Orbital state of excited electron identified by polarization-analyzed resonant inelastic X-ray scattering

Strongly correlated transition metal compounds attract great interest because they exhibit a variety of interesting phenomena, such as high-temperature superconductivity in cuprates and colossal magnetoresistance in manganites [1]. It is widely recognized that the orbital degree of freedom of the *d* electrons often plays a crucial role in the occurrence of these phenomena. For example, it controls the anisotropy of electron mobility and the propagation of interactions. Orbital excitations, where the orbital state changes by gaining energy, at zero momentum transfer can be observed by Raman scattering, but an experimental technique with momentum resolution is crucial to the complete understanding of the elementary orbital excitation, the so-called orbiton. Recently, resonant inelastic X-ray scattering (RIXS) using brilliant synchrotron radiation X-rays has been developed as a new spectroscopic technique to measure excitations of correlated electrons [2], and it is a potent method to observe momentum-resolved orbital excitations. However, various excitations are often entangled in the spectrum of RIXS, and it has been difficult to distinguish between them experimentally.

To identify the orbital excitations, we utilize polarization, which is an inherent and important characteristic of the photon [3]. So far, most RIXS studies have focused on energy and momentum dependences and the polarization has been overlooked. Although the role of the incident photon polarization was investigated in relation with the resonant conditions in a few experimental and theoretical studies, the scattered photon polarization has not been identified at all. Similarly to conventional Raman spectroscopy, polarization in RIXS must be connected to the symmetry of the excitations. Because the symmetry argument is rigorous and independent of the parameters in theoretical models, the polarization can be very useful for the assignment of the excitations in RIXS.

The experiments were carried out at **BL11XU** beamline. We measured the orbital excitations of single-crystalline $KCuF_3$, which is an archetypal material with orbital order, at the Cu *K*-edge. Linearly polarized incident X-rays were monochromatized by a double crystal Si(111) monochromator and a secondary Si(400) channel-cut monochromator, and irradiated on the sample. The energy of scattered X-rays was analyzed using spherically bent Ge(800) crystals. The total energy resolution was about 600 meV. To resolve the polarization of the scattered X-rays, we developed a polarization analyzer system which is schematically shown in Fig. 1 and installed in the spectrometer. A pyrolytic graphite (PG) crystal was placed in front of the detector and the (006) reflection of PG was measured. The polarization extinction ratio of the reflection ($\sin^2 2\theta_P$, where θ_P is the Bragg angle) is 0.94. The experimental reflectivity of the (006) reflection was about 0.02. By rotating the PG crystal and the detector about the axis of the beam, one can select the polarization of the scattered photon.

Polarization-analyzed RIXS spectra are shown in Figs. 2(a) and 2(b); these spectra were measured under the two polarization conditions of $\pi \rightarrow \pi'$ and $\pi \rightarrow \sigma'$, where π is the incident photon polarization parallel to the scattering plane, and π' and σ' denote the scattered photon polarizations parallel and perpendicular to the scattering plane, respectively. The incident photon energy is fixed at 8994 eV, near the peak of the X-ray absorption spectrum. The incident photon polarization (ε_i) lies in the scattering plane and the scattering angle (2θ) is chosen to be close to 90° in order to reduce the elastic scattering. The incident and scattered polarizations are therefore orthogonal to each other, which is the so-called depolarized configuration.

Orbital excitations are observed at 1.0–1.5 eV. There are two types of orbital excitations in $KCuF_3$: One excitation is a transition of an electron from the t_{2g} orbital to the e_g orbital (t_{2g} excitation) and the other one is a transition of an electron between the e_g orbitals (e_g excitation). The latter corresponds to the orbital degree of freedom in $KCuF_3$. In Fig. 2(a), the 1.4 eV peak in the red spectrum of the $\pi \rightarrow \sigma'$ condition corresponds to an orbital excitation. From a phenomenological consideration of the symmetry of the RIXS process, we can assign the excitation as the t_{2g} excitation. On the other hand, in addition to the peak at 1.4 eV, a spectral weight exists at around 1.0 eV for the blue spectrum of the $\pi \rightarrow \pi'$ condition, and it comes from the e_g excitation. This implies that the two

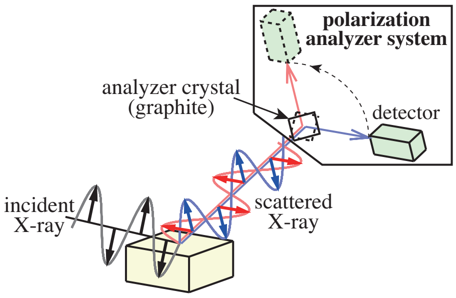

Fig. 1. Schematic view of polarization analyzer system installed at BL11XU.

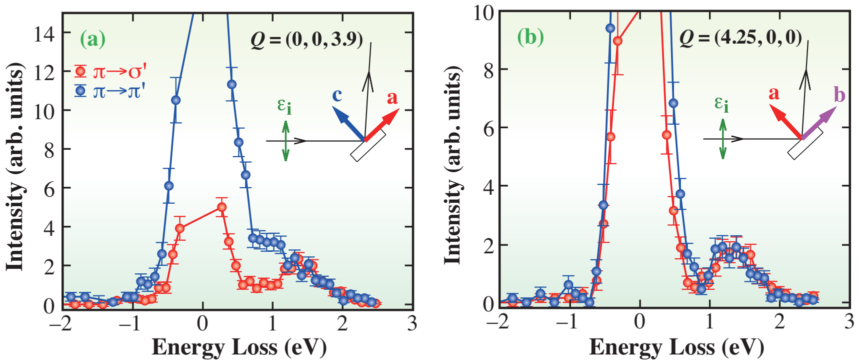

Fig. 2. Polarization-analyzed RIXS spectra. Spectra with red and blue circles are measured under the π → σ' and π → π' and conditions, respectively. The momentum transfer (*Q*) is represented by the Miller indices in the tetragonal unit cell of the primitive perovskite structure (a = 4.1410 Å and c = 3.9237 Å) and corresponding experimental geometries are shown in insets.

orbital excitations show clear dependence on the scattered photon polarization. Our assignments based on the results of polarization analysis are consistent with a recent optical absorption study, where different orbital excitations were identified and their respective energies were estimated. When we change the polarization relative to the crystal orientation, both π → π' and π → σ' spectra become identical, as shown in Fig. 2(b), namely, the e_g excitation disappears under this polarization condition.

Now that we are able to distinguish the e_g excitation from the t_{2g} excitation, it becomes possible to investigate the momentum dependence of each orbital excitation separately. Figures 3(a) and 3(b) show the polarization-analyzed RIXS spectra obtained near the high-symmetry points of the Brillouin zone. The excitation energy of the orbital excitations is analyzed by fitting the spectra and the excitations are found to be dispersionless within our experimental resolution. Since the improvement in energy resolution is still in progress, the dispersion relation of orbital excitations should become observable by *K*-edge RIXS in the future.

In summary, we have performed a polarization-analyzed RIXS study of the orbital excitations in $KCuF_3$ at the Cu *K*-edge. The polarization of the scattered photons in RIXS was identified for the first time. Our result demonstrates that the polarization analysis is quite useful for the identification of the excitations.

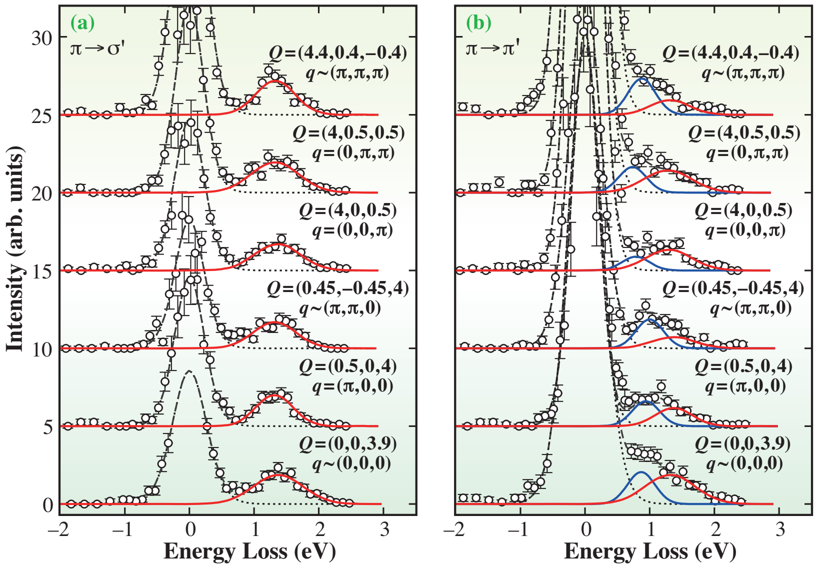

Fig. 3. Momentum dependence of polarization-analyzed RIXS spectra. ***Q*** and ***q*** are the absolute and reduced momentum transfer, respectively. Open circles correspond to the experimental data. Red and blue solid-line spectra are the fitted t_{2g} and e_g excitations, respectively. Dashed-line spectra represent the sum of the fitted elastic line (dotted line) with the fitted orbital excitations (solid line). [3]

Kenji Ishii[a,*], Sumio Ishihara[b] and Yoichi Murakami[c]

[a]SPring-8/JAEA
[b]Department of Physics, Tohoku University
[c]High Energy Accelerator Research Organization (KEK)

*E-mail: kenji@spring8.or.jp

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