Probing chirality with high energy synchrotron light

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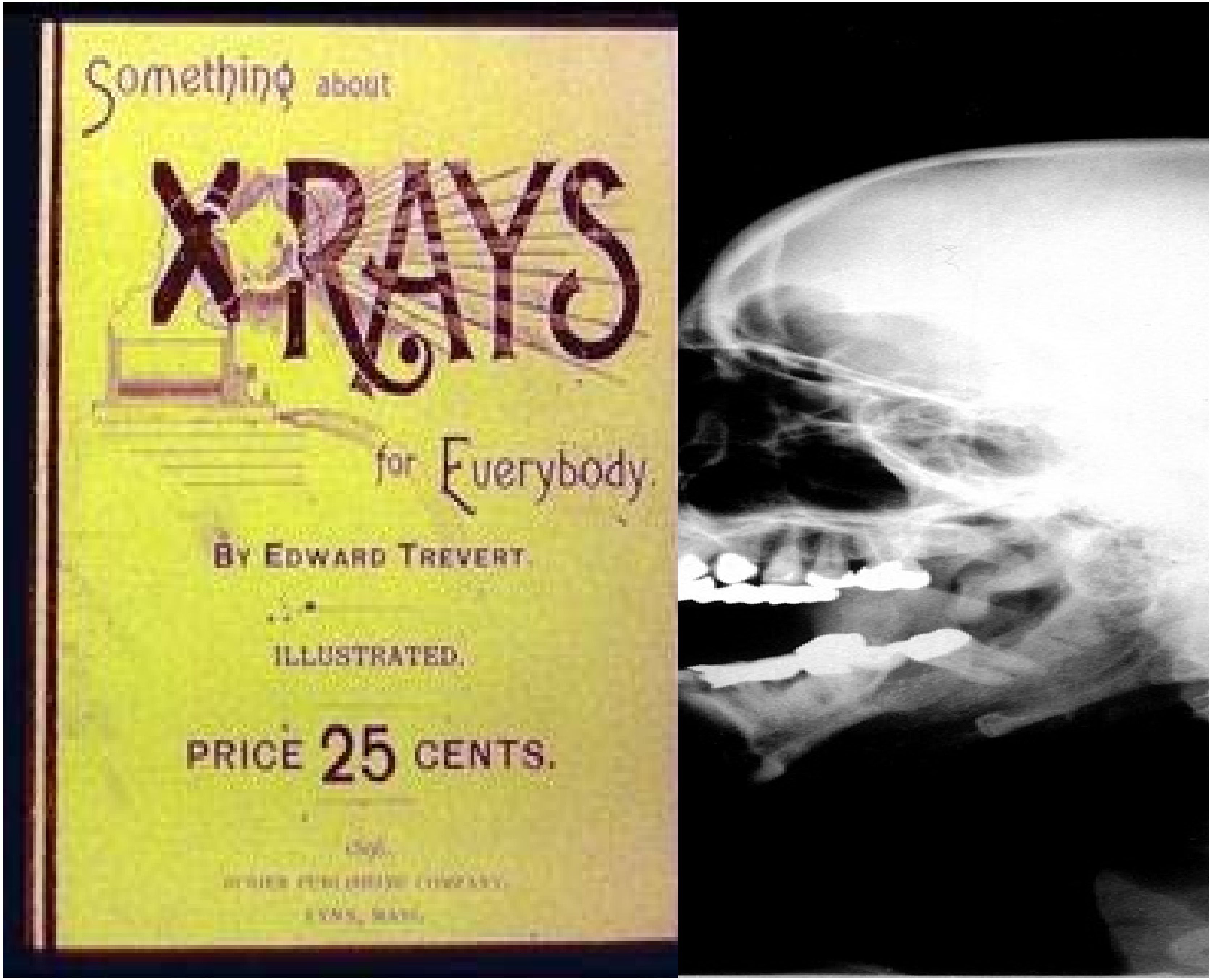
Outline


Something about
X-RAYS
for Everybody.
By Edward Trevert.
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Phase information

$$\rho(\boldsymbol{R}) = \rho_A(\boldsymbol{R}) + \rho_S(\boldsymbol{R})$$

Scattering density – two parts

$$F(\boldsymbol{Q}) = \sum_A f_A(\boldsymbol{Q}) \exp(i\boldsymbol{Q}\boldsymbol{R}_A) + \sum_S f_S(\boldsymbol{Q}) \exp(i\boldsymbol{Q}\boldsymbol{R}_S)$$

$$F(\boldsymbol{Q}) = F_A(\boldsymbol{Q}) + F_S(\boldsymbol{Q})$$

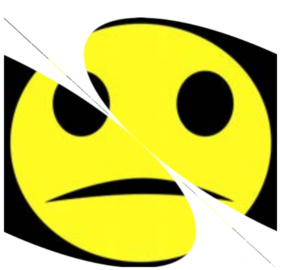
Structure factor – two parts

Scattered intensity – three contributions

$$I(\boldsymbol{Q}) \propto |F(\boldsymbol{Q})|^2 = |F_A(\boldsymbol{Q})|^2 + |F_S(\boldsymbol{Q})|^2 + 2|F_A(\boldsymbol{Q})||F_S(\boldsymbol{Q})|\cos(\phi_A - \phi_S)$$

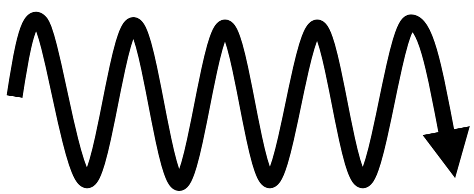
Direct phase information is lost in diffraction experiment but we have the cross-term – and structure solution is possible!

$\cos(\phi_A - \phi_S)$ Cos is even function....

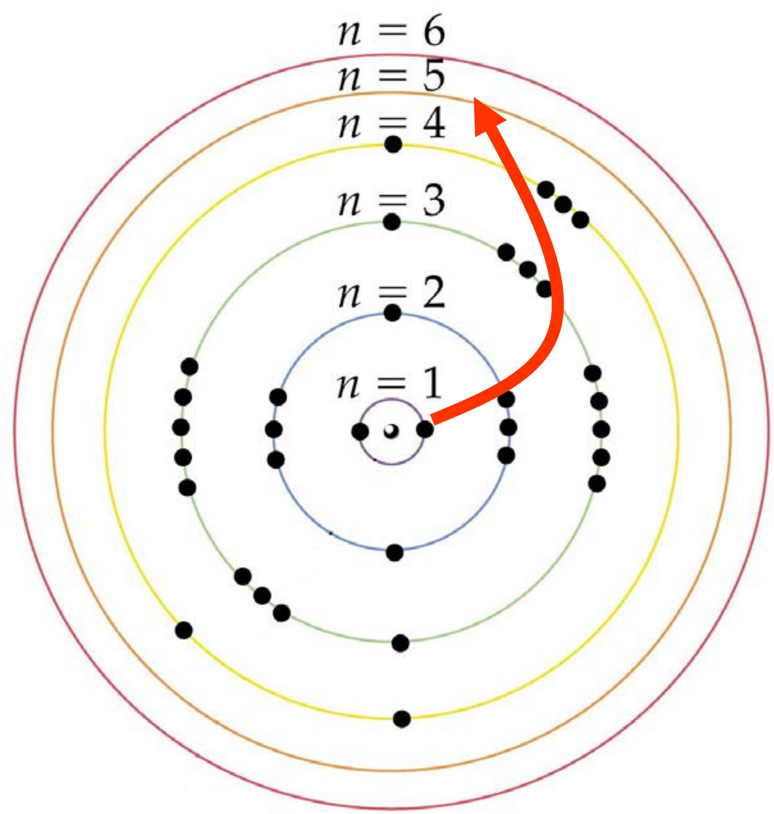


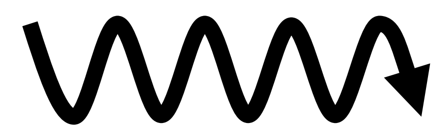
Resonant scattering

$$f = f_o + \Delta f' + i\Delta f''$$



Incident X-ray





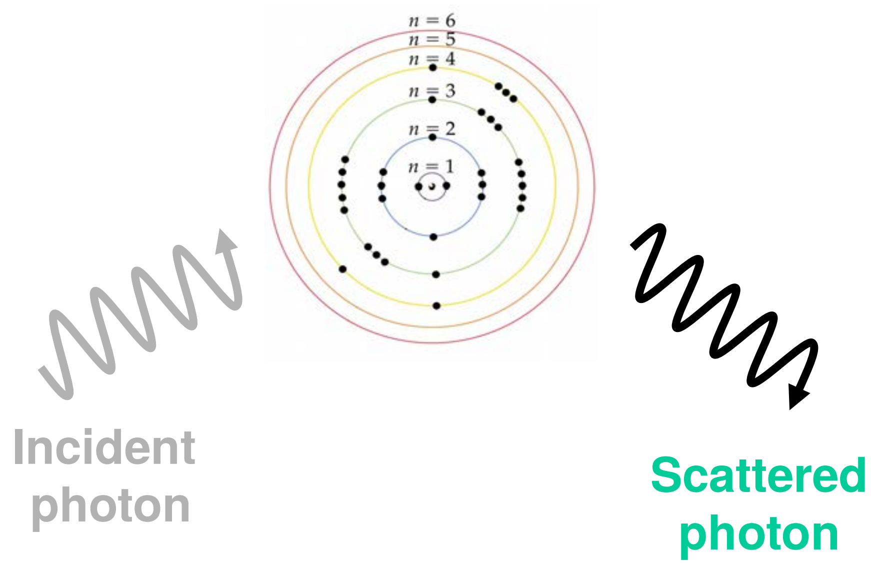
Anomalously Scattered X-ray

-90° phase shift diminished amplitude

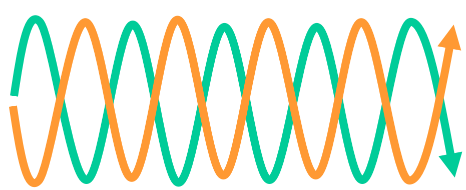
Selenium atom

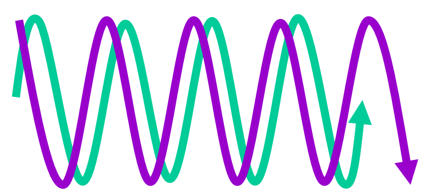
Excited state

Resonant scattering



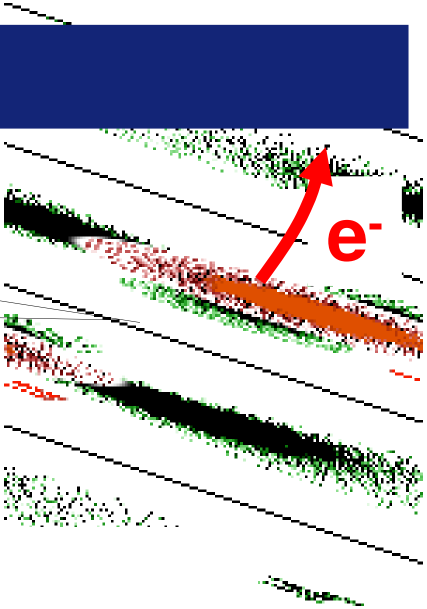
$$f = f_o + \Delta f' + i\Delta f''$$





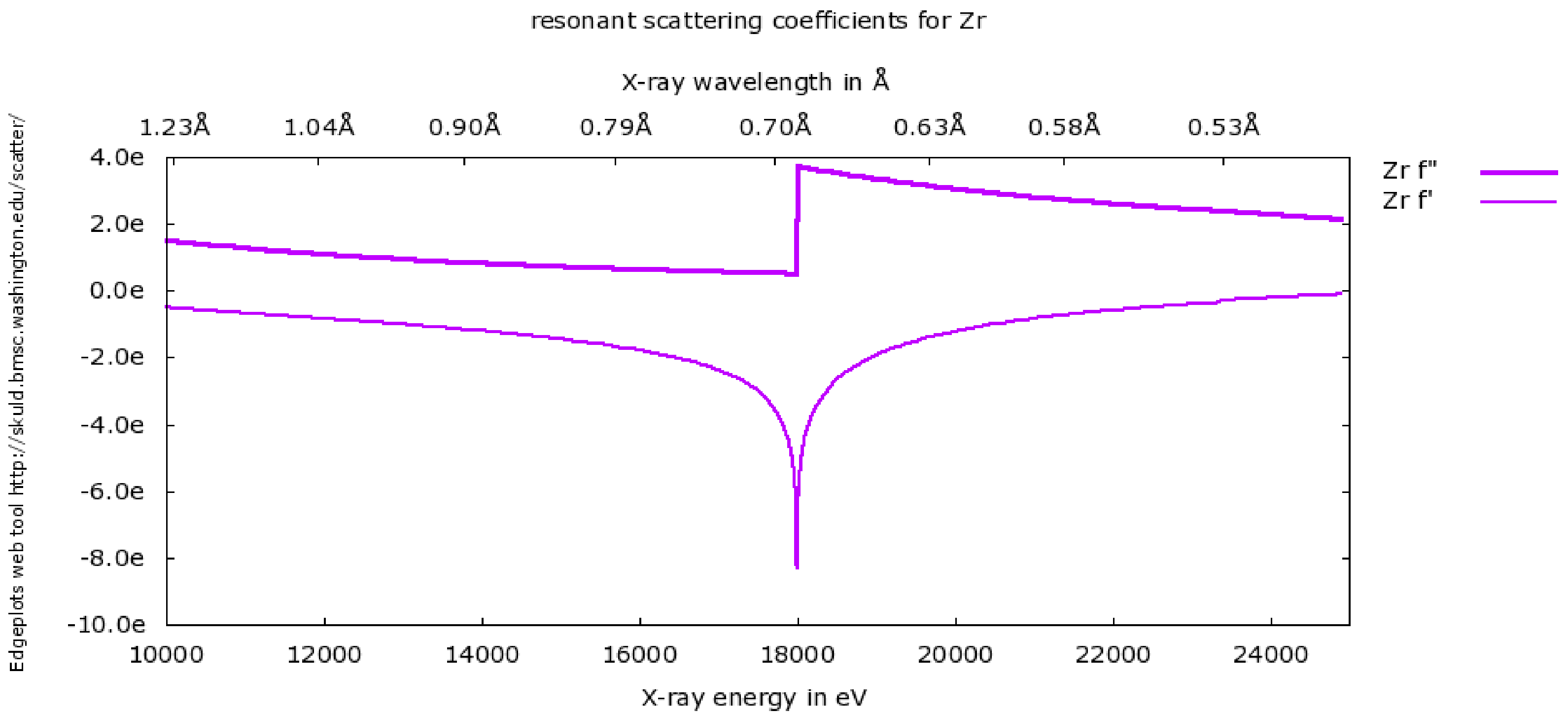
Resonant scattering

$$f = f_o + \Delta f' + i\Delta f''$$



$f_o \leftarrow$

$$f(\boldsymbol{q}) = \int d\boldsymbol{r}\, \rho(\boldsymbol{r}) \exp(i\,\boldsymbol{q}\,\boldsymbol{r}_i)$$



Resonant scattering

$$f = f_o + \Delta f' + i\Delta f''$$

$$\rho(\boldsymbol{R}) = \rho_J(\boldsymbol{R}) + \rho_K(\boldsymbol{R})$$

$$F(\boldsymbol{Q}) = \sum_j \left(f_0^j + \Delta f'^j\right)\exp\left(i\boldsymbol{Q}\boldsymbol{R}_j\right) + i\sum_k \left(\Delta f''^k\right)\exp\left(i\boldsymbol{Q}\boldsymbol{R}_k\right)$$

$$i\,e^{(i\phi)} = e^{(i(\phi+\pi/2))}$$

$$i\,F_K(\boldsymbol{Q}) = |F_K(\boldsymbol{Q})|\,e^{i(\phi_K+\pi/2)}$$

Resonant scattering

$$\mathbf{f} = \mathbf{f_o} + \Delta\mathbf{f'} + i\Delta\mathbf{f''}$$

$$F(\boldsymbol{Q}) = F_J(\boldsymbol{Q}) + i\,F_K(\boldsymbol{Q})$$

$$i\,e^{(i\phi)} = e^{(i(\phi+\pi/2))}$$

$$i\,F_K(\boldsymbol{Q}) = |F_K(\boldsymbol{Q})|\,e^{i(\phi_K+\pi/2)}$$

$$I(\boldsymbol{Q}) = |F(\boldsymbol{Q})|^2 = |F_J(\boldsymbol{Q}) + i\,F_K(\boldsymbol{Q})|^2$$

$$I(\boldsymbol{Q}) = |F_J(\boldsymbol{Q})|^2 + |F_K(\boldsymbol{Q})|^2 + 2|F_J(\boldsymbol{Q})||F_K(\boldsymbol{Q})|\cos(\phi_J - \phi_K + \pi/2)$$

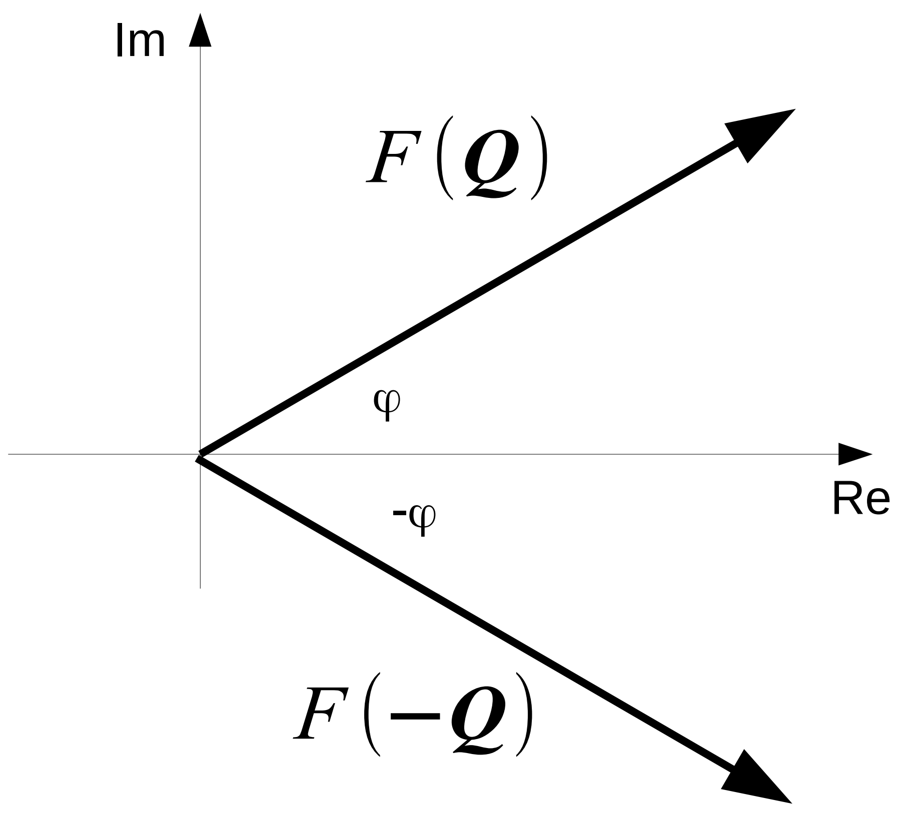
$$I(\boldsymbol{Q}) = |F_J(\boldsymbol{Q})|^2 + |F_K(\boldsymbol{Q})|^2 + 2|F_J(\boldsymbol{Q})||F_K(\boldsymbol{Q})|\sin(\phi_J - \phi_K)$$

$\sin(\phi_J - \phi_K)$ - is odd function!

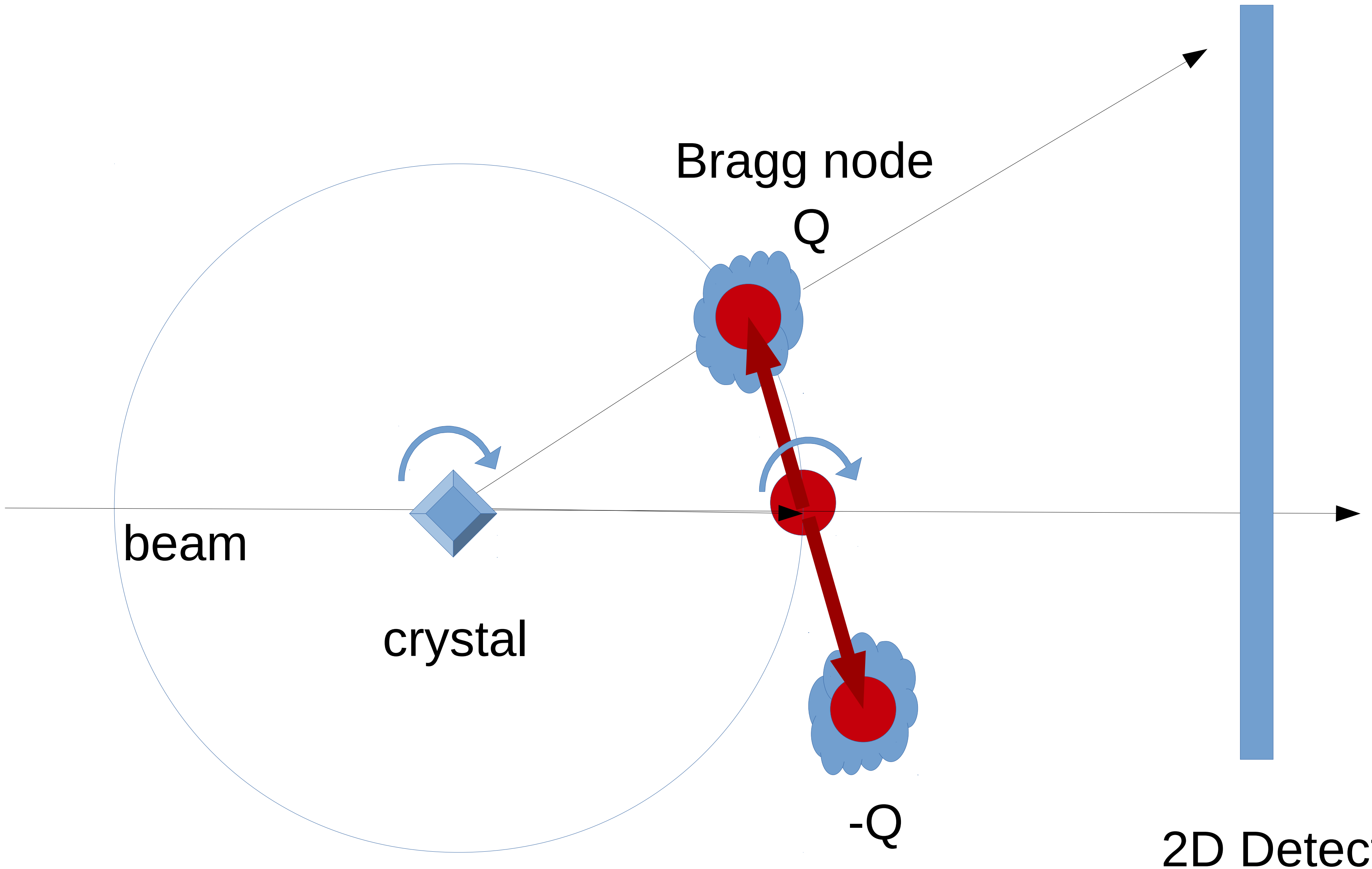
Friedel pairs: Q and -Q

$$F(\boldsymbol{Q}) = \sum_i f_i(Q)\exp(i\boldsymbol{Q}(\boldsymbol{r}_i))$$

$$F(\boldsymbol{Q}) = |F(\boldsymbol{Q})|\exp(i\phi)$$

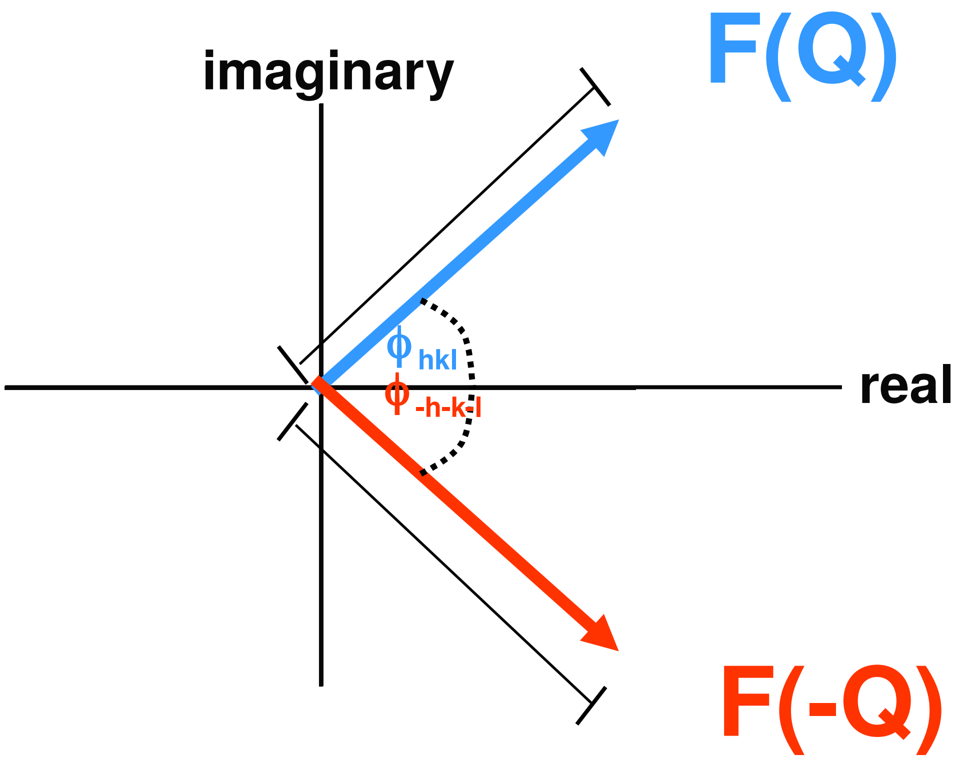


Friedel pairs: Q and -Q



Friedel law

$$|F(\vec{Q})| = |F(-\vec{Q})|$$
$$I(\vec{Q}) = I(-\vec{Q})$$

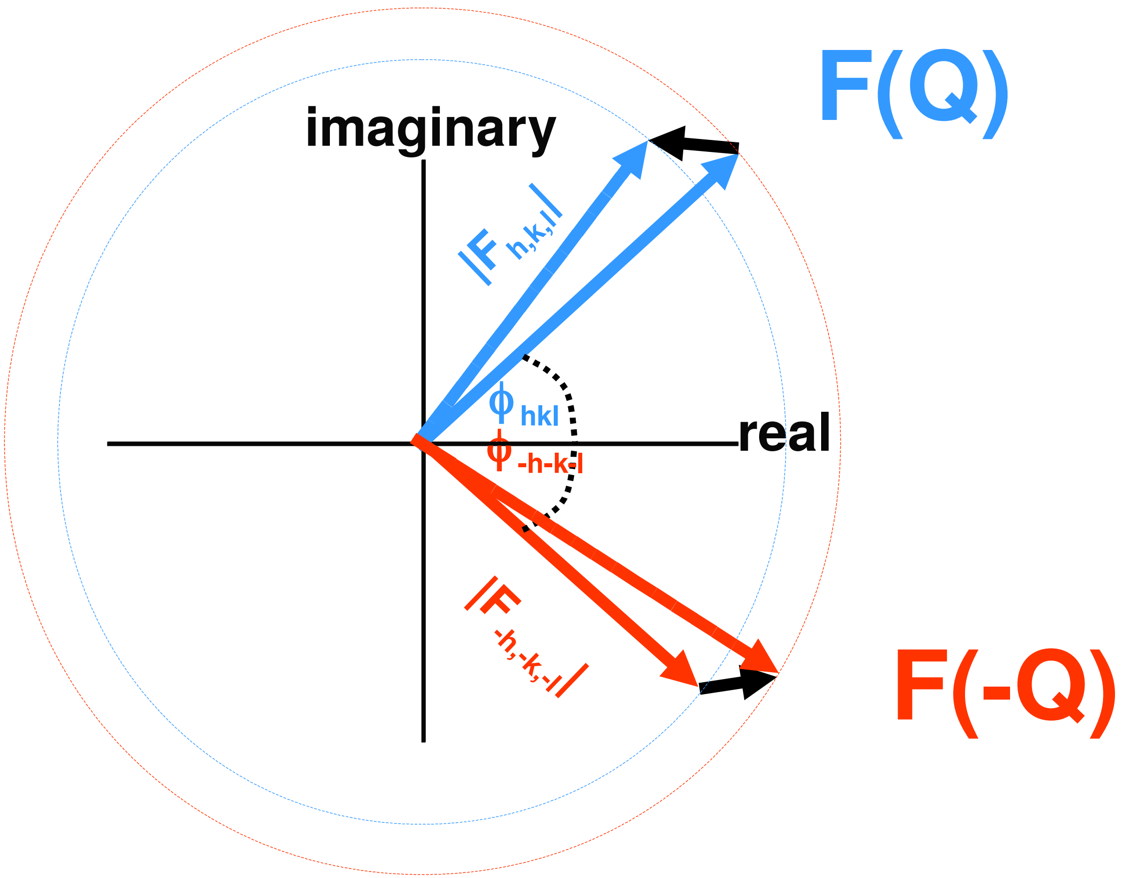


$$I(Q) = |F(Q)|^2 = |F_A(Q)|^2 + |F_S(Q)|^2 + 2|F_A(Q)||F_S(Q)|\cos(\phi_A - \phi_S)$$

$\cos(\phi_A - \phi_S)$ Cos is even function....

Friedel law: close to resonance

$$|F(\vec{Q})| \neq |F(-\vec{Q})|$$
$$I(\vec{Q}) \neq I(-\vec{Q})$$



$$I(Q) = |F(Q)|^2 = |F_J(Q) + i F_K(Q)|^2$$

$$I(Q) = |F_J(Q)|^2 + |F_K(Q)|^2 + 2|F_J(Q)||F_K(Q)|\sin(\phi_J - \phi_K)$$

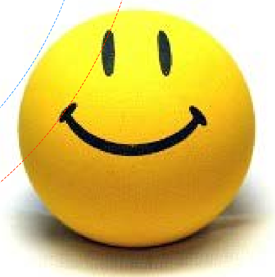
$\sin(\phi_J - \phi_K)$ - is odd function!

How to solve phase problem

$$I(\mathbf{Q}) = |F(\mathbf{Q})|^2 = |F_J(\mathbf{Q}) + i F_K(\mathbf{Q})|^2$$

$$I(\mathbf{Q}) = |F_J(\mathbf{Q})|^2 + |F_K(\mathbf{Q})|^2 + 2|F_J(\mathbf{Q})||F_K(\mathbf{Q})|\sin(\phi_J - \phi_K)$$

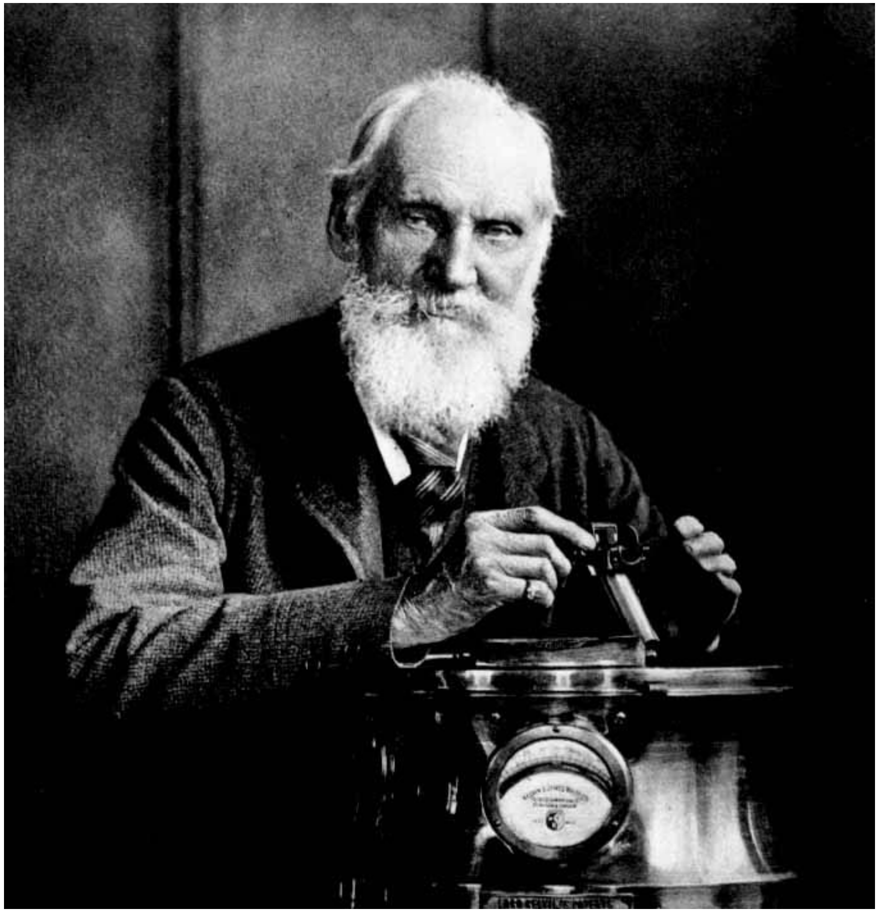
$$I(\mathbf{Q}) - I(-\mathbf{Q}) = 4|F_J(\mathbf{Q})||F_K(\mathbf{Q})|\sin(\phi_J - \phi_K)$$



$\sin(\phi_J - \phi_K)$ - is odd function!

To get phase information from resonance scattering one has to be able to manipulate X-ray energy
This is what synchrotron can do!

Chirality

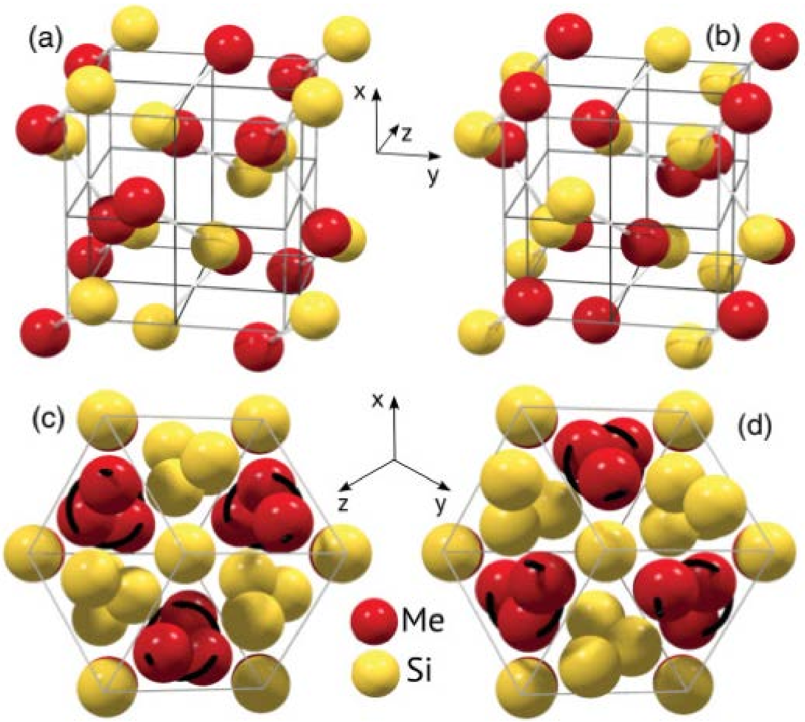


Chirality in MnSi

Left and Right forms are related by the inversion operation

$$(x, y, z)_L = (-x, -y, -z)_R$$
$$\phi_L = -\phi_R$$

X (Mn)	X (Si)
0.137	0.846 L
0.887	0.154 R



$$I(\boldsymbol{Q}) - I(-\boldsymbol{Q}) = \pm 2 |F_J(\boldsymbol{Q})| |F_K(\boldsymbol{Q})| \sin(\phi_J - \phi_K)$$

$\sin(\phi_J - \phi_K)$ - is odd function!

Opposite enantiomeric forms give an interference contribution of he different sign. They are distinguishable due to the resonant contribution.

Absolute structure determination

1. Resonance contribution

$$f(\vec{Q}) = f_0(\vec{Q}) + f'(\lambda) + i f''(\lambda)$$

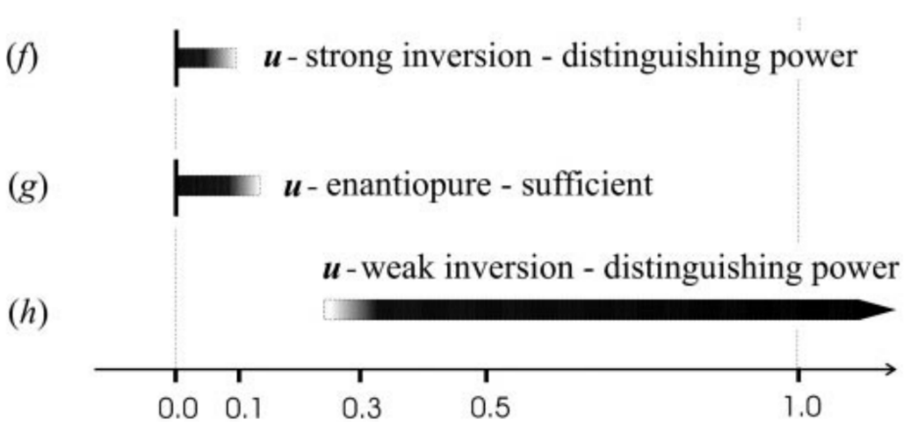
2. Violation of Friedel law

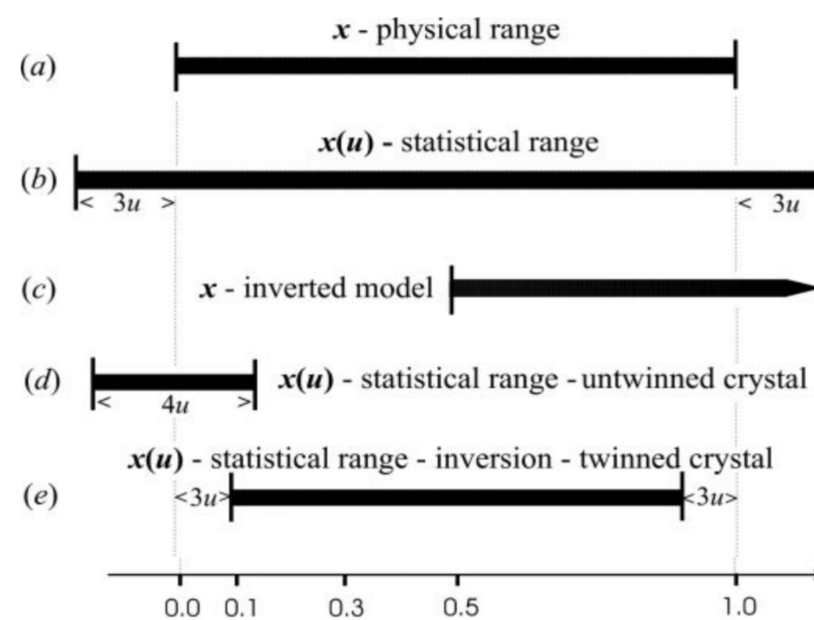
$$|F(\vec{Q})| \neq |F(-\vec{Q})|$$

$$I(\vec{Q}) - I(-\vec{Q}) \neq 0$$

3. Flack parameter

$$I_d(\vec{Q}) = (1-x)|F(\vec{Q})|^2 + x|F(-\vec{Q})|^2$$





H. D. Flack and G. Bernardinelli (2008). Chirality **20,** 681

Parsons' quotients

Observed: $$q_{\mathrm{obs}}(\mathbf{h}) = \frac{I_{\mathrm{obs}}(\mathbf{h}) - I_{\mathrm{obs}}(\bar{\mathbf{h}})}{I_{\mathrm{obs}}(\mathbf{h}) + I_{\mathrm{obs}}(\bar{\mathbf{h}})}$$

Calculated: $$q_{\mathrm{calc}}(\mathbf{h}) = \frac{I_{\mathrm{calc}}(\mathbf{h}) - I_{\mathrm{calc}}(\bar{\mathbf{h}})}{I_{\mathrm{calc}}(\mathbf{h}) + I_{\mathrm{calc}}(\bar{\mathbf{h}})}$$

Structural chirality: $$\Gamma = 1 - 2x_F = \frac{q_{\mathrm{obs}}}{q_{\mathrm{calc}}}$$

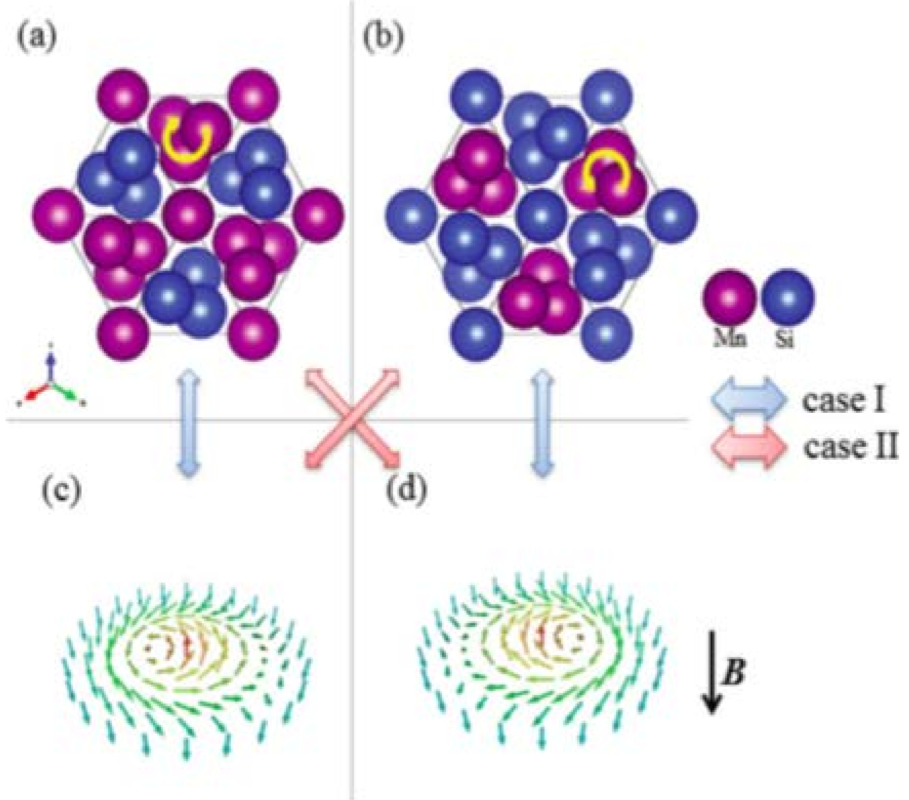
S. Parsons et al., Acta Cryst. (2013). B69, 249–259

Absolute structure determination

$$\frac{I(H)-I(-H)}{I(H)+I(-H)}=\gamma_c\frac{|F_M(H)|^2-|F_M(-H)|^2}{|F_M(H)|^2+|F_M(-H)|^2}$$

$$\gamma_c=(1-2x)$$

Structural chirality – from X-ray diffraction data close to a resonance

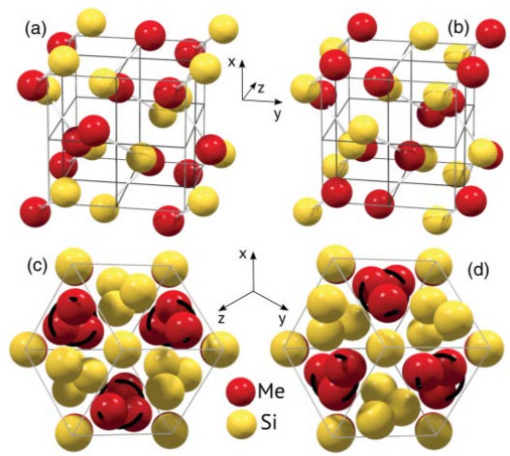


$$\frac{I\uparrow(Q)-I\downarrow(Q)}{I\uparrow(Q)+I\downarrow(Q)}=\gamma_m(\mathbf{P}_0\mathbf{e}_0)$$

Magnetic chirality – from scattering of polarized neutron

Chirality in MnSi at 18 keV

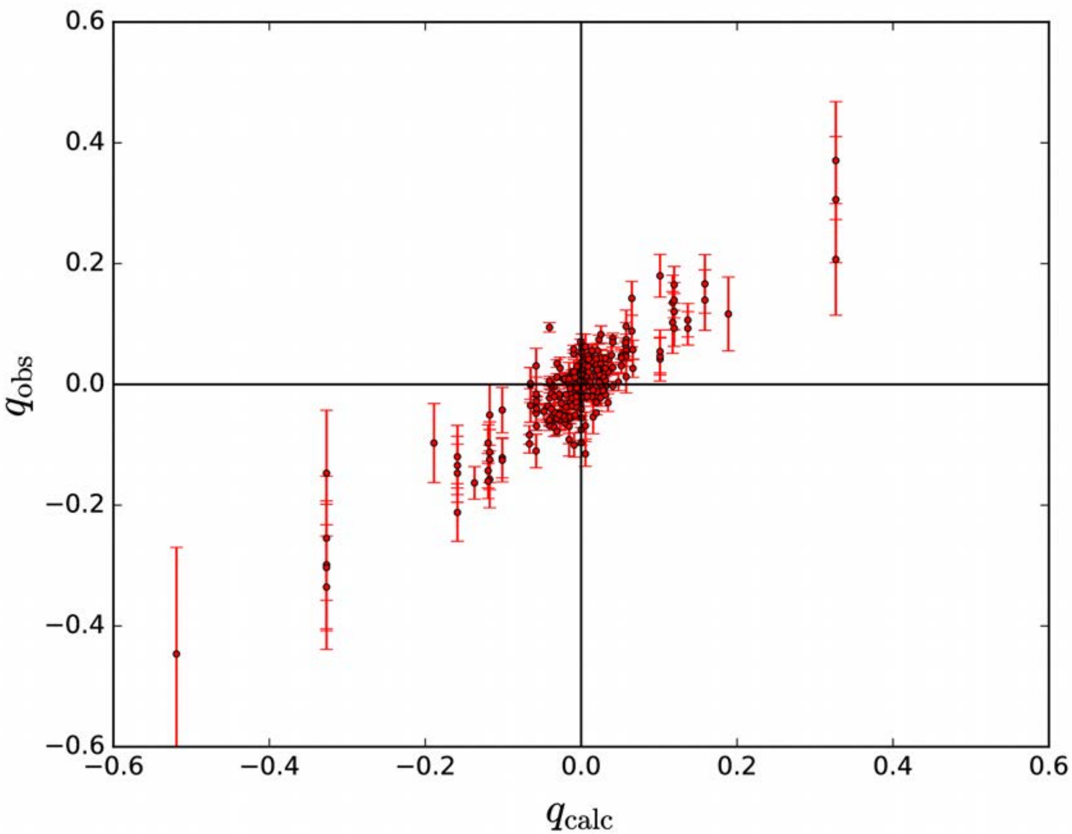
X (Mn)	X (Si)
0.137	0.846 L
0.887	0.154 R



Mn k-edge: 6.5390 keV
Wavelength: 18 keV (0.7 Å)
R_1: 1 – 2%
Flack: 0.01(1)

f'(Mn) = 0.2858, f''(Mn) = 0.6739

f'(Si) = 0.0653, f''(Si) = 0.0646



$$q_{\mathrm{obs}}(\mathbf{h}) = \frac{I_{\mathrm{obs}}(\mathbf{h}) - I_{\mathrm{obs}}(\bar{\mathbf{h}})}{I_{\mathrm{obs}}(\mathbf{h}) + I_{\mathrm{obs}}(\bar{\mathbf{h}})}$$

$$q_{\mathrm{calc}}(\mathbf{h}) = \frac{I_{\mathrm{calc}}(\mathbf{h}) - I_{\mathrm{calc}}(\bar{\mathbf{h}})}{I_{\mathrm{calc}}(\mathbf{h}) + I_{\mathrm{calc}}(\bar{\mathbf{h}})}$$

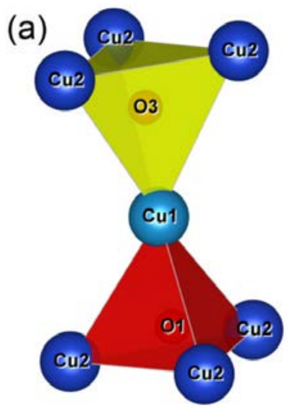
$$\Gamma = 1 - 2x_F = \frac{q_{\mathrm{obs}}}{q_{\mathrm{calc}}}$$

Chirality of Cu_2OSeO_3 (Cu k-edge: 8.9789 keV)

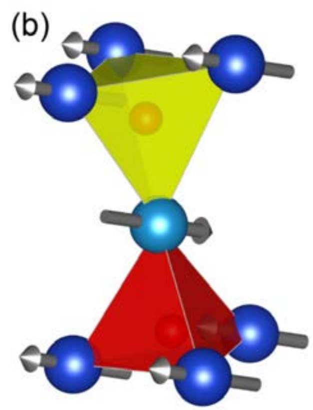
PHYSICAL REVIEW B **89**, 140409(R) (2014)

Chirality of structure and magnetism in the magnetoelectric compound Cu_2OSeO_3

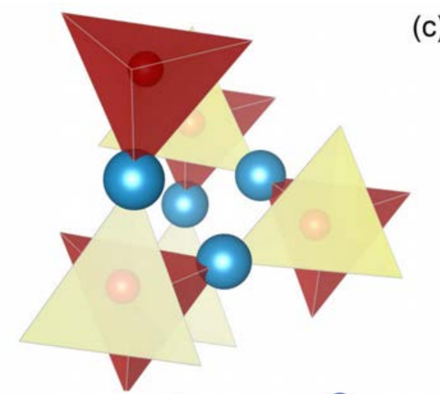
V. Dyadkin,[1,2,*] K. Prša,[3] S. V. Grigoriev,[2,4] J. S. White,[3,5] P. Huang,[3] H. M. Rønnow,[3] A. Magrez,[6]
C. D. Dewhurst,[7] and D. Chernyshov[1]



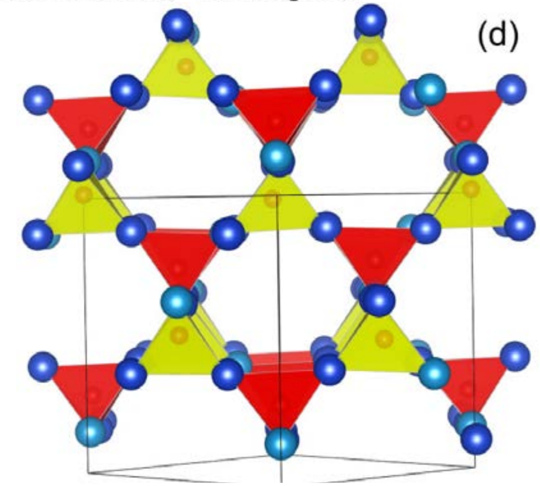
Anion-centered dimer



Magnetically ordered dimer



Structural spiral propagating along [111]



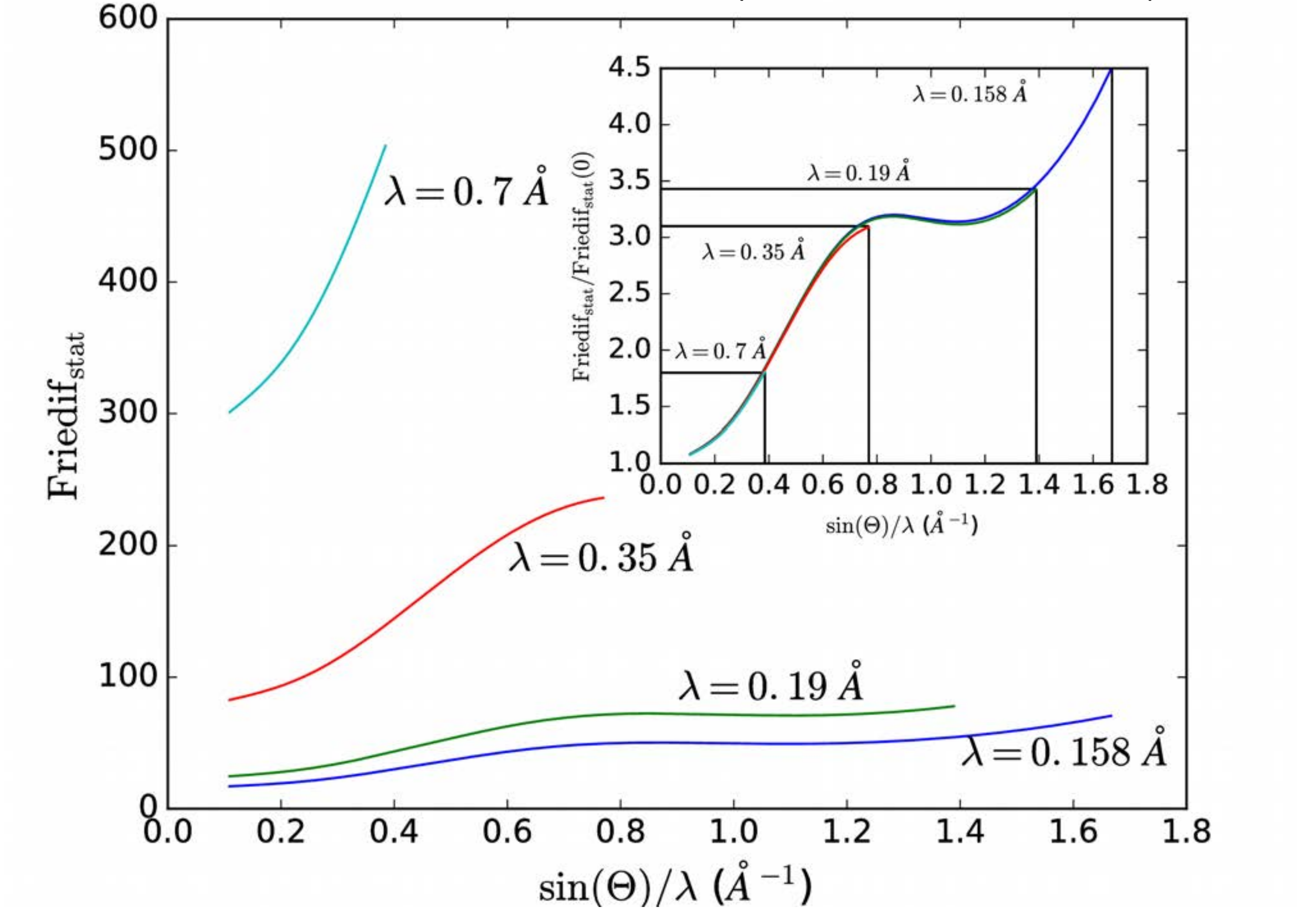
3D-framework of corner-shared dimers

TABLE I. Crystal data and structure refinement for Cu_2OSeO_3.

Temperature	293 K
Crystal system	cubic
Space group	$P2_13$
Wavelength	0.69156 Å
Unit cell dimension a	8.9080(5) Å
θ range for data collection	$\theta_{min} = 3.147^\circ$, $\theta_{max} = 32.252^\circ$
	$-13 \leqslant h \leqslant 13$
Limiting indices	$-11 \leqslant k \leqslant 11$
	$-13 \leqslant l \leqslant 13$
Reflections collected / unique	5255/886 [$R_{int} = 0.0367$]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0312$, $wR_2 = 0.0685$
Absolute structure parameter	$-0.028(12)$

Friedif$_{stat}$

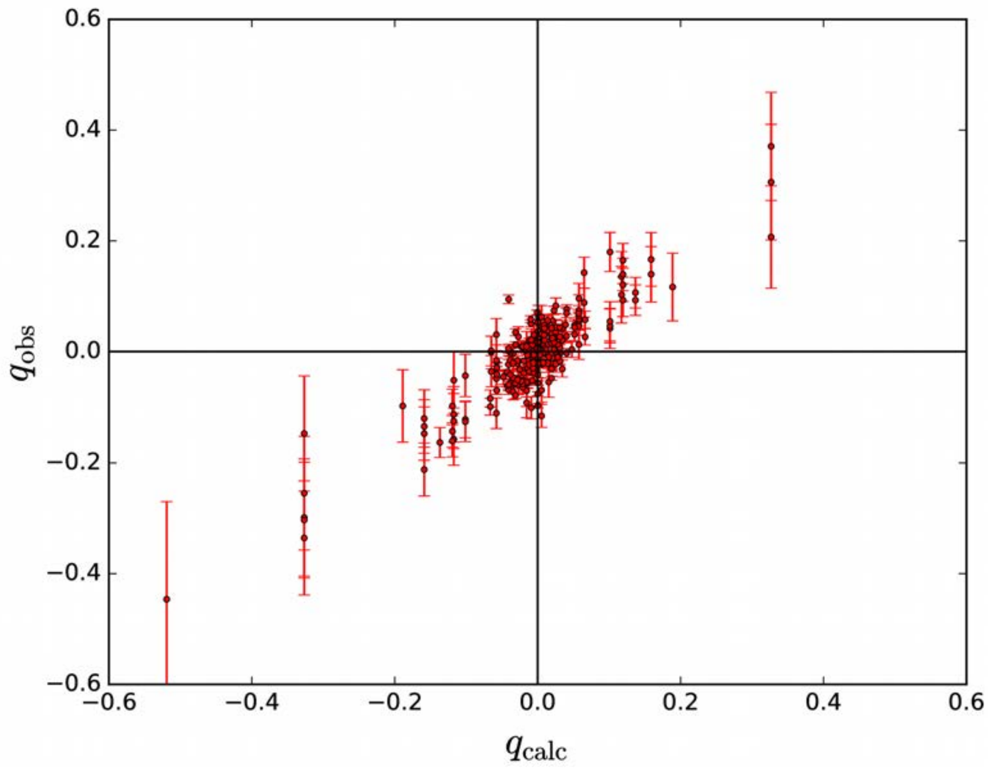
$$\mathrm{Friedif}_{\mathrm{stat}} = 2 \times 10^4 \times \frac{\sqrt{\sum_{j=1}^{N}\sum_{l=1}^{N}\left(f_j f_l'' - f_l f_j''\right)^2 - \sum_{j=1}^{M}\sum_{l=1}^{M}\left(f_j f_l'' - f_l f_j''\right)^2}}{\left(\sum_{j=1}^{N} f_j^2 + \sum_{j=1}^{N} f_j''^2\right)}$$



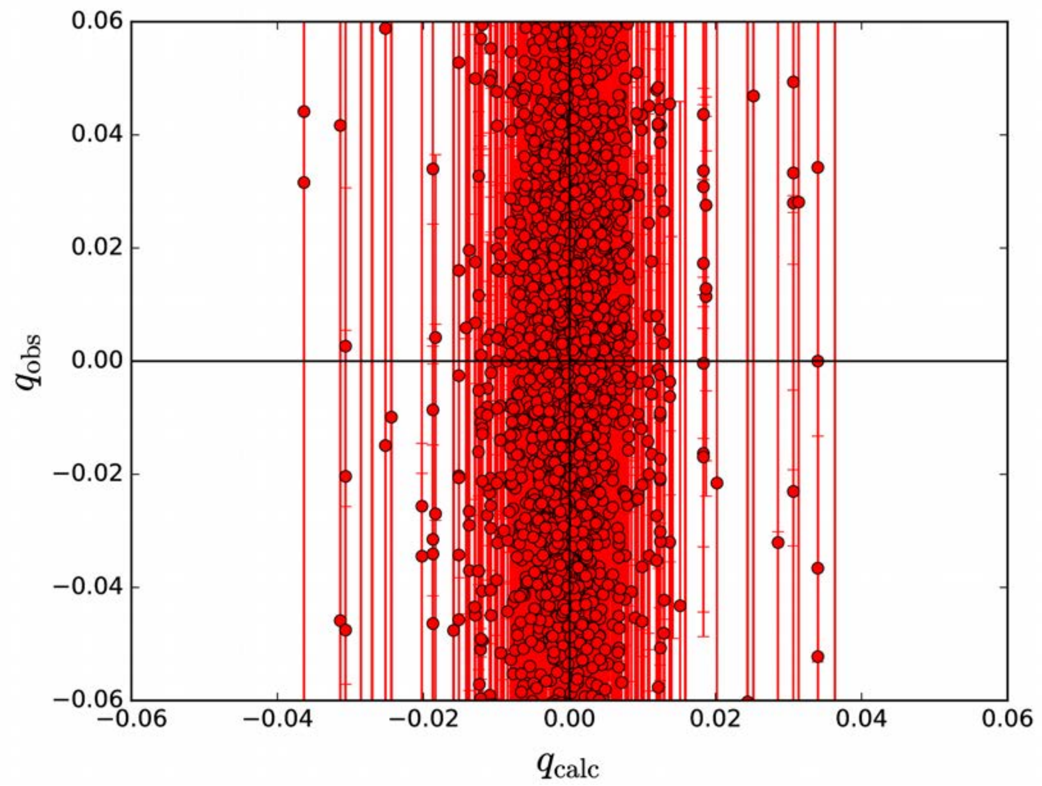
H.D. Flack and U. Shmueli, Acta Cryst. (2007) A63, 257

Parsons' plot for MnSi

18 keV



78 keV



f'(Mn) = 0.2858, f''(Mn) = 0.6739

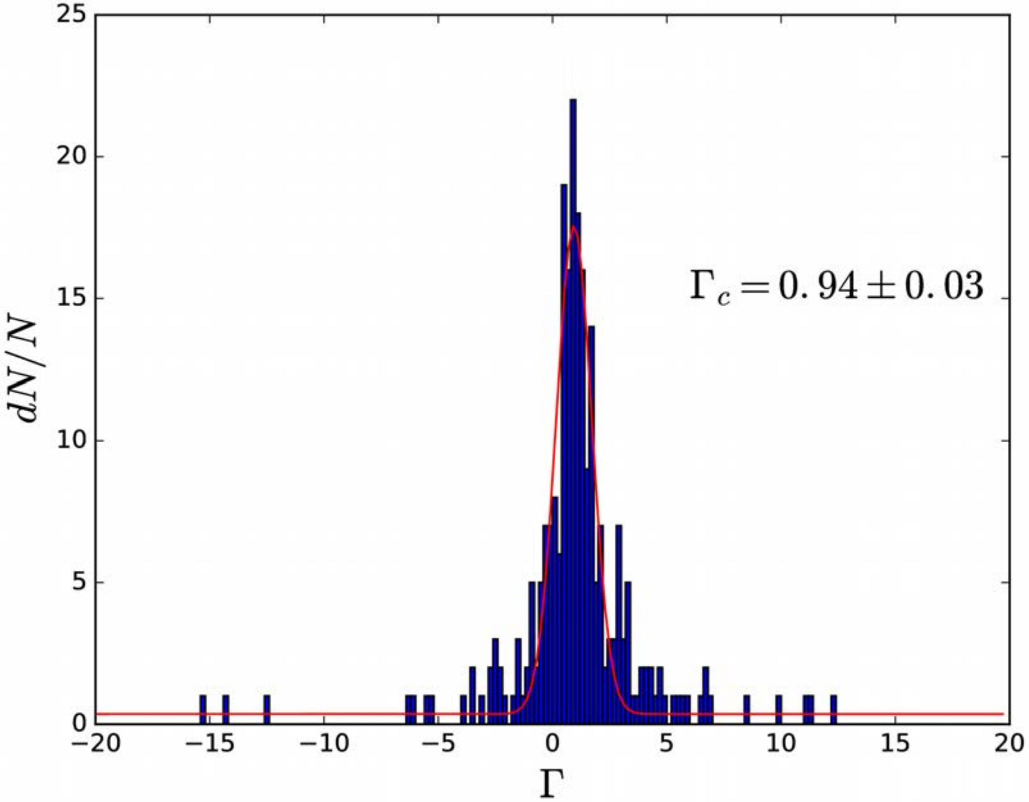
f'(Si) = 0.0653, f''(Si) = 0.0646

f'(Mn) = -0.0397, f''(Mn) = 0.0385

f'(Si) = -0.0197, f''(Si) = 0.0027

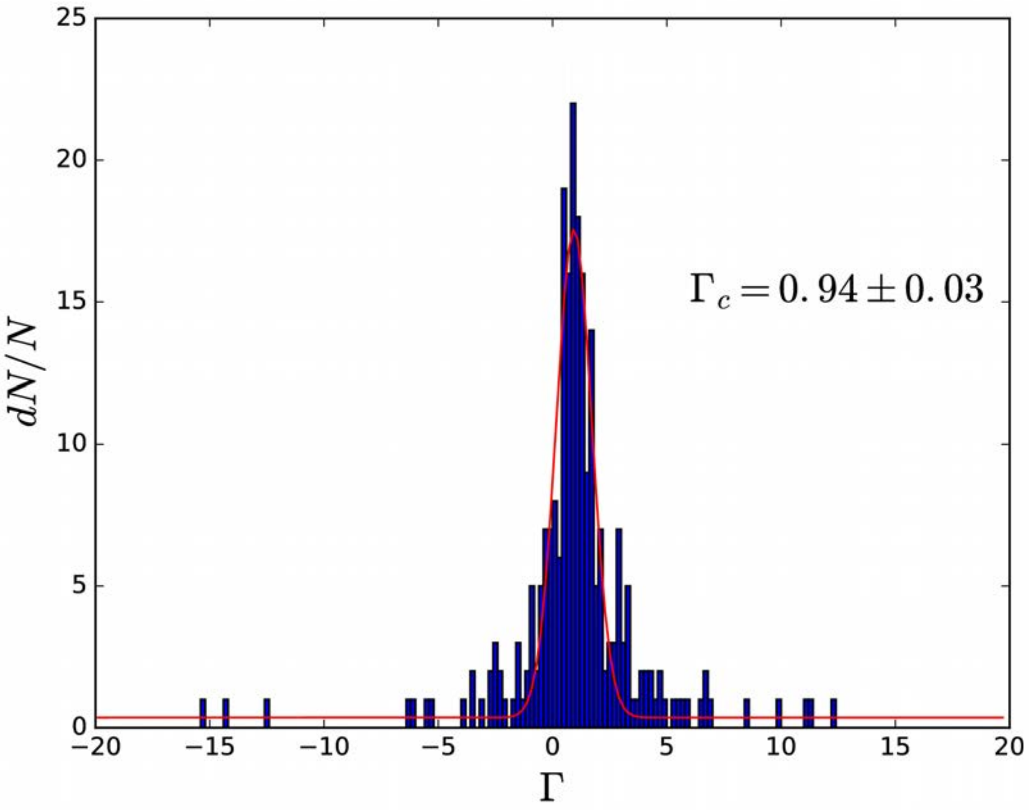
Γ-histogram

18 keV

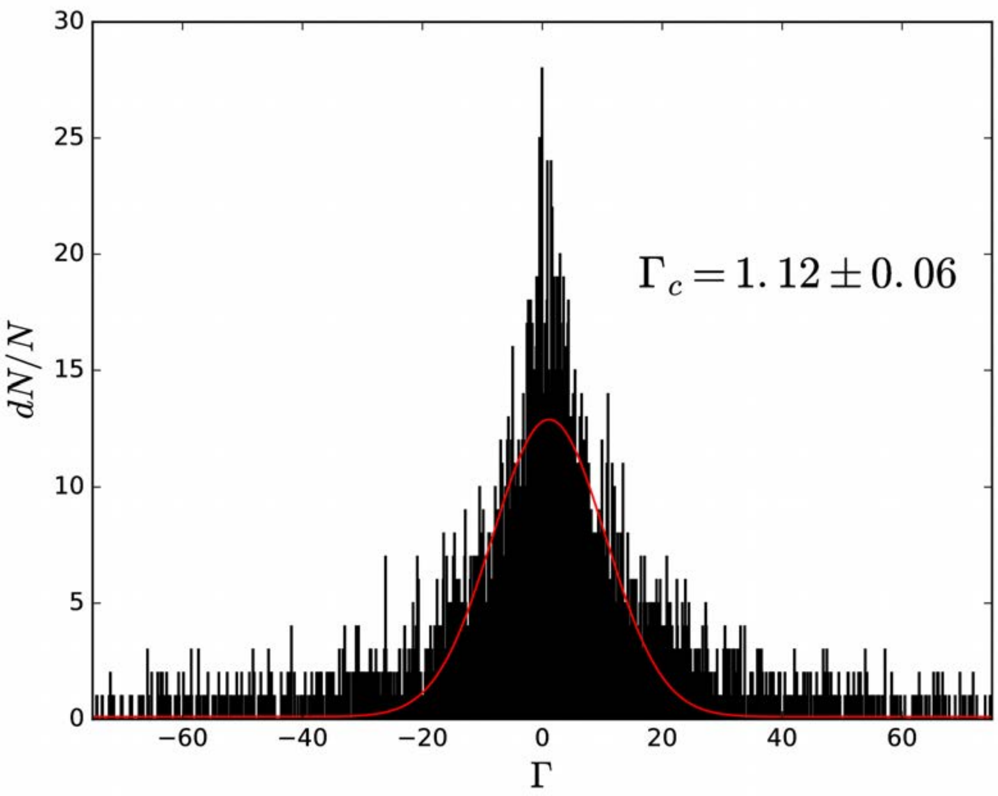


Γ-histogram

18 keV



78 keV



Weighted Γ-histogram

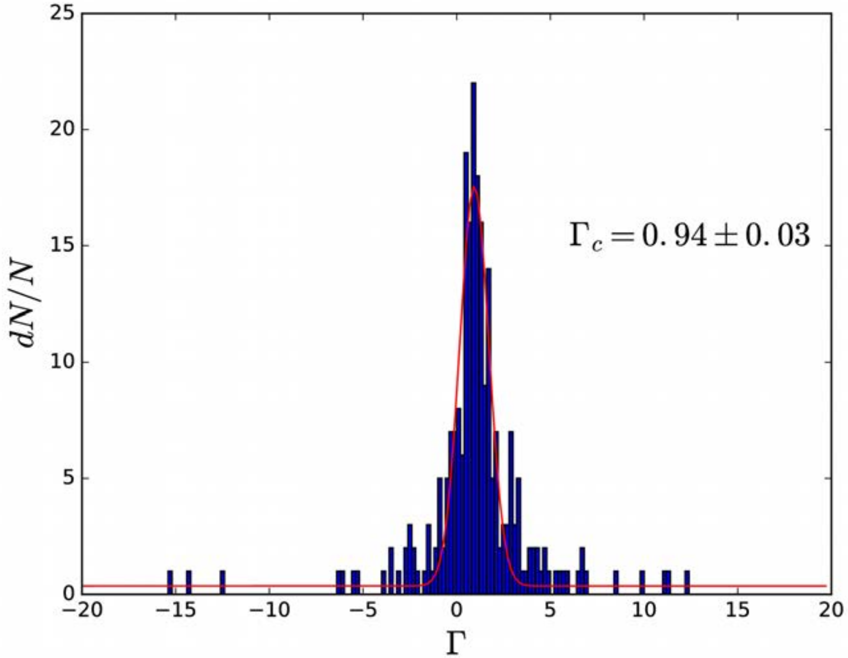
$$\sigma^2(\Gamma) = \sum_{i=1}^{n} \left(\Delta I_i \frac{\partial \Gamma}{\partial I_i} \right)^2$$

$$= \Delta I_{\mathrm{o}}^{+} \left[\frac{I_{\mathrm{c}}^{+} + I_{\mathrm{c}}^{-}}{(I_{\mathrm{c}}^{+} - I_{\mathrm{c}}^{-})(I_{\mathrm{o}}^{+} + I_{\mathrm{o}}^{-})} - \frac{(I_{\mathrm{c}}^{+} + I_{\mathrm{c}}^{-})(I_{\mathrm{o}}^{+} - I_{\mathrm{o}}^{-})}{(I_{\mathrm{c}}^{+} - I_{\mathrm{c}}^{-})(I_{\mathrm{o}}^{+} + I_{\mathrm{o}}^{-})^2} \right]^2$$

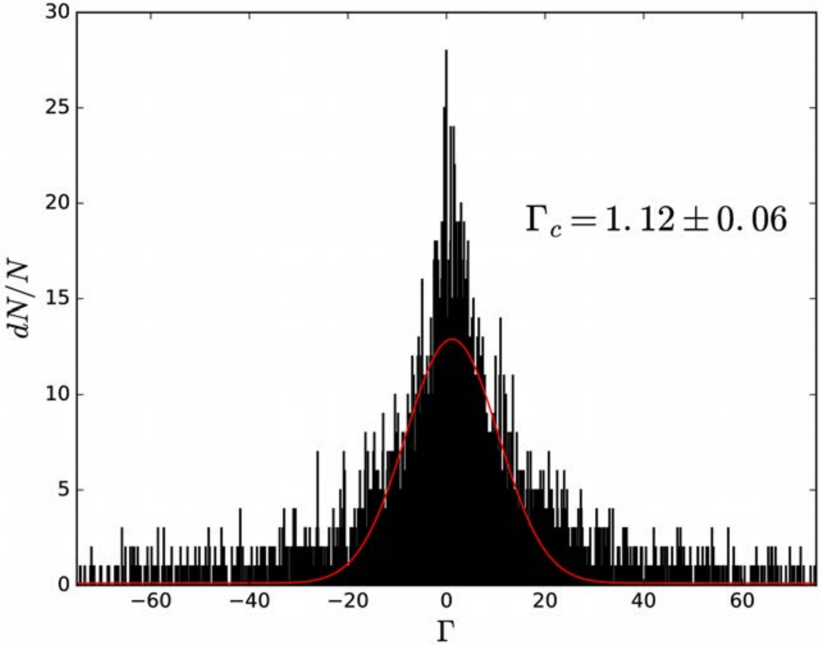
$$+ \Delta I_{\mathrm{o}}^{-} \left[- \frac{(I_{\mathrm{c}}^{+} + I_{\mathrm{c}}^{-})(I_{\mathrm{o}}^{+} - I_{\mathrm{o}}^{-})}{(I_{\mathrm{c}}^{+} - I_{\mathrm{c}}^{-})(I_{\mathrm{o}}^{+} + I_{\mathrm{o}}^{-})^2} - \frac{I_{\mathrm{c}}^{+} + I_{\mathrm{c}}^{-}}{(I_{\mathrm{c}}^{+} - I_{\mathrm{c}}^{-})(I_{\mathrm{o}}^{+} + I_{\mathrm{o}}^{-})} \right]^2$$

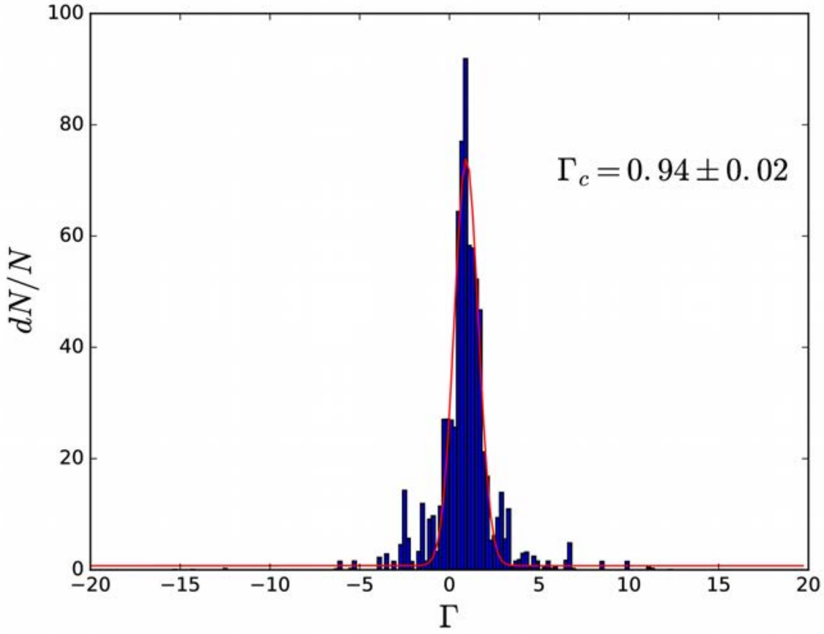
Weighted Γ-histogram

18 keV



78 keV





Weighted Γ-histogram

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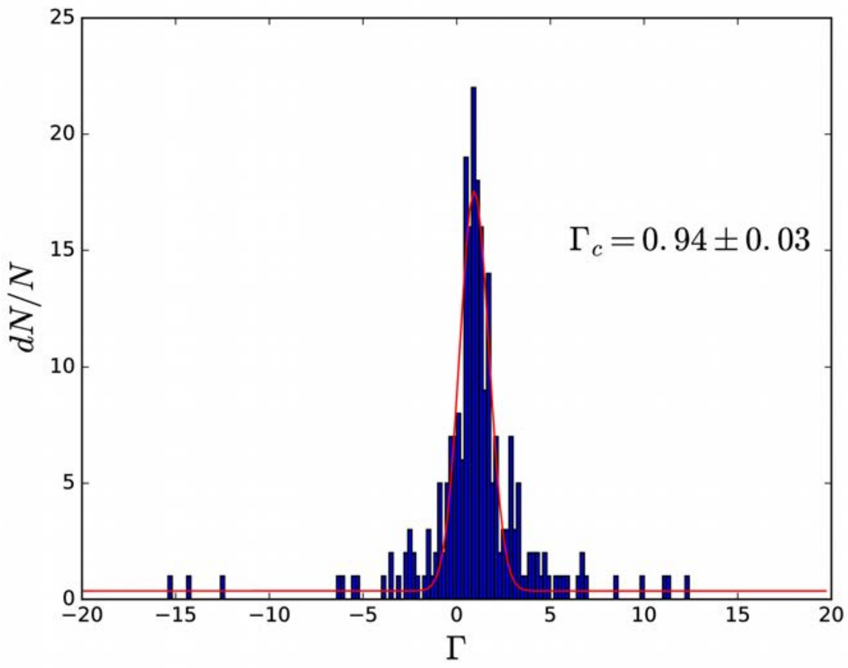
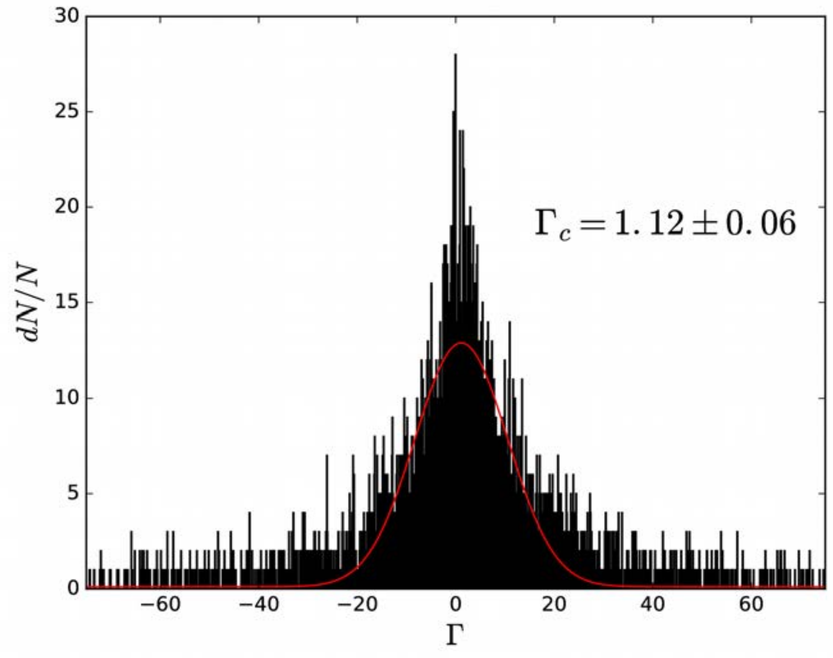
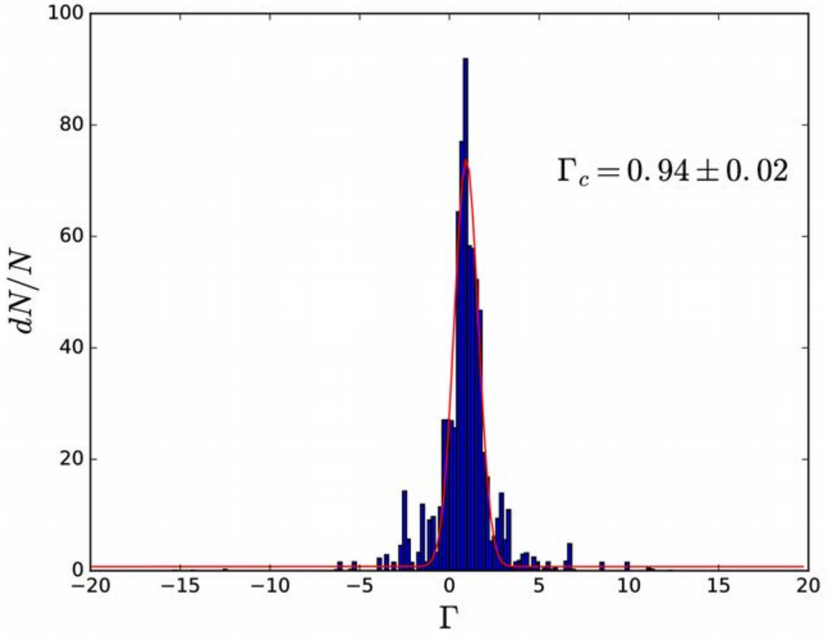
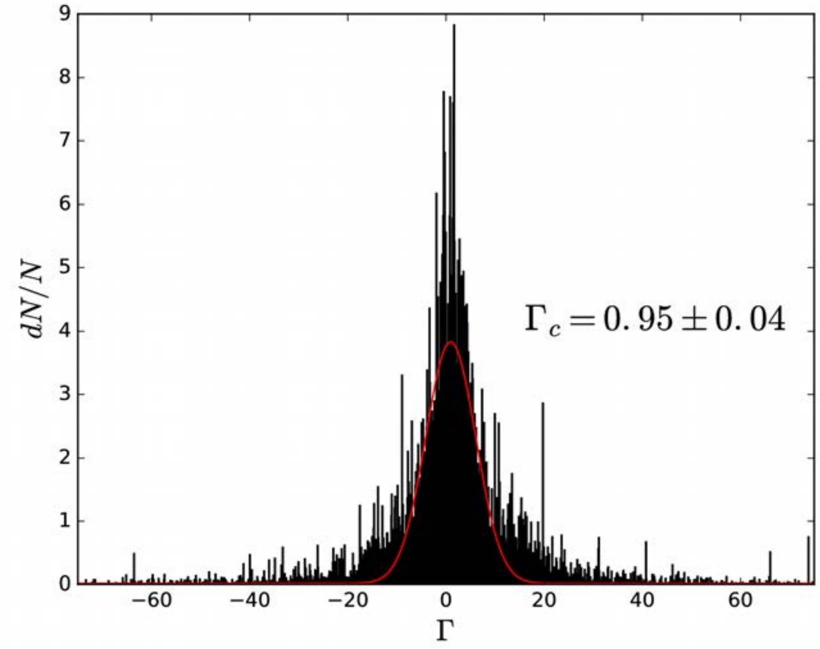
78 keV









Conclusion

- Determination of absolute structure using the Flack parameter and Parsons quotients for low energy x-rays is a routine procedure.

- Determination of absolute structure far from the resonant scattering is also possible if we apply statistical methods to the quotients distribution.

Bleeding edge

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Absolute structure determination using *CRYSTALS*

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