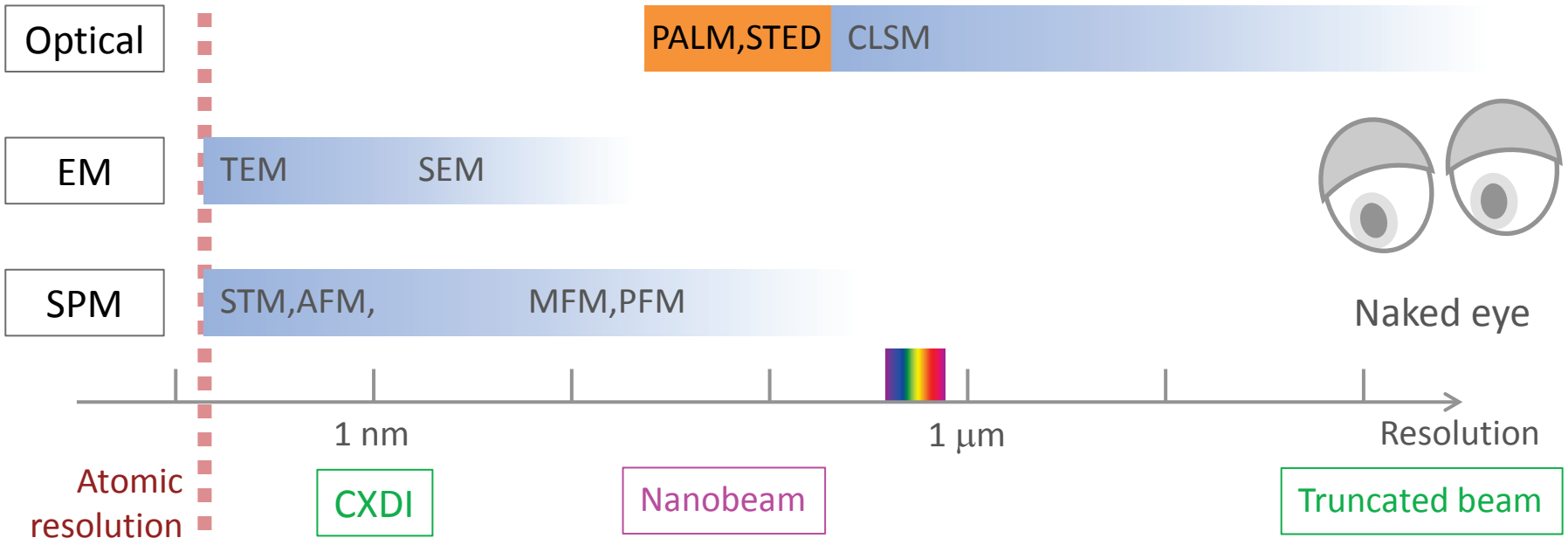
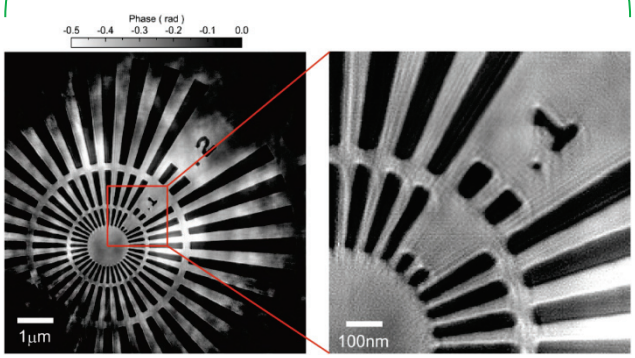
顕微計測が実現する マルチスケール構造物性研究

理研放射光科学総合研究センター　大隅寛幸

Microscopy

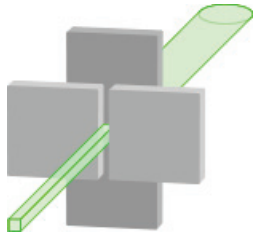




Y. Takahashi et al,. PRB83, 214109(2011).

Prospective utilization

- Microanalysis
- Visualization of something other than appearance (analytical imaging)



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   - Antiferromagnetic domain structure of $Cd_2Os_2O_7$
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   - Evaluation of *L*/*S* by NRXMS: Sr_2IrO_4
   - Discrimination of spin chirality by NRXMS: $DyMnO_3$
   - Improvement in the photon flux density

Collaborators

SPring-8

T. Arima (*RSC / Univ. of Tokyo*)
S. Tardif (*RSC*)
T. Komesu (*RSC*)
N. Kawamura (*JASRI*)
H. Ohashi (*JASRI*)
M. Takata (*RIKEN SPring-8 Center*)
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H. Yumoto (*JASRI*)
T. Koyama (*JASRI*)

$CsCuCl_3$

Y. Kousaka (*Aoyama-Gakuin Univ.*)
Y. Nakao (*Aoyama-Gakuin Univ.*)
J. Akimitsu (*Aoyama-Gakuin Univ.*)
T. Yokobori (*Aoyama-Gakuin Univ.*)

$Cd_2Os_2O_7$

Z. Hiroi (*Univ.of Tokyo*)
N. Torimoto (*Kwansei-Gakuin Univ.*)
J. Yamaura (*Tokyo tech*)
S. Kawase (*Kwansei-Gakuin Univ.*)

Sr_2IrO_4

B. J. Kim (*Univ.of Tokyo*)
S. Fujiyama (*RIKEN*)
H. Takagi (*Univ. of Tokyo*)
D. Hirai (*Univ. of Tokyo*)

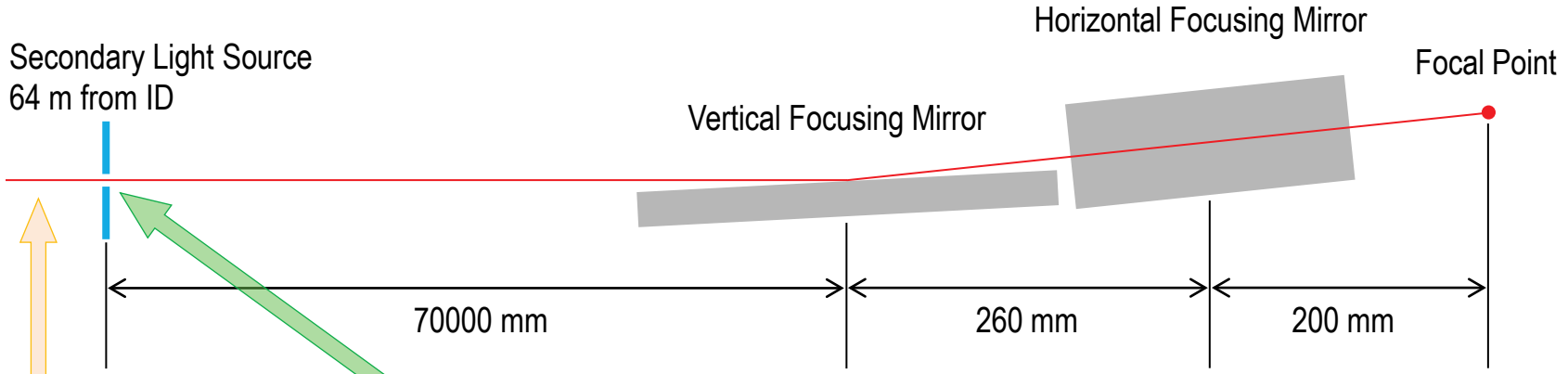
$DyMnO_3$

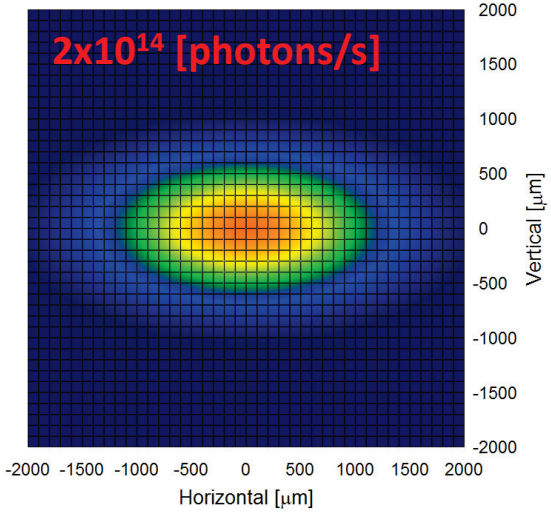
H. Sagayama (*Tohoku Univ.*)
N. Abe (*Tohoku Univ.*)
K. Taniguchi (*Tohoku Univ.*)
Y. Tokura (*Univ. of Tokyo*)
D. Okuyama (*RIKEN ASI*)
Y. Yamasaki (*Univ. of Tokyo*)

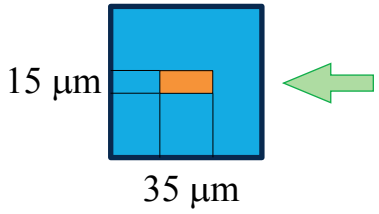
RIKEN SPring-8

X-ray focusing optics in BL19LXU/SPring-8

BL19LXU/SPring-8







Slit Size

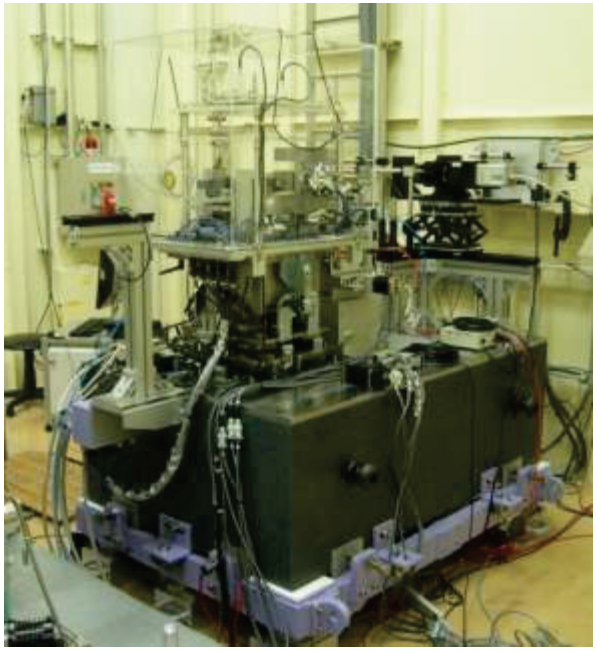
$$\text{Horizontal}: \quad 35\,[\mu\text{m}] = \frac{70260\,[\text{mm}]}{200\,[\text{mm}]} \times 100\,[\text{nm}]$$

$$\text{Vertical}: \quad 15\,[\mu\text{m}] = \frac{70000\,[\text{mm}]}{460\,[\text{mm}]} \times 100\,[\text{nm}]$$

H. Yumoto, H.O *et al.*, AIP Conf. Proc. **1365**, 200 (2011).

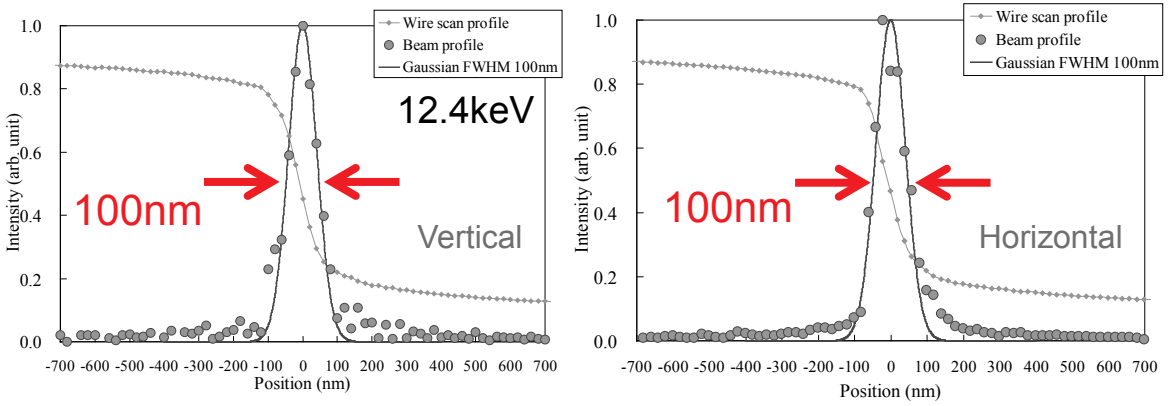
X-ray nanobeam available at BL19LXU/SPring-8

BL19LXU/SPring-8

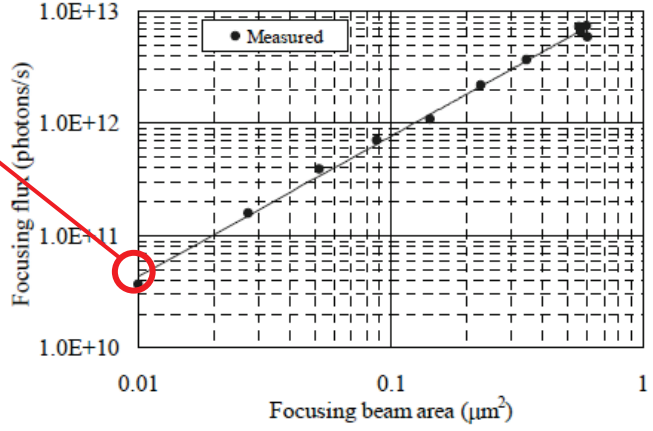


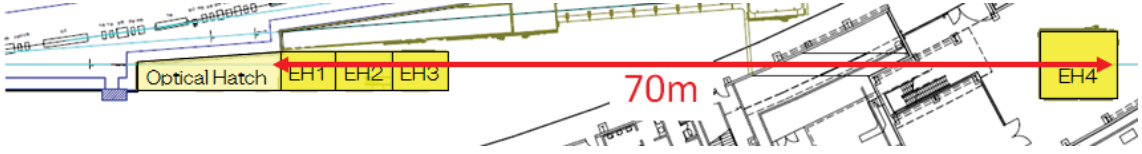
KB mirror optics

Focusing intensity profile and photon flux



3.7×10^{10} photons/s
@ 100×100 nm^2





H. Yumoto, H.O *et al.*, AIP Conf. Proc. **1365**, 200 (2011).

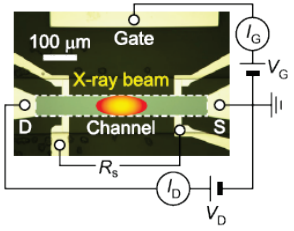
Operand XRD measurement on an EDLT device

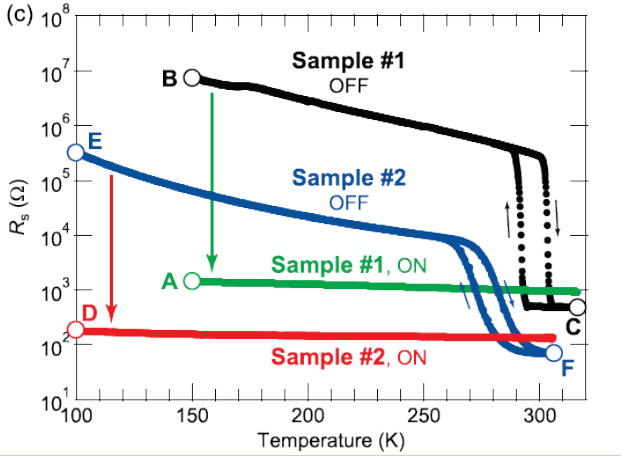
VO_2 – electric-double layer transistor

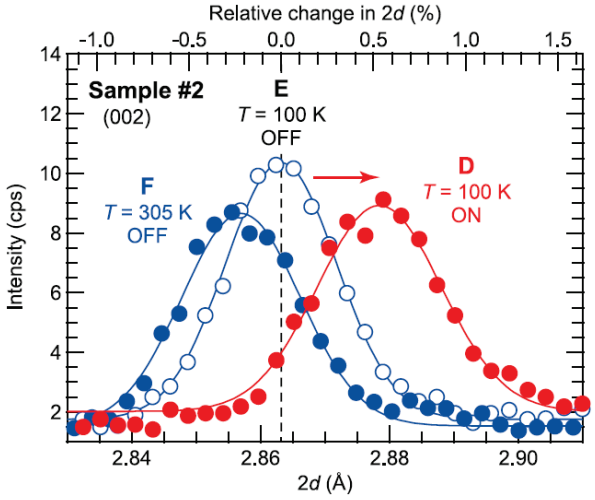
(a)

	Sample #1	Sample #2
Substrate	TiO_2 (001)	TiO_2 (001)
Film	VO_2	$V_{0.98}W_{0.02}O_2$
Thickness	10 nm	40 nm
Condition	Vacuum	N_2 flow

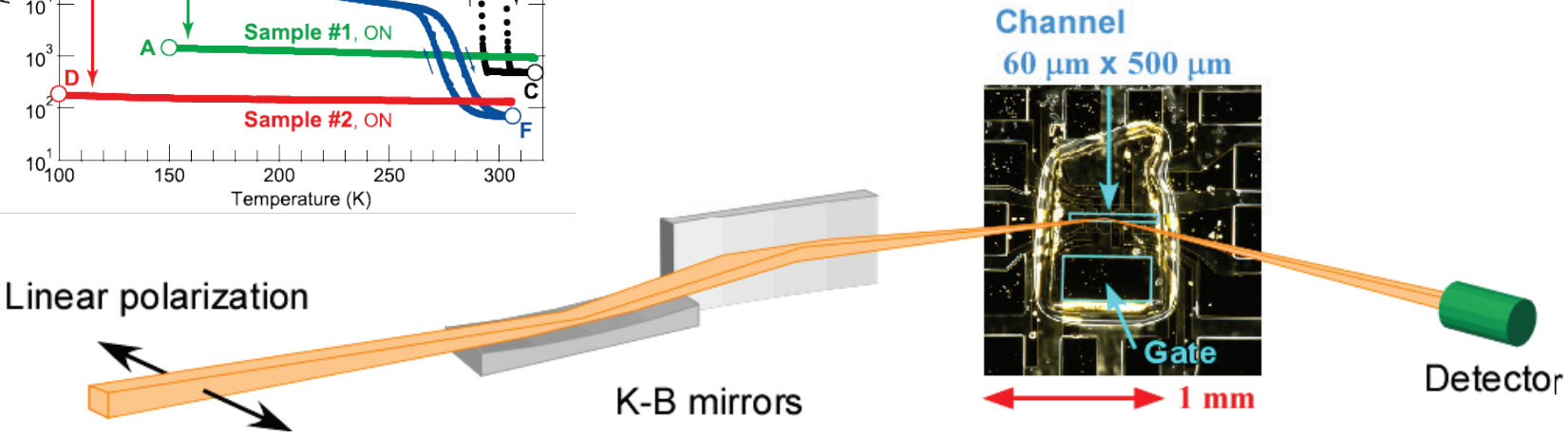
(b)







XRD patterns of the 002 reflection



D. Okuyama, H.O *et al.*, APL**104**, 023507 (2014).

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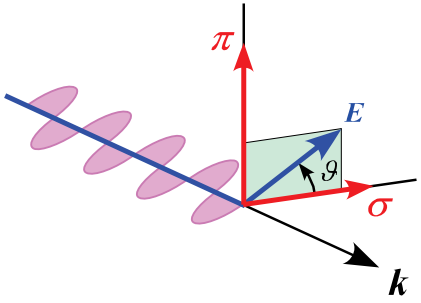
Matrix representation of polarization

Electric field

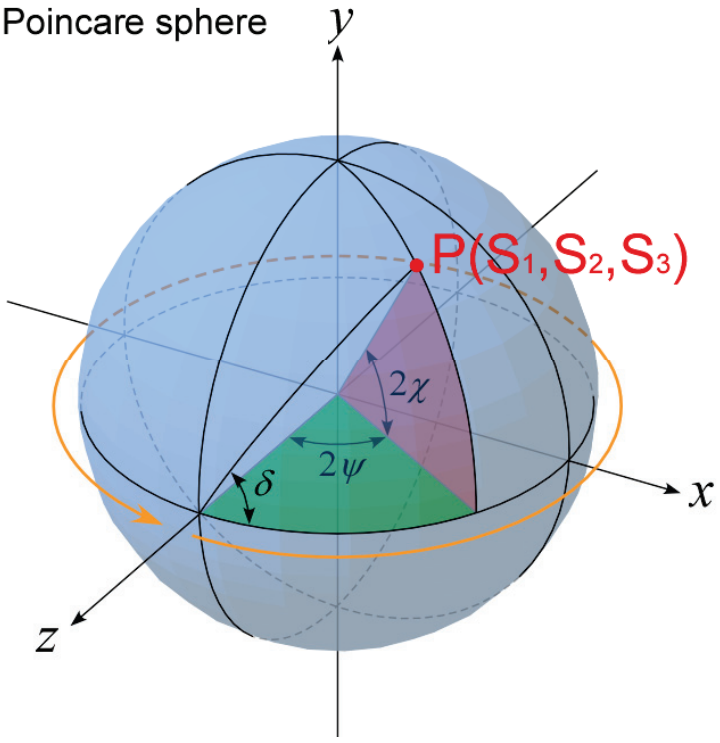
$$\boldsymbol{E}(\boldsymbol{r},t)=\begin{pmatrix}E_\sigma e^{i\delta_\sigma}\\ E_\pi e^{i\delta_\pi}\end{pmatrix}e^{i(\omega t-\boldsymbol{k}\cdot\boldsymbol{r})}$$



Density matrix

$$\hat{\rho}=\frac{\boldsymbol{E}(\boldsymbol{r},t)\boldsymbol{E}^{\dagger}(\boldsymbol{r},t)}{E_\sigma{}^2+E_\pi{}^2}$$

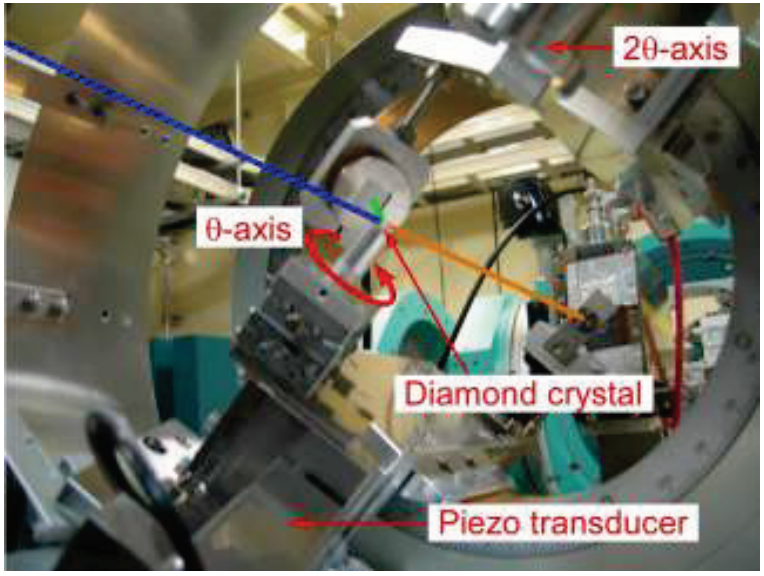
$$=\frac{1}{2}\left[\begin{pmatrix}1&0\\0&1\end{pmatrix}+P_{45}\begin{pmatrix}0&1\\1&0\end{pmatrix}+P_{\mathrm{C}}\begin{pmatrix}0&-i\\i&0\end{pmatrix}+P_{\mathrm{L}}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\right]$$

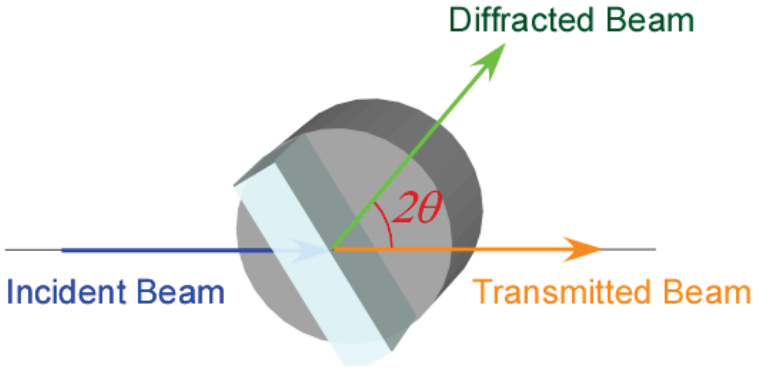


Stokes parameters

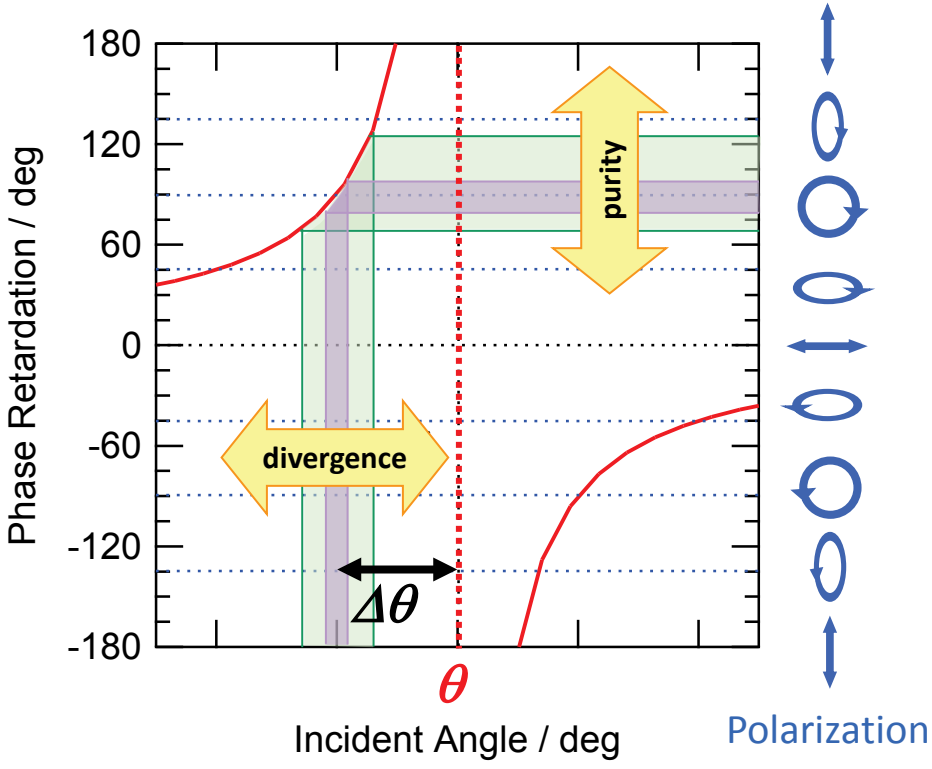
$$\boldsymbol{P}=(P_{45},P_{\mathrm{C}},P_{\mathrm{L}})=\left(\frac{2E_\sigma E_\pi}{E_\sigma{}^2+E_\pi{}^2}\cos(\delta_\sigma-\delta_\pi),\quad -\frac{2E_\sigma E_\pi}{E_\sigma{}^2+E_\pi{}^2}\sin(\delta_\sigma-\delta_\pi),\quad \frac{E_\sigma{}^2-E_\pi{}^2}{E_\sigma{}^2+E_\pi{}^2}\right)$$

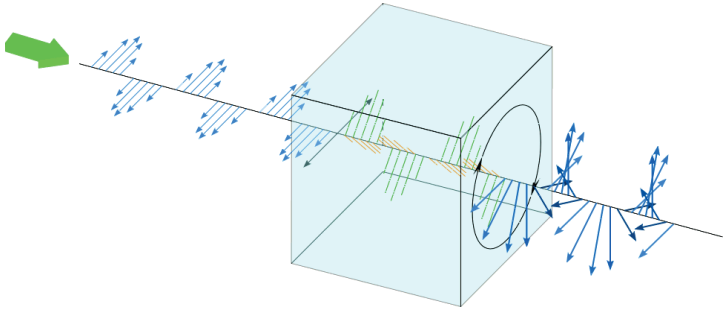
Manipulation of X-ray polarization



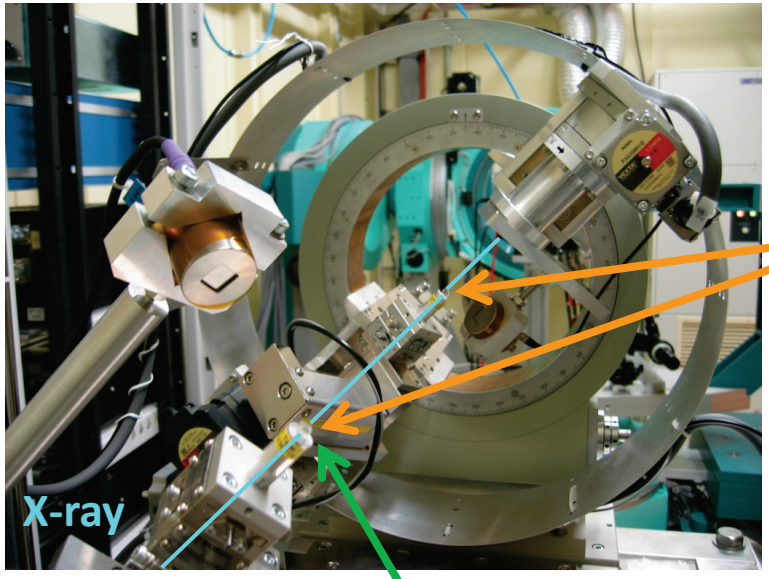


X-ray phase retarder

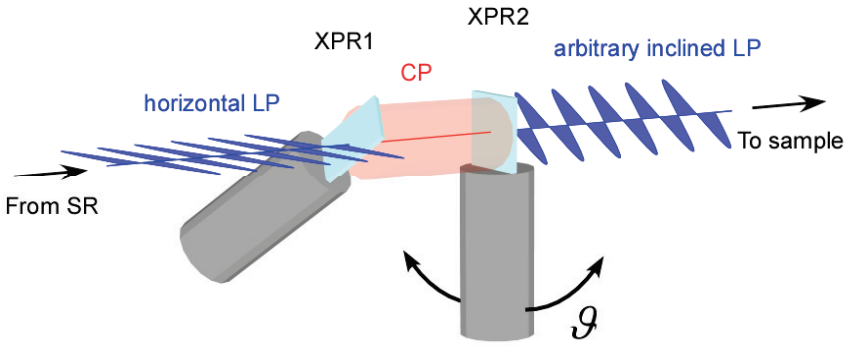




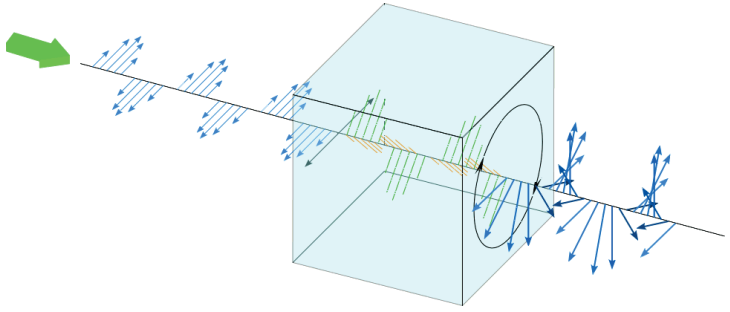
Manipulation of X-ray polarization

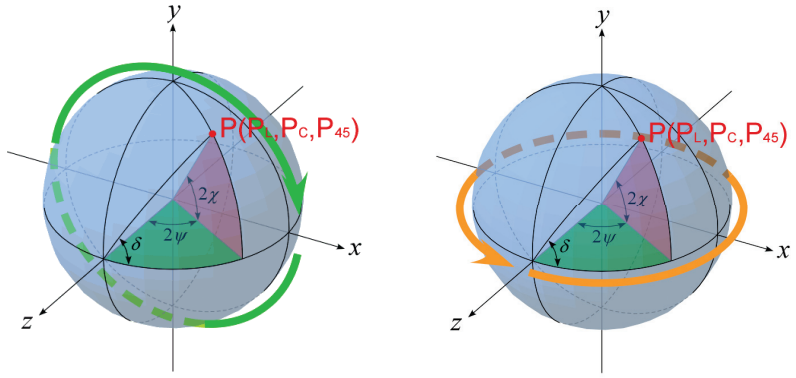


Inclined linear polarization ($P_{45}^2+P_L^2=1$)



Elliptical polarization ($P_C^2+P_L^2=1$)





Transformation into arbitrary polarization

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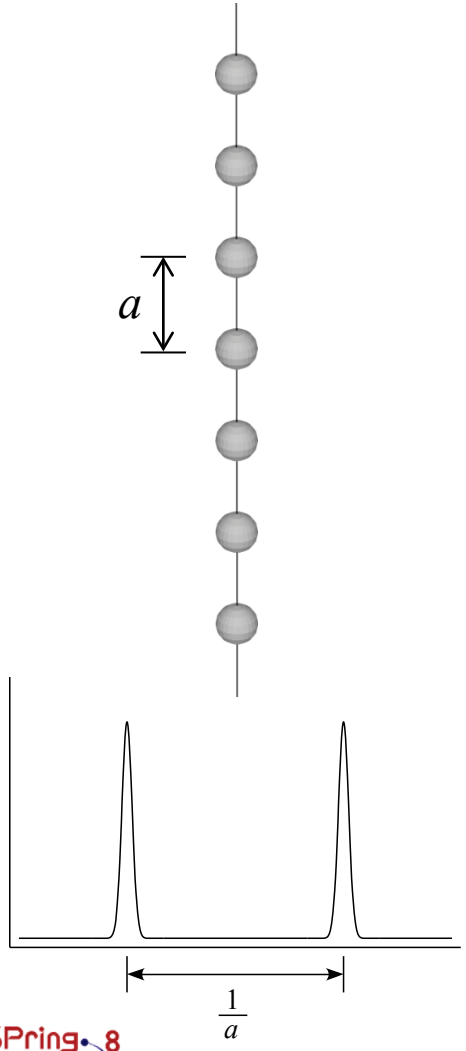
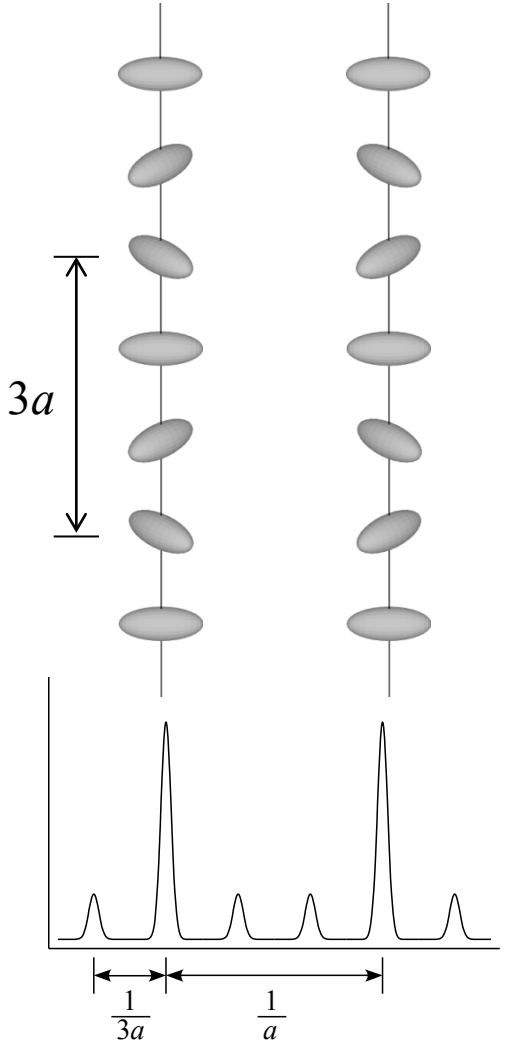
Resonant circularly polarized X-Ray diffraction

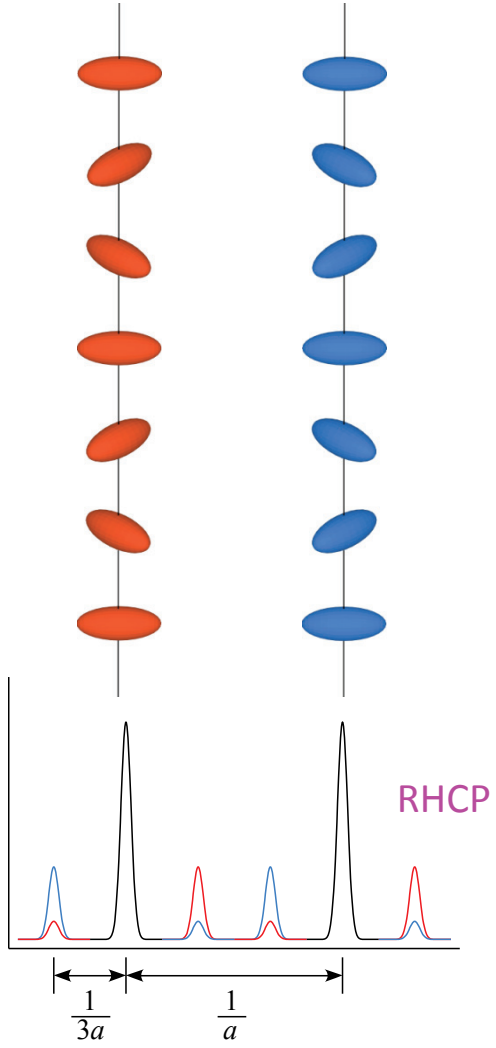
Non Resonant XRD



Resonant LP XRD



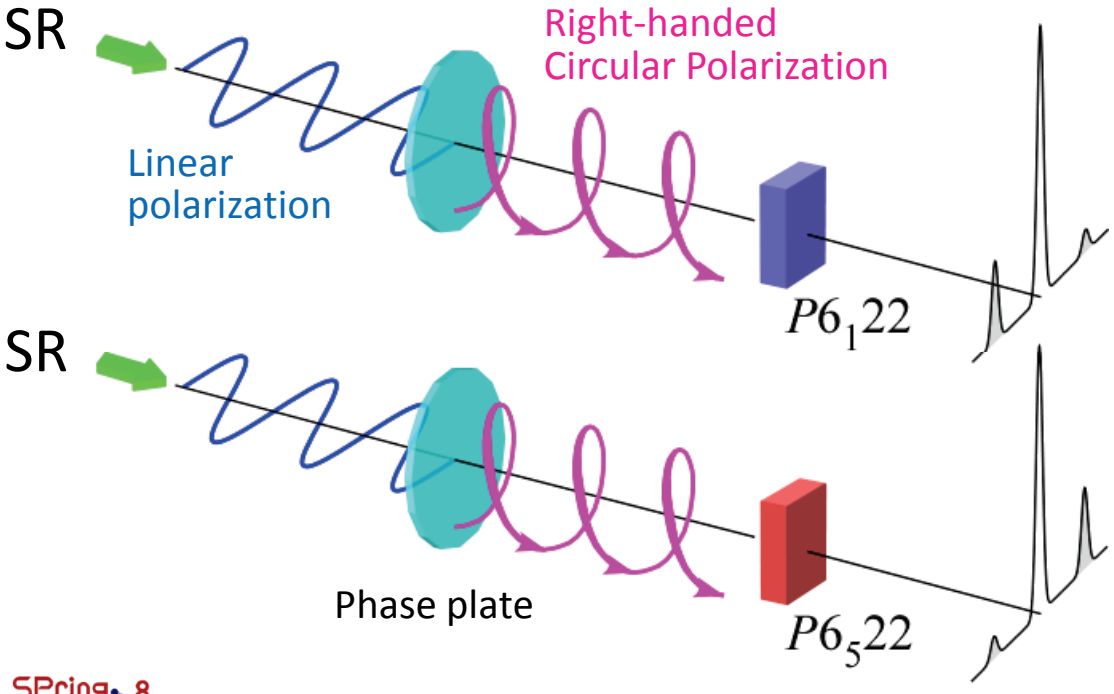
Resonant CP XRD

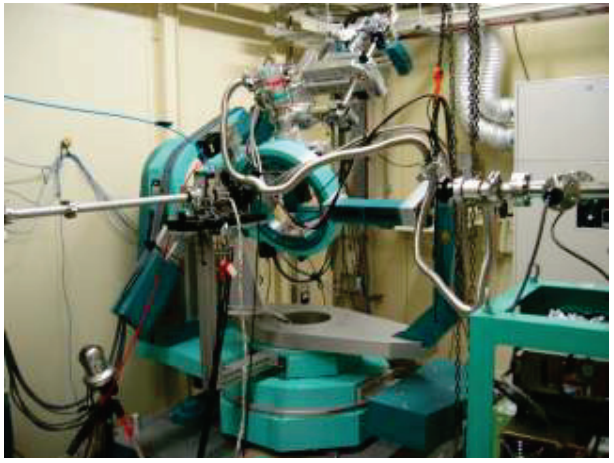


SPring-8

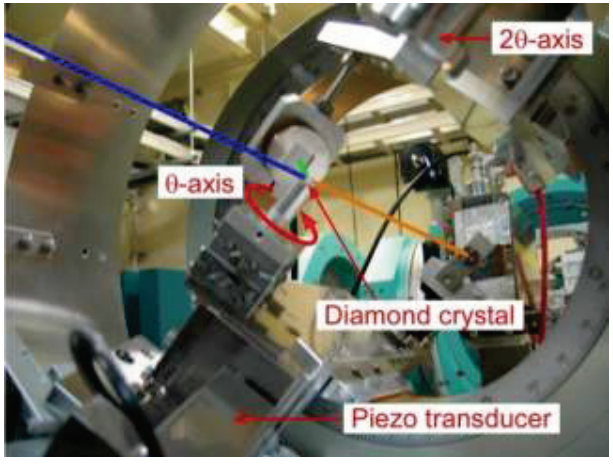
Experimental detail

Beamline:	BL19LXU/SPring-8
X-ray energy:	Cu *K*-edge
Phase Plate:	C(001) t=1.0mm
X-ray detector:	AMPTEK XR100-CR (Si-PIN)
Sample cooling:	Closed-cycle He gas refrigerator





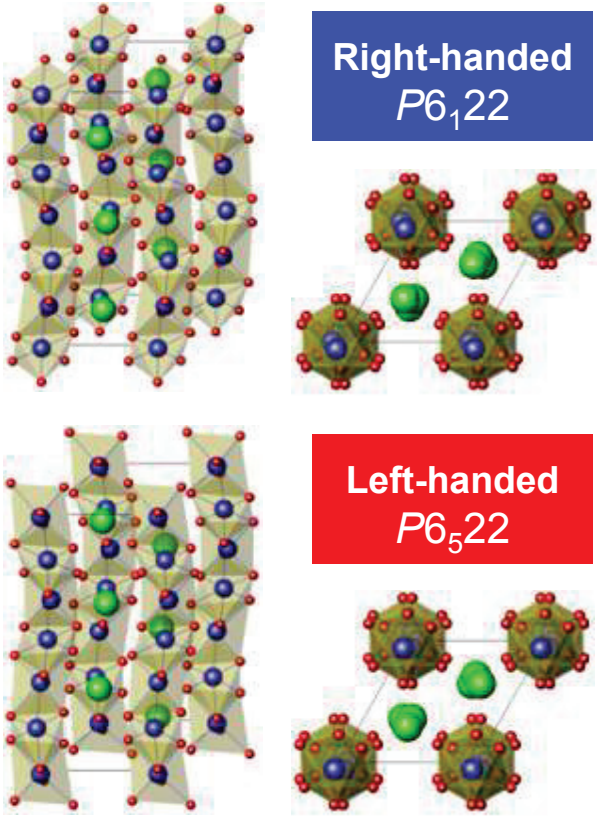
Six-circle diffractometer



X-ray phase retarder

Discrimination of enantiomorph crystals

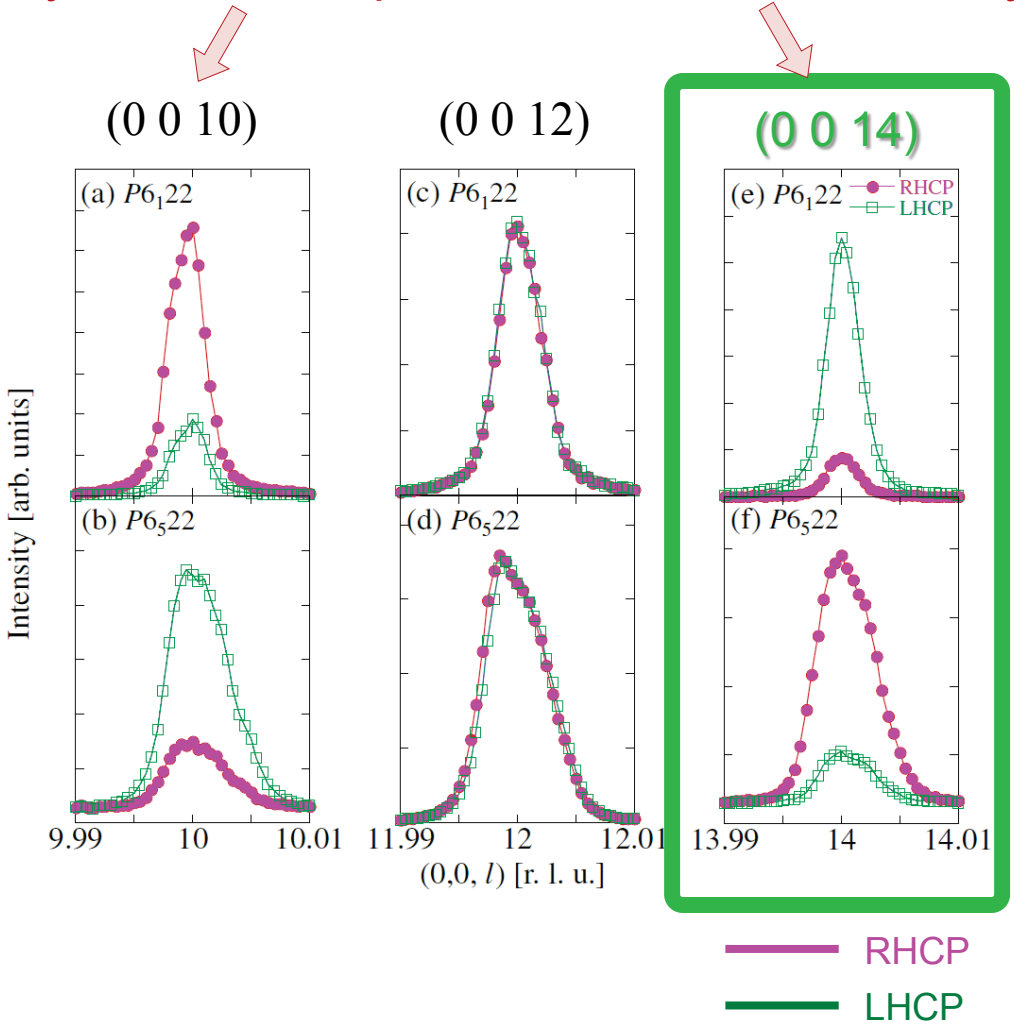
$CsCuCl_3$



Right-handed
$P6_122$

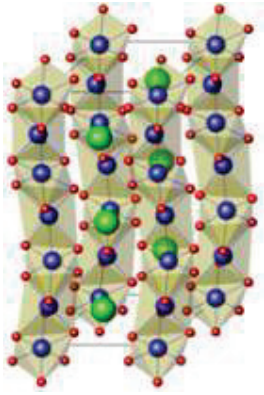
Left-handed
$P6_522$

Asymmetrical superlattice reflection intensity

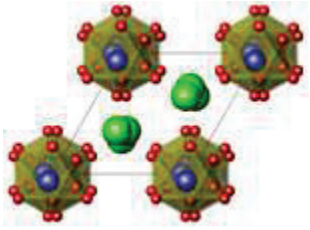


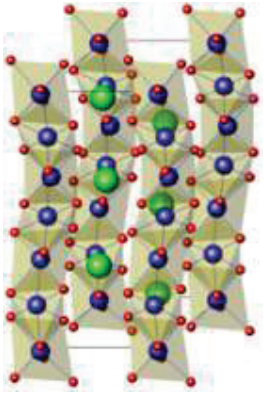
Y. Kousaka, H.O *et al.*, JPSJ **78**, 123601 (2009).

Flipping ratio (measure of handedness)

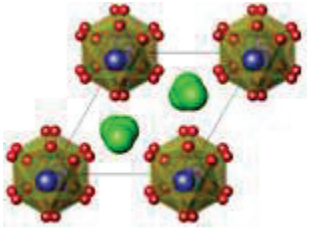


Right-handed
$P6_122$





Left-handed
$P6_522$

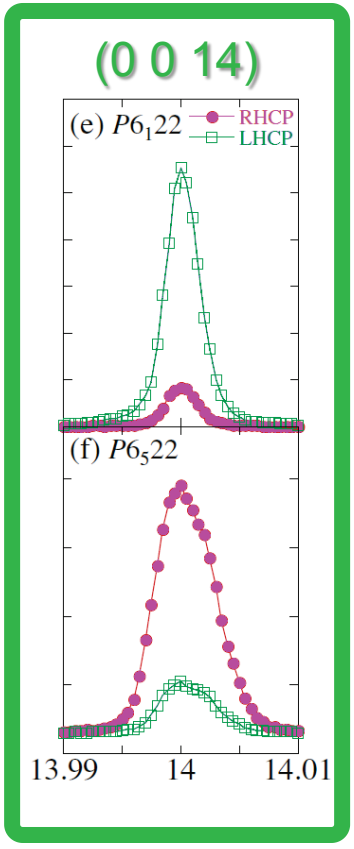


$FR < 0$

$FR > 0$

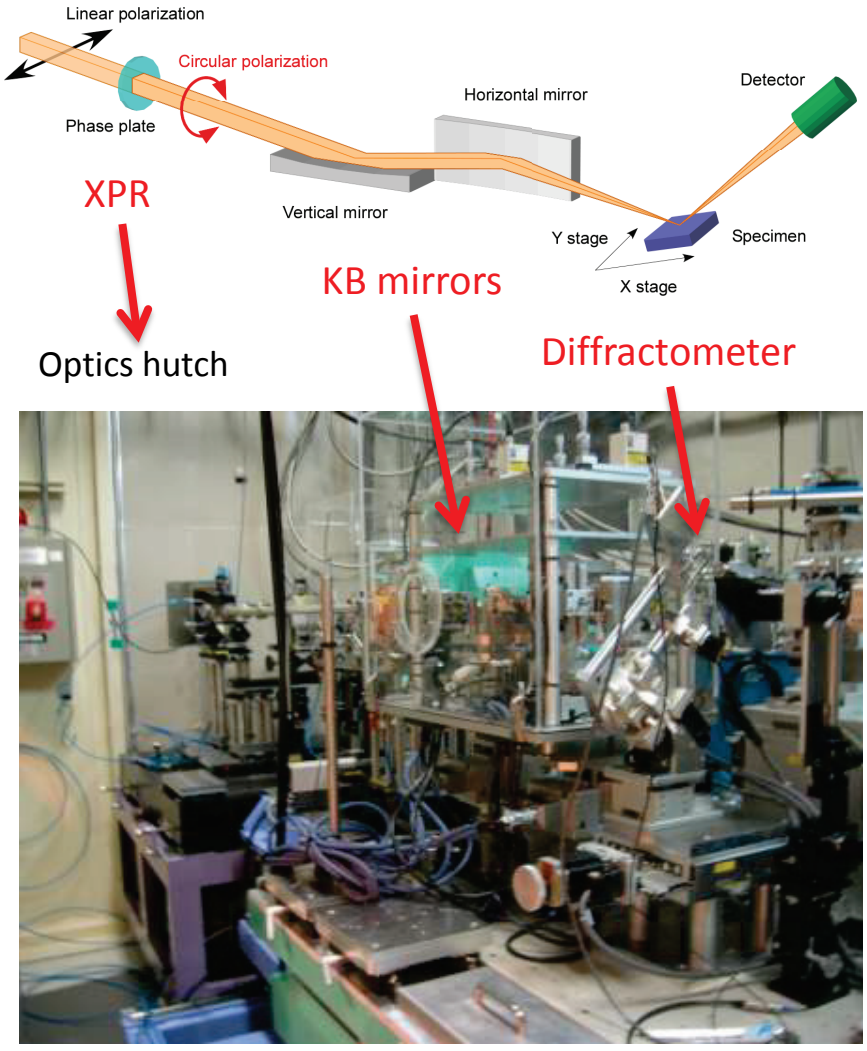
Flipping Ratio

$$FR = \frac{I(RHC) - I(LHC)}{I(RHC) + I(LHC)}$$



Y. Kousaka, H.O *et al*., JPSJ **78**, 123601 (2009).

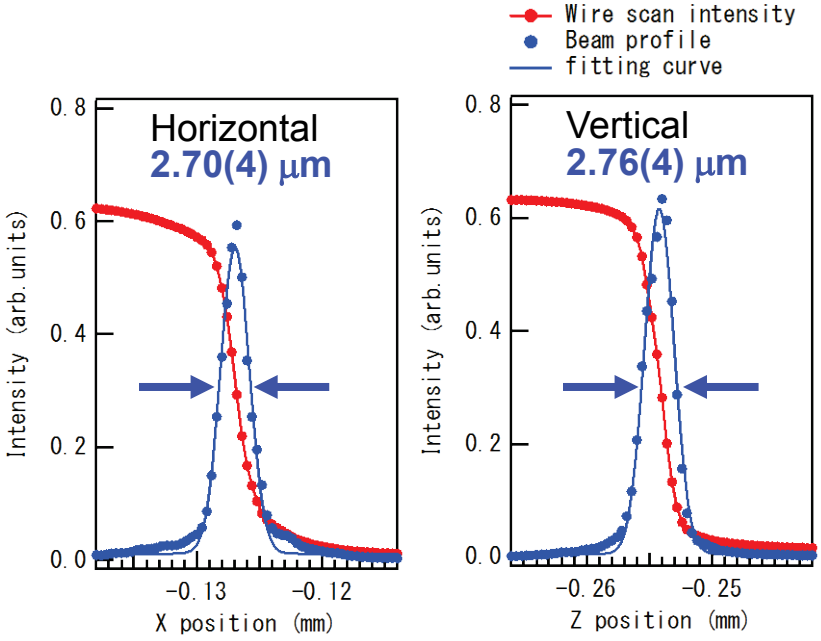
Experimental detail



KB mirrors optics installed at BL39XU

BL39XU/SPring-8

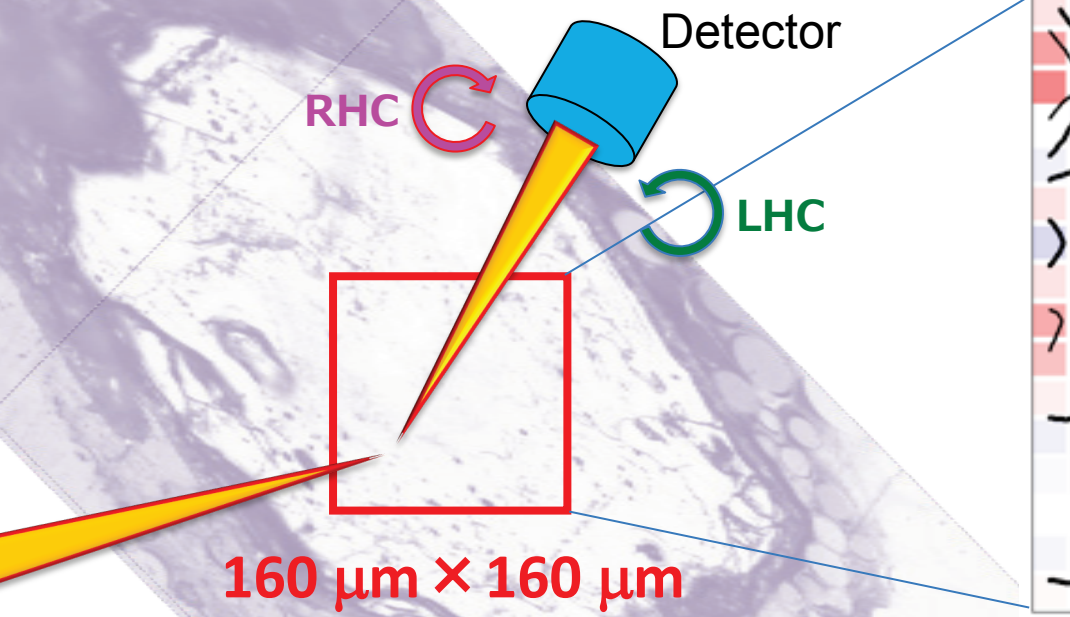
- X-ray (Cu *K*-edge)
- Detector (SDD)
- *Pc*≈±0.993 (simulation)
- Beam size @ sample position



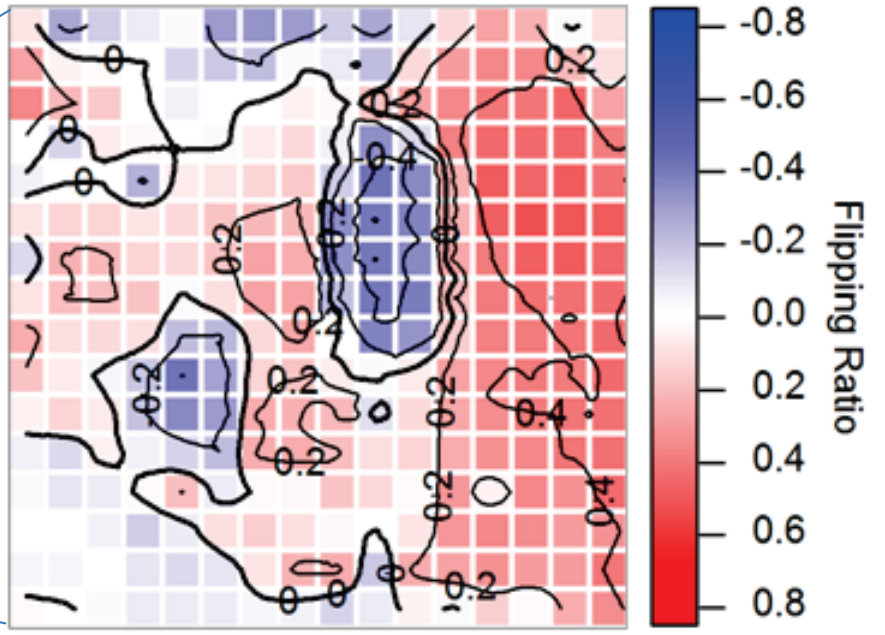
Focusing intensity profiles

Chirality domain structure on the (001) surface

$$FR = \frac{I(RHC) - I(LHC)}{I(RHC) + I(LHC)}$$



8.986 keV



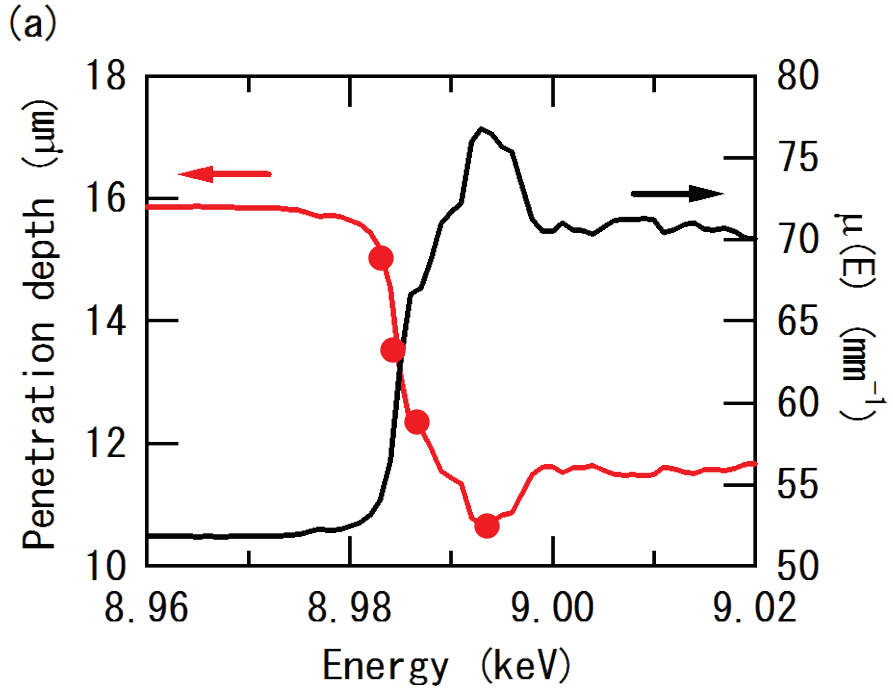
Right-handed $P6_122$

Left-handed $P6_522$

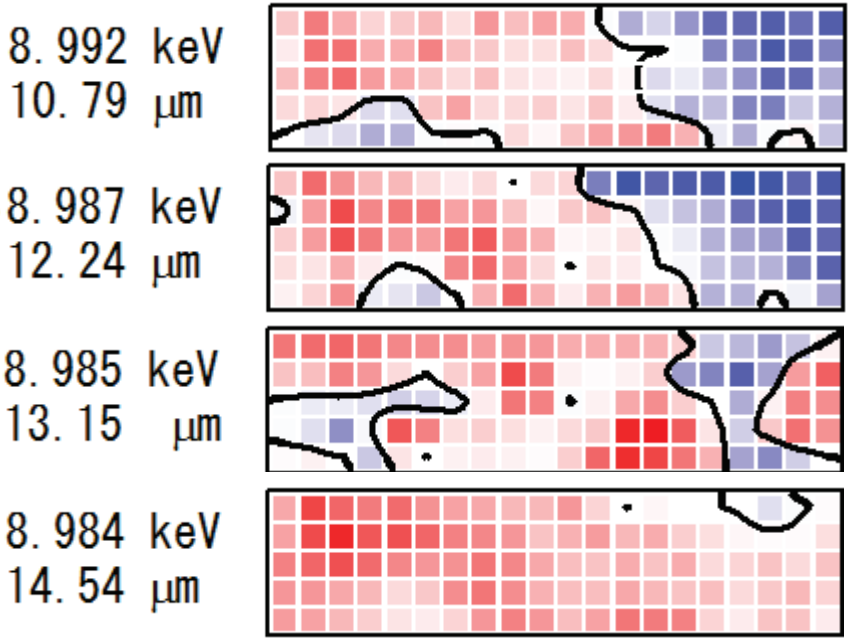
Beamsize: 2.7 × 2.7 μm²
Pitch: 10 μm
Probing depth: 10.5 μm

RIKEN SPring-8

Depth profiling by controlling X-ray penetration



Penetration depth depends on photon energy

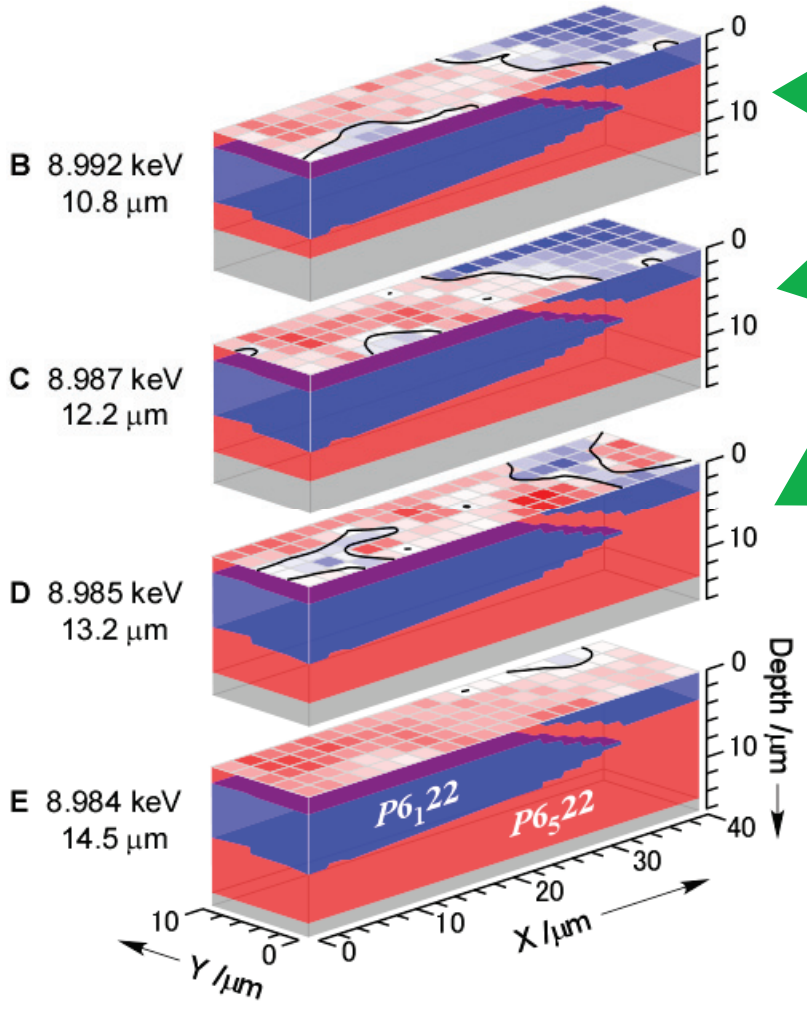


Observed Images depend on photon energy

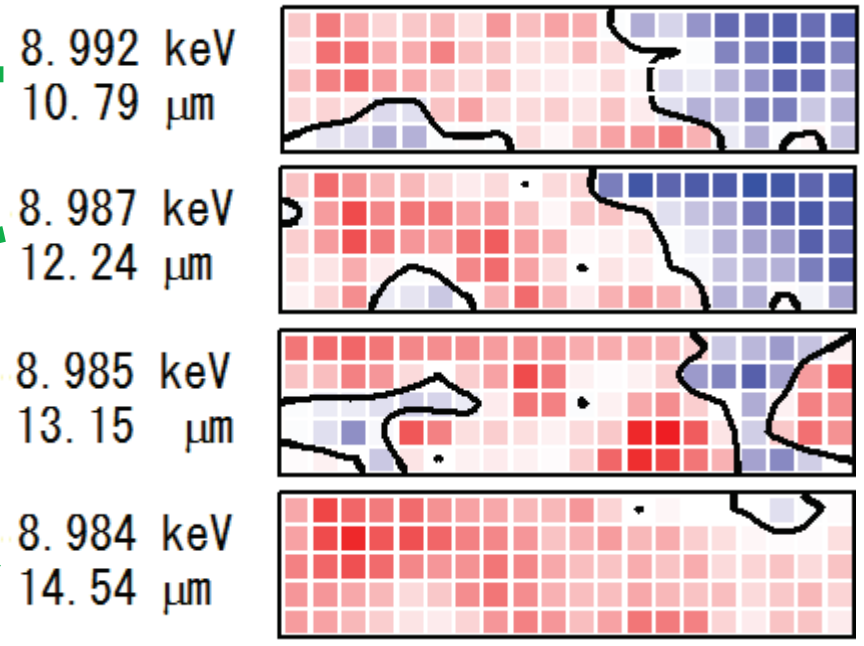
Raster Image + Depth profile = 3D Image

RIKEN SPring-8

3D imaging of chirality domain structure



Reconstructed 3D Image



Observed Images depend on photon energy

Morphological features

In-plane : several tens of microns

Out-of-plane : few microns

H. Ohsumi *et al.*, Angew. Chem. Int. Ed **52**, 8718 (2013).

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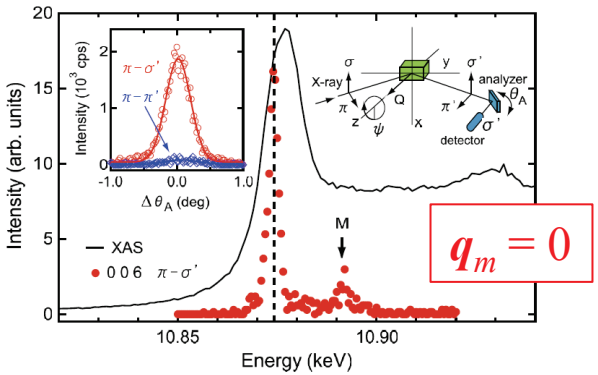
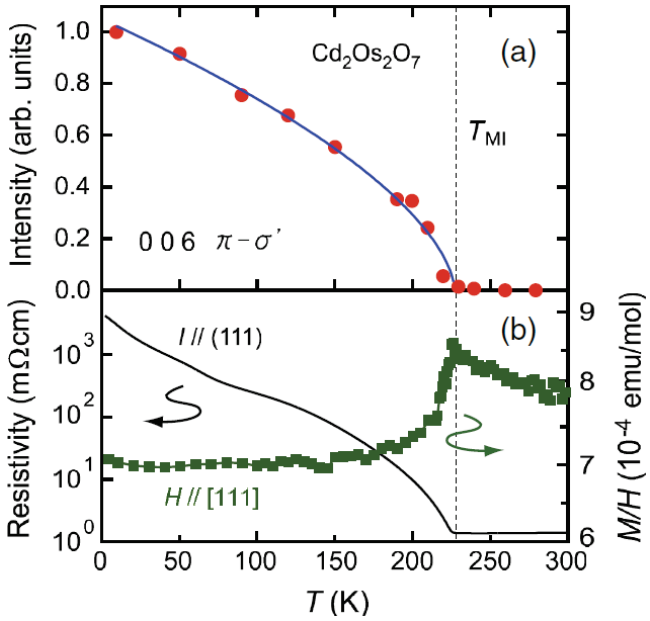
   - Improvement in the photon flux density

Determined magnetic structure of $Cd_2Os_2O_7$

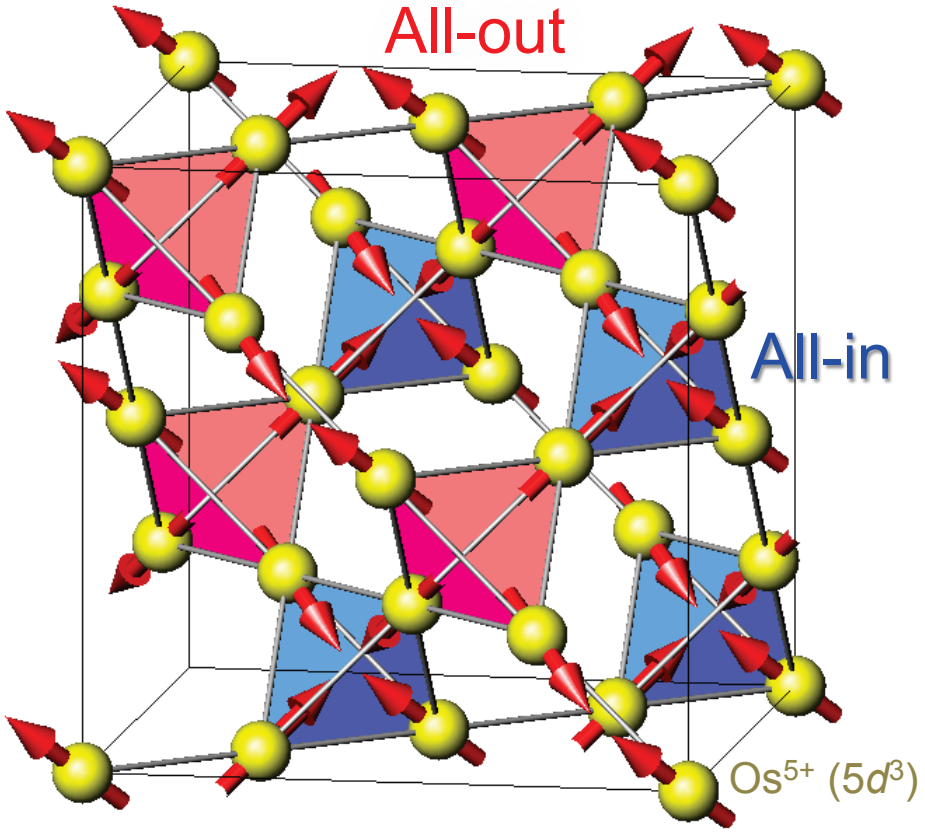


Spectra of the 006 reflection intensity



T dependence of the 006 reflection intensity

all-in-all-out type

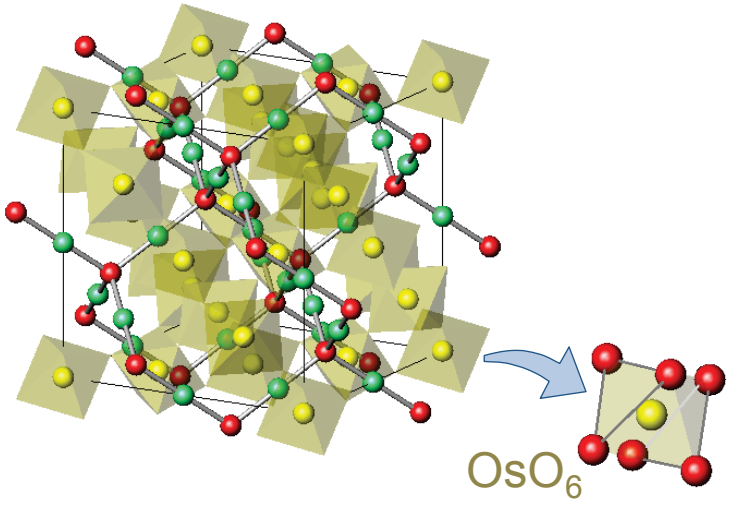


Pyrochlore lattice of Os

J. Yamaura, H.O *et al.*: PRL **108**, 247205 (2012).

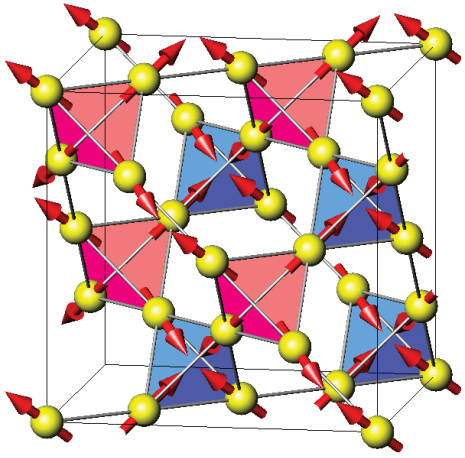
Circularly polarized X-rays distinguish between AIAO and AOAI

Anisotropy in Tensor Susceptibility



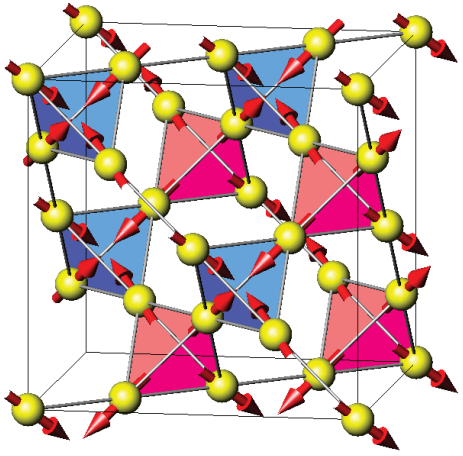
$$F_{\mathrm{ATS}}\begin{pmatrix} \sin 2\Psi & -\sin\theta\cos 2\Psi \\ \sin\theta\cos 2\Psi & \sin^2\theta\sin 2\Psi \end{pmatrix}$$

All-In/All-Out



$$F_{\mathrm{mag}}\begin{pmatrix} 0 & i\sin\theta \\ i\sin\theta & 0 \end{pmatrix}$$

All-Out/All-In



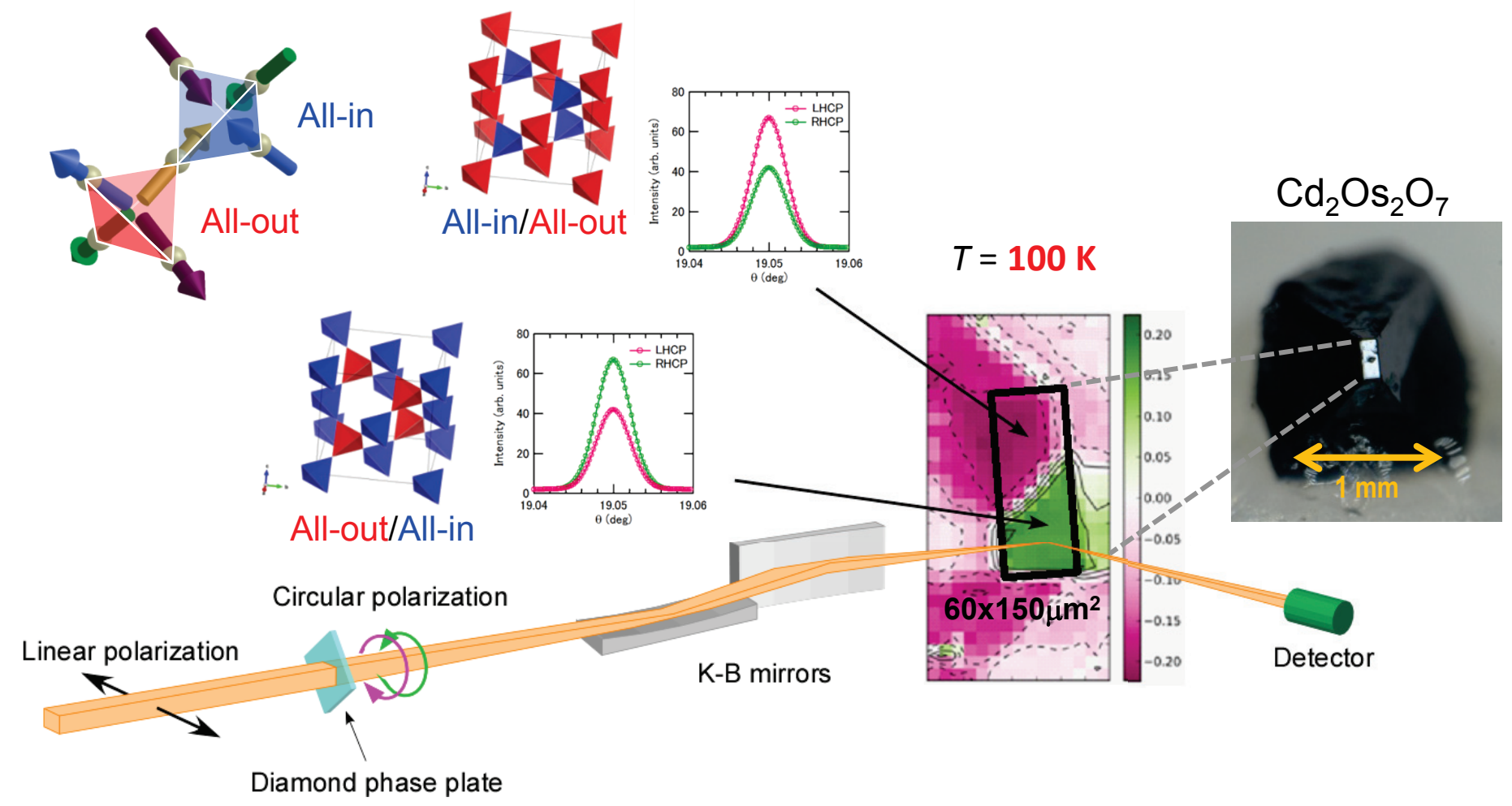
$$-F_{\mathrm{mag}}\begin{pmatrix} 0 & i\sin\theta \\ i\sin\theta & 0 \end{pmatrix}$$

$$I_{004n+2}(P_C) \propto \left|F_{\mathrm{ATS}}\right|^2\left[\sin^2\theta + 2\sin^2\Psi\cos^2\Psi\cos^4\theta\right] + \left|F_{\mathrm{mag}}\right|^2\sin^2\theta \mp P_C \,\mathrm{Re}\left[F_{\mathrm{ATS}}{}^{*}F_{\mathrm{mag}}\right]\sin 2\Psi\sin\theta\cos^2\theta$$

P_c = +1: RHCP
P_c = −1: LHCP

RIKEN SPring-8

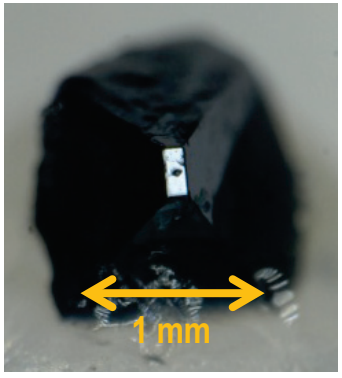
Magnetic domain structure on the (001) surface

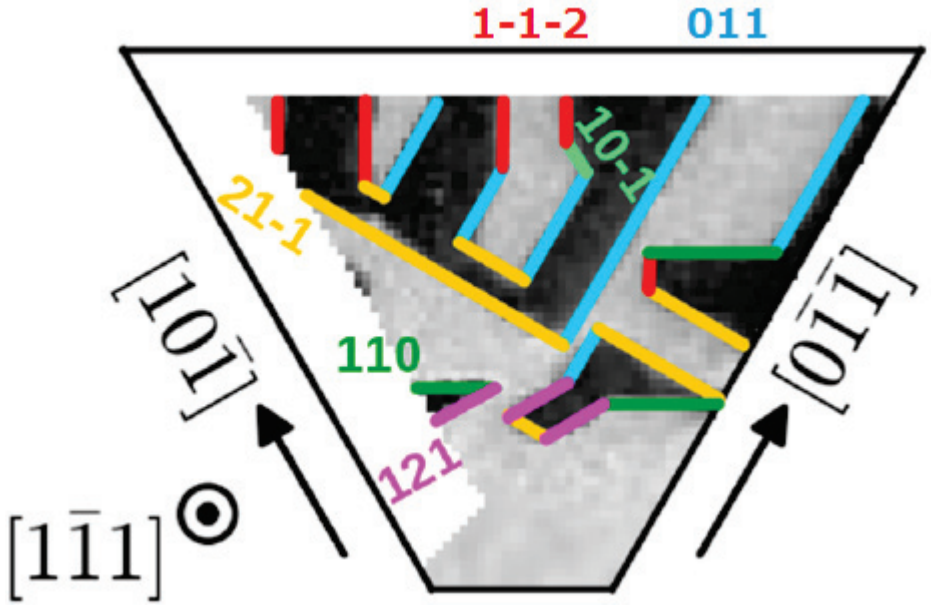


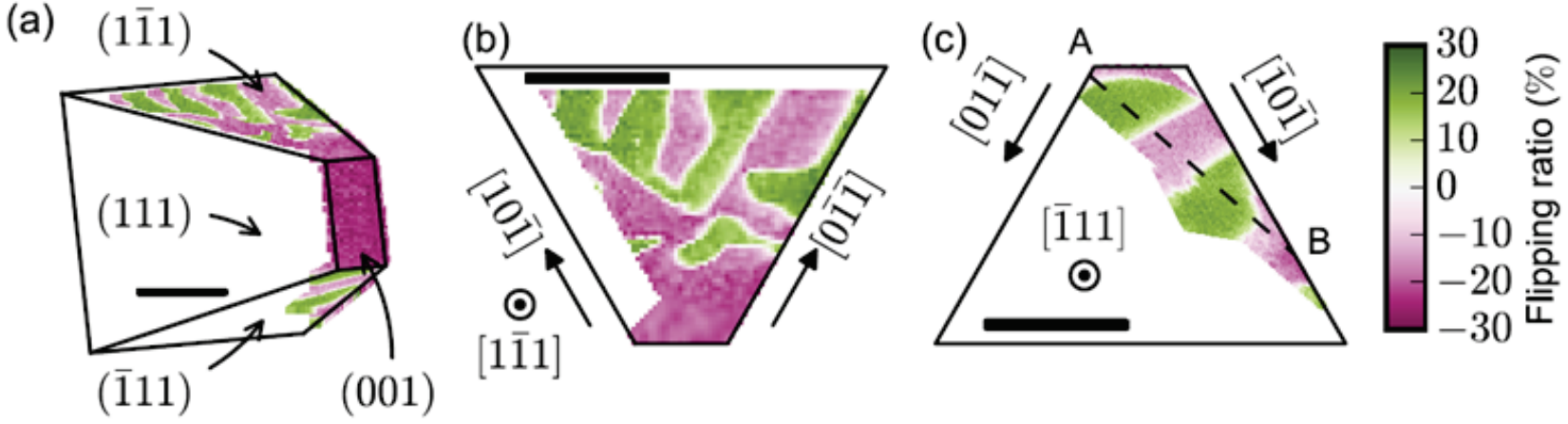
S. Tardif, H.O *et al.*, PRL **114**,147205 (2015).

Magnetic domain structure on the other facets

$Cd_2Os_2O_7$

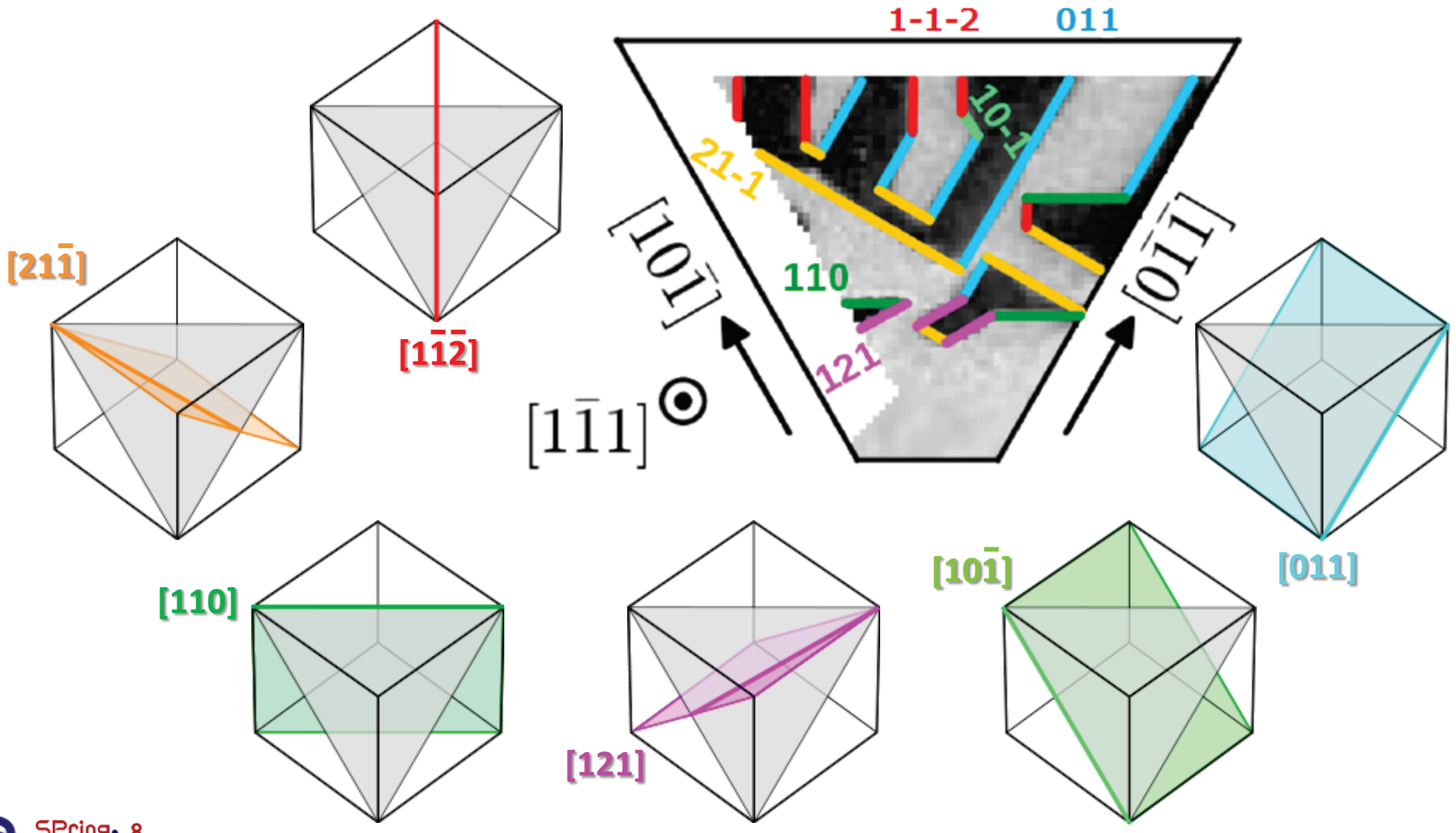






S. Tardif, H.O *et al.*, PRL **114**,147205 (2015).

Identification of magnetic domain walls



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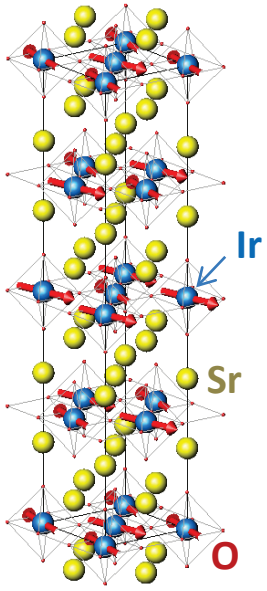
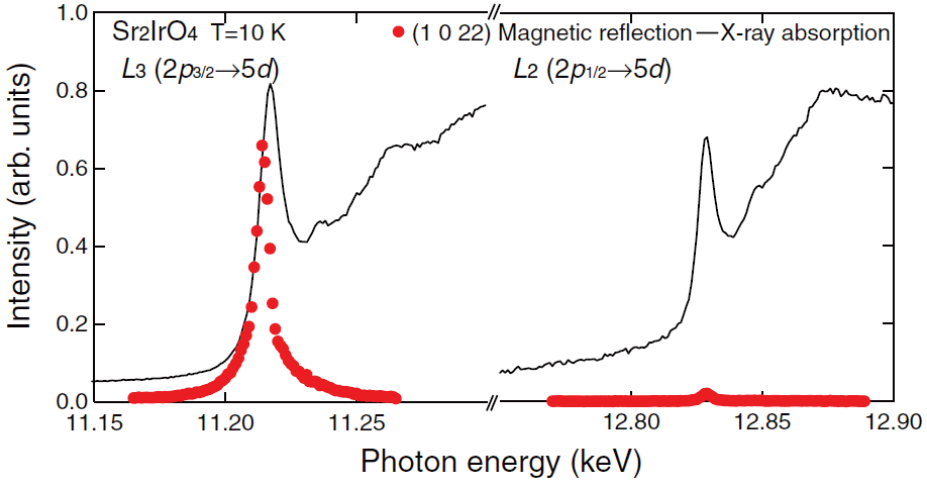
Relativistic Mott insulator Sr_2IrO_4



Magnetic structure



Energy profiles of Resonance Peaks

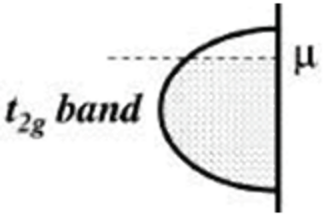
S=1/6, L=2/3

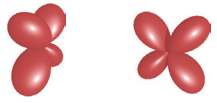
$\mu_{\mathrm{eff}} = 0.77\ \mu_{\mathrm{B}}$

Ir^{4+} ($5d^5$)

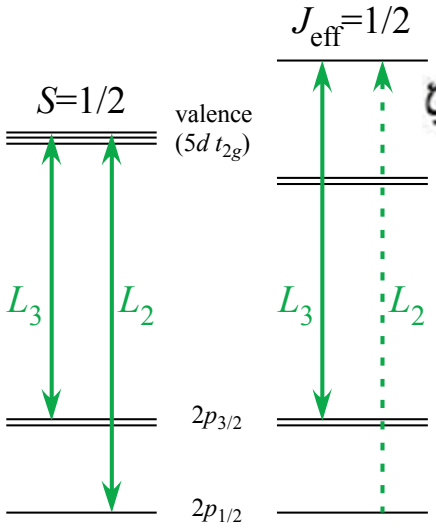
$\mu_{\mathrm{eff}} \sim 0.5\ \mu_{\mathrm{B}}$

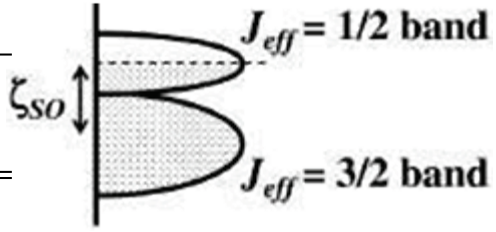
Insulator

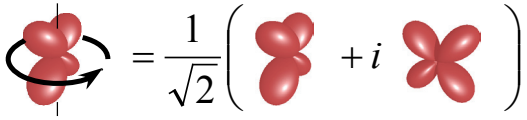




S=1/2 state



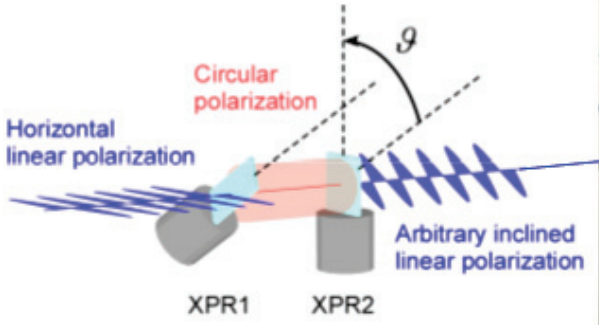


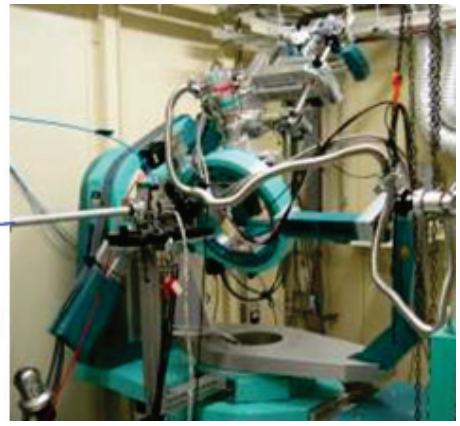


J_{eff}=1/2 state

B. J. Kim, H.O *et al.*, Science **323**, 1329 (2009).

Evaluation of *L*/*S* by non-resonant X-ray magnetic scattering





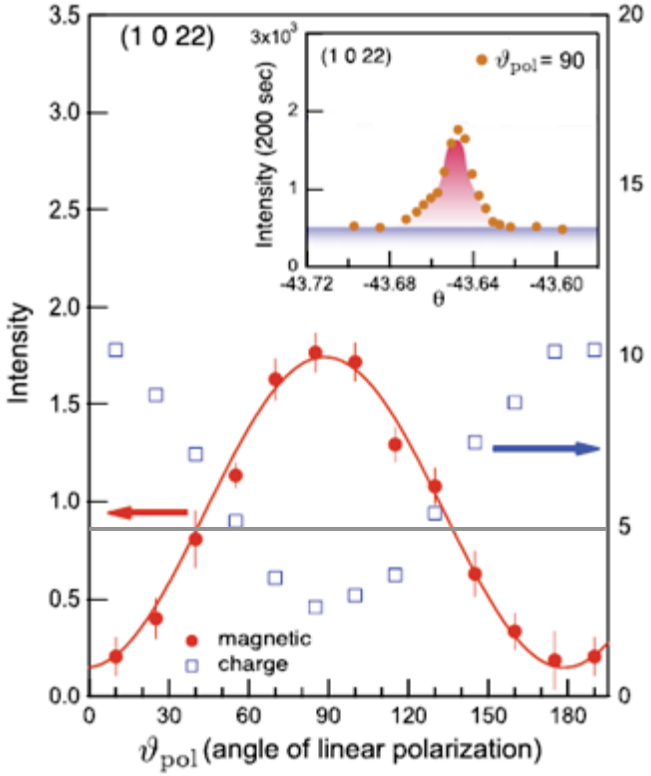
$$I(\vartheta) = I_0 + I_{45}\sin 2\vartheta + I_L \cos 2\vartheta$$

Charge

$$\begin{cases} I_0 = |F(K)|^2 \left(\sin^4\theta + \cos^4\theta\right) \\ I_{45} = 0, \quad I_L = |F(K)|^2 2\sin^2\theta\cos^2\theta \end{cases}$$

Magnetic

$$\begin{cases} I_0 = \left(\dfrac{\hbar\omega}{mc^2}\sin\theta\sin 2\theta\right)^2 |S(K)|^2 \left[\left(\dfrac{1}{\sin\theta} + \dfrac{2L\sin\theta}{S}\right)^2 - \left(\dfrac{2L\sin\theta}{S}\right)\left(\dfrac{1}{\sin\theta} + \dfrac{L\sin\theta}{S}\right)\right] \\ I_{45} = 0, \quad I_L = -\left(\dfrac{\hbar\omega}{mc^2}\sin\theta\sin 2\theta\right)^2 |S(K)|^2 \left[\left(\dfrac{2L\sin\theta}{S}\right)\left(\dfrac{1}{\sin\theta} + \dfrac{L\sin\theta}{S}\right)\right] \end{cases}$$

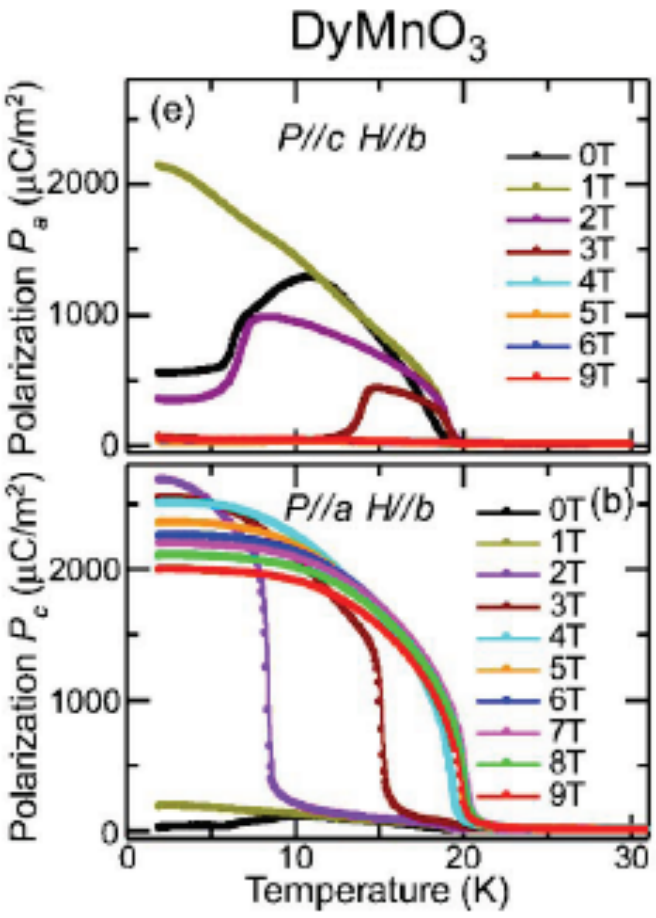


$$J_{eff} = \frac{1}{2}, \quad \frac{L}{S} = 5.0 \pm 0.7$$

$$S = \frac{1}{2}, \quad \frac{L}{S} = 0$$

S. Fujiyama, H. O *et al.*, PRL **112**, 016405 (2014).

Multiferroic material $DyMnO_3$

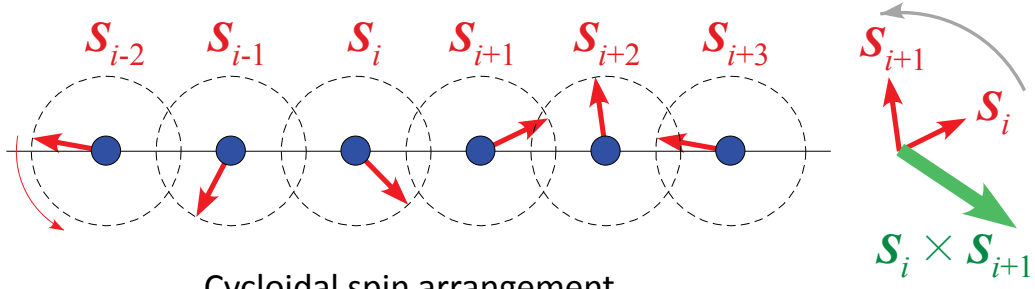


Temperature dependence of polarization.

T. Kimura et al., PRB **71**, 224425 (2005).

Spin-chirality driven ferroelectrics

Magnetic structure having vector spin chirality



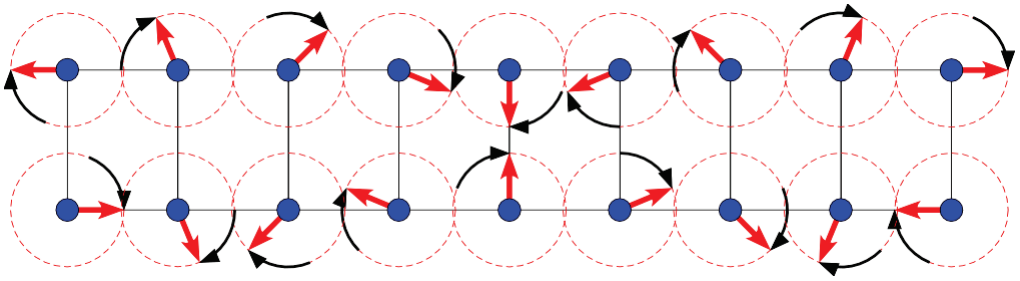
Cycloidal spin arrangement

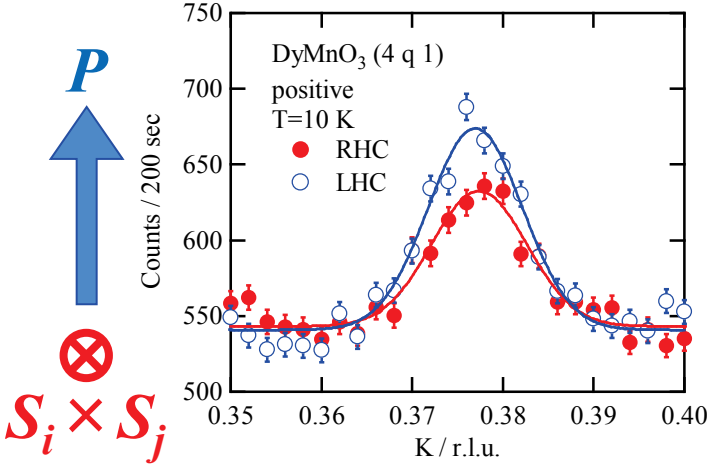
Spontaneous activation of Dzyaloshinskii-Moriya interaction in order to reduce total energy. $\mathcal{H}_{DM} = \boldsymbol{D} \cdot (\boldsymbol{S}_1 \times \boldsymbol{S}_2)$

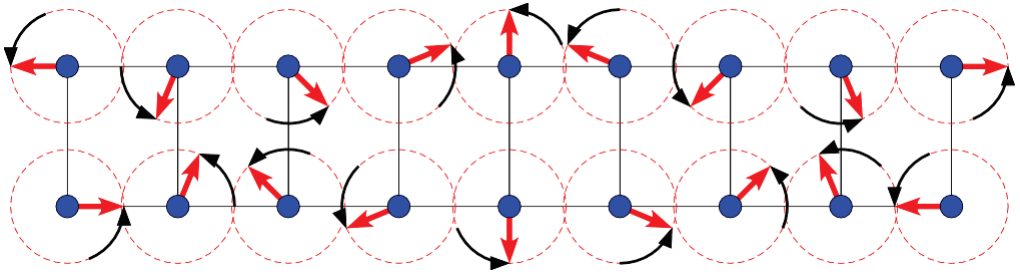
$\boldsymbol{D} = 0$ centrosymmetric non-polar	⇒	$\boldsymbol{D} \neq 0$ non-centrosymmetric local polarization

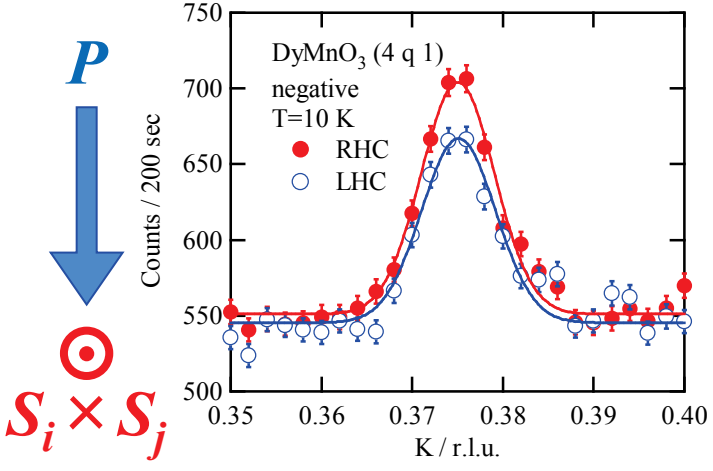
Violation of inversion symmetry

Discrimination of vector spin chirality by NRXMS





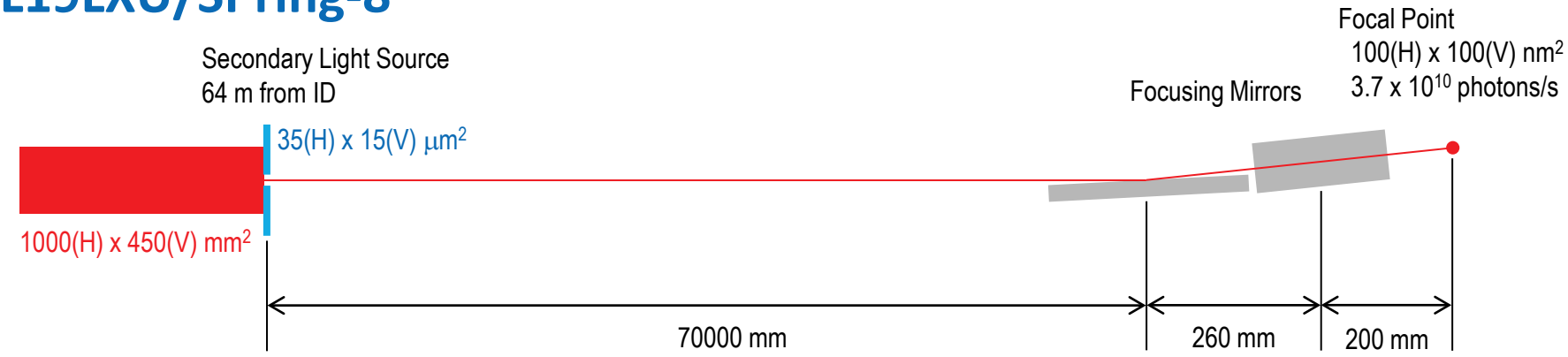




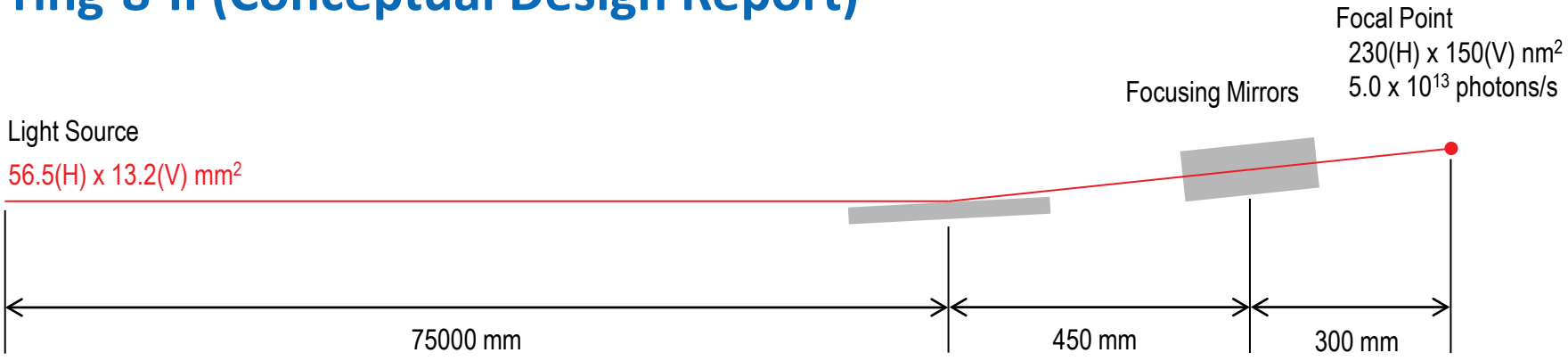
H. Sagayama, H.O *et al.*: JPSJ **79**, 043711 (2010).

The flux density will increase three orders of magnitude

BL19LXU/SPring-8



SPring-8-II (Conceptual Design Report)



Future prospects

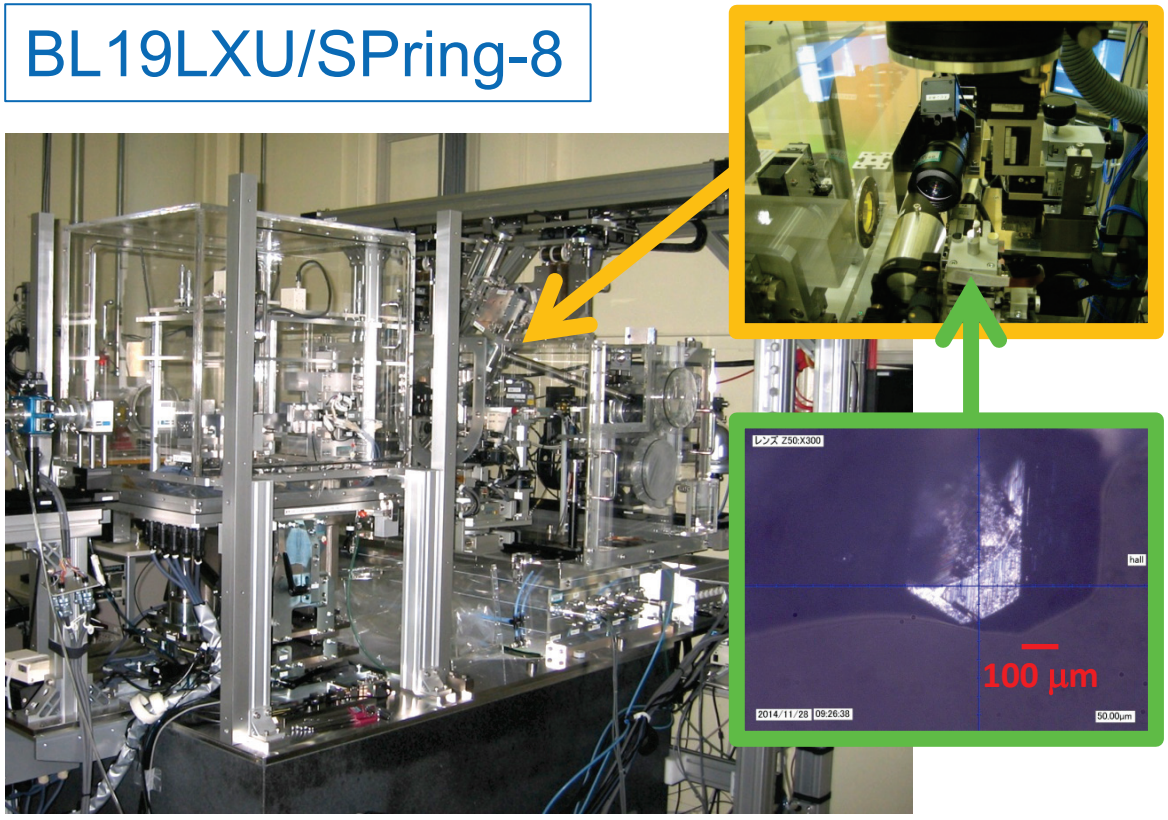
Polarized nanobeam X-ray diffraction techniques offer new opportunities to investigate hierarchical structures in real materials.

One of the most promising applications is the visualization of spatial variation of order parameters.

A thousand times more intense X-ray nanobeam allows the visualization of order parameters using NRXMS.

High-resolution scanning X-ray microscope

BL19LXU/SPring-8



KB mirror optics and diffractometer

3.7×10^{10} photons/s @ 100×100 nm^2

For LT experiments