

## Intermediate Spin State in Cobalt Oxides Studied by Resonant X-Ray Scattering Technique

The existence of the intermediate-spin (IS) state in cobalt oxides has long been a disputed problem. Recent resonant X-ray scattering experiments have clearly elucidated  $\text{Co}^{3+} e_g$  orbital ordering in  $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ , which has the highest ferromagnetic transition temperature among perovskite Co oxides. This result provides not only a clue to understanding the magnetism but also the first clear evidence of the existence of the IS state of  $\text{Co}^{3+}$ . This discovery is expected to open a new field of materials physics, which will combine the IS state concept with many interesting magnetic and electronic properties.

A strongly correlated electron system shows various intriguing physical properties due to the close interplay among the charge, spin, and orbital degrees of freedom. In cobalt oxides, spin-state degrees of freedom such as low-spin (LS), high-spin (HS), and the IS state emerge additionally, and a wide variety of physical properties associated with the spin-state are expected. In particular, the existence of the intermediate-spin (IS) state is highly controversial because the IS state never becomes the ground state in conventional theory, whereas the existence of the IS state was reported experimentally. To date, there has been no decisive evidence of the existence of the IS state.

$\text{Sr}_{4-x}\text{R}_x\text{Co}_4\text{O}_{10.5}$  ( $R = \text{Y}$  and lanthanide,  $0.8 < x < 1.0$ ) was recently discovered as a room-temperature ferromagnet with  $T_c \sim 370$  K, which is the highest  $T_c$  among perovskite-type cobalt oxides [1]. This material has a unique crystal structure as shown in Fig. 1: the Sr and Y ions form an ordered structure with four times the size of the ideal perovskite structure, and the  $\text{CoO}_6$  octahedral layers and oxygen vacant  $\text{CoO}_{4.25}$  layers are alternately stacked in the direction of the  $c$ -axis. As an origin of the ferromagnetism, the importance of the spin-state degrees of freedom of  $\text{Co}^{3+}$  ( $3d^6$ ), namely HS ( $t_{2g}^4 e_g^2$ ),

LS ( $t_{2g}^6$ ), and IS ( $t_{2g}^5 e_g^1$ ), was proposed on the basis of recent powder X-ray diffraction experiments [2]. Therefore, not only the existence of the IS state of  $\text{Co}^{3+}$  but also the  $e_g$  orbital ordering of the IS state were investigated by a resonant X-ray scattering (RXS) experiment near the Co  $K$  absorption edge energy [3], which is a unique technique for combining diffraction with spectroscopy. This experiment was performed at BL-4C and 3A.

To clarify the orbital ordering in the ferromagnetic phase, the energy dependence of the scattering intensity has been measured at several reciprocal lattice points. The signals resonating near the Co  $K$ -edge energy were found at  $(h00)$ :  $h = 4n \pm 1$  reflection. The energy dependence of scattering intensity at (500) is shown in Fig. 2. Moreover, the RXS signals show a large  $h$  dependence of the scattering intensity. The polarization and azimuthal angle dependence of the RXS signal was also measured at 7.727 keV corresponding to the  $1s \rightarrow 4p$  transition energy. These results clearly indicate the existence of anisotropic Co-site ordering as shown in Fig. 3. However, it was difficult to distinguish between the  $e_g$  and  $t_{2g}$  orbital ordering of  $\text{Co}^{3+}$ , since the signal contains information of the Co  $4p$  state.

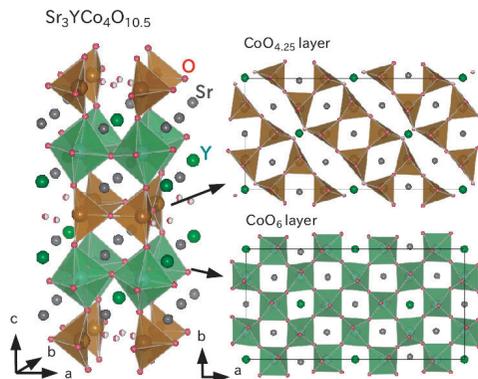


Figure 1  
Crystal structure of  $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$ . Sr, Y, Co, and O atoms are drawn by gray, green, brown and red balls, respectively.

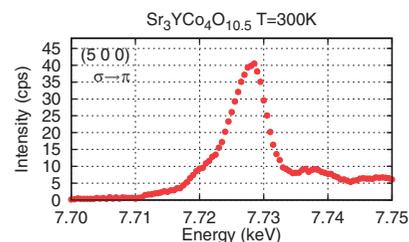


Figure 2  
Energy dependence of the scattering intensity at (500), which was measured in the ferromagnetic phase at 300 K.

In order to clarify the existence of the  $e_g$  orbital ordering of the IS state, the RXS signal at the pre-edge region ( $1s \rightarrow 3d$  transition energy) was noted. The RXS signal at  $1s \rightarrow e_g$  transition energy, which is stronger than that at  $1s \rightarrow t_{2g}$  transition energy, was discovered. This is direct evidence of not only  $e_g$  orbital ordering but also the presence of the IS state, because the signal at the  $1s \rightarrow e_g$  transition energy reflects the anisotropy of the  $e_g$  orbital, and only the IS state of  $\text{Co}^{3+}$  ion has the  $e_g$  orbital degrees of freedom.

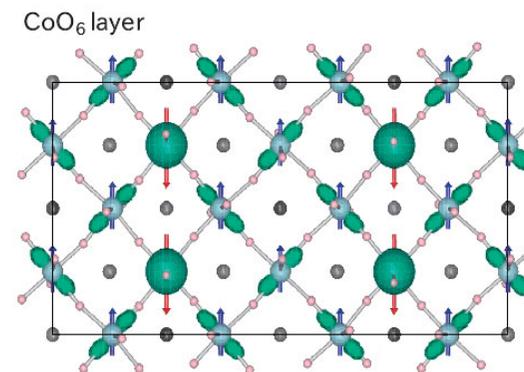


Figure 3  
Determined orbital ordering and proposed magnetic structure in the  $\text{CoO}_6$  layer. Anisotropic Co sites ( $x^2-z^2 / y^2-z^2$  type  $e_g$  orbital) of the intermediate spin state and isotropic Co sites of the high spin state are drawn.

A peculiar spin-state ordering (HS/IS states) and a ferrimagnetic structure based on the determined orbital structure (Fig. 3) were also proposed. To understand the interesting orbital and spin-state ordering, further studies are strongly desired. A neutron scattering experiment to determine the magnetic structure and a resonant soft X-ray scattering experiment to elucidate the Co electric state directly are now in progress in J-PARC and Photon Factory, respectively.

### REFERENCES

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### BEAMLINES

4C and 3A

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