light Source of Brookhaven National Lab. Inelastic scattering was measured by varying q along the Cu-chain direction of single crystalline Li_2CuO_2, $GeCuO_3$ and $SrCuO_2$. A simplified version of the structural (rather topological) differences between these compounds is shown in Fig.1. In case of the Li and the Ge-cuprate, being edge-sharing systems Cu-O-Cu bonds are about 94 and 99 degrees, respectively, giving rise to small Cu to Cu hopping and effective quasi-zero dimensionality (q-0D) at room temperatures. In contrast, $SrCuO_2$, or Sr_2CuO_3, the corner sharing systems, Cu-O-Cu bond is almost linear leading to a large hopping integral and rather quasi-one dimensionality (q-1D). The basic electronic structures of these compounds are further described elsewhere [14-19]. The scattered beam was reflected from a diced Ge-based analyzer for energy analysis and focused onto a solid-state detector. The detector was thermoelectrically cooled to achieve low level of random background. For q-scans, the incident energy was kept fixed to keep the resonant condition invariant and q was varied by rotating the entire spectrometer around the scattering center either in the horizontal plane or vertical plane. Overall energy resolution was maintained from 300-400 meV for this experiment.

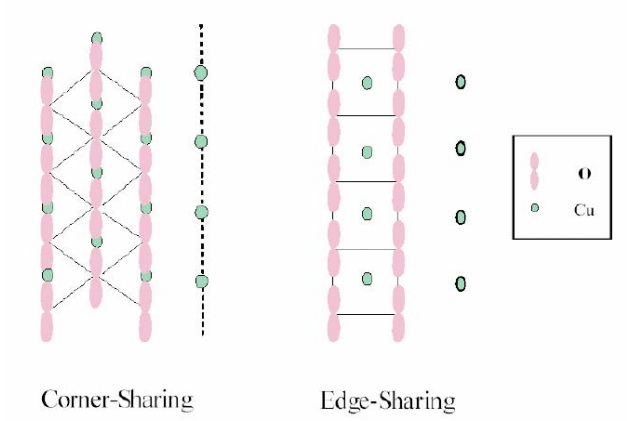

FIG. 1: Topology of the lattice determines the nature of the electronic excitations. In case of $GeCuO_3$, an edge-sharing system (right) Cu-O-Cu bonds are 99 degrees giving rise to small Cu to Cu hopping and quasi-zero dimensionality. In contrast, in $SrCuO_2$,-a corner-sharing system (left), Cu-O-Cu bond is almost 180 degrees leading to large hopping integral and quasi one dimensionality.

Results

Fig.2(right) shows inelastic x-ray scattering spectra in Li_2CuO_2 with varying momentum transfers along the chain direction with incident energy fixed near Cu K-edge (E0 = 9 KeV) where largest resonance enhancement was observed. Each spectrum, bottom to top reflecting q changing from near π to 2π, shows a

strong feature around 5.5 eV -excitations to the antibonding states (involving the upper Hubbard band) which are the analogs of the 6 eV excitations observed in two dimensional insulating cuprates[6, 8]. The second weak and broad feature is seen around 2 eV which broadens near 2π but does not disperse much with a change of q. Fig.2(middle) shows inelastic x-ray scattering spectra in $GeCuO_3$. Similar to Li_2CuO_2, bonding to antibonding state excitation was found at around 6.4 eV. Particle-hole pair excitation is around 3.8 eV which coincides with the excitations seen in optical studies. Although the lineshape of the excitation has some q-dependence this excitation has very weak energy dispersion within the level of our energy resolution. This strongly suggests the localized character of this pair involving a hole of Zhang-Rice character and an electron with upper Hubbard band character. We also see some weak excitations inside the Mott gap. These are most likely due to the fluctuations in the orbital degrees of freedom coupling weakly to the resonance process[17]. Fig.2(left) shows inelastic excitation spectra in the Sr-cuprate along the Cu-O-Cu direction. These results are improvements over our earlier work on related systems[7]. At low-q near 2π (bottom spectrum) it shows an excitation feature near 2 eV, which increases in energy as one goes from 2π to 3π (upward). The total dispersion is about 1 eV.

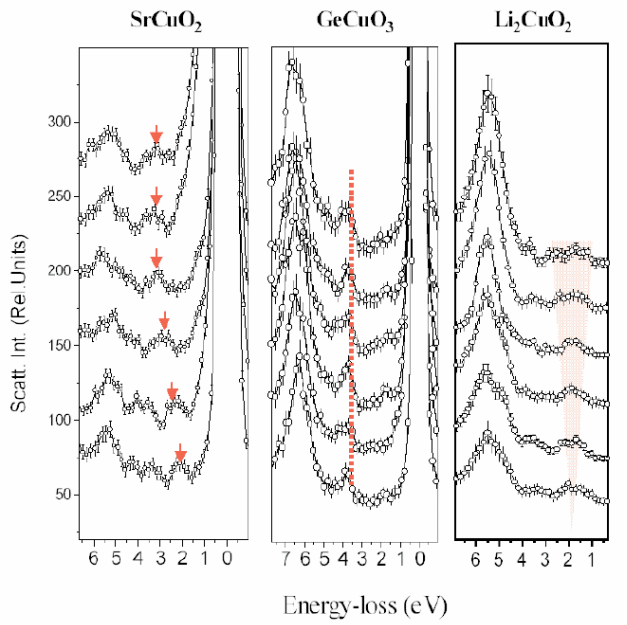

FIG. 2: q-dependence of charge excitations in $SrCuO_2$ (left), $GeCuO_3$ (middle) and Li_2CuO_2 (right). For $GeCuO_3$, the approx. value of q (bottom to top) 1, 1.2, 1.3, 1.5, 1.6, 1.9 (in units of 2π/a) where as for $SrCuO_2$:the value of q (bottom to top) 2.05, 2.4, 2.6, 2.8, 3.02, 3.1 and Li_2CuO_2 the values of q (bottom to top) 0.7, 0.8, 0.9, 1, 1.5 and 1.7 (in units of π/a_0, a_0 being the lattice constant along the chain).

Discussion

In order to understand the origin of these low energy charge excitations in these prototype Mott insulators we perform theoretical calculations based on many-body Hubbard-type Hamiltonians with realistic parameters obtained from other experiments to understand the momentum dependence. We consider the scattering to have the following components: (i) absorption of an x-ray photon brings about the dipole transition of an electron from copper 1s to 4p states, (ii) in the intermediate states, the 1s-core-hole is screened due to the oxygen 2p electrons, which is a consequence of strong attractive Coulomb interaction between the copper 1s-core hole and 3d electrons and this perturbation induces the excitations across the Mott gap, (iii) the 4p electron goes back to the 1s state and a photon is emitted out. Then via the energy and momentum conservations, the differences of the energies and the momenta between incident and emitted photons are related to the excitations across the Mott gap -defining the lowest energy charge fluctuation in the system. The Hamiltonian then contains copper $3d_{y^2-x^2}$, 1s and oxygen 2p states. In the edge-sharing geometry (Li-and Ge-cuprate), two oxygen 2p orbitals at the same site are included, whereas only one oxygen 2p orbital is taken into account in the corner-sharing geometry (Sr-cuprate). The hopping amplitudes and the energy level separations are taken based on different types of spectroscopies for an overall consistency check [17]. The on-site and inter-site Coulomb interactions are also the same as those in Ref. [11], except for copper 1s-3d interaction which is taken to be 4.5 eV. The momentum-dependence of the resonant scattering spectra is calculated for clusters with 6 units of CuO_4 by using the Lanczos and conjugate-gradient algorithms[11, 12].

Novel aspect of the present results is the momentum dependence. We plot the q-dependence (dispersion relations) of the Mott excitations in these model systems in Fig.3(left). It shows the dramatic difference in dispersions due to the difference in the effective dimensionality. For the quasi-1-D case (Sr-cuprate) Mott gap is direct in the sense that the energy of the pair excitations is lowest at $q \sim 0$. This may not necessarily be the case for Li-or Ge-cuprates. Due to the experimental error bars it is hard to conclude the lowest energy pair excitations in those systems but the experimental data

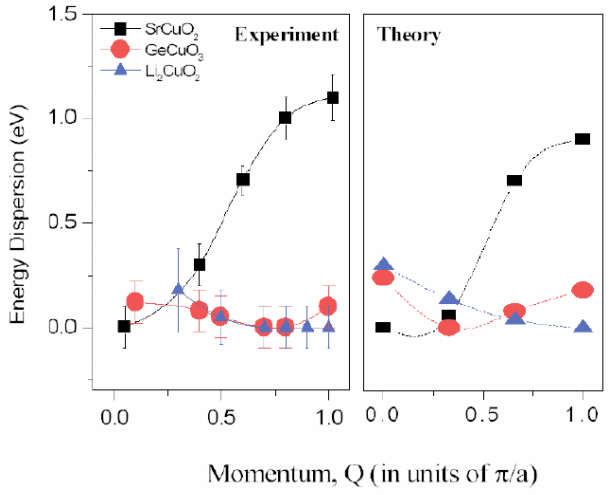

FIG. 3: (Left) Momentum-structure of the Mott-gap excitations in q-1D ($SrCuO_2$)and q-0D (Li_2CuO_2 and $GeCuO_3$) cuprates. (Right) Dispersion relations of charge excitations in Hubbard model. Both for experimental data (Left) and model calculations (Right) lowest energy of the excitation was taken to as the reference and the momentum is measured in units of π/a_0 along the chain directions where a_0 is the lattice constant in that direction.

points have a systematic tendency to suggest that the Mott gap might be indirect in quasi-zero dimensional systems. Fig.3(right) shows the dispersion relations in theoretical calculations based on Hubbard model which are broadly consistent with experimental results.

Results can be summarized with a simplistic view : the core-hole created by the photon near the absorption edge causes electronic excitations in the Hubbard bands which is composed of having a hole in the occupied band and an electron in the unoccupied upper Hubbard band across the gap in Mott insulators. The particle-hole pair formed in the process absorbs the energy and momentum lost from the incident photons and exhibits its intrinsic dynamics. The detail momentum dependence of such a complex provides information about the unoccupied upper Hubbard bands. In case of $GeCuO_3$ effective Coulomb interaction is large (due to large Madelung potential) resulting in a larger effective Mott gap but Cu-O-Cu interaction is weak resulting in a weak dispersion. In case of $SrCuO_2$, the insulating charge gap again scales with effective electron-electron interaction but a larger dispersion results from larger Cu-O-Cu interactions. A comparison of quasi-zero dimensional compounds and quasi-one dimensional compound shows that the momentum structure of charge excitations over the Brillouin zone dramatically reflects the effective dimensionality of the lattice. Wide-scale momentum tunability of high energy x-rays allowing to probe the complete Brillouin zones made such detailed study possible for the first time. Comparison with numerical calculations suggests that momentum structure of the Mott gap can be understood in the context of the Hubbard model.

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