# Ferro-type Orbital State in Mott Transition System $Ca_{2-x}Sr_xRuO_4$ Revealed by Resonant X-ray Scattering Interference Technique

Among 4*d* electron systems, $Ca_{2-x}Sr_xRuO_4$ has especially attracted attention because of its rich and novel ground states such as in Mott transition [1-3]. Since $Ca_{2-x}Sr_xRuO_4$ has four 4*d* electrons in the $t_{2g}$ orbitals, the significance of orbital degree of freedom is invoked. Nevertheless, few works have been carried out on orbital ordering in 4*d* electron system so far.

The anisotropic tensor of an X-ray susceptibility signal is enhanced near an absorption edge. However, conventional resonant X-ray scattering (RXS) measurement is not useful for the observation of a *ferro-type* orbital state, in which charges are distributed with the same local symmetry at each Ru ion site. This is because it is difficult to extract the signal for a ferro-type orbital state at Γ points, which is accompanied with large magnitude of a fundamental reflection by Thomson scattering. However, the RXS interference technique can offer unique access to observing the *ferro-type* orbital state, in which the signal of the ferro-type orbital state is magnified by the interference with a fundamental signal. In the present study, it is revealed that the observation of orbital states by a resonant X-ray scattering interference technique is significant for understanding the rich phase diagram of $Ca_{2-x}Sr_xRuO_4$ [4].

Figure 1(a) shows the resonant X-ray scattering configuration at beamline **BL46XU**. ψ is an azimuthal angle, which is the angle around scattering vector *Q*, while $\varphi_A$ indicates the detector angle. The X-ray absorption of Ru is observed around 22.15 keV in Fig. 1(b). Figure 1(c) shows the energy profiles at *Q* = (0 2 6) with polarization angles of $\varphi_A$ = 98° (dotted thick line) and 82° (thin line) at ψ = 270° at 305 K.

The *interference term* for ferro-type orbital ordering is obtained by subtracting the intensity at $\varphi_A$ = 82° from that at $\varphi_A$ = 98°: for $\varphi_A$ = 90° ± Δφ (Δφ = 8°), $I(90° + \Delta\varphi) - I(90° - \Delta\varphi) \propto 2Re\,[F_{\sigma\sigma}\ F_{\sigma\pi}]\ \sin^2 2\theta_A \sin 2\Delta\varphi$, in which $F_{\sigma\sigma}$ and $F_{\sigma\pi}$ denote the scattering factors for the $\sigma \rightarrow \sigma$ and $\sigma \rightarrow \pi$ scattering processes, respectively, and $2\theta_A$ is the scattering angle in the analyzer crystal.

$F_{\sigma\pi}$ has information on the asphericity of 4*d* charge distribution, while $F_{\sigma\sigma}$ corresponds to a fundamental signal. Noticeable point is that $F_{\sigma\pi}$ is enhanced by $F_{\sigma\sigma}$. Therefore, a small signal for a ferro-type ordering is detectable. The resonant signal for ferro-type orbital ordering in Fig. 1(c) appears near the *K* absorption edge. Near the *K* absorption edge, an atomic scattering factor is represented by a tensor and the RXS signal has an azimuthal angle dependence.

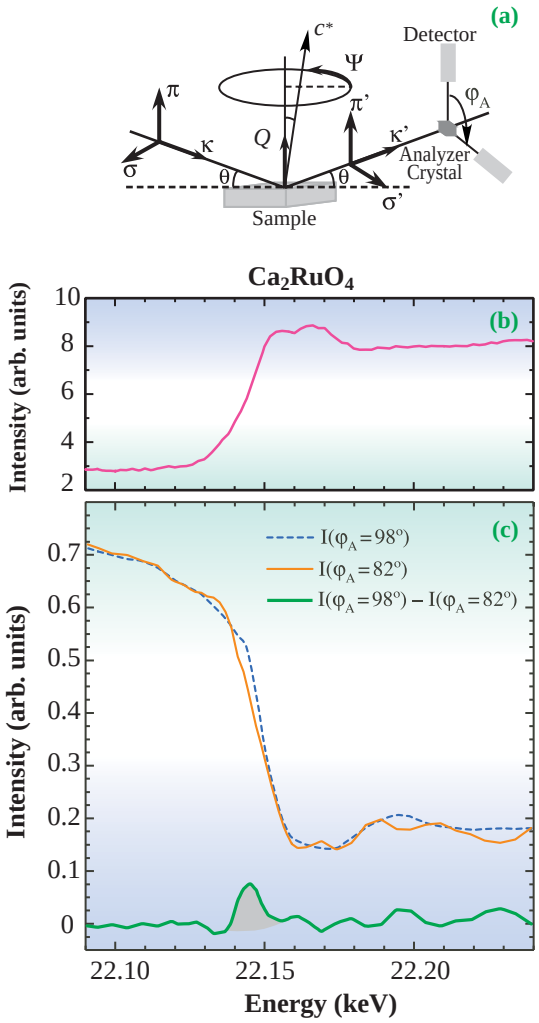


Fig. 1. **(a)** Schematic picture of resonant X-ray scattering configuration. **(b)** Incident energy dependence of X-ray fluorescence in $Ca_2RuO_4$. **(c)** Energy scans at 305 K for $\varphi_A$ = 98° (dotted thick line) and $\varphi_A$ = 82° (thin line) at azimuthal angle ψ = 270° at *Q* = (0 2 6). The bottom thick line is obtained by subtracting the energy spectrum at $\varphi_A$ = 82° from that at $\varphi_A$ = 98°, which corresponds to the interference term.

In order to further verify that the observed resonant signal corresponds to the orbital ordering in $Ca_2RuO_4$, the azimuthal angle dependence has been observed. The magnitude of the signal at the main edge peak at 305 K exhibits the characteristic oscillation with the 360º period (Fig. 2). $F_{\sigma\pi}$ mainly contributes to the ψ dependence of the interference signal.

The observed ψ dependence shows the minimum and maximum at around ψ = 90º and 270º, respectively, while the intensity approaches zero at ψ = 0º and 180º. These features are well explained by the analysis for a ferro-type $d_{xy}$ ordering, as shown in Fig. 2. In addition, we analyzed the ψ-dependence of the resonant signal at $Q$ = (0 2 14), which is also consistent with the behavior of the $d_{xy}$ orbital.

Figure 3 shows the temperature dependence of the RXS signal. Above 200 K, the magnitude gradually decreases and then disappears near a metal-insulator transition ($T_{MI}$ ~ 357 K). Note that the RXS signal is observed at room temperature. Braden *et al.* showed that at around 300 K, the apical bond length RuO(2) is almost equal to the averaged equatorial bond length RuO(1) [5]. Therefore, the Jahn-Teller distortion is unreasonable for the main origin of the orbital ordering in $Ca_2RuO_4$. As discussed in ref. [6], it is possible that a two-dimensional crystal field as well as a superexchange interaction play a significant role in stabilizing the ferro-type orbital ordering, in addition to the Jahn-Teller effect of a $RuO_6$ octahedron.

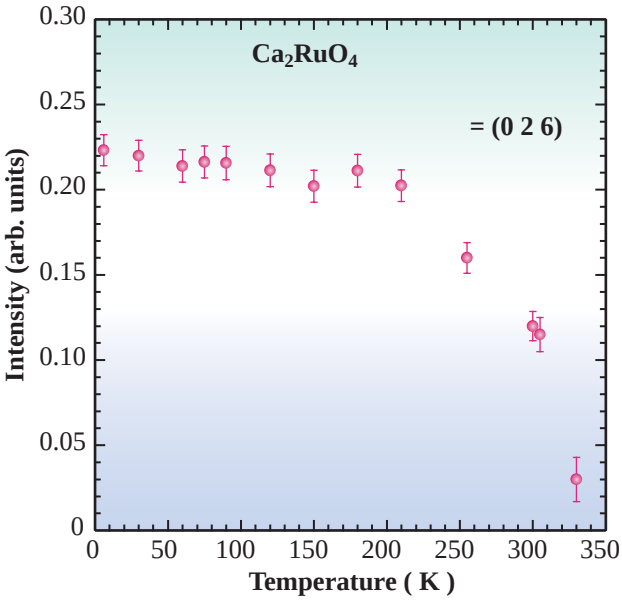


Fig. 3. Temperature dependence of *interference term* at $Q$ = (0 2 6) with ψ = 270º in $Ca_2RuO_4$.

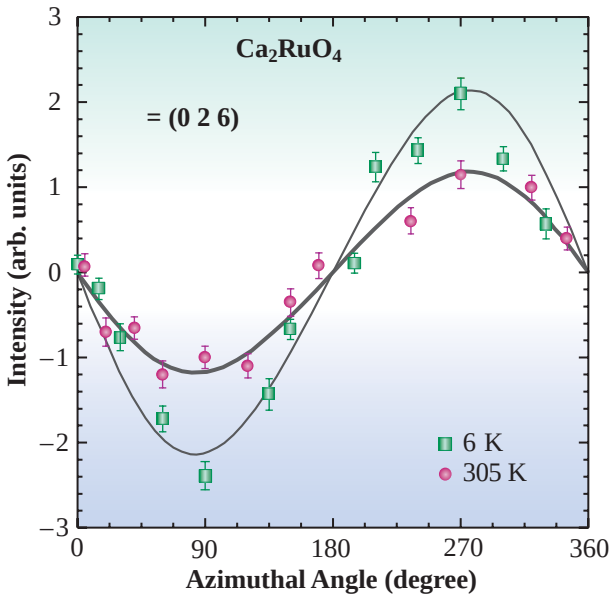


Fig. 2. Azimuthal angle dependences of *interference term* for main edge peak at 305 K and 6 K at $Q$ = (0 2 6).

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## References

[1] Y. Maeno *et al.*: Nature **372** (1994) 532.
[2] S. Nakatsuji *et al.*: J. Phys. Soc. Jpn. **66** (1997) 1868.
[3] S. Nakatsuji and Y. Maeno: Phys. Rev. Lett. **84** (2000) 2666.
[4] *M. Kubota, Y. Murakami, M. Mizumaki, H. Ohsumi, N. Ikeda, S. Nakatsuji, H. Fukazawa and Y. Maeno: Phys. Rev. Lett.* ***95*** *(2005) 026401.*
[5] M. Braden *et al.*: Phys. Rev. B **58** (1998) 847.
[6] Fang *et al.*: Phys. Rev. B **69** (2004) 045116.