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Mott Gap Excitations in Twin-Free $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($T_c = 93$ K) Studied by Resonant Inelastic X-Ray Scattering

K. Ishii,^{1,*} K. Tsutsui,² Y. Endoh,^{1,3} T. Tohyama,² K. Kuzushita,¹ T. Inami,¹ K. Ohwada,¹ S. Maekawa,² T. Masui,⁴ S. Tajima,⁴ Y. Murakami,^{1,5} and J. Mizuki¹

¹*Synchrotron Radiation Research Center, Japan Atomic Energy Research Institute, Hyogo 679-5148, Japan*

²*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

³*International Institute for Advanced Studies, Kizugawadai, Kizu, Kyoto 619-0025, Japan*

⁴*Superconducting Research Laboratory, ISTEK, Tokyo 135-0062, Japan*

⁵*Department of Physics, Tohoku University, Sendai 980-8578, Japan*

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Mott gap excitations in the optimally doped high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($T_c = 93$ K) have been studied by the resonant inelastic x-ray scattering method. Anisotropic spectra in the ab plane are observed in a twin-free crystal. The excitation from the one-dimensional CuO chain is enhanced at 2 eV near the zone boundary of the b^* direction, while the excitation from the CuO_2 plane is broad at 1.5–4 eV and almost independent of the momentum transfer. Theoretical calculations based on the one-dimensional and two-dimensional Hubbard model reproduces the observed spectra when different values of the on-site Coulomb energy are assumed. The Mott gap of the CuO chain site is found to be much smaller than that of the CuO_2 plane site.

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Of the various superconducting copper oxides, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) is still recognized as useful for elucidating the mechanism by which unconventional superconductivity at high transition temperature arises. However, the unique crystal structure, particularly the one-dimensional (1D) CuO chains running along the crystalline b axis next to the double CuO_2 planes, complicates matters. The CuO chains contribute to the bulk electronic properties such as optical conductivity [1] and dc electric conductivity [2]. Furthermore, a substantial anisotropic character in the superconducting state observed in the far infrared spectra [3] and the thermal conductivity [4] suggests that the superfluid density is induced in the CuO chains, even though it is generally recognized that the two-dimensional (2D) CuO_2 planes play the most important role in the superconductivity of YBCO. It is still uncertain what role the CuO chains might play in the superconductivity. The CuO chains might behave as unstable 1D metals and thus relax to a charge modulation of twice of the Fermi wave vector ($2k_F$) [5–7], but other factors than the simple proximity effect of superconductivity in the CuO_2 planes might also appear. The experimental evidence so far has been explained either by the proximity-effect induced chain superconductivity with magnetic impurities [8] or by Friedel oscillation in the fragmentary CuO chain due to partial oxygen depletion [9]. Therefore any experimental evidence that clarifies the role of the CuO chain would contribute significantly to understanding the general causes of high transition temperature in YBCO.

As a first step to solve this issue, the intrinsic electronic structure of the chain should be clarified. One reason why the electronic structure remains unclear is the lack of experimental tools to distinguish the electronic states of

the chain from those of the plane. Here we applied the resonant inelastic x-ray scattering (RIXS) method, which measures the momentum dependence of the electronic excitations unlike the conventional optical method. Angle-resolved photoemission spectroscopy (ARPES), which also gives momentum-resolved spectra, presented the dispersion relation below the Fermi energy (E_F) in the CuO chain [10], but the excitations across E_F have not been searched yet. ARPES essentially yields the one-particle spectra for the occupied states below E_F , while RIXS gives the two-particle excitations. The RIXS results from Mott insulators such as cuprates [11–15] and a manganite [16] show a peak structure in the excitation spectra across the so-called Mott gap. Furthermore, recent RIXS measurements of hole-doped manganites showed that a salient peak feature of the Mott gap remains even in the metallic state and that the energy gap is partly filled at the same time [17], which really demonstrates the capability of RIXS to explore the electronic excitations in the metallic state of the transition metal oxides.

In this Letter, we present the RIXS spectra of twin-free YBCO at optimal doping ($T_c = 93$ K), from which we can successfully distinguish the electronic excitations between the CuO_2 planes and the CuO chain. We also show the anisotropic x-ray absorption spectra near the Cu K edge. It is noted that we selected optimally doped YBCO because the anisotropy in both the normal conductivity and the superconductivity is saturated. A twin-free crystal is indispensable to elucidate the anisotropy as demonstrated in the recent neutron scattering experiment [18].

The experiments were carried out at the beam line 11XU of SPring-8 [19]. A Si(111) double-crystal monochromator and a Si(400) channel-cut secondary monochromator were used. Horizontally scattered x rays were analyzed in en-

ergy by a spherically bent Ge(733) crystal. Overall energy resolution is about 400 meV as estimated from the full width at half maximum (FWHM) of the quasielastic scattering. Momentum resolution is $\sim 0.17 \text{ \AA}^{-1}$ at maximum, which corresponds to about 1/10 of a^* . The c axis of the crystal was kept perpendicular to the scattering plane. Our use of π polarization of the incident x ray enables us to reduce the intensity of the elastic scattering when the scattering angle (2θ) is close to 90 degrees. It is crucially important to measure the low energy excitation without being disturbed by the tail of the elastic scattering, so that the Brillouin zone measured is chosen at a value of 2θ near 90 degrees. We used two single crystals. One is a twinned crystal, which is used for the incident energy (E_i) dependence. The x-ray absorption spectra and the momentum dependence of RIXS were measured with a twin-free crystal. The twin-free single crystal was grown by a crystal pulling technique [20] and detwinned under uniaxial pressure. All the spectra were collected at room temperature.

First we measured the spectra by varying the energy of the incident x ray to determine the resonant energy, as shown in Fig. 1(a). The scattering vector is fixed at $\mathbf{Q} = (4.5, 0, 0)$ corresponding to the superposition of $\mathbf{q} = (\pi, 0)$ and $(0, \pi)$, where \mathbf{q} represents the reduced wave vector in the ab plane. A peak at 2 eV was observed at $E_i = 8990$ eV. There are other resonant features between 4 and 9 eV at higher E_i . We can see two peaks at 5.5 and 8 eV in the spectra of $E_i = 8996$ eV. Hereafter we fixed E_i at 8990 eV to focus on the excitation at low energy (~ 2 eV).

In Fig. 1(b), we show the x-ray absorption spectra of the twin-free crystal near the Cu-K absorption edge. The spectra were measured by the fluorescence method. Clear differences between $\epsilon \parallel a$ and $\epsilon \parallel b$ were observed. ϵ is the polarization vector of the x ray. By analogy with the spectra of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ [21], we can assign the peaks as follows: The peak at 8980 eV [labeled A in Fig. 1(b)] originates from the electric quadrupole transition from the $1s$ to the $3d$ state. A pair of peaks at 8984 and 8990 eV (B and C) is assigned as the dipole transition from $1s$ to $4p_\pi$, along which there is no ligand oxygen. The final state of peak B is well screened and that of peak C is poorly screened. The peaks at 8997 and 9003 eV (D and E) correspond to the transition to $4p_\sigma$, whose orbital extends toward the ligand oxygens. In the case of $\epsilon \parallel b$, the Cu atoms in both the CuO_2 plane and the CuO chain have ligand oxygen atoms along the direction of ϵ , and only the transition to $4p_\sigma$ is observed. On the other hand, because the Cu atoms in the chain have no oxygen along the a axis, the transition to the $4p_\pi$ state appears in $\epsilon \parallel a$. The fact that the peak at 2 eV appears resonantly at the intermediate state of $4p_\pi$ indicates that the peak originates from the chain.

Figure 2 shows the momentum dependence of the RIXS spectra in which \mathbf{q} is parallel to $[100]$, $[010]$, and $[110]$. The absolute momentum transfer (\mathbf{Q}) is represented as $\mathbf{Q} = \mathbf{G} + \mathbf{q}/2\pi$ where $\mathbf{G} = (0, 4, 0)$. Apart from the peak

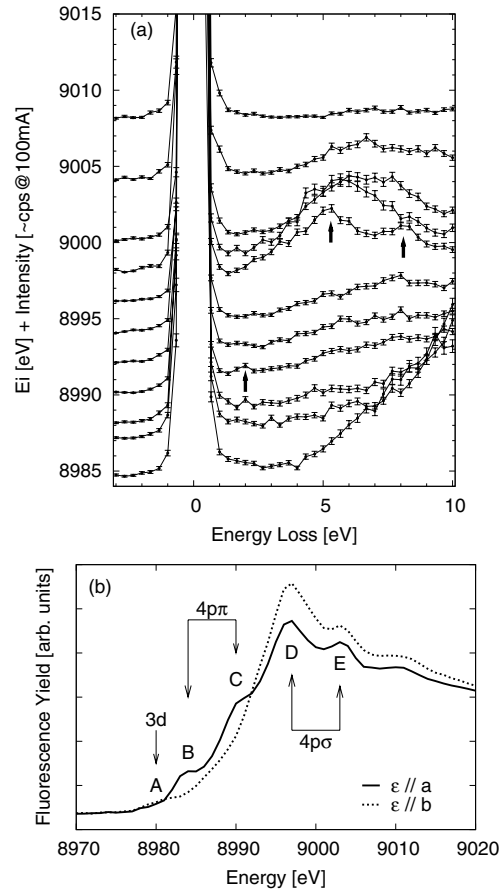


FIG. 1. (a) Resonant inelastic x-ray scattering spectra of twinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as a function of energy loss at some representative incident x-ray energies (E_i). The scattering vector is fixed at $\mathbf{Q} = (4.5, 0, 0)$. Three resonantly enhanced excitations are indicated by the arrows. The strong intensity above 10 eV in the spectrum of $E_i = 8984.5$ eV comes from the Cu $K\beta_5$ emission line. (b) Absorption spectra of twin-free $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ near the Cu-K absorption edge.

at 5.5 eV, we found two characteristics in the low energy region which are considered to be excitations across the Mott gap. One is a broad excitation at 1.5–4 eV that is almost independent of the momentum transfer. The other is an excitation at 2 eV which is prominent at the zone boundary in the b^* direction, that is, the intensity is enhanced near $(0, \pi)$ and (π, π) . The excitation along the a^* and b^* axes should be equivalent in the planes. On the other hand, the momentum dependence along the b^* axis can be stronger than that along the a^* axis in the chains, because the chains run along the b axis. Accordingly, a clear momentum dependence of the 2 eV peak along the b^* axis is direct evidence that this is the excitation across the Mott gap in the chain, while the broad feature at 1.5–4 eV is the excitation in the plane. We note that the scans at $(\pi, 0)$, $(0, \pi)$, and (π, π) are duplicated at different beam times in order to affirm the small 2 eV feature. We also measured at the different Brillouin zones and confirmed that these characteristics are independent of the selection of the Brillouin zone. Detailed data are presented in [22].

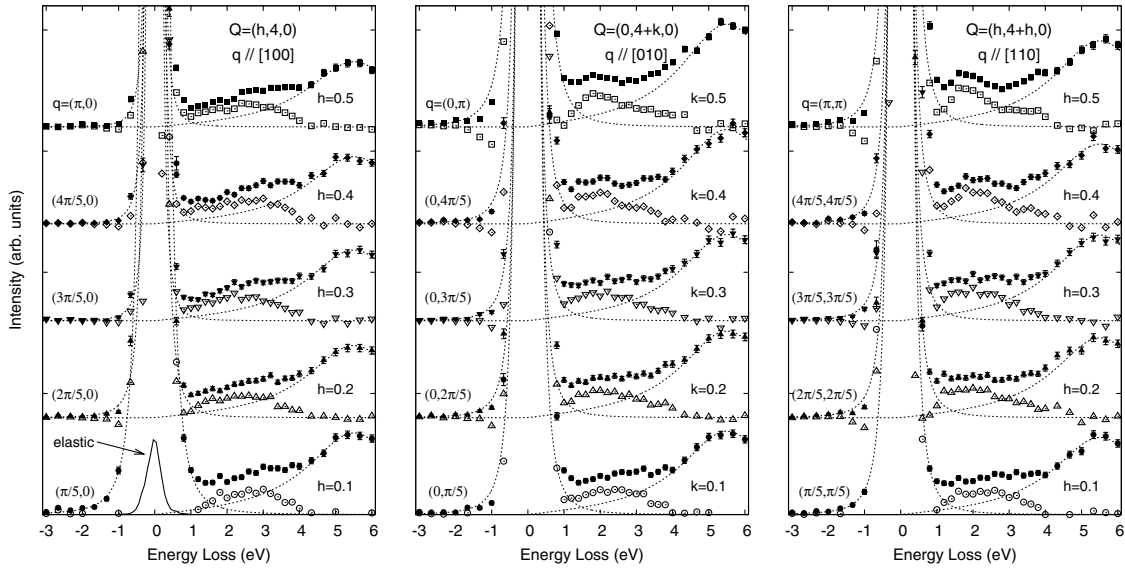


FIG. 2. Momentum dependence of the RIXS spectra of a twin-free crystal for q along [100], [010], and [110], respectively. The energy of the incident x ray is 8990 eV. The filled marks are the raw data, and the open marks are the data from which the elastic scattering and the peak at 5.5 eV (indicated by dotted lines) are subtracted. The solid curve in the left panel is a peak shape of the elastic line which shows the instrumental energy resolution.

In order to consider the origin of the peak structures more accurately, we carried out the calculation of the RIXS spectrum by using the numerically exact diagonalization technique on small clusters [23]. We consider the one-dimensional Hubbard model for the CuO_3 chain, where the Zhang-Rice band (ZRB) is regarded as the lower Hubbard band (LHB). The model includes the hopping term of the electrons (t) and the on-site Coulomb interaction term (U). Because the band calculations and the angle-resolved photoemission indicate that the filling of the electrons on the chain is close to $1/4$ [10,24], we assume this amount of filling in the 12-site Hubbard chain. The RIXS spectrum is expressed as the second-order process of the dipole transition between Cu $1s$ and $4p$ orbitals, where the Coulomb interaction (U_c) between Cu $1s$ core hole and the “ $3d$ system” is explicitly included in the process. The values of the model parameters are set to be $U/t = 4$, $U_c/t = 6$, and $\Gamma/t = 1$ with $t = 0.3$ eV, where Γ is the inverse of the lifetime of the intermediate state, in order for the theoretical data to reproduce the 2 eV structure in Fig. 2. In order to choose the incident energy for the RIXS calculation, we first calculated the x-ray absorption spectrum (not shown here) expressed by Eq. 3 in Ref. [25], and found the three-peak structure similar to that of the hole-doped two-dimensional case [25]: The peaks of the well-screened and the poorly-screened states are located at around $\omega = U - 2U_c$ and $-U_c$, respectively, and the peak that the core hole is created at the hole-doped sites is located at around zero. The incident energy of 8990 eV in the experiment is suggested to be set to the energy of the poorly-screened state, and thus the incident energy for the calculation is set to that same energy.

Figure 3 shows the theoretical result of the RIXS for the chain (solid lines), together with the spectrum yielded by

the sum of the chain and the plane components (dotted lines). Here the spectrum for the plane is the same as shown in Ref. [25]. The spectrum with zero momentum transfer of the chain site is plotted for all the momenta along [100] (the left panel in Fig. 3). The spectrum along [110] is the average of the spectra along [100] and [010]. The spectrum below the energy $\Delta\omega \sim 4t = 1.2$ eV ($4t$ is the band width of the free electron) is due to the excitation within the LHB, which is swallowed up by the quasielastic peak. Note that its spectral weight is severely reduced when the incident energy is set to that of the well-screened state. This feature may be observed by using much better energy resolution in the future. The spectrum above $\sim 4t$ is due to the excitation from the LHB to the upper Hubbard band

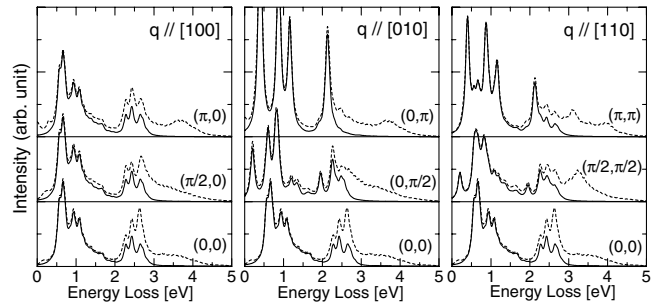


FIG. 3. Theoretical result of the momentum dependence of the chain component of the RIXS presented by solid lines. The left, middle, and right panels show the spectra along [100], [010], and [110], respectively. The dotted lines denote the sum of the chain and the plane components of the spectra, where the model parameters for the chain are $U/t = 4$, $U_c/t = 6$, and $\Gamma/t = 1$ with $t = 0.3$ eV. The δ functions are convoluted with a Lorentzian broadening of $0.2t$.

(UHB). At $(0, 0)$, it spreads over the energy region between 2 and 3 eV. The spectrum becomes more intense with increasing momentum transfer of the chain state, and the spectral weight becomes concentrated in the narrow energy region at $(0, \pi)$. The feature is similar to that in the undoped chain case [26]. We believe that this intense feature of the chain component appears as the peak structure of 2 eV in the experimental data.

As shown by the dotted lines in Fig. 3, there appear broad spectra in the energy region up to 4 eV that originate from the Mott gap excitation in the plane [25]. The broad-peak structures correspond to the broad excitations at 1.5–4 eV seen in Fig. 2. The broadness of the Mott gap excitations in hole-doped CuO_2 planes in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ contrasts greatly with that of the undoped CuO_2 planes in $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ [11] and La_2CuO_4 [13], in which a sharp peak can be seen at 2–4 eV. We can estimate the magnitude of the dispersion in the plane from the spectra along the $[100]$ direction in Fig. 2 because there is no dispersion in the chain along this direction. The dispersion in hole-doped CuO_2 planes is much smaller than that in undoped planes, which has been predicted in the theoretical calculation [25].

Our experimental results and theoretical calculations demonstrate that the charge gap of the chain is smaller than that of the plane. In order to compare the theoretical peak position at $(0, \pi)$ with that of the experimental data, we have to set the value of U to $4t$ for the chain rather than the value of $10t$ for the plane. The small value of U suggests that the charge transfer parameter Δ of the chain is small compared with that of the plane. The reason for the different values of Δ is that the Cu atom in the plane has five ligand oxygen atoms while the Cu in the chain has four, so that the electric environment around the Cu and O sites of the chain is different from that of the plane [27]. Optical measurements for insulating cuprates show that the charge transfer gap decreases with decreasing number of ligand oxygen atoms [28], which is qualitatively consistent with the present case. We also note that the small Δ for the chain is consistent with a recent study [9] where it is shown that the $2k_F$ Friedel oscillation of the charge density, instead of the $4k_F$ one, dominates at small Δ . It is believed that this oscillation can explain the STM results [5–7].

Individual calculations of the chain and the plane reproduce the experimental spectra well. It may suggest that the coupling between the CuO chain and the neighboring CuO_2 planes is rather weak.

In summary, we have performed a RIXS study for optimally doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and found two characteristic excitations. The excitation from the CuO_2 plane shows a broad feature at 1.5–4 eV and is almost independent of the momentum transfer, as is consistent with the theoretical prediction. On the other hand, the excitation from the CuO chain is enhanced at 2 eV near the zone boundary of the b^* direction. The result indicates that the Mott gap in the chain is smaller than that in the plane.

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*Electronic address: kenji@spring8.or.jp

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