Resonant soft X-ray scattering study of the magnetic structures in La$_{1.5}$Ca$_{0.5}$CoO$_4$ using a high vacuum diffractometer with a 4-blade-slit detector system

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Abstract. In resonant soft X-ray scattering measurement, we need the detector which can tune its solid angle continuously in vacuum. We have constructed a 4-blade-slit detector system for high vacuum and set it in the quasi-3-axis diffractometer. With this system, we have studied two magnetic structures in antiferromagnetic insulator La$_{1.5}$Ca$_{0.5}$CoO$_4$ by Co $L_{2,3}$-edge resonant soft X-ray scattering. We revealed that the underlying Co electronic structures for these magnetic structures are the same, since the observed energy spectra take the same lineshape.

1. Introduction
Resonant soft X-ray scattering (RSXS) of superstructures is a powerful method to make clear the underlying electronic structures. This is one of the experimental methods which have developed in the last decade with the help of progress in the synchrotron radiation technique. RSXS at $3d$ transition-metal (TM) $L_{2,3}$-edges enhances the cross-section of magnetic scattering through the $p$-$d$ transition process [1]. Therefore, RSXS study of $3d$ TM oxides are sensitive to the magnetic moment of TM $3d$ electrons, allowing us to probe the magnetic structures with high sensitivity. On the other hand, wave number of the light is relatively long (~ 10-20 Å) and probing depth is relatively short (~ 100 nm) in soft X-ray (SX) region. Therefore, RSXS measurements are limited to the structures with long periods and required to set the whole diffractometer inside the vacuum chamber.

In scattering measurement, we need detectors with large solid angles in searching peaks roughly and those with small solid angles in observing tiny superstructures precisely by subtracting backgrounds, such as fluorescence. We ordinarily cope with this by mounting a 4-blade-slit system in front of the detector in hard X-ray scattering. For SX case, however, it is not easy to do the same because the diffractometer is set inside the vacuum. Outgas from the motors and the volume of 4-blade-slit system become problems. These problems were so far answered by preparing detectors with different solid angles or changing apertures in front of the detector [2]. But both of them have demerits; in the former case geometry of the each detector is different and in the latter case solid angle...
of the detector cannot be tuned continuously. We constructed a SX scattering system whose detector can change its solid angle continuously by introducing a tiny 4-blade-slit system for high vacuum.

La$_{2-x}$Ca$_x$CoO$_4$ system has been controversial for its Co$^{3+}$ spin states. Co$^{2+}$ always takes high-spin (HS) state but Co$^{3+}$ takes various spin states, estimated from magnetization measurements; HS for $x < 0.5$ and intermediate-spin (IS) state for $x > 0.7$ [3]. Neutron scattering [4] observed two magnetic structures below Neel temperature ($T_N \sim 50$ K) in La$_{2-x}$Ca$_x$CoO$_4$ system with scattering vector $q$ of $(1/2, 0, 1/2)$ for $x \leq 0.5$ and $(1/2, 0, 1)$ for $x \geq 0.5$; both structures were observed only in La$_{1.5}$Ca$_{0.5}$CoO$_4$. It needs to reveal the underlying Co electronic structures of these two magnetic structures to know the relationship between the magnetic structures and the magnetizations in La$_{2-x}$Ca$_x$CoO$_4$ system. We have studied these magnetic structures in La$_{1.5}$Ca$_{0.5}$CoO$_4$ by Co L$_{2,3}$-edge RSXS measurements. We revealed that the underlying Co electronic structures for those two magnetic structures are the same, since the energy spectra of scattering peaks take the same lineshape.

2. Instruments

Figure 1 shows the illustrations of the 4-blade-slit system and the quasi-3-axis diffractometer for high vacuum. There exists a square window of $15 \times 15$ mm$^2$ in the center of the 4-blade-slit system. The top and bottom blades move from end to end of this window independently. The right and left blades can open the window completely but can close by 3 mm from the center. With these blades, we can adjust the inhomogeneous sensitivity of the detector and slight shift in the alignment of the detector position by moving the cross point of the four blades from the center of the square window within the movable region. A micro-channel plate with its detection area of $10 \times 10$ mm$^2$ is set behind the square window. The detector position is away from the rotating center of $2\theta$ axis by 100 mm. The acceptance angles are $\pm 2.8^\circ$ in and orthogonal to the scattering plane.

This quasi-3-axis diffractometer has a quasi $\chi$ axis in addition to the usual $\theta$ and $2\theta$ rotation axes by moving the 4-blade-slit detector orthogonal to the scattering plane as shown in Fig. 1 (b). This moving range is $\pm 40$ mm, which is $\sim \pm 20^\circ$ of the $\chi$ axis. The 4-blade-slit system cut the incident light in the higher angles of the $2\theta$ axis owing to its dimensions of $160 \times 160 \times 34$ mm$^3$. In order to decrease the undetectable region of $2\theta$ axis, horizontal windows of $5 \times 65$ mm$^2$ are made next to the square window to pass the incident light. The detectable region of this diffractometer is $2\theta \leq 130^\circ$ with $\chi$ of $\sim \pm 20^\circ$ and $140^\circ \leq 2\theta \leq 165^\circ$ with $\chi$ of $\sim \pm 1.5^\circ$. The incident light is cut by the frame of the 4-blade-slit system $(130^\circ \leq 2\theta \leq 140^\circ)$ and the detector itself $(165^\circ \leq 2\theta \leq 180^\circ)$.

3. Experimental

La$_{1.5}$Ca$_{0.5}$CoO$_4$ single crystals were grown by floating-zone method. The growing procedure was explained in the other article precisely [4]. Single crystals La$_{1.5}$Ca$_{0.5}$CoO$_4$ (100) were cut and polished to make a mirror-like surface. All directions in this paper are expressed in orthorhombic system.
Lattice parameters are \( a = b = 5.418 \) Å and \( c = 12.469 \) Å at room temperature [4]. The samples are mounted on the quasi-3-axis diffractometer by setting \( ac \) plane as a scattering plane. In \( \sigma \) (\( \pi \)) polarization, the electric-field vector of the incident light was adjusted parallel (orthogonal) to the \( b \) axis which is orthogonal to the \( ac \) scattering plane. The base pressure of the diffractometer was \( 1 \times 10^{-5} \) Pa at room temperature. Samples can be cooled down to 25 K by liq. He flow. The \( 2\theta \) angles of \((1/2, 0, 1/2)\) and \((1/2, 0, 1)\) at Co \( L_{2,3} \)-edge (770 - 800 eV) were \( 102 - 108^\circ \) and \( 142 - 160^\circ \), respectively. Therefore, RSXS of \((1/2, 0, 1)\) were measured by using the horizontal window of the 4-blade-slit system. RSXS measurements were done at the soft X-ray undulator beamline BL-16A in the Photon Factory, KEK. Energy resolution was \( \sim 0.1 \) eV in the energy range of 500 - 1500 eV. Beam size was \( \sim 300 \) \( \mu \)m in horizontal direction and \( \sim 100 \) \( \mu \)m in vertical direction at the focal point.

![Figure 2](image)

**Figure 2.** (a) H scans and (b) L scans of the RSXS of \((1/2, 0, 1/2)\) with different horizontal slit sizes. (c) Energy scans of RSXS of \((1/2, 0, 1/2)\), background and subtracted BG.

### 4. Results and Discussions

Figure 2 shows the RSXS peaks of \( \text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_{4} \) with \( q \) of \((1/2, 0, 1/2)\) scanned along \( q_x \) (H scan) and \( q_z \) (L scan) direction at 25 K and at 773 eV under \( \pi \) polarization. RSXS lineshapes measured with different horizontal slit sizes are compared. FWHM and ratio of signal to background S/B of these scans are summarized in Table 1. In both scans S/B increases clearly since backgrounds are cut effectively by closing horizontal slit from 2 mm to 0.2 mm. FWHM also becomes narrower in both scans, although difference in H scans is small since correlation in \( ab \) plane is relatively strong [4]. This means that the 4-blade-slit detector system works well in measuring scattering signal effectively. We have obtained RSXS energy spectra of magnetic structures by subtracting background spectra from energy scans of RSXS intensities as in Fig. 2 (c).

| H \times V (mm) | H scan | L scan |
|-----------------|--------|--------|
|                 | FWHM (r.l.u) | S/B     | FWHM (r.l.u) | S/B     |
| 0.2 \times 0.4  | 0.00436 | 3.4 ± 0.1 | 0.035 | 3.3 ± 0.7 |
| 2 \times 0.4    | 0.0046  | 1.7 ± 0.1 | 0.051 | 0.95 ± 0.2 |

Co \( L_{2,3} \)-edge RSXS energy spectra of the two magnetic structures and Co \( L_{2,3} \)-edge XAS are compared in Fig. 3. Red and blue bars correspond to the XAS structures of Co\(^{2+}\) and Co\(^{3+}\), respectively. RSXS spectra are normalized by the maximum peak intensity. Self-absorption effect in RSXS spectra
are corrected by multiplying XAS spectra on the RSXS spectra subtracted BG [5]. RSXS spectra of the two magnetic structures show nearly the same features. Most of the RSXS structures correspond to the Co\(^{2+}\) XAS structures not the Co\(^{3+}\) ones. Co \(L_2\)-edge RSXS structures are negligibly small. This means existence of finite orbital moments since magnetic scattering intensities are roughly linear to square of XMCD intensities [1]. From Co \(L_{2,3}\)-edge RSXS measurement, we reveal that the both magnetic structure are originated from the Co electronic structures which are mainly composed from Co\(^{2+}\) and have finite orbital moments.

![Figure 3](image_url)

**Figure 3.** (a) Co \(L_{2,3}\)-edge XAS and (b) RSXS energy spectra of the magnetic structures of La\(_{1.5}\)Ca\(_{0.5}\)CoO\(_4\) at 30 K. Red (blue) bars correspond to XAS structures of Co\(^{3+}\) (Co\(^{2+}\)).

5. **Conclusions**

We have studied two magnetic structures of La\(_{1.5}\)Ca\(_{0.5}\)CoO\(_4\) with different propagation vectors by the Co \(L_{2,3}\)-edge resonant soft X-ray scattering measurement. We have measured the energy spectra of the magnetic scattering peaks clearly with use of a 4-blade-slit detector system for high vacuum. We reveal that the underlying Co electronic structures of the two magnetic structures are almost the same, since the spectral lineshapes match very well with each other.

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