Application of Resonant Inelastic X-ray Scattering (RIXS) Method to Materials Physics

Resonant inelastic X-ray scattering (RIXS) is a promising tool to probe the momentum dependence of low-energy excitations in solids [1,2]. A schematic process of RIXS for Cu 1*s*-4*p* excitation is illustrated in Fig. 1, in which the labels (I), (II), and (III) stands for the respective step of the RIXS process. The incident light excites the Cu 1*s* electron to the Cu 4*p* states in step (I). In the step (II) of the de-excitation, the Cu 3*d* electron is excited across the Fermi level (red circle). When the Cu 4*p* electron relaxes into the Cu 1*s* state with the Cu 3*d* excitation, the corresponding energy is emitted in the form of photons (step (III)). The emitted energy is smaller than the excitation energy by the amount of the energy loss for the Cu 3*d* excitation as explained above. Namely, RIXS measurements probe second-order optical processes.

In RIXS, an electron is excited from the occupied core state to the unoccupied state, and the energy ($h\nu$-dependence) and momentum (Δk-dependence) differences between the occupied and unoccupied states are probed. In general, the excitation of valence electrons in inelastic X-ray scattering is too weak to be distinguished from other excitation processes with good statistics. Therefore, resonance enhancement near the core excitation threshold is utilized in RIXS. As a great advantage for studying the momentum dependence of the electronic energies, RIXS is much more bulk sensitive than photoemission and is applicable to insulators. Another advantage of RIXS measurement is the freedom to change the photon energy near the core absorption threshold to select different intermediate states [2].

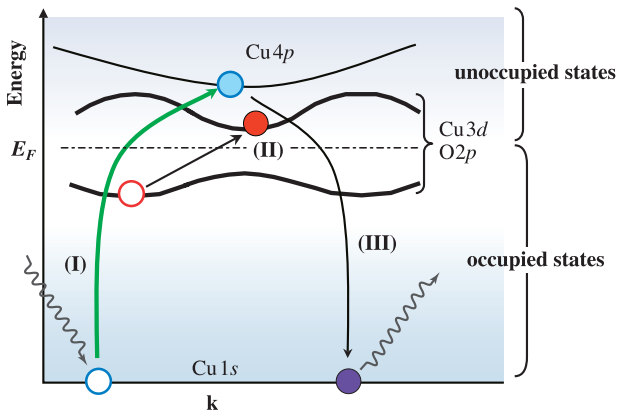

Fig. 1. Schematic picture of inelastic resonant X-ray scattering for Cu 1*s* - 4*p* absorption [3].

The experiment was carried out in the third hutch of beamline **BL19LXU** [4]. Figure 2 shows the experimental setup designed for RIXS in the Cu 1*s* absorption region around 9 keV. In this figure, all the components shown in the top view are set on a single optical bench with a size of 1 m × 2 m. The linearly polarized undulator radiation was tuned to a proper monochromatic energy using two Si (111) crystals. It was further monochromatized by two channel-cut Si (220) crystals, with the energy resolution of 360 meV full width at half maximum (FWHM). Then, the light was focused by a bimorph mirror with a focusing length of about 1 m. The horizontal focus size was smaller than 100 μm on the sample. The monochromatic light was incident onto the polished surface of the sample, which was kept in an evacuated chamber with polyimid windows (shown in Fig. 2, photo 1). Horizontally scattered radiation was analyzed by a setup constructed on an arm rotating around the sample position. The angle of the arm determines the scattering vector and therefore the momentum transferred to the excited electron. The energy of the scattered radiation was analyzed by a spherically bent Si (553) crystal (shown in Fig. 2, photo 2), which was mounted on a biaxial goniometer enabling both energy analysis and adjustment of the tilting angle. The diameter of the Rowland circle was 1 m. The analyzed light was focused on a NaI scintillation detector. The size of the slit in front of the detector was set to 0.4 mm. The slit and the detector were put on the same plate, which is moved

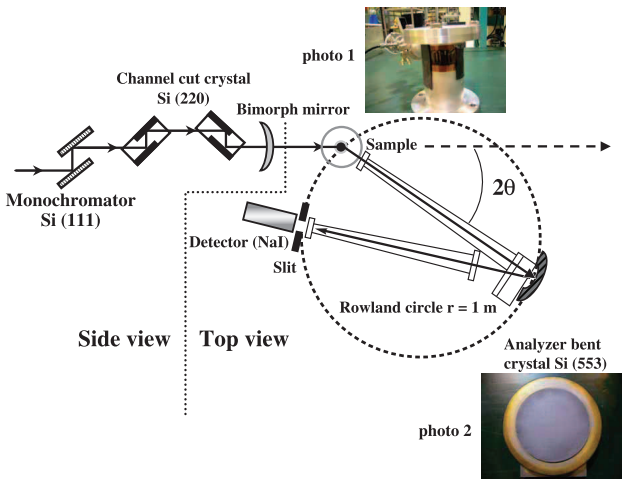

Fig. 2. Schematic picture of our experimental setup at BL19LXU (photo 1). Sample chamber with polyimid windows (photo 2). Spherically bent Si (553) crystal.

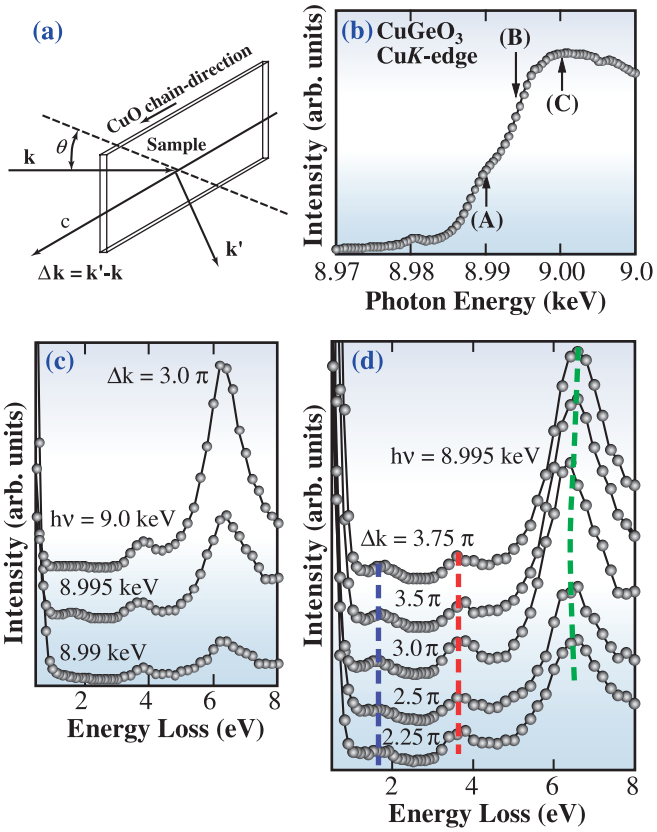

Fig. 3. **(a)** Schematic diagram for explaining RIXS in the transmission mode **(b)** Cu 1*s* - 4*p* absorption spectrum in $CuGeO_3$ **(c)** $h\nu$-dependence of RIXS spectra at $\Delta k = 3.0\pi$. **(d)** Δk-dependence of RIXS spectra at $h\nu = 8.995$ keV.

horizontally so that the slit followed the Roland circle. The total energy resolution, determined from the width (FWHM) of the quasi-elastic scattering peak, was about 440 meV. Most parts of the optical path from the sample position to the detector were evacuated using of polyimid windows to minimize the loss due to the scattering by air.

As an example of application, we show the RIXS spectra of $CuGeO_3$. This sample is one-dimensional insulator and has a single chain with the edge-sharing CuO_2 plaquettes configuration. For a thin film $CuGeO_3$ sample, the chain axis is oriented by Laue diffraction measurement, where the naturally grown surface was used for measurement. The measurement has been performed at room temperature in the transmission mode as shown in Fig. 3(a). The Δk measurement for single chain direction has been performed by changing both 2θ and θ angles as shown in Fig. 2 and Fig. 3(a).

Figure 3(b) shows the Cu 1*s*-4*p* XAS spectrum measured by means of the fluorescence yield. The labels in XAS indicate the incident photon energies used for RIXS measurement shown in Figs. 3(c) and 3(d). In Fig. 3(b), the Cu 1*s*-3*d* quadrupole peak is located at $h\nu = 8.98$ keV. The label (A) corresponds mainly to the Cu 1*s*-4*p*π transition, whereas the Cu 1*s*-4*p*σ absorption is dominant in the regions of label (B) and (C). Figure 3(c) shows the $h\nu$-dependence of the RIXS spectra at $\Delta k = 3.0\pi$. In Fig. 3(c), each spectrum reflects the difference in the intermediate states. These spectra have some characteristic features. For example, the spectrum at $h\nu = 8.995$ keV shows a low-energy loss peak around 1.6 eV. To investigate the character in detail, we performed the measurement of Δk-dependence for RIXS spectrum at $h\nu = 8.995$ keV as shown in Fig. 3(d). Figure 3(d) shows three dispersions around 1.6 eV (blue dashed line), 3.5 eV (red dashed line), and 6.5 eV (green dashed line). To clarify the origins of these features, we compare our result with the theoretical calculation. As a result, the features around 3.5 eV and 6.5 eV correspond to the excitation states from the Zhang-Rice singlet made of the Cu 3*d* hole coupled with the O 2*p* hole and the bonding state between Cu 3*d* and O 2*p* states to the upper Hubbard band, respectively. The feature around 1.6 eV is described as the *d*-*d* transition on the same Cu site [5].

RIXS measurement can thus provide bulk information of not only occupied states but also unoccupied states with the momentum dependence. Therefore, this method is a very powerful tool for materials science.

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