Orbital Ordering Studied by Resonant X-Ray Scattering

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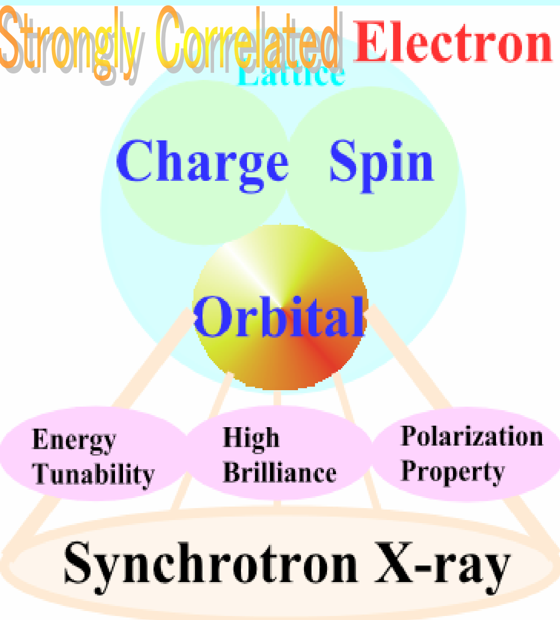
Prof. T. Iga (Hiroshima Univ.)

OUTLINE

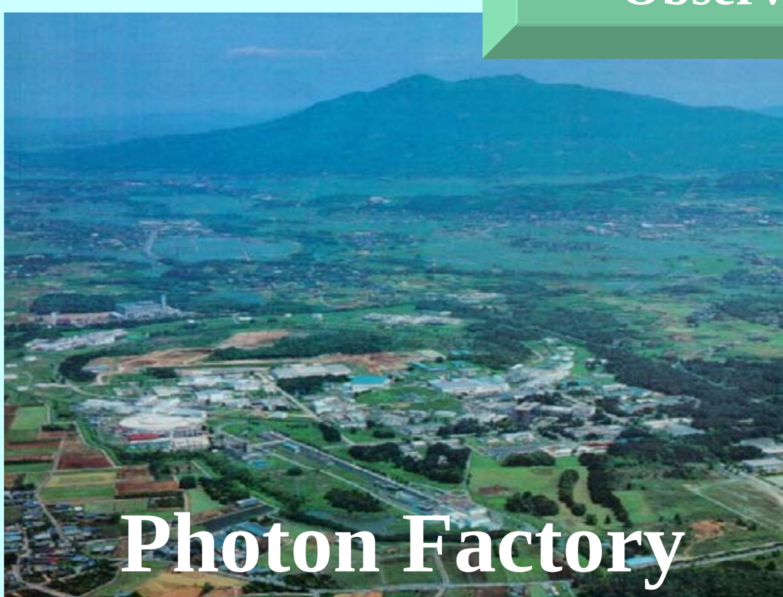


Introduction
Resonant X-ray Scattering to Observe Orbital Ordering

Recent Development of Resonant X-ray Scattering
1. Short Range Orbital Ordering
2. Orbital Ordering of *f*-electron Systems
3. Observation of Ferro-Orbital Ordering

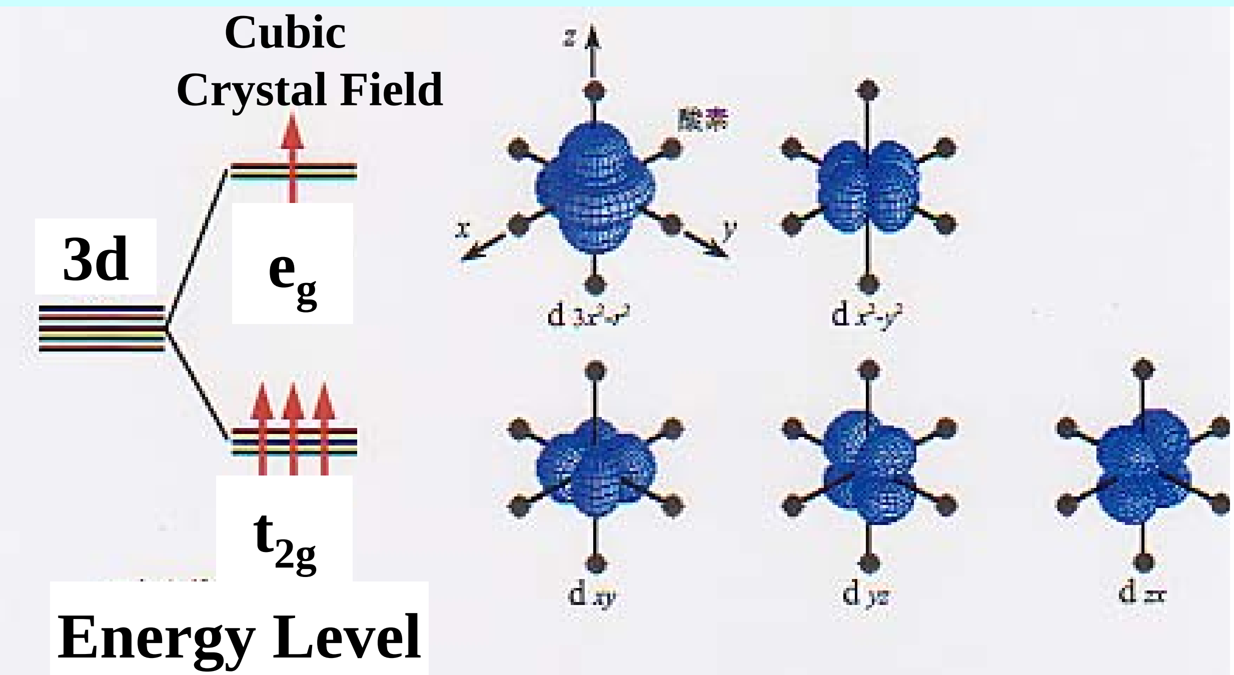
Orbital Ordering near the Mott Transition in t_{2g} Electron Systems, Titanates

Resonant Inelastic X-ray Scattering
Observation of Orbital Excitation in Manganites

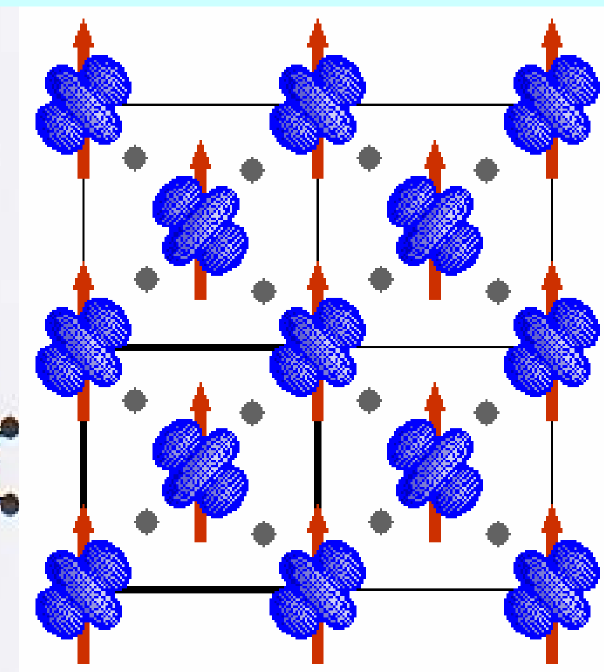


Orbital Degree of Freedom and Orbital Ordering in Manganite

Orbital Degree of Freedom of Mn^{3+} in Perovskite-type Manganese Oxide



Orbital Ordering in ab-plane of $LaMnO_3$



Cooperative Jahn Teller effect and/or
the super-exchange interaction between Mn sites

→ **Orbital Ordering**

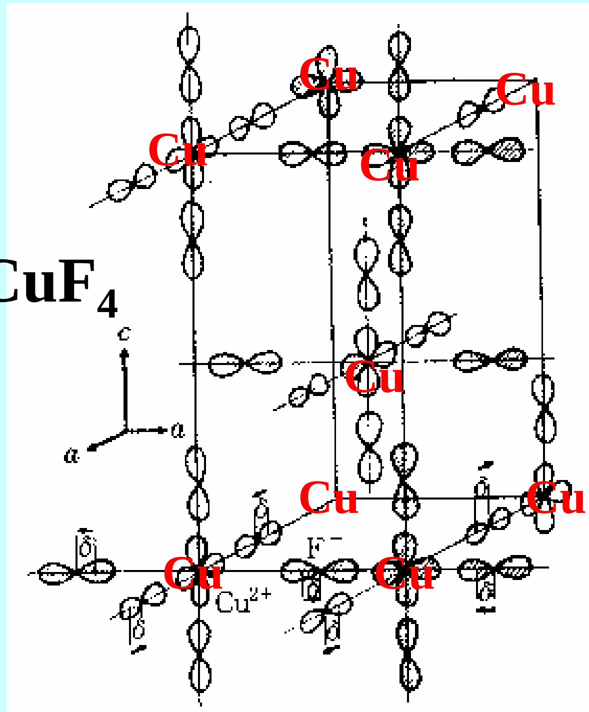
Polarized Neutron Diffraction

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)^{\pm\pm} = |F_N \pm F_M|^2$$

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)^{\pm\mp} = 0$$

First Observation of the Orbital Ordering

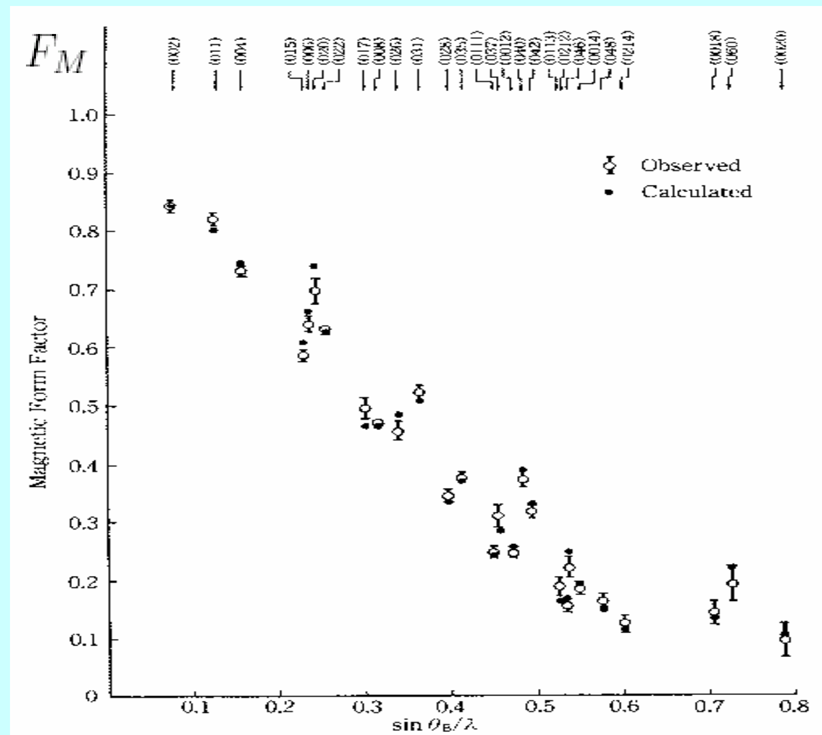
K_2CuF_4



Flipping Ratio R

$$R = \left(\frac{F_N + F_M}{F_N - F_M}\right)^2 = \left(\frac{1+\gamma_0}{1-\gamma_0}\right)^2$$

$$\gamma_0 = F_M/F_N$$



Problems

1. The magnetic order is required.

2. Temperature dependence of the order parameter

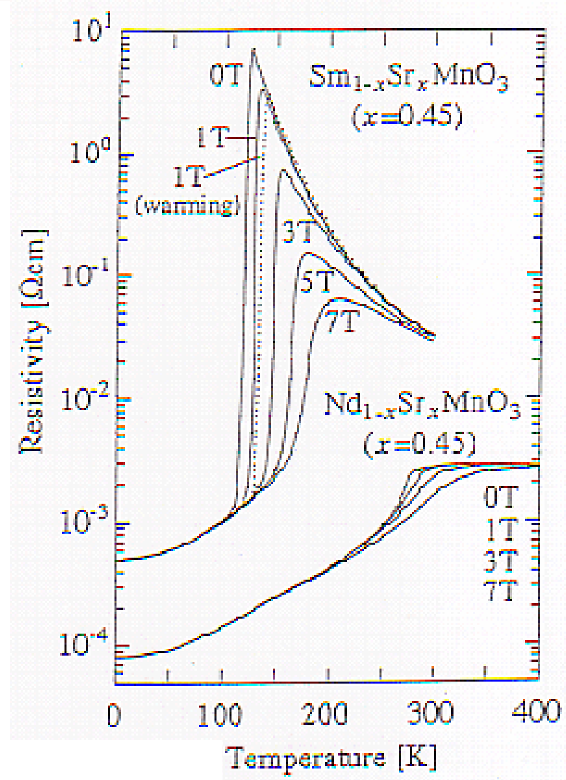
3. The correlation Length

Y. Ito and J. Akimitsu, J. Phys. Soc. Jpn., 40 (1976) 1621.

CMR
(Colossal Magneto-Resistance) Compound

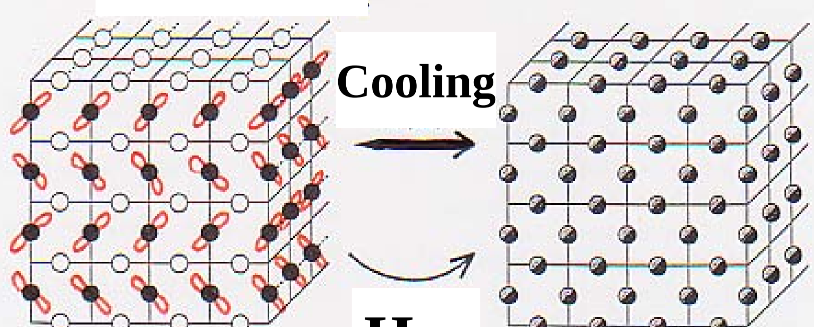
Importance of Orbital degree of freedom

$Sm_{1-x}Sr_xMnO_3$

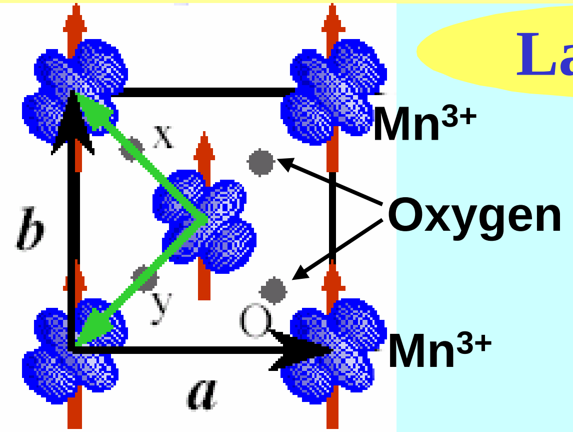


Tokura Group

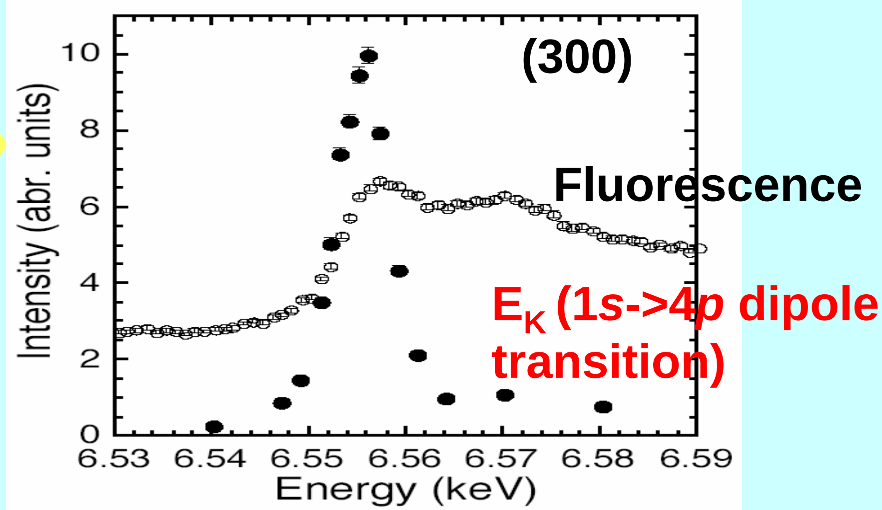
The revival of exprimental and theoretical interest in the manganites has occurred in 1990's by the discovery of CMR.



Resonant X-ray Scattering



1. Resonant Nature



$$\hat{f}(n=+1) = \begin{pmatrix} f_{\perp} & 0 & 0 \\ 0 & f_{\parallel} & 0 \\ 0 & 0 & f_{\perp} \end{pmatrix}$$

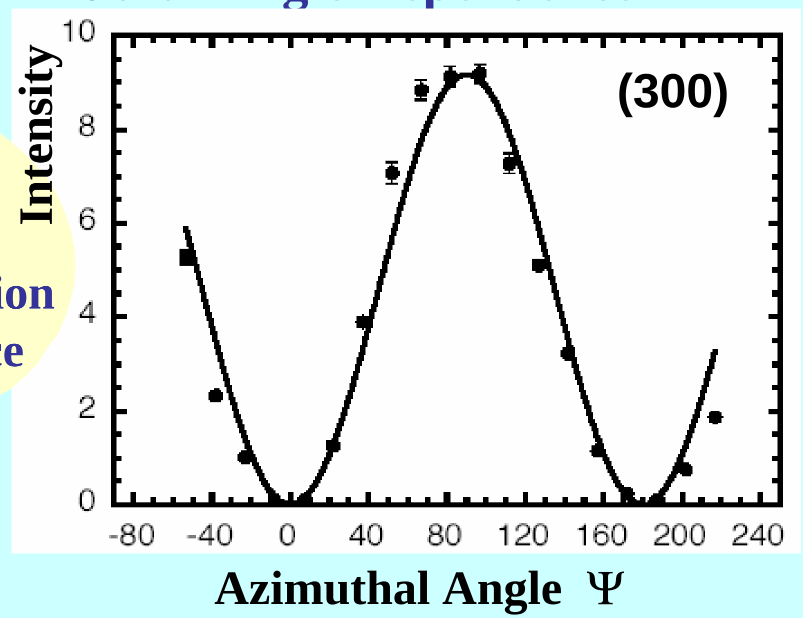
$$\hat{f}(n=-1) = \begin{pmatrix} f_{\parallel} & 0 & 0 \\ 0 & f_{\perp} & 0 \\ 0 & 0 & f_{\perp} \end{pmatrix}$$

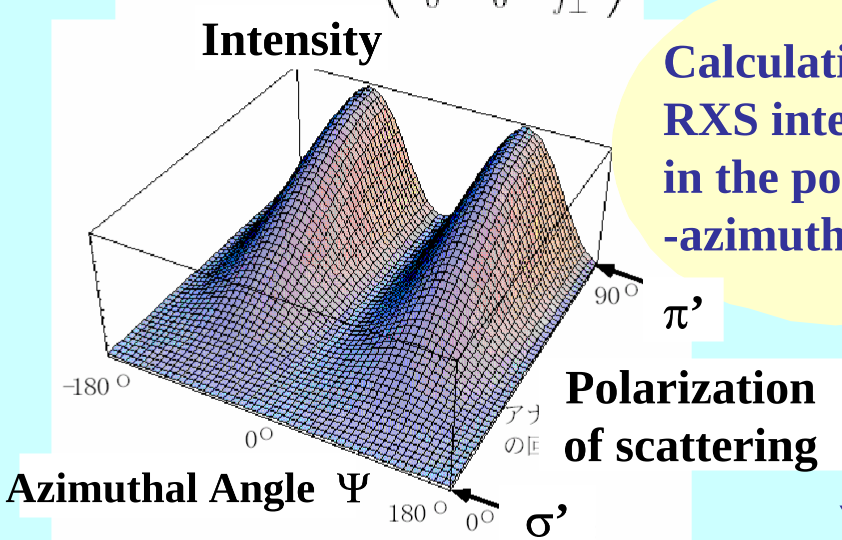
Atomic Scattering Tensor

2. Polarization Dependence

The polarization of x-ray rotates (σ→π).

3. Azimuthal Angle Dependence





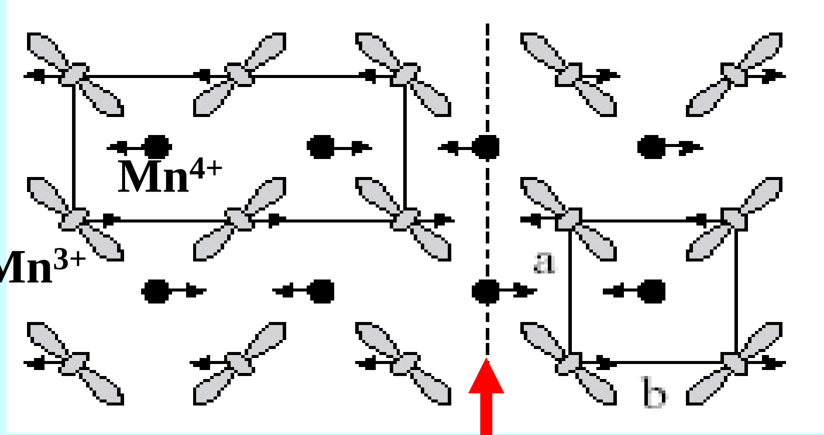
Calculation of RXS intensity in the polarization -azimuthal space

Y. Murakami et al. PRL 80, 1932 (1998), PRL 81, 582 (1998).

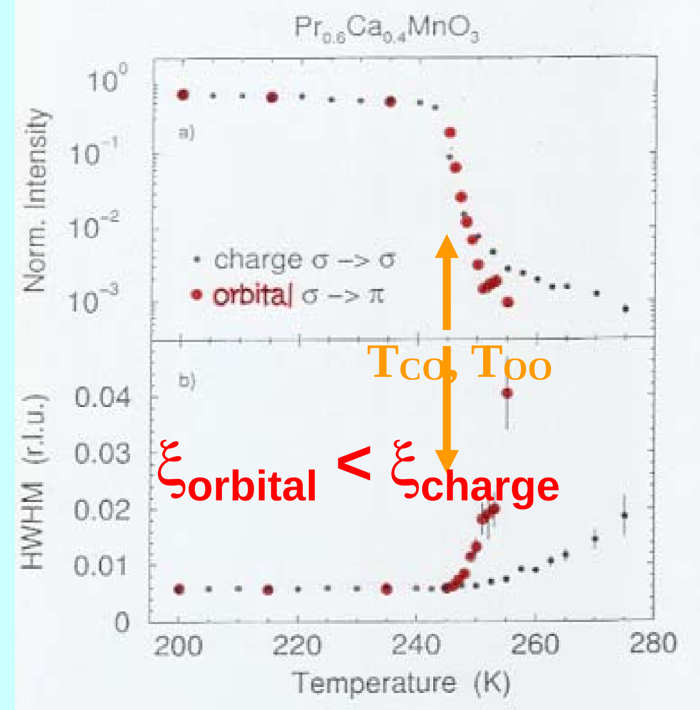
Recent Development of RXS

1. **Observation of short-range orbital ordering:**
   $Pr_{1-x}Ca_xMnO_3$,

   M.v.Zimmermann , PRL 83, 4872 (1999)
   (A team of BNL scientists) PRB 64, 195133 (2001)



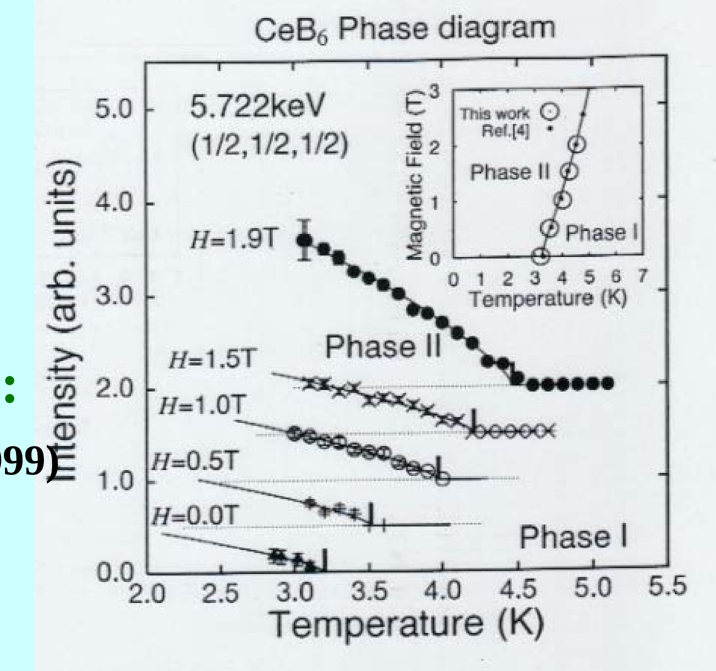
Orbital antiphase domain boundary



2. **Observation of orbital ordering in f-electron system (quadrupolar ordering):**

   DyB_2C_2, Y. Tanaka, J. Phys. Cond. Matter. 11, L505 (1999)
   K.Hirota, PRL 84, 2706 (2000)
   T. Matsumura, PRB 65, 094420 (2002)

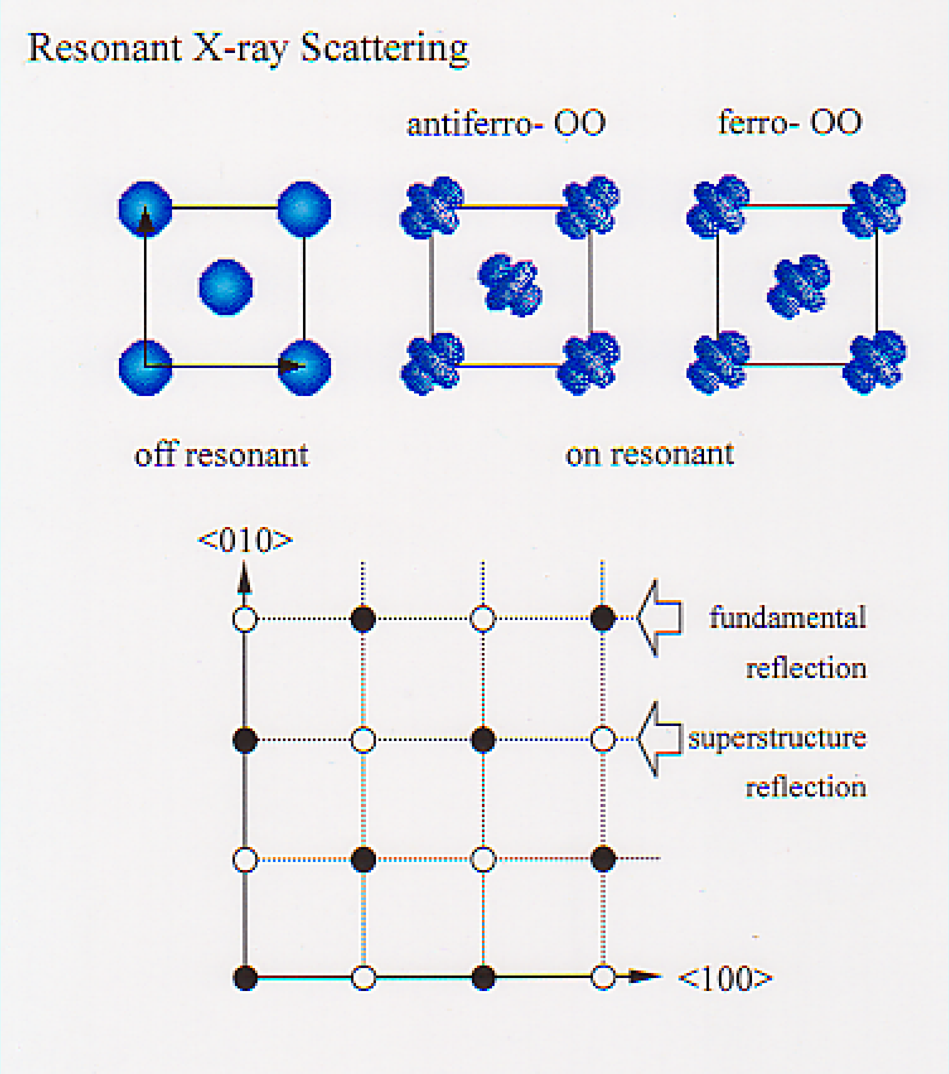
   CeB_6, H.Nakao , JPSJ 70, 1857 (2001)



3. Observation of Ferro-Orbital Ordering

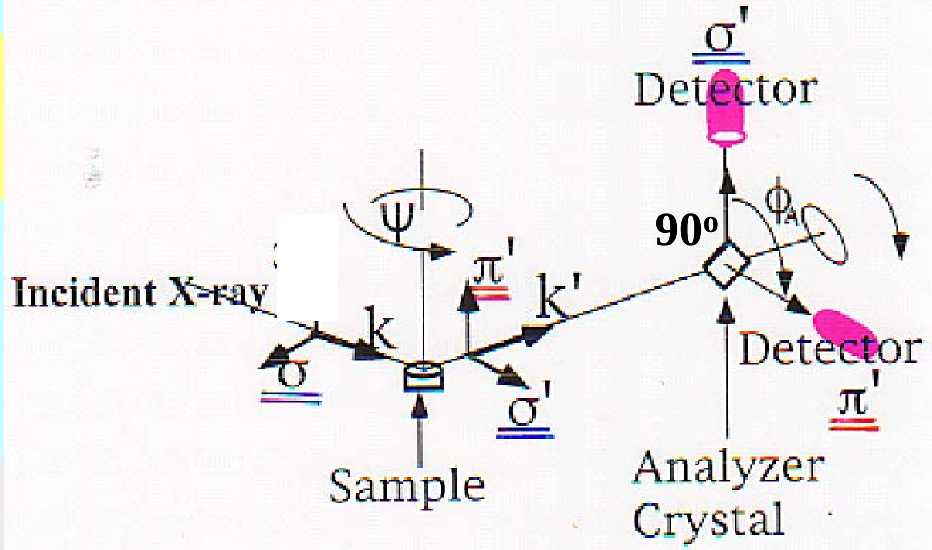
$La_{0.5}Sr_{0.5}MnO_3$ thin films, H. Ohsumi et al., **JPSJ 72, 1006 (2003).**

$La_{1-x}Sr_xMnO_3$ superlattice, T. Kiyama et al., **JPSJ 72, 785 (2003).**



Interference Technique using Resonant X-ray Scattering

T. Kiyama et al., **JPSJ 72, 785 (2003).**
H. Ohsumi et al., **JPSJ 72, 1006 (2003).**



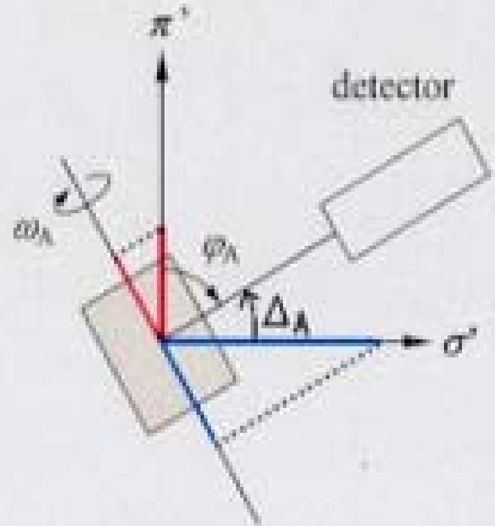
Cu(220)
for manganites

New Technique to Observe Ferro-Orbital Ordering

Polarization analysis $(2\theta_A = 90°)$

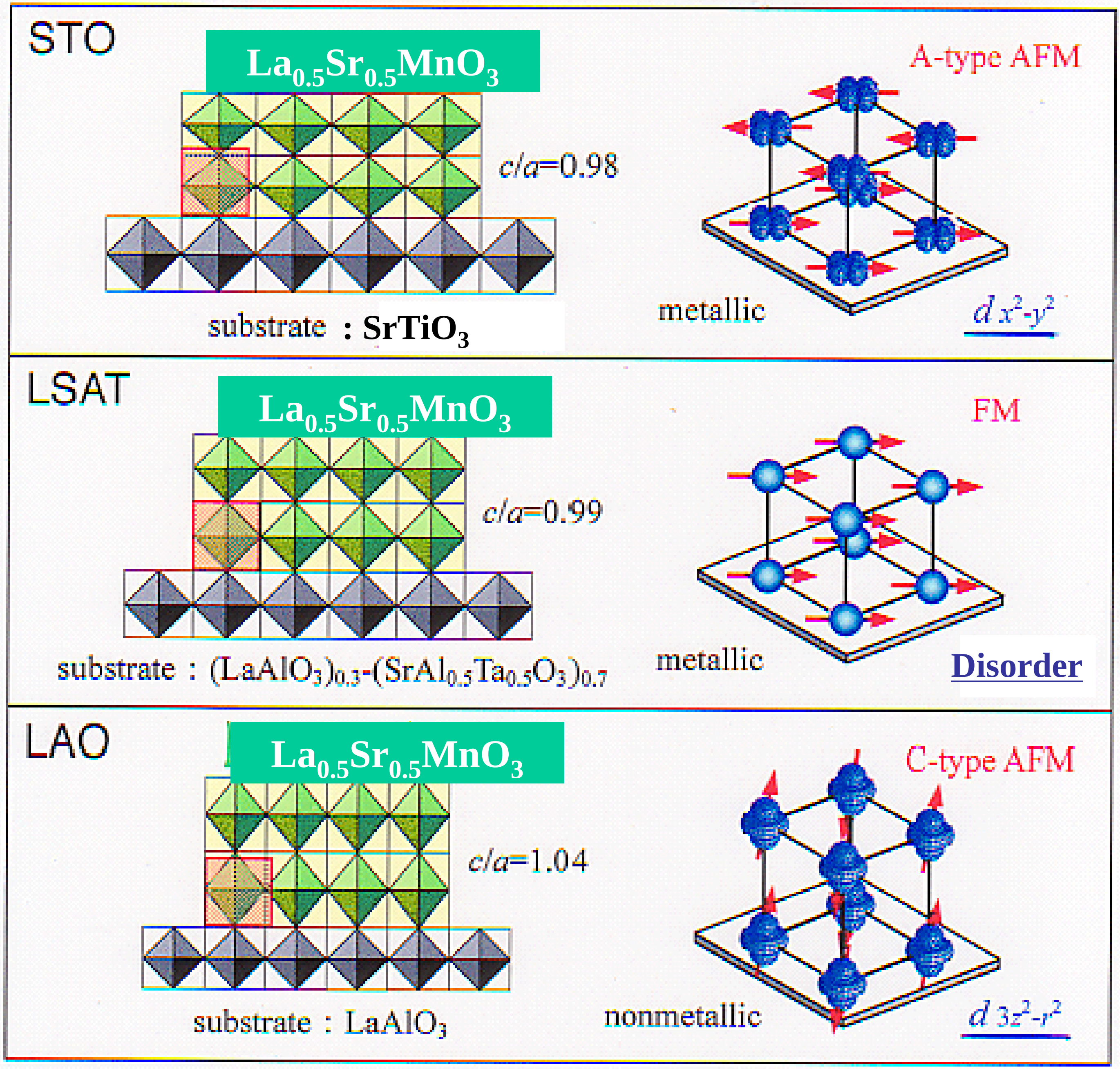
$$I(\varphi_A) \propto \left| (\sigma \hat{F} \sigma) \cos\varphi_A - (\pi \hat{F} \sigma) \sin\varphi_A \right|^2$$

amplitude of electric field along the ω_A-axis

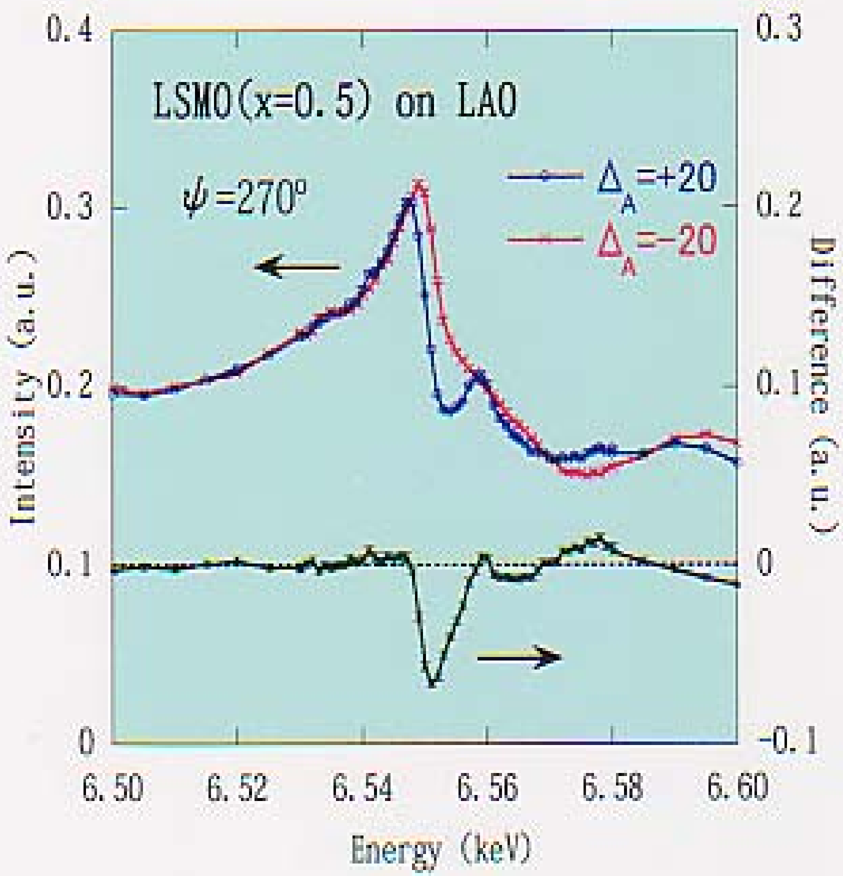


Interference Term

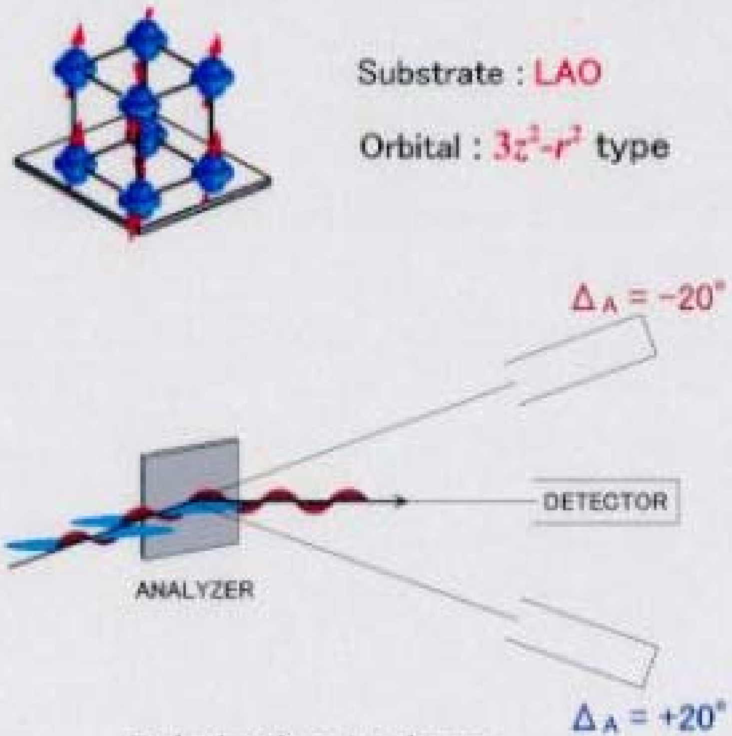
$$I(90° + \Delta_A) - I(90° - \Delta_A) \propto \left| (\sigma \hat{F} \sigma) \sin\Delta_A + (\pi \hat{F} \sigma) \cos\Delta_A \right|^2 - \left| (\sigma \hat{F} \sigma) \sin\Delta_A - (\pi \hat{F} \sigma) \cos\Delta_A \right|^2$$
$$= 2\,\mathrm{Re}\left[(\sigma \hat{F} \sigma)(\pi \hat{F} \sigma)^* \right] \sin 2\Delta_A$$



Y. Konishi *et al.*, J. Phys.Soc. Jpn. **68**, 3790 (1999).

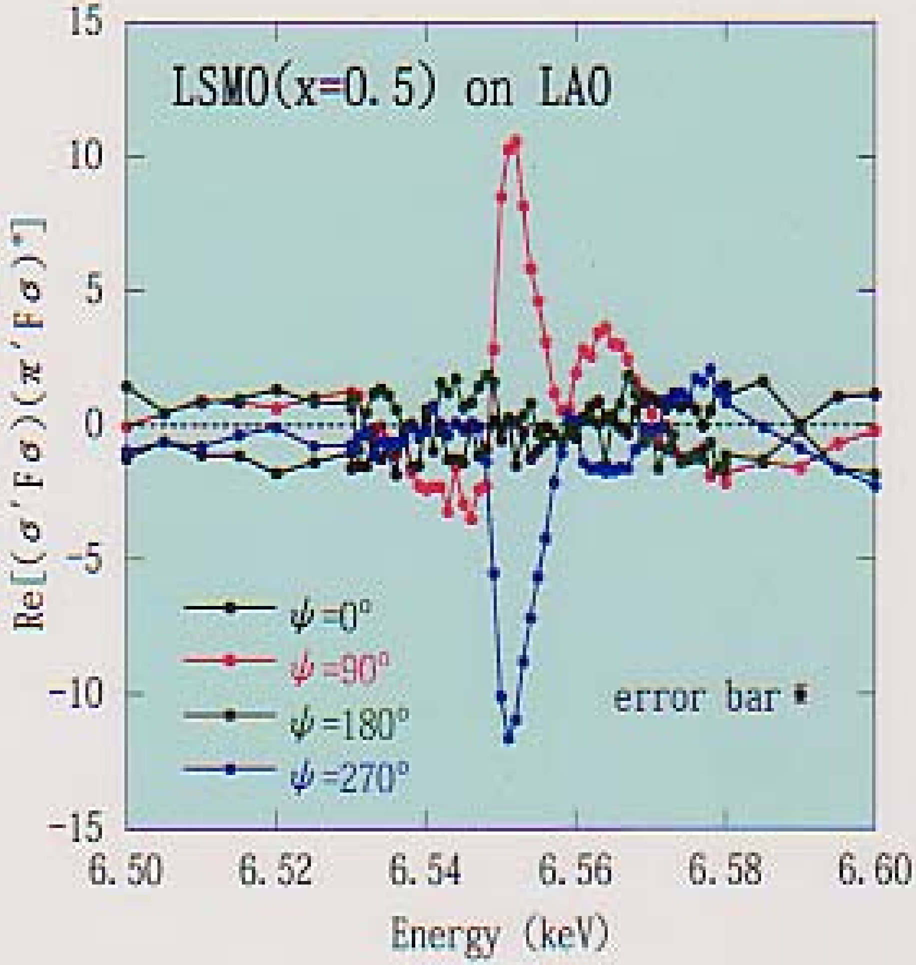


Energy dependence of the (012) Bragg reflection near the manganese *K*-absorption edge.

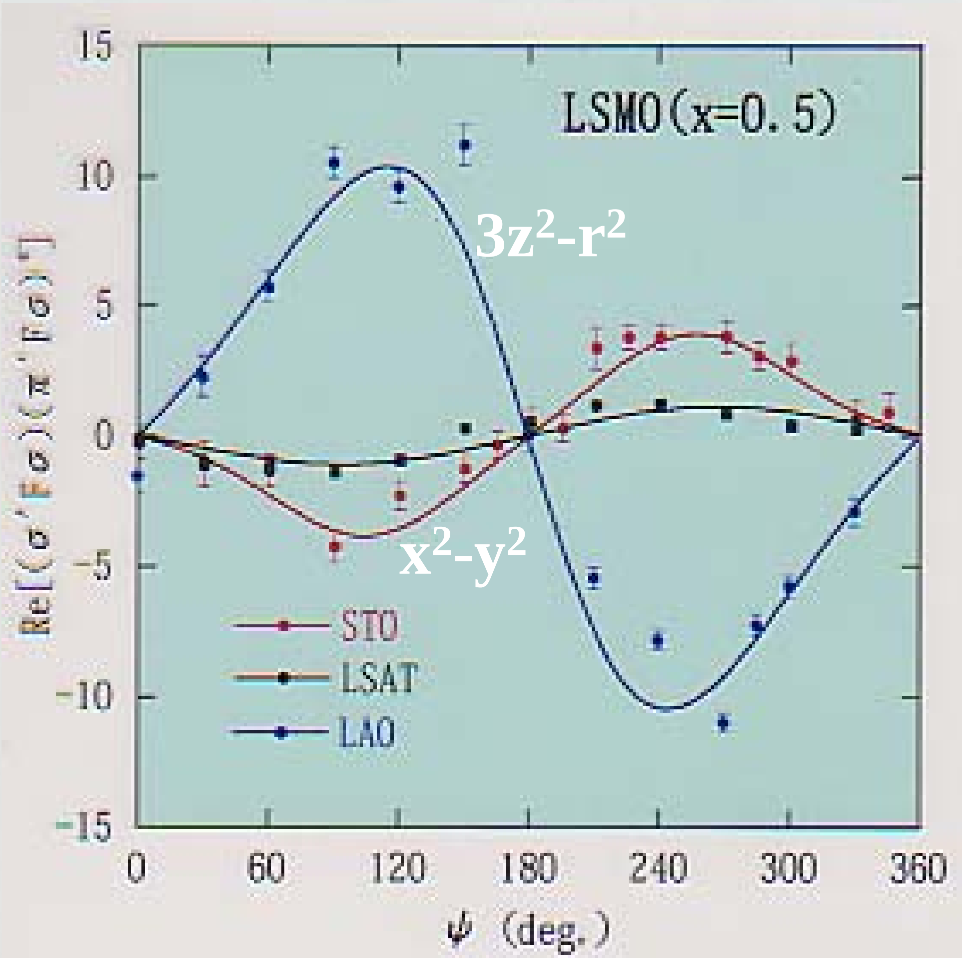


Polarization Analyzer

H. Ohsumi et al., **JPSJ 72, 1006 (2003).**



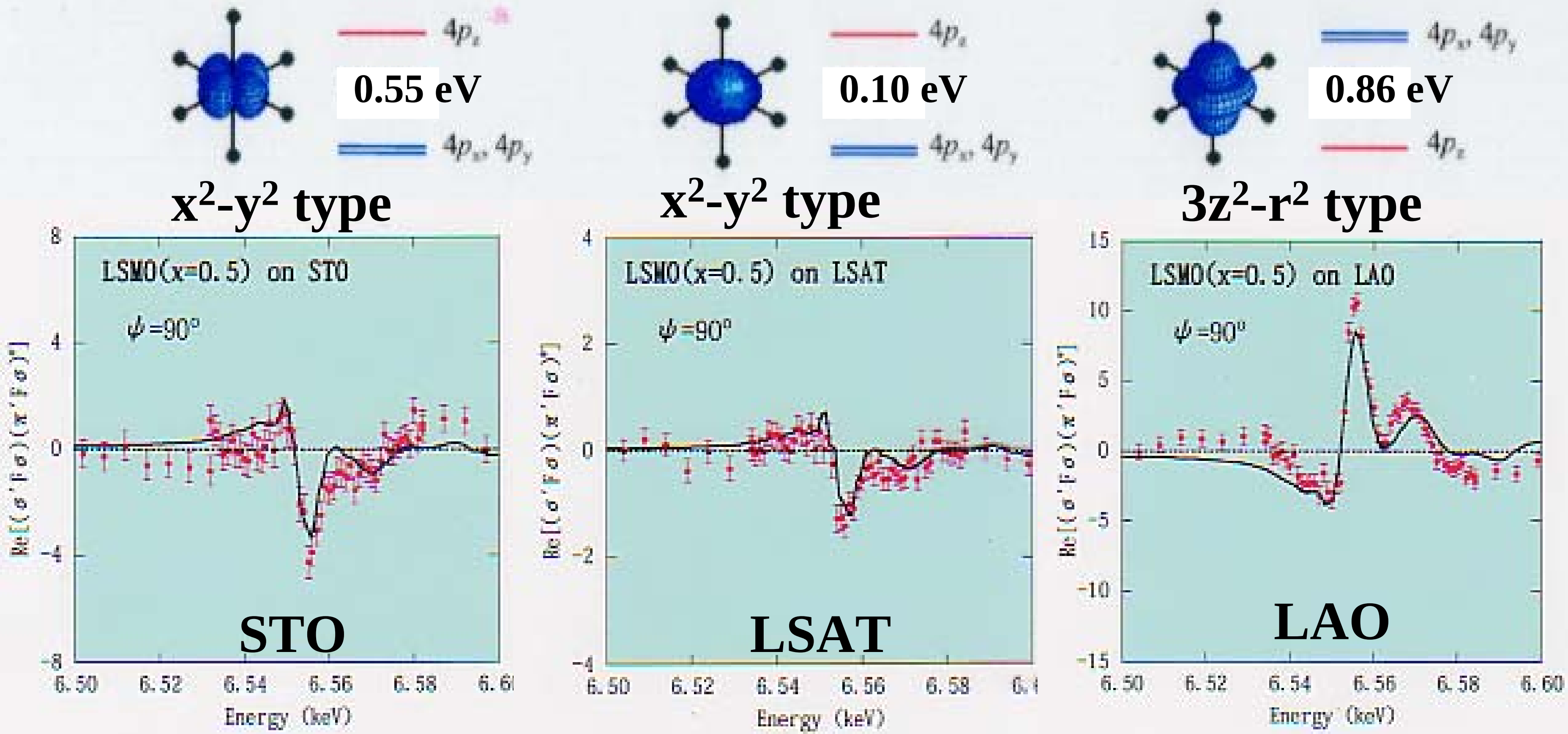
Energy Dependence



Azimuthal Angle Dependence

H. Ohsumi et al., JPSJ 72, 1006 (2003).

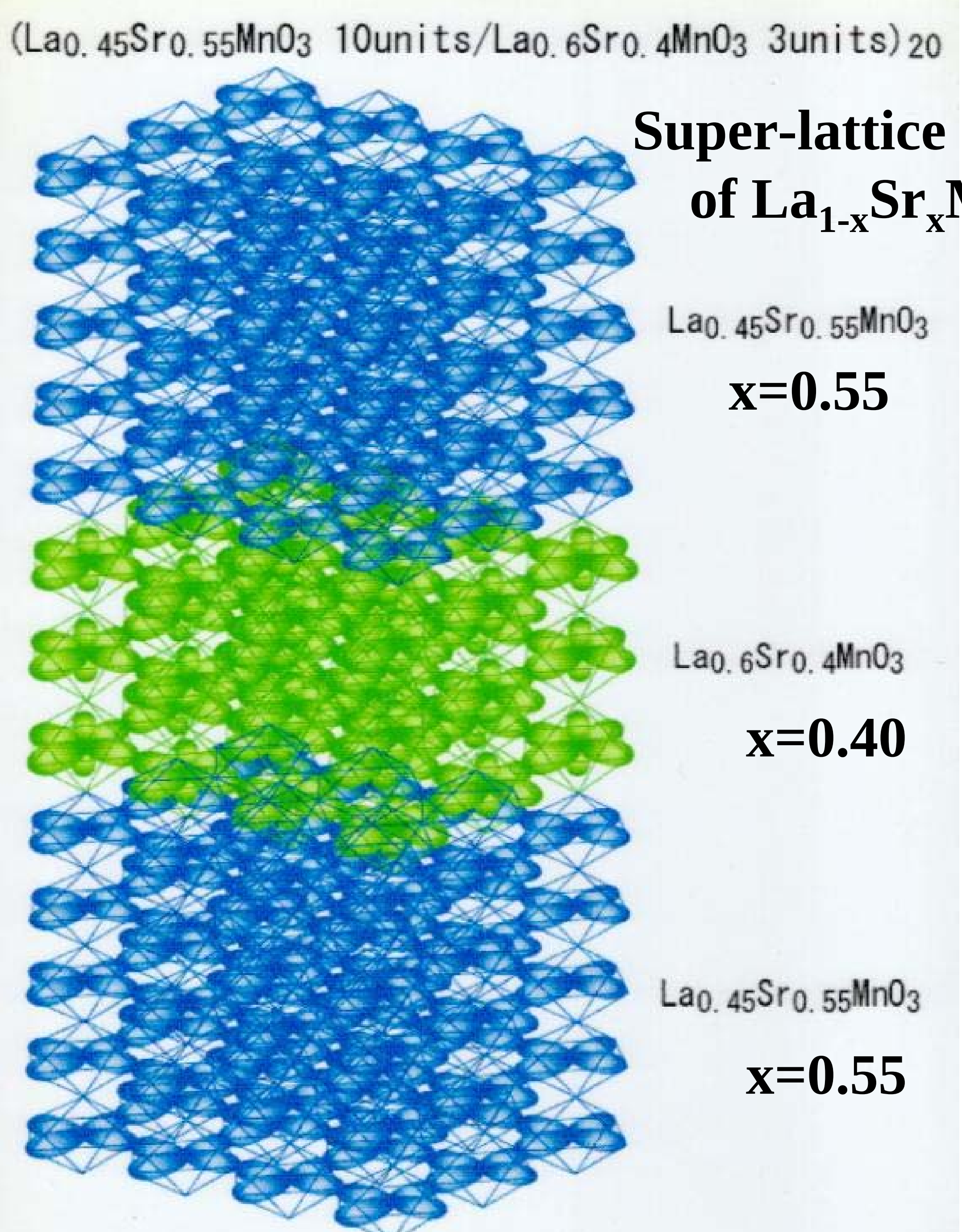
Electric Structure of 4*p* state



Energy Dependence of the Interference Term

H. Ohsumi et al., **JPSJ 72, 1006 (2003).**

Orbital-Super-lattice



Super-lattice Structure of $La_{1-x}Sr_xMnO_3$

x=0.55

x=0.40

x=0.55

T. Kiyama et al., **JPSJ 72, 785 (2003).**

Orbital Ordering Systems Studied by RXS

e_g Electron System

- $La_{0.5}Sr_{1.5}MnO_4$
- $La_{1-x}Sr_{1+x}MnO_4$
- $LaMnO_3$
- $La_{1-x}Sr_xMnO_3$
- $La_{2-2x}Sr_{1+2x}Mn_2O_7$
- $Nd_{1-x}Sr_xMnO_3$
- $Pr_{1-x}Ca_xMnO_3$
- $KCuF_3$
- $KCu_xZn_{1-x}F_3$
- K_2CuF_4

(1*s* → 4*p*)

t_{2g} Electron System

- $YTiO_3$
- $Y_{1-x}Ca_xTiO_3$
- $RTiO_3$
- (R=Gd, Sm, Nd, La)
- YVO_3
- $LaVO_3$
- V_2O_3

(1*s* → 4*p*)

f Electron System

- DyB_2C_2
- HoB_2C_2
- TbB_2C_2
- CeB_6
- $PrFe_4P_{12}$

(2*p* → 5*d*)

- UPd_3, UGa_3
- NpO_2

(3*d* → 5*f*)

This list is rapidly increasing.

We can know the temperature dependence of the orbital state and its correlation length from the width of the resonant x-ray reflections

Orbital Ordering near the Mott Transition in t_{2g} Electron Systems

Manganites

Orbital Ordered State
Antiferro-Insulator

Low Hole Doping

CMR

Orbital Liquid State
Ferro-Metal

$YTiO_3$
$Ti^{3+}(3d^1)$

$CaTiO_3$
$Ti^{4+}(3d^0)$

0 — *1* — *x*

Hole doping

Orbital Ordering ?

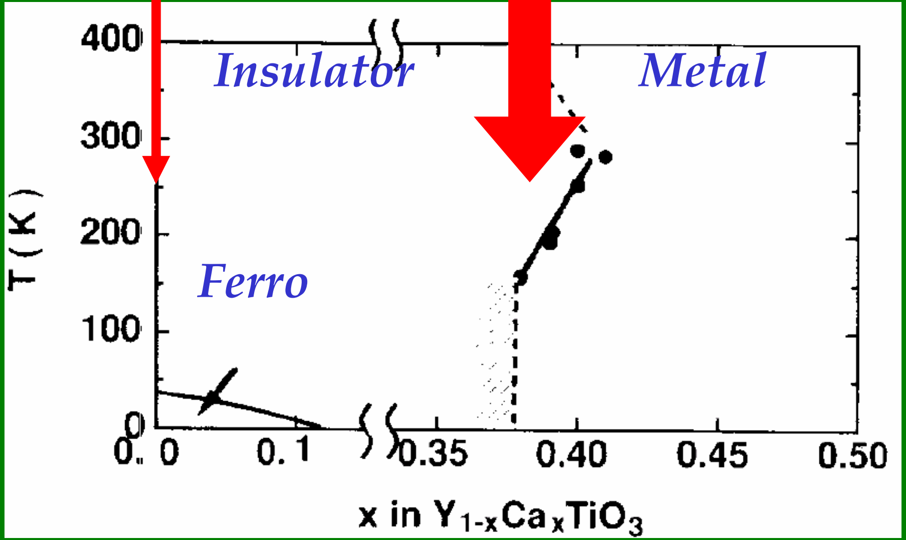
$Y_{1-x}Ca_xTiO_3$

Questions

1. **Why does the ferromagnetic state become unstable in the insulative phase with the hole doping?**

2. **Why is the system still insulator in the high hole doped region?**

→ **Orbital states**

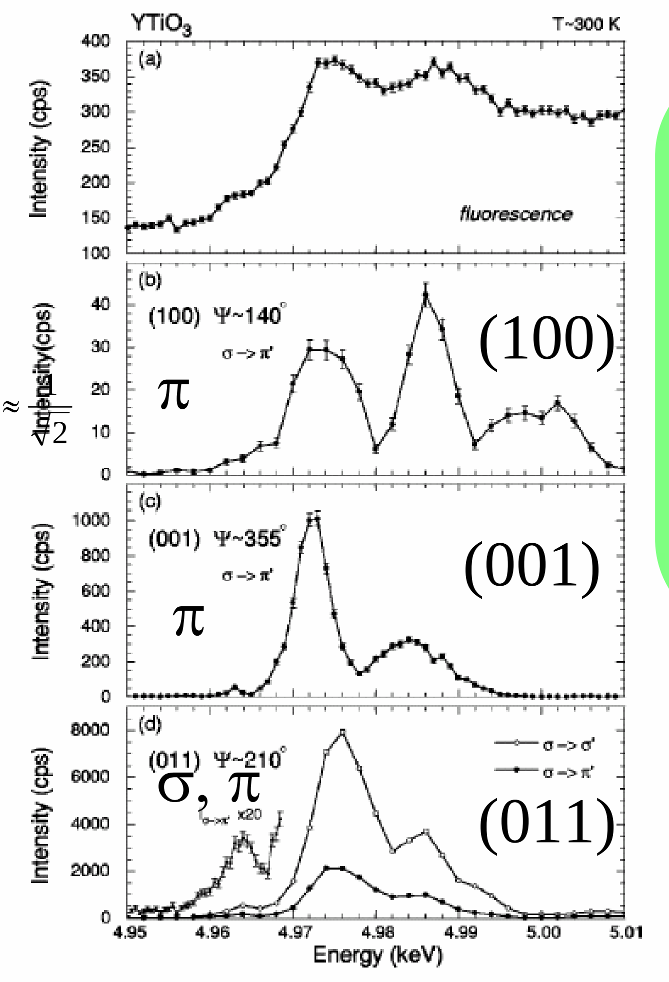


F. Iga et al., Physica B 223&224 (1996) 526.

Orbital State of YTiO3

Azimuthal angle dependence

Energy Dependence of (100), (001), (011)



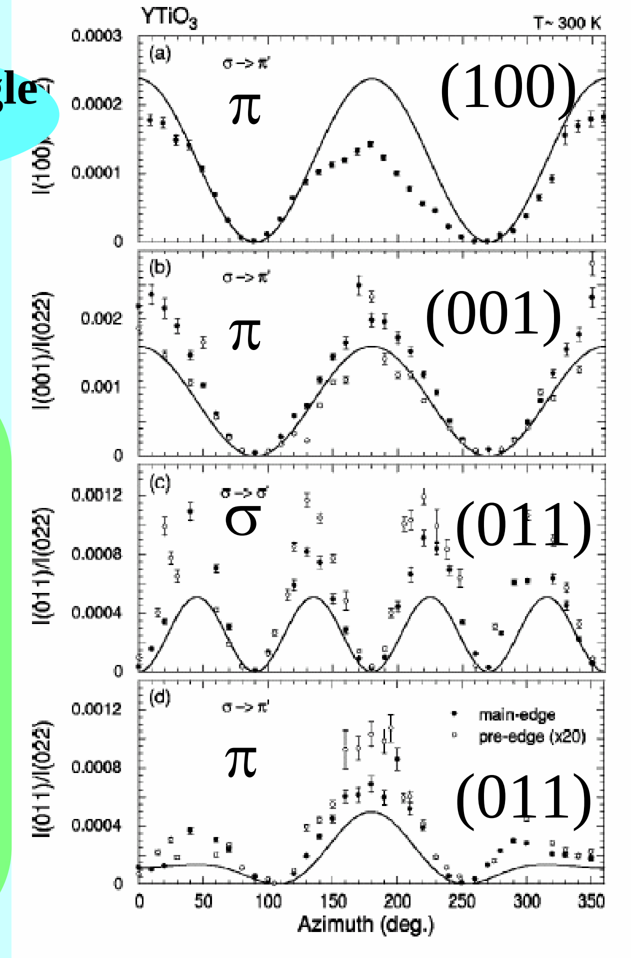
Site1: $c_1 d_{zx} - c_2 d_{xy}$

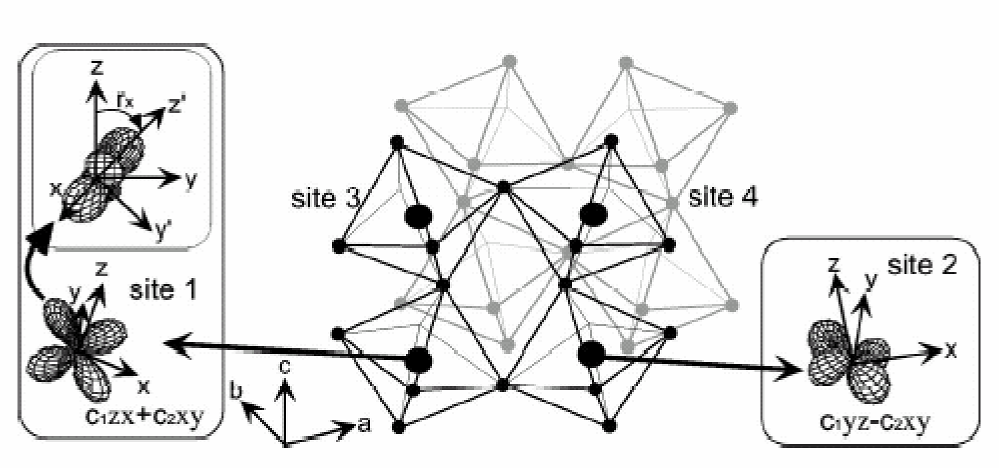
Site2: $c_1 d_{yz} + c_2 d_{xy}$

Site3: $c_1 d_{zx} + c_2 d_{xy}$

Site4: $c_1 d_{yz} - c_2 d_{xy}$

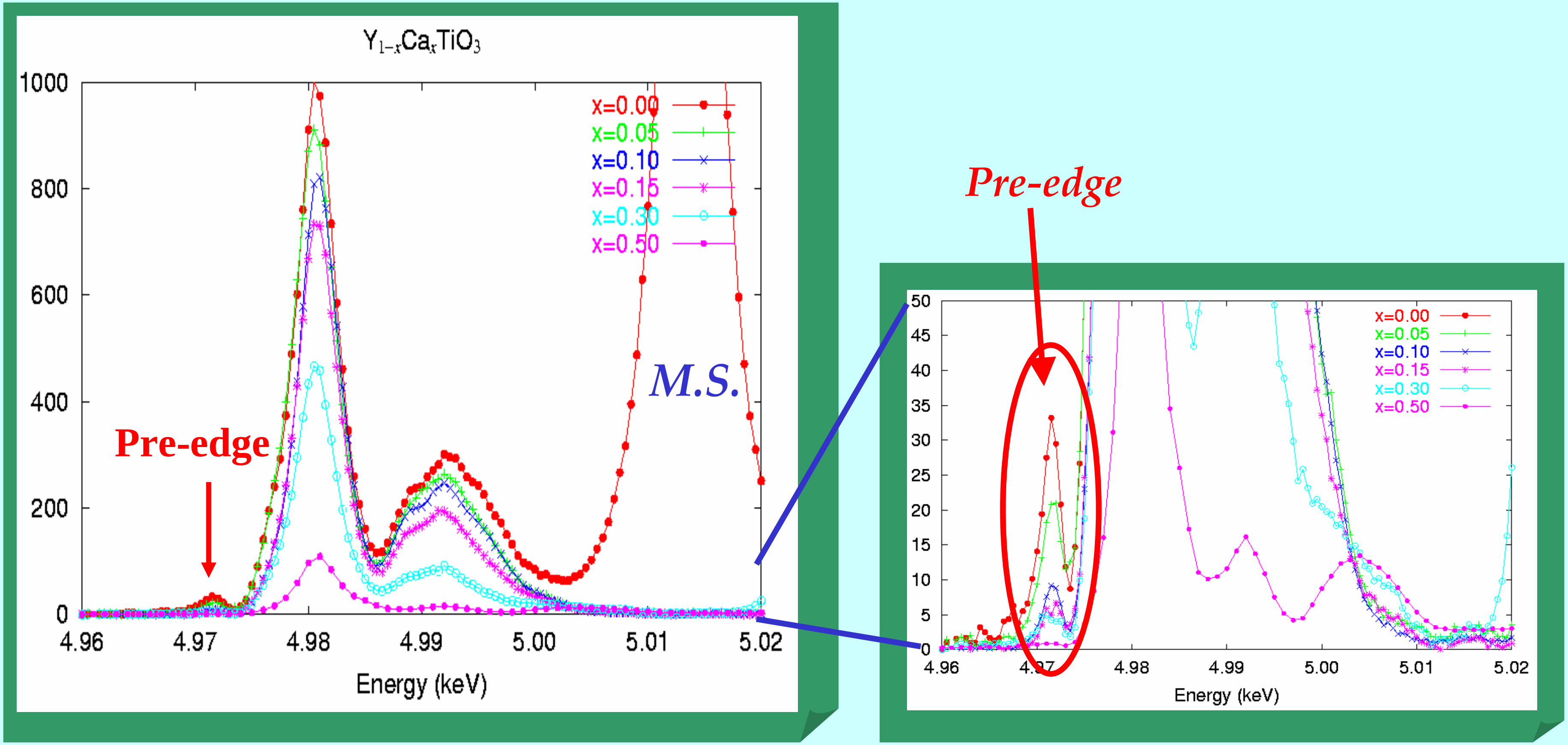
$$c_1 = c_2 \approx \frac{1}{\sqrt{2}}$$



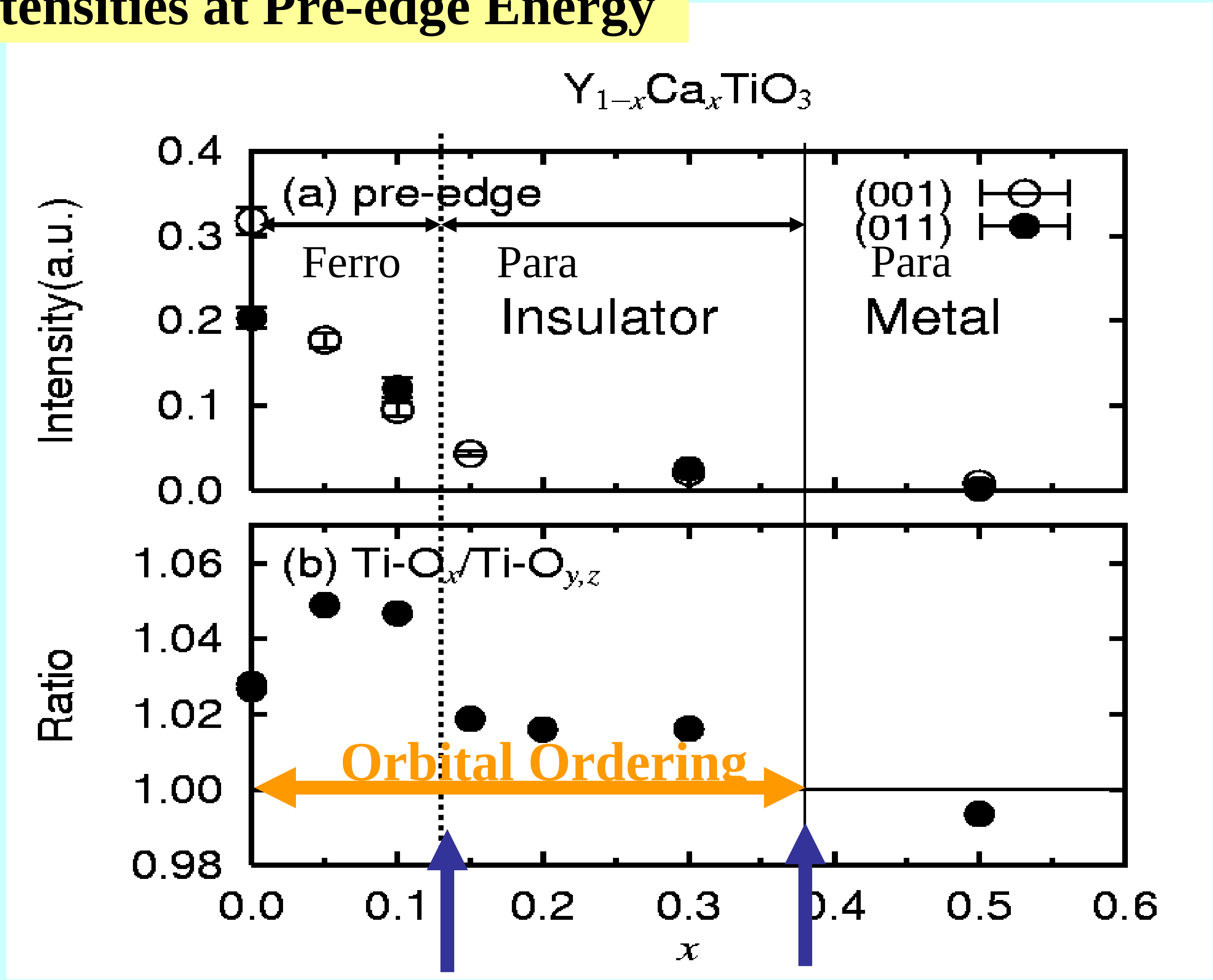


H. Nakao, PRB 66, 184419 (2002).

Energy Dependence of (001) Signals



Concentration *x* Dependence of RXS Intensities at Pre-edge Energy



Magnetic Transition Mott Transition

Resonant Inelastic X-ray Scattering (RIXS)

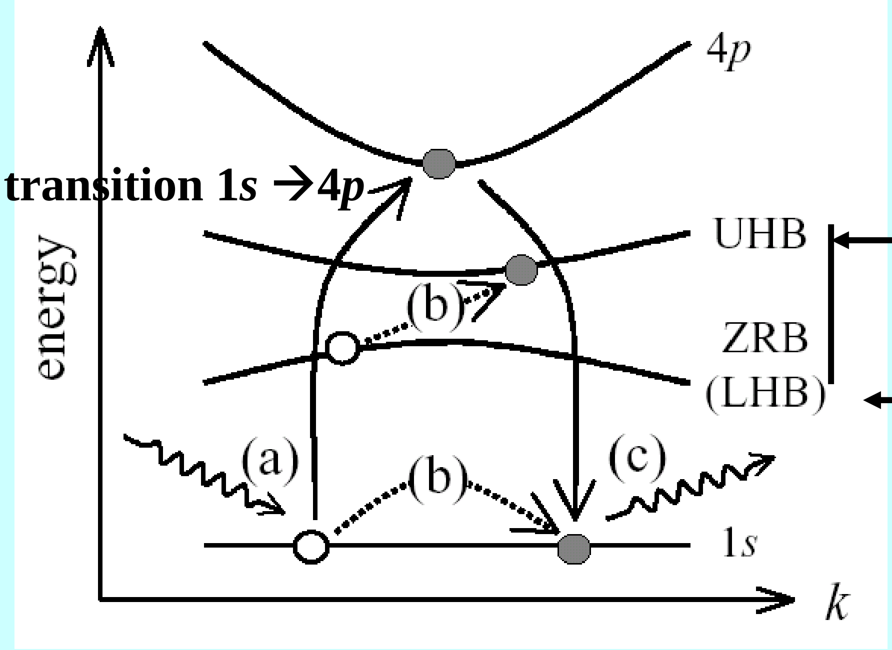
The RIXS is a powerful technique to obtain information on the momentum dependence of the elementary excitations.

Transition metal Oxides like manganites and cuprates

Ex. Charge Transfer excitation between the transition metal and oxygen

***d-d* excitation on the transition metal site**

Dipole transition 1*s* → 4*p*



RIXS Experiments

Angle-Resolved Photoemission Spectroscopy Experiments

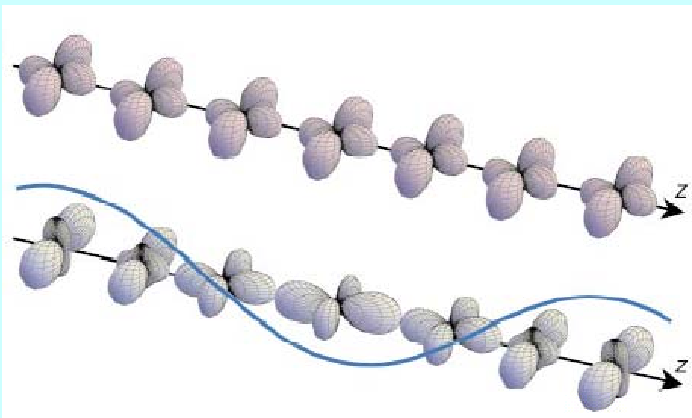
K. Tsutsui, T. Tohyama, and S. Maekawa, PRL 83, 3705 (1999).

Schematic view of RIXS process in the case of the cuprate

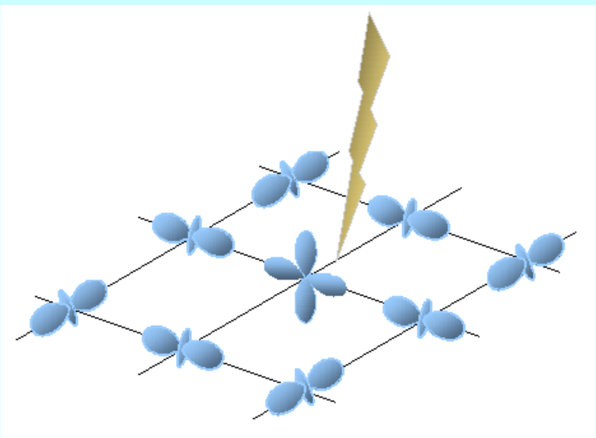
Observation of Orbital Excitations

Collective Orbital Excitation

Individual Orbital Excitation



E. Saitoh, Nature 410, 180 (2001)



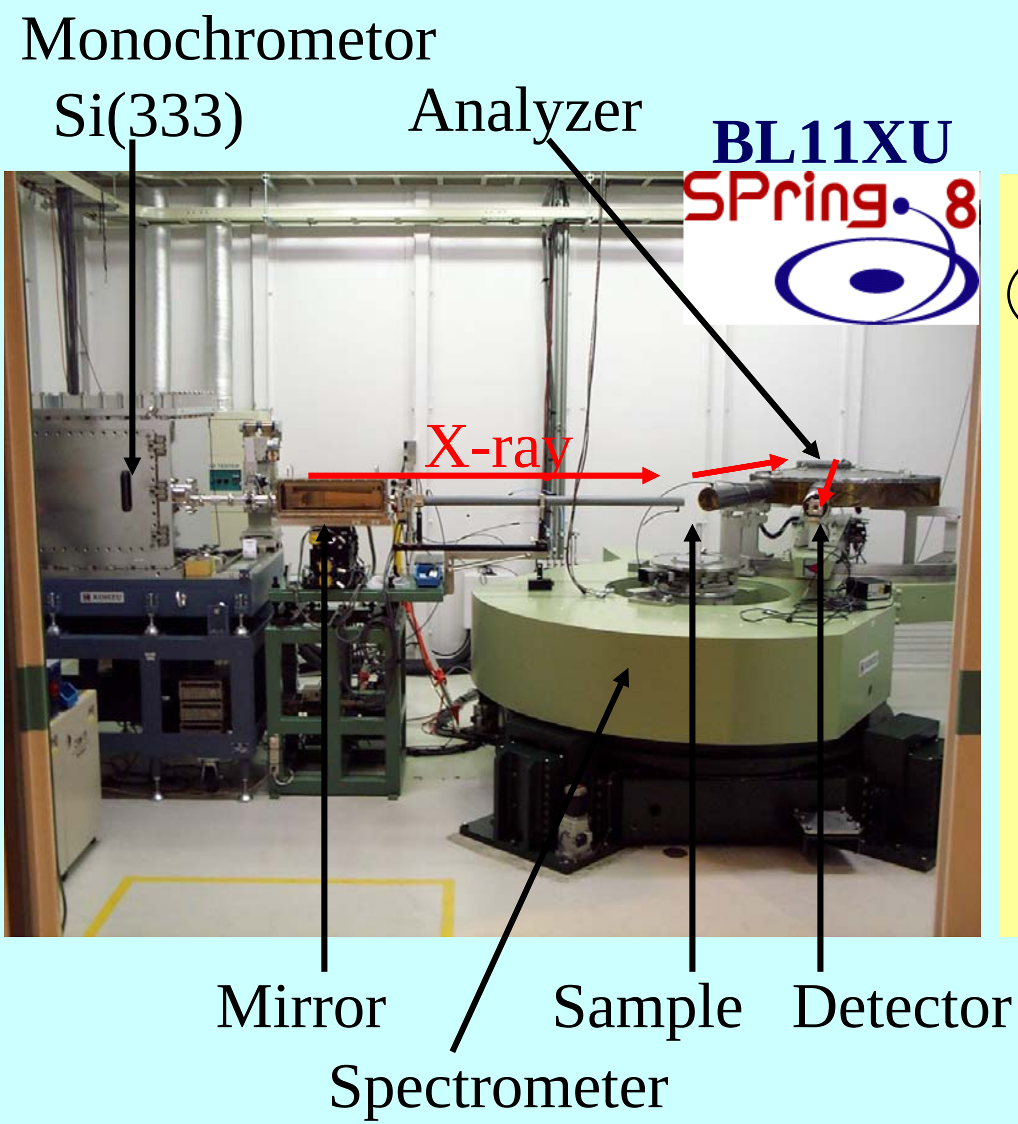
by S. Ishihara & S. Maekawa

Orbital Wave
cf. Spin Wave

Particle-hole Excitation
cf. Stoner Excitation

in magnetically ordered systems

Resonant Inelastic X-ray Scattering (RIXS)



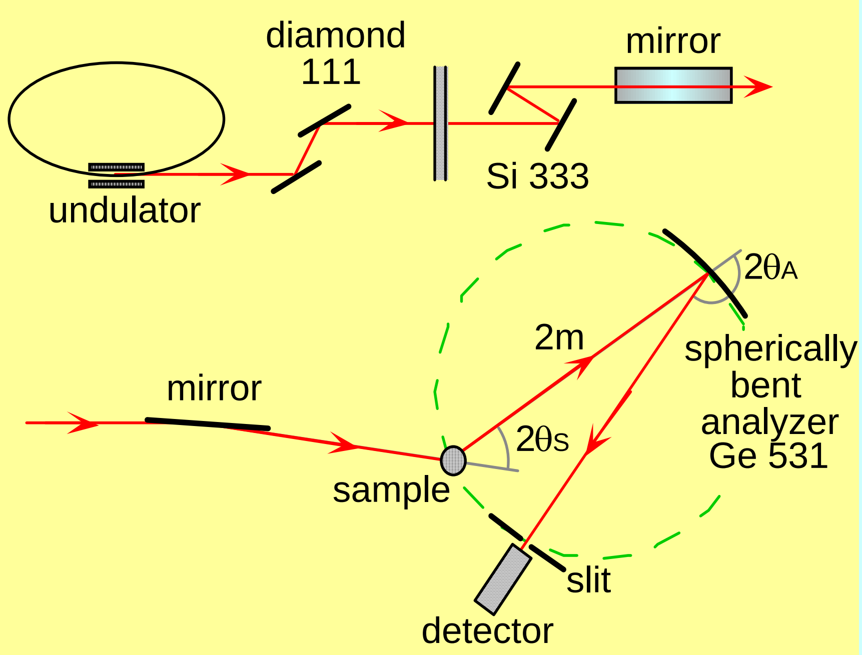
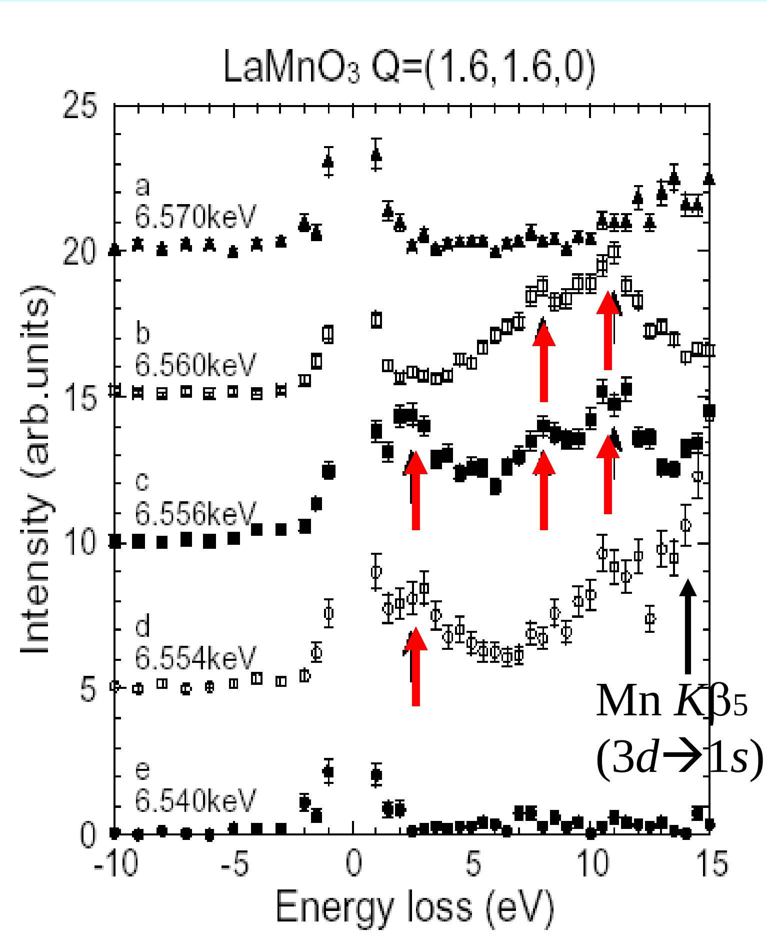


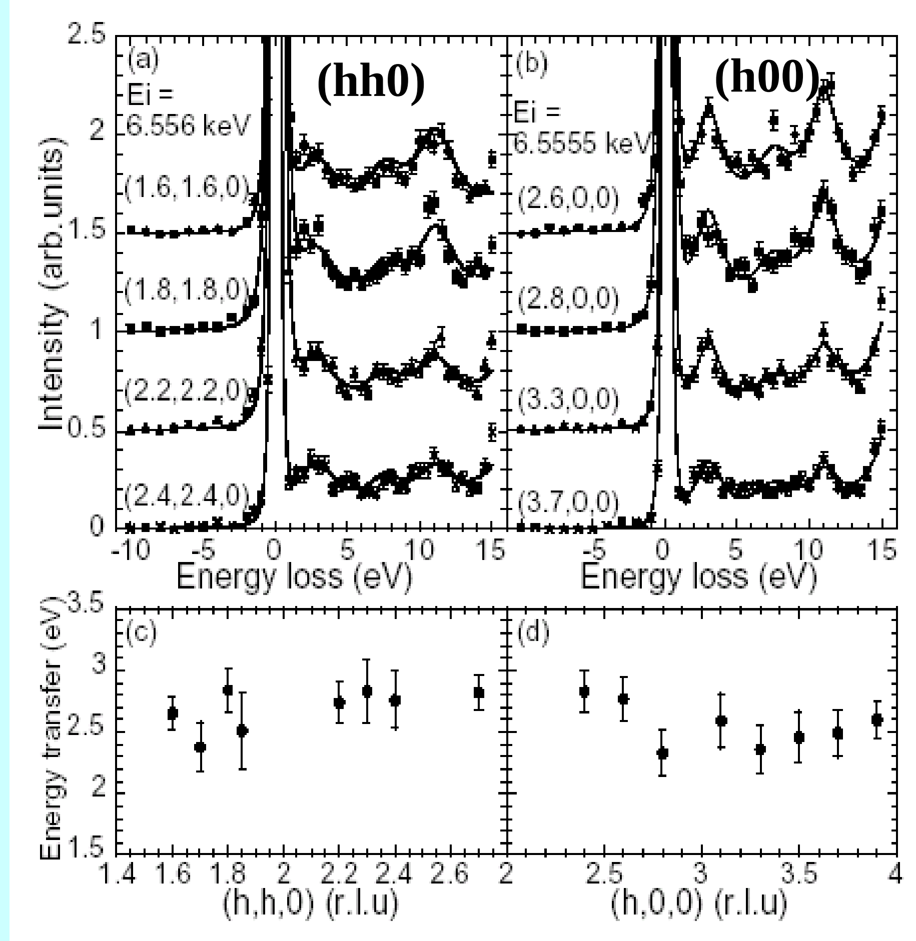
Fig.1 Schematic layout of the spectrometer. Side view to the mirror (above) and top view after the mirror (below).

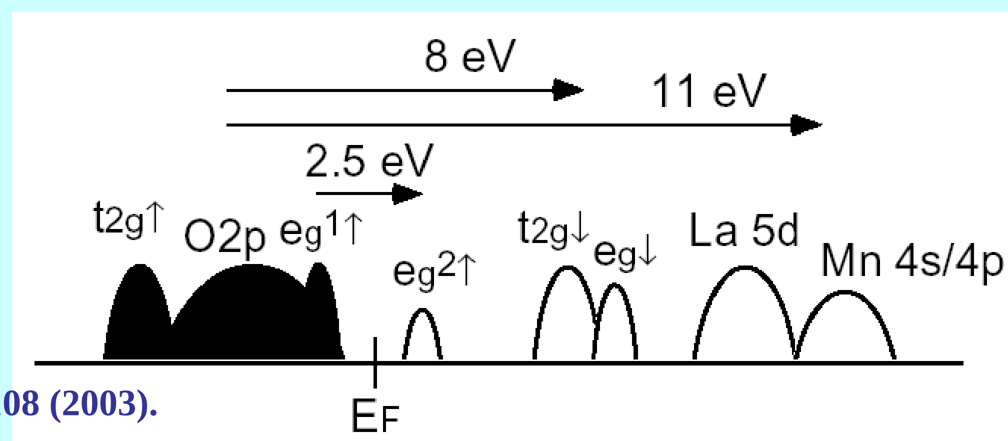
Normal Resolution: 500 meV

High Resolution : 130 meV FWHM

Electronic Excitations in $LaMnO_3$ Observed by RIXS

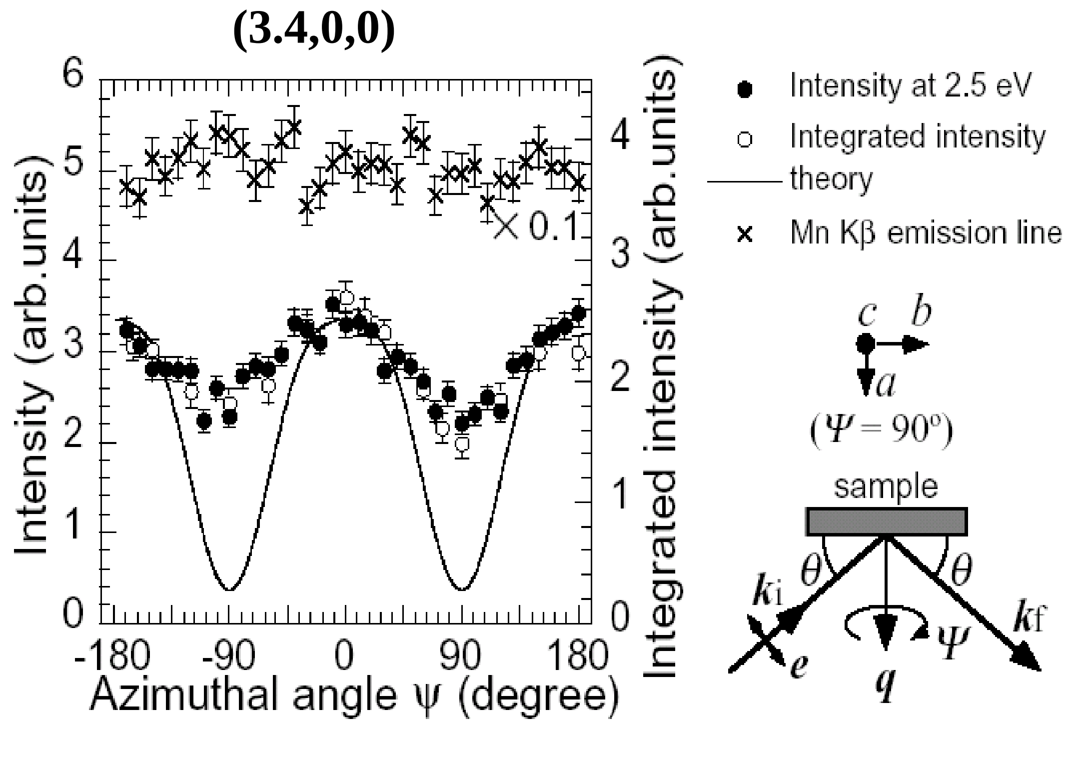


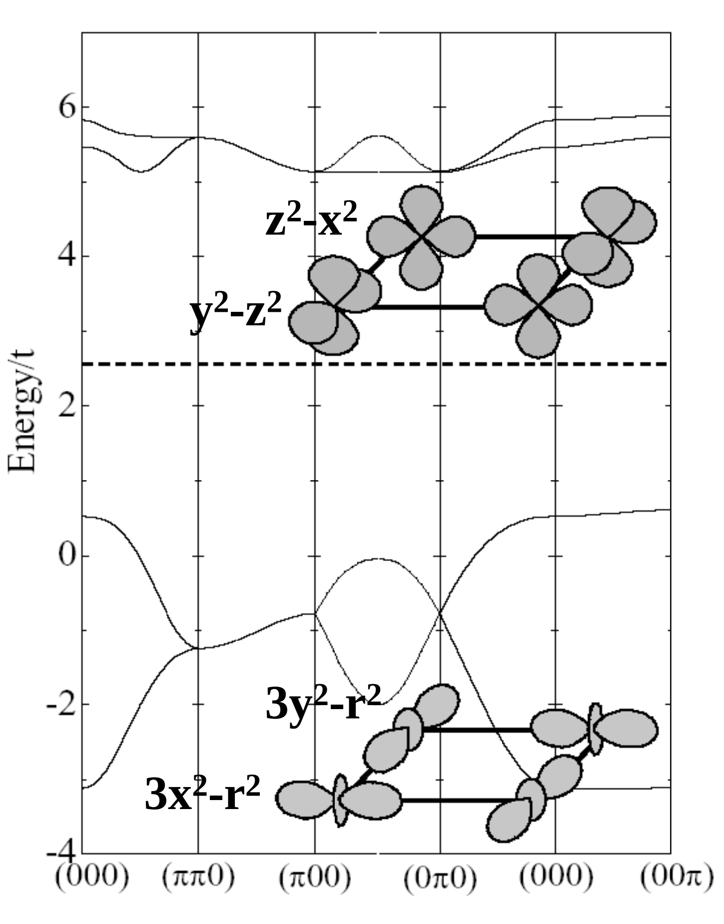




T. Inami, S. Ishihara et. al., Phys. Rev. B 67, 045108 (2003).

Azimuthal angle dependence of the Orbital Excitation and the electronic band structure for $LaMnO_3$





T. Inami, S. Ishihara et. al., Phys. Rev. B 67, 045108 (2003).

Summary

We have developed resonant RXS (RIXS) Technique to observe the orbital ordering and its excitations.

Short Range Order
Quadrupole Order
Ferro-Orbital Order

The magnetism is controlled by the orbital ordering, which make the system insulative in the titanates.

$Y_{1-x}Ca_xTiO_3$
$RTiO_3$

We have observed the individual orbital excitation from $d_{3x^2-r^2}/d_{3y^2-r^2}$ to $d_{y^2-z^2}/d_{z^2-x^2}$.

$LaMnO_3$
$La_{1-x}Sr_xMnO_3$