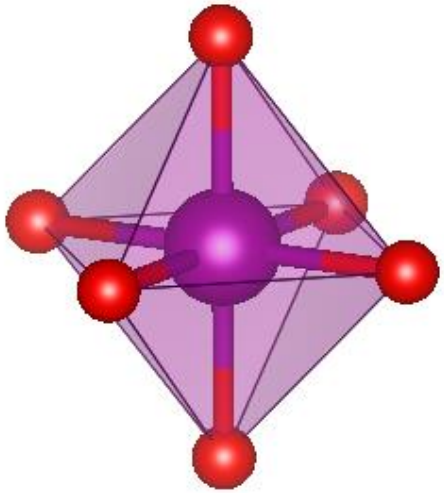
電荷、軌道自由度と構造パラメーター

Bond valence sum　(BVS)

イオン結晶中で各イオンがもっている電荷（形式電荷）qi は配位している結合ごとに割り振るこ とができる

$$V = \sum v_i$$

$$v_i = exp\left(\frac{R_0 - R_i}{b}\right)$$



Mn 2	O	-2	1.790	0.37	a ?
Mn 2	O	-2	1.740	0.417	bs ?
Mn 2	O	-2	1.765	0.37	j ?
Mn 2	O	-2	1.762	0.40	ap 'R0 fixed by Mn2O7'
Mn 2	S	-2	2.22	0.37	e unchecked
Mn 2	F	-1	1.698	0.37	a ?
Mn 2	Cl	-1	2.133	0.37	a ?
Mn 2	Br	-1	2.34	0.37	e unchecked
Mn 2	I	-1	2.52	0.37	e unchecked
Mn 2	N	-3	1.84	0.37	bq 'high spin'
Mn 2	N	-3	1.68	0.37	bq 'intermediate spin'
Mn 2	N	-3	1.53	0.37	bq 'low spin'
Mn 2	N	-3	1.849	0.37	j 'from transition metal complexes'
Mn 3	O	-2	1.760	0.37	a ?
Mn 3	O	-2	1.823	0.247	bs ?
Mn 3	O	-2	1.732	0.37	j 'from transition metal complexes'
Mn 3	O	-2	1.762	0.35	ap 'R0 fixed by Mn2O7'
Mn 3	F	-1	1.66	0.37	b ?
Mn 3	F	-1	1.666	0.36	at ?
Mn 3	Cl	-1	2.14	0.37	b ?
Mn 3	N	-3	1.82	0.37	bq 'high spin'
Mn 3	N	-3	1.71	0.37	bq 'low spin'
Mn 3	N	-3	1.837	0.37	j 'from transition metal complexes'
Mn 4	O	-2	1.753	0.37	a ?
Mn 4	O	-2	1.750	0.374	bs ?
Mn 4	O	-2	1.750	0.37	j 'from transition metal complexes'
Mn 4	O	-2	1.762	0.34	ap 'R0 fixed by Mn2O7 Small sample'

https://www.iucr.org/resources/data/datasets/bond-valence-parameters

BOND VALENCE PARAMETERS

INFORMATION ABOUT 'BVPARM*XXXX*.CIF' (*XXXX* IS THE YEAR OF REVISION OF THE FILE)

bvparm*xxxx*.cif files are text files that list the parameters R_O and B in the equation:

$$\text{bond valence} = \exp((R_O - R)/B) \qquad (1)$$

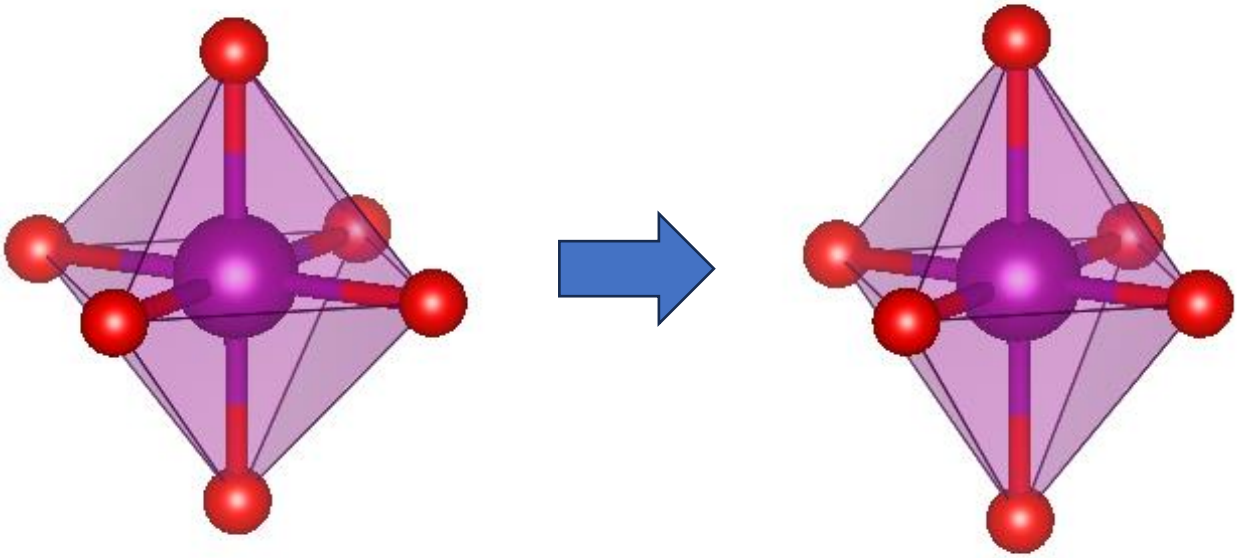
where R is the length of a bond between the two given atoms and the bond valence is a measure of the strength of the bond. The bond valence has the property that its sum around each atom in a compound is equal to the valence (oxidation state) of that atom. The bond valence is frequently used to validate newly determined crystal structures, but it has many other uses in the analysis and modelling of crystal structures.

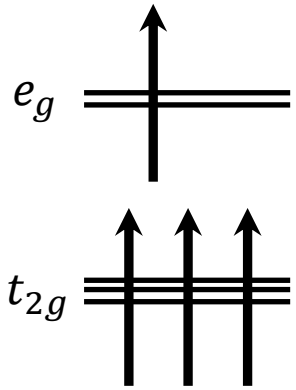
Full details of the bond valence model can be found in I. D. Brown, *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*, published by Oxford University Press, 2002.

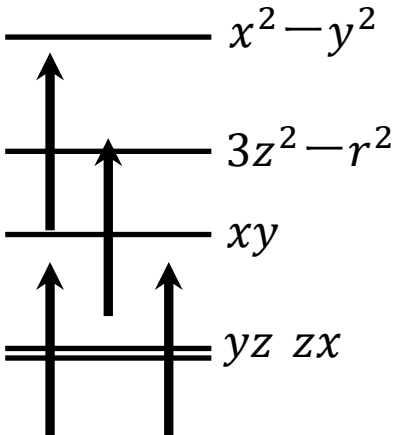
I have compiled this list from values of bond valence parameters reported in the papers cited in the file. The list is reasonably comprehensive, but I omitted some earlier parameter determinations that did not differ significantly from values that were already in the list. Where significantly different values have been reported in the literature, I have listed them in what I believe to the decreasing order of reliability. In that way a reading program can default to a bond's first occurrence in the list. In some cases, where no parameters are available in the literature I have suggested values. These carry the comment 'unchecked' and should be used with caution.

歪モード解析

MnO_6 八面体

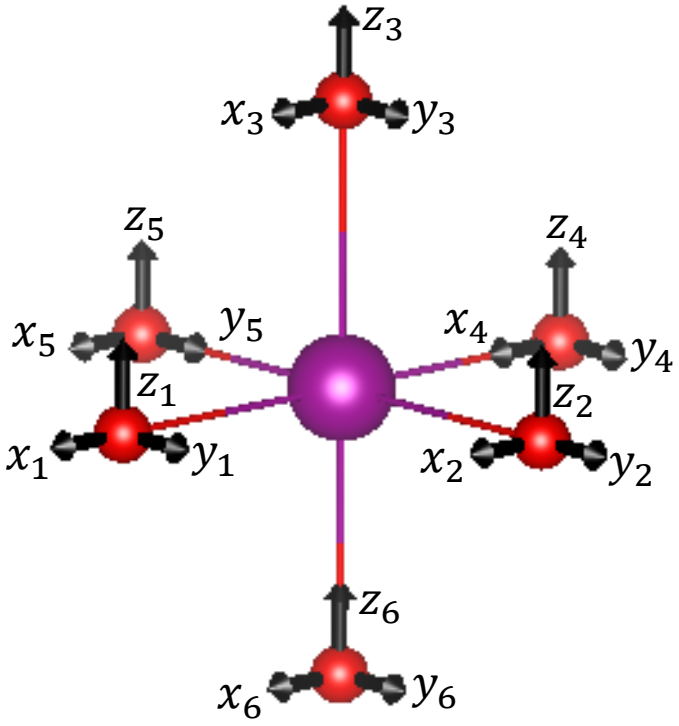






MX_6の歪みの基準振動モード

$$\Gamma_{vib} = a_{1g} + e_g + 2t_{1u} + t_{2g} + t_{2u} + \Gamma_{rot}$$



Q_1	a_{1g}	$(x_1 - x_4 + y_2 - y_5 + z_3 - z_6)/\sqrt{6}$
Q_2	e_g	$(x_1 - x_4 - y_2 + y_5)/2$
Q_3	e_g	$(2z_3 - 2z_6 - x_1 + x_4 - y_2 + y_5)/2\sqrt{3}$
Q_4	t_{2g}	$(z_2 - z_5 + y_3 - y_6)/2$
Q_5	t_{2g}	$(x_3 - x_6 + z_1 - z_4)/2$
Q_6	t_{2g}	$(y_1 - y_4 + x_2 - x_5)/2$
Q_7	t_{1u}^a	$(x_2 + x_3 + x_5 + x_6)/2$
Q_8	t_{1u}^a	$(y_1 + y_3 + y_4 + y_6)/2$
Q_9	t_{1u}^a	$(z_1 + z_2 + z_4 + z_5)/2$
Q_{10}	t_{1u}^b	$(x_1 + x_4)/\sqrt{2}$
Q_{11}	t_{1u}^b	$(y_2 + y_5)/\sqrt{2}$
Q_{12}	t_{1u}^b	$(z_3 + z_6)/\sqrt{2}$
Q_{13}	t_{2u}	$(x_2 + x_5 - x_3 - x_6)/2$
Q_{14}	t_{2u}	$(y_3 + y_6 - y_1 - y_4)/2$
Q_{15}	t_{2u}	$(z_1 + z_4 - z_2 - z_5)/2$

加えて、回転のモードが三個存在する。
（中心イオンMの自由度は考えていないので、並進モード（三個）は存在しない。）

ReO6の酸素6個の座標をを一つのベクトルで記述すると、
任意の歪みは基準振動モードの線形結合で表せる。

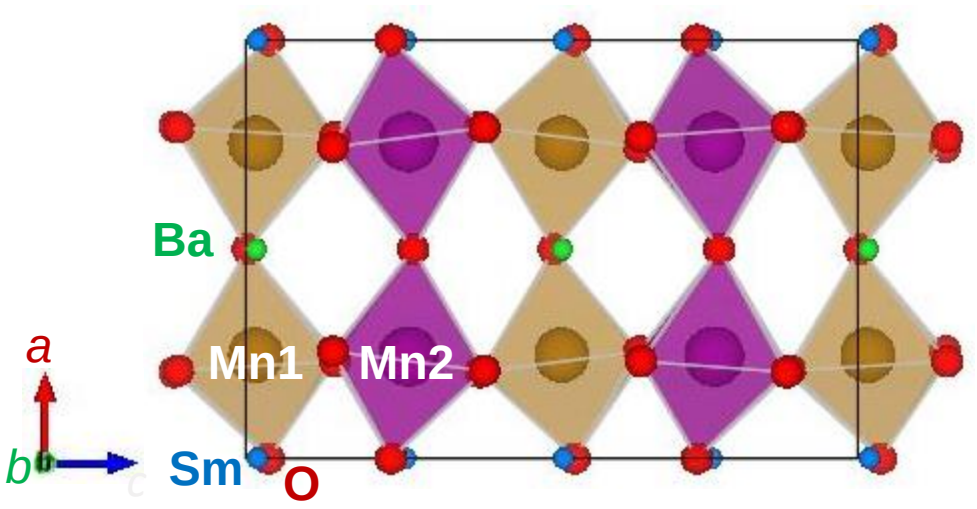
$$\Delta\mathbf{r} = \sum_i a_i \mathbf{Q}_i = \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \\ x_4 \\ y_4 \\ z_4 \\ x_5 \\ y_5 \\ z_5 \\ x_6 \\ y_6 \\ z_6 \end{pmatrix} = a_1 \frac{1}{\sqrt{6}} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 1 \\ -1 \\ 0 \\ 0 \\ 0 \\ -1 \\ 0 \\ 0 \\ 0 \\ -1 \end{pmatrix} + a_2 \frac{1}{2} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \\ -1 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} + a_3 \frac{1}{2\sqrt{3}} \begin{pmatrix} -1 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 2 \\ 1 \\ 0 \\ 0 \\ 0 \\ -1 \\ 0 \\ 0 \\ 0 \\ -2 \end{pmatrix} + \ldots$$

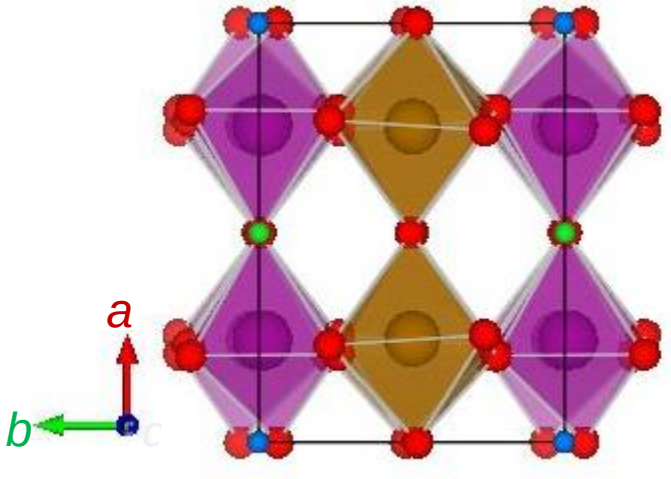
異なる基準振動モードは直交するので、酸素6個の座標と規格化された基準振動モード$\mathbf{Q}_i$の内積をとればa_iが得られる。

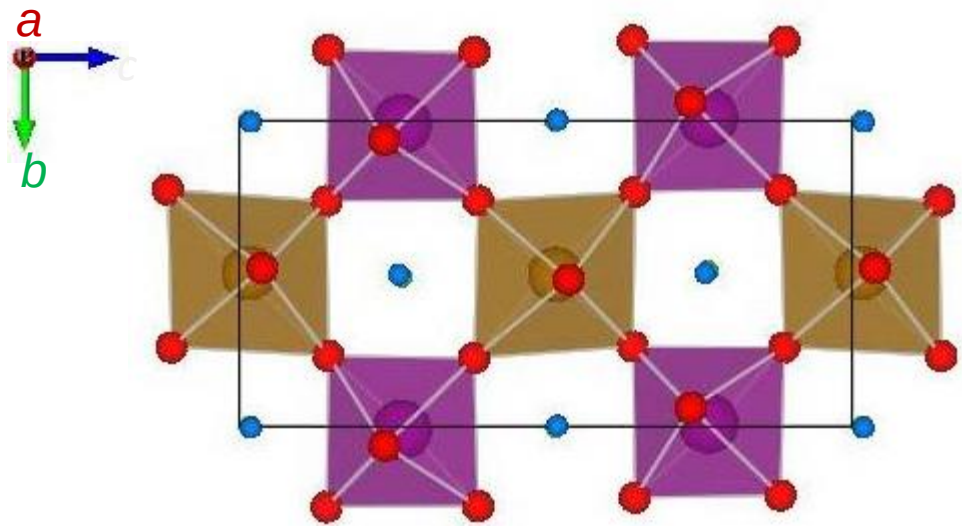
$SmBaMn_2O_6$

HS et al., Physical Review B 90(24), 241113(R)(1)-(4) (2014.12).

Crystal structure analysis at 150 K (LT ferroelectric)







Space group: $Pmc2_1$

a = 7.5814(3) Å

b = 5.5435(2) Å

c = 11.0957(5) Å

V = 466.32(3) Å^3

GOF = 1.036

R_1 ($I > 2.0\ \sigma(I)$) = 0.0420

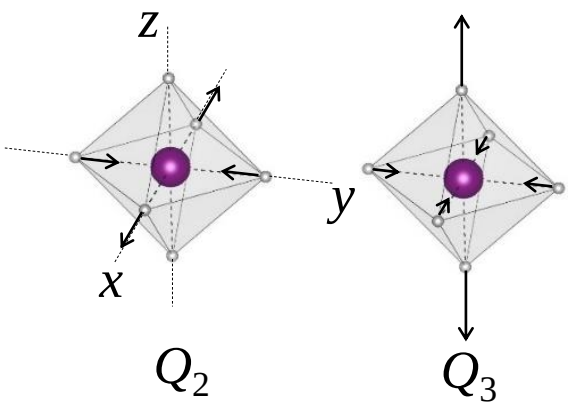
wR_2 (all data) = 0.1321

Reflection number : 7718

3.13668 (r_0 = 1.732 (Mn^{3+})
3.78675 (r_0 = 1.750 (Mn^{4+})

$$BV = \sum_{i=1}^{n} \exp\left(\frac{r_0 - r_i}{0.37}\right)$$

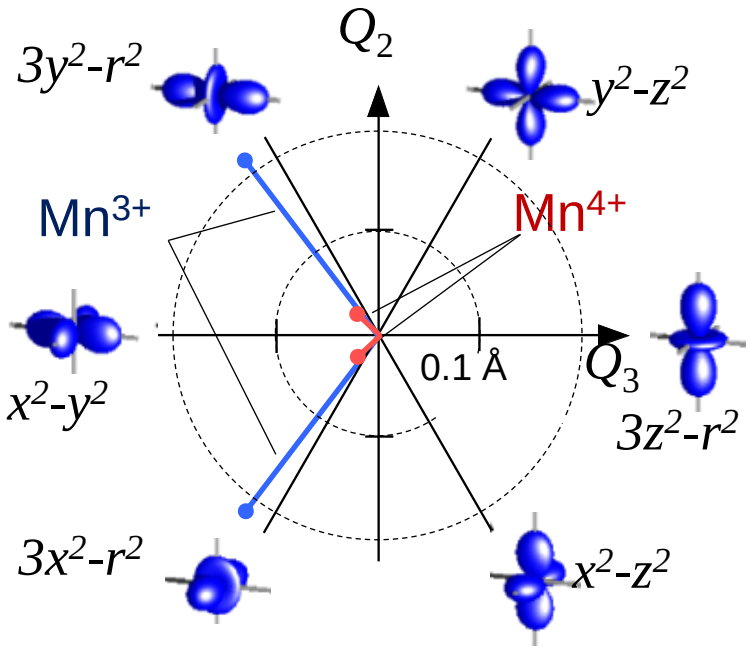
Mode analysis



Distortion mode

	Mn^{3+}	Mn^{4+}
Q2	-0.172113	-0.0199958
Q3	-0.129564	-0.021337

$\Phi=\cos(\varphi/2)|d3z^2\text{-}r^2\rangle + \sin(\varphi/2)|dx^2\text{-}y^2\rangle$



波動関数

Bond valence sum

$$BV = \sum_{i=1}^{n} \exp\left(\frac{r_0 - r_i}{0.37}\right)$$

r_0 = 1.732 (Mn^{3+}), 1.750 (Mn^{4+})

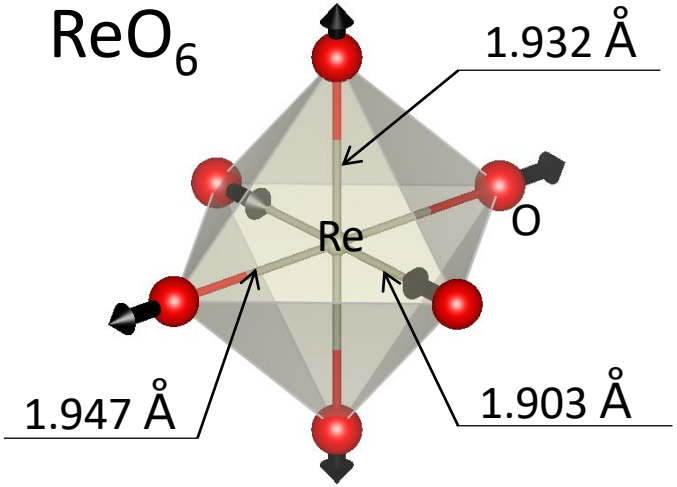
```
l(Mn1-O8) =  1.879(8) Å
l(Mn1-O7) =  1.888(6) Å
l(Mn1-O3) =  1.8883(16) Å
l(Mn1-O5) =  1.987(7) Å
l(Mn1-O6) =  1.943(8) Å
l(Mn1-O2) =  1.9480(8) Å

l(Mn2-O7) =  2.123(6) Å
l(Mn2-O4) =  1.8915(13) Å
l(Mn2-O5) =  1.937(7) Å
l(Mn2-O8) =  2.091(8) Å
l(Mn2-O6) =  1.928(8) Å
l(Mn2-O1) =  1.9229(9) Å
```

3.13668 (Mn^{3+})

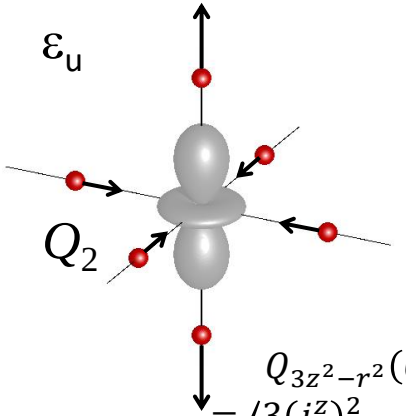
3.78675 (Mn^{4+})

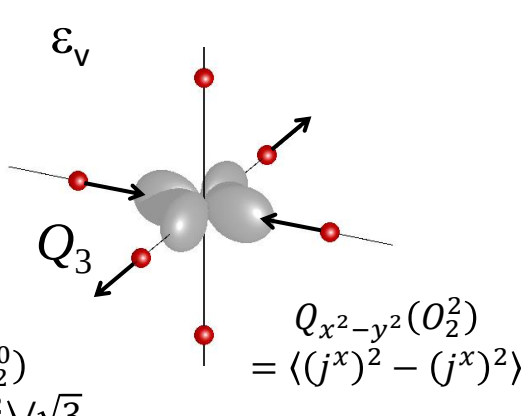
Ba_2MgReO_6 D. Hirai, HS, et al., Phys. Rev. Research 2, 022063(R) (2020).

Crystal structure analysis at LT phase

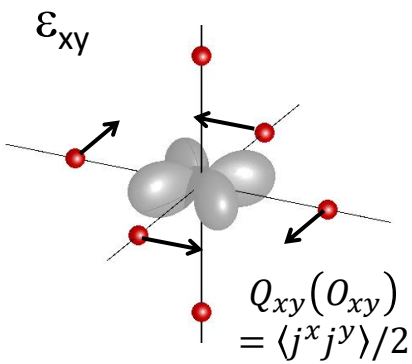


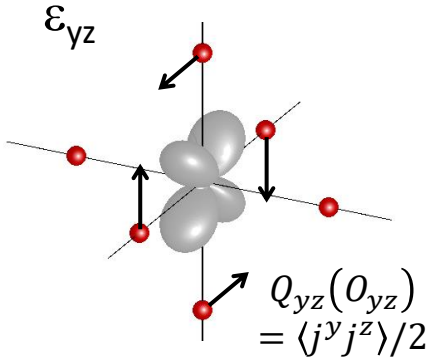
Γ_3

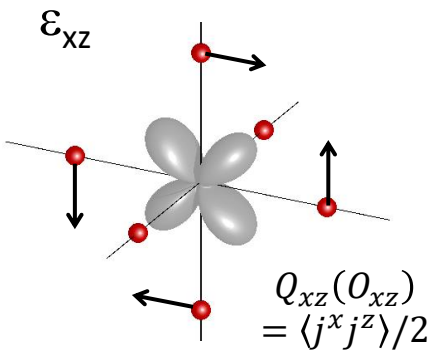




Γ_5

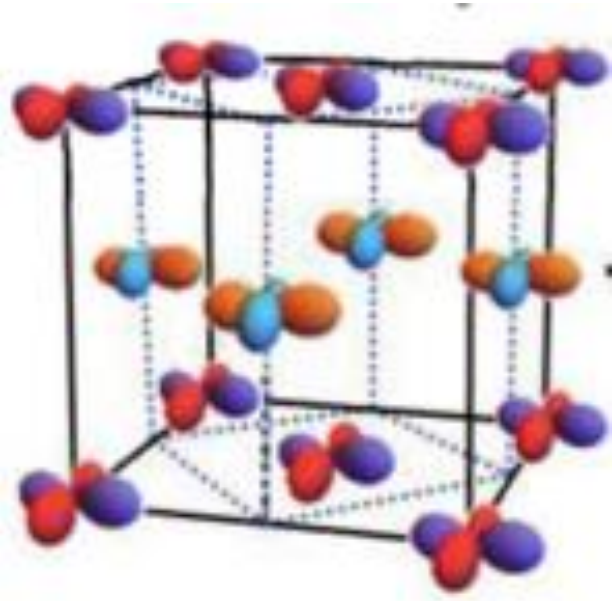




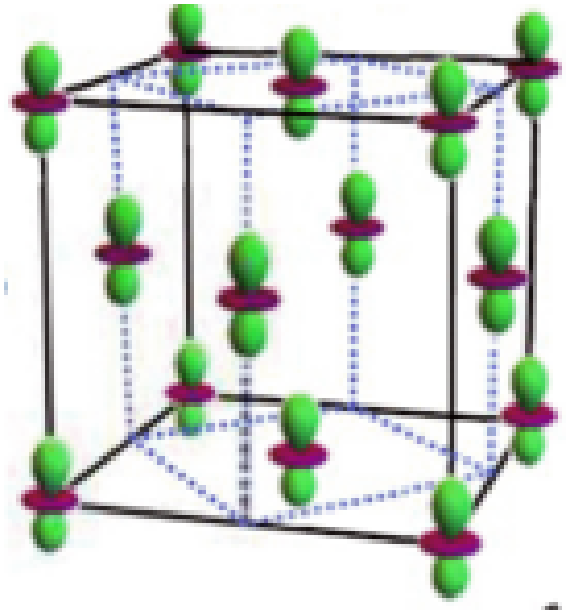


電子の存在確立

Mode	Amp. (Å)	OP
ε_u	0.045	$Q_{3z2\text{-}r2}$
ε_v	0.006	$Q_{x2\text{-}y2}$
ε_{xy}	0	Q_{xy}
ε_{yz}	0	Q_{yz}
ε_{xz}	0	Q_{xz}



Antiferro (0 0 1) $Q_{x2\text{-}y2}$
(0.045 Å)



Ferro (0 0 0) $Q_{3z2\text{-}r2}$
(0.006 Å)

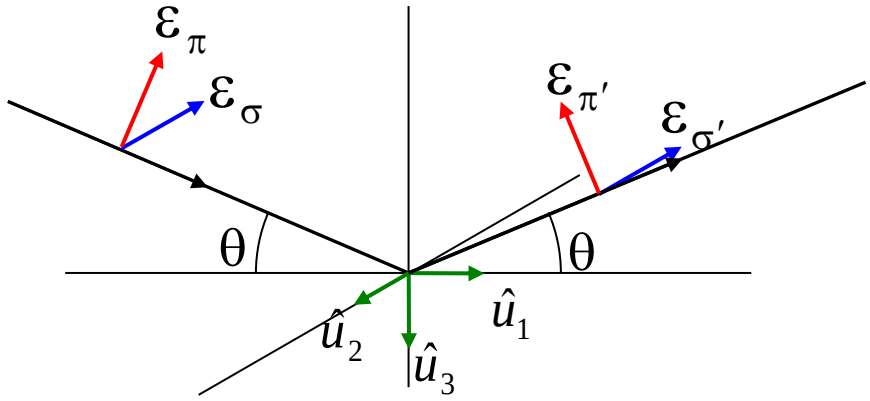
円偏光非共鳴磁気散乱

スピン散乱断面積　M. Blume and D. Gibbs, Phys. Rev. B **37**, 1779 (1988).

$$\frac{\partial\sigma}{\partial\Omega}=\left(\frac{e^2}{mc^2}\right)^2\left|\left(-i\frac{\hbar\omega}{mc^2}\right)\begin{pmatrix}\langle M\rangle_{\sigma'\sigma} & \langle M\rangle_{\sigma'\pi}\\ \langle M\rangle_{\pi'\sigma} & \langle M\rangle_{\pi'\pi}\end{pmatrix}\right|^2$$

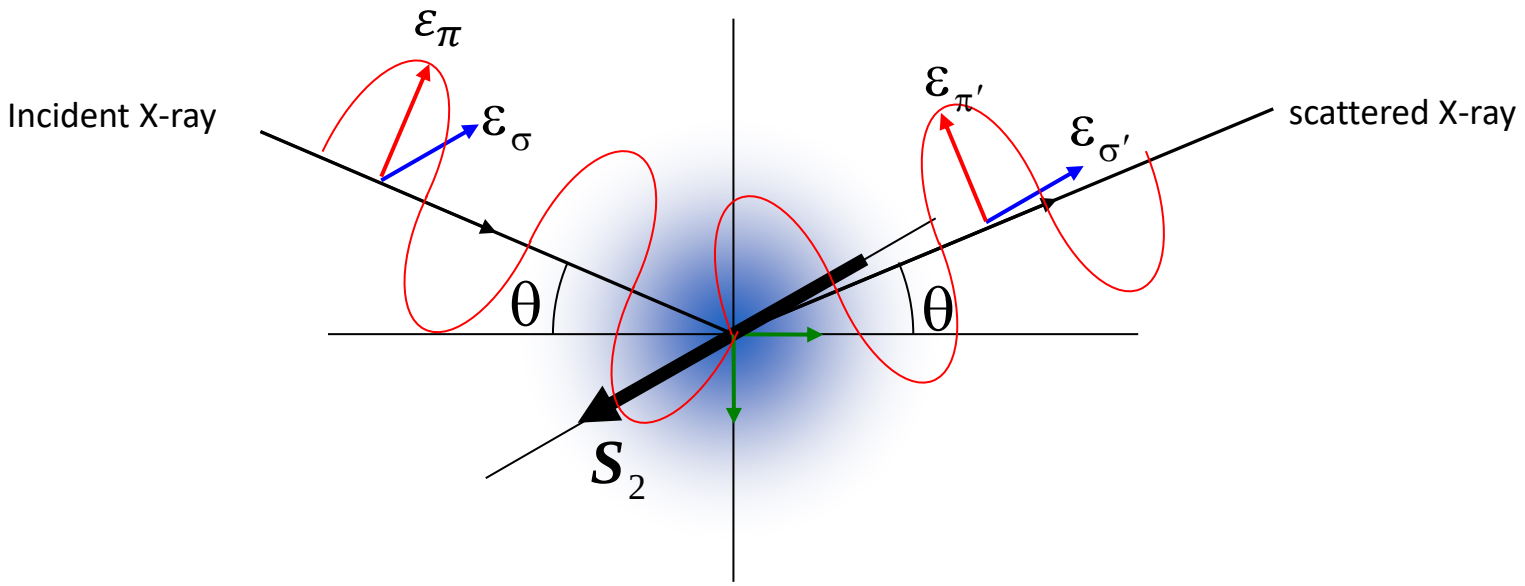
$$=\left(\frac{e^2}{mc^2}\right)^2\left(\frac{\hbar\omega}{mc^2}\right)^2\left|\begin{pmatrix}(\sin 2\theta)S_2 & -2(\sin^2\theta)[(\cos\theta)S_1-(\sin\theta)S_3]\\ 2(\sin^2\theta)[(\cos\theta)S_1+(\sin\theta)S_3] & (\sin 2\theta)S_2\end{pmatrix}\right|^2$$

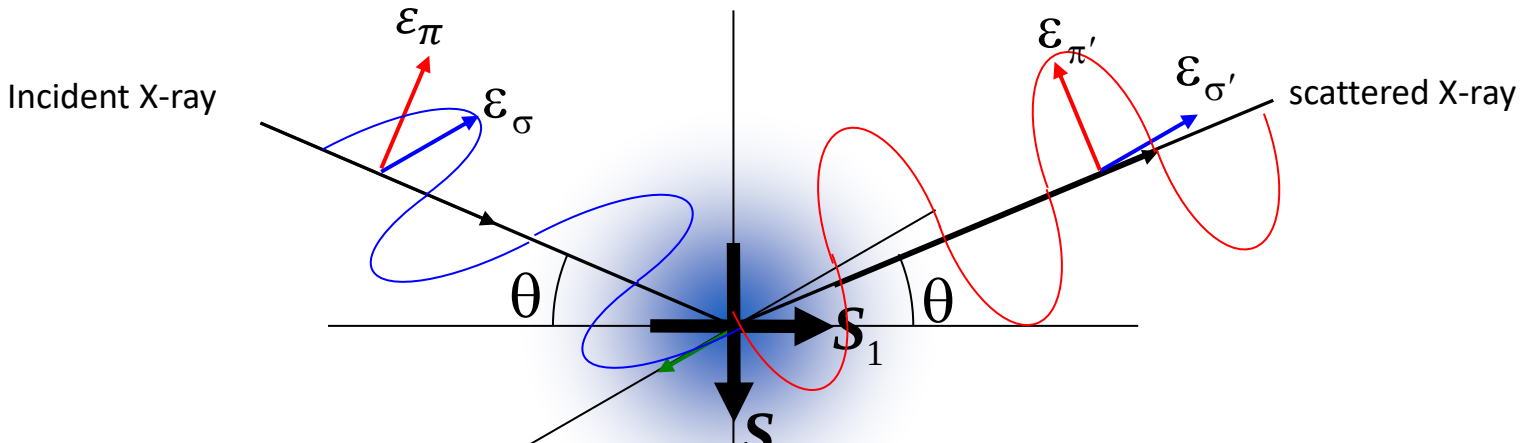
$$\boldsymbol{S}=\sum_j \exp(2\pi i\boldsymbol{Q}\cdot\boldsymbol{r})\langle a|\boldsymbol{s}_i|a\rangle$$

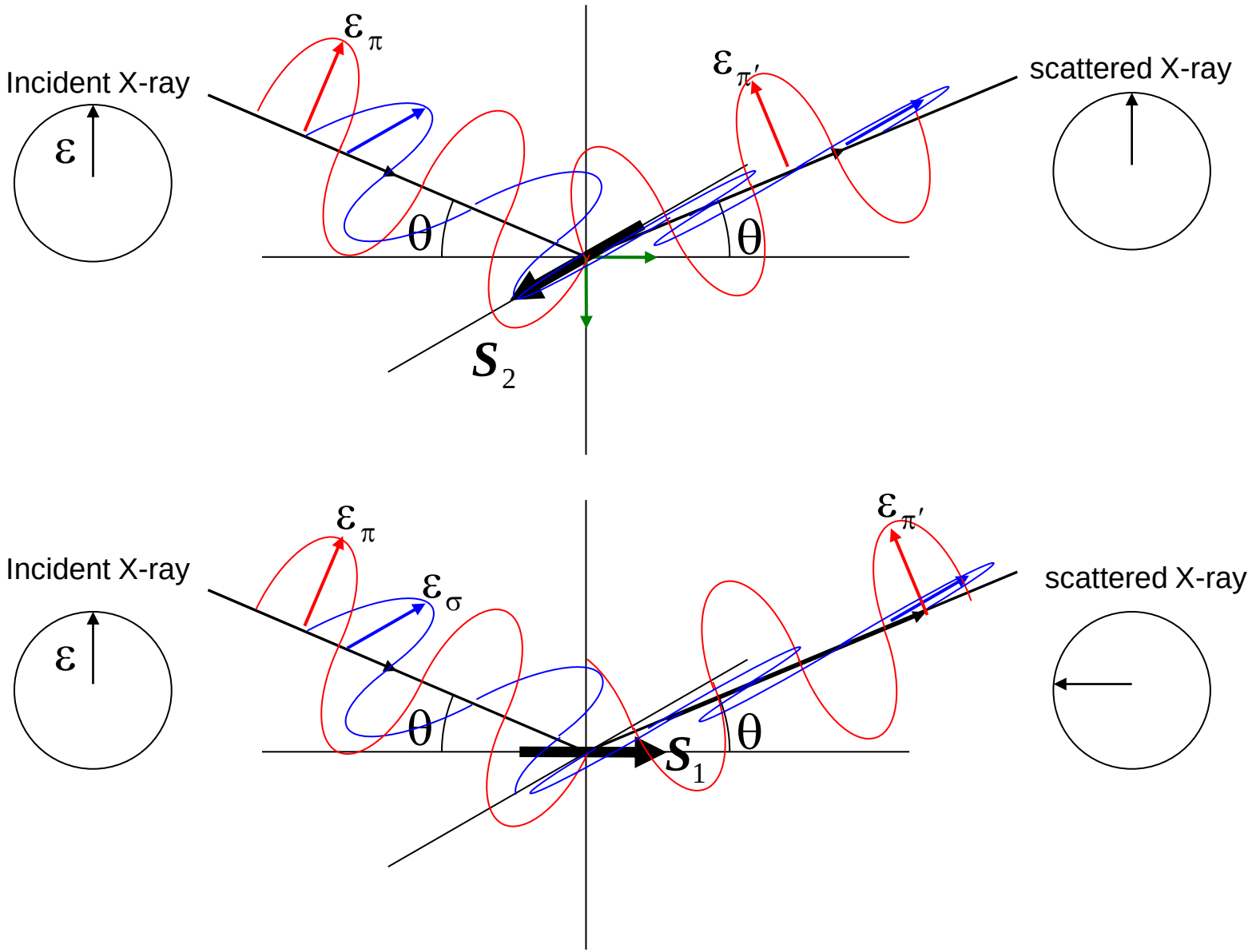


X線磁気散乱の偏光依存性

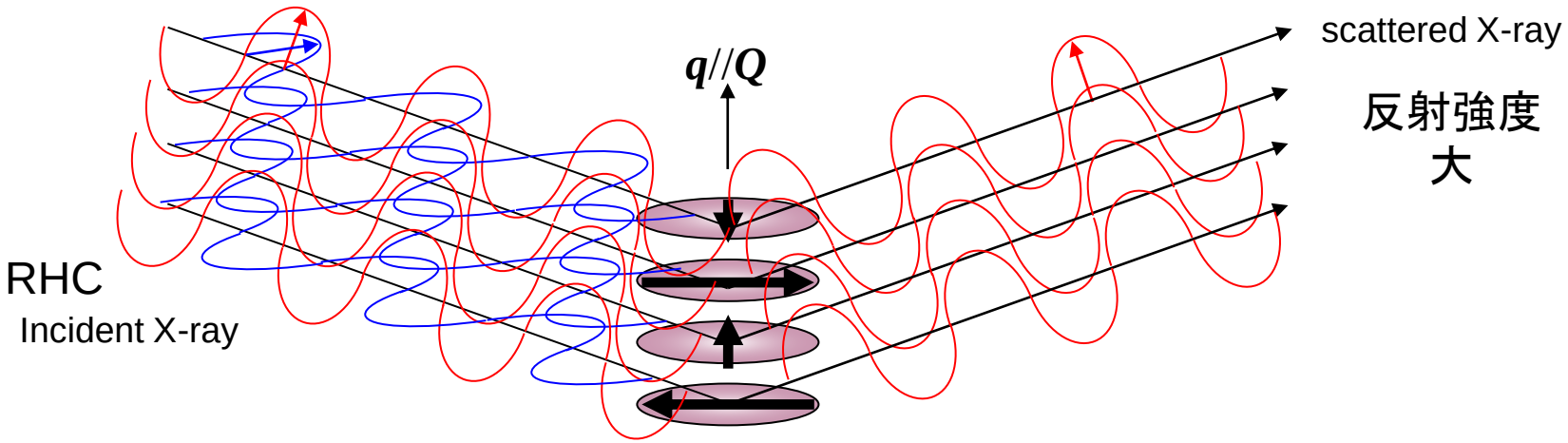
$$\langle M_m \rangle = \begin{pmatrix} \langle M_m \rangle_{\sigma\sigma} & \langle M_m \rangle_{\sigma\pi} \\ \langle M_m \rangle_{\pi\sigma} & \langle M_m \rangle_{\pi\pi} \end{pmatrix} = \sin 2\theta \begin{pmatrix} S_2 & -S_1 \sin\theta + S_3 \sin\theta \tan\theta \\ S_1 \sin\theta + S_3 \sin\theta \tan\theta & S_2 \end{pmatrix}$$



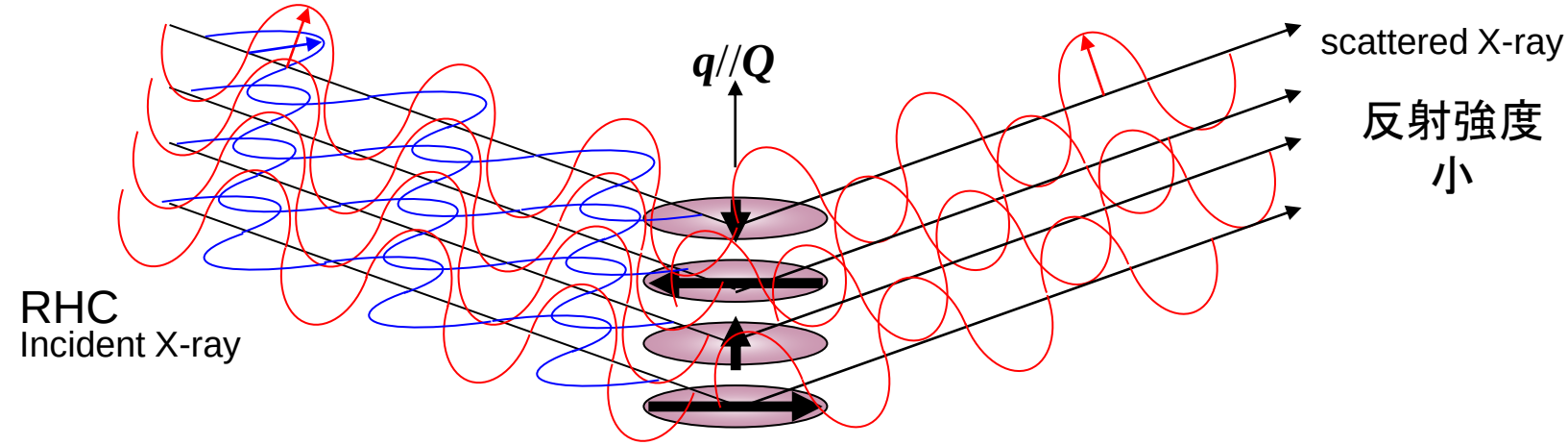



Incident X-ray
ε
ε_π
ε_π′
scattered X-ray
θ
θ
S_2
Incident X-ray
ε
ε_π
ε_σ
ε_π′
scattered X-ray
θ
θ
S_1

Left-handed Spin Screw

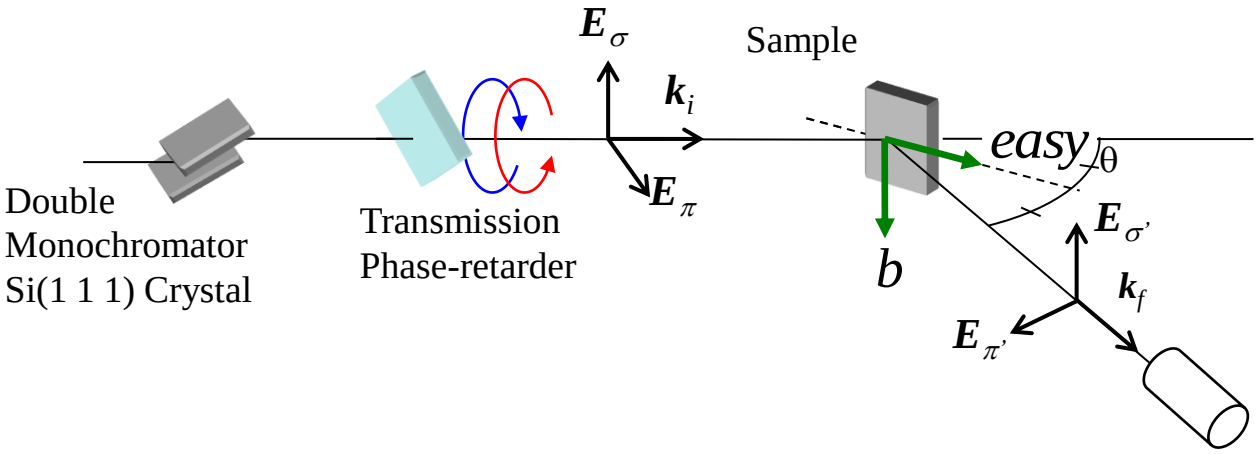


Right-handed Spin Screw



Experimental details

X-ray diffraction measurement @BL19XLU, SPring-8

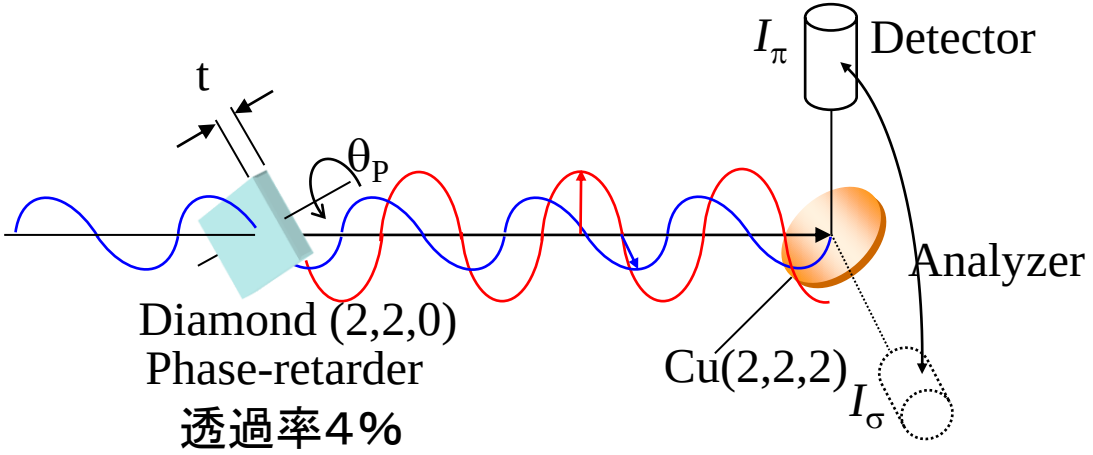


Single crystal : FZ method

Size ϕ 4mm, t = 2.5 mm

Electric Field cooling

Conversion from liner to circular using a transmission phase-retarder

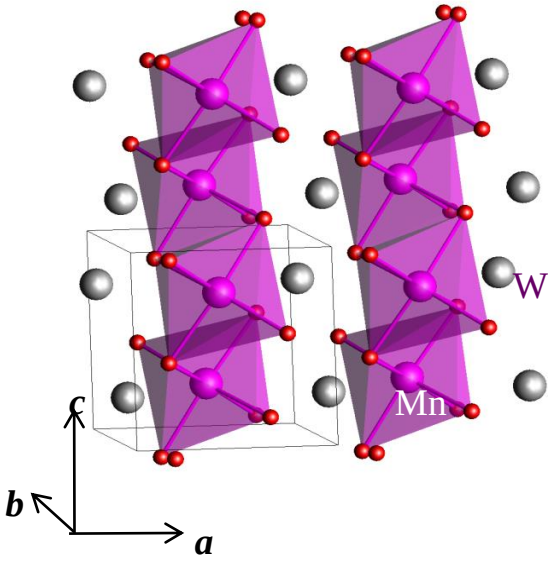


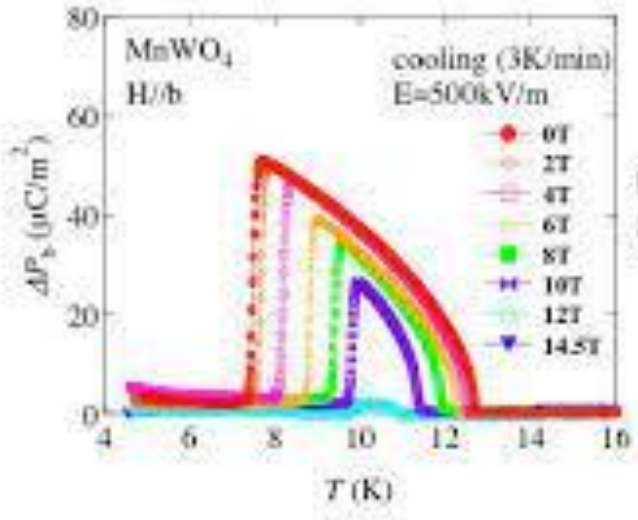
$$\mathbf{P}_{circ} = \pm 0.9968$$

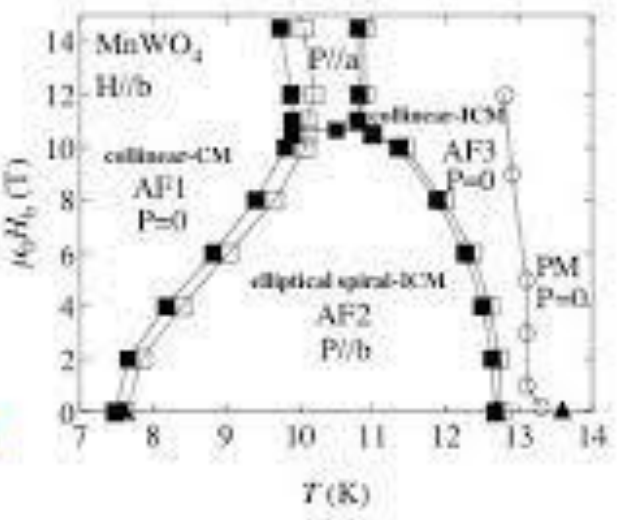
$MnWO_4$ Simple Spin-Spiral Multiferroics

K. Taniguchi *et al*., Phys. Rev. Lett. **97**, 097203 (2006),
A. H. Arkenbout *et al*., Phys. Rev. B **74**, 184431 (2006).

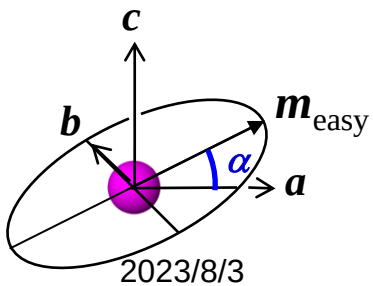
Crystal structure



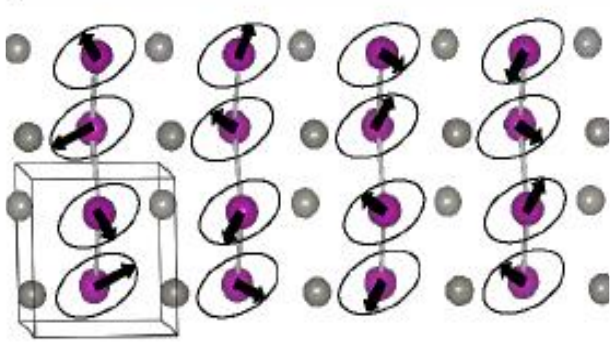




Monoclinic P2/c
Quasi 1D spin system



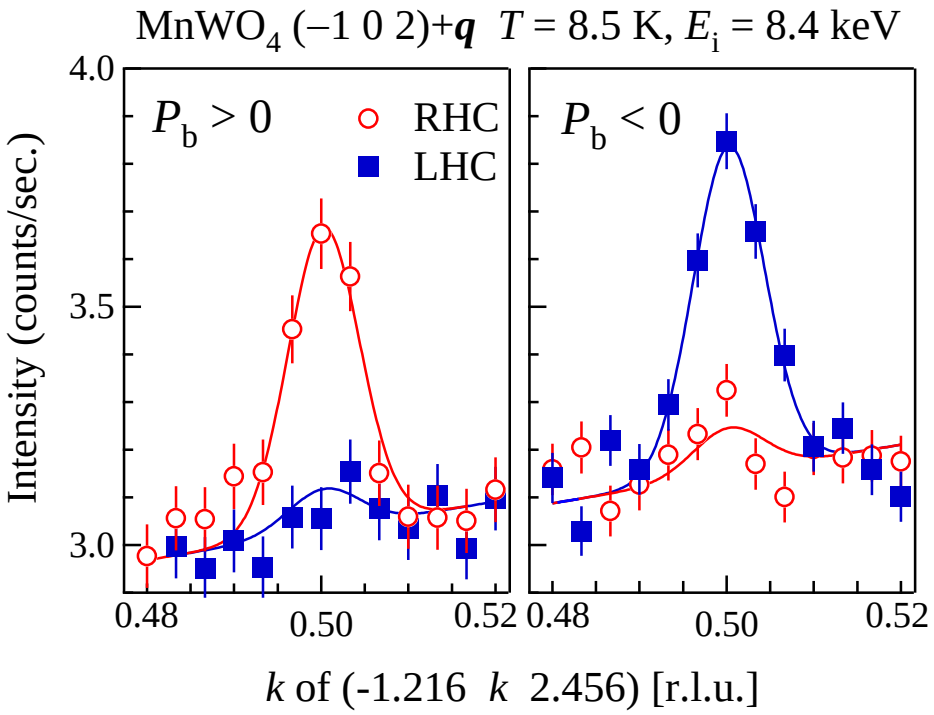
AF2 *Helical Spin*

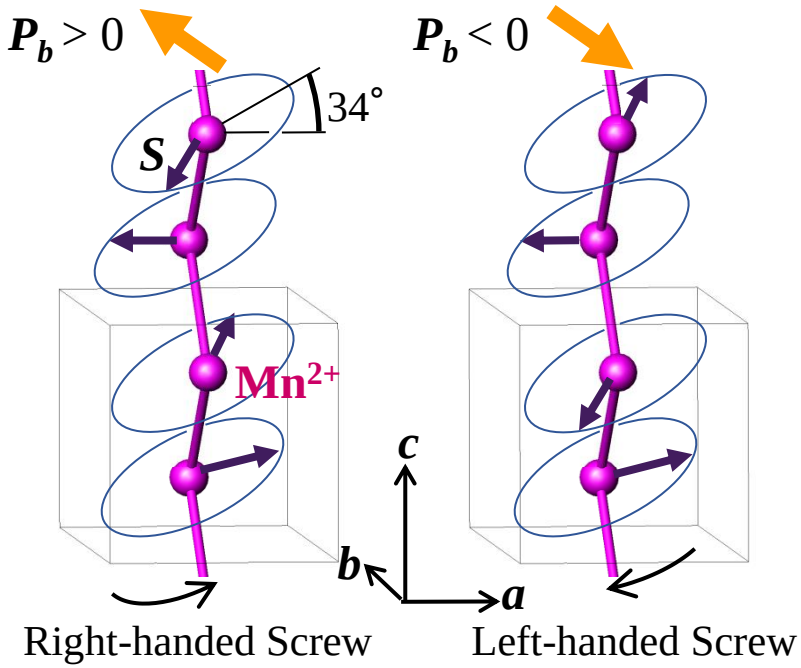


G.Lautenschlager *et al*., PRB (1993).

$MnWO_4$

HS et al., JPSJ 79, 043711(2010).





$I_L/I_R=7$

楕円率 $m_b/m_{easy}= 0.9$