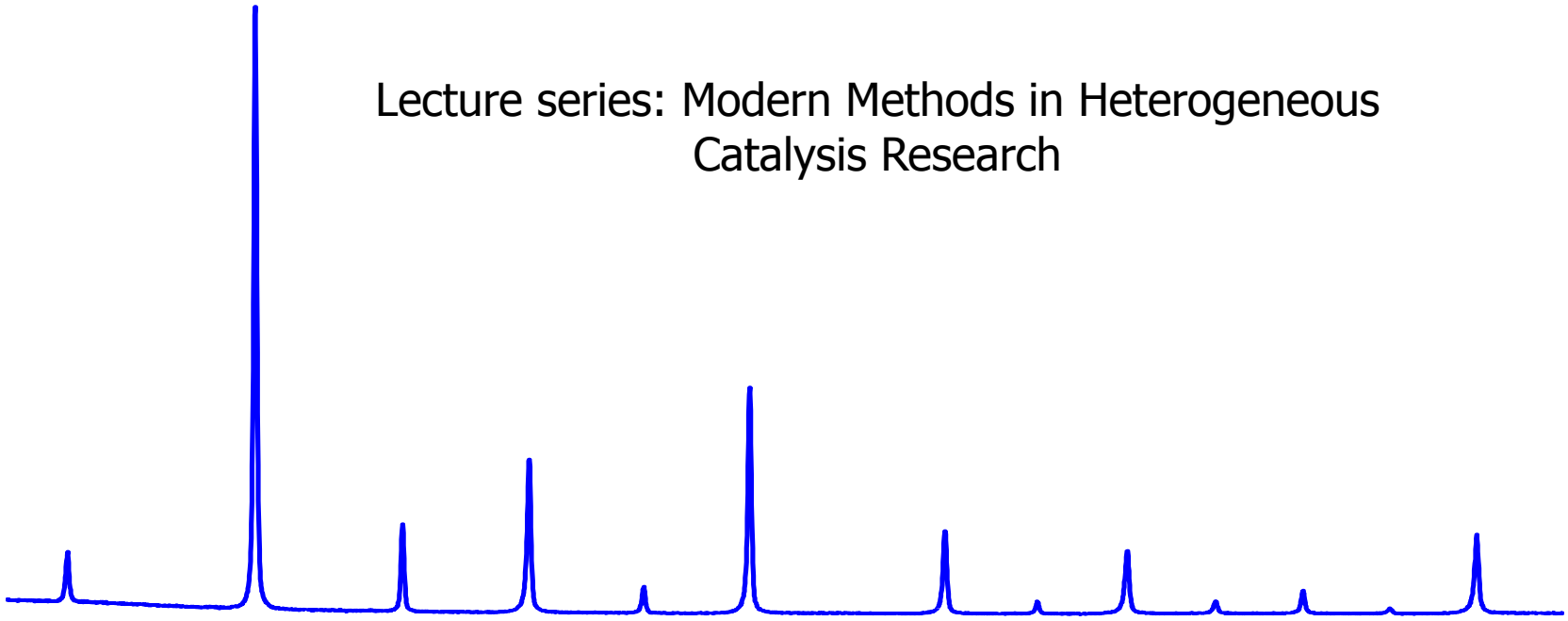
Fundamentals of X-ray diffraction

Elena Willinger

Lecture series: Modern Methods in Heterogeneous Catalysis Research

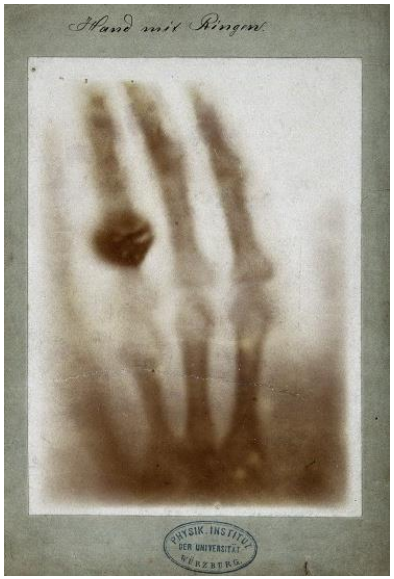


Outline

- History of X-ray
- Sources of X-ray radiation
- Physics of X-ray scattering
- Fundamentals of crystallography
- X-ray diffraction methods
- X-ray diffraction in material science: examples

History of X-rays

Anna Bertha Röntgen



In 1895 Röntgen discovers X-rays

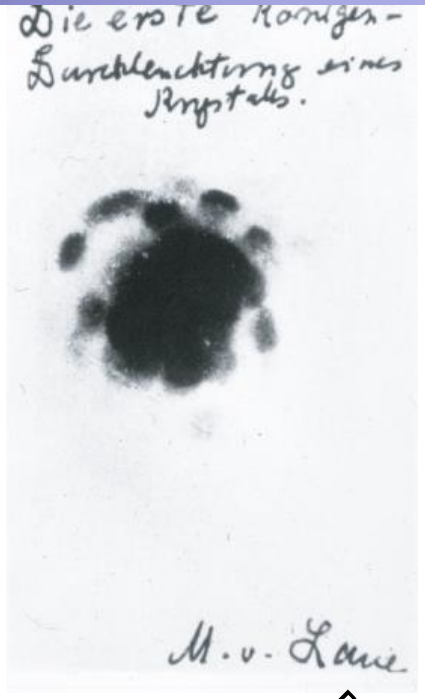
Wilhelm Röntgen

1901: The First Nobel Prize in Physics

Wilhelm Conrad Röntgen

Prize motivation: "in recognition of the extraordinary services he has rendered by the discovery of the remarkable rays subsequently named after him"

History of X-ray

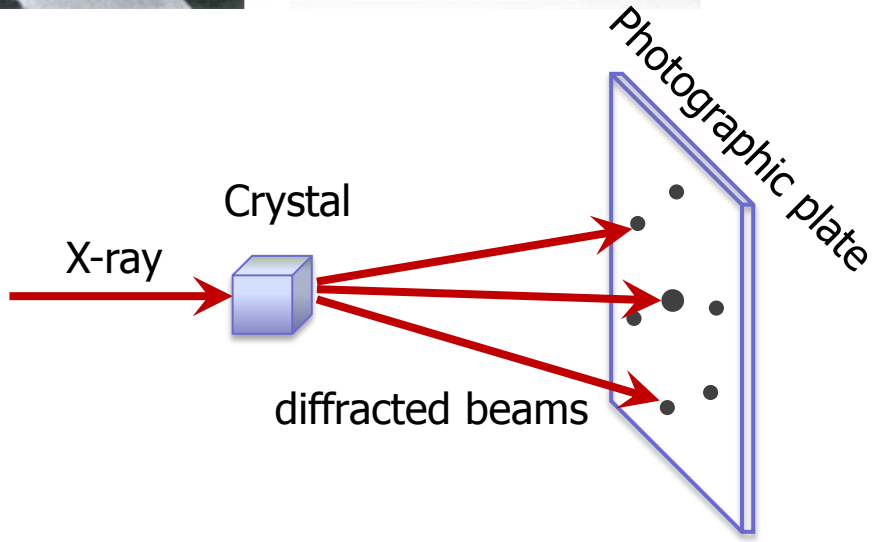


Max von Laue

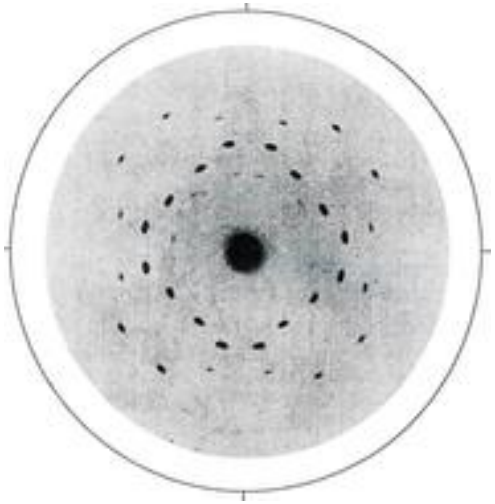
1914: The Nobel prize for physics

Prize motivation: "for his discovery of the diffraction of X-rays by crystals"

Director at the FHI (1951-1959)

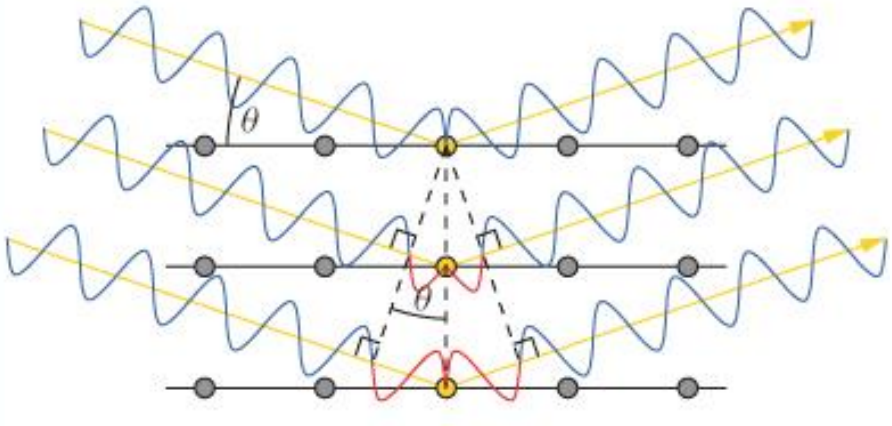


Diffraction pattern



History of X-ray

W. H. Bragg and his son W. L. Bragg and the diffraction of x-rays by crystals.

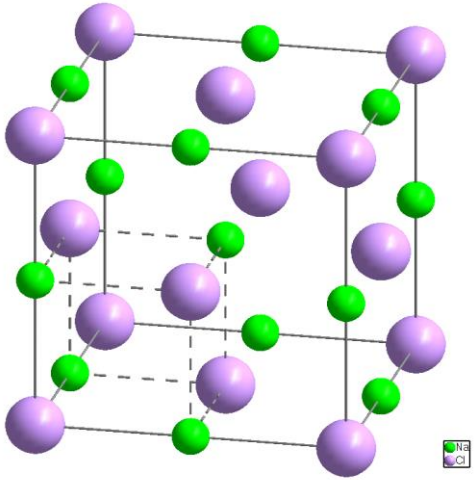


$2d\sin\theta=n\lambda$

1915: The Nobel prize for physics

Prize motivation: "for their services in the analysis of crystal structure by means of X-rays"

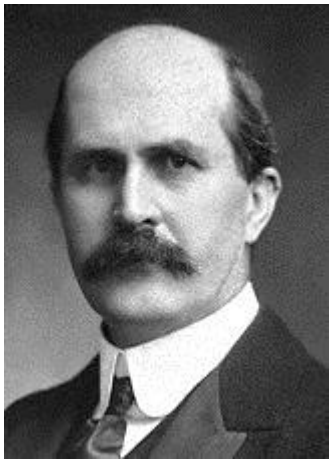
The progress in crystalline structure determination



NaCl – fcc lattice

Fm-3m
a= 5.64 Å

Bragg:
In sodium chloride there appear
To be no molecules represented by NaCl. The equality in number of sodium and chloride atoms is arrived at by a chess-board pattern of these atoms; it is a result of geometry and no of a pairing off of the atoms



William H. Bragg

Henry Armstrong

This statement is…absurd to the n^{th} degree; not chemical cricket.
Chemistry is neither chess nor geometry, whatever X-ray physics may be. […]

It is time that chemists took charge of chemistry once more and protected neophytes against the worship of false gods…

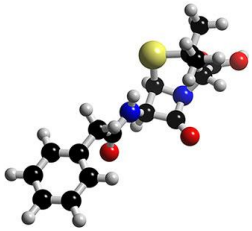
The progress in crystalline structure determination

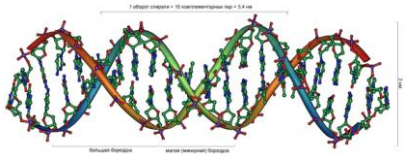
1912 NaCl (2 atoms)

Iron Pyrite FeS2 (3 atoms)

Calcite CaCO3 (5 atoms)

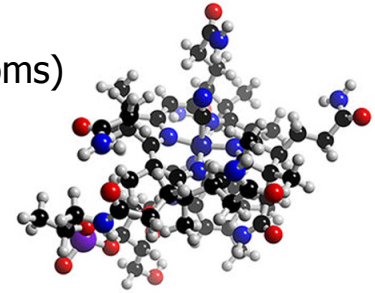
1945 Penicillin, Dorothy Hodtkins (41 atoms)



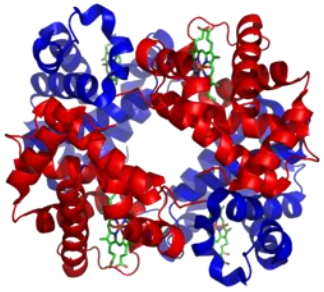


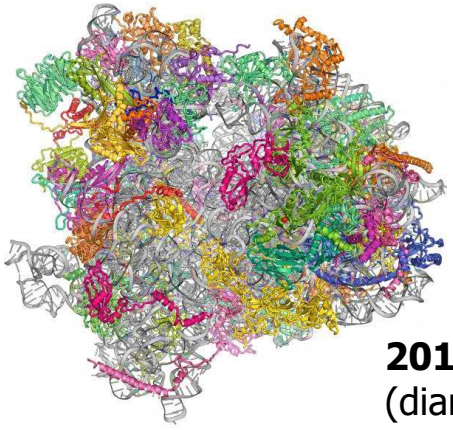
1953 DNA, James Watson and Francis Crick (77 atoms, diameter~20 Å)

1954 Vitamin B12, Dorothy Hodtkins (181 atoms)

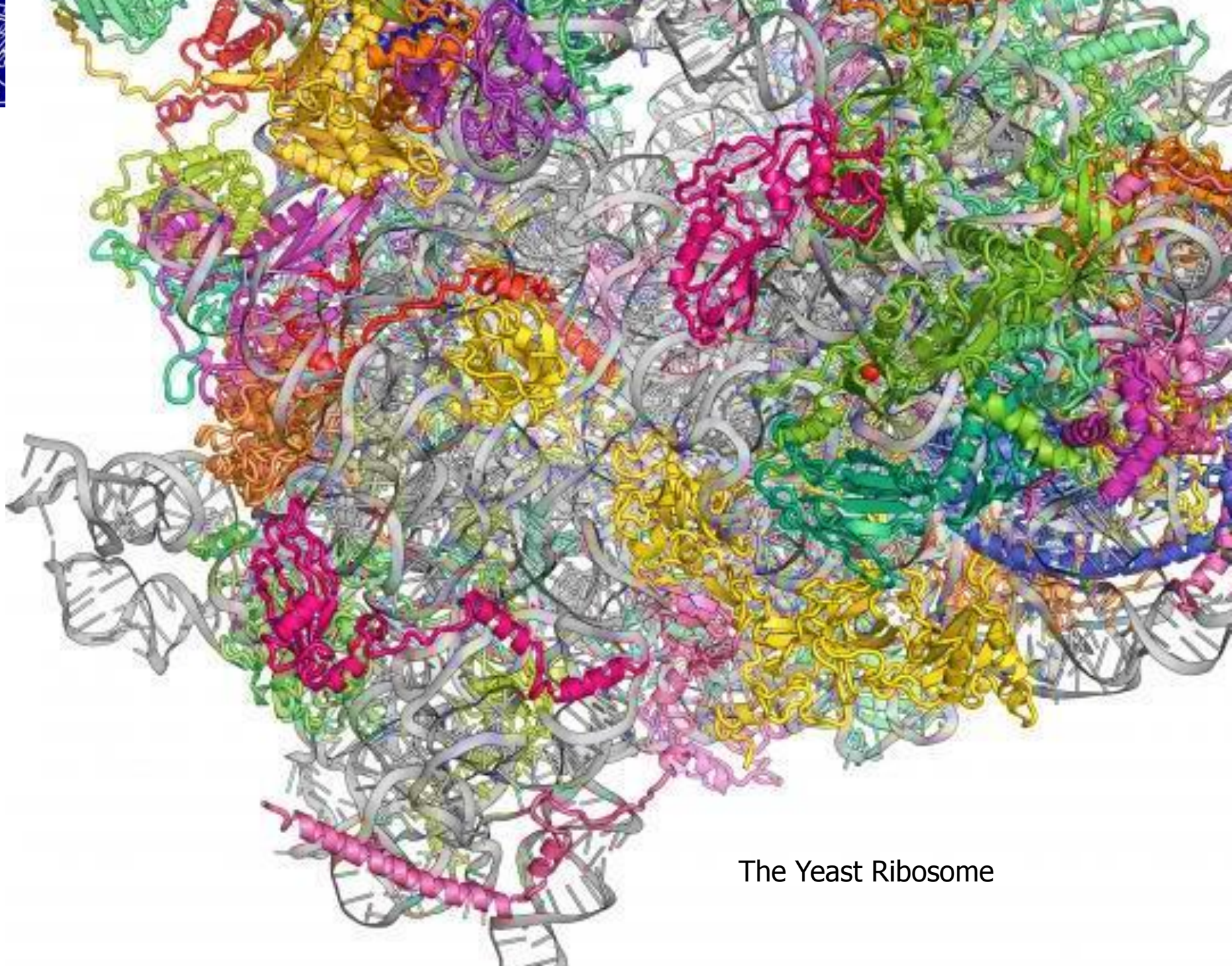


1962 Hemoglobin structure (diameter 50 Å)





2011 Yeast Ribosome structure (diameter ~250-300 Å) 404714 atoms



The Yeast Ribosome

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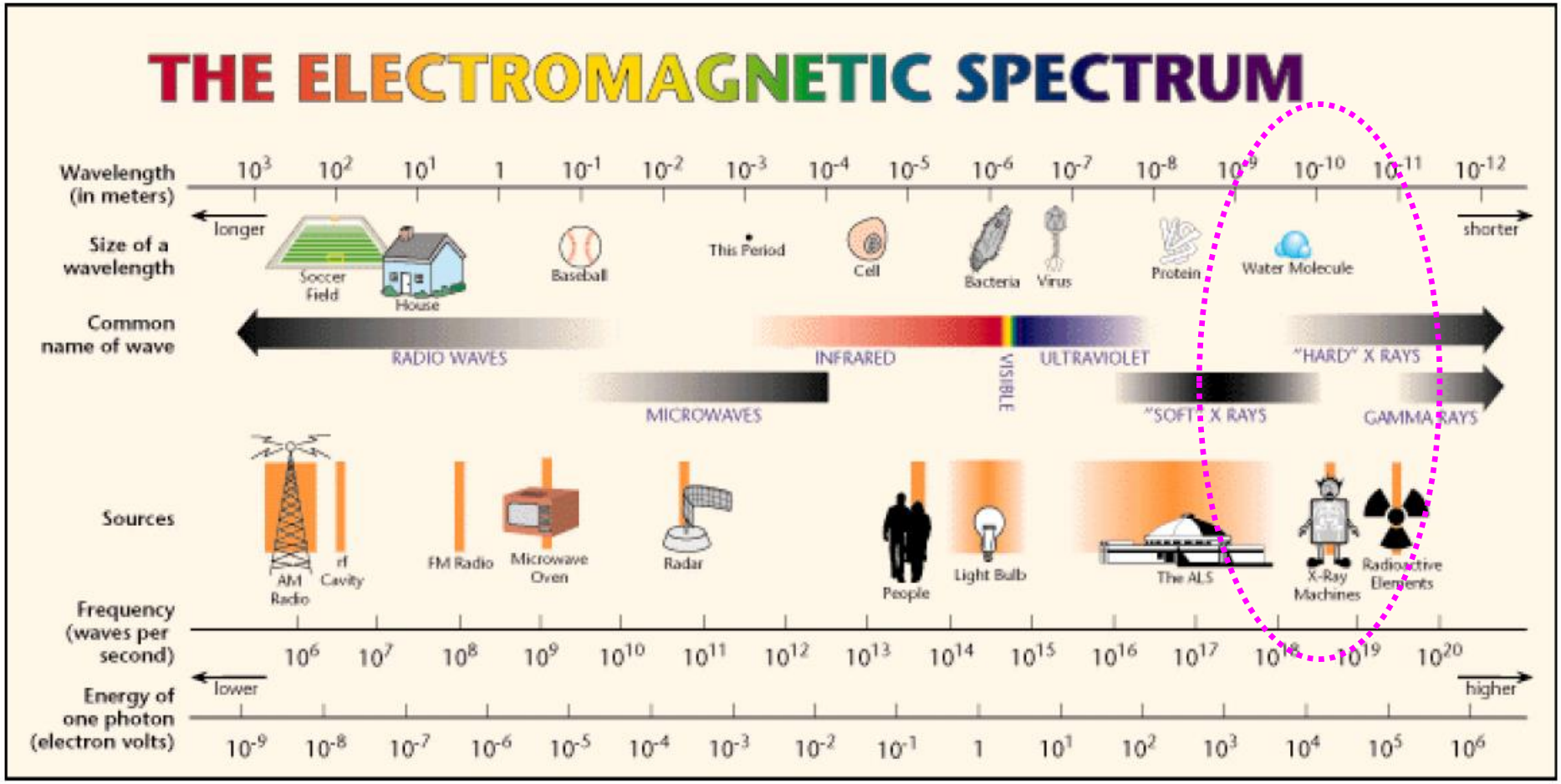
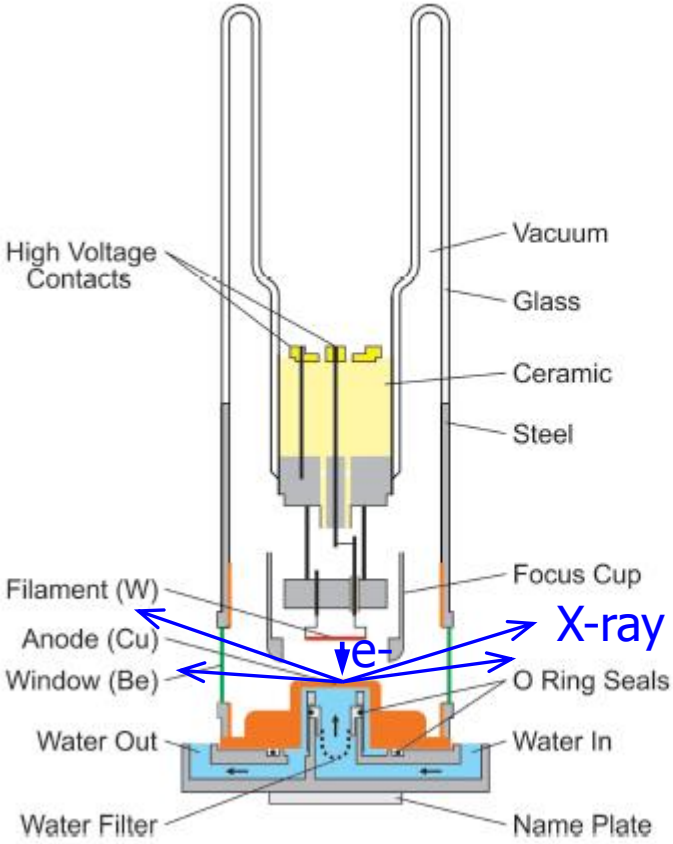
X-ray



X-rays are electromagnetic waves

X-ray sources

Conventional X-ray laboratory source



Electrostatic potential 20 to 60 kV

Anode current 10 to 50 mA

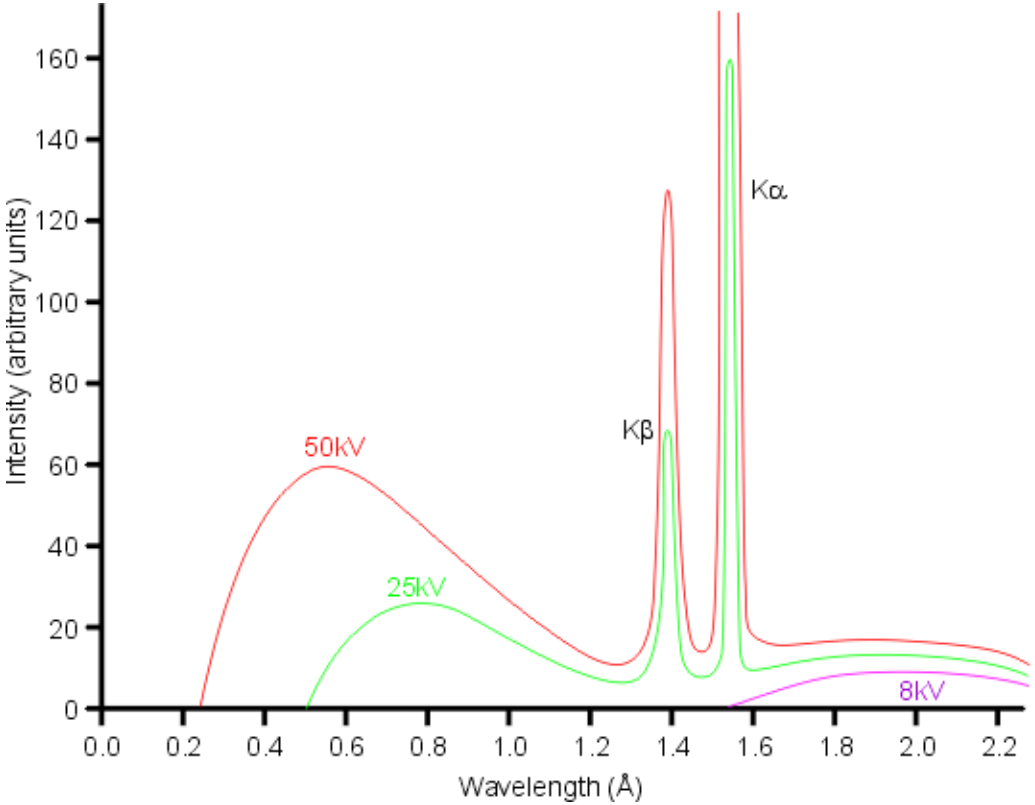
Input power ~ 0.5 to 3 kW

Only 0.1% transforms into X-ray beam

The wavelengths, most commonly used in crystallography: 0.5-2.5 Å

X-ray spectra

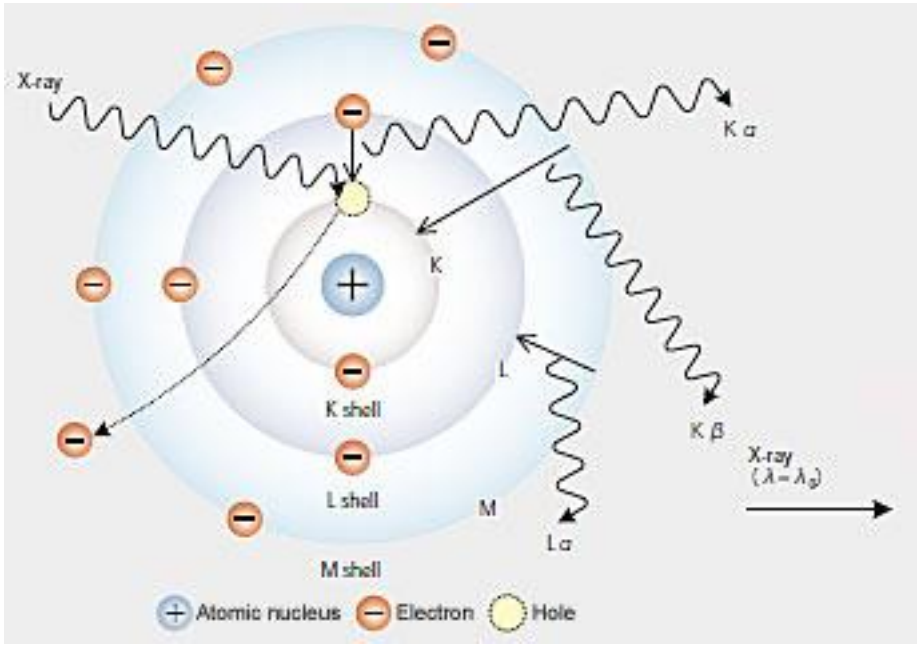
A typical x-ray spectrum from a Cu target

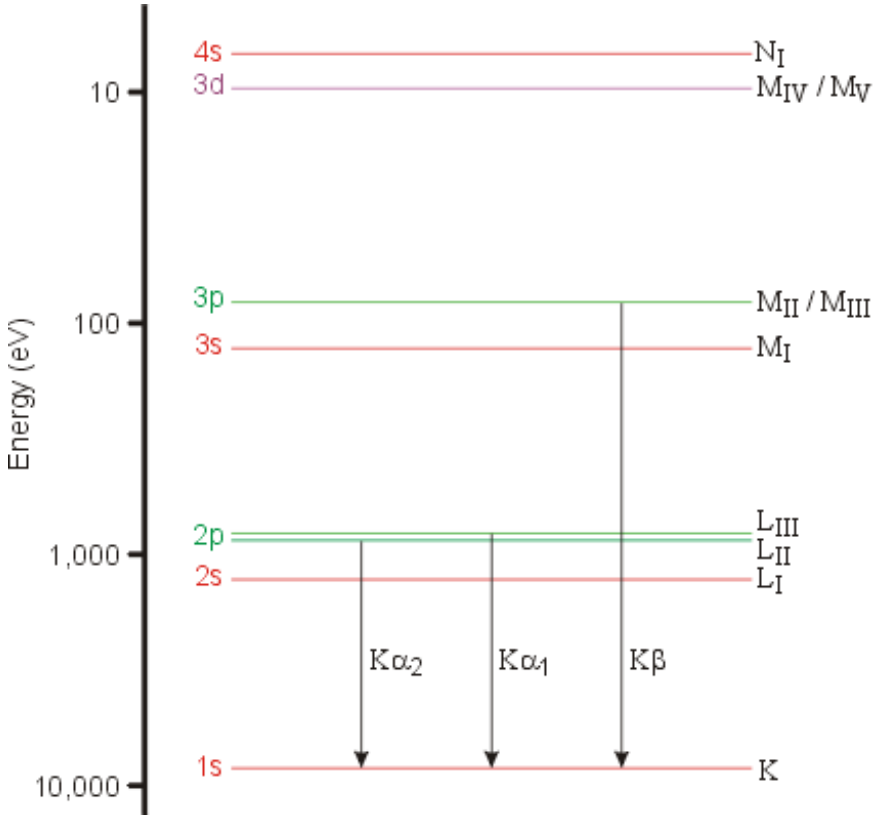


$$eV = h\nu = \frac{hc}{\lambda}$$

$$\lambda_c = \frac{12.4}{V, kV}\ \text{Å}$$

Characteristic X-ray lines

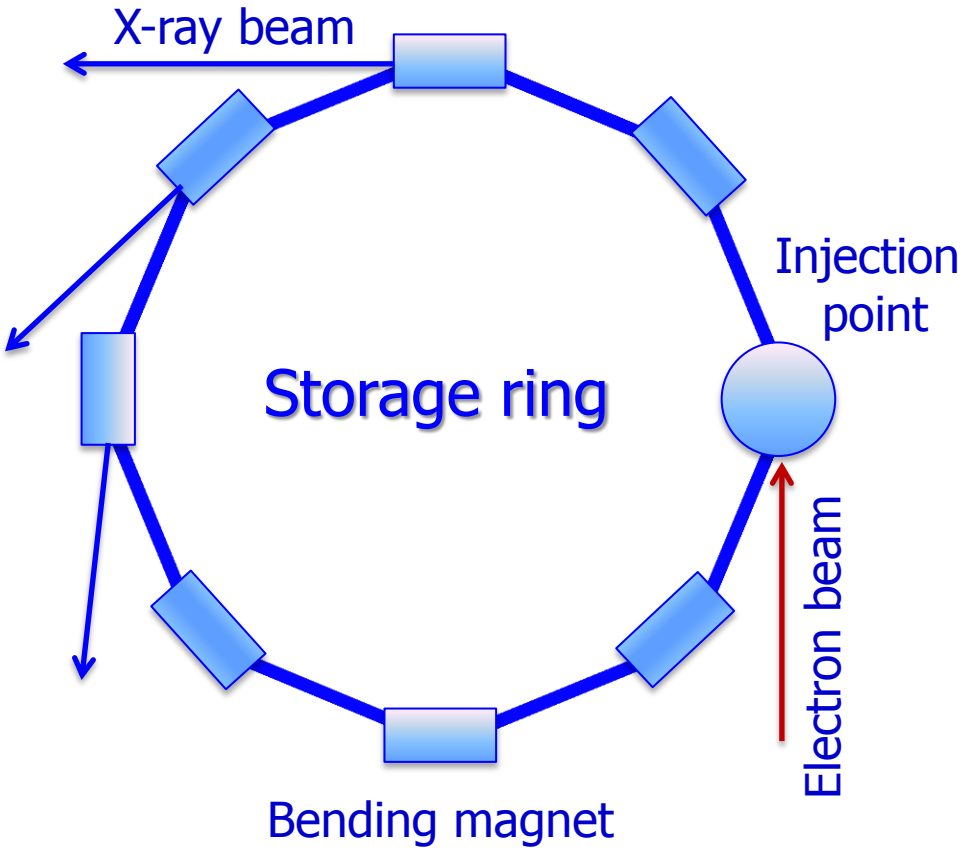




Anode	Kα	Kβ
Cu	1.54184 Å	1.39222 Å
Mo	0.71073 Å	0.63229 Å

Synchrotron X-ray Sources

The Berlin Electron Storage Synchrotron radiation (BESSY)



Advantages:

High brightness ⟶ small samples
High collimation ⟶ high resolution of 2θ
Continuous spread of wavelengths

Disadvantage:

the synchrotron sources are not available on a daily basis

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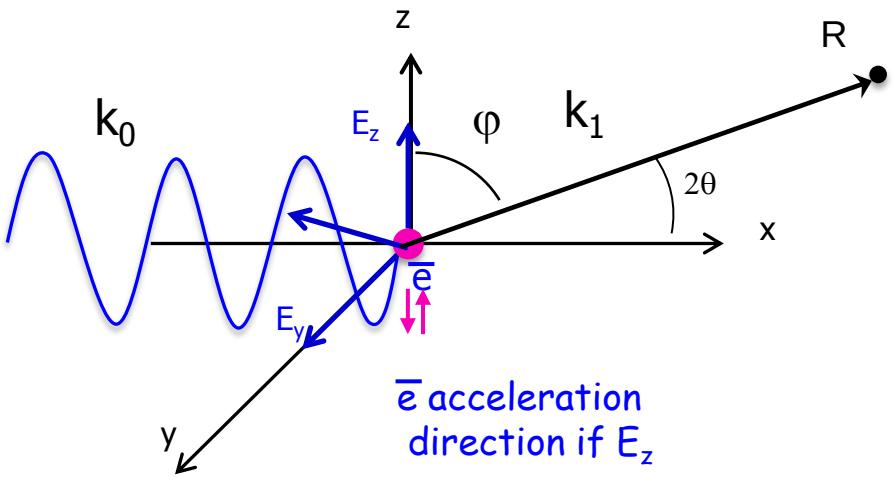
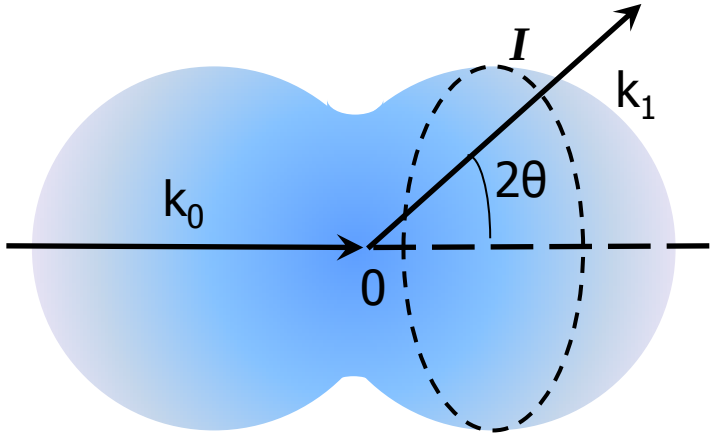
Elementary scattering



Scattering intensity distribution

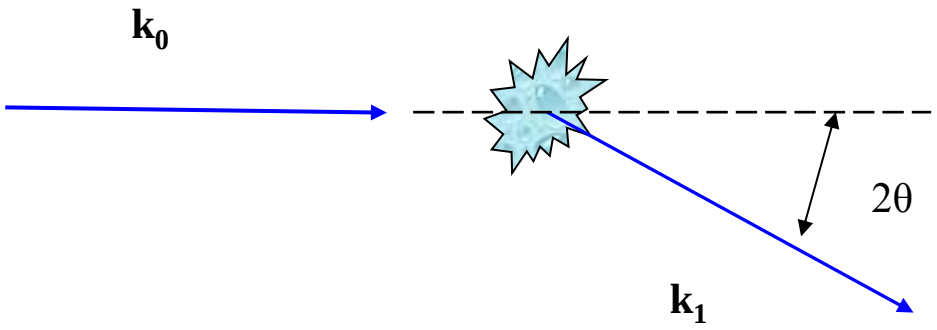


Thomson scattering formula

$$I = I_0 \frac{e^4}{r^2 m^2 c^4} \left(\frac{1+\cos^2 2\theta}{2} \right)$$

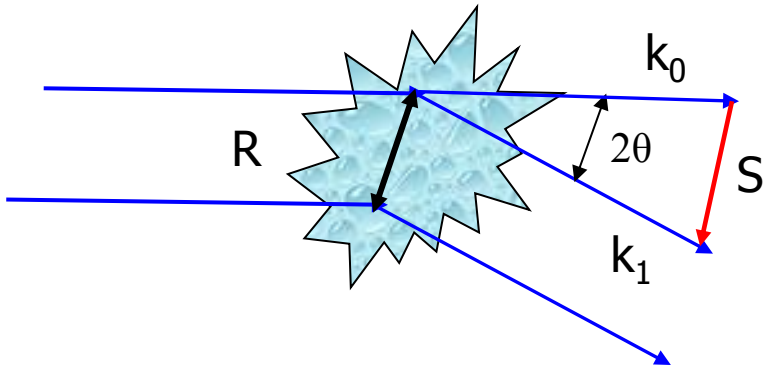
X-ray scattering physics

Plane wave approximation → the source and detector are far away from the object
the object is small



Elastic - no energy loss
coherent - no random phase shift
scattering

X-ray scattering physics



$S = 2|k|\sin\theta$ scattering vector

$\Delta\varphi = S \bullet R$ phase shift

Scattering intensity

$$I(\mathbf{S}) = \Sigma A_j e^{-2\pi i (\mathbf{S} \bullet \mathbf{R}_j)} \bullet \Sigma A_k e^{2\pi i (\mathbf{S} \bullet \mathbf{R}_k)} = \Sigma\Sigma A_j A_k e^{-2\pi i (\mathbf{S} \bullet (\mathbf{R}_j - \mathbf{R}_k))}$$

$$= A^2 \Sigma\Sigma e^{-2\pi i (\mathbf{S} \bullet (\mathbf{R}_j - \mathbf{R}_k))}$$

$\{\mathbf{R}_j - \mathbf{R}_k\}$ – Object property (unique set)

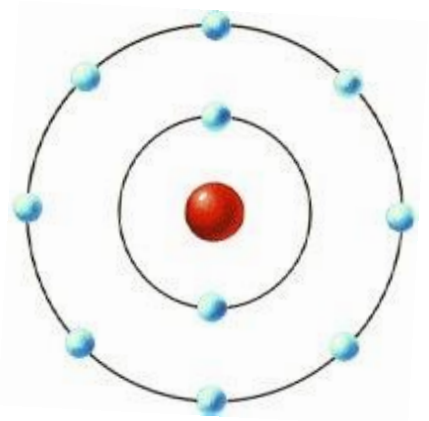
X-ray scattering physics

Atomic scattering amplitude E(s)

E(s) is the sum of all the electrons scattering amplitudes

$$A_{at}(s) = \sum_{j=0}^{z-1} A_e(s) e^{-2\pi i(sr)}$$

Atomic scattering factor f(s)



$$f(s) = A_{at}(s) / A_e(s)$$

$$f(s) = \sum_{j=0}^{z-1} e^{-2\pi i(sr)}$$

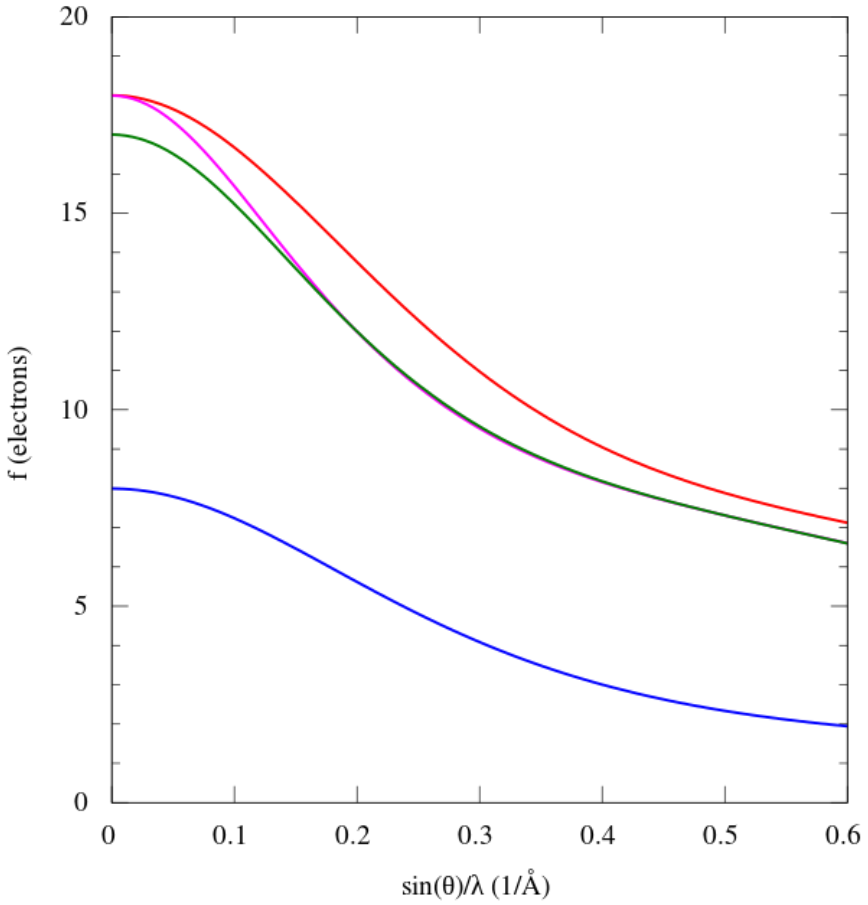
$$s=0,\ f(s)=Z$$

$$r_j=0\ ,\ f(s)=Z \text{ and doesn't depend on } s$$

↓

Since electrons are not concentrated in one point *f(s)* depends on $s = 2\sin\theta/\lambda$

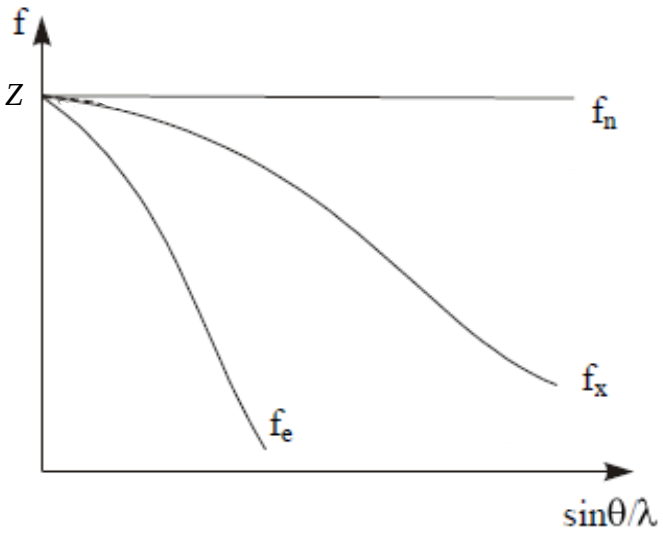
Atomic scattering factor

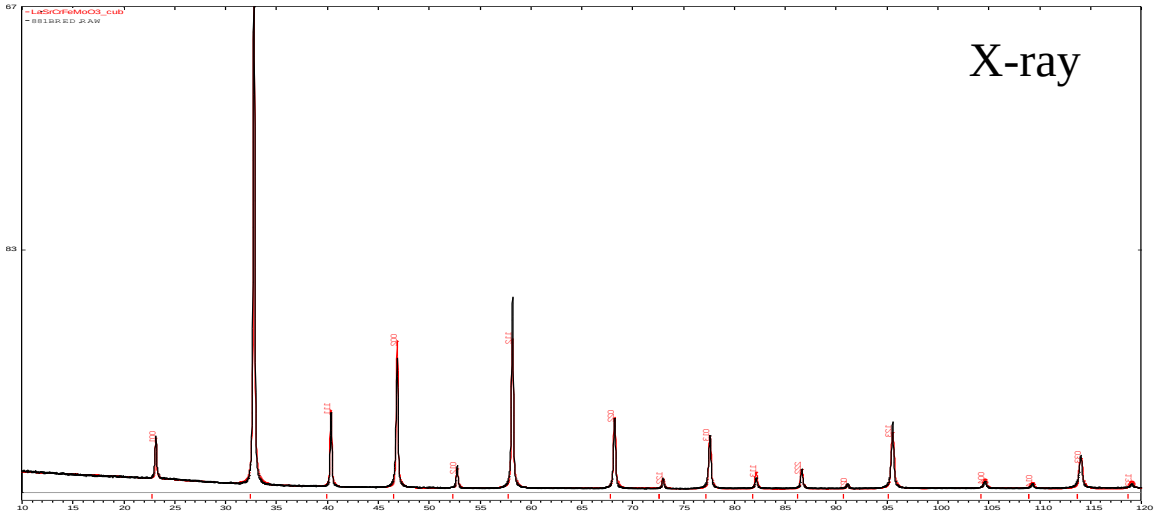


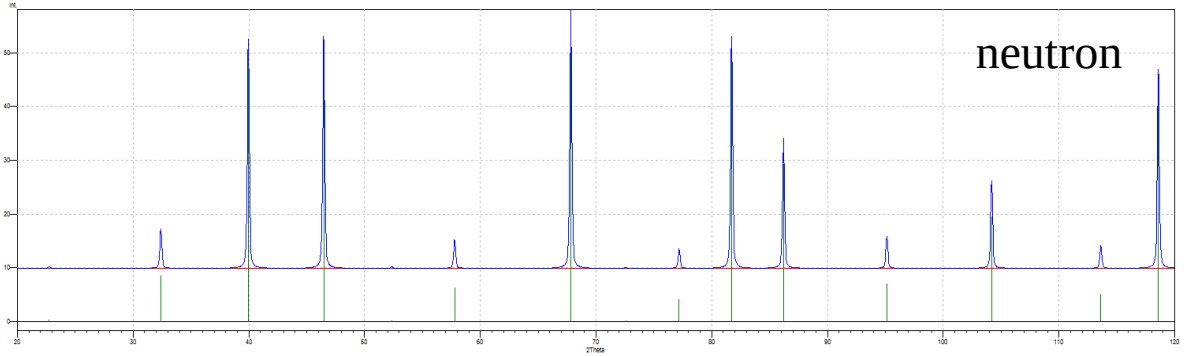
O, z=8, atomic radius =0.66
Cl, z=17, atomic radius=1
Cl-, z=18, radius= 1.81
K, z = 19, atomic radius=2.02
K+ =18, radius= 1.33

X-ray atomic factors of O, Cl , Cl^- and K^+ ; smaller charge distributions have a wider atomic factor.

Atomic scattering factor

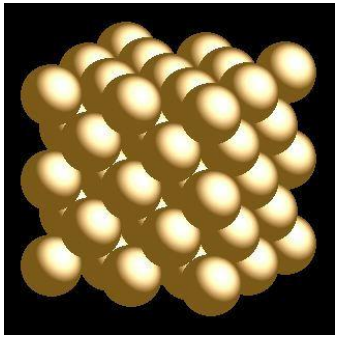


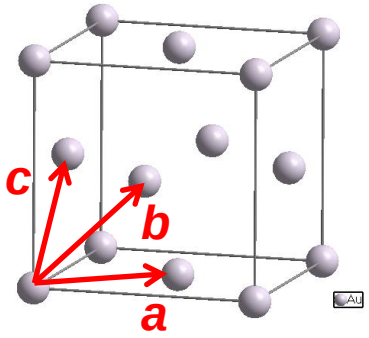




X-ray scattering physics

X-ray scattering by crystalline (periodic) ensemble of atoms





$\mathbf{R}_{mnp} = m\mathbf{a} + n\mathbf{b} + p\mathbf{c}$

Periodic arrangement of atoms is given by lattice with the basis vectors ***a,b,c***

Scattering amplitude $A(\mathbf{S}) = A_e \Sigma f_j e^{-i2\pi(\mathbf{S}\cdot\mathbf{R}_j)} = -A_e f \Sigma e^{i2\pi(\mathbf{S}\cdot\mathbf{R}_{mnp})}$

In general $A(\mathbf{S}) \sim 0$ for infinite crystal, i.e. m, n and $p \rightarrow \infty$

But if $(\mathbf{S}\cdot\mathbf{R}_{mnp}) = (\mathbf{S}\cdot\mathbf{a})m + (\mathbf{S}\cdot\mathbf{b})n + (\mathbf{S}\cdot\mathbf{c})p = q$ – integer

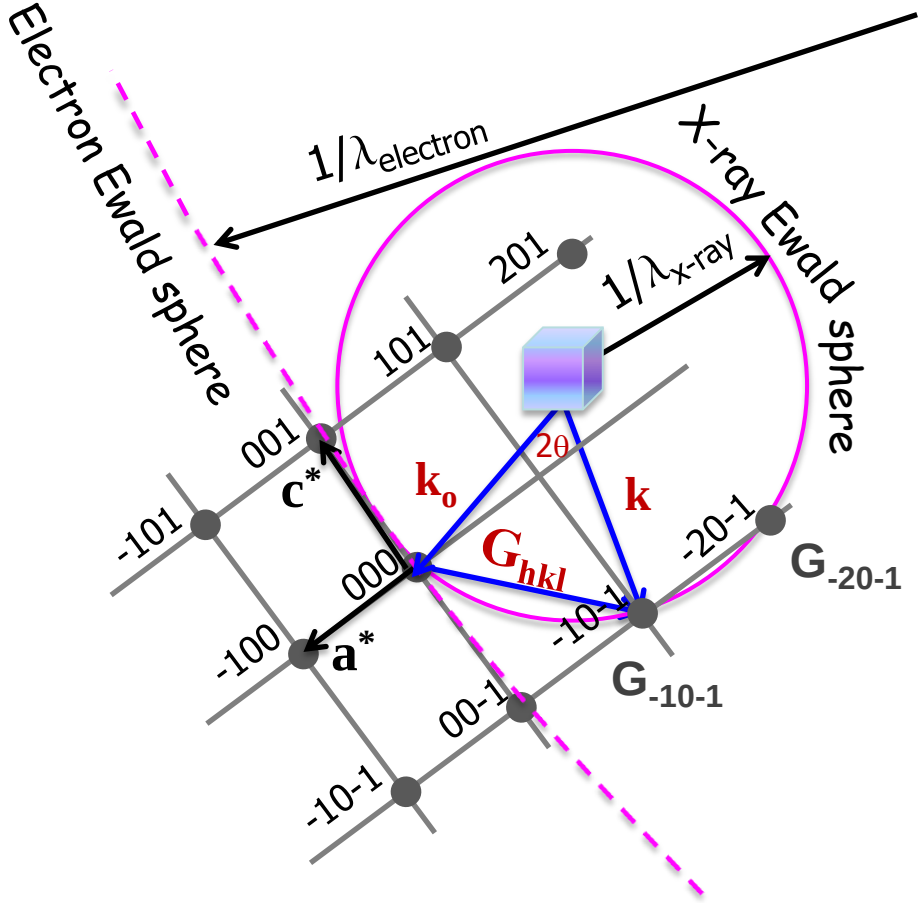
then $e^{i2\pi(\mathbf{S}\cdot\mathbf{R}_{mnp})} = 1$ and $|A(\mathbf{S})| = N A_e f(s)$, N – number of atoms,

There is the only solution: $\mathbf{S} = \{\mathbf{G}_{hkl}\} = \{h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*\}$

with $\mathbf{a}^* = [\mathbf{b}\times\mathbf{c}]/V$, $\mathbf{b}^* = [\mathbf{c}\times\mathbf{a}]/V$, $\mathbf{c}^* = [\mathbf{a}\times\mathbf{b}]/V$, $V = (\mathbf{a}[\mathbf{b}\times\mathbf{c}])$

Ewald construction

Space of wave vectors - Ewald construction



$G_{hkl} = ha^* + kb^* + lc^*$

$G_{hkl} = 2|k|\sin\theta$

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Crystal periodic structures

Quartz

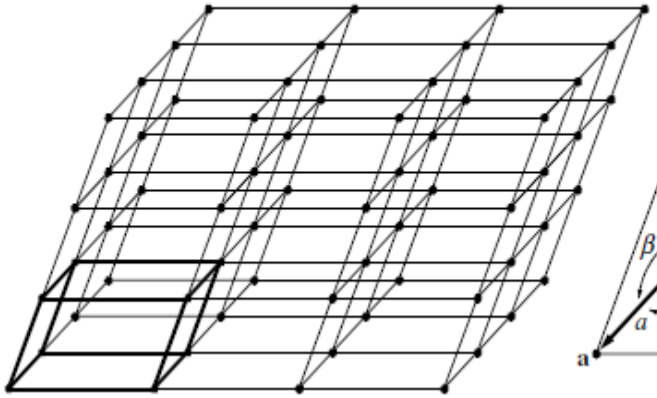
Trigonal

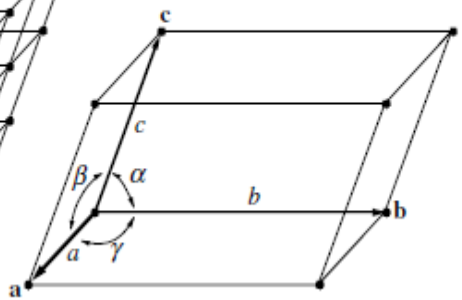
Pyrite

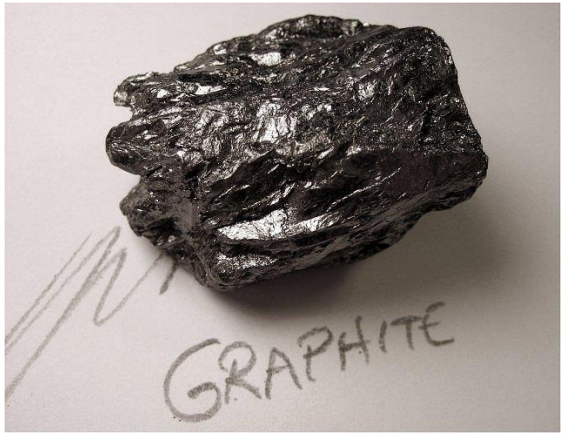
cubic

Rocksalt

cubic







Bravais lattices

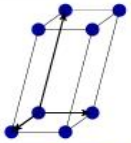
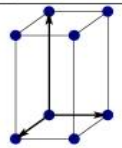
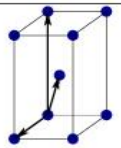
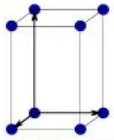
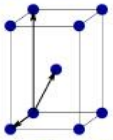
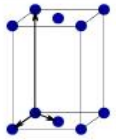
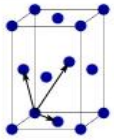
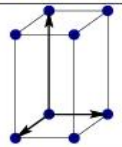
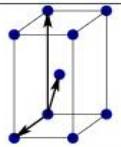
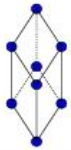
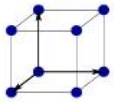
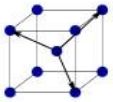
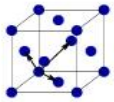
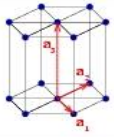
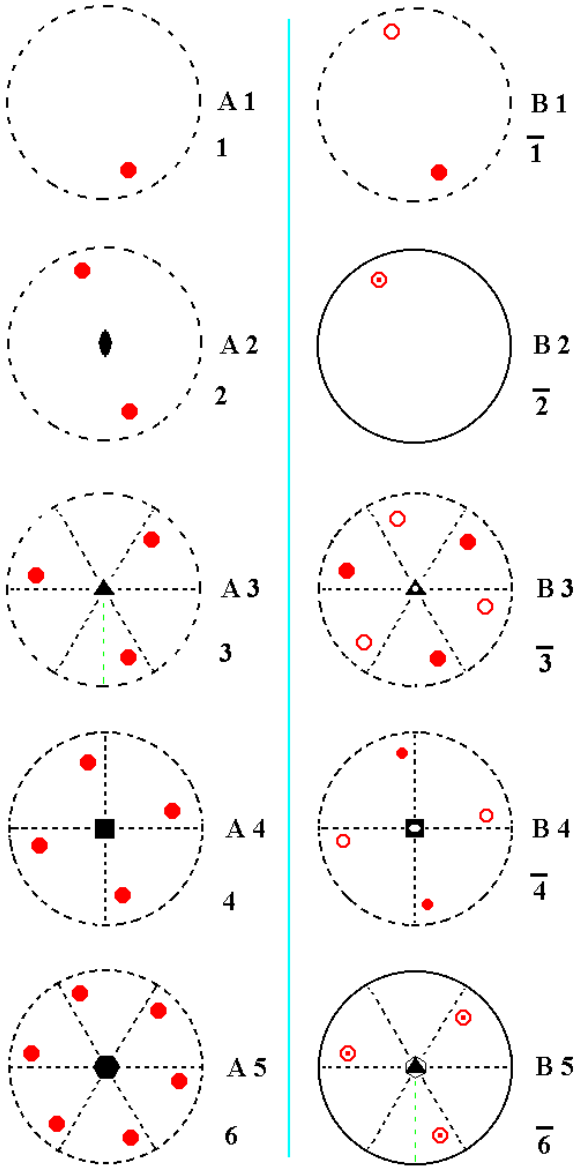
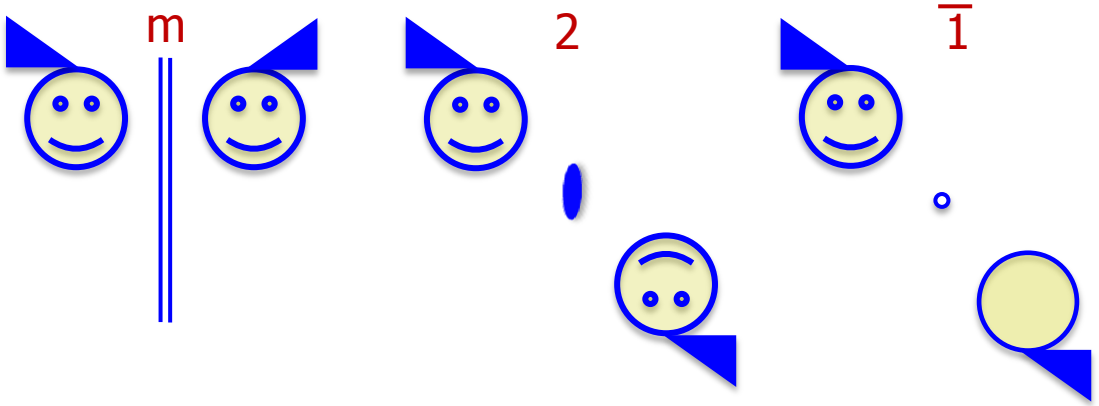
Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

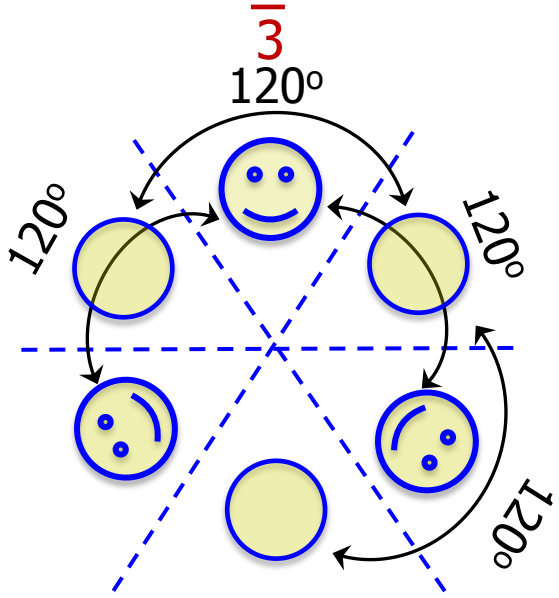
Table 1.1: Bravais lattices in three-dimensions.

http://www.theory.nipne.ro/~dragos/Solid/Bravais_table.jpg

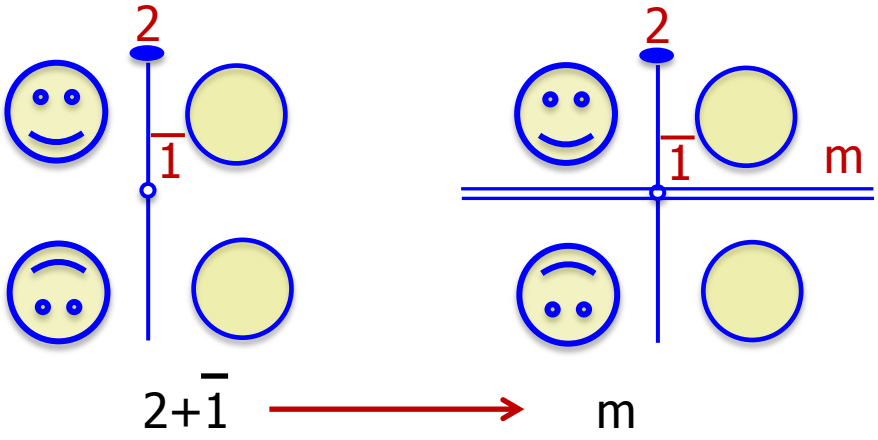
Symmetry elements



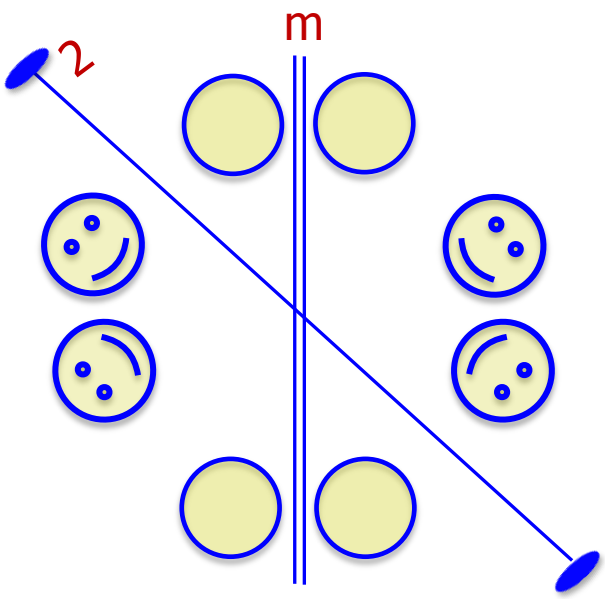


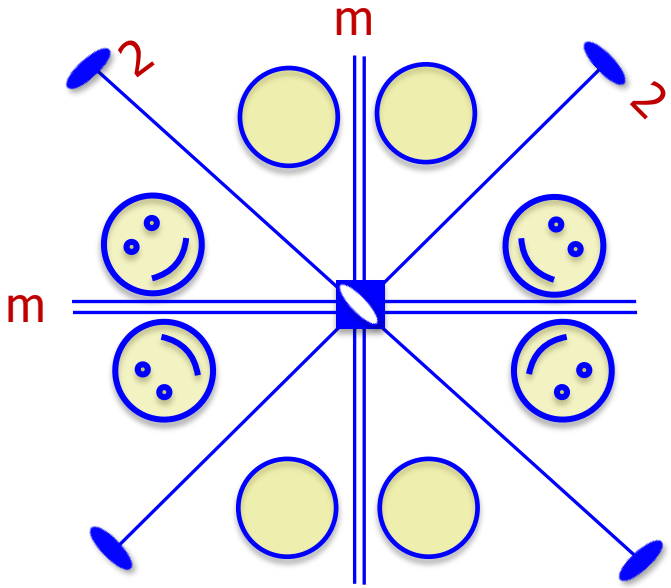


Interaction of symmetry elements



2+m → 2+m+4̄





32 Point groups

Table 1.8. Symbols of crystallographic point groups.

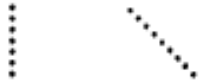
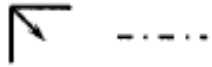
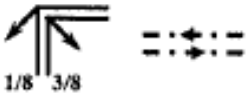
Crystal system	First position		Second position		Third position		Point group
	element	direction	element	direction	element	direction	
Triclinic	1 or $\bar{1}$	any	none		none		1, $\bar{1}$
Mono-clinic	2, m or 2/m	*Y*	none		none		2, m, 2/m
Ortho-rhombic	2 or m	*X*	2 or m	*Y*	2 or m	*Z*	222, mm2, mmm
Tetragonal	4, $\bar{4}$ or 4/m	*Z*	none or 2 or m	*X*	none or 2 or m	base diagonal	4, $\bar{4}$, 4/m, 422, 4mm, $\bar{4}$2m, 4/mmm
Trigonal	3 or $\bar{3}$	*Z*	none or 2 or m	*X*	none		3, $\bar{3}$, 32, 3m, $\bar{3}$m
Hexagonal	6, $\bar{6}$ or 6/m	*Z*	none or 2 or m	*X*	none or 2 or m	base diagonal	6, $\bar{6}$, 6/m, 622, 6mm, $\bar{6}$2m, 6/mmm
Cubic	2, m, 4 or $\bar{4}$	*X*	3 or $\bar{3}$	body diagonal	none or 2 or m	face diagonal	23, m3, 432, $\bar{4}$3m, m$\bar{3}$m

We want to know where in the 3D periodic structure the symmetry element is located!

Translational symmetry elements

Reflection + translation = glide planes

Table 1.15. Crystallographic glide planes

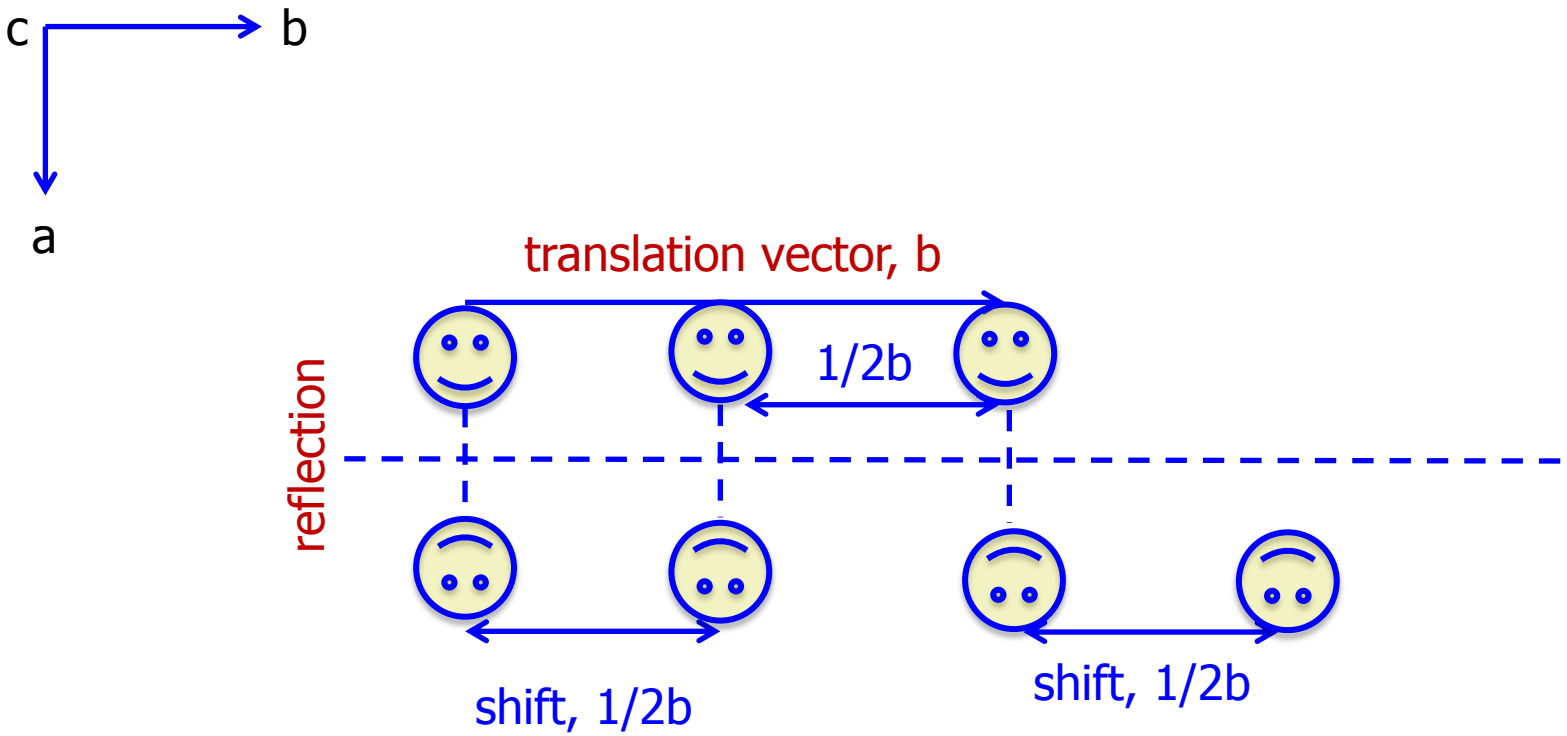
Plane symbol	Order	Graphical symbol[a]	Translation vector
a	2		**a**/2
b	2		**b**/2
c	2		**c**/2
n	2		**d**/2[b]
d	4		**d**/4[b]

a ⊥ [010] or [001]
a || [100]

b ⊥ [100] or [001]
b || [010]

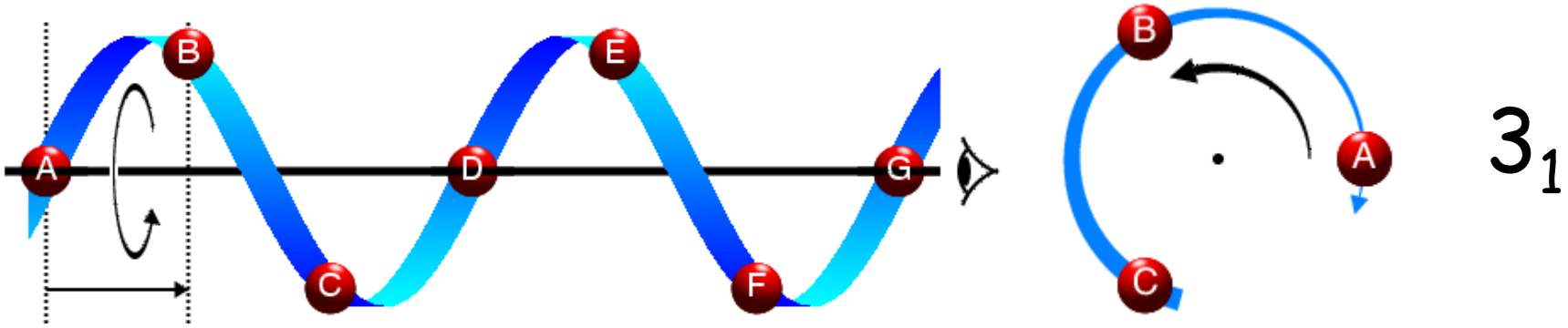
c ⊥ [100] or [010]
c || [001]

Glide planes



Translational symmetry elements

Rotation + translation = screw axis



3_1

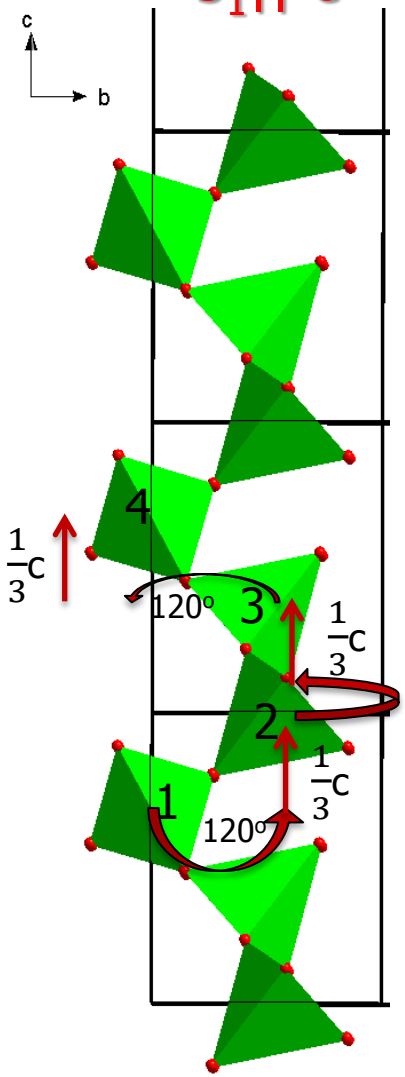
X_y

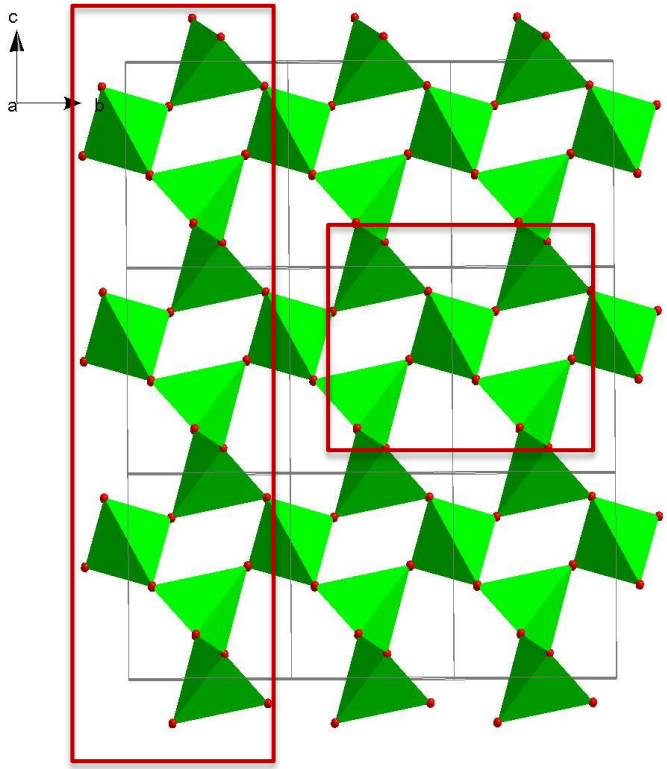
The degree of rotation is **360/x**
The translation is **y/x** units
along screw axis

Order	Screw axes
2	2_1
3	3_1, 3_2
4	4_1, 4_2, 4_3
6	6_1, 6_2, 6_3, 6_4, 6_5

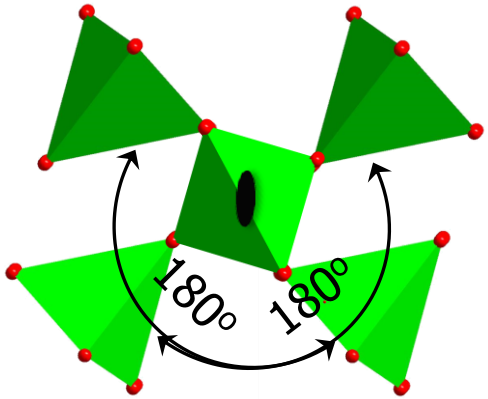
Screw axis in Quartz

$3_1 \parallel c$





$2 \parallel a$



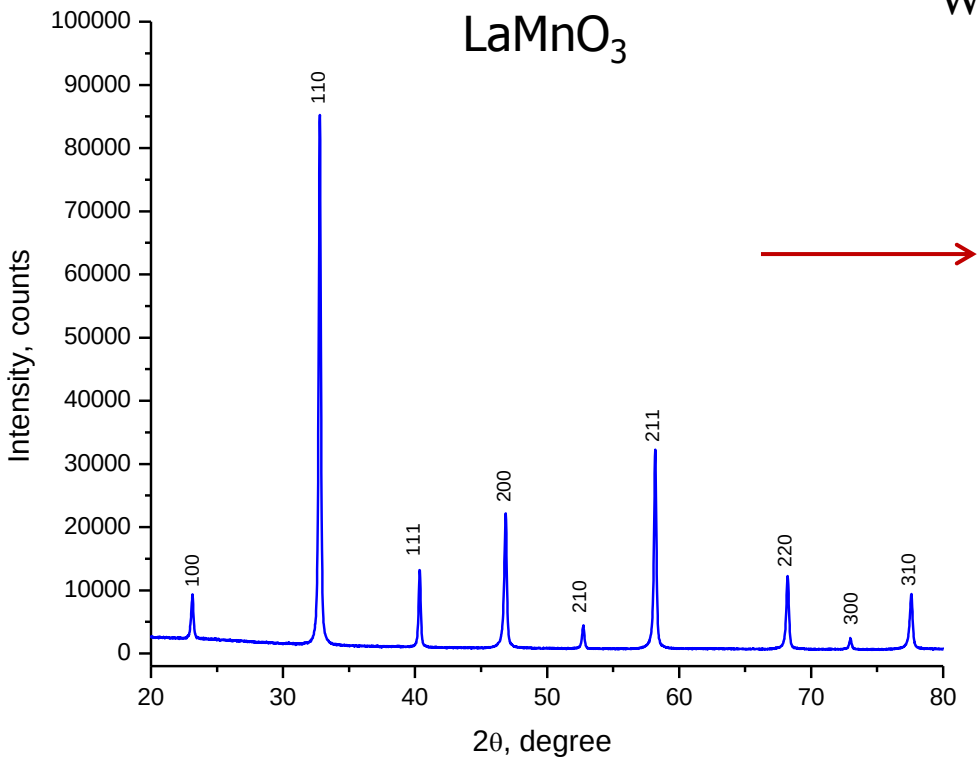
S.G.: $P3_121$
trigonal
Z: 3

Space group

The combination of all available symmetry operations (32 point groups), together with translation symmetry, within the all available lattices (14 Bravais lattices) lead to 230 Space Groups that describe the only ways in which identical objects can be arranged in an infinite lattice.

Cubic	*23*	$P23^{195}$, $F23^{196}$, $I23^{197}$, $P2_13^{198}$, $I2_13^{199}$
(36)	**m$\bar{3}$**	**Pm$\bar{3}^{200}$, Pn$\bar{3}^{201}$, Fm$\bar{3}^{202}$, Fd$\bar{3}^{203}$, Im$\bar{3}^{204}$, Pa$\bar{3}^{205}$, Ia$\bar{3}^{206}$**
	432	$P432^{207}$, $P4_232^{208}$, $F432^{209}$, $F4_132^{210}$, $I432^{211}$, $P4_332^{212}$, $P4_132^{213}$, $I4_132^{214}$
	$\bar{4}$3m	P$\bar{4}$3m^{215}, F$\bar{4}$3m^{216}, I$\bar{4}$3m^{217}, P$\bar{4}$3n^{218}, F$\bar{4}$3c^{219}, I$\bar{4}$3d^{220}
	m$\bar{3}$m	**Pm$\bar{3}$m^{221}, Pn$\bar{3}$n^{222}, Pm$\bar{3}$n^{223}, Pn$\bar{3}$m^{224}, Fm$\bar{3}$m^{225}, Fm$\bar{3}$c^{226}, Fd$\bar{3}$m^{227}, Fd$\bar{3}$c^{228}, Im$\bar{3}$m^{229}, Ia$\bar{3}$d^{230}**

Intenational tables for Crystallography



We know specific density, ρ, of the sample

Pm-3m (221) – cubic
a=3.905 Å
V=59.56 Å^3

$$Z = \frac{\rho V}{m}$$

Z = 1

Z - number of molecules in the unit cell

m – molecular mass

Intenational tables for Crystallography

CONTINUED No. 221 $Pm\bar{3}m$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5); (13); (25)

Positions

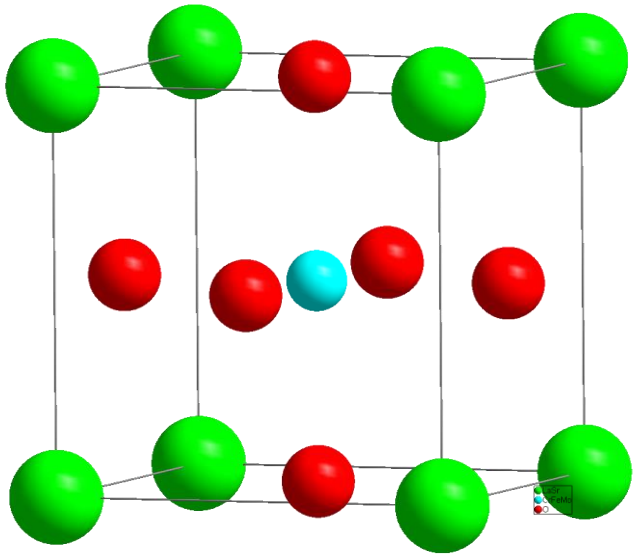
Multiplicity, Wyckoff letter, Site symmetry		Coordinates					
48	n 1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{x},y,\bar{z}$	(4) $x,\bar{y},\bar{z}$		
		(5) z,x,y	(6) $z,\bar{x},\bar{y}$	(7) $\bar{z},\bar{x},y$	(8) $\bar{z},x,\bar{y}$		
		(9) y,z,x	(10) $\bar{y},z,\bar{x}$	(11) $y,\bar{z},\bar{x}$	(12) $\bar{y},\bar{z},x$		
		(13) $y,x,\bar{z}$	(14) $\bar{y},\bar{x},\bar{z}$	(15) $y,\bar{x},z$	(16) $\bar{y},x,z$		
		(17) $x,z,\bar{y}$	(18) $\bar{x},z,y$	(19) $\bar{x},\bar{z},\bar{y}$	(20) $x,\bar{z},y$		
		(21) $z,y,\bar{x}$	(22) $z,\bar{y},x$	(23) $\bar{z},y,x$	(24) $\bar{z},\bar{y},\bar{x}$		
		(25) $\bar{x},\bar{y},\bar{z}$	(26) $x,y,\bar{z}$	(27) $x,\bar{y},z$	(28) $\bar{x},y,z$		
		(29) $\bar{z},\bar{x},\bar{y}$	(30) $\bar{z},x,y$	(31) $\bar{z},\bar{x},y$	(32) $\bar{z},x,\bar{y}$		
		(33) $\bar{y},\bar{z},x$	(34) $y,\bar{z},\bar{x}$	(35) $\bar{y},z,\bar{x}$	(36) y,z,x		
		(37) $\bar{y},\bar{x},z$	(38) y,x,z	(39) $\bar{y},x,\bar{z}$	(40) $y,\bar{x},\bar{z}$		
		(41) $\bar{x},\bar{z},y$	(42) $x,\bar{z},\bar{y}$	(43) x,z,y	(44) $\bar{x},z,\bar{y}$		
		(45) $z,\bar{y},x$	(46) $\bar{z},y,x$	(47) $z,\bar{y},\bar{x}$	(48) $\bar{z},y,\bar{x}$		
24	m . . m	x,x,z	$\bar{x},\bar{x},z$	$\bar{x},x,\bar{z}$	$x,\bar{x},\bar{z}$	z,x,x	$z,\bar{x},\bar{x}$
		$z,\bar{x},x$	$z,x,\bar{x}$	$x,z,\bar{x}$	$\bar{x},z,x$	$x,z,\bar{x}$	$\bar{x},z,x$
		$x,x,\bar{z}$	$\bar{x},\bar{x},\bar{z}$	$\bar{x},x,z$	$x,\bar{x},z$	$x,\bar{z},x$	$\bar{x},\bar{z},x$
		$\bar{x},z,\bar{x}$	x,z,x	$x,\bar{z},\bar{x}$	$\bar{x},\bar{z},\bar{x}$	$\bar{z},x,x$	$\bar{z},\bar{x},x$
24	l m . .	$\frac{1}{2},y,z$	$\frac{1}{2},\bar{y},z$	$\frac{1}{2},y,\bar{z}$	$\frac{1}{2},\bar{y},\bar{z}$	$z,\frac{1}{2},y$	$z,\frac{1}{2},\bar{y}$
		$z,\frac{1}{2},y$	$z,\frac{1}{2},\bar{y}$	$y,\frac{1}{2},z$	$\bar{y},\frac{1}{2},z$	$y,\frac{1}{2},\bar{z}$	$\bar{y},\frac{1}{2},\bar{z}$
		$y,\frac{1}{2},z$	$\bar{y},\frac{1}{2},z$	$y,\frac{1}{2},\bar{z}$	$\bar{y},\frac{1}{2},\bar{z}$	$\frac{1}{2},z,y$	$\frac{1}{2},z,\bar{y}$
		$\frac{1}{2},z,y$	$\frac{1}{2},z,\bar{y}$	$z,y,\frac{1}{2}$	$z,\bar{y},\frac{1}{2}$	$z,y,\frac{1}{2}$	$z,\bar{y},\frac{1}{2}$
24	k m . .	$0,y,z$	$0,\bar{y},z$	$0,y,\bar{z}$	$0,\bar{y},\bar{z}$	$z,0,y$	$z,0,\bar{y}$
		$z,0,y$	$z,0,\bar{y}$	$y,z,0$	$\bar{y},z,0$	$y,z,0$	$\bar{y},z,0$
		$y,0,z$	$\bar{y},0,z$	$y,0,\bar{z}$	$\bar{y},0,\bar{z}$	$0,z,\bar{y}$	$0,z,y$
		$0,z,\bar{y}$	$0,z,y$	$z,y,0$	$z,\bar{y},0$	$z,y,0$	$z,\bar{y},0$
12	j m . $m2$	$\frac{1}{2},y,y$	$\frac{1}{2},\bar{y},y$	$\frac{1}{2},y,\bar{y}$	$\frac{1}{2},\bar{y},\bar{y}$	$y,\frac{1}{2},y$	$y,\frac{1}{2},\bar{y}$
		$\bar{y},\frac{1}{2},y$	$\bar{y},\frac{1}{2},\bar{y}$	$y,y,\frac{1}{2}$	$\bar{y},\bar{y},\frac{1}{2}$	$y,\bar{y},\frac{1}{2}$	$\bar{y},\bar{y},\frac{1}{2}$
12	i m . $m2$	$0,y,y$	$0,\bar{y},y$	$0,y,\bar{y}$	$0,\bar{y},\bar{y}$	$y,0,y$	$y,0,\bar{y}$
		$\bar{y},0,y$	$\bar{y},0,\bar{y}$	$y,y,0$	$\bar{y},y,0$	$y,\bar{y},0$	$\bar{y},\bar{y},0$
12	h m m 2 . .	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$	$0,x,\frac{1}{2}$	$0,\bar{x},\frac{1}{2}$	$\frac{1}{2},0,x$	$\frac{1}{2},0,\bar{x}$
		$\frac{1}{2},x,0$	$\frac{1}{2},\bar{x},0$	$x,0,\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$	$0,\frac{1}{2},x$	$0,\frac{1}{2},\bar{x}$
8	g . 3 m	x,x,x	$\bar{x},\bar{x},x$	$\bar{x},x,\bar{x}$	$x,\bar{x},\bar{x}$		
		$x,x,\bar{x}$	$\bar{x},\bar{x},\bar{x}$	$x,\bar{x},x$	$\bar{x},x,x$		
6	f 4 m . m	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},x,\frac{1}{2}$	$\frac{1}{2},\bar{x},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},x$	$\frac{1}{2},\frac{1}{2},\bar{x}$
6	e 4 m . m	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	$0,0,x$	$0,0,\bar{x}$
3	d 4/m m . m	$\frac{1}{2},0,0$	$0,\frac{1}{2},0$	$0,0,\frac{1}{2}$			
3	c 4/m m . m	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			
1	b $m\bar{3}m$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$					
1	a $m\bar{3}m$	$0,0,0$					

Reflection conditions

h,k,l permutable
General:

no conditions

Special: no extra conditions



La
Mn
O

La	1a	m-3m	0 0 0			
Mn	1b	m-3m	½ ½ ½			
O	3c	4/mm.m	0 ½ ½	½ 0 ½	½ ½ 0	

Outline

- History of X-ray
- Sources of X-ray radiation
- Physics of X-ray scattering
- Fundamentals of crystallography
- X-ray diffraction methods
- X-ray diffraction in material science: examples

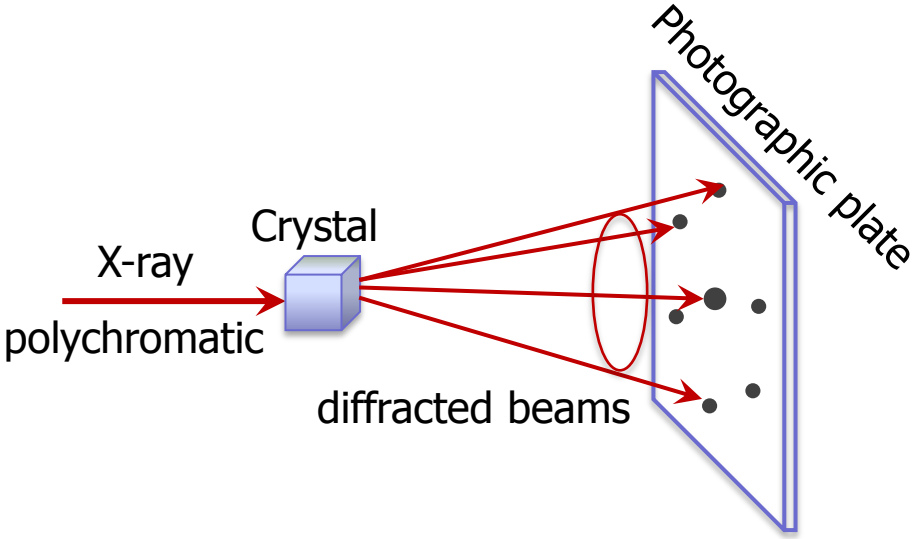
The diffraction scheme

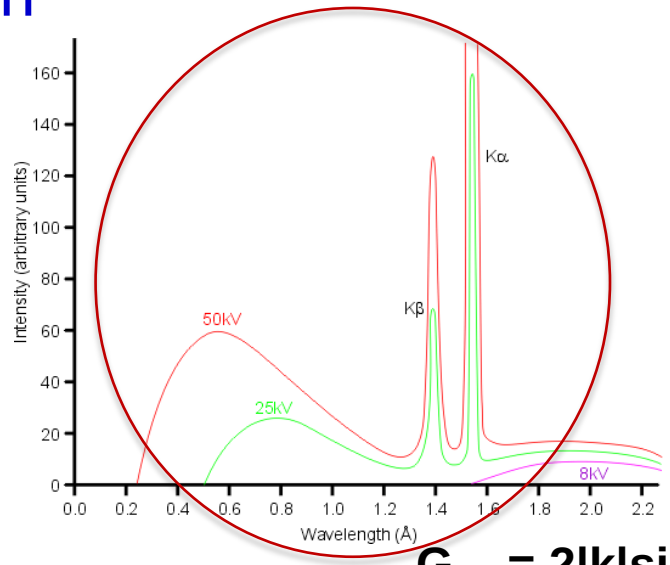
Laue diffraction

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

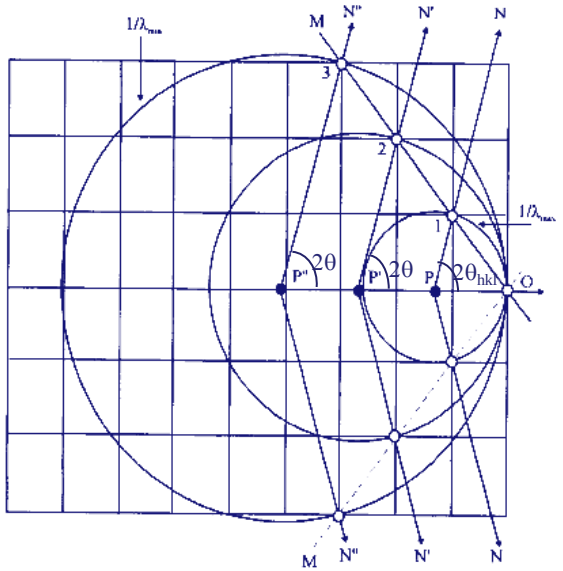
θ_{hkl} is fixed ⟶ polychromatic radiation

The crystal position is fixed





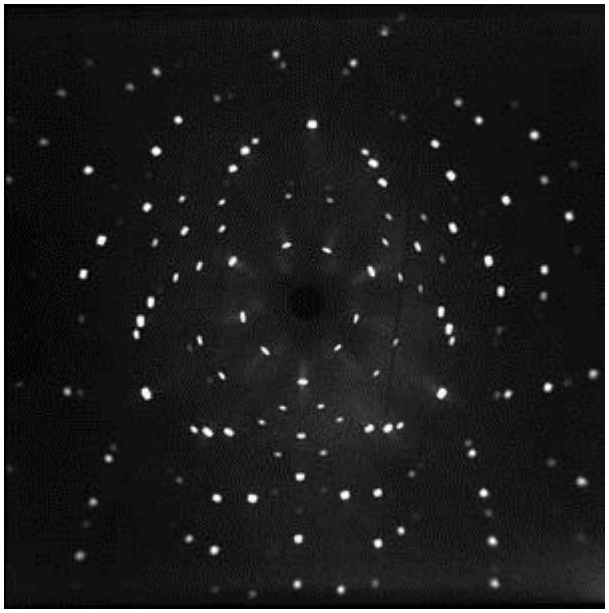
$G_{hkl} = 2|k|\sin\theta$



The diffraction scheme

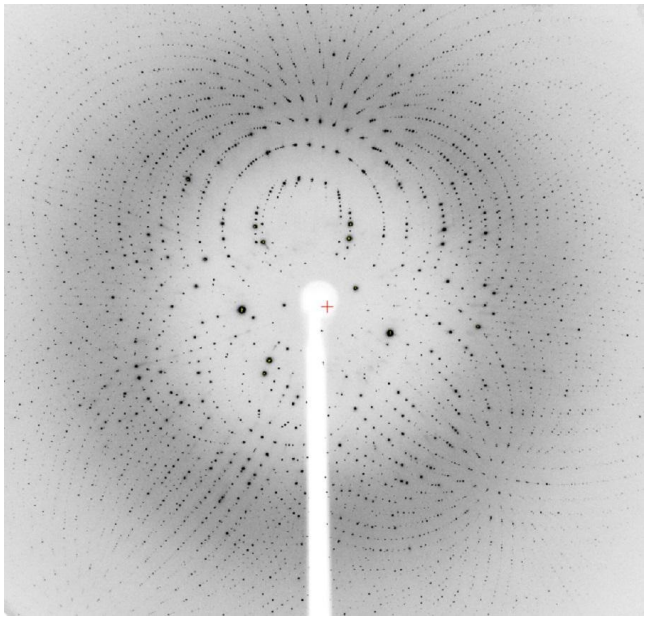
Laue diffraction

Historical X-ray photograph



Silicon crystal, 3-fold [111]* axis
S.Gr.: Fd-3m
face-centered cubic (*fcc*)

Modern XRD pattern of Hemoglobin obtained with the CCD detector



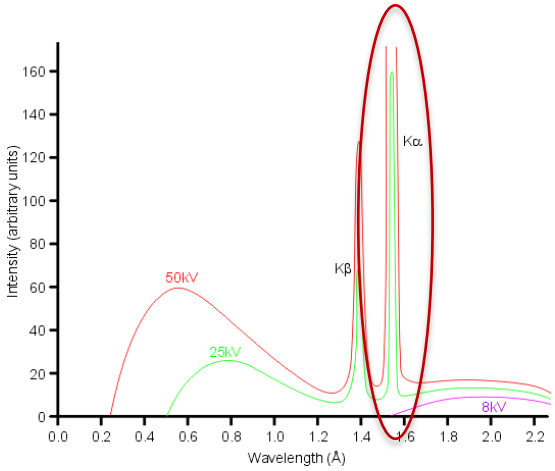
The diffraction scheme

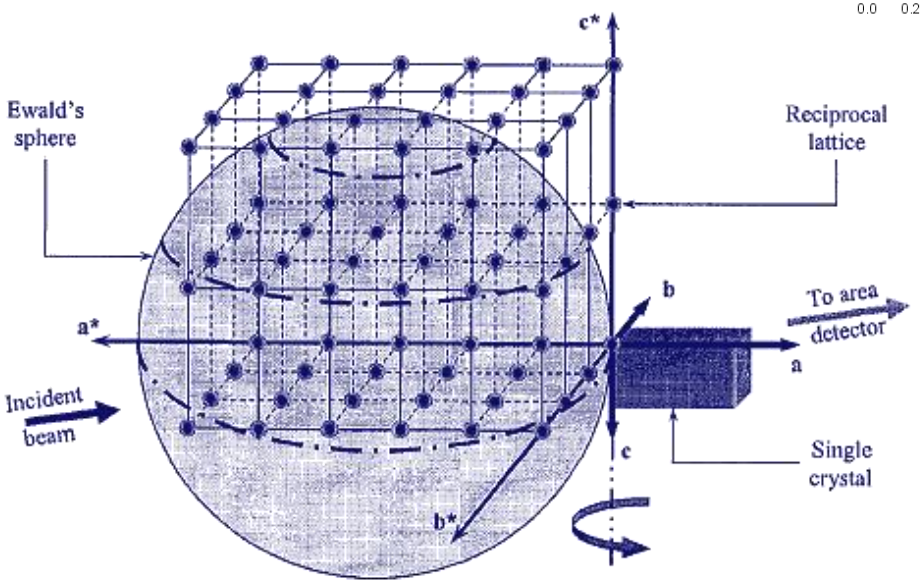
Bragg diffraction (oscillating crystal)

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

λ is fixed ⟶ monochromatic radiation

The crystal is rotating (oscillating)

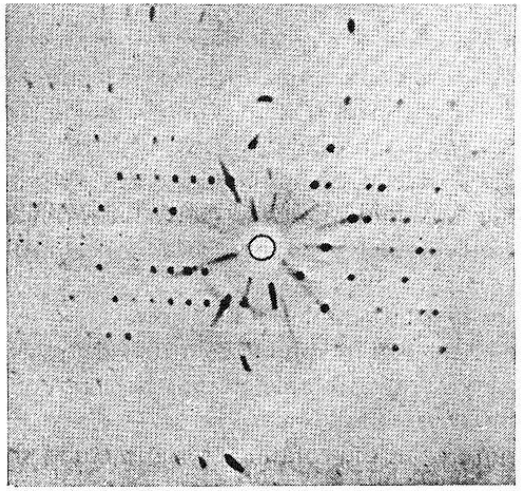


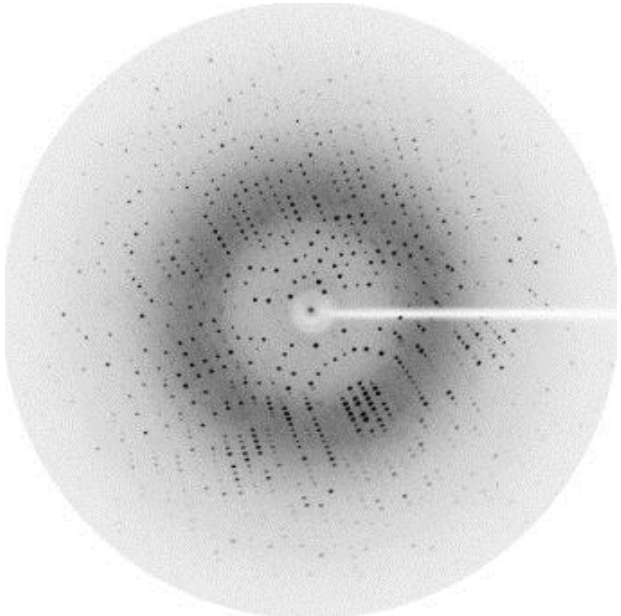


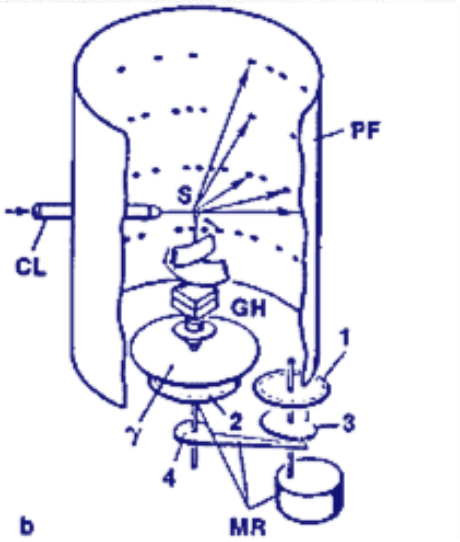
$$G_{hkl} = 2|k|\sin\theta$$

The diffraction scheme

Bragg diffraction (the crystal rotating)







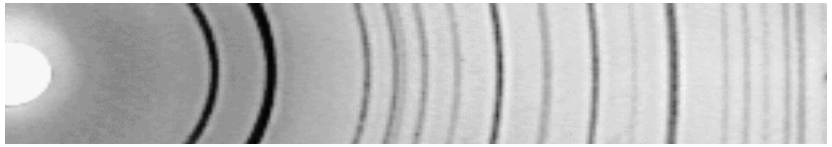
The diffraction scheme

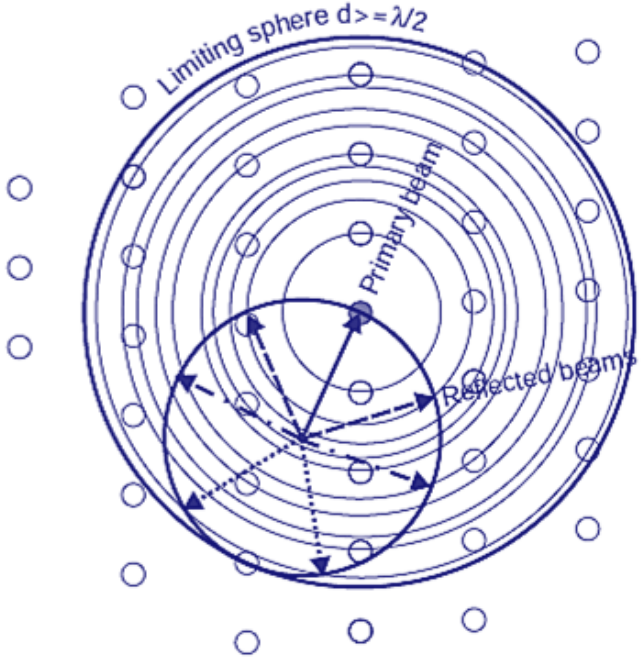
Debye-Scherrer diffraction

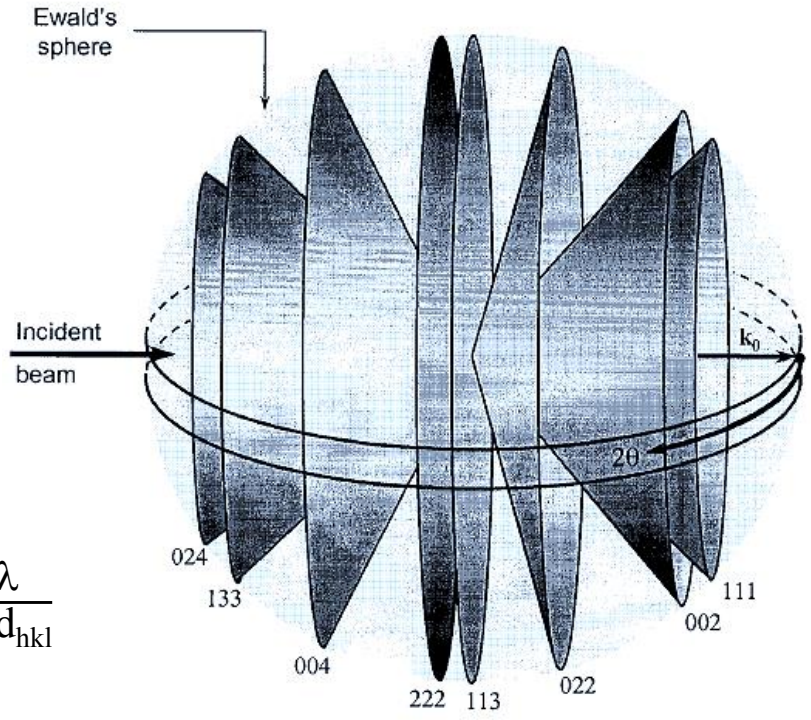
$$2d_{hkl}\sin\theta_{hkl} = \lambda$$

λ is fixed ⟶ monochromatic radiation

Quartz



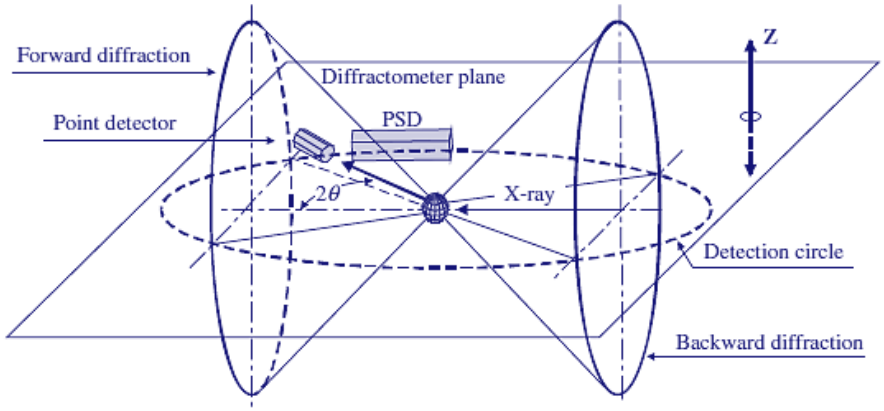




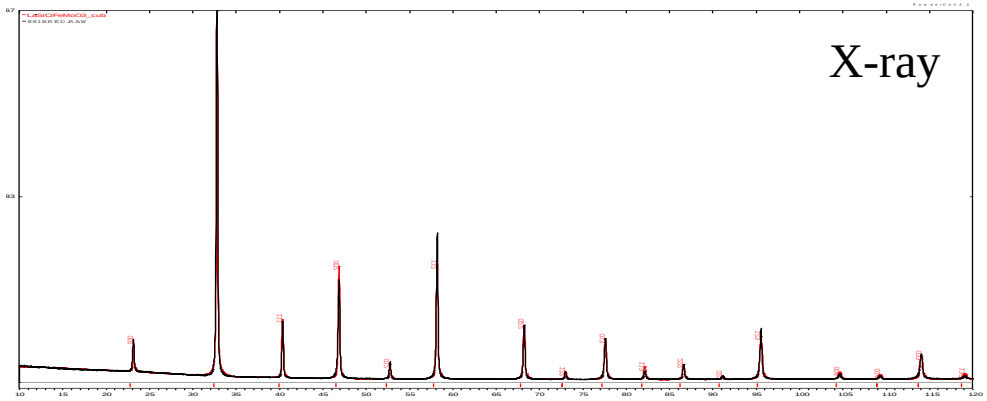
$$\sin\theta_{hkl} = \frac{\lambda}{2d_{hkl}}$$

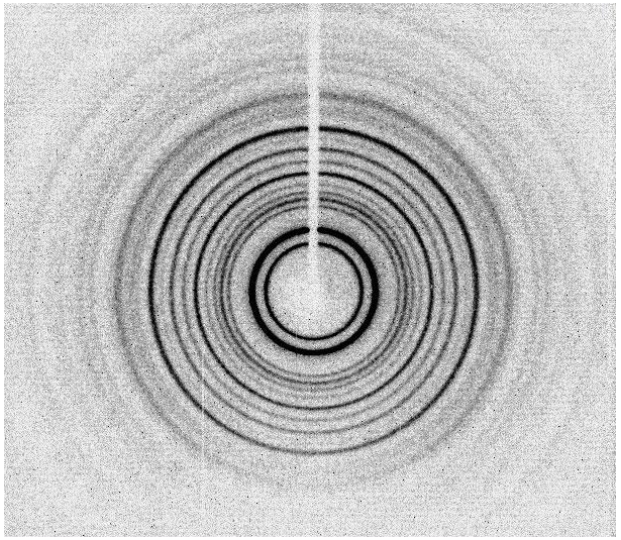
The diffraction scheme

Debye-Scherrer diffraction



CCD detector

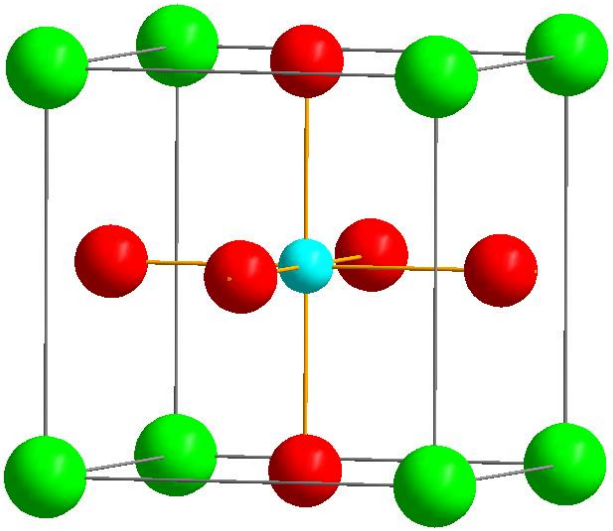


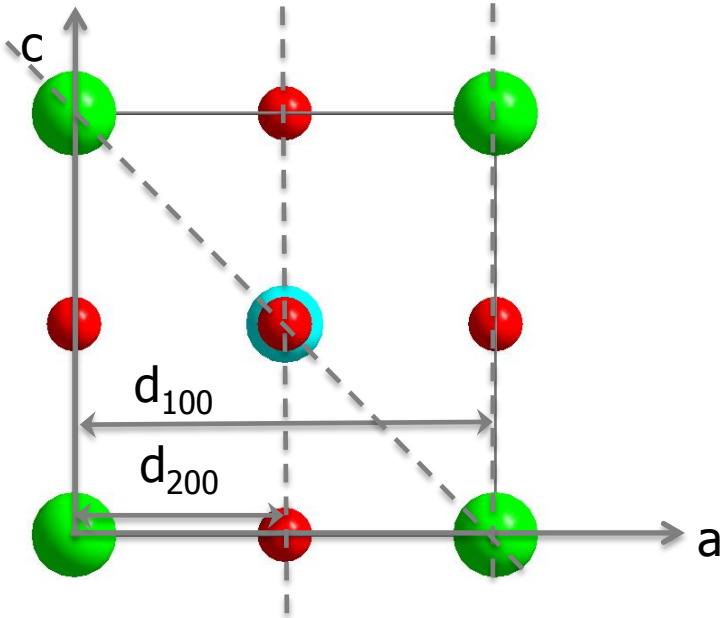


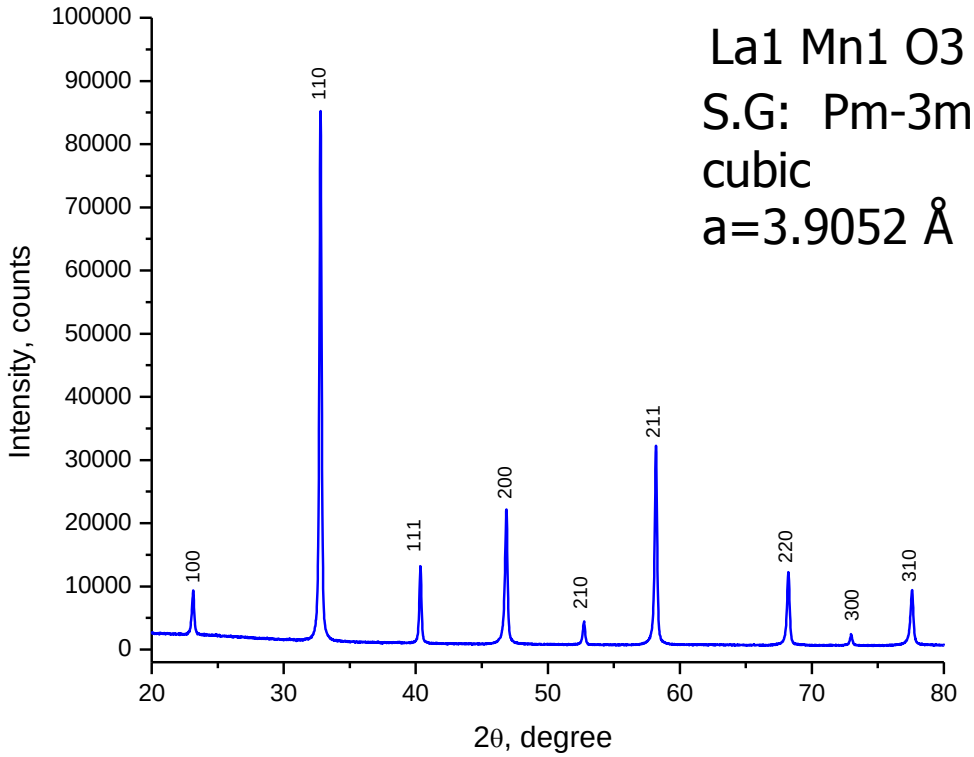
Outline

- History of X-ray
- Sources of X-ray radiation
- Physics of X-ray scattering
- Fundamentals of crystallography
- X-ray diffraction methods
- X-ray diffraction in material science: examples

Structure factor







$$F(hkl)=\sum_{i=1}^{N} f_i e^{i2\pi(hx_i+ky_i+lz_i)}$$

$F_{100}= f_{La}+f_O-f_{Mn}-2f_O=f_{La}-f_{Mn}-f_O= 22$

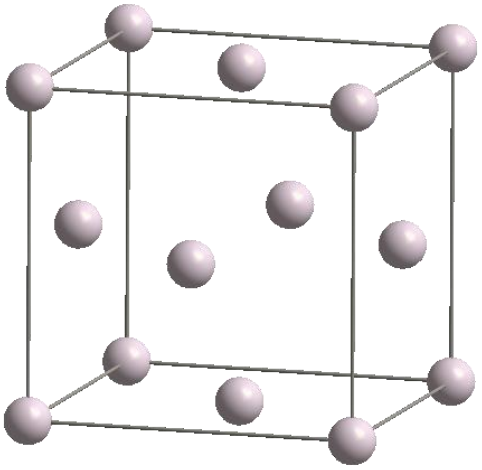
$F_{200}= f_{La}+f_{Mn}+3f_O =75$

$F_{110}= f_{La}+f_{Mn}-f_O =60$

Systematic absences

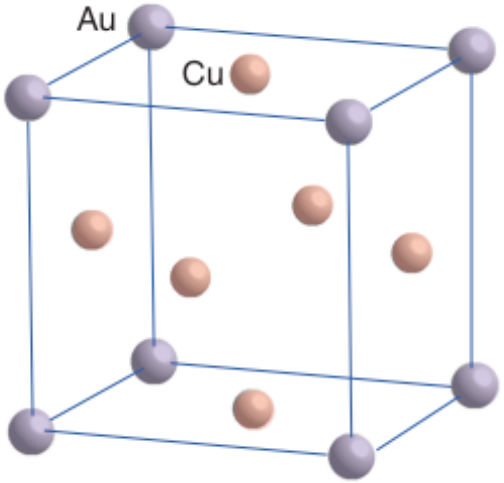
AuCu- face-centred cubic (F), fcc
disordered solid solution

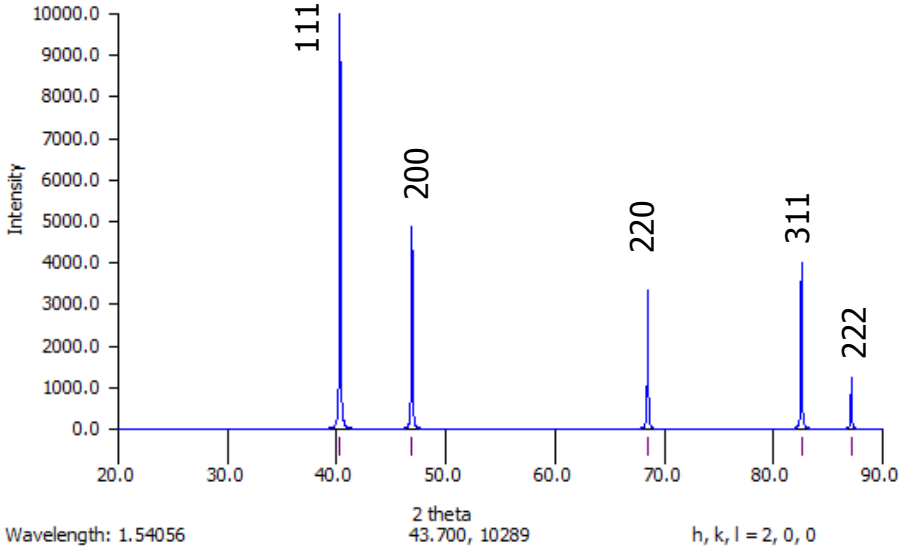
Fm-3m
a= 3.872 Å

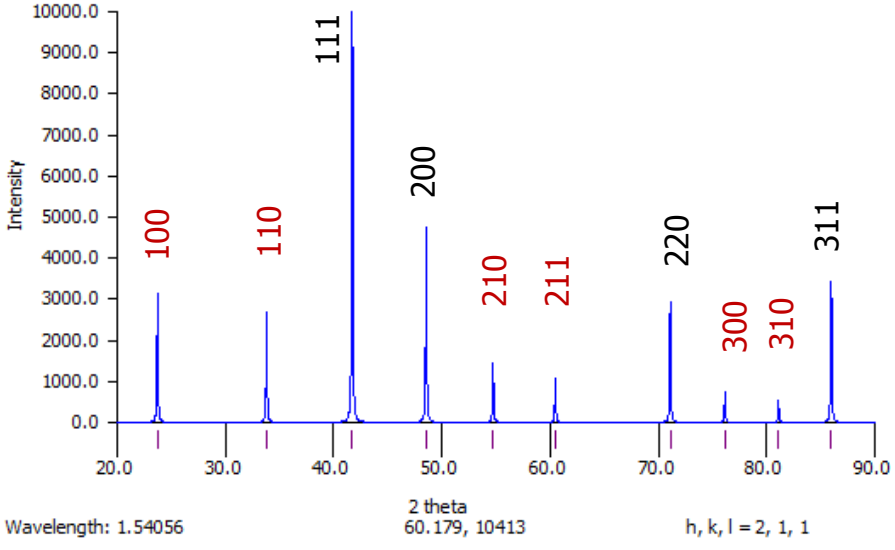


AuCu3- primitive cubic (P)
ordered solid solution

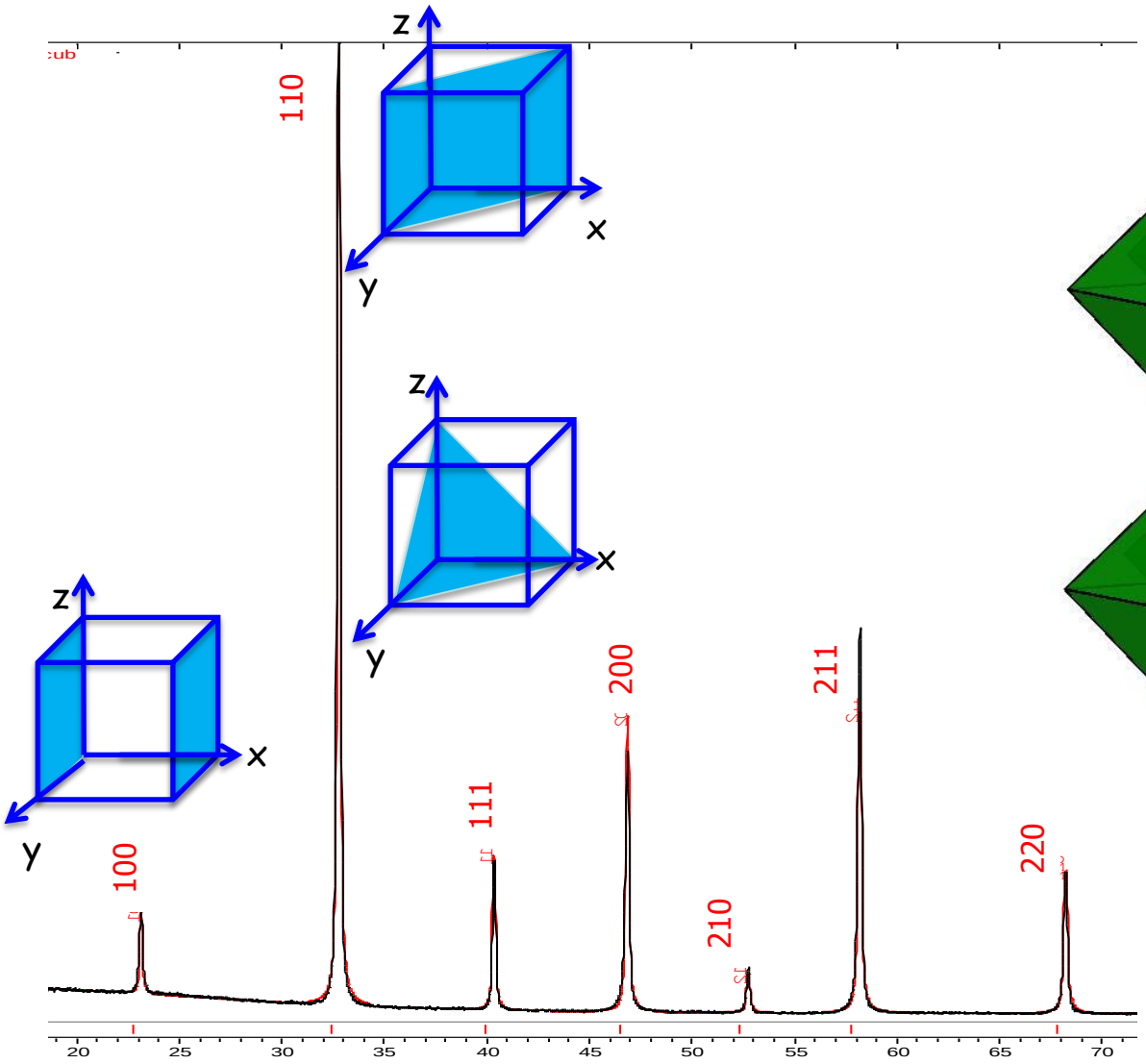
Pm-3m
a= 3.747 Å

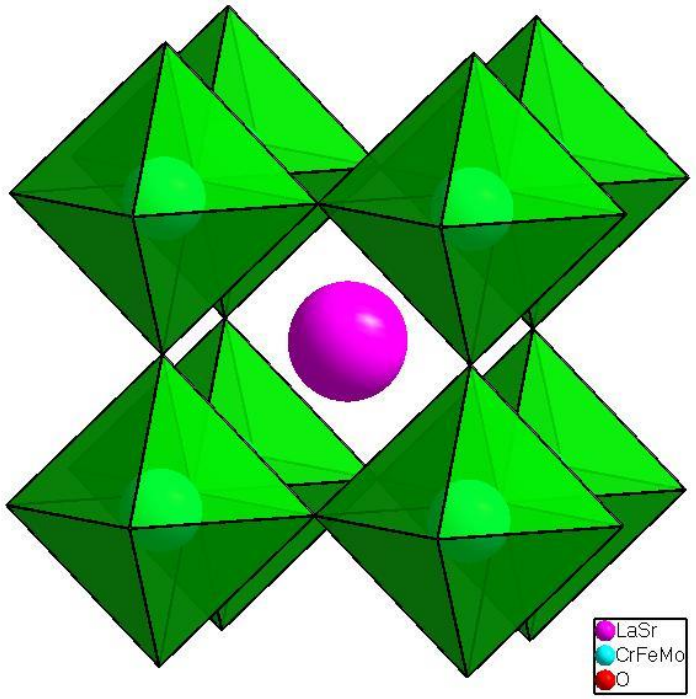






Perovskites





Pm-3m (221) – cubic

a=3.905 Å

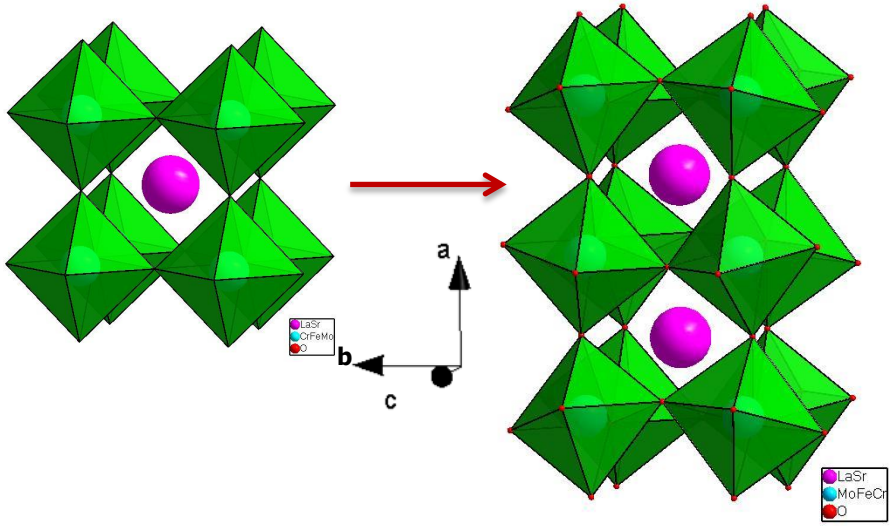
V=59.56 Å^3

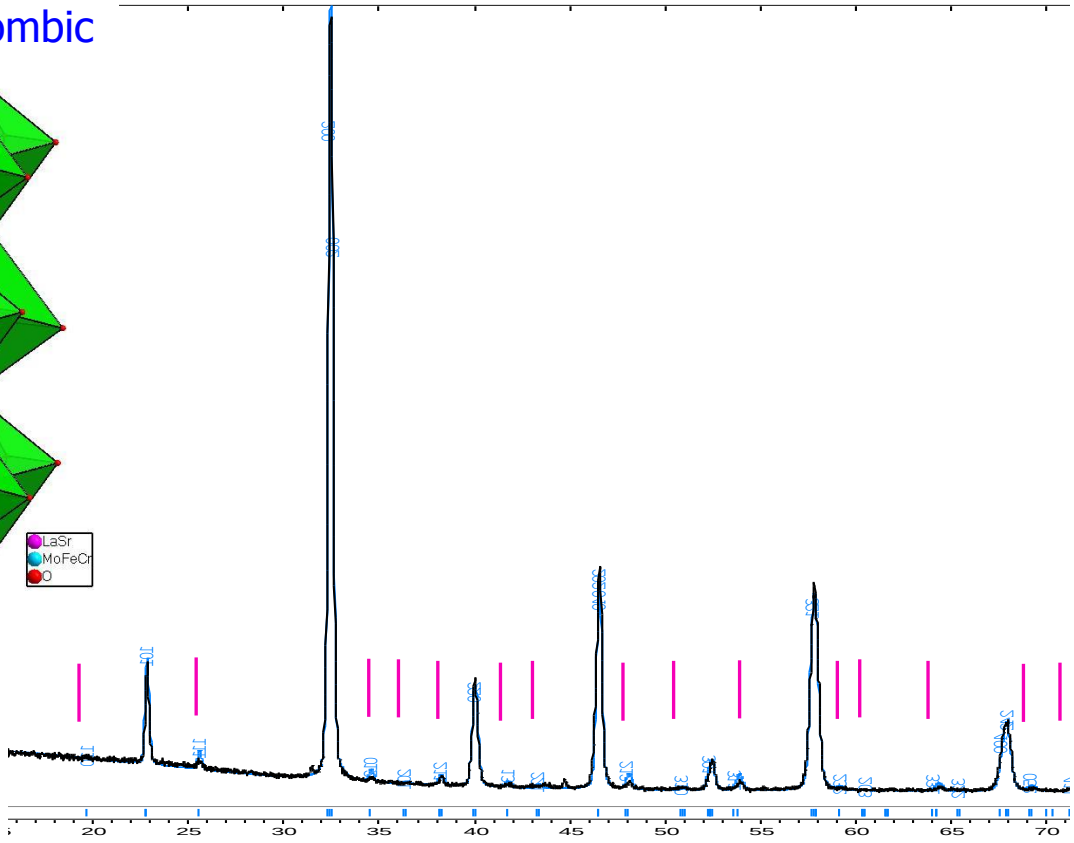
Z = 1

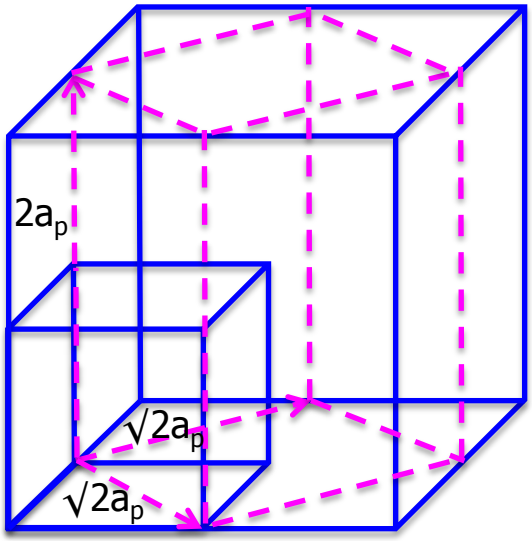
Perovskites

Pm-3m, cubic

Pnma, orthorhombic



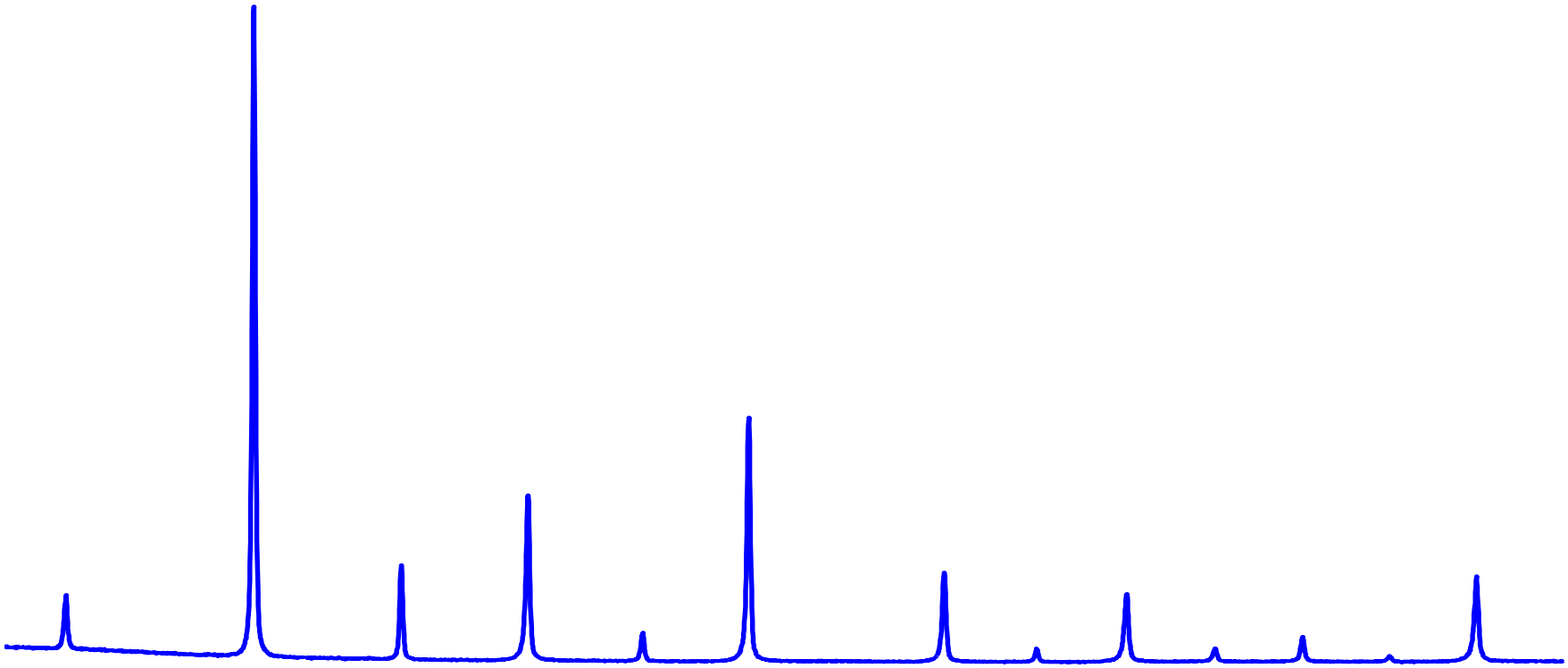




Pnma, a = $\sqrt{2}a_p$, b = $\sqrt{2}a_p$, c = $2a_p$

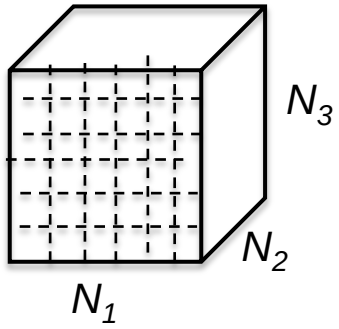
Pnma (62)
a=5.539 Å, b=5.489 Å, c=7.793 Å
V=236.96 Å^3
Z= 4

Conclusions



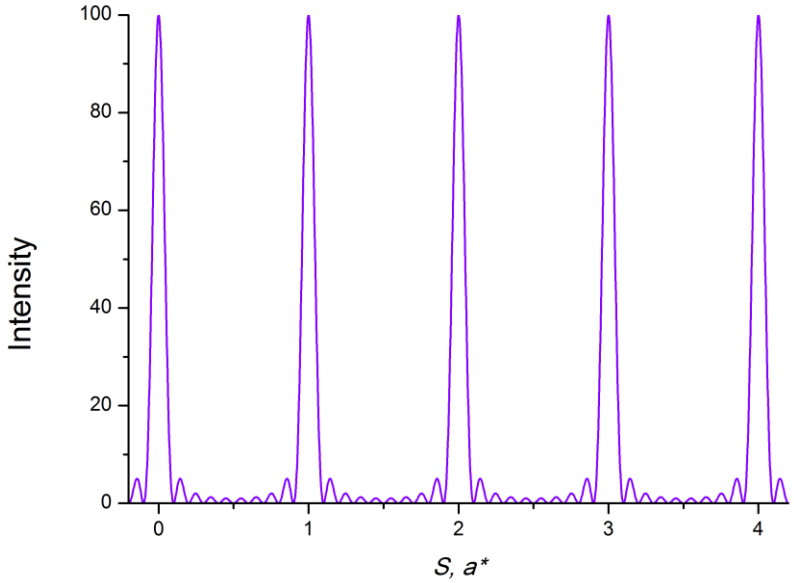
X-ray scattering physics

Finite crystal



$$I \sim \frac{\sin^2(N_1\varphi_1)}{\sin^2\varphi_1} \cdot \frac{\sin^2(N_2\varphi_2)}{\sin^2\varphi_2} \cdot \frac{\sin^2(N_3\varphi_3)}{\sin^2\varphi_3}$$

$$\varphi_1 = \pi(\boldsymbol{S}\cdot\boldsymbol{a}),\ \varphi_2 = \pi(\boldsymbol{S}\cdot\boldsymbol{b}),\ \varphi_3 = \pi(\boldsymbol{S}\cdot\boldsymbol{c})$$



$N_1 = 10$

*There are high peaks in I(S) when (**S**·**a***) - integer*

$$N \longrightarrow \infty$$

$$I \sim N_1^2 \cdot \delta(\boldsymbol{S}-n\cdot\boldsymbol{a}^*)$$