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Optical excitations in Sr_2CuO_3

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We investigated excitation spectra of the one-dimensional chain compound Sr_2CuO_3. The small peak at 2.3 eV in the loss function turned out to correspond to the strong charge-transfer transition at 1.8 eV in conductivity. It has the excitonic character expected in one-dimensional extended Hubbard model of the transition from the lower Hubbard band to the Zhang-Rice singlet state. The strongest peak at 2.7 eV in the loss function is attributed to the continuum excitation of the excitonic charge-transfer transition. The spectral weight sum rule is satisfied within these transitions.

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Superconducting cuprates have a CuO_2 plane in common which is composed of a two-dimensional (2D) corner-sharing network of CuO_4 plaquettes. The electronic property of an undoped CuO_2 plane should be metallic without strong on-site Coulomb repulsion at Cu sites, which divides the Cu $d_{x^2-y^2}$ state into two Hubbard bands of upper Hubbard band (UHB) and lower Hubbard band (LHB) opening a charge-transfer gap between LHB (from a hole point of a view) and O $2p$ states. Charge doping changes the electronic structure of the CuO_2 plane finally giving rise to the high-temperature superconductivity. It is important to understand the properties of insulating cuprates to solve the mystery of the high-temperature superconductivity.

Optical spectroscopy is one of fundamental tools to investigate electronic structure, which can directly measure the charge-transfer gap. By absorbing light, holes in LHB can be excited to O $2p$ states. When a hole is introduced into the CuO_2 plane, the ground state becomes a well-known Zhang-Rice singlet (ZRS) state evenly residing at surrounding O $2p$ orbitals.[1] Because an optical excitation is a charge-conserving process, to be involved in optical excitations for the ZRS state, one CuO_4 plaquette should give a hole to a neighboring CuO_4 plaquette, which is possible in corner-sharing CuO_4 plaquette structures. Therefore, the first optical excitation crossing the charge-transfer gap should be from LHB to the ZRS state in the CuO_2 plane as depicted in Fig. 1. The second excitation is expected to be from LHB to nonbonding (NB) O $2p$ states in the CuO_2 plane, which is localized within one plaquette. Energies of these two excitations are essential to model the electronic structure of the CuO_2 plane.

However, the electronic structure of insulating cuprates remains still unclear. Optical spectra of insulating cuprates of one-dimensional (1D) and 2D corner-sharing structure show similar spectral feature of two peaks around 2 eV such as peaks A and B in Fig. 2. It is clear that the lowest-energy peak, which is rather sharp and has a large spectral weight in common, should be the charge-transfer transition α from LHB to ZRS. But the origin of the other peak, which comes at about 0.5 eV higher, is still unclear. This peak is relatively broad and the strength varies depending on materials. It is rather small and appears as a humplike shape in RE_2CuO_4 (RE: rare-earth ions) and Sr_2CuO_3.[2,3] Imada *et al.*[2] attributed this peak to a sideband transition with spin excitation via the strong Kondo coupling between the $2p$ hole and the $3d$ spin in the final state. On the other hand this peak has a comparable or even larger weight than the first peak in $YBa_2Cu_3O_6$ and $Sr_2CuO_2Cl_2$.[4,5] Choi *et al.*[5] attributed this peak to the β transition from LHB to NB state. Therefore further studies are required to reveal the nature of those peaks and to understand the electronic structure of insulating cuprates.

Sr_2CuO_3 has a corner-sharing CuO_4 plaquette 1D chain structure. Its electronic properties along the chain direction should have a common character with the CuO_2 plane, while only localized phenomena within one plaquette are expected in the direction perpendicular to the chain. This chain structure provides a unique chance to investigate the electronic structure of CuO_4 plaquette networks telling the difference between localized and delocalized excitations in a single material. In addition, the one dimensionality of this material enriches its physics attracting many researchers with interesting phenomena such as the spin-charge separation, a large optical nonlinear effect, and Wannier-type bound excitons.[6–9] All these factors make the excitation spectra of this system of great interest.

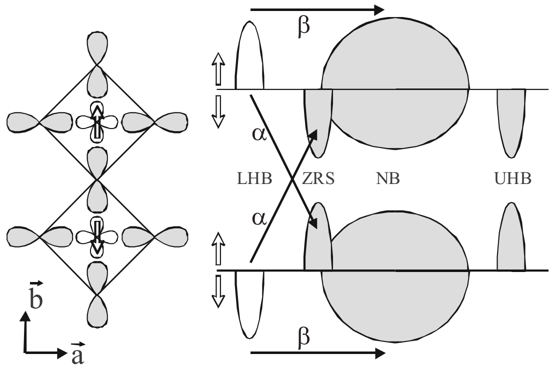

FIG. 1. Schematic diagram of DOS and optical excitations in a corner-sharing CuO_4 plaquette structure with the antiferromagnetic background from a hole point of view. The grayed DOS are occupied by electrons. Note that the notations of two Hubbard bands of LHB and UHB are exchanged in the electron point of view. The axes of Sr_2CuO_3 are given with respect to the chain.

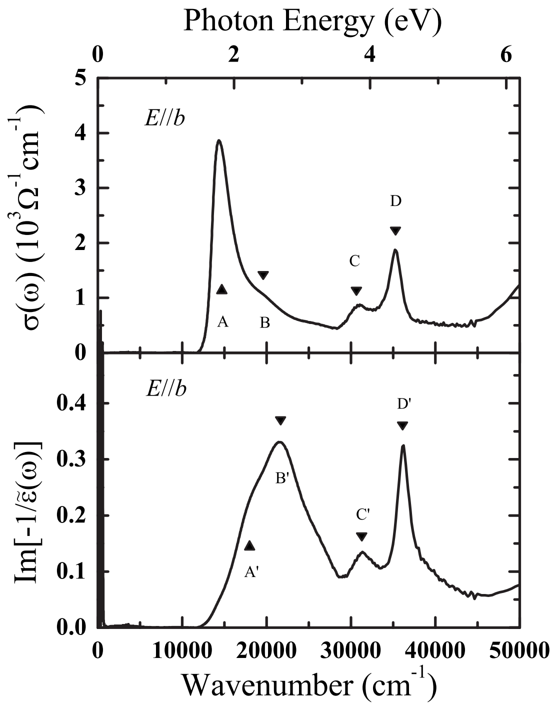

FIG. 2. Optical conductivity and loss function along the chain direction of Sr_2CuO_3. Four excitations are observed in both spectra.

Moskvin *et al.* investigated the electronic structure of Sr_2CuO_3 along and perpendicular to the chain direction by electron-energy-loss spectroscopy (EELS).[10] Peaks unique along the chain direction are considered to be the ZRS state involved transitions, while structures common in both directions are attributed to transitions localized within one plaquette. Interestingly, the strong charge-transfer excitation right above the gap was found to be composed of two peaks. The first small peak above the gap was argued to be a localized excitation within one plaquette. This observation has put more importance on the multiband model accounting details of orbitals over the simple one-band Hubbard model approach. Unfortunately optical experiment along *a* axis is lacking. It is because this material is cleaved along *bc* plane and its strongly reactive nature in air makes polishing for *a*-axis troublesome. There is only one optical absorption report along *a*-axis measured on a thin film grown with *ab* plane utilizing the anisotropic property of a $LaSrAlO_4$ substrate.[11] Although EELS experiment has detected an energy loss at 2.0 eV along *a* axis, no corresponding absorption feature was observed. This discrepancy demands further investigations on this system.

In this paper we report optical spectra along the chain direction of Sr_2CuO_3 measured by reflectivity measurement. The optical conductivity spectra $\sigma(\omega)$ and the loss function agree with previously reported data. However, we notice that the observed small peak just above the gap in the loss function is not a localized excitation within one CuO_4 plaquette but the ZRS state involved charge-transfer excitation which appears as a strong peak at 1.8 eV in $\sigma(\omega)$. This peak is an excitonic peak due to the strong intersite Coulomb interaction expected in the extended Hubbard model. The strong peak at 2.7 eV in the loss function is also attributed to the excitation from LHB to the ZRS state, which is the continuum excitation of the excitonic peak.

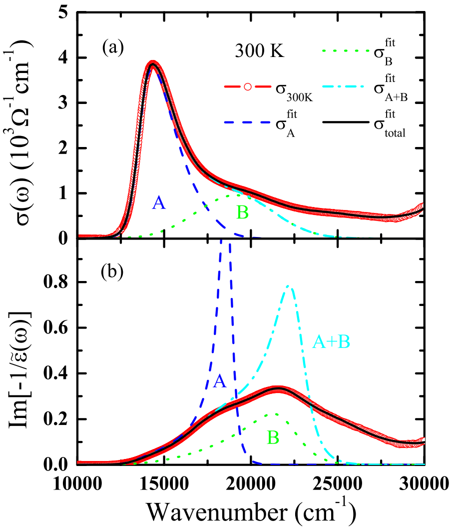

FIG. 3. (Color online) Gaussian fitting of $\sigma(\omega)$ for peaks A, B, and corresponding loss functions along the chain direction of Sr_2CuO_3.

Single crystalline samples were grown using the traveling-solvent floating zone method. Temperature-dependent polarized reflectivity spectra were carefully measured over a wide energy range. In a low-energy region of 30–24000 cm^{-1} (4 meV to 3 eV) an *in situ* evaporation technique was adopted in the overfilling method on Bruker 66 v/S Fourier transform spectrometer. In 4000–50 000 cm^{-1} (0.5 eV to about 6 eV) Cary5 grating spectrometer was used in the underfilling method. High-energy spectra in 6–30 eV were measured at room temperature utilizing synchrotron radiation from the normal-incidence monochromator beam line at Pohang Light Source (PLS). All measurements were done on freshly cleaved surfaces. The complex optical conductivity spectra $\tilde{\sigma}(\omega)$ were obtained from Kramers-Kronig transformation of reflectivity $R(\omega)$.

Figure 2 shows $\sigma(\omega)$ and the loss function along the chain direction of Sr_2CuO_3. Note that the loss function $\mathrm{Im}[-1/\tilde{\epsilon}(\omega)]$, which corresponds to EELS spectrum at zone center, can be obtained also from $\tilde{\sigma}(\omega)=\frac{i\omega}{4\pi}[1-\tilde{\epsilon}(\omega)]$. There are four clear peaks, respectively, marked as A-D and A′-D′. All these peaks were observed in previous studies on $\sigma(\omega)$ and EELS spectra, respectively.[2,10,12] It can be easily noticed that C and D in $\sigma(\omega)$ should correspond to C′ and D′ in the loss function. However coming to A, B and A′, B′ their strengths and energies do not allow a simple conclusion.

To find a direct relationship between peaks in $\sigma(\omega)$ and the loss function, $\tilde{\sigma}(\omega)$ was fitted with Gaussian functions. Note that the strongly asymmetric line shape of peak A does not allow Lorentzian with a long tail. Neither it is possible to fit peak A with a single Gaussian but at least three Gaussians are required for a decent fitting. Figure 3(a) shows the fitting result together with an individual peak corresponding to peaks A and B. The complex dielectric function $\tilde{\epsilon}(\omega)$ can be decomposed with individual modes as $\tilde{\epsilon}(\omega)=1+\Sigma_n\tilde{\epsilon}_n(\omega)$. If all modes are separated far away from each other then the loss function of each mode can be obtained simply with its own dielectric function $\tilde{\epsilon}_i(\omega)$ together with $\epsilon_\infty \equiv 1 + \Sigma_{E_n > E_i} \epsilon_n(0)$ which accounts the contribution by higher-energy modes. In a real system, however, some modes are located close to each other such that the loss functions obtained in this way become slightly different from peaks observed in the total loss function. That is, differently from $\sigma(\omega)$ the sum of respective loss functions obtained in this way does not become the total loss function. Figure 3(b) shows corresponding loss functions of peaks A and B obtained as described above. Because two modes A and B are not completely separated, the obtained loss function for each mode is different from the respective peaks in the total loss function. Although their peak heights are much different, however, their peak energies are well reproduced. Note that the loss function of the sum of those two modes obtained in the same way already explains even the peak height quite well for the peak A′. This clearly shows that peaks A′ and B′ correspond to peaks A and B.

In this corner-sharing chain structure, the first strong peak A should be the ZRS transition α. Note that the strength has to be considered in $\sigma(\omega)$ not in the loss function. Then, how can we understand the observed EELS spectra? In the reported EELS spectra, there is one more excitation at 5.2 eV which is missing in the loss function shown in Fig. 2.[10,12] Note that peak C′ was observed only with $q \sim 0$. Although the peak at 5.2 eV is missing in our measurement, the previously reported $\sigma(\omega)$ by Imada *et al.*[2] also shows a small peak there. However, although this peak is common in both spectra along b and c axes, it is much stronger along c axis. This makes it suspicious that the weak feature along b axis might come from c axis due to slightly misaligned polarization. Likewise the 2 eV excitation along a axis in EELS spectra could come from partially mixed b axis.

The low dimensional character of Sr_2CuO_3 allows a direct comparison of the experiment and a theory. The strongly asymmetric line shape has been understood based on 1D one-band extended Hubbard model (EHM) including on-site Coulomb repulsion U and the nearest-neighbor interaction V, which has explained many other properties of 1D charge-transfer insulators including Sr_2CuO_3, Ca_2CuO_3, and Ni-halogen-bridged 1D materials.[7,9,11–13] However, a close look on $\sigma(\omega)$ of those 1D charge-transfer insulators finds another common feature which is not pronounced in 1D EHM. That is, like the peak B in Sr_2CuO_3, they have a hump structure in the long tail above the excitonic peak. Although it does not appear as a separated peak when $V < 2t$, if the excitonic peak becomes a bound exciton ($V > 2t$), the theory expects a separated continuum excitation above the excitonic peak. The continuum nature of those peaks was clearly demonstrated in the Ni-Br-Br compound, which forms a bound exciton at low temperature.[14] Note that the continuum excitation in the Ni-Br-Br compound appears as a hump even at high temperature, which is clearly manifested in reflectivity spectra.[7] Therefore peak B could be attributed to the continuum excitation. That is, if there were no intersite Coulomb interaction, peak B would be the only transition from LHB to the ZRS state. However, sizable intersite Coulomb interaction makes the excitonic peak A take most of the spectral weight, leaving relatively small weight for the continuum excitation B.[15]

This assignment of peak B contrasts to previous assignments in insulating cuprates.[2,5] To be assigned as a spin excitation sideband or the β transition, peak B has to be either weak or strong, which does not hold true among insulating cuprates. However, if peaks A and B were induced by a strong excitonic effect, the strength variation could be understood by different strength of the excitonic effect. Because the intersite Coulomb interaction V in 1D EHM lies close to the critical boundary of $V \sim 2t$ in Sr_2CuO_3, a small lattice and/or chemical environment change may affect the electronic structure rather strongly[9] Even though the intersite interaction has been considered as an important parameter in 1D cases, it has seldom been considered in 2D cuprates for the simplicity in theoretical treatments. However, the importance of the excitonic effect in the CuO_2 plane has been recognized by a simplified calculation on CuO_4 plaquettes clusters. Hanamura *et al.*[16] elaborated to explain the discrepancy of the strengths of two peaks A and B among cuprates by considering the intersite interaction between Cu and O. They argued that the A peak is a charge-transfer exciton between Cu d electron and O $2p$ hole, while the B peak has a continuum character delocalized over a few plaquettes, which is similar to the assignment in the previous paragraph.[16] However, they did not consider the ZRS state but treated with the O $2p$ state at each O site for the O $2p$ hole. As a result, the excitonic peak A can be obtained even in a single CuO_4 plaquette in their calculation, which cannot explain the observed anisotropy between a and b axes of Sr_2CuO_3 and much larger gaps of edge-sharing chain compounds.[17,18] Nevertheless their discussion could be qualitatively valid if a single O $2p$ state could stand for the ZRS state at the neighboring plaquette as Zhang and Ng[19] assumed to explain the dispersion of the excitonic peak A. Further theoretical efforts are required to understand the charge-transfer excitations and the excitonic effect in various insulating cuprates.

Because both peaks A and B have the ZRS transition character, the next higher-energy peaks C and D are expected to be β transitions from LHB to NB states. Without spectrum along a axis, it is necessary to rely on general features observed in insulating cuprates. To investigate the β excitation, an edge-sharing chain system such as Li_2CuO_2 should be ideal because the β transition should be the first pronounced excitation in the edge-sharing chain. In Li_2CuO_2 the first strong peak is observed at about 4.2 eV in $\sigma(\omega)$.[17] Recently Málek *et al.*[20] did detailed calculation for Li_2CuO_2 on clusters within a three-band (pd) Hubbard model. Interestingly, a single plaquette, of which behavior should correspond to that of the a axis of Sr_2CuO_3, shows two peaks similar to peaks C and D. The antiferromagnetic background in the corner-sharing chain, which should suppress the Zhang-Rice triplet (ZRT) transition, could make these β transitions along the chain direction similar to those of a single plaquette. Note that many 2D insulating cuprates also have a strong peak in this energy range.[2–4] Therefore peaks C and D are attributed to β transitions from LHB to NB states.

Málek *et al.*[20] argued also that the spectral weight of the ZRS excitation at high temperature should decrease due to the thermally excited ZRT transition, which comes around 4 eV, even in antiferromagnetic CuO_4 plaquette systems in-

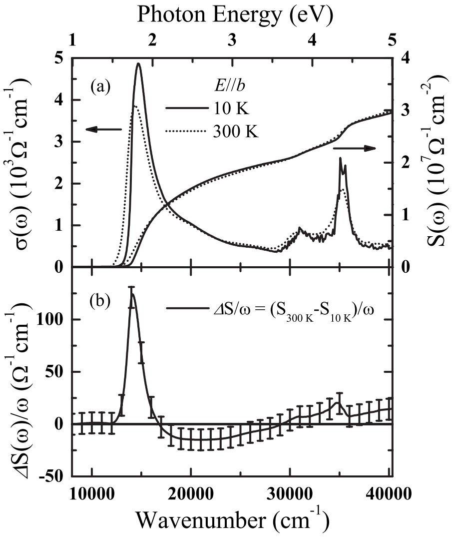

FIG. 4. (a) Optical conductivity and spectral weight along the chain direction of Sr_2CuO_3 at 300 and 10 K and (b) its difference normalized by the energy. The error bar is assumed from the conductivity value in the gap region.

cluding Sr_2CuO_3. Figure 4(a) shows temperature-dependent $\sigma(\omega)$ up to 5 eV and integrated spectral weight. Because $\sigma(\omega)$ was obtained by Kramers-Kronig transformation from $R(\omega)$, it is difficult to estimate the error. Only in the gap region, where is no absorption, the error could be estimated rather easily. Comparison of the values in the gap region with other reported data suggests a rather small error in our spectra.[2,7,9] To examine the spectral weight redistribution, the spectral weight change between 300 and 10 K normalized by energy is shown in Fig. 4(b). Note that the normalized spectral weight will have the error similar to that in $\sigma(\omega)$ because the spectral weight is an integrated value over energy. There is strong temperature dependence in peak A, which has been understood by the electron-phonon coupling.[7] The spectral weight sum rule is satisfied at about 3.5 eV within experimental error. This implies that the ZRT excitation in this material is absent. Its robust antiferromagnetic configuration with the largest exchange energy among cuprates may not allow the ZRT transition which requires finite ferromagnetic interaction. Because it is difficult to separate peaks A and B in a consistent way at all temperatures (note that even peak A itself requires a few Gaussians for a decent fitting) it would be meaningless to discuss further details on the spectral weight. However, it has been noticed that $\sigma(\omega)$ can be simply scaled by the peak height and width right above the gap.[9] Best scaling factors expect decrease in spectral weight at low temperature. But it should be noted that peak A could be composed of a few peaks due to electron-phonon coupling.[21] In addition, bound exciton peaks appear at low temperature of which spectral weight is not taken into account in the scaling argument.[9] Therefore, it could be stated that spectral weight of the bound excitons may come mainly from a lower part of peak A. But any further argument is beyond current observations.

In summary, optical conductivity spectra and the loss function of Sr_2CuO_3 were analyzed in detail. Four excitations below 5 eV were attributed to the ZRS state and NB O 2*p* states involved excitations, respectively. The small peak at 2.3 eV in EELS spectra, which had been believed to be a localized excitation within single CuO_4 plaquette, turned out to correspond to the strong excitonic charge-transfer excitation at 1.8 eV in $\sigma(\omega)$. Another ZRS state involved transition was addressed, which appears as the strongest peak at 2.7 eV in the loss function and corresponds to the continuum excitation in 1D EHM. The spectral weight sum rule is satisfied within ZRS involved excitations below 3.5 eV. This finding of the existence of an excitonic peak and its continuum excitation demands reexamination of the electronic structure of 2D cuprates.

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[15] It is worth noting that Matsueda *et al.* (Ref. 22) interpreted the hump structure (a long tail above the excitonic peak) as another peak based on one-dimensional two-band Hubbard model. They claimed that the excitonic peak corresponds to the excitation from the lower Hubbard band (from the hole point of view) to the singlet bound state while the hump structure originates by the excitation from the lower Hubbard band to the unbound state, which correspond to the α and β excitations, respectively (see Ref. 22). However, this scenario cannot explain the observed anisotropy between a and b axes of Sr_2CuO_3, neither the much larger charge-transfer gaps of edge-sharing chain compounds than those of compounds with corner-sharing structures (Ref. 17).

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