Spectral analysis of resonant x-ray scattering from the multipolar ordering phase

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Outline

1. Introduce a simple formula of the resonant x-ray scattering (RXS) amplitude

   Advantage : energy profile

2. Applications

   $Ce_{0.7}La_{0.3}B_6$ (phase IV), CeB_6(phase II)

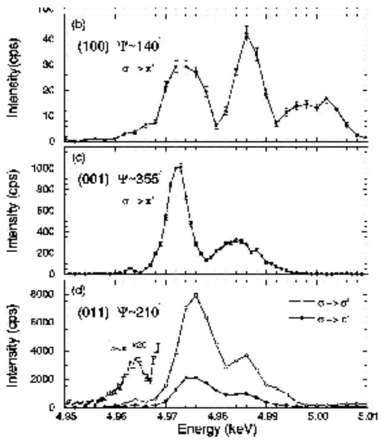
   (NpO_2,$U_{1-x}Np_xO_2$:triple-**k** multipole order)

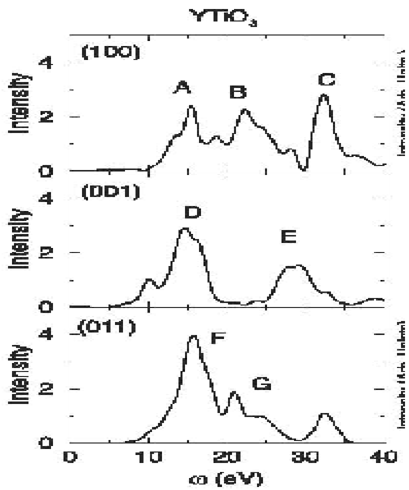
   Importance of the spectral shape analysis

   in the f electron systems

Spectral shape analysis

3d system





Ti K-edge in YTiO3
Exp.: H. Nakao et al. (PRB '02)
M. Takahashi & J. Igarashi(PRB '02)

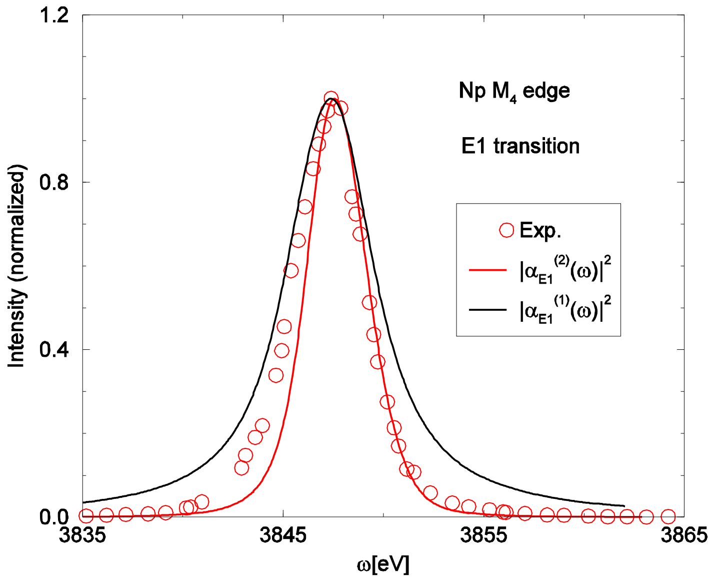
Mn K-edge in $LaMnO_3$

Exp. : Y. Murakami et al. (PRL '98)

Cluster calc.: S. Ishihara & S.Maekawa (PRB '98)

Band structure calc.:
M. Takahashi, J. Igarashi & P. Fulde (JPSJ '99)

f system

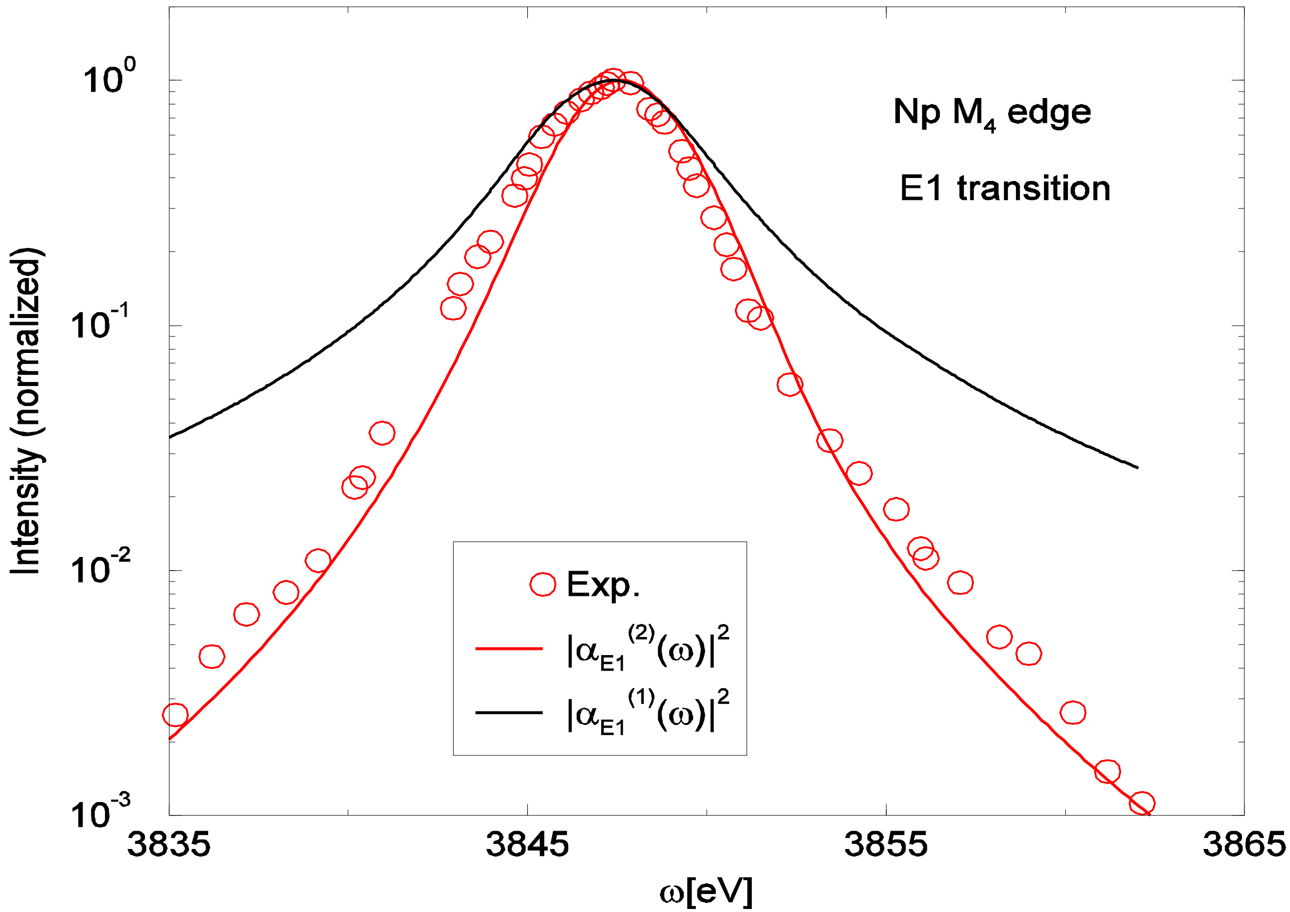


Np M4-edge (NpO_2 , E1)

Exp. : J.A.Paixao et al. (PRL '02)

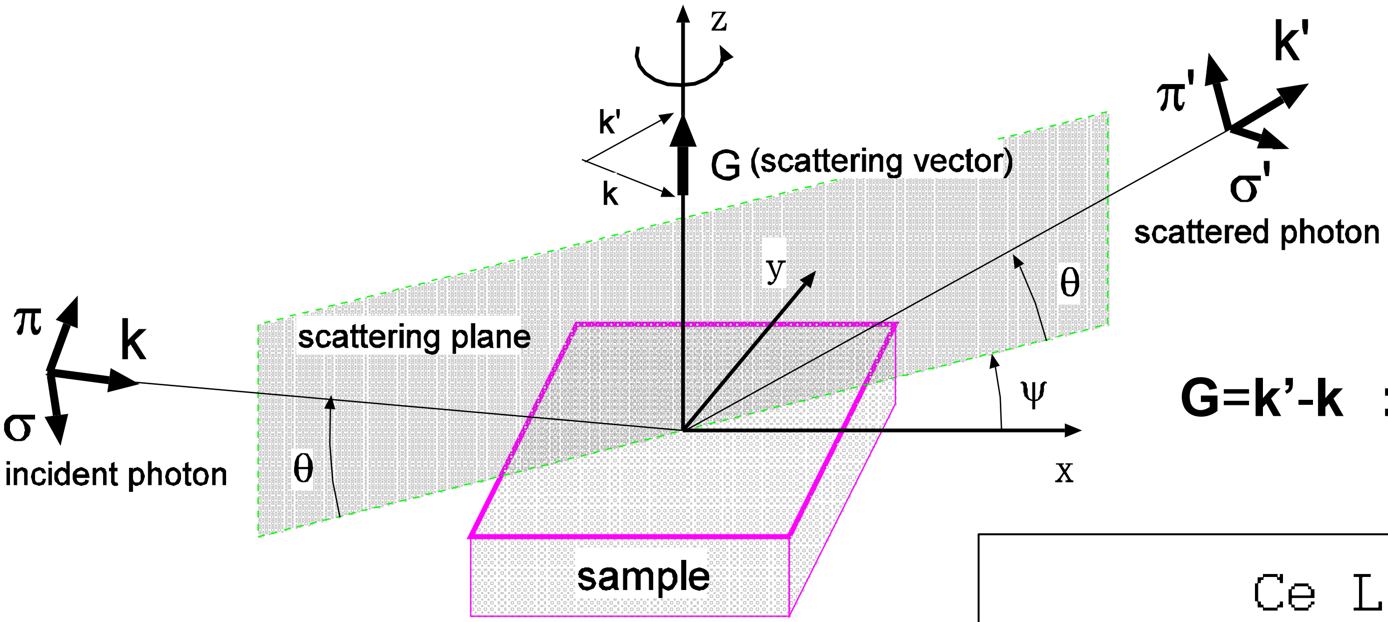
Theory :T. Nagao & J. Igarashi (PRB '05)

Simple form & single-peak



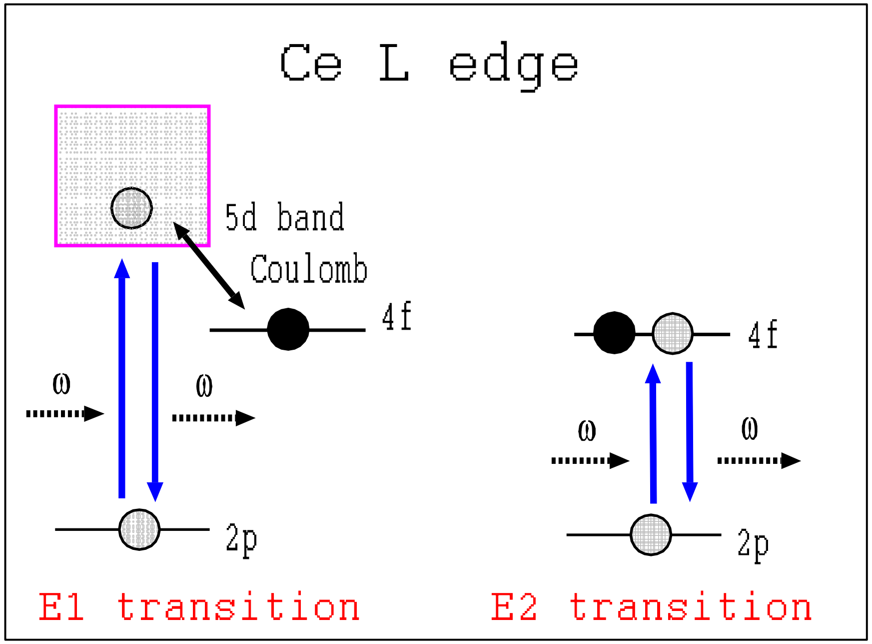
Data : Courtesy of Prof. G. H. Lander & Dr. Mannix (unpublished, ’00)

Resonant x-ray scattering (RXS)



G=k'-k :scattering vector

2nd order optical process



How to get direct information about f level

- Photon wavelength : a few Å→ a few 10^3eV

	E1	E2
Rare earth		
L_2,L_3	2p↔5d	2p↔4f
Actinides		
M_2,M_3	3p↔6d	3p↔5f
M_4,M_5	3d↔5f	3d↔6g

E1 (dipole) transition: up to rank two (quadrupole)
E2 (quadrupole) transition : up to rank four (hexadecapole)

RXS amplitude formula

- Electric dipole (E1) transition

$$\sum_{\mu,\mu'} \varepsilon_\mu \varepsilon_{\mu'} \sum_\Lambda \frac{\langle 0|x_\mu|\Lambda\rangle\langle\Lambda|x_{\mu'}|0\rangle}{\hbar\omega - (E_\Lambda - E_0) + i\Gamma}$$

$$x_\mu = \begin{cases} x, & \mu = 1 \\ y, & \mu = 2 \\ z, & \mu = 3 \end{cases}$$

- Electric quadrupole (E2) transition

$$\frac{k^2}{9} \sum_{\mu,\mu'} q_\mu(\hat{\mathbf{k}}', \boldsymbol{\varepsilon}') q_{\mu'}(\hat{\mathbf{k}}, \boldsymbol{\varepsilon}) \sum_\Lambda \frac{\langle 0|\tilde{z}_\mu|\Lambda\rangle\langle\Lambda|\tilde{z}_{\mu'}|0\rangle}{\hbar\omega - (E_\Lambda - E_0) + i\Gamma}$$

$$\tilde{z}_\mu = \begin{cases} \frac{\sqrt{3}}{2}(x^2 - y^2), & \mu = 1 \\ \frac{1}{2}(3z^2 - r^2), & \mu = 2 \\ \sqrt{3}yz, & \mu = 3 \\ \sqrt{3}zx, & \mu = 4 \\ \sqrt{3}xy, & \mu = 5 \end{cases} \qquad q_\mu(\mathbf{A}, \mathbf{B}) = \begin{cases} \frac{\sqrt{3}}{2}(A_x B_x - A_y B_y), & \mu = 1 \\ \frac{1}{2}(3A_z B_z - \mathbf{A}\cdot\mathbf{B}), & \mu = 2 \\ \frac{\sqrt{3}}{2}(A_y B_z + A_z B_y), & \mu = 3 \\ \frac{\sqrt{3}}{2}(A_z B_x + A_x B_z), & \mu = 4 \\ \frac{\sqrt{3}}{2}(A_x B_y + A_y B_x), & \mu = 5 \end{cases}$$

ε_μ : **photon polarization**

Γ : **core hole lifetime width broadening**

Previous theories

J.P.Hannon et al.(PRL ’88)
J.Luo et al. (PRL ’93)
P.Carra & B.T.Thole (RMP ’94)
J.P.Hill & D.F.McMorrow (Acta Cryst. ’96)
S.W.Lovesey & E.Balcar (JPCM ’96)

Fast collision approximation

$$\sum_{\Lambda} \frac{\langle 0|x_{\mu}|\Lambda\rangle\langle\Lambda|x_{\mu'}|0\rangle}{\hbar\omega-(E_{\Lambda}-E_{0})+i\Gamma}$$

$$\Downarrow$$

$$\frac{\sum_{\Lambda} \langle 0|x_{\mu}|\Lambda\rangle\langle\Lambda|x_{\mu'}|0\rangle}{\hbar\omega-(\Delta-E_{0})+i\Gamma}$$

Give up the energy profile!

Spherical symmetric intermediate State Hamiltonian

Justified in the localized f electron systems
(weak CEF & inter-site interactions)

X

Our treatment

T. Nagao & J. Igarashi (PRB ’05) : E1
T. Nagao & J. Igarashi (cond-mat/0605288) : E2

Fast collision approx. is not necessary !

Results

- E1 $$\sum_{\nu=0}^{2} \alpha_{E1}^{(\nu)}(\omega) \sum_{\mu=1}^{2\nu+1} \langle 0 | z_{\mu}^{(\nu)} | 0 \rangle P_{\mu}^{(\nu),E1}(\boldsymbol{\varepsilon}', \boldsymbol{\varepsilon})$$

Energy profile

Expectation value of multipole op.

Geometrical factor

- E2 $$\sum_{\nu=0}^{4} \alpha_{E2}^{(\nu)}(\omega) \sum_{\mu=1}^{2\nu+1} \langle 0 | z_{\mu}^{(\nu)} | 0 \rangle P_{\mu}^{(\nu),E2}(\boldsymbol{\varepsilon}', \mathbf{k}'; \boldsymbol{\varepsilon}, \mathbf{k})$$

- exact **energy dependence**
- summarized the components of the multipolar operator in the **Cartesian basis**

For instance, v=2

$$\alpha^{(2)}_{E1}(\omega) = \tfrac{4}{3}\left[-F^{(E1)}_{J-1}(\omega) - F^{(E1)}_{J}(\omega) - F^{(E1)}_{J+1}(\omega)\right]$$

$$\begin{aligned}\alpha^{(2)}_{E2}(\omega) = {} & 2\sqrt{\tfrac{2}{7}}\Big[4(2J-3)(J-1)F^{(E2)}_{J-2}(\omega) \\ & + (J-5)(J-1)F^{(E2)}_{J-1}(\omega) \\ & - \tfrac{1}{3}(2J-3)(2J+5)F^{(E2)}_{J}(\omega) \\ & + (J+2)(J+6)F^{(E2)}_{J+1}(\omega) \\ & + 4(2J+5)(J+2)F^{(E2)}_{J+2}(\omega)\Big]\end{aligned}$$

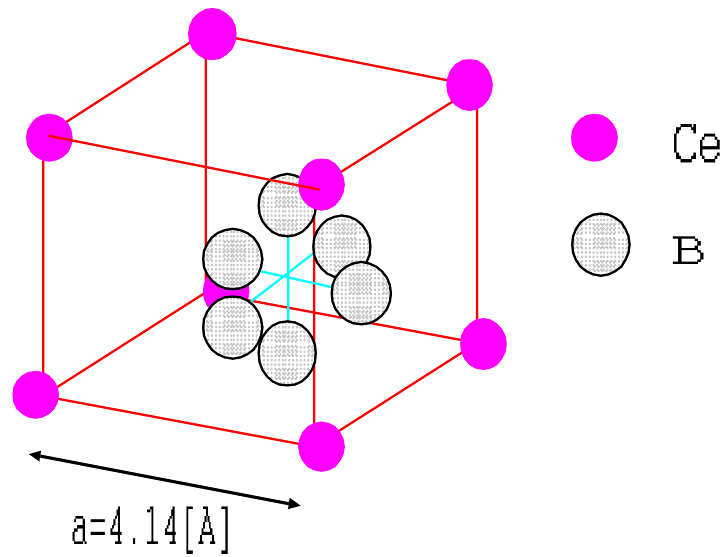
$$\begin{aligned}F^{(En)}_{J'}(\omega) = {} & {}_{n}C_{n+|J-J'|}\sqrt{(2J+1)(2J'+1)}\,\frac{(J+J'-n)!}{(J+J'+1+n)!} \\ & \times |(J\|V_n\|J)|^2 \sum_{i=1}^{N_{J'}} \frac{1}{\hbar\omega - (E_{J',i}-E_0) + i\Gamma}\end{aligned}$$

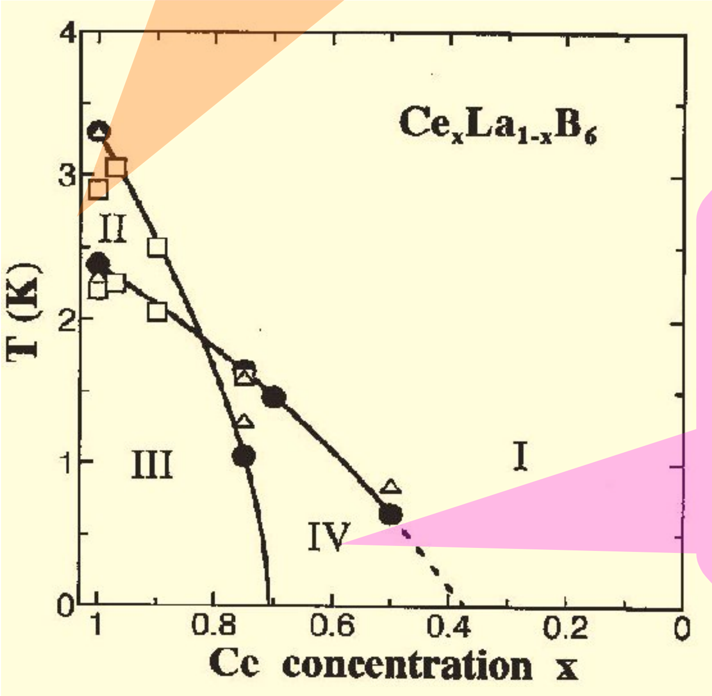
$$P^{(2),E1}_{\mu}(\boldsymbol{\varepsilon}',\boldsymbol{\varepsilon}) = q_{\mu}(\boldsymbol{\varepsilon}',\boldsymbol{\varepsilon})$$

$$\begin{aligned}P^{(2),E2}_{\mu}(\boldsymbol{\varepsilon}',\mathbf{k}';\boldsymbol{\varepsilon},\mathbf{k}) = {} & -\frac{3}{2\sqrt{14}}\Big[(\boldsymbol{\varepsilon}'\cdot\boldsymbol{\varepsilon})q_{\mu}(\hat{\mathbf{k}}',\hat{\mathbf{k}}) + (\hat{\mathbf{k}}'\cdot\hat{\mathbf{k}})q_{\mu}(\boldsymbol{\varepsilon}'\cdot\boldsymbol{\varepsilon}) \\ & + q_{\mu}(\hat{\mathbf{k}}'\times\hat{\mathbf{k}},\boldsymbol{\varepsilon}'\times\boldsymbol{\varepsilon})\Big]\end{aligned}$$

CeB_6 (phase II) and $Ce_{1-x}La_xB_6$ (phase IV)

CeB_6 : phase II
Antiferroquadrupole(AFQ) phase
RXS: H. Nakao et al.(JPSJ '01)
F. Yakhou et al.(PLA '01)



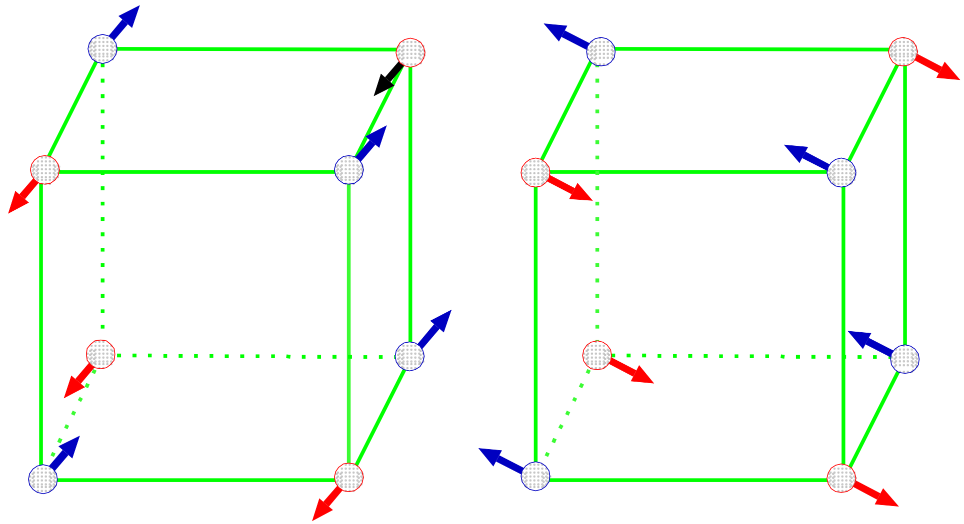


$Ce_{1-x}La_xB_6$: phase IV

- No magnetic moment
- Breaking time-reversal symmetry
- Lattice distortion // (111)

Antiferrooctupole (AFO) phase ?
K.Kubo & Y.Kuramoto(JPSJ '03,'04)

Ordering pattern ($Ce_{1-x}La_xB_6$ in phase IV)



T_{111} $\qquad$ $T_{\bar{1}\bar{1}1}$

$$\mathbf{Q} = \left(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\right)$$

$$\left(\langle T_x^\beta \rangle, \langle T_y^\beta \rangle, \langle T_z^\beta \rangle\right) // p$$

$$T_p^\beta = \begin{cases} \frac{1}{\sqrt{3}}(T_x^\beta + T_y^\beta + T_z^\beta), & p = 111 \\ \frac{1}{\sqrt{3}}(T_x^\beta - T_y^\beta - T_z^\beta), & p = 1\bar{1}\bar{1} \\ \frac{1}{\sqrt{3}}(-T_x^\beta + T_y^\beta - T_z^\beta), & p = \bar{1}1\bar{1} \\ \frac{1}{\sqrt{3}}(-T_x^\beta - T_y^\beta + T_z^\beta), & p = \bar{1}\bar{1}1 \end{cases}$$

$$T_x^\beta = \frac{\sqrt{6}}{15}\overline{J_x(J_y^2 - J_z^2)}$$

$$T_y^\beta = \frac{\sqrt{6}}{15}\overline{J_y(J_z^2 - J_x^2)}$$

$$T_z^\beta = \frac{\sqrt{6}}{15}\overline{J_z(J_x^2 - J_y^2)}$$

Dipole operators J_p Quadrupole operators O_p

$$\mathbf{J}_{111} = \frac{1}{\sqrt{3}}(\mathbf{J}_x + \mathbf{J}_y + \mathbf{J}_z)$$
$$\mathbf{J}_{1\bar{1}\bar{1}} = \frac{1}{\sqrt{3}}(\mathbf{J}_x - \mathbf{J}_y - \mathbf{J}_z)$$
$$\mathbf{J}_{\bar{1}1\bar{1}} = \frac{1}{\sqrt{3}}(-\mathbf{J}_x + \mathbf{J}_y - \mathbf{J}_z)$$
$$\mathbf{J}_{\bar{1}\bar{1}1} = \frac{1}{\sqrt{3}}(-\mathbf{J}_x - \mathbf{J}_y + \mathbf{J}_z)$$

$$\mathbf{O}_{111} = \frac{1}{\sqrt{3}}(\mathbf{O}_{yz} + \mathbf{O}_{zx} + \mathbf{O}_{xy})$$
$$\mathbf{O}_{1\bar{1}\bar{1}} = \frac{1}{\sqrt{3}}(\mathbf{O}_{yz} - \mathbf{O}_{zx} - \mathbf{O}_{xy})$$
$$\mathbf{O}_{\bar{1}1\bar{1}} = \frac{1}{\sqrt{3}}(-\mathbf{O}_{yz} + \mathbf{O}_{zx} - \mathbf{O}_{xy})$$
$$\mathbf{O}_{\bar{1}\bar{1}1} = \frac{1}{\sqrt{3}}(-\mathbf{O}_{yz} - \mathbf{O}_{zx} + \mathbf{O}_{xy})$$

$$\mathbf{O}_{yz} = \frac{\sqrt{3}}{2}(\mathbf{J}_y\mathbf{J}_z + \mathbf{J}_z\mathbf{J}_y)$$
$$\mathbf{O}_{zx} = \frac{\sqrt{3}}{2}(\mathbf{J}_z\mathbf{J}_x + \mathbf{J}_x\mathbf{J}_z)$$
$$\mathbf{O}_{xy} = \frac{\sqrt{3}}{2}(\mathbf{J}_x\mathbf{J}_y + \mathbf{J}_y\mathbf{J}_x)$$

ground quartet Γ_8 (J=5/2:Ce^{3+} f^1 config.)

$$|+,\uparrow\rangle = \sqrt{\tfrac{5}{6}}\,|+\tfrac{5}{2}\rangle + \sqrt{\tfrac{1}{6}}\,|-\tfrac{3}{2}\rangle$$

$$|+,\downarrow\rangle = \sqrt{\tfrac{5}{6}}\,|-\tfrac{5}{2}\rangle + \sqrt{\tfrac{1}{6}}\,|+\tfrac{3}{2}\rangle$$

$$|-,\uparrow\rangle = |+\tfrac{1}{2}\rangle$$

$$|-,\downarrow\rangle = |-\tfrac{1}{2}\rangle$$

$$T_p^{\beta} = \begin{pmatrix} -\sqrt{90} & 0 & 0 & 0 \\ 0 & \sqrt{90} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix},$$

$$J_p = \begin{pmatrix} 0 & \frac{1+11\sqrt{2}i}{6\sqrt{3}} & 0 & 0 \\ \frac{1-11\sqrt{2}i}{6\sqrt{3}} & 0 & 0 & 0 \\ 0 & 0 & -\frac{7}{6} & 0 \\ 0 & 0 & 0 & \frac{7}{6} \end{pmatrix},$$

$$O_p = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} (\propto H_p^{\beta})$$

$$\sum_{\nu=0}^{4} \alpha_{E2}^{(\nu)}(\omega) \sum_{\mu=1}^{2\nu+1} \langle 0|z_{\mu}^{(\nu)}|0\rangle P_{\mu}^{(\nu),E2}(\varepsilon',k';\varepsilon,k)$$

pure $\alpha_{E2}^{(3)}(\omega)$

Single-**k** AF type order

primary	secondary	profiles	Materials
$\mathbf{J}_{x,y,z}$	$\mathbf{T}^{\alpha}_{x,y,z}$	$\alpha^{(1,3)}_{E2}(\omega)$	
$\mathbf{O}_{yz,zx,xy}$	$\mathbf{H}^{\beta}_{x,y,z}$	$\alpha^{(2,4)}_{E2}(\omega)$	$\mathbf{CeB_6}$, **phaseII**
$\mathbf{T}^{\beta}_{p}$	-	$\alpha^{(3)}_{E2}(\omega)$	$\mathbf{Ce_{0.7}La_{0.3}B_6}$, **phaseIV**

Triple-**k** AF type order

primary	secondary	profiles	Materials
$\mathbf{J}_{p}$	$\mathbf{T}^{\alpha}_{p}, \mathbf{O}_{p} (\mathbf{H}^{\beta}_{p})$	$\alpha^{(1,2,3,4)}_{E2}(\omega)$	$\mathbf{UO_2}$, $\mathbf{U_{0.75}Np_{0.25}O_2}$
$\mathbf{O}_{p}$	$\mathbf{H}^{\beta}_{p}$	$\alpha^{(2,4)}_{E2}(\omega)$	
$\mathbf{T}^{\beta}_{p}$	$\mathbf{O}_{p} (\mathbf{H}^{\beta}_{p})$	$\alpha^{(2,3,4)}_{E2}(\omega)$	$\mathbf{NpO_2}$

RXS experiment

(phase IV in $Ce_{0.7}La_{0.3}B_6$)

Ce L_2 edge

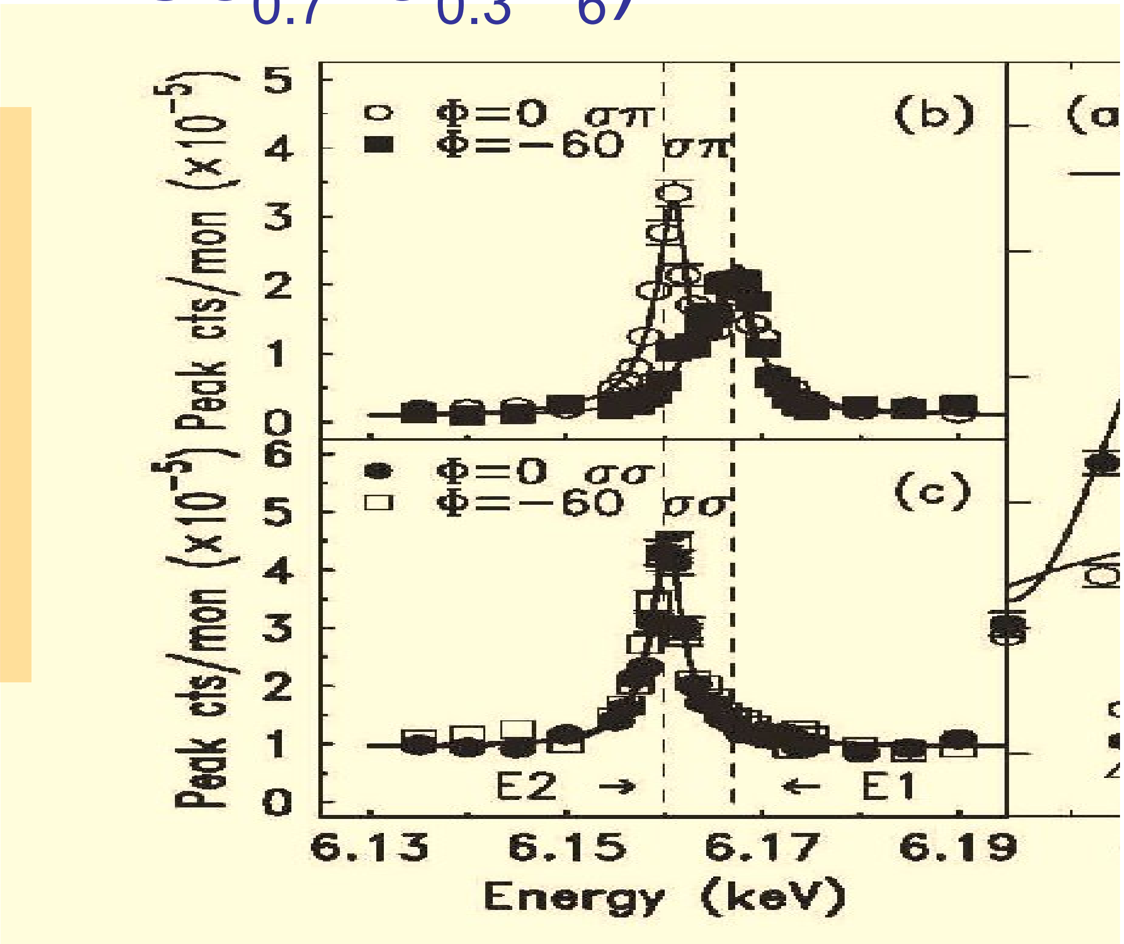
σ-σ':

E2 + (background)

σ-π' :

E1 + E2

$$G = \left(\frac{3}{2} \quad \frac{3}{2} \quad \frac{3}{2}\right)$$



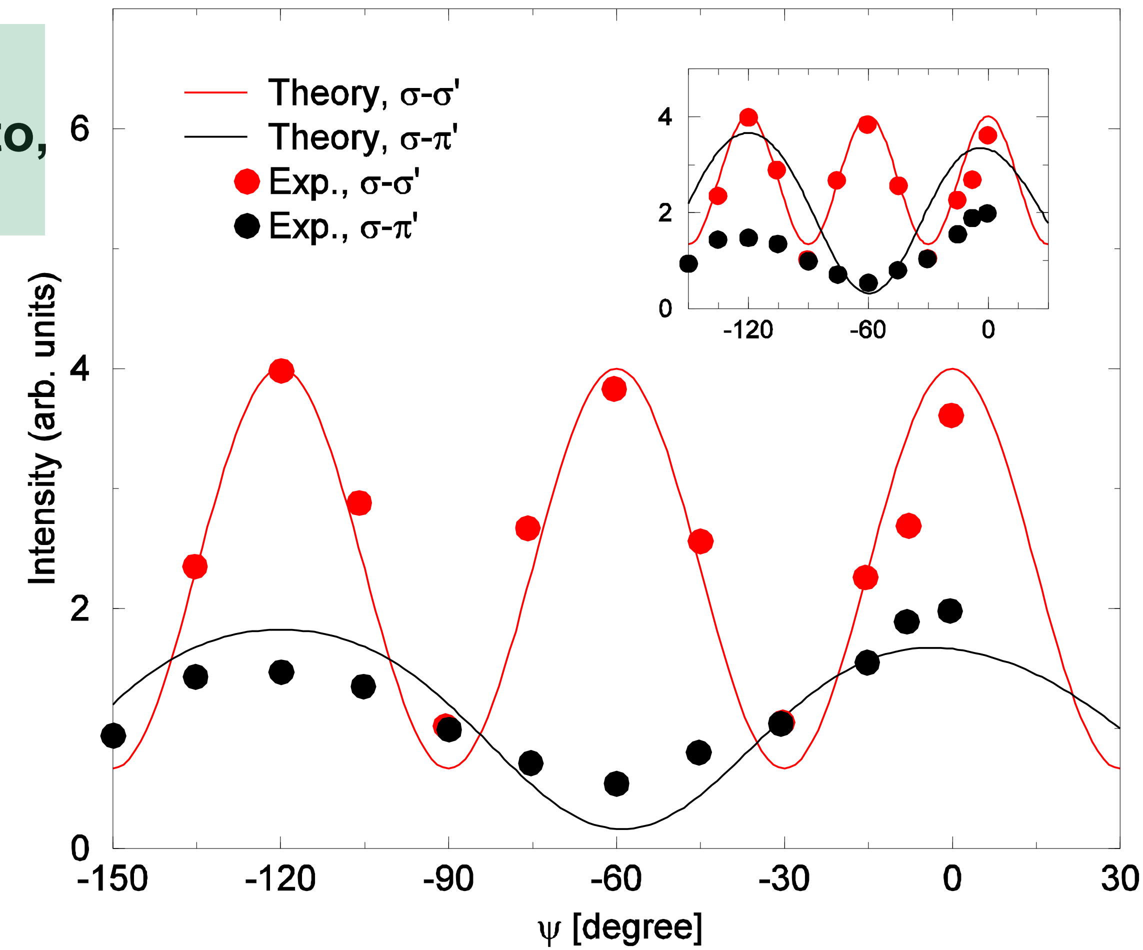
- D. Mannix et al. (PRL '05)

Azimuthal angle dependence

Theory :
H. Kusunose & Y. Kuramoto,
(JPSJ, '05)

$$\left[\frac{I_{\sigma\to\sigma'}}{I_{\sigma\to\pi'}}\right]_{\text{Theory}} \approx 1$$

$$\left[\frac{I_{\sigma\to\sigma'}}{I_{\sigma\to\pi'}}\right]_{\text{Exp.}} \approx 2$$



Domain effect

$T_{111}:T_{1\bar{1}\bar{1}}:T_{\bar{1}1\bar{1}}:T_{\bar{1}\bar{1}1} = 3:1:1:1$

→ **T. Nagao & J. Igarashi (cond-mat/0605288)**

Energy profile

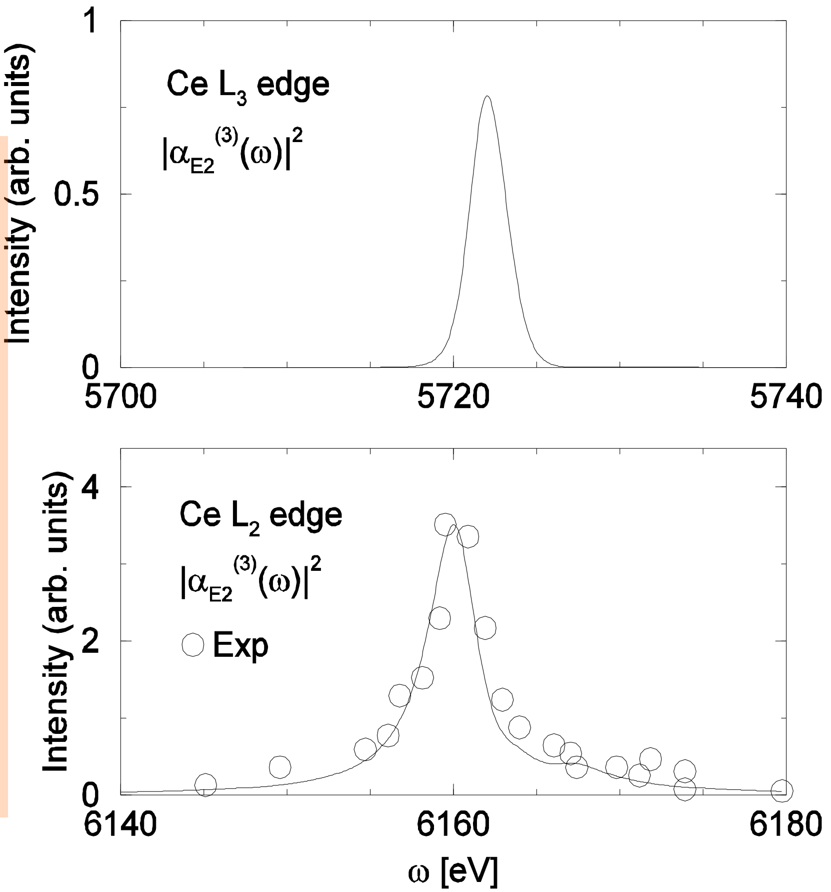
Intermediate states:

$(2p)^5(4f)^2$ configuration

- intra-atomic Coulomb interactions between 2p-2p, 2p-4f and 4f-4f
- spin-orbit(SO) interactions of 2p & 4f

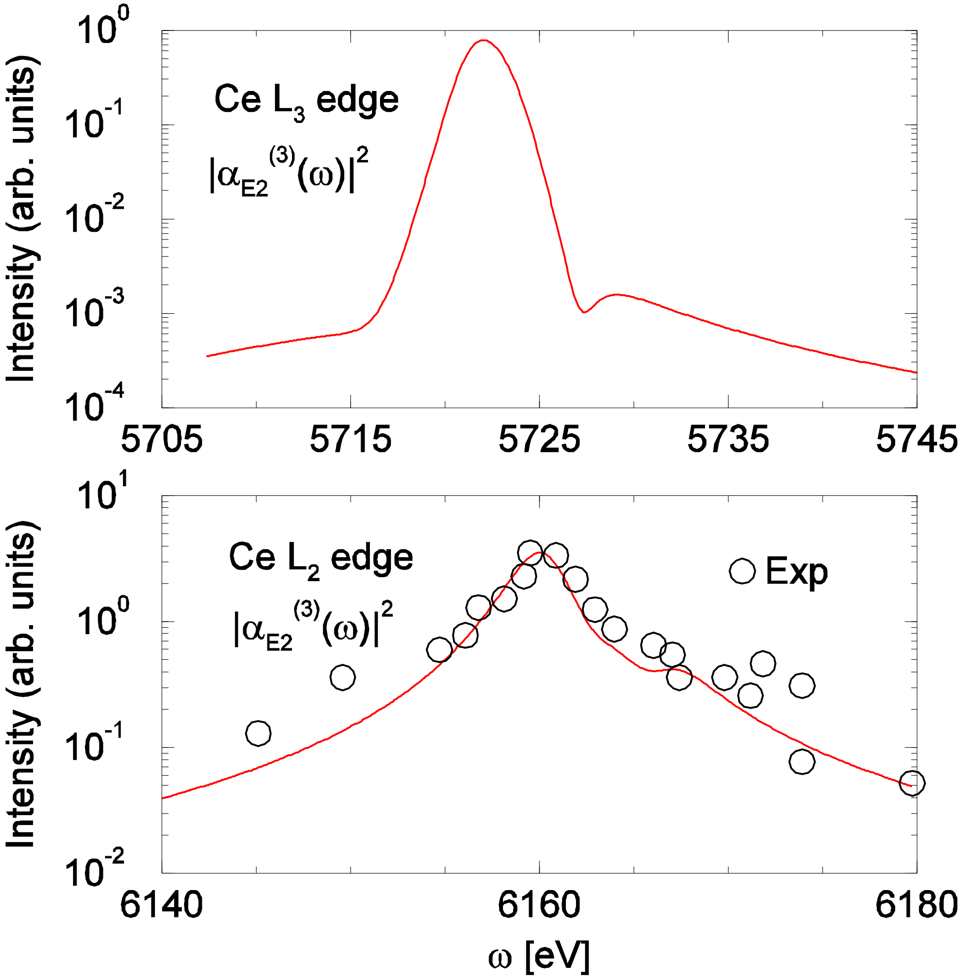
the Slater integrals and the SO coupling.

⇒ Cowan code (Hartree-Fock) with screening



Γ=2 eV

Profile of the octupole operator



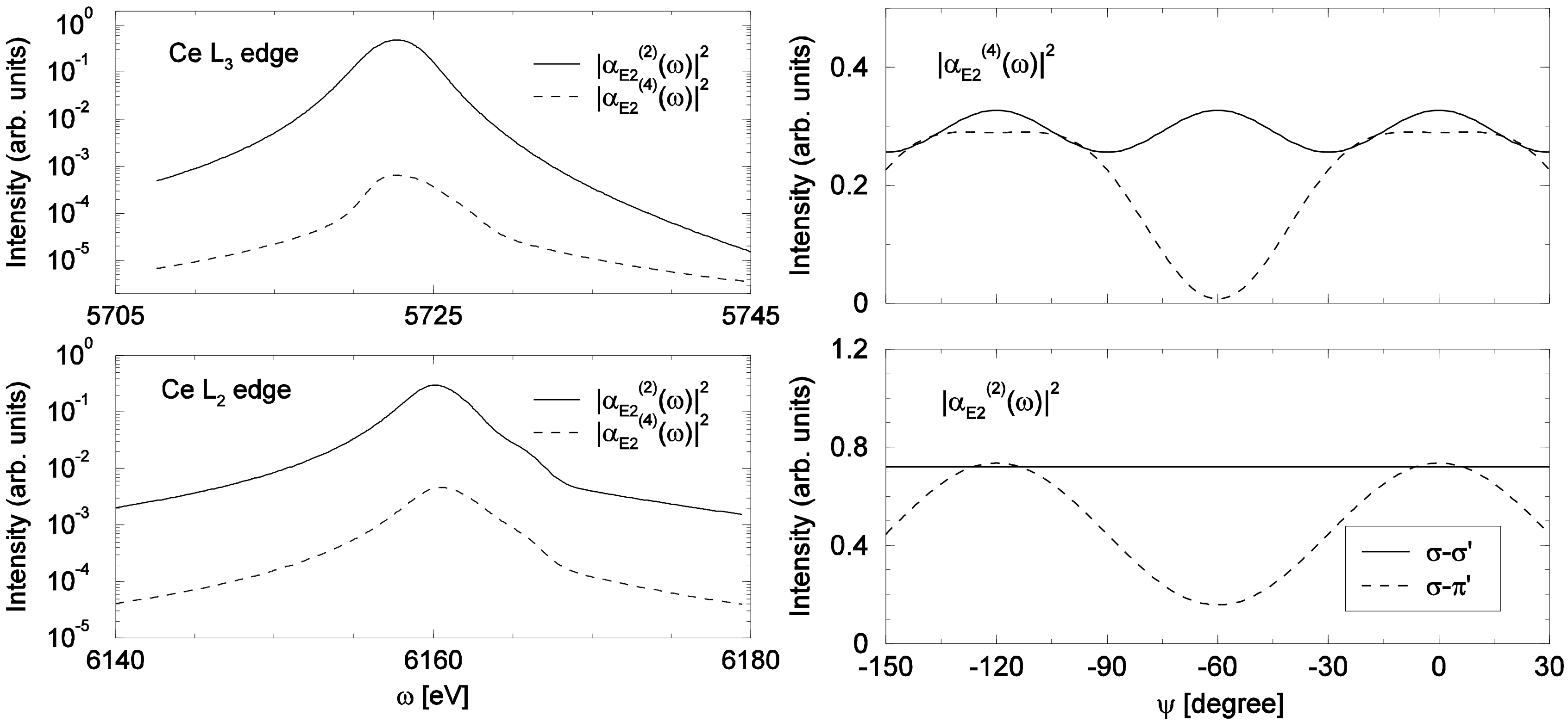
- **Detectable at the L3 edge**
- **L2 profile is different from L3 profile**

  (T. Nagao & J. Igarashi, cond-mat/0605288)

- **energy profile: domain indep.**

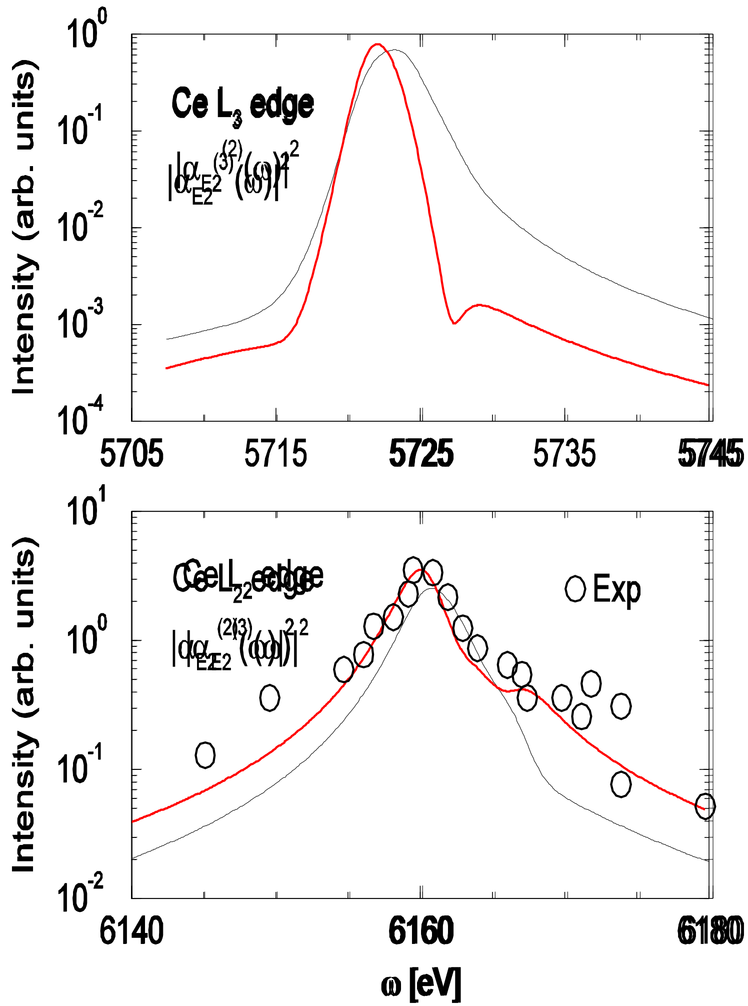
  (Ψ-dep.: $I_{\sigma\text{-}\sigma'}/\ I_{\sigma\text{-}\pi'}$ domain sensitive)

CeB_6 phase II （antiferroquadrupole）

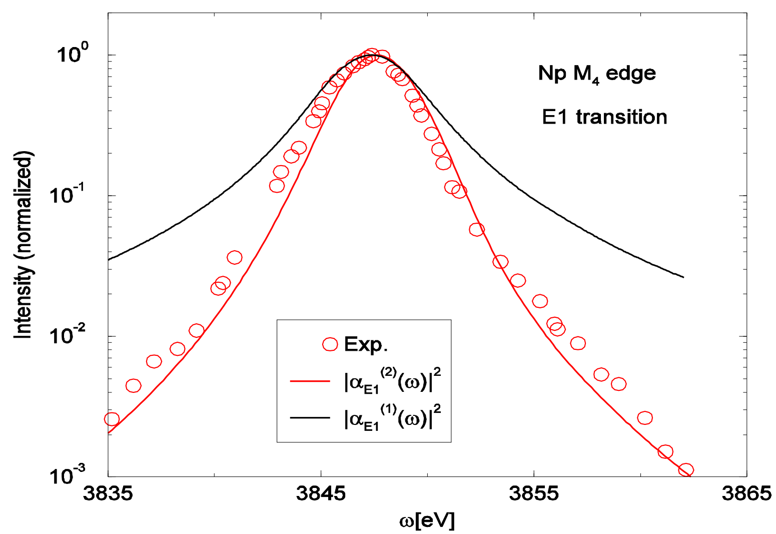


Domain sum : O_{yz} : O_{zx} : O_{xy} = 1:1:1

Are they really distinguishable ?

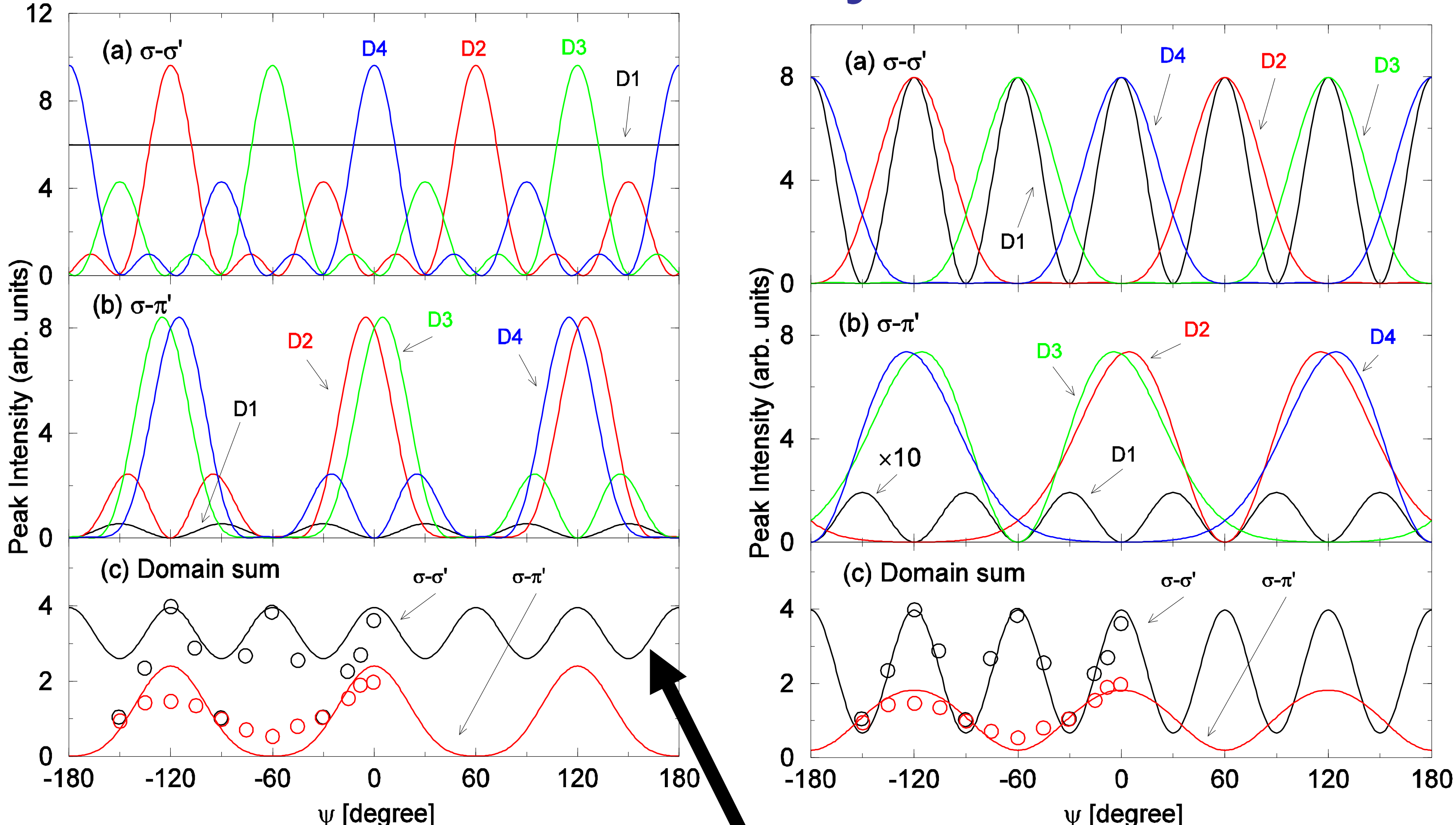


Ce $L_{2,3}$ edges, AFO v.s. AFQ



Np M_4 edges,
AFO (=AFQ) v.s. AFM

Six- & three-fold symmetries



$O_{yz} : O_{zx} : O_{xy} = 1:1:1$

$T_{111} : T_{1\bar{1}\bar{1}} : T_{\bar{1}1\bar{1}} : T_{\bar{1}\bar{1}1} = 3:1:1:1$

Oscillation in the σ-σ’ channel : due to hexadecapole profile

Summary

- Derived a useful formula of the resonant x-ray scattering amplitude including the exact energy profile.
- Phase IV in $Ce_{0.7}La_{0.3}B_6$

  Reproduced the E2 spectrum at the Ce L_2 edge.

  E2 signal at the Ce L_3 edge is detectable ?

  Domain control may be crucial…
- Energy profile may provide useful information in identifying the order parameter in the f electron system.