Resonant X-ray Scattering Study of Rare-earth Tertraborides

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- Resonant X-ray Scattering
  : magnetic, structural ATS and orbital order
- GdB_4 : mode-selective spectroscopic probe
- DyB_4 : quadrupole-strain interaction
- Summary

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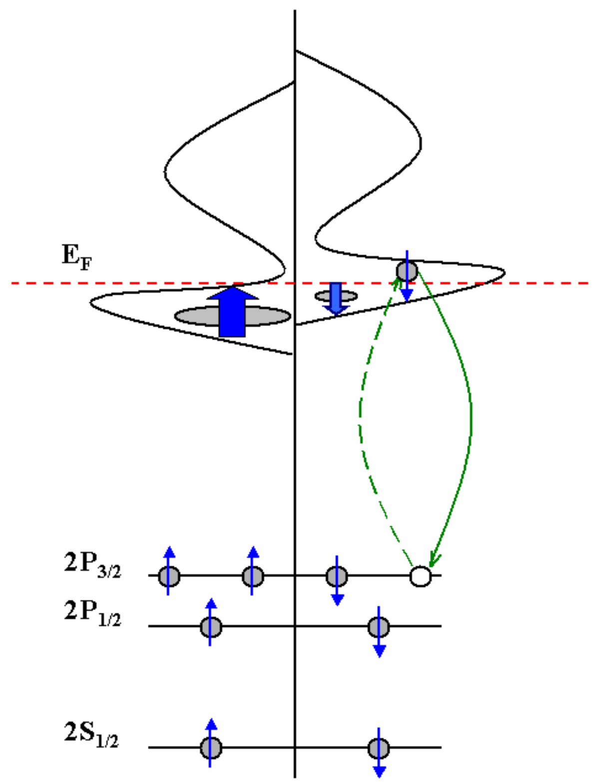
Collaborations with

- X-ray diffraction : POSTECH & PAL
  - Prof. K.-B. Lee
  - Dr. C. Song (UCLA)
  - Dr. Japil Koo
  - Yong Jun Park
- Neutron diffraction : SKKU & HANARO
  - Prof. J.-G. Park.
  - Dr. Seongsu Lee (Rutgers Univ.)
  - Dr. G. Hong
  - C.-H. Lee
- Crystal growth : GIST & Hiroshima Univ.
  - Prof. B. K. Cho
  - J. Y. Kim
  - Prof. F. Iga

Resonance effects in magnetic & ATS reflections



schematics depicting the resonant scattering process emphasizing the spin polarized magnetic scattering process

On tuning the photon energy to an absorption edge of the target ion, an electron in the core level becomes excited to an empty valence shell and eventually de-excited to the core level by emitting the photon of the same energy. This resonance process explores a valence shell through the intermediate states giving rise to an enhanced sensitivity to valence charges.

Especially, the valence shell experiences spin polarizations (**magnetic** ion) as well as anisotropic charge distortion (**ATS**) due to the crystalline electric field, or various bondings/ hybridizations surrounded by other ions in solids.

Consequently, spin and chemical charge anisotropy can be effectively investigated by resonance x-ray scattering technique.

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RXS for charge and spin anisotropy

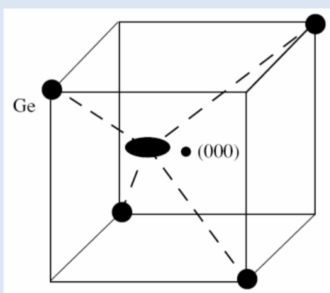
Scattering length of the electric dipole (E1) transition can be expressed with a 2nd rank tensor

$$f^{E1} \propto \varepsilon_{out}^{+,\beta} \varepsilon_{inc}^{\alpha} \sum_n p_a \frac{\langle b=a | R_\beta | n \rangle \langle n | R_\alpha | a \rangle}{E_n - E_a - \hbar\omega - i\Gamma_c}$$

$$f^{E1} \propto \varepsilon_{out}^{+} \bullet \varepsilon_{inc} \mathrm{T} + i\left(\varepsilon_{out}^{+} \times \varepsilon_{inc}\right) \bullet \vec{\mathrm{M}} + \varepsilon_{out}^{T} \overleftrightarrow{\Phi} \varepsilon_{inc}$$

$$\overleftrightarrow{\Phi} \approx \frac{1}{2}\left(R_{\alpha\beta} + R_{\beta\alpha}\right) - \frac{1}{3} R_{\alpha\beta} \delta_{\alpha\beta}$$

Symmetric (traceless) part :
Structural ATS



(0 0 4n+2):
Bragg forbidden
ATS allowed

$(R_{\alpha\beta} - \ldots$

metri

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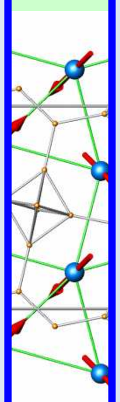
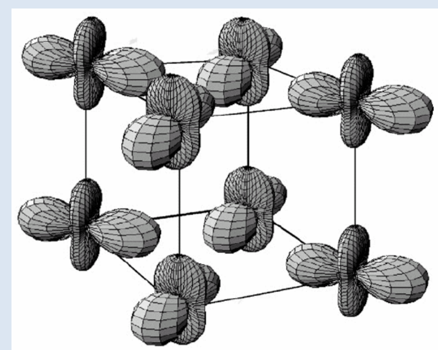


$$\overleftrightarrow{\Phi} \approx \frac{1}{2}\left(R_{\alpha\beta} + R_{\beta\alpha}\right) - \frac{1}{3} R_{\alpha\beta} \delta_{\alpha\beta}$$

Symmetric (traceless) part :
Orbital (quadrupolar) order



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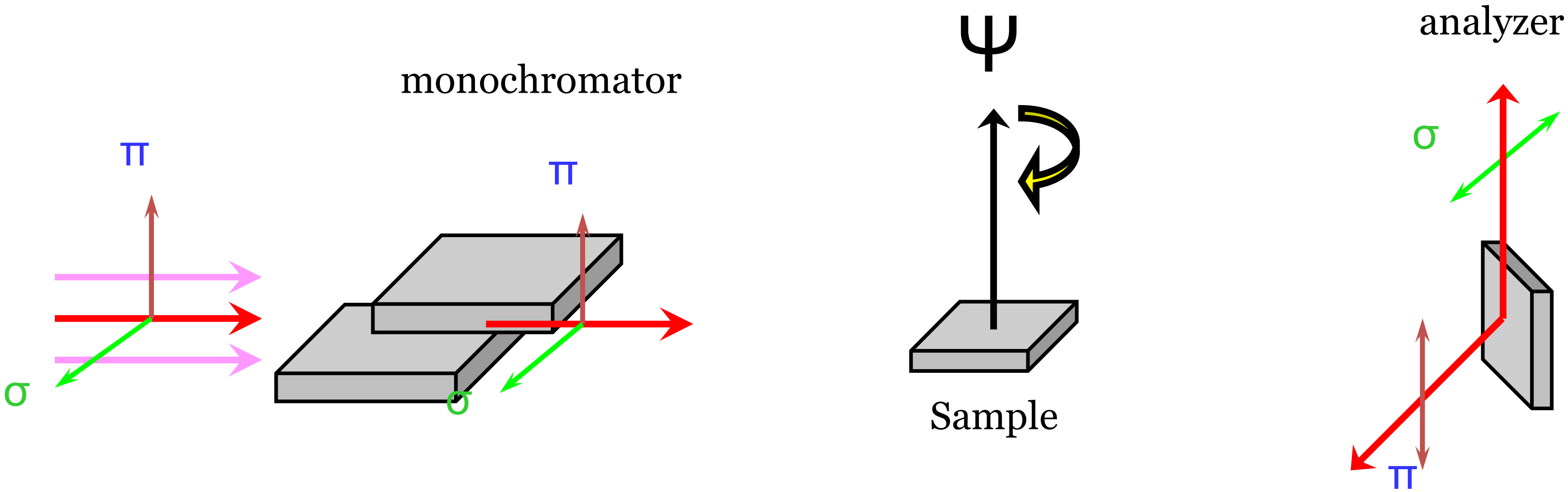
Three distinctive features of RXS:

Experimental configurations



- Polarization dependence can be achieved by the choice of proper analyzer crystal
  - Choose a proper analyzer crystal which has ~90 degree Bragg reflection at given x-ray energy.
  - Magnetic : σ – π
  - ATS : σ – σ and σ – π
- Azimuthal angle dependence reflects the electronic local symmetry of sample
- Element specific: ex)) K-edge of 4d transition metal for hard x-ray

Brief review of past works and quests

Resonant X-ray Scattering: magnetic structure

✓1985 M. Blume
theoretical basis
✓1985 K. Namikawa, *et al.*
magnetic enhancement in Ni
(Zeeman interaction)
✓1986 G. van der Laan, *et al.*
MXD at M_5-edge of TbIG
✓**1988 Doon Gibbs, *et al.***
AF modulation in Ho: XRES

Has been complementary to neutron scattering

Resonant X-ray Scattering: chemical anisotropy (ATS)

✓1982 Templeton & Templeton
✓1983 Dmitrienko
formalism of ATS-symmetry
✓1992 Finkelstein, *et al.*
ATS in α-Fe_2O_3
✓**1998 Murakami, *et al.***
orbital orderings in $LaMnO_3$
✓2000 Hirota *et al.*
quadrupolar orderings in DyB_2C_2

Has been fascinating tools to characterize orbital physics

No works have been reported dealing with:

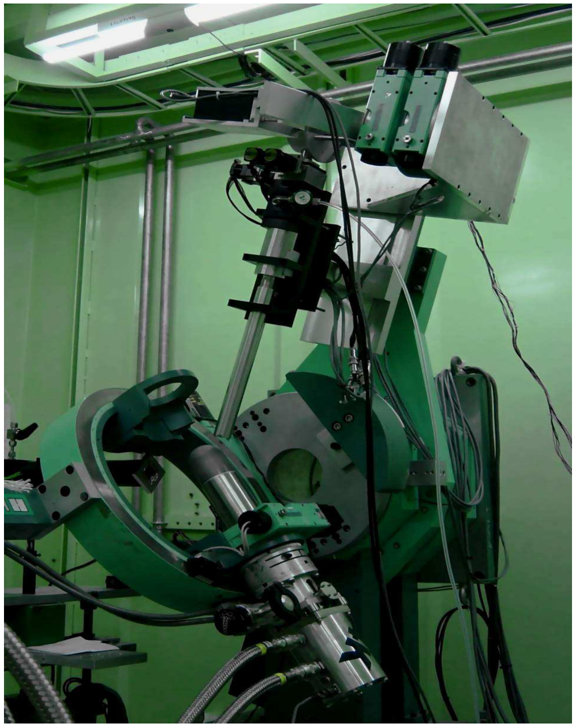
1. combined effects of magnetic and chemical anisotropy
2. possibility of RXS as a spectroscopic probe.
3. relation between orbital and lattice degrees of freedom

Synchrotron experiment – Pohang Light Source, 3C2

Pohang Light Source

✓Power: 2.5GeV & 180mA

✓Beamlines in operation
: 5 IDs & 22 BMs



3C2 Beamline

✓E: 4keV~13keV, ΔE~2eV

✓~10^9 photons/sec (BM)

✓Polarization analysis, 5K displex

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Combined effects & Mode Selective Spectroscopy : GdB4

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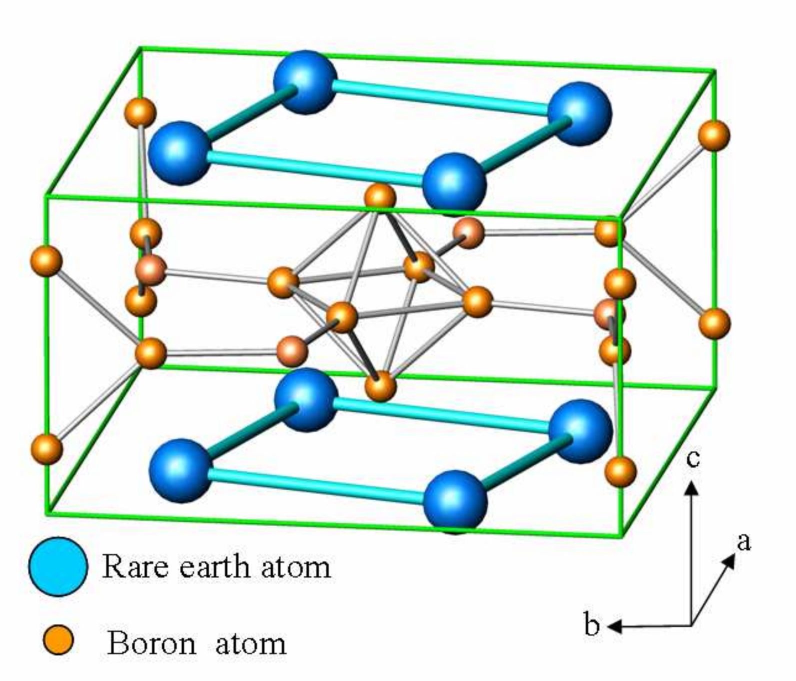
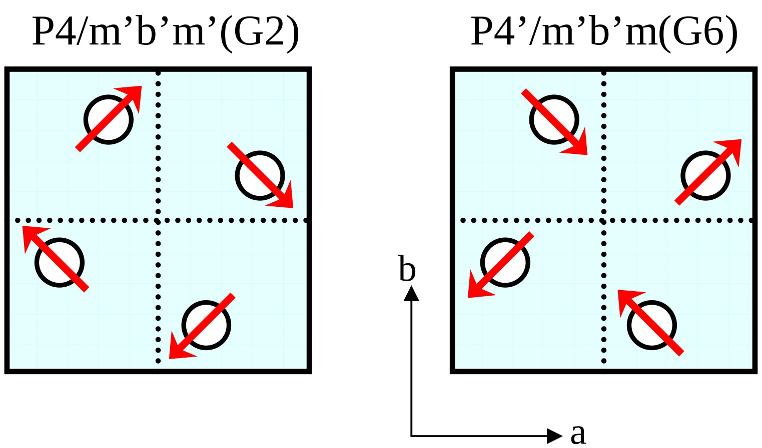
GdB_4: coexistence of magnetic & ATS resonance

Crystal and magnetic structure of GdB4





✓Tetragonal structure (P4/mbm) with Gd ions at the 4g symmetry position

✓Only one magnetic ion and antiferromagnetic ordering below 42K with *ab*- plane moments and a propagation vector of [1 0 0]
→ magnetic RXS is expected at (2n+1 0 0)

✓(2n+1 0 0) reflections are glide-plane symmetry forbidden
→ Structural ATS is expected at the same Q-positions

Good candidate to demonstrate

1. the combined effects between magnetic and ATS RXS
2. spectroscopic probe for spin and chemical anisotropy

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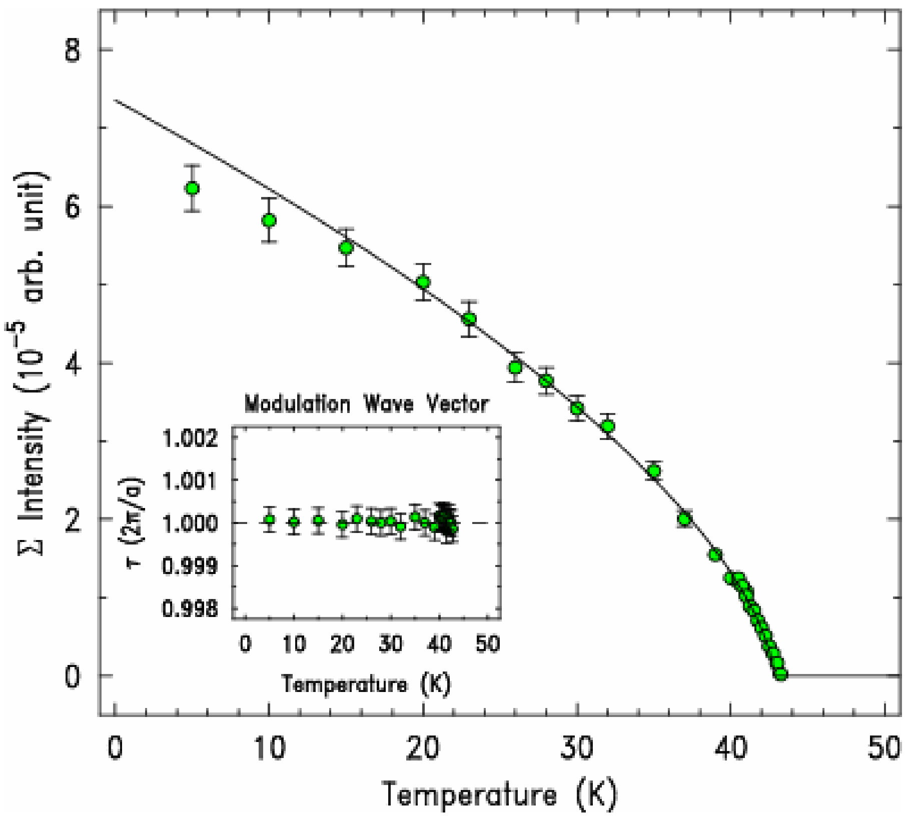
Some results of magnetic scattering



- ✓Resonance signal enhancement at E=7.245keV which is 2~3 eV above the absorption edge implying the E1 transition process
- ✓Scattering performed on σ–to–π polarization channel using the PG (0 0 6) reflections
- ✓Sample mounted with the flat (*h* 0 0) planes parallel to the Q and the *ab*-plane is in the scattering plane (defining Ψ =0)
- ✓Magnetic order parameter obtained with T_N=43K. The solid line is a power law fit used as an eye- guide
- ✓Modulation wave vector=[1 0 0]

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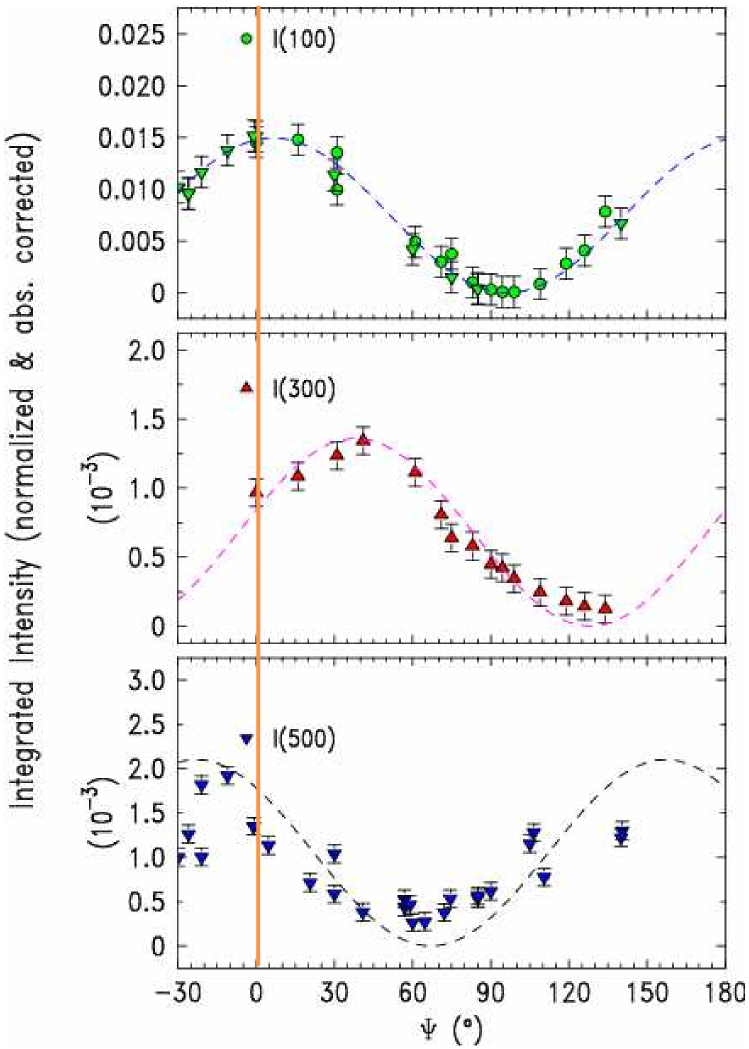
Azimuthal rotation dependence



✓The azimuthal dependence of the superstructure peaks, (*h* 0 0), at 5K displays a sinusoidal modulation with the phase shifted from zero and the shifted phases are different for each reflection plane

✓Modulation can be realized for a transverse spin ordering, but the phase shifts and Q-dependence of shifted phase is not possible from magnetic reflection only

✓The broken lines are from a derived scattering factor considering both magnetic and ATS reflections whose details are described below

✓Azimuthal rotation (Ψ) along [1 0 0]
: Ψ =0 (***c***-axis // ***y***)

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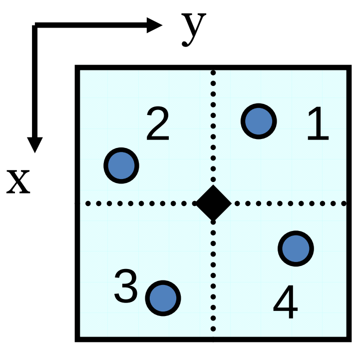
Analysis 1: ATS reflection (E1 transition)



$$r_1 = \left(x, \frac{1}{2} + x, 0\right) \quad r_2 = \left(\frac{1}{2} - x, x, 0\right) \quad r_3 = \left(-x, \frac{1}{2} - x, 0\right) \quad r_4 = \left(\frac{1}{2} + x, -x, 0\right)$$

$$F(h = 2n+1, 0, 0) = \varepsilon^+_{out} \left[(f_1 - f_4) e^{i2\pi(2n+1)x} + (f_3 - f_2) e^{-i2\pi(2n+1)x} \right] \varepsilon_{inc}$$

$$\propto \varepsilon^+_{out} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \varepsilon_{inc} \cos[2\pi(2n+1)x]$$

Symmetric traceless

$$f_n = \begin{pmatrix} a & b & c \\ b & d & e \\ c & e & -a-d \end{pmatrix} \longrightarrow (f_1 - f_4) = (f_3 - f_2) \propto \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Symmetry invariant :

$$f(r') = R^+ f(r) R$$

$$R(\sigma_{001}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Reflection (001)

$$R(\sigma_{110}) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Reflection (110)

$$R(C_4) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

4-fold rotation (001)

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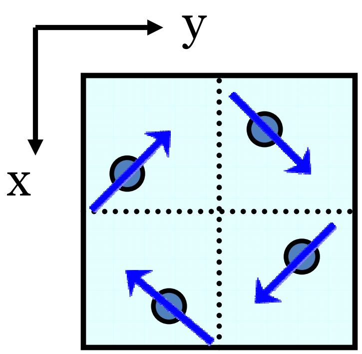
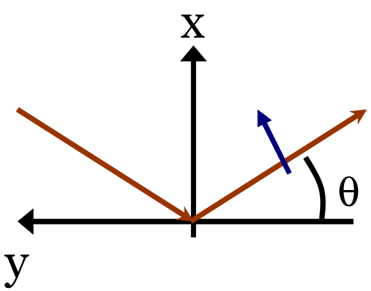
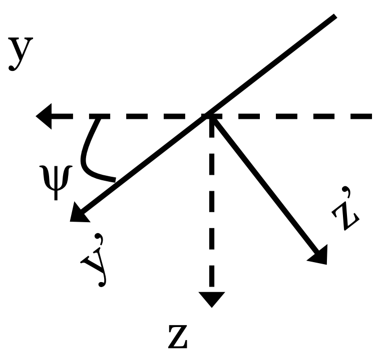
Analysis 2: magnetic structure & photon polarizations



$$F_{\mathrm{MAG}}(h=2n+1,0,0)=\left(\varepsilon_{out}^{+}\times\varepsilon_{inc}\right)_y \mathrm{M}\sin[2\pi(2n+1)x]$$





$$\varepsilon_{\sigma}^{inc}(\Psi)=\begin{pmatrix}0\\-\sin\Psi\\\cos\Psi\end{pmatrix}$$

$$\varepsilon_{\pi}^{out}(\Psi)=\begin{pmatrix}\cos\theta\\\sin\theta\cos\Psi\\\sin\theta\sin\Psi\end{pmatrix}$$

rotated

$$R(\hat{\Psi}\parallel\hat{a})=\begin{pmatrix}1&0&0\\0&\cos\Psi&-\sin\Psi\\0&\sin\Psi&\cos\Psi\end{pmatrix}$$

Rotation matrix

$$\varepsilon_{\sigma}^{inc}(0)=\begin{pmatrix}0\\0\\1\end{pmatrix}$$

$$\varepsilon_{\pi}^{out}(0)=\begin{pmatrix}\cos\theta\\\sin\theta\\0\end{pmatrix}$$

unrotated

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The azimuthal dependence with interference

$$F(\Psi)_{\sigma\to\pi}^{E1,\mathrm{MAG}} = \mathrm{M}_{\mathrm{MAG}} \cos\left(2\theta/2\right)\sin\left(2\pi(2n+1)x\right)\cos(\Psi)$$

$$\& \qquad F(\Psi)_{\sigma\to\pi}^{E1,\mathrm{ATS}} = \Phi_{\mathrm{ATS}} \cos\left(2\theta/2\right)\cos\left(2\pi(2n+1)x\right)\sin(\Psi)$$

$$F(\Psi)_{\sigma\to\pi}^{E1,\mathrm{M\&A}} = [\mathrm{M},\Phi]\cos\left(2\theta/2\right)\cos[\Psi-\Delta(Q,\xi)]$$

$$\text{with} \qquad \tan\Delta = \frac{\{\mathrm{M},\Phi\}}{[\mathrm{M},\Phi]}\cot[2\pi(2n+1)x]$$

$$\text{for } |a|\rangle|b| \Rightarrow [a,b]=a \text{ and } \{a,b\}=b$$

✓σ-to-σ polarization remains forbidden for the E1 transition

✓Coherent interference between magnetic and ATS reflections leads to phase shifted azimuthal dependence where the shifted phase (Δ) has Q-dependence

✓The derived scattering factors well reproduce the experimental results
:three data set with parameters of ***x*** (atomic position) and ξ, relative strength of magnetic and ATS. (***x***=0.317, taken from TbB4)

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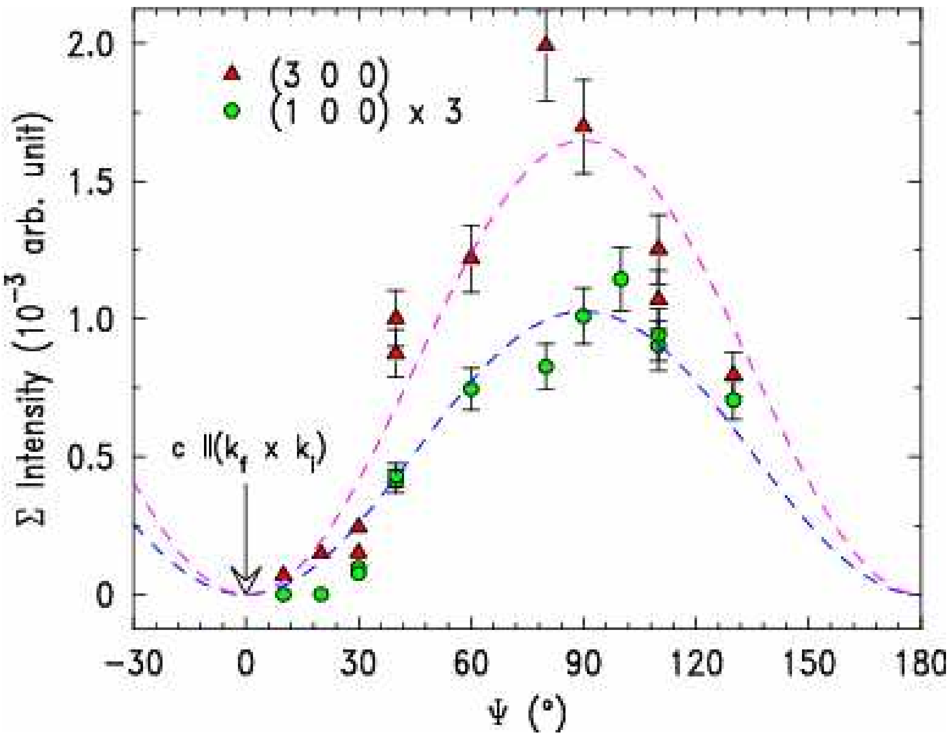
Azimuthal dependence of pure ATS reflections



✓To further confirm the results, azimuthal dependence of pure ATS reflections are obtained at 99K (above the T_N=43K)

✓Azimuthal dependence displays **in-phase modulation** with a maximum intensity at Ψ =90 degree

✓Broken lines are from the derived scattering factor, but now having only the ATS scattering

✓Overall, the results are self-consistent supporting that inclusion of the ATS reflection is inevitable to interpret the phase shifted azimuthal dependences in magnetic phase.

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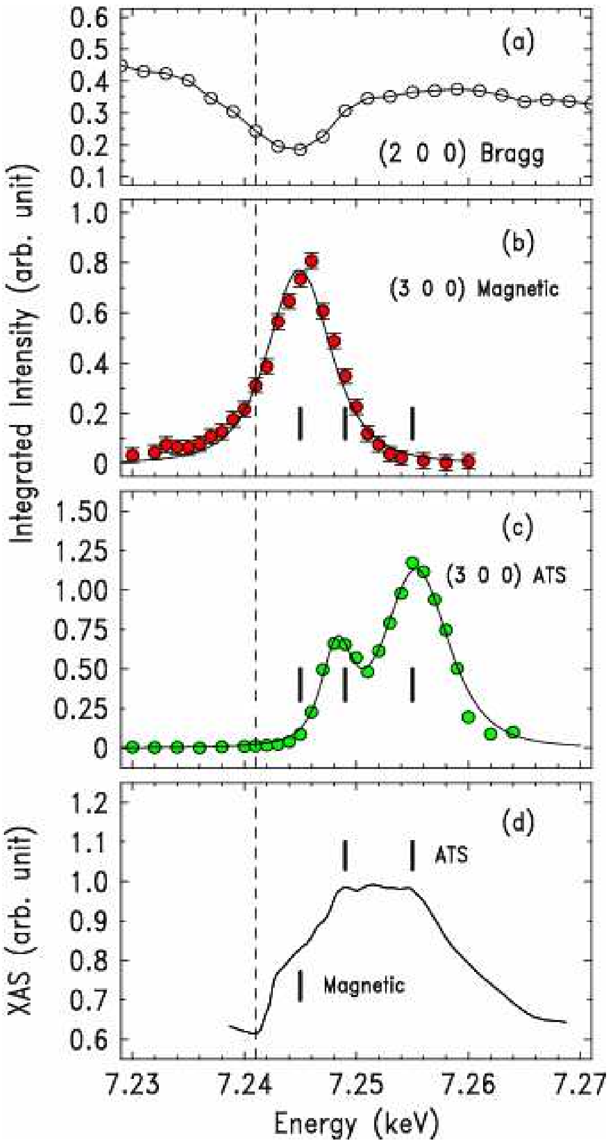
Resonance energy profiles



✓Separation of the energy profiles becomes enabled by rotating the azimuthal angle:
- pure magnetic: $\Psi = 0$
– pure ATS : $\Psi = 90$

✓Different resonance energies
E_{MAG}=7.245keV
E_{ATS} =7.249keV & 7.255keV

✓Involved transition: Gd $2p_{3/2}$-to-5d
- resonance energy profile (w/ three main peaks) reflects the electronic structure of Gd 5d band

✓Ample distribution of the Gd 5d state shifted upward due to bonding with B 2p state: confirmation from the x-ray absorption spectrum near B K-edge

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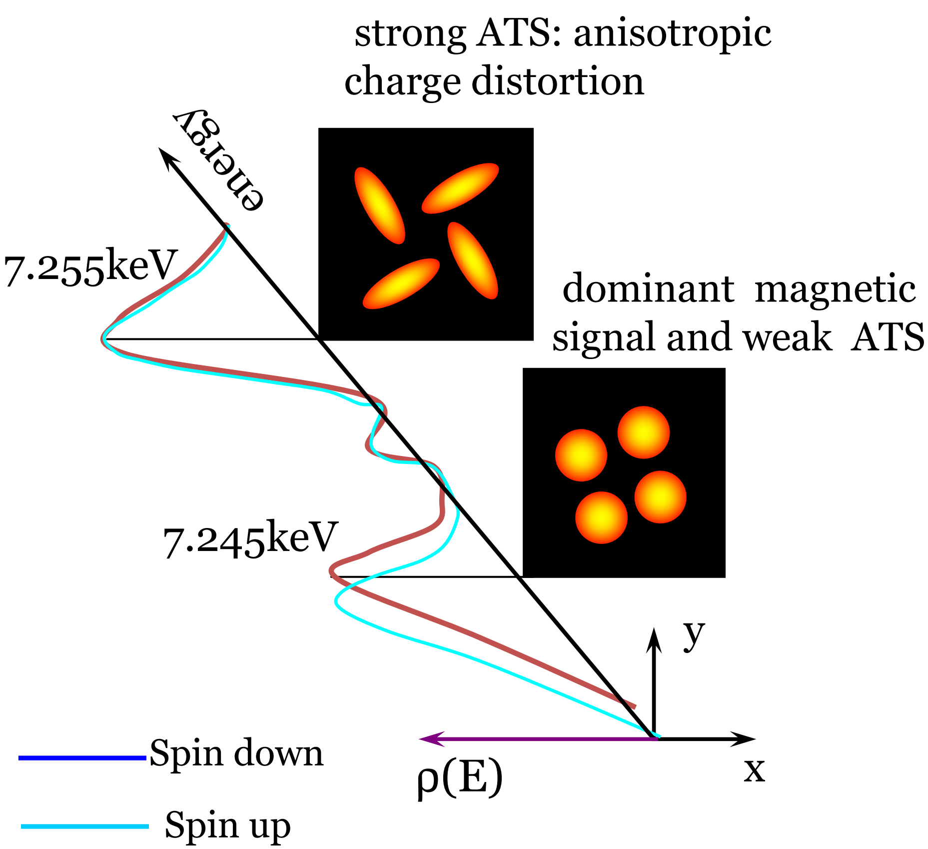
RXS: a mode-selective spectroscopy probe



Schematics of Gd 5d-state deduced from energy profiles of RXS

- ✓Intra- & inter-atomic hybridizations of Gd 5d-states with Gd, 4f and B, 2p- state lead to a major split of Gd 5d -orbital
  - Gd 4f & 5d -> magnetic contribution
  - B 2p & Gd 5d -> ATS
- ✓Higher energy state: Anisotropic charge distortion of the Gd 5d states after a bonding with B 2p states as observed from the B, 2p absorption spectrum
- ✓Lower energy state:dominant magnetic resonance and weak ATS
  -> exchange split comes from direct hybridizations with spherical Gd 4f-state

Implications of the current works

✓Anisotropy of the valence charge is sensitively reflected in RXS

✓Distortion of the local environment:
- hybridization with neighbor atoms
- crystal electric field effect
- thermal motion & point defects
- displacive lattice modulations, etc

✓Interplay of magnetic ordering and crystalline anisotropy

✓**Resonant X-ray Scattering as a local environment sensitive probe**

✓**Resonant X-ray Scattering as a mode selective spectroscopy probe**

✓X-ray absorption spectroscopy
- somewhat averaged information (Q=0)

✓Angle resolved PES
- energy level dispersion: E(k)

✓Resonant X-ray Scattering
- explicit visualization of a given orbital's physical characteristics
- intrinsic Q-dependence

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Direct Observation of Quadrupole-Strain Interaction : DyB_4

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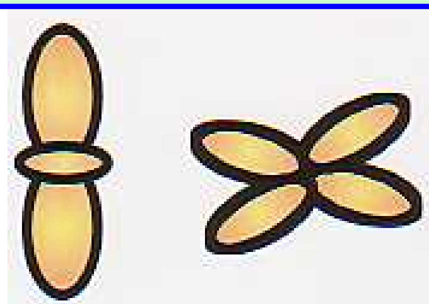
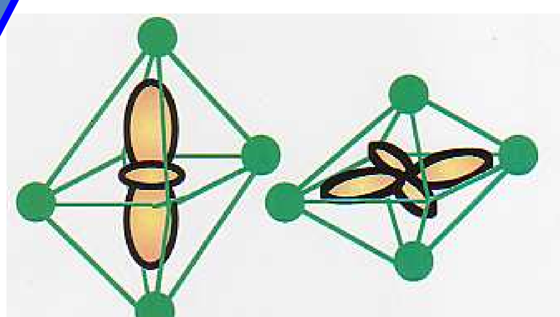
Quadrupole-Strain interaction

Orbital order : microscopic



Lattice-orbit coupling

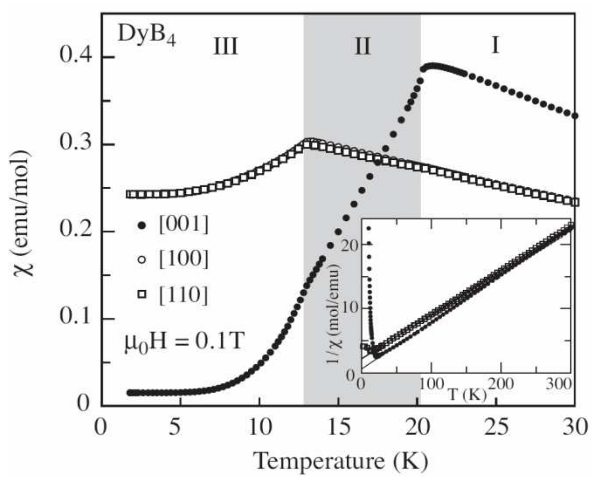
$$\varepsilon_{ij} \propto Q_{ij}$$



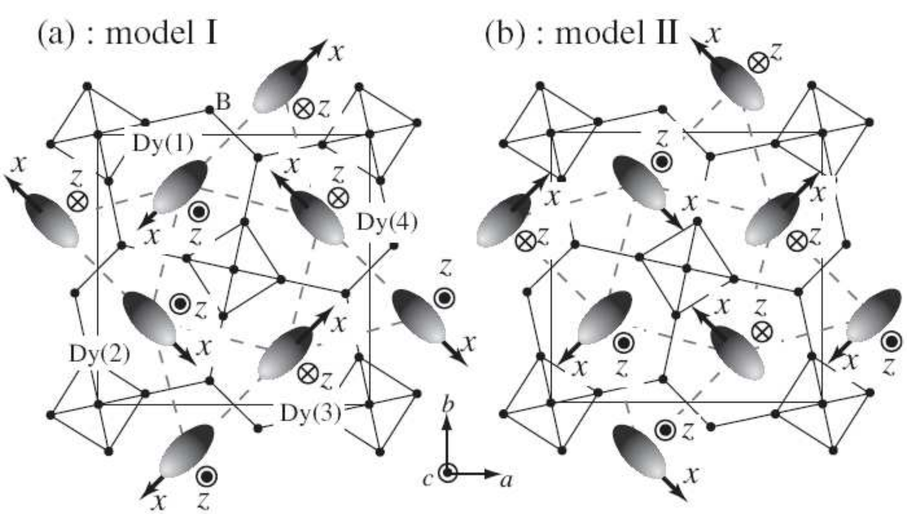
Lattice distortion : macroscopic

- Orbital and strain related phenomena in 3*d*- and 4*f*-electron systems
  - ✓ Magnetoelasticity
  - ✓ Jahn-Teller transition, etc.
- Quadrupole-Strain (Q-S) interaction
  - ✓ well known in 60's
  - ✓ analyzed mostly by strain
- No direct demonstration by experiments
  - ✓ Difficult to observe quadrupolar order
- Q-S interaction was investigated using resonant x-ray scattering.

DyB4: quadrupolar ordered system



R. Watanuki *et. al.,* JPSJ 74, 2169 (2005)



D. Okuyama *et. al.,* JPSJ 74, 2434 (2005)

- Phase I ($T > T_{N1} = 21$ K)
  - paramagnet with tetragonal structure (P4/mbm)
- Phase II ($T_{N1} > T > T_{N2} = 12$ K)
  - collinear AFM (c-axis moments)
- **Phase III : AFQ + FQ**
  - Change of crystal & magnetic structures
  - bc-plane : AFQ <-> RXS
  - ac-plane : FQ <-> strain
- **Good candidate** to demonstrate the relation between quadrupole order and strain

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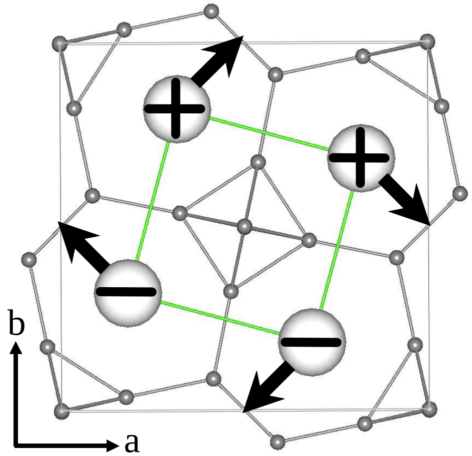
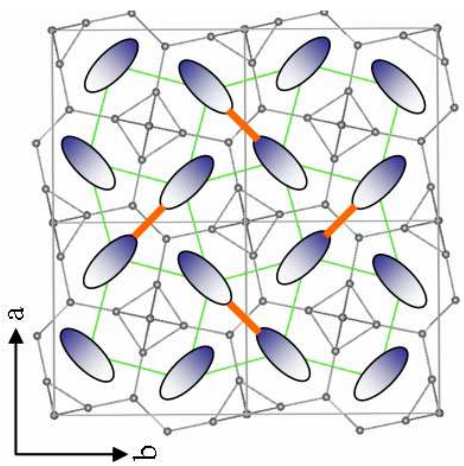
Crystal & Magnetic Structures in phase III

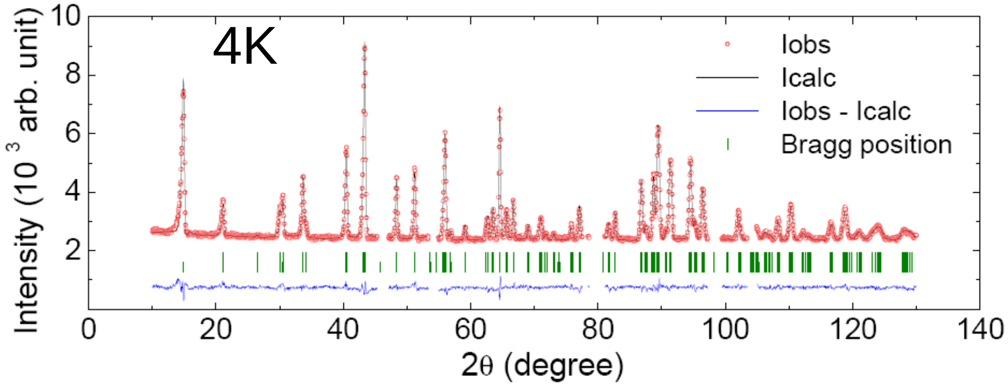
Monoclinic : $P\,1\,2_1/a'\,1$

spin



Quadrupole moments





- Dy ion at each site has canted **[110]'s** local magnetic easy axes due to boron surroundings
- Due to strong LS coupling, principal axes of quadrupole moment **coincide with** spin directions
- AFQ (*bc*-plane) and FQ (*ac*-plane) are **proportional** to each other.

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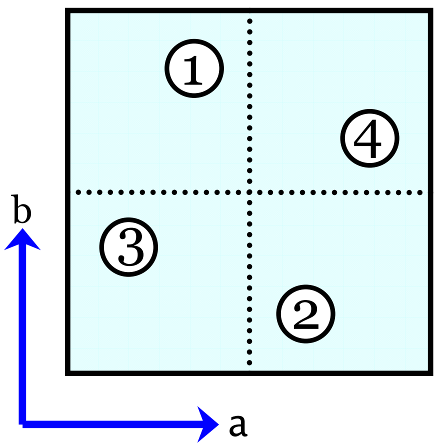
RXS factor calculation in phase III

Under monoclinic (P 1 2_1/a 1) symmetry

Atomic scattering factor of Dy via *E*1 transition



$$f_1 = f_2 = \begin{pmatrix} 0 & f_{ab} & f_{ac} \\ f_{ab} & 0 & f_{bc} \\ f_{ac} & f_{bc} & 0 \end{pmatrix} \qquad f_3 = f_4 = \begin{pmatrix} 0 & -f_{ab} & f_{ac} \\ -f_{ab} & 0 & -f_{bc} \\ f_{ac} & -f_{bc} & 0 \end{pmatrix}$$

exist even in tetragonal structure : structural ATS

Ferro-type

Can not be measured

Antiferro-type

Measurable by RXS

Structure factor : (h=2n+1 0 0)

$$(f_1 - f_4)e^{2\pi i h x} + (f_2 - f_3)e^{-2\pi i h x}$$

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RXS factor calculation in phase III (continued)

Structure factors of forbidden reflection (h,k=odd integer)
for each domain and scattering channel:

For (h 0 0) domain,

$$F_{\sigma-\sigma} \propto f_{bc}\sin(2\Psi)\cos(2\pi hx),$$

$$F_{\sigma-\pi} \propto \cos(2\pi hx)\left(f_{ab}\sin\Psi\cos\theta - f_{bc}\cos 2\Psi\sin\theta\right)$$
$$-\sin(2\pi hx)M_b\cos\Psi\cos\theta$$

For (0 k 0) domain,

$$F_{\sigma-\sigma} = 0,$$

$$F_{\sigma-\pi} \propto \cos(2\pi ky)\left(f_{ab}\sin\Psi\cos\theta - f_{bc}\cos\Psi\cos\theta\right)$$
$$+\sin(2\pi ky)(M_a\cos\Psi\cos\theta + M_c\sin\Psi\cos\theta)$$

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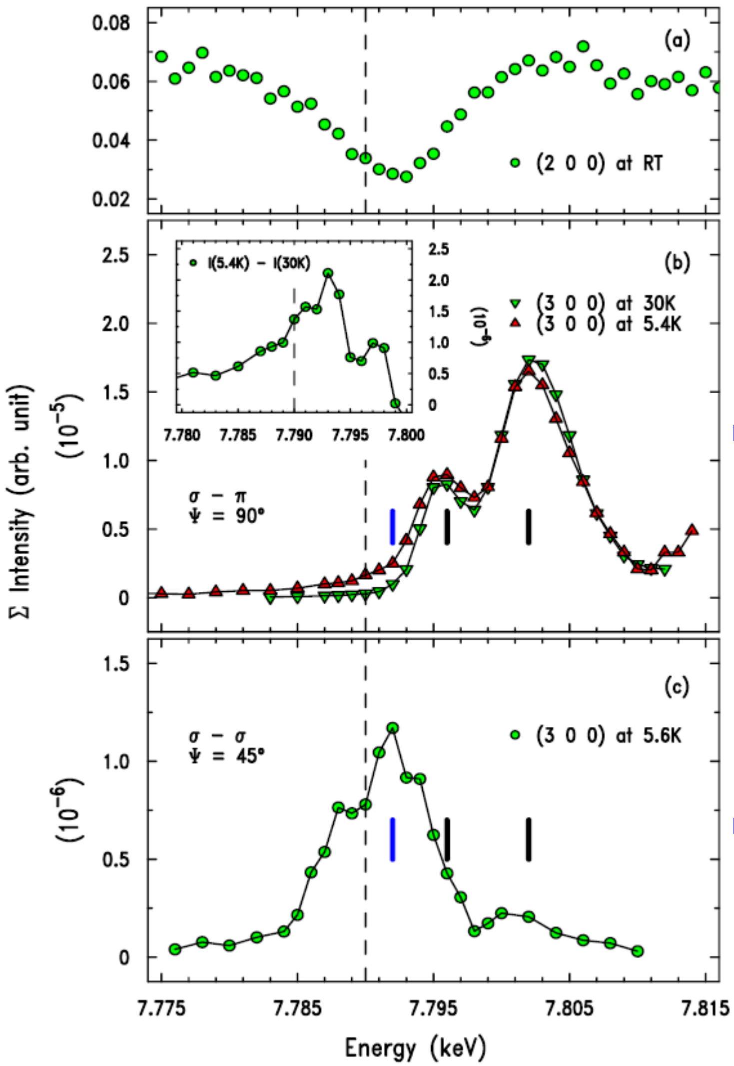
Energy Profiles: observation of AFQ order



Near Dy L_3-edge,

at (3 0 0) forbidden reflection

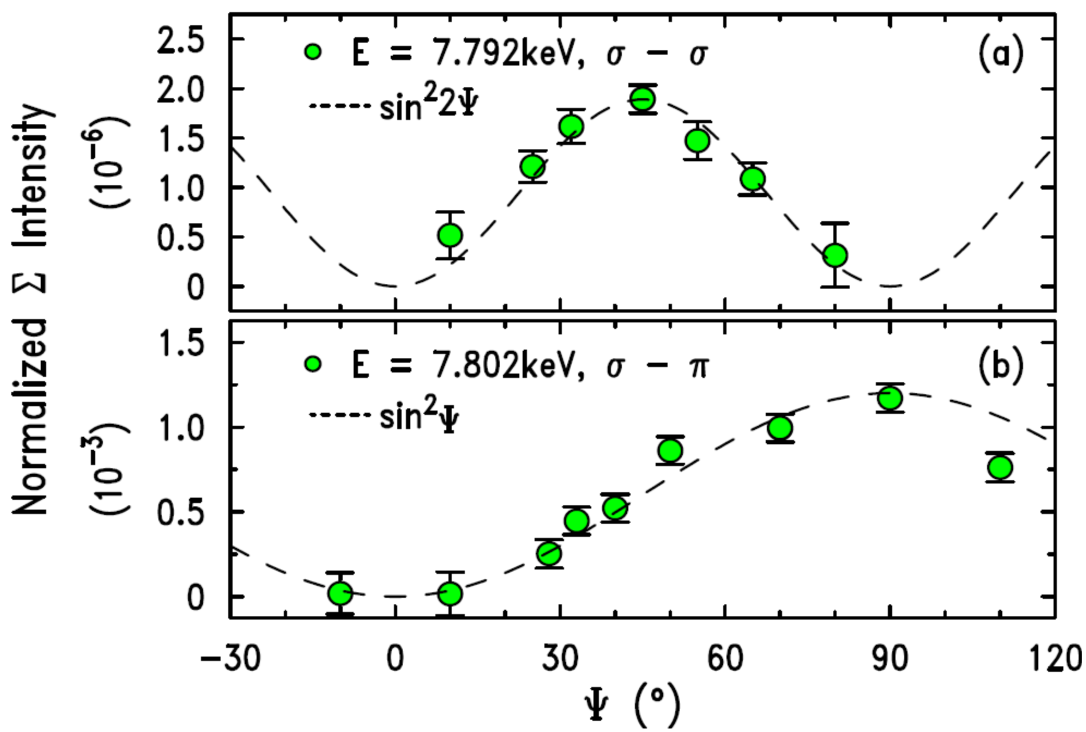
σ -π channel

- dominant Structural ATS
  - 7.796 and 7.802 keV
  - Hybridization of B 2*p* and Dy 5*d*
- MAG + f_{bc} : 7.792 keV
  - Hybridization of Dy 4*f* and 5*d*

σ - σ channel

- f_{bc} component only
- f_{bc} reflect AFQ order of Dy 4*f* electrons

Observation of AFQ order : azimuthal dependence



E = 7.792 keV

AFQ $f_{bc}\sin(2\Psi)$

E = 7.802 keV

Structural ATS $f_{ab}\sin\Psi$

- confirm that f_{bc} originates from AFQ order of Dy 4*f* electrons

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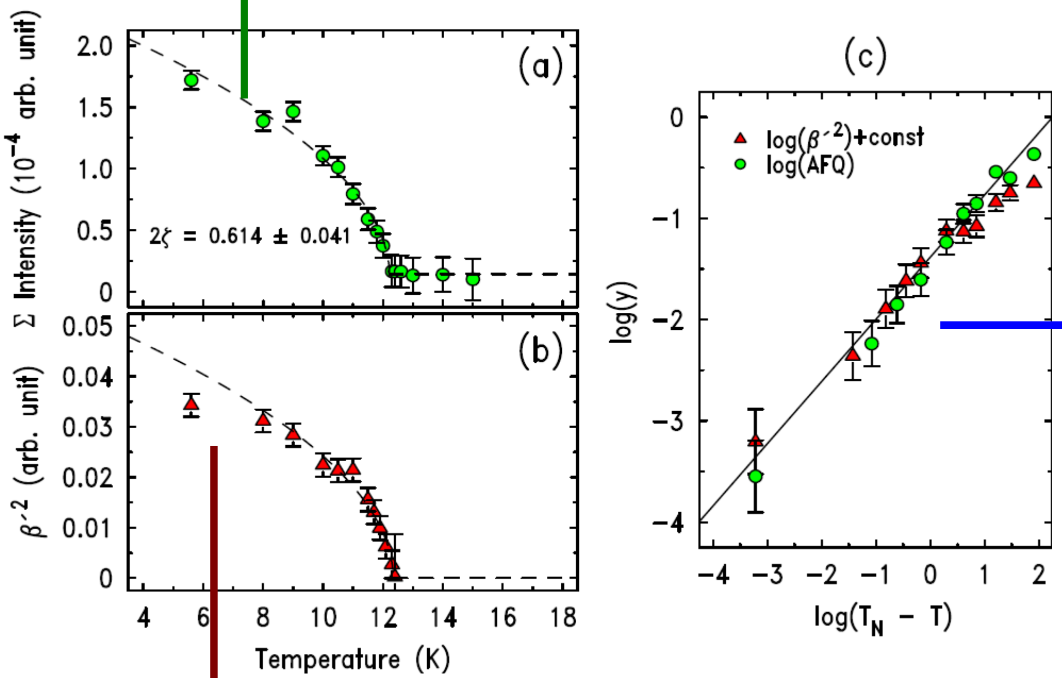
AFQ order and Strain

T-dep of AFQ order: $I_{Q.O.} \propto \langle f_{bc} \rangle^2 \propto \langle Q_{bc} \rangle^2$

obtained from (300) AFQ reflection



AFQ proportional to strain

$\langle Q_{bc} \rangle \propto \varepsilon_{ca}$

T-dep of monoclinicity: $\beta^2 \propto \varepsilon_{ca}^2$

Obtained from (401) Bragg peak splittings

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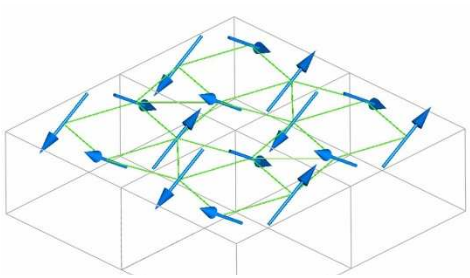
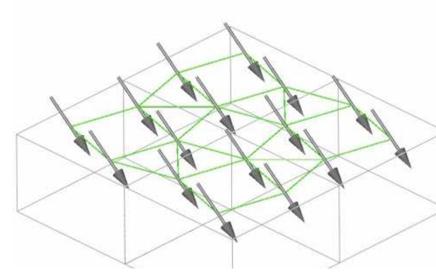
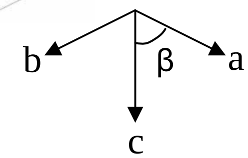
Conclusion:

Direct demonstration of Q-S interaction



NPD





AFQ (Q_{bc})

FQ (Q_{ca})

RXS

strain (e_{ca})

Proportional to each other!!!

- NPD results: AFQ order is proportional to FQ order
- RXS results: strain is proportional to AFQ order
- Consequently, monoclinic strain is proportional to FQ order.

The quadrupole-strain coupling is directly demonstrated in DyB_4

S. Ji *et al.*, PRL 99, 076401 (2007)

Summary

Through the RXS study of rare-earth tetraborides, we show followings:

✓Explicit evidence of interference between magnetic and chemical anisotropy (ATS) reflections

✓Resonance energy profiles of magnetic, structural ATS and quadrupolar order are separately obtained which explain physical characteristics of split rare-earth 5d-band

- lower energy band: intra-atomic mixing (with Gd/Dy 4f)
  -> reflect magnetic and orbital anisotropy dominantly.
- upper band : inter-atomic mixing (with B 2p)
  -> major contribution to the structural ATS : anisotropic distortion due to bonding with B

✓Quadrupole-strain interaction which has been understood theoretically or phenomenologically can be measured directly.

POSTECH