From a diffraction experiment to the crystal structure

Sébastien Pillet

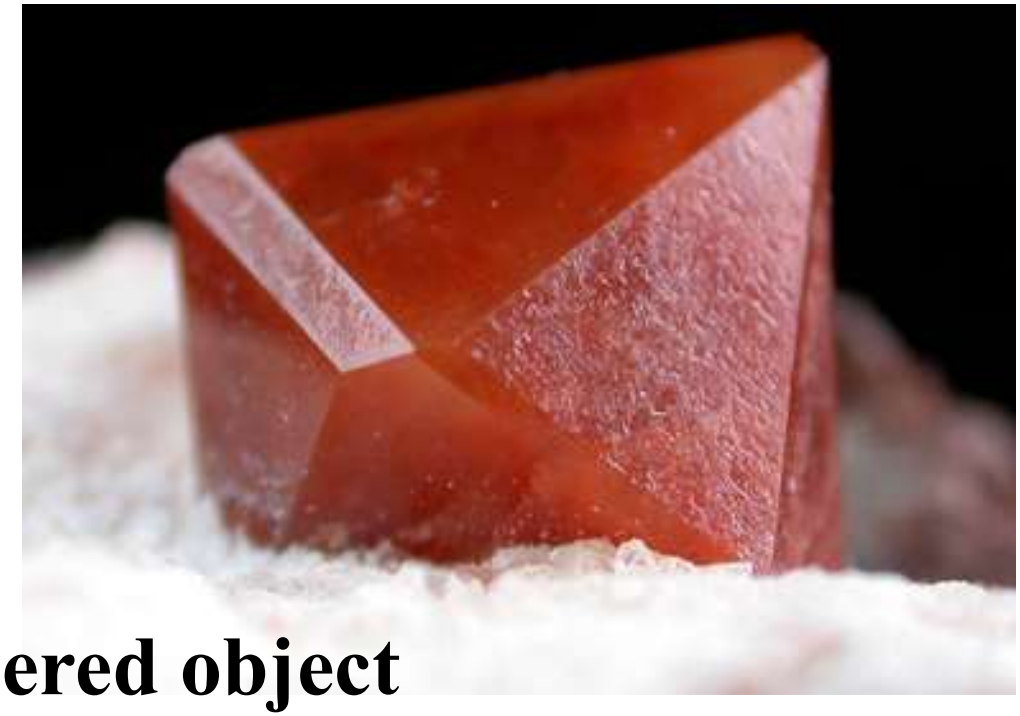
Laboratoire de Cristallographie, Résonance Magnétique et Modélisations
Université de Lorraine

CLSF School – November 3rd 2026

Outline

- Motivations
- Some fundamentals
- Measuring diffraction data
- Solving the crystal structure
- The structural model
- Analysing structural properties : scientific cases

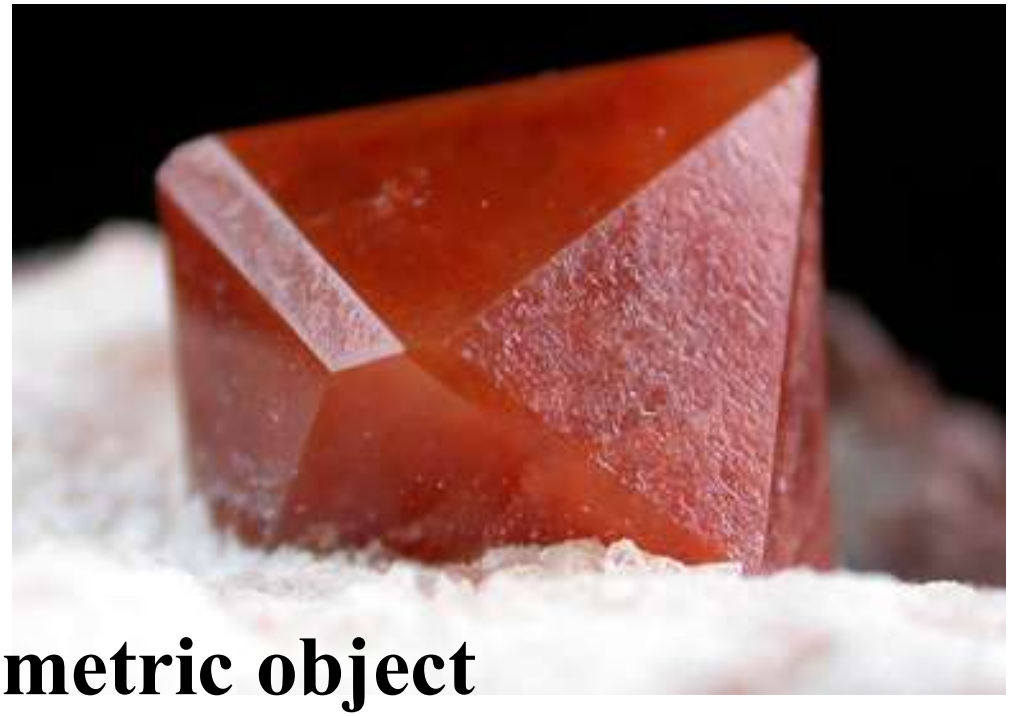
What is a crystal?



Ordered object

N ~ 10^{18} atoms

What is a crystal?



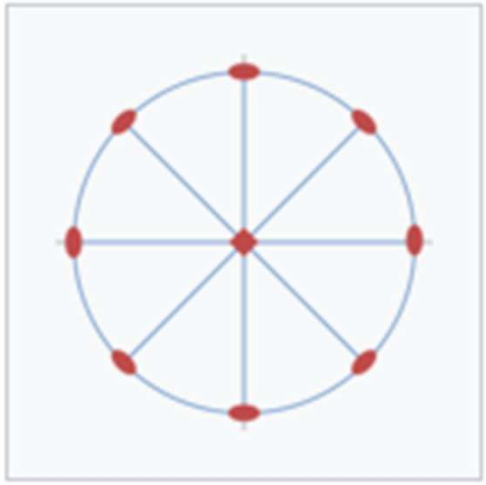
Symmetric object

Point group vs space group

A **point group** is a group of symmetry operations all of which leave at least one point unmoved

We do not consider the motif

Symmetry of the crystal lattice



$$\frac{4}{m}\frac{2}{m}\frac{2}{m}\,(D_{4h})$$

32 **point groups** in three dimensions

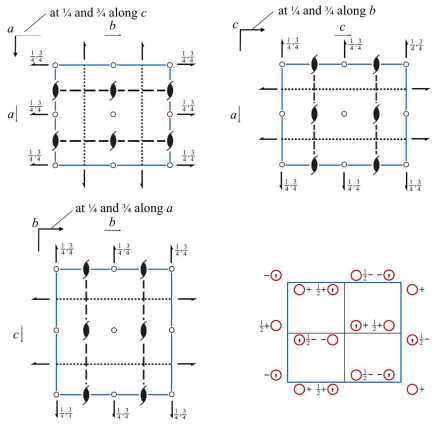
The symmetry group of a three-dimensional crystal pattern is called its **space group**

We consider the motif (asymmetric unit)

Symmetry of the crystal structure

Pbca $P\frac{2_1}{b}\frac{2_1}{c}\frac{2_1}{a}$ Orthorhombic

No. 61 *mmm*



Origin at $\bar{1}$

Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{2}$; $0 \le z \le \frac{1}{2}$;

Symmetry operations

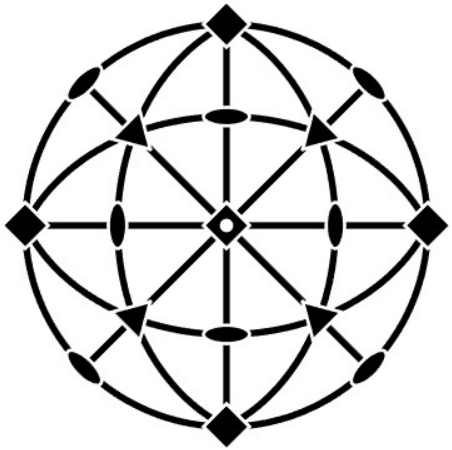
(1) 1 (2) 2 $(0,0,\frac{1}{2})$ $\frac{1}{4},0,z$ (3) 2 $(0,\frac{1}{2},0)$ $0,y,\frac{1}{4}$ (4) 2 $(\frac{1}{2},0,0)$ $x,\frac{1}{4},0$

(5) $\bar{1}$ 0,0,0 (6) *a* $x,y,\frac{1}{4}$ (7) *c* $x,\frac{1}{4},z$ (8) *b* $\frac{1}{4},y,z$

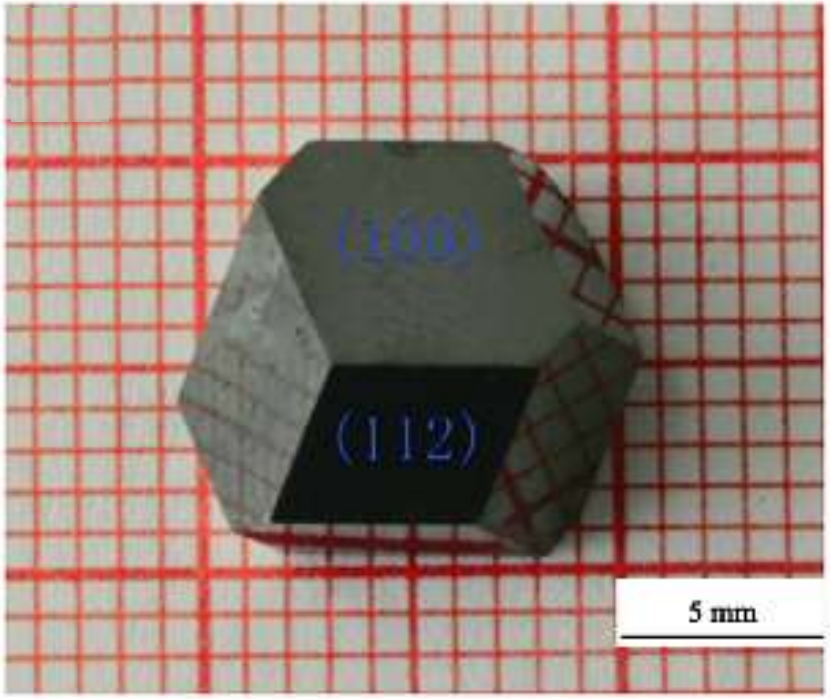
230 **space groups** in three dimensions

Neumann's principle

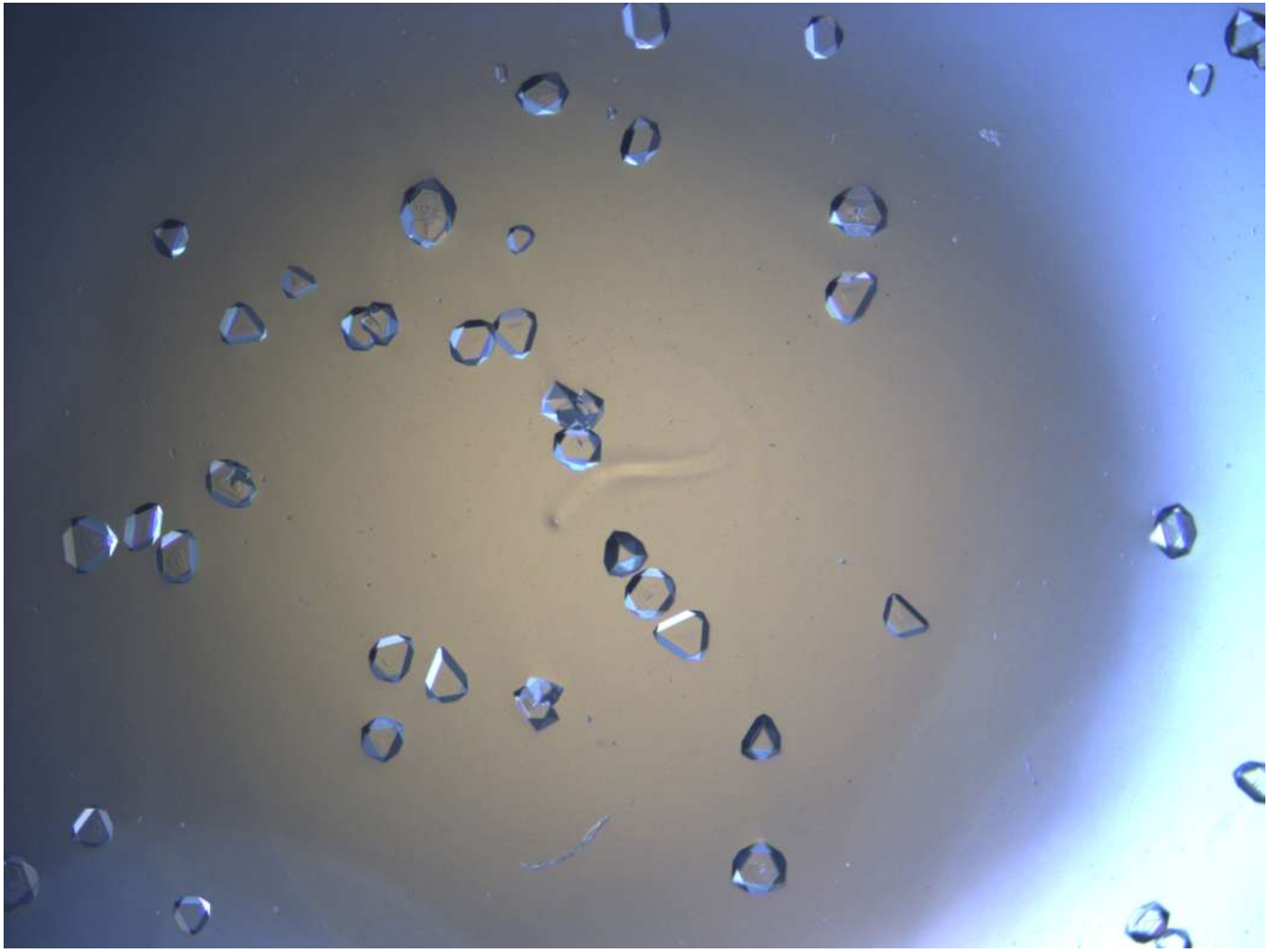
Neumann's principle :
the symmetry operations of any physical property of a crystal must include the symmetry operations of the point group of the crystal
Any physical property should be invariant with respect to the crystal point-group symmetry operations



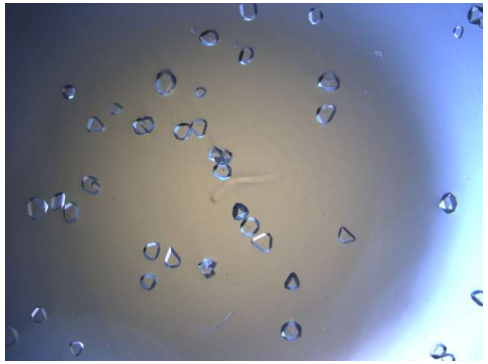
Space group (350K) : Pm-3m
Point group (350K) : m-3m



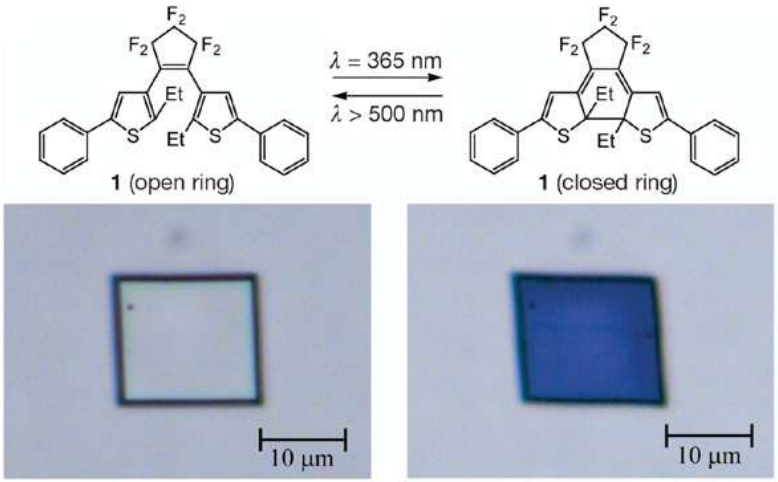
Use of single crystal X-ray diffraction



Use of single crystal X-ray diffraction

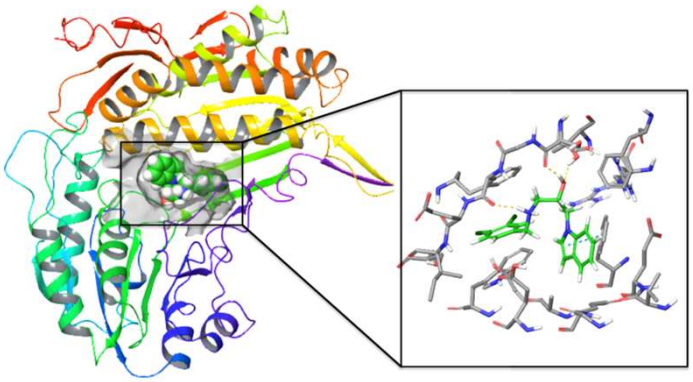


optical

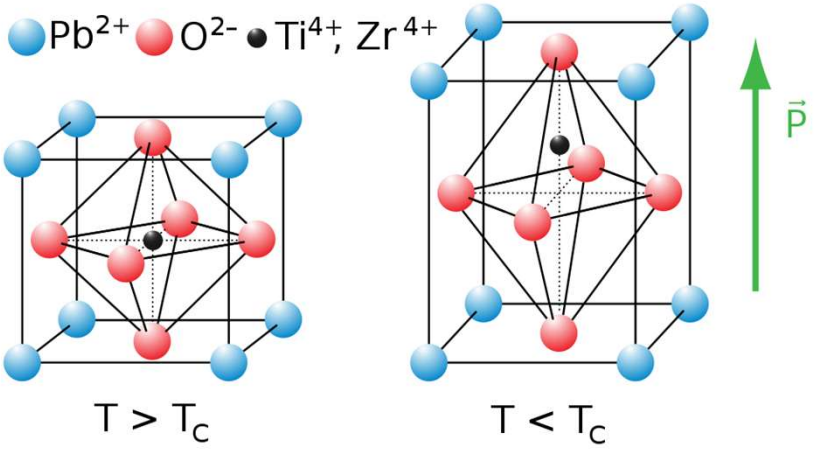


Structure-properties relationship

Biological activity

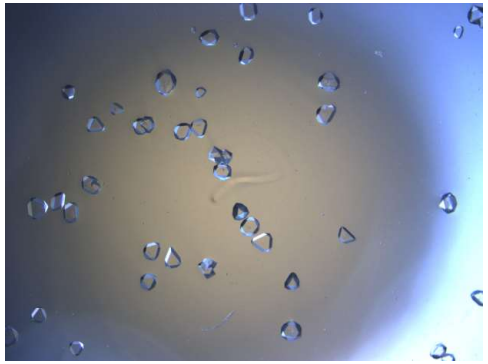


electrical



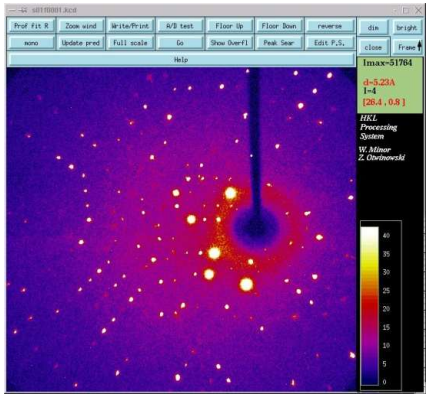
Use of single crystal X-ray diffraction

Direct space



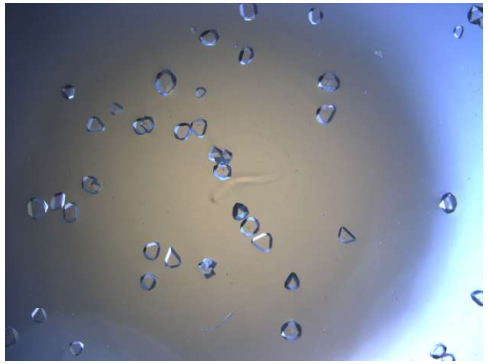
Diffraction experiment

Reciprocal space



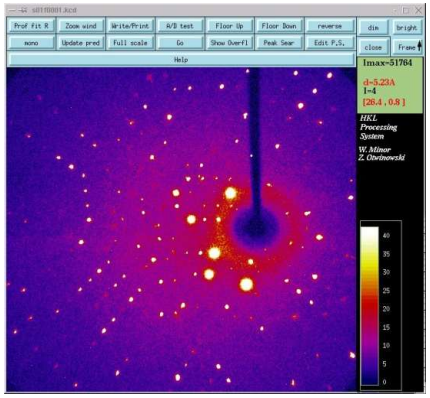
Use of single crystal X-ray diffraction

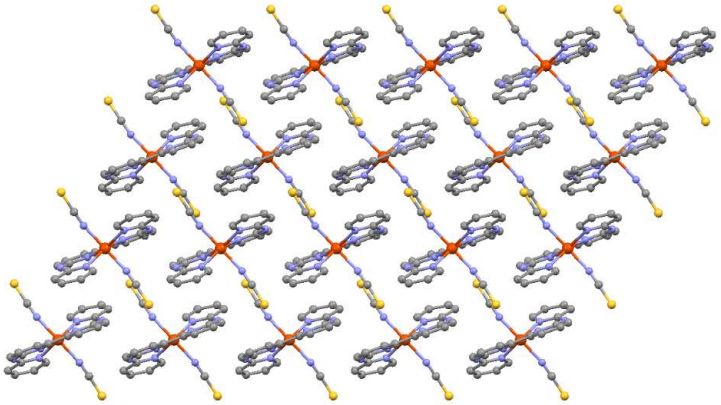
Direct space



Diffraction experiment

Reciprocal space

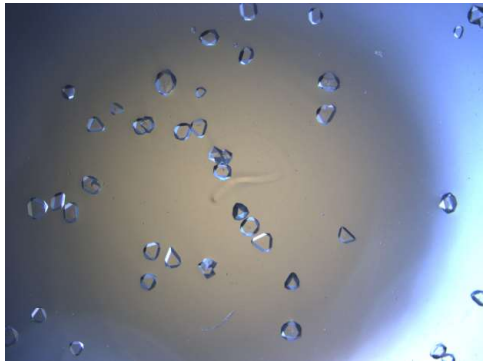




Structural model

Use of single crystal X-ray diffraction

Direct space

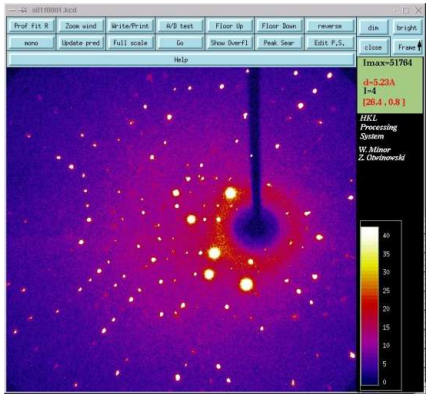


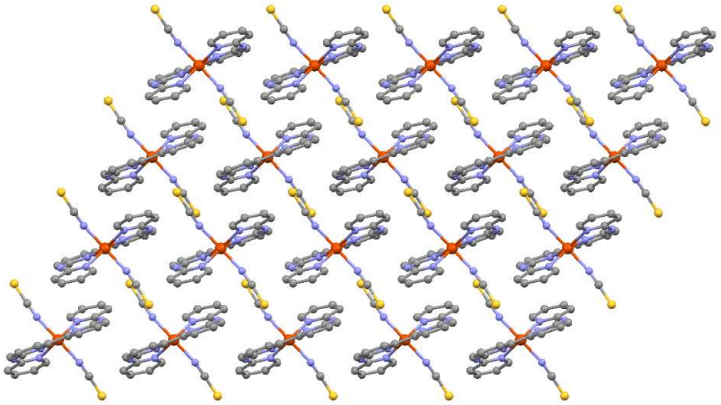
Symmetry
Bond distances
Bond angles
Disorder
Thermal smearing / dynamics

At thermodynamic equilibrium or out of equilibrium

Diffraction experiment

Reciprocal space

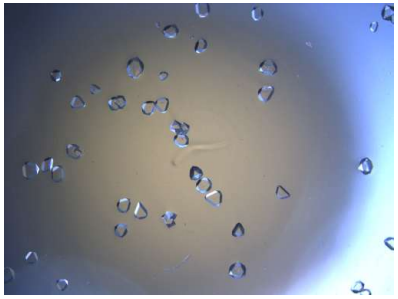




Structural model

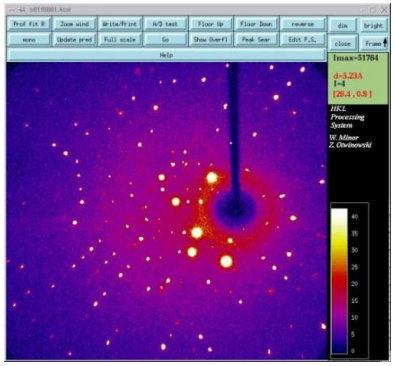
Use of single crystal X-ray diffraction

Direct space



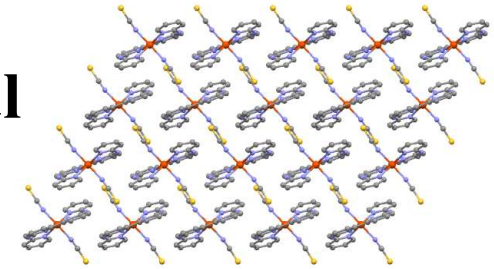
- Symmetry : determination of point group
- Twins?
- Polymorphism?

Reciprocal space



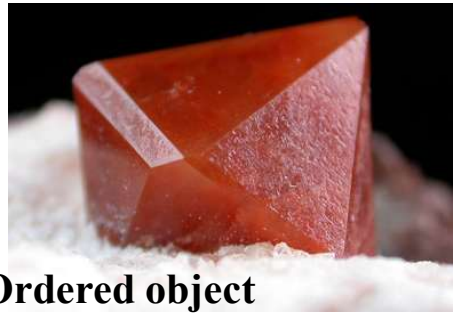
- Crystal quality
- Microstructure
- Diffuse scattering (=disorder)
- Twins?
- Symmetry (determination of certain translational symmetry elements, lattice mode)

Structural model



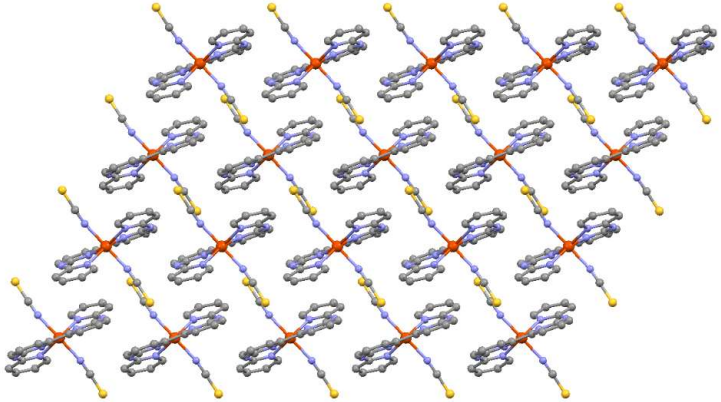
- Chemical composition
- Symmetry (determination of space group)
- Structural organisation
- Studies as a function of T, P, hv, …

What is a crystal?



Ordered object

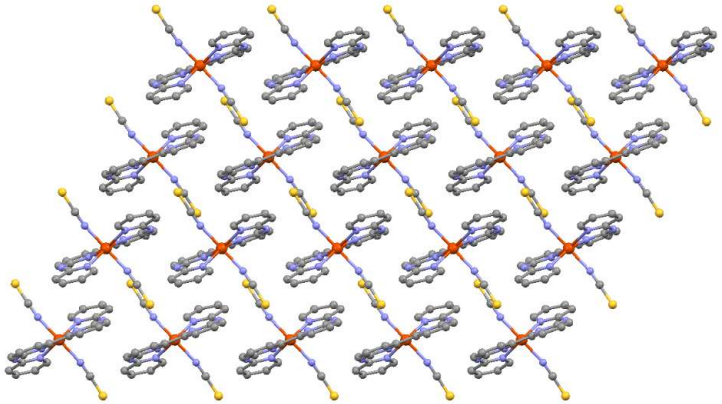
N ~ 10^{18} atoms



What is a crystal?

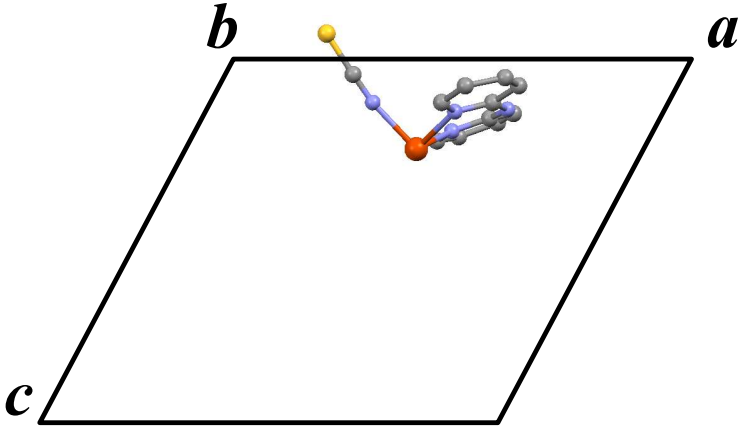


Ordered object
N ~ 10^{18} atoms

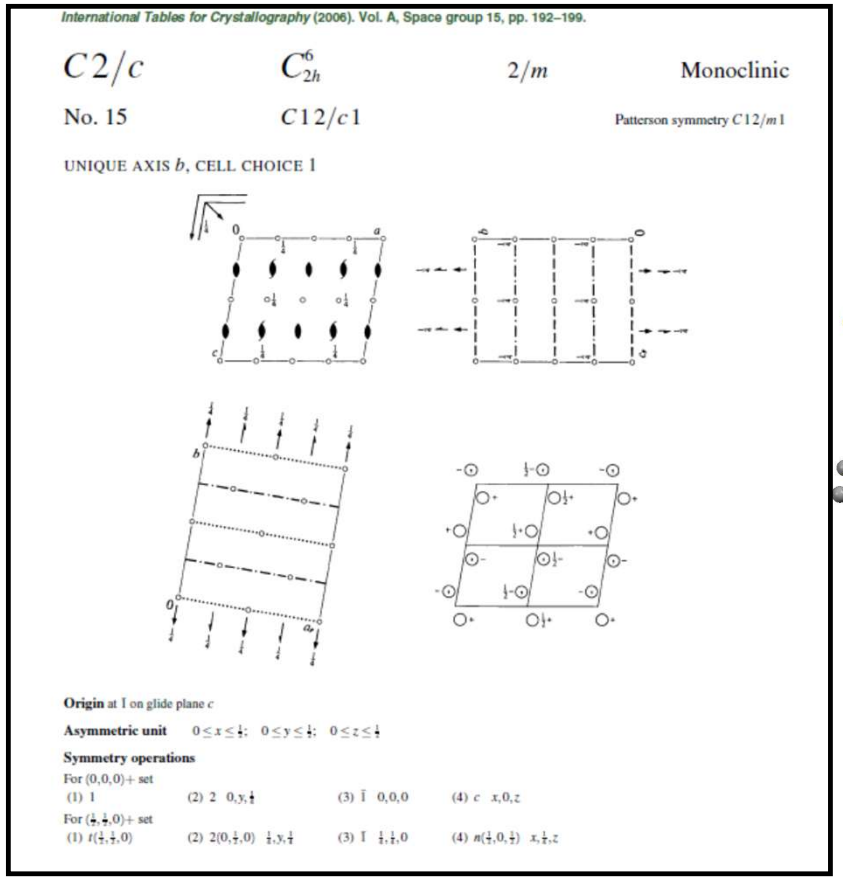


1. Asymmetric unit = motif

Asymmetric unit



What is a crystal?



International Tables for Crystallography (2006). Vol. A, Space group 15, pp. 192–199.

$C2/c$ C_{2h}^6 $2/m$ Monoclinic

No. 15 $C12/c1$ Patterson symmetry $C12/m1$

UNIQUE AXIS b, CELL CHOICE 1

Origin at $\bar{1}$ on glide plane c

Asymmetric unit $0 \le x \le \frac{1}{4}$; $0 \le y \le \frac{1}{4}$; $0 \le z \le \frac{1}{4}$

Symmetry operations

For (0,0,0)+ set

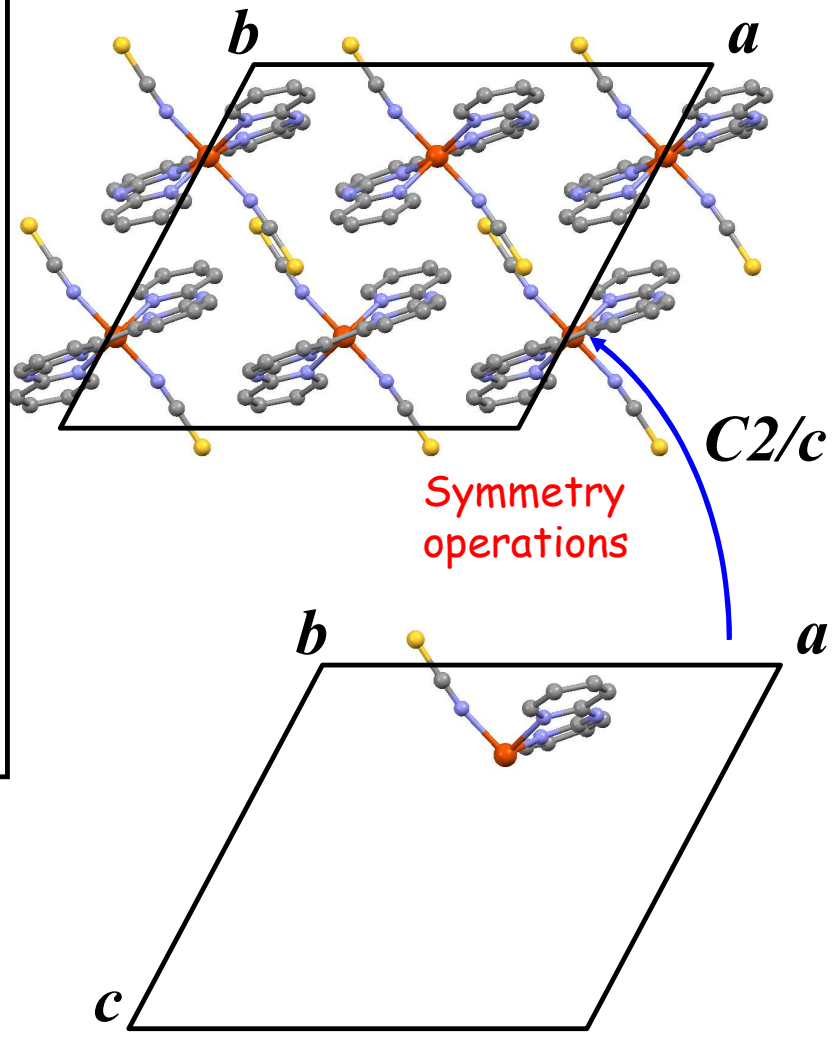
(1) 1 (2) 2 $0,y,\frac{1}{4}$ (3) $\bar{1}$ 0,0,0 (4) c $x,0,z$

For $(\frac{1}{2},\frac{1}{2},0)$+ set

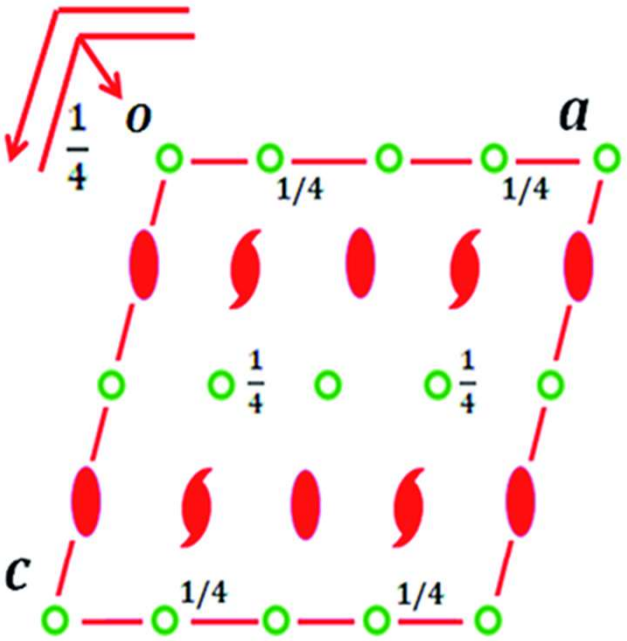
(1) $t(\frac{1}{2},\frac{1}{2},0)$ (2) $2(0,\frac{1}{4},0)$ $\frac{1}{2},y,\frac{1}{4}$ (3) $\bar{1}$ $\frac{1}{2},\frac{1}{4},0$ (4) $n(\frac{1}{2},0,\frac{1}{2})$ $x,\frac{1}{4},z$

1. Asymmetric unit = motif
2. Space group

Unit cell



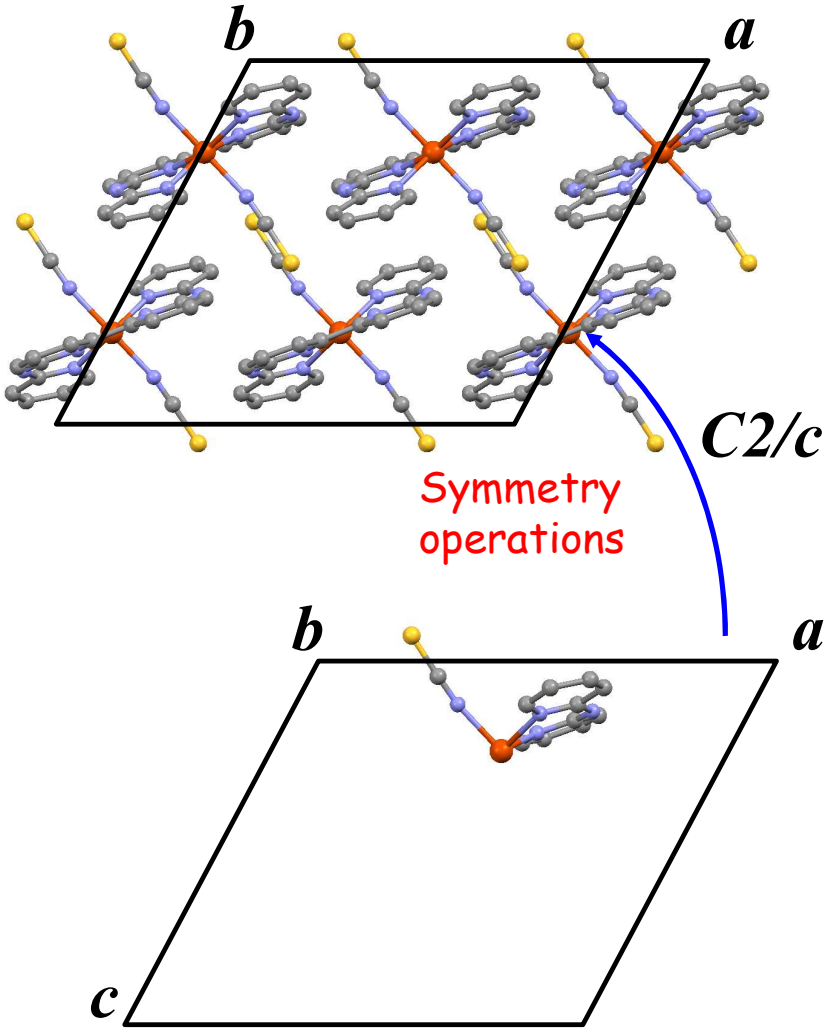
What is a crystal?



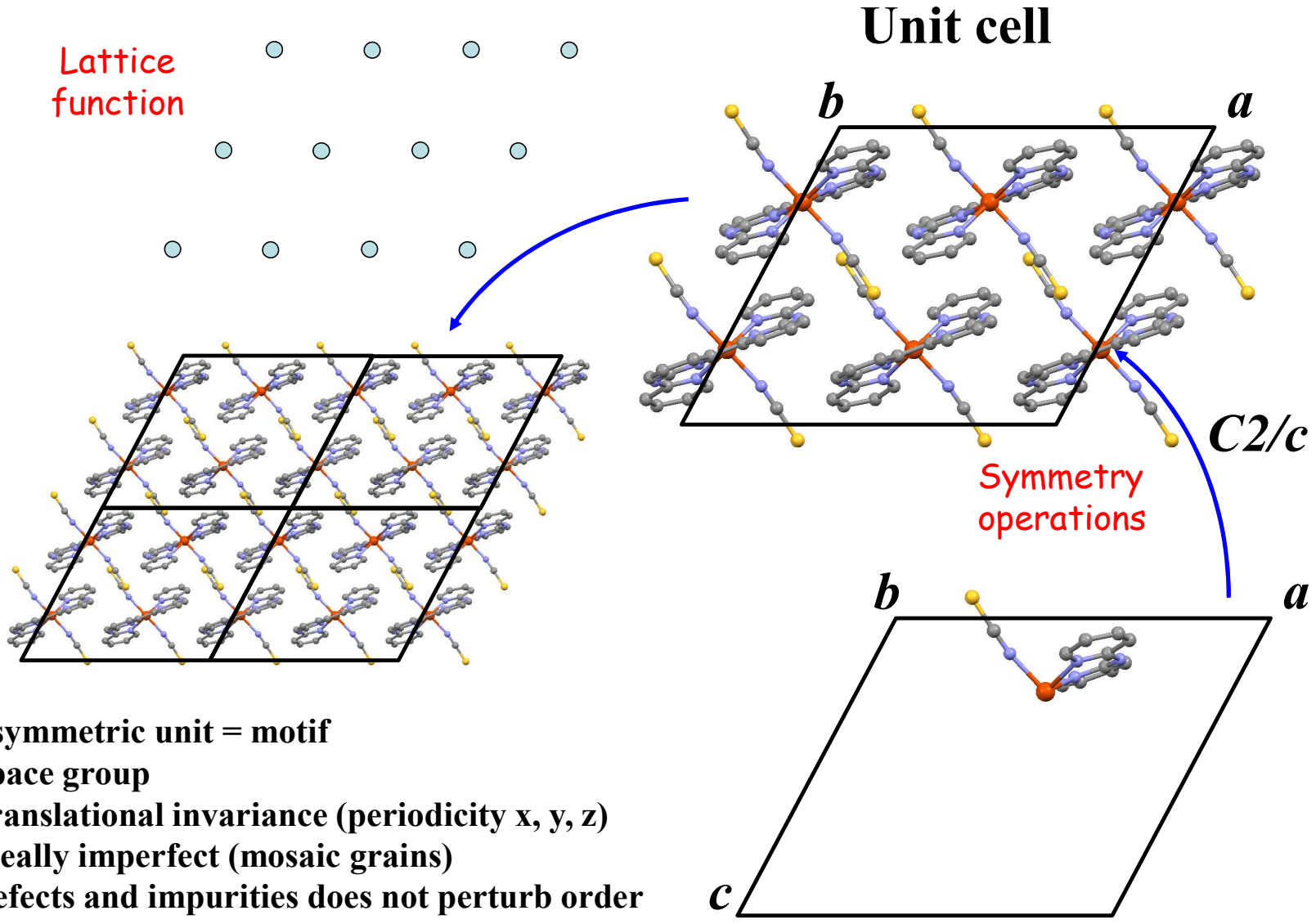
Space group *C* 2/*c* (No. 15)

1. Asymmetric unit = motif
2. Space group

Unit cell



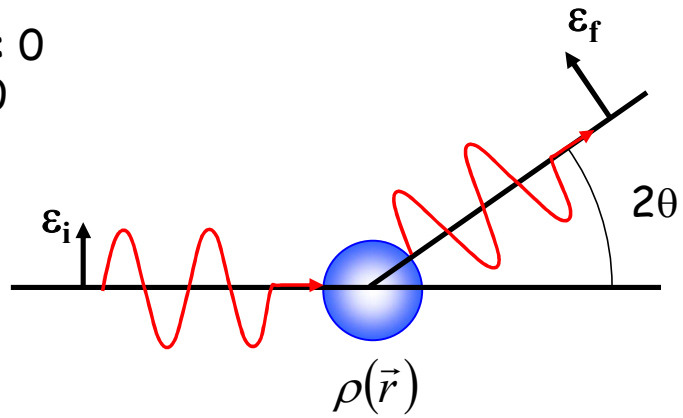
What is a crystal?



1. Asymmetric unit = motif
2. Space group
3. Translational invariance (periodicity x, y, z)
4. Ideally imperfect (mosaic grains)
5. Defects and impurities does not perturb order

Principle of X-ray diffraction

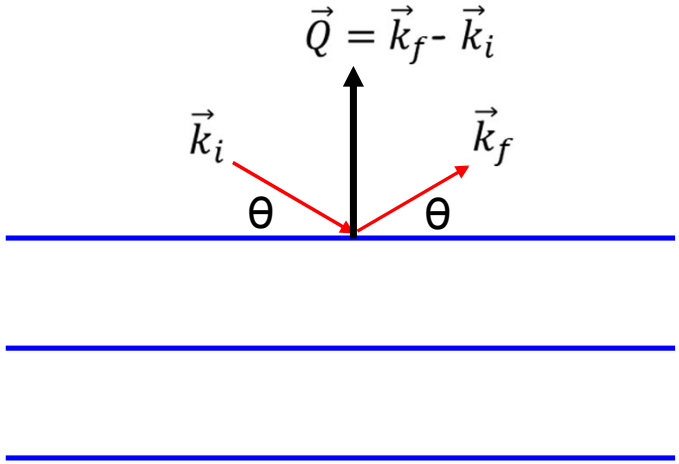
Charge : 0
Mass : 0
Spin : 1



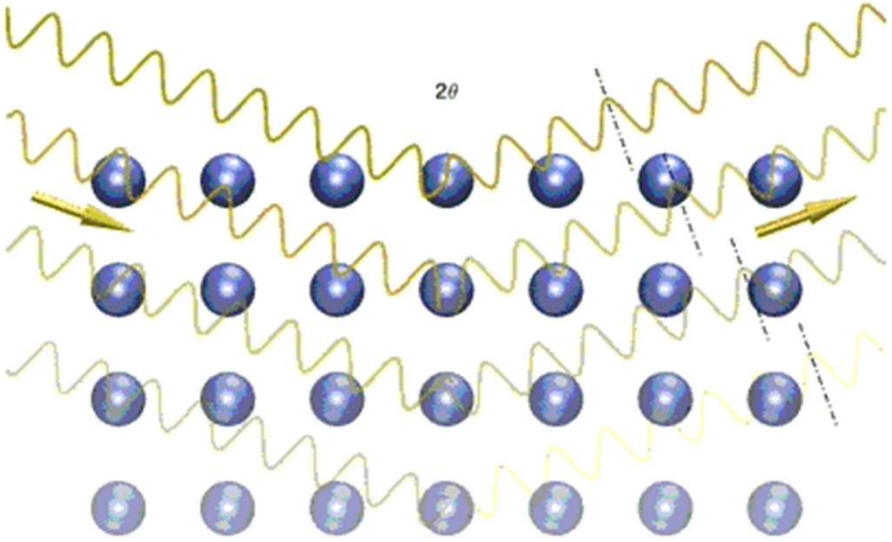
Thomson elastic scattering

Radial process

$$\lambda\,[\text{Å}] = \frac{12.398}{\varepsilon\,[\text{keV}]} \qquad |\vec{k}_i| = |\vec{k}_f| \quad (\lambda_i = \lambda_f)$$

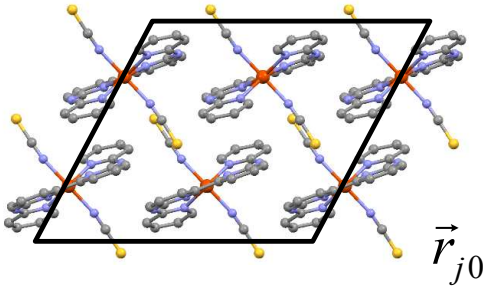


Bragg's law



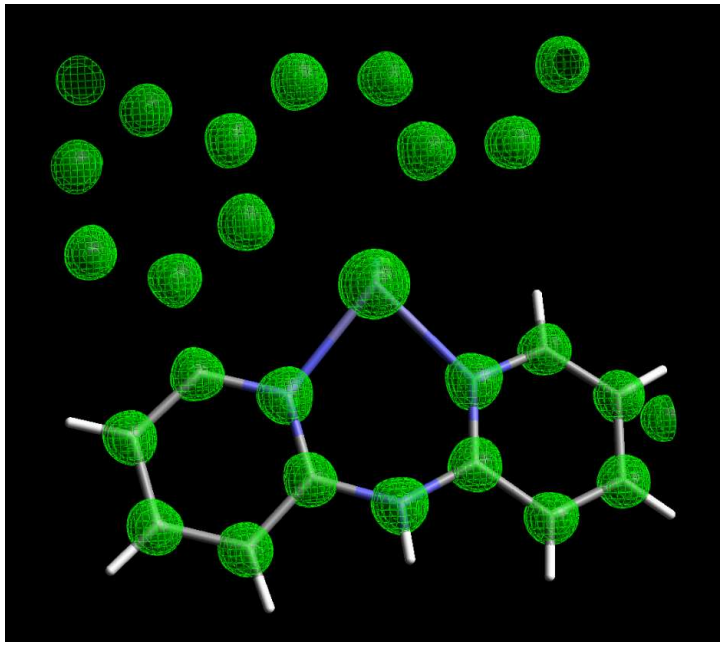
Taken from Philip Willmott (Paul Scherrer Institute, Switzerland)

Unit cell structure factors

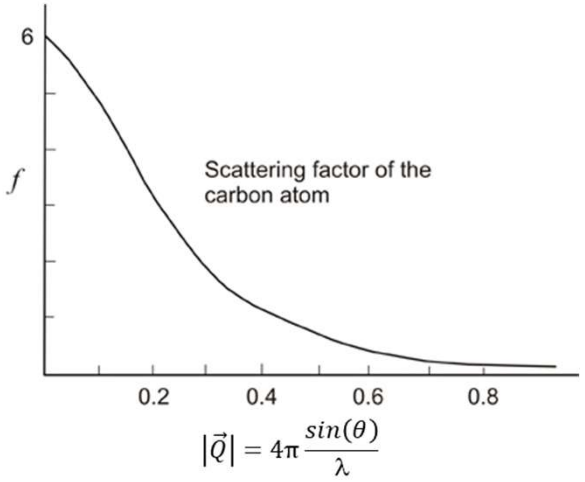


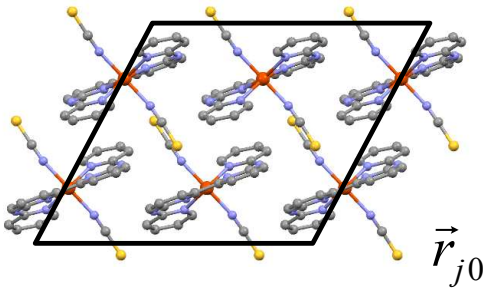
Scattering object: $\rho_{unit\,cell}(\vec{r})$

$$\rho_{unit\,cell}(\vec{r}) = \sum_{j}^{unit\,cell} \rho_j(\vec{r})$$



Unit cell structure factors





Scattering object: $\rho_{unit\,cell}(\vec{r})$

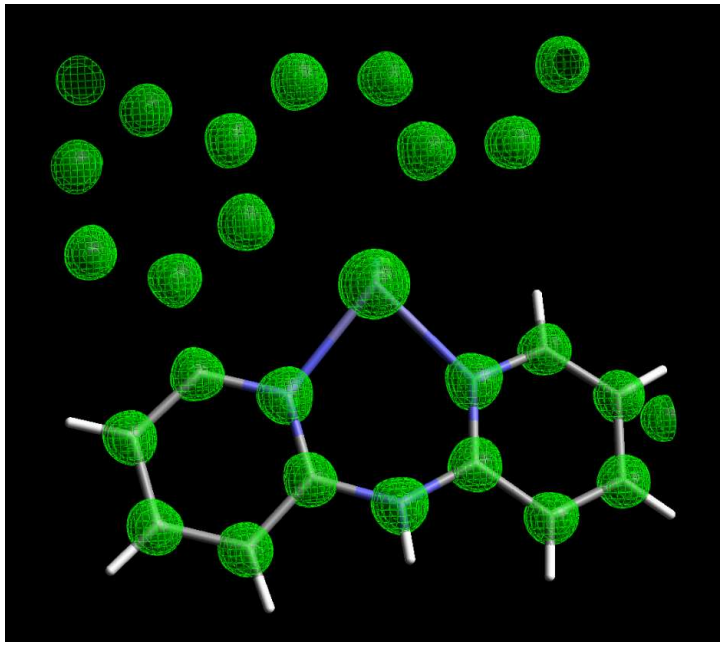
$$\rho_{unit\,cell}(\vec{r}) = \sum_{j}^{unit\,cell} \rho_j(\vec{r})$$

TF

Unit-cell structure factors

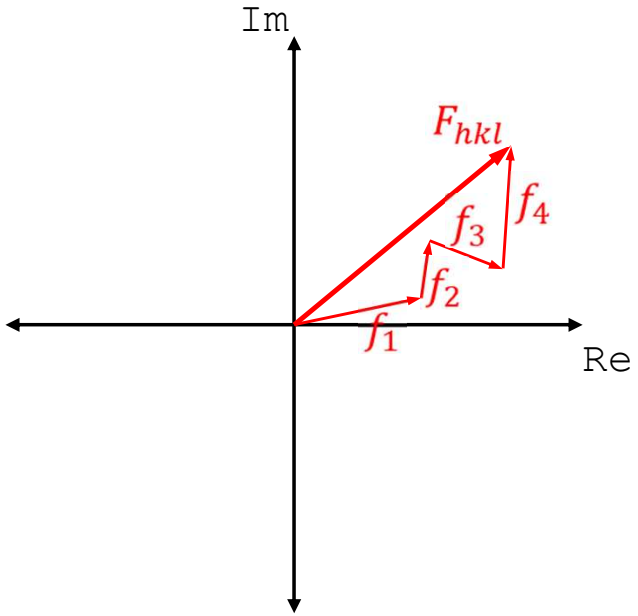
$$F_{unit\,cell}(\vec{Q}) = \sum_{j}^{unit\,cell} f_j e^{-i\vec{Q}.\vec{r}_j}$$

f_j : atomic scattering factor

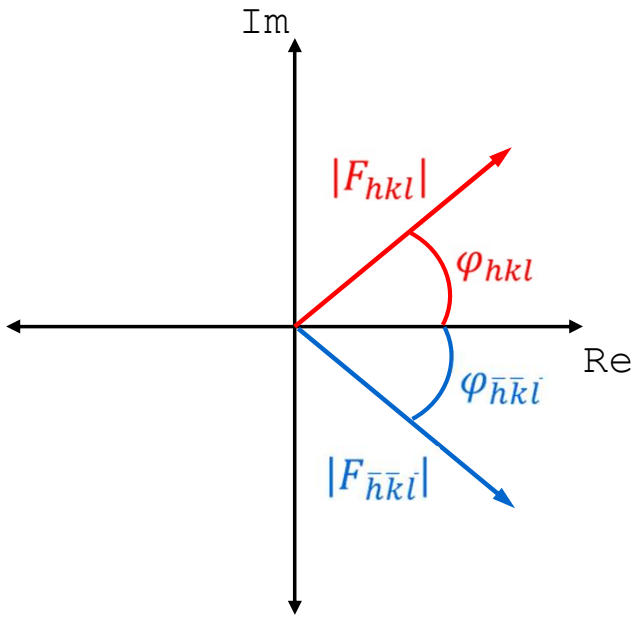


Unit cell structure factors

$$F_{unit\ cell}(\vec{Q}) = \sum_{j}^{unit\ cell} f_j e^{-i\vec{Q}.\vec{r}_j} = |F(\vec{Q})|e^{i\varphi(\vec{Q})}$$



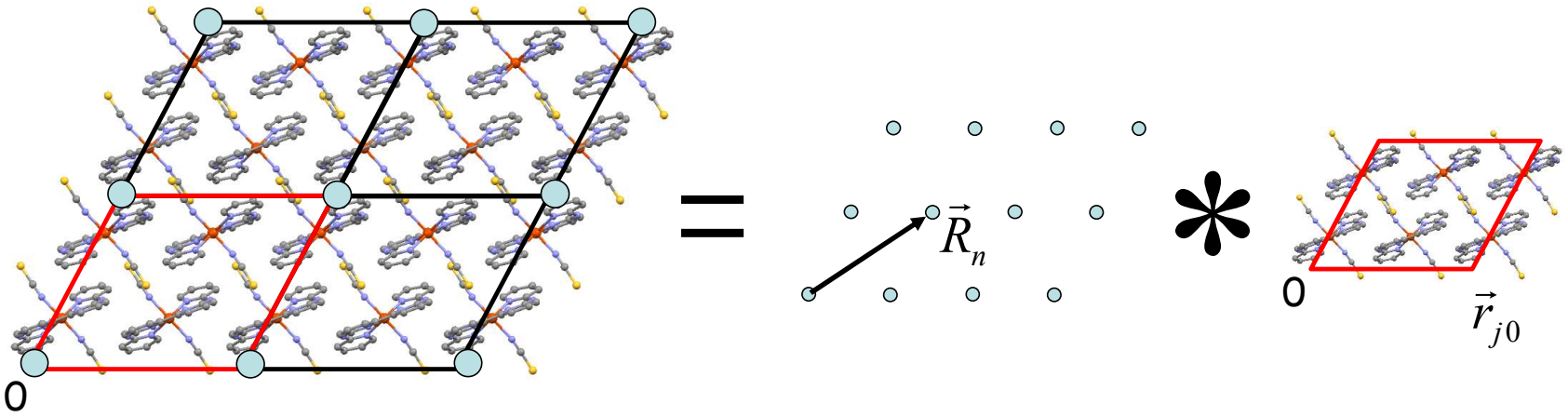
Argand diagram



$$|F_{hkl}| = |F_{\bar{h}\bar{k}\bar{l}}|$$

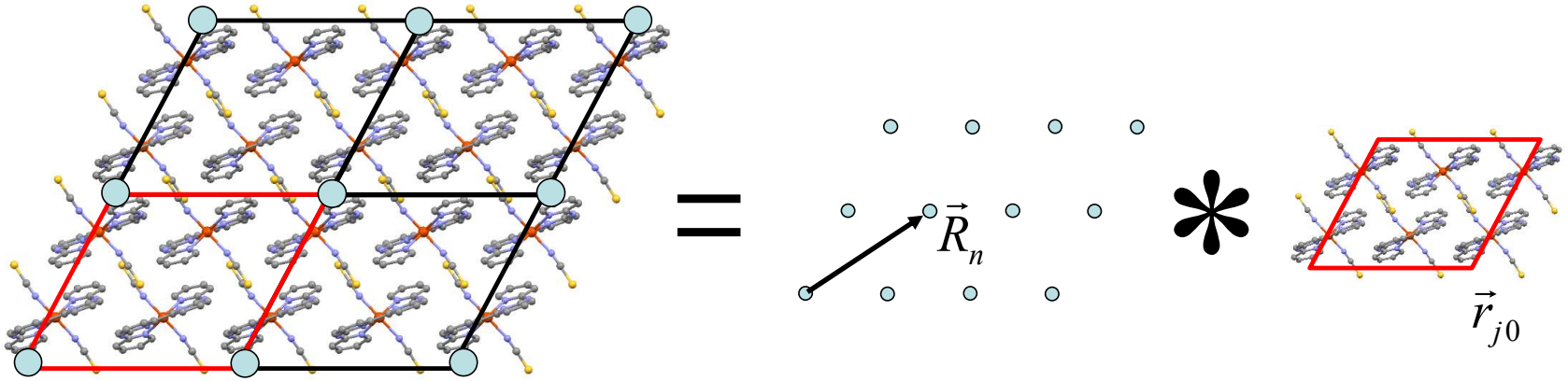
$$\varphi_{hkl} = -\varphi_{\bar{h}\bar{k}\bar{l}}$$

Structure factor and interference function



$$\vec{r}_{jn} = \vec{r}_{j0} + \vec{R}_n$$

Structure factor and interference function

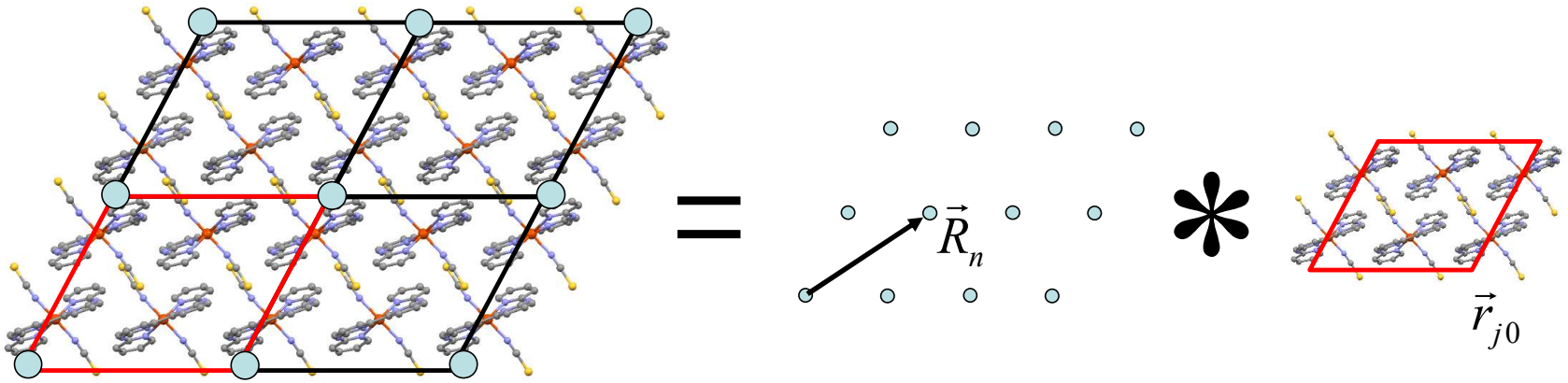


$$\vec{r}_{jn} = \vec{r}_{j0} + \vec{R}_n$$

Crystal periodicity

$$\rho_{crystal}(\vec{r}) = \sum_{crystal} \rho_{atomic}(\vec{r}) = \left[\sum_{u,v,w=-\infty}^{+\infty} \delta(\vec{r} - \vec{r}_{u,v,w})\right] * \left[\sum_{unit\ cell} \rho_{atomic}(\vec{r})\right]$$

Structure factor and interference function



$$\vec{r}_{jn} = \vec{r}_{j0} + \vec{R}_n$$

Crystal periodicity

$$\rho_{crystal}(\vec{r}) = \sum_{crystal} \rho_{atomic}(\vec{r}) = \left[\sum_{u,v,w=-\infty}^{+\infty} \delta(\vec{r} - \vec{r}_{u,v,w})\right] * \left[\sum_{unit\ cell} \rho_{atomic}(\vec{r})\right]$$

TF

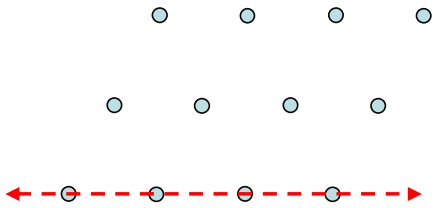
$$F_{crystal}(\vec{Q}) = \sum_{n_a}\sum_{n_b}\sum_{n_c}\sum_{j}^{unit\ cell} f_j e^{-i\vec{Q}.\vec{r}_{jn}}$$

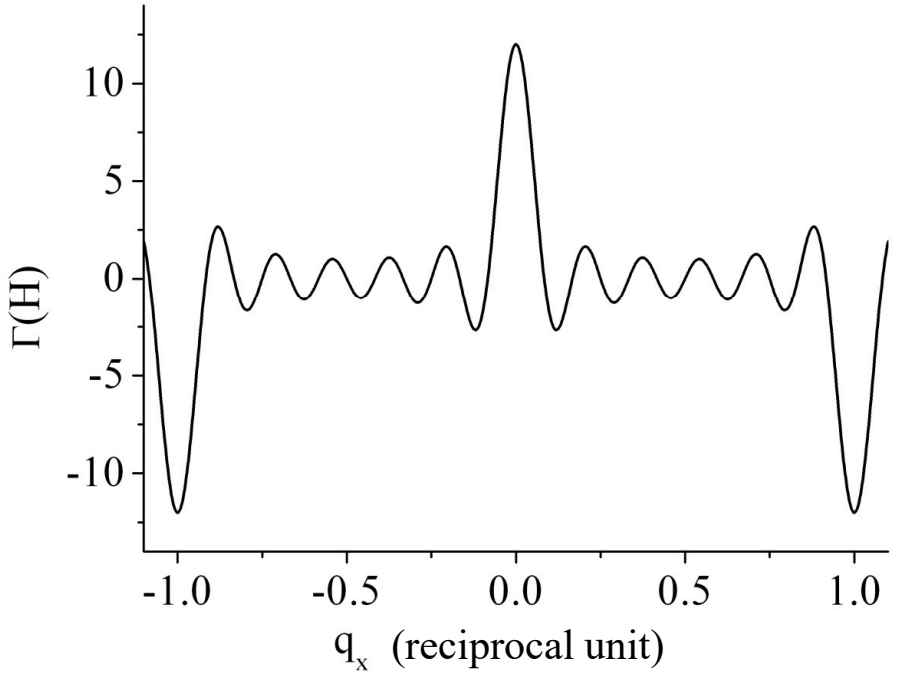
$$= \sum_{n_a}\sum_{n_b}\sum_{n_c} e^{i\vec{Q}.(x_n\vec{a}+y_n\vec{b}+z_n\vec{c})} \sum_{j}^{unit\ cell} f_j e^{-i\vec{Q}.\vec{r}_{j0}} = \Gamma(\vec{Q}) \cdot F_{unit\ cell}(\vec{Q})$$

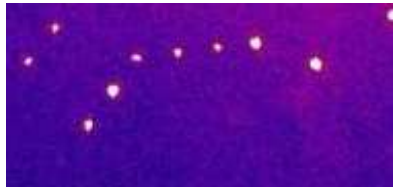
The interference function

$$\Gamma(\vec{Q}) = \sum_{n_a}\sum_{n_b}\sum_{n_c} e^{i\vec{Q}.(x_n\vec{a}+y_n\vec{b}+z_n\vec{c})} = \frac{sin(\pi n_a q_x)}{\pi q_x}\cdot\frac{sin(\pi n_b q_y)}{\pi q_y}\cdot\frac{sin(\pi n_c q_z)}{\pi q_z}$$

$$\vec{Q} = q_x\vec{a}^* + q_y\vec{b}^* q_z$$





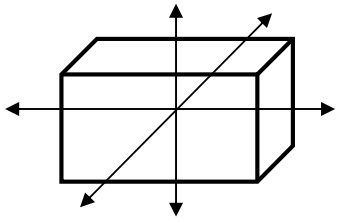


Extrema for integer values q_x=h, q_y=k, q_z=l (hkl)

Finite size effects

Influence of finite size on the scattering process :

$$\rho_{crystal}(\vec{r}) = \rho_{crystal\,\infty}(\vec{r}) \cdot [box(\vec{r})] = \left[\sum_{u,v,w=-\infty}^{+\infty} \delta\left(\vec{r} - \vec{r}_{u,v,w}\right)\right] * \left[\sum_{unit\ cell} \rho_{atomic}(\vec{r})\right] \cdot [box(\vec{r})]$$



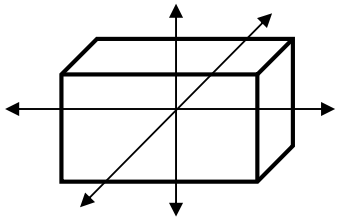
Finite size effects

Influence of finite size on the scattering process :

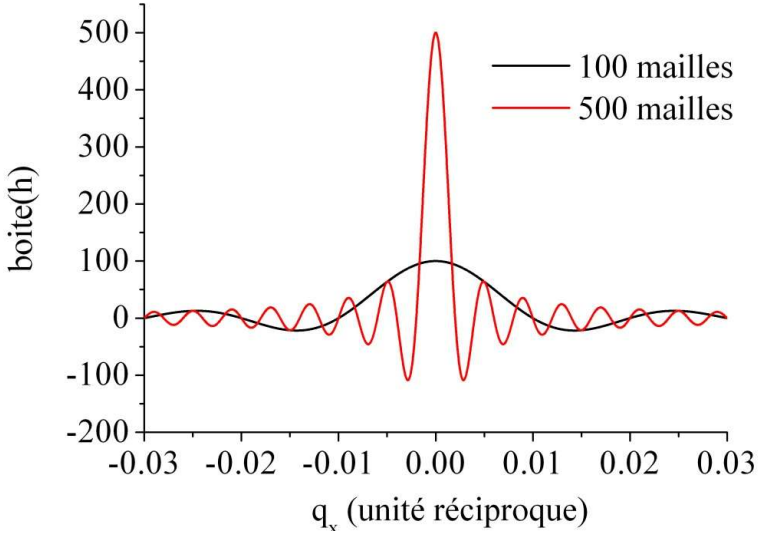
$$\rho_{crystal}(\vec{r}) = \rho_{crystal\,\infty}(\vec{r}) \cdot [box(\vec{r})] = \left[\sum_{u,v,w=-\infty}^{+\infty} \delta\left(\vec{r} - \vec{r}_{u,v,w}\right)\right] * [\sum_{unit\ cell} \rho_{atomic}(\vec{r})] \cdot [box(\vec{r})]$$

TF

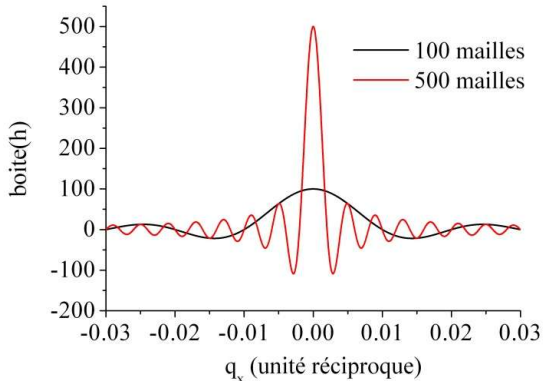
$$F_{crystal}(\vec{Q}) = \Gamma(\vec{Q}) \cdot F_{unit\,cell}(\vec{Q}) * B(\vec{Q})$$

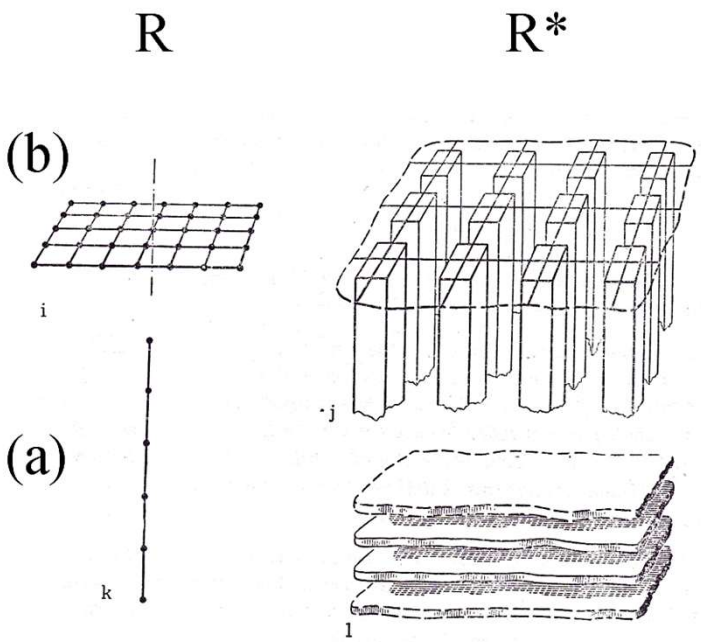


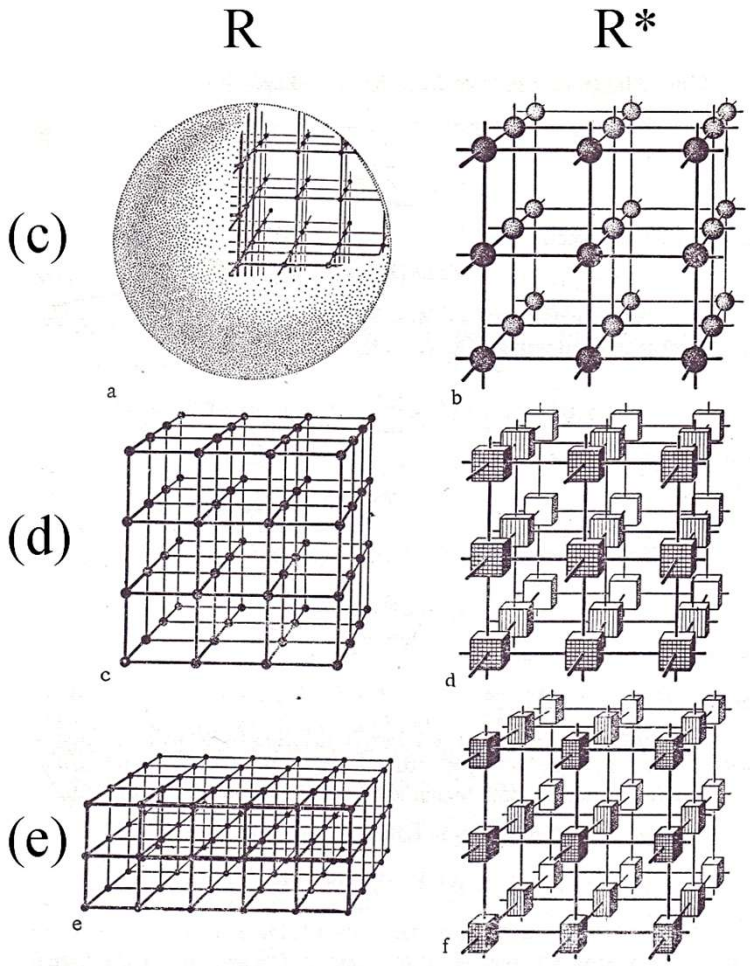
$$\mathrm{B}(\vec{Q}) = \frac{sin(\pi L_a q_x)}{\pi L_a q_x} \cdot \frac{sin(\pi L_b q_y)}{\pi L_b q_y} \cdot \frac{sin(\pi L_c q_z)}{\pi L_c q_z}$$



Reciprocal lattice associated to a single crystal







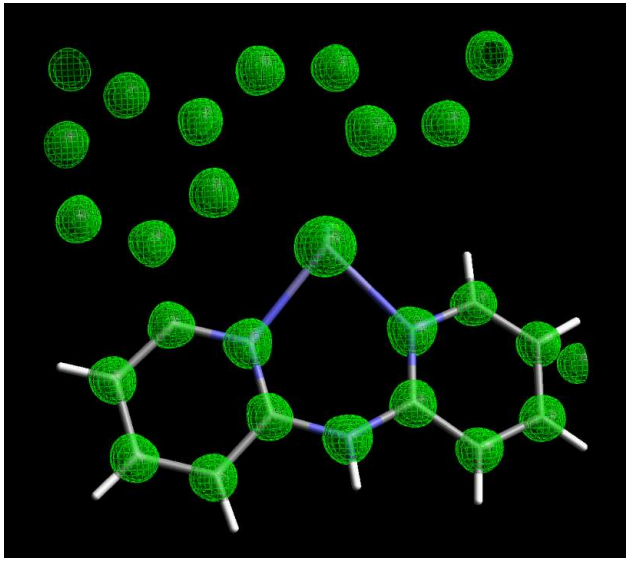
The structure factors

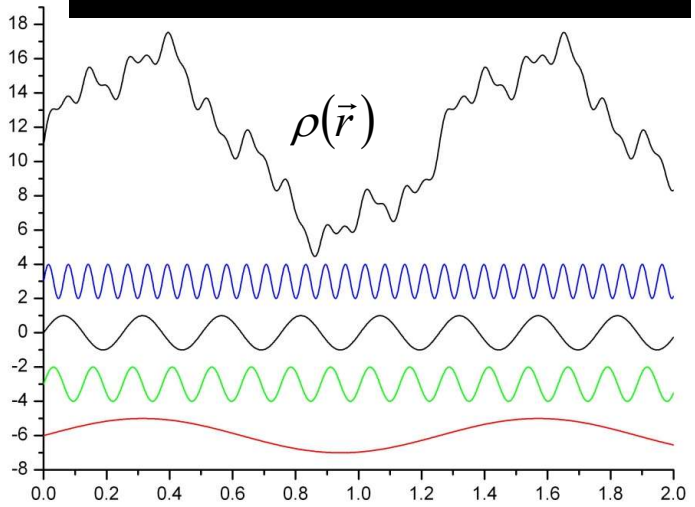
$$F_{unit\ cell}(\vec{Q}) = FT(\rho(\vec{r}))$$

$$FT^{-1}$$

$$\rho(\vec{r}) = \frac{1}{V} \sum_{h,k,l=-\infty}^{+\infty} F(\vec{Q}) e^{-i\vec{Q}\cdot\vec{r}}$$

with $F(\vec{Q}) = |F(\vec{Q})| e^{i\varphi(\vec{Q})}$





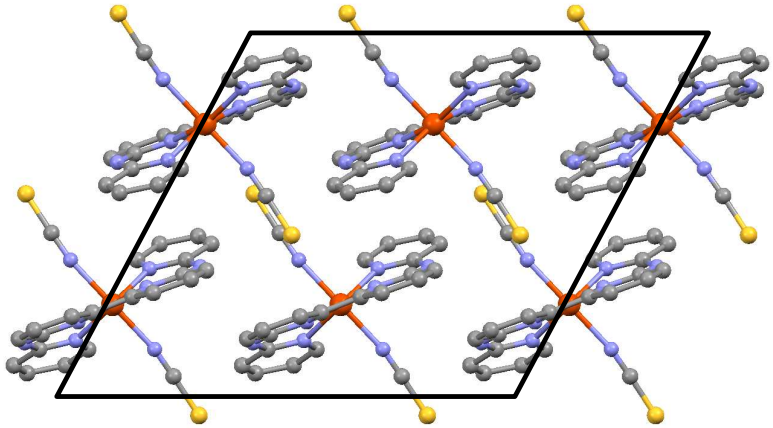
The structure factors

$$F_{unit\ cell}(\vec{Q}) = \sum_{j}^{unit\ cell} f_j e^{-i\vec{Q}.\vec{r}_j} = |F(\vec{Q})|e^{i\varphi(\vec{Q})}$$

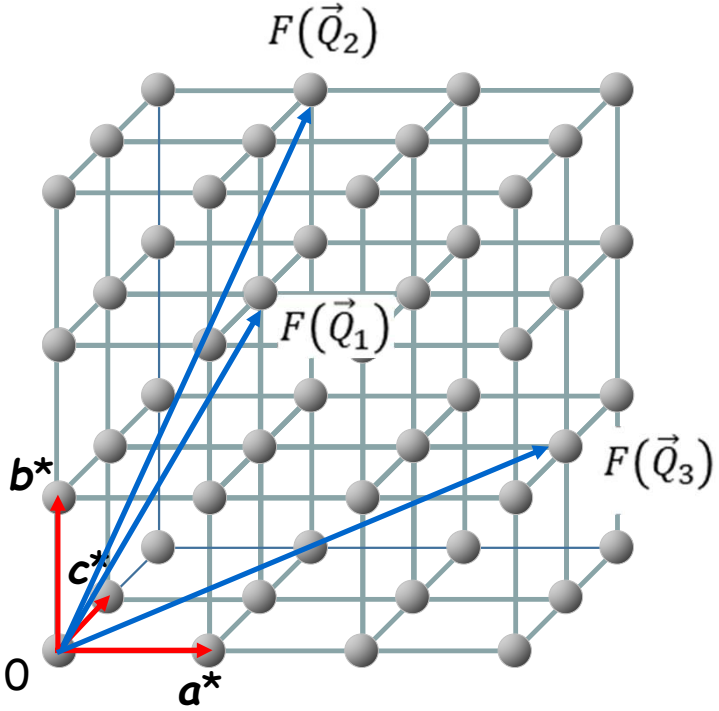
atom type

atom position

Direct space

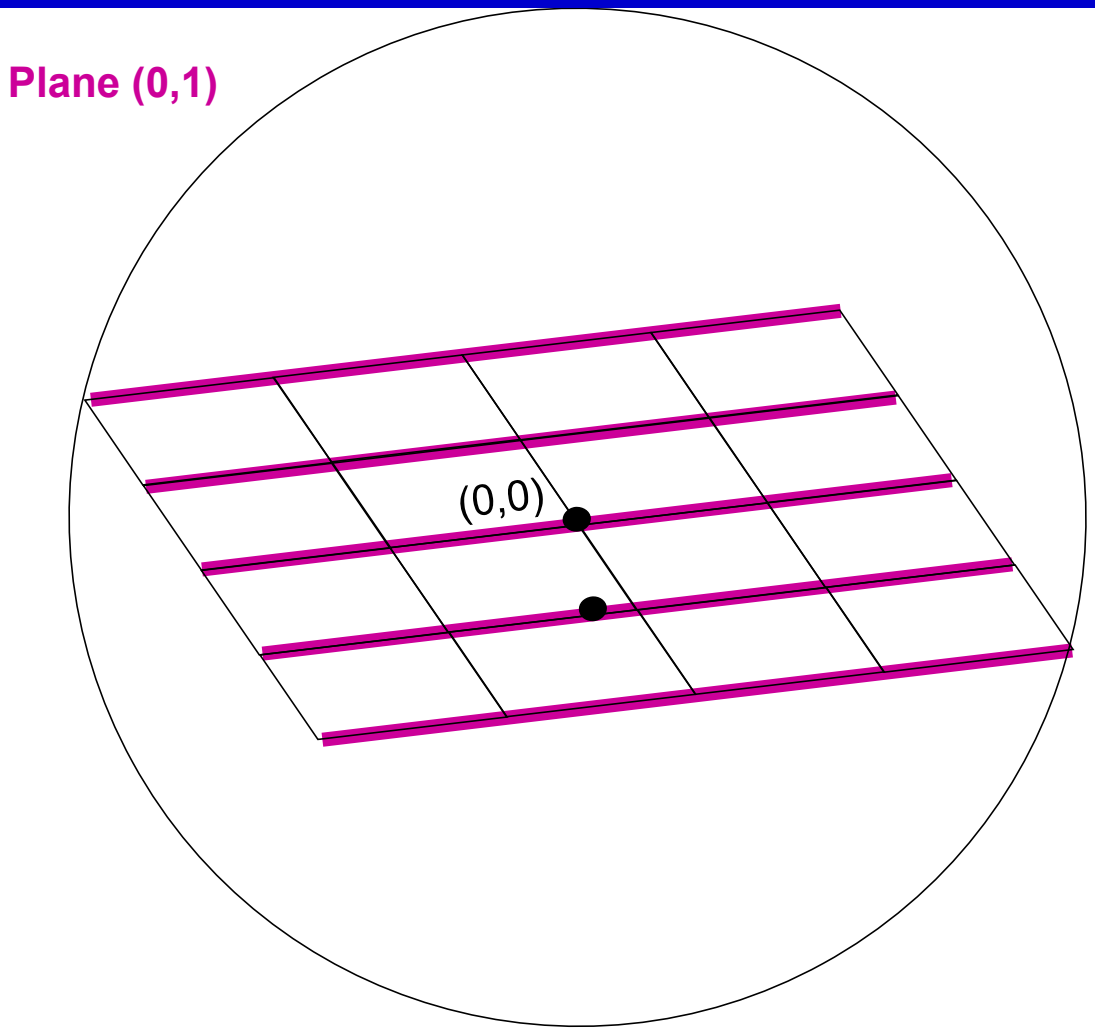


Reciprocal space

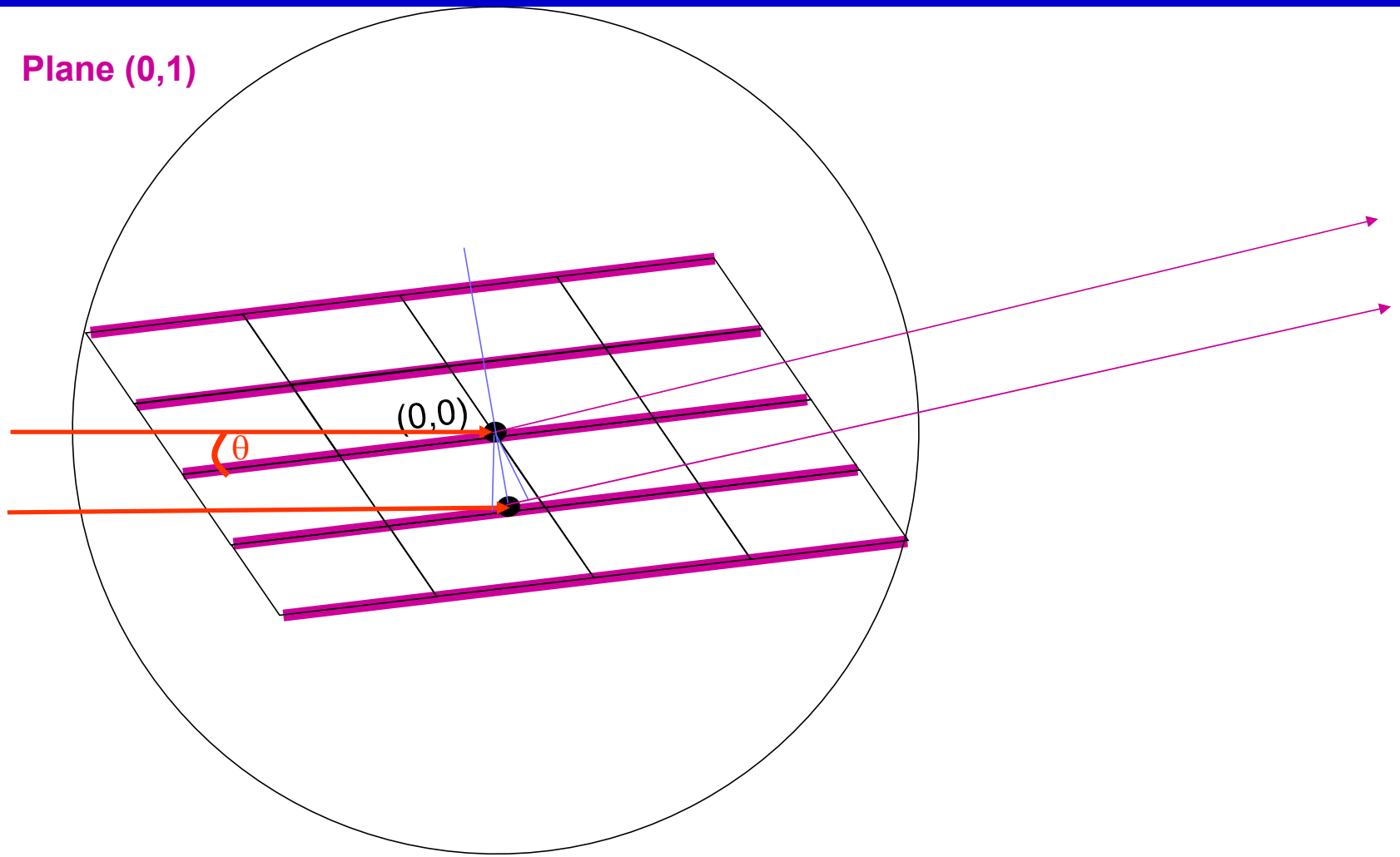


- Each structure factor $F(\vec{Q})$ is related to a family of planes (hkl)
- All atoms contribute to each structure factor
- The entire crystal structure is described by the whole set of structure factors

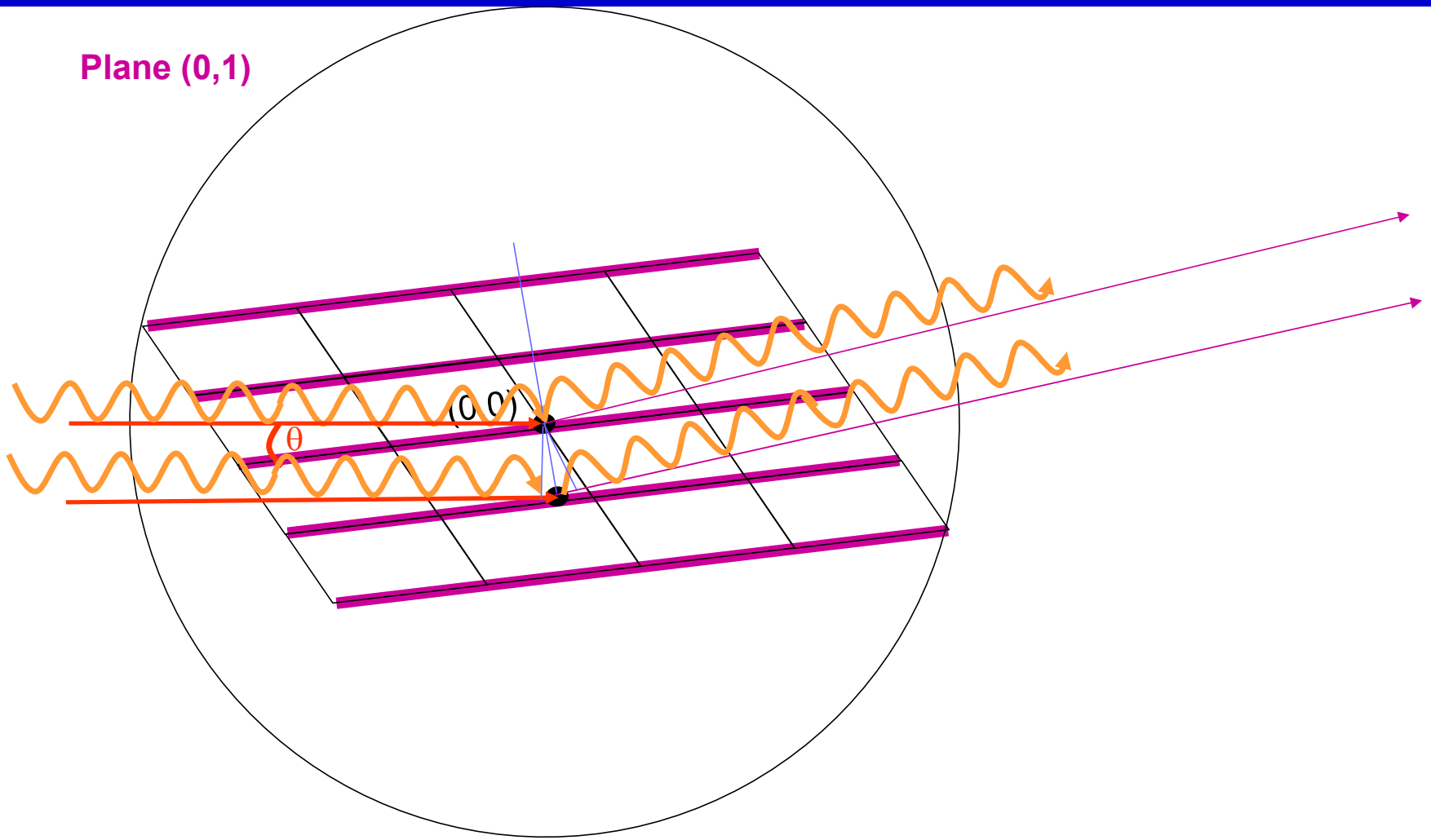
Geometry of diffraction, Bragg condition



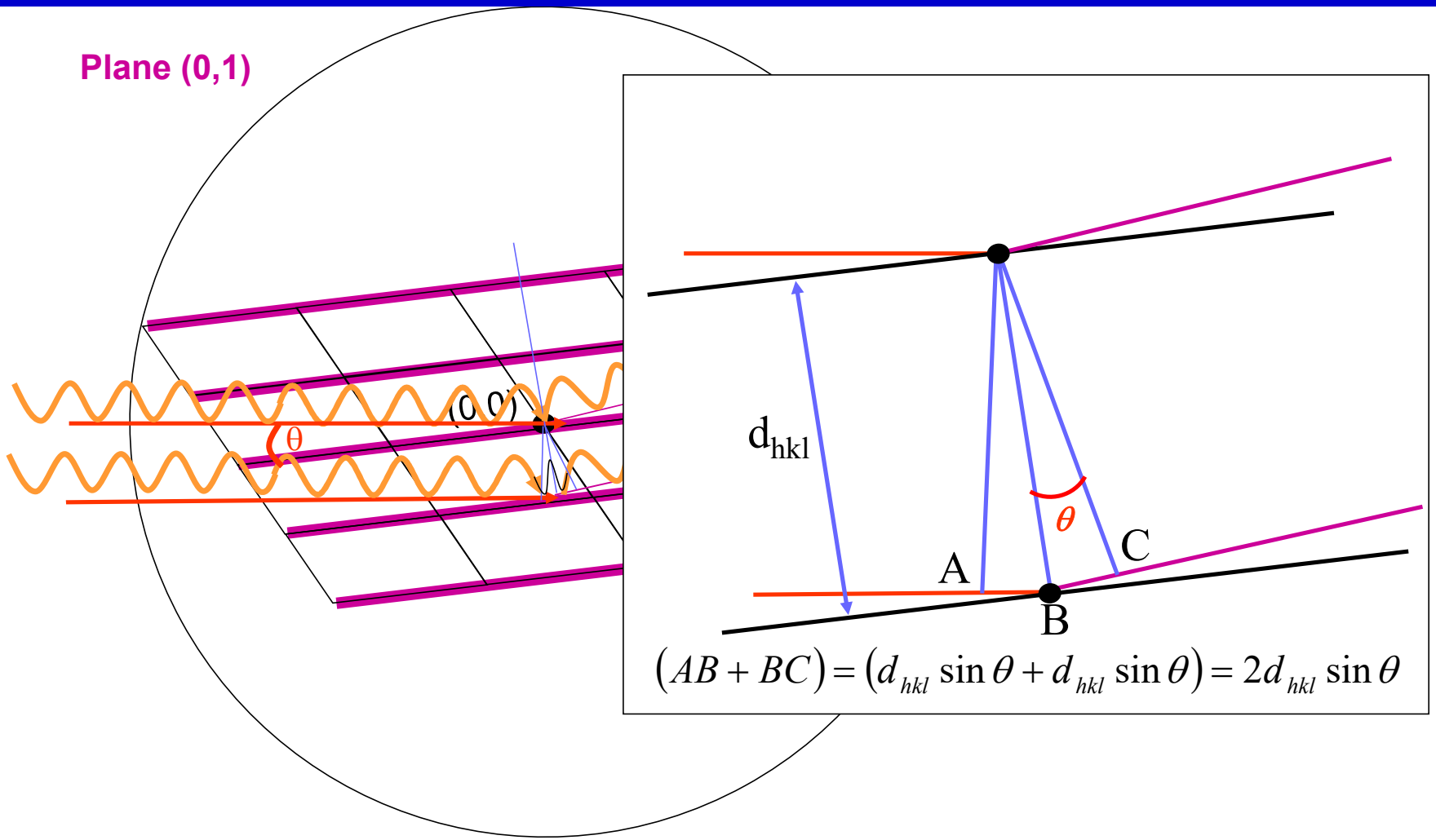
Geometry of diffraction, Bragg condition



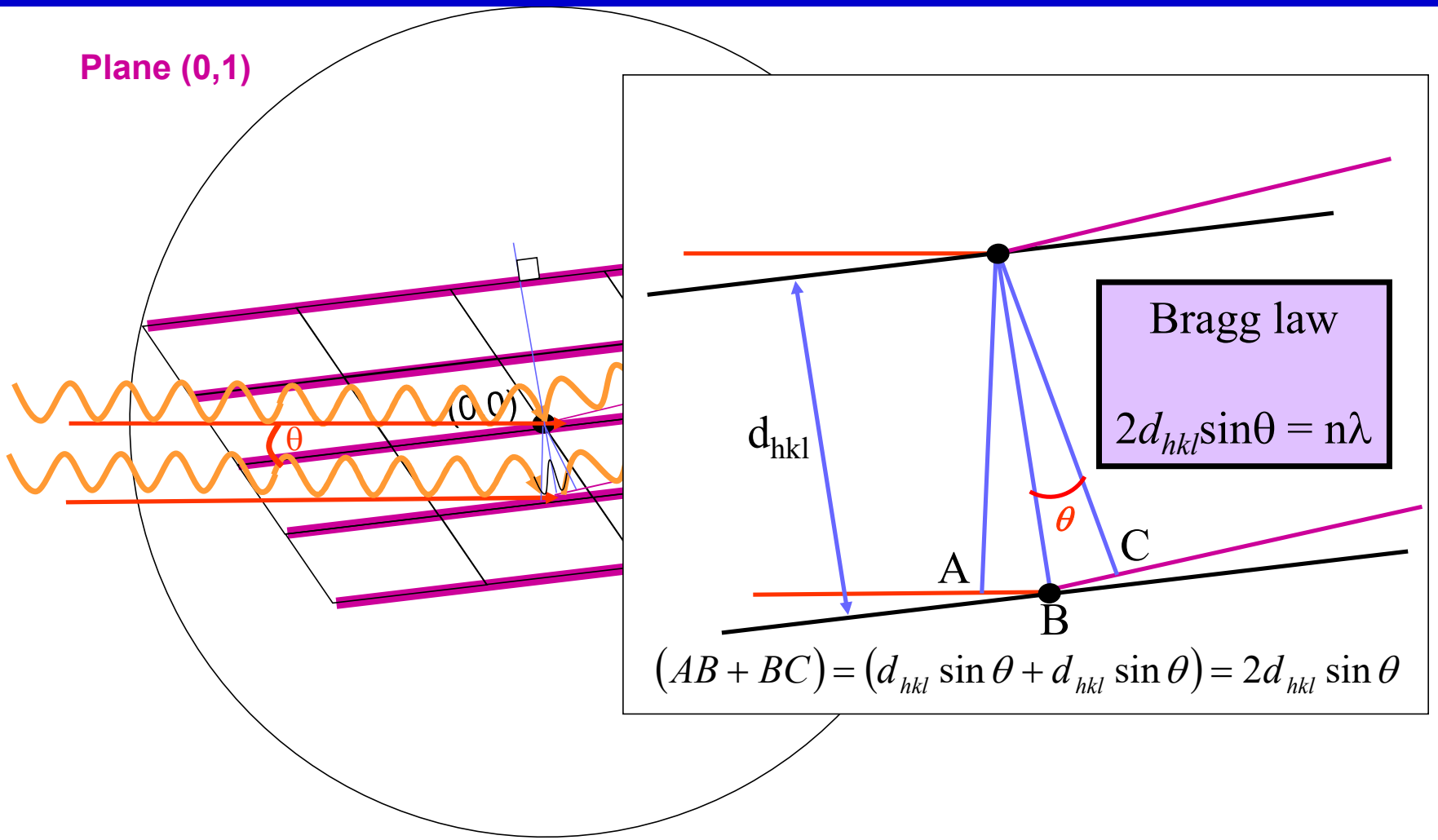
Geometry of diffraction, Bragg condition



Geometry of diffraction, Bragg condition

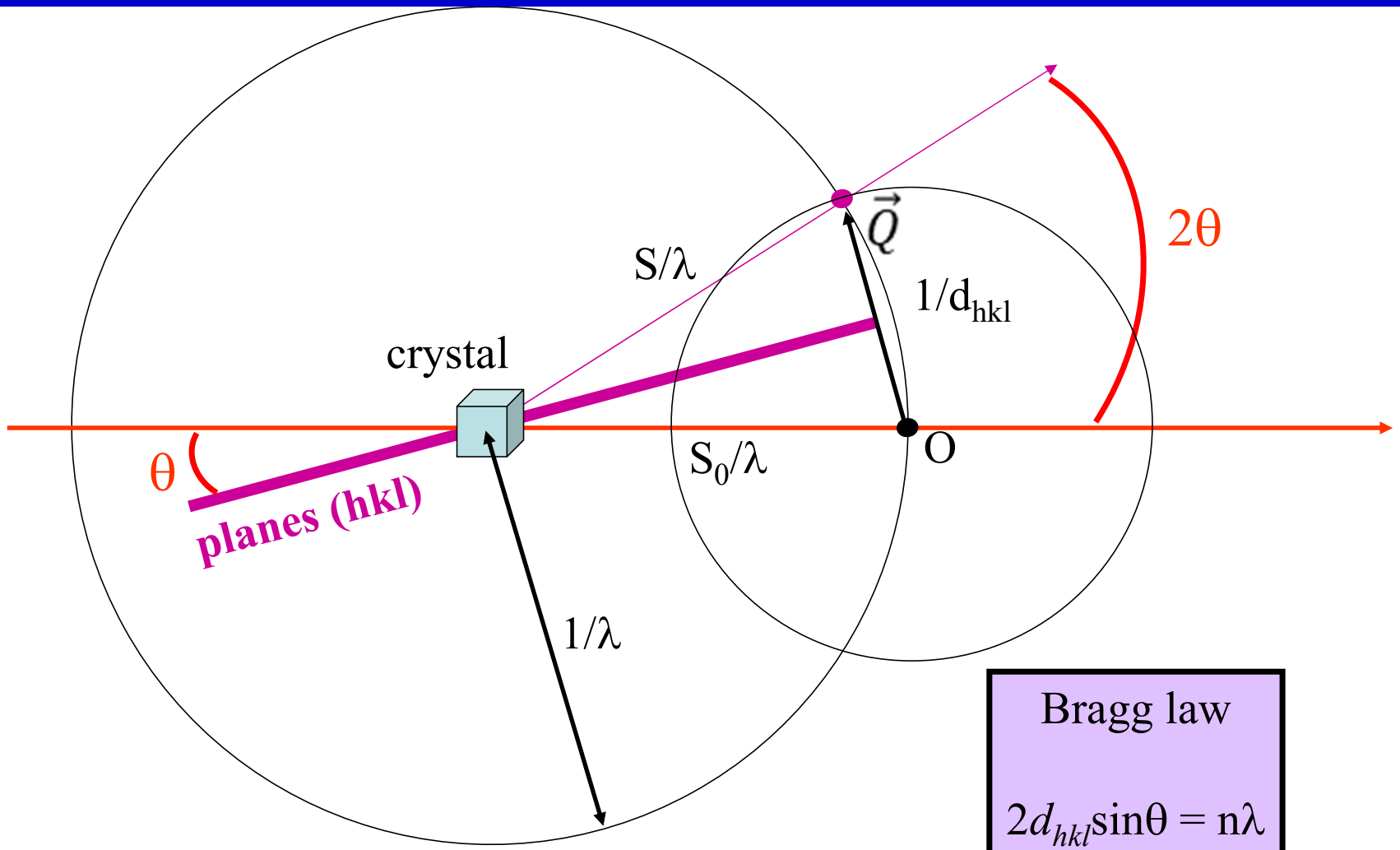


Geometry of diffraction, Bragg condition



Bragg condition : the path difference between two waves must be equal to n times the wavelength

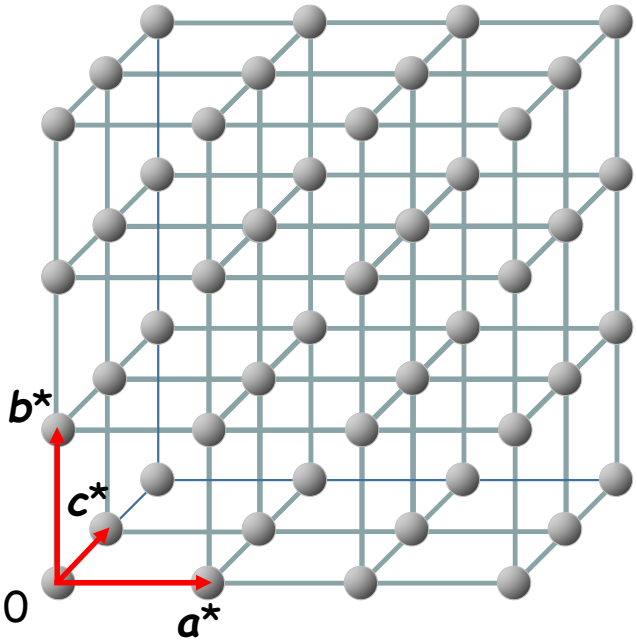
Geometry of diffraction, Ewald construction



Bragg law

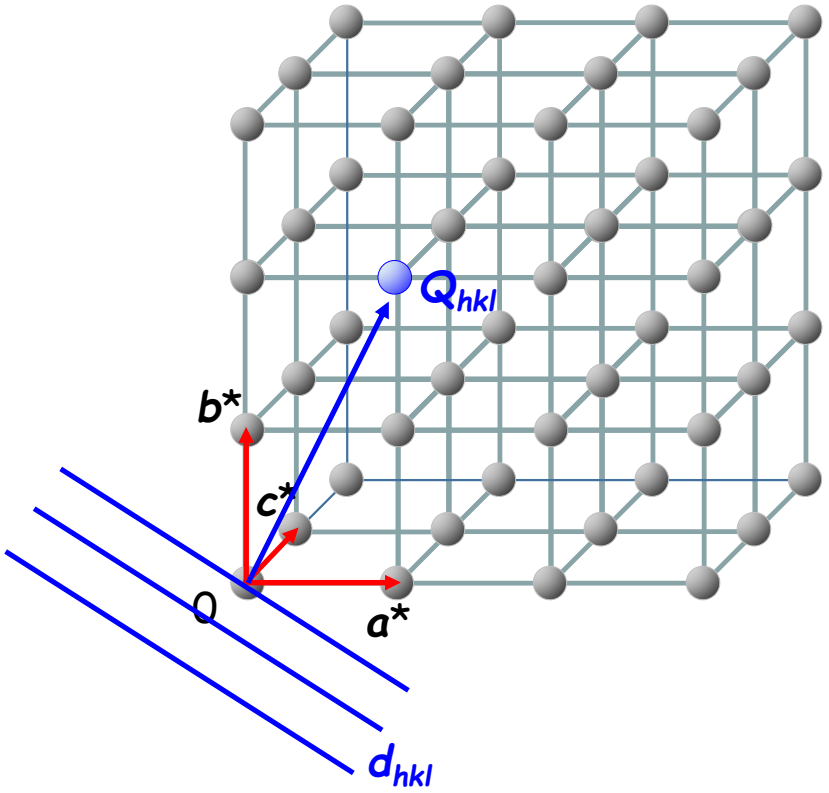
$2d_{hkl}\sin\theta = n\lambda$

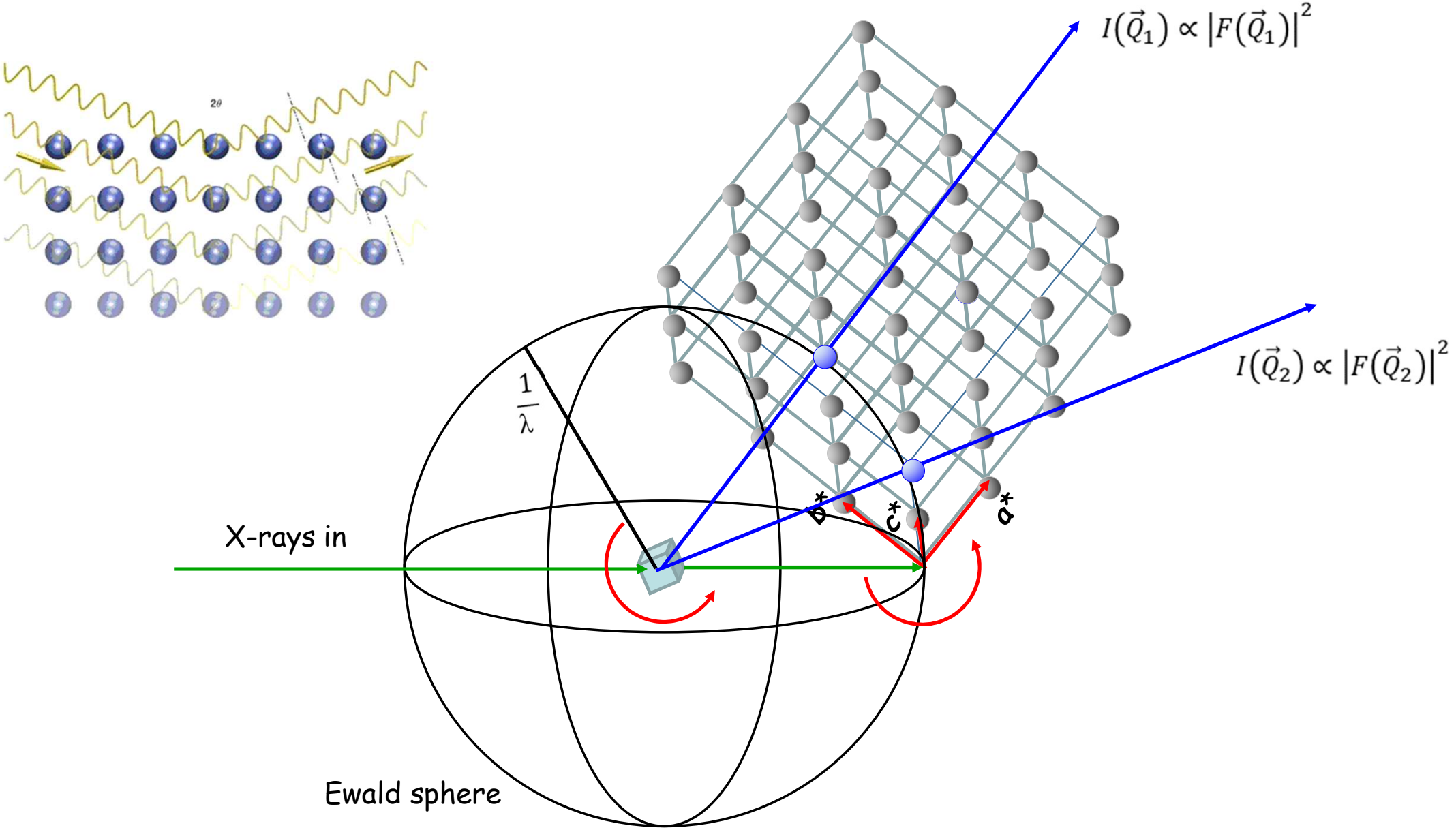
Single crystal x-ray diffraction experiment



Single crystal diffraction experiment

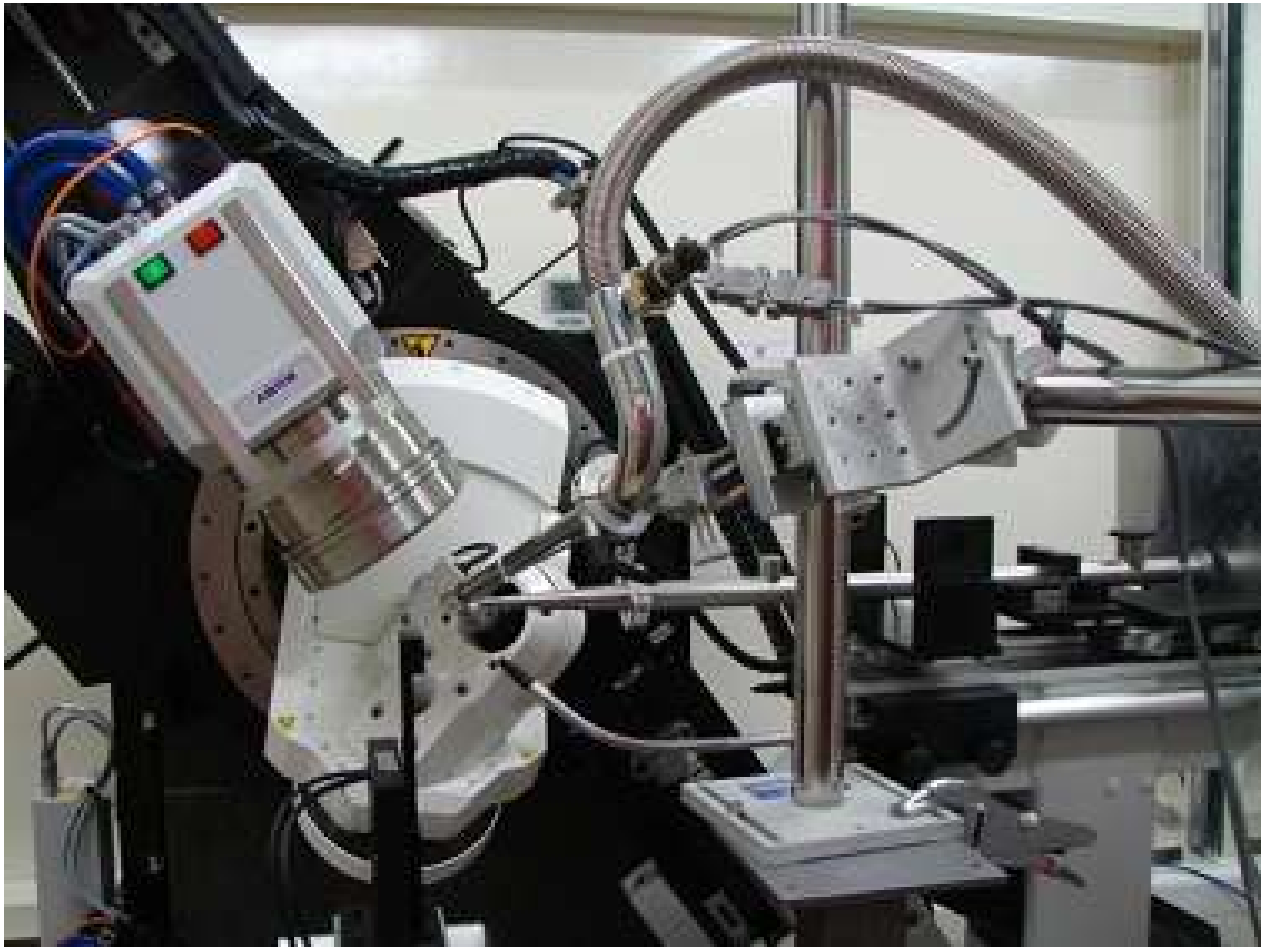
$$I(\vec{Q}) \propto F(\vec{Q}) \cdot F^*(\vec{Q}) \propto |F(\vec{Q})|^2$$



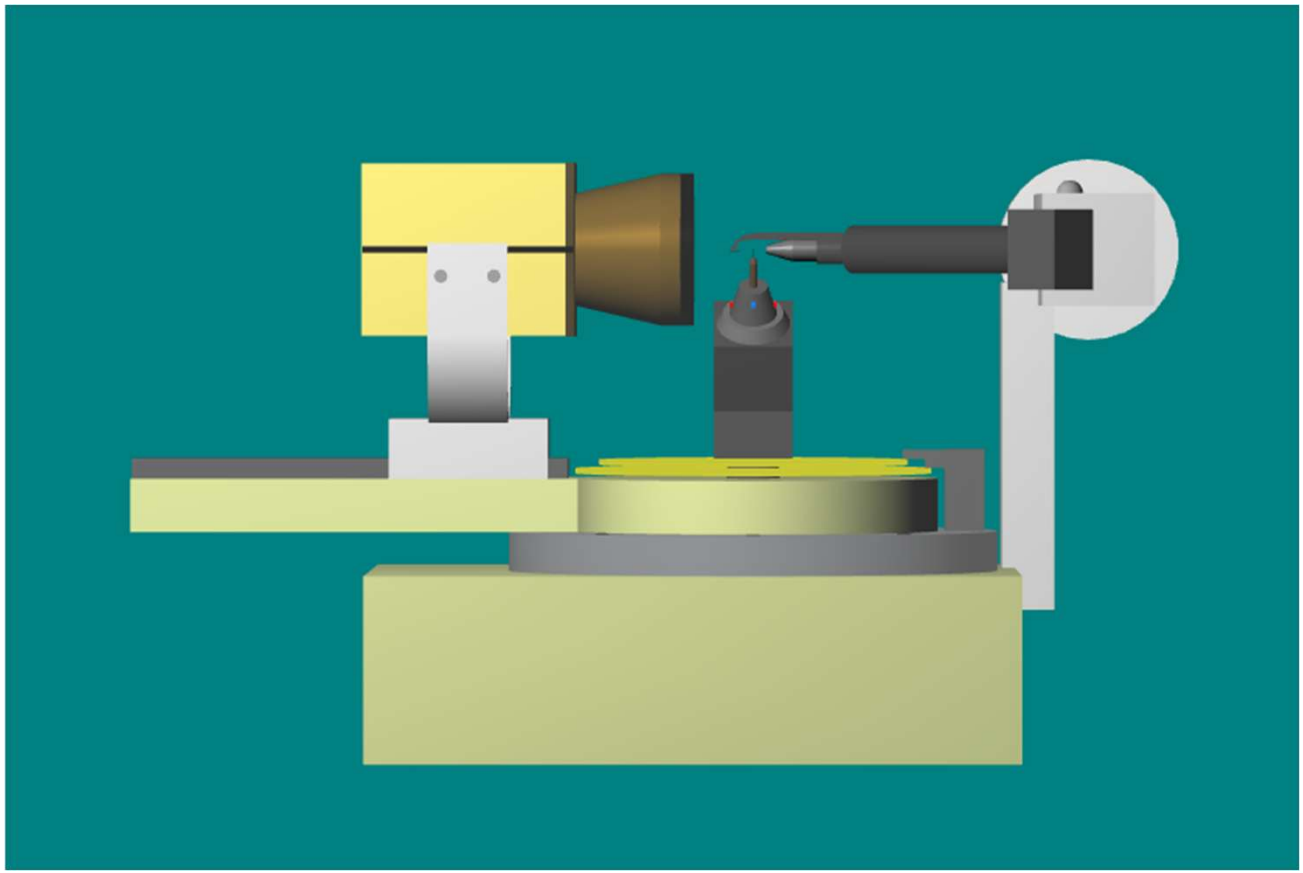

$I(\vec{Q}_1) \propto |F(\vec{Q}_1)|^2$
$I(\vec{Q}_2) \propto |F(\vec{Q}_2)|^2$
$\frac{1}{\lambda}$
X-rays in
Ewald sphere
b*
c*
a*

Picture of a diffraction instrument

CRISTAL @SOLEIL



Animation : Ewald construction

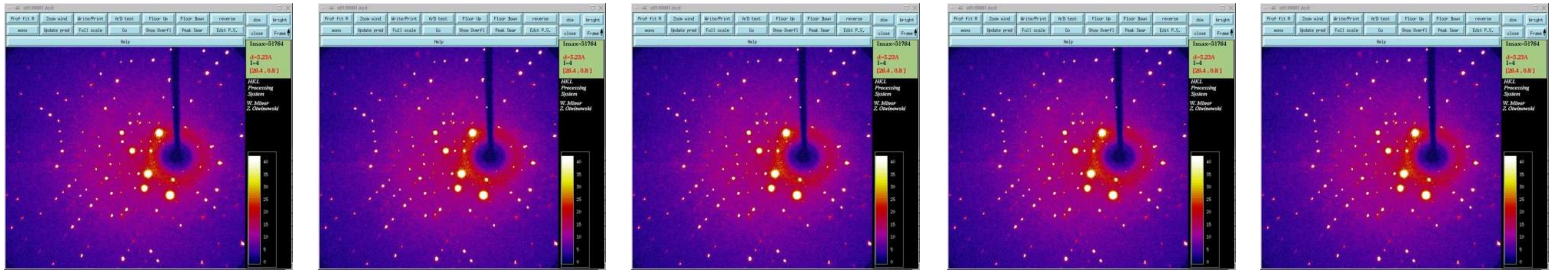


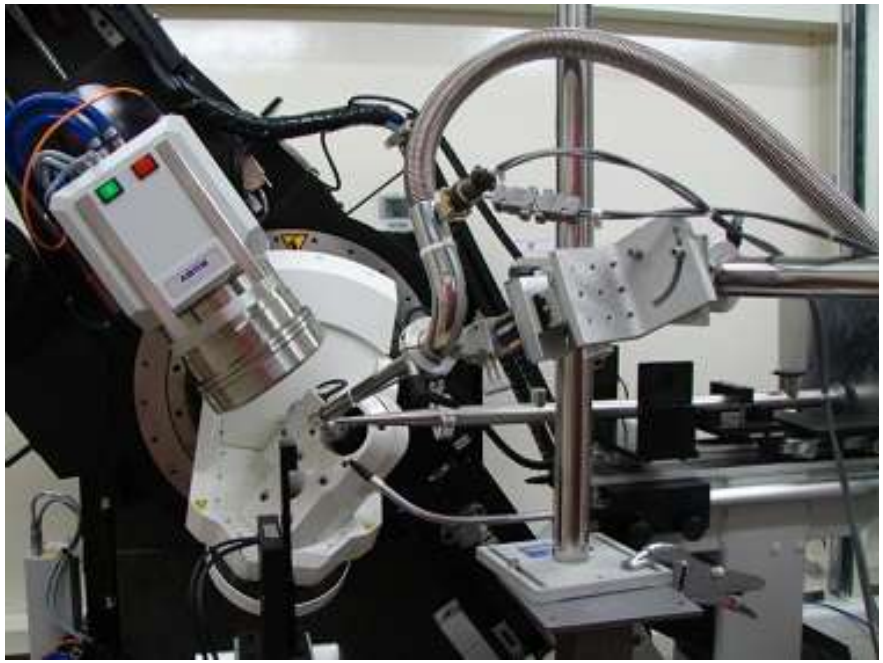
EwaldSphere.exe

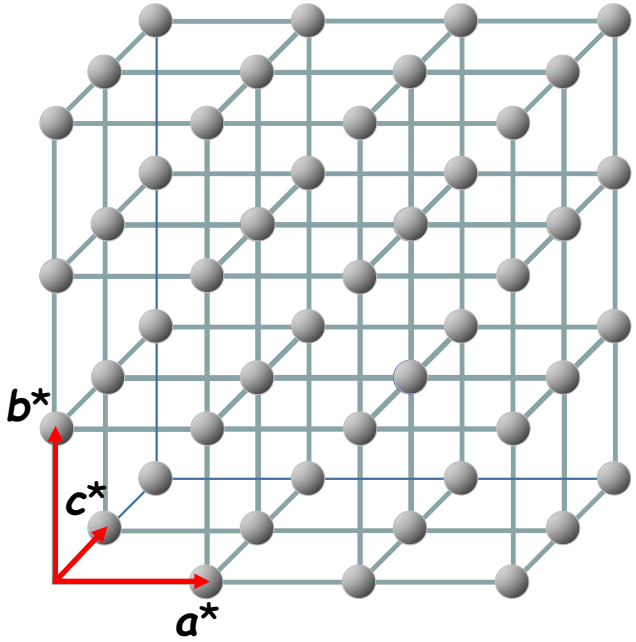
http://www.doe-mbi.ucla.edu/~sawaya/m230d

Collecting diffraction frames

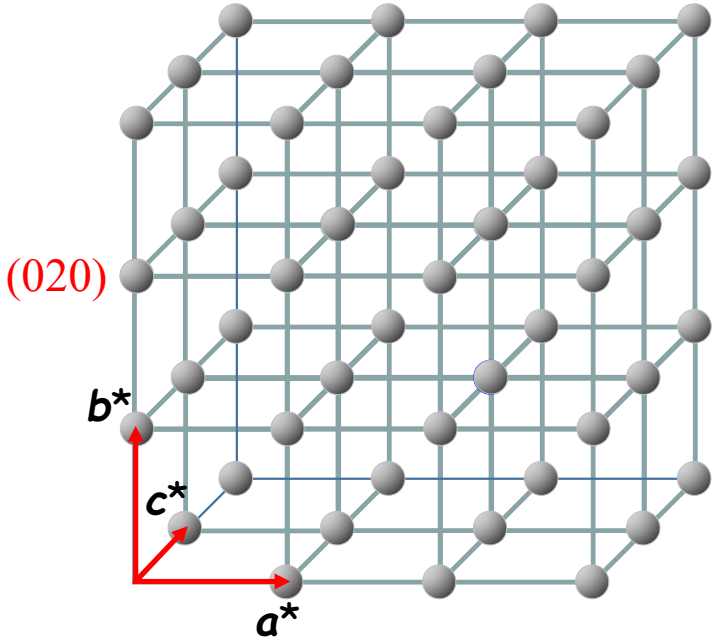
$0 < \omega < 1$ $1 < \omega < 2$ $2 < \omega < 3$ $3 < \omega < 4$ $4 < \omega < 5$





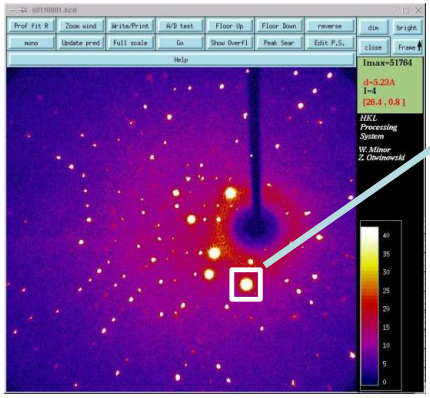


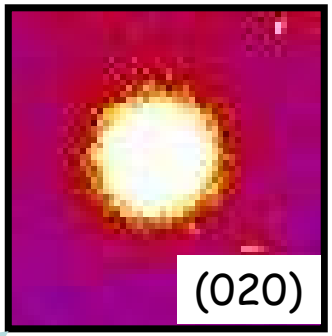
Indexing and data integration

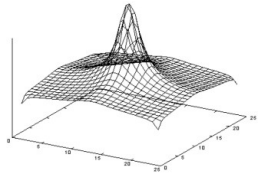


Indexing : determine orientation matrix and unit cell parameters a*, b*, c*, α*, β*, γ* so that the Miller indices h,k,l which define the position of each Bragg peak in reciprocal space are integers :

$$\vec{Q} = q_x\vec{a}^* + q_y\vec{b}^* + q_z\vec{c}^*$$

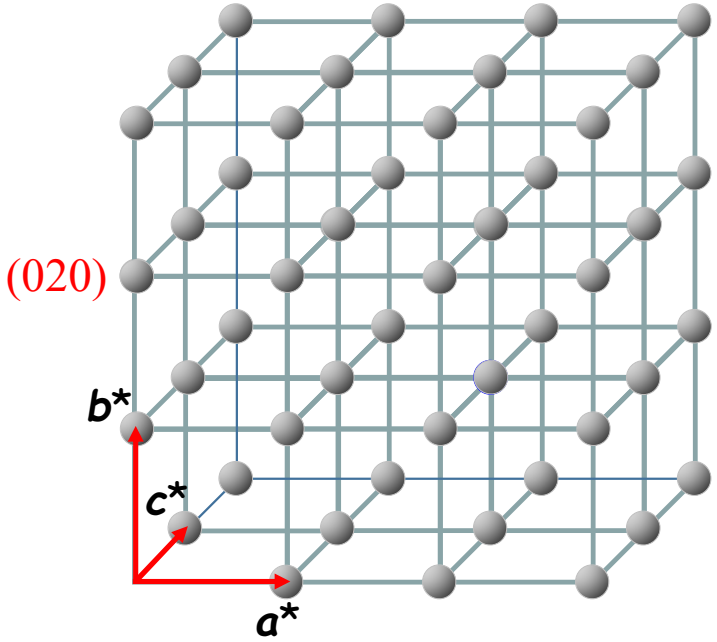






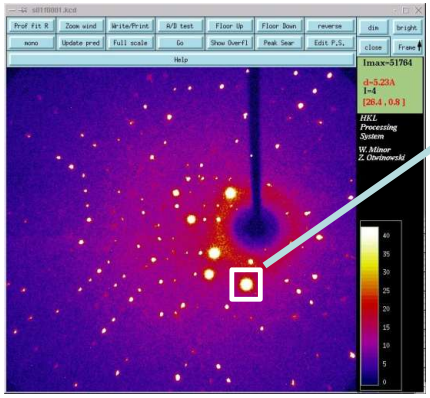
$$\{\vec{Q} \quad I(\vec{Q}) \quad \sigma(I(\vec{Q}))\}$$

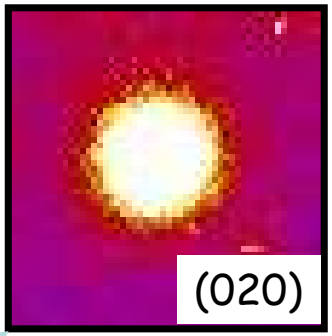
Indexing and data integration

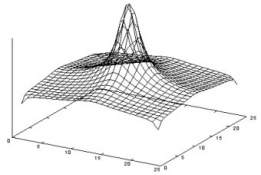


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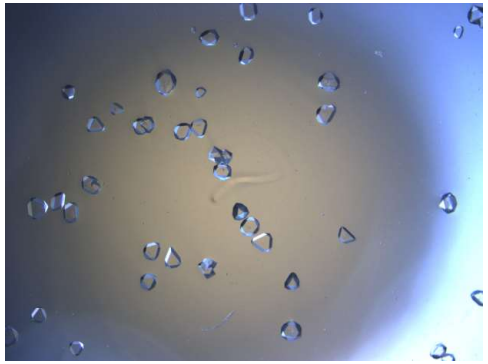




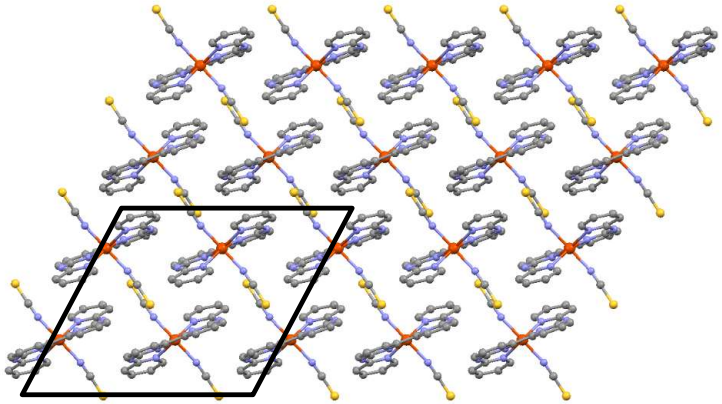
h	k	l	I(Q)	σ(I(Q))
0	0	1	5.10	0.2
0	0	1	6.30	0.4
0	0	2	47.40	2.3
-5	2	-9	159.39	7.8
…				

$$\{\vec{Q} \quad I(\vec{Q}) \quad \sigma\left(I(\vec{Q})\right)\}$$

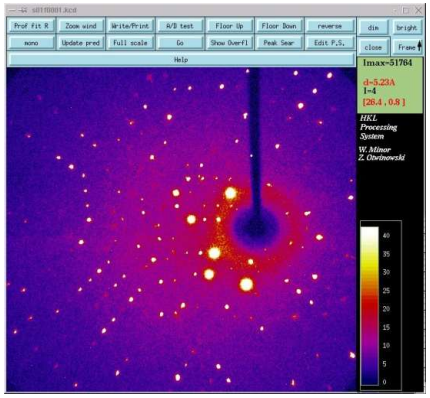
Use of single crystal diffraction



Structural model



Diffraction experiment



$$\{\vec{Q} \quad I(\vec{Q}) \quad \sigma\left(I(\vec{Q})\right)\}$$

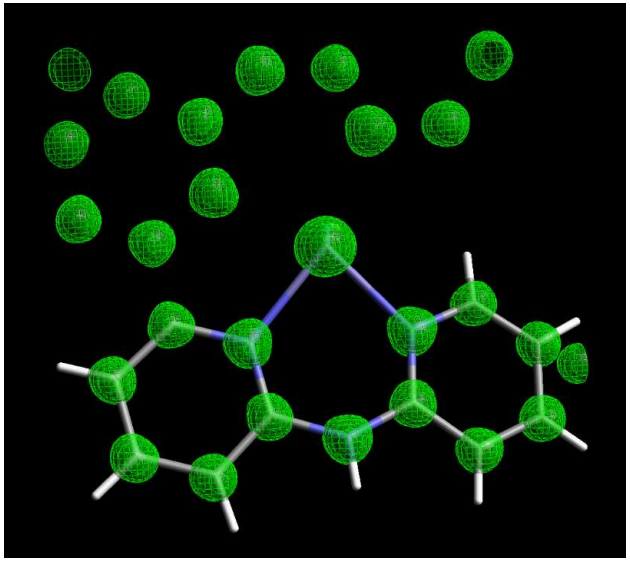
Structure solution methods

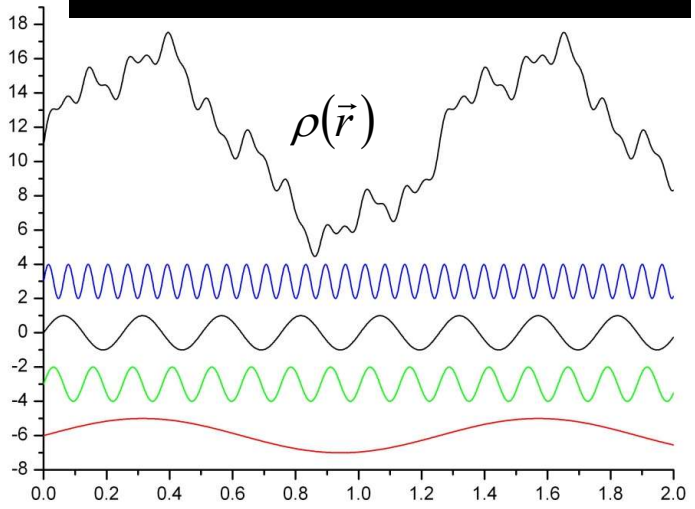
Objective : determine the distribution of atomic electron density in the unit cell from diffraction data :

$$I(\vec{Q}) \propto F(\vec{Q}) \cdot F^*(\vec{Q}) \propto |F(\vec{Q})|^2$$

$$\rho(\vec{r}) = \frac{1}{V} \sum_{h,k,l=-\infty}^{+\infty} F(\vec{Q}) e^{-i\vec{Q}\cdot\vec{r}}$$

with $F(\vec{Q}) = |F(\vec{Q})| e^{i\varphi(\vec{Q})}$





Structure solution methods

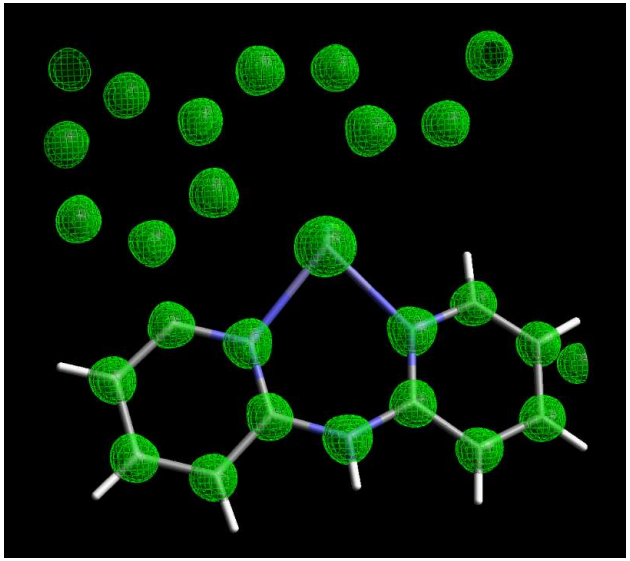
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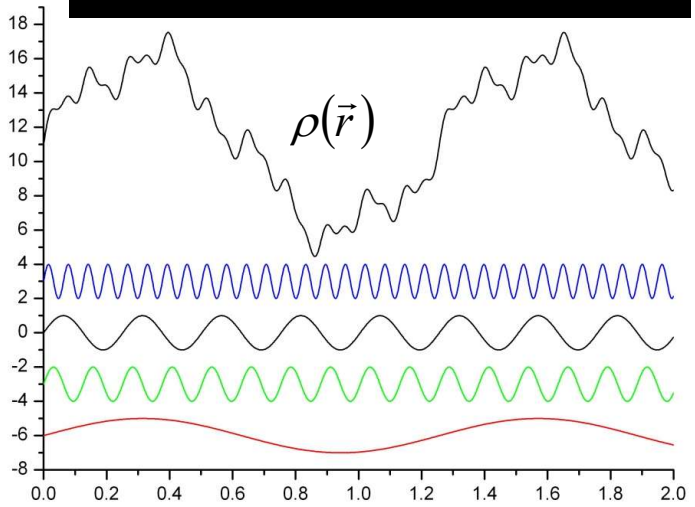
$$I(\vec{Q}) \propto F(\vec{Q}) \cdot F^*(\vec{Q}) \propto |F(\vec{Q})|^2$$

$$\rho(\vec{r}) = \frac{1}{V} \sum_{h,k,l=-\infty}^{+\infty} F(\vec{Q}) e^{-i\vec{Q}\cdot\vec{r}}$$

with $F(\vec{Q}) = |F(\vec{Q})| e^{i\varphi(\vec{Q})}$

fondamental problem = phases are lost





Structure solution methods

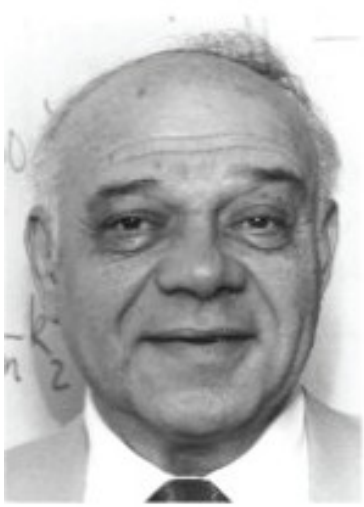
Jerome Karle
Chemistry Nobel prize 1985



Herbert Hauptman
Chemistry Nobel prize 1985

Structure solution methods

Jerome Karle
Chemistry Nobel prize 1985





Herbert Hauptman
Chemistry Nobel prize 1985

$$|F_K(\vec{Q})|e^{i\varphi_K(\vec{Q})} = FT^{-1}[\rho_K(x,y)]$$

$$|F_H(\vec{Q})|e^{i\varphi_H(\vec{Q})} = FT^{-1}[\rho_H(x,y)]$$

Structure solution methods

Jerome Karle
Chemistry Nobel prize 1985



Herbert Hauptman
Chemistry Nobel prize 1985

$$|F_K(\vec{Q})|e^{i\varphi_K(\vec{Q})} = FT^{-1}[\rho_K(x,y)]$$

$$|F_H(\vec{Q})|e^{i\varphi_H(\vec{Q})} = FT^{-1}[\rho_H(x,y)]$$

$$\rho(x,y) = FT\left[|F_K(\vec{Q})|e^{i\varphi_H(\vec{Q})}\right]$$

$$\rho(x,y) = FT\left[|F_H(\vec{Q})|e^{i\varphi_K(\vec{Q})}\right]$$

R. Blessing, HWI, Buffalo

Structure solution methods

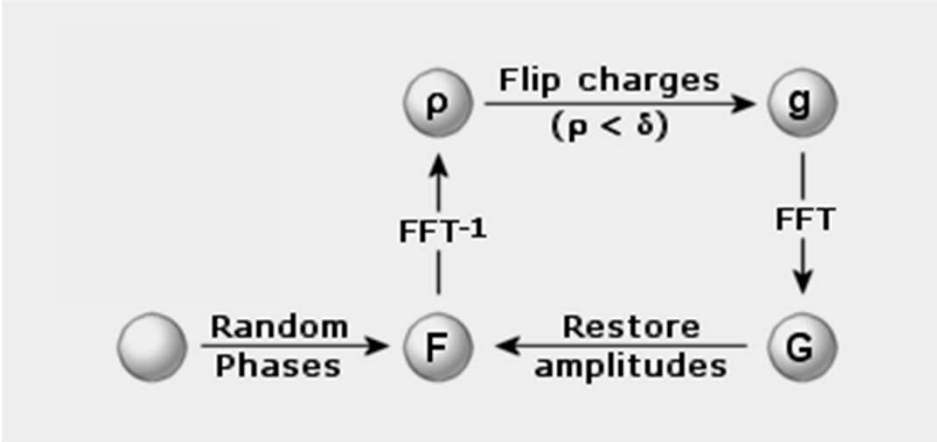
- Molecular replacement method:
  - prior knowledge of molecular fragments : use of a data base of known molecular fragments

- Heavy atom method / Patterson : Dirdif, Shelx
  - prior knowledge = the structure contains at least one heavy element. Use of contrast effect

- **Direct methods**: Shelx, Sir
  - prior knowledge = the crystal structure consists of discret atoms : accumulation of electron density in certain region of space (atomicity), chemical composition, symmetry

- **Charge flipping** : Superflip
  - prior knowledge = the crystal structure consists of discret atoms : accumulation of electron density in certain region of space (atomicity)

Animation charge flipping methods (2004)



https://www.epfl.ch/schools/sb/research/iphys/teaching/crystallography/charge-flipping/

Improvement (refinement) of the structure

Observables

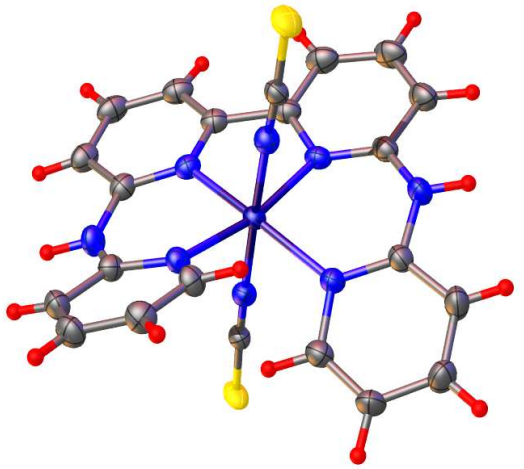
$$\left\{\left|F_{obs}(\vec{Q})\right| \quad \sigma\left(F_{obs}(\vec{Q})\right)\right\}$$

Improvement (refinement) of the structure

Observables

$$\left\{ |F_{obs}(\vec{Q})| \quad \sigma\left(F_{obs}(\vec{Q})\right) \right\}$$

Structural model



$$p_j \quad \left\{ \begin{pmatrix} x \\ y \\ z \end{pmatrix}, B_{iso}, \begin{pmatrix} U_{11} & U_{12} & U_{13} \\ U_{21} & U_{22} & U_{13} \\ U_{31} & U_{32} & U_{33} \end{pmatrix}, occ \right\}$$

Least-squares refinement : optimization

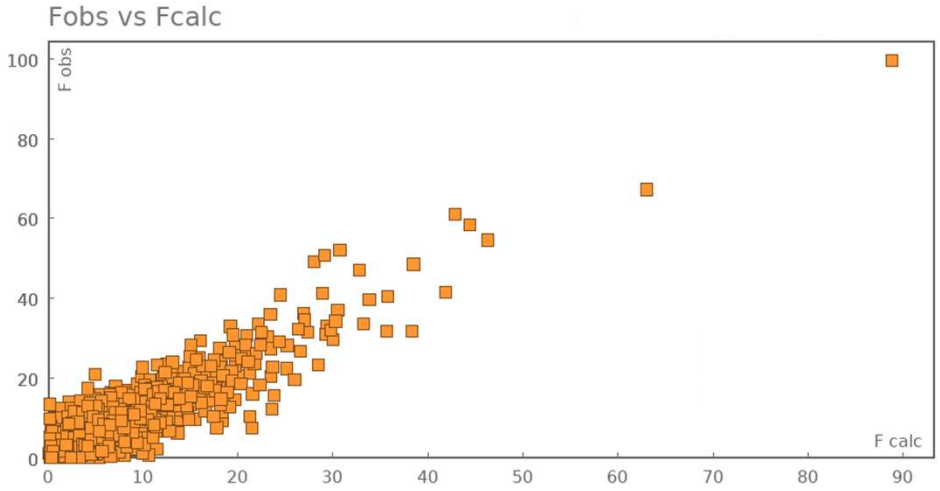
$$\chi^2 = \sum_Q \left[\frac{F_{obs} - F_{calc}(p_j)}{\sigma(F_{obs})} \right]^2$$

$$F_{calc}(\vec{Q}) = \sum_{j=1}^{N_{at}} f_j \cdot occ_j \cdot e^{i\vec{Q}\cdot\vec{r}} \cdot e^{-2\pi^2 \vec{Q}^T \cdot \tilde{U} \cdot \vec{Q}}$$

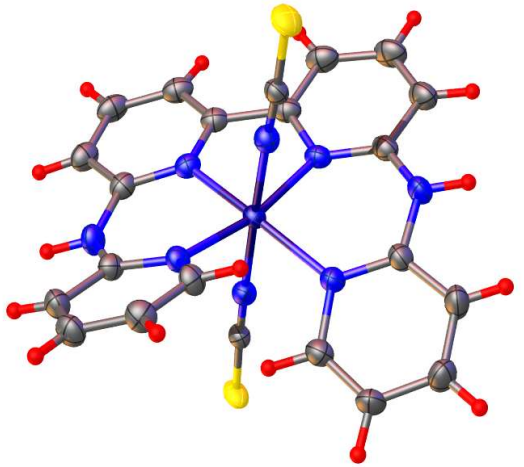
Improvement (refinement) of the structure

Observables

$$\left\{ |F_{obs}(\vec{Q})| \quad \sigma\left(F_{obs}(\vec{Q})\right) \right\}$$



Structural model



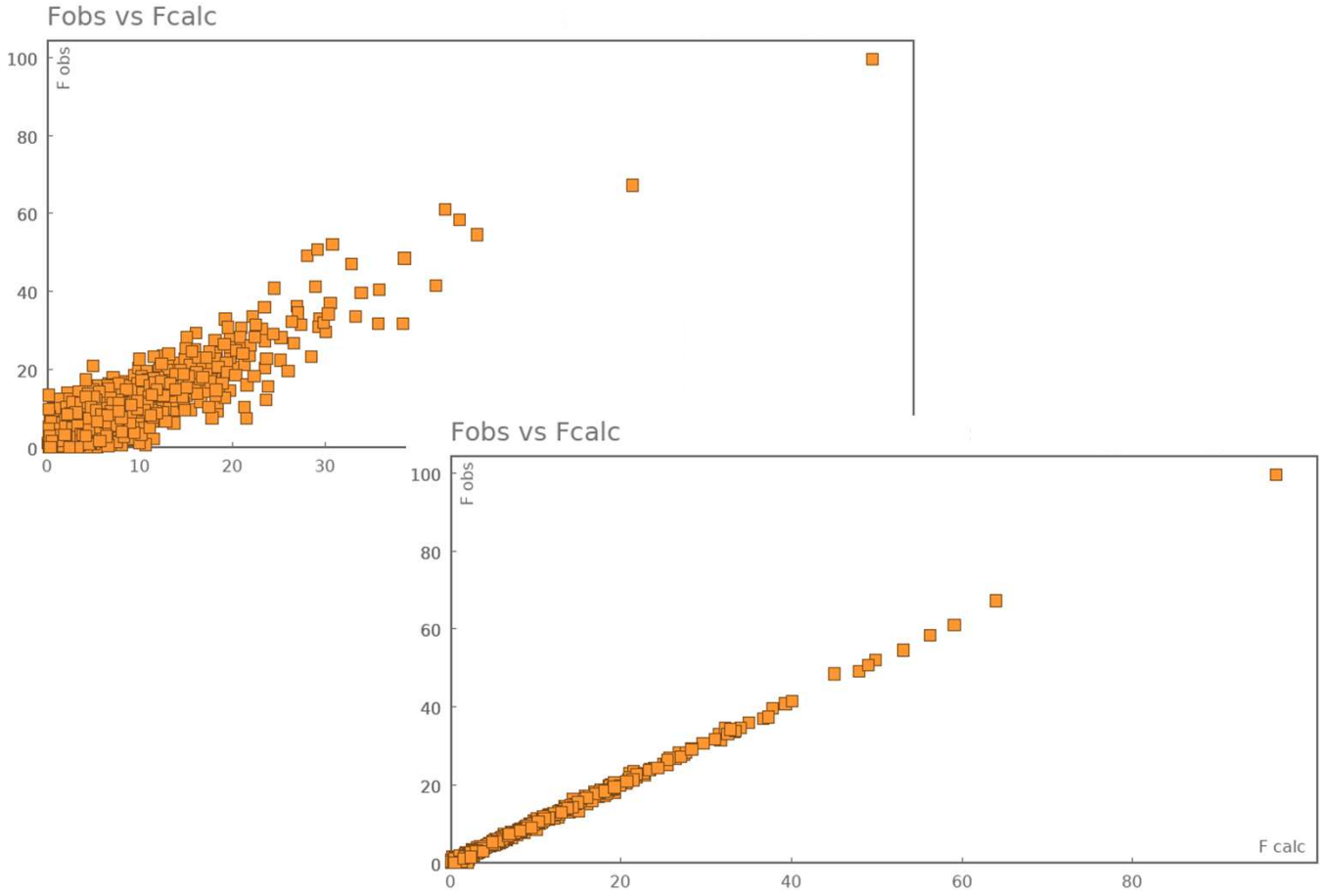
$$p_j \quad \left\{ \begin{pmatrix} x \\ y \\ z \end{pmatrix}, B_{iso}, \begin{pmatrix} U_{11} & U_{12} & U_{13} \\ U_{21} & U_{22} & U_{13} \\ U_{31} & U_{32} & U_{33} \end{pmatrix}, occ \right\}$$

$$F_{calc}(\vec{Q}) = \sum_{j=1}^{N_{at}} f_j \cdot occ_j \cdot e^{i\vec{Q}\cdot\vec{r}} \cdot e^{-2\pi^2 \vec{Q}^T \cdot \tilde{U} \cdot \vec{Q}}$$

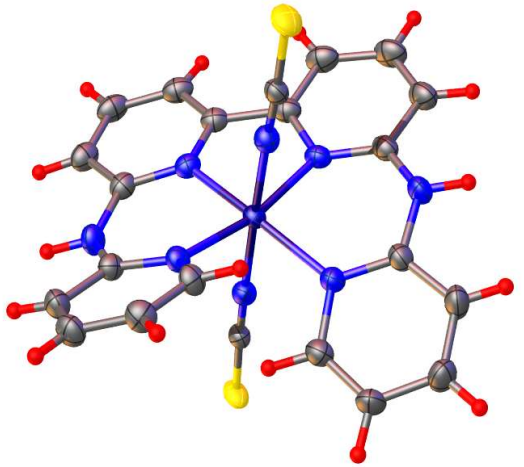
Improvement (refinement) of the structure

Observables

$$\left\{ |F_{obs}(\vec{Q})| \quad \sigma\left(F_{obs}(\vec{Q})\right) \right\}$$



Structural model

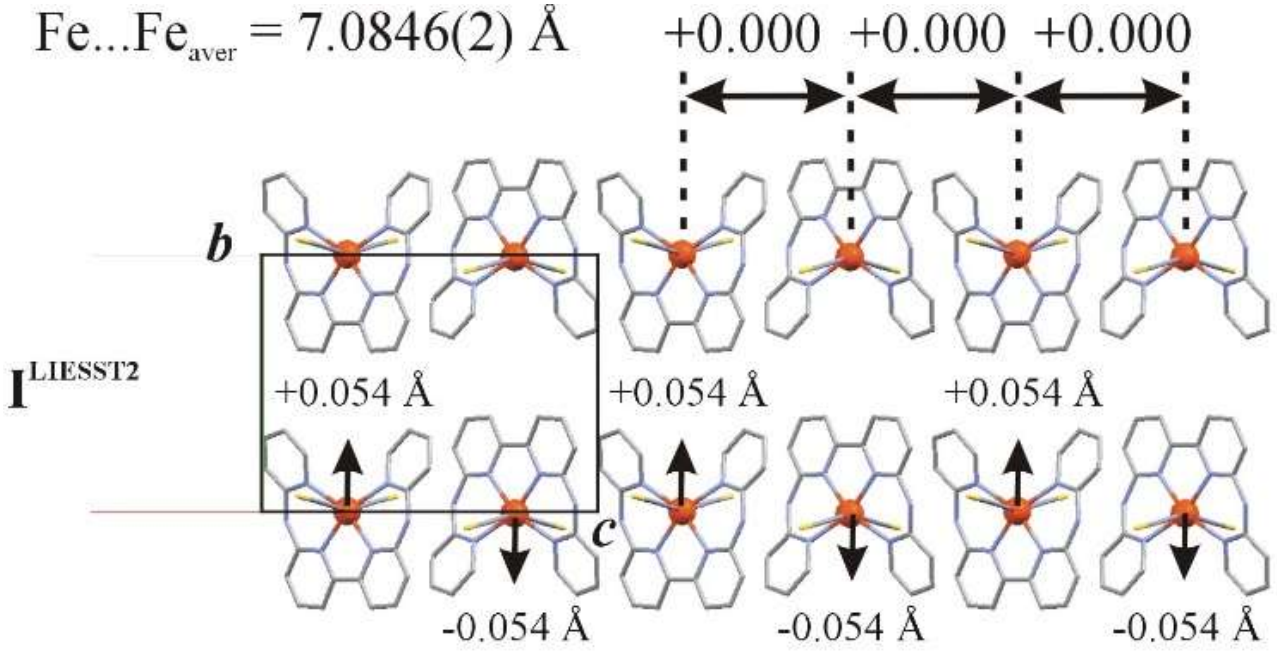


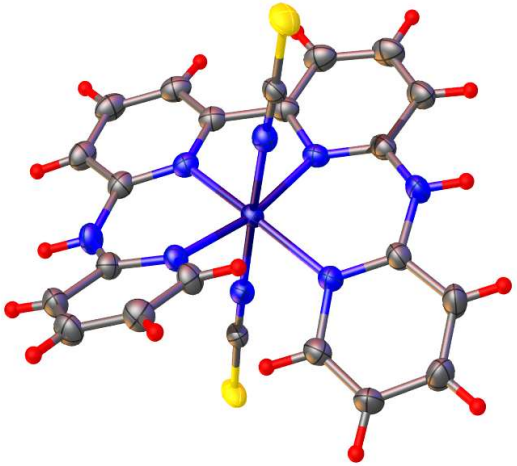
$$p_j \quad \left\{ \begin{pmatrix} x \\ y \\ z \end{pmatrix}, B_{iso}, \begin{pmatrix} U_{11} & U_{12} & U_{13} \\ U_{21} & U_{22} & U_{13} \\ U_{31} & U_{32} & U_{33} \end{pmatrix}, occ \right\}$$

$$F_{calc}(\vec{Q}) = \sum_{j=1}^{N_{at}} f_j \cdot occ_j \cdot e^{i\vec{Q}\cdot\vec{r}} \cdot e^{-2\pi^2 \vec{Q}^T \cdot \tilde{U} \cdot \vec{Q}}$$

Structural analysis

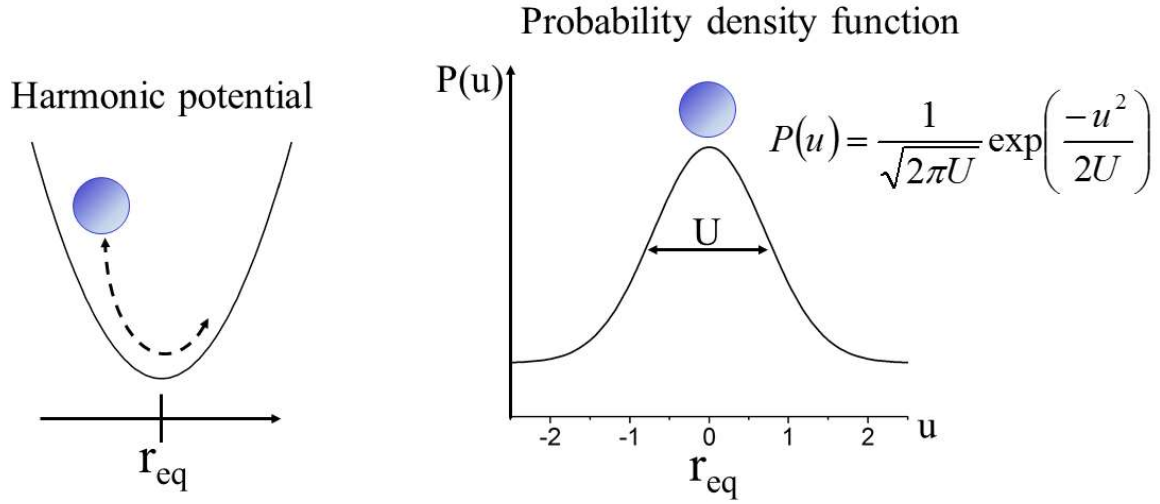
- Bond distances
- Bond angles
- Torsion angles
- Atomic displacement ellipsoids
- Intermolecular contacts





Dynamics and the Debye Waller factor

Born-Hoppenheimer approximation : the electron density follows the displacement of nucleus



$$\rho_{dynamic}(\vec{r}) = \int \rho_{static}(\vec{r}-\vec{u})\mathrm{p}(\vec{u})\mathrm{d}(\vec{u}) = \rho_{static}(\vec{u}) * \mathrm{p}(\vec{u})$$

Probability density function : $p(u)=\frac{1}{\sqrt{2\pi U}}\exp\left(\frac{-u^2}{2U}\right)$ in the spherical harmonic approximation

$U=\langle u^2\rangle$ is the quadratic mean displacement of the atom from its equilibrium position

Dynamics and the Debye Waller factor

$$\rho_{dynamic}(\vec{r}) = \int \rho_{static}(\vec{r}-\vec{u})\mathrm{p}(\vec{u})\mathrm{d}(\vec{u}) = \rho_{static}(\vec{u}) * \mathrm{p}(\vec{u})$$

TF

$$f(\vec{Q}) = F_{static}(\vec{Q}) \cdot \mathrm{T}(\vec{Q})$$

$$\begin{pmatrix} U_{11} & U_{12} & U_{13} \\ & U_{22} & U_{23} \\ & & U_{33} \end{pmatrix}$$

In the isotropic harmonic approximation :

$$\mathrm{T}(\vec{Q}) = e^{(-2\pi^2 U H^2)} = e^{\left(-8\pi^2 U \frac{sin^2\theta}{\lambda^2}\right)}$$

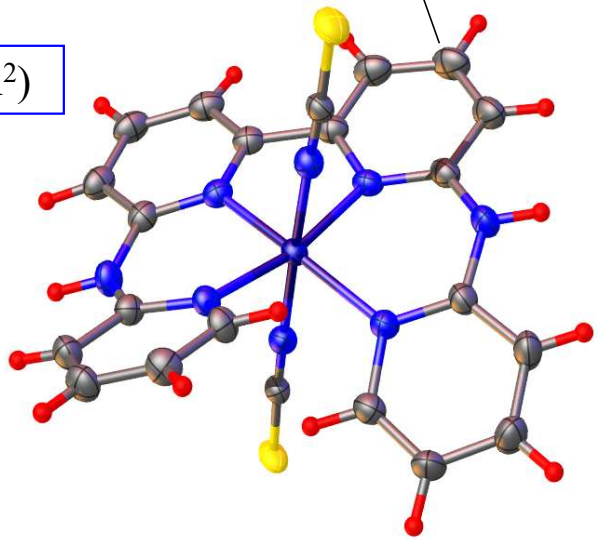
$$\mathrm{T}(\vec{Q}) = e^{\left(-B\frac{sin^2\theta}{\lambda^2}\right)}$$

B ~ 3-10 Å^2 (U ~ 0.02-0.12 Å^2)

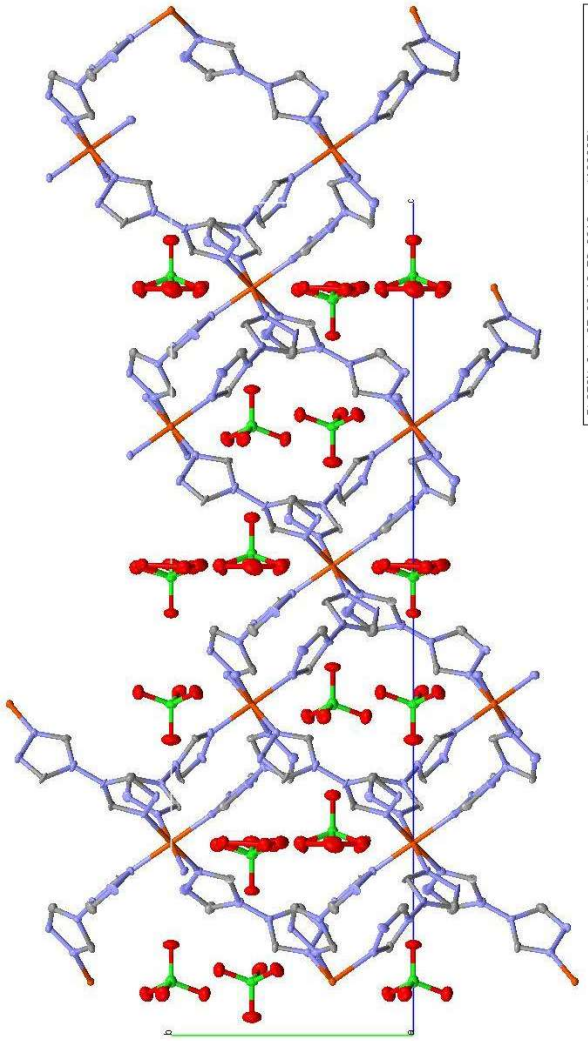
In the anisotropic harmonic approximation :

$$\mathrm{T}(\vec{Q}) = e^{-2\pi^2 \vec{Q}^T \cdot \tilde{U} \cdot \vec{Q}} = e^{\left(-\sum_{i,j} 2\pi^2 h_i h_j a_i^* a_j^* U_{ij}\right)}$$

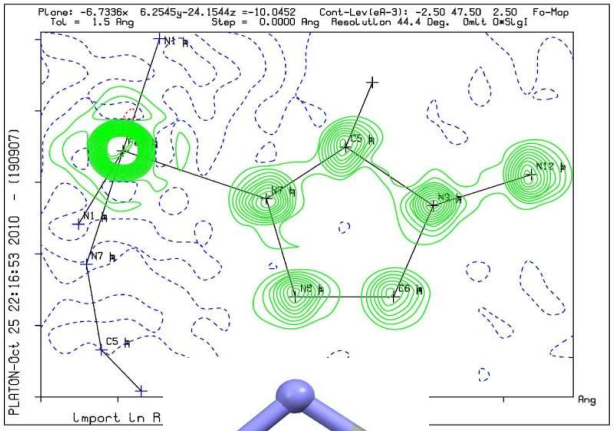
$\tilde{U}$ Is the atomic displacement tensor (symmetric)

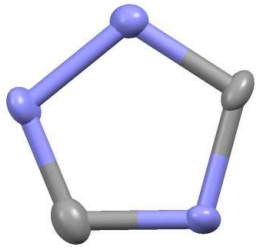


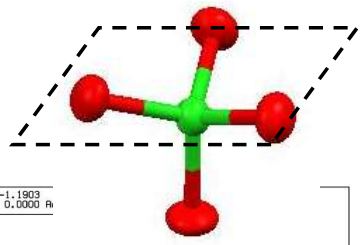
Structural disorder

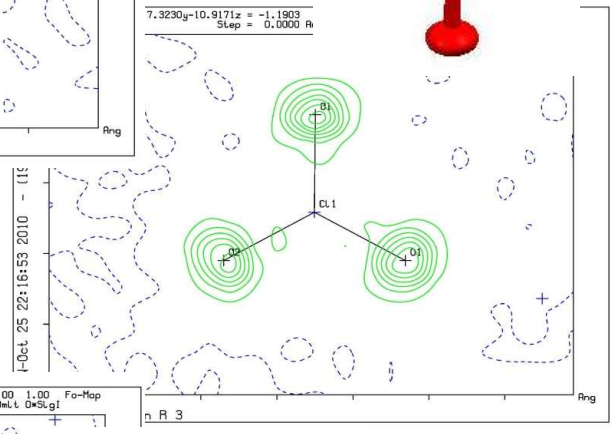


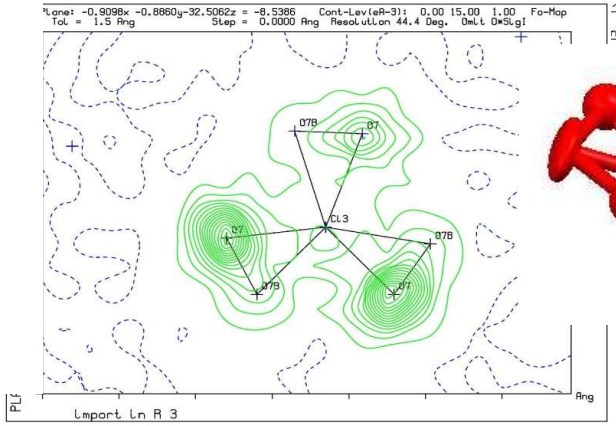
$[Fe(btr)_3].(ClO_4)_2$

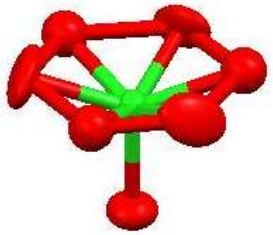






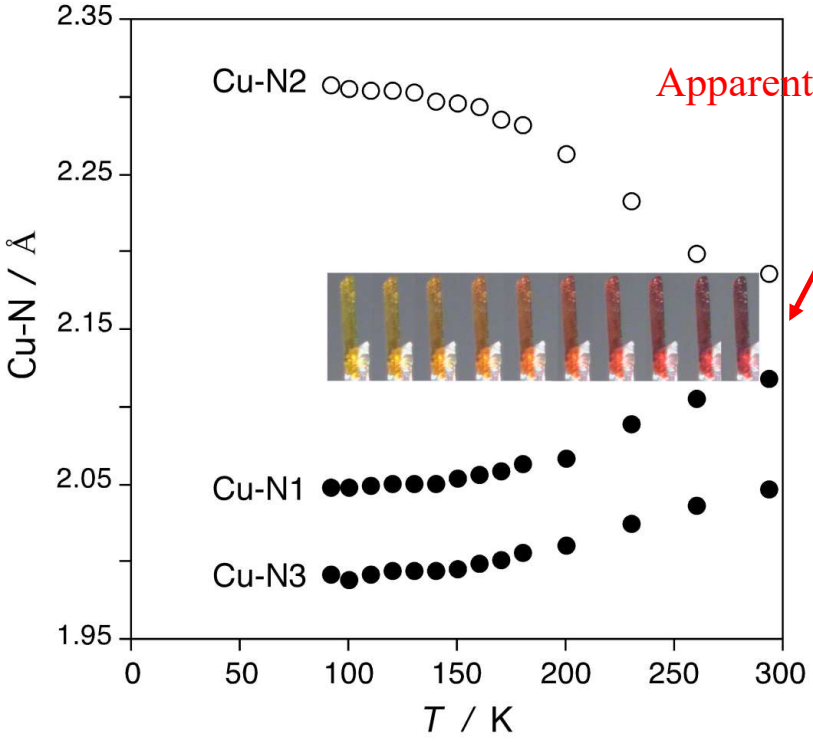




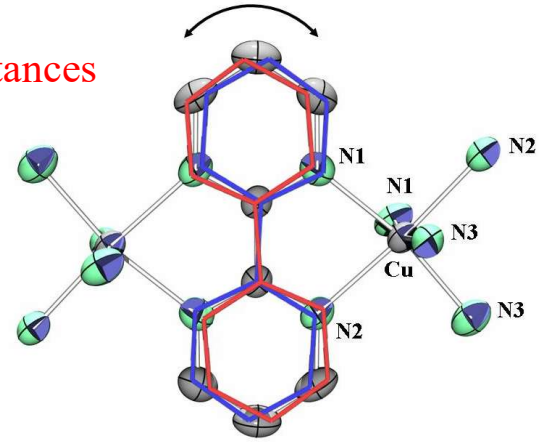


Static disorder ?
or dynamical disorder ?

Average structure and local structure



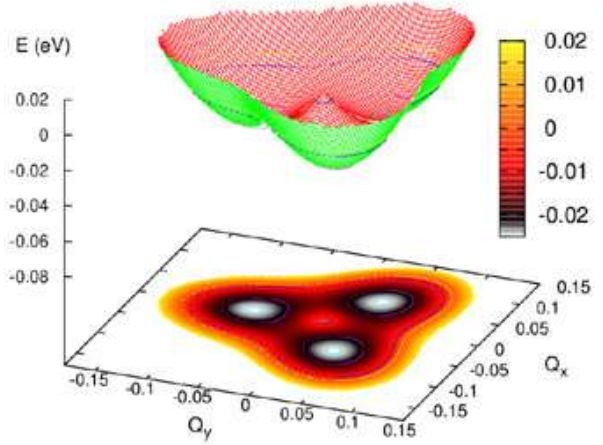
Apparent Cu-N distances



Dynamical Jahn-Teller effect

Vibronic coupling leads to a degeneracy between 3 nuclear configurations

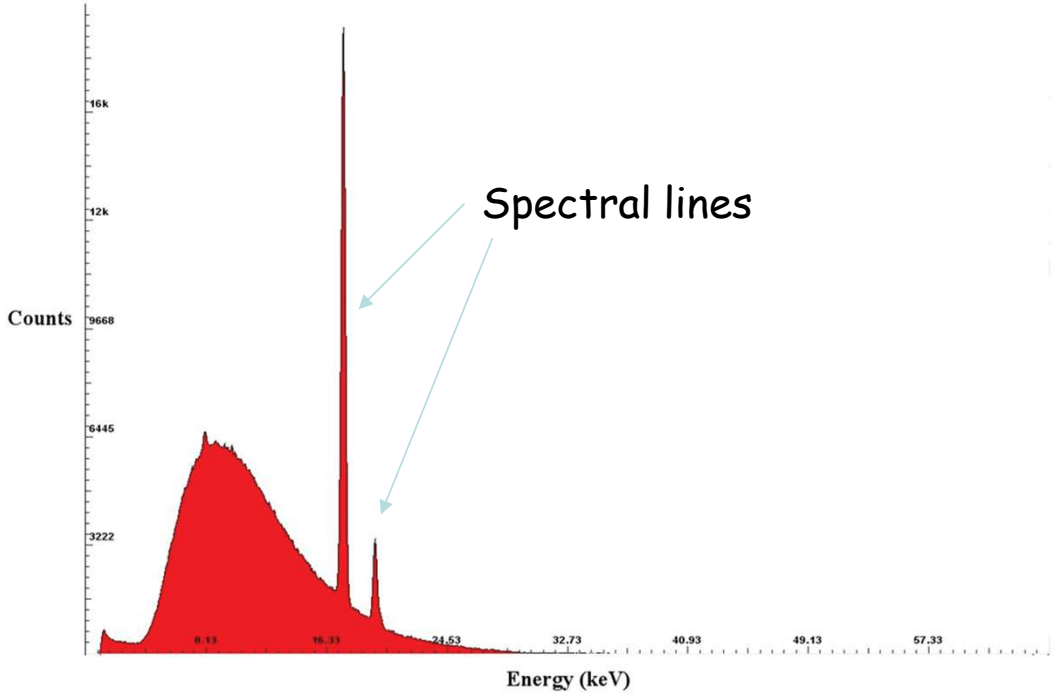
Potential energy surface



Scientific cases

X-ray source emission wavelength

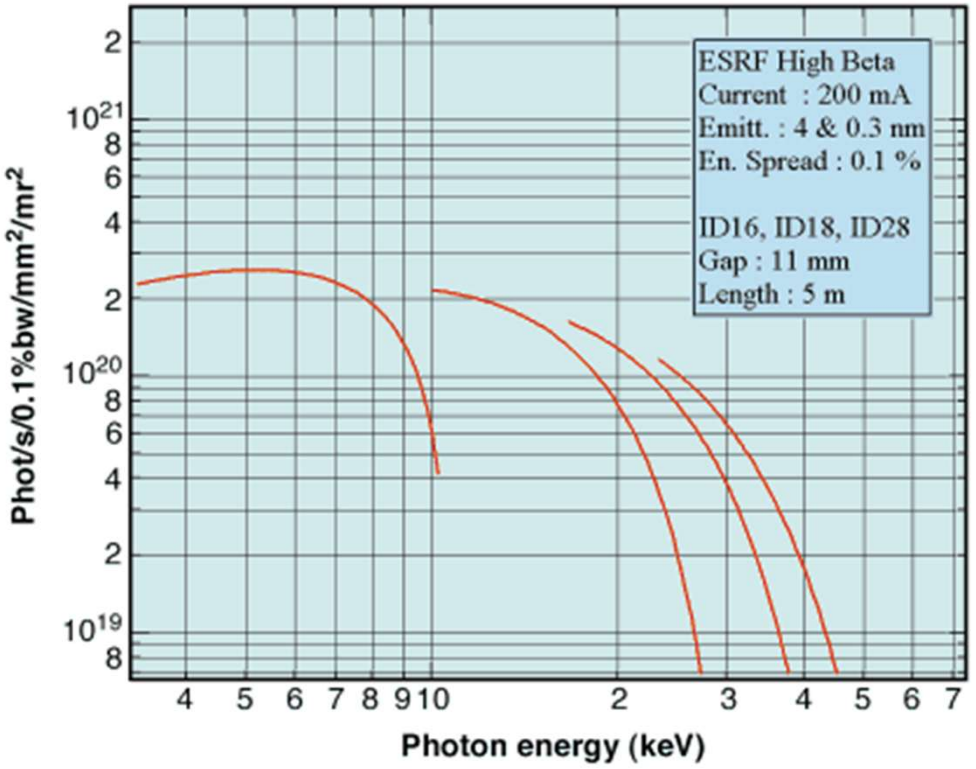
Laboratory X-ray sources
(Mo X-ray tube)



Source : https://xray.oxinst.com/

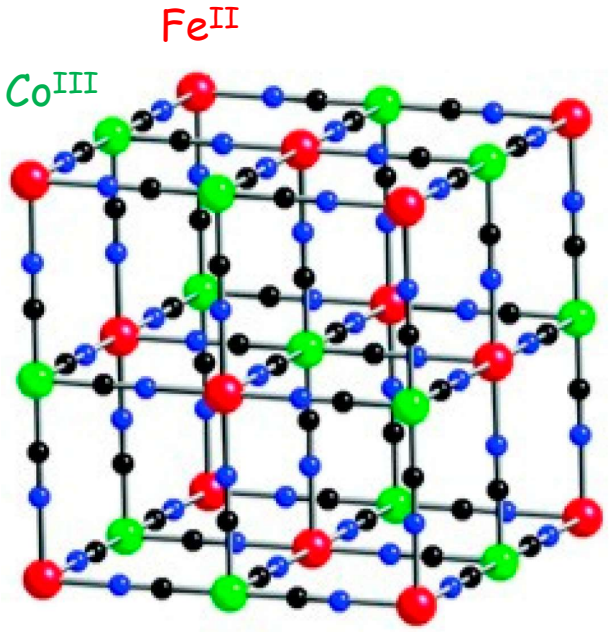
Fixed wavelength

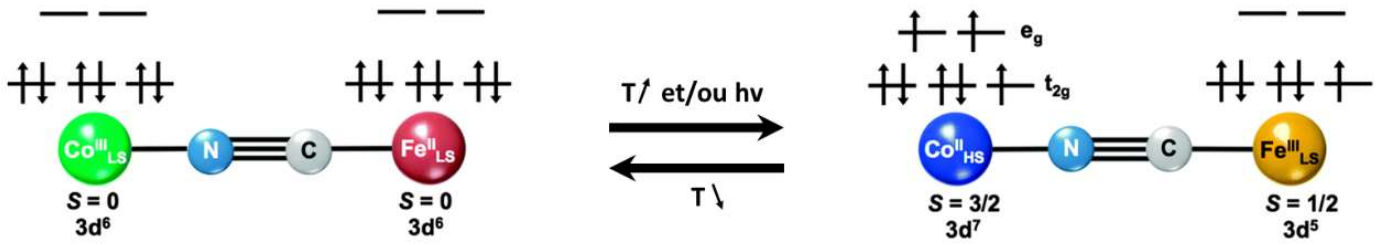
Synchrotron radiation facilities



Tunable wavelength

X-ray source emission wavelength



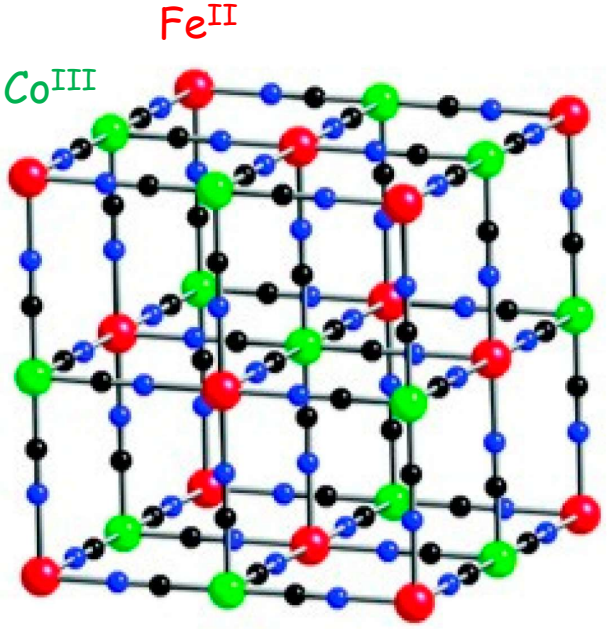


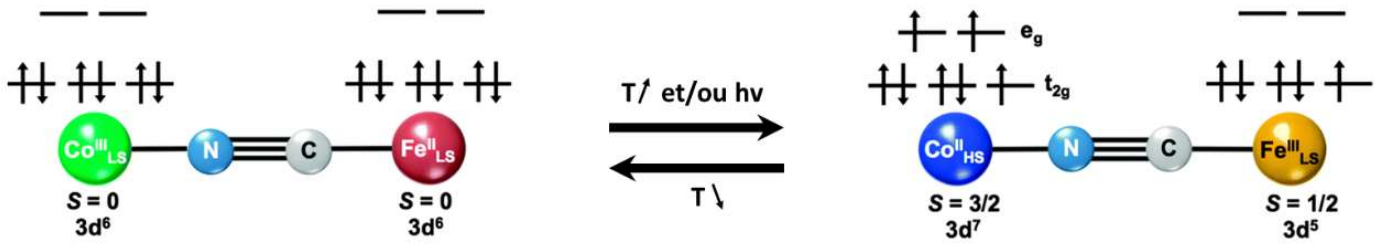
Co^{III} : 24 electrons Co^{II} : 25 electrons
Fe^{II} : 24 electrons Fe^{III} : 23 electrons

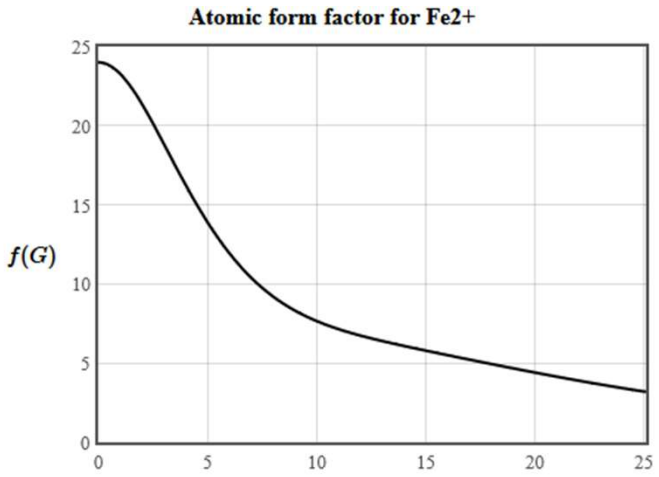
Co^{III}-Fe^{II} pairs have the same number of electrons !

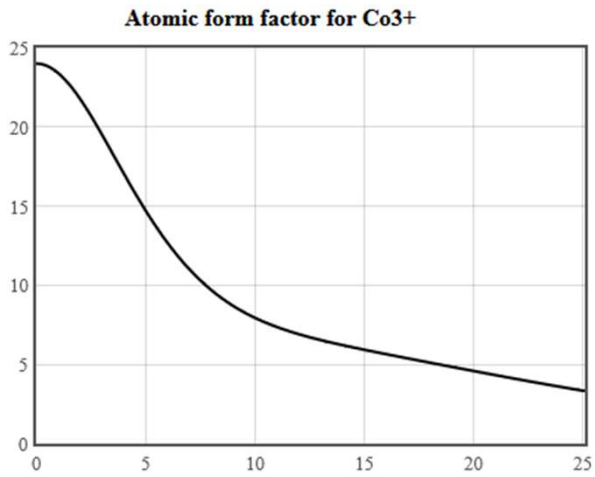
→ https://physics.nist.gov/

X-ray source emission wavelength









Co^{III} : 24 electrons
Fe^{II} : 24 electrons

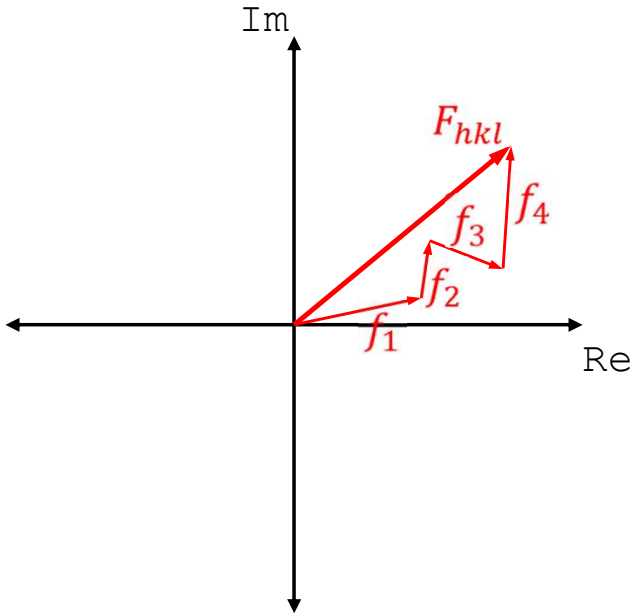
Co^{II} : 25 electrons
Fe^{III} : 23 electrons

Co^{III}-Fe^{II} pairs have the same number of electrons !

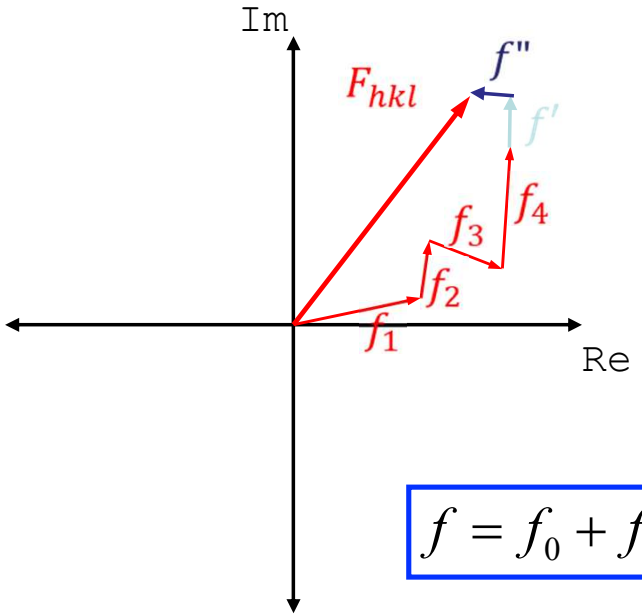
→ https://physics.nist.gov/

Unit cell structure factor

$$F_{unit\ cell}(\vec{Q}) = \sum_{j}^{unit\ cell} f_j e^{-i\vec{Q}.\vec{r}_j} = |F(\vec{Q})| e^{i\varphi(\vec{Q})}$$



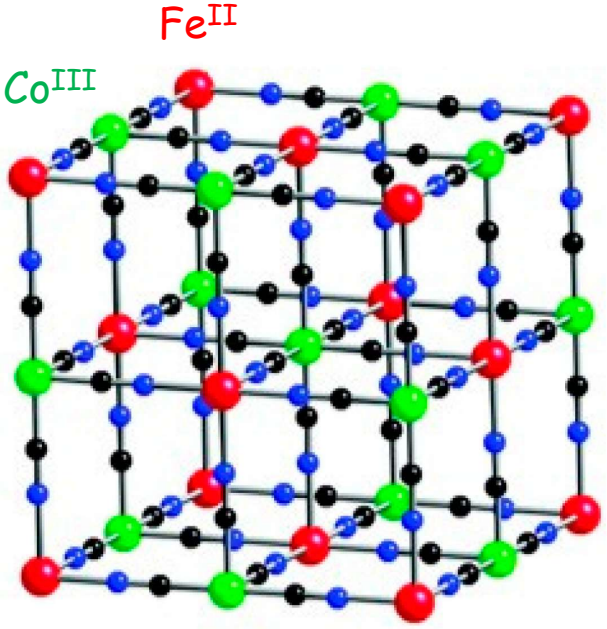
Argand diagram

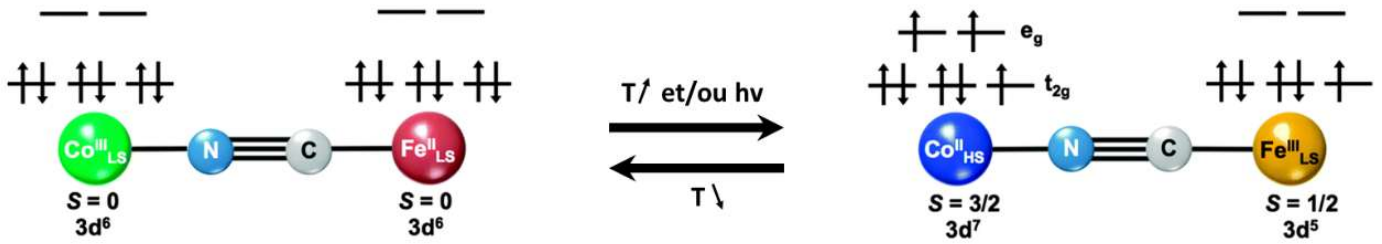


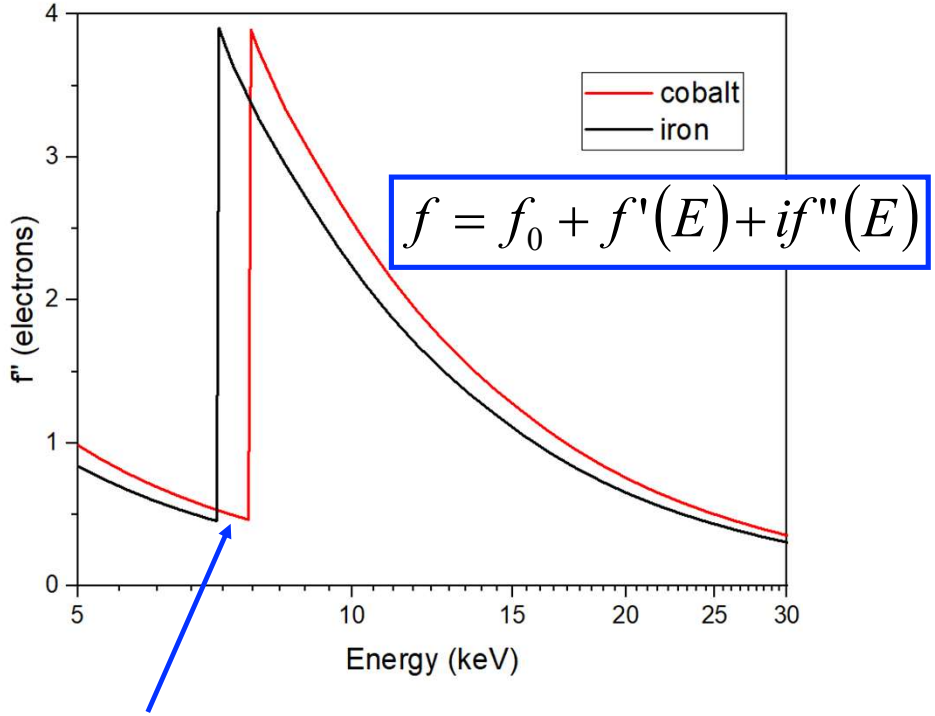
$$f = f_0 + f'(E) + if''(E)$$

Accounting for anomalous dispersion

X-ray source emission wavelength







Co^{III} : 24 electrons Co^{II} : 25 electrons

Fe^{II} : 24 electrons Fe^{III} : 23 electrons

Co^{III}-Fe^{II} pairs have the same number of electrons !

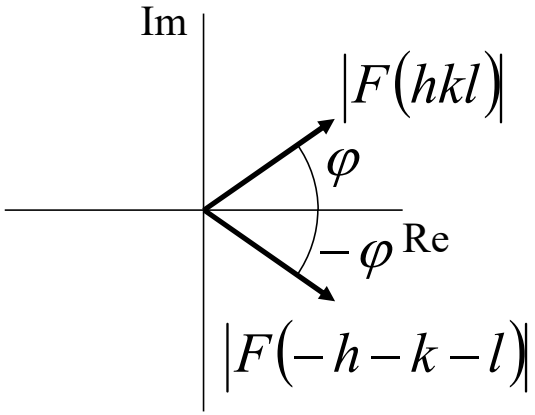
→ https://physics.nist.gov/

Tune the energy to enhance scattering contrast

Absolute structures

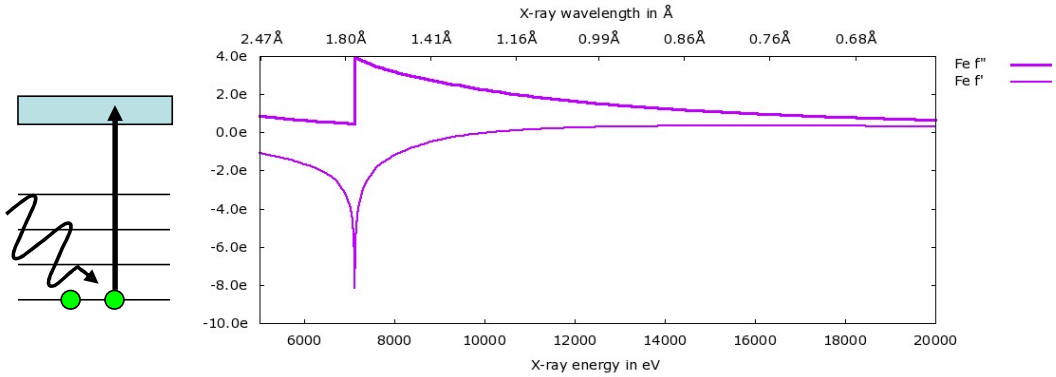
Friedel law : $\mathbf{I}(hkl) = \mathbf{I}(-h-k-l)$

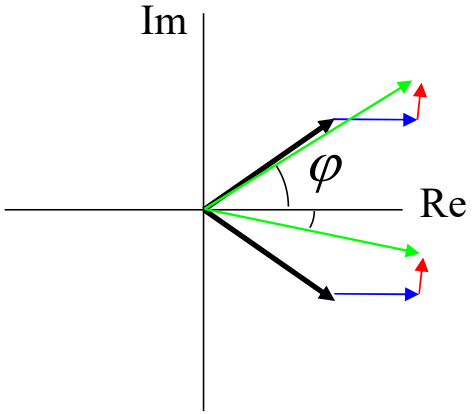
In the absence of anomalous dispersion,
the diffraction pattern is centrosymetric :
Two structures containing two different
enantiomers are not distinguishable



In presence of anomalous dispersion :
Resonance phenomenon (EXAFS, XANES)

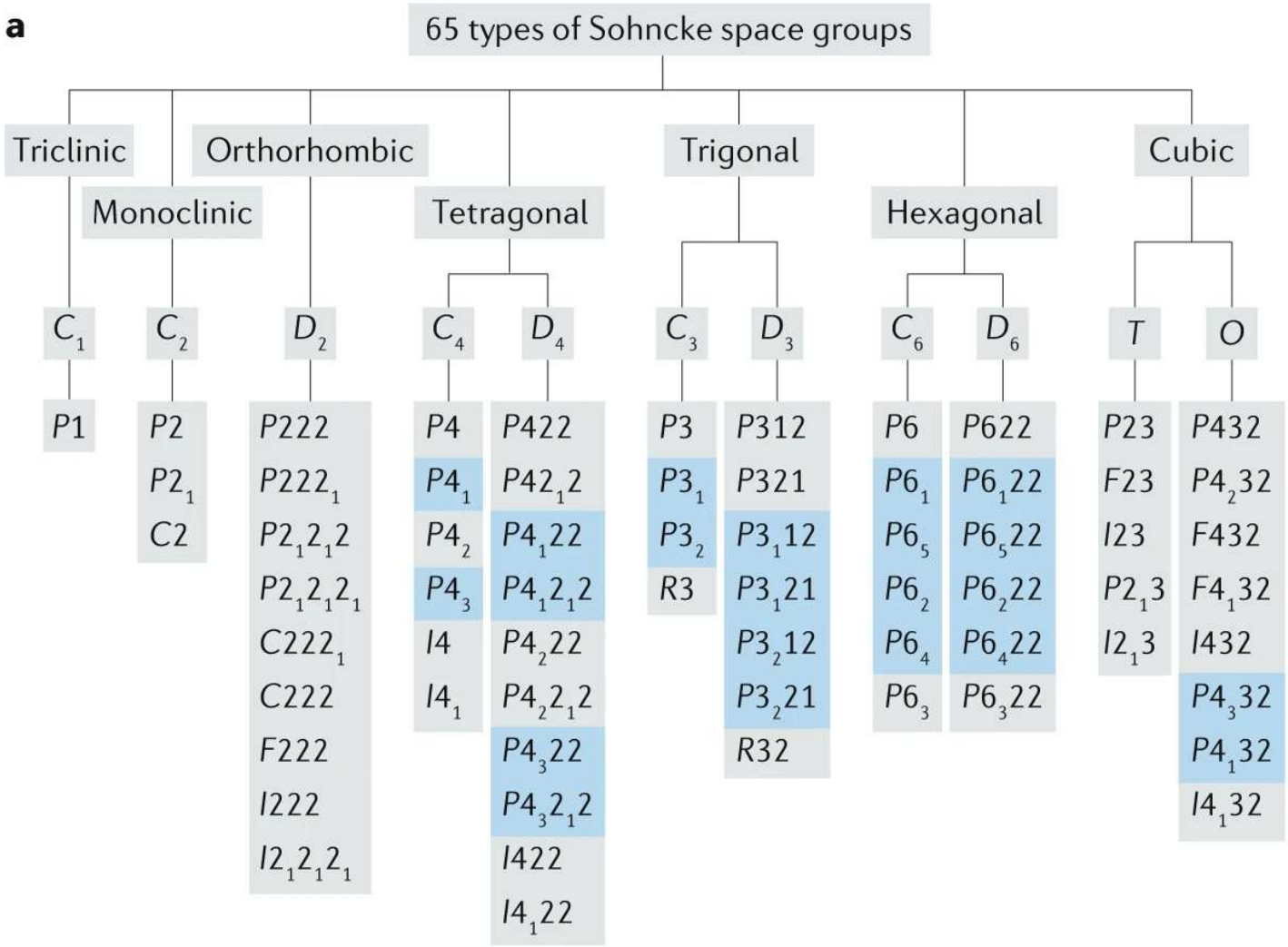
$$f = f_0 + f'(E) + if''(E)$$





$\mathbf{I}(hkl) \neq \mathbf{I}(-h-k-l)$

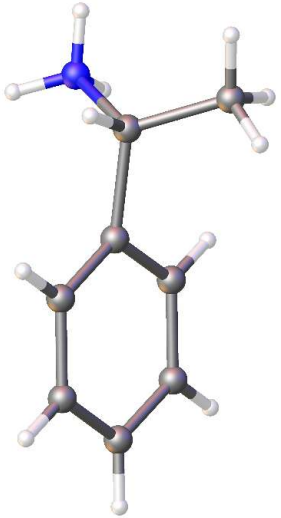
Chirality : 65 Sohncke space groups

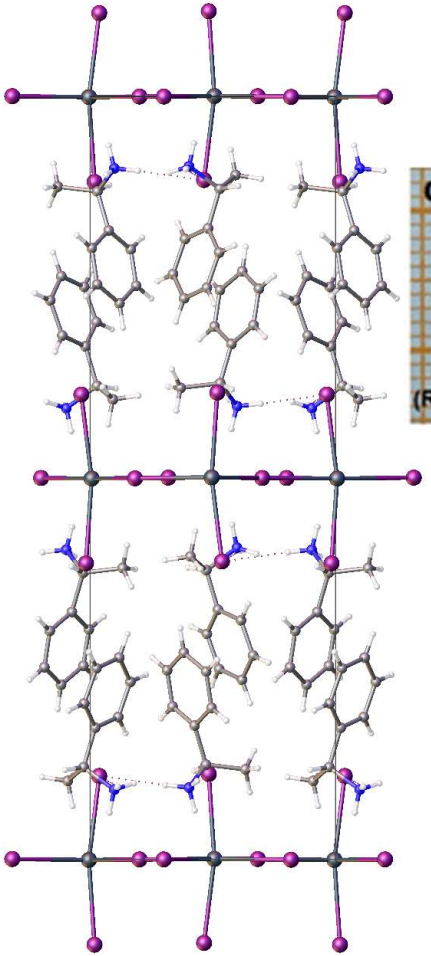


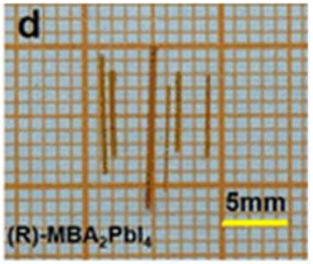
G. Long et al., Nat. Rev. Mater., (2020), 5, 423.

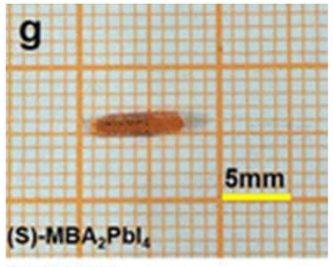
Chirality with chiral organic cation : $(MBA)_2PbI_4$

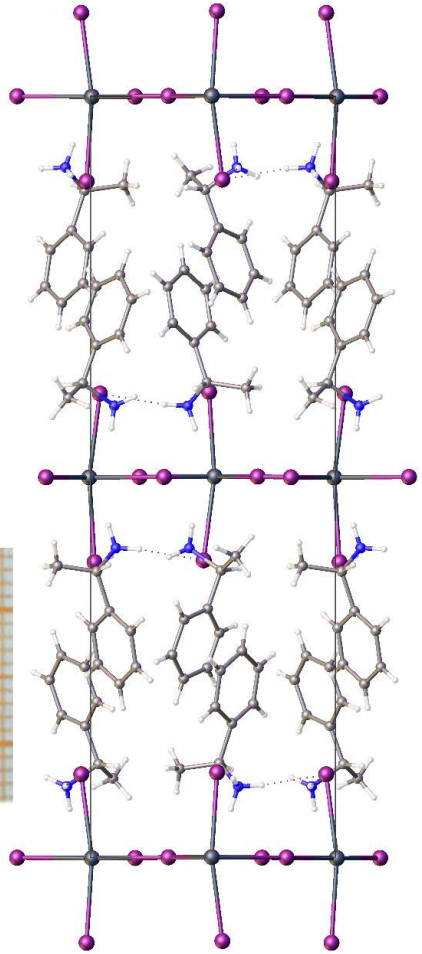
$(R\text{-}MBA)_2PbI_4$



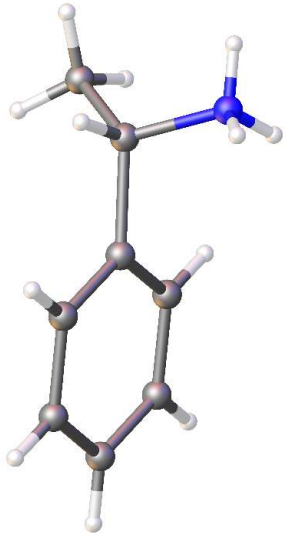








$(S\text{-}MBA)_2PbI_4$



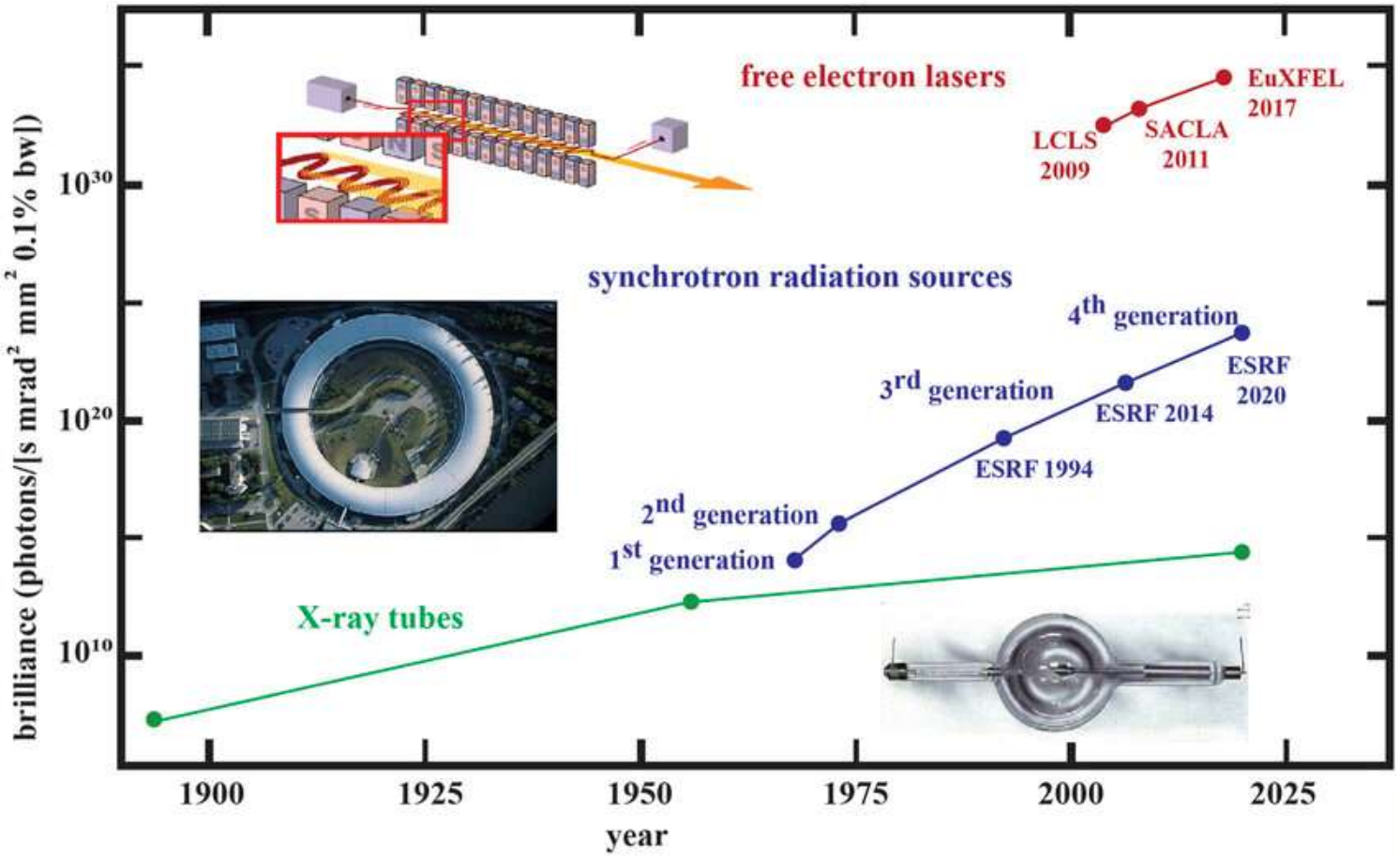
$P2_12_12_1$ space group

$P2_12_12_1$ space group

$$F^2(hkl,x) = (1-x)\left|F(hkl)\right|^2 + x\left|F(-h-k-l)\right|^2$$

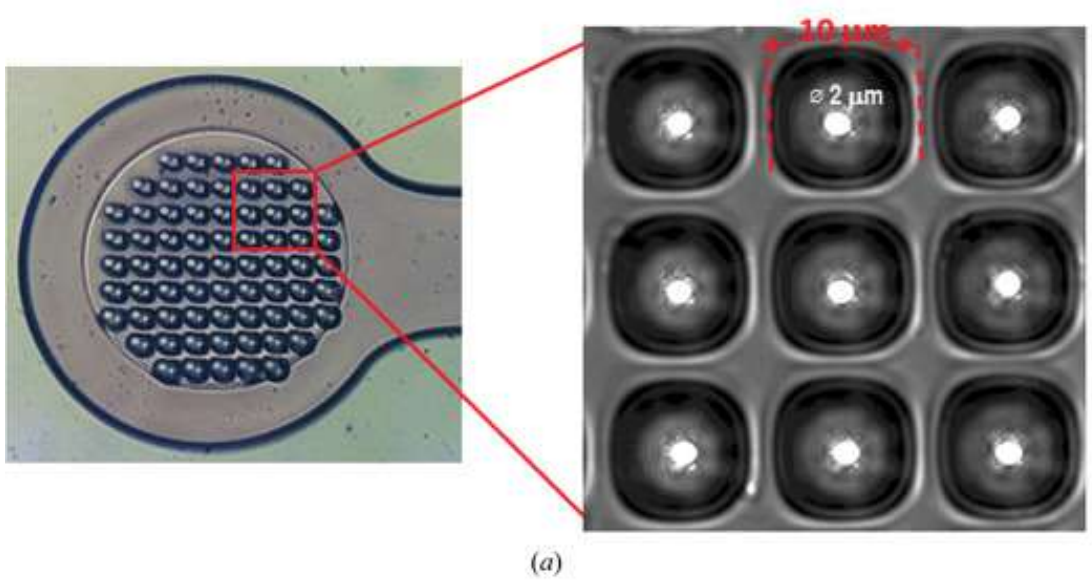
Flack parameter : x

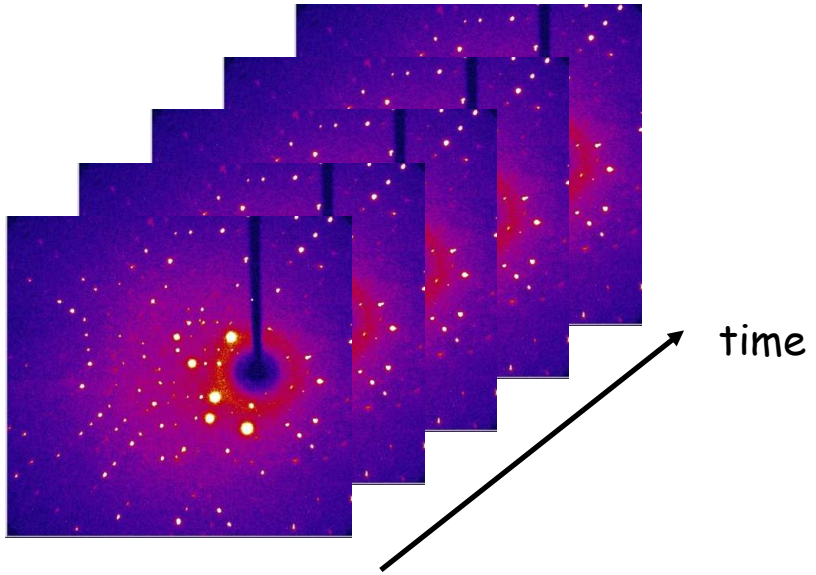
X-ray source brilliance



V. Cerentola et al., J. Phys. Cond. Mat. (2021), 33, 274003

X-ray source brilliance





G. Guo et al., IUCrJ (2018), 5, 238.

Measure tiny crystals
(1-5 μm)

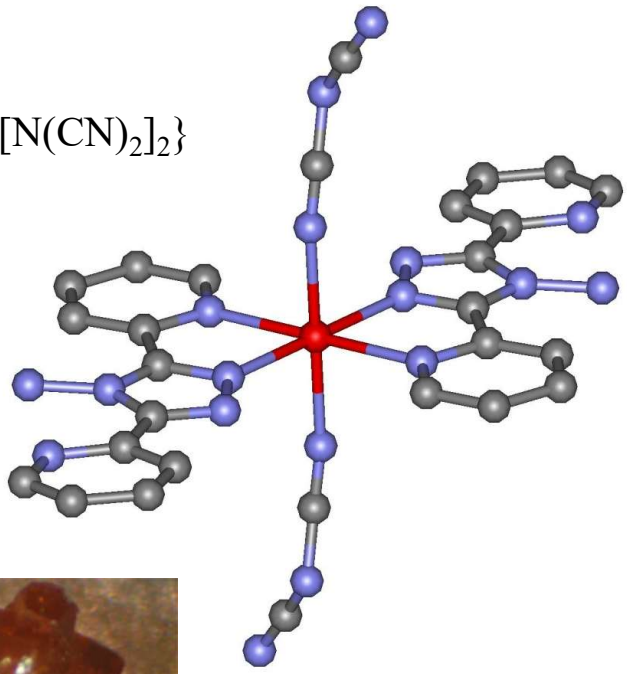
Cannot grow big crystals
Single domain tiny crystals

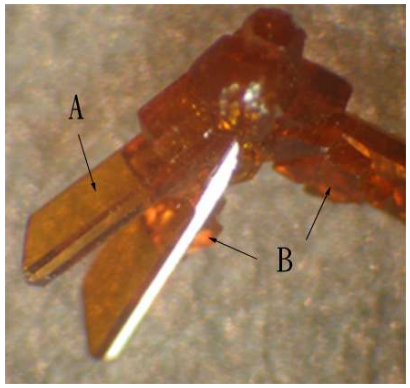
Measure fast
Shutterless modes

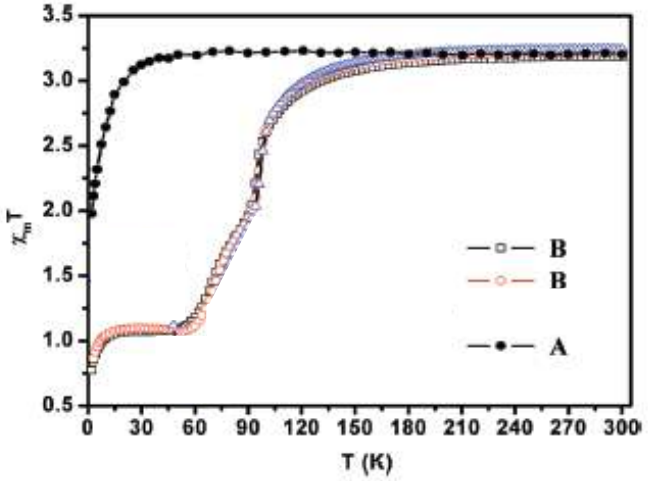
Fast completeness
Reduce radiation dommage
Kinetic irreversible effects

Polymorphism

$\{Fe(abpt)_2[N(CN)_2]_2\}$







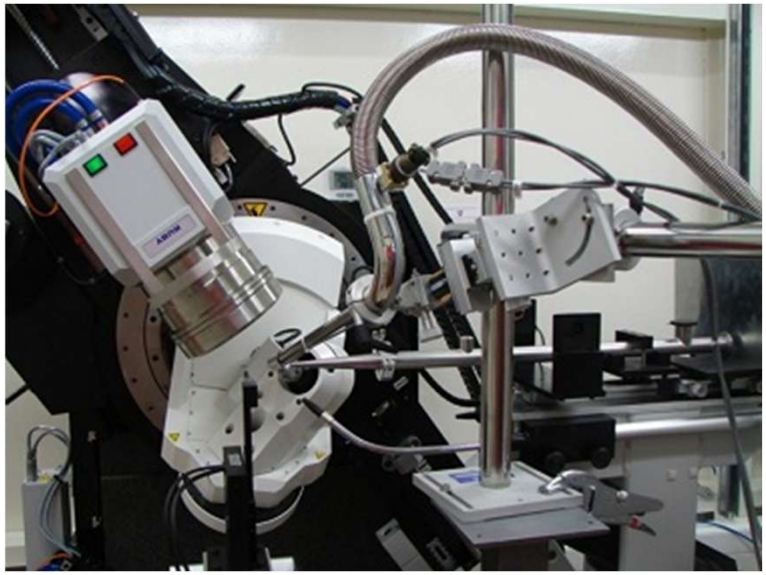
Polymorph A:
P-1
a=8.4618(5)Å, b=9.6086(3)Å, c=9.6381(7)Å
V =710.44(7)Å^3, Z =1

Polymorph B:
P-1
a=9.599(2)Å, b=9.989(2)Å, c=16.106(2)Å
V =1491.6(4)Å^3, Z =2

Single crystal combined to powder diffraction

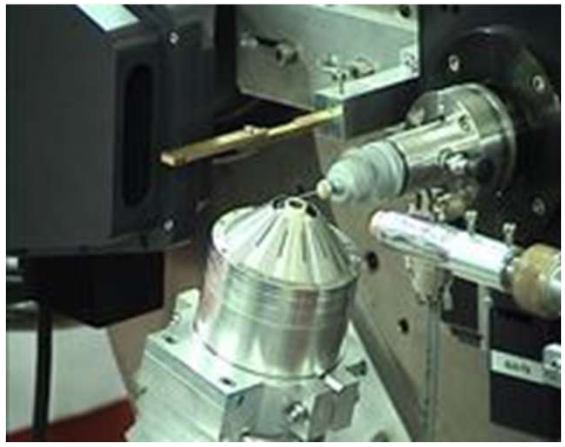
Moliner *et al*., (2001), *Inorg Chem*, **40**, 3986.
Sheu *et al*., (2008), *Inorg Chem*, **47**, 10866.

As a function of temperature …



He or N2 cryostream

High T blower



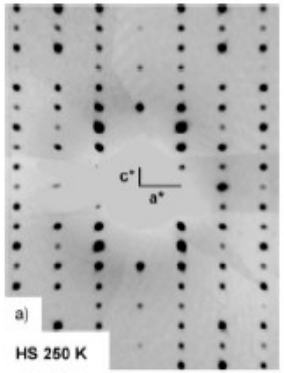


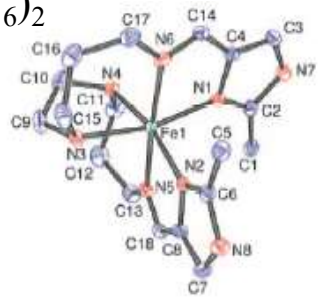
Close cycle cryostat

Symmetry breaking, development of a surstructure

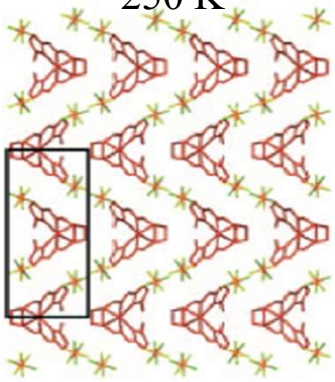
$[FeH_2L_2Me]$-$(PF_6)_2$

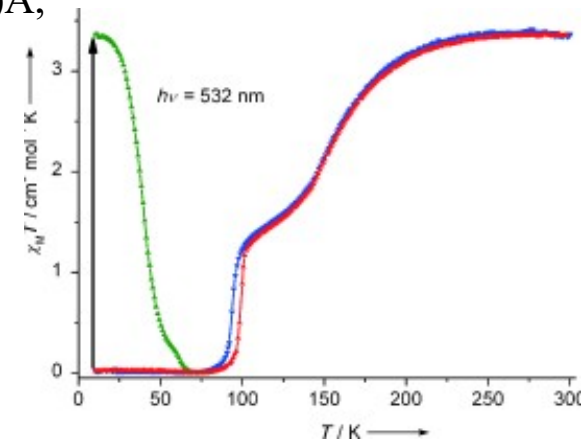
$P22_12_1$, a=8.405(1)Å, b=9.469(2)Å,
c=17.399(3)Å , V=1384.7(4)Å^3
Z=2





250 K

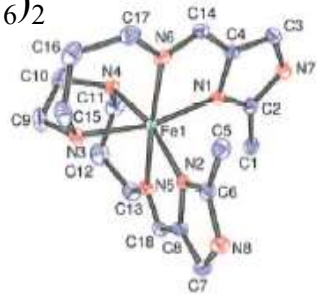




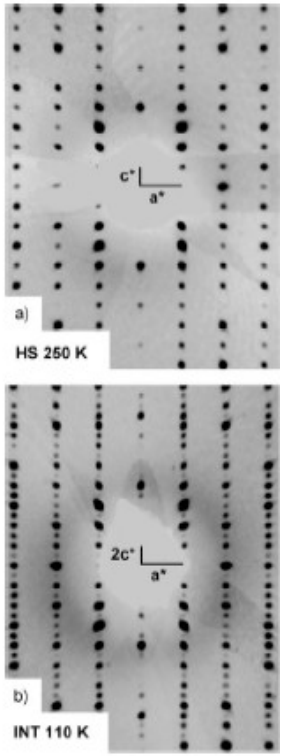
Bréfuel et al. Angew. Chem. (2009), 48, 9304

Symmetry breaking, development of a surstructure

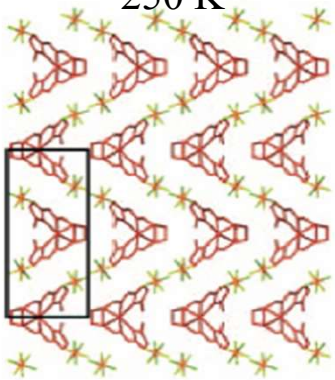
$[FeH_2L_2Me]$-$(PF_6)_2$



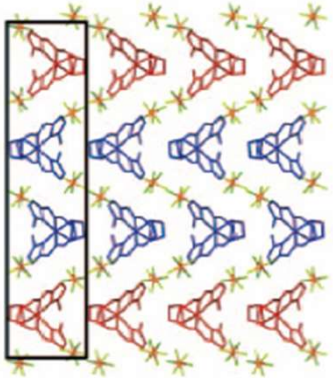
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c=17.399(3)Å , V=1384.7(4)Å^3
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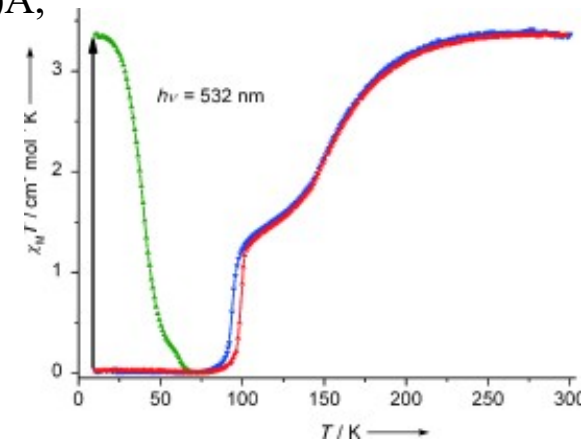
250 K

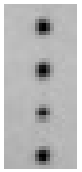


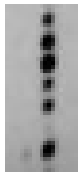
110 K



$P2_1$, c=35.543(2)Å,
V=2655(2)Å^3, Z=4





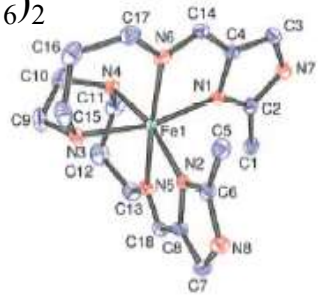


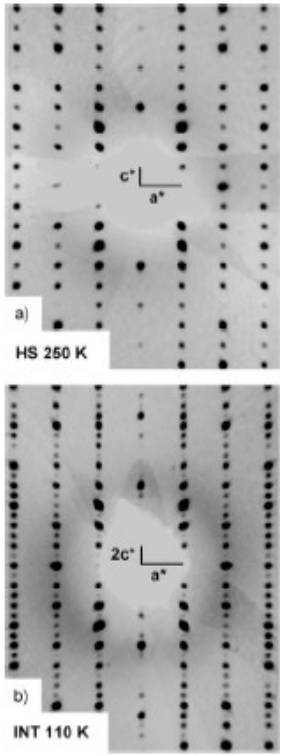
Bréfuel et al. Angew. Chem. (2009), 48, 9304

Symmetry breaking, development of a surstructure

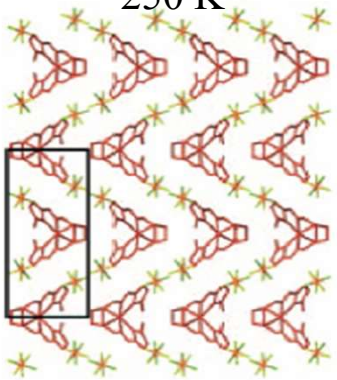
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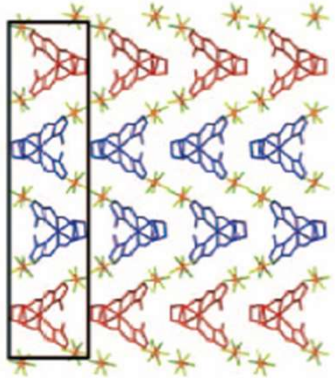




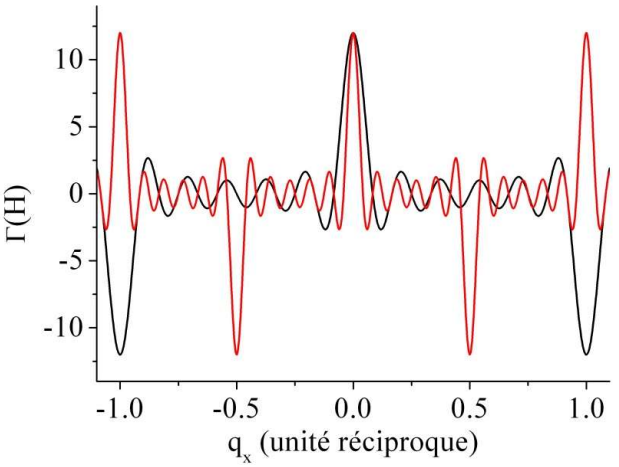
250 K



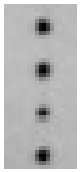
110 K



$P2_1$, c=35.543(2)Å,
V=2655(2)Å^3, Z=4

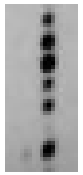


Additional 3D order



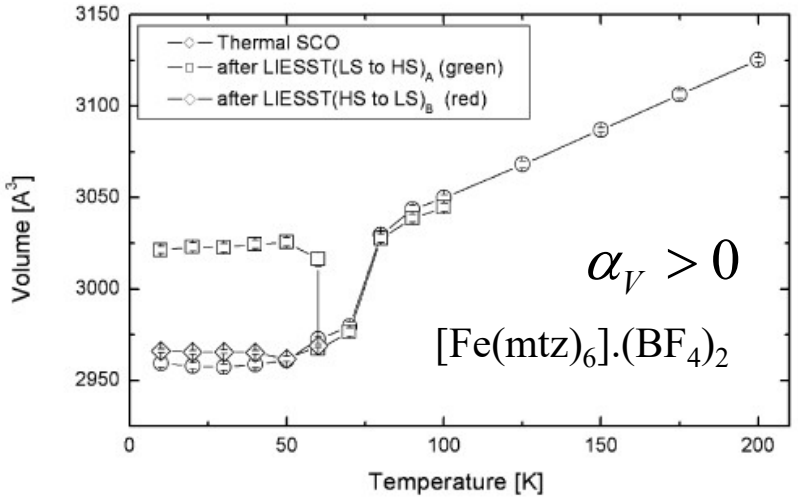


New periodicity



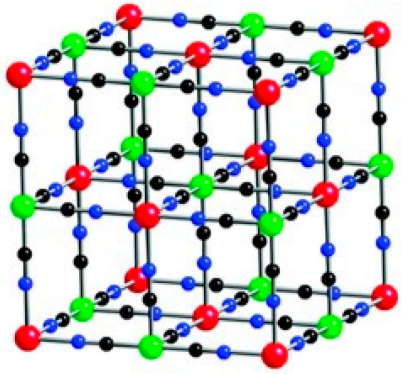
Bréfuel et al. Angew. Chem. (2009), 48, 9304

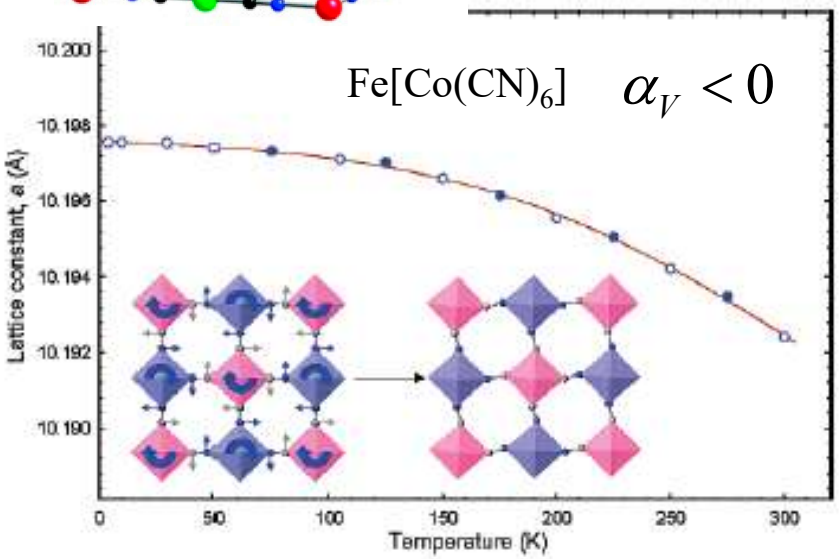
Isobaric expansion

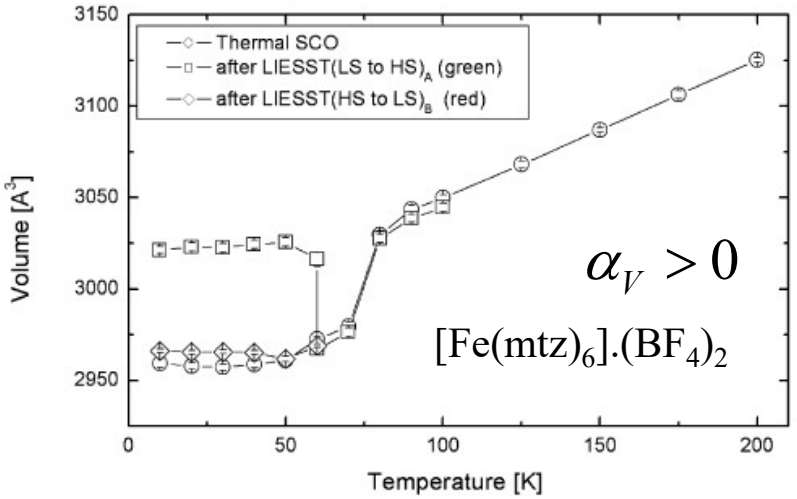


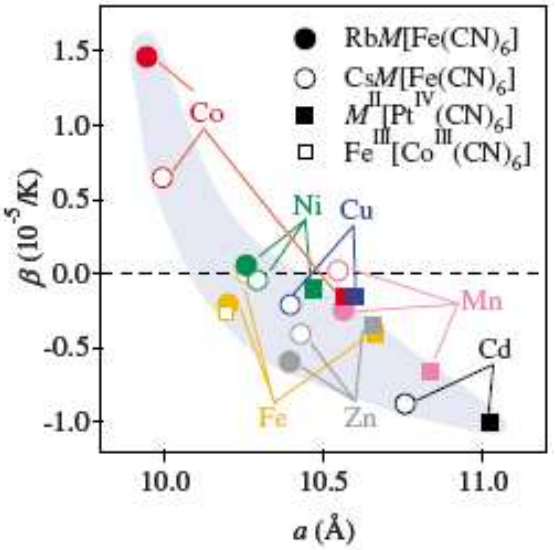
Matsuda et al. Phys. Rev B79, 172302 (2009)
Margadonna et al., J. Am. Chem. Soc. 126, 15390 (2004)
Kusz et al. *J Appl Cryst.,* **34**, 229, (2001)

Isobaric expansion



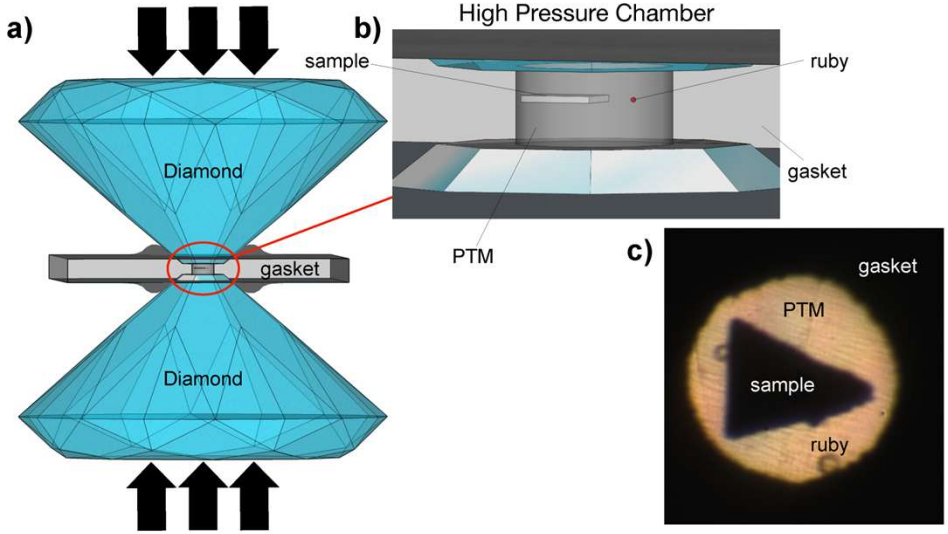


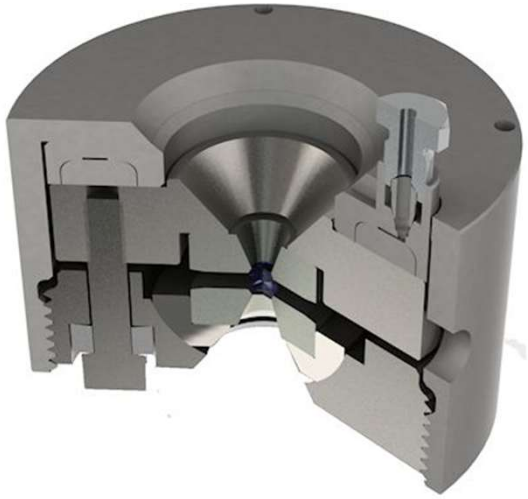




Matsuda et al. Phys. Rev B79, 172302 (2009)
Margadonna et al., J. Am. Chem. Soc. 126, 15390 (2004)
Kusz et al. *J Appl Cryst.*, **34**, 229, (2001)

Single crystal diffraction under pressure

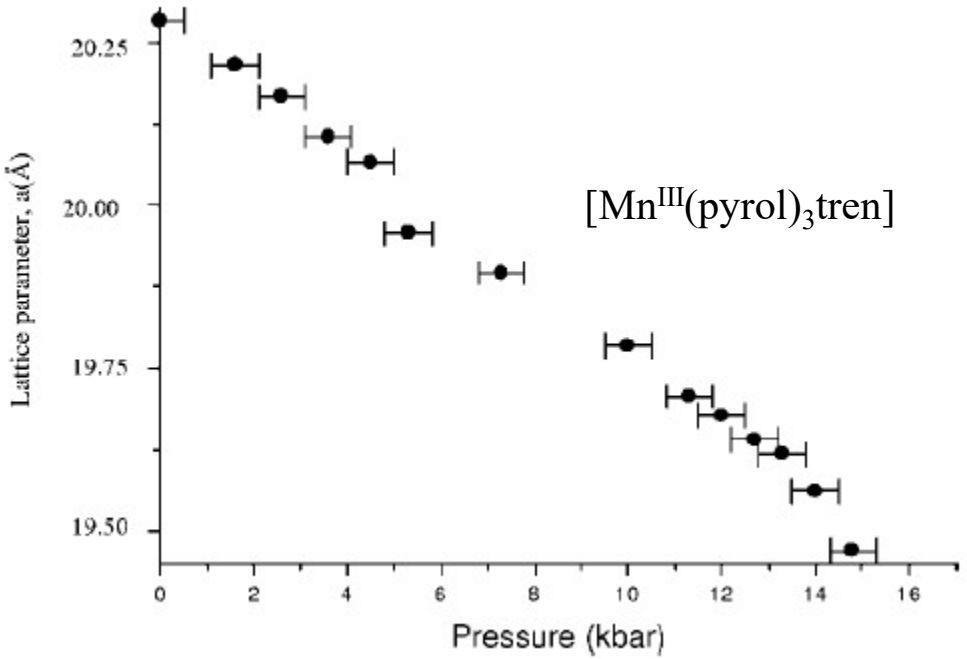


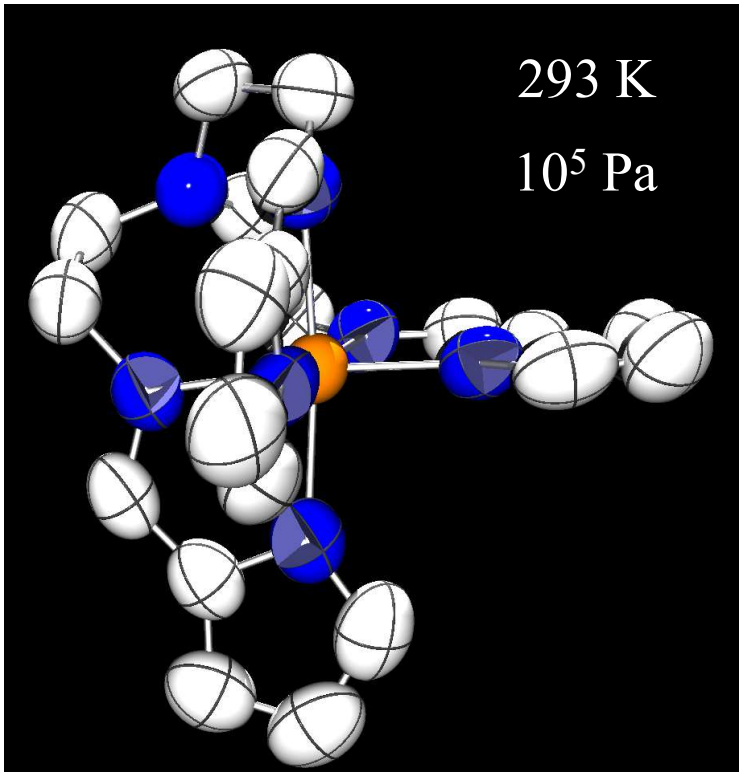






Single crystal diffraction under pressure





P. Guionneau *et al., Phys. Rev*. (2005) **B72**, 214408

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- diffraction geometry, 4 cercles diffractometer, indexing

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Direct methods

Direct determination of the phases of structure factors from structure factor moduli using mathematical and probabilist formulas

- **positivity** of the electron/nuclear density $\rho(\mathbf{r})>0$ (Hauptman & Karle, 1953) : gives a restraint on the set of physically acceptable phases (Hauptman determinant ≥ 0)

- **atomicity** of the electron/nuclear density (Sayre, 1951)

- **symmetry** of the crystal structure (origin)

- **chemical composition** of the unit cell

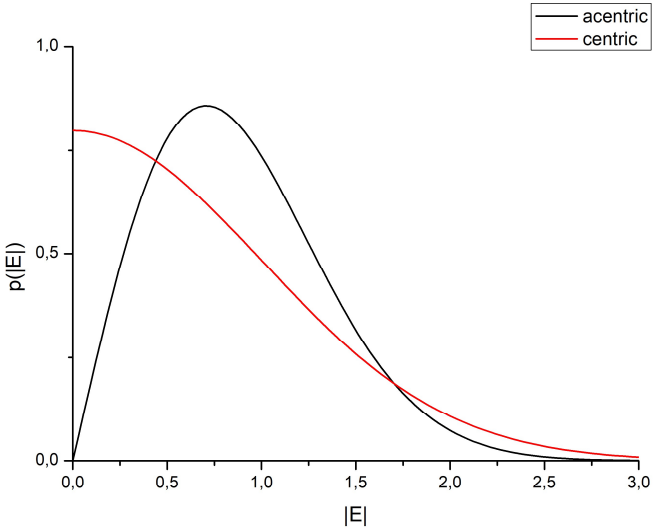
Normalized structure factors : $$E(\vec{Q}) = \sum_{j=1}^{N_{at}} \frac{f_j}{\sqrt{\sum f_j^2}} exp[i\vec{Q}.\vec{r_j}] = \frac{F(\vec{Q})}{\sqrt{\langle F^2(\vec{Q})\rangle_{\substack{resolution \\ slices}}}}$$

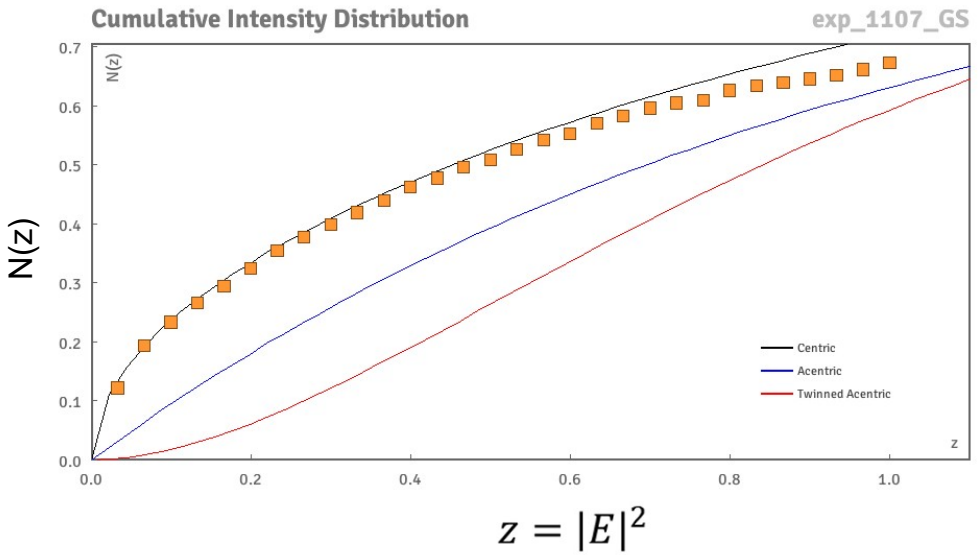
Allows to get rid of thermal smearing, and consider point atoms

Direct methods, detection of inversion center

$$E(\vec{Q}) = \sum_{j=1}^{N_{at}} \frac{f_j}{\sqrt{\sum f_j^2}} exp[i\vec{Q}.\vec{r_j}] = \frac{F(\vec{Q})}{\sqrt{\langle F^2(\vec{Q})\rangle_{\substack{resolution \\ slices}}}}$$

$P(E)$ allows to distinguish a centrosymmetric structure from a non-centrosymmetric one

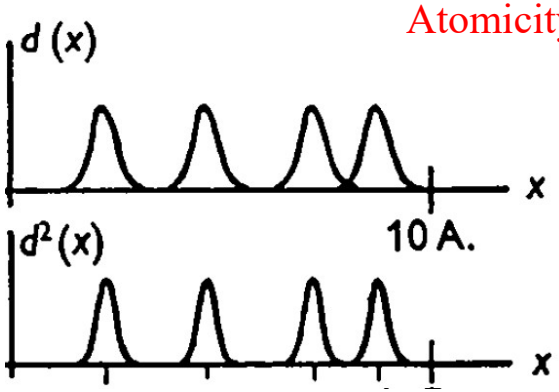




$z = |E|^2$

We can also analyze the various moments of the distribution E : $|E|^2, |E|^3, |E|^4, |E|^5, |E|^6$

Direct methods, Sayre equation



Atomicity hypothesis $\rho(\vec{r}) = \frac{1}{V} \sum_{h,k,l=-\infty}^{+\infty} F(\vec{H}) e^{-2i\pi \vec{H}.\vec{r}}$

$$\rho^2(\vec{r}) = \frac{1}{V} \sum_{h,k,l=-\infty}^{+\infty} G(\vec{H}) e^{-2i\pi \vec{H}.\vec{r}} \propto \rho(\vec{r})$$

Sayre equation : $F(\vec{H}) = \frac{\gamma(\vec{H})}{V} \sum_{\vec{K}} F(\vec{K}) F(\vec{H}-\vec{K})$ self-convolution

$\times F(-\vec{H})$

$$|F(\vec{H})|^2 = \frac{\gamma(\vec{H})}{V} \sum_{\vec{K}} |F(-\vec{H}) F(\vec{K}) F(\vec{H}-\vec{K})| \exp\left[i\left(\varphi(-\vec{H}) + \varphi(\vec{K}) + \varphi(\vec{H}-\vec{K})\right)\right]$$

For strong values of $|F(\vec{H})|$, $|F(\vec{H})|^2$ is also strong, real and positive. It is thus highly probable that the most important terms of the Fourier summation are also real and positive.

Thus if $F(\vec{K})$ and $F(\vec{H}-\vec{K})$ are also high,

$$\varphi(-\vec{H}) + \varphi(\vec{K}) + \varphi(\vec{H}-\vec{K}) \approx 0 \quad \Rightarrow \quad P\left(\varphi(-\vec{H}) \middle| \varphi(\vec{K}), \varphi(\vec{H}-\vec{K})\right)$$

Direct methods, tangent formula

If we rewrite the Sayre equation $F(\vec{H}) = \frac{\gamma(\vec{H})}{V} \sum_{\vec{K}} F(\vec{K}) F(\vec{H} - \vec{K})$

$$|F(\vec{H})| \exp[i\varphi(\vec{H})] = \frac{\gamma(\vec{H})}{V} \sum_{\vec{K}} |F(\vec{K}) F(\vec{H} - \vec{K})| \exp[i(\varphi(\vec{K}) + \varphi(\vec{H} - \vec{K}))]$$

$$|F(\vec{H})| \exp[i\varphi(\vec{H})] = A(\vec{H}) + iB(\vec{H})$$

$$A(\vec{H}) = \frac{\gamma(\vec{H})}{V} \sum_{\vec{K}} |F(\vec{K}) F(\vec{H} - \vec{K})| \cos(\varphi(\vec{K}) + \varphi(\vec{H} - \vec{K}))$$

$$B(\vec{H}) = \frac{\gamma(\vec{H})}{V} \sum_{\vec{K}} |F(\vec{K}) F(\vec{H} - \vec{K})| \sin(\varphi(\vec{K}) + \varphi(\vec{H} - \vec{K}))$$

Tangent formula

$$\tan\varphi(\vec{H}) = \frac{\sum_{\vec{K}} |F(\vec{K}) F(\vec{H} - \vec{K})| \sin(\varphi(\vec{K}) + \varphi(\vec{H} - \vec{K}))}{\sum_{\vec{K}} |F(\vec{K}) F(\vec{H} - \vec{K})| \cos(\varphi(\vec{K}) + \varphi(\vec{H} - \vec{K}))}$$

Direct methods, tangent formula

Tangent formula

$$\tan\varphi\left(\vec{H}\right)=\frac{\sum_{\vec{K}}\left|F\left(\vec{K}\right)F\left(\vec{H}-\vec{K}\right)\right|\sin\left(\varphi\left(\vec{K}\right)+\varphi\left(\vec{H}-\vec{K}\right)\right)}{\sum_{\vec{K}}\left|F\left(\vec{K}\right)F\left(\vec{H}-\vec{K}\right)\right|\cos\left(\varphi\left(\vec{K}\right)+\varphi\left(\vec{H}-\vec{K}\right)\right)}$$

Allows to explore the phase space by correlating phase largely distributed : iterative method of refinement and extension of phases

Direct methods : reciprocal space



Cyclization in dual space

(SnB, SHELXD, SHELXT)

- Phases are refined in reciprocal space
- Direct space imposes a strong atomicity constraint on phases