Theoretical Study on Resonant Inelastic X-Ray Scattering in Quasi-One-Dimensional Cuprates

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We study theoretically the resonant inelastic x-ray scattering in quasi-one-dimensional insulating copper oxides, where the incident photon energy is tuned to the Cu1s-4p absorption energy. Our attention is focused particularly on the strong momentum-transfer dependence of the spectral shape observed in recent experiments. We describe the antiferromagnetic ground state within the Hartree-Fock theory, and consider charge excitations from the ground state within the random phase approximation. By taking account of the electron correlation effects perturbatively, we obtain detailed momentum-transfer dependence of the spectra in a semi-quantitative agreement with the experiments.

KEYWORDS: Resonant inelastic x-ray scattering, One-dimensional copper oxide, Sr2CuO3, SrCuO2

Resonant inelastic x-ray scattering (RIXS) measurements are now becoming a promising and unique experimental technique to clarify the detailed charge excitation spectra of solids in a relatively high-energy range, owing to high brilliance of synchrotron radiation. In particular, the RIXS measurements in the hard x-ray regime could be a new powerful tool to detect momentum dependent charge excitations in solids. A number of compounds have been investigated by this technique. Among them, the RIXS in cuprates utilizing the Cu1s-4p absorption edge attracts much interest recently, since relatively large momentum dependence was indeed observed in the charge excitation spectra.

The electronic properties of the quasi-one-dimensional (Q1D) insulating cuprates Sr2CuO3 (SCO213) and SrCuO2 (SCO112) are well characterized by the one-dimensional chain consisting of the Cu-O plaquettes. The Cu-O chains are expected only weakly coupled with each other. In SCO213 the Cu-O plaquettes are aligned with sharing the corner oxygen atoms with the nearest plaquettes, as shown in Fig. 1. It was reported that SCO213 shows antiferromagnetic order below about 5 K with reduced staggered magnetization along the chain. The strong fluctuations are responsible for the extremely reduced Néel temperature and magnetization, but the ground state of SCO213 is an antiferromagnetic (AF) insulator. Concerning SCO112, the Cu-O plaquettes form a zigzag chain by sharing the edges with the nearest plaquettes. The zigzag chain can be regarded approximately as being constructed by combining two independent Cu-O chains sharing the edges with each other. Therefore we study the RIXS properties of these two cuprates by considering the corner-sharing Cu-O chain as in Fig. 1 in the present article.

Recently, RIXS measurements were performed for the Q1D cuprates SCO213 and SCO112. In the both Q1D cuprates, characteristic spectral weight was obtained for energy transfer \( \omega \approx 2, 5.6 \) (eV), but the origin of the spectral peaks are still unclear. The aim of the present article is to provide a quantitative understanding on the RIXS, particularly on the position of the peaks and the highly momentum-dependent behaviors of the spectra in these one-dimensional cuprates. We calculate the intensity in the RIXS spectra as a function of energy-momentum transfer, using the perturbation theory developed by Platzman and Isaacs. We describe the antiferromagnetic (AF) ground state by the Hartree-Fock (HF) theory, and take account of the excitations from the ground state within the random phase approximation (RPA). As a result, we obtain a semi-quantitative agreement with experiments, regarding the peak positions and the momentum dependent behaviors.

The essential microscopic process of the RIXS in the cuprates is considered to be as follows. The incident photon excites resonantly the Cu1s core electrons to the upper empty Cu4p bands. Since the core Cu1s orbitals are well localized to be coupled strongly to the Cu3d electrons by the interorbital Coulomb interaction, the created Cu1s core hole scatters the Cu3d electrons, which occupy the bands relatively close to the chemical potential (As a result of the scattering, the most probably only one electron-hole pair is created on the Cu3d band). In order to describe this process specifically, we consider the total Hamiltonian of the form, 

\[
H = H_{dp} + H_{1s-3d} + H_{1s} + H_{4p} + H_z.
\]

The dp-Hamiltonian describing the electronic properties of the Cu3d-O2p bands is given in the form, 

\[
H_{dp} = H_0 + H'.
\]

\( H_0 \) and \( H' \) are the Hartree-Fock Hamiltonians with and without the creation of the Cu1s core hole, respectively. The RPA correction is considered by using the transfer integrals.

Fig. 1. Schematic figure of the Cu-O chain presenting the definition of the transfer integrals.
are the noninteracting and the interaction parts, respectively.

\[ H_0 = \sum_{k\sigma} d^\dagger_{k\sigma} \begin{pmatrix} \varepsilon_d & \zeta_1(k) t_2 & -t_2 \\ -\zeta_1(k) t_2 & \varepsilon_p & \zeta_1'(k) & -\zeta_1'(k) \\ t_2 & -\zeta_1'(k) & \varepsilon_p & 0 \\ -t_2 & \zeta_1'(k) & 0 & \varepsilon_p \end{pmatrix} d_{k\sigma}, \]

(1)

where \( d_{k\sigma} = (d_{k\sigma}, p_{k\sigma}, p_{2k\sigma}, p_{22k\sigma}) \), and \( d_{k\sigma}, p_{k\sigma}, p_{2k\sigma} \) and \( p_{22k\sigma} \) are the electron annihilation operators in the atomic \( d_{x^2-y^2} \) or \( px,py \) orbits at the Cu, O(1), O(2) and O(2') atoms, respectively. The dispersions are \( \zeta_1(k) = 2it_1 \sin \frac{k}{2} \) and \( \zeta_1'(k) = 2it' \sin \frac{k}{2} \). The hopping parameters are \( t_1 = -1.45 \) eV, \( t_2 = -1.8 \) eV and \( t' = -0.7 \) eV (See Fig. 1), as determined for SCO213 by the LDA first principle calculation.\(^{13} \) The interacting part is

\[ H' = \frac{U_d}{N} \sum_{kk'q} d^\dagger_{k-q} d^\dagger_{k'+q} d_{k'} d_{k}. \]

(2)

The Coulomb energy is taken to be \( U_d = 11 \) eV in the present study. Regarding the one-particle level, we take \( \varepsilon_{p2} - \varepsilon_{p1} = 0.5 \) eV, \( \varepsilon_d^{HF} - \varepsilon_{p1} = -0.5 \) eV, where \( \varepsilon_d^{HF} \) is the screened Cu3d one-electron energy within the HF theory. For this parameters, we obtain the AF ground state with the staggered magnetization \( \omega_{\text{stagg}} = 0.43 \mu_B \). The scattering of the Cu3d electrons by the Cu1s core hole is described by

\[ H_{1s-3d} = \frac{V}{N} \sum_{kk'q\sigma\sigma'} d^\dagger_{k'q\sigma'} s^\dagger_{k-q\sigma} s_{k\sigma'} d_{k\sigma}, \]

(3)

where \( s_{k\sigma} \) (\( s^\dagger_{k\sigma} \)) is the annihilation (creation) operator for the Cu1s electrons with momentum \( k \) and spin \( \sigma \), and \( V \) is the so-called core-hole potential. \( H_{4p} \) and \( H_{1s} \) describe the kinetics of the electrons on the Cu4p and Cu1s bands. Since the Cu1s electrons are well localized, we take completely flat dispersion for them. For the Cu4p electrons, we use simple two-dimensional cosine-shaped band for simplicity. This simplification does not affect the spectral shape so drastically, because the factor containing the Cu4p dispersion function is integrated up in momentum, as seen later in eq. (5). \( H_x \) describes the transitions between the Cu1s and Cu4p states, involving the photon absorption and inverse emission processes. \( H_x \) is of the form

\[ H_x = \sum_{k\sigma\sigma'} (w(q; k)p^\dagger_{k+q\sigma} s_{k\sigma} + \text{h.c.}), \]

(4)

where \( p^\dagger \) is the creation operator of the Cu4p electron. In the present study, we ignore the momentum dependence of the matrix elements \( w(q; k) \), i.e., \( w(q; k) = w \).

The main spectral weight of the RIXS is evaluated by the diagram shown in Fig. 2. In Fig. 2(a), the effective three point vertex function \( \Lambda \) represented by the shaded triangle is calculated within the RPA, and this vertex part is inserted into the diagram Fig. 2(b) representing the total scattering probability. In Fig. 2(b), note that the off-diagonal components of the Keldysh Green’s functions are assigned to the solid lines which connect the upper normally-time-ordered branch and the lower reversely-time-ordered branch, while the usual causal (normally-time-ordered) Green’s functions are assigned to the solid lines in the upper branch and the

![Fig. 2](image-url)

(a) Vertex renormalization in the RPA. The solid lines, the shaded triangle and the empty square are the Green’s function for Cu3d electrons, the renormalized vertex and the anti-symmetrized bare Coulomb interaction, respectively. (b) The diagrammatic representation of the RIXS intensity. The wavy and the dashed lines denote photons and the 1s-core-hole potential, respectively. The Green’s functions for Cu3d, Cu1s and Cu4p electrons are assigned to the solid lines marked with ‘3d’, ‘1s’ and ‘4p’, respectively.

reversely-time-ordered Green’s functions are assigned to the solid lines in the lower branch.\(^{15} \) Regarding the core hole potential \( V \), we take only the first order term in \( V \) (i.e., Born scattering). The effect of higher orders in \( V \) is briefly mentioned later. The analytic expression for the diagram Fig. 2(b) is obtained as

\[ W(j, \omega; j', \omega') = (2\pi)^3 N |w|^4 \sum_{k_{ijj'}} \delta(E_{j}(k) + \omega - E_{j'}(k + q)) \times n_{j}(k)(1 - n_{j'}(k + q)) \sum_{\sigma'\sigma} U_{j,\sigma}(k)A_{\sigma\sigma'}(\omega, q)U_{j',\sigma'}^{\dagger}(k + q) \]

\[ \times \sum_{k_{ij}} \left| \frac{\omega_{i} + \varepsilon_{1s} + i\Gamma_{1s} - \varepsilon_{4p}(k_{ij})}{\omega_{i} + \varepsilon_{1s} + i\Gamma_{1s} - \varepsilon_{4p}(k_{ij})} \right|^2, \]

(5)

where \( q_{f} \) and \( q_{f} \) (\( \omega_{i} \) and \( \omega_{f} \)) are the momenta (energies) of the initially absorbed and the finally emitted photons, respectively. \( q_{i} - q_{f} \) and \( \omega = \omega_{i} - \omega_{f} \) are the momentum transfer and the energy loss, respectively. \( E_{j}(k) \) and \( n_{j}(k) \) are the energy dispersion and the electron occupation number of the band \( j \), respectively, obtained by diagonalizing the HF Hamiltonian for \( H_{4p} \). \( U_{j,\sigma}(k) \) is the \( (j, \sigma) \)-element of the unitary matrix diagonalizing the HF Hamiltonian for \( H_{4p} \). \( \varepsilon_{1s}(k) \) and \( \varepsilon_{4p}(k) \) are the kinetic energies of the Cu1s and Cu4p electrons, respectively. In the present study the incident photon energy \( \omega_{i} \) is tuned to the Cu1s-4p absorption energy \( \omega_{i} \approx \varepsilon_{4p}(0) - \varepsilon_{1s} \), for which the intensity of the spectrum is enhanced by the resonance. The decay rate \( \Gamma_{1s} \) of the core hole is 0.8 eV in the present study.

The numerical results of the RIXS intensity by the formula eq. (5) are shown as a function of energy loss \( \omega \) for momentum transfers \( q = 0, \frac{Q}{2} \) and \( \pi \) in Fig. 3. We see that there are three characteristic peaks in the calculated RIXS spectra around \( \omega \approx 2, 6, 10 \) eV. In the experiments, two peaks are observed around the momentum transfer \( \omega \approx 2 \) and 5.6 eV, which are in agreement with the present numerical results. The high-energy 10eV
peak gives only small contribution to the total spectral weight, and the intensity around $\omega \approx 2$ and 6 eV covers the main part of the spectral weight. In Fig. 4, the contourplots of the calculated RIXS spectra are shown as a function of the momentum transfer $q$ and the energy loss $\omega$, and the experimental data read from ref. 6 are also displayed for comparison. We can see that the 2eV peak shows a relatively large sinusoidal dispersion, while the other two do not. This sinusoidal dispersion of the 2eV peak quantitatively agrees with the experimental spectrum read from ref. 6, and the arrows point the two peaks.

In order to inspect the origin of the peaks in the RIXS spectra, we should turn back to the formula (5). Comparing the results modified by the correlations (the solid lines in Fig. 3) with the uncorrected results (the dashed lines in Fig. 3), we can see that the overall spectral shape is well reproduced by the calculation. Although the detailed spectral structure are of course affected by the correlation effects, the momentum dependence of the 6eV peak position is well captured even without any correlation effects, although the detailed spectral structure are of course affected by the correlation effects. Therefore we might expect that the overall spectral shape is determined by the other factors rather than the correlation effects on the scattering process, and thus expect naturally that the factor $n_j(k)(1 - n_{j'}(k + q))|U_{j',d\sigma}(k)U_{d\sigma,j}(k + q)|^2$ is essential for determining the overall spectral shape. It is very interesting to note that this factor is the product of the partial electron occupation number of the band $j$ at the momentum $k$ and the partial hole occupation number of the band $j'$ with the momentum $k + q$. Thus the Cu$3d$-4$p$ RIXS spectra in cuprates are closely related to the partial occupation number of the Cu$3d$ electrons in each band. From this point of view, the RIXS spectra reflect the charge excitation processes in which Cu$3d$ electrons are selectively excited from the lower occupied bands to the upper unoccupied bands. In Fig. 5, the total and the Cu$3d$ partial density of states (DOS) are shown. We find only one DOS weight around $\omega \approx 1$ eV above the chemical potential, and four DOS weights around $\omega \approx -2, -4, -6, -9$ eV below the chemical potential. We can consider naturally that the three RIXS weights around 2, 6 and 10 eV in Fig. 3 are attributable to the excitation processes in which the electrons occupying the

\[ \frac{\partial}{\partial q} \text{Energy Loss (eV)} = \frac{\partial}{\partial \omega} \text{Energy Loss (eV)} \]

\[ \text{RIXS Intensity (arb. units)} \]

\[ \text{Momentum Transfer} \]

\[ \text{Energy Loss (eV)} \]

\[ \text{RIXS spectra as a function of momentum transfer and energy loss. The light and dark regions correspond to high and low RIXS intensity, respectively. The hatched lines are the results with and without the RPA corrections, respectively. The thick solid and the thin broken lines are the results with and without the RPA corrections, respectively. The inset shows a typical experimental spectrum read from ref. 6, and the arrows point the two peaks.} \]

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bands $\omega \approx -2, -6,$ and $-9$ eV are excited to the upper unoccupied band. Of interest is that the sharp peak in the total DOS around $\omega \approx -4$ eV, which corresponds to the non-bonding oxygen band, is not reflected in the RIXS spectra at all. This is because the oxygen non-bonding band does not contain any components of the Cu3d orbitals and the other orbitals which are enough localized at the Cu-sites to be coupled strongly to the Cu1s orbitals. In this sense, the Cu1s-4p RIXS measures the Cu3d-orbital-selective charge excitations. In general, only the bands which are hybridized with the localized orbitals strongly coupled to the core hole are observable in the RIXS spectra.

We should make a distinction between the 2, 6 eV peaks and the 10 eV peak in the RIXS spectra (Fig. 3). Since the DOS peaks around $\omega \approx 1$ and $-9$ eV correspond respectively to the upper and lower Hubbard bands, the RIXS spectral weight around 10 eV in Fig. 3 is related to the charge excitation process across the Mott-Hubbard energy gap, which is usually of the order of $U_d$. On the other hand, the RIXS spectral weights around 2 and 6 eV are related to the charge transfer (CT) process in which the Cu3d electrons mixed in the wide O2p bands are excited to the upper empty Cu3d Hubbard band. This energy scale of the CT excitation is basically connected to the CT energy $\varepsilon_p - \varepsilon_d$. We should note that the main spectral weight originates from the CT process, and the excitations across the Mott-Hubbard gap provides only minor contribution to the RIXS spectra. Therefore, the validity of the theoretical analyses based on the single-band Hubbard model, which consider only Cu sites, is unclear.

We give some remarks on the present calculations. At first, we discuss the validity of the application of the HF theory to the present system. Although the experiments are usually performed above the Néel temperature, the HF analysis is valid in principle only at the absolute zero temperature. In actual low-dimensional systems including the cuprates, the fluctuations are very strong to reduce the Néel temperature and the magnitudes of order parameters. However we would like to stress that it is not so important for the RIXS spectra whether the AF long range order is attained or only short range AF correlation exists. The reasons are as follows. (i) The AF transition does not affect the RIXS spectra so drastically, since the RIXS spectra basically reflect only the charge sector in the scattering process. (ii) The RIXS occurs, basically being well localized in the space, due to the localized nature of the Cu1s core hole. In addition to these points, by noting that the AF ground states in Mott insulators may be continued adiabatically to the HF AF ground state at the absolute zero temperature in the limit of strong Coulomb repulsion, we consider that the AF HF theory provides a good starting point to the analysis. But we should note here the following point. As we have mentioned, the RIXS spectral weight is roughly determined by the product of the Cu3d partial occupation numbers in the occupied and the unoccupied bands. Since the HF theory usually underestimates the magnitude of the localized moment, the product of Cu3d electron and hole occupation numbers $n_{p\sigma}(1-n_{p\sigma})$ in the local picture is overestimated. Thus the intensity around 10 eV in the RIXS spectra is overestimated within the HF theory. It is natural to consider that the CT excitations, rather than the charge excitation process across the Mott-Hubbard gap, provide the main contribution to the spectral weight, and the 10 eV peak might not be observable in reality.

We have considered only the first order terms in the core hole potential $V$. Actually we investigated the effects of higher orders in $V$ within the $T$-matrix approximation as in usual single impurity problems (Results are not shown). However we found that the spectral shape is not so drastically changed by the higher orders of $V$, although the absolute magnitude of the spectra is changed.

In the present work, we have analyzed theoretically the RIXS spectra in the Q1D cuprates. The peak positions and the momentum-transfer dependence of the RIXS spectra are explained in a semiquantitative agreement with the experimental results. We have shown that the RIXS measurement in cuprates is a unique technique to clarify the Cu3d-orbital-selective charge excitations.

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