Structural analysis by single crystal X-ray diffraction

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SOLEIL SYNCHROTRON

UNIVERSITÉ DE LORRAINE

CRM²

cnrs

A crystal

Ordered object

N ~ 10^{18} atoms

A crystal

Symmetric object

Neumann principle **: «** *the symmetry elements of any* ***physical property*** *of a crystal* ***should include all the symmetry elements of the symmetry point group of that crystal*** **»**

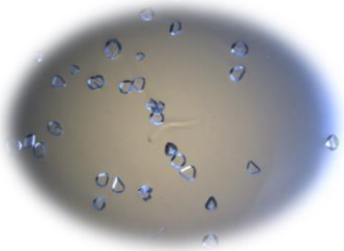
Fundamental Concepts

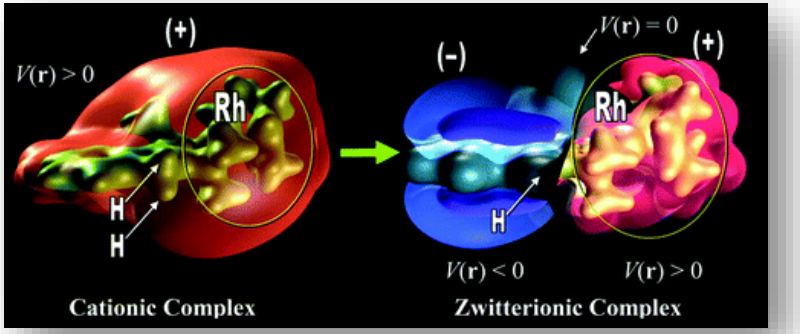
Two pillars of crystallography

1- The symmetry of ideal crystalline structures: a better understanding of crystalline architectures and the consequences for their physical properties

2- The phenomenon of diffraction: the investigative tool of choice for fine, detailed structural analysis of atomic and molecular arrangements in ordered crystalline solids

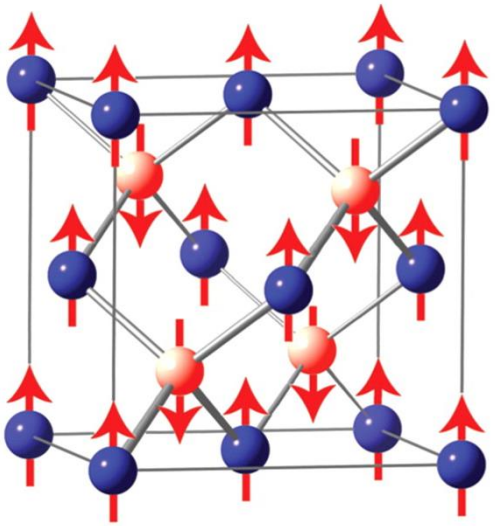
Use of single crystal X-ray diffraction





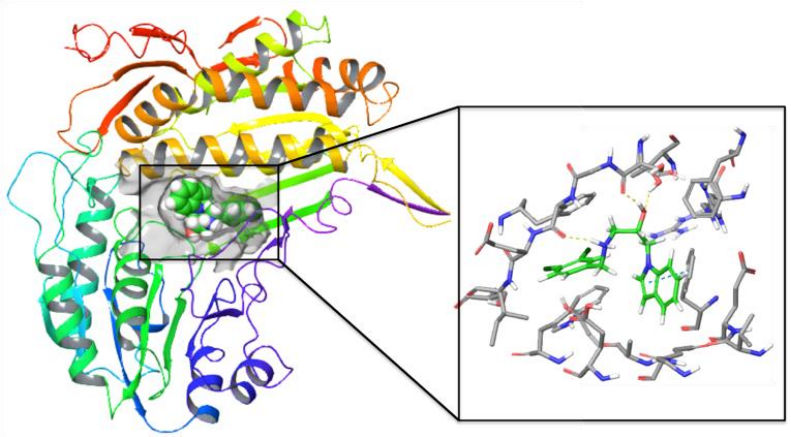
Catalytic

Magnetic

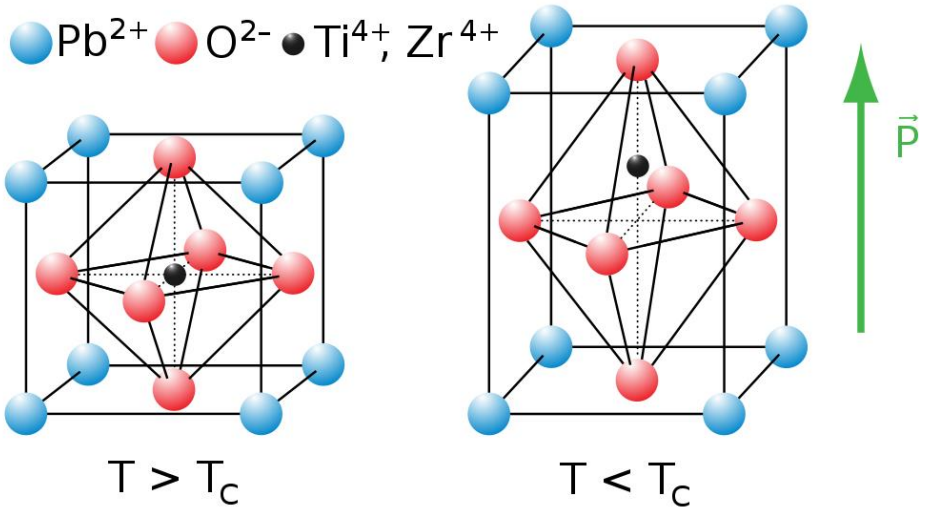


Structure-properties relationship

Biological activity

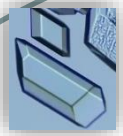


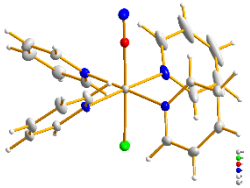
Electrical

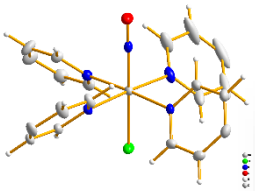


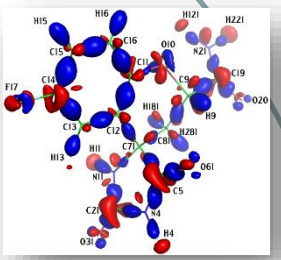
Structure-Properties

Sample



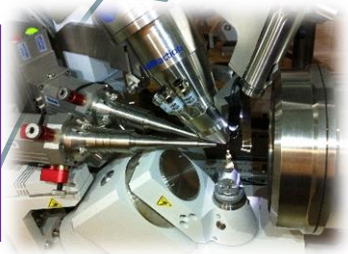




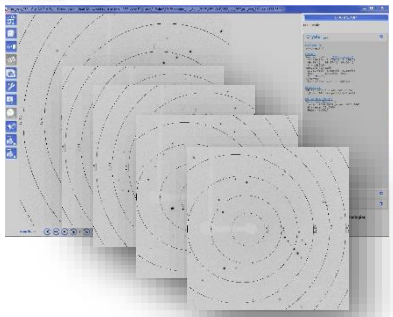


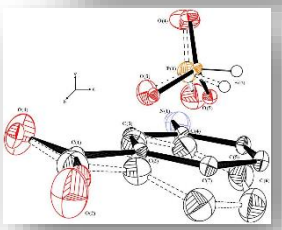
Structural Model

X-ray diffraction experiment



- Data Collection
- Optimal conditions

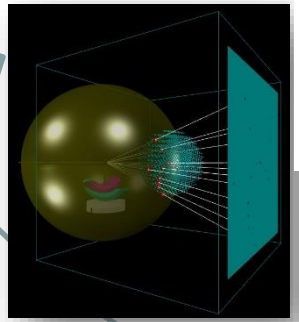


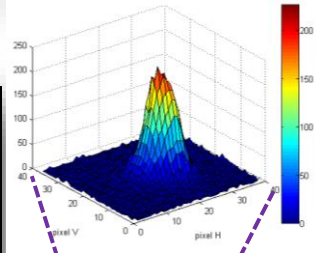


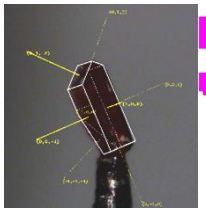
Resolution

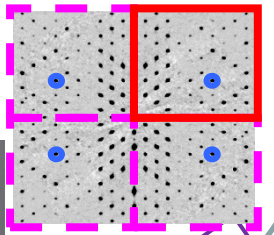
Refinement

Data analysis







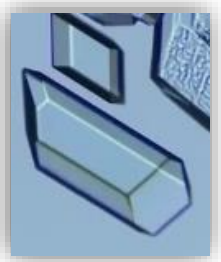


Data reduction

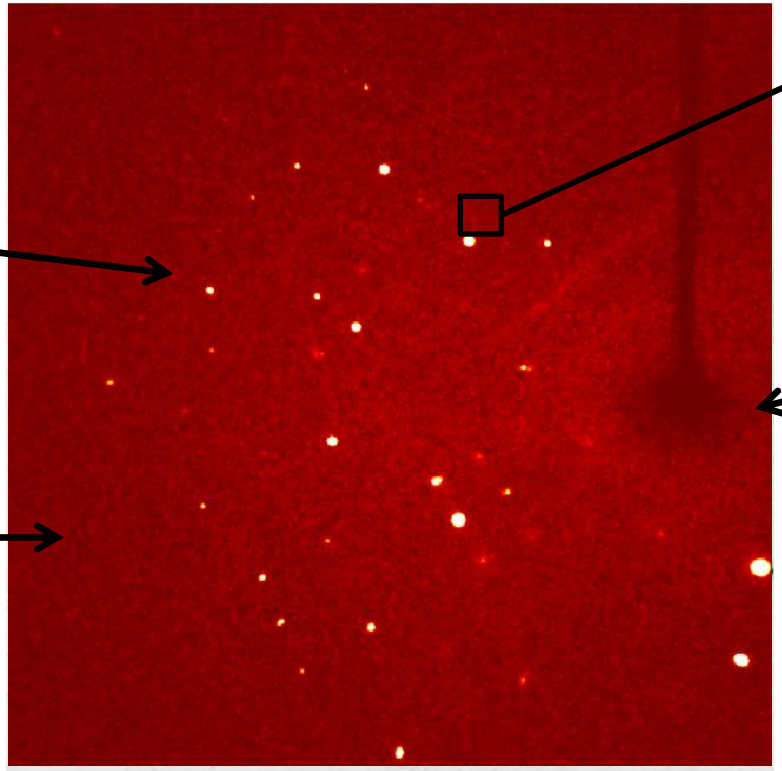
Corrections

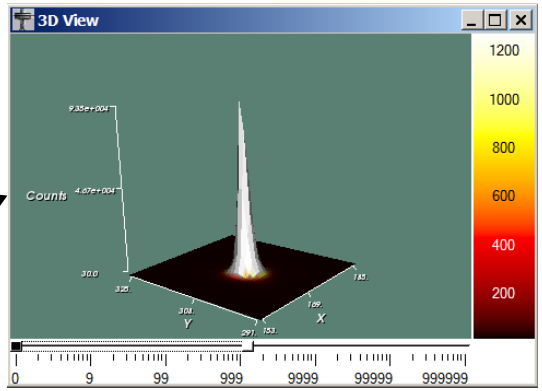
- Indexation
- Integration

Use of single crystal X-ray diffraction



XRD





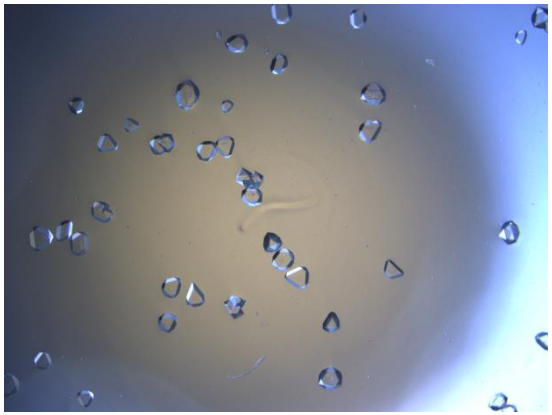
Diffraction peak(*hkl*)

Background noise

Shadow of the beamstop(or well, which masks the direct beam)

Reciprocal space

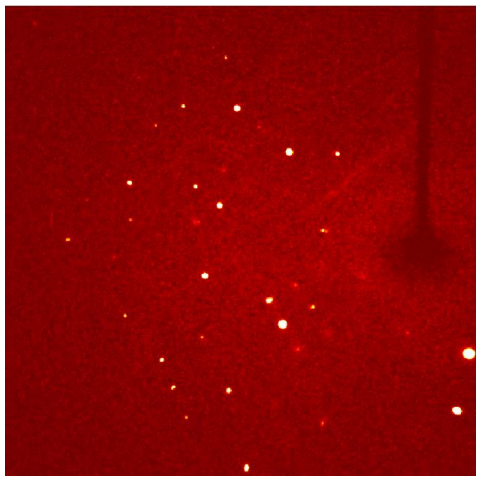
Use of single crystal X-ray diffraction

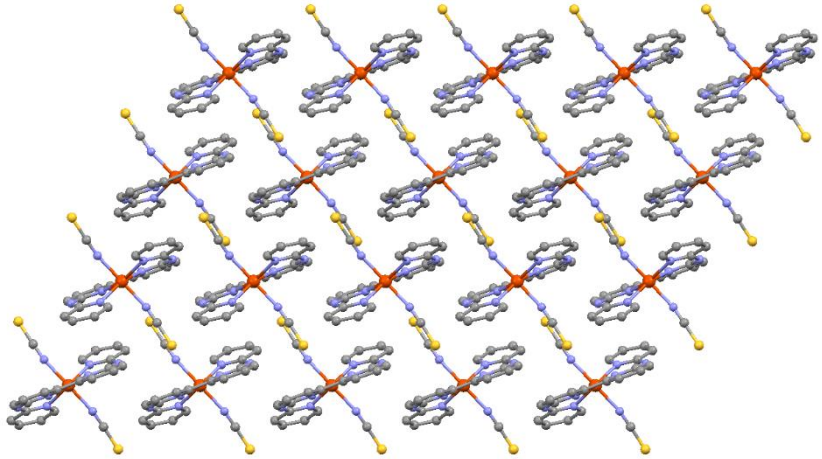


Symmetry
Bond distances
Bond angles
disorder
Thermal smearing

At thermodynamic equilibrium or out of equilibrium

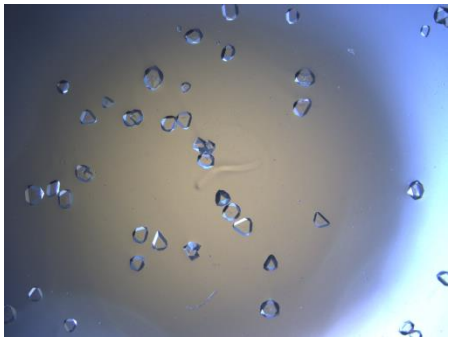
XRD



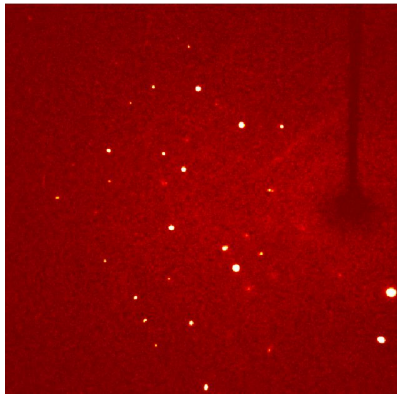


Structural model

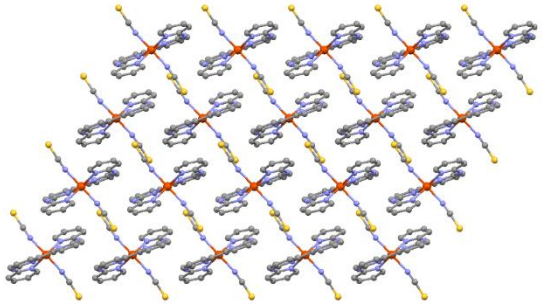
Use of single crystal X-ray diffraction



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



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

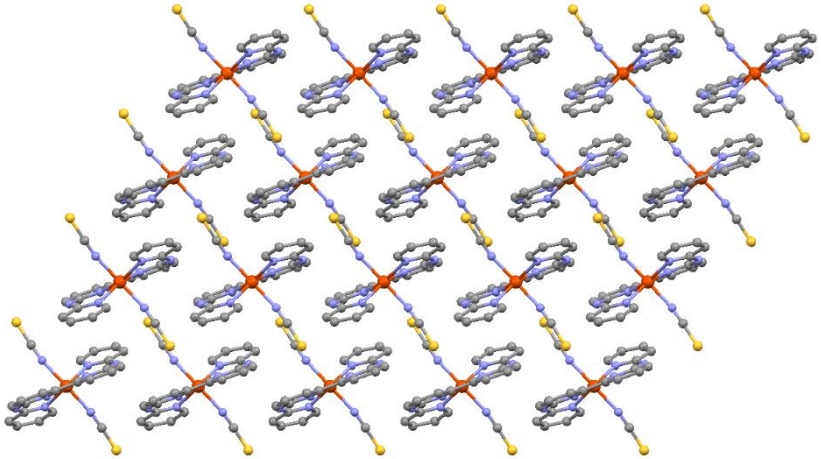


- Chemical composition
- Symmetry (determination of space group)
- Structural organisation
- Studies as a function of T, P, …

A crystal

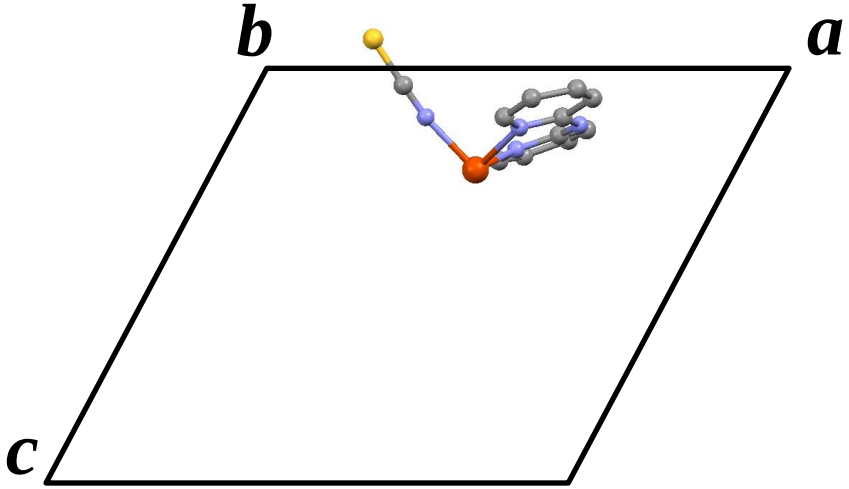
Ordered object

N ~ 10^{18} atoms

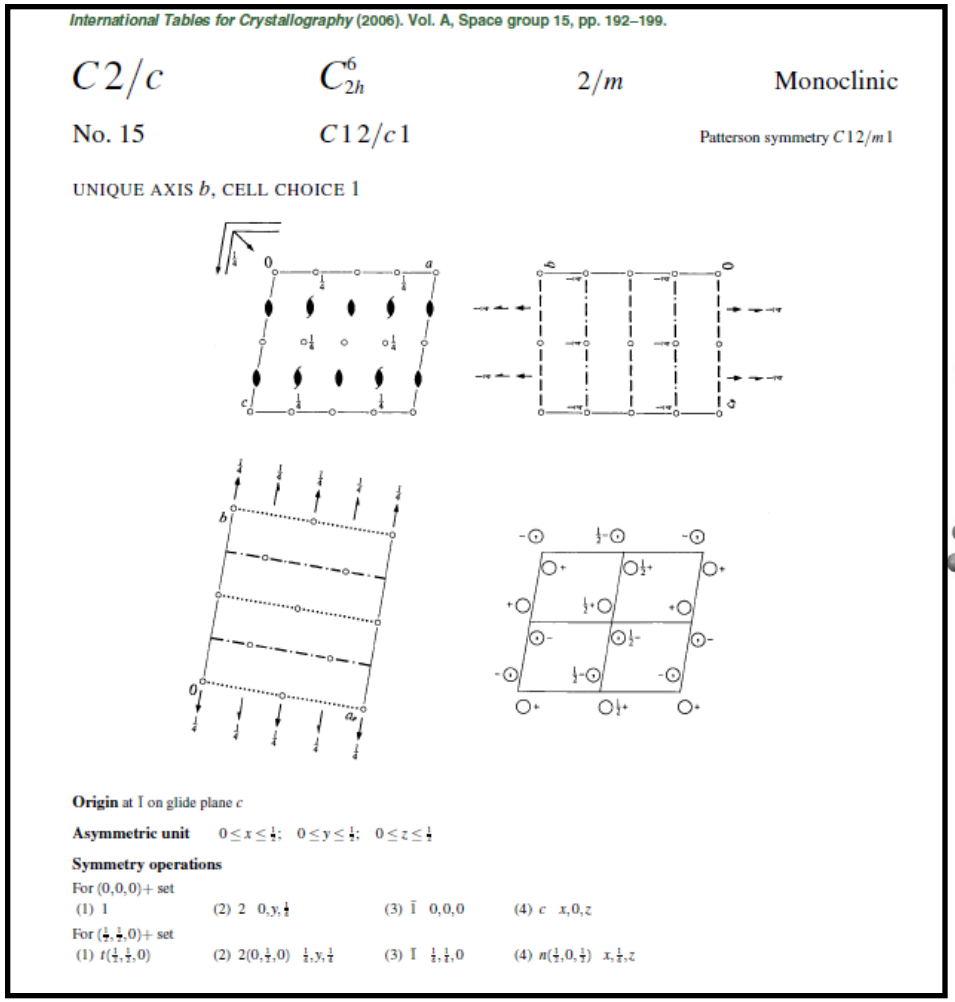


1. Asymmetric unit = motif

Asymmetric unit



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 1 on glide plane c

Asymmetric unit $0 \le x \le \frac{1}{4}$; $0 \le y \le \frac{1}{4}$; $0 \le z \le \frac{1}{2}$

Symmetry operations

For (0,0,0)+ set

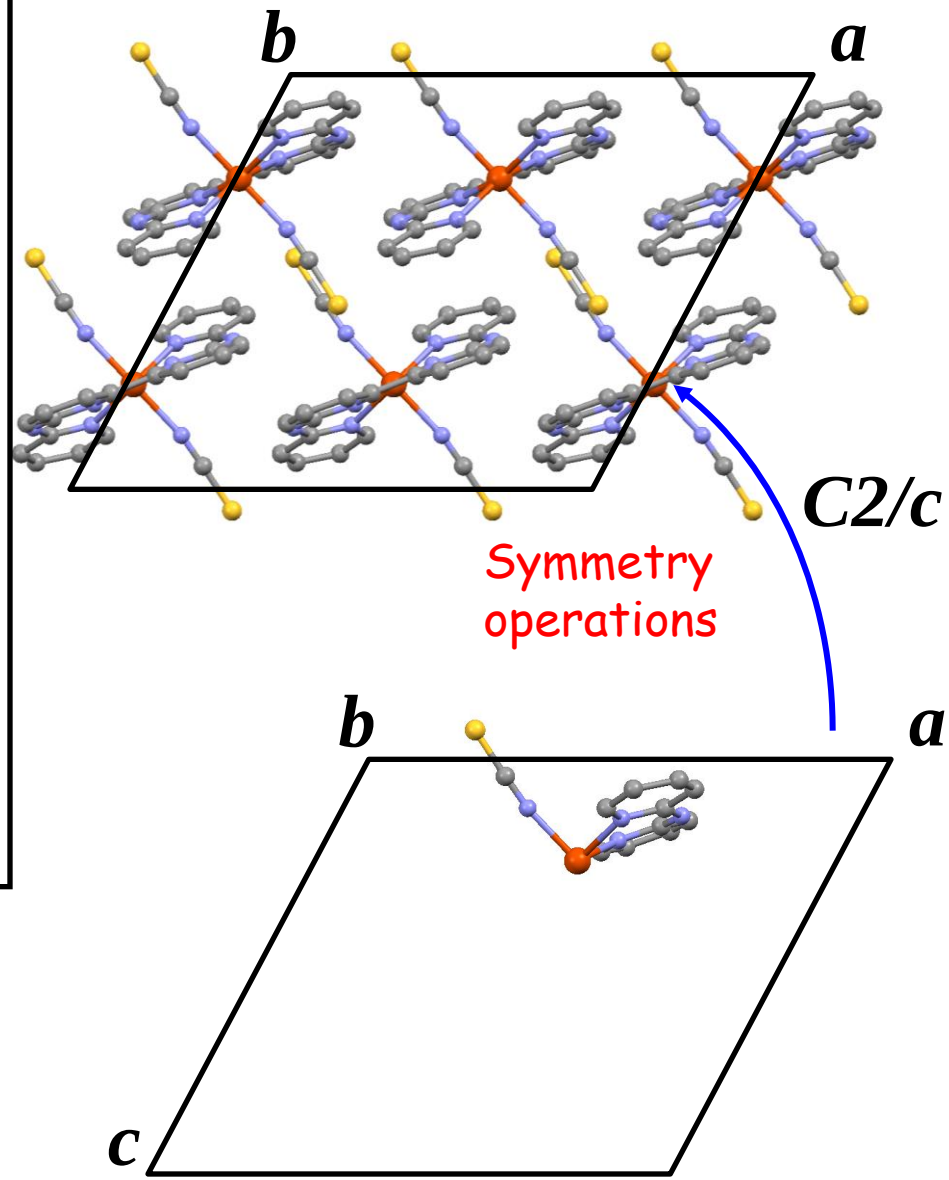
(1) 1 (2) 2 $0,y,\frac{1}{4}$ (3) $\bar{1}$ 0,0,0 (4) c $x,0,z$

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

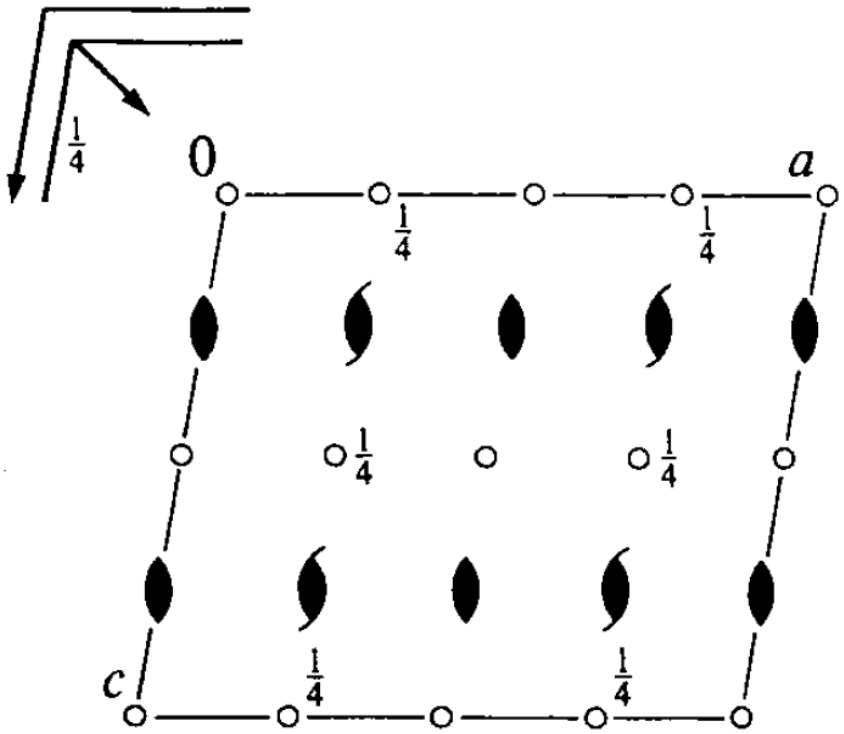
(1) $t(\frac{1}{2},\frac{1}{2},0)$ (2) $2(0,\frac{1}{2},0)$ $\frac{1}{4},y,\frac{1}{4}$ (3) $\bar{1}$ $\frac{1}{2},\frac{1}{2},0$ (4) $n(\frac{1}{2},0,\frac{1}{2})$ $x,\frac{1}{4},z$

1. Asymmetric unit = motif
2. Space group

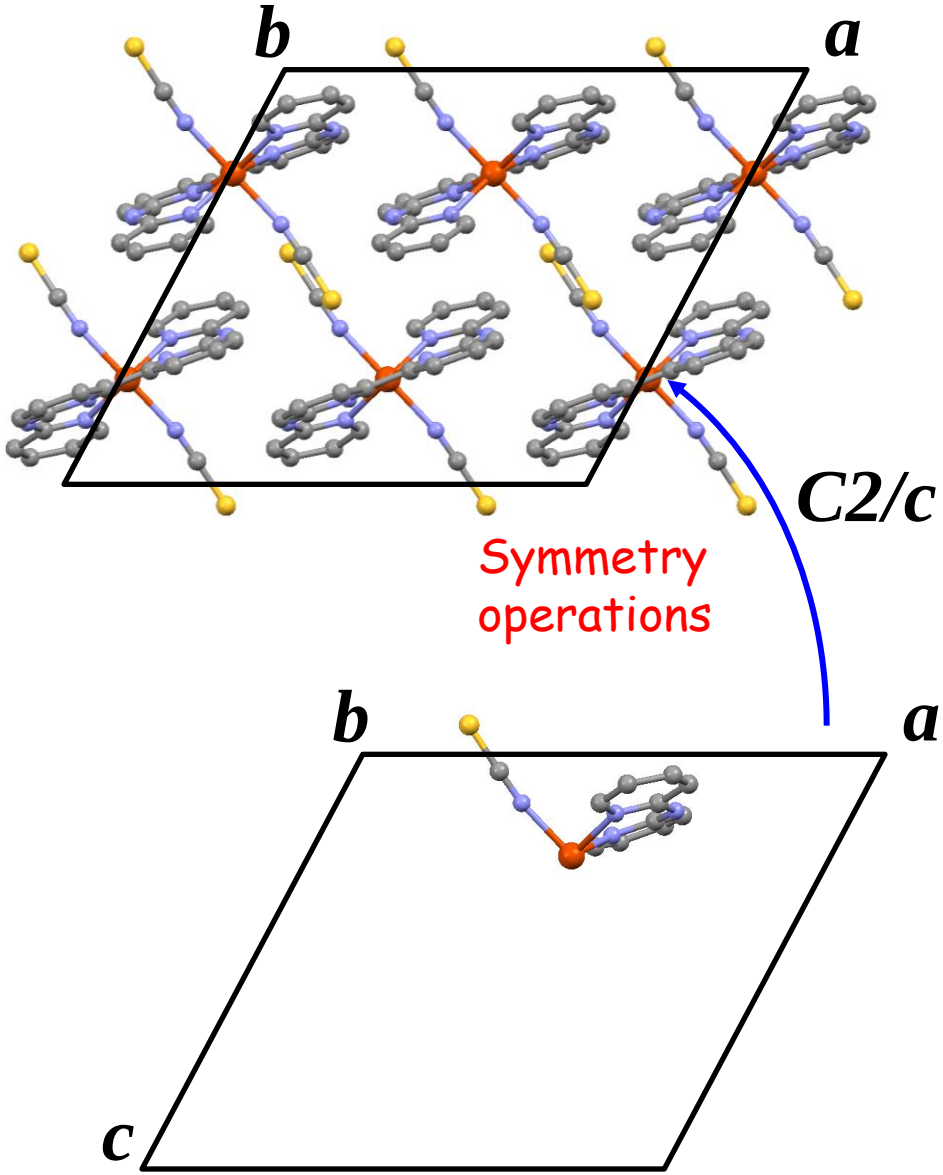
Unit cell



A crystal

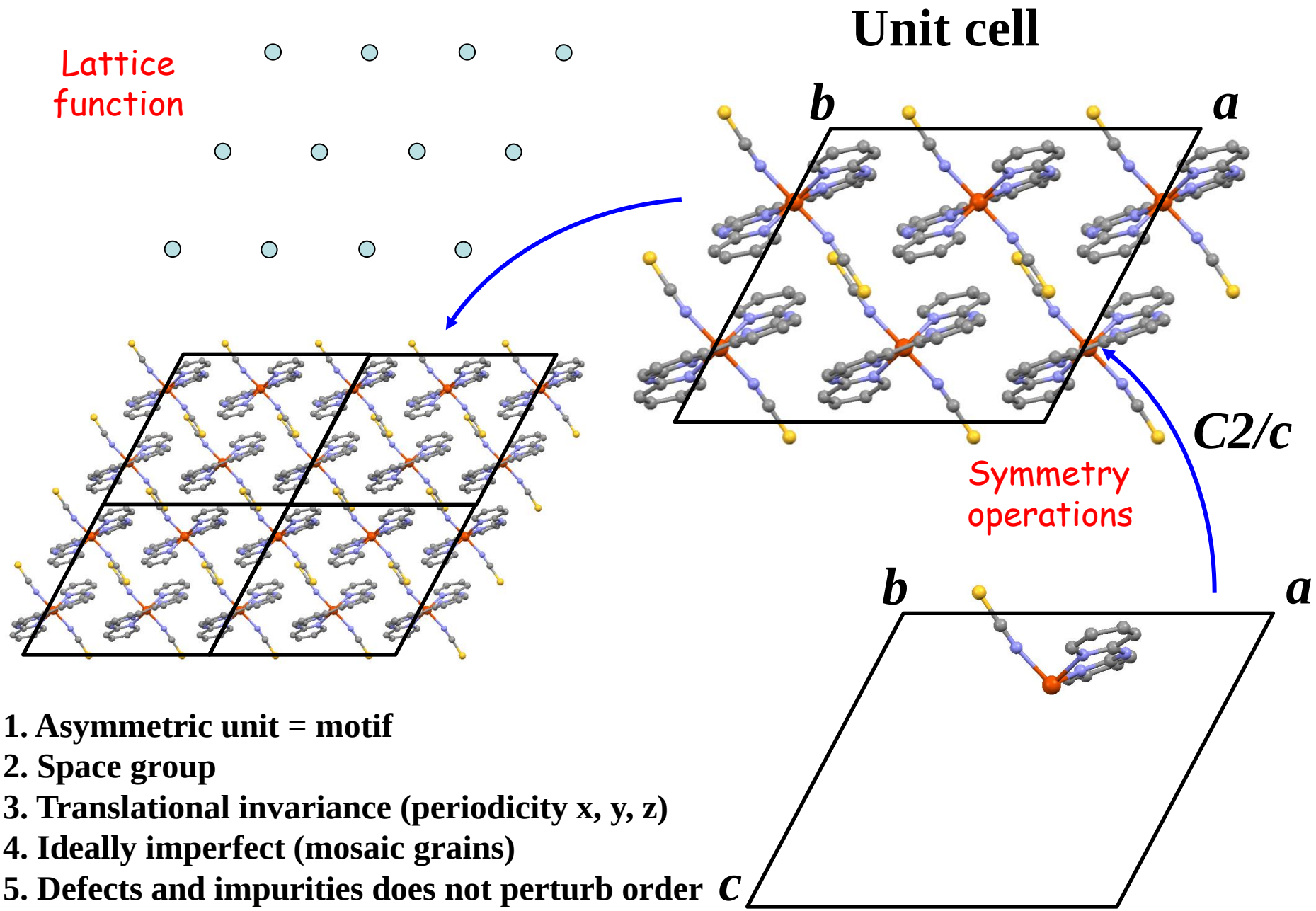


Unit cell



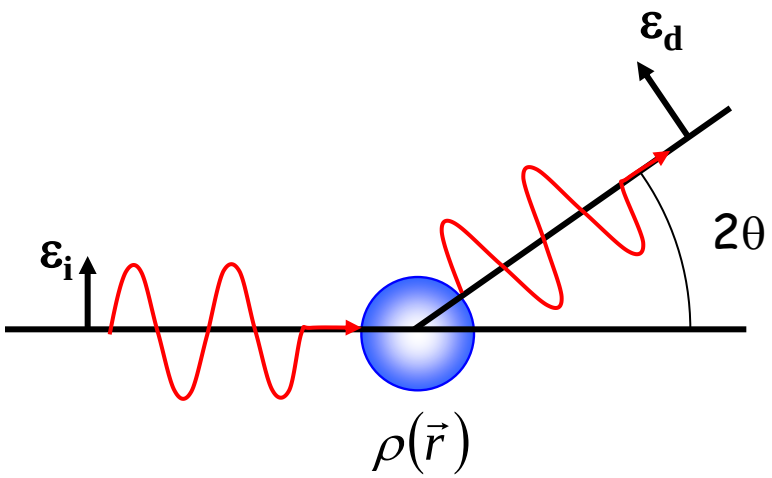
1. Asymmetric unit = motif
2. Space group

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 single crystal x-ray diffraction

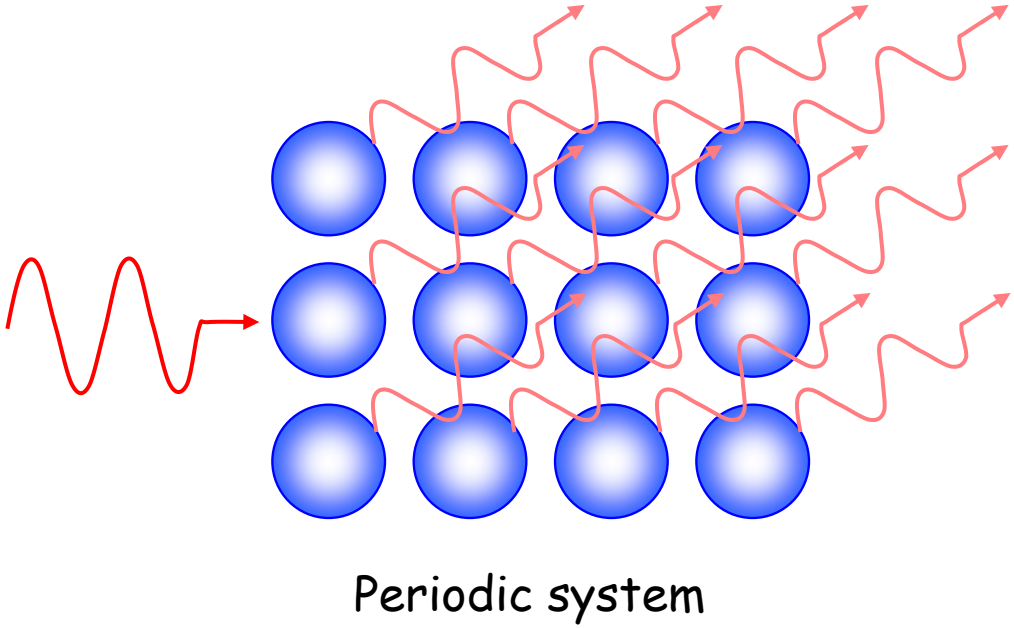


Thomson elastic scattering

Radial process

$$\lambda\,[\text{Å}] = \frac{12.398}{\varepsilon\,[\text{keV}]}$$

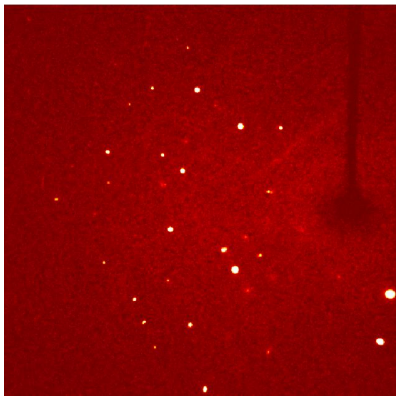
$k_i = k_d\ (\lambda_i = \lambda_d)$



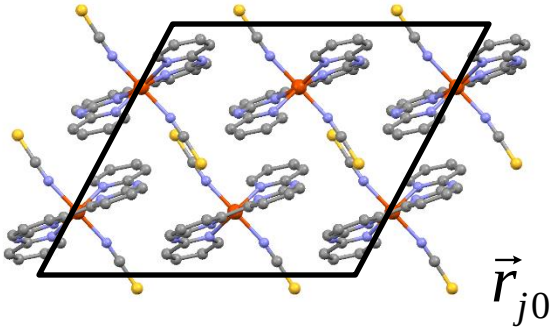
Periodic system

Diffraction

(constructives interferences between scattered waves by all the electrons)



Unit cell structure factor



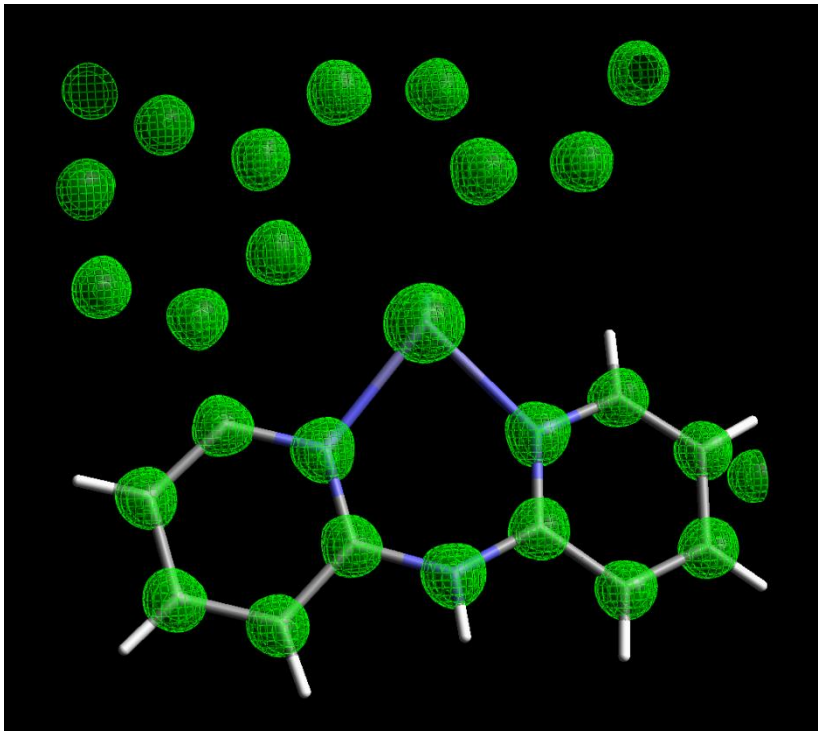
Scattering object: $\rho_{unit\,cell}(\vec{r})$

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

FT

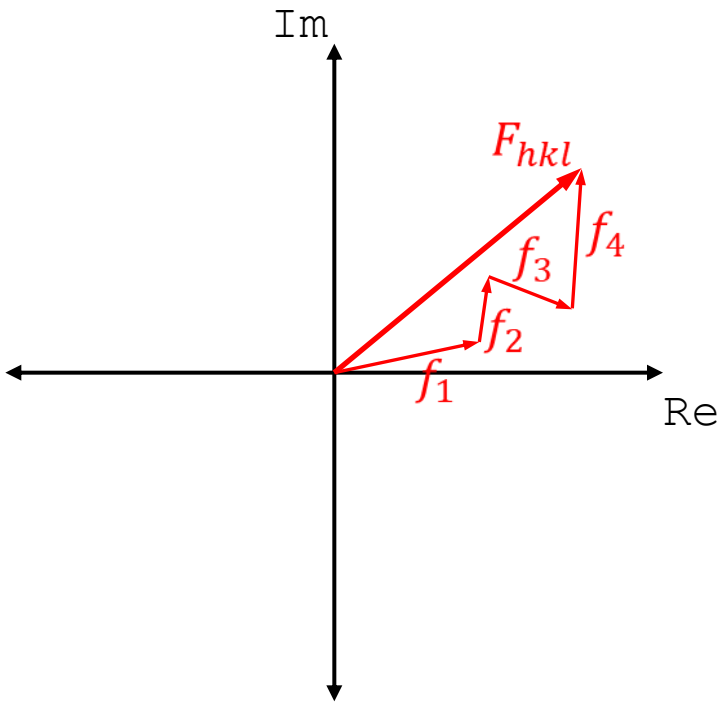
$$F_{unit\,cell}(\vec{H}) = \sum_{j}^{unit\ cell} f_j e^{-2i\pi\vec{H}.\vec{r}_j}$$

f_j : atomic scattering factor

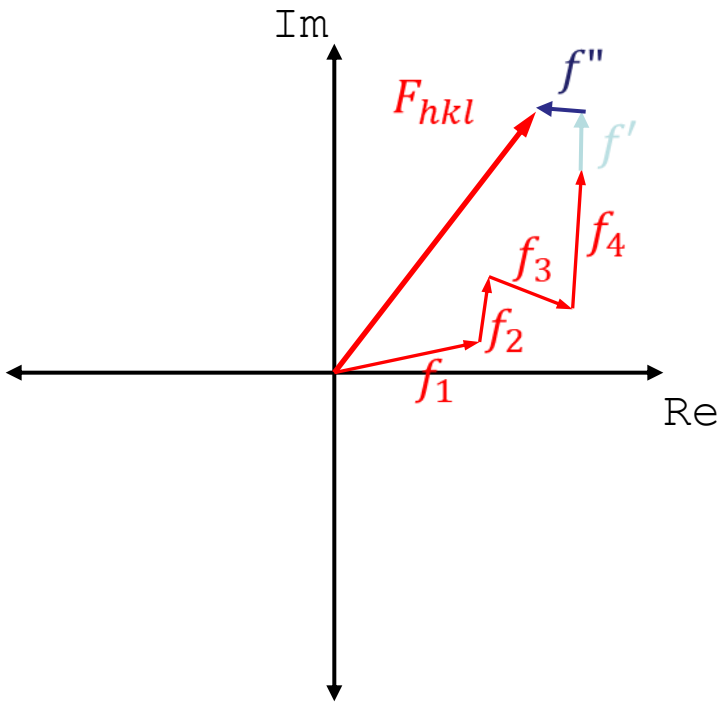


Unit cell structure factor

$$F_{unit\,cell}(\vec{H}) = \sum_{j}^{unit\,cell} f_j e^{-2i\pi \vec{H}.\vec{r}_{j0}} = |F(\vec{H})| e^{i\varphi(\vec{H})}$$

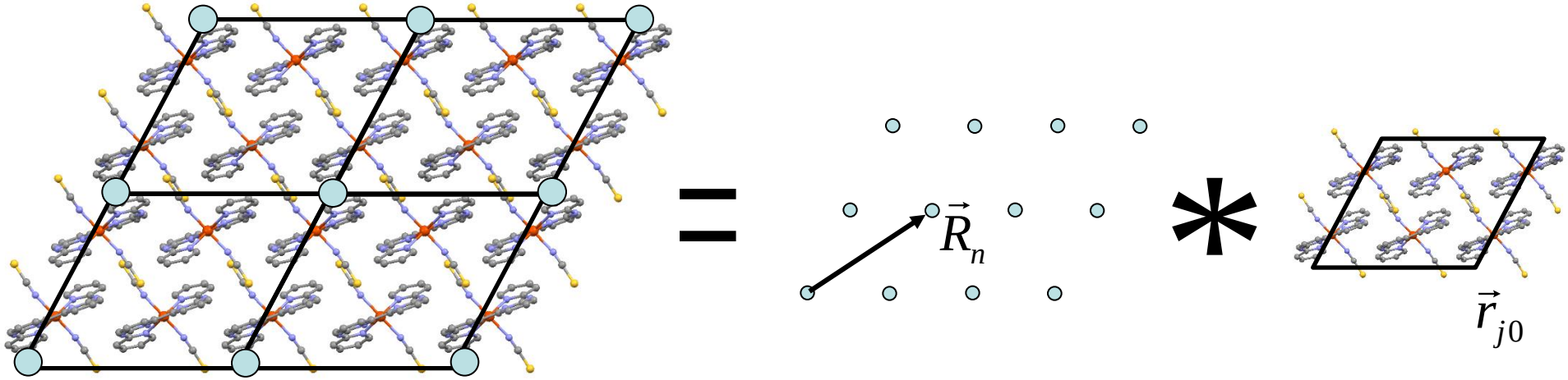


Argand diagram



Accounting for anomalous dispersion

Structure factor and interference function



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

Crystal periodicity

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

FT

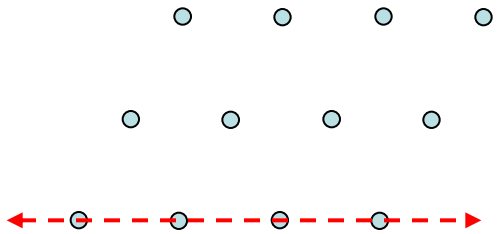
$$F_{crystal}(\vec{H}) = \sum_{n_a}\sum_{n_b}\sum_{n_c}\sum_{j}^{unit\ cell} f_j e^{-2i\pi\vec{H}.\vec{r}_{jn}}$$

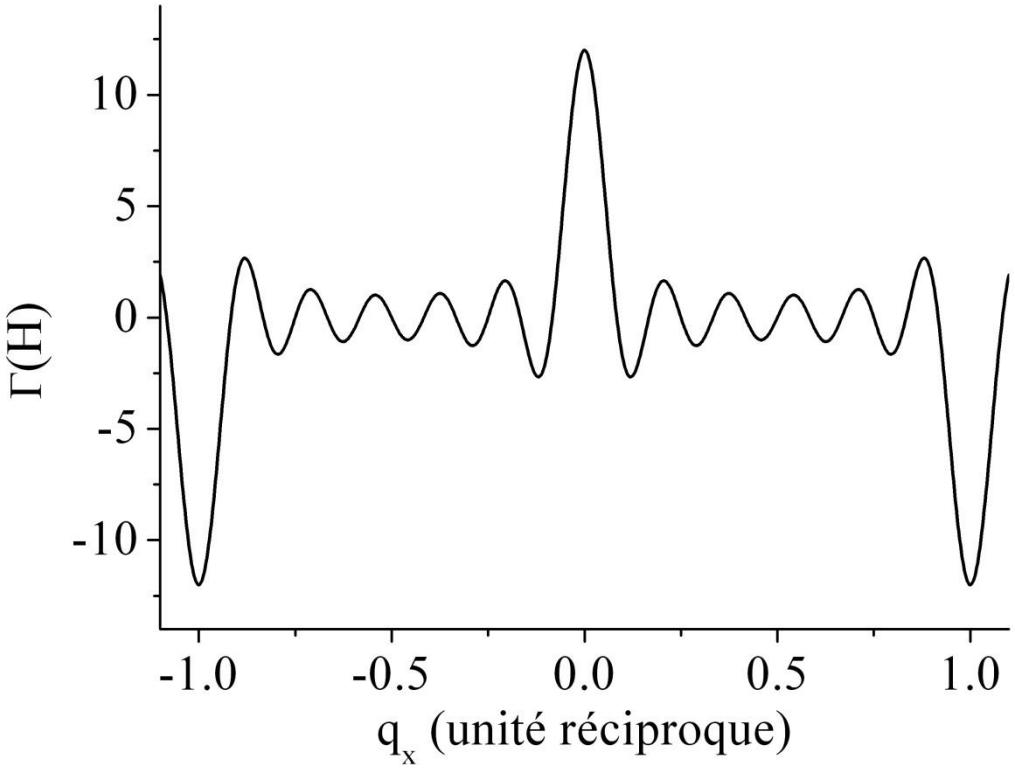
$$= \sum_{n_a}\sum_{n_b}\sum_{n_c} e^{2i\pi\vec{H}.(x_n\vec{a}+y_n\vec{b}+z_n\vec{c})} \sum_{j}^{unit\ cell} f_j e^{-2i\pi\vec{H}.\vec{r}_{j0}} = \Gamma(\vec{H}) \cdot F_{unit\ cell}(\vec{H})$$

Interference function

$$\Gamma(\vec{H}) = \sum_{n_a}\sum_{n_b}\sum_{n_c} e^{2i\pi\vec{H}\cdot\left(x_n\vec{a}+y_n\vec{b}+z_n\vec{c}\right)} = \frac{\sin(\pi n_a q_x)}{\sin(\pi q_x)}\frac{\sin(\pi n_b q_y)}{\sin(\pi q_y)}\frac{\sin(\pi n_c q_z)}{\sin(\pi q_z)}$$

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





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

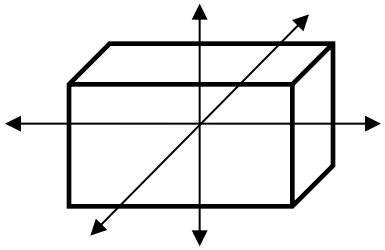
Finite size effects

Influence of finite size on the scattering process :

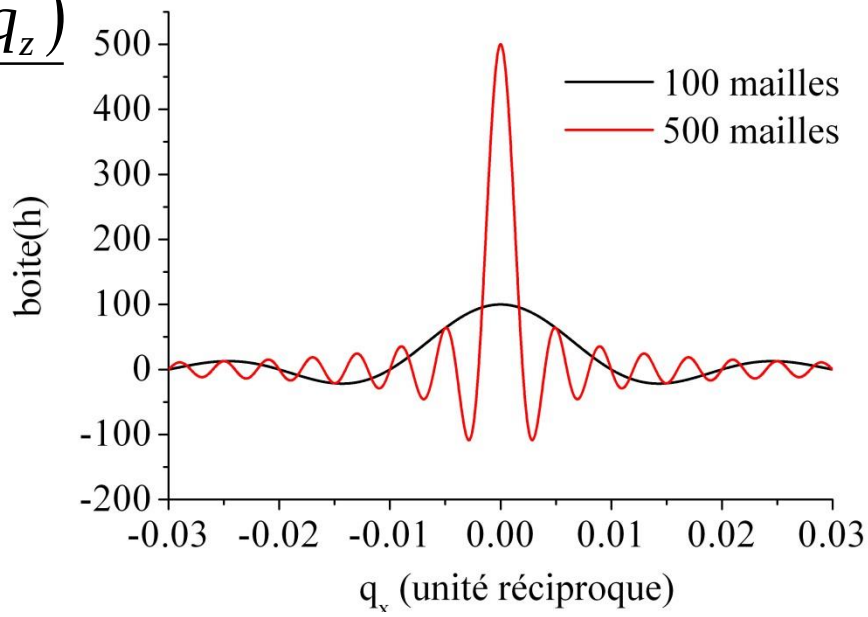
$$\rho_{crystal}(\vec{r}) = \rho_{crystal\,\infty}(\vec{r}) \cdot [boite(\vec{r})] = \left[\sum_{u,v,w=-\infty}^{+\infty} \delta(\vec{r} - \vec{r}_{u,v,w})\right] * \left[\sum_{unit\ cell} \rho_{atomic}(\vec{r})\right] \cdot [boite(\vec{r})]$$

FT

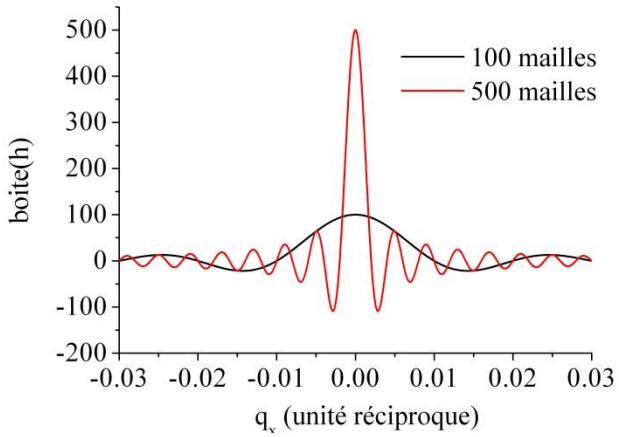
$$F_{crystal}(\vec{H}) = \Gamma(\vec{H}) \cdot F_{unit\,cell}(\vec{H}) * B(\vec{H})$$



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

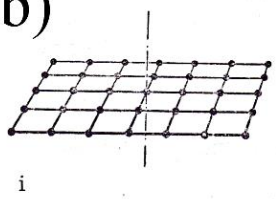


Reciprocal lattice associated to a single crystal

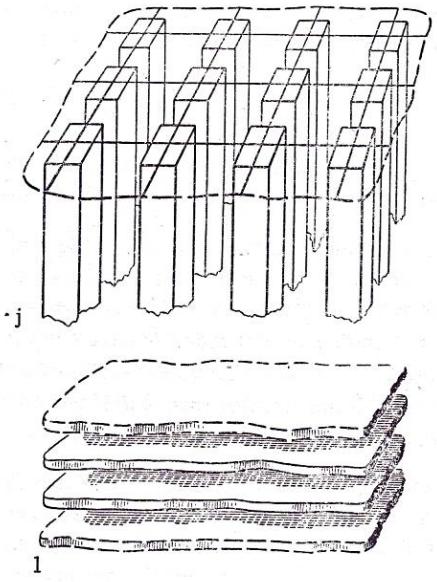


R R*

(b)

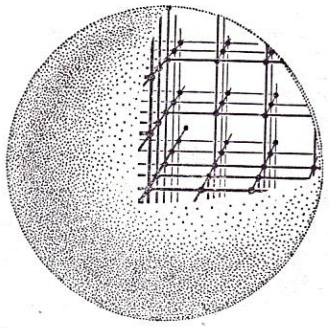


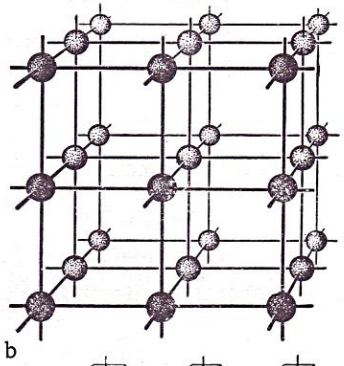
(a)



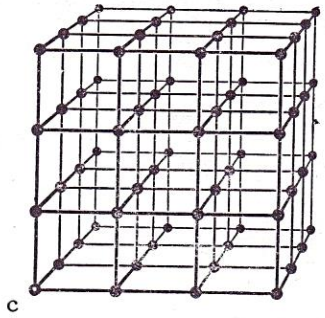
R R*

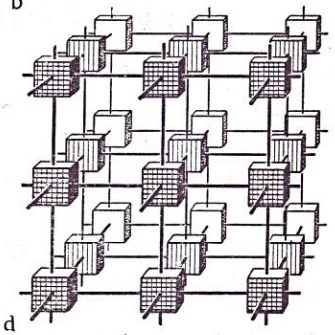
(c)



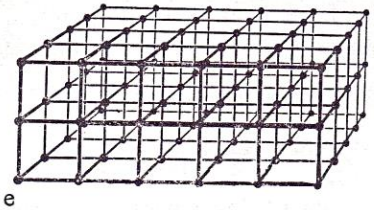


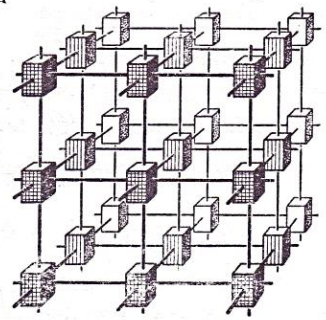
(d)





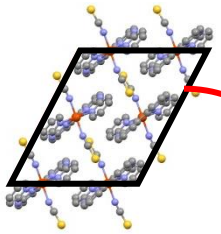
(e)

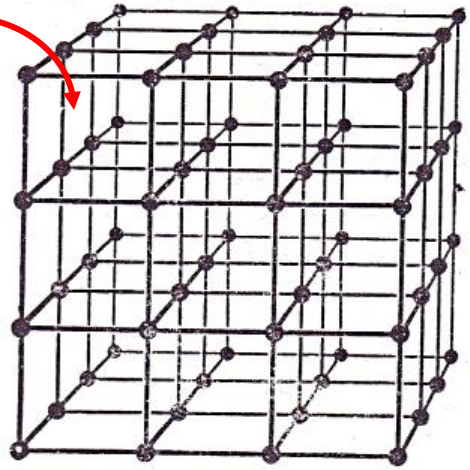


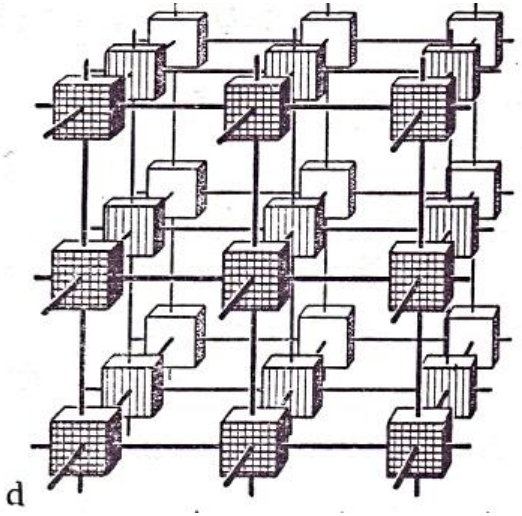


Principle of a single crystal diffraction experiment

$$F_{crystal}(\vec{H}) = \Gamma(\vec{H}) \cdot F_{unit\,cell}(\vec{H})$$



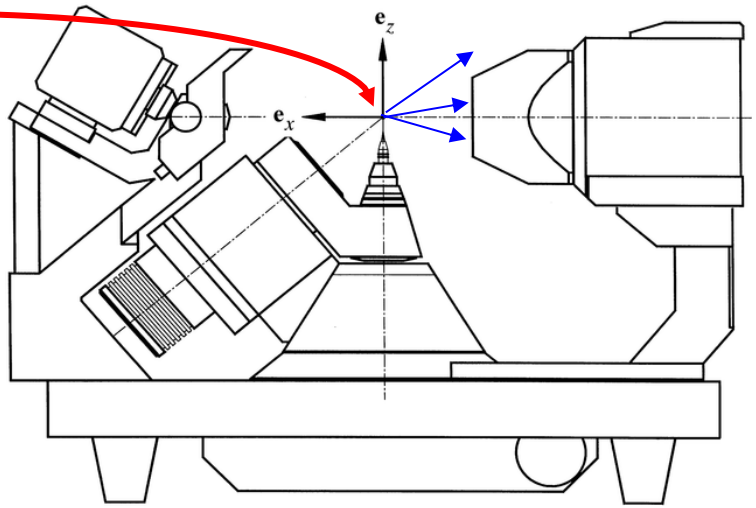


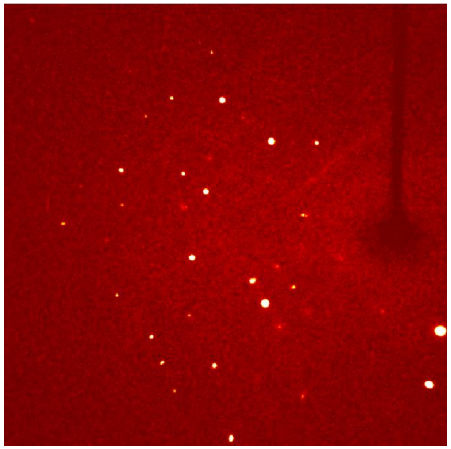


Peak positions
=
Unit cell parameters

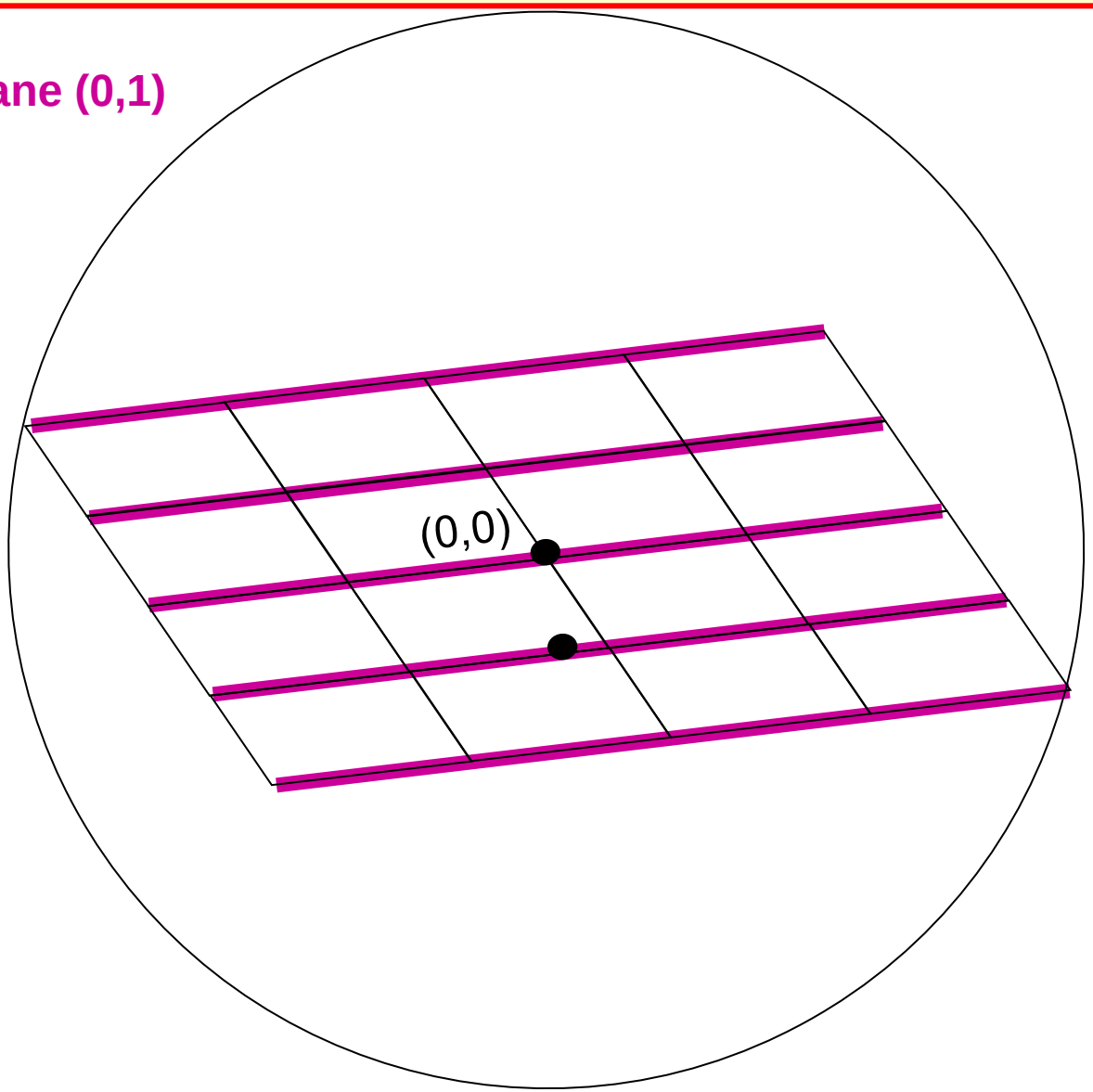
Peak intensity
=
Unit cell content

Peak shape
=
Microstructure

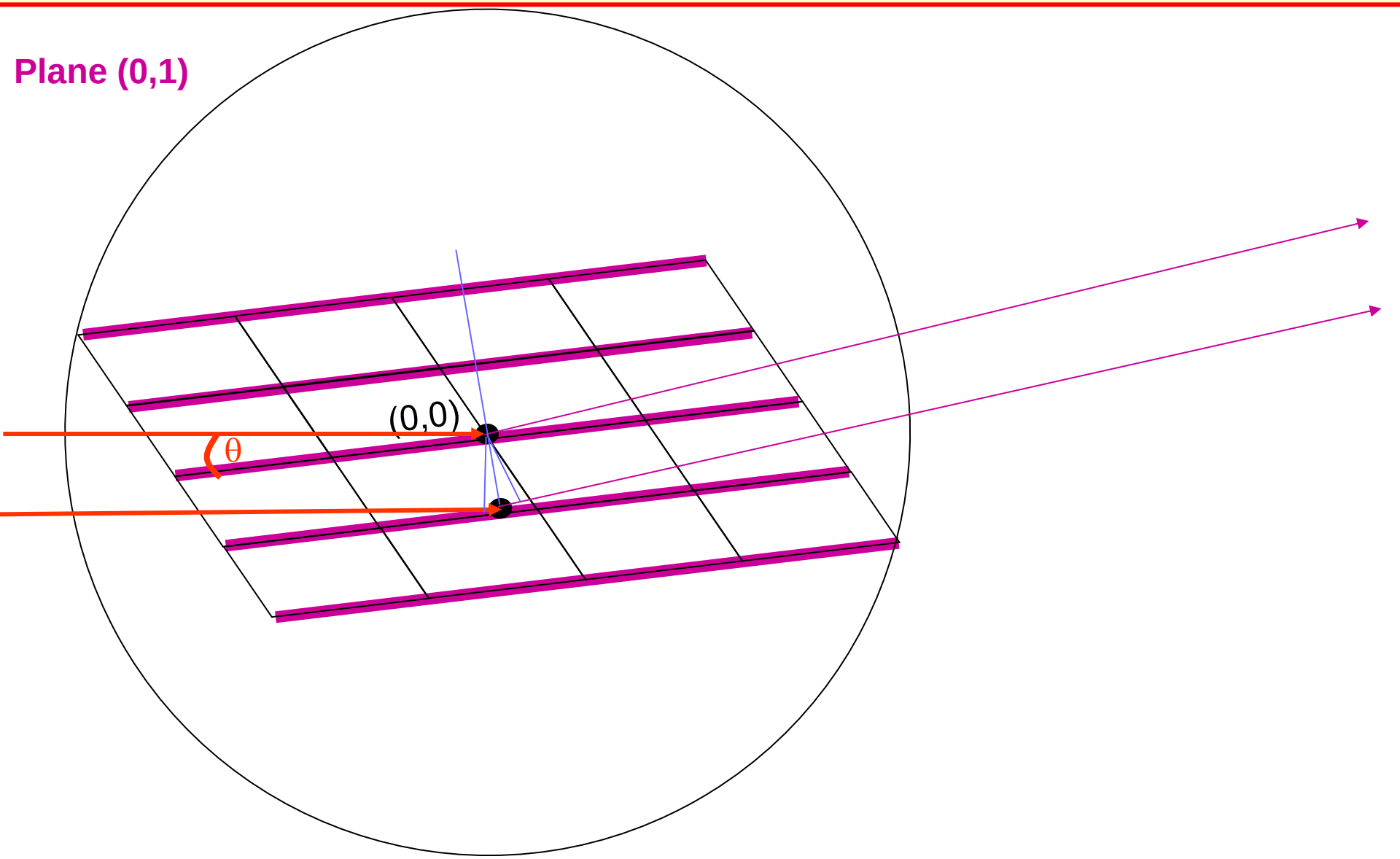




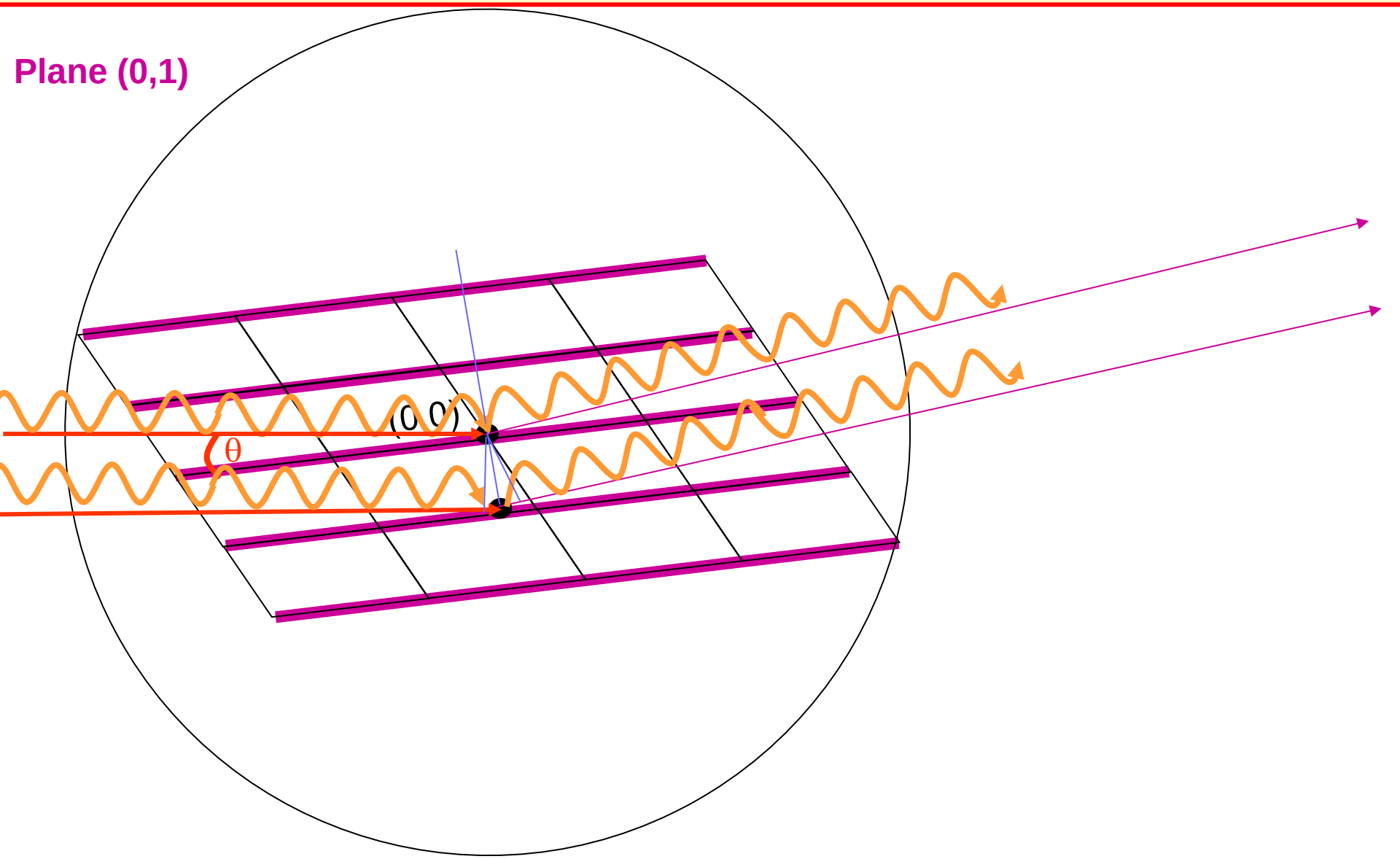
Geometry of diffraction, Bragg condition



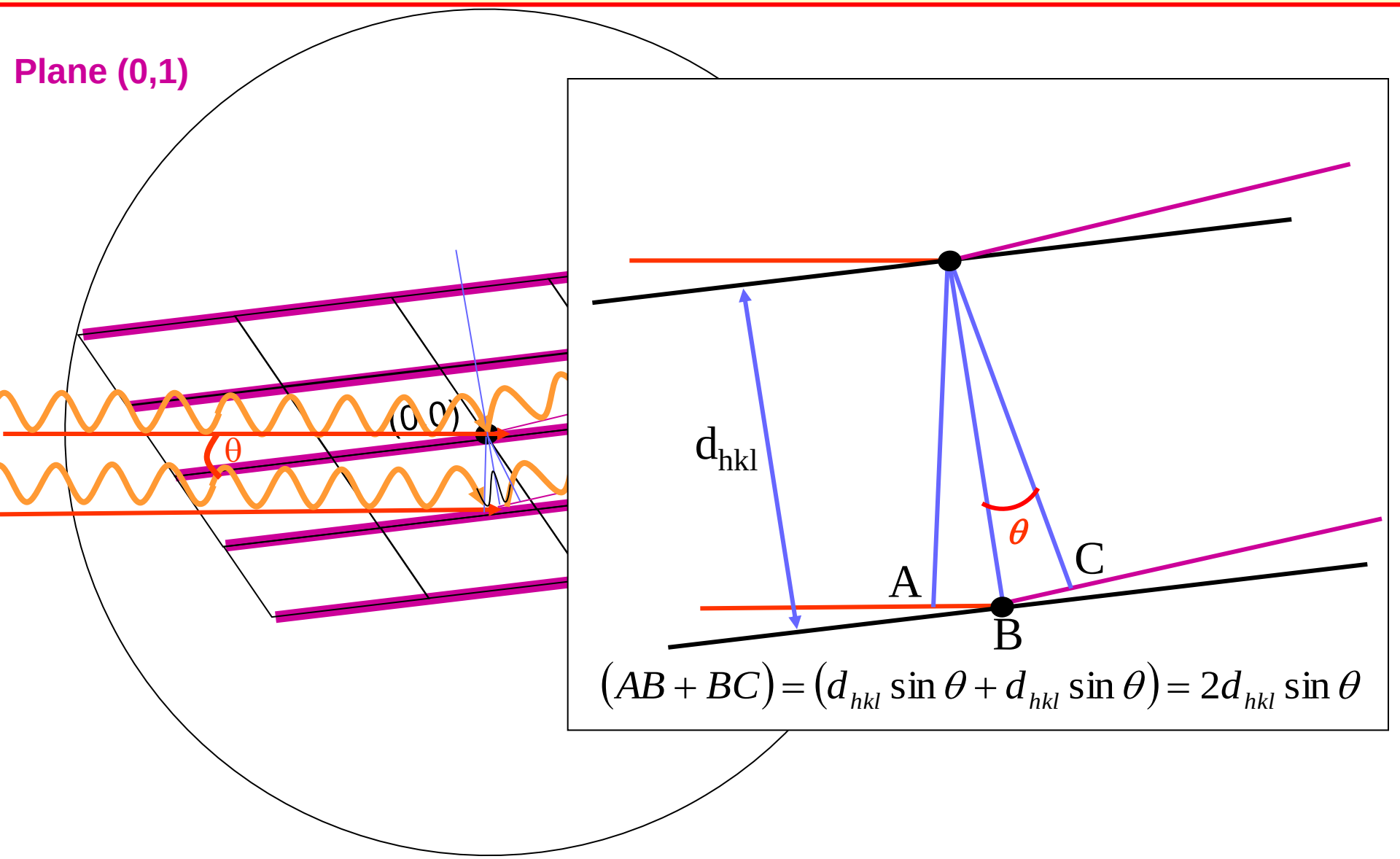
Geometry of diffraction, Bragg condition



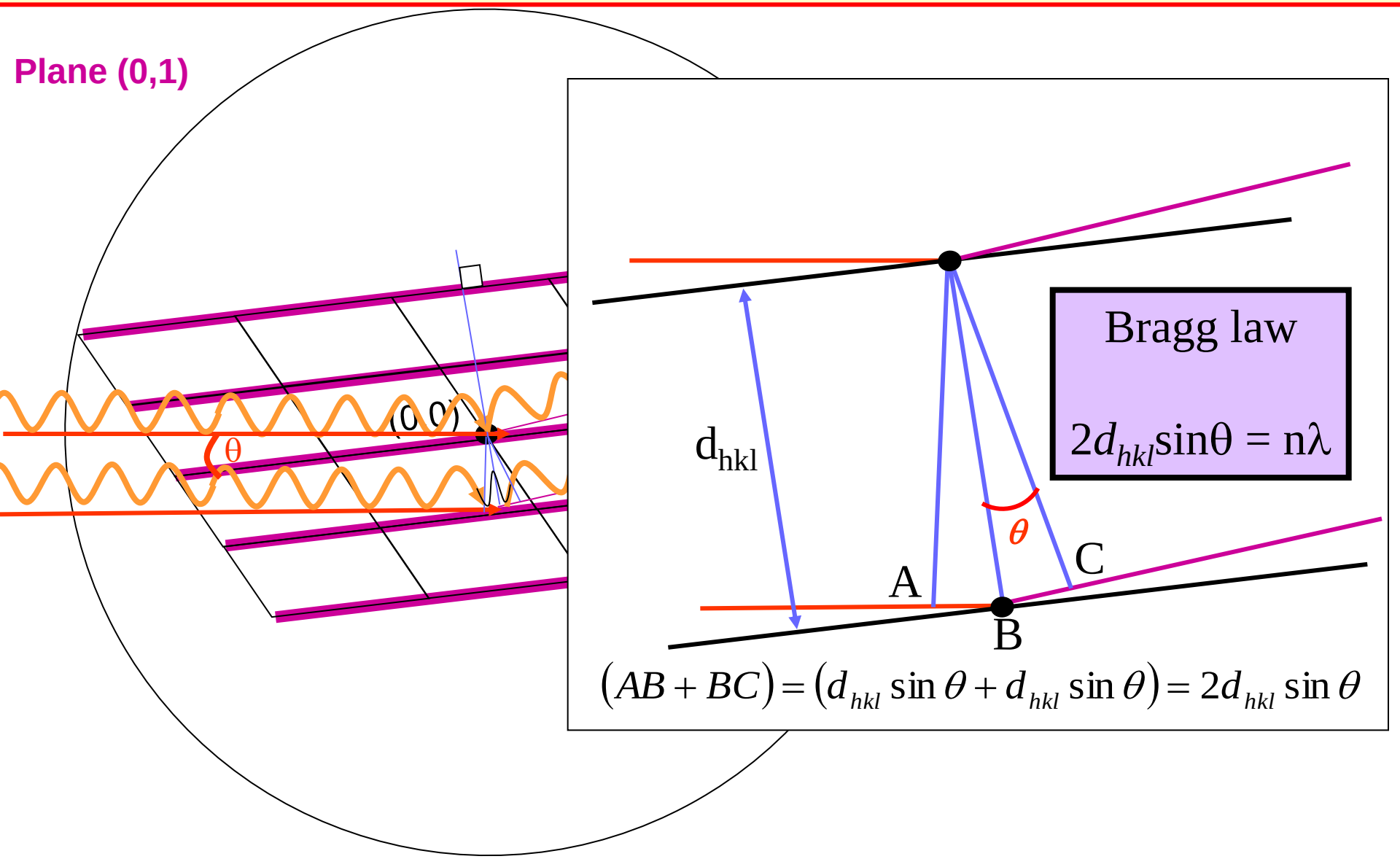
Geometry of diffraction, Bragg condition



Geometry of diffraction, Bragg condition

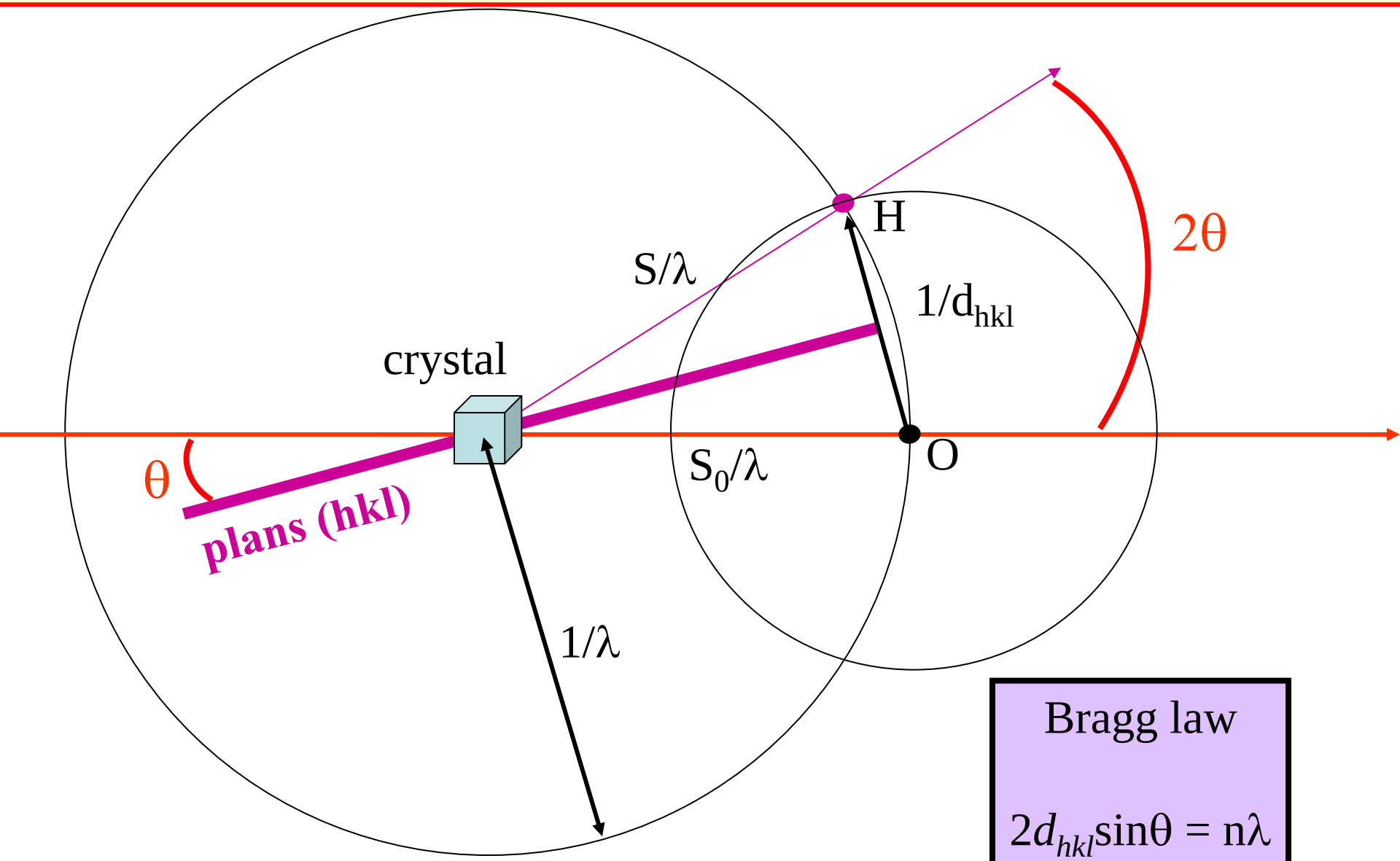


Geometry of diffraction, Bragg condition



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

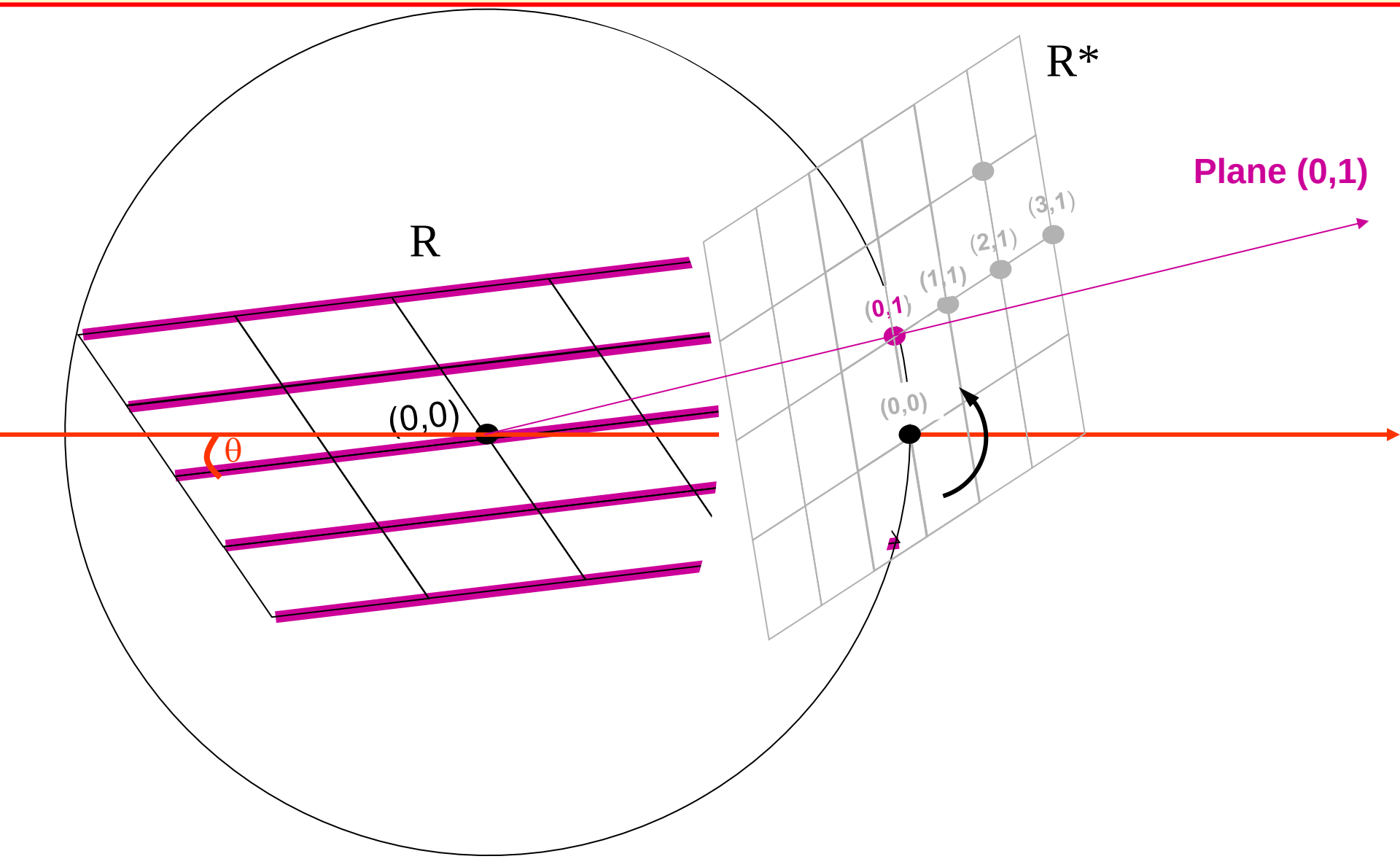
Geometry of diffraction, Ewald construction



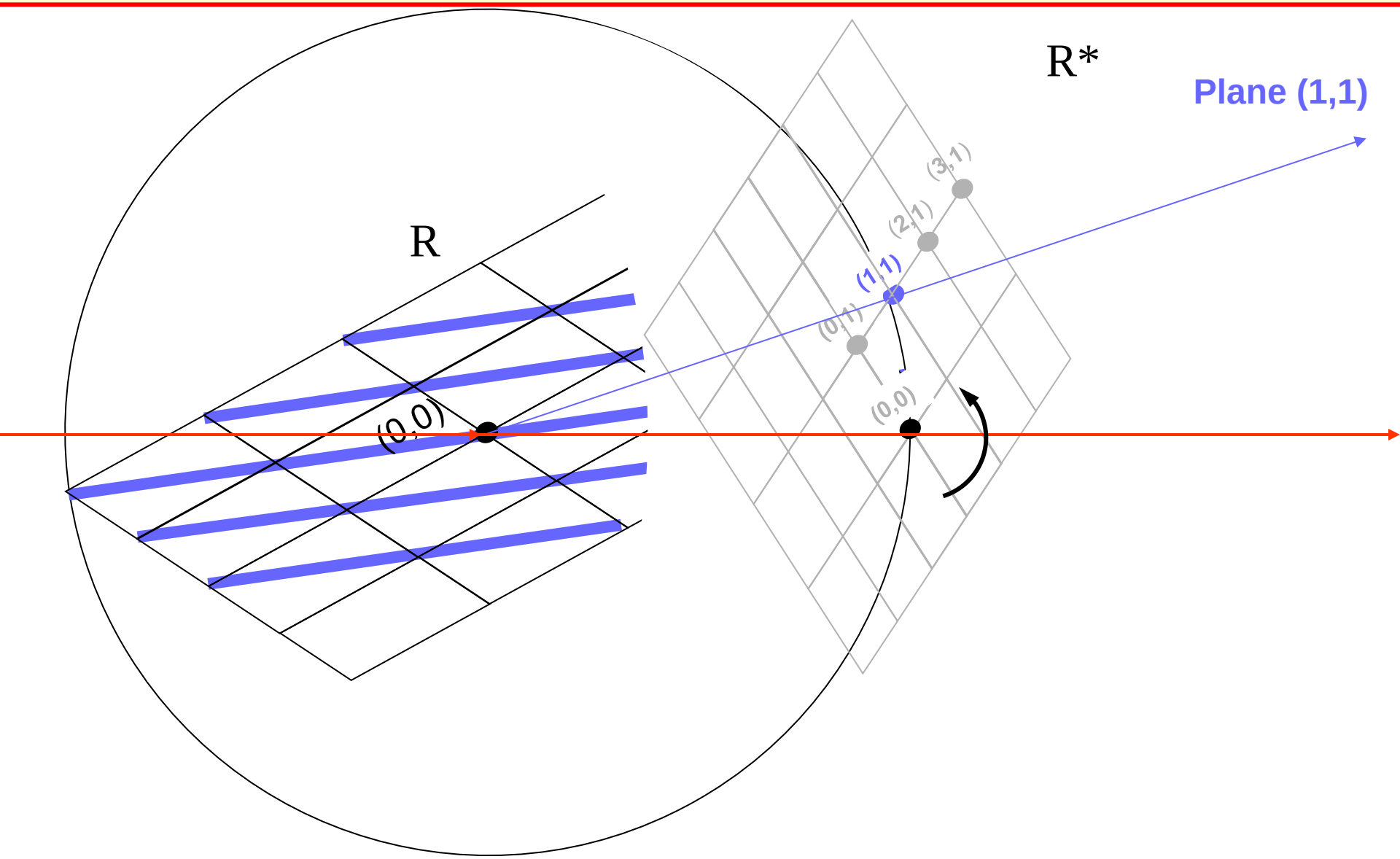
Bragg law

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

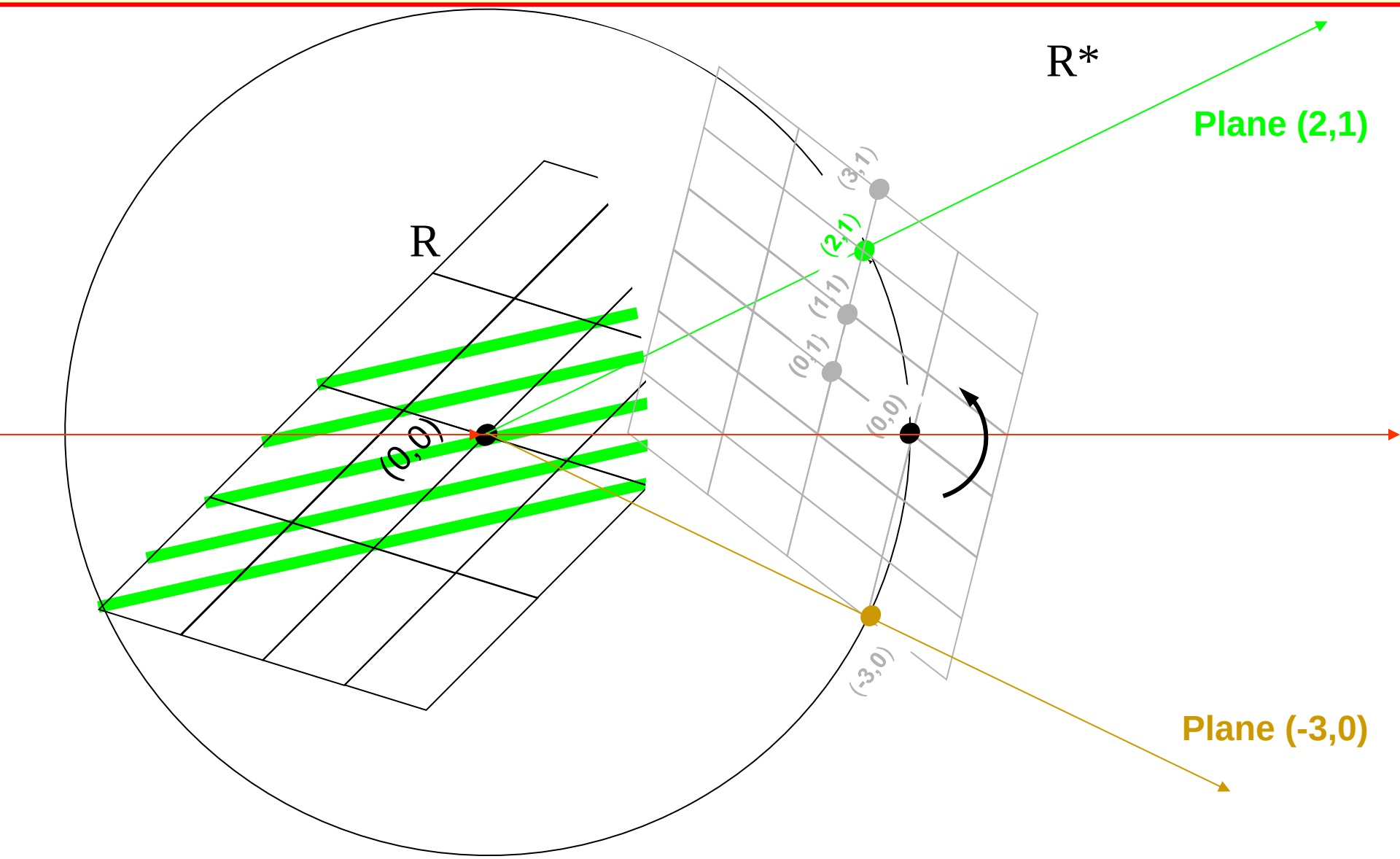
Geometry of diffraction, Ewald construction



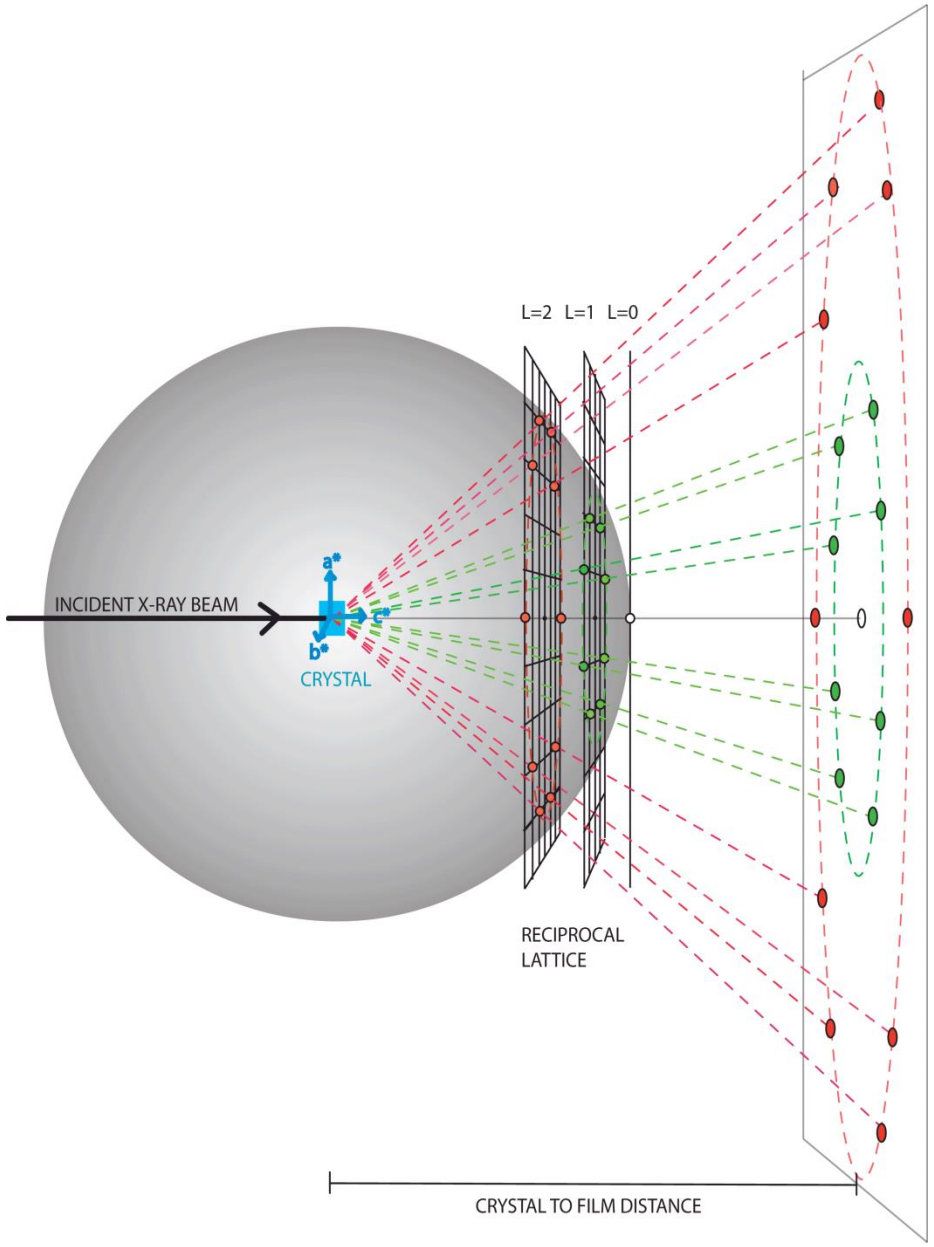
Geometry of diffraction, Ewald construction



Geometry of diffraction, Ewald construction



Collecting diffraction frames



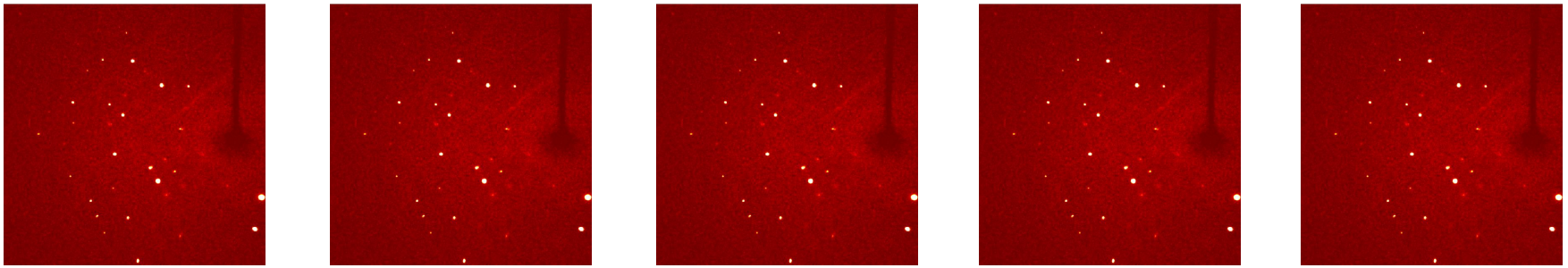
animation

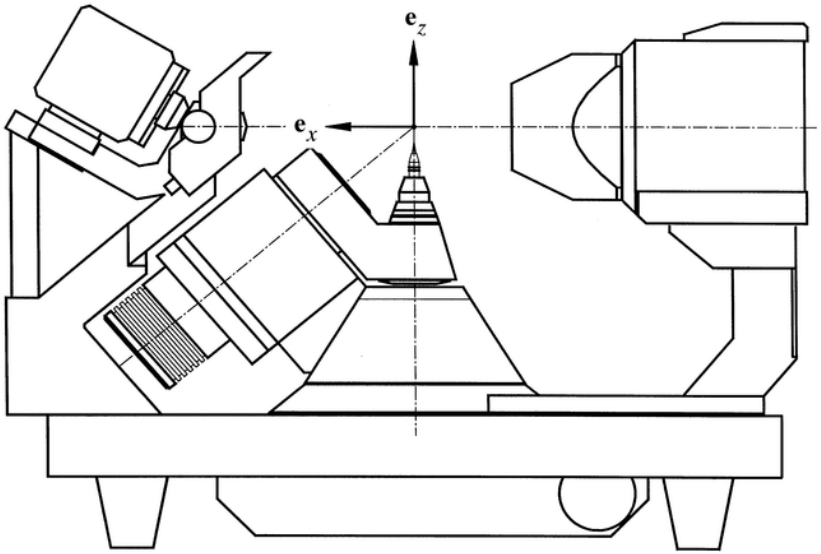
EwaldSphere.exe

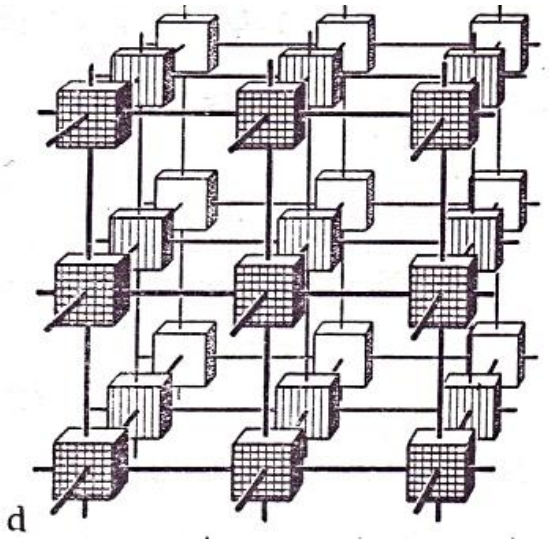
http://www.doe-mbi.ucla.edu/~sawaya/m230d

Collecting diffraction frames

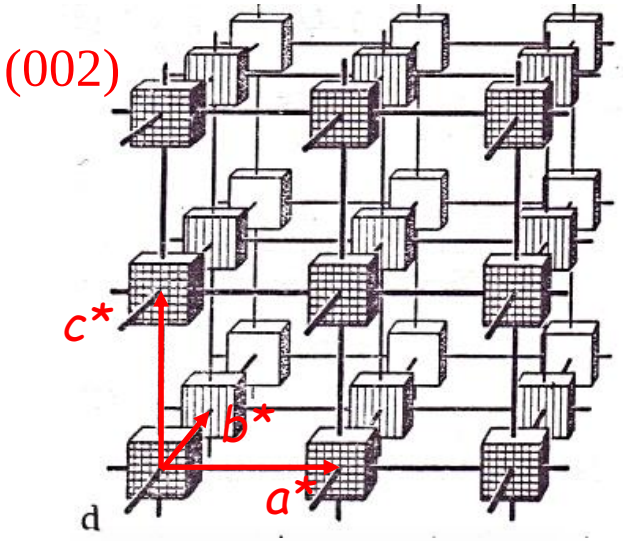
$0 < \omega < 1$ $1 < \omega < 2$ $2 < \omega < 3$ $3 < \omega < 4$ $4 < \omega < 5$





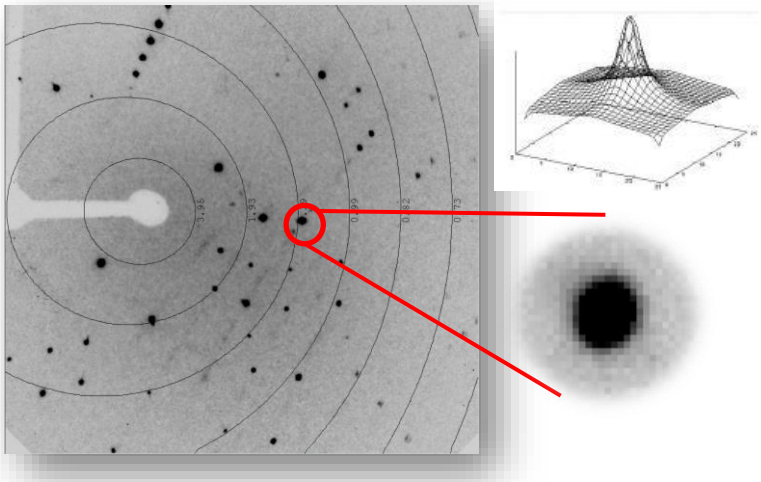


Indexing and data integration



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 :

$$\vec{H} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$$



Integration

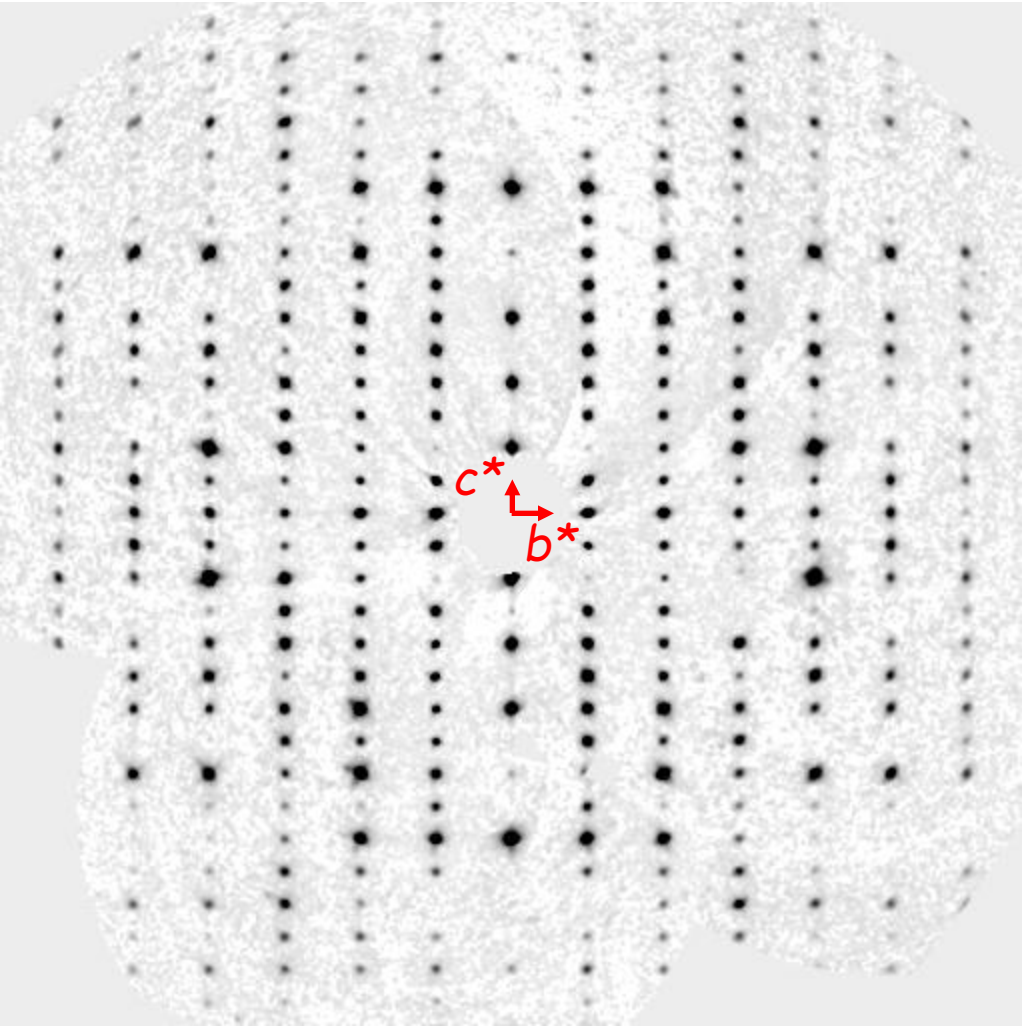
h	k	l	I(H)	σ(I(H))
0	0	1	5.10	0.2
0	0	1	6.30	0.4
0	0	2	47.40	2.3
-5	2	-9	159.39	7.8
…				

$$\vec{H},\ I(\vec{H}),\ \sigma\left(I(\vec{H})\right)$$

- Pixel-by-pixel summation over an integration volume
- Application of a 2D or 3D profile / profile fitting and learnt profile
- Background noise estimation

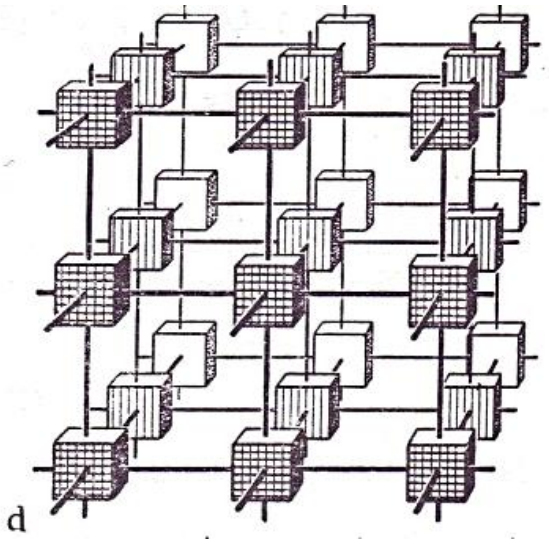
Collecting diffraction frames

(0kl) layer



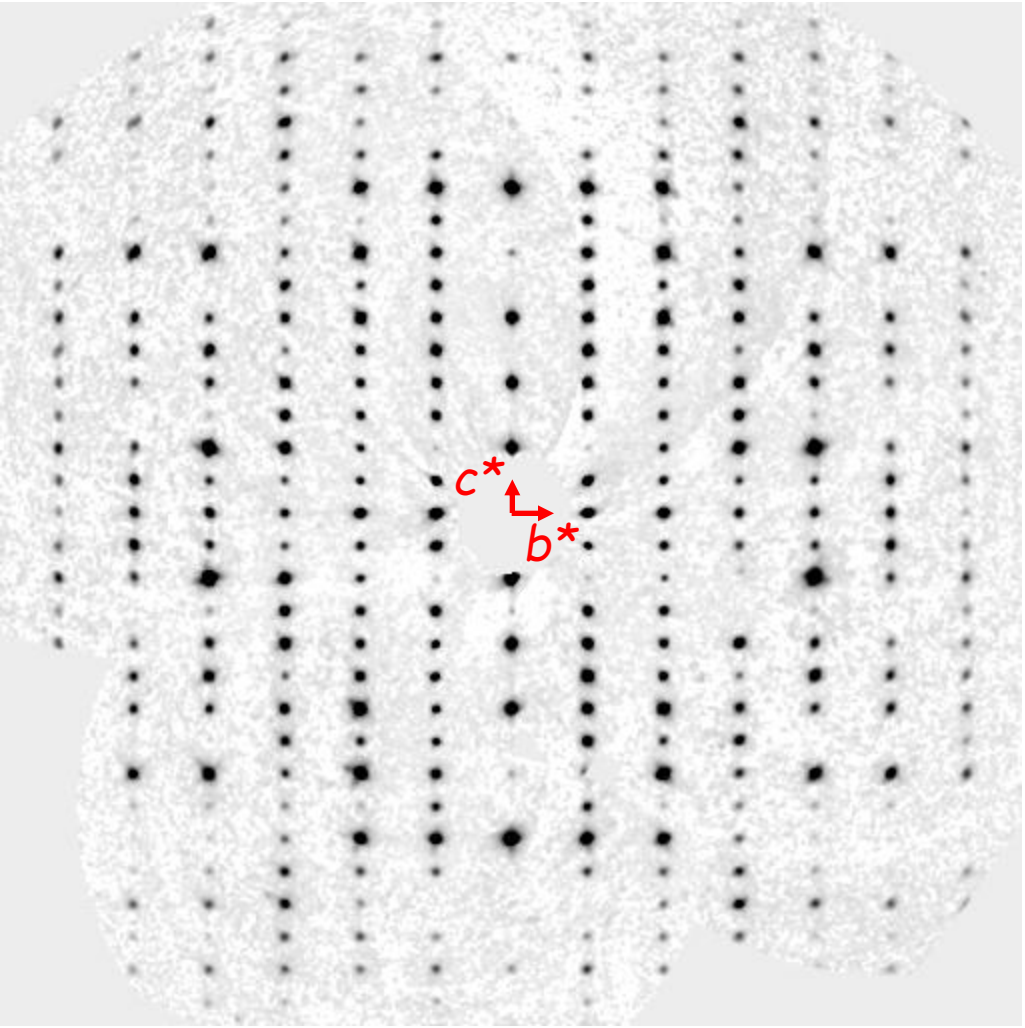
Space group C2/c

Systematic absence :
(0kl) with k=2n+1
(00l) with l=2n+1



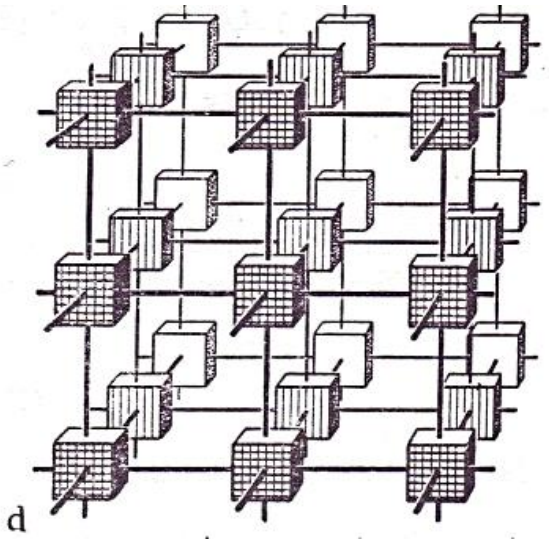
Collecting diffraction frames

(0kl) layer

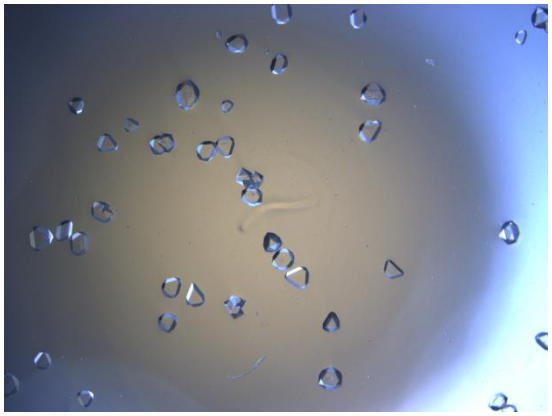


Space group C2/c

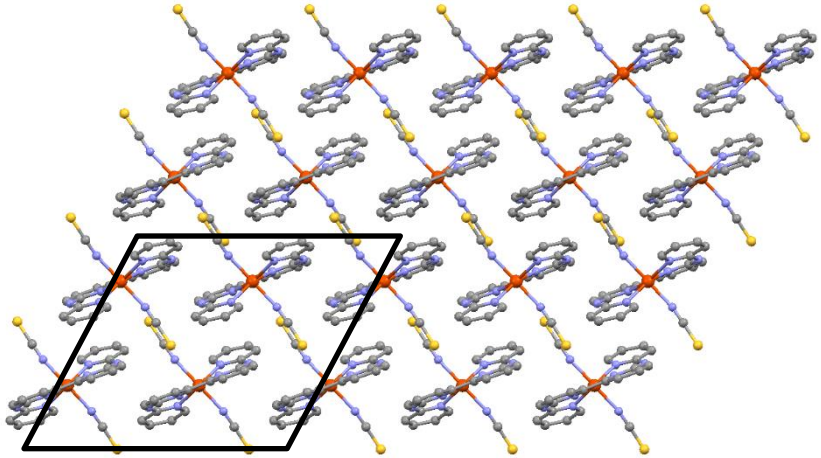
Systematic absence :
(0kl) with k=2n+1 : C lattice mode
(00l) with l=2n+1 : mirror c perp. To b



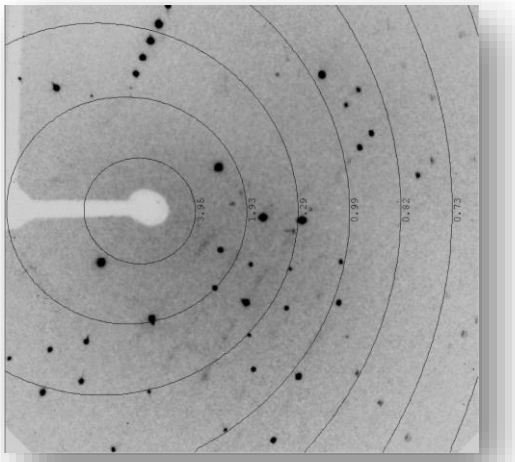
Use of single crystal x-ray diffraction



Structural model



XRD



$$\left\{\vec{H},\ I(\vec{H}),\ \sigma\left(I(\vec{H})\right)\right\}$$

Structure solution methods

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

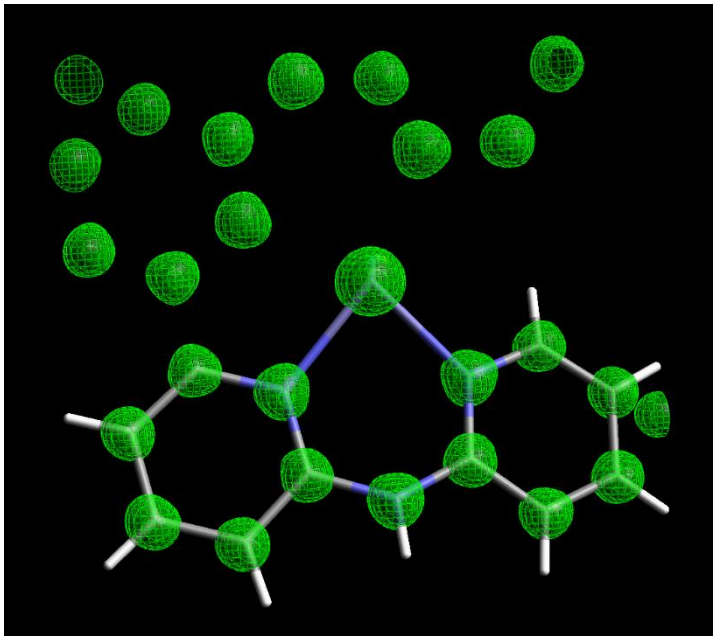
$$F_{unit\,cell}(\vec{H}) = TF(\rho(\vec{r}))$$

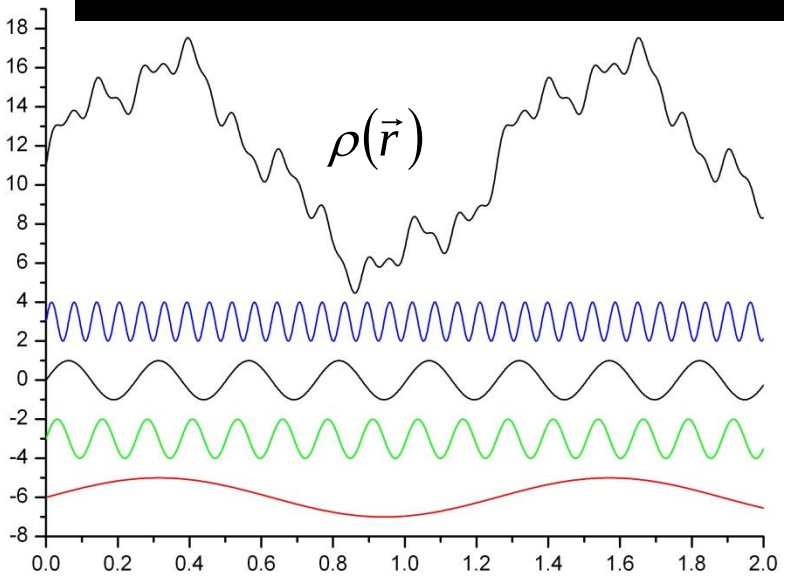
$$\rho(\vec{r}) = \frac{1}{V}\sum_{h,k,l=-\infty}^{+\infty} F(\vec{H})\exp\left[-2i\pi\vec{H}.\vec{r}\right]$$

with $$F(\vec{H}) = \left|F(\vec{H})\right|\exp\left[i\varphi(\vec{H})\right]$$

fondamental problem = phases are lost

$$I(\vec{H}) \propto F(\vec{H}) \bullet F^{*}(\vec{H}) \propto \left|F(\vec{H})\right|^{2}$$





Structure solution methods

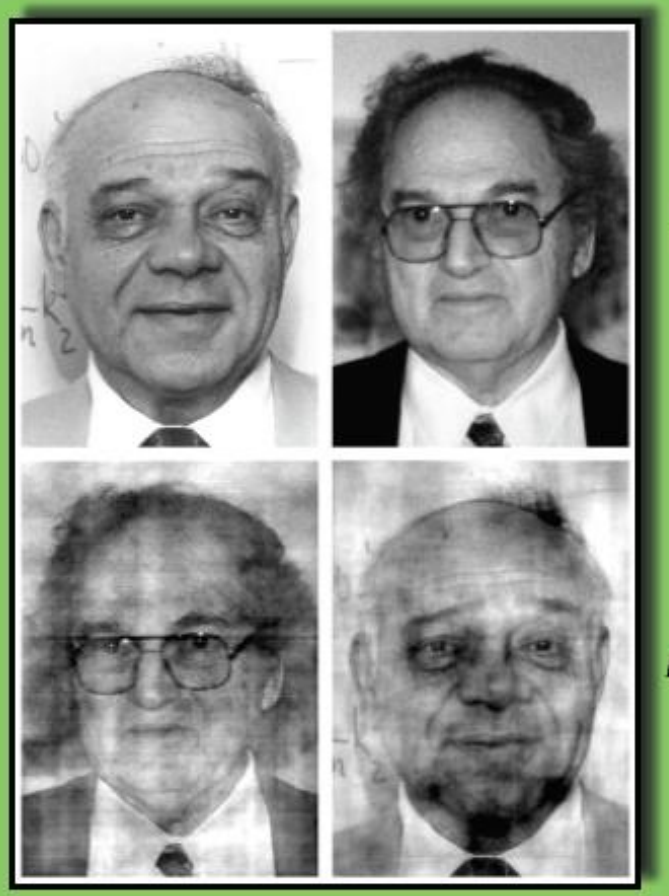
Amplitudes *versus* Phases

Karle

$$|F_{\mathrm{K}}|e^{i\varphi_{\mathrm{K}}} = \hat{\mathcal{F}}^{-1}\left[\rho_{\mathrm{K}}(x,y)\right]$$

$$\rho(x,y) = \hat{\mathcal{F}}\left[|F_{\mathrm{K}}|e^{i\varphi_{\mathrm{H}}}\right]$$

~ Hauptman



Hauptman

$$|F_{\mathrm{H}}|e^{i\varphi_{\mathrm{H}}} = \hat{\mathcal{F}}^{-1}\left[\rho_{\mathrm{H}}(x,y)\right]$$

$$\rho(x,y) = \hat{\mathcal{F}}\left[|F_{\mathrm{H}}|e^{i\varphi_{\mathrm{K}}}\right]$$

~ Karle

Randy J. Read (1997). Model Phases: Probabilities and Bias. *Methods in Enzymology*, vol. **277**, edited by Charles W. Carter, Jr., and Robert M. Sweet, pp. 110-128. New York: Academic Press.

Structure solution methods

- Molecular replacement method:
  - prior knowledge of 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)

Direct methods

Direct determination of the phases of structure factors from structure factor moduli using mathematical and probabilist relations that come from **some obvious features of the electron density,**

- **positivity** of the electron 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 density (Sayre, 1951): the electron densities of different atoms do not overlap
- **symmetry** of the crystal structure (origine)
- **chemical composition** of the unit cell

Normalized structure factors :

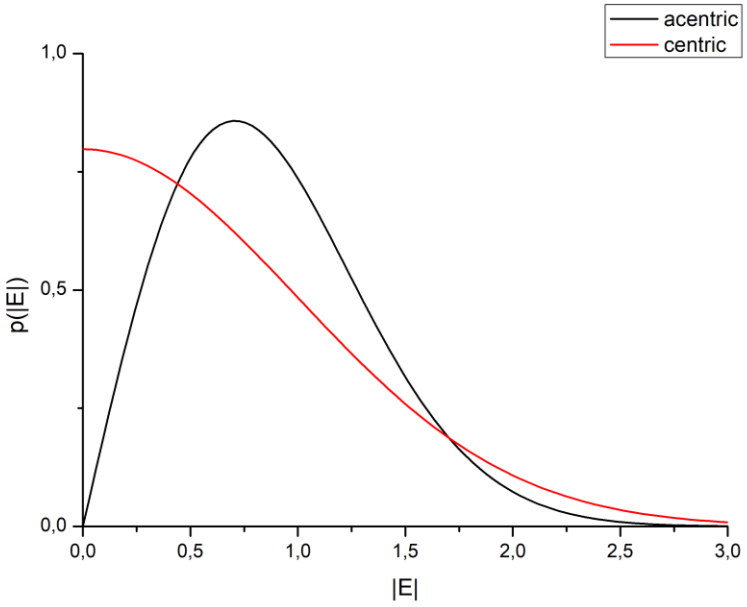
$$E(\vec{H}) = \sum_{j=1}^{N_{at}} \frac{f_j}{\sqrt{\sum f_j^2}} exp\left[2i\pi \vec{H}.\vec{r}_j\right] = \frac{F(\vec{H})}{\sqrt{\langle F^2(\vec{H})\rangle_{\substack{resolution \\ slices}}}}$$

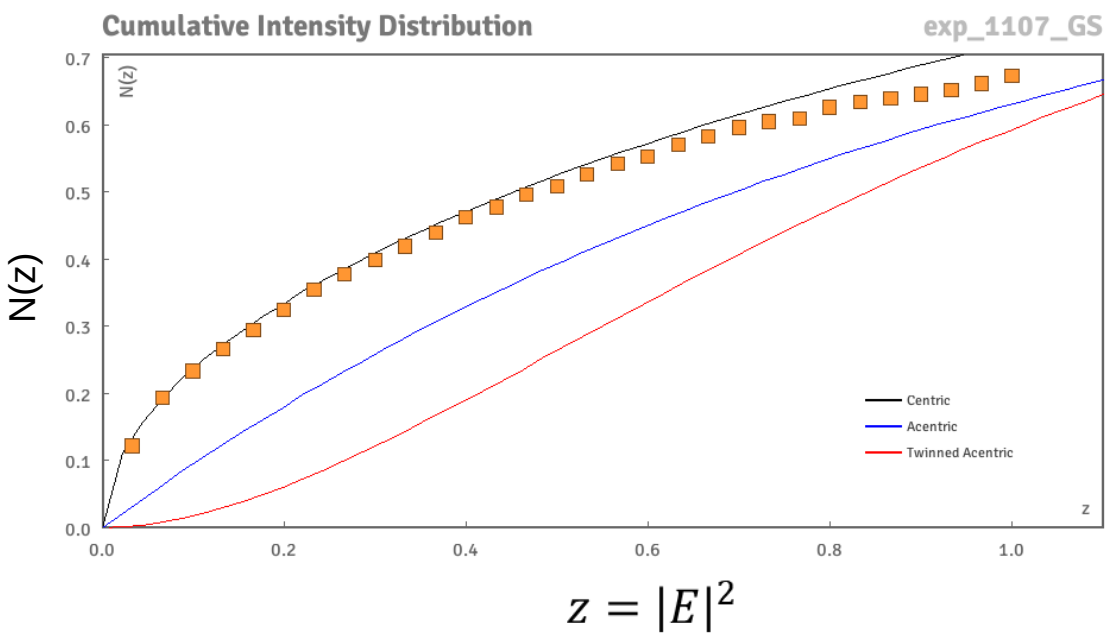
Allows to get rid of thermal smearing, and consider point atoms

Direct methods : detection of inversion center

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

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

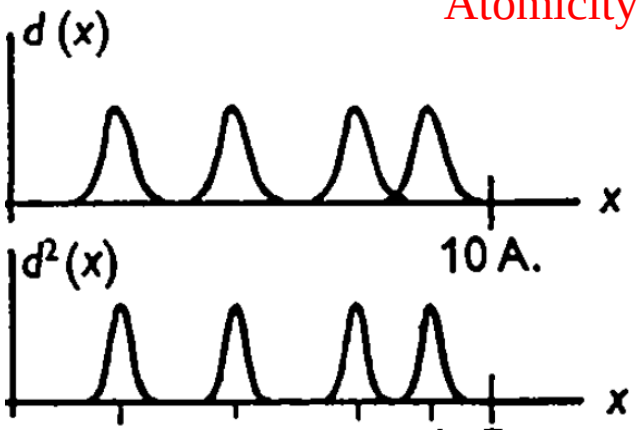




$$z = |E|^2$$

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 $\rho(\vec{r}) = \frac{1}{V} \sum_{h,k,l=-\infty}^{+\infty} F(\vec{H}) \exp\left[-2i\pi \vec{H}.\vec{r}\right]$

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

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

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

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

For strong values of $\left|F(\vec{H})\right|$, $\left|F(\vec{H})\right|^2$ 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,

$$\varphi(-\vec{H}) + \varphi(\vec{K}) + \varphi(\vec{H}-\vec{K}) \approx 0$$

$$P\left(\varphi(-\vec{H}) \middle| \varphi(\vec{K}), \varphi(\vec{H}-\vec{K})\right)$$

Direct methods : tangent formula

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

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

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

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

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

Tangent formula

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

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 impose a strong atomicity constraint on phases

Direct methods : Advantages & Disadvantages

Advantages:

- This set of methods is **very efficient** and most of the small molecules crystal structures are determined with this approach.
- Quick in practice, direct methods give a high proportion of the atomic positions, facilitating the refinement step.
- Figure of merits are associated to the results, this allows the result to be appreciated with **hindsight**.
- Direct methods are a matter of equations, they are fully automated, thus **easy to use** especially because decades of experience have allowed to have defaults parameters well optimized.

Disadvantages:

- **Difficult** to understand due to the mathematical aspects behind. Very often used as black-boxes.
- The **space-group must be determined** prior to applying direct methods.
- The phase relationships become a minor feature as the number of atoms in the structure increases. **Above 2000** atoms in the unit-cell, direct methods are inefficient. **This method is not applicable for proteins and large macromolecules.**

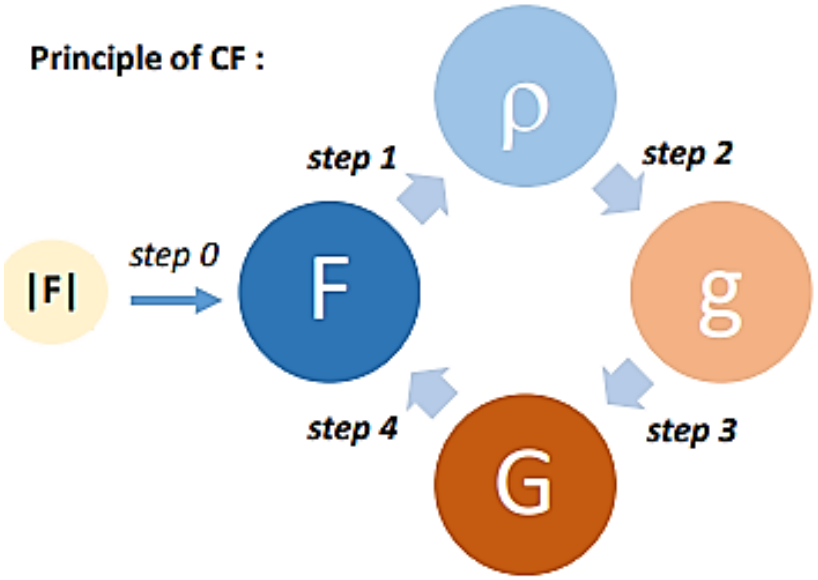
Initial references for direct methods :
Karle, J. and Hauptman, H., *Acta Cryst*. 3 (1950), 181-187

Charge Flipping (CF) method (2004)

General concept : the idea is to calculate anyway the inverse Fourier Transform of the structure factors and to correct the **wrong phases** obtained by a succession of iterations based on the fact that an **electron density must be positive**

- ab-initio determination of crystal structure (periodic and aperiodic structures, single crystal and powder diffraction, X and N diffraction)

Principle of CF :



|F | : experimental amplitude of structure factors, without phase

F : structure factors with phase

ρ : electron density with potential negative values

g : electron density with only positive values

G : structure factors with phase

Sequence of the CF algorithm

Step 0 : random phases are attributed to the experimental data.

Step 1 : electron density in the unit-cell is calculated from F.

Step 2 : the electron densities that are negative are inverted to positive. This is the "***charge flipping***" that names the method

Step 3 : new structure factors, **G**, with their phases are calculated.

Step 4 : the phases of G are kept while their amplitudes are replaced by the experimental ones, giving new F,

Charge Flipping (CF) method (2004)

Advantages:

- CF needs **no preliminary information** on the crystal, except the Unit-cell parameters. **The space group is NOT required** since all calculation are made in P1, the space group is deduced at the end of the process. No need of information on the chemical composition.
- CF is tolerant to imperfects experimental data, though high noise may be problematic.
- CF proved to **be very efficient** in the case of aperiodic structures. Superspace crystallographers use it.
- CF is also of help in powder diffraction since the space group is often difficult to obtain in powder and CF does not need the space group.
- CF is easy to understand

Disadvantages:

- Data with bad resolution **may not be pertinent** for CF.
- **Not much parameters that the user can adjust** to converge towards the result

Basic references for CF :
The method was proposed in *G. Oszlanyi and A. Suto, Acta Cryst A 60, 134, 2004*
The implementation was developed in *L. Palatinus, Acta Cryst B 69, 1, 2013*

Improvement (refinement) of the structure

Observables

$$\left\{\left|F_{obs}(\vec{H})\right|, \sigma\left(\left|F_{obs}(\vec{H})\right|\right)\right\}$$

Least-squares refinement

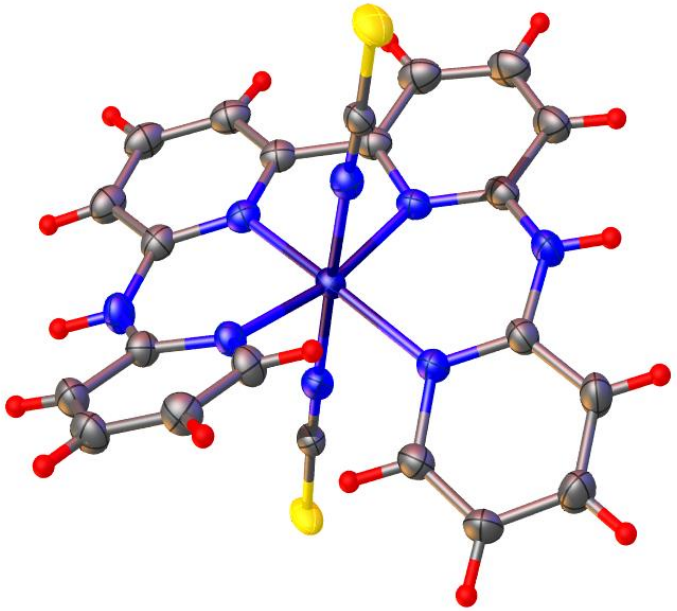
$$\left\{\left|F_{calc}(\vec{H})\right|, \varphi_{calc}(\vec{H})\right\}$$

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

$$\min \chi^2 \quad \Rightarrow \quad \frac{\partial \chi^2}{\partial p_j} = -2\sum_{\vec{H}} \frac{F_{obs} - F_{calc}}{\sigma^2(F_{obs})} \frac{\partial F_{calc}}{\partial p_j} = 0, \quad j = 1,2,\ldots,m$$

$$F_{calc}(\vec{H}) = \sum_{j=1}^{Nat} f_j occ_j \exp\left[2i\pi \vec{H}.\vec{r}_j\right] \exp\left[-2\pi^2 \vec{H}^T.\tilde{U}.\vec{H}\right]$$

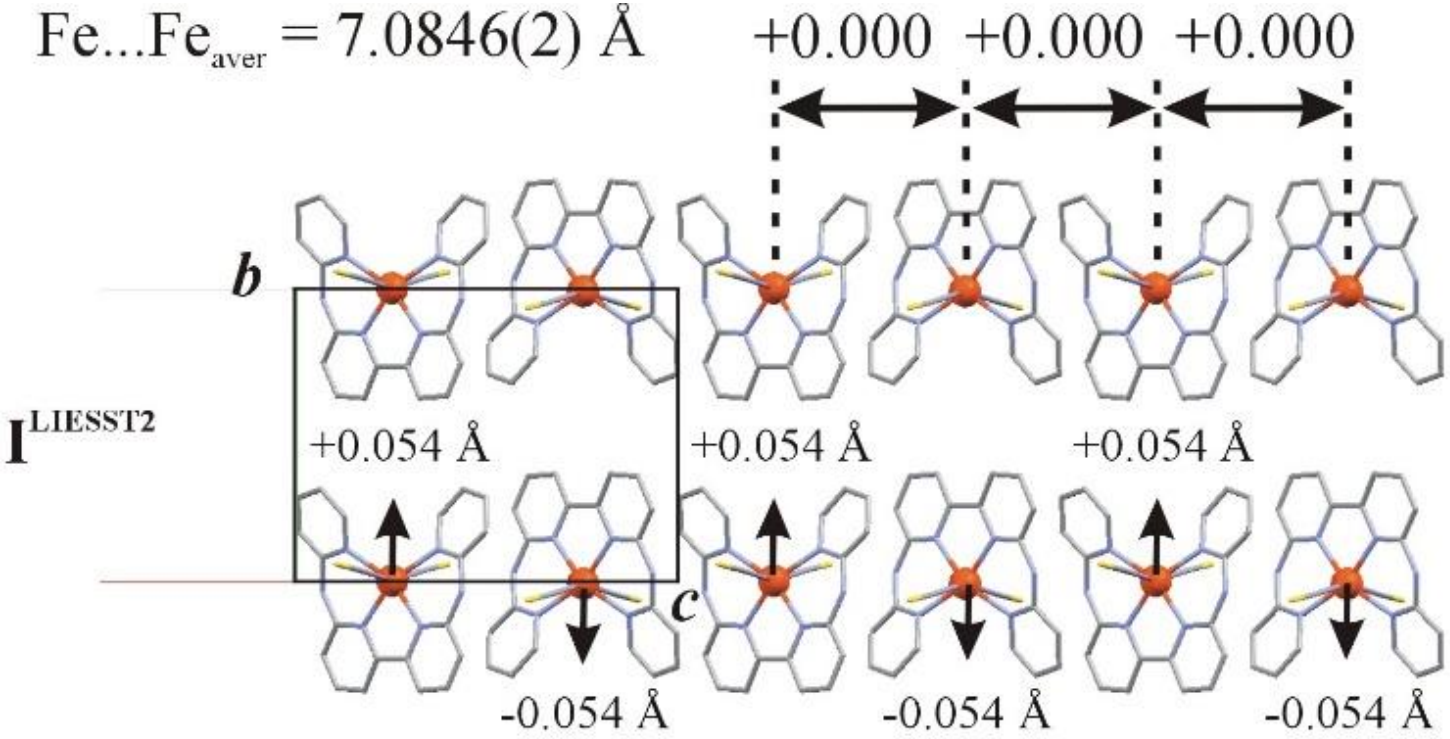
Structural model



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

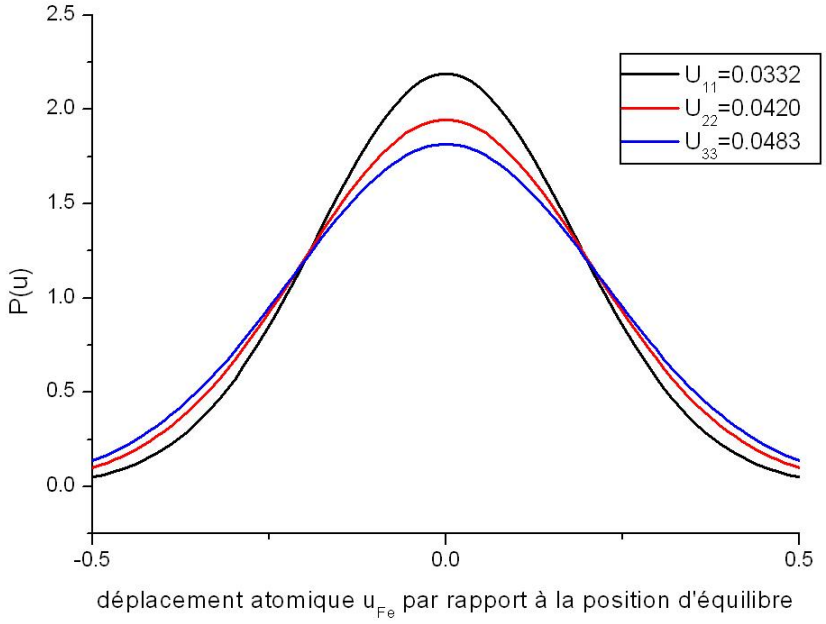
Structural analysis

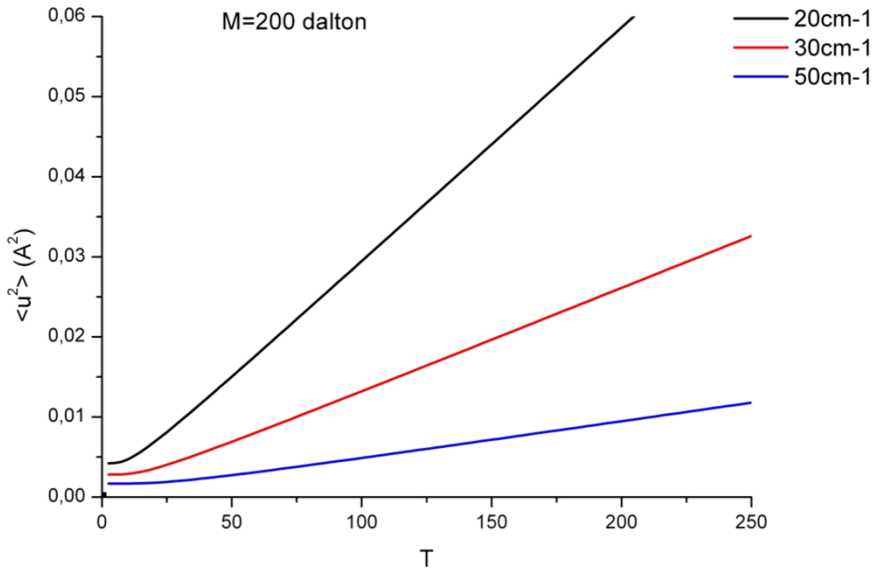
- Bond distances
- Bond angles
- Torsion angles
- Thermal smearing ellipsoids
- Intermolecular contacts



Thermal smearing and 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

Thermal smearing and Debye Waller factor

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

FT

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

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

In the isotropic harmonic approximation :

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

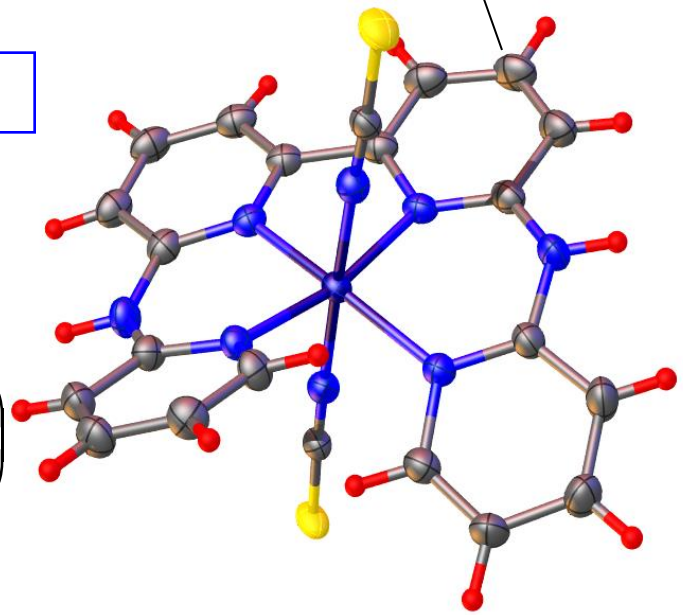
$$= \exp\left(-B\frac{\sin^2\theta}{\lambda^2}\right)$$

B~3-10 Å^2 (U~ 0.02-0.12 Å^2)

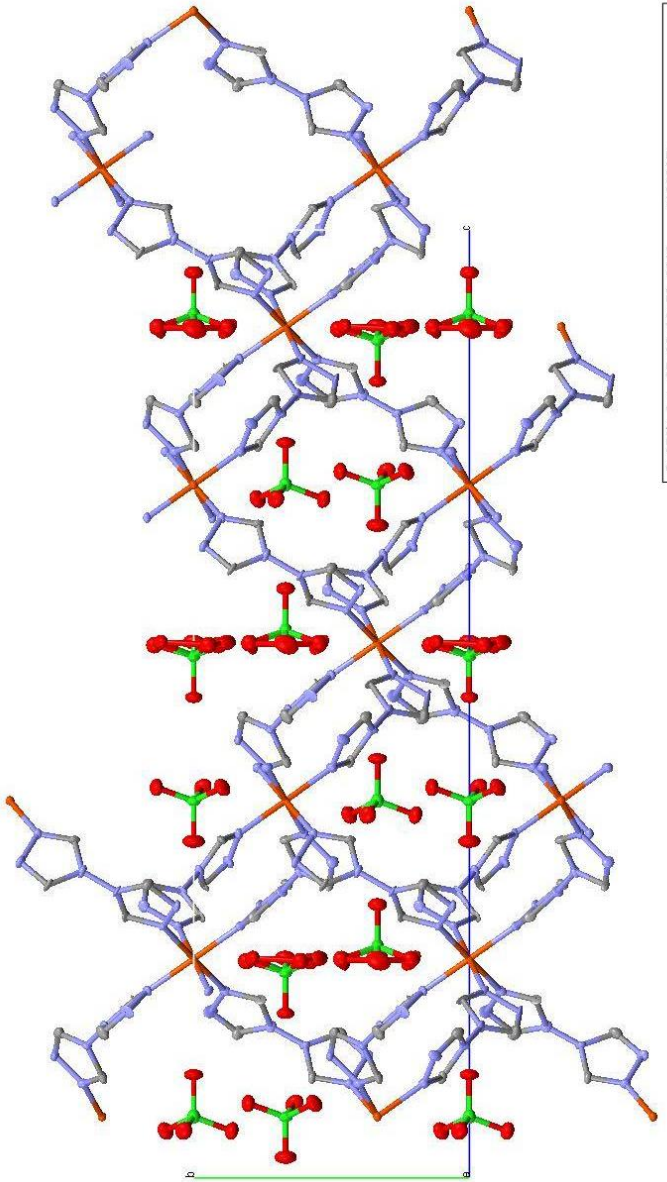
In the anisotropic harmonic approximation :

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

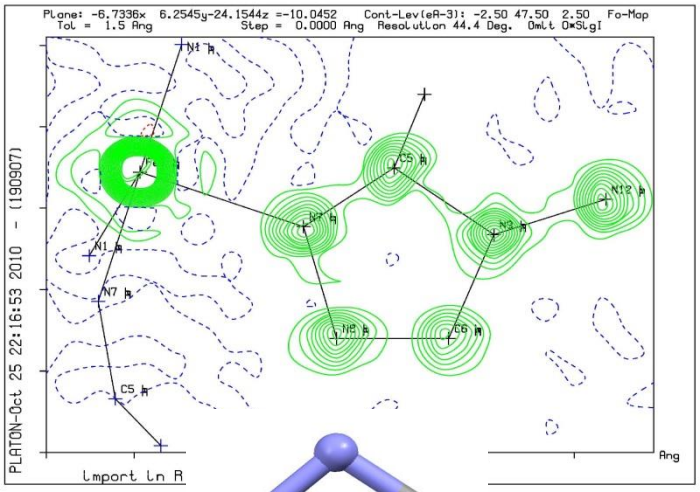
$\tilde{U}$ Is the atomic displacement tensor (symmetric)

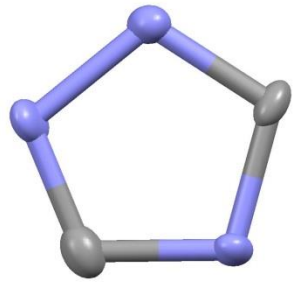


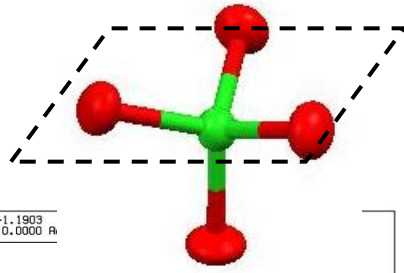
Structural disorder

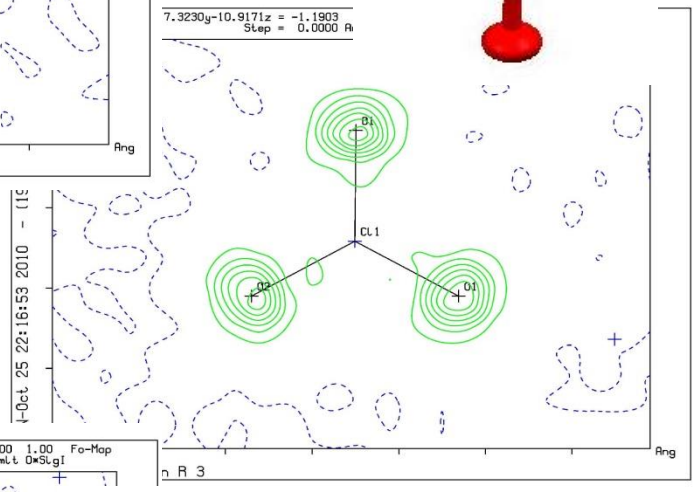


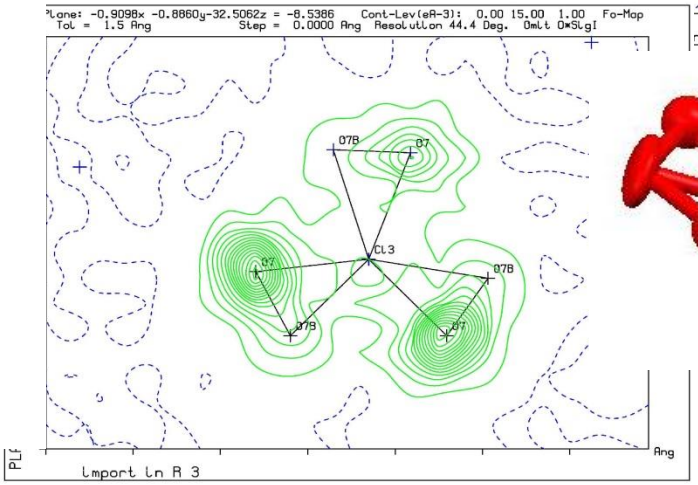
$[Fe(btr)_3].(ClO_4)_2$

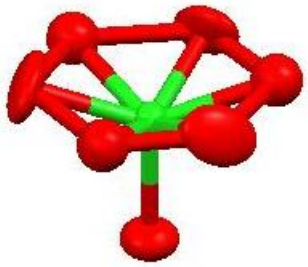












Static disorder ?

or dynamical disorder ?

Absolute structures

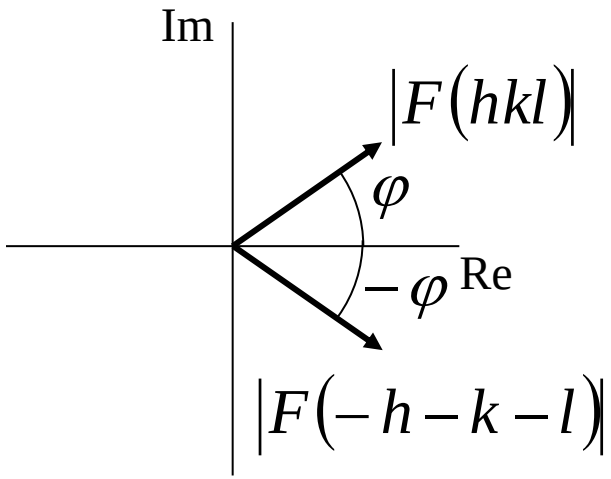
Friedel law : $\mathbf{I}(hkl) = \mathbf{I}(-h-k-l)$

In the absence of anomalous dispersion,

the diffraction pattern is centrosymetric :

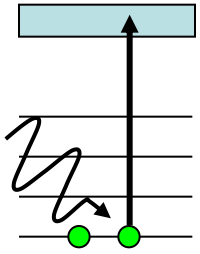
Two structures containing two different

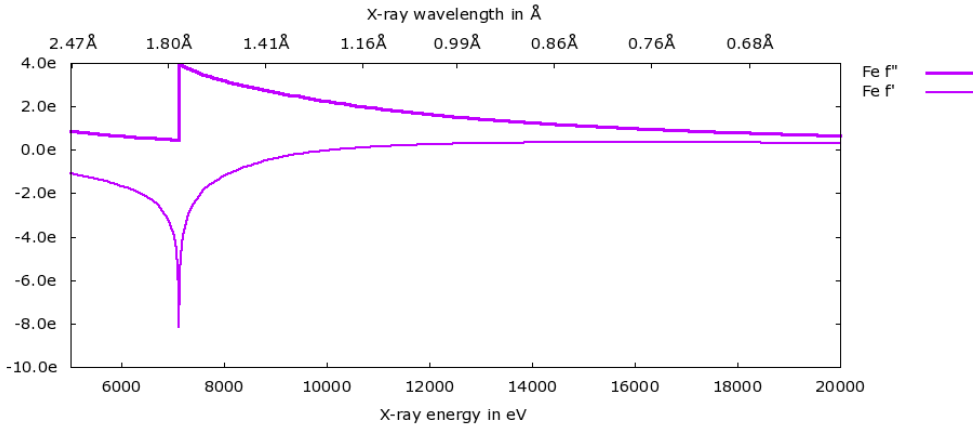
enantiomers are not distinguishable

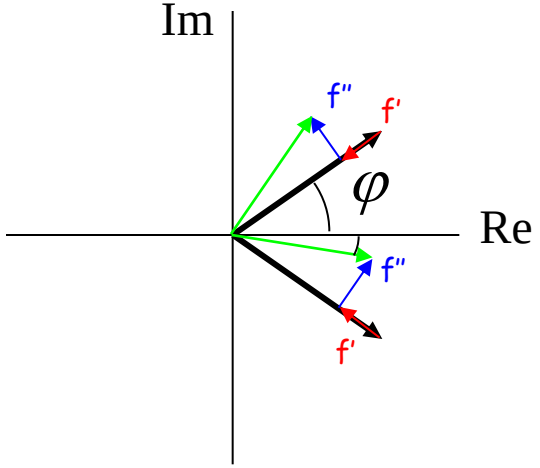


In presence of anomalous dispersion :
Resonance phenomenon (EXAFS, XANES)

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







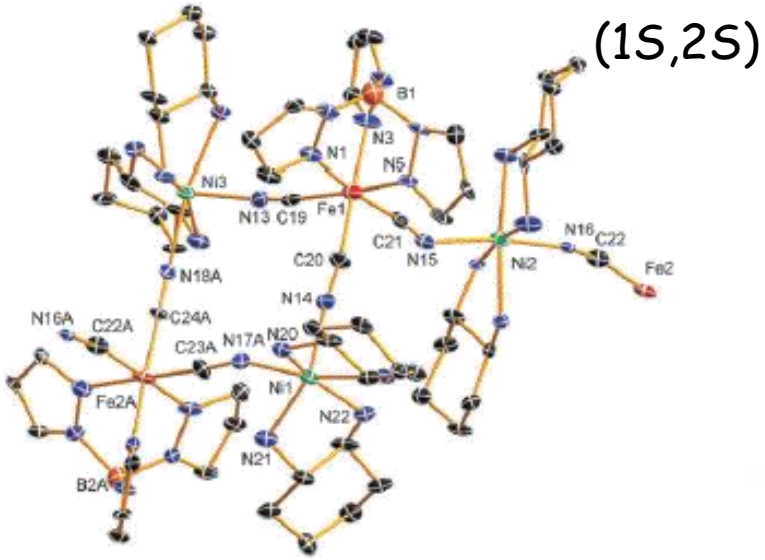
$\mathbf{I}(hkl) \neq \mathbf{I}(-h-k-l)$

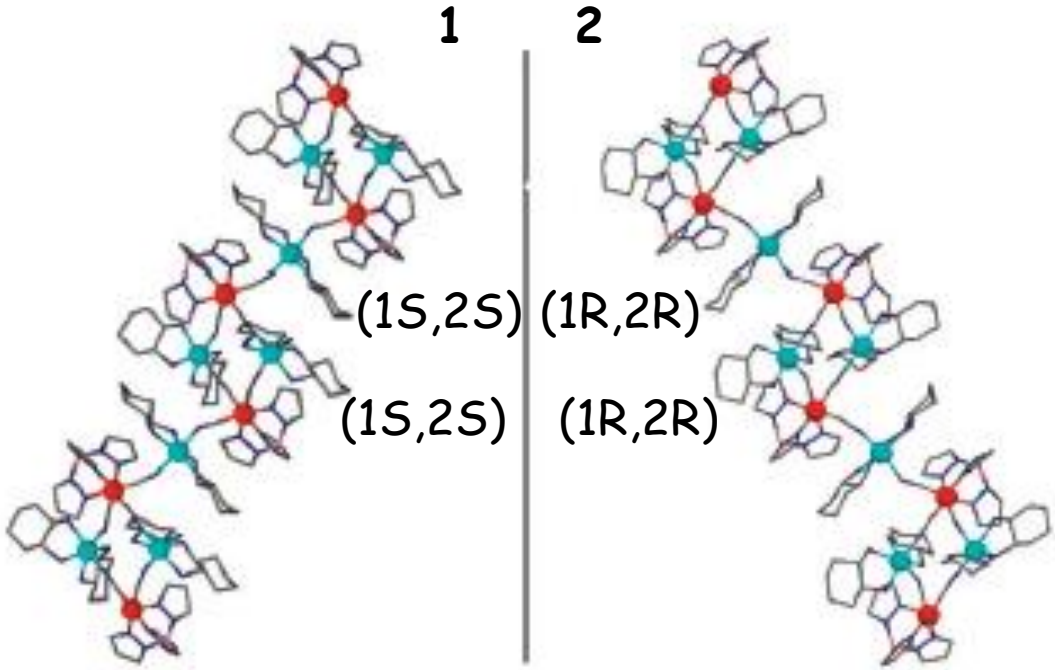
Absolute structures and optical activities

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

Flack parameter : x

requires a heavy atom and an appropriate choice of wavelength λ



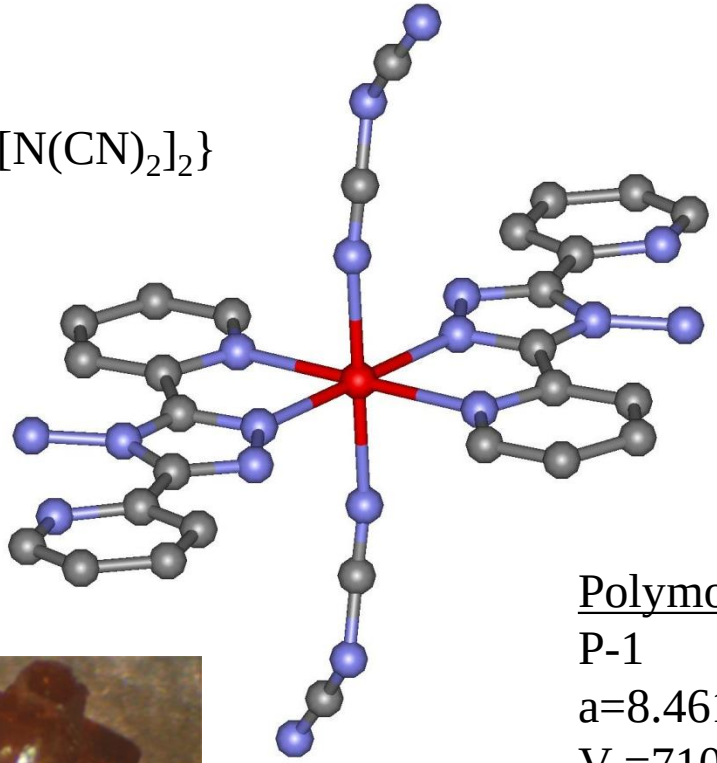


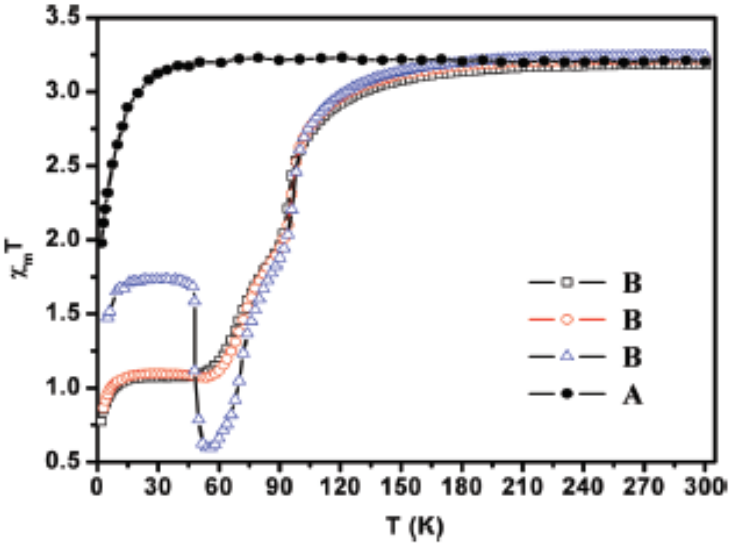
	1	2
Non centrosymmetric space group:	P1	P1
Flack parameter x	0.012(1)	0.018(15)

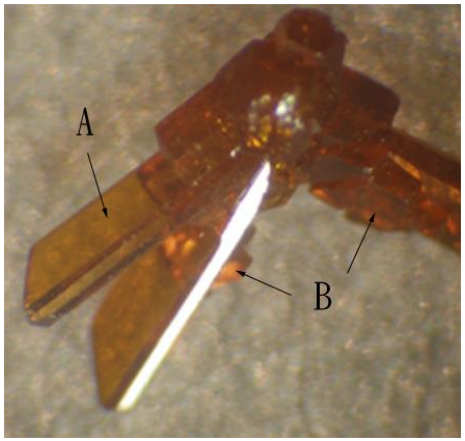
Wang et al. *Chem. Commun.*, (2009), 6940

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 XRD

Moliner *et al*., (2001), *Inorg Chem*, **40**, 3986.

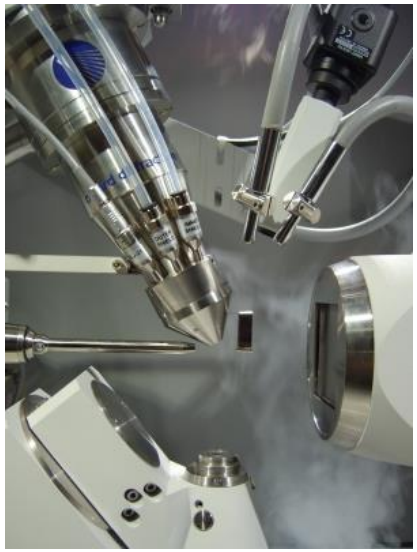
Sheu *et al*., (2008), *Inorg Chem*, **47**, 10866.

Single crystal diffraction as a funciton of T

N_2 cryostream

90K < T < 300K

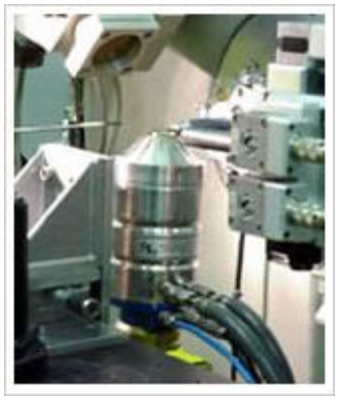
He cryostream



10K < T < 70K

displex

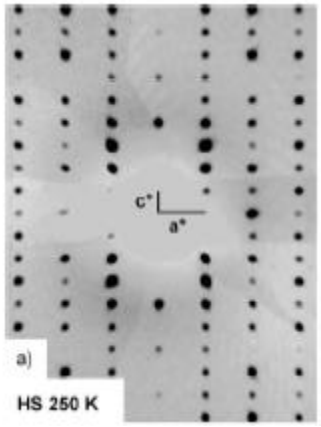
300K < T < 1000K

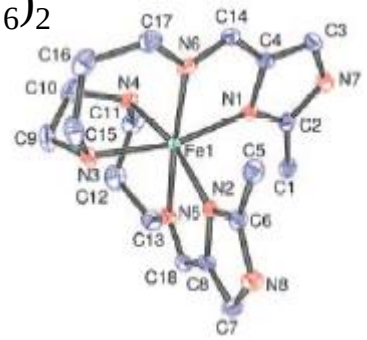


Symmetry breaking : development of a surstructure

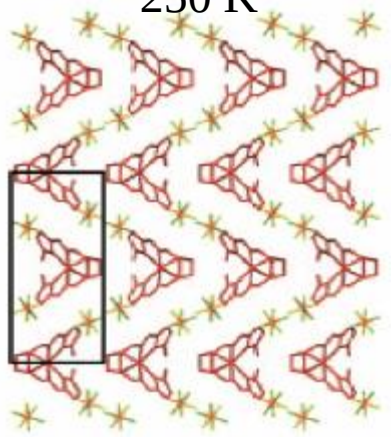
$[FeH_2L_2Me]$-$(PF_6)_2$

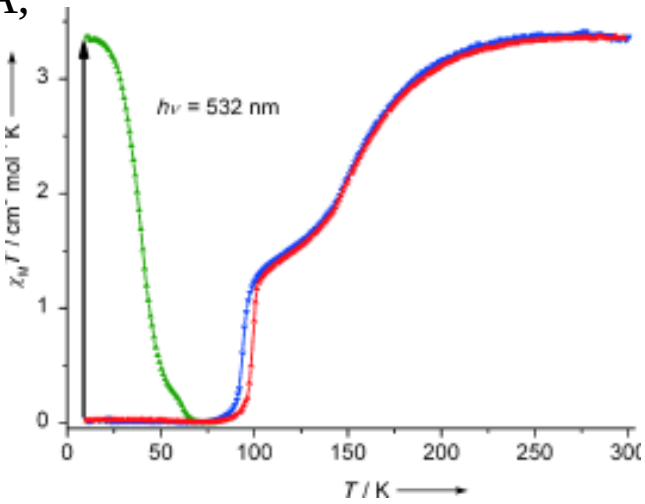
$P22_12_1$, a=8.405(1)Å, b=9.469(2)Å,
c=17.399(3)Å , V=1384.7(4)Å^3
Z=2





250 K





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

Symmetry breaking : development of a surstructure

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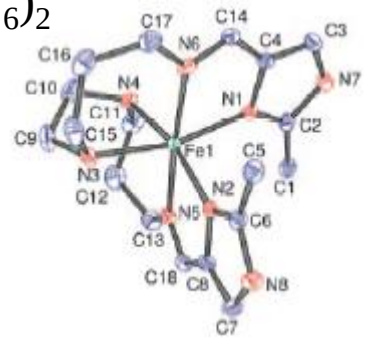
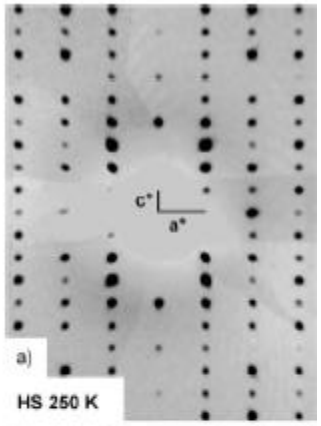
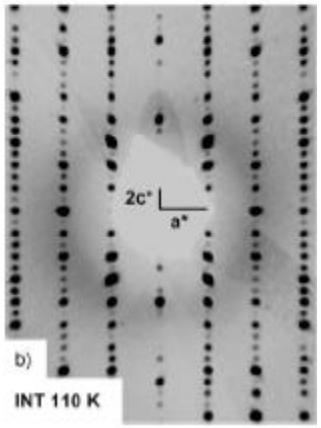
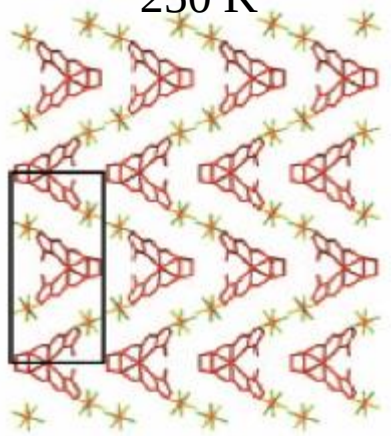
Z=2



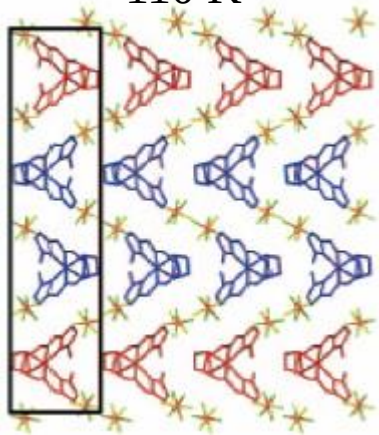


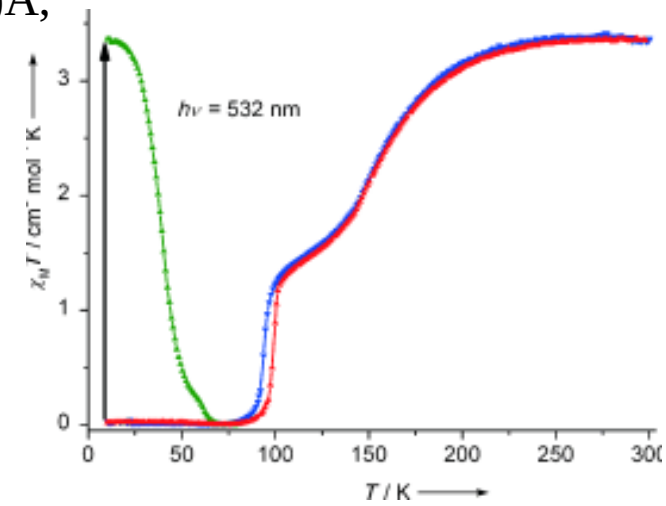


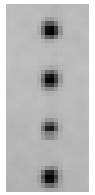
250 K

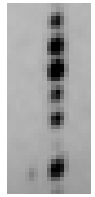


110 K







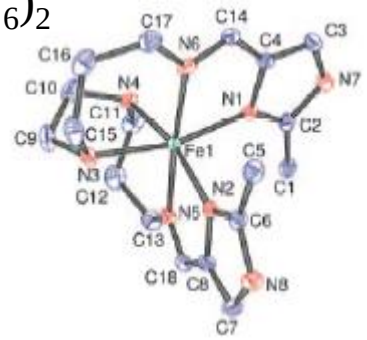


$P2_1$, c=35.543(2)Å,
V=2655(2)Å^3, Z=4

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

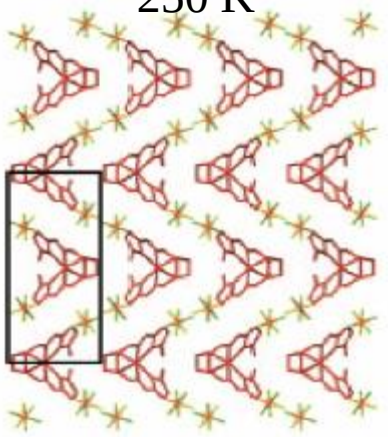
Symmetry breaking : development of a surstructure

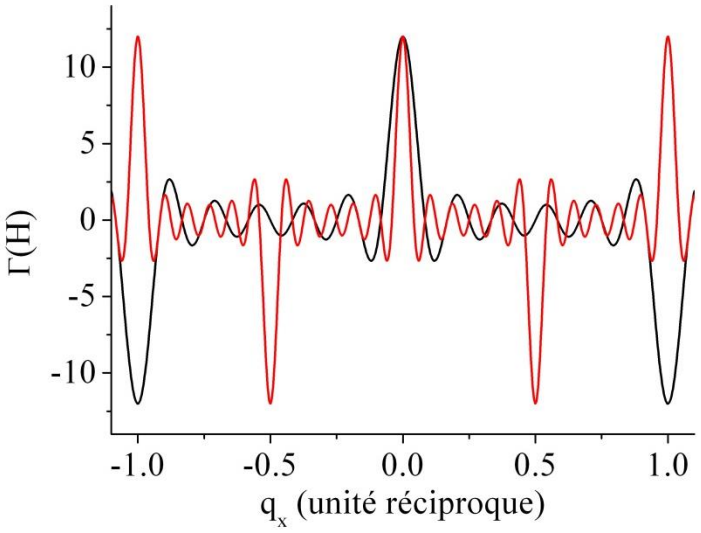
$[FeH_2L_2Me]-(PF_6)_2$

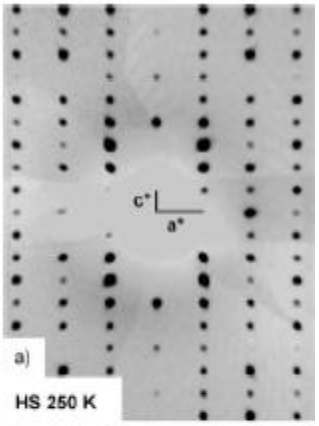


$P22_12_1$, a=8.405(1)Å, b=9.469(2)Å,
c=17.399(3)Å , V=1384.7(4)Å^3
Z=2

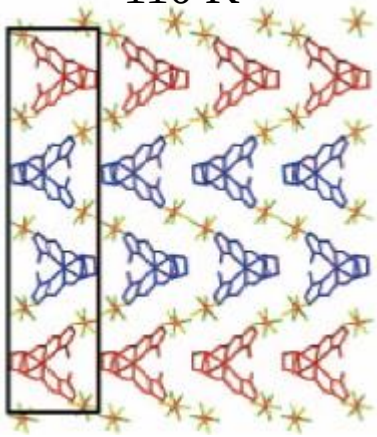
250 K



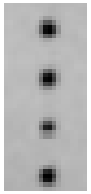


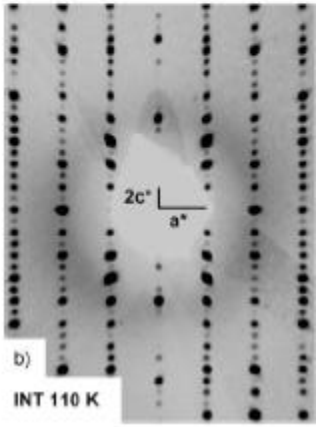


110 K

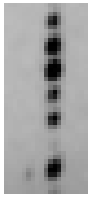


Additional 3D order





New periodicity

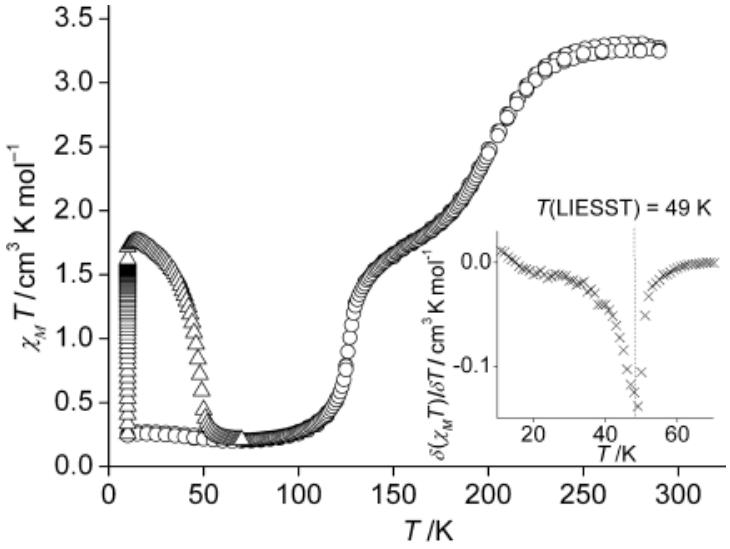


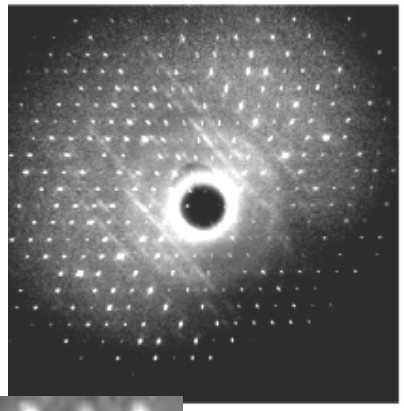
$P2_1$, c=35.543(2)Å,
V=2655(2)Å^3, Z=4

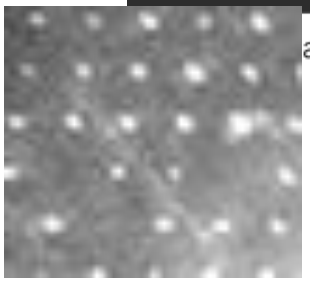
Bréfuel et al. Angew. Chem. (2009), 48, 9304

Diffuse scattering and disorder

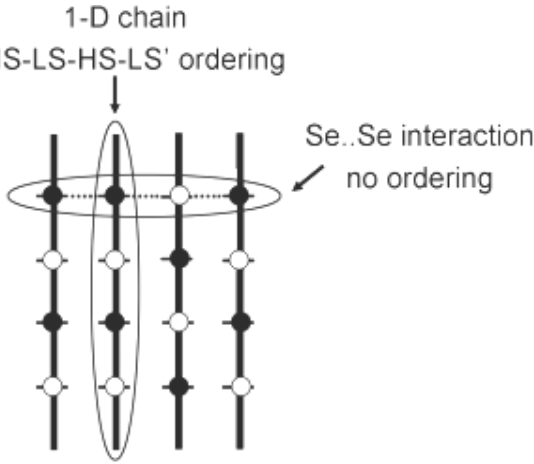
[Fe(NCSe)$_2$(bdpp)]





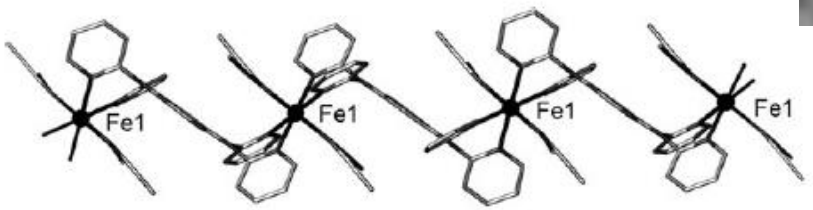


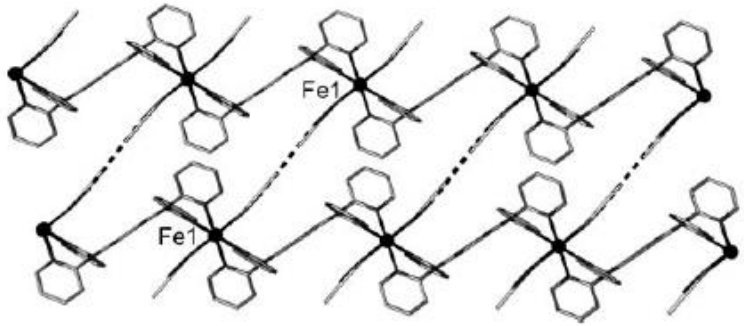
a)



b)

[101]





Diffuse planes ⊥ to [101]

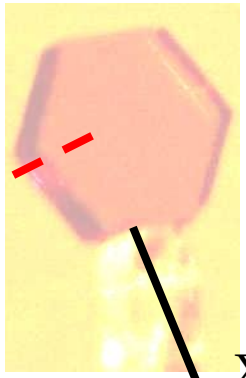
→ Strong 1D correlations along [101]

HS-LS-HS-LS ordering

No correlations between chains

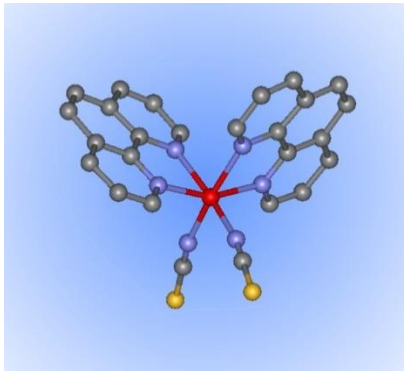
S. Neville *et al.*, *Chem. Eur. J.* (2008), **14**, 10123

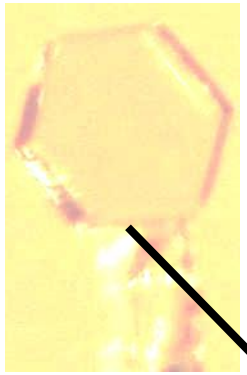
Photo-crystallography: principles



XRD

$\rho_{fond}(r)$





XRD

$\rho_{excited}(\vec{r})$

modèle

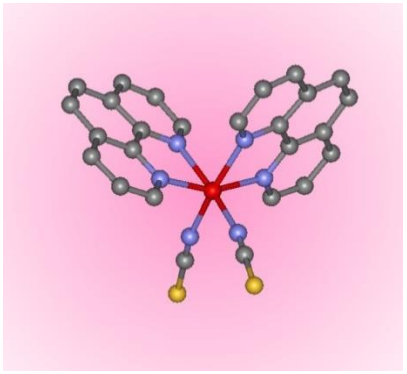
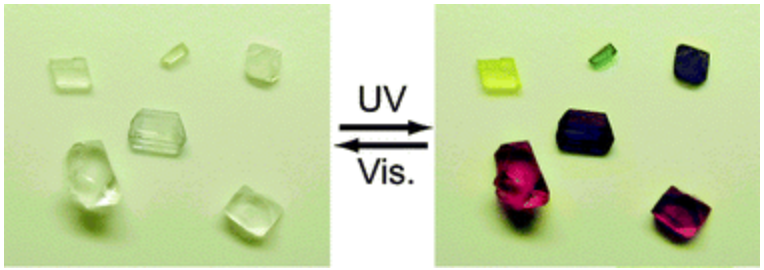
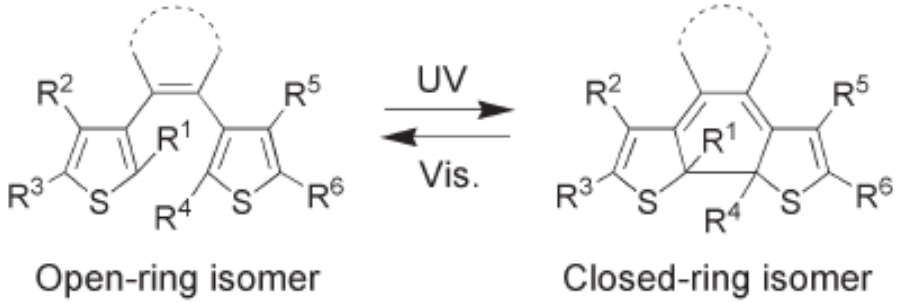


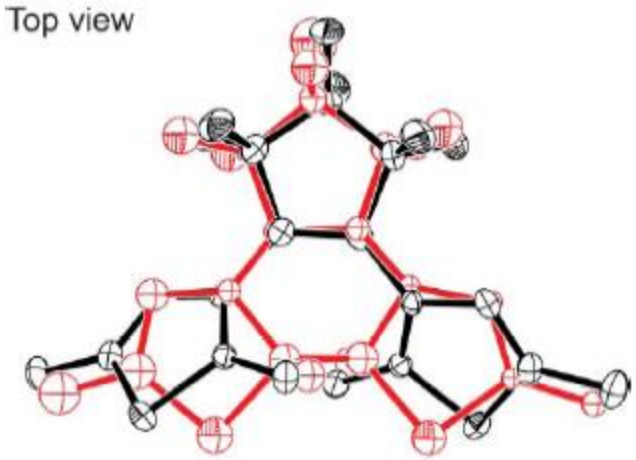
Photo-chromism

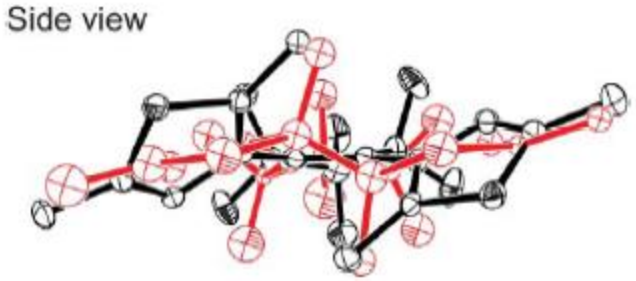
Diarylethen derivatives



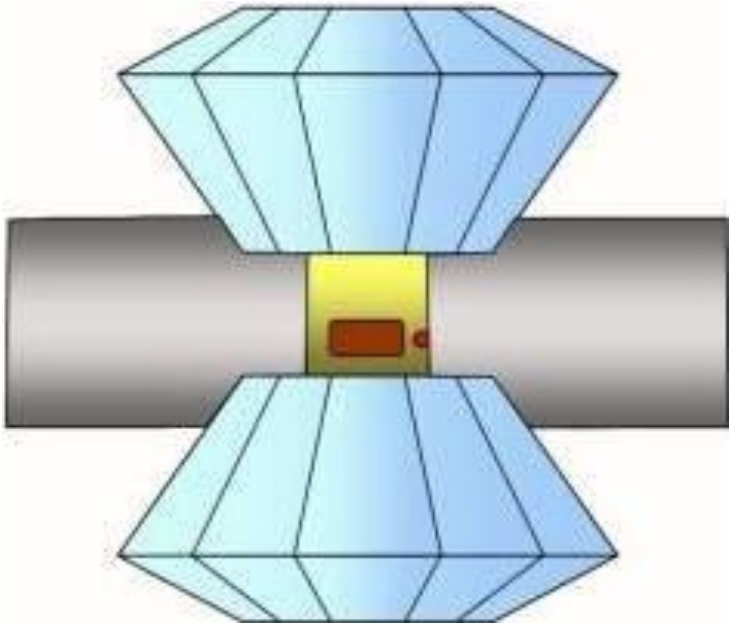


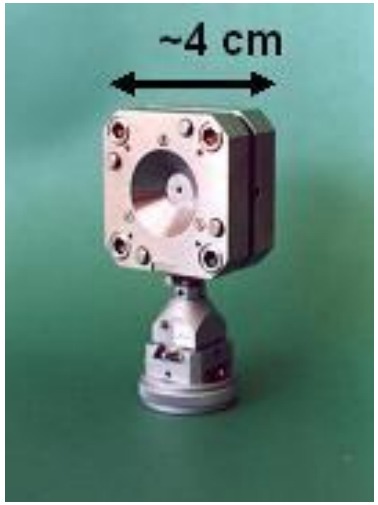
Scheme 1 Photochromism of diarylethene.

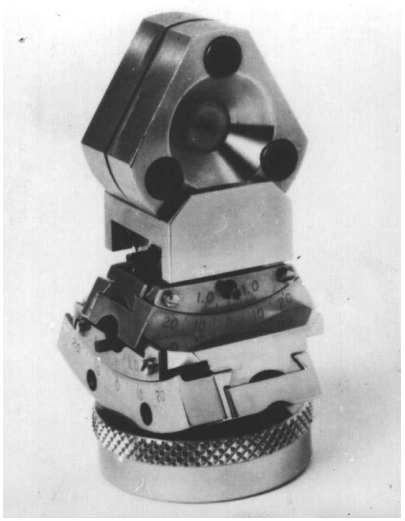




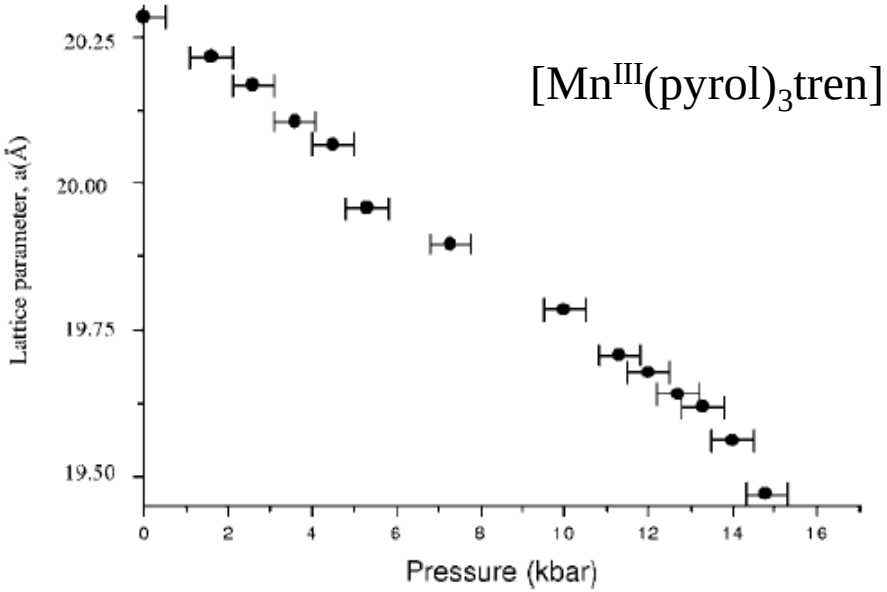
Single crystal diffraction under pressure

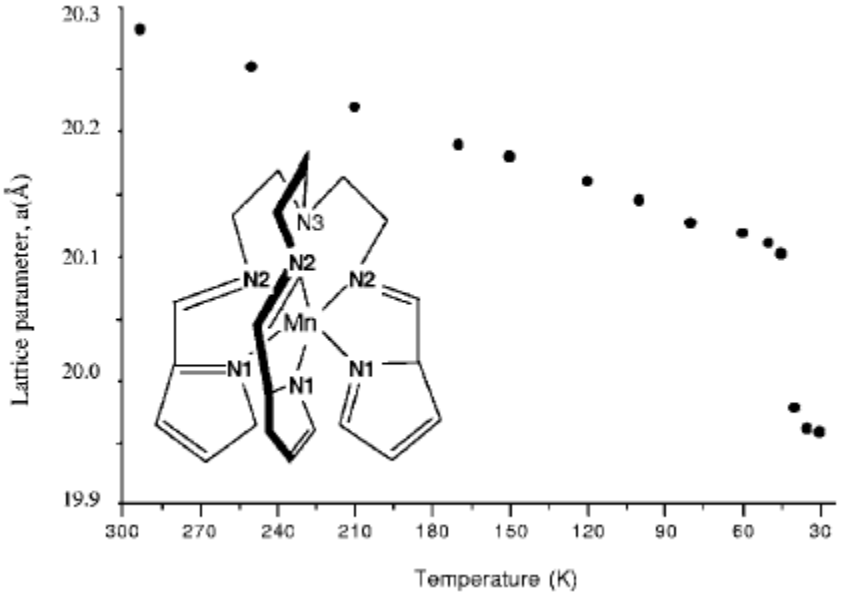


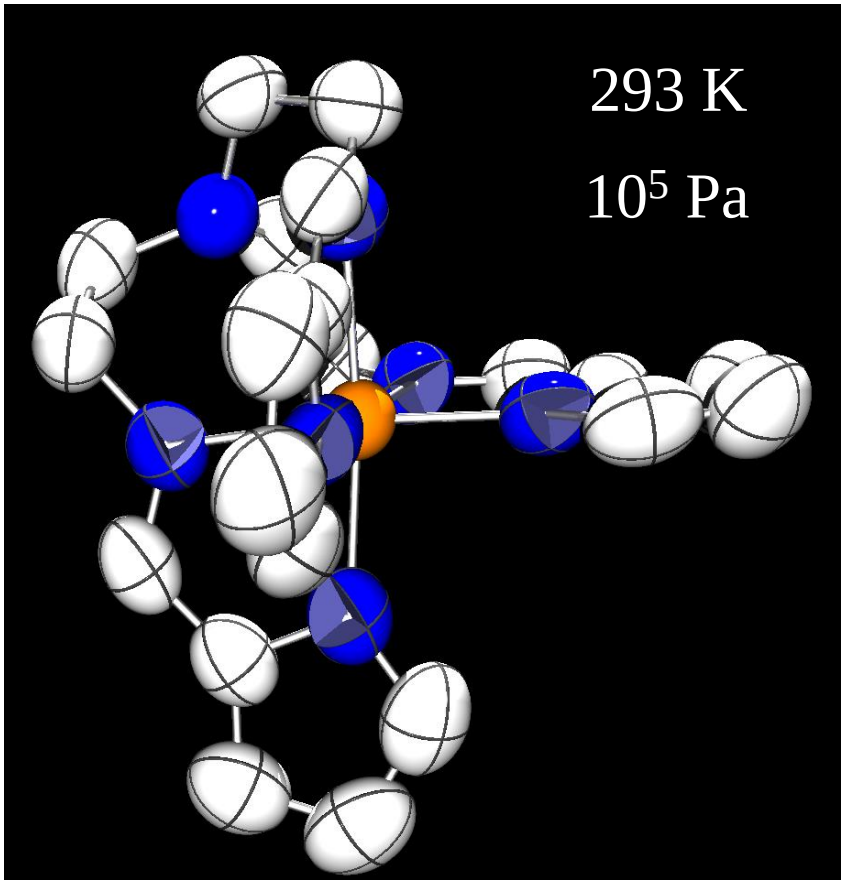




Single crystal diffraction under pressure



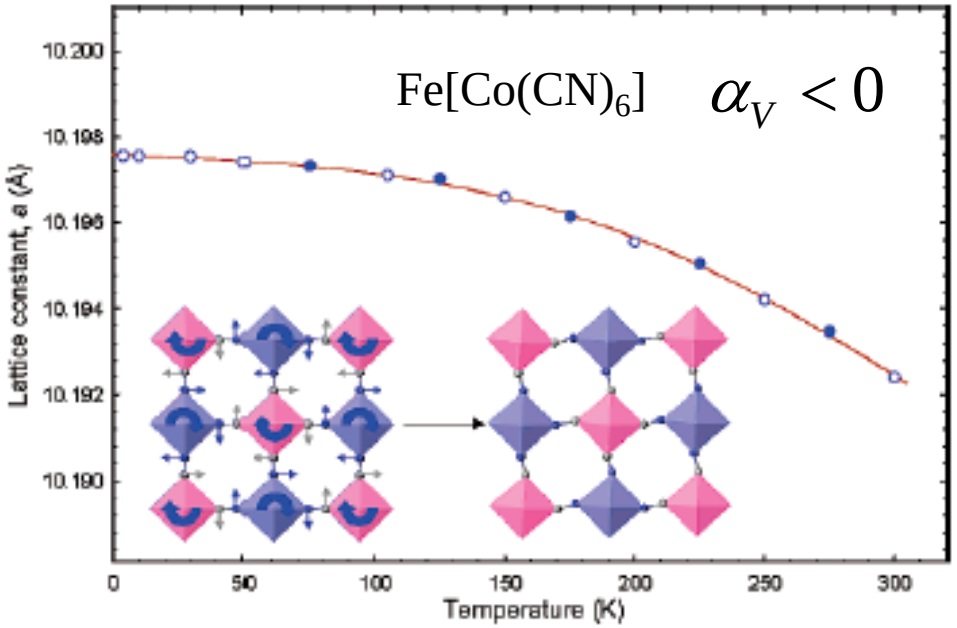


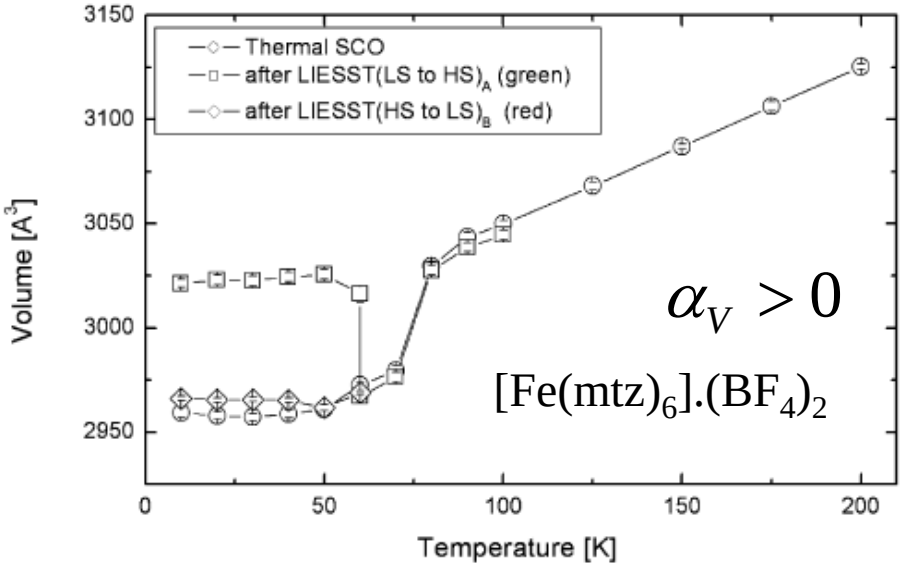


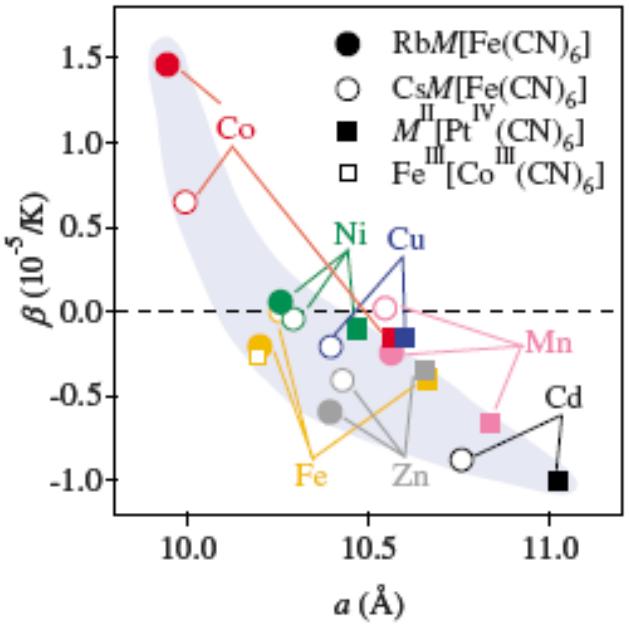
P. Guionneau *et al.*, *Phys. Rev.* (2005) **B72**, 214408

Isobaric expansion

$$\vec{x}(T) = \left[1 + \tilde{\tilde{\alpha}} \cdot (T - T_0) + \tilde{\tilde{\varepsilon}}_{HB} \cdot \gamma_{HS}(T)\right] \vec{x}_{BS}(T_0)$$







Matsuda et al. Phys. Rev B79, 172302 (2009)

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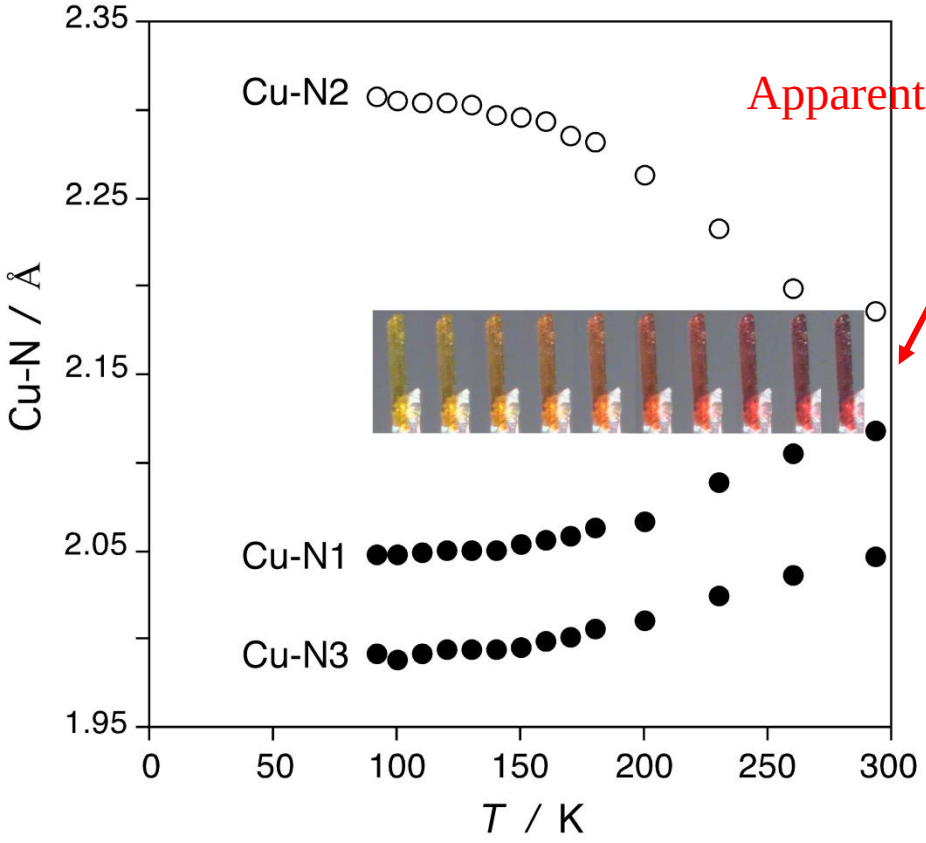
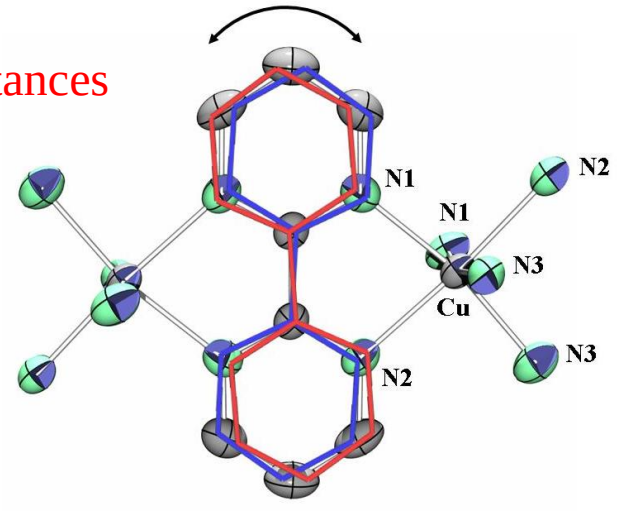
THANK
YOU

Average structure and local structure

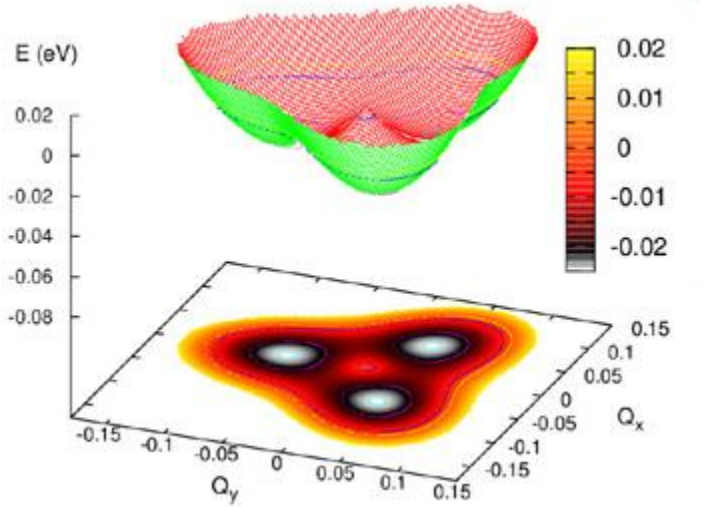


Apparent Cu-N distances



Dynamical Jahn-Teller effect

Potential energy surface



Vibronic coupling leads to a degeneracy between 3 nuclear configurations

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