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Charge dynamics in strongly correlated one-dimensional Cu-O chain systems revealed by inelastic x-ray scattering

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We report on the Cu 1*s* resonant inelastic x-ray scattering (RIXS) of Cu-O one-dimensional strongly correlated insulator systems with contrasting atomic arrangements, namely edge-sharing $CuGeO_3$ and corner-sharing Sr_2CuO_3. Owing to good statistics of the high-resolution RIXS data, so far unresolved fine structures are revealed. Detailed photon-energy and momentum dependence of the RIXS spectra in comparison with theoretical calculations has clarified the natures of the low-energy charge excitations and hybridization of the electronic states.

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Resonant inelastic x-ray scattering (RIXS) is a powerful tool to probe the momentum dependence of low-energy excitations in solids.[1,2] This technique is intriguing to clarify bulk electronic states of strongly correlated insulators, which have attracted a keen general interest in decades.[3–5] For metallic systems, high-resolution angle-resolved photoemission (ARPES) is promising to detect their occupied states. Nowadays both surface-sensitive low-energy[6] and bulk-sensitive high-energy[7,8] ARPES measurements are feasible. Compared to ARPES, RIXS is really bulk sensitive and applicable to insulators with high resistivity, where the electron correlation is even stronger.[1,2,5,9] However, high-energy resolution RIXS is rather demanding because of their poor count rate. For this purpose, high photon flux in a small spot size and a highly efficient analyzer crystal are required.

Here we report photon-energy ($h\nu$) and momentum (Δk) dependence of the Cu 1*s* RIXS with good statistics for two contrasting Cu-O one-dimensional (1D) insulating systems $CuGeO_3$ (Ref. 10) and Sr_2CuO_3 (Ref. 2) with dominantly divalent Cu. As shown in Fig. 1(c), $CuGeO_3$ has a single chain with the edge-sharing CuO_2 plane configuration with the Cu-O-Cu angle (θ) of 99°, where the Cu-Cu chain axis is taken as the *x* axis and the CuO_2 plane corresponds to the *x*-*y* plane. The $3d_{xy}$ orbital is unoccupied because it has the highest energy among the whole *d* orbitals according to an extended *d*-*p* model calculation.[11,12] The transfer energy between the neighboring Cu 3*d* sites via O 2*p* sites is thought to be very small because of the orthogonality of the Cu $3d_{xy}$ orbitals on the neighboring sites coupled to the O 2*p* orbitals in the edge-sharing $CuGeO_3$. On the other hand, Sr_2CuO_3 has a single Cu-O chain with the corner-sharing configuration as shown in Fig. 2(b). The transfer energy is thought to be large in this case, in which the Cu 3*d* hole is thought to be in the $3d_{x^2-y^2}$ state. Therefore, very different behavior of charge dynamics is expected in these systems.

A RIXS experiment was performed at BL19LXU of SPring-8 with a 27-m-long x-ray linear undulator. By use of two channel cut crystal monochromators, the resolution of the incident $h\nu$ was better than 300 meV. A horizontal focusing was better than 100 μm on the sample. The instrument with a 1-m Rowland circle was used for the measurement. The total resolution of 400 meV (full width at half maximum) was achieved by using a spherically bent Si(553) analyzer crystal. Transmission (reflection) mode was employed for $CuGeO_3$(Sr_2CuO_3) kept at room temperature. In both cases, the polarization of the light and the Cu-O chain were in the horizontal plane which corresponds to the scattering plane. For a thin-film $CuGeO_3$ sample, the chain axis was oriented by Laue diffraction. A surface perpendicular to the Cu-O chain was oriented and polished for a Sr_2CuO_3 sample. For a dipole excitation, the Cu 1*s* state is excited to the Cu 4*p* states, where an electron in a certain occupied state is excited to a certain unoccupied state while emitting the scattered x rays with the corresponding energy loss. The photon momentum *k* is large in the x-ray region and the momentum difference Δk between the incident and scattered photons can easily cover few Brillouin zones.

The experimental results of edge-sharing $CuGeO_3$ are shown in Fig. 1. The inset in Fig. 1(c) shows the Cu 1*s* absorption spectrum measured by fluorescence yield. The quadrupole excitation peak is observed at $h\nu$=8.980 keV, whereas the main absorption band is rather wide. The RIXS spectra are measured for $\Delta k = 3\pi$ at three $h\nu$ of 8.990, 8.995, and 9.000 keV as shown in Figs. 1(a) and 1(b). Three RIXS structures are observed near 6.3, 3.7, and 1.6 eV. It is recognized that the intensity ratio between the structures at 3.7 and 6.3 eV is the smallest at $h\nu$=9.000 keV and the structure at 1.6-eV above the smooth tail of the elastic peak is negligible at $h\nu$=8.990 keV. Then the Δk dependence of the RIXS is measured at different $h\nu$. A typical result at $h\nu$=8.995 keV [Fig. 1(c)] shows very small dispersion of all RIXS peaks.

The results of Sr_2CuO_3 are shown in Fig. 2. The inset of Fig. 2(a) shows the Cu 1*s* absorption spectrum. Two peak

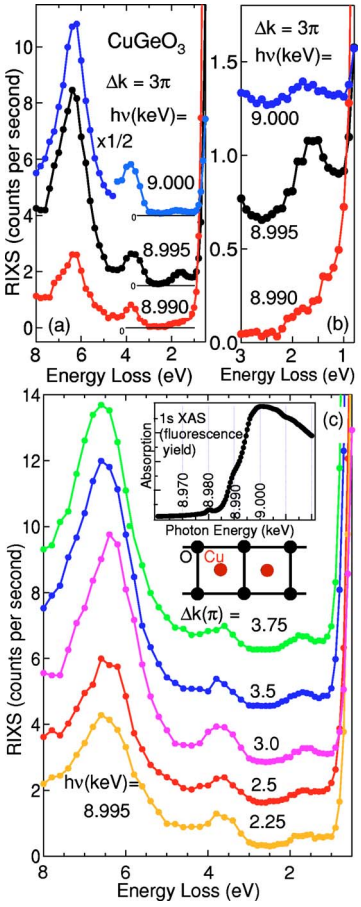

FIG. 1. (Color online) RIXS spectra of edge-sharing $CuGeO_3$ at room temperature. The error bar of the intensity is within the size of symbols. (a) $h\nu$ dependence measured at $\Delta k=3\pi$. (b) Same spectra as (a) but expanded in the low-energy region. (c) Δk-resolved RIXS spectra at $h\nu=8.995$ keV. The inset shows the Cu 1*s* absorption spectrum.

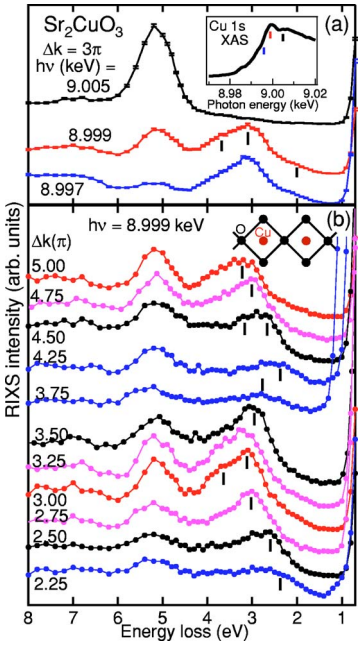

FIG. 2. (Color online) RIXS spectra of corner-sharing Sr_2CuO_3 at room temperature. The error bar is shown, for example, at $h\nu=9.005$ keV. (a) $h\nu$ dependence measured at $\Delta k=3\pi$. The inset shows the Cu 1*s* absorption spectrum. (b) Δk-resolved RIXS spectra at $h\nu=8.999$ keV. Some representative structures are indicated by vertical bars for a guide to the eye.

structures are recognized near 8.999 and 9.005 keV in addition to an absorption hump near 8.985 keV (the quadrupole excitation threshold is near 8.980 keV). Figure 2(a) shows clear differences of RIXS at $h\nu=8.997$, 8.999, and 9.005 keV for $\Delta k=3\pi$. For excitations at 8.997 and 8.999 keV, three broad energy-loss structures are observed at around 3.2, 5.2, and ~6.7 eV. One can further recognize a shoulder near 2 eV for $h\nu=8.997$ and 8.999 keV, and near 3.7 eV for $h\nu=8.999$ keV owing to the good statistics compared with Ref. 2. It is remarkable that the 3.2-eV structure is dramatically suppressed at $h\nu=9.005$ keV. Figure 2(b) shows the Δk dependence of the RIXS at $h\nu=8.999$ keV. A clear Δk dependence is observed for the above-mentioned peak located at 3.2 eV at $\Delta k=3\pi$. Its dispersion is found to have a minimum close to 2.3 eV around $\Delta k=4\pi$ and 2π and a maximum close to 3.2 eV around $\Delta k=5\pi$ and 3π, where shoulders near 3.7 and 2.0 eV are also seen. The Δk-dependent shift of the structure near 5.2 eV is much less prominent.

We now discuss the observed complex RIXS structures in comparison with theoretical calculations. The extended *d-p* model calculation by a rigorous numerical diagonalization method for finite-size clusters[11,12] predicts a two-peak structure separated by about 4 eV in the Cu 1*s* absorption spectrum, reflecting different intermediate states in the RIXS processes. The low-energy peak corresponds mainly to the "$|1s^1 3d^{10} L 4p^1\rangle$" states ($L$ denotes the hole in the O 2*p* states), where the Cu 3*d* hole is transferred to the O 2*p* state in order to reduce the on-site Coulomb repulsive energy between the Cu 1*s* and 3*d* holes. The higher-energy peak originates mainly from the "$|1s^1 3d^9 4p^1\rangle$" state with the Cu 3*d* hole on the Cu site. The energy separation between these two peaks depends upon the Cu 3*d*-O 2*p* hopping energy and on-site Coulomb energy between the Cu 1*s* and 3*d* holes.

We have calculated the electronic structures as well as the charge excitations of the edge- and corner-sharing CuO_2 planes within a Hartree-Fock (HF) theory by using a random-phase approximation, in which the electron correlation effects are perturbatively taken into account.[13] The antiferromagnetic ground state of Mott insulators is well described by the HF theory. Then the charge-excitation energy in Mott insulators can be generally regarded as the antiferromagnetic gap energy within the HF theory. For $CuGeO_3$, two RIXS peaks located near 3.5 and 6.5 eV with very small dispersions of less than 0.2 eV against Δk are predicted, where the spectral weight near 3.5 eV is much smaller than that near 6.5 eV. The Slate-Koster hopping parameters for $CuGeO_3$ were chosen as $V(pd\sigma)=-1.6$ eV and $V(pd\pi)=0.65$ eV. The $V(pp\sigma)=0.5$ eV parallel to the chain (0.7 eV perpendicular to the chain) and $V(pp\pi)=-0.25\ V(pp\sigma)$. The 3.5-eV peak corresponds to the excitation from the so-called Zhang-Rice singlet (ZRS), which is made of the Cu 3*d* hole coupled with the O 2*p* hole,[14] to the upper Hubbard band (UHB). The energy loss near 6.5 eV is ascribed to the exci-

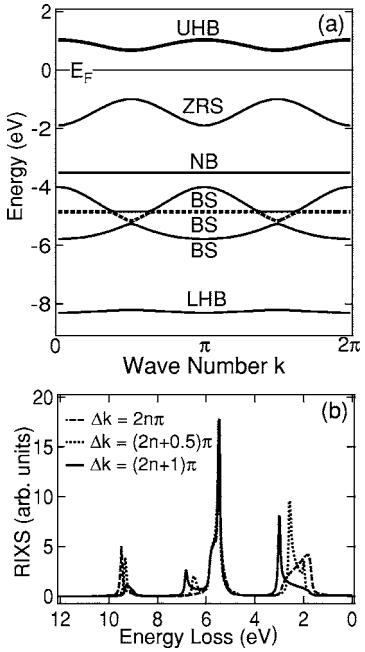

FIG. 3. (a) Electronic structure predicted by the Hartree-Fock calculation (depicted in the electron presentation). Hopping parameters are taken as $t_{x,dp}=-1.4$ eV, $t_{y,dp}=-1.4$ eV, and $t'_{pp}=-0.7$ eV with the correlation energy $U_{dd}=11$ eV. (b) predicted RIXS spectra at three typical $\Delta k=2n\pi$, $(2n+0.5)\pi$ and $(2n+1)\pi$ with integer n.

tation from the bonding state (BS) (in terms of the electron character) between the Cu $3d$ and O $2p$ states to the UHB. These structures are in a good agreement with the experimental spectra. Furthermore, the extended d-p model suggests that the intensity ratio between the ZRS→UHB to BS→UHB is enhanced when the low-energy absorption ($|1s^13d^{10}L4p^1\rangle$) peak is excited, which is in a qualitative agreement with the $h\nu$-dependent experimental result in Fig. 1(a). On the other hand, the experimentally observed peak at 1.6 eV in the RIXS spectra of $CuGeO_3$ cannot be predicted from both theories. We interpret the 1.6-eV structure as the d-d transition taking place on the same Cu site, as implied from the electron-energy-loss spectroscopy (EELS) (Ref. 15) and soft x-ray O $1s$ RIXS (Ref. 16). Since the $d_{x^2-y^2}$ and d_{xy} orbitals can hybridize via the O $2p$ orbital in edge-sharing $CuGeO_3$ with $\theta=99°$, the d-d transition takes place between these states. The strong suppression of this peak at $h\nu=8.990$ eV in RIXS is decisively understood because the $|1s^13d^{10}L4p^1\rangle$ is dominant at this $h\nu$ and the d-d transition does not take place in the $3d^{10}$ configuration.

Figure 3 shows the calculated results for Sr_2CuO_3 with $t_{x,dp}=-1.4$ eV, $t_{y,dp}=-1.4$ eV, and $t'_{pp}=-0.7$ eV; and $U_{dd}=11$ eV in the HF theory. The incident $h\nu$ is fixed to 8.999 keV. We have obtained a better fitting for the peak positions than in the previous calculation[13] by using another reasonable parameter set as above. Both UHB and ZRS have noticeable dispersions caused by the strong hybridization between the Cu $3d$ and O $2p$ states and large transfer energies. The dispersions show the π periodicity reflecting the antiferromagnetic ground state. The calculated RIXS spectra in Fig. 3(b) for typical Δk values of $2n\pi, (2n+0.5)\pi$ and $(2n+1)\pi$ with integer n show the 2π periodicity[13] instead of π periodicity, reflecting the partial occupation number of the Cu $3d_{x^2-y^2}$ electrons for each spin component in the band. The 2π periodicity is in full agreement with the experimental results. The 2π periodicity was already reported in Sr_2CuO_3 (Ref. 2) and $SrCuO_2$ (Ref. 17). According to Fig. 3(b), ZRS→UHB excitation is predicted to have a large dispersion and more than two components (the dispersion of the RIXS features is quantitatively different but qualitatively similar to Fig. 4 of Ref. 13). It is noticed that its spectral weight shifts toward smaller energies near $\Delta k=2n\pi$ ($n=0$, 1, 2, …) in agreement with the experimentally observed dispersive feature through 2.3–3.2 eV. In this calculation the ZRS→UHB excitation at $\Delta k=(2n+1)\pi$ has a weak low-energy shoulder near the energy loss of 2 eV, which is also consistent with the experimental results. Although several arguments have been paid to this threshold structure,[17,18,2] it is demonstrated that this structure is inherent in the ZRS→UHB excitation. The upper and lower BS between the Cu $3d$ and O $2p$ states have also noticeable dispersions, whereas the O $2p$ nonbonding band (NB) at −3.5 eV, the middle BS at −4.8 eV, and the Cu $3d$ lower Hubbard band (LHB) at −8.3 eV have very small dispersions as predicted in Fig. 3(a). The smallness of the Δk dependence of the 5.2-eV structure in Fig. 2(b) is ascribable to the small dispersion of the middle branch BS→UHB excitation. The excitation from the NB and upper BS states is not strong in RIXS because of the little partial occupation number of the Cu $3d_{x^2-y^2}$ electrons. According to this calculation, an additional structure due to the lower BS→UHB excitation is predicted around 6.0–7.0 eV. Although there is some hint of such a structure in the region between 6 and 8 eV in Fig. 2(a), further studies are necessary to confirm the prediction. The intensity of ZRS→UHB excitation is dramatically reduced at $h\nu=9.005$ keV. This is because this $h\nu$ corresponds to the intermediate $|1s^13d^94p^1\rangle$ state and further Cu $3d$ excitation requiring the correlation energy U_{dd} is very unfavorable. The distinct d-d excitation is not observed in corner-sharing Sr_2CuO_3 because the hybridization is strong between the Cu $3d_{x^2-y^2}$ and O $2p$ states and then the hole is not localized on the Cu site, making the on-site d-d transition not a well-defined excitation. On the other hand, the intensity of the ZRS→UHB excitation relative to the BS→UHB excitation is much stronger than $CuGeO_3$, reflecting the easy formation of the ZRS in corner-sharing system. Although the observed structures in the RIXS spectra and their $h\nu$ dependence for Sr_2CuO_3 are mostly explained, there is still an unsolved problem with respect to the weak shoulder structure near 3.7 eV for $\Delta k=3\pi$ [Fig. 2(a)]. Further theoretical study is required to interpret this weak structure, even though it seems to be related to the main ZRS→UHB branch excitation. Finally, in order to make a complete discussion on the $h\nu$ dependence of RIXS, we require more detailed information on the Cu $4p$ electronic structure. Such a discussion will be reported in a future work.

In conclusion, clear contrasts between the edge-sharing $CuGeO_3$ and corner-sharing Sr_2CuO_3 are revealed by virtue of the $h\nu$-dependent and Δk-resolved RIXS, reflecting the different natures of the electronic states. The high potential of RIXS for the study of strongly correlated insulator systems is thus demonstrated.

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