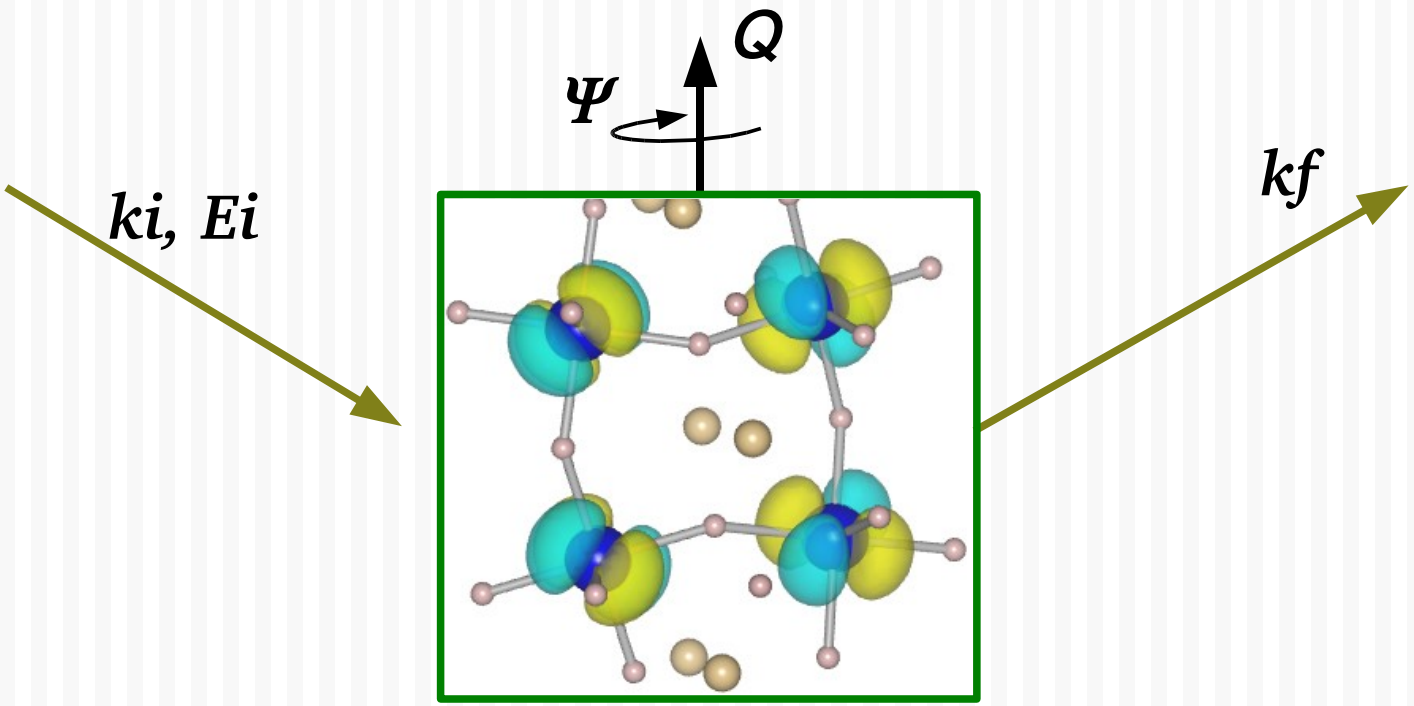
Orbital orderings in transition metal oxides studied by a resonant x-ray scattering technique

Tohoku University H. Nakao



Outline

- Introduction

  Resonant x-ray scattering (RXS) technique

  How to detect anisotropy of an orbital.

- Application

  Orbital ordering in $YTiO_3$ and $Y_{1-x}Ca_xTiO_3$

  - RXS at 1s -> 3d transition energy (pre-edge)

    Order parameter of orbital ordering

    ⇒ Relation between orbital state and physical properties

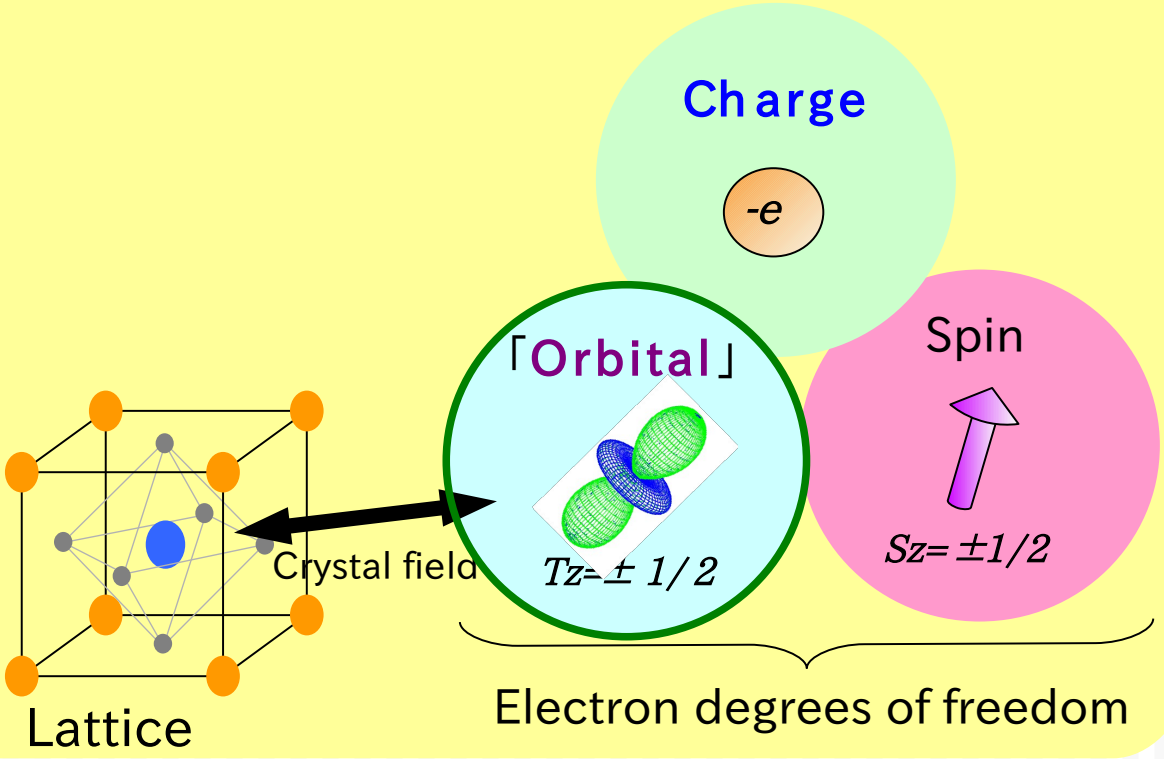
  - RXS at 1s -> 4p transition energy (main edge)

    Origin: 3d orbital state vs. octahedral tilting

    ⇔ RXS in RVO_3

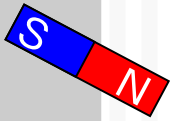
    Quantitative estimation of ordered orbital

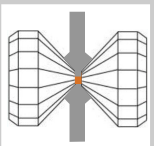
Strongly correlated electron system



External Field

Magnetic field
Electric field
Pressure
Light ....





Various remarkable physical properties

- High Tc superconductivity,
- Colossal magnetoresistance effect,
- Gigantic magnetoelectric effect,
- .....

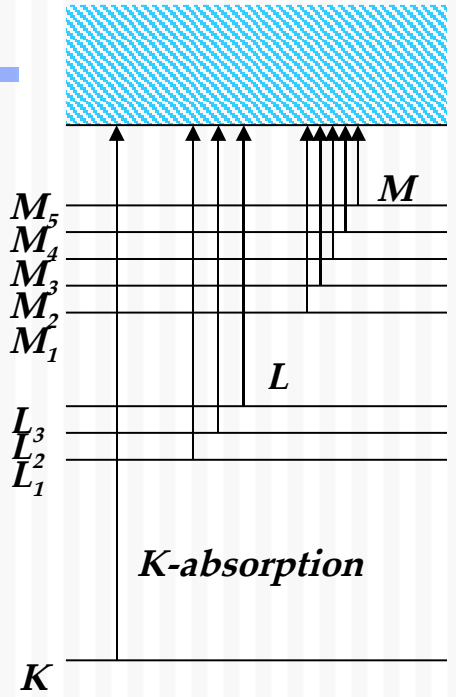
RXS technique

Resonant x-ray scattering technique

Atomic scattering factor (ASF)

$$f = f_0(Q) + f'(E) + if''(E)$$

Anomalous scattering term



Selective information:

Element: Absorption energy depends on the atom

Shell: *K*-, *L*-, *M*-….. edge

Local state around the absorbed atom

- Chemical shift - Charge state
- Tensor of ASF - Strongly reflect the local symmetry
  - Orbital state
  - Chemical bond
- Spin state

X-ray diffraction → Periodicity

Y. Murakami et al., PRL **81** (1998) 582.

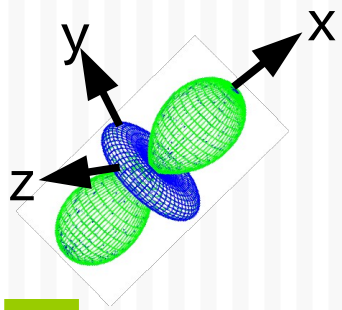
Resonant x-ray scattering technique

Atomic scattering factor on Mn ion

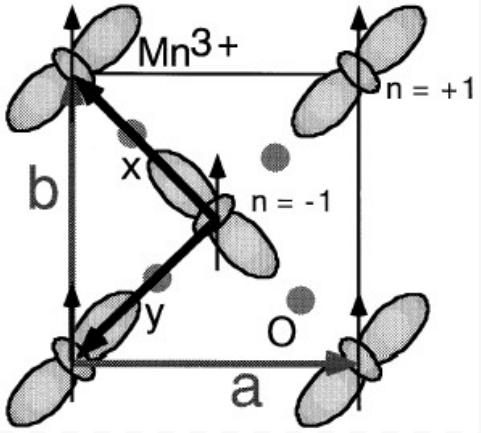
→ Tensor at Mn *K*-edge

$$f = f_0(Q) + f' + i f''$$

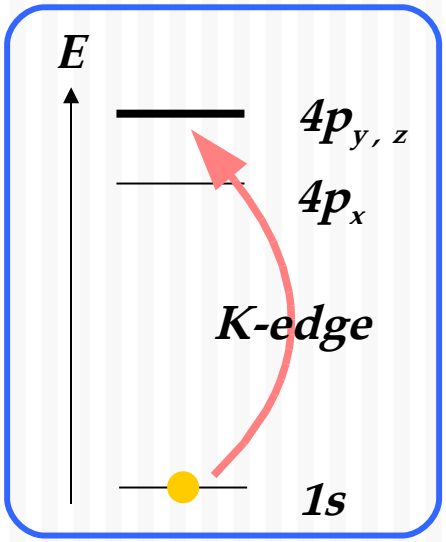
$$f_a = \begin{pmatrix} f_{//} & 0 & 0 \\ 0 & f_{\perp} & 0 \\ 0 & 0 & f_{\perp} \end{pmatrix}$$



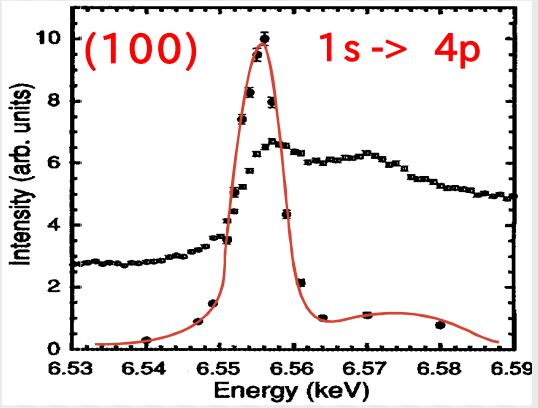
$LaMnO_3$



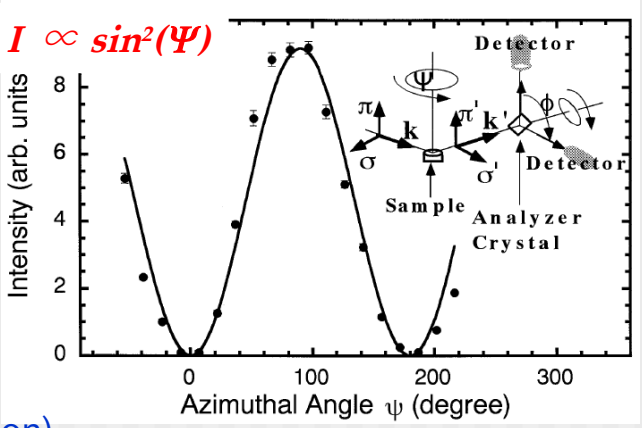
Orbital selective technique



1. Resonant phenomenon at absorption energy



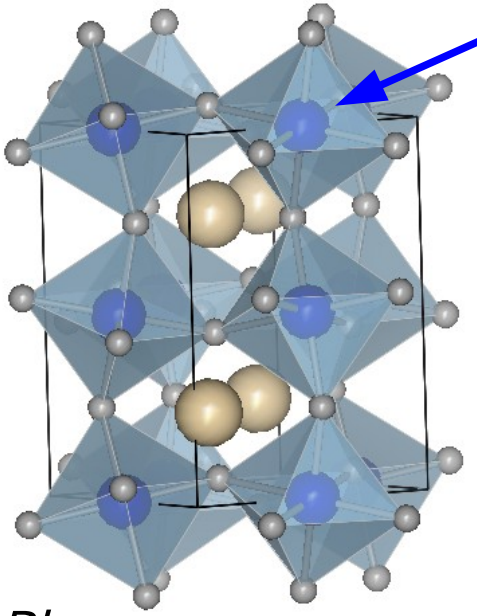
3. Azimuthal angle, Polarization dependence



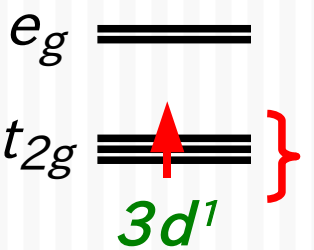
2. Space group× (Observation of forbidden reflection)

$YTiO_3$

Perovskite structure



Ti^{3+}



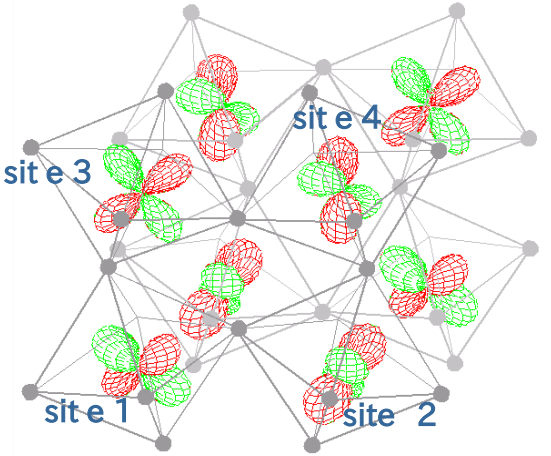
Orbital degree of freedom

Mott insulator

Pbnm

($GdFeO_3$ type structure)

Orbital ordering



<site 1-4>
$c_1 d_{zx} - c_2 d_{xy}$
$c_1 d_{yz} + c_2 d_{xy}$
$c_1 d_{zx} + c_2 d_{xy}$
$c_1 d_{yz} - c_2 d_{xy}$

$c_1 \sim 0.71$

Ferromagnetism: $T_c \sim 30$ K

Theory

Experiment ($T < T_c$)

Polarized neutron scattering

*J. Akimitsu et al., JPSJ **70** (2001) 3475.*

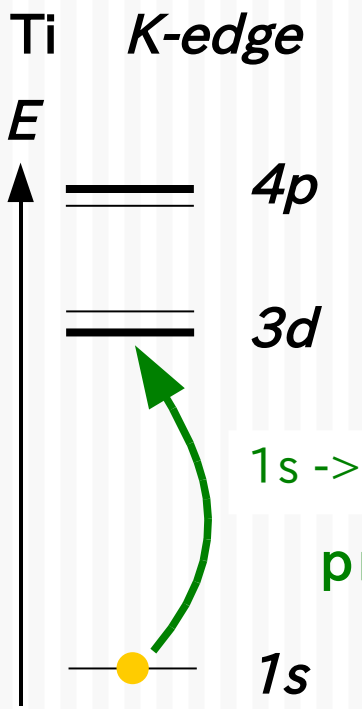
^{47,49}*Ti NMR*

*M. Ito et al., JPSJ **68** (1999) 2783.*

Orbital ordering in $YTiO_3$

RXS sign als

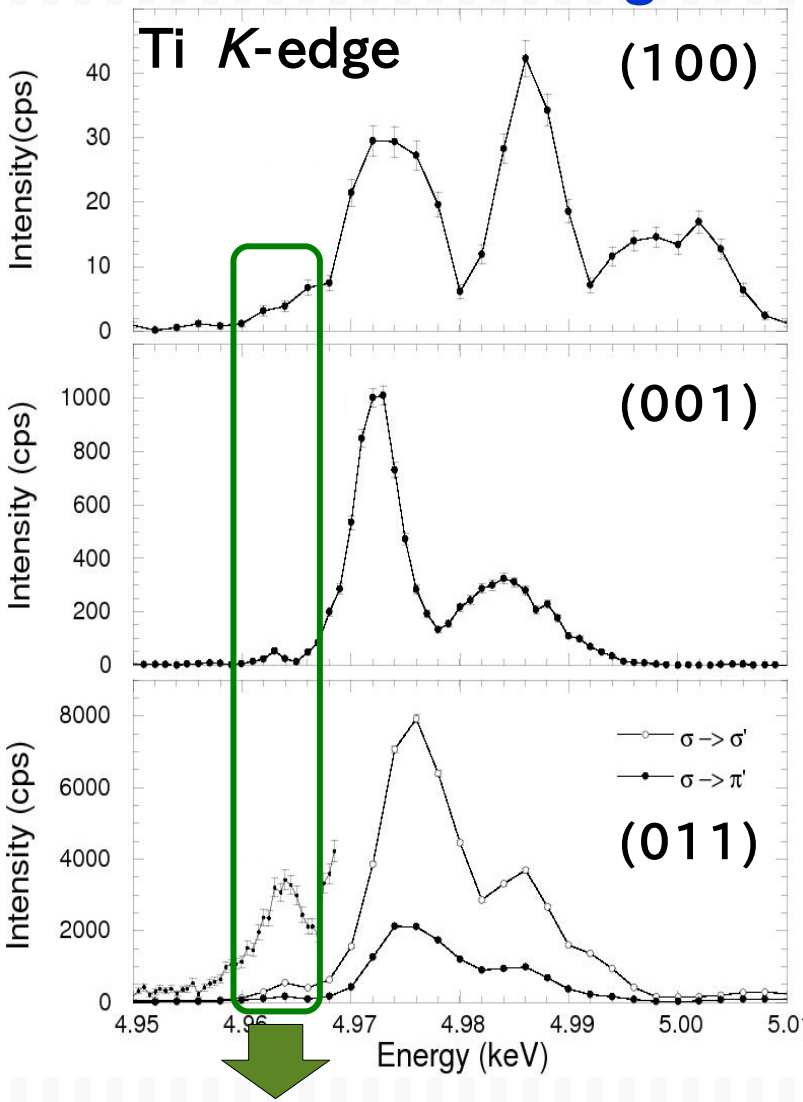
Resonant x-ray scattering:
orbital selective technique



1s -> 3d transition energy

pre-e dge

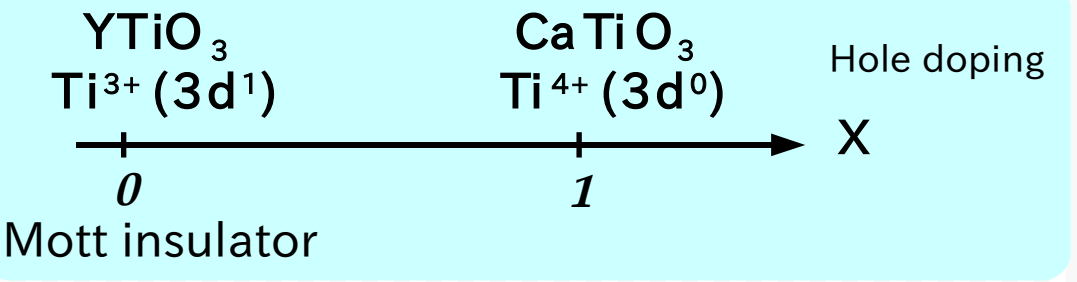
Tensor:
Anisotropic Ti 3d state



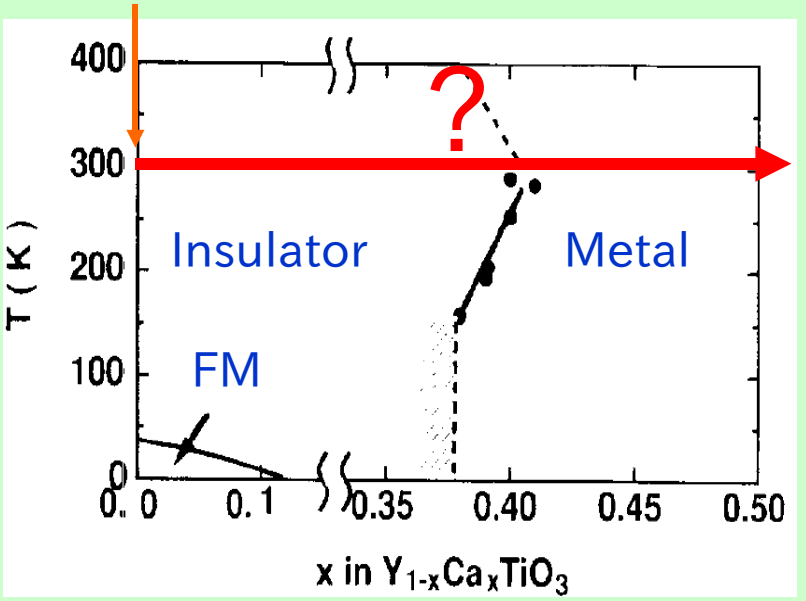
Direct evidence of 3d orbital ordering

H. Nakao et al., PRB **66** (2002) 184419.

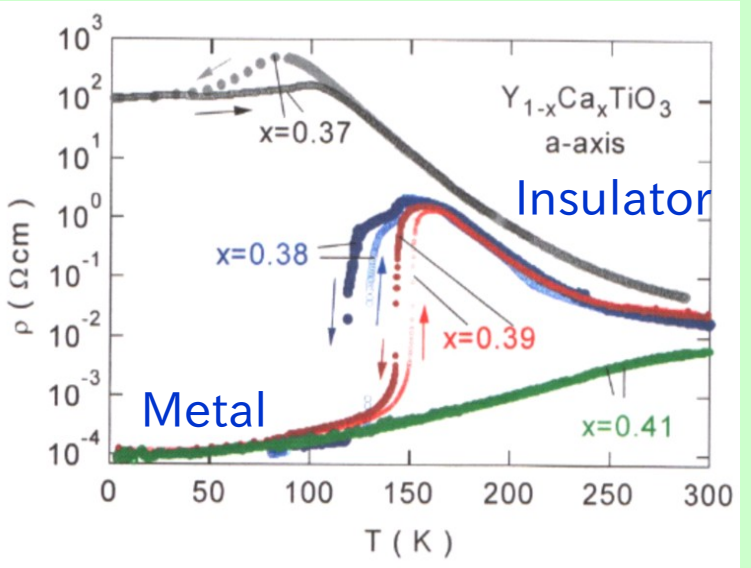
Hole doping: $Y_{1-x}Ca_xTiO_3$



Orbital ordering



*F. Iga et al., Physica B **223&224** (1996) 526.*

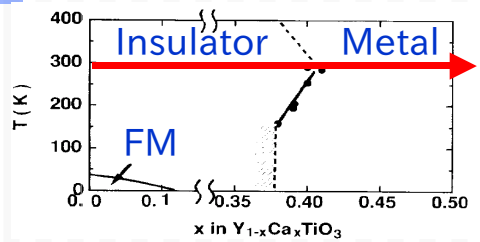


*M. Tsubota et al., JPSJ **72** (2003) 3182.*

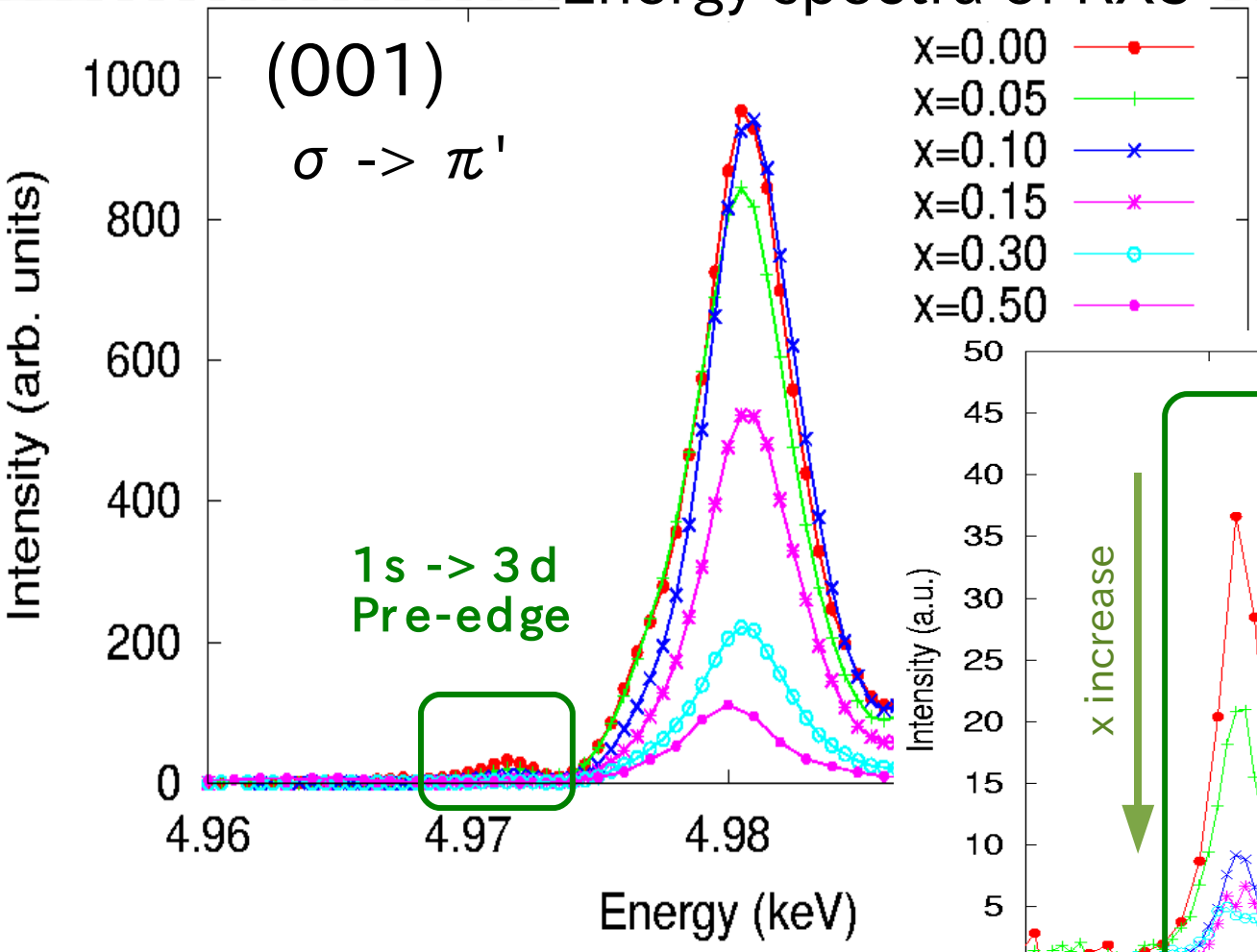
Relation between physical properties and orbital ordering ?

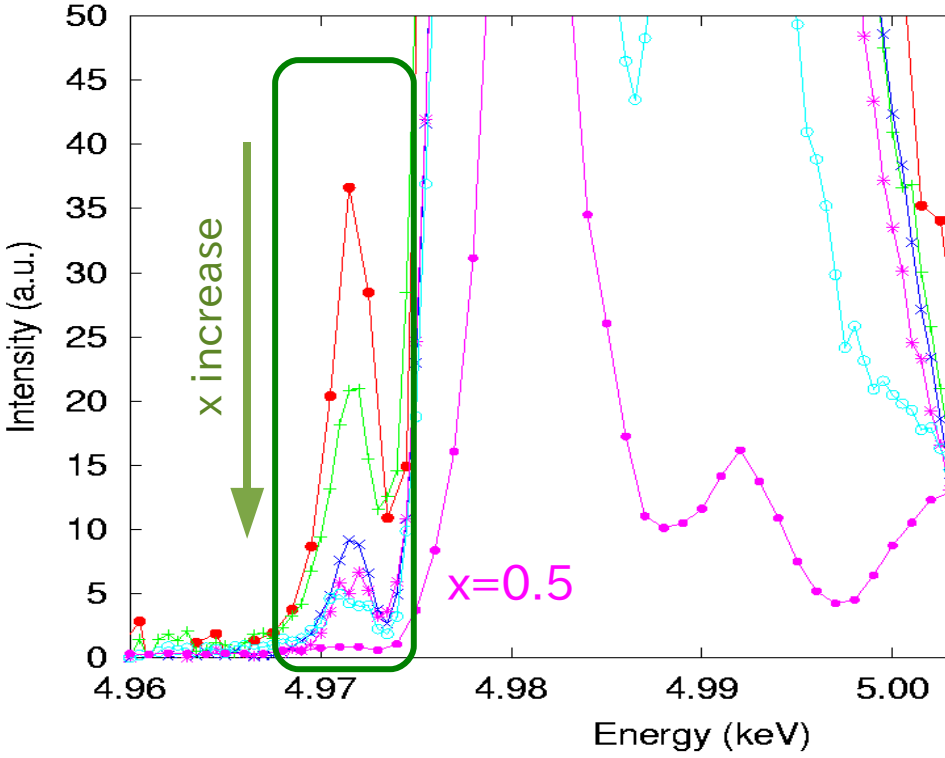
Hole doping ⇔ Orbitally ordered state

$Y_{1-x}Ca_xTiO_3$



Energy spectra of RXS

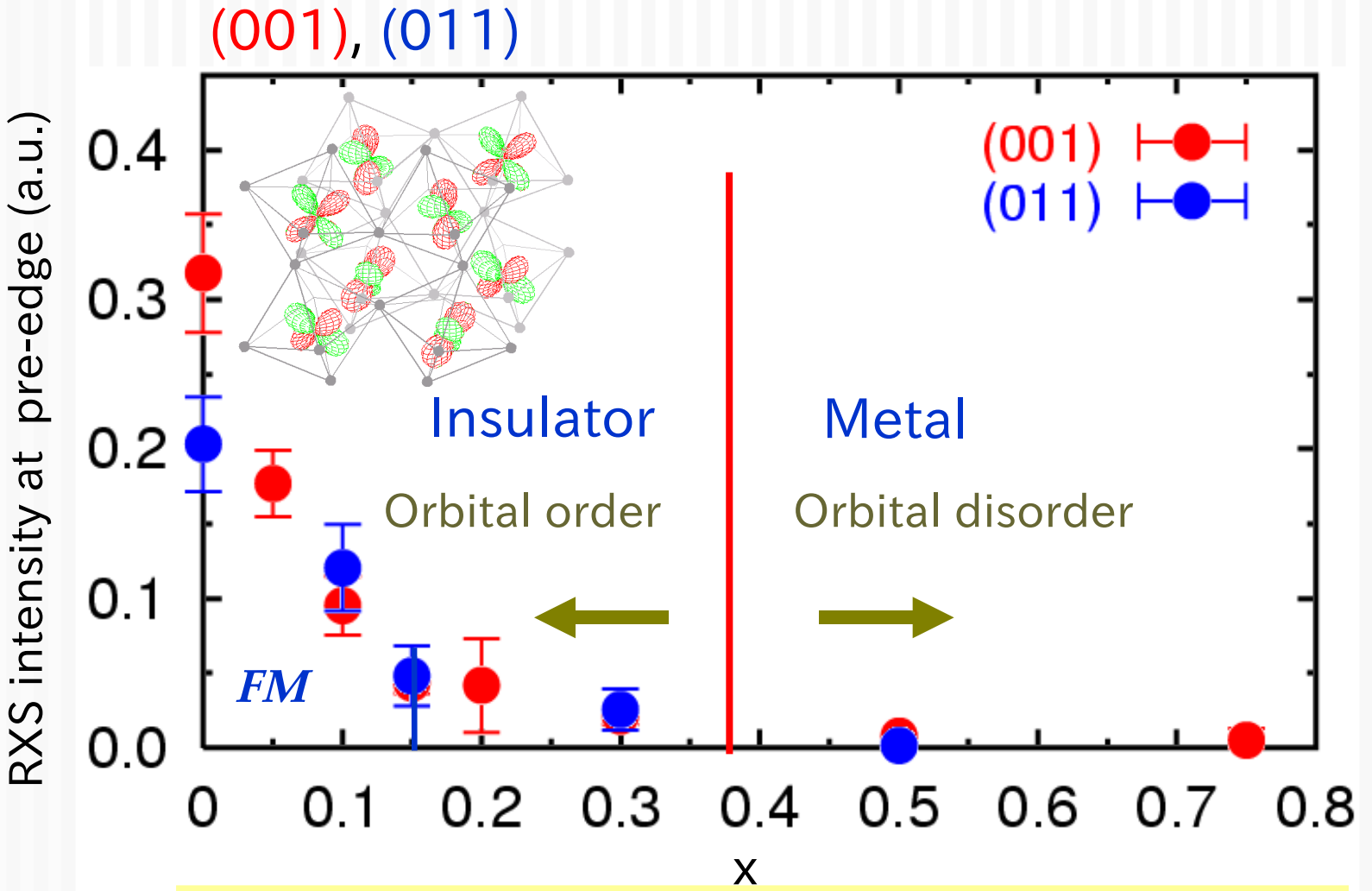




Order parameter of orbital ordering

H. Nakao et al., JPSJ **73** (2004) 2620.

Ti^{3+} ($3d^1$) Orbital state studied by RXS at pre-edge



Orbital ordering strongly suppressed in $0<x<0.15$

Insulator phase ⟷ orbital ordering

RXS at pre-edge: 1s-> 3d transition energy

⇨ Existence of anisotropic 3d orbital

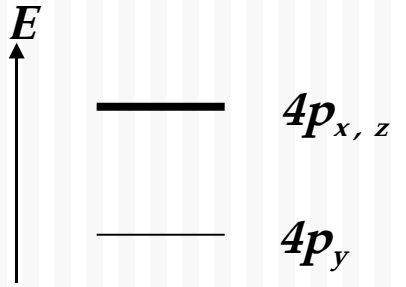
⇔ Order parameter of orbital ordering

~~Anisotropy of ordered 3d orbital~~

(Wave function of ordered orbital)

RXS at main edge: 1s -> 4p transition energy

Anisotropic Ti 4p state



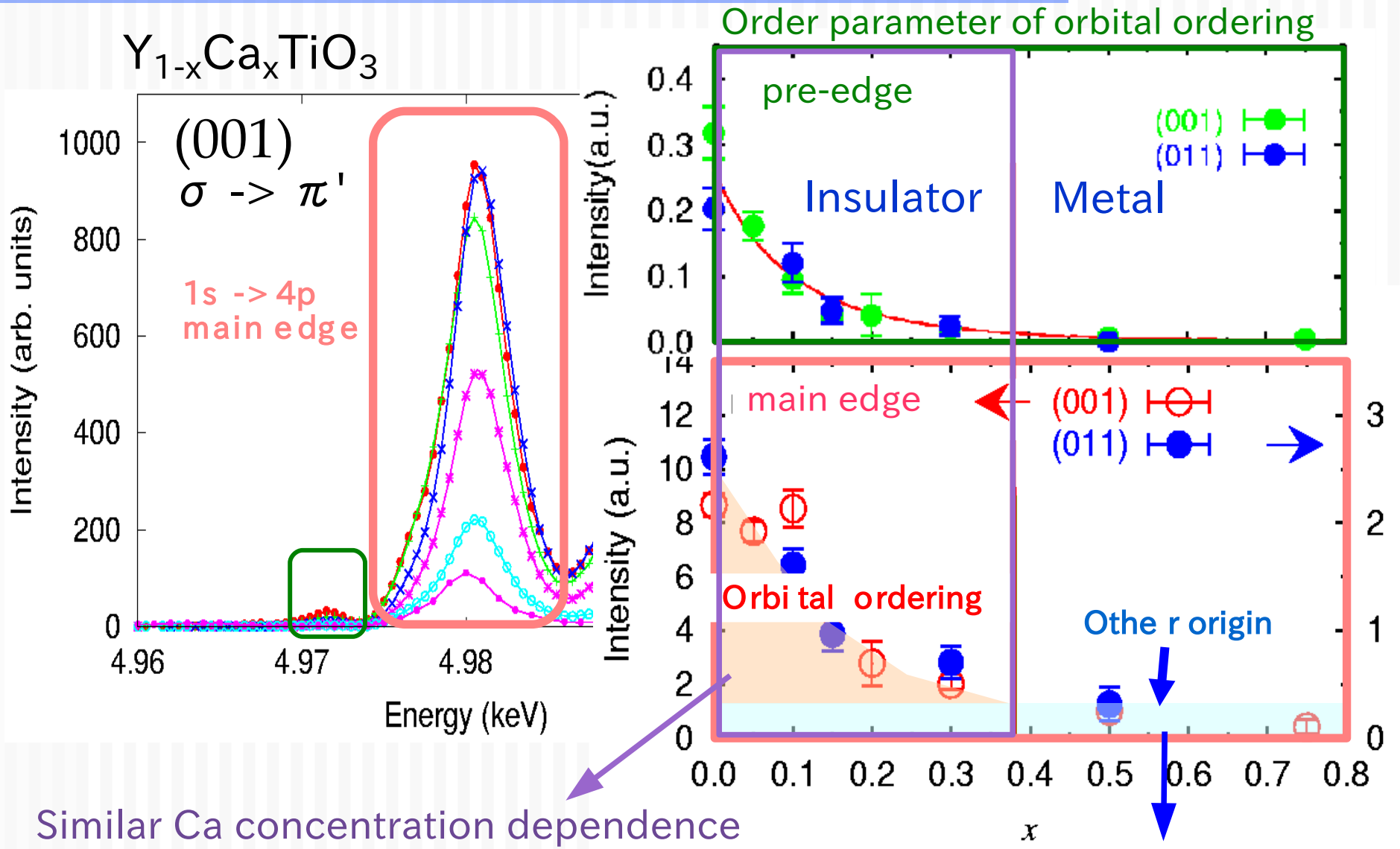
Origin:

3d orbital state,

Structural anisotropy: octahedral tilting

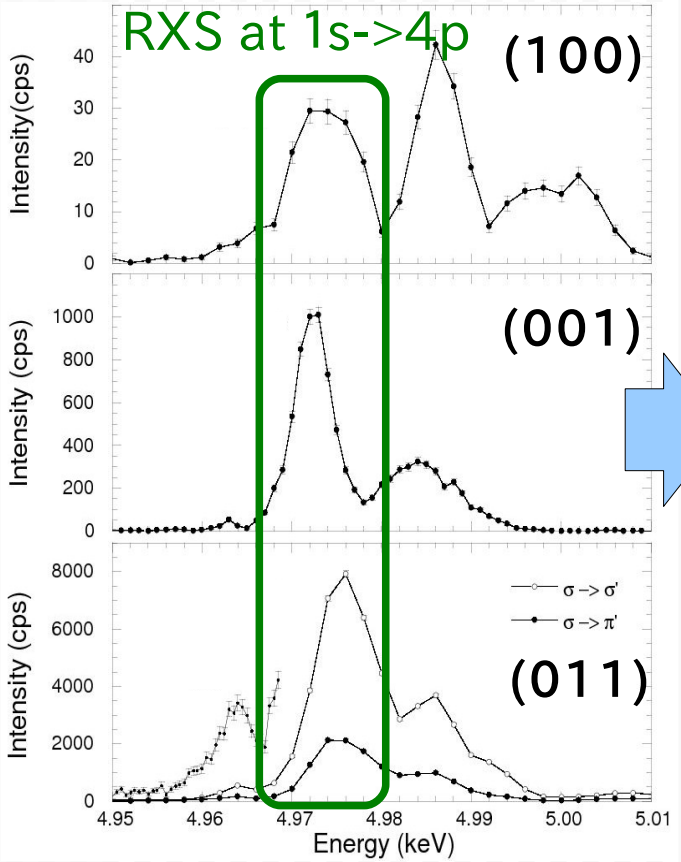
RXS at main edge

(1s -> 4p transition energy)



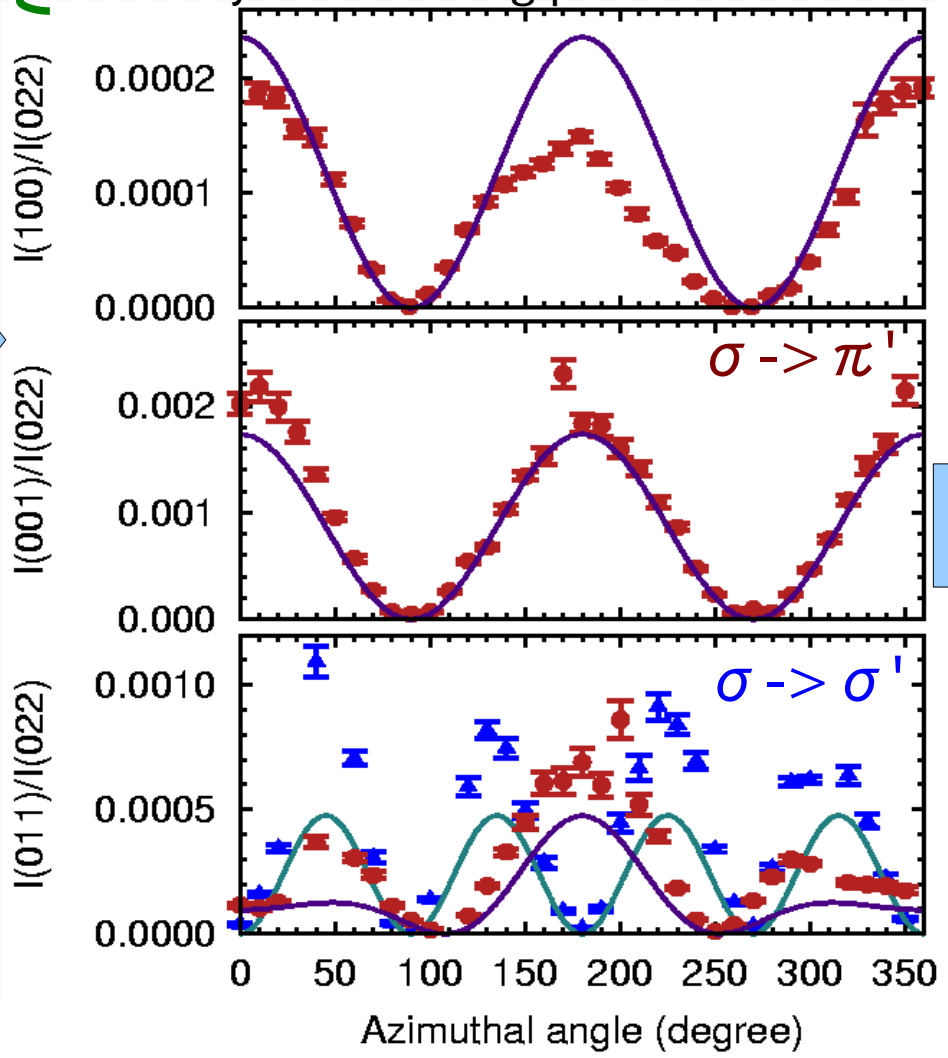
RXS at main edge ($YTiO_3$)

To estimate anisotropic 4p states



$$\begin{cases} (100): & f_1 - f_2 + f_3 - f_4 \\ (001): & f_1 + f_2 - f_3 - f_4 \\ (011): & f_1 - f_2 - f_3 + f_4 \end{cases}$$

Azimuthal angle / polarization dependence
Intensity ratio among peaks



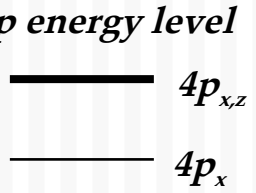
Tensor of Atomic scattering factor

H. Nakao et al., PRB **66** (2002) 184419.

Wave function of ordered orbital in $YTiO_3$

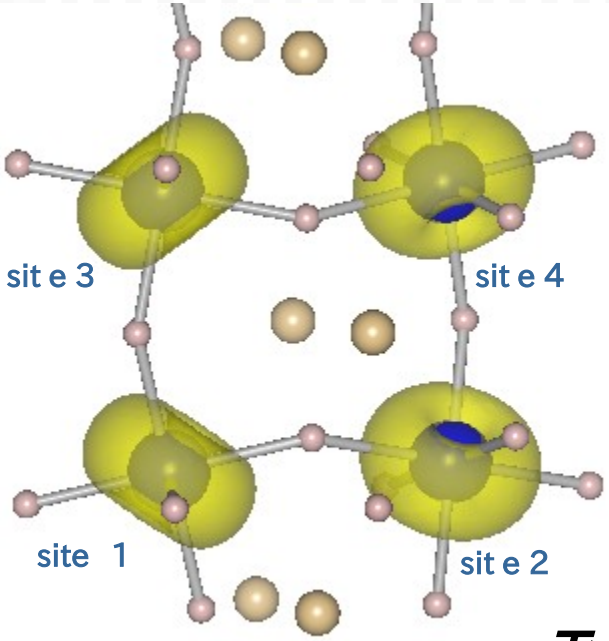
Tensors of Anomalous scattering factor at each Ti sites

$$f = \begin{pmatrix} f_{//} & 0 & 0 \\ 0 & f_{\perp} & 0 \\ 0 & 0 & f_{//} \end{pmatrix}$$

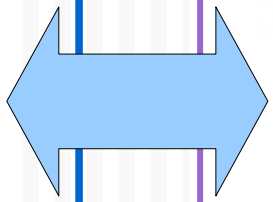


Energy level splitting of Ti 4p orbital
(Anisotropic 4p band structure)

Anisotropic Ti 4p states

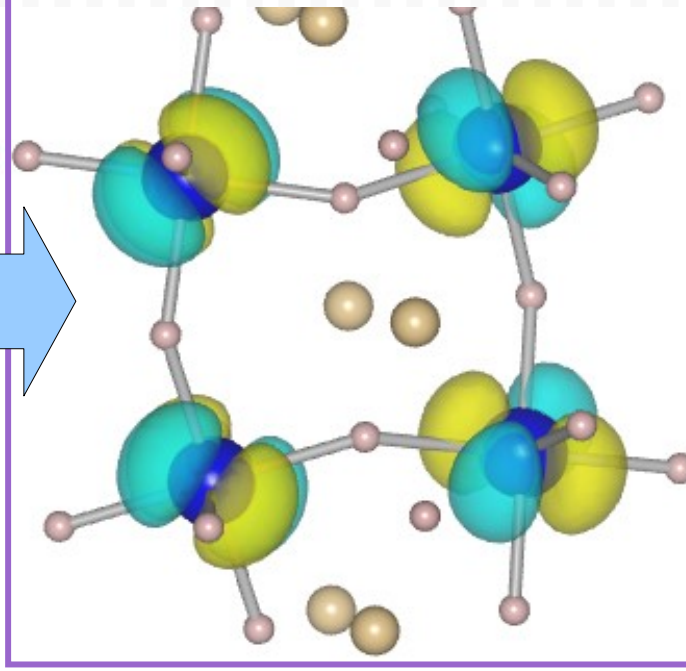


T> *T*c



Wave function of ordered orbital

Theories and previous experiments (*T*< *T*c)



$c_1 d_{zx}$-$c_2 d_{xy}$

$c_1 d_{yz}$+$c_2 d_{xy}$

$c_1 d_{zx}$+$c_2 d_{xy}$

$c_1 d_{yz}$-$c_2 d_{xy}$

$c_1 = c_2 \sim 0.71$

Summary

1. RXS at 1s -> 3d transition (pre-edge)

Anisotropic 3d energy level

→ Order parameter of ordered orbital

- $YTiO_3$ Direct evidence of orbital ordering
- $Y_{1-x}Ca_xTiO_3$ Orbital state & physical properties

2. RXS at 1s -> 4p transition (main edge)

Anisotropic 4p energy level

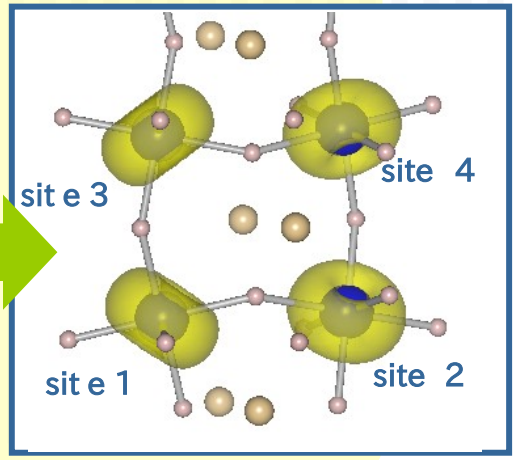
Origin: 3d orbital state and octahedral tilting

- $YTiO_3$

→ Quantitative estimation of 4p orbitals

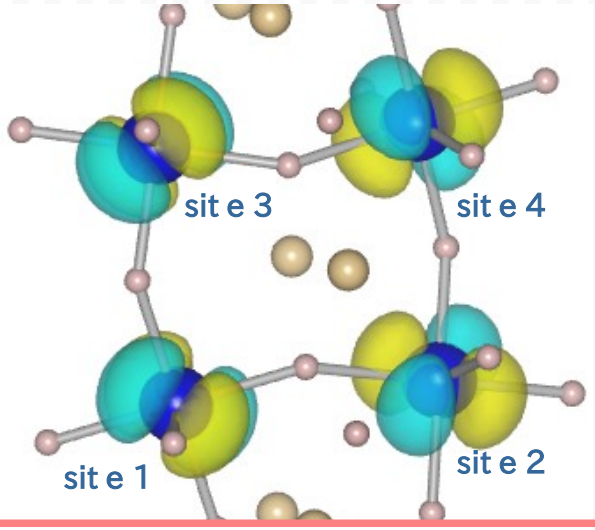
⟷ Wave function of ordered orbital

(Theoretical support is strongly desired.)

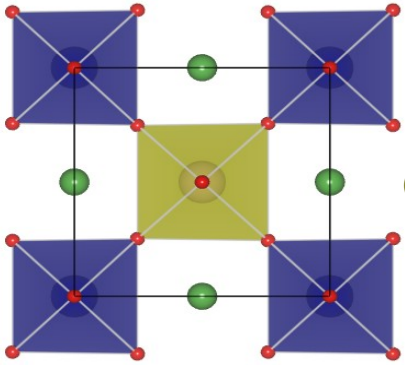


Future: Quantitative estimation of RXS

Anisotropy of ordered orbital



Absolute value of valence



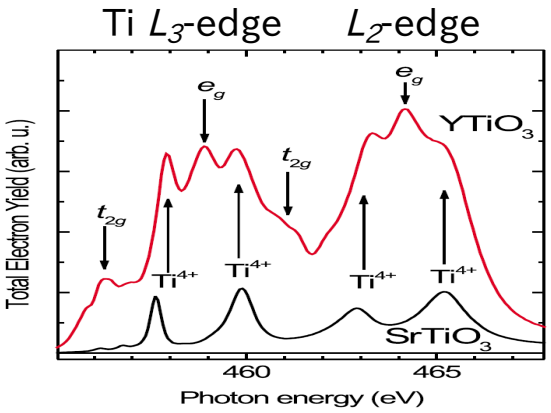
$\delta = 0.50 \pm 0.08$

Resonant soft X-ray scattering

Transition metal:
$L_{2,3}$-edge 2p-3d

Rare earth metal:
$M_{4,5}$-edge 3d-4f

Light element(O,S):
K-edge 1s-2p



Spectroscopic study

(energy spectrum)

Crystal field splitting:
t_{2g} , e_g

Orbital hybridization

Transition metal oxide
TM3d - O 2p hybridization

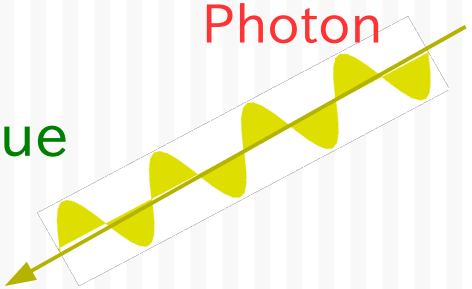
Covalencey

Future

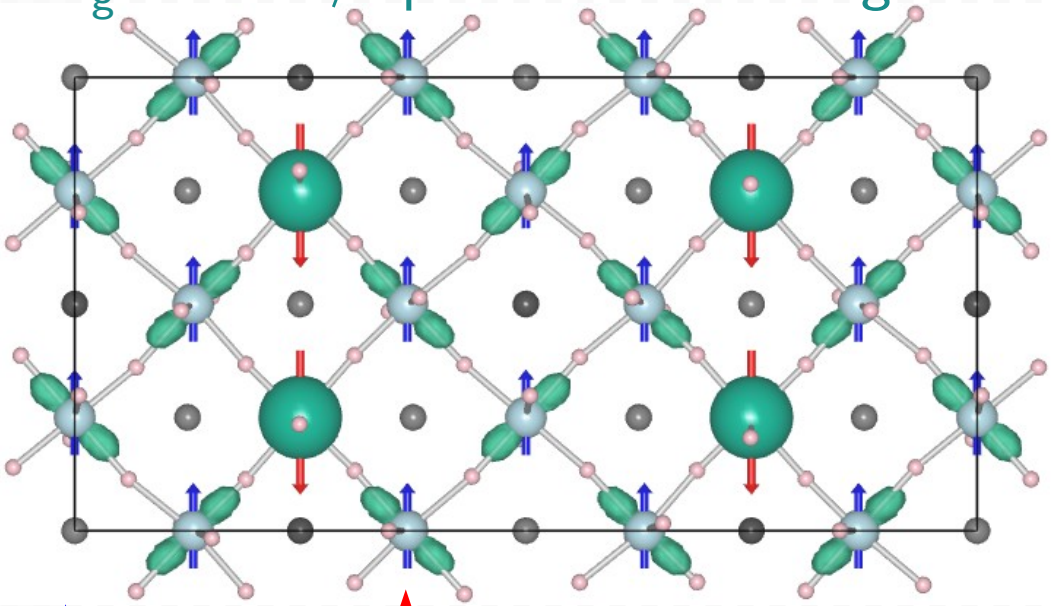
Multi-probes in IMSS

$Sr_3YCo_4O_{10.5}$

RXS technique



e_g-orbital / spin-state ordering



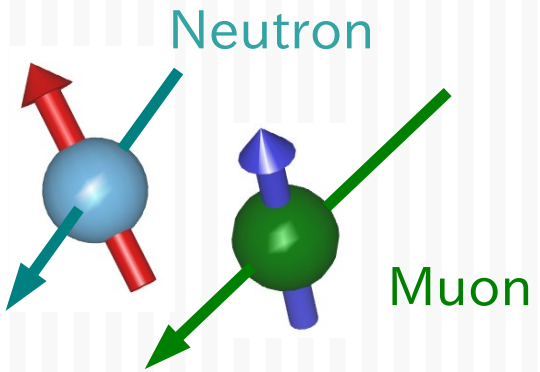
IS state　HS state

Resonant soft x-ray scattering

Respective information: t_{2g} , e_g

→ Spin-state

Co3d-O2p hybridization



Magnetic structure

→ Spin-state

Charge/orbital/spin states ⟺ Not only by RXS, but also by complementary use of multi-probes

Collaborators

Thank you for your attention.

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