The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
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Advanced School on Synchrotron and Free Electron Laser Sources and their Multidisciplinary Applications

7 - 25 April 2008

Single crystal crystallography (Basic Aspects)

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Basic crystallography for X-ray diffraction

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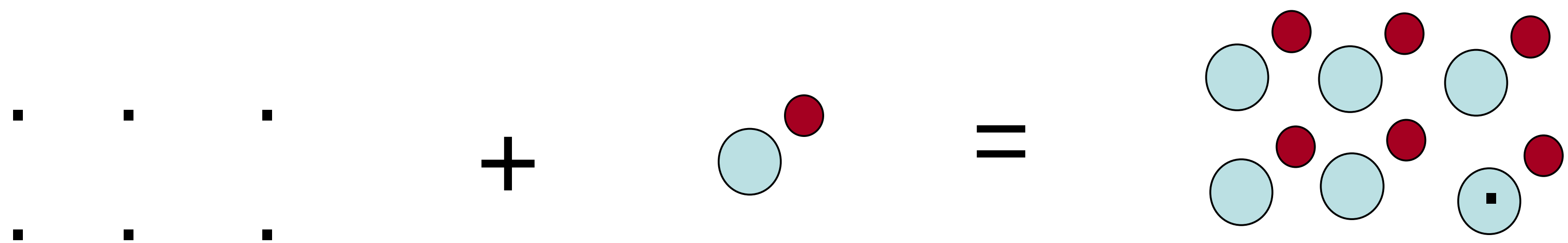
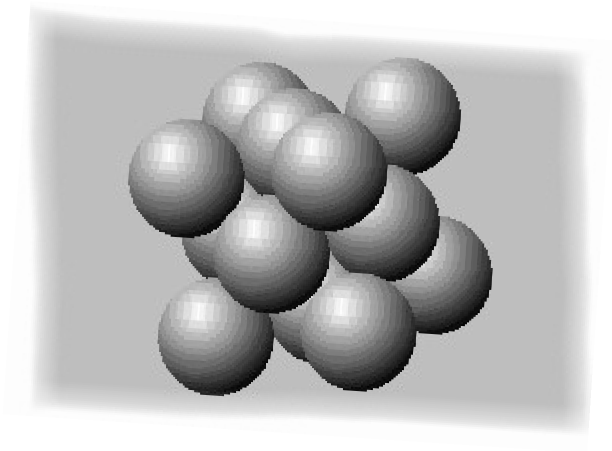
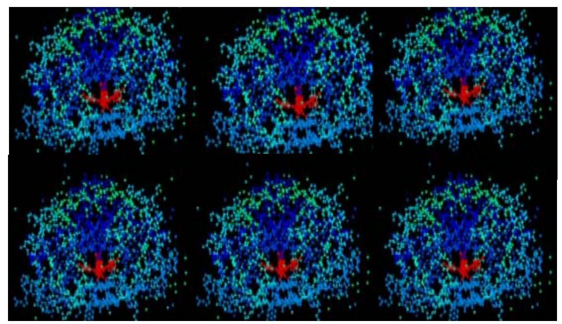
Point lattice + motif of atoms = Structure



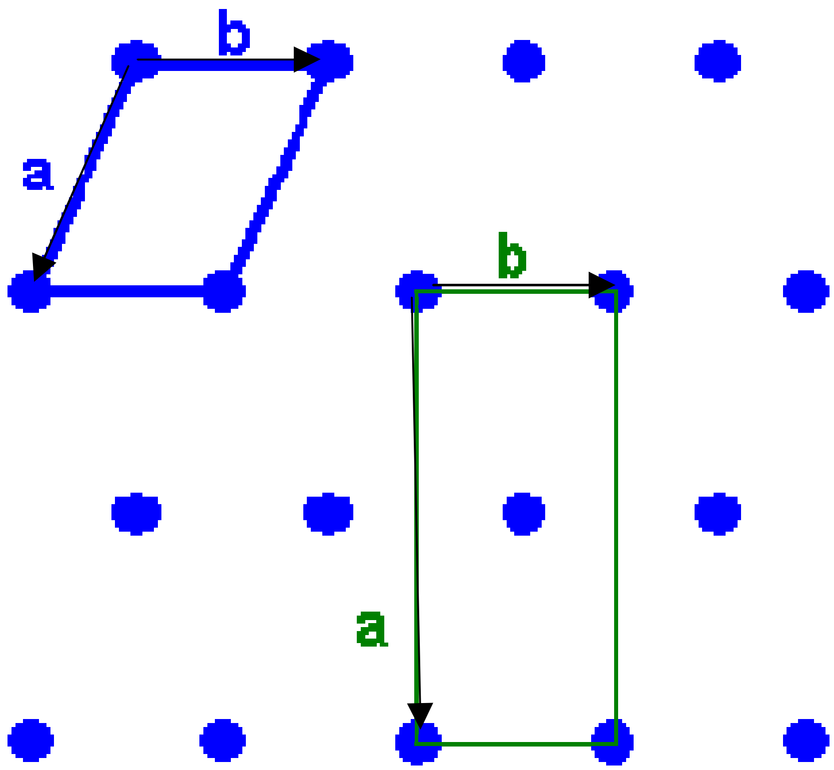


Cu, Au, Ag, …



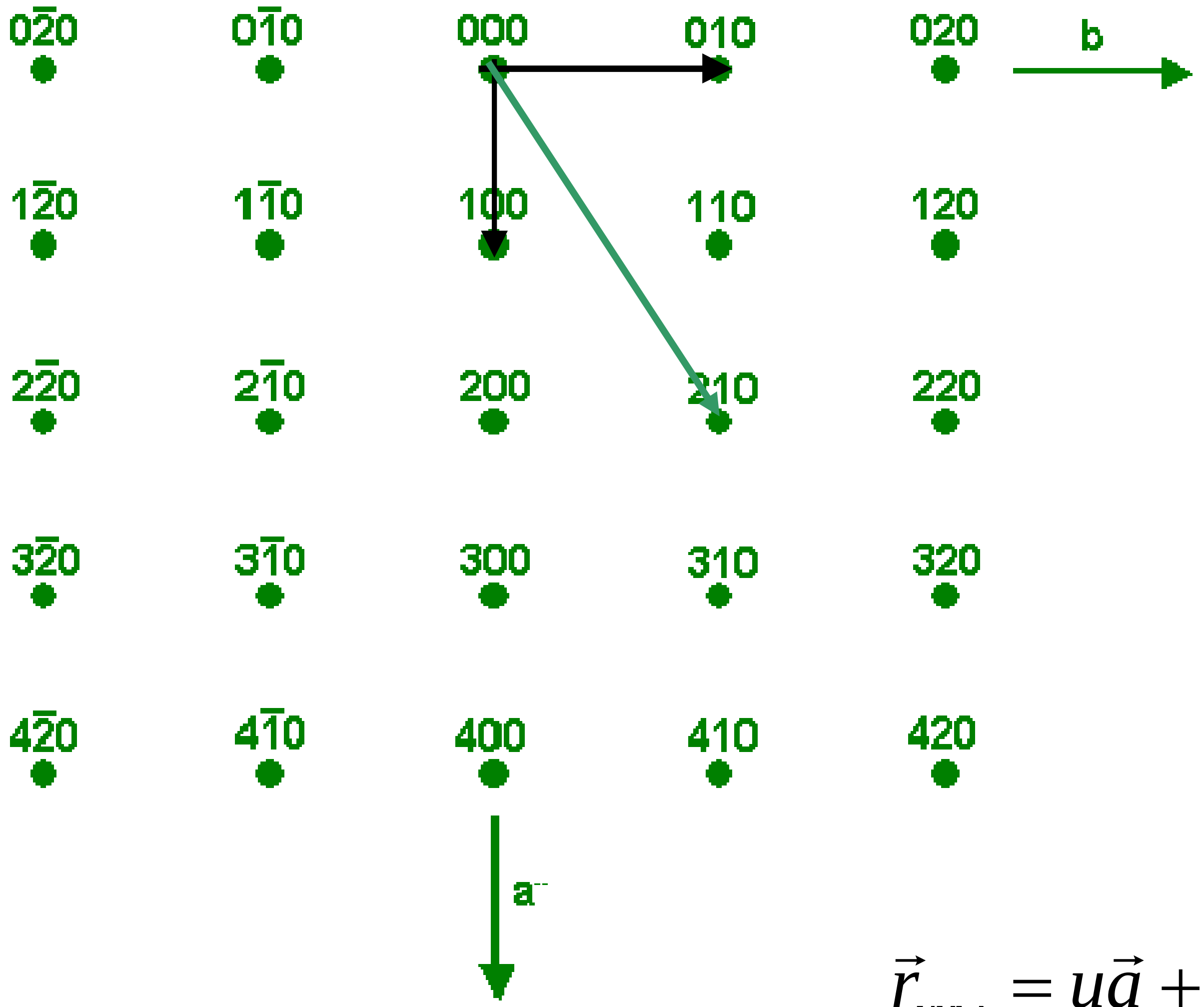
A protein crystal

Point lattices and unit cells



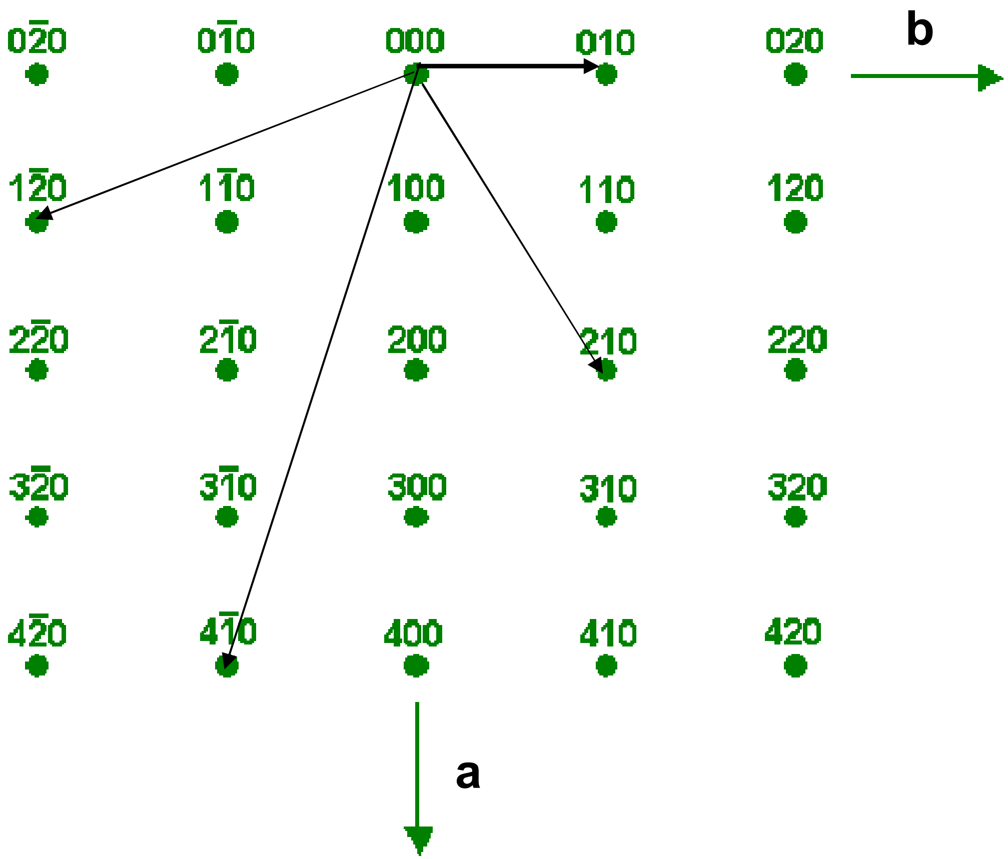
Primitive and non-primitive unit cells

Lattice points



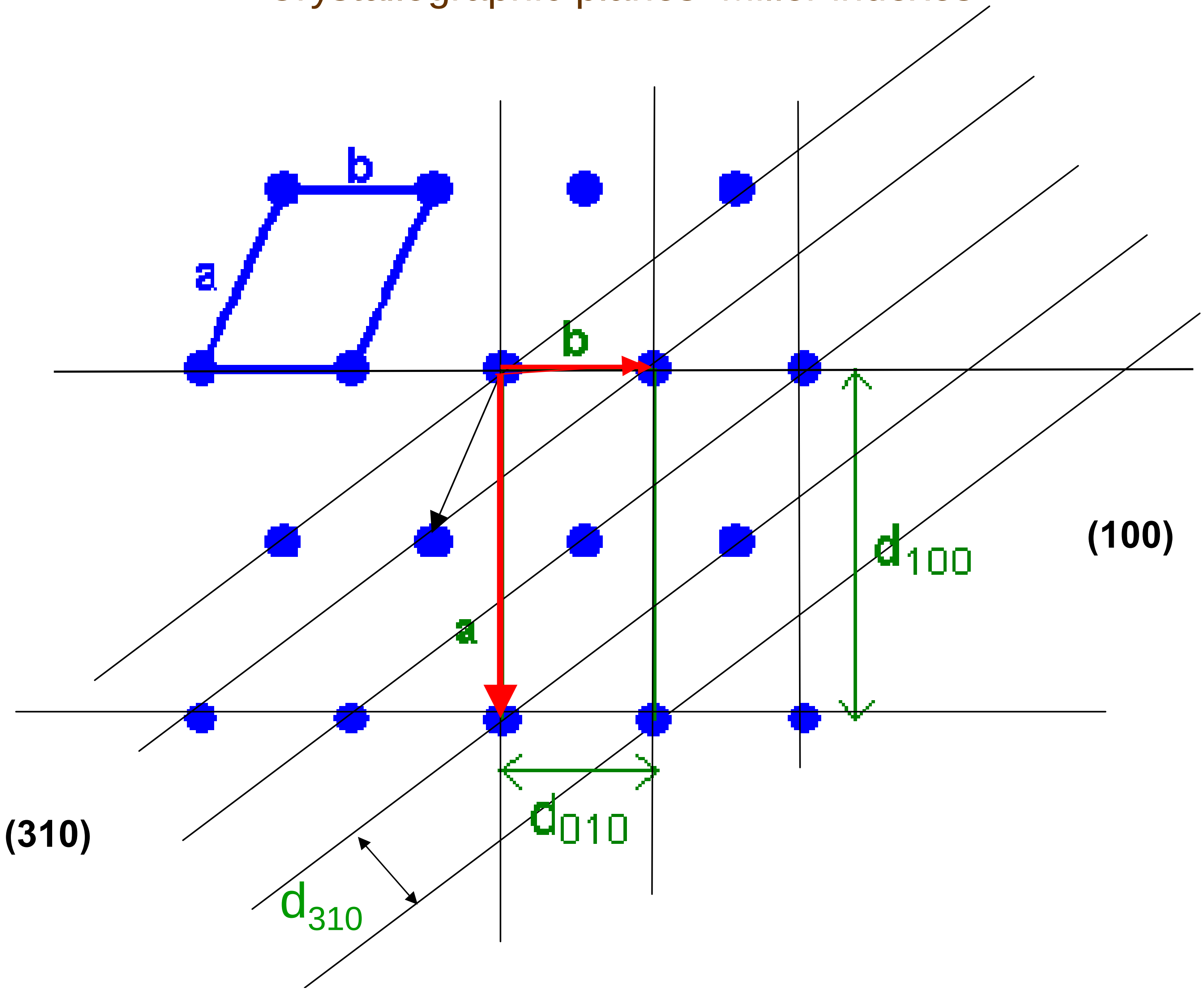
$$\vec{r}_{uvw} = u\vec{a} + v\vec{b} + w\vec{c}$$

Crystallographic directions

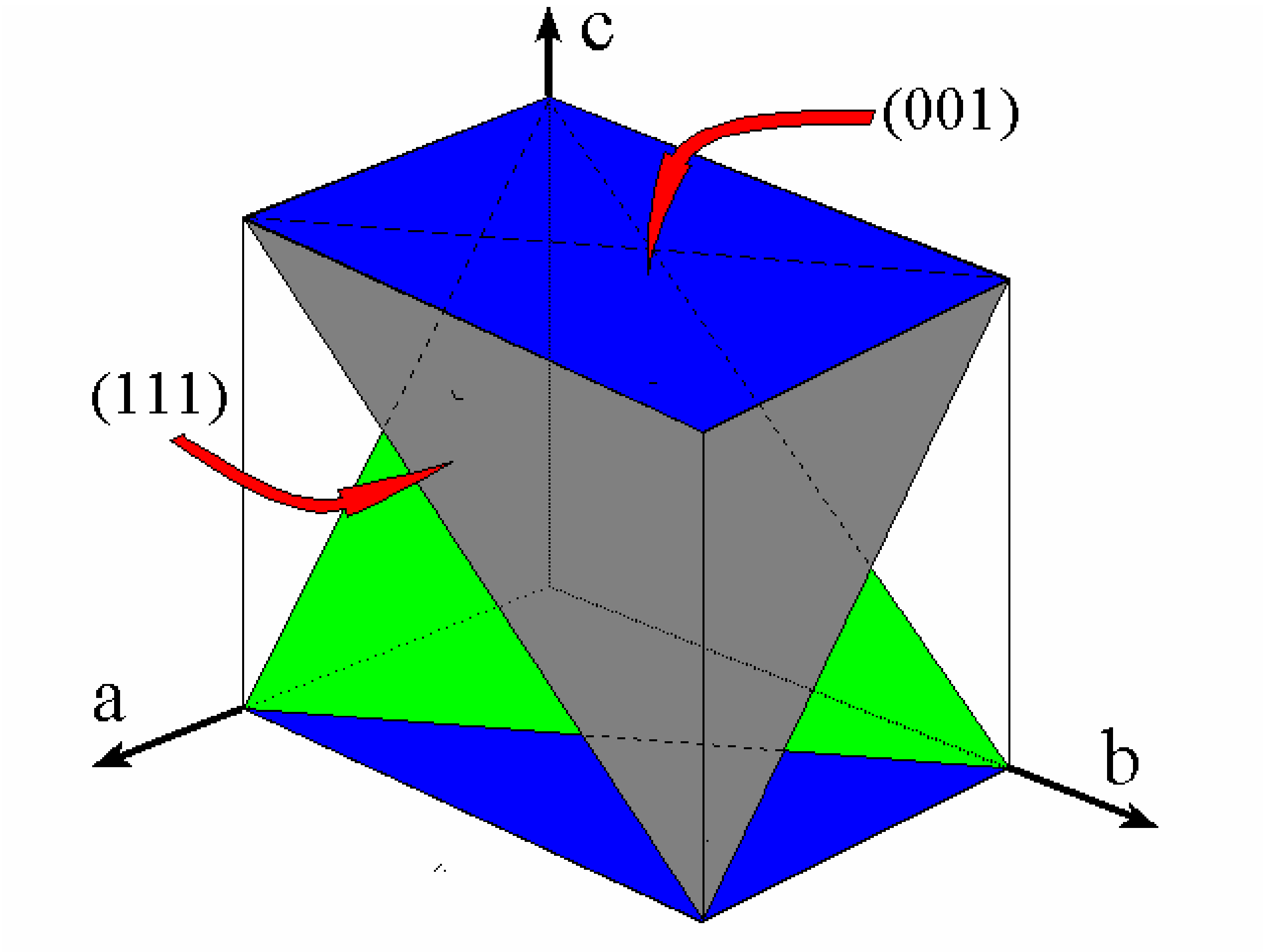


$$\vec{r}_{uvw} = u\vec{a} + v\vec{b} + w\vec{c}$$

Crystallographic planes Miller indexes



Miller indexes



Crystal systems
defined by the relationships between unit cell edge length and angles between these edges

- **Triclinic:** **$a \neq b \neq c$**
  $\alpha \neq \beta \neq \gamma$

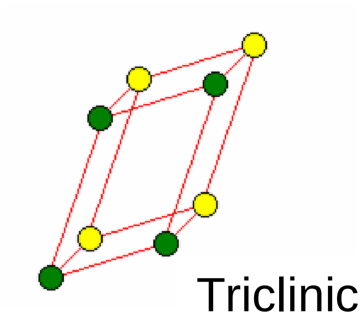
- **Monoclinic:** **$a \neq b \neq c$**
- $\alpha = \gamma = 90^o$ $\beta \neq$ **90^o**

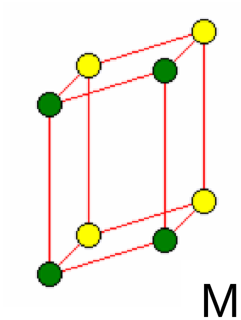
- **Orthorhombic:** **$a \neq b \neq c$**
  $\alpha = \beta = \gamma = 90^o$

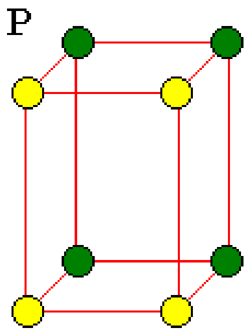
- **Tetragonal:** **$a = b \neq c$**
  $\alpha = \beta = \gamma = 90$

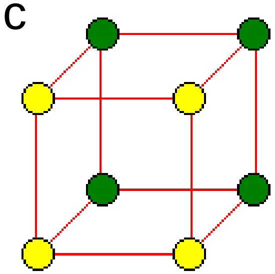
- **Hexagonal:** **$a = b = c$**
  $\alpha = \beta = 90^o$ $\gamma = 120^o$

- **Cubic:** **$a = b = c$**
  $\alpha = \beta = \gamma = 90^o$


Triclinic

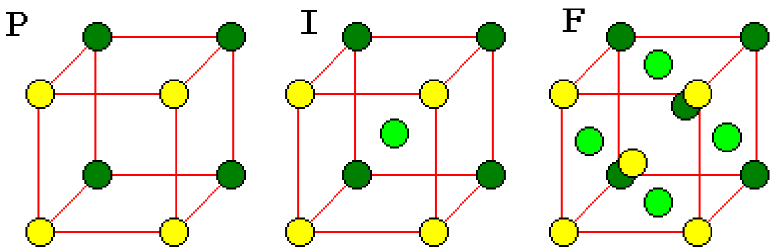

Monoclinic

Tetragonal


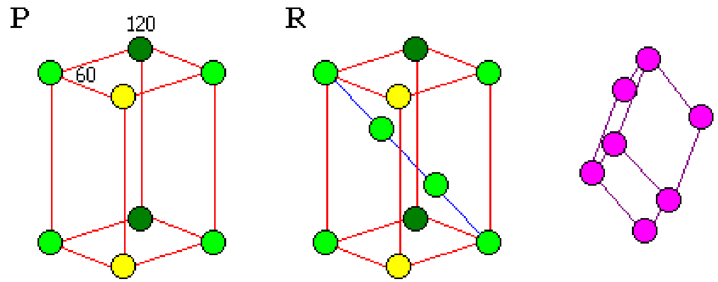
Cubic


Bravais lattices

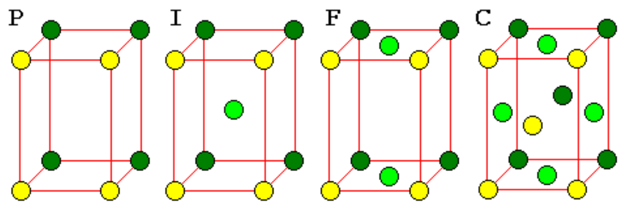
Cubic (3)



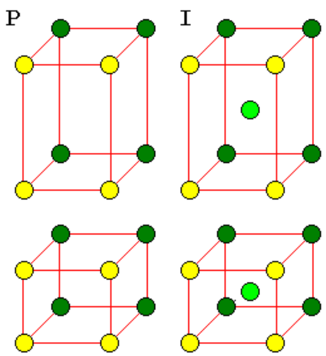
Hexagonal (2)



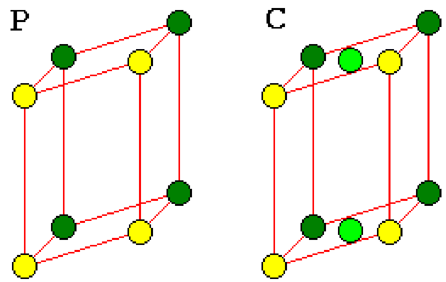
Tetragonal (4)



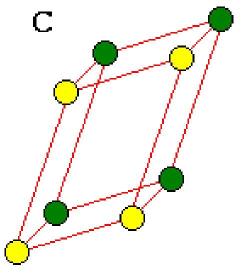
Orthorhombic (2)



Monoclinic (2)

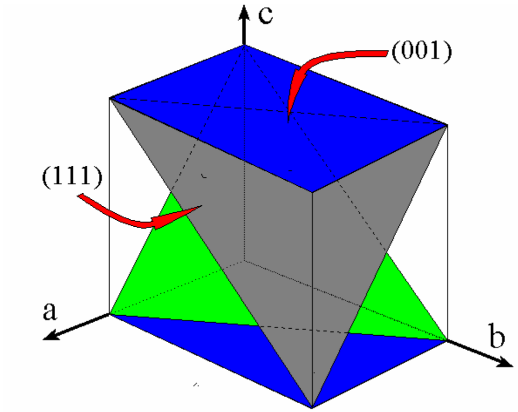


Triclinic (1)



Interplanar spacing d_{hkl} for the different crystal systems

Cubic: $$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$



Orthorhombic: $$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

Hexagonal: $$d_{hkl} = \frac{1}{\sqrt{\frac{4}{3a^2}(h^2 + hk + l^2) + \frac{l^2}{c^2}}}$$

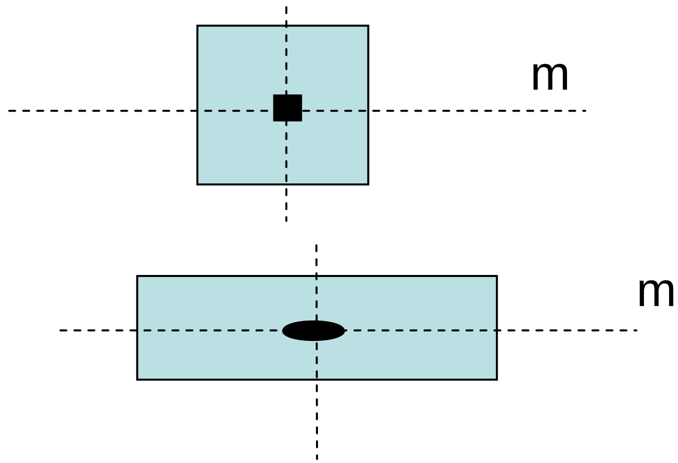
- etc

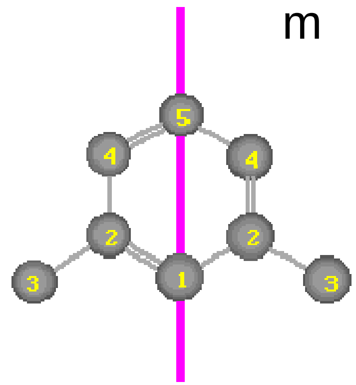
Symmetry properties

Point group operations

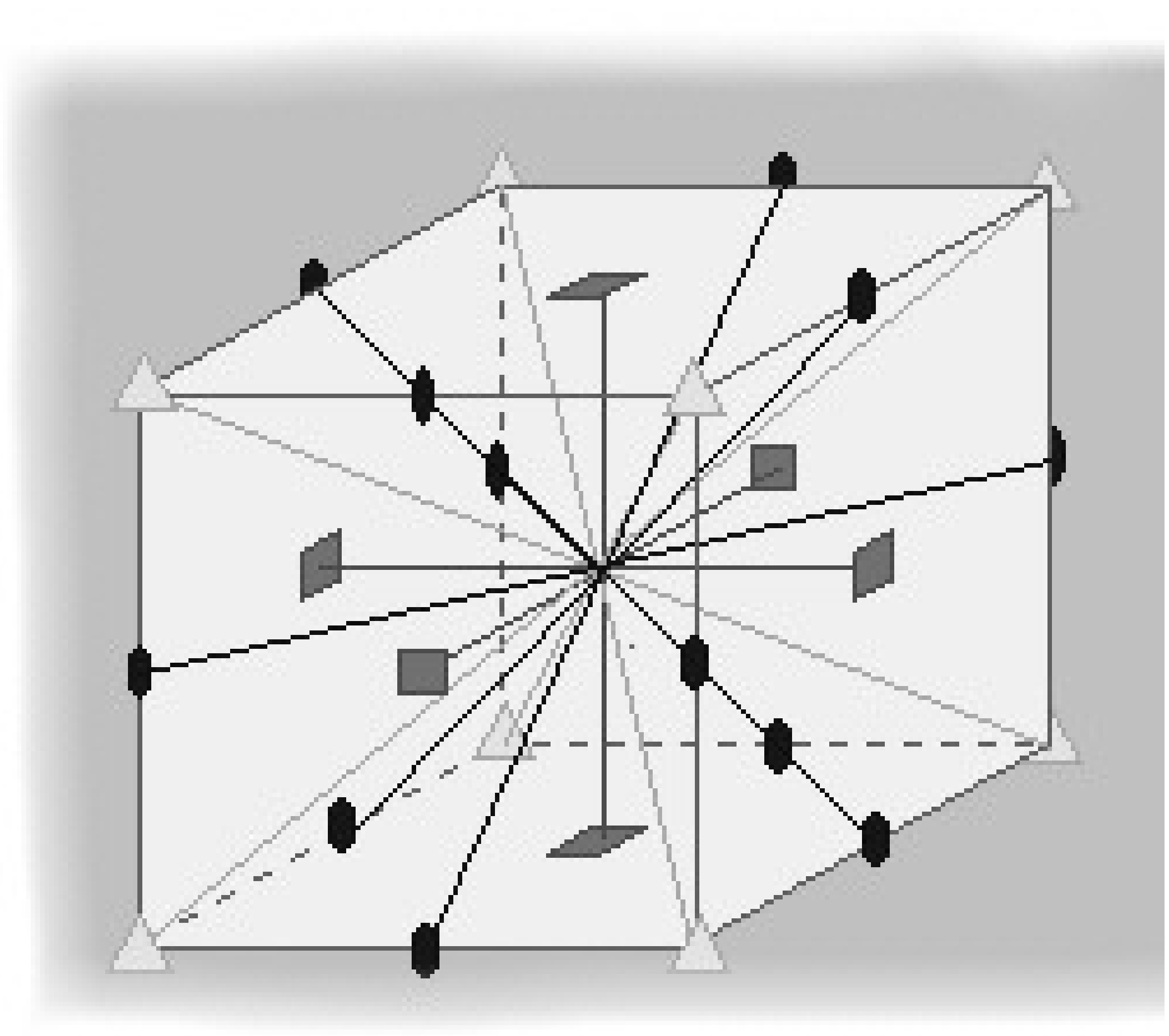
- Rotations 1, 2, 3, 4, 6
- Mirrors m
- Inversion: i
- Rotation-inversion $\bar{2}$

…





Symmetry operations



9 mirror planes

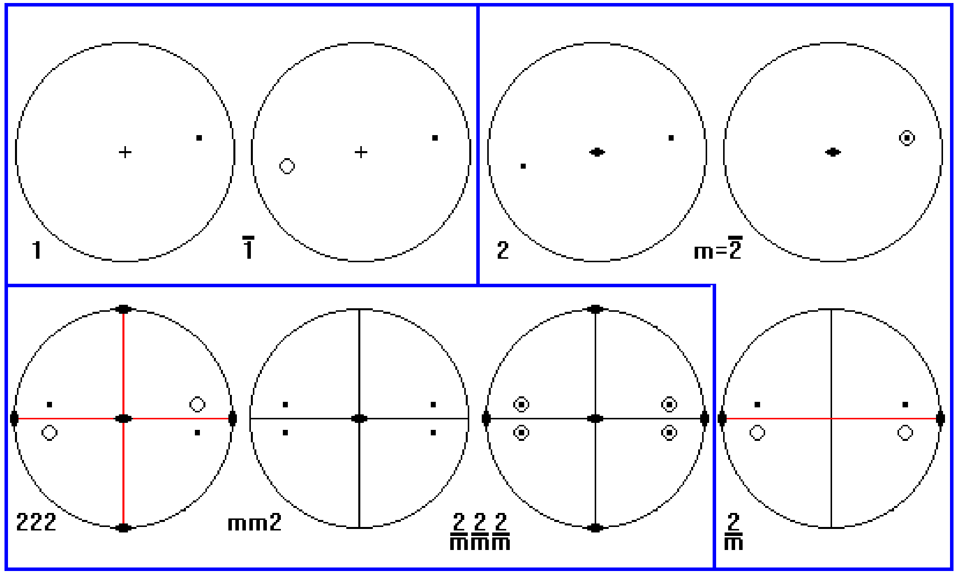
3 tetrad axes

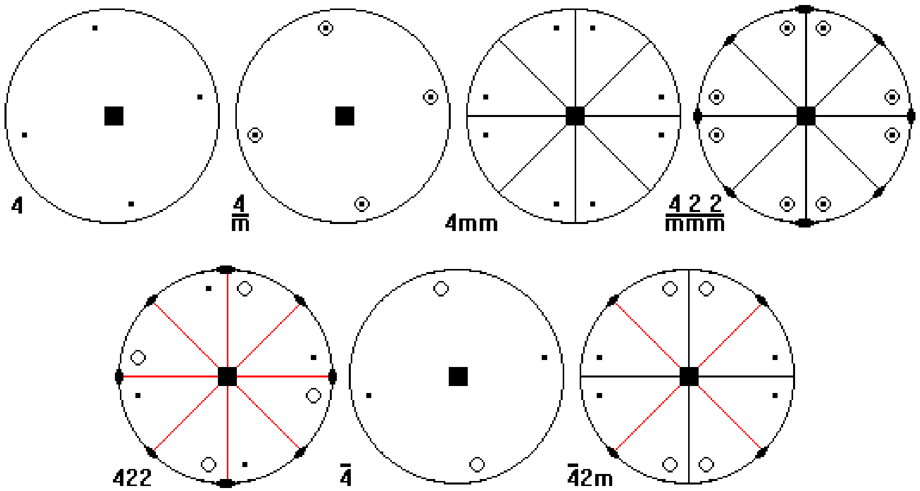
4 triad axes

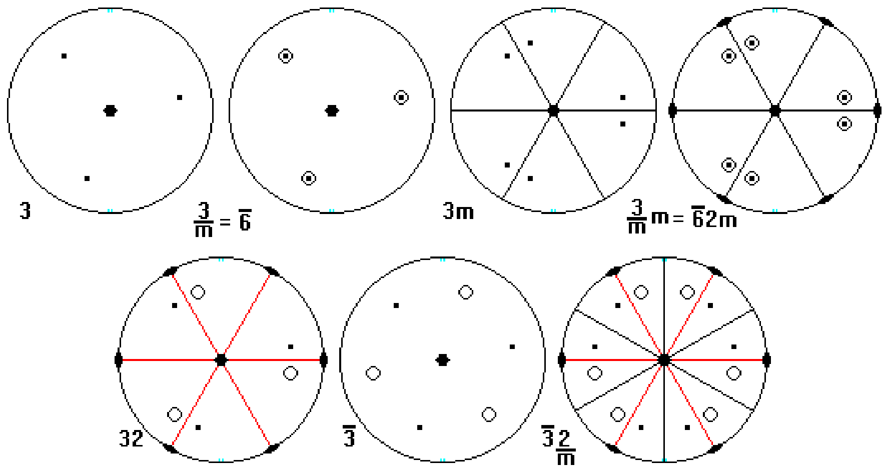
6 diad axes

32 crystallographic point groups

Triclinic,
Monoclinic and
orthorombic





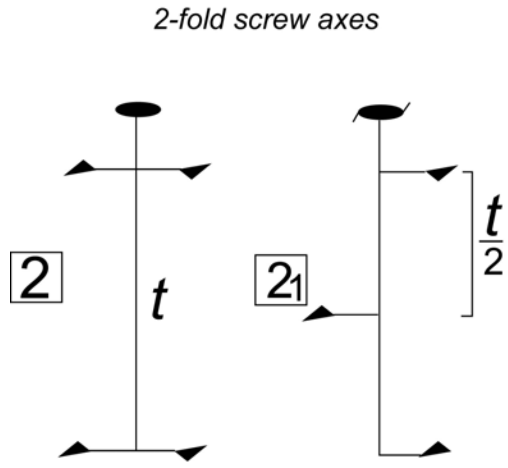


Tetragonal

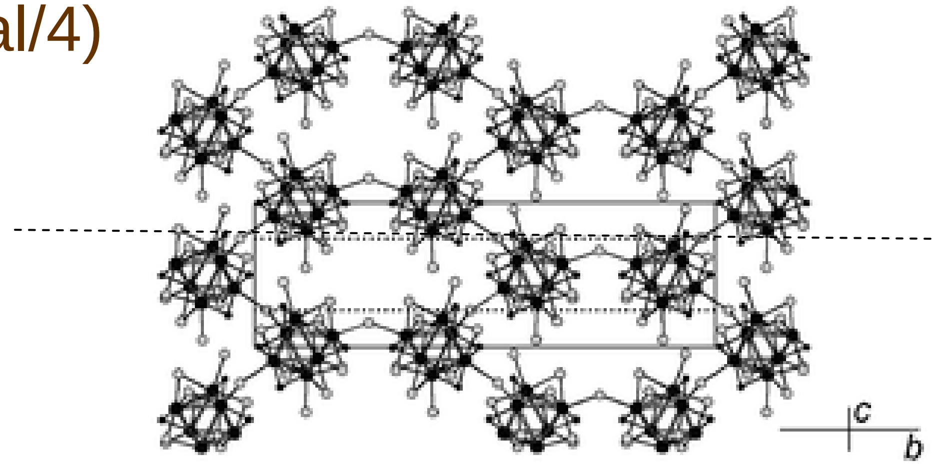
Hexagonal (Trigonal)

Translational symmetry operations

- Screw axis
- (Examples: 2_1, 4_1, 4_2 ...)



- Glide plane a/2, b/2, c/2, n (2D diagonal/2), d (3D diagonal/4)



230 space groups

- **Triclinic**

1. *P* 1   2. *P* -1

- **Monoclinic**

3. *P* 1 2 1   4. *P* 1 21 1   5. *C* 1 2 1

6. *P* 1 *m* 1   7. *P* 1 *c* 1   8. *C* 1 *m* 1

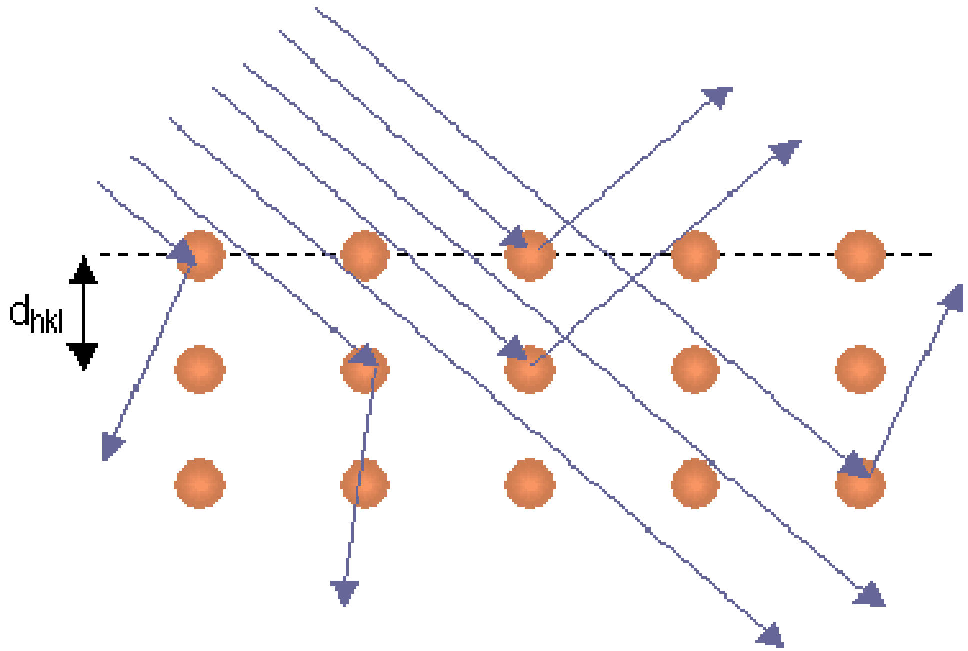
9. *C* 1 *c* 1   10. *P* 1 2 / *m* 1   11. *P* 1 21 / *m*1

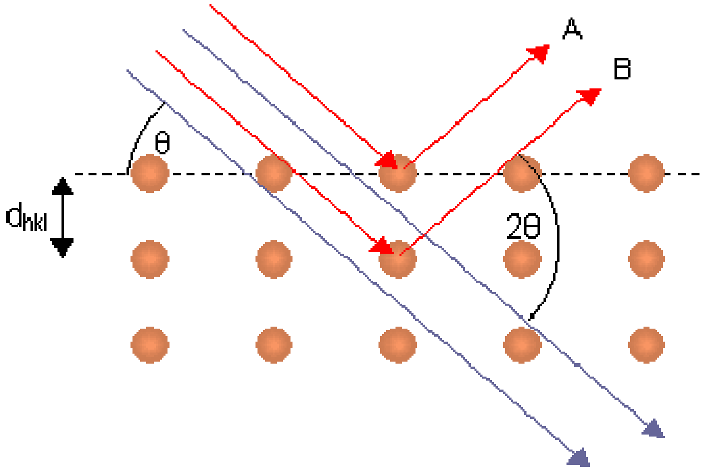
12. *C* 1 2 / *m* 1   13. *P* 1 2 / *c* 1

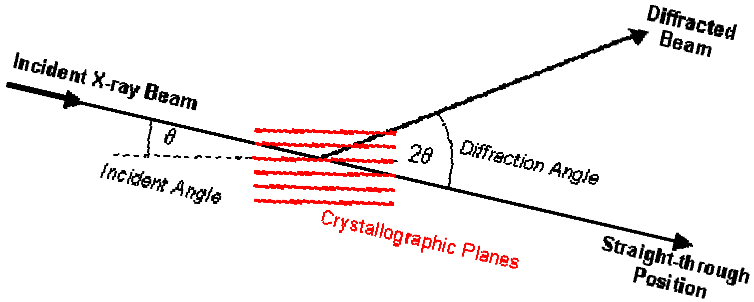
14. *P* 1 21 / *c* 1   15. *C* 1 2 / *c* 1

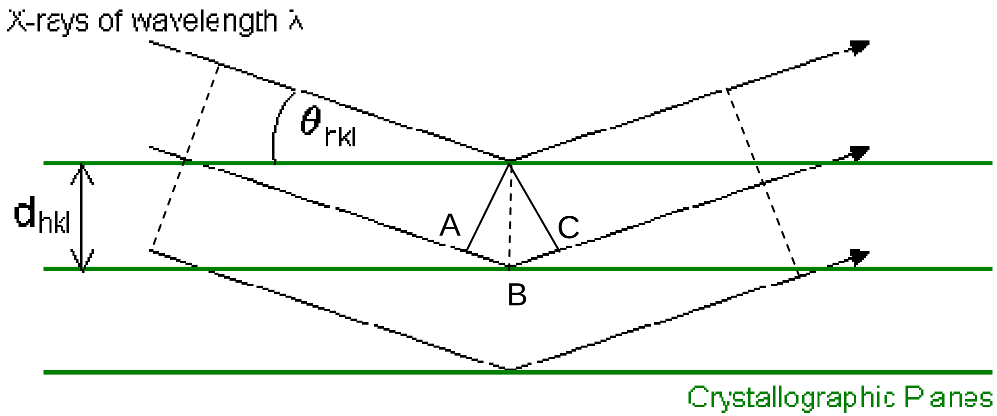
- **Cubic**

195. *P* 2 3	196. *F* 2 3	197. *I* 2 3
198. *P* 21 3	199. *I* 21 3	200. *P m* -3
201. *P n* -3	202. *F m* -3	203. *F d* -3
204. *I m* -3	205. *P a* -3	206. *I a* -3
207. *P* 4 3 2	208. *P* 42 3 2	209. *F* 4 3 2
210. *F* 41 3 2	211. *I* 4 3 2	212. *P* 43 3 2
213. *P* 41 3 2	214. *I* 41 3 2	215. *P* -4 3 *m*
216. *F* -4 3 *m*	217. *I* -4 3 *m*	218. *P* -4 3 *n*
219. *F* -4 3 *c*	220. *I* -4 3 *d*	221. *P m* -3 *m*
222. *P n* -3 *n*	223. *P m* -3 *n*	224. *P n* -3 *m*
225. *F m* -3 *m*	226. *F m* -3 *c*	227. *F d* -3 *m*
228. *F d* -3 *c*	229. *I m* -3 *m*	230. *I a* -3 *d*


d_{hkl}







$$\overline{AB} + \overline{BC} = 2d_{hkl} \sin\theta_{hkl} = n\lambda$$

Bragg law : $\boxed{2d_{hkl} \sin\theta_{hkl} = n\lambda}$

Reciprocal lattice

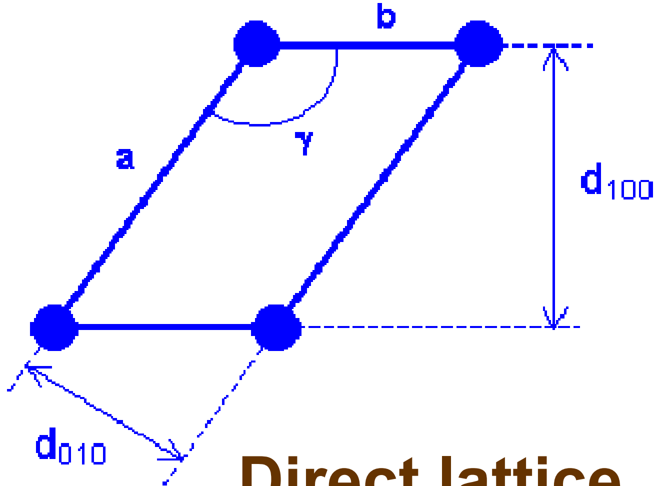
Let be a direct lattice defined by $\vec{r}_{uvw} = u.\vec{a} + v.\vec{b} + w.\vec{c}$

Definitions of the unit vectors of the reciprocal lattice:

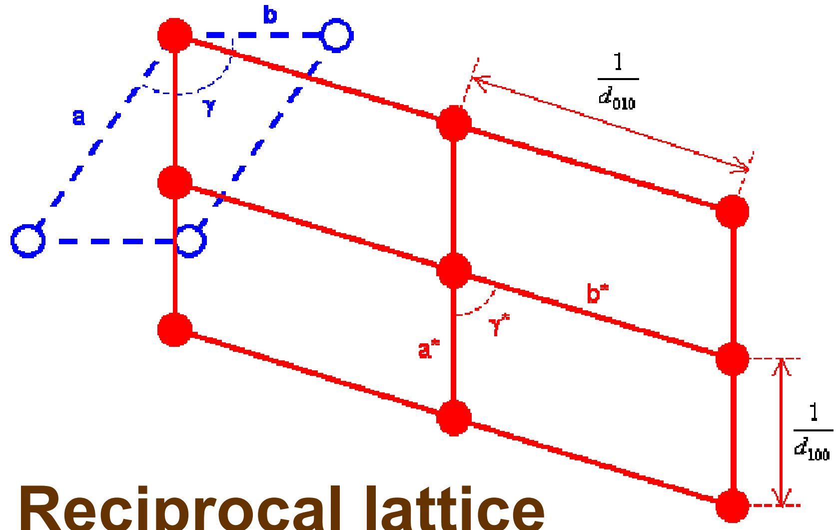
$$\vec{a}^* = \frac{\vec{b} x \vec{c}}{V_c} \qquad \vec{b}^* = \frac{\vec{c} x \vec{a}}{V_c} \qquad \vec{c}^* = \frac{\vec{a} x \vec{b}}{V_c}$$

Reciprocal space vector: $\vec{s} = s_x.\vec{a}^* + s_y.\vec{b}^* + s_z.\vec{c}^*$

Reciprocal lattice vector: $\vec{r}^*_{hkl} = h.\vec{a}^* + k.\vec{b}^* + l.\vec{c}^*$ h, k, l integers



Direct lattice



Reciprocal lattice

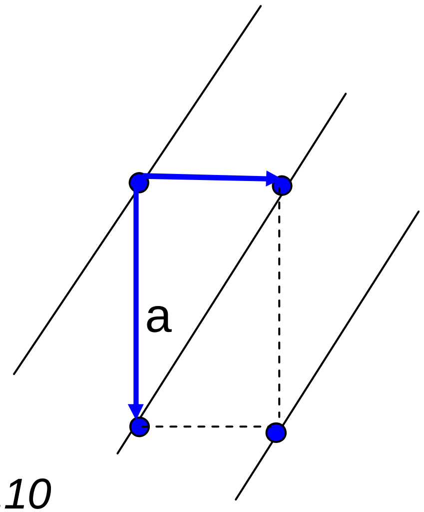
Properties

i) $\vec{a}.\vec{a}^* = 1 \qquad \vec{b}^*.\vec{b} = 1 \qquad \vec{c}^*.\vec{c} = 1$

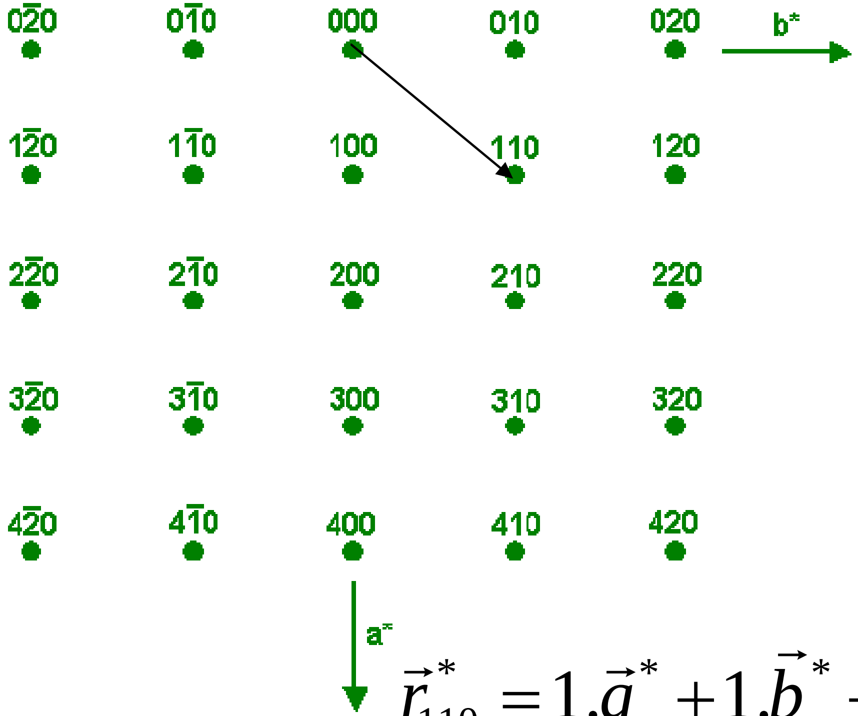
ii) $\vec{a}^*\vec{b} = 0 \qquad \vec{b}^*\vec{c} = 0 \qquad \vec{a}^*\vec{c} = 0$

iii) $\boxed{\vec{r}^{\,*}_{hkl} = h.\vec{a}^* + k.\vec{b}^* + l.\vec{c}^* \quad \text{is perpendicular to the planes (hkl)}}$

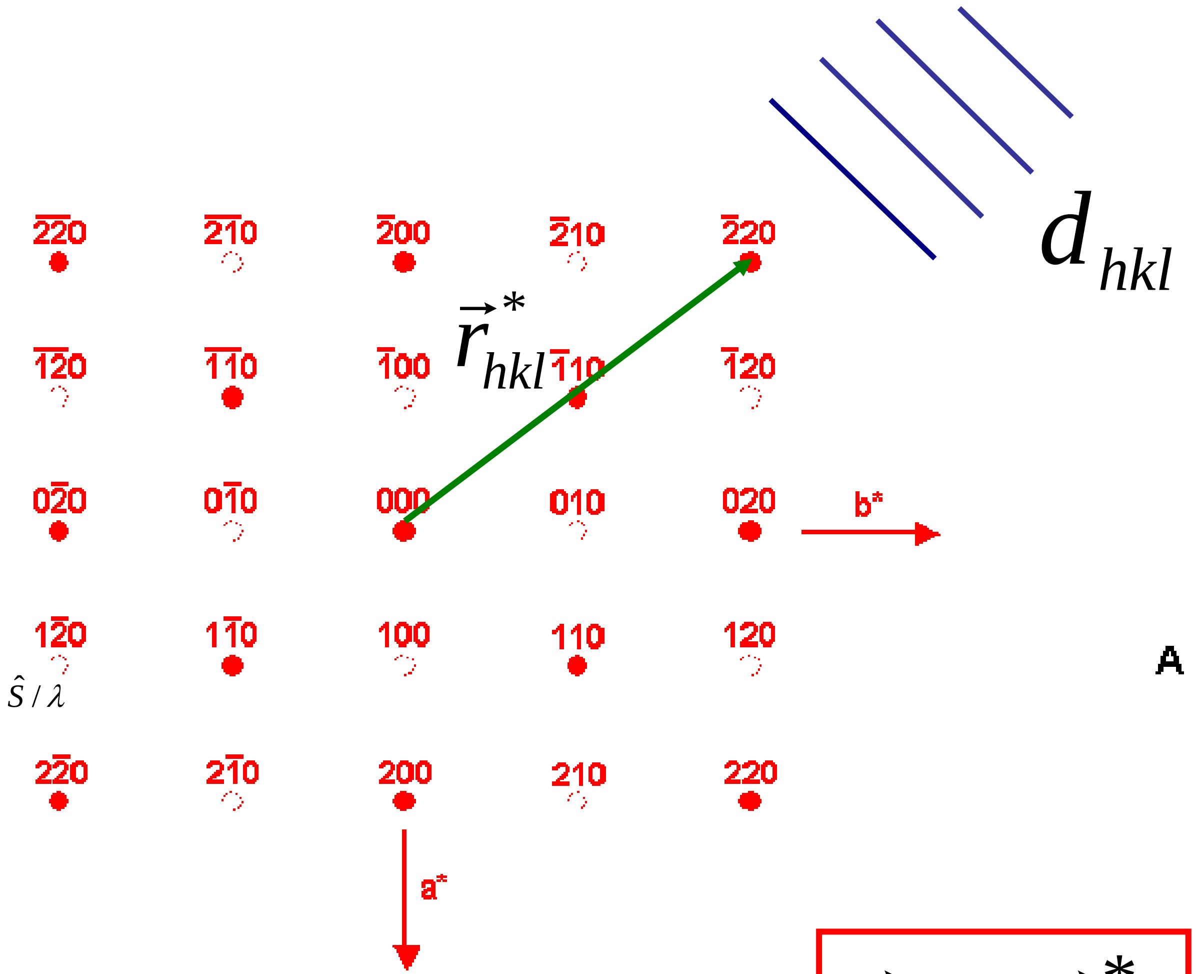
iv) $\boxed{d_{hkl} = 1/\vec{r}^{\,*}_{hkl}}$



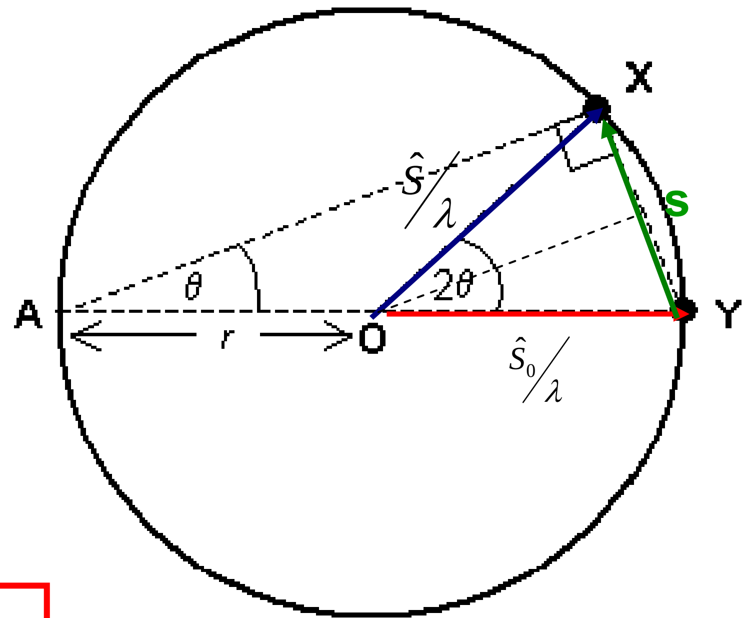
d_{110}



$$\vec{r}^{\,*}_{110} = 1.\vec{a}^* + 1.\vec{b}^* + 0.\vec{c}^*$$



Ewald construction



Bragg law in reciprocal space:

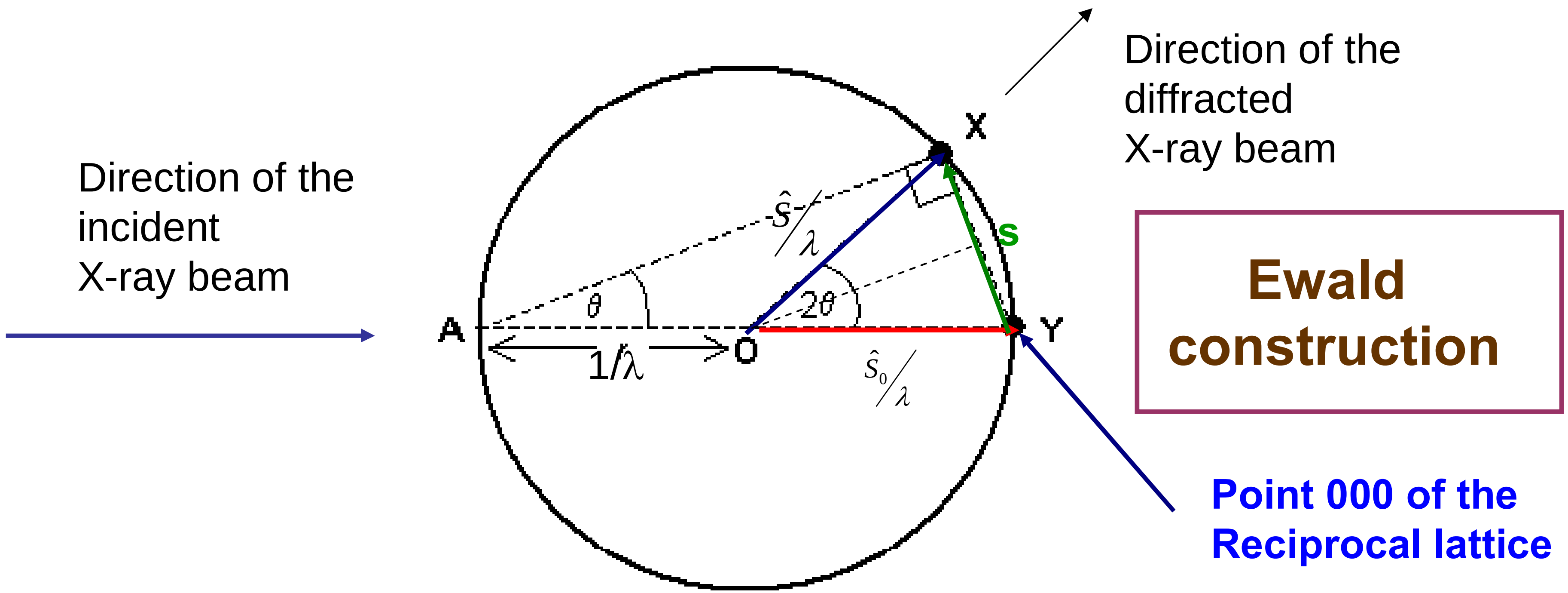
$$\boxed{\vec{s} = \vec{r}^{\,*}_{hkl}}$$

... is equivalent to:

$$\boxed{\lambda = 2.d_{hkl}.\sin\theta_{hkl}}$$

(classical Bragg law)

Ewald construction



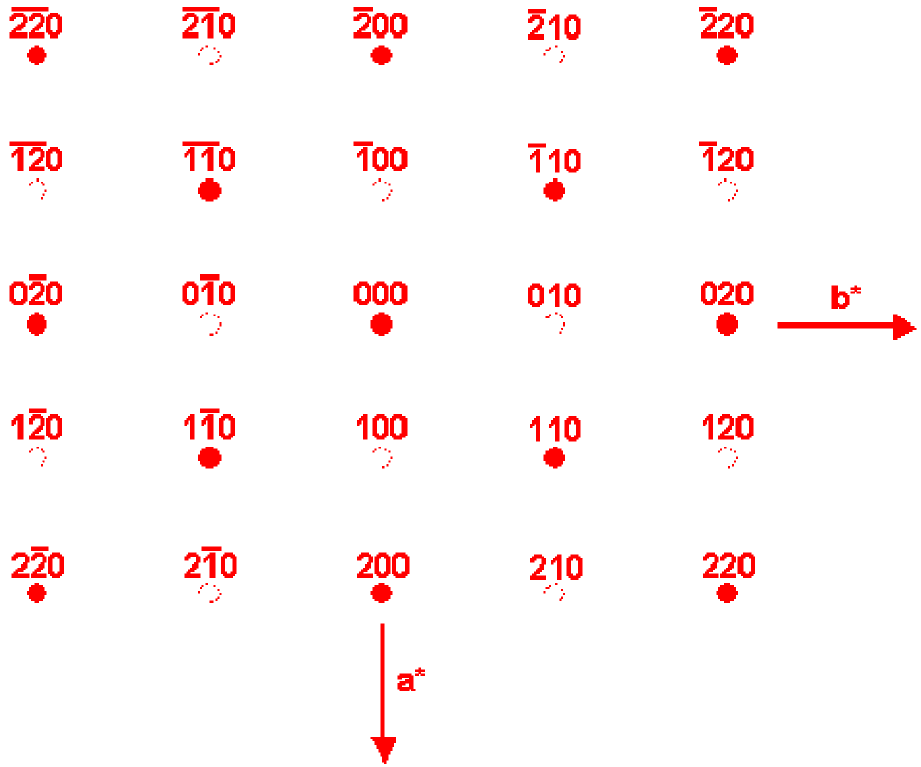
If $\boxed{\vec{s} = \vec{r}^{\,*}_{hkl}}$ **(Bragg law in the reciprocal space)**

$$2.\frac{1}{\lambda}.\sin\theta_{hkl} = \left|\vec{r}^{\,*}_{hkl}\right| = \frac{1}{d_{hkl}} \longrightarrow \boxed{2.d_{hkl}\sin\theta_{hkl} = \lambda}$$

(Bragg law in the direct space)

Application of Bragg law in reciprocal space

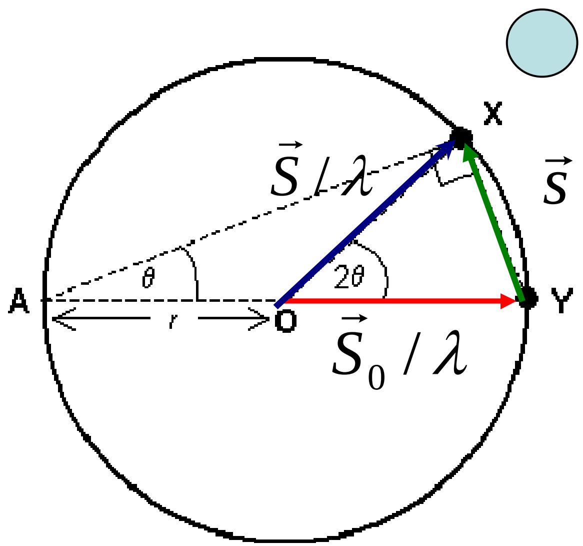
($\vec{s} = \vec{r}^{\,*}_{hkl}$) : **Ewald construction**



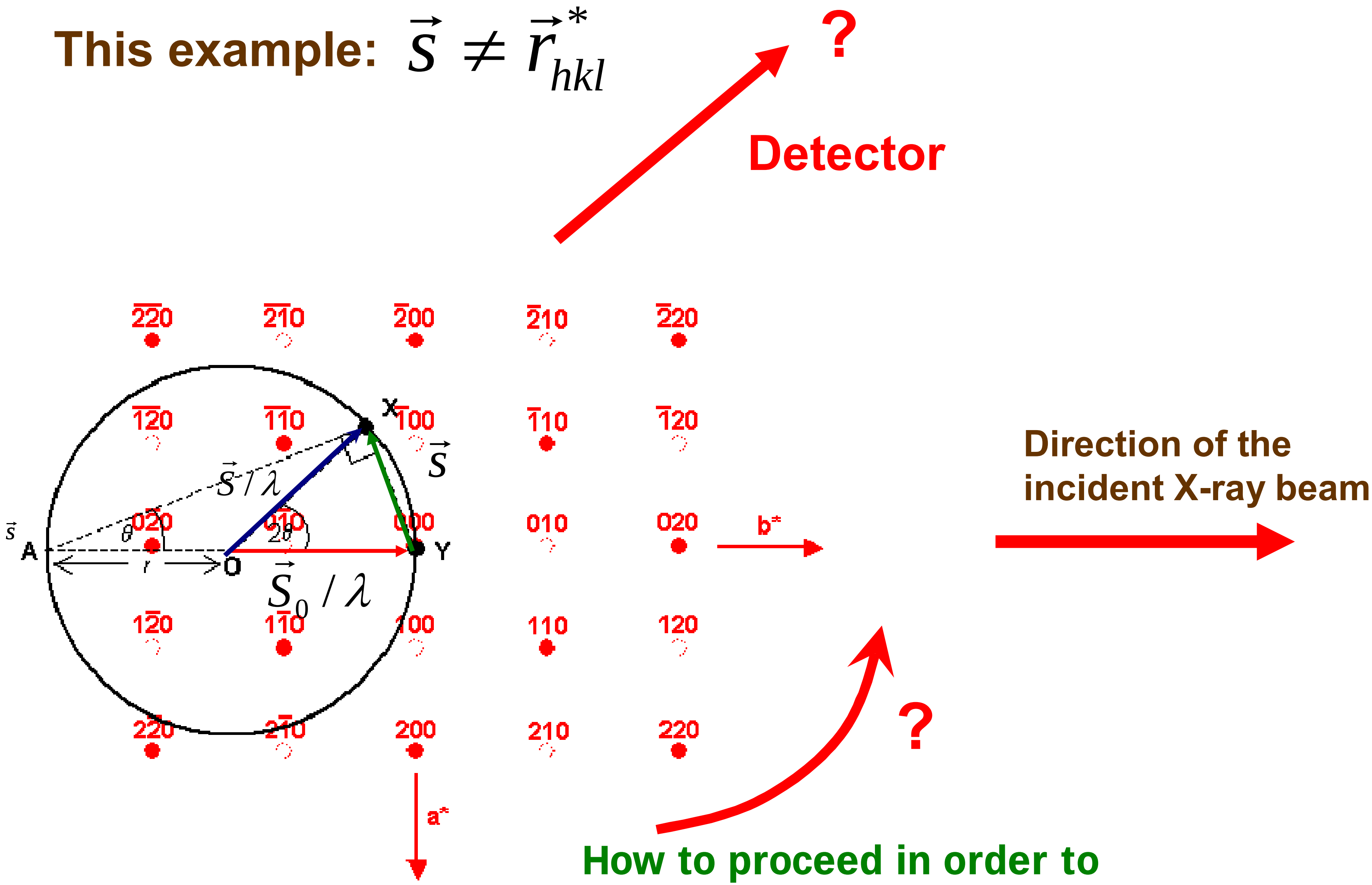
$\vec{s}$

Direction of the incident X-ray beam

Detector

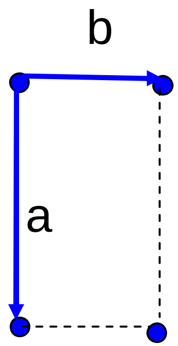


This example: $\vec{S} \neq \vec{r}^{\,*}_{hkl}$



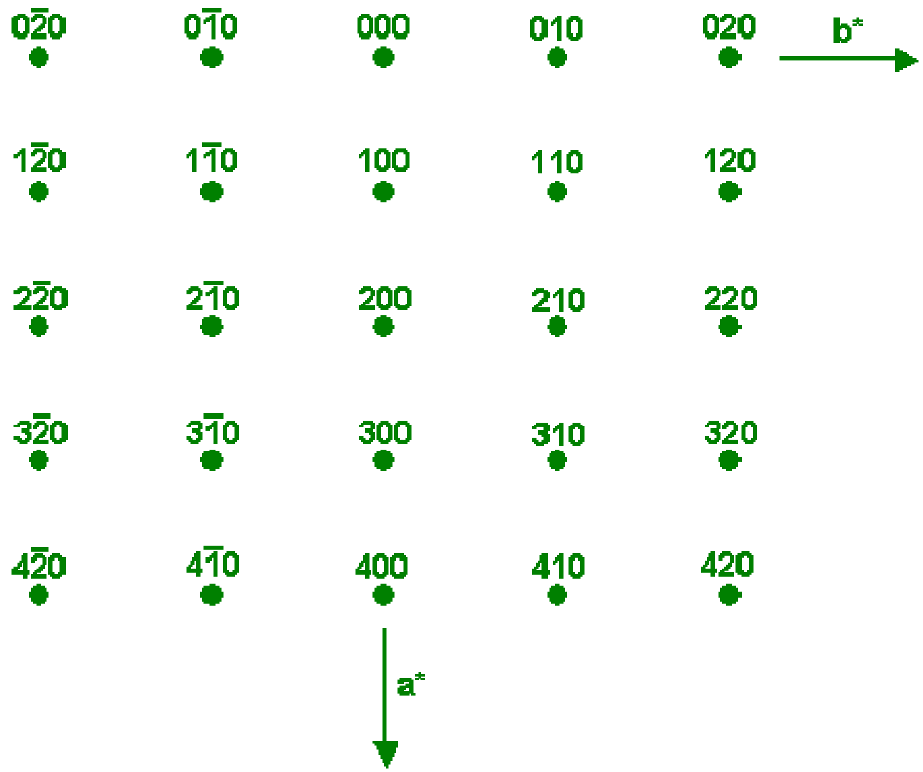
How to proceed in order to determine the right crystal orientation and angular position of the X-ray detector to satisfy Bragg conditions?

Ewald construction   Step 1



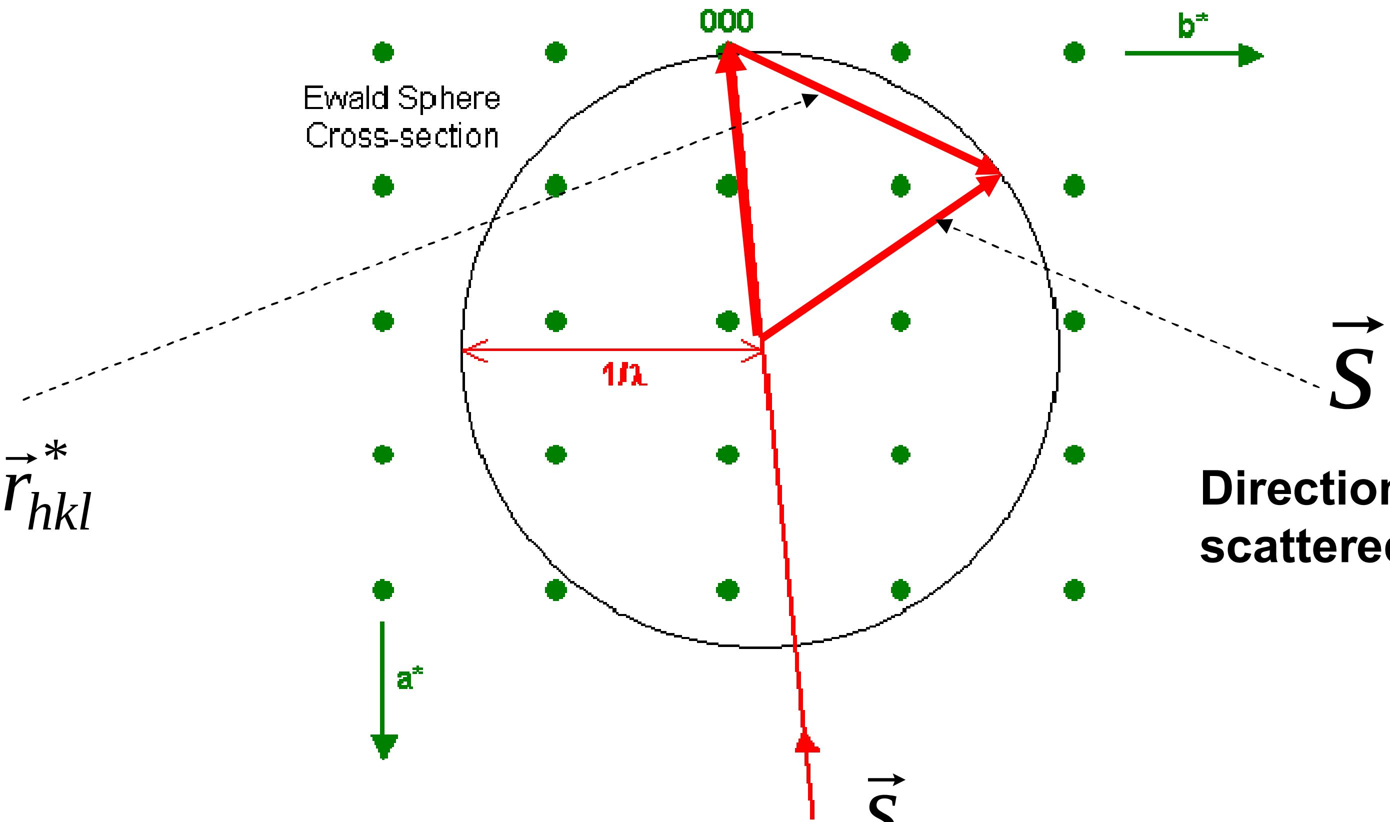
Direct unit cell

- Ewald construction   Step 2



$$\vec{a}^* = \frac{\vec{b}x\vec{c}}{V_c} \qquad \vec{b}^* = \frac{\vec{c}x\vec{a}}{V_c} \qquad \vec{c}^* = \frac{\vec{a}x\vec{b}}{V_c}$$

Ewald construction   Step 3



$\vec{s} \neq \vec{r}^{\,*}_{hkl}$

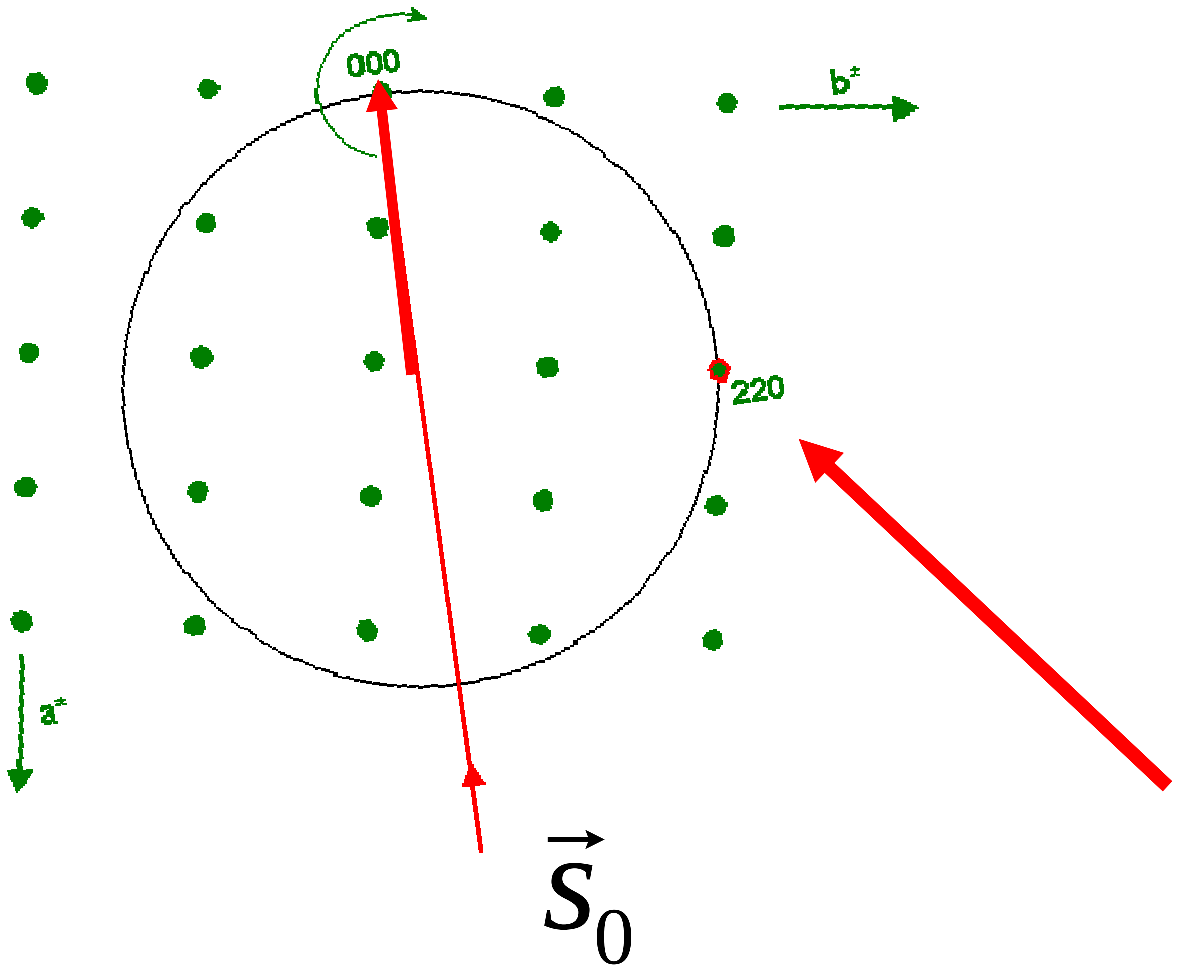
$\vec{S}$

Direction of the scattered beam

$\vec{S}_0$

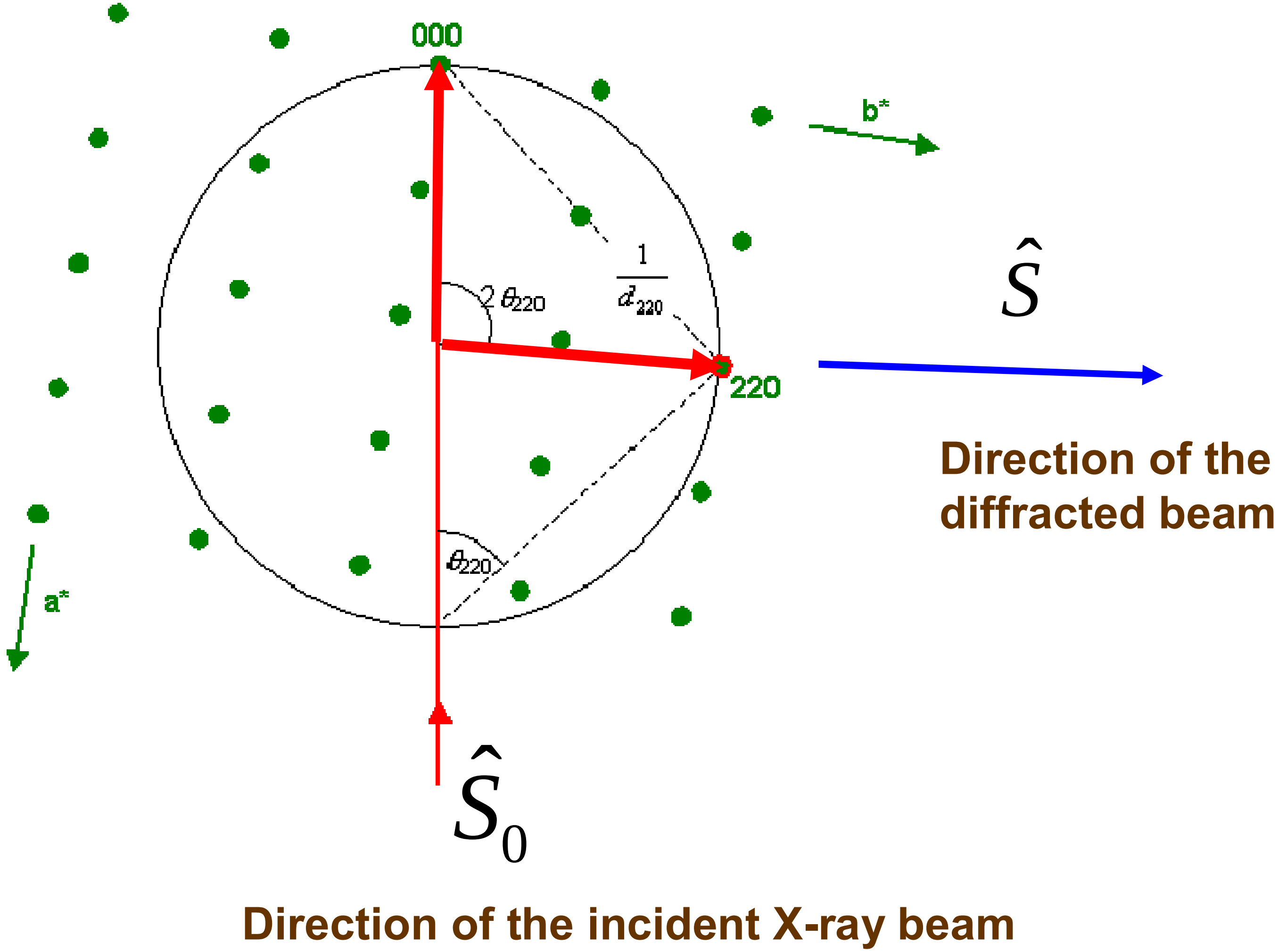
Direction of the incident X-ray beam

- **Ewald construction   Step 4**

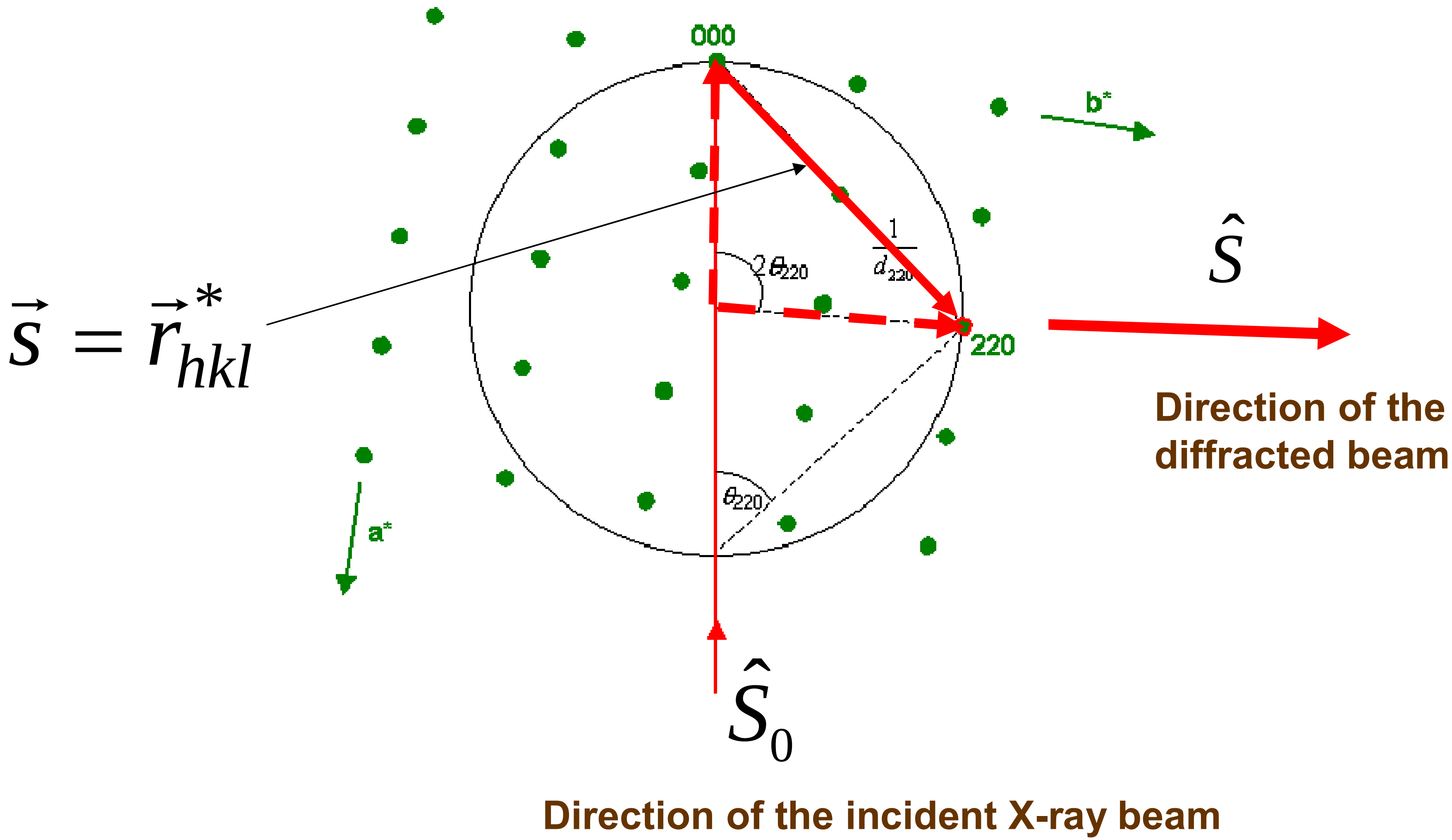


Direction of the incident X-ray beam

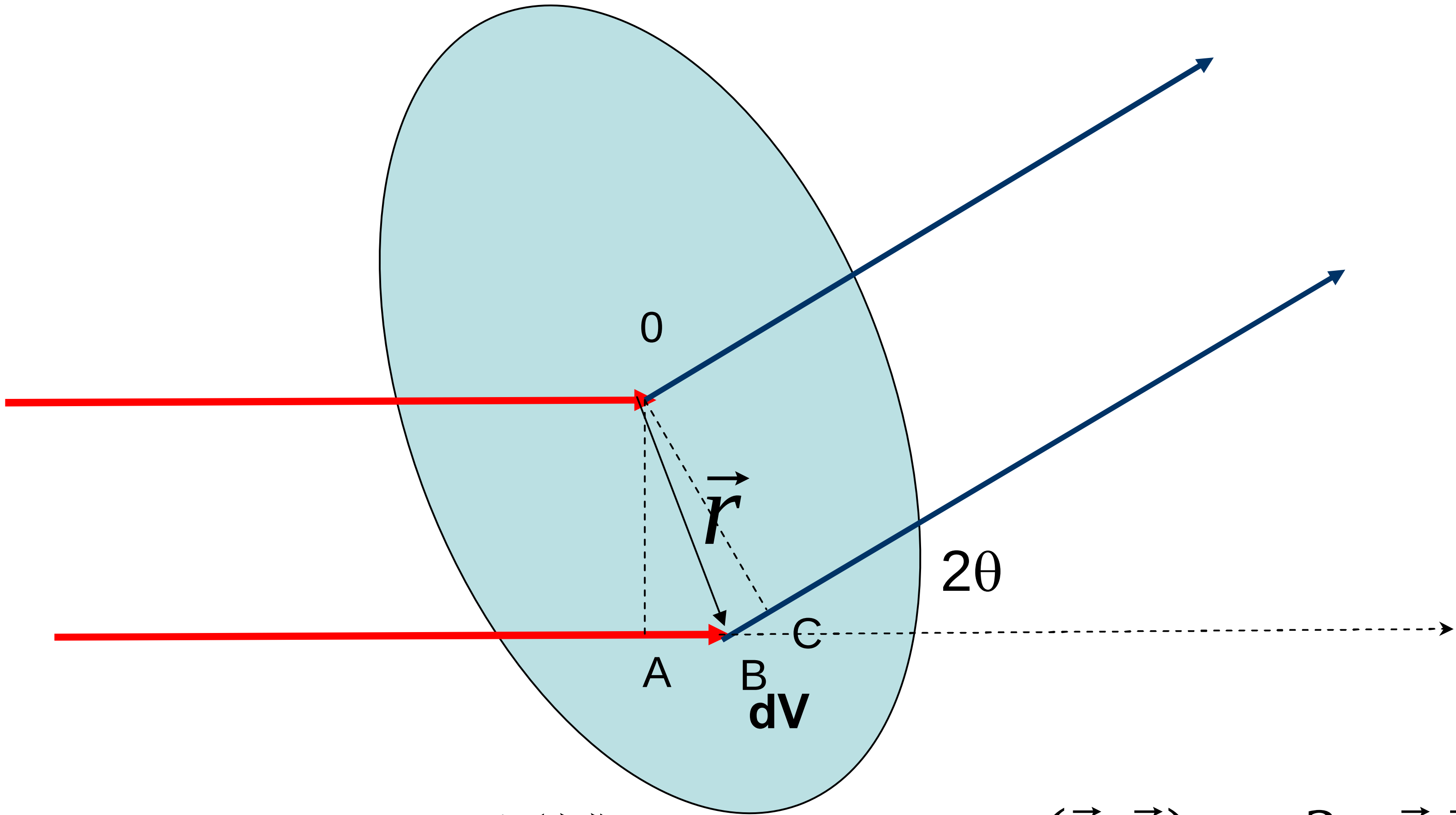
- **Ewald construction   Step 5**



- **Ewald construction   Step 5**



Amplitude of beams diffracted by materials of arbitrary structure



$$dA(\vec{s}) = A_e.\rho(\vec{r}).d\vec{r}.e^{i\varphi(\vec{r},\vec{s})}$$

$$\varphi(\vec{s},\vec{r}) = -2\pi.\vec{s}.\vec{r}$$

ρ(r) ↔ A(s) and Fourier transforms:

$$\boxed{A(\vec{s})_N = A_e\int \rho(\vec{r}).e^{-2\pi i.\vec{s}.\vec{r}}\, d\vec{r}}$$

$$\boxed{\rho(\vec{r}) = (1/A_e)\int A(\vec{s})_N.e^{2\pi i\vec{z}.\vec{r}}\, d\vec{s}}$$

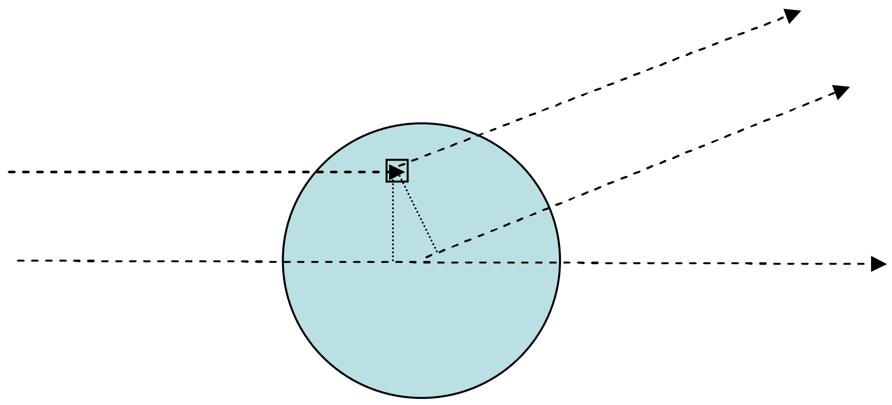
X-ray diffraction by crystals (3D periodic structures)

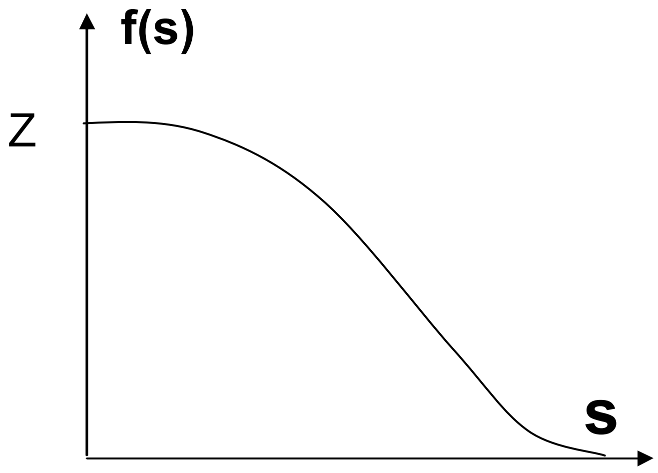
Atomic factor

$$f(\vec{s}) = \frac{Amplitude.scattered.by.one.atom}{Amplitude.scattered.by.one.electron} = \int \rho(\vec{r}).e^{-2\pi i\vec{s}.\vec{r}} d\vec{r}$$

Atomic factor for
Isotropic atoms:

$$f(s) = \int 4\pi.r^2 \rho(r) \frac{\sin 2\pi sr}{2\pi sr} dr$$





Structure factor

$$F(\vec{s} = \vec{r}^{\,*}_{hkl}) = \frac{Amplitude.scattered.by.an.unit.cell}{Amplitude.scattered.by.one.electron} = \int \rho(\vec{r}).e^{-2\pi i \vec{r}^{\,*}_{hkl}.\vec{r}}\, d\vec{r}$$

$$F(\vec{s}) = \sum_i f_i.e^{-2\pi.i.(\vec{s}.\vec{r}_i)}$$

fi= atomic scattering factor

$$F(\vec{s} = \vec{r}^{\,*}_{hkl}) = F_{hkl} = \sum_i f_i e^{-2.\pi.i(h.x_i^{'} + k.y_i^{'} + l.z_i^{'})}$$

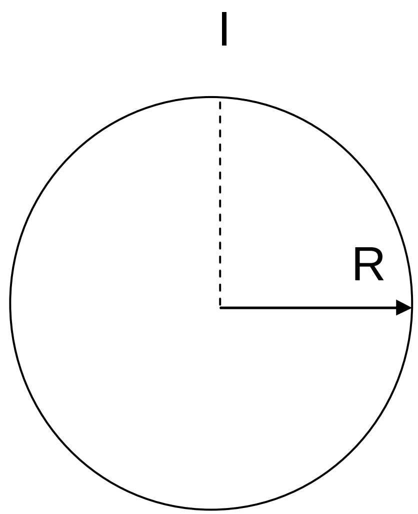
$$[\rho(\vec{r})]_{unit.cell} = \sum\sum\sum F_{hkl} e^{2\pi.i.\vec{r}^{\,*}_{hkl}.\vec{r}}$$

(F_{hkl} are complex numbers)

$$A_{hkl} = A_e \sum\sum\sum F_{hkl}.e^{i\varphi_{uvw}} = A_e N.F_{hkl}$$

$$\varphi(uvw,hkl) = 2\pi.\vec{r}^{\,*}_{hkl}.\vec{r}_{uvw} = 2\pi.n$$

$$A_{hkl} = A_e \sum\sum\sum F_{hkl}.e^{2\pi i(\vec{r}^{\,*}_{hkl}.\vec{r}_{uvw})} = A_e N.F_{hkl}$$



$$\boxed{(I_N)_{hkl} = N^2.\left|F_{hkl}\right|^2}$$

$$\boxed{\left|F_{hkl}\right| = (1/N).\sqrt{I(\vec{r}^{\,*} = \vec{r}^{\,*}_{hkl})}}$$

$$\boxed{F_{hkl} = \sum_i f_i e^{-2.\pi.i(h.x_i' + k.y_i' + l.z_i')}}$$

$$[\rho(\vec{r})]_{unit.cell} = \sum\sum\sum F_{hkl} e^{2\pi.i.\vec{r}^{*}_{hkl}.\vec{r}}$$

$$F_{hkl} = |F_{hkl}|.e^{-i.\varphi_{hkl}}$$

COMPLEX !!!

The phase problem

$$(I_N)_{hkl} = N^2.|F_{hkl}|^2$$

$$|F_{hkl}| = (1/N).\sqrt{I(\vec{r}^{*} = \vec{r}^{*}_{hkl})}$$

Experiment

$$F_{hkl} = \sum_{i} f_i e^{-2.\pi.i(h.x_i^{'} + k.y_i^{'} + l.z_i^{'})}$$

$$\boxed{[\rho(\vec{r})]_{unit.cell} = \sum\sum\sum F_{hkl} e^{2\pi .i.\vec{r}^{*}_{hkl}.\vec{r}}}$$

$$F_{hkl} = |F_{hkl}|.e^{-i.\varphi_{hkl}}$$ COMPLEX !!!

$$\boxed{(I_N)_{hkl} = N^2.|F_{hkl}|^2}$$

$$\boxed{|F_{hkl}| = (1/N).\sqrt{I(\vec{r}^{*} = \vec{r}^{*}_{hkl})}}$$

Experiment

$$\boxed{F_{hkl} = \sum_i f_i e^{-2.\pi.i(h.x_i^{'} + k.y_i^{'} + l.z_i^{'})}}$$

Structure

CRYSTALLOGRAPHIC LATTICES

-Point lattices
-Crystallographic directions [uvw]
-Crystallographic planes. Miller indexes (hkl)
-Reciprocal point lattices:
-Relationship between direct and reciprocal lattices

SYMMETRY

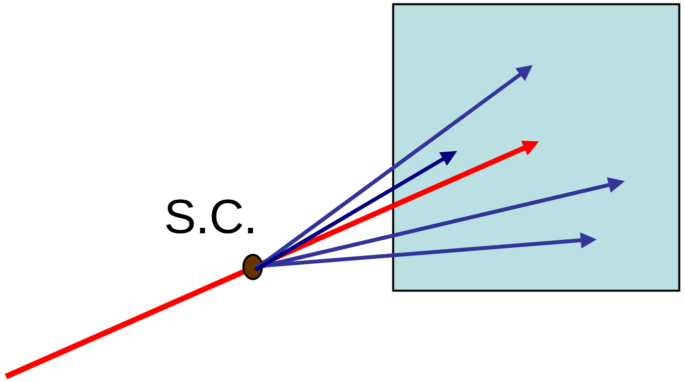
-Crystal systems (6)
-Bravais lattices (14)
-Crystal classes. Point groups (32)
-Space groups (230)

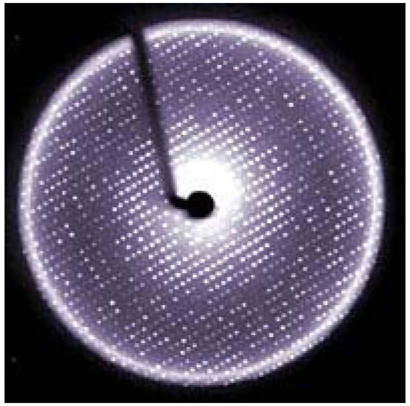
X-RAY DIFFRACTION

-Ewald construction
-Thompson scattering. (Scattering amplitude by an electron) = Ae
-Atomic scattering factor. f (s) (Scattering amplitude by an atom)/Ae
-Structure factor: F_{hkl} (Scattering amplitude by an unit cells)/Ae

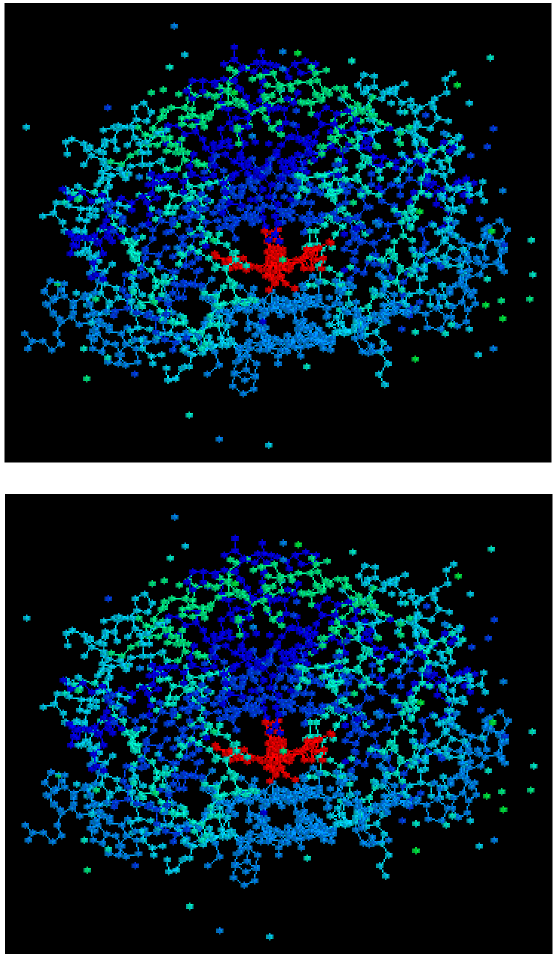
-The phase problem

Structure of crystallized proteins; Coordinates of atoms inside the unit cell



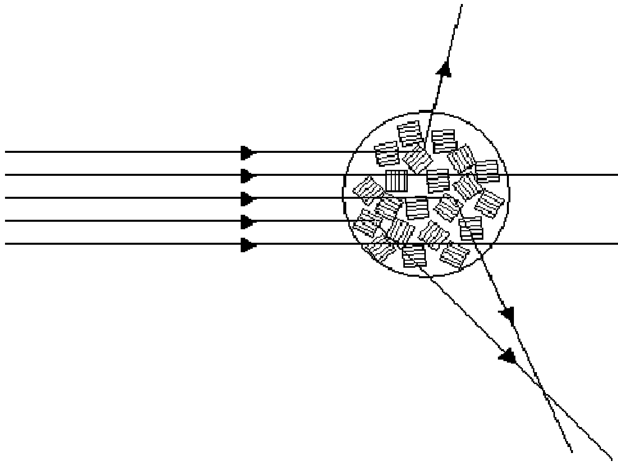


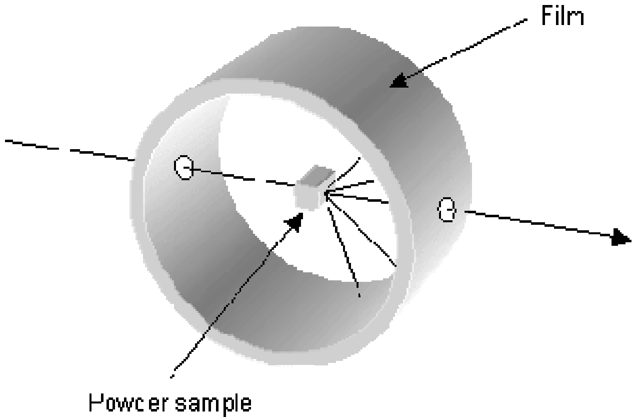
X-ray diffraction patterns

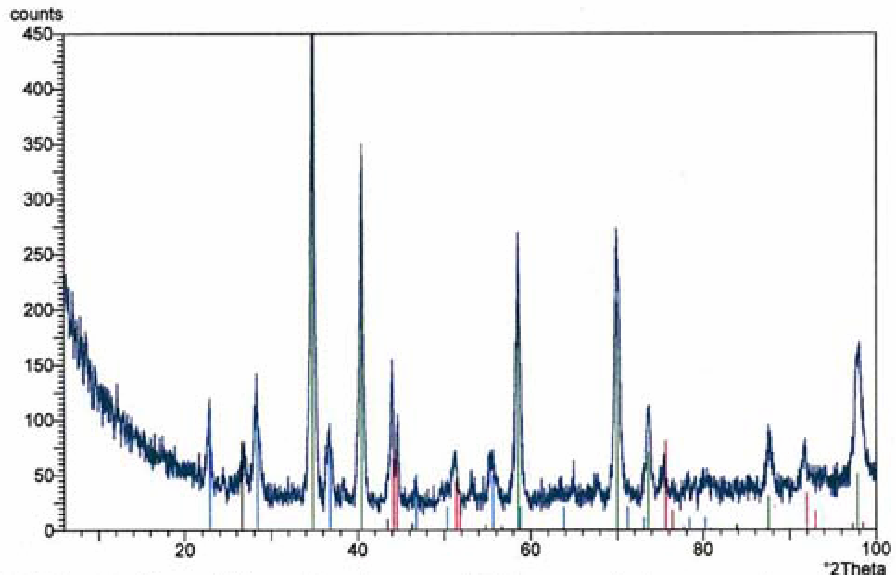


HIV1

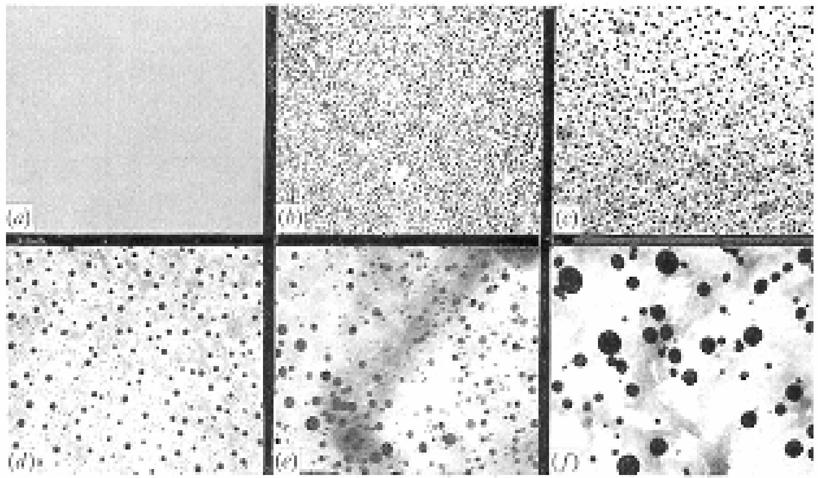
Powder diffraction: Determination of lattice parameters, lattice thermal expansion, phase analysis, average crystal size and stress measurements, texture determination



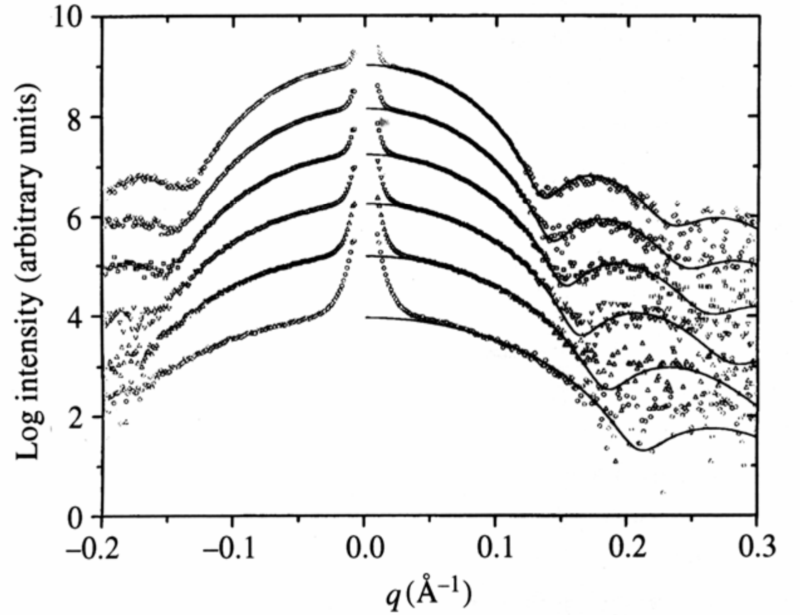




Small – angle X-ray scattering (SAXS)

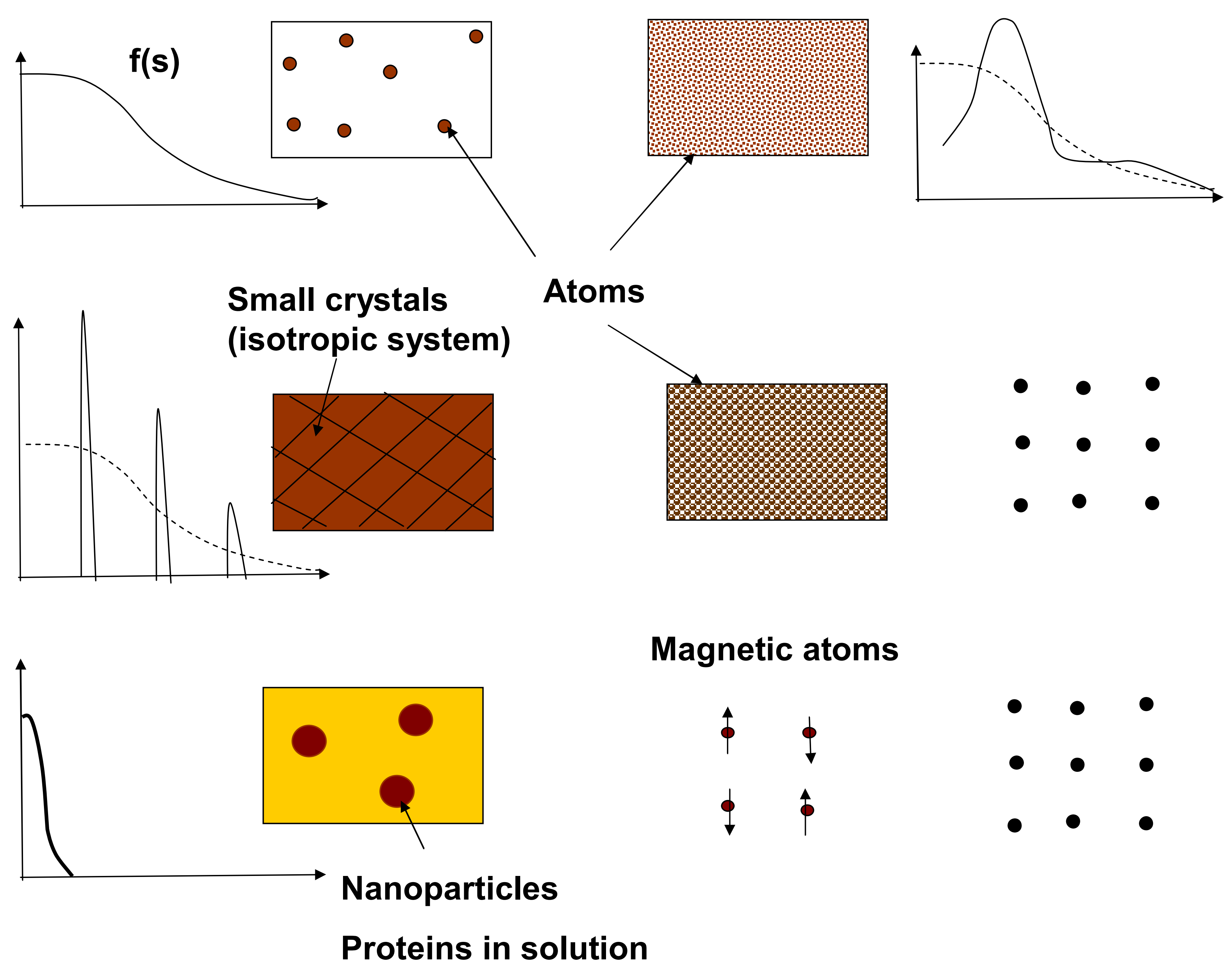


10 nm



Lectures and Tutorials on X-ray Scattering

- Single Crystal Crystallog. Basic Aspects *(A. Craievich)*
- Protein Crystallography. Basic Aspects *(D. Lamba)*
- Protein Crystallography. Applications *(M. Polentarutti)*
- Wide-angle scattering. Basic Aspects *(P. Scardi)*
- Powder X-ray Diffraction. Applications *(P. Scardi)*
- Powder X-ray Diffraction. *Tutorial*
- Small-angle X-ray Scattering (SAXS). Basic Aspects *(A. Craievich).*
- SAXS. Applications *(A. Craievich).*
- SAXS. Structure transformations *(A. Craievich)*
- SAXS. Nanomaterials and proteins in solution *(H. Amenitsch)*
- SAXS under extreme conditions *(H. Amenitsch)*
- SAXS. Tutorial *(H. Amenitsch)*
- Inelastic scattering *(G. Monaco)*
- Magnetic X-ray Scattering *(N. Binggeli)*


f(s)
Small crystals
(isotropic system)
Atoms
Magnetic atoms
Nanoparticles
Proteins in solution