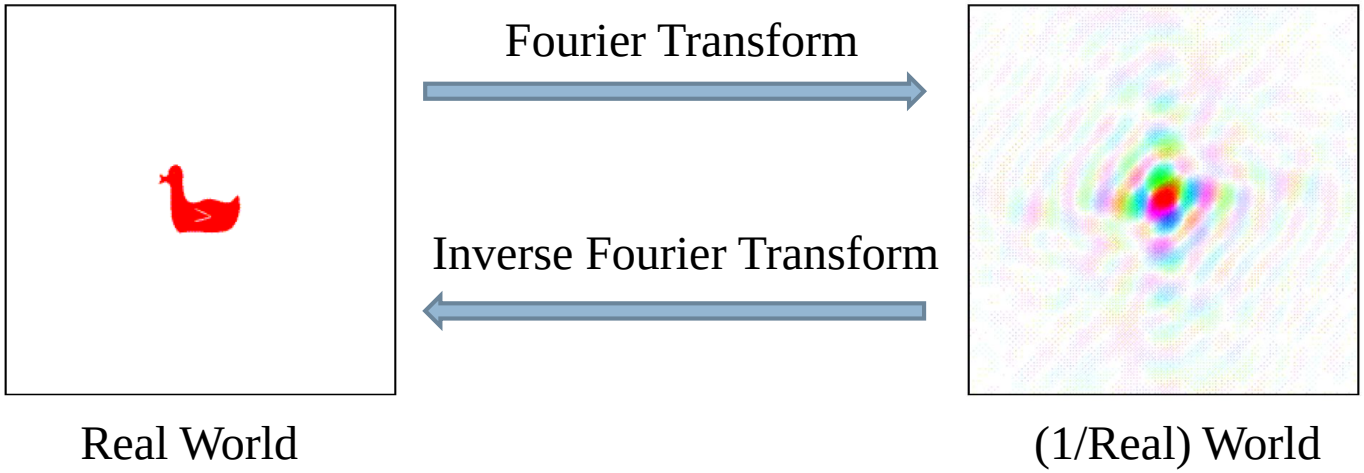
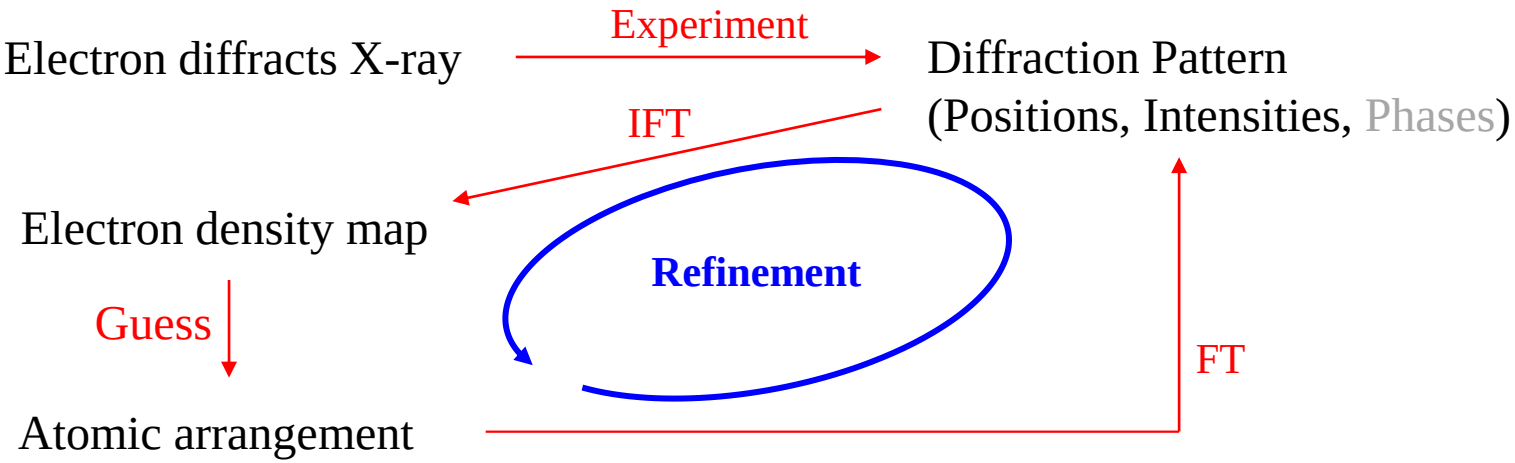
Nutshells of X-ray Crystallography

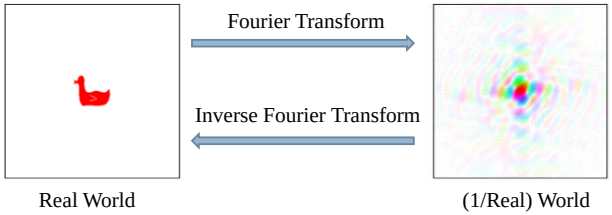
Line up!
We will catch you !

X-ray Crystallography

What do we want to do?







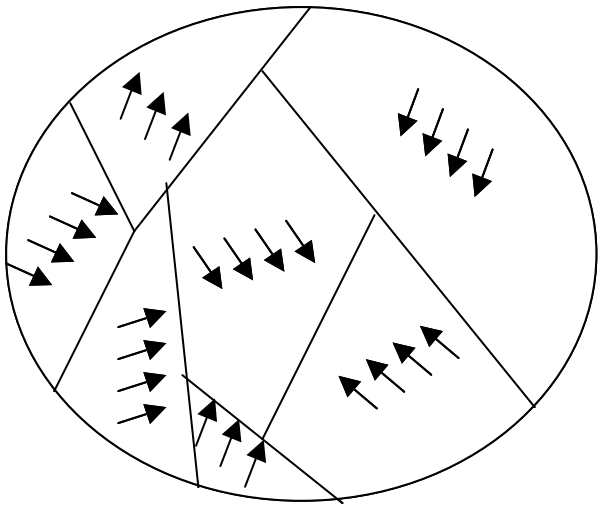
What is this ?
How does it look like?

Solid

Gas, Liquid
No structure of ordering or stacking
Structure in molecule or atom

Solid
All solids in the universe have a certain number of ways of packing – **crystalline solid**

비정형 고체 (Amorphous solid)
결정형 고체 (Crystalline solid)
준결정 (Quasicrystal)



Solid Structure (Crystal Structure)

CRYSTAL STRUCTURE

The periodic arrangement of atoms in the crystal.

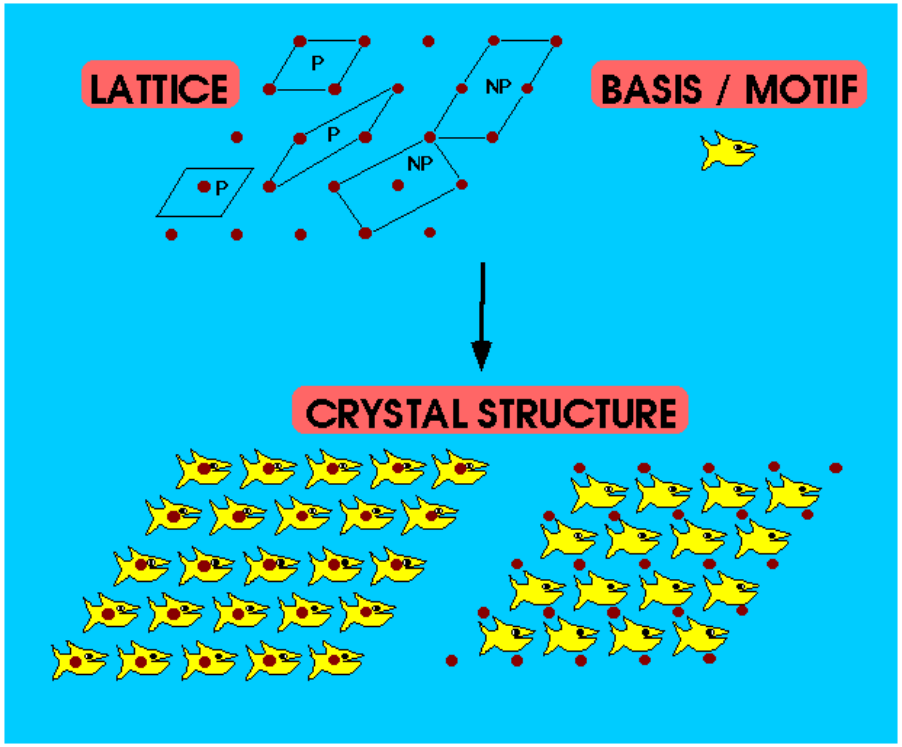
LATTICE

An infinite array of points in space, in which each point has identical surroundings to all others.
(= Lattice points are all equivalent.)

UNIT CELL

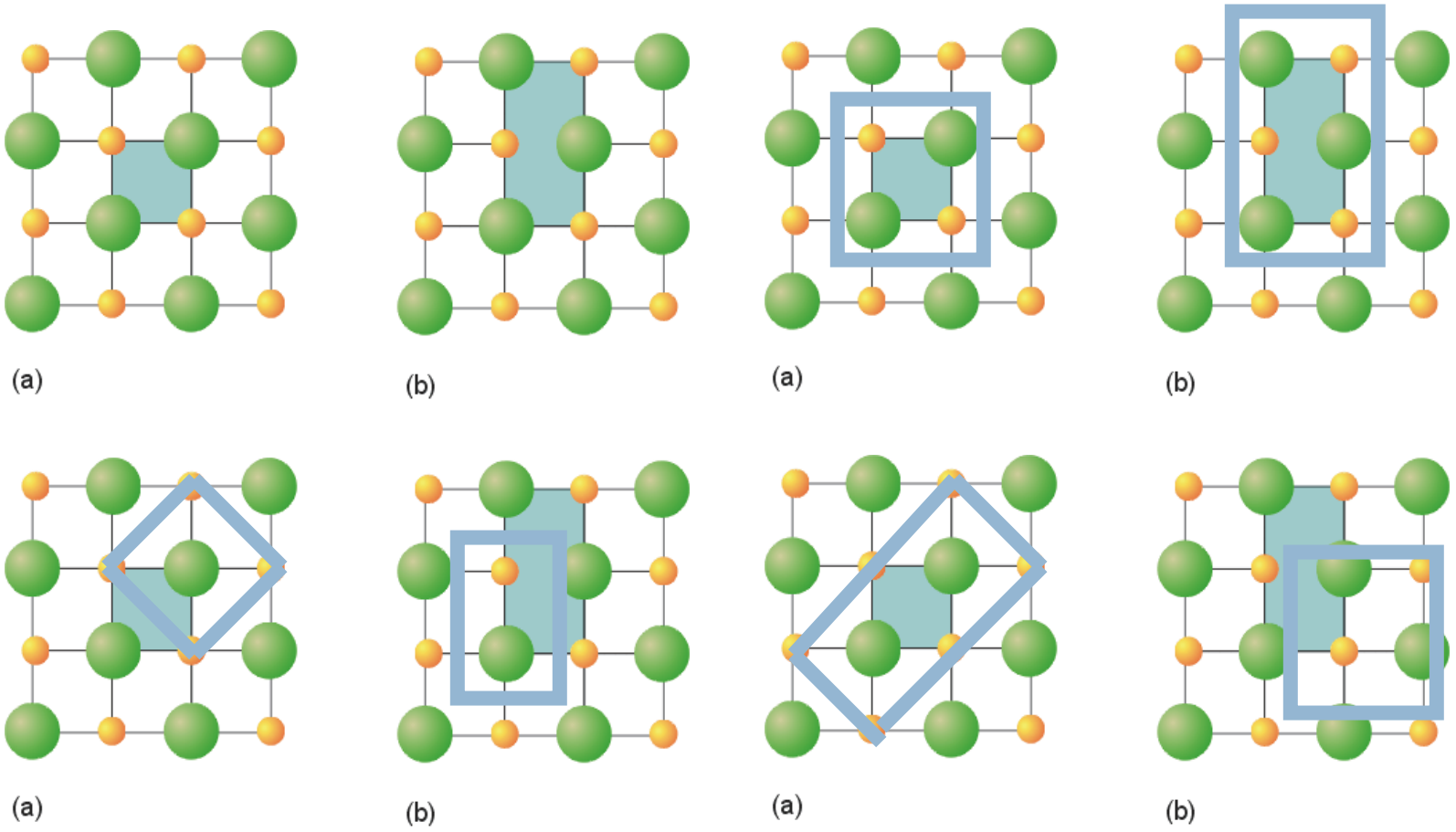
A component of the crystal, which when stacked together with pure translational repetition reproduces the whole crystal.

PRIMITIVE (P) UNIT CELLS contain only a ***single lattice point***



Crystal Structure

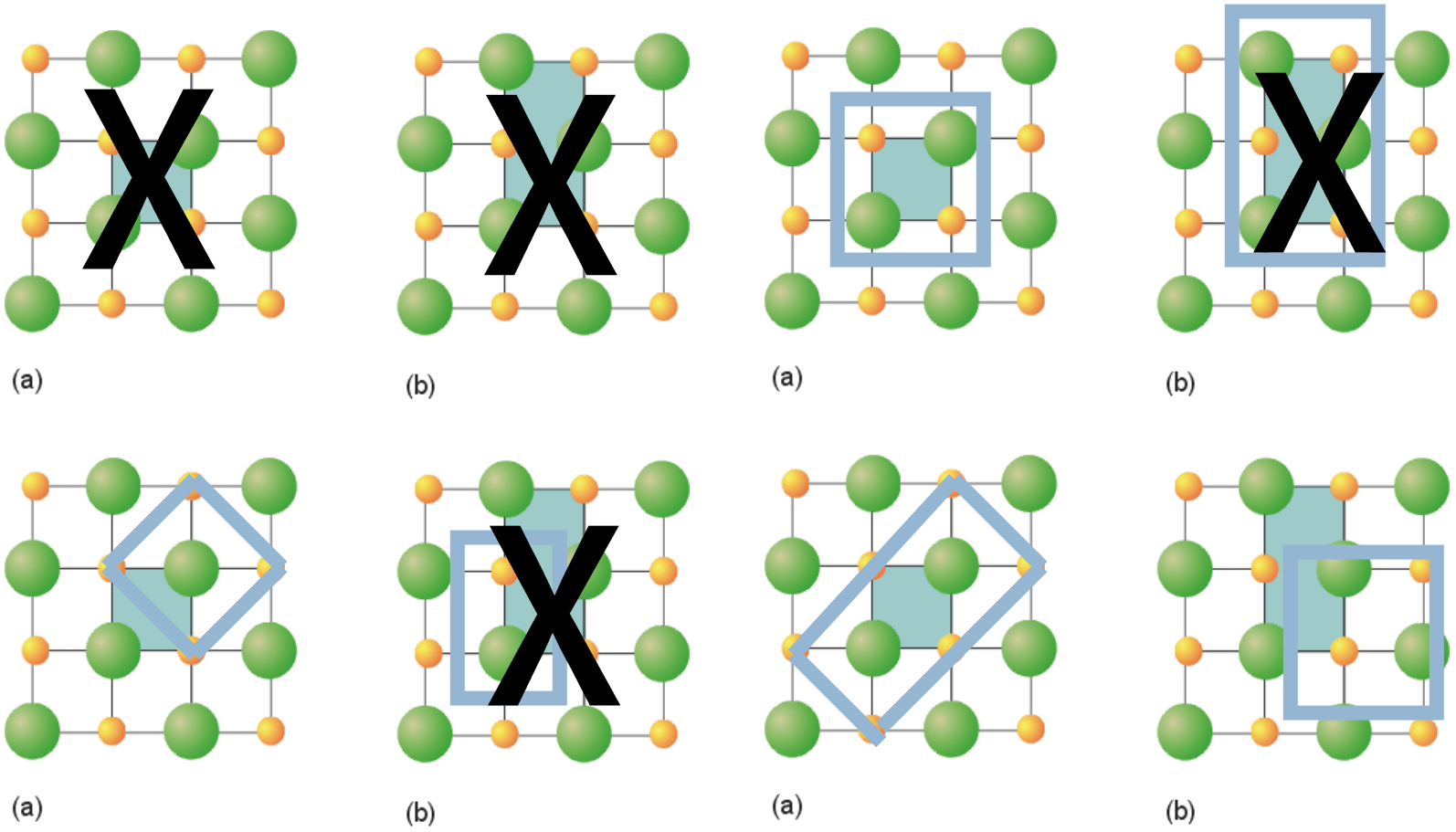
Unit Cell



Unit cell ?

Crystal Structure

Unit Cell



Unit cell ?

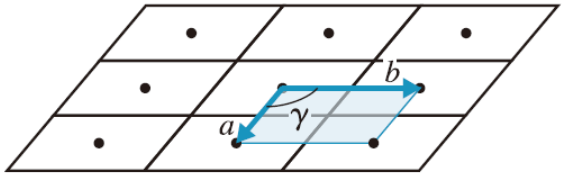
Crystal Structure

Requirement of Unit Cell (How to fill the space)

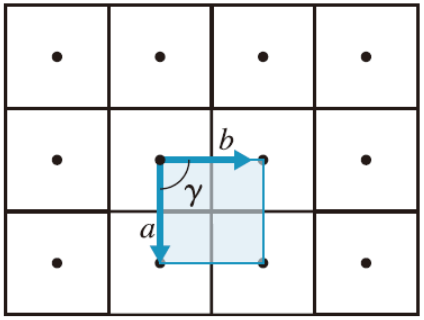
Crystallographic restriction theorem:

Must have 2-, or 3- fold axes => C_2, C_3, C_4, C_6 axes (except for quasicrystal)

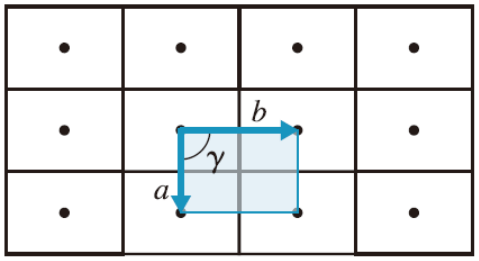
2차원 격자의 종류



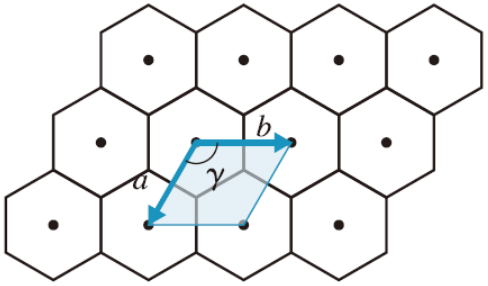
평행사변형 격자 ($a \neq b, \gamma =$ 임의)



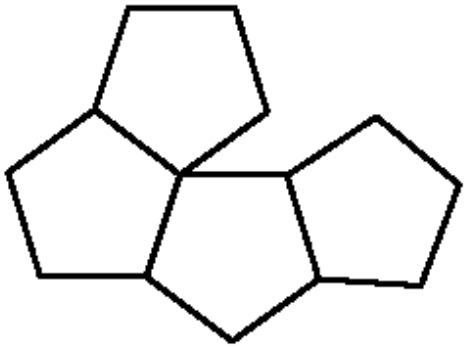
정사각형 격자 ($a = b, \gamma = 90°$)



직사각형 격자 ($a \neq b, \gamma = 90°$)

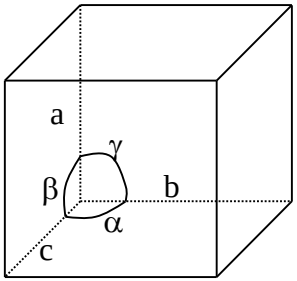


정육각형 격자 ($a = b, \gamma = 120°$)

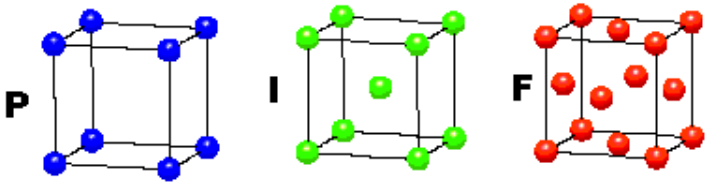


Crystal Structure

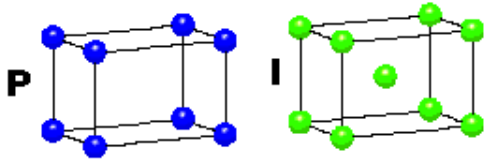
7 Crystal Systems (14 Bravais Lattices)



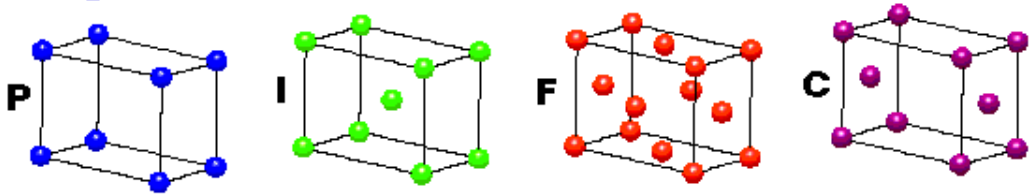
CUBIC
$a = b = c$
$\alpha = \beta = \gamma = 90°$



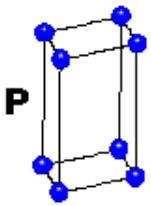
TETRAGONAL
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$



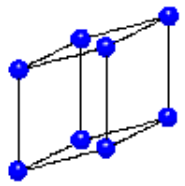
ORTHORHOMBIC
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$



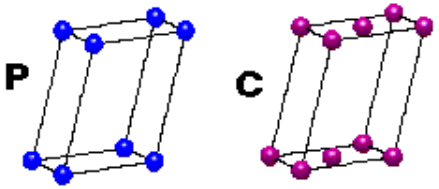
HEXAGONAL
$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$



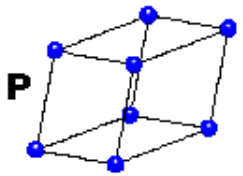
TRIGONAL
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$



MONOCLINIC
$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$



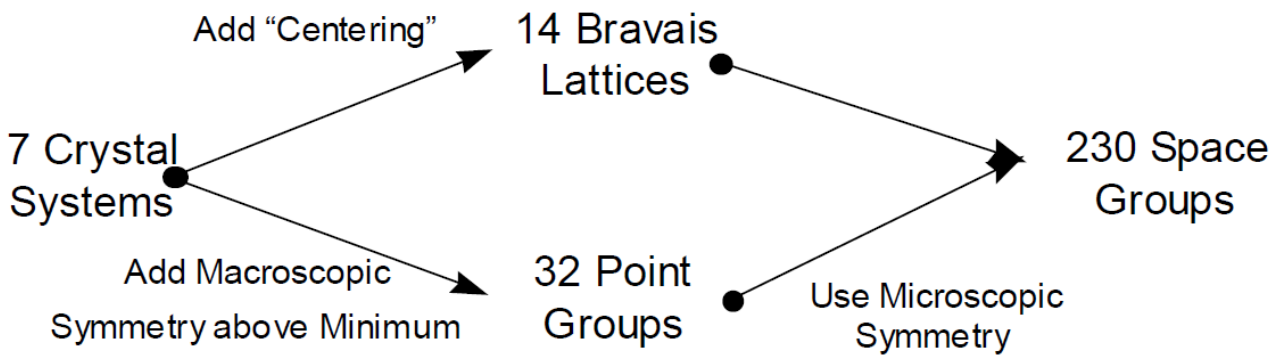
TRICLINIC
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$



4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices

Crystal Structure

32 Point Groups, 230 Space groups



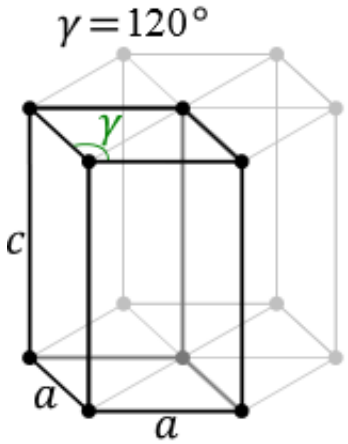
A point group is defined by the symmetry operations of

Symmetry Operations	Symmetry Elements
Rotation (C_n)	Rotational axis
Reflection (σ)	Mirror plane
Inversion (i)	Center of symmetry
Improper rotation (S_n)	Improper rotational axis

Crystal Structure

Theoretically, there are infinite number of point groups, but the crystallographic restriction theorem gives only **32 point groups** in the crystal systems.

Point group symmetry defines the symmetry of an isolated object or group of objects.



Hexagonal lattice

If **only lattice points** are considered, the point group of hexagonal lattice is $\boldsymbol{D_{6h}}$.

Depending on the motif, it can have $\boldsymbol{C_6}$, $\boldsymbol{C_{3h}}$, $\boldsymbol{C_{6h}}$, $\boldsymbol{D_6}$, $\boldsymbol{C_{6v}}$, $\boldsymbol{D_{3h}}$.

Crystal Structure

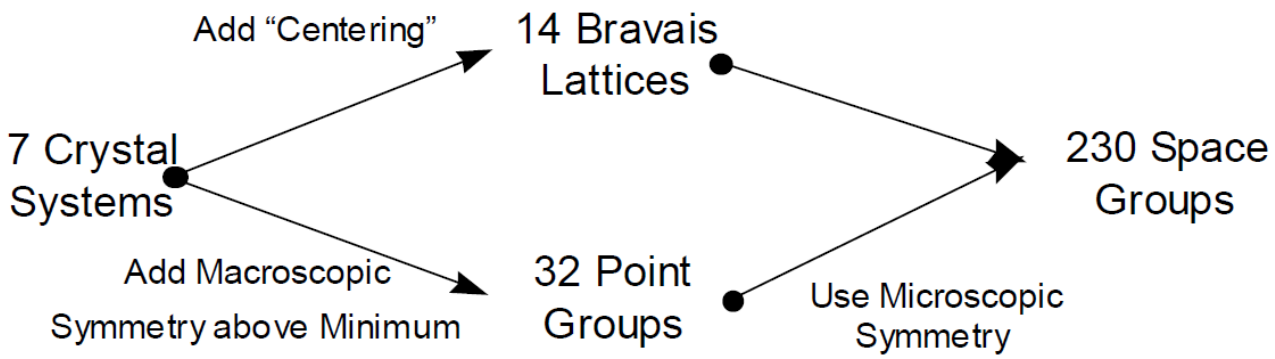
32 Point Groups

Crystal Systems	Hermann-Mauguin (full)	Hermann-Mauguin (short)	Shubnikov	Schoenflies	Orbifold	Coxeter	Order
Triclinic	1	1	1	C_1	11	$[\,]^+$	1
	①	①	$\tilde{2}$	$C_i = S_2$	×	$[2^+,2^+]$	2
Monoclinic	2	2	2	C_2	22	$[2]^+$	2
	m	m	m	$C_s = C_{1h}$	*	$[\,]$	2
	$\frac{2}{m}$	2/m	$2:m$	C_{2h}	2*	$[2,2^+]$	4
Orthorhombic	222	222	$2:2$	$D_2 = V$	222	$[2,2]^+$	4
	mm2	mm2	$2\cdot m$	C_{2v}	*22	$[2]$	4
	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$	mmm	$m\cdot 2:m$	$D_{2h} = V_h$	*222	$[2,2]$	8
Tetragonal	4	4	4	C_4	44	$[4]^+$	4
	④	④	$\tilde{4}$	S_4	2×	$[2^+,4^+]$	4
	$\frac{4}{m}$	4/m	$4:m$	C_{4h}	4*	$[2,4^+]$	8
	422	422	$4:2$	D_4	422	$[4,2]^+$	8
	4mm	4mm	$4\cdot m$	C_{4v}	*44	$[4]$	8
	④2m	④2m	$\tilde{4}\cdot m$	$D_{2d} = V_d$	2*2	$[2^+,4]$	8
	$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	4/mmm	$m\cdot 4:m$	D_{4h}	*422	$[4,2]$	16
Trigonal	3	3	3	C_3	33	$[3]^+$	3
	③	③	$\tilde{6}$	$S_6 = C_{3i}$	3x	$[2^+,6^+]$	6
	32	32	$3:2$	D_3	322	$[3,2]^+$	6
	3m	3m	$3\cdot m$	C_{3v}	*33	$[3]$	6
	$③\frac{2}{m}$	③m	$\tilde{6}\cdot m$	D_{3d}	2*3	$[2^+,6]$	12
Hexagonal	6	6	6	C_6	66	$[6]^+$	6
	⑥	⑥	$3:m$	C_{3h}	3*	$[2,3^+]$	6
	$\frac{6}{m}$	6/m	$6:m$	C_{6h}	6*	$[2,6^+]$	12
	622	622	$6:2$	D_6	622	$[6,2]^+$	12
	6mm	6mm	$6\cdot m$	C_{6v}	*66	$[6]$	12
	⑥m2	⑥m2	$m\cdot 3:m$	D_{3h}	*322	$[3,2]$	12
	$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	6/mmm	$m\cdot 6:m$	D_{6h}	*622	$[6,2]$	24
Cubic	23	23	$3/2$	T	332	$[3,3]^+$	12
	$\frac{2}{m}③$	m③	$\tilde{6}/2$	T_h	3*2	$[3^+,4]$	24
	432	432	$3/4$	O	432	$[4,3]^+$	24
	④3m	④3m	$3/\tilde{4}$	T_d	*332	$[3,3]$	24
	$\frac{4}{m}③\frac{2}{m}$	m③m	$\tilde{6}/4$	O_h	*432	$[4,3]$	48

(n) means $\overline{n}$

Crystal Structure

32 Point Groups, 230 Space groups



To generate an infinite 3D lattice from an object it is necessary to add translational symmetry to point group symmetry.

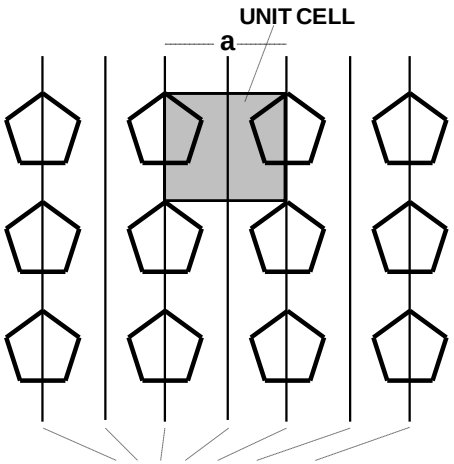
Symmetry Operations	Defined
Rotation (C_n) Reflection (σ) Inversion (i) Improper rotation (S_n)	Point group
+ Glide plane (= translation + reflection) Screw axis (= translation + rotation)	Space group

Crystal Structure

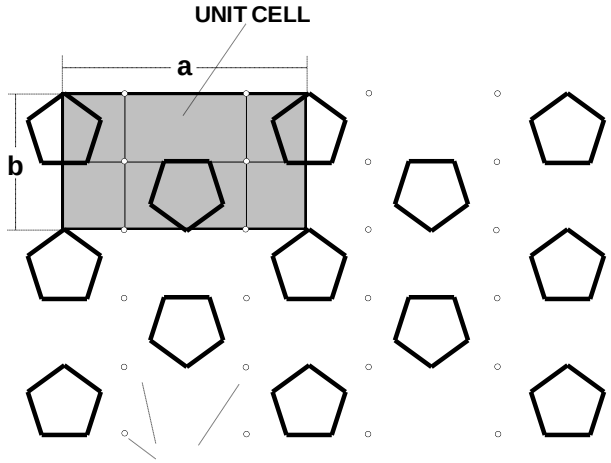
230 Space groups

Glide plane is a symmetry operation describing how a reflection in a plane, followed by a translation (**less than a unit cell vector**) parallel with that plane, may leave the crystal unchanged.

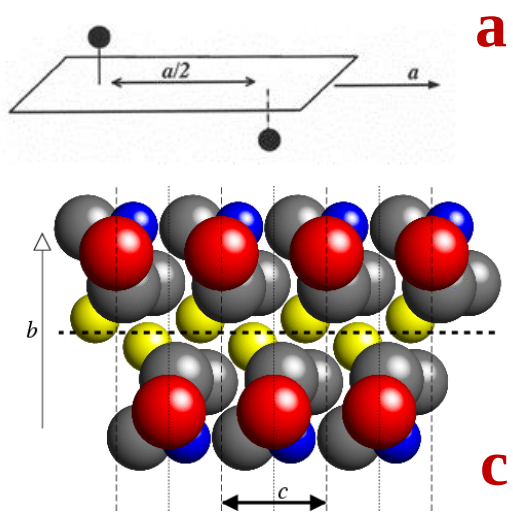
a: reflection followed by ½ **a** translation
b: reflection followed by ½ **b** translation
c: reflection followed by ½ **c** translation
n : reflection followed by ½ **a** + ½ **b** or ½ **a** + ½ **c** or ½ **b** + ½ **c** translation (diagonal glide)
d : reflection followed by ¼ **a** + ¼ **b** or ¼ **a** + ¼ **c** or ¼ **b** + ¼ **c** translation (diamond glide)



no glide



a



c

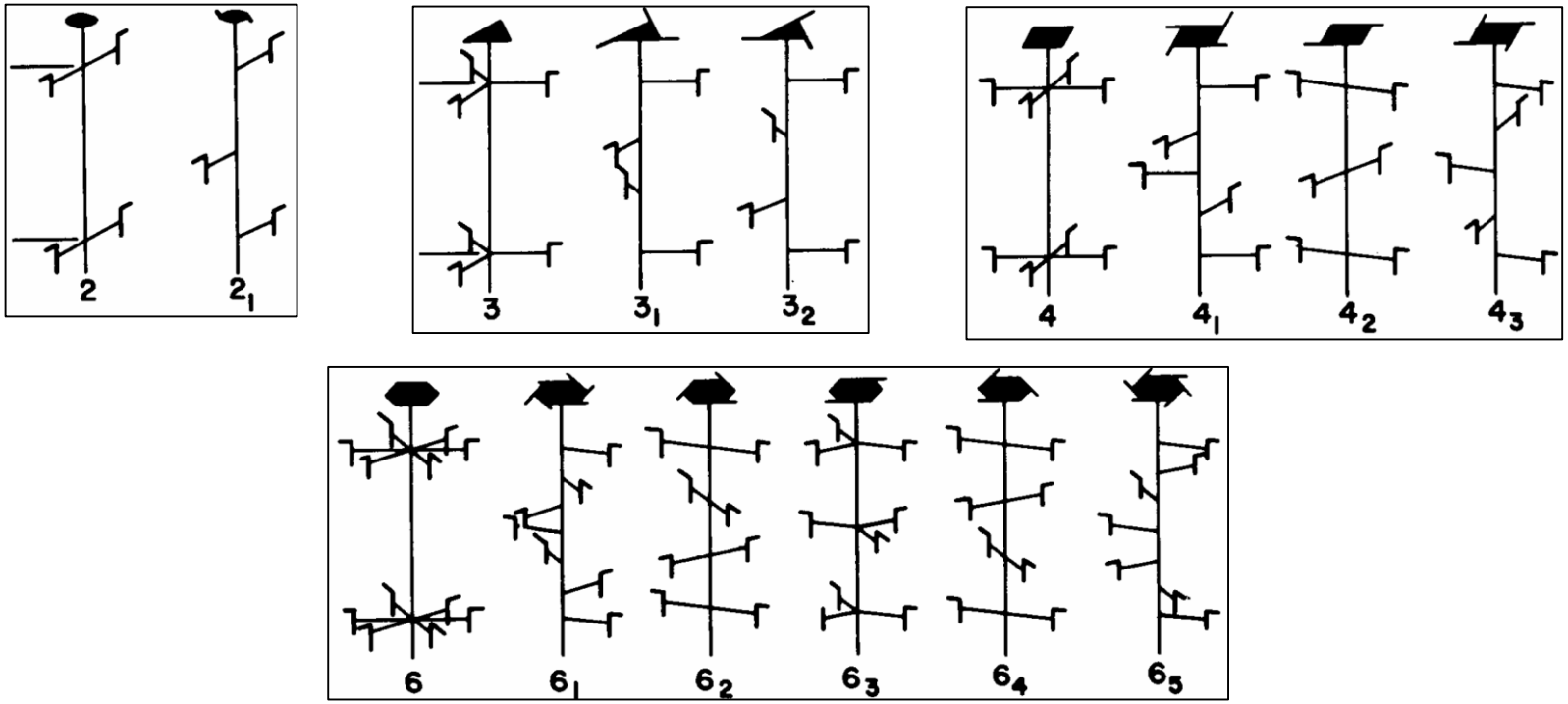
Crystal Structure

230 Space groups

Screw axis is a symmetry operation describing how a rotation about an axis, followed by a translation (**less than a unit cell vector**) parallel with that axis, may leave the crystal unchanged.

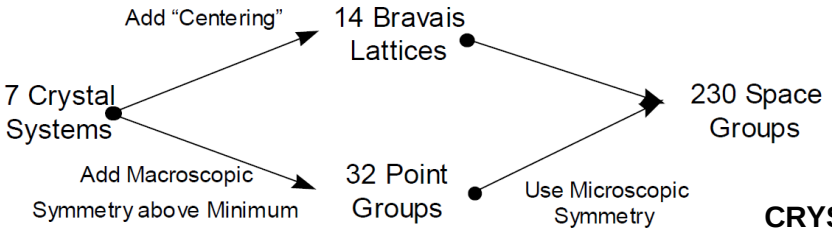
11 unique screw axes: **2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5**

(n_m: counter clockwise C_n + m/n translation)



Crystal Structure

Crystal systems, Bravais lattices
Point Groups, Space groups



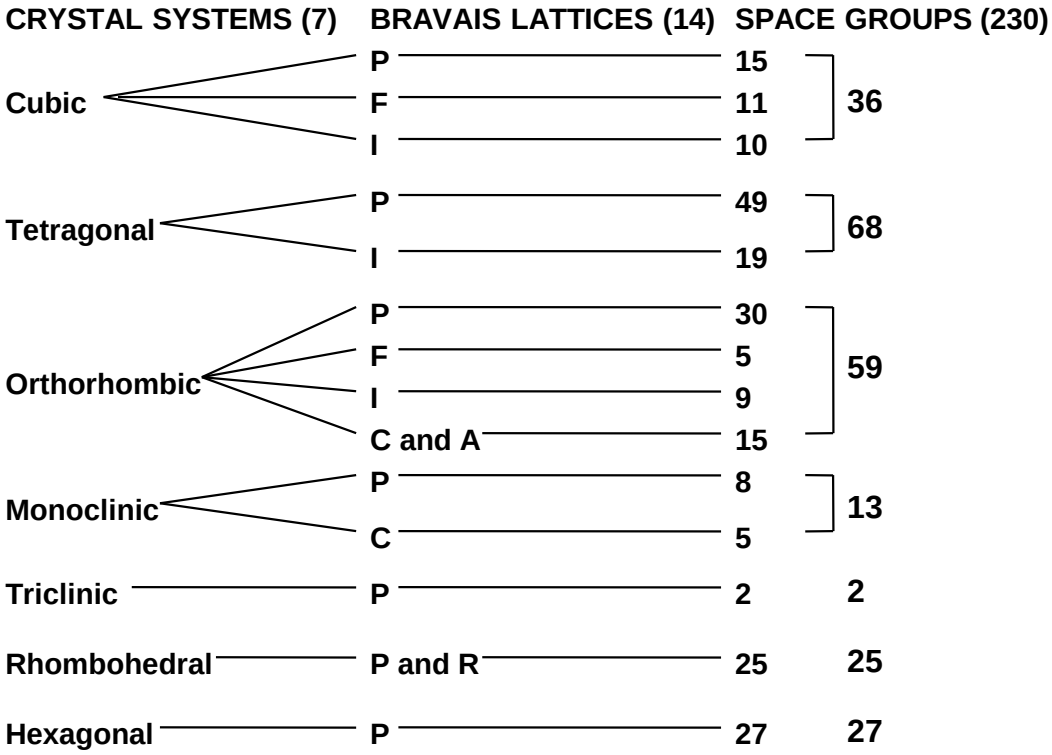
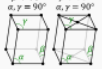
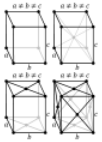
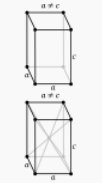


Fig. 9

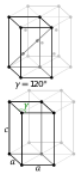
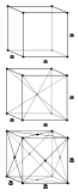
Crystal Structure

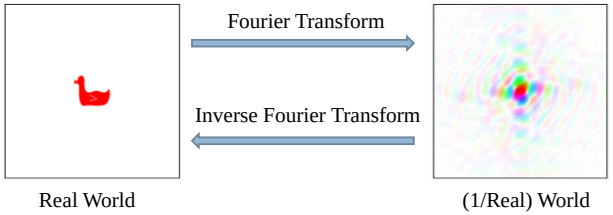
Crystal systems, Bravais lattices
Point Groups, Space groups

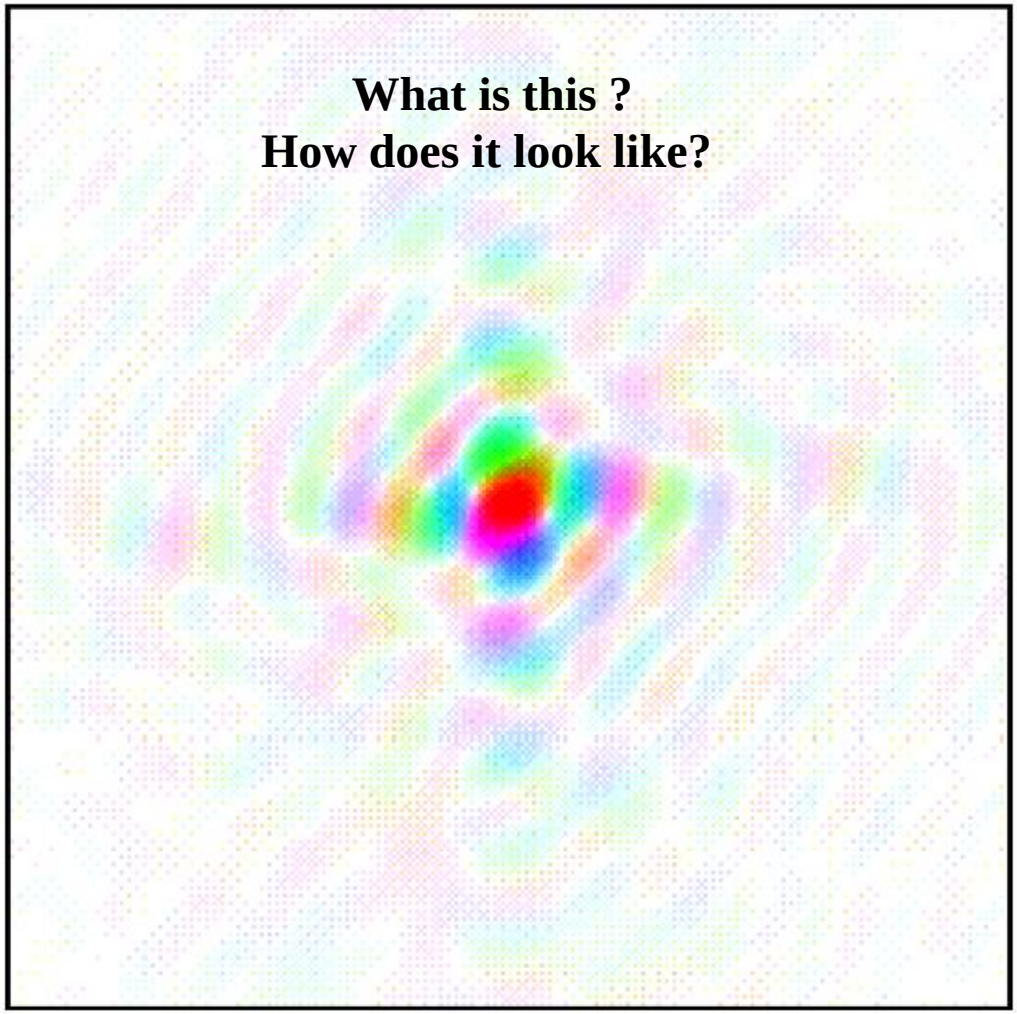
#	Crystal system (count) Bravais lattice	Point group					Space groups (international short symbol)
		Intl	Schön.	Orbifold notation	Cox.	Ord.	
1	Triclinic (2) 	1	C_1	11	[ ]$^+$	1	P1
2		$\bar{1}$	C_i	1×	[2$^+$,2$^+$]	2	P$\bar{1}$
3-5	Monoclinic (13) 	2	C_2	22	[2]$^+$	2	P2, P2_1 C2
6-9		m	C_s	*11	[ ]	2	Pm, Pc Cm, Cc
10-15		2/m	C_{2h}	2*	[2,2$^+$]	4	P2/m, P2_1/m C2/m, P2/c, P2_1/c C2/c
16-24	Orthorhombic (59) 	222	D_2	222	[2,2]$^+$	4	P222, P222_1, P2_12_12, P$2_12_12_1$, C222_1, C222, F222, I222, I$2_12_12_1$
25-46		mm2	C_{2v}	*22	[2]	4	Pmm2, Pmc2_1, Pcc2, Pma2, Pca2_1, Pnc2, Pmn2_1, Pba2, Pna2_1, Pnn2 Cmm2, Cmc2_1, Ccc2, Amm2, Aem2, Ama2, Aea2 Fmm2, Fdd2 Imm2, Iba2, Ima2
47-74		mmm	D_{2h}	*222	[2,2]	8	Pmmm, Pnnn, Pccm, Pban, Pmma, Pnna, Pmna, Pcca, Pbam, Pccn, Pbcm, Pnnm, Pmmn, Pbcn, Pbca, Pnma Cmcm, Cmce, Cmmm, Cccm, Cmme, Ccce Fmmm, Fddd Immm, Ibam, Ibca, Imma
75-80	Tetragonal (68) 	4	C_4	44	[4]$^+$	4	P4, P4_1, P4_2, P4_3, I4, I4_1
81-82		$\bar{4}$	S_4	2×	[2$^+$,4$^+$]	4	P$\bar{4}$, I$\bar{4}$
83-88		4/m	C_{4h}	4*	[2,4$^+$]	8	P4/m, P4_2/m, P4/n, P4_2/n I4/m, I4_1/a
89-98		422	D_4	224	[2,4]$^+$	8	P422, P42_12, P4_122, P4_12_12, P4_222, P4_22_12, P4_322, P4_32_12 I422, I4_122
99-110		4mm	C_{4v}	*44	[4]	8	P4mm, P4bm, P4_2cm, P4_2nm, P4cc, P4nc, P4_2mc, P4_2bc I4mm, I4cm, I4_1md, I4_1cd
111-122		$\bar{4}$2m	D_{2d}	2*2	[2$^+$,4]	8	P$\bar{4}$2m, P$\bar{4}$2c, P$\bar{4}2_1$m, P$\bar{4}2_1$c, P$\bar{4}$m2, P$\bar{4}$c2, P$\bar{4}$b2, P$\bar{4}$n2 I$\bar{4}$m2, I$\bar{4}$c2, I$\bar{4}$2m, I$\bar{4}$2d
123-142		4/mmm	D_{4h}	*224	[2,4]	16	P4/mmm, P4/mcc, P4/nbm, P4/nnc, P4/mbm, P4/mnc, P4/nmm, P4/ncc, P4_2/mmc, P4_2/mcm, P4_2/nbc, P4_2/nnm, P4_2/mbc, P4_2/mnm, P4_2/nmc, P4_2/ncm I4/mmm, I4/mcm, I4_1/amd, I4_1/acd

Crystal Structure

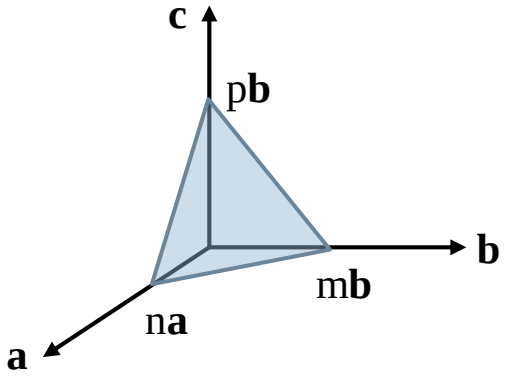
Crystal systems, Bravais lattices
Point Groups, Space groups

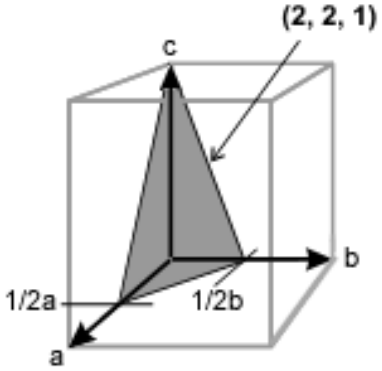
#	Crystal system (count) Bravais lattice	Point group					Space groups (international short symbol)
		Intl	Schön.	Orbifold notation	Cox.	Ord.	
143–146	Trigonal (25) 	3	C_3	33	[3]$^+$	3	P3, $P3_1$, $P3_2$ R3
147–148		$\bar{3}$	S_6	3×	[2$^+$,6$^+$]	6	$P\bar{3}$, $R\bar{3}$
149–155		32	D_3	223	[2,3]$^+$	6	P312, P321, $P3_112$, $P3_121$, $P3_212$, $P3_221$ R32
156–161		3m	C_{3v}	*33	[3]	6	P3m1, P31m, P3c1, P31c R3m, R3c
162–167		$\bar{3}$m	D_{3d}	2*3	[2$^+$,6]	12	$P\bar{3}$1m, $P\bar{3}$1c, $P\bar{3}$m1, $P\bar{3}$c1 $R\bar{3}$m, $R\bar{3}$c
168–173	Hexagonal (27) 	6	C_6	66	[6]$^+$	6	P6, $P6_1$, $P6_5$, $P6_2$, $P6_4$, $P6_3$
174		$\bar{6}$	C_{3h}	3*	[2,3$^+$]	6	$P\bar{6}$
175–176		6/m	C_{6h}	6*	[2,6$^+$]	12	P6/m, $P6_3$/m
177–182		622	D_6	226	[2,6]$^+$	12	P622, $P6_122$, $P6_522$, $P6_222$, $P6_422$, $P6_322$
183–186		6mm	C_{6v}	*66	[6]	12	P6mm, P6cc, $P6_3$cm, $P6_3$mc
187–190		$\bar{6}$m2	D_{3h}	*223	[2,3]	12	$P\bar{6}$m2, $P\bar{6}$c2, $P\bar{6}2$m, $P\bar{6}2$c
191–194		6/mmm	D_{6h}	*226	[2,6]	24	P6/mmm, P6/mcc, $P6_3$/mcm, $P6_3$/mmc
195–199	Cubic (36) 	23	T	332	[3,3]$^+$	12	P23, F23, I23 $P2_13$, $I2_13$
200–206		m$\bar{3}$	T_h	3*2	[3$^+$,4]	24	Pm$\bar{3}$, Pn$\bar{3}$, Fm$\bar{3}$, Fd$\bar{3}$, Im$\bar{3}$, Pa$\bar{3}$, Ia$\bar{3}$
207–214		432	O	432	[3,4]$^+$	24	P432, $P4_232$ F432, $F4_132$ I432 $P4_332$, $P4_132$, $I4_132$
215–220		$\bar{4}$3m	T_d	*332	[3,3]	24	$P\bar{4}$3m, $F\bar{4}$3m, $I\bar{4}$3m $P\bar{4}$3n, $F\bar{4}$3c, $I\bar{4}$3d
221–230		m$\bar{3}$m	O_h	*432	[3,4]	48	Pm$\bar{3}$m, Pn$\bar{3}$n, Pm$\bar{3}$n, Pn$\bar{3}$m Fm$\bar{3}$m, Fm$\bar{3}$c, Fd$\bar{3}$m, Fd$\bar{3}$c Im$\bar{3}$m, Ia$\bar{3}$d

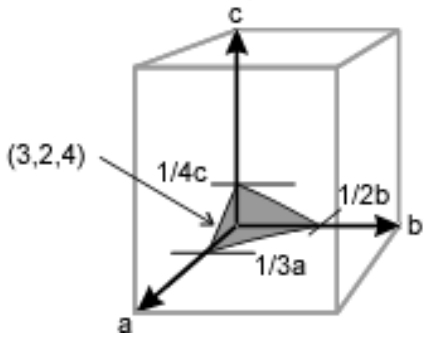

Fourier Transform
Inverse Fourier Transform
Real World
(1/Real) World


What is this ?
How does it look like?

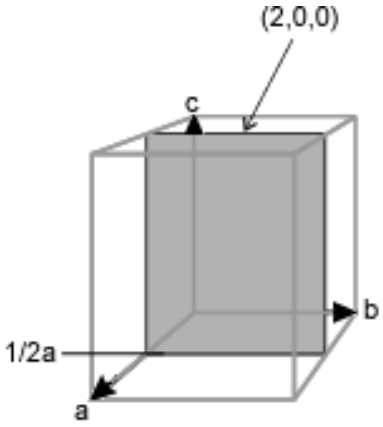
Basic Principle of Diffraction Pattern

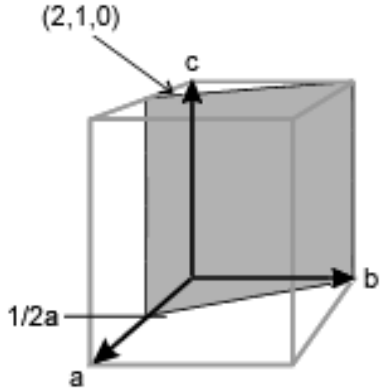


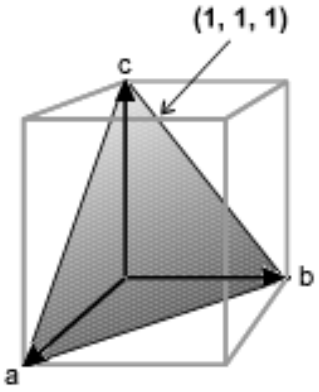


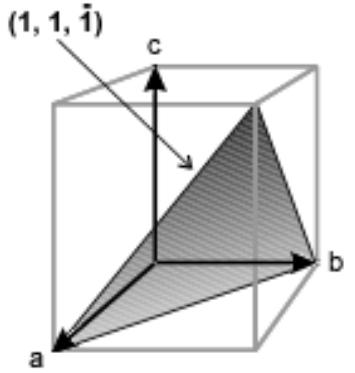


Miller index of the crystal plane:
(1/n 1/m 1/p) => smallest integer ***(h k l)***



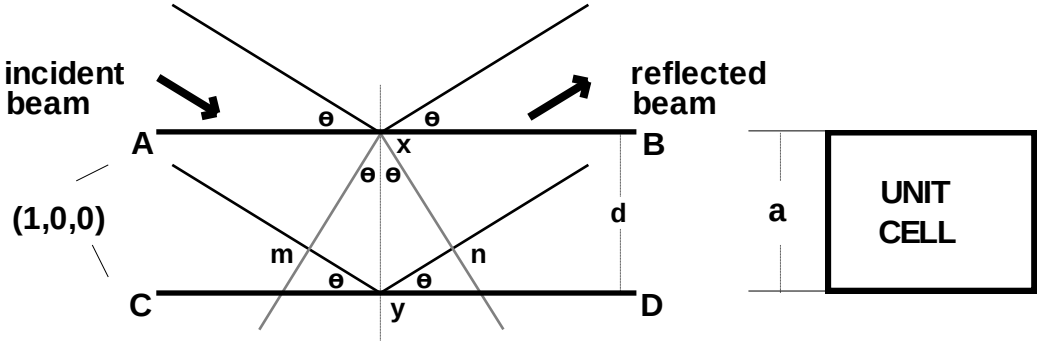


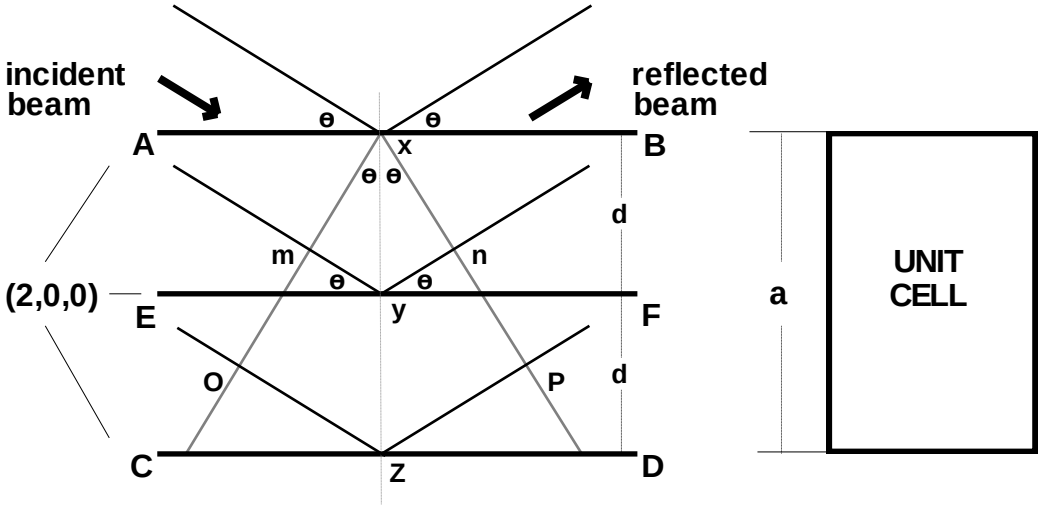




Basic Principle of Diffraction Pattern

Bragg's Law





Constructive interference

$$2d \sin\theta = n\lambda$$

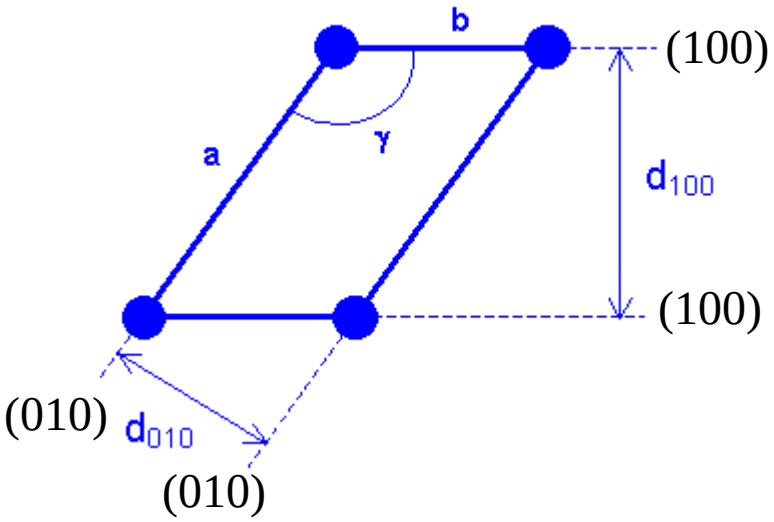
$$2d \sin\theta = \lambda$$

1st order reflection

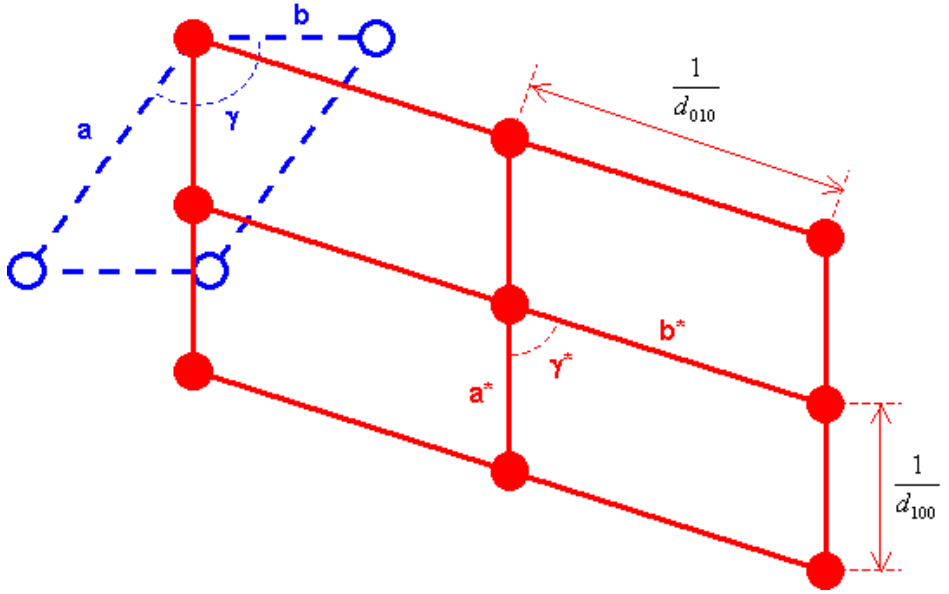
$$2d \sin\theta = 2\lambda$$

2nd order reflection

Basic Principle of Diffraction Pattern



Direct (real) lattice



Reciprocal lattice

Reciprocal vector **a*** ⊥ (100)
Reciprocal vector **b*** ⊥ (010)
| **a*** | = $1/d_{100}$
| **b*** | = $1/d_{010}$
angle $\gamma^* = 180^o - \gamma$

Basic Principle of Diffraction Pattern

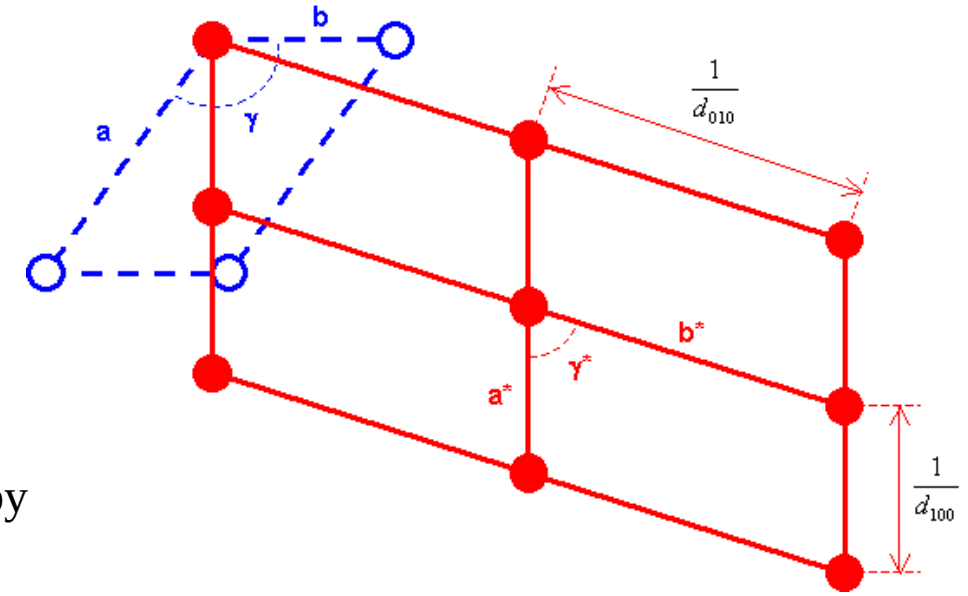
Due to the linear relationship between planes (ex, $d_{200} = (1/2)d_{100}$), a periodic lattice is generated. In general, the periodicity in the reciprocal lattice is given by

$$\rho^*_{hkl} = 1/d_{hkl}$$

In vector form, the general reciprocal lattice vector for the (*hkl*) plane is given by

$$g_{hkl} = \mathbf{n}_{hkl}/d_{hkl}$$

$\mathbf{n}_{hkl}$: unit vector normal to the (*hkl*) planes.



Reciprocal lattice

Reciprocal vector **a*** ⊥ (100)
Reciprocal vector **b*** ⊥ (010)
$|\mathbf{a}^*| = 1/d_{100}$
$|\mathbf{a}^*| = 1/d_{010}$
angle $\gamma^* = 180^o - \gamma$

Basic Principle of Diffraction Pattern

Direct and Reciprocal Cell Relationships

Orthorhombic

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90^o$

$$a^* = \frac{1}{a} \qquad a = \frac{1}{a^*}$$

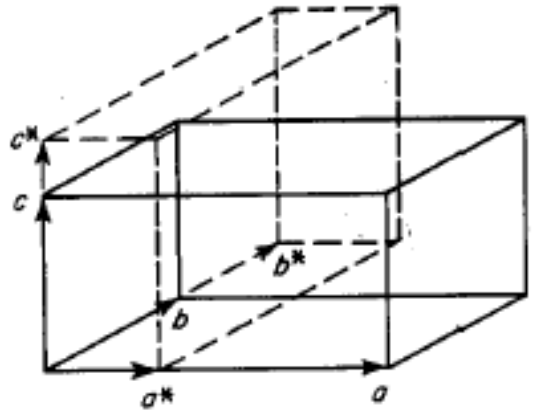
$$b^* = \frac{1}{b} \qquad b = \frac{1}{b^*}$$

$$c^* = \frac{1}{c} \qquad c = \frac{1}{c^*}$$

$$V^* = \frac{1}{V} = a^* b^* c^*$$

$$V = \frac{1}{V^*} = abc$$

$$\alpha = \beta = \gamma = \alpha^* = \beta^* = \gamma^* = 90^\circ$$



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

Tetragonal $a = b \neq c,\ \alpha = \beta = \gamma = \alpha* = \beta* = \gamma* = 90^o$

Basic Principle of Diffraction Pattern

Direct and Reciprocal Cell Relationships

Monoclinic

$a \neq b \neq c$

$\alpha = \gamma = 90^o$

$\beta \neq 120^o$

$$a^* = \frac{1}{a \sin \beta} \qquad a = \frac{1}{a^* \sin \beta^*} \qquad \alpha = \gamma = \alpha^* = \gamma^* = 90^\circ$$

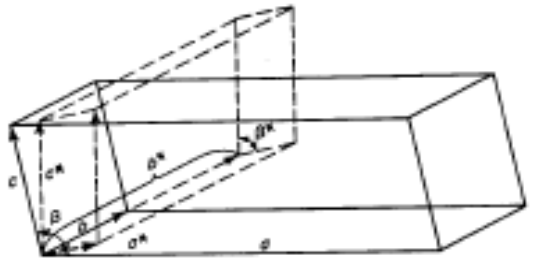
$$b^* = \frac{1}{b} \qquad b = \frac{1}{b^*} \qquad \beta^* = 180^\circ - \beta$$

$$c^* = \frac{1}{c \sin \beta} \qquad c = \frac{1}{c^* \sin \beta^*}$$

N.B.: $\sin \beta^* = \sin \beta$, $\cos \beta^* = -\cos \beta$

$$V^* = \frac{1}{V} = a^* b^* c^* \sin \beta^*$$

$$V = \frac{1}{V^*} = abc \sin \beta$$



Hexagonal $a = b \neq c$, $\alpha = \beta = \alpha* = \beta^* = 90^o$, $\gamma = 120^o$, $\gamma^* = 60^o$,

Basic Principle of Diffraction Pattern

Direct and Reciprocal Cell Relationships

Triclinic

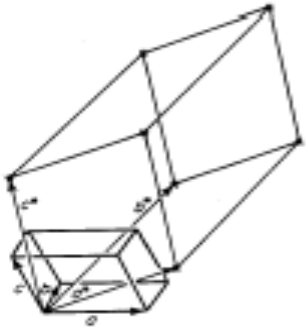
$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90^o$

$$a^* = \frac{bc \sin \alpha}{V} \qquad a = \frac{b^*c^* \sin \alpha^*}{V^*}$$

$$b^* = \frac{ac \sin \beta}{V} \qquad b = \frac{a^*c^* \sin \beta^*}{V^*}$$

$$c^* = \frac{ab \sin \gamma}{V} \qquad c = \frac{a^*b^* \sin \gamma^*}{V^*}$$



$$V = \frac{1}{V^*} = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

$$V^* = \frac{1}{V} = a^*b^*c^*\sqrt{1 - \cos^2\alpha^* - \cos^2\beta^* - \cos^2\alpha^* + 2\cos\alpha^*\cos\beta^*\cos\gamma^*}$$

$$\cos\alpha^* = \frac{\cos\beta\cos\gamma - \cos\alpha}{\sin\beta\sin\gamma} \qquad \cos\alpha = \frac{\cos\beta^*\cos\gamma^* - \cos\alpha^*}{\sin\beta^*\sin\gamma^*}$$

$$\cos\beta^* = \frac{\cos\alpha\cos\gamma - \cos\beta}{\sin\alpha\sin\gamma} \qquad \cos\beta = \frac{\cos\alpha^*\cos\gamma^* - \cos\beta^*}{\sin\alpha^*\sin\gamma^*}$$

$$\cos\gamma^* = \frac{\cos\alpha\cos\beta - \cos\gamma}{\sin\alpha\sin\beta} \qquad \cos\gamma = \frac{\cos\alpha^*\cos\beta^* - \cos\gamma^*}{\sin\alpha^*\sin\beta^*}$$

Trigonal $a = b = c,\ \alpha = \beta = \gamma \neq 90^o$

Basic Principle of Diffraction Pattern

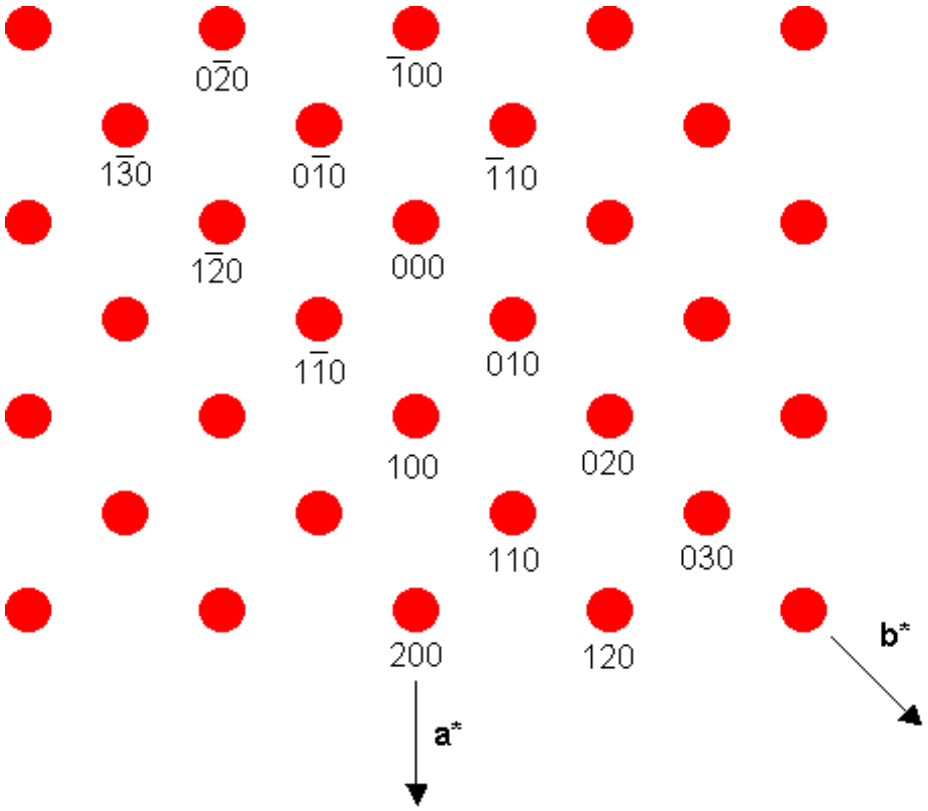
Due to the linear relationship between planes (ex, $d_{200} = (1/2)d_{100}$), a periodic lattice is generated. In general, the periodicity in the reciprocal lattice is given by

$$\rho^*_{hkl} = 1/d_{hkl}$$

In vector form, the general reciprocal lattice vector for the (*hkl*) plane is given by

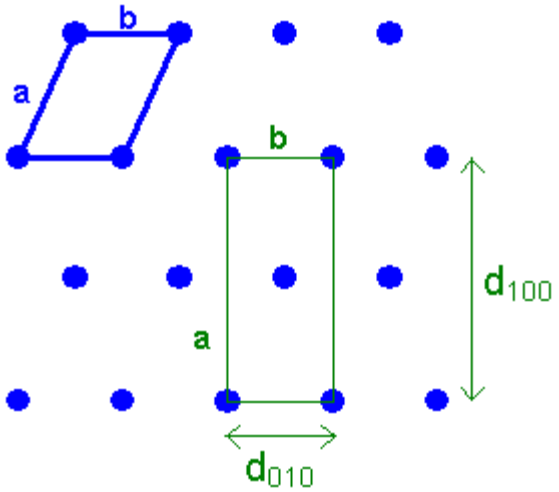
$$g_{hkl} = \mathbf{n}_{hkl}/d_{hkl}$$

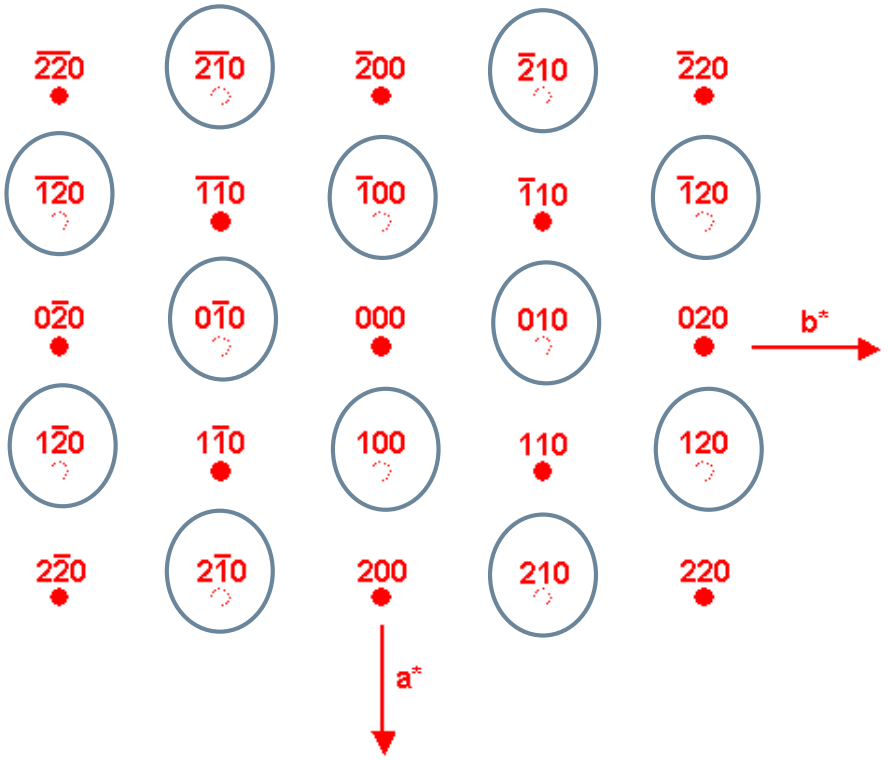
$\mathbf{n}_{hkl}$: unit vector normal to the (*hkl*) planes.



Basic Principle of Diffraction Pattern

Absence in reciprocal lattice





High symmetry can lead to reflections being systematically absent from the data set.

For non-primitive lattices, such as a C-centred lattice, systematic absences can occur in the reciprocal lattice (and in diffraction pattern) due to the construction of the lattices.

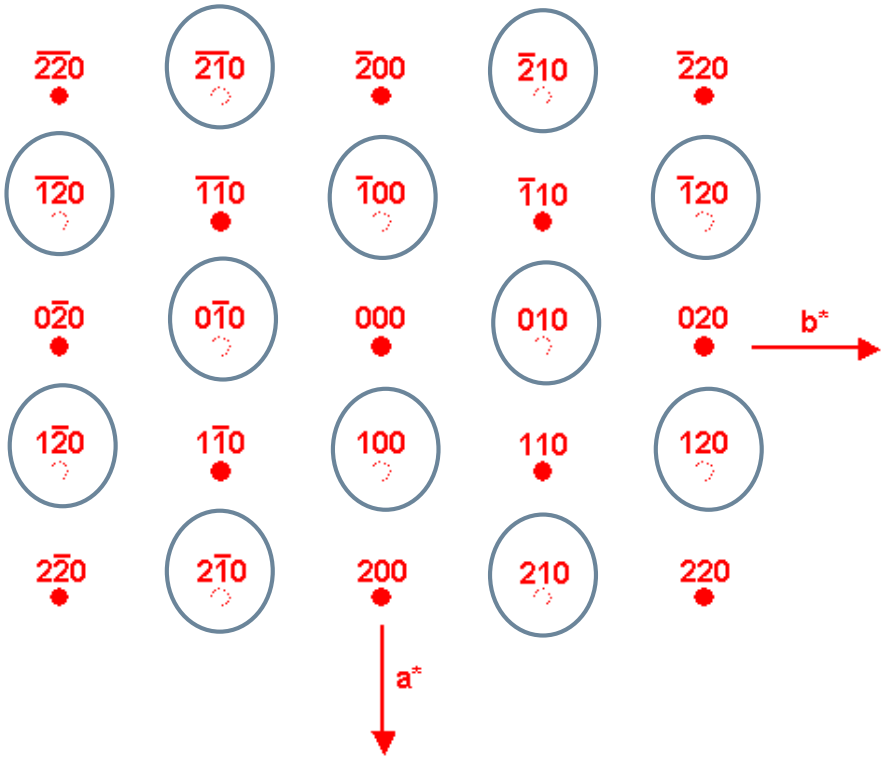
Basic Principle of Diffraction Pattern

Absence in reciprocal lattice

General absences determine the lattice type;
Primitive (**P**) has no general absences.
End Centered (**C**) h+k=2n+1 are all absent.
Face Centered (**F**) only h, k, l, all even or all odd are observed.
Body Cantered (**I**) h+k+l=2n+1 are all absent.

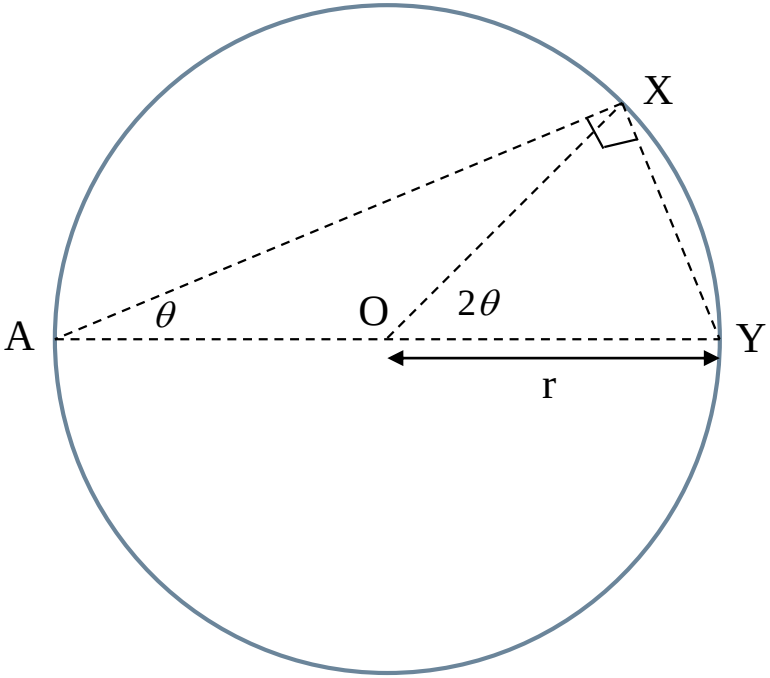
Special absences refer to specific sets of reflections and are used to detect the presence of glide planes and screw axes.

Give information for determining space groups



Basic Principle of Diffraction Pattern

Ewald Sphere



$$2r \sin\theta = XY$$

If this geometry is constructed **in reciprocal space** with

r = 1/λ
Y is 000 point
X is a general *hkl* point

=> XY = $1/d_{hkl}$

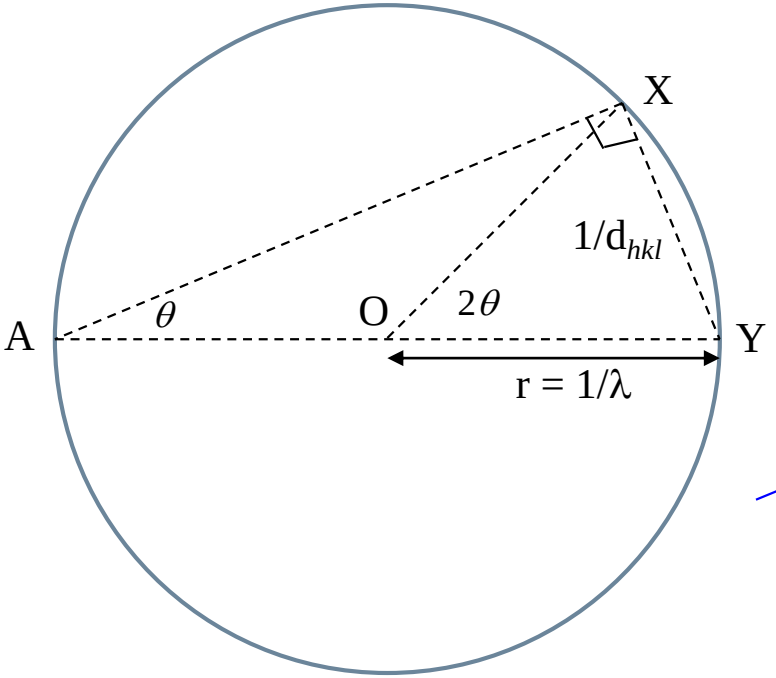
$$\frac{2}{\lambda}\sin\theta = 1/d_{hkl}$$

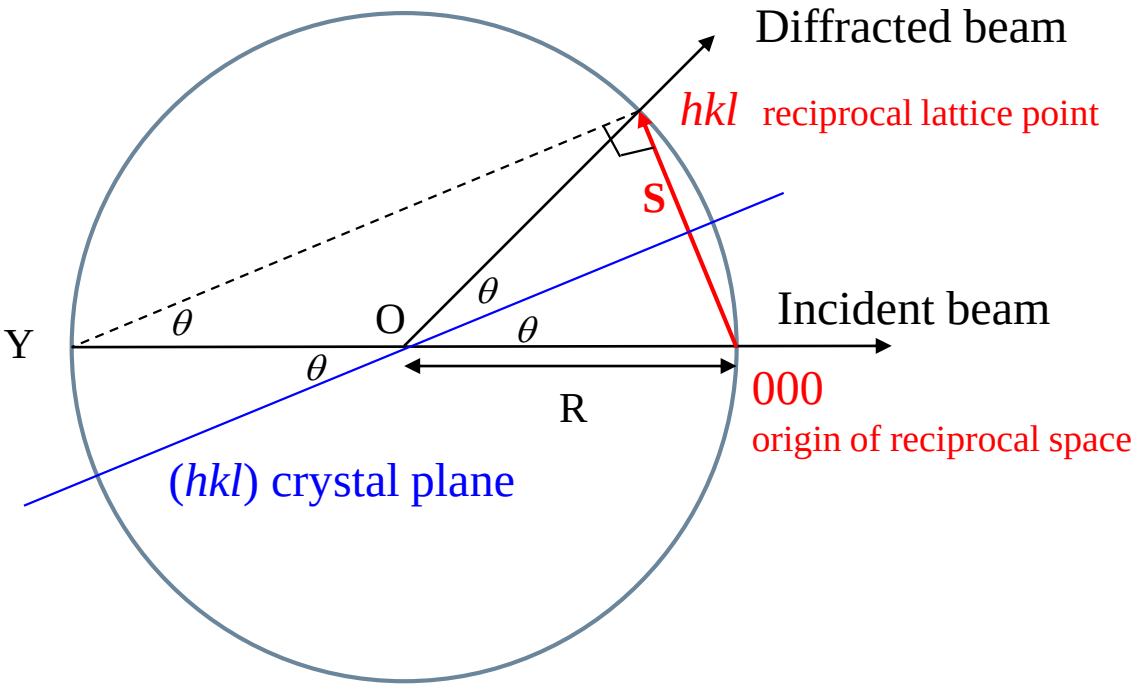
$$2d_{hkl}\sin\theta = \lambda$$ **Bragg's Law**

In 3D, it's a sphere, called **Ewald Sphere**.
Even though the Ewald sphere is in reciprocal space (inverse distance) and we are in real space, we can use the predicted angles of diffraction (2θ) to predict the diffraction pattern.

Basic Principle of Diffraction Pattern

Ewald Sphere





Since $|\mathbf{S}| = 1/d_{hkl}$, if we let $R = 1/\lambda$,

$$\frac{2}{\lambda}\sin\theta = 1/d_{hkl}$$

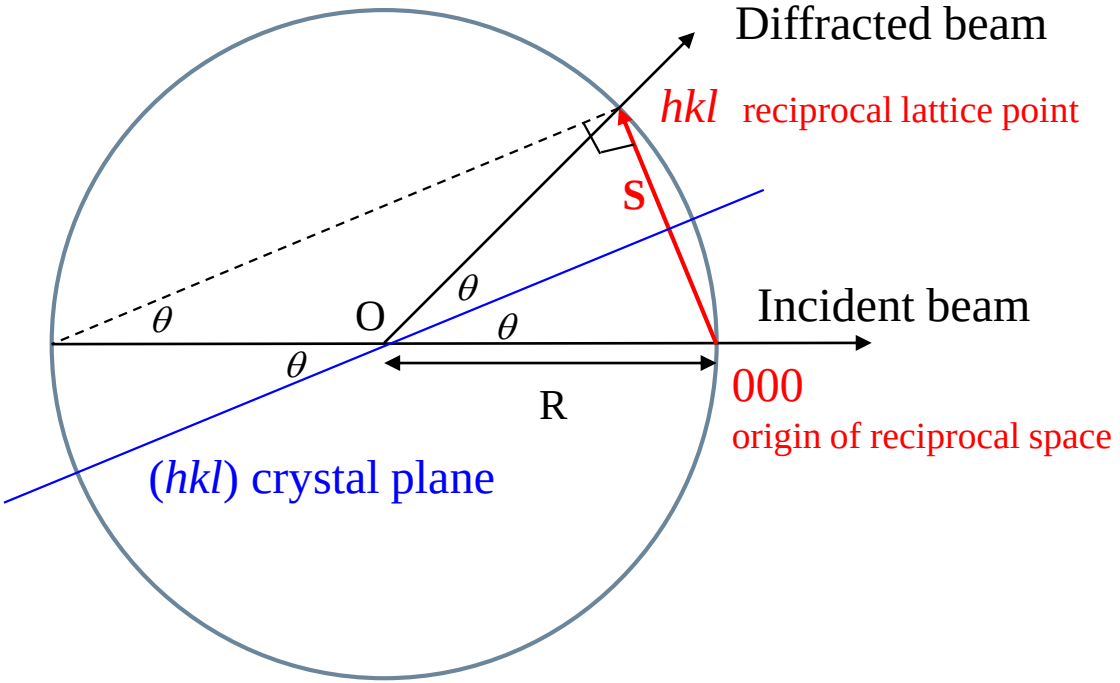
$$2d_{hkl}\sin\theta = \lambda$$ **Bragg's Law**

Basic Principle of Diffraction Pattern

Ewald Sphere

Even though the Ewald sphere is in reciprocal space (inverse distance) and we are in real space, we can use the predicted angles of diffraction (2θ) to predict the diffraction pattern.

➔ **Diffraction occurs when a reciprocal lattice point intersects Ewald sphere.**



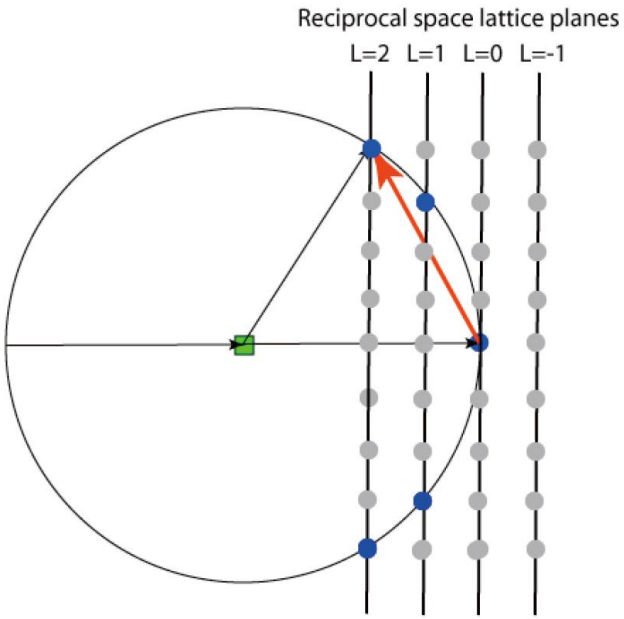
Since $|\mathbf{S}| = 1/d_{hkl}$, if we let $R = 1/\lambda$,

$$\frac{2}{\lambda}\sin\theta = 1/d_{hkl}$$

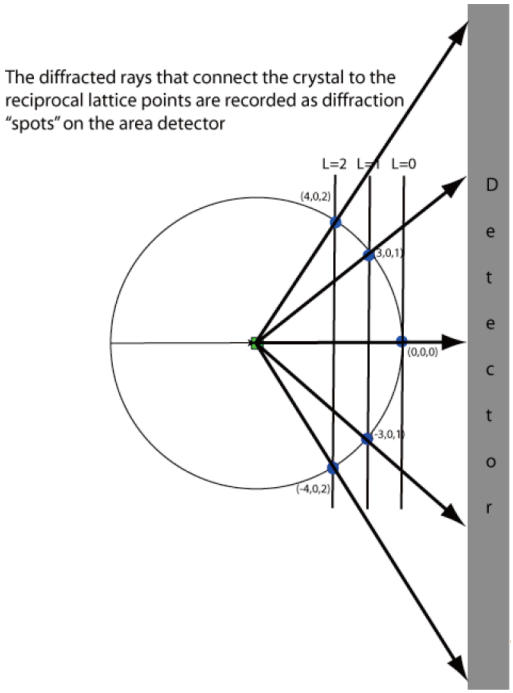
$$2d_{hkl}\sin\theta = \lambda$$ **Bragg's Law**

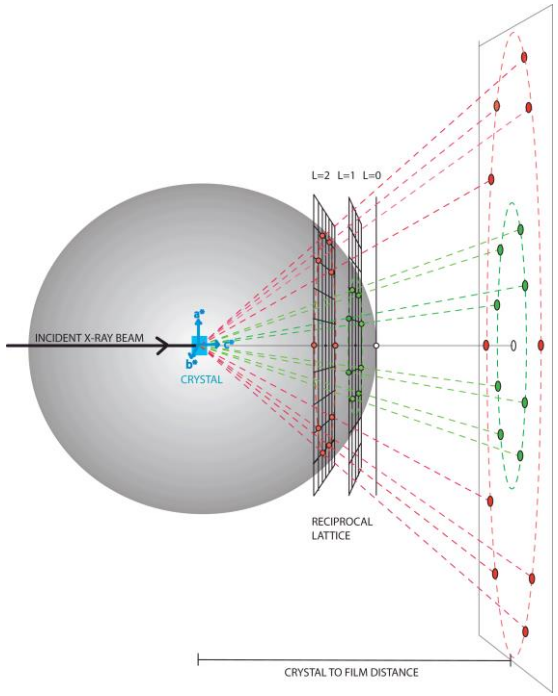
Basic Principle of Diffraction Pattern

Ewald Sphere



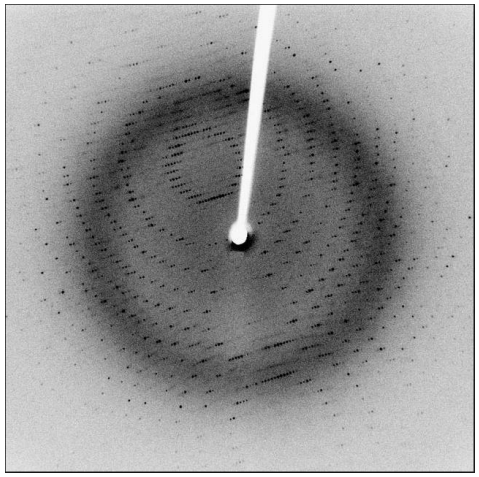
A perfectly-aligned crystal shooting down the C* axis
Only spots lying on the Ewald sphere are diffracting

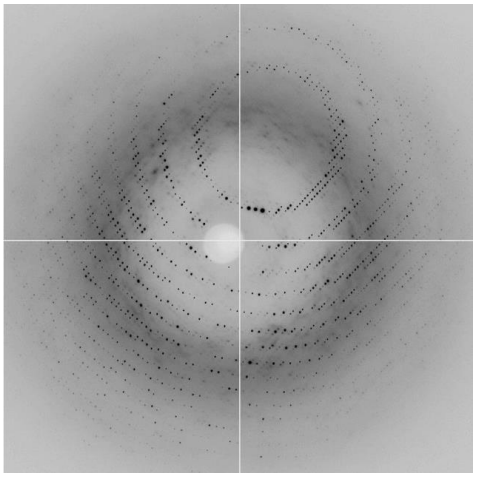


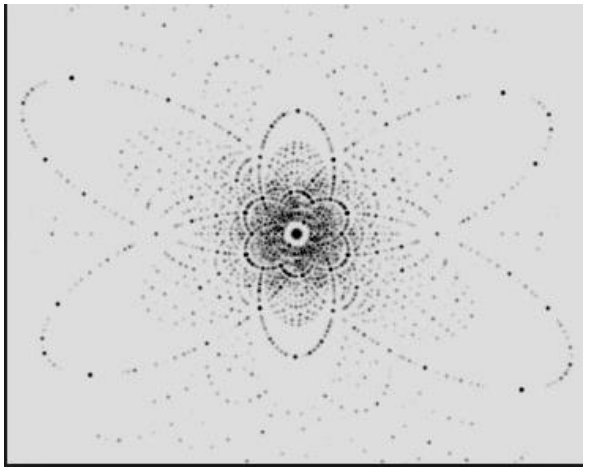


Basic Principle of Diffraction Pattern

Examples

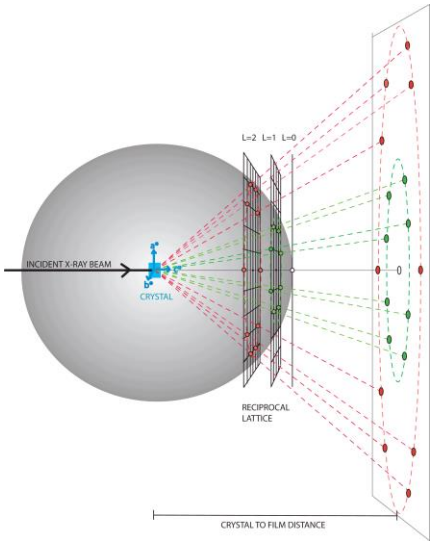


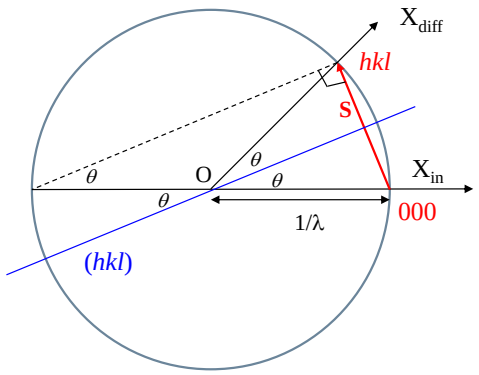




Basic Principle of Diffraction Pattern

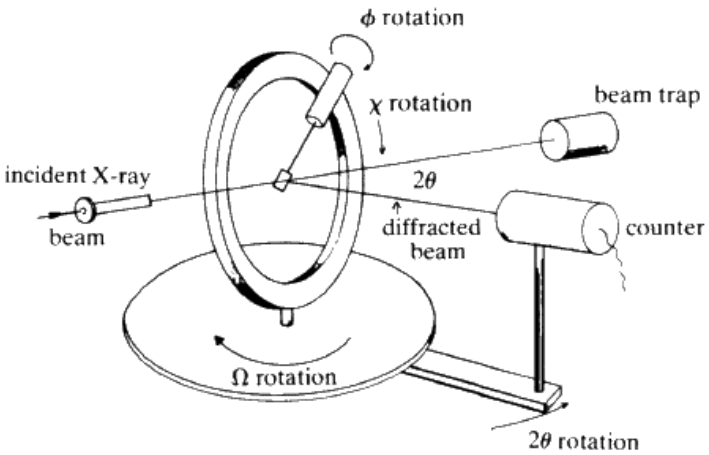
Limiting Sphere

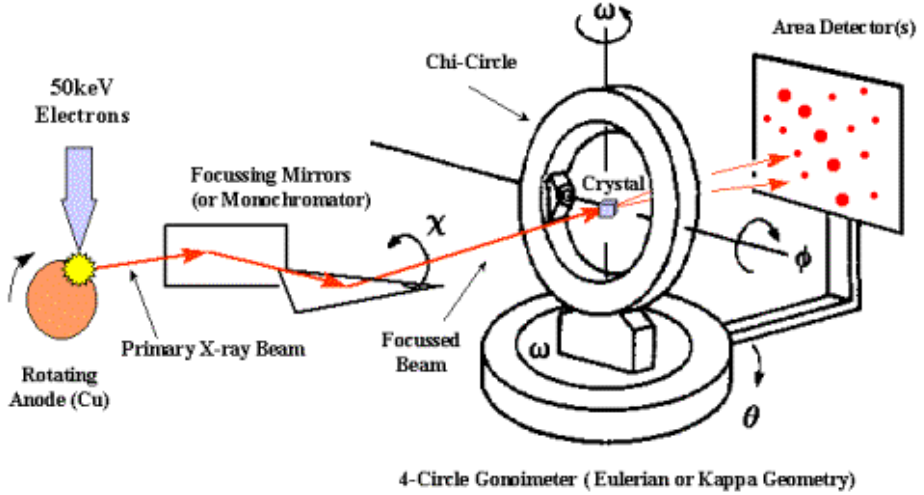




Ewald Sphere

We have to collect diffraction patterns in all possible angles.



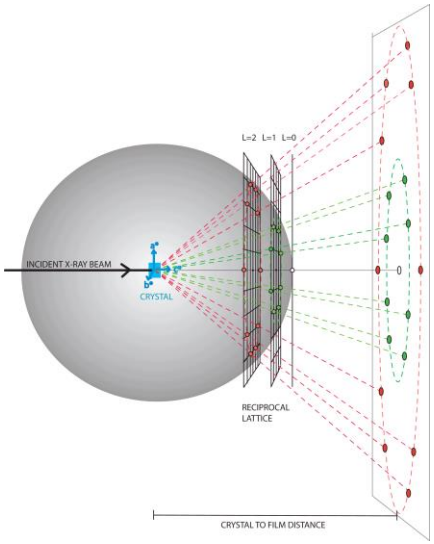


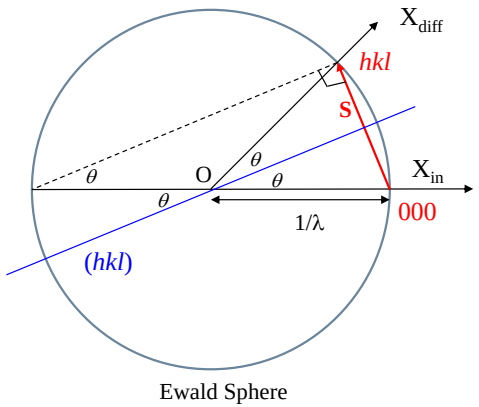
4-Circle Goniometer (Eulerian or Kappa Geometry)

4-circle diffractometer

Basic Principle of Diffraction Pattern

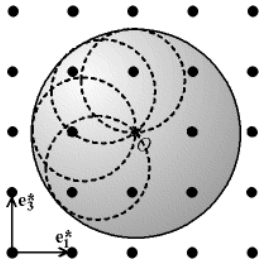
Limiting Sphere

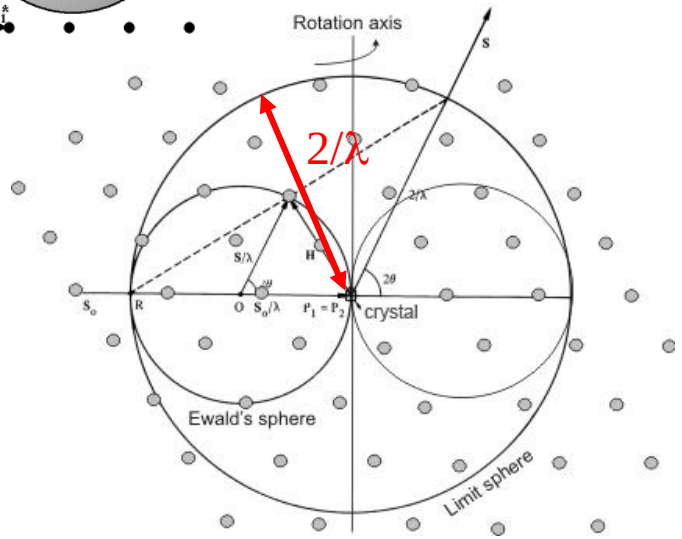




Ewald Sphere

We have to collect diffraction patterns in all possible angles.
Then **how many diffraction spots can we get theoretically**?





If one rotates the Ewald sphere completely about the (000) reciprocal lattice point in all three dimensions, the larger sphere (of radius 2/λ) contains all of the reflections that it is possible to collect using that wavelength of X-rays. This construction is known as the "**Limiting sphere**" and it defines the complete data set. Any reciprocal lattice points outside of this sphere can not be observed.

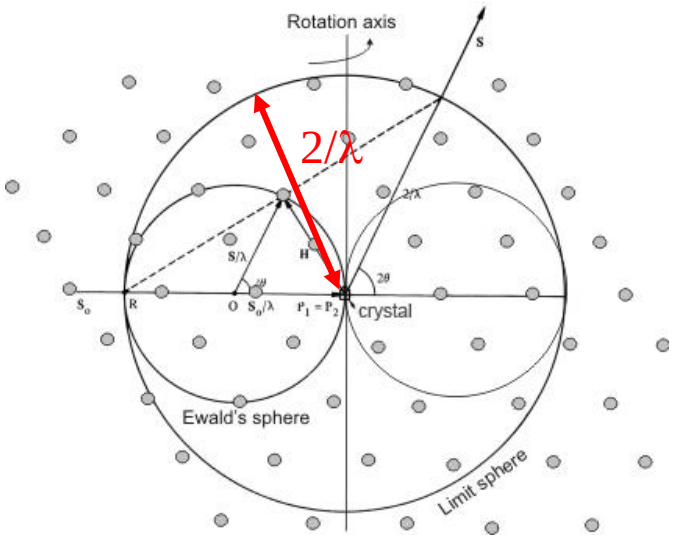
Basic Principle of Diffraction Pattern

Limiting Sphere

Complete Data Set: total # of reciprocal lattice points within the limiting sphere
= theoretically possible total # of reflection points

$$\approx \frac{\frac{4}{3}\pi r^3}{V^*} = \frac{4}{3}\pi(2/\lambda)^3 V \approx 33.5\, V/\lambda^3 = 33.5/V^*\lambda^3$$

(V^*: volume of reciprocal unit cell
V: volume of unit cell. λ = X-ray wavelength



Basic Principle of Diffraction Pattern

Limiting Sphere

Resolution:

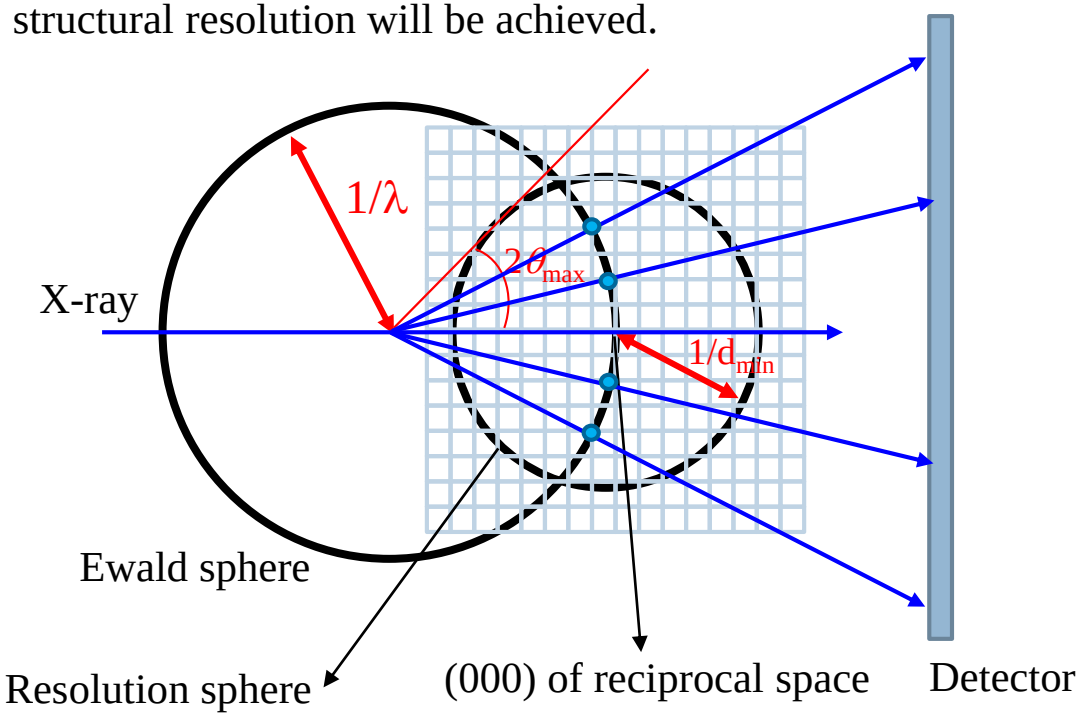
Theoretical maximum resolution: when $\sin\theta = 1$, $\mathbf{d_{res} = \lambda/2}$

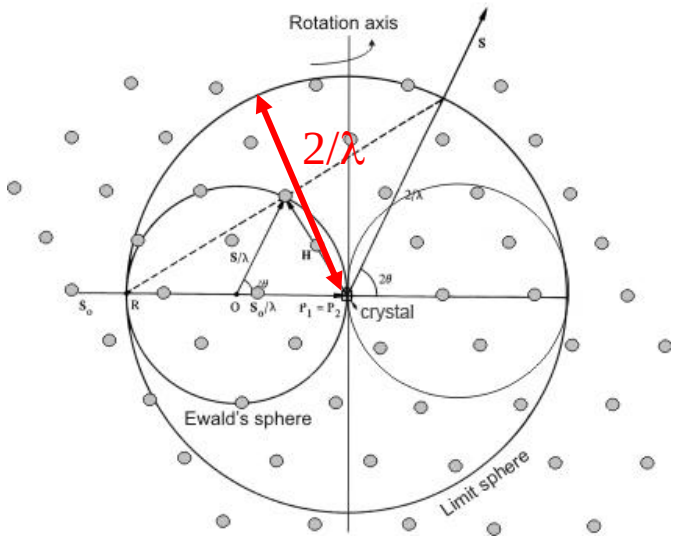
Real maximum resolution: $\mathbf{d_{res} = (\lambda/2)\sin\theta_{max}}$

$$2d\sin\theta = \lambda$$

$$\sin\theta_{max} = \lambda/2d_{min}$$

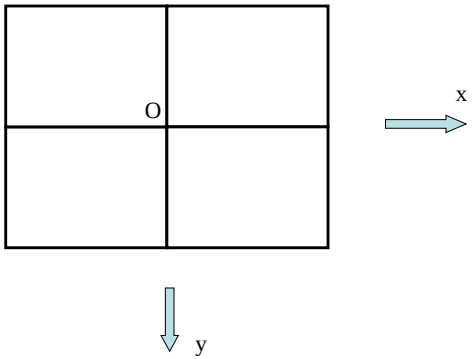
By reducing the wavelength, Bragg's Law indicates that the diffraction angles (θ) will decrease; the spectrum shrinks, but on the other hand, more diffraction data will be obtained, and therefore a better structural resolution will be achieved.

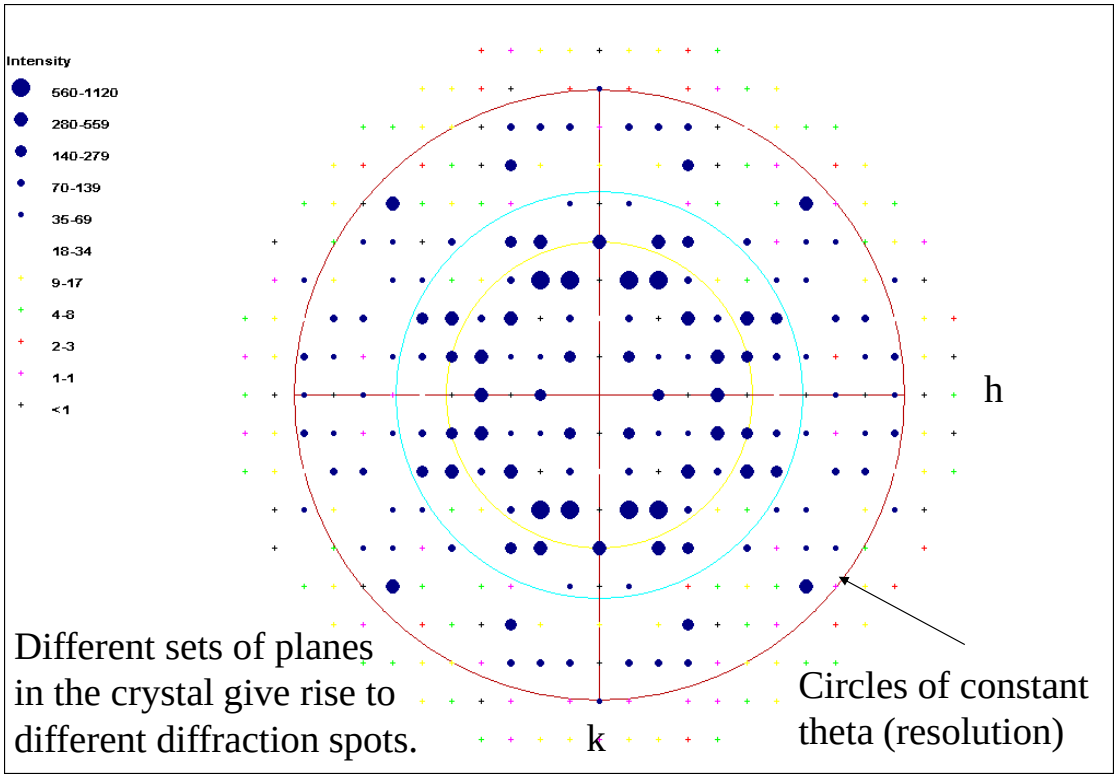




Basic Principle of Diffraction Pattern

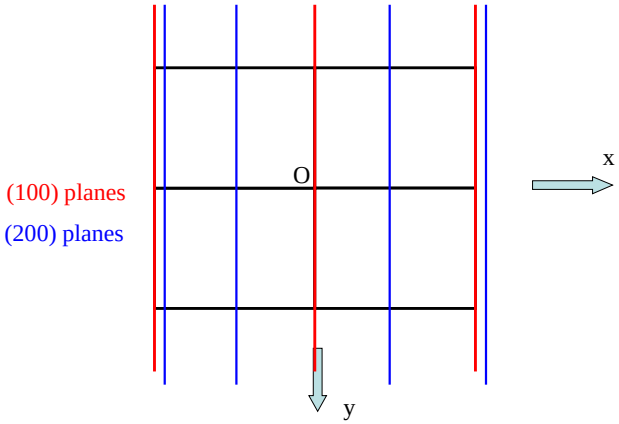
Examples





Basic Principle of Diffraction Pattern

Examples



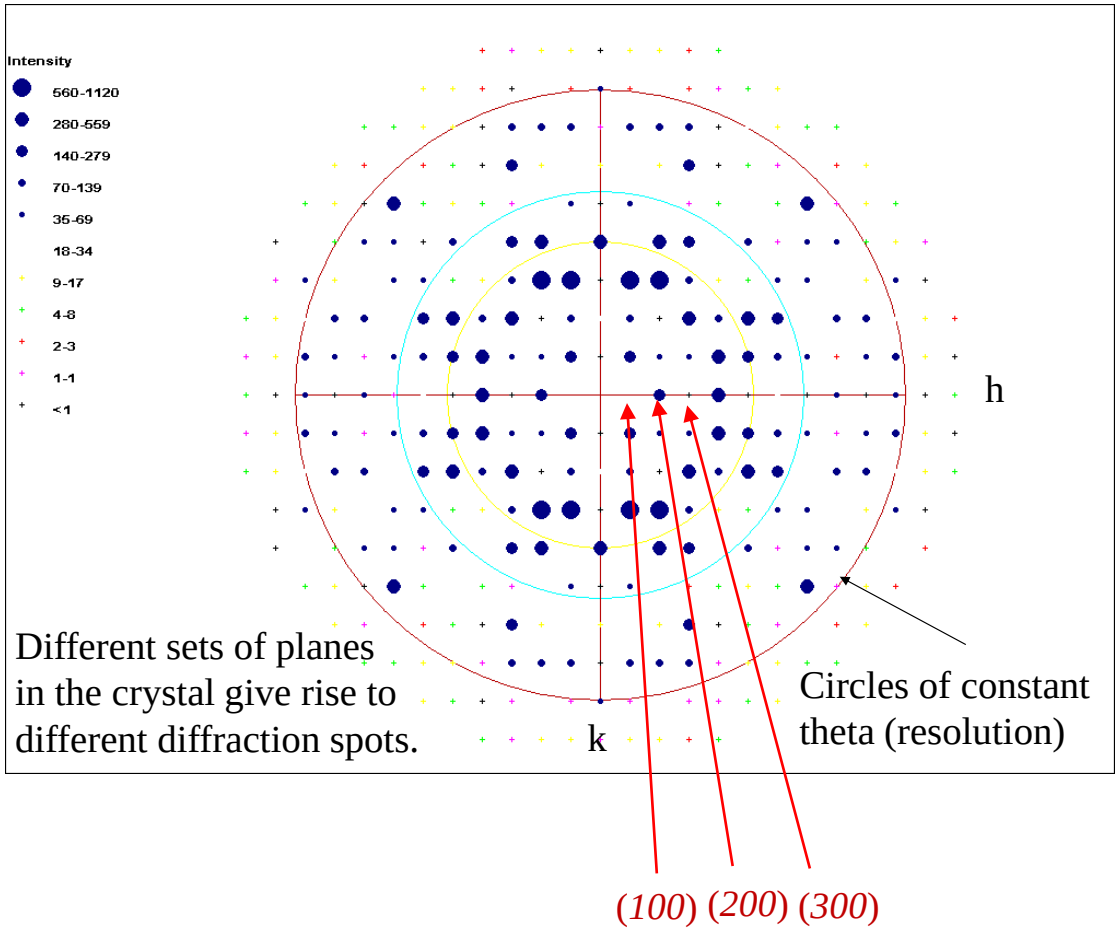
$$2d \sin\theta = n\lambda$$

$$2d_{(1,0,0)} \sin\theta = \lambda$$

$$2d_{(2,0,0)} \sin\theta = \lambda$$

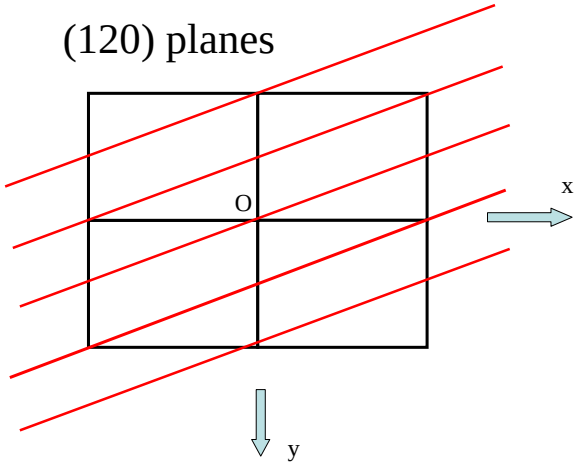
$$d_{(2,0,0)} = (1/2)d_{(1,0,0)}$$

θ increases

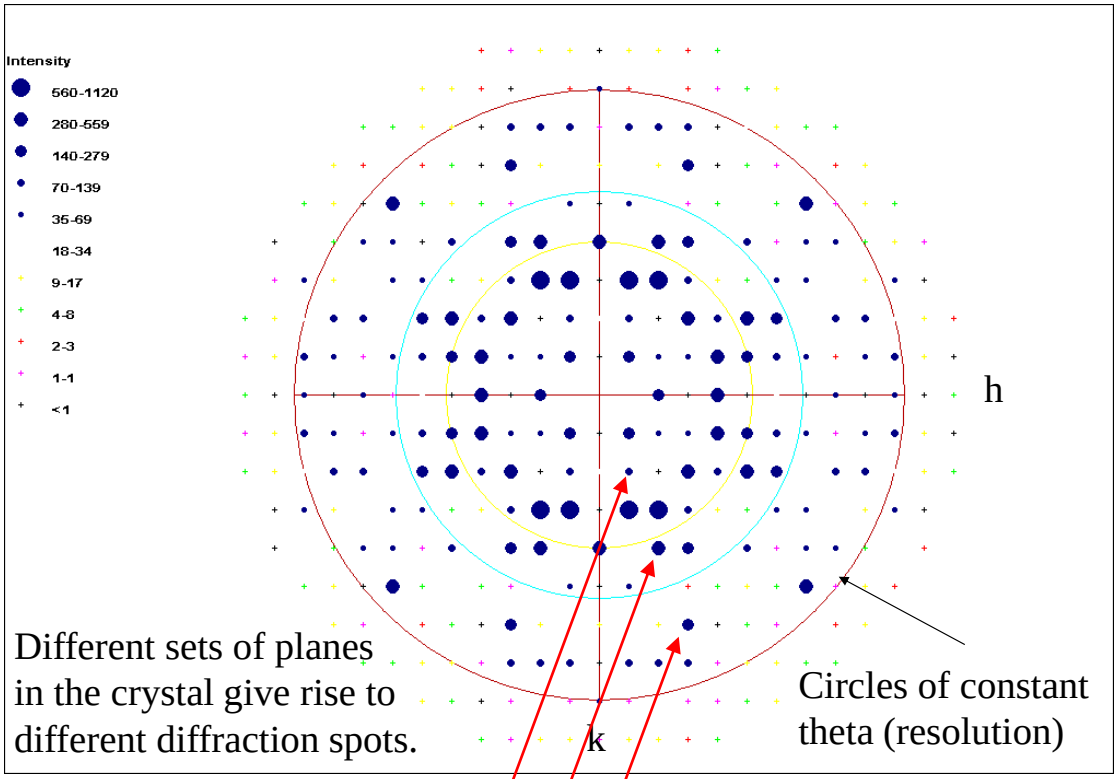


Basic Principle of Diffraction Pattern

Examples

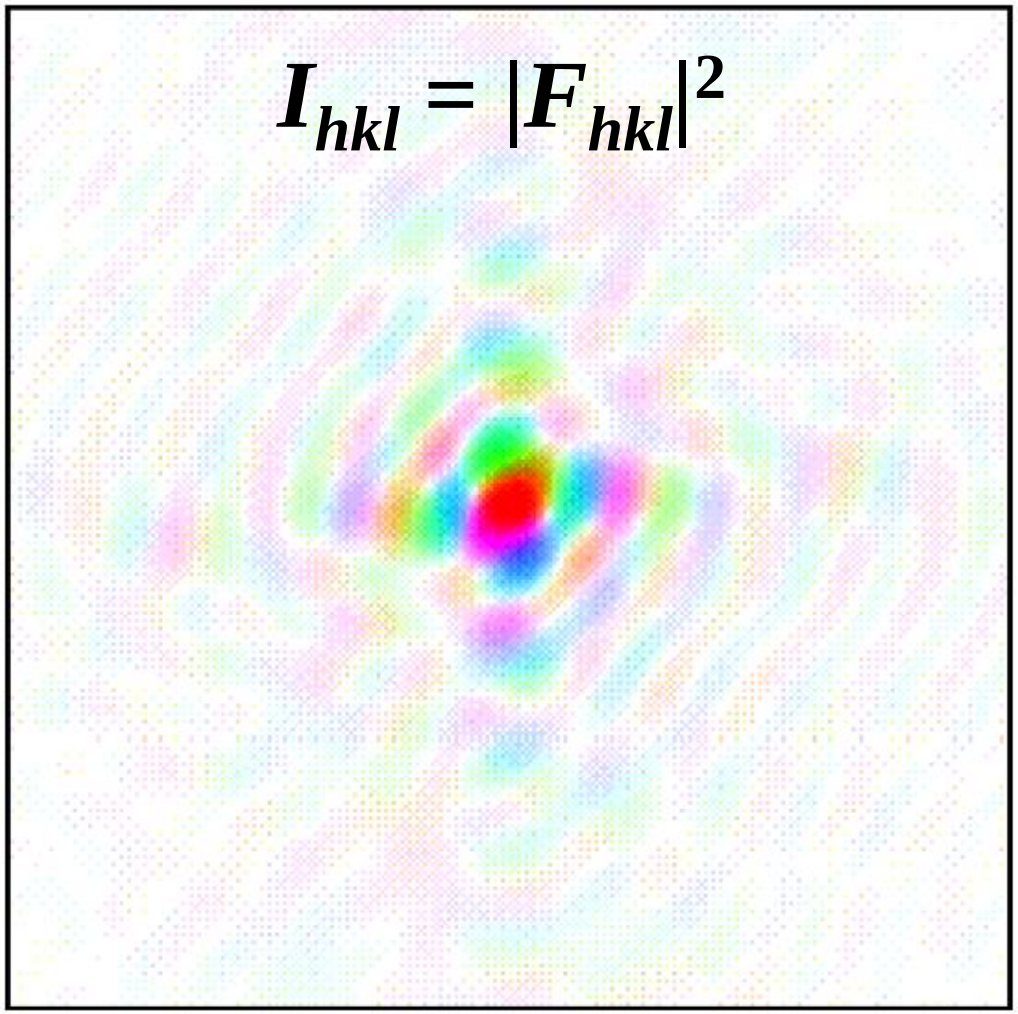


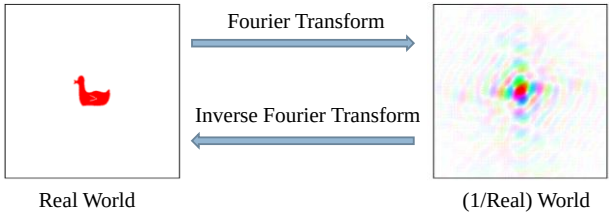
$$2d \sin\theta = n\lambda$$



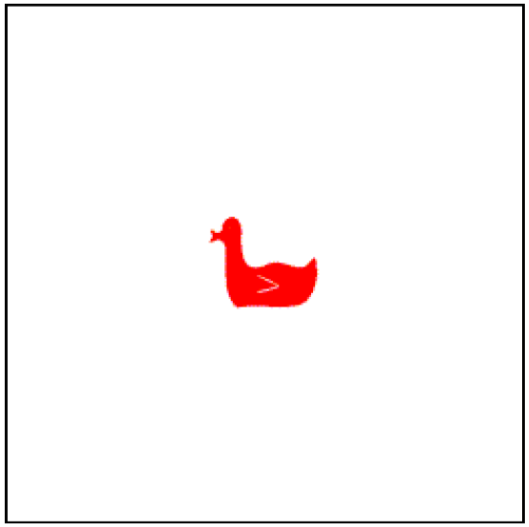
Basic Principle of Diffraction Pattern

Outcomes of Experiment

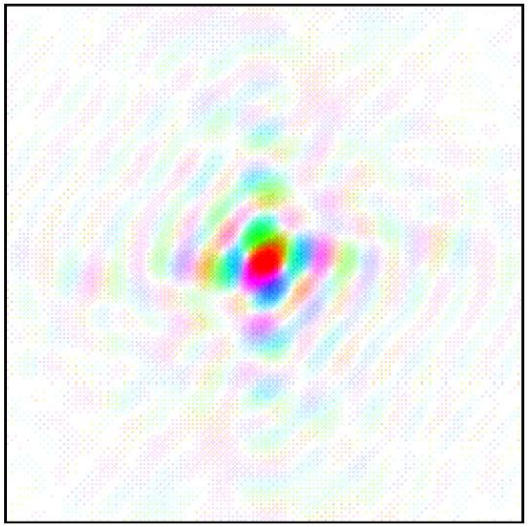




How to get this ?



From this ?



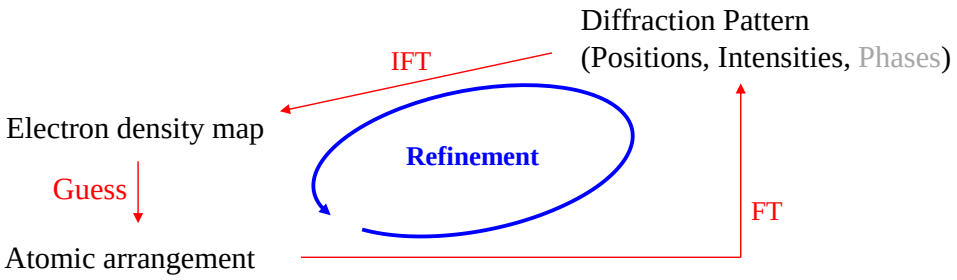
Diffraction Pattern to Electron Density Map

To get ρ_{xyz}, we have to know the **structure factor, F_{hkl}**.
F_{hkl} contains amplitude (**$|F_{hkl}|$**) and phase (**ϕ_{hkl}**) at *hkl*.

$$F_{hkl} = |F_{hkl}|\cos\phi_{hkl} + i\,|F_{hkl}|\sin\phi_{hkl}$$

- What we measure in the experiment, $|F_{hkl}|$
- What we still need, φ_{hkl} (the phase problem)

Methods for solving the phase problem (Initial Phasing)
- *Ab initio* phasing (Direct methods)
- Molecular Replacement (MR)
- Multiple/Single Isomorphous replacement (MIR/SIR) (=Heavy Metal Method)
- Multiple/Single wavelength Anomalous Diffraction (MAD/SAD)



After final refinements, try to achieve R factor (relative index)

$$\mathbf{R} = \frac{\sum ||F_o| - |F_c||}{|F_o|} \leq 0.05$$

Diffraction Pattern to Electron Density Map

Structure Factor

$$F_{(h,k,l)} = \sum_{j=1}^{atoms} f_{(j)} \exp\left[2\pi \cdot i(hx_{(j)} + ky_{(j)} + lz_{(j)})\right]$$

j = j-*th* atom

- Describes how atomic arrangement (*xyz*) influences the intensity of the scattered beam.

- It tells us which reflections (i.e., peaks, *hkl*) to expect in a diffraction pattern.
- Structure factor is independent of the shape and size of the unit cell.

$$|F_{hkl}| = \frac{\text{amplitude of the wave scattered by all atoms of in a unit cell}}{\text{amplitude of the wave scattered by one electron}}$$

By definition, $|F_{000}|$ is the sum of all electrons in a unit cell.

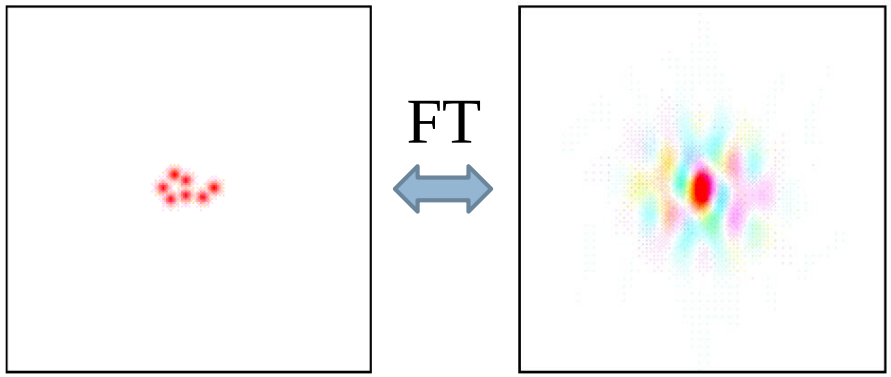
Selection Rules

Crystal Type	Bravais Lattice	Reflections Present	Reflections Absent
Simple	Primitive, P	Any *h,k,l*	None
Body-centered	Body centered, I	$h+k+l$ = even	$h+k+l$ = odd
Face-centered	Face-centered, F	*h,k,l* unmixed	*h,k,l* mixed
NaCl	FCC	*h,k,l* unmixed	*h,k,l* mixed
Zincblende	FCC	Same as FCC, but if all even and $h+k+l \neq 4N$ then absent	*h,k,l* mixed and if all even and $h+k+l \neq 4N$ then absent
Base-centered	Base-centered	*h,k* both even or both odd	*h,k* mixed
Hexagonal close-packed	Hexagonal	$h+2k=3N$ with *l* even $h+2k=3N\pm1$ with *l* odd $h+2k=3N\pm1$ with *l* even	$h+2k=3N$ with *l* odd

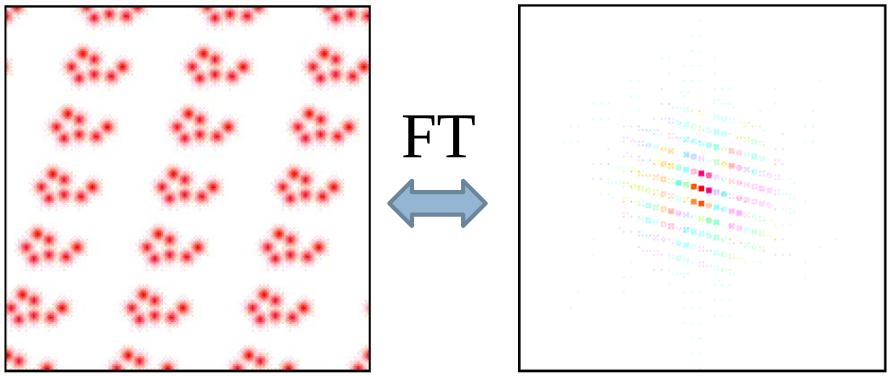
Diffraction Pattern to Electron Density Map

Fourier Transform (Inverse Fourier Transform)

$$\rho(xyz) = \frac{1}{V}\sum_{h}\sum_{k}\sum_{l} | F_{hkl} | \exp[-2\pi \cdot i(hx + ky + lz) + i\varphi_{hkl}]$$



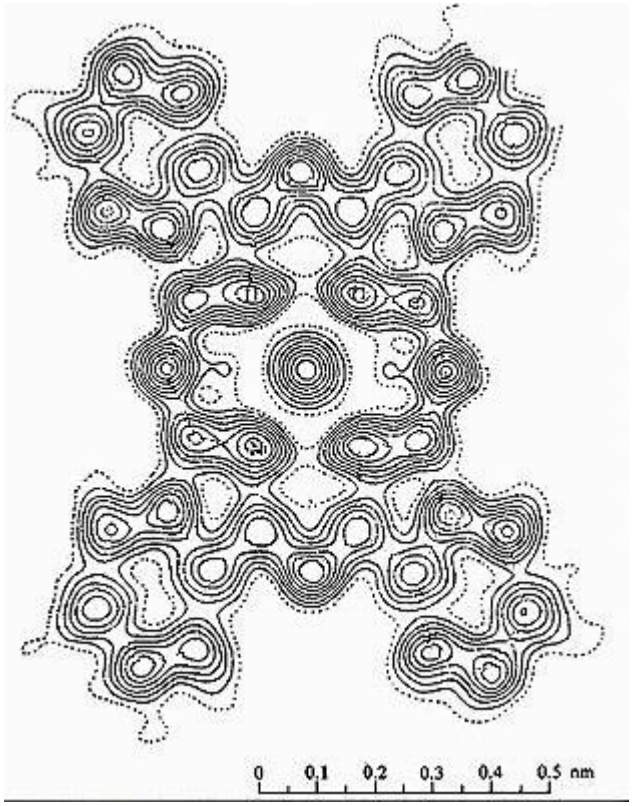
Electron Density Map Diffraction Pattern



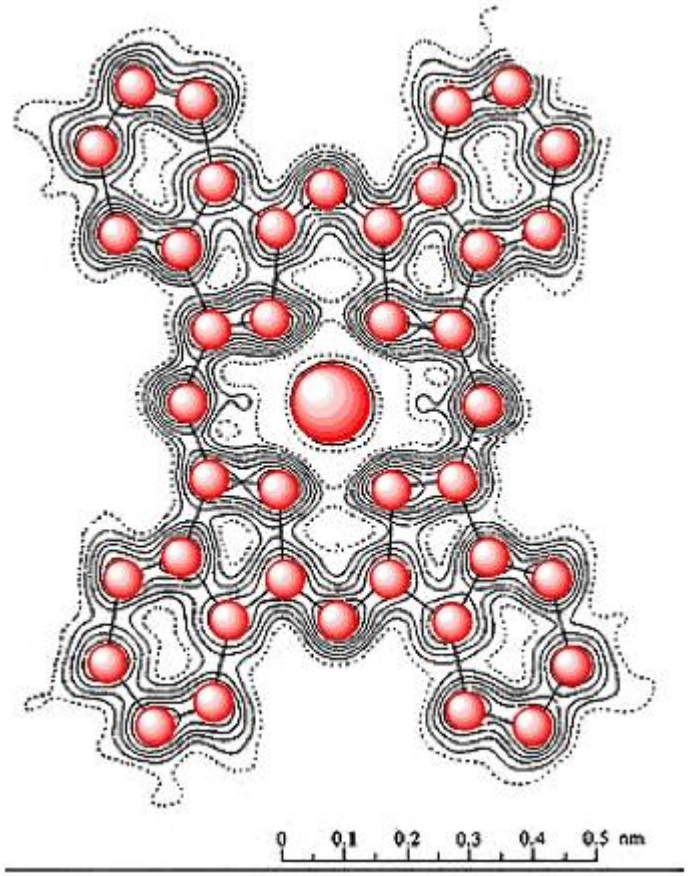
Electron Density Map Diffraction Pattern

Electron Density Map to Structure

Initial Guess



Electron Density Map



Atomic Arrangement (Structure)

Refinements

Procedure

1. Use whatever atoms you have that look OK to generate an electron density map.
2. The known atoms are subtracted from this to generate a difference map.
3. Any atoms that have been missed should be in the difference map.
4. The refinement process minimises the difference between observed (F_o)and calculated (F_c)reflection intensities.
5. In the final difference map there should be no peaks larger than a H atom
   i.e. > 1e/Å ^{3}. (A H atom has a volume of about 1Å ^{3} and has 1 e.)

Refinements

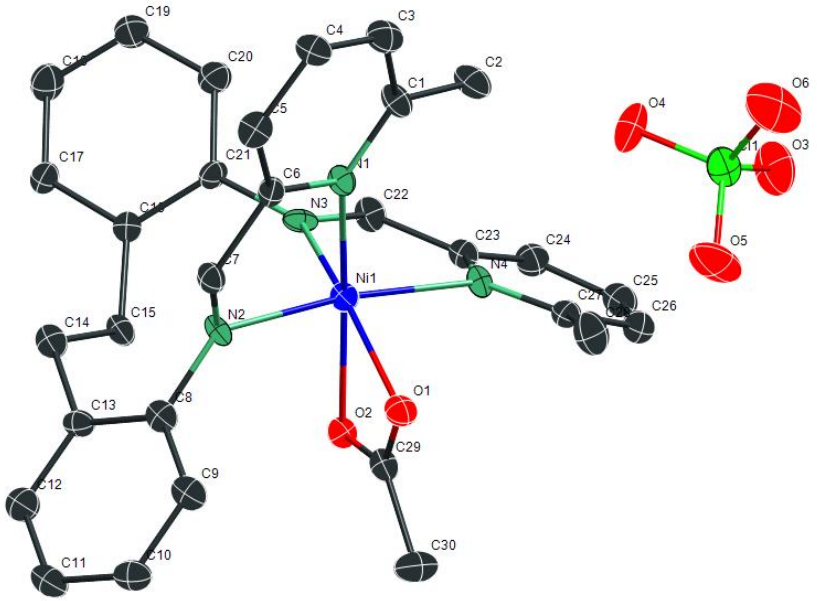
Final Stage

Addition of hydrogen atoms – Hydrogen atoms have only 1 electron and are often not seen in difference maps. It is best to include them at calculated positions. This is easy to do and it will improve the "R factor".

Anisotropic refinement of the non-hydrogen atoms – In the early stages atoms are refined as if they were spheres. Since atoms vibrate in a way that is controlled by chemical bonds and interactions with their neighbours, it is better to refine then as ellipsoids. One parameter (the radius) is enough to define a sphere this with x,y,z means that isotropic refinement requires 4 parameters per atom. An ellipsoid needs 6 parameters thus an anisotropic atom requires 9 parameters.

Report

Details of the crystallization - solvent, temperature, how did you obtain the crystal
Details of the data collection - instrument, number of reflections, crystal size
Details of the solution/refinement - confidence factors, hydrogen treatment
Details of the structure - atom positions, thermal parameters, bond distances and angles
A figure showing the atom numeration
A figure showing the thermal ellipsoid (ORTEP) (could be combined)



Files from Crystallographers

.raw – raw reflection data; used as input file for XPREP
._ls – statistical analysis of raw reflection data
.prp – a listing of what was done while running XPREP
.p4p – data collection parameter file; used as input file for XPREP
.hkl – reflection intensity table created by XPREP.
.ins – instruction file containing cell parameters, etc. created by XPREP; input file for XS, XL, and XSHELL
.res – results file created by running XS or XL; updated form of .ins file
.lst – a listing of what was done in the last computer run.
.fcf – structure factors
.cif – crystallographic information file

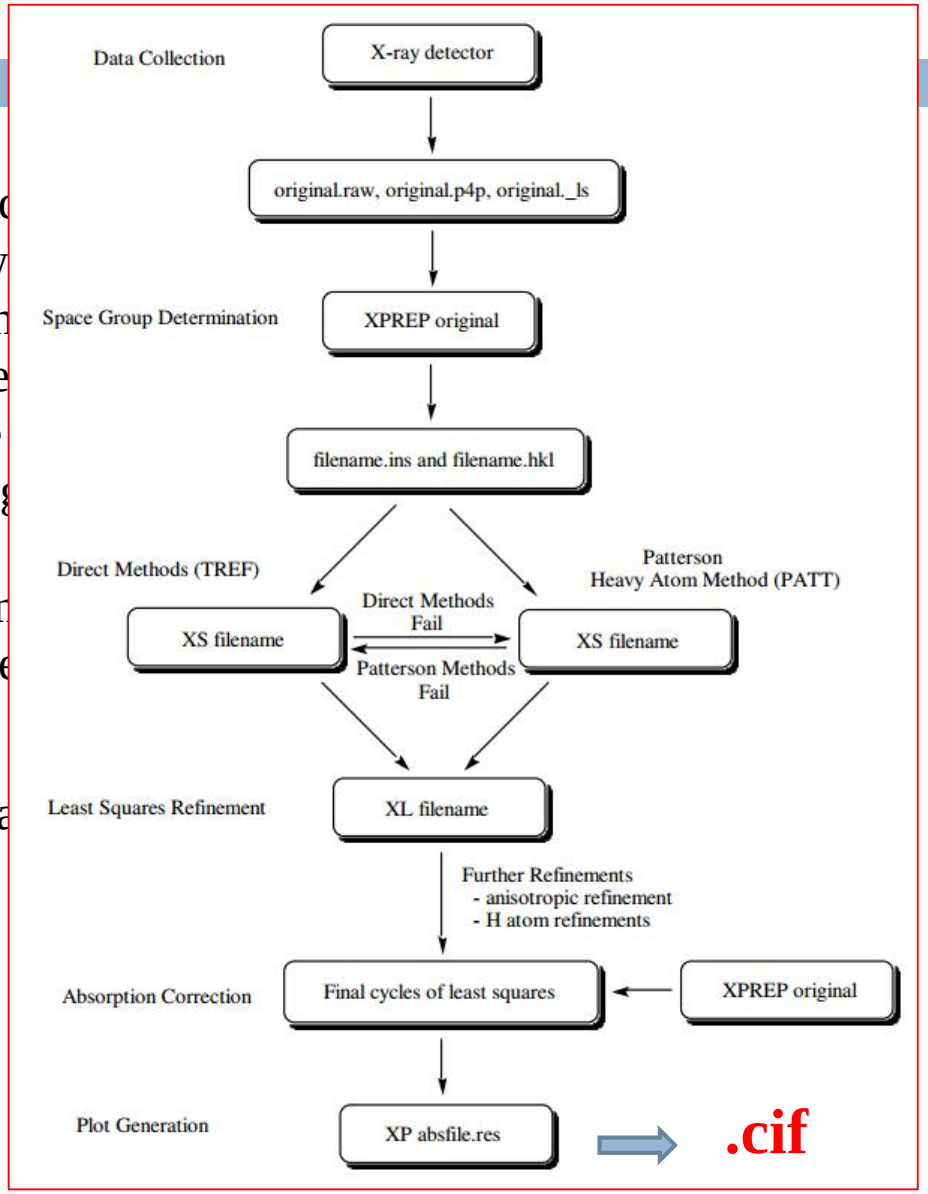
Files from Crystallographers

.raw – raw reflection data; used as input file for XPREP
._ls – statistical analysis of raw reflection data
.prp – a listing of what was done while running XPREP
.p4p – data collection parameter file; used as input file for XPREP
.hkl – reflection intensity table created by XPREP.
.ins – instruction file containing cell parameters, etc. created by XPREP; input file for XS, XL, and XSHELL
.res – results file created by running XS or XL; updated form of .ins file
.lst – a listing of what was done in the last computer run.
.fcf – structure factors
.cif – crystallographic information file

Files from Crystallographers

.raw – raw reflection data; usec
._ls – statistical analysis of raw
.prp – a listing of what was don
.p4p – data collection paramete
.hkl – reflection intensity table
.ins – instruction file containing
XL, and XSHELL
.res – results file created by run
.lst – a listing of what was done
.fcf – structure factors
.cif – crystallographic informa

file for XS,



.hkl File

.hkl – reflection intensity table

0	0	1	26.52	1.32	n
0	0	3	184.29	7.70	n
0	0	−3	222.51	8.41	n
0	0	4	23.58	1.06	n
0	0	−5	295.17	12.09	n
0	0	6	64.41	3.14	n
0	0	−7	1132.81	37.85	n
0	0	8	251.32	11.96	n
0	0	9	141.26	6.23	n
0	0	−9	123.48	3.48	n
0	0	10	36.25	2.34	n
0	0	−10	36.58	1.83	n

Batch numbers (0, 1…) sometimes missing

Miller indices *h k l*

Intensities I_{hkl}

Standard deviations of intensities $\sigma(I_{hkl})$

.fcf File

.fcf – structure factors

```
#
# h,k,l, Fc-squared, Fo-squared, sigma(Fo-squared) and status flag
#
data_new
_shelx_title ' ZnBC-DT in Pbna'
_shelx_refln_list_code          4
_shelx_F_calc_maximum       86.03
_exptl_crystal_F_000       616.00
_refIns_d_resolution_high  0.8902

loop_
 _symmetry_equiv_pos_as_xyz
 'x, y, z'
 '-x+1/2, -y, z+1/2'
 'x, -y+1/2, -z'
 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x-1/2, y, -z-1/2'
 '-x, y-1/2, z'
 'x-1/2, -y-1/2, z-1/2'

_cell_length_a     7.7950
_cell_length_b     9.8090
_cell_length_c    15.4210
_cell_angle_alpha  90.000
_cell_angle_beta   90.000
_cell_angle_gamma  90.000

_shelx_F_squared_multiplier     1.000

loop_
 _refln_index_h
 _refln_index_k
 _refln_index_l
 _refln_F_squared_calc
 _refln_F_squared_meas
 _refln_F_squared_sigma
 _refln_observed_status
   2   0   0     746.13     668.00     11.11 o
   4   0   0    4605.89    4926.42     77.02 o
   6   0   0    2432.20    2797.27     44.05 o
   8   0   0      19.47      21.95      2.17 o
   4   1   0    3584.50    3326.54     36.70 o
   6   1   0     653.33     755.05      9.65 o
   8   1   0       6.15       9.79      1.00 o
   2   2   0     191.20     173.97      2.44 o
   4   2   0    3179.93    3277.39     36.15 o
```

Miller indices
h k l

F_c^2

F_o^2

$\sigma(F_o^2)$

Status - Classification of a reflection indicating its status with respect to inclusion in the refinement and the calculation of R factors

CIF (Crystallographic Information File) File

http://www.iucr.org/__data/iucr/cifdic_html/1/cif_core.dic/index.html

Table A. Crystal data and structure refinement for $[Cu_4L_4]\cdot 4\,CH_3OH$		Cif file line
Empirical formula	$C_{116}H_{104}Cu_4N_4O_{12}$	_chemical_formula_sum
Formula weight	2056.23	_chemical_formula_weight
Temperature, K	100	_cell_measurement_temperature
Wavelength, Å	0.71073	_diffrn_radiation_wavelength
Crystal system	Monoclinic	_symmetry_cell_setting
Space group	$P2_1/n$	_symmetry_space_group_name_H-M
a, Å	15.0138(10)	_cell_length_a
b, Å	23.9417(16)	_cell_length_b
c, Å	28.5907(19)	_cell_length_c
α, °	90	_cell_angle_alpha
β, °	104.426(2)	_cell_angle_beta
γ, °	90	_cell_angle_gamma
Volume, Å ^{3}	9953.1(11)	_cell_volume
Z	4	_cell_formula_units_Z
D_{cacl}, (g cm^{-3})	1.372	_exptl_crystal_density_diffrn
μ, mm^{-1}	0.911	_exptl_absorpt_coefficient_mu
F(0 0 0)	4272	_exptl_crystal_F_000
Crystal Size, mm^3	0.50 x 0.03 x 0.02	_exptl_crystal_size_max, mid, min
Reflection collected	161621	_diffrn_reflns_number
Independent Reflections	24480 (R_{int} = 0.1466)	_reflns_number_total (R_{int} = _diffrn_reflns_av_R_equivalents)
Completeness to θ	___% (=___°)	_diffrn_measured_fraction_theta_full (_diffrn_reflns_theta_full)
Max. and min. transmission	0.9820 and 0.6582	_exptl_absorpt_correction_T_max and _exptl_absorpt_correction_T_min
No. of data	24480	_refine_ls_number_reflns
No. of restraints	0	_refine_ls_number_restraints
No. of parameters	1261	_refine_ls_number_parameters
Absorption correction	Mutiscan	_exptl_absorpt_correction_type
Goodness-of-fit on F^2	1.021	_refine_ls_goodness_of_fit_ref
Final R indices [I > 2σ(I)][a,b]	R1 = 0.0672, wR2 = 0.1478	R1 = _refine_ls_R_factor_gt, wR2 = _refine_ls_wR_factor_gt
R indices (all data)	R1 = 0.1633, wR2 = 0.1884	R1 = _refine_ls_R_factor_all, wR2 = _refine_ls_wR_factor_ref
Absolute structure parameters		_refine_ls_abs_structure_Flack
Largest diff. peak and hole, e·Å $^{-3}$	1.321 and -0.920	_refine_diff_density_max and _refine_diff_density_min

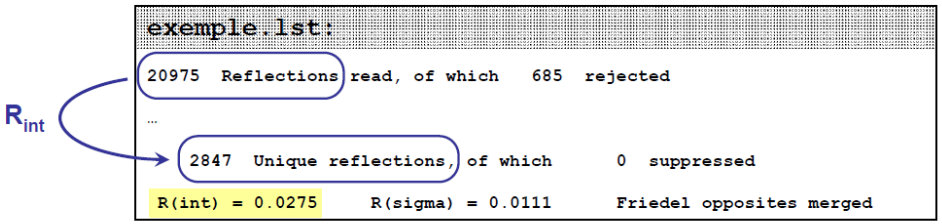
CIF (Crystallographic Information File) File

Table A. Crystal data and structure refinement for $[Cu_4L_4]\bullet 4CH_3OH$	
Empirical formula	$C_{116}H_{104}Cu_4N_4O_{12}$
Formula weight	2056.23
Temperature, K	100
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	15.0138(10)
b, Å	23.9417(16)
c, Å	28.5907(19)
α, °	90
β, °	104.426(2)
γ, °	90
Volume, Å ^{3}	9953.1(11)
Z	4
D_{cacl}, (g cm^{-3})	1.372

CIF (Crystallographic Information File) File

F(0 0 0)	4272
Crystal Size, mm^3	0.50 x 0.03 x 0.02
Reflection collected	161621
Independent Reflections	24480 (R_{int} = 0.1466)

F(000) = sum of all electrons in the unit cell (effective number of electrons in the unit cell)



$$R_{int} = \frac{\sum \left| F_o^2 - F_o^2(mean) \right|}{\sum F_o^2}$$

$$R_{sigma} = \frac{\sum \sigma(F_o^2)}{\sum F_o^2}$$

R_{int} = Merging error (measure of the precision/reproducibility) **Values = 0 ~ infinity**

R_{σ} = Measure of the signal-to-noise ratio

The less R_{int}, the better. [If $R_{int} >> R_{\sigma}$ (more than 2-3 times), problem !!]

CIF (Crystallographic Information File) File

Completeness to θ	**___% (=___º)**
Max. and min. transmission	0.9820 and 0.6582
No. of data	24480

Fraction of unique (symmetry-independent) reflections measured out to _diffrn_reflns_theta_full. Values = 0 ~ 100 %

The theta angle (in degrees) at which the measured reflection count is close to complete. The fraction of unique reflections measured out to this angle is given by _diffrn_measured_ fraction_ theta_full. Values = 0 ~ 90

The maximum and minimum transmission factors applied to the diffraction pattern measured in this experiment. These factors are also referred to as the absorption correction A or 1/A*. As this value is the one that is applied to the measured intensities, it includes the correction for absorption by the specimen mount and diffractometer as well as by the specimen itself. Values = 0 ~ 1

The number of unique reflections contributing to the least-squares refinement calculation. Values = 0 ~ infinity

CIF (Crystallographic Information File) File

No. of parameters	**1261**
Absorption correction	Mutiscan
Absolute structure parameters	

The number of parameters refined in the least-squares process. If possible, this number should include some contribution from the restrained parameters. The restrained parameters are distinct from the constrained parameters (where one or more parameters are linearly dependent on the refined value of another). Least-squares restraints often depend on geometry or energy considerations and this makes their direct contribution to this number, and to the goodness-of-fit calculation, difficult to assess. Values = 0 ~ infinity

The measure of absolute structure as defined by Flack (1983). For centrosymmetric structures, the only permitted value, if the data name is present, is 'inapplicable', represented by '.' . For noncentrosymmetric structures, the value must lie in the 99.97% Gaussian confidence interval -3u =< x =< 1 + 3u and a standard uncertainty (e.s.d.) u must be supplied. The _enumeration_range of 0.0:1.0 is correctly interpreted as meaning (0.0 - 3u) =< x =< (1.0 + 3u). Ref: Flack, H. D. (1983). Acta Cryst. A39, 876-881. Values = 0 ~ 1

CIF (Crystallographic Information File) File

Goodness-of-fit on F^2	**1.021**
Final *R* indices [I > 2σ(I)][a,b]	$R_1 = 0.0672$, $wR_2 = 0.1478$
***R* indices (all data)**	$R_1 = 0.1633$, $wR_2 = 0.1884$
Largest diff. peak and hole, e·Å $^{-3}$	1.321 and -0.920

$$GooF = S = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{N_{Ref.} - N_{Par.}}}$$

$N_{Ref.}$: number of independent reflections
$N_{Par.}$: number of parameters

$$R_1 = \frac{\sum \left| |F_o| - |F_c| \right|}{\sum |F_o|}$$

$$wR_2 = R_w(F^2) = \sqrt{\frac{\sum w\left(F_o^2 - F_c^2\right)^2}{\sum w(F_o^2)^2}}$$

The largest and smallest values in electrons per angstrom cubed of the final difference electron density.

CIF (Crystallographic Information File) File

Validations

Factors	Good	Acceptable	Problematic	Really Problematic
R_1 (I>2σ(I))	< 5%	< 7%	> 10%	> 15%
wR_2 (all data)	< 12%	< 20%	> 25% (or 2R_1)	> 35%
S	0.9-1.2	0.8-1.5	< 0.8 or > 2	< 0.6 or > 4

S should be around 1.
S > 1: bad model or bad data/parameter ratio
S < 1: model is better than the data: problems with the absorption correction, space group problems

R-factor depends on the signal-to noise ratio.
S is relatively independent from the noise.

Acceptable values for residual electron density:

- For light atom structures (H – F) : **< 0.5 e^-/Å 3**
- For heavy atom structures : 10% of the electrons of the heavy atom per Å ^{3} in a distance smaller 1.2 Å from the heavy atom. (Fourier truncation errors)
- Accumulation of electron density on special positions
  Usually should be less than 1 (-1)

test.lst:

Electron density synthesis with coefficients Fo-Fc
Highest peak 0.42 at 0.2140 0.0398 0.5135 [0.40 A from C2]
Deepest hole -0.56 at 0.1424 0.4014 0.6865 [0.53 A from F3]