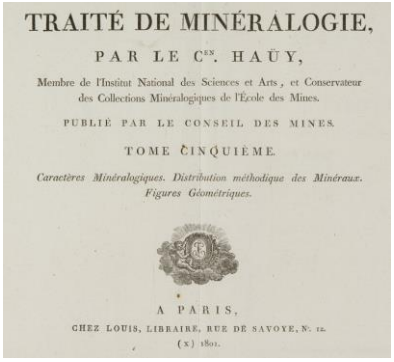
Introduction to X-Ray Powder Diffraction

Riccardo Vivani
Department of Pharmaceutical Sciences
Perugia University

Aim of these lessons:

- introduce some useful concepts for better understand the next lesson/tutorial on Rietveld refinement with Fullprof
- help to extract some information from powder diffraction data
- help setup a powder diffraction experiment by yourself

CRYSTAL a solid structure consisting of atoms, molecules or ions having a geometrically regular arrangement, which is repeated indefinitely in the three spatial dimensions, called the crystal lattice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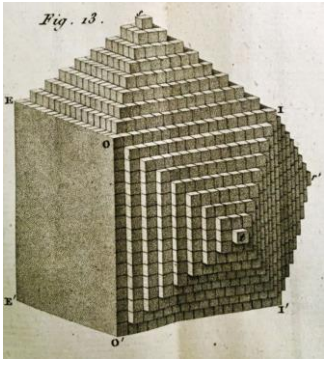
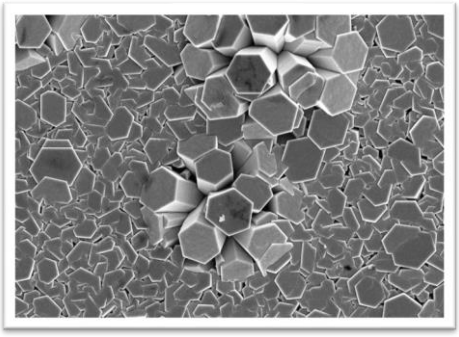


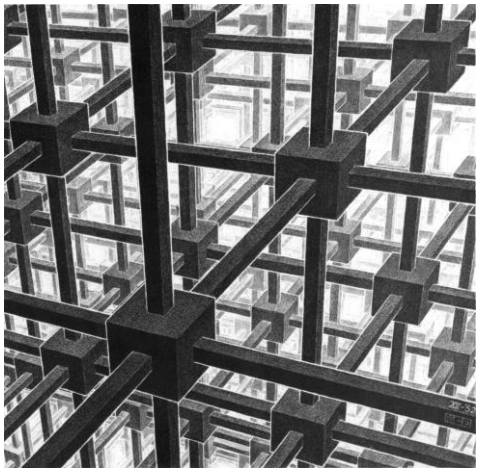
René Just Haüy
(1743-1822)

Large crystals



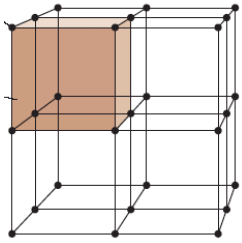
Small crystals

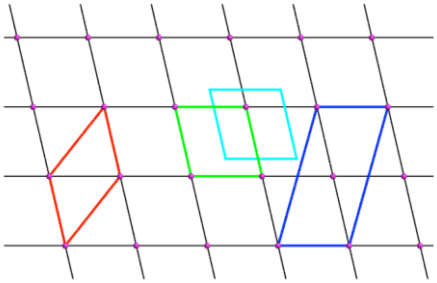
THE CRYSTAL LATTICE



M.C. Escher
(1898-1972)

THE CRYSTAL LATTICE AND THE UNIT CELL

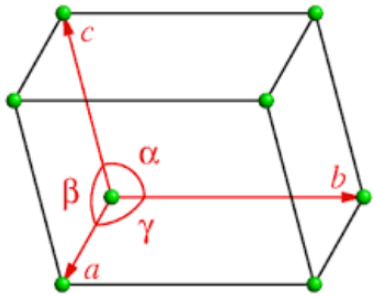




- Many options to choose the unit cell
- Rules:
  - minimum number of lattice points (not the blue one)
  - Origin on one lattice point
  - Angles as close to 90 deg as possible

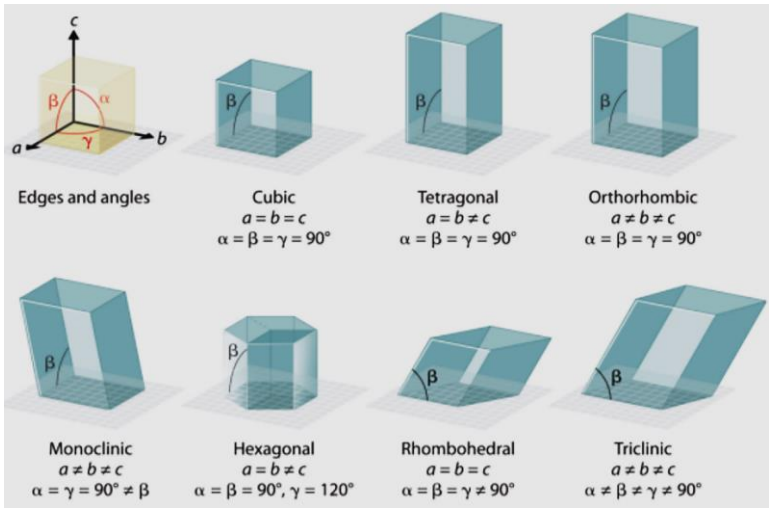
THE UNIT CELL

A unit cell is represented by a parallelepiped, characterized by three non coplanar vectors (***a***, ***b***, ***c***) and three angles (α, β, γ)

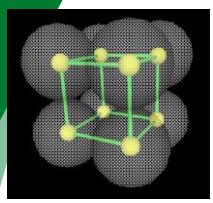


Depending on the relation among vectors and angles, there are **seven types of unit cells**, forming the **seven crystal systems**

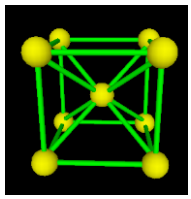
THE SEVEN CRYSTAL SYSTEMS



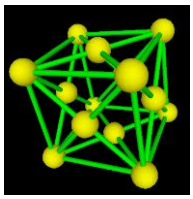
In some crystalline systems the lattice nodes are not found only in the vertices of the unit cell (primitive, P), but there are also others:
- in the center (body centered, I)
- in the center of all faces (face centered, F)
- in two opposite faces (base centered C).



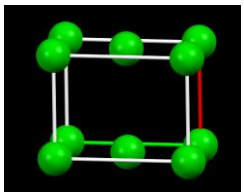
primitive



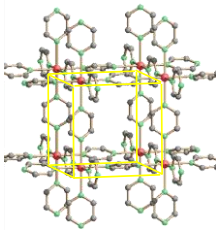
body centered



all face-centered



base centered



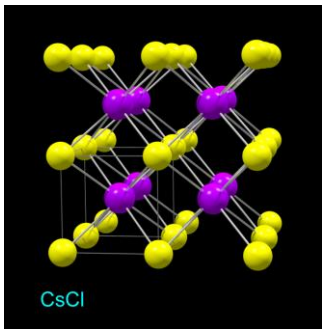
Metal organic framework

Iron (the Atomium, Bruxelles)

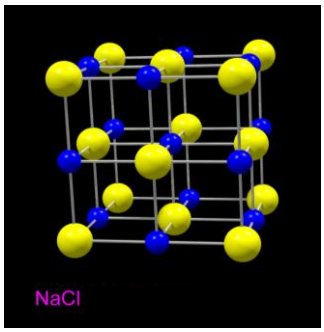
Buckminsterfullerene - C_{60}

Barium

Other examples

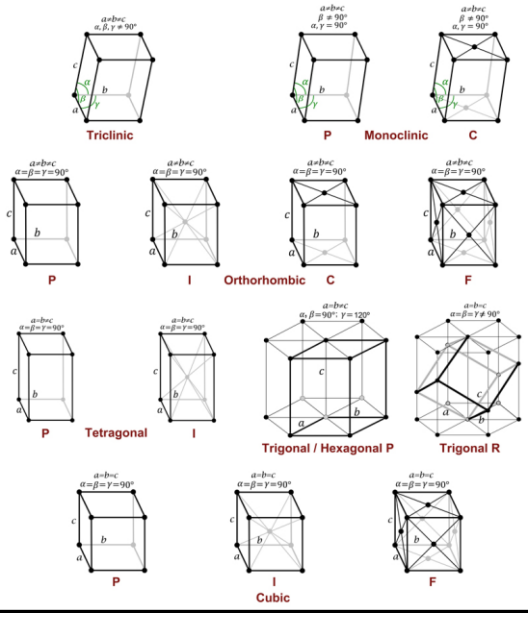


Two interpenetrated P lattices

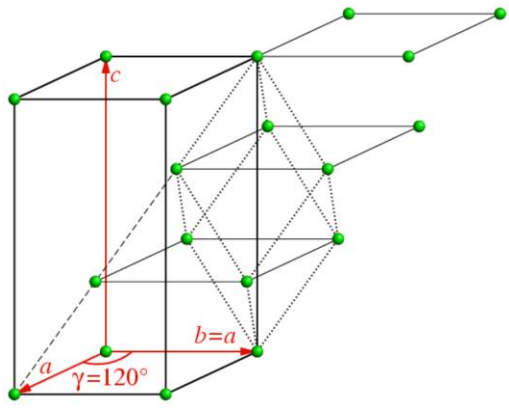


Two interpenetrated F lattices

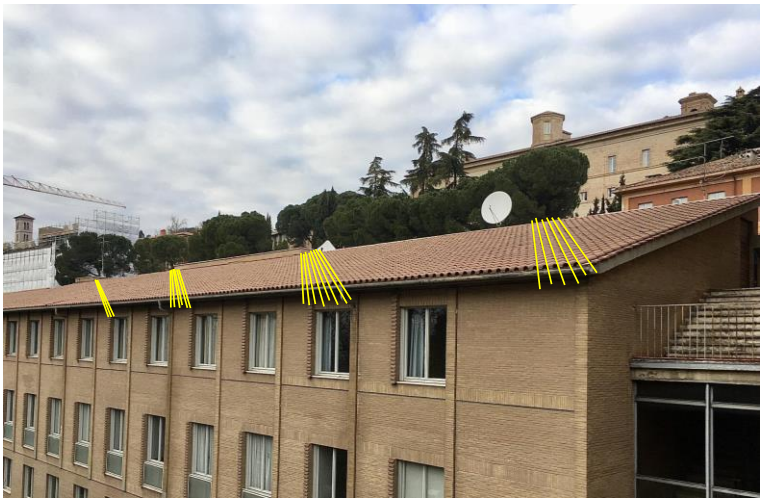
THE 14 BRAVAIS LATTICES

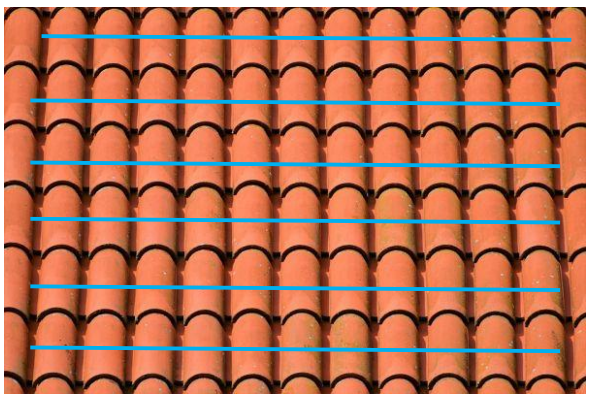


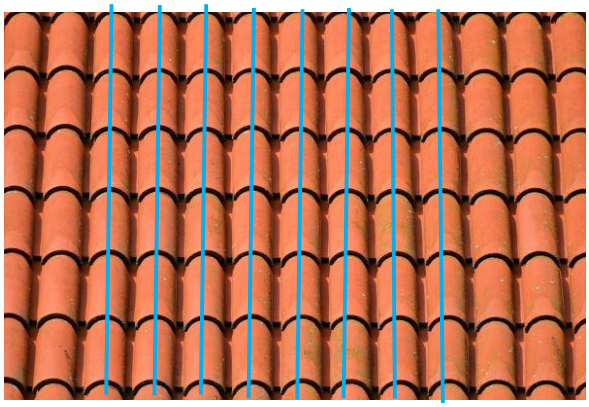
TRIGONAL AND ROMBOHEDRAL UNIT CELL

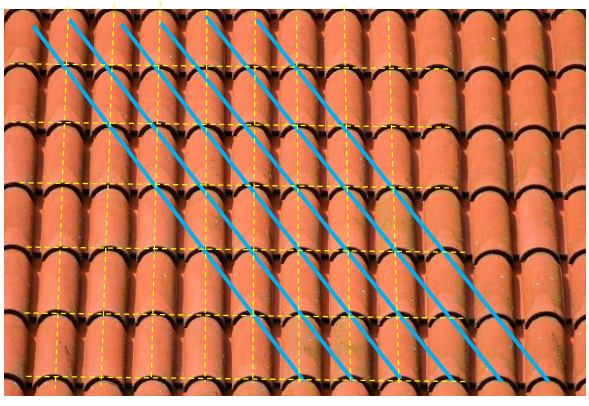


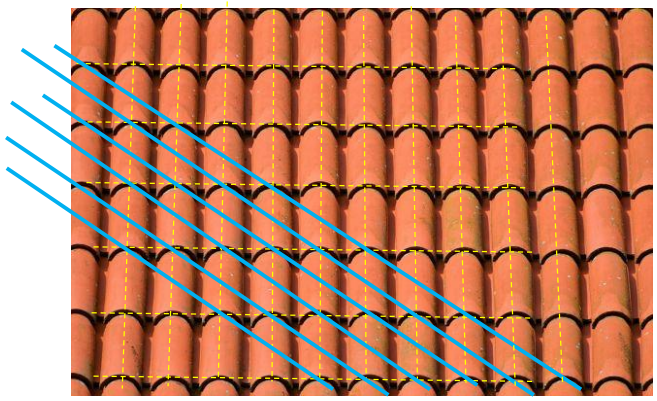
The translational periodicity of the crystals generates families of lattice planes



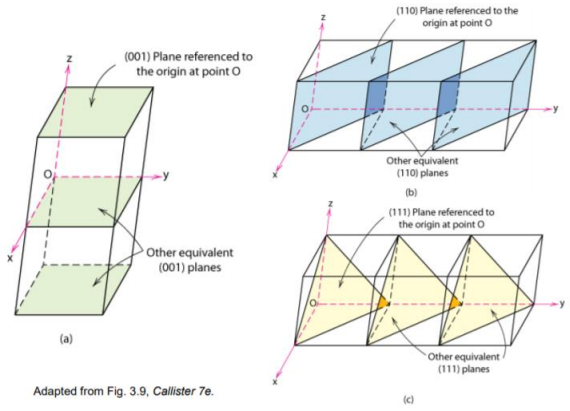








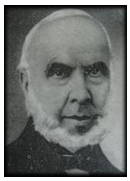
The translational periodicity of the crystals generates families of lattice planes



Adapted from Fig. 3.9, *Callister 7e.*

How can we mark them?

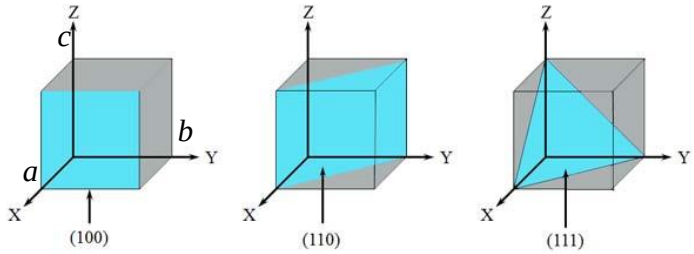
The Miller Indices



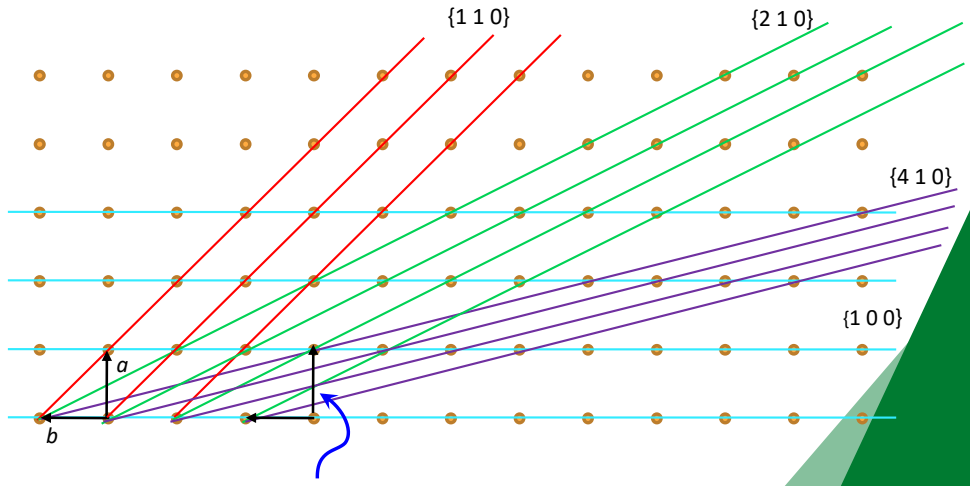
William Hallowes Miller
(1801-1880)

Given the three unit vectors of the crystal lattice, a, b, and c, and given x, y, and z, the intercepts of a plane on them, this plane is indicated by three integers, h, k, and l such that

$$h = \frac{1}{\frac{x}{a}} \qquad k = \frac{1}{\frac{y}{b}} \qquad l = \frac{1}{\frac{z}{c}}$$

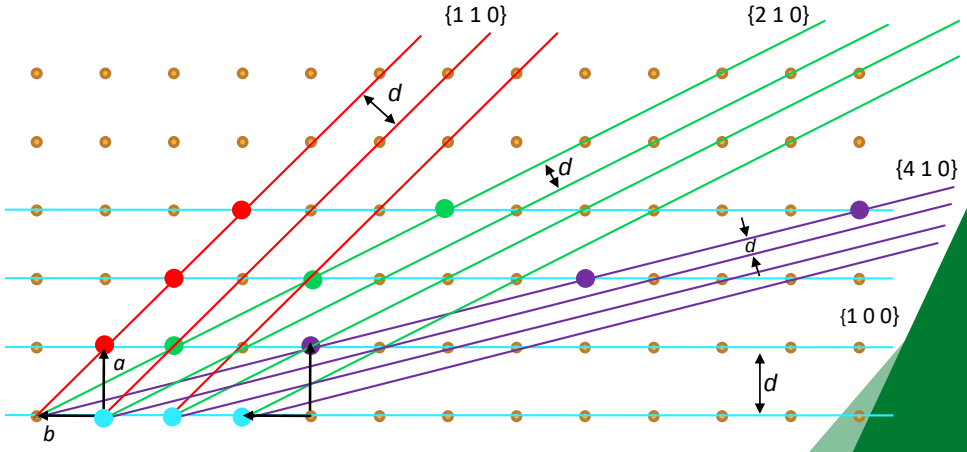


Given a plane (h k l) the translational symmetry of the crystal lattice generates a family of planes (indicated with curly brackets {hkl}, all having the same Miller indices h, k, l of the generating plane, equally spaced by a distance *d* which depends on the Miller indices.



The {hkl} family of planes intersects h times the *a* axis, k times the *b* etc.

Given a plane (h k l) the translational symmetry of the crystal lattice generates a family of planes (indicated with curly brackets {hkl}, all having the same Miller indices h, k, l of the generating plane, equally spaced by a distance *d* which depends on the Miller indices.



Note that when the Miller indices increase, the *d* spacing decreases, and the planes have a lower density of lattice nodes

Interplanar spacing

The interplanar distances *d* can be calculated with simple geometric considerations; they are a function of the cell parameters and contain the values of *h, k*, and *l* of the considered family of planes

System	d_{hkl}
Cubic	$\left[\frac{1}{a^2}(h^2+k^2+l^2)\right]^{-1/2}$
Tetragonal	$\left[\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}\right]^{-1/2}$
Orthorhombic	$\left[\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}\right]^{-1/2}$
Hexagonal	$\left[\frac{4}{3a^2}(h^2+hk+k^2)+\frac{l^2}{c^2}\right]^{-1/2}$
	$\left[\frac{1}{a^2}\frac{(h^2+k^2+l^2)\sin^2\alpha+2(hk+kl+lh)(\cos^2\alpha-\cos\alpha)}{1-2\cos^3\alpha+3\cos^2\alpha}\right]$
Monoclinic	$\left[\frac{(h^2/a^2)+(l^2/c^2)-(2hl\cos\beta/ac)}{\sin^2\beta}+\frac{k^2}{b^2}\right]^{-1/2}$
Triclinic	$\left[\left(\frac{h^2}{a^2}\sin^2\alpha+\frac{k^2}{b^2}\sin^2\beta+\frac{l^2}{c^2}\sin^2\gamma+\frac{2hk}{ab}(\cos\alpha\cos\beta-\cos\gamma)\right.\right.$ $\left.\left.+\frac{2kl}{bc}(\cos\beta\cos\gamma-\cos\alpha)+\frac{2lh}{ca}(\cos\gamma\cos\alpha-\cos\beta)\right)\Big/$ $(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma)\right]^{-1/2}$

Interplanar spacing

or with another formalism:

$Q = (1/d_{hkl})^2 = h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2kl\ b^*c^*\cos\alpha^* + 2hl\ a^*c^*\cos\beta^* + 2hk a^*b^*\cos\gamma^*$

where:

$$a^* = \frac{b \times c}{V}; \quad \cos\alpha^* = \frac{\cos\beta \,.\, \cos\gamma - \cos\alpha}{\sin\beta \,.\, \sin\gamma}$$

$$b^* = \frac{c \times a}{V}; \quad \cos\beta^* = \frac{\cos\alpha \,.\, \cos\gamma - \cos\beta}{\sin\alpha \,.\, \sin\gamma}$$

$$c^* = \frac{a \times b}{V}; \quad \cos\gamma^* = \frac{\cos\alpha \,.\, \cos\beta - \cos\gamma}{\sin\alpha \,.\, \sin\beta}$$

REDUCED FORMULAS

Cubic:

$1/d^2 = (h^2 + k^2 + l^2)/a^2$

Tetragonal:

$1/d^2 = \{(h^2 + k^2)/a^2\} + (l^2/c^2)$

Orthorhombic:

$1/d^2 = (h^2/a^2) + (k^2/b^2) + (l^2/c^2)$

Hexagonal:

$1/d^2 = (4/3)\{(h^2 + hk + k^2)/a^2\} + (l^2/c^2)$

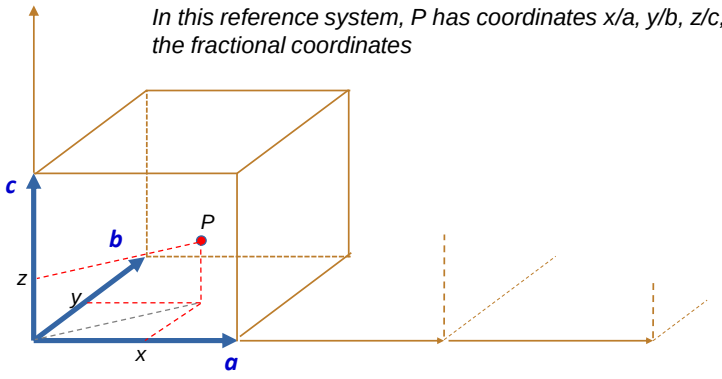
Monoclinic:

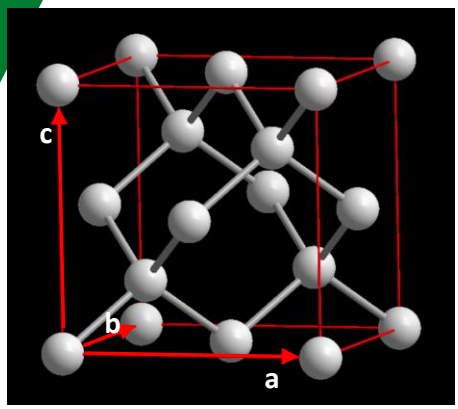
$1/d^2 = (1/\sin^2\beta)\{(h^2/a^2) + (k^2\sin^2\beta/b^2) + (l^2/c^2) - (2hl\cos\beta/ac)\}$

The crystallographic, or fractional, coordinates

a, b, and c vectors defining the unit cell, identify the unit vectors of a reference system, not necessarily orthogonal, which is used to indicate the position of a point in the cell

In this reference system, P has coordinates x/a, y/b, z/c, the fractional coordinates





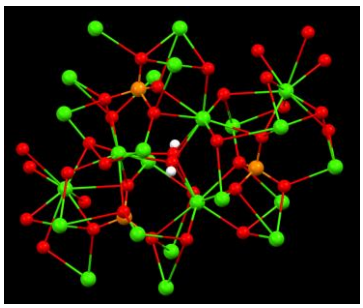
Unit cell of diamond and fractional coordinates of the atoms contained in it, compared with their cartesian coordinates.

Diamond, face centered cubic structure
a = b = c = 3.559 Å

No	name	crystal coordinates x	y	z	cartesian coordinates x	y	z
1*	C	0.0000	0.0000	0.0000	-1.7798	-1.7798	-1.7797
2	C	0.0000	0.5000	0.5000	-1.7797	0.0000	0.0000
3	C	0.5000	0.5000	0.0000	0.0000	0.0000	-1.7797
4	C	0.5000	0.0000	0.5000	0.0000	-1.7797	0.0000
5	C	0.7500	0.2500	0.7500	0.8899	-0.8899	0.8899
6	C	0.2500	0.2500	0.2500	-0.8899	-0.8899	-0.8899
7	C	0.2500	0.7500	0.7500	-0.8899	0.8899	0.8899
8	C	0.7500	0.7500	0.2500	0.8899	0.8899	-0.8899

Site Occupancy Factor

Sometimes a crystallographic position within a unit cell is not fully occupied by an atom, i.e. that atom is not present in that position in all unit cells of the crystal.
Its site occupancy factor (*s.o.f.*) will be less than 1.
This can happen for various reasons:
- **static or dynamic disorder:** some atoms are displaced in several positions. On average, each of these positions is occupied by a fraction of the atom
Ex. Hydroxylapatite → model structure → CIF file



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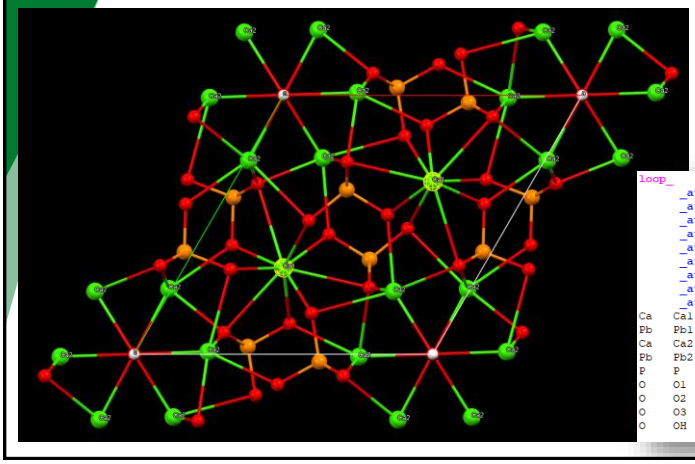
# ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS

loop_
   _atom_site_type_symbol
   _atom_site_label
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_occupancy
   _atom_site_thermal_displace_type
   _atom_site_U_iso_or_equiv
   _atom_site_symmetry_multiplicity
Ca   Ca1   0.66667     0.33333     -0.00166(23)   1.0   Uiso   0.00780(32)   4
Ca   Ca2   0.24735(15)  0.99255(18)  0.25          1.0   Uiso   0.00581(21)   6
P    P     0.39864(17)  0.36992(15)  0.25          1.0   Uiso   0.00385(22)   6
O    O1    0.32595(33)  0.48671(34)  0.25          1.0   Uiso   0.00385(22)   6
O    O2    0.5809(4)    0.4537(4)    0.25          1.0   Uiso   0.00385(22)   6
O    O3    0.34046(25)  0.25886(30)  0.06906(25)   1.0   Uiso   0.00385(22)   12
O    OH    0.0          0.0          0.1895(8)     0.5   Uiso   0.00385(22)   4
H    H     0.0          0.0          0.0658(9)     0.5   Uiso   0.01185(22)   4
```

Site Occupancy Factor

- substitutional disorder: elements with similar binding properties can occupy equivalent sites. Isomorphic substitution - solutions
Ex. Pb-Hydroxylapatite, Zn-Cd-S-Se systems, Mg-Calcite, Clays



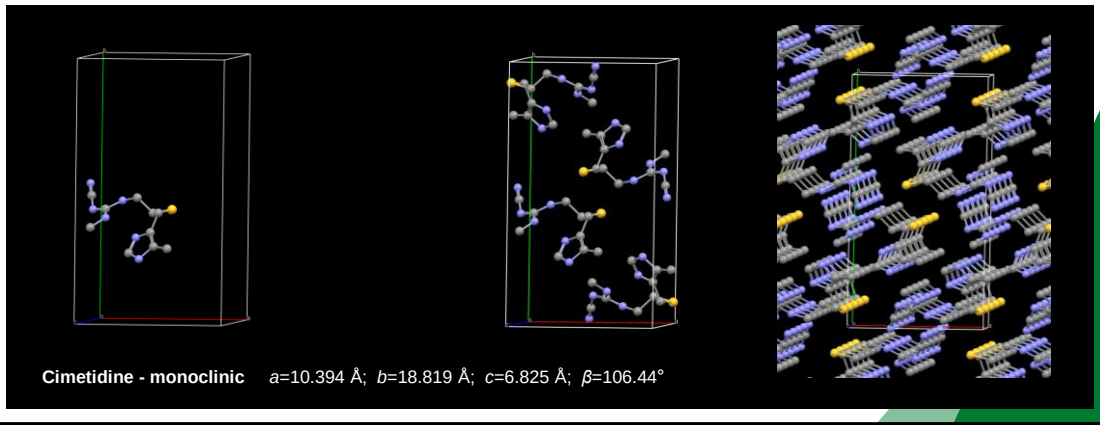
estimated standard deviation

S.O.F.(Ca1) + SO.F.(Pb1) = 1
S.O.F.(Ca2) + SO.F.(Pb2) = 1

```
loop_
   _atom_site_type_symbol
   _atom_site_label
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_occupancy
   _atom_site_thermal_displace_type
   _atom_site_U_iso_or_equiv
   _atom_site_symmetry_multiplicity
Ca   Ca1   0.66667      0.33333      0.0064(11)   0.8572(26)  Uiso  0.0111(12)  4
Pb   Pb1   0.66667      0.33333      0.0064(11)   0.1428(26)  Uiso  0.0111(12)  4
Ca   Ca2   0.24083(15)  0.99317(26)  0.25         0.209(5)    Uiso  0.01762(28) 6
Pb   Pb2   0.24083(15)  0.99317(26)  0.25         0.791(5)    Uiso  0.01762(28) 6
P    P     0.4076(8)    0.3878(6)    0.25         1.0         Uiso  0.0080(16)  6
O    O1    0.3736(16)   0.5295(11)   0.25         1.0         Uiso  0.0383(24)  6
O    O2    0.5921(11)   0.4622(15)   0.25         1.0         Uiso  0.0383(24)  6
O    O3    0.3576(7)    0.2580(8)    0.0923(10)   1.0         Uiso  0.0383(24)  12
O    OH    0.0          0.0          0.1041(26)   0.5         Uiso  0.0383(24)  4
```

The content of a crystal

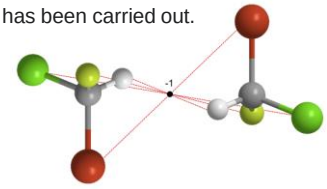
Asymmetric Unit → (symmetry operations of the space group) **Unit Cell Content** → (simple translation along *a*, *b*, and *c*) **Crystal**

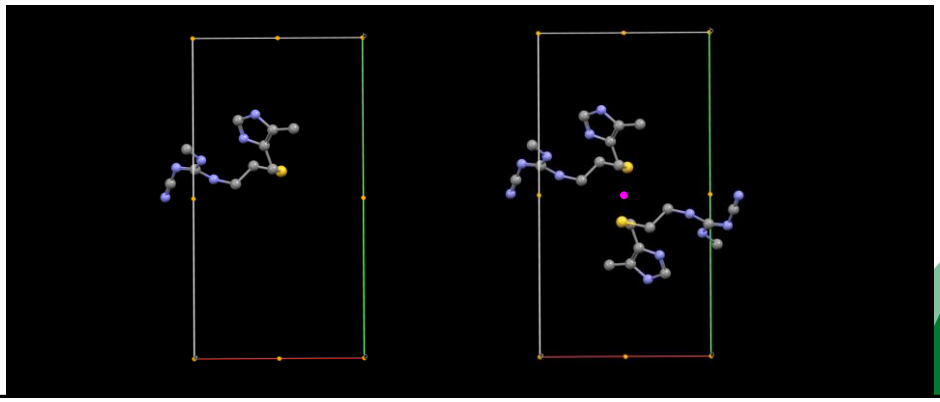


Symmetry elements

Symmetry operation
a transformation that leaves an object looking the same after it has been carried out.

Inversion i -1 P(x,y,z) → P'(-x,-y,-z)





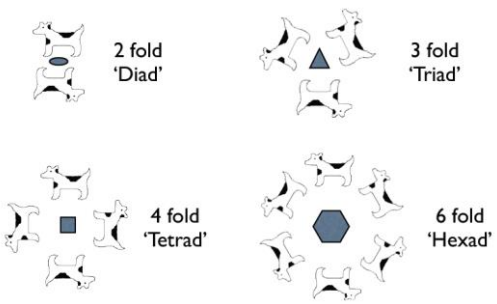
SYMMETRY ELEMENTS

Rotation Axes | Mirror Planes

X = rotation order,
in which the rotation angle is 360/X °

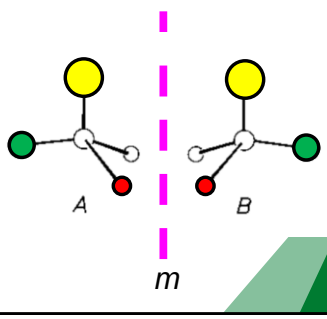
Es. X = 2 P(x, y, z) → P'(-x, y, -z)

In crystals the rotation order can be only 1, 2, 3, 4, or 6



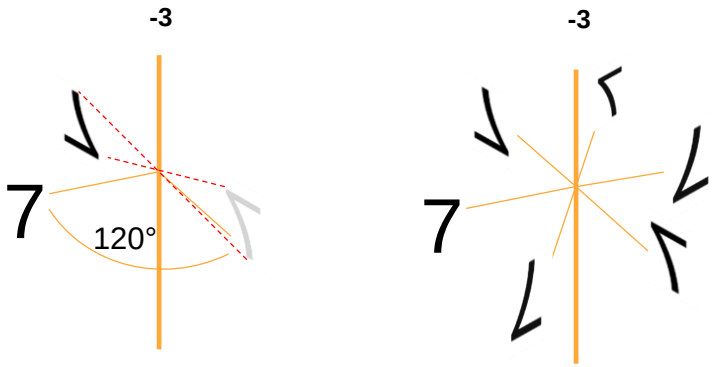
m

Es. m P(x, y, z) → P'(x, -y, z)



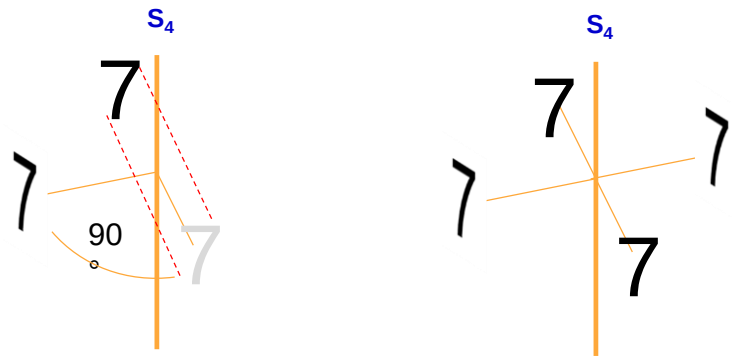
Combined Symmetry Operations

Rotoinversion axes -X



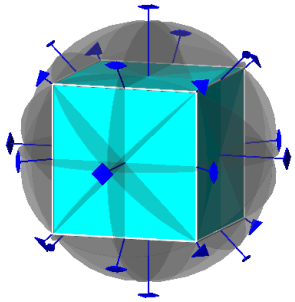
Combined Symmetry Operations

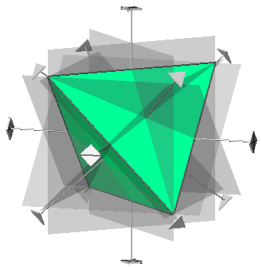
Rotoreflection axes S_X



Combining symmetry operations

In real crystals these symmetry operations can only be combined in 32 possible ways, defining 32 crystallographic point groups

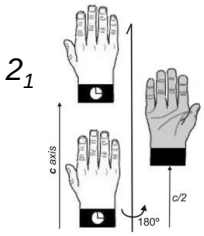




Of the 32 crystal classes, only 11 contain the operator *center of symmetry*, and these 11 centro-symmetric crystal classes are known as **Laue groups.**

Symmetry Elements and Translation

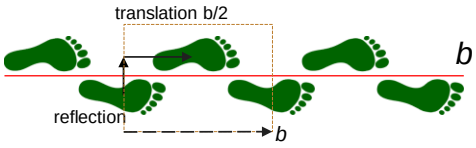
Screw Axes



The combination of a rotation by 360°/n about an axis and a translation along the axis by a multiple of the distance of the translational symmetry, divided by n

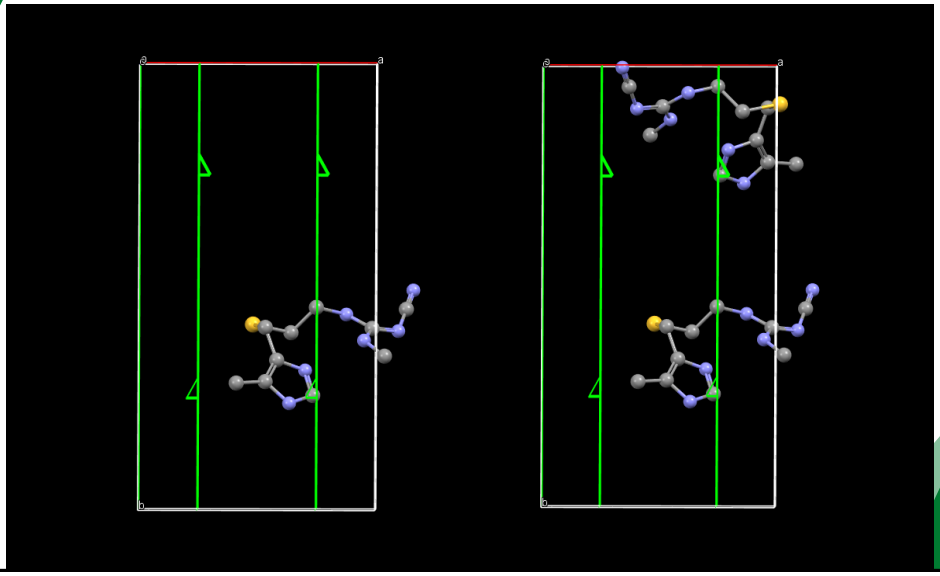
2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, 6_3, 6_4, 6_5

Glide planes

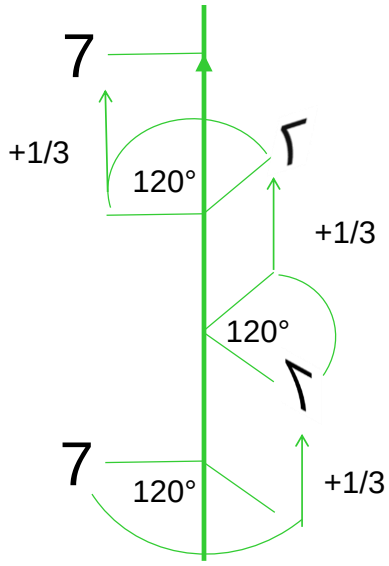


The combination of a reflection in a plane followed by a parallel with that plane

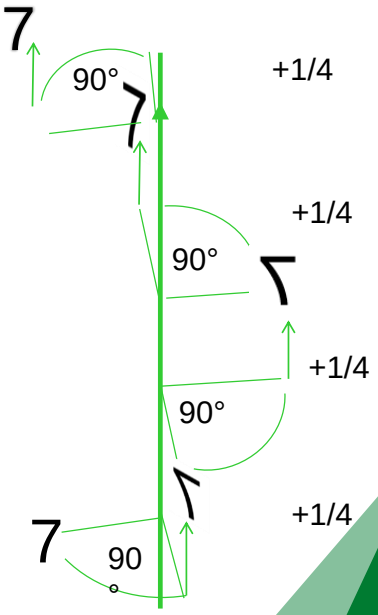
Symmetry Elements and Translation
Screw Axis 2_1



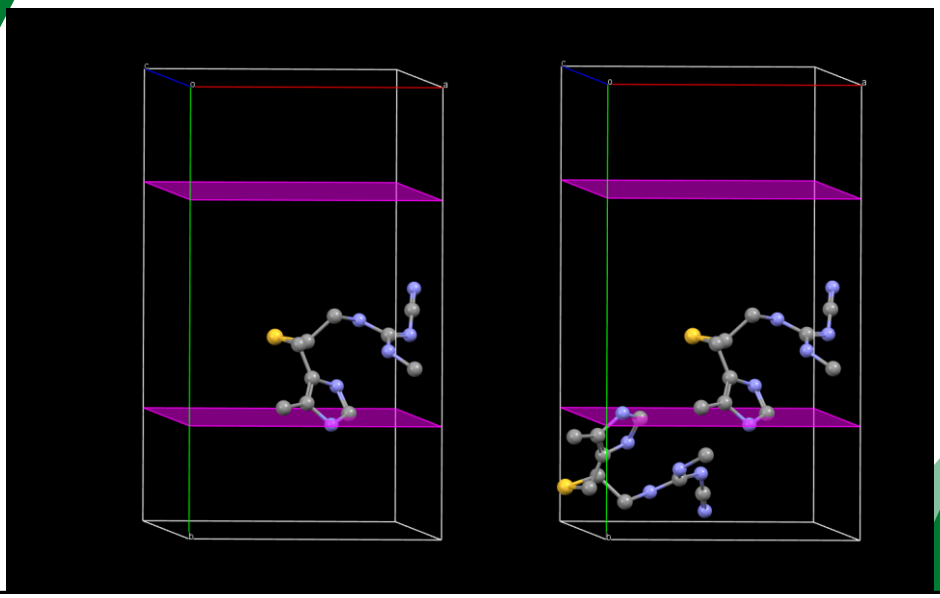
Screw Axis 3_1



Screw Axis 4_1



Glide Plane **a**



Combination of Symmetry Elements with Translation

Finally, combining the ***32 crystal classes*** (crystallographic point groups) with the ***14 Bravais lattices***, we find up to 230 different ways to replicate a finite object (motif) in 3-dimensional space. These ***230 ways to repeat patterns in space***, which are compatible with the 32 crystal classes and with the 14 Bravais lattices, ***are called space groups***, and represent the 230 different ways to fit the Bravais lattices to the symmetry of the objects.

https://crystalsymmetry.wordpress.com/2014/08/15/the-space-group-list-project-as-a-poster/

Site Symmetry and Special Positions

The action of symmetry elements of a space group on each point of the unit cell will reproduce it n times. This n value is called "site multiplicity"

The points placed over one or more point symmetry elements will be unaffected by those operations. Therefore a special position has a reduced site multiplicity
→ Escher web sketch

A space group can include different special positons, called Wyckoff positions

Unit cell content $= \sum_i (s.o.f.)_i \times (site\ mult.)_i$

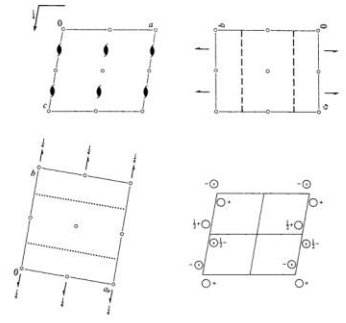
The characters of the 230 space groups are resumed in the International Tables for Crystallography (IUCr)

One example

$P2_1/c$ C_{2h}^5 2/m Monoclinic

No. 14 $P12_1/c1$ Patterson symmetry $P12/m1$

UNIQUE AXIS b, CELL CHOICE 1



Origin at $\bar{1}$

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

Symmetry operations

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

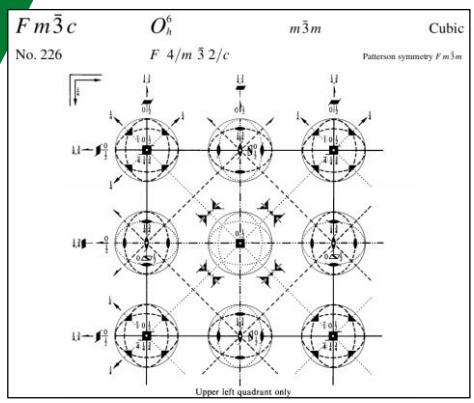
number of atoms (multiciplity) and their positions generated by the space group symmetry when an atom occupies a general position...

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\frac{z}{2}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	$h0l$: $l=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
							Special: as above, plus
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			hkl : $k+l=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$			hkl : $k+l=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$

...and a special position (that is it is placed over a point symmetry element)

general position: multiplicity = 192



special positions
reduced multiplicity

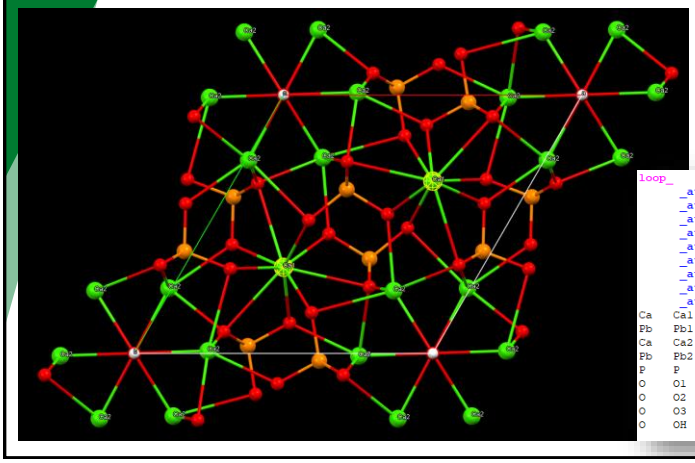
Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates			
	$(0,0,0)+$	$(0,\frac{1}{2},\frac{1}{2})+$	$(\frac{1}{2},0,\frac{1}{2})+$	$(\frac{1}{2},\frac{1}{2},0)+$
192 i 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) $y+\frac{1}{2},x+\frac{1}{2},\bar{z}+\frac{1}{2}$	(14) $\bar{y}+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2}$	(15) $y+\frac{1}{2},\bar{x}+\frac{1}{2},z+\frac{1}{2}$	(16) $\bar{y}+\frac{1}{2},x+\frac{1}{2},z+\frac{1}{2}$
	(17) $x+\frac{1}{2},z+\frac{1}{2},\bar{y}+\frac{1}{2}$	(18) $\bar{x}+\frac{1}{2},z+\frac{1}{2},y+\frac{1}{2}$	(19) $\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2},\bar{y}+\frac{1}{2}$	(20) $x+\frac{1}{2},\bar{z}+\frac{1}{2},y+\frac{1}{2}$
	(21) $z+\frac{1}{2},y+\frac{1}{2},\bar{x}+\frac{1}{2}$	(22) $z+\frac{1}{2},\bar{y}+\frac{1}{2},x+\frac{1}{2}$	(23) $\bar{z}+\frac{1}{2},y+\frac{1}{2},x+\frac{1}{2}$	(24) $\bar{z}+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{x}+\frac{1}{2}$
	(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) $z,x,\bar{y}$	(32) $z,\bar{x},y$
	(33) $\bar{y},\bar{z},\bar{x}$	(34) $y,\bar{z},x$	(35) $\bar{y},\bar{z},x$	(36) $y,z,\bar{x}$
	(37) $\bar{y}+\frac{1}{2},\bar{x}+\frac{1}{2},z+\frac{1}{2}$	(38) $y+\frac{1}{2},x+\frac{1}{2},z+\frac{1}{2}$	(39) $\bar{y}+\frac{1}{2},x+\frac{1}{2},\bar{z}+\frac{1}{2}$	(40) $y+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2}$
	(41) $\bar{x}+\frac{1}{2},\bar{z}+\frac{1}{2},y+\frac{1}{2}$	(42) $x+\frac{1}{2},\bar{z}+\frac{1}{2},\bar{y}+\frac{1}{2}$	(43) $x+\frac{1}{2},z+\frac{1}{2},y+\frac{1}{2}$	(44) $\bar{x}+\frac{1}{2},z+\frac{1}{2},\bar{y}+\frac{1}{2}$
	(45) $\bar{z}+\frac{1}{2},\bar{y}+\frac{1}{2},x+\frac{1}{2}$	(46) $\bar{z}+\frac{1}{2},y+\frac{1}{2},\bar{x}+\frac{1}{2}$	(47) $z+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{x}+\frac{1}{2}$	(48) $z+\frac{1}{2},y+\frac{1}{2},x+\frac{1}{2}$
96 i m..	$0,y,z$ $z,0,y$ $y,z,0$ $y+\frac{1}{2},\bar{z},\bar{x}+\frac{1}{2}$ $\frac{1}{2},z+\frac{1}{2},\bar{y}+\frac{1}{2}$ $z+\frac{1}{2},y+\frac{1}{2},\frac{1}{2}$	$0,\bar{y},z$ $z,0,\bar{y}$ $\bar{y},z,0$ $\bar{y}+\frac{1}{2},\frac{1}{2},\bar{x}+\frac{1}{2}$ $\frac{1}{2},z+\frac{1}{2},y+\frac{1}{2}$ $z+\frac{1}{2},\bar{y}+\frac{1}{2},\frac{1}{2}$	$0,y,\bar{z}$ $\bar{z},0,y$ $y,\bar{z},0$ $y+\frac{1}{2},\frac{1}{2},z+\frac{1}{2}$ $\frac{1}{2},\bar{z}+\frac{1}{2},\bar{y}+\frac{1}{2}$ $\bar{z}+\frac{1}{2},y+\frac{1}{2},\frac{1}{2}$	$0,\bar{y},\bar{z}$ $\bar{z},0,\bar{y}$ $\bar{y},\bar{z},0$ $\bar{y}+\frac{1}{2},\frac{1}{2},z+\frac{1}{2}$ $\frac{1}{2},\bar{z}+\frac{1}{2},y+\frac{1}{2}$ $\bar{z}+\frac{1}{2},\bar{y}+\frac{1}{2},\frac{1}{2}$	no
96 h ..2	$\frac{1}{2},y,y$ $\bar{y},\frac{1}{2},y$ $\frac{1}{2},\bar{y},\bar{y}$ $y,\frac{1}{2},\bar{y}$	$\frac{1}{2},\bar{y},y$ $y,\frac{1}{2},\bar{y}$ $\frac{1}{2},y,\bar{y}$ $\bar{y},\frac{1}{2},y$	$\frac{1}{2},\bar{y},\bar{y}$ $\bar{y},y,\frac{1}{2}$ $\frac{1}{2},y,y$ $y,\bar{y},\frac{1}{2}$	$y,\frac{1}{2},\bar{y}$ $y,\bar{y},\frac{1}{2}$ $\bar{y},\frac{1}{2},y$ $\bar{y},y,\frac{1}{2}$	hk
64 g .3.	x,x,x $\bar{x},\bar{x},x$ $x+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2}$ $\bar{x}+\frac{1}{2},x+\frac{1}{2},x+\frac{1}{2}$	$\bar{x},\bar{x},\bar{x}$ $x,x,\bar{x}$ $\bar{x}+\frac{1}{2},x+\frac{1}{2},\bar{x}+\frac{1}{2}$ $x+\frac{1}{2},\bar{x}+\frac{1}{2},x+\frac{1}{2}$			hk
48 f 4..	$x,\frac{1}{2},\frac{1}{2}$ $\bar{x},\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$ $x,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},x,\frac{1}{2}$ $\frac{1}{2},\bar{x},\frac{1}{2}$	$\frac{1}{2},\bar{x},\frac{1}{2}$ $\frac{1}{2},x,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},x$ $\frac{1}{2},\frac{1}{2},\bar{x}$	$\frac{1}{2},\frac{1}{2},\bar{x}$ $\frac{1}{2},\frac{1}{2},x$	hk
48 e $mm2$..	$x,0,0$ $0,0,x$ $x+\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$\bar{x},0,0$ $0,0,\bar{x}$ $\bar{x}+\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$0,x,0$ $\frac{1}{2},x+\frac{1}{2},\frac{1}{2}$	$0,\bar{x},0$ $\frac{1}{2},\bar{x}+\frac{1}{2},\frac{1}{2}$			hk
24 d $4/m$..	$0,\frac{1}{2},\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},0$	hk
24 c $\bar{4}m.2$	$\frac{1}{4},0,0$	$\frac{3}{4},0,0$	$0,\frac{1}{4},0$	$0,\frac{3}{4},0$	$0,0,\frac{1}{4}$	$0,0,\frac{3}{4}$	hk
8 b $m\bar{3}$.	$0,0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$					hk
8 a 432	$\frac{1}{4},\frac{1}{4},\frac{1}{4}$	$\frac{3}{4},\frac{3}{4},\frac{3}{4}$					hk

693

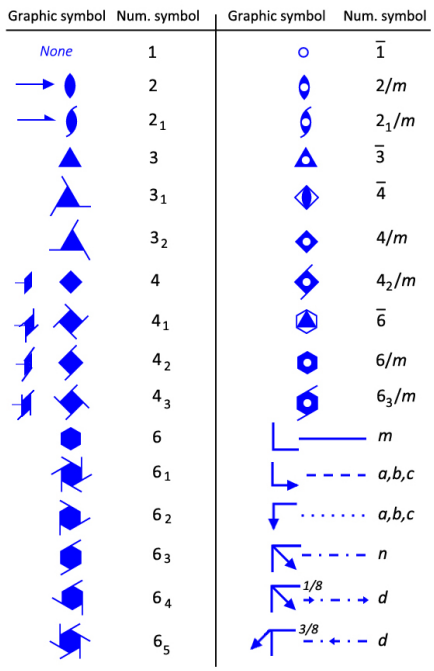
Unit cell content

Pb-Hydroxylapatite



Unit cell content $= \sum_i (s.o.f.) \times (site\ mult.)$

```
loop_
   _atom_site_type_symbol
   _atom_site_label
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_occupancy
   _atom_site_thermal_displace_type
   _atom_site_U_iso_or_equiv
   _atom_site_symmetry_multiplicity
Ca   Ca1    0.66667     0.33333     0.0064(11)   0.8572(26)  Uiso  0.0111(12)   4
Pb   Pb1    0.66667     0.33333     0.0064(11)   0.1428(26)  Uiso  0.0111(12)   4
Ca   Ca2    0.24083(15) 0.99317(26) 0.25         0.209(5)    Uiso  0.01762(28)  6
Pb   Pb2    0.24083(15) 0.99317(26) 0.25         0.791(5)    Uiso  0.01762(28)  6
P    P      0.4076(8)   0.3878(6)   0.25         1.0         Uiso  0.0080(16)   6
O    O1     0.3736(16)  0.5295(11)  0.25         1.0         Uiso  0.0383(24)   6
O    O2     0.5921(11)  0.4622(15)  0.25         1.0         Uiso  0.0383(24)   6
O    O3     0.3576(7)   0.2580(8)   0.0923(10)   1.0         Uiso  0.0383(24)   12
O    OH     0.0         0.0         0.1041(26)   0.5         Uiso  0.0383(24)   4
```



The CIF file (Crystallographic Information File)

Hall, Allen & Brown (1991)

CIF Format

The CIF contains the crystallographic information for a structure in a well-defined and standardised format.
The information for one structure/experiment is called a *data block*.
A CIF can contain multiple data blocks. A data block begins with the string ' `data_` ' to signify the start of the structural information
For example:

```
data_ZP3
```

Within a data block, each piece of information is stored in a *CIF field*. A CIF field is made up of a *data name*, which describes a piece of information about the structure, and a *data item*, the information related to the data name.
For example:

```
_cell_volume 1513.980(15)
_symmetry_space_group_name_H-M  "R -3 c"
```

The CIF file (Crystallographic Information File)

Hall, Allen & Brown (1991)

CIF Format

Data items can also be stored as part of a loop. This is usually used to store a table of values, such as atom coordinates. The loop begins with ' `loop_` ', which is then followed on subsequent lines by the data names in the table. After that, the value data is stored: each line will contain a data item for each of the data names listed.

```
loop_
      _atom_site_type_symbol
      _atom_site_label
      _atom_site_fract_x
      _atom_site_fract_y
      _atom_site_fract_z
      _atom_site_occupancy
      _atom_site_thermal_displace_type
      _atom_site_U_iso_or_equiv
      _atom_site_symmetry_multiplicity
Zr   Zr1     0.0           0.0          0.0           1.0   Uiso  0.01390(24)   6
P    P2      0.66875(30)   0.0          0.25          1.0   Uiso  0.0355(6)     18
O    O3      0.5108(6)    -0.1098(5)    0.21303(14)   1.0   Uiso  0.0261(10)    36
O    O4      0.7183(6)    -0.1255(5)    0.28148(7)    1.0   Uiso  0.0718(15)    36
```

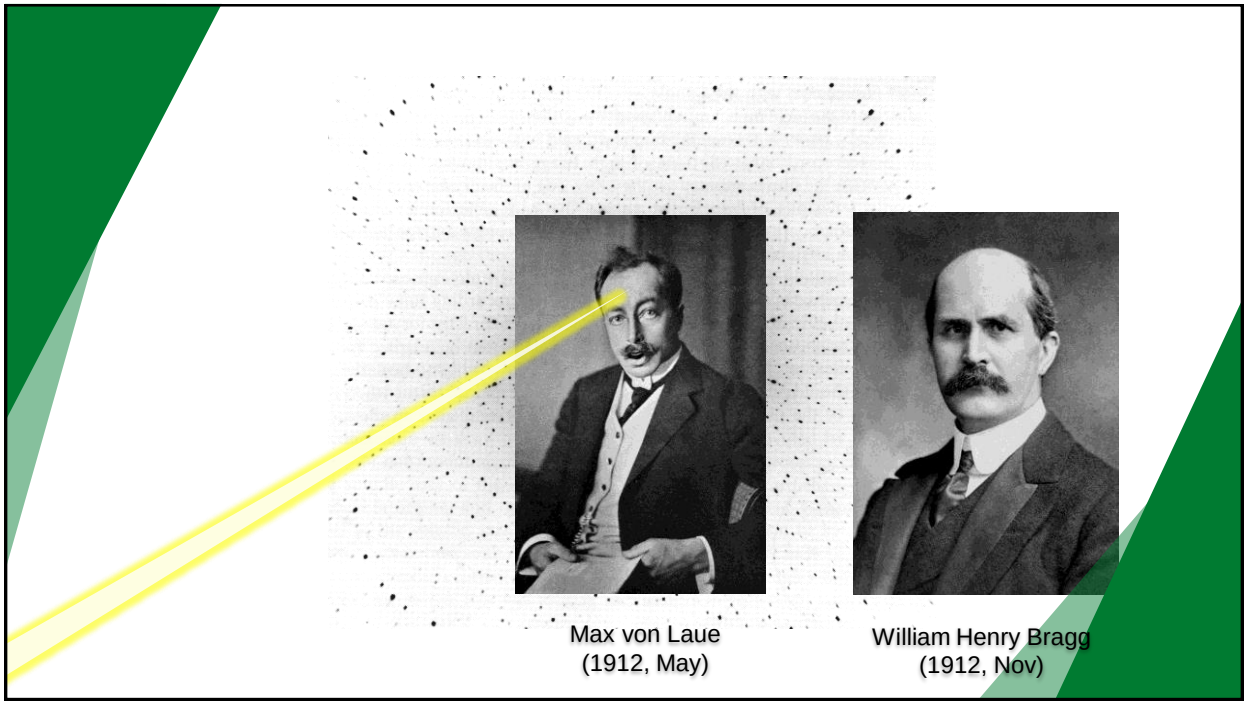
A CIF file can be read by almost any crystallographic program

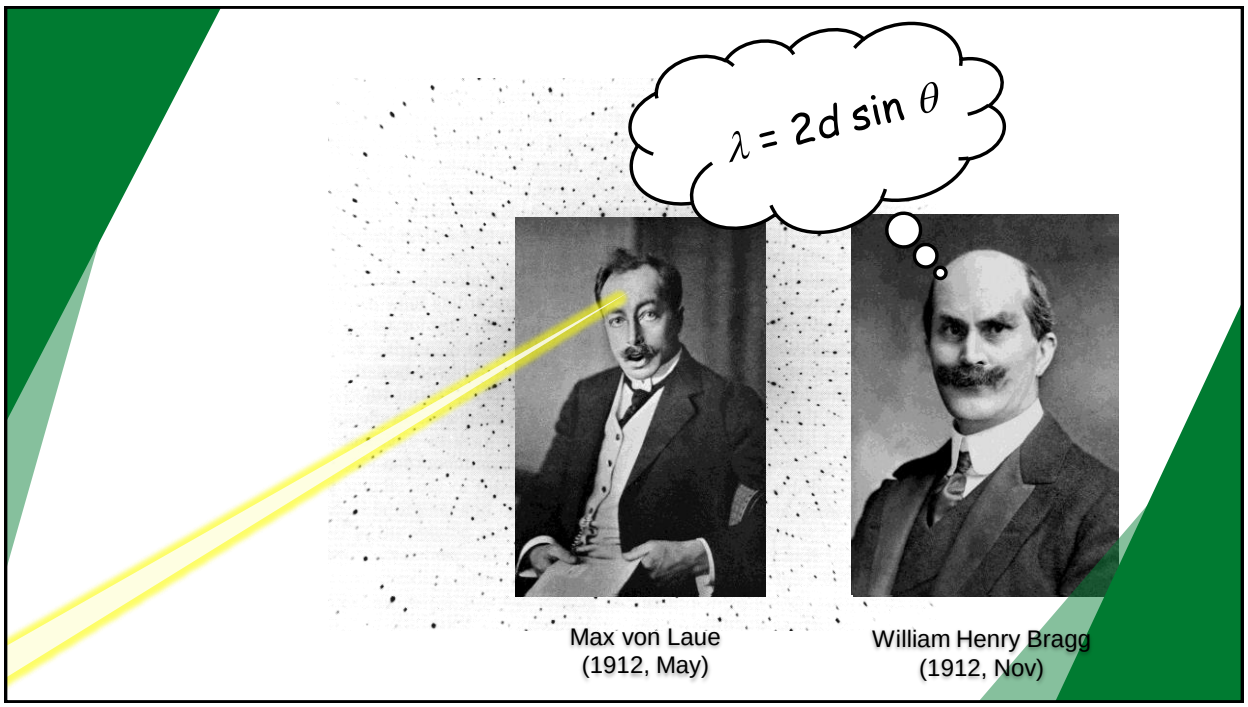
enCIFer : https://www.ccdc.cam.ac.uk/Community/csd-community/encifer/
Mercury: https://www.ccdc.cam.ac.uk/support-and-resources/Downloads/
Vesta: https://jp-minerals.org/vesta/en/

X-RAY DIFFRACTION

Max von Laue
(1912, May)

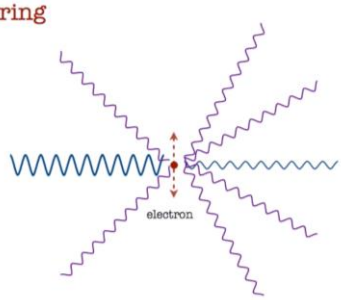
Max von Laue
(1912, May)


Max von Laue
(1912, May)
William Henry Bragg
(1912, Nov)

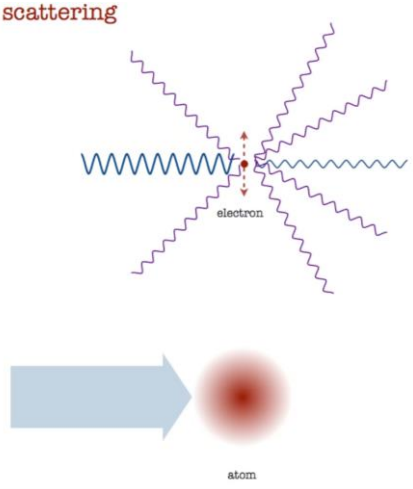

$\lambda = 2d \sin \theta$
Max von Laue
(1912, May)
William Henry Bragg
(1912, Nov)

X-ray scattering

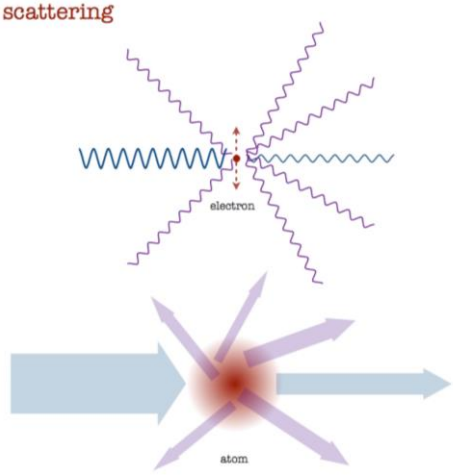
X-ray scattering



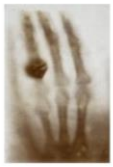
X-ray scattering

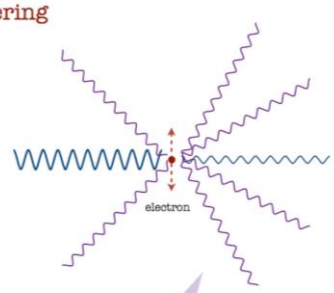


X-ray scattering



X-ray scattering





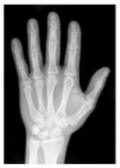
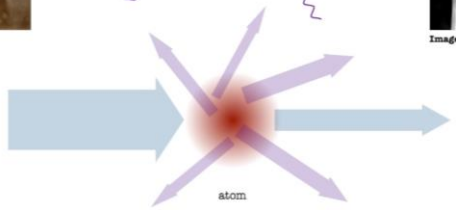
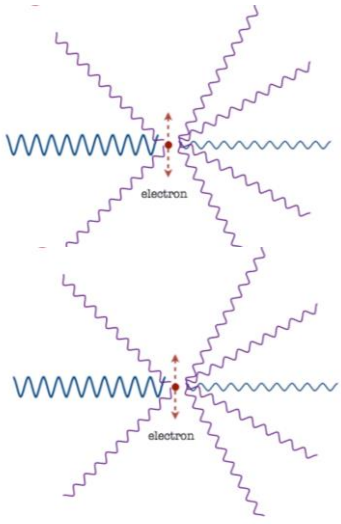
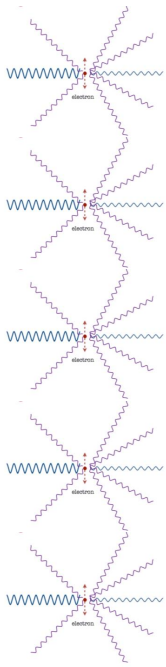


Image: Trace Meek/flickr



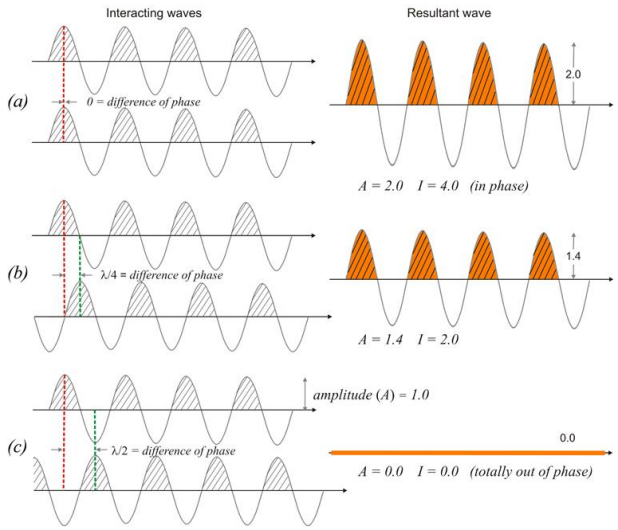


X-ray

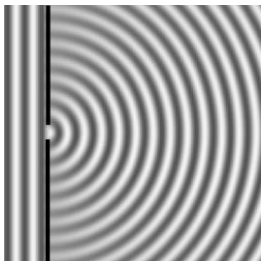


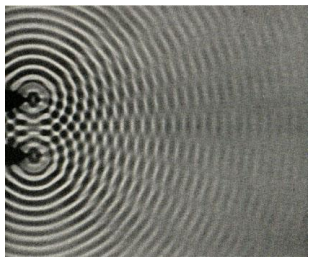
DIFFRACTION

Superimposition of waves - Interference

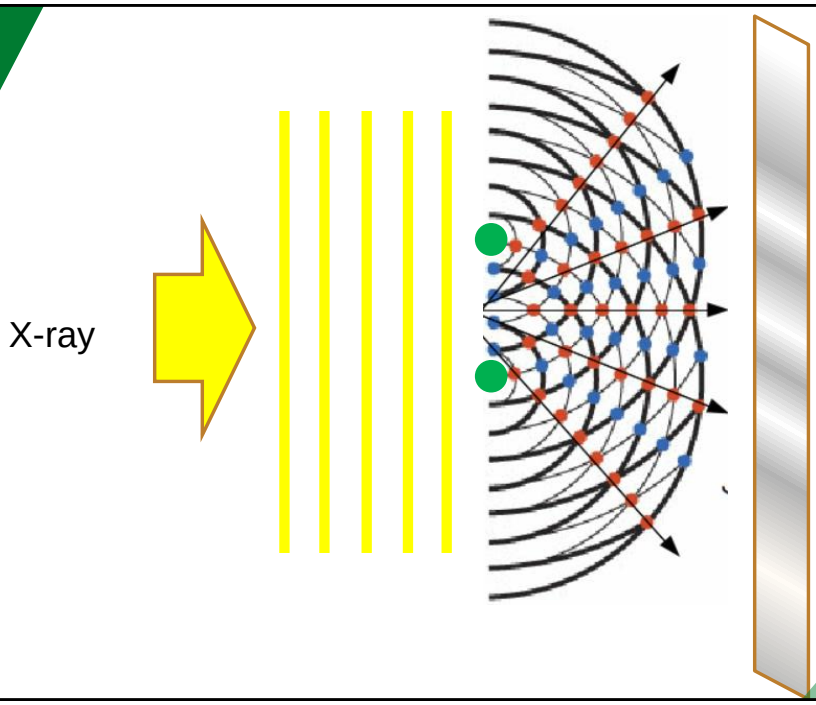


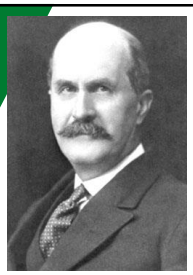
Superimposition of waves - Interference





https://javalab.org/en/superposition_en/

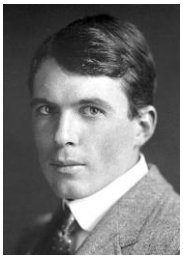




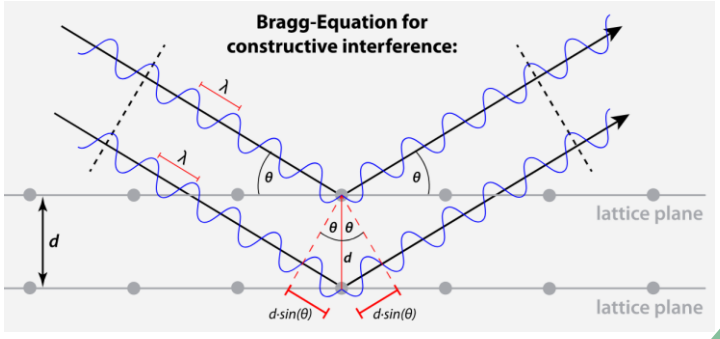
William Henry Bragg
(1862-1942)

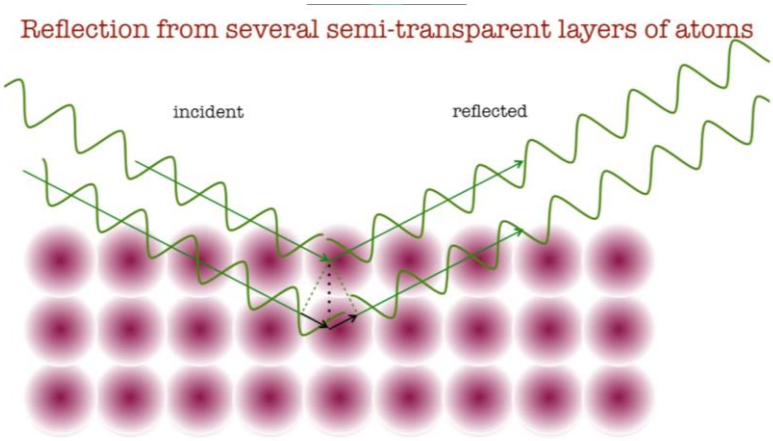
The Bragg Equation

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

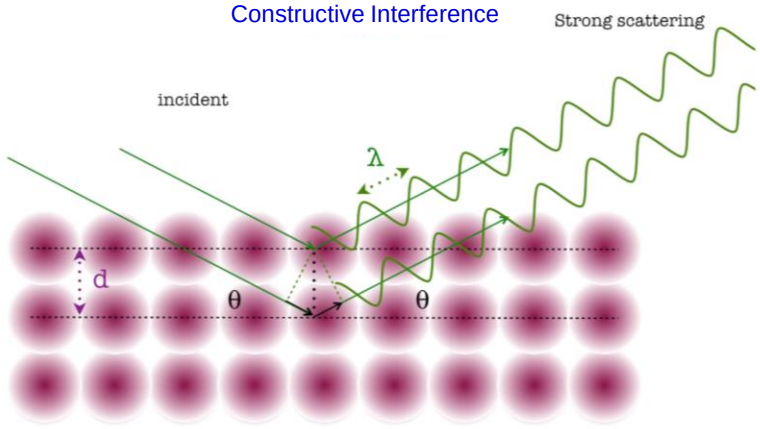


William Lawrence Bragg
(1890-1971)





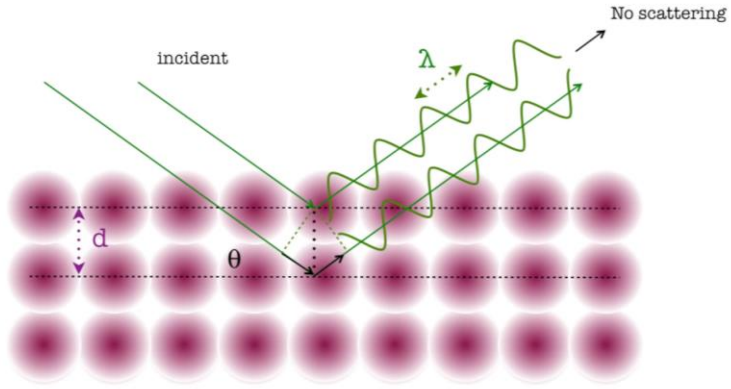
Constructive Interference



Path difference = $2d\sin\theta$

Strong diffraction if $2d\sin\theta = n\lambda$

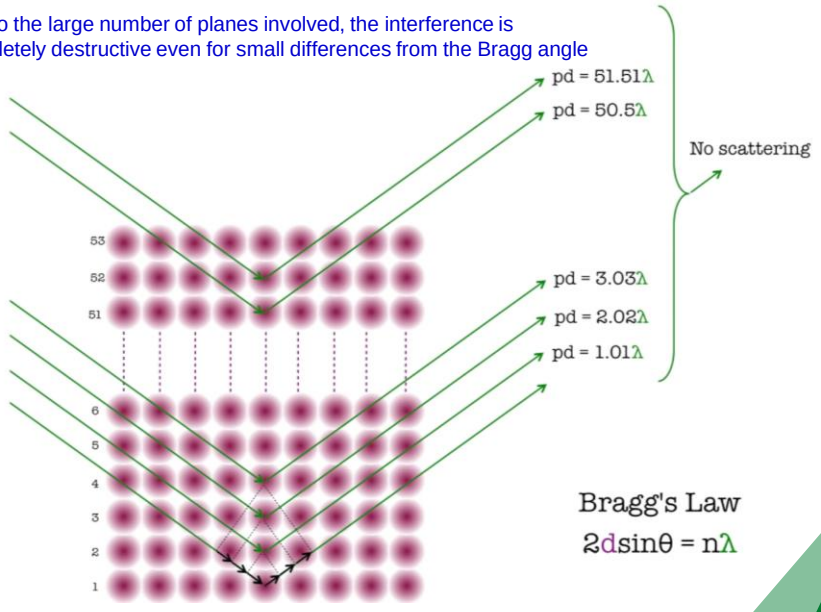
Destructive Interference



Path difference = $2d\sin\theta$

In this case, $2d\sin\theta = (2n-1)\lambda/2$

Due to the large number of planes involved, the interference is completely destructive even for small differences from the Bragg angle



Bragg's Law

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

Intensity of a diffraction peak

$$I_{hkl} = \frac{1}{2}\frac{K_e K_{hkl}}{\mu}$$

I_{hkl} is directly proportional to the Structure Factor F_{hkl} (contained in K_{hkl}) and inversely proportional to the linear absorption coefficient μ

- K_e = experimental constant containing I_0, e, m_e, c, λ, and a scale factor S
- $K_{(hkl)}$ = constant specific of the given crystalline phase, contanining:
  - m_{hkl} = multiplicity of the hkl reflection,
  - V = Unit cell volume
  - V_s = Irradiated volume of sample
  - Lp = Lorentz - polarization factor
  - F_{hkl} = Structure Factor
- μ = linear absorption coefficient

F_{hkl} = Structure factor $\quad F_{hkl} = \sum_{j=1}^{N} f_j \, e^{2\pi i(hx_j + ky_j + lz_j)}$

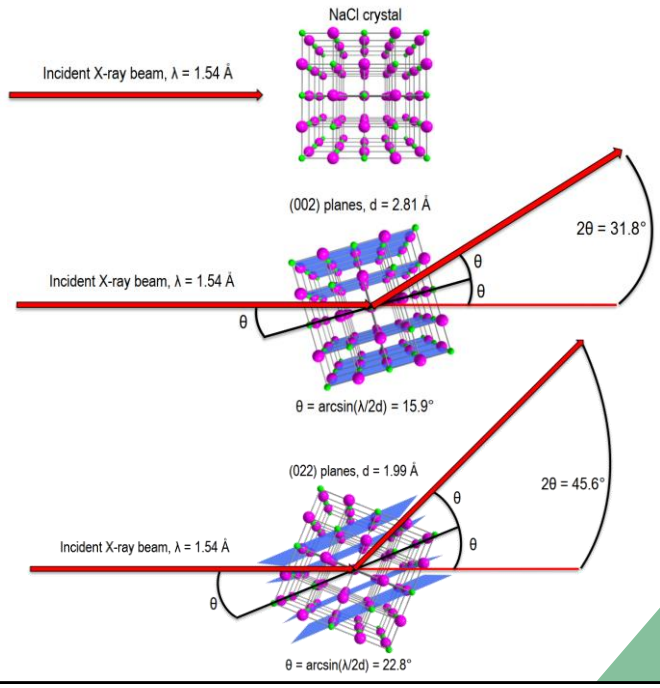
in which

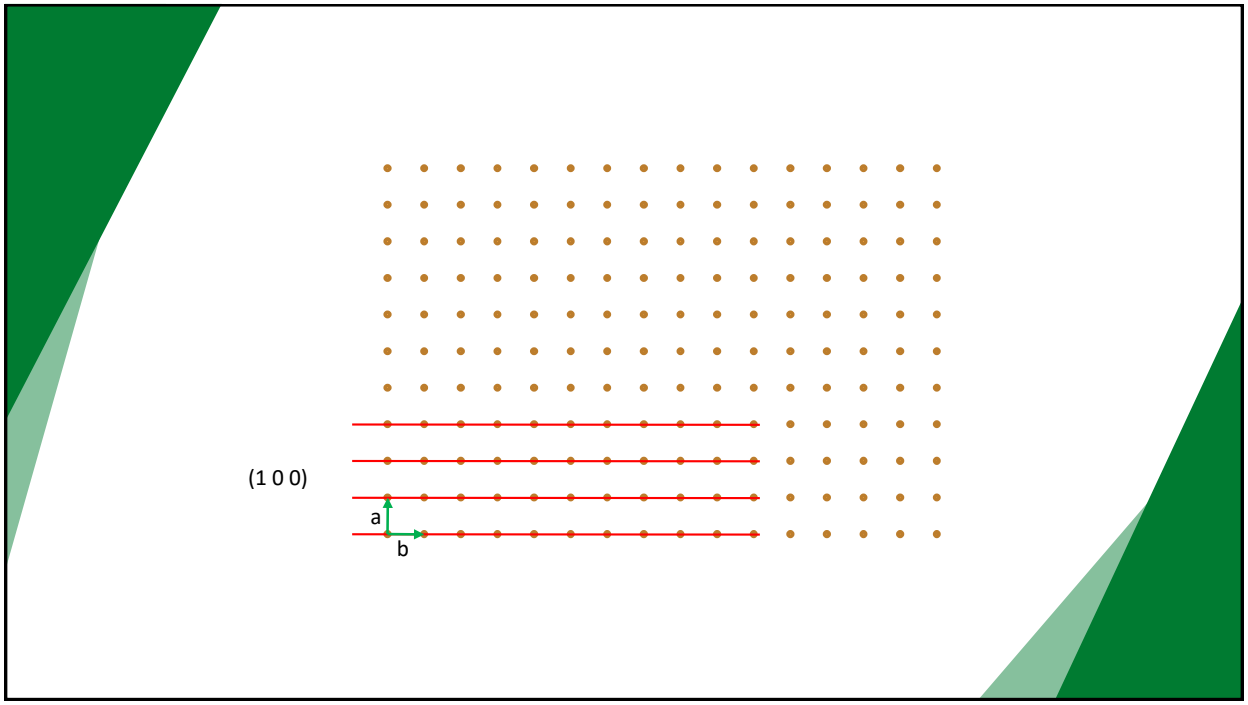
- $x_j\, y_j\, z_j$ = *crystal coordinates of the N atoms in the asymmetric unit*
- f_j = *atomic scattering factors*

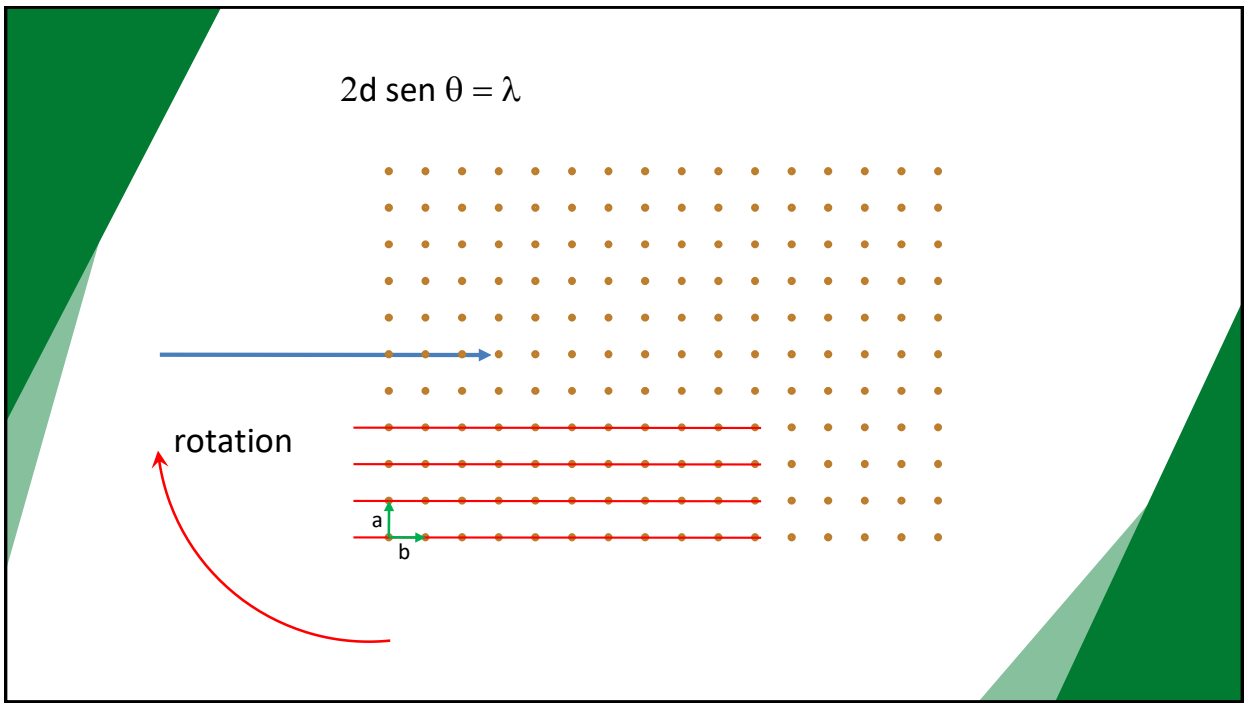
Single Crystal X-ray Diffraction

Large crystals (...not so large!)

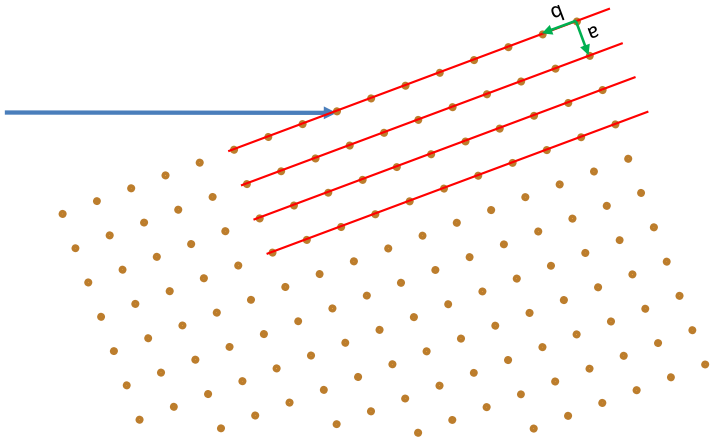
Naica, Mexico



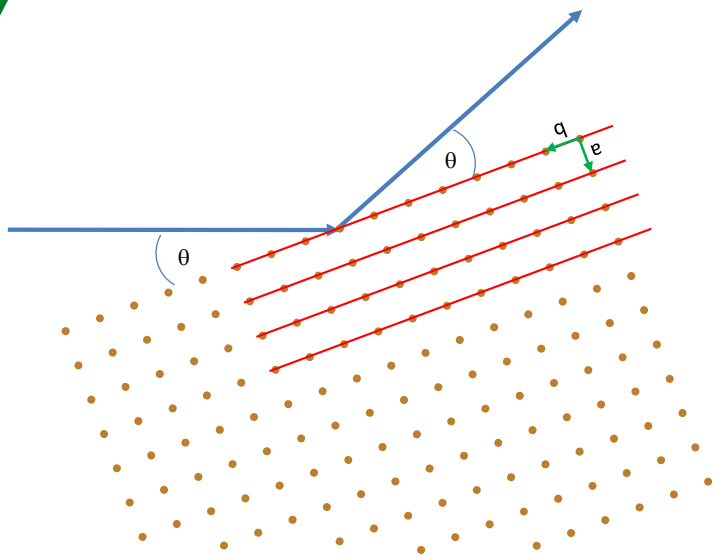

(1 0 0)
a
b

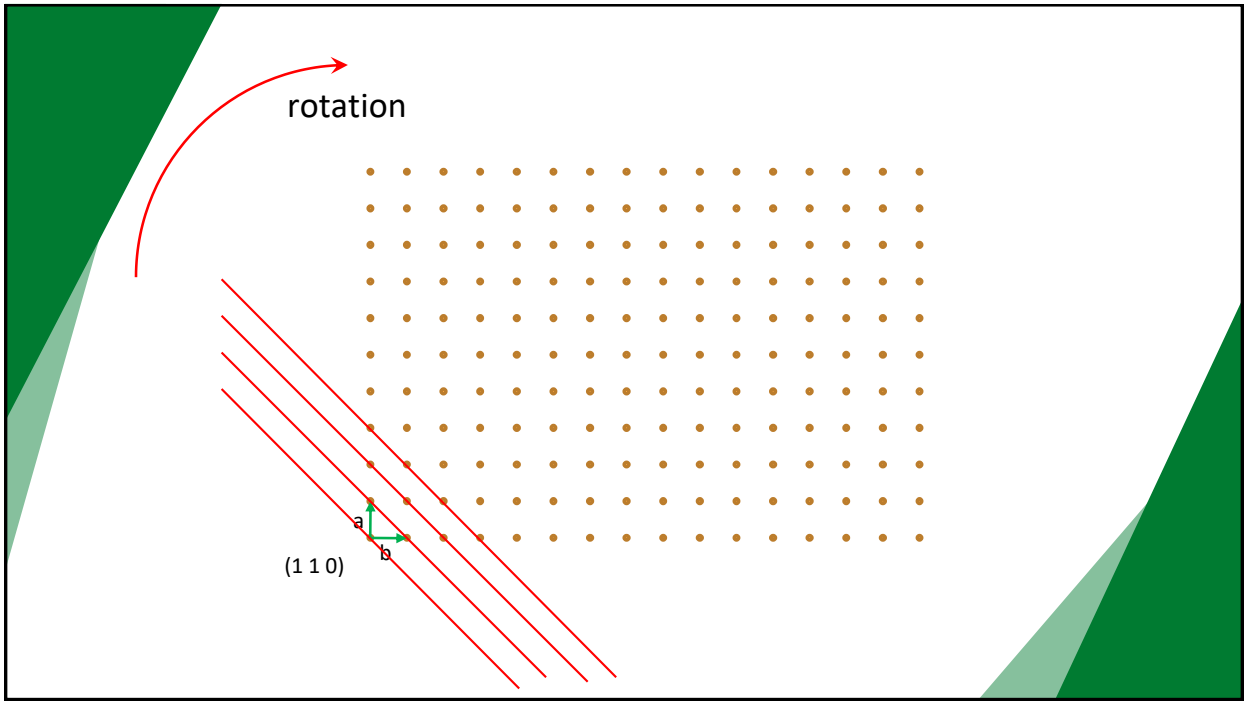

2d sen θ = λ
rotation
a
b

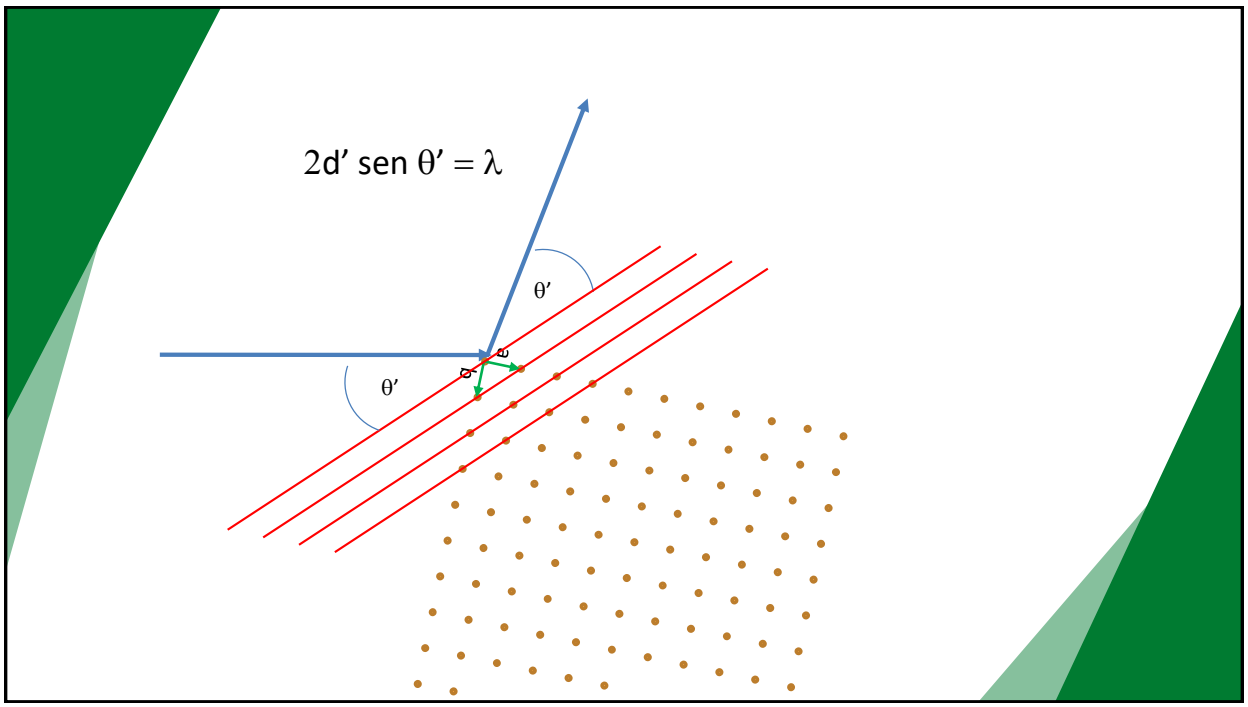
$2d \text{ sen } \theta = \lambda$

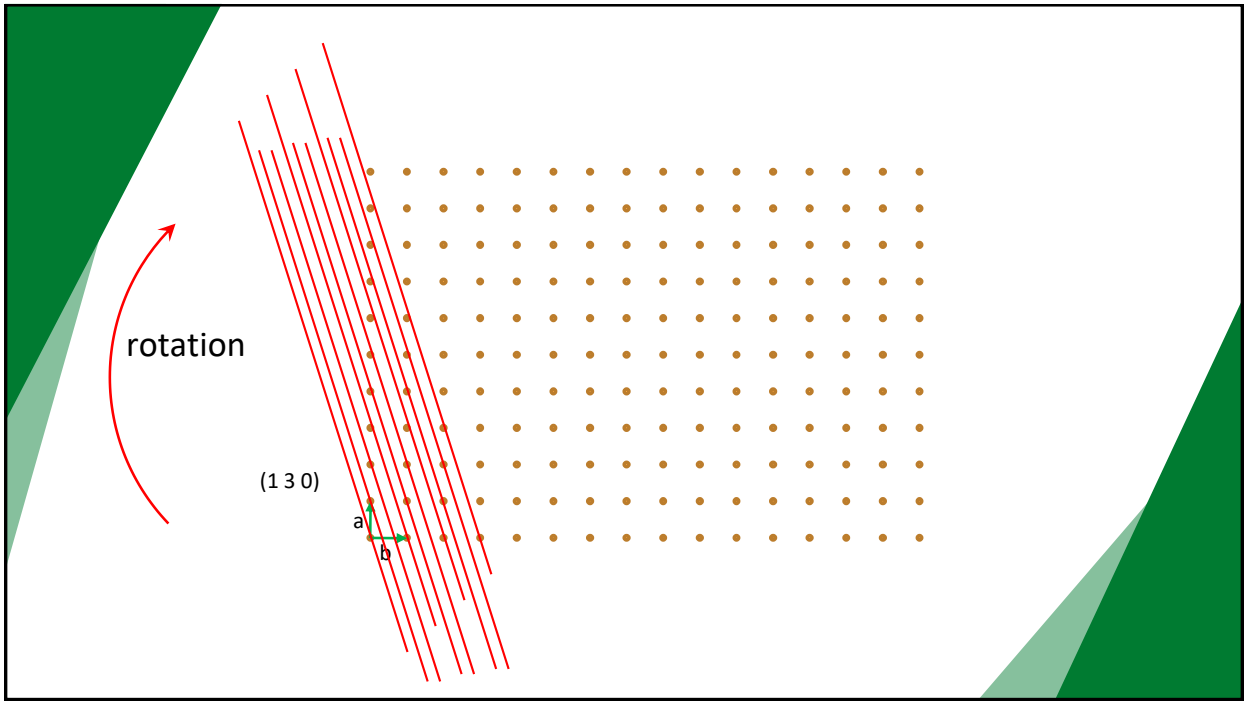


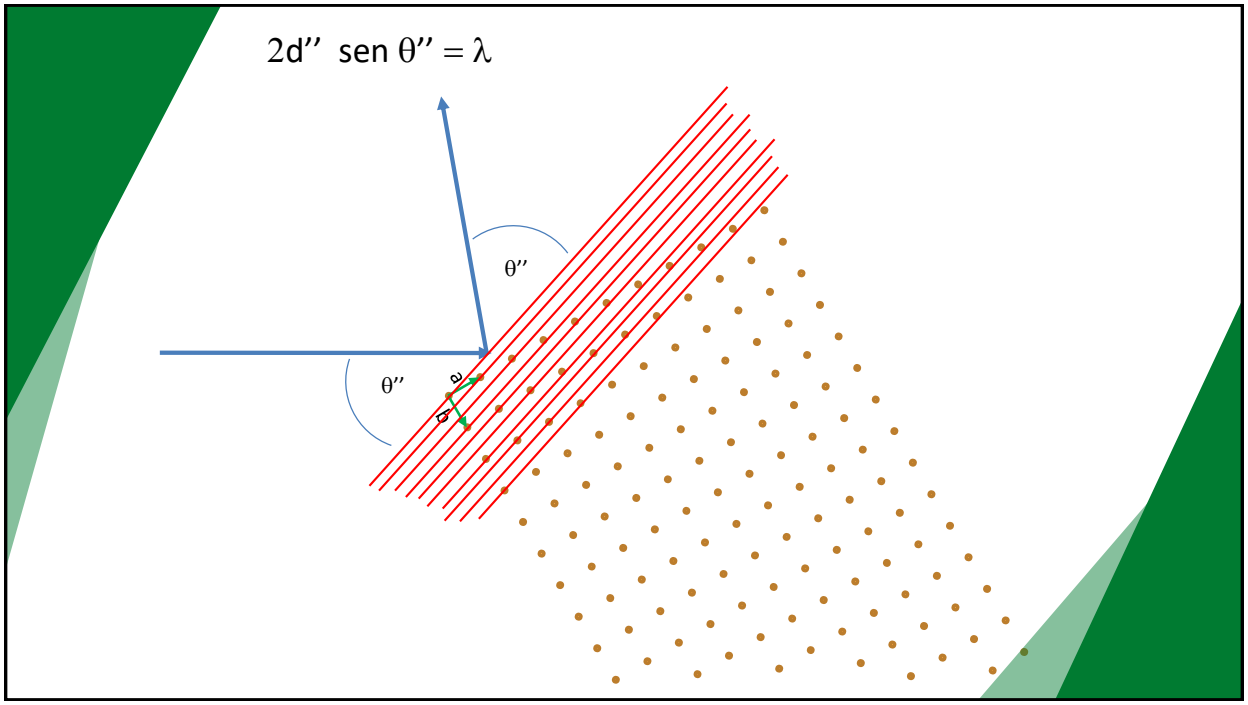
$2d \text{ sen } \theta = \lambda$




rotation
a
b
(1 1 0)

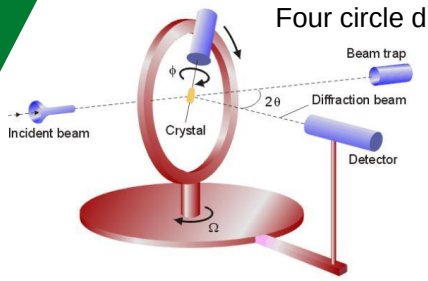

2d' sen θ' = λ
θ'
θ'
d'

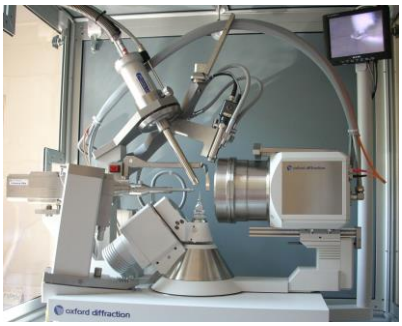

rotation
(1 3 0)
a
b


2d'' sen θ'' = λ
θ''
θ''
a
b

Single Crystal X-ray Diffraction

Four circle diffractometer





The diffraction effects are spread in 3D
Many data (5000 - 10000 reflections)

↓

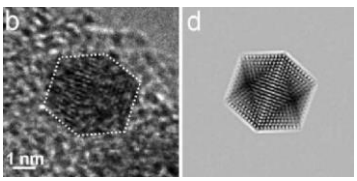
Many calculations

↓

Accurate and complete description of the structure

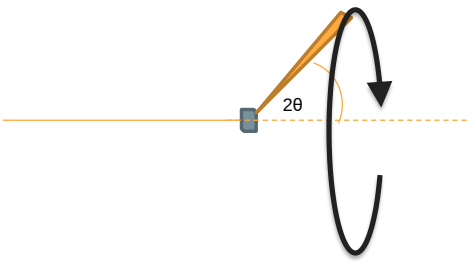
Powder X-ray Diffraction

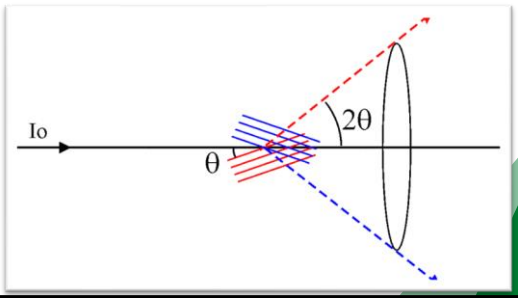
Small crystals (...not so small!)



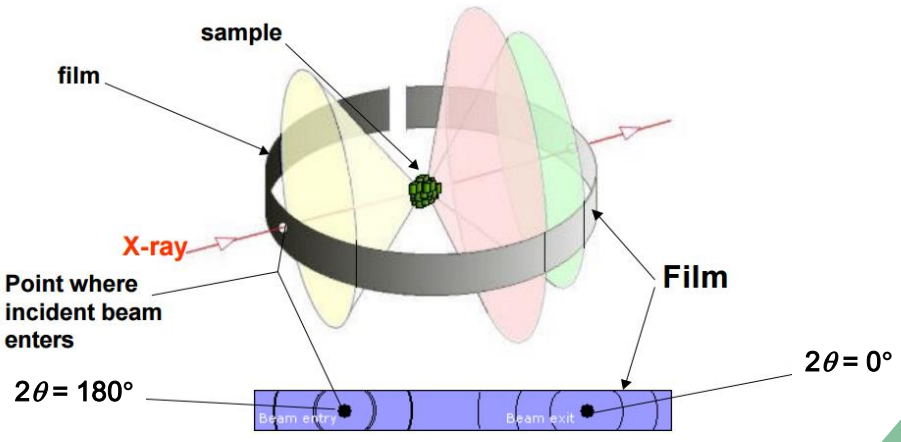
N. Dahal et al. *Chem. Mater.* 2008, 20, 6389

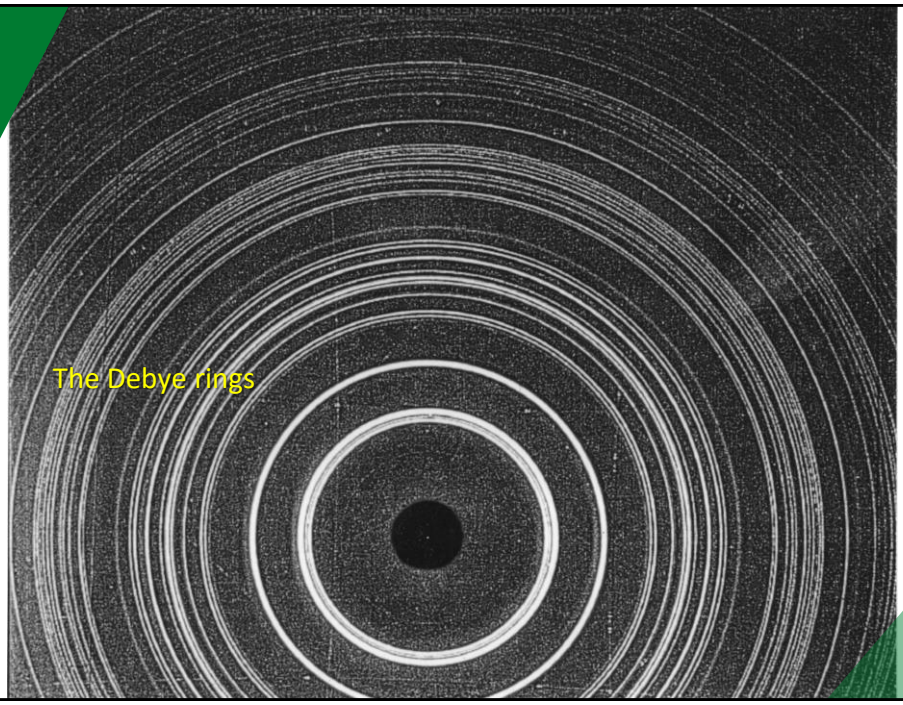
In a microcrystalline , a large number of crystallites are randomly oriented.
When a family of hkl planes are in diffraction condition at a given theta angle, all crystallites produce diffracted beams with rotational symmetry with respect to the incident beam. Each single diffracted reflection degenerates into a diffraction cone.
3 D → 1 D



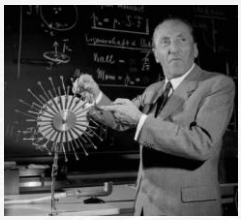


Powder X-ray Diffraction - diffraction cones and Debye rings





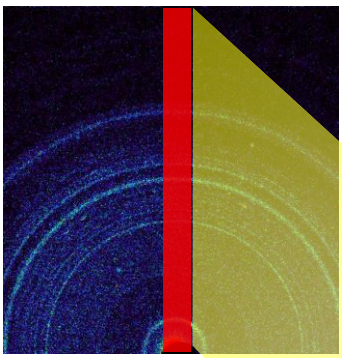
Peter Debye
(1884-1966)



Paul Scherrer
(1890-1969)

The Debye rings

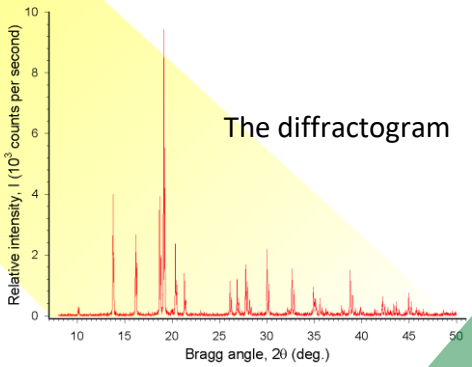
Powder X-ray Diffraction



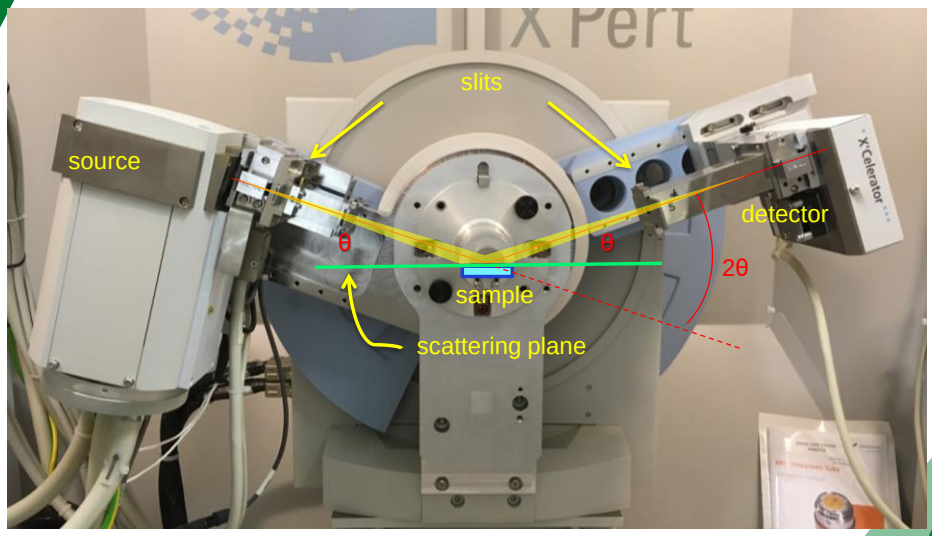
X-ray powder pattern of Mars soil

All the information contained in the diffraction figure is compressed into 1D, and a lot of information is lost, due to peak overlapping.
However, the instrumental apparatus is much simpler than single-crystal diffraction, and can give a statistical image of a multi-phase material

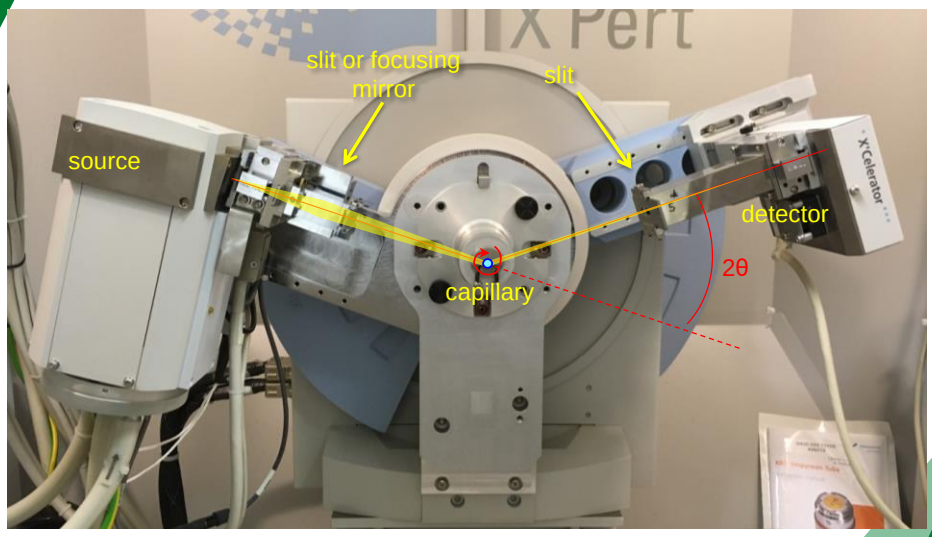
The diffractogram



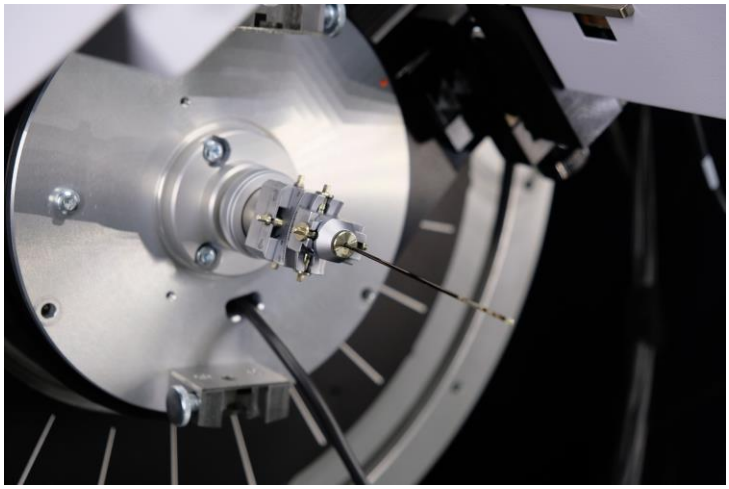
A Lab Diffractometer (Panalytical)
in reflection (Bragg-Brentano) geometry - flat sample



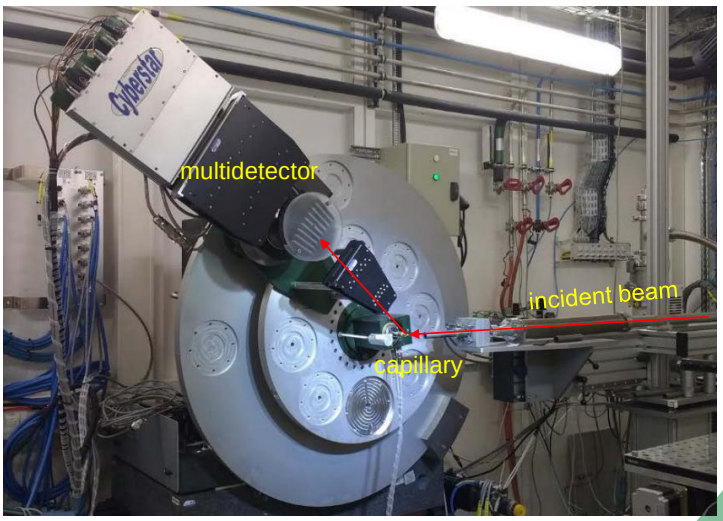
A Lab Diffractometer (Panalytical)
in transmission geometry - sample in capillary



A Lab Diffractometer (Bruker)
in transmission geometry - sample in capillary

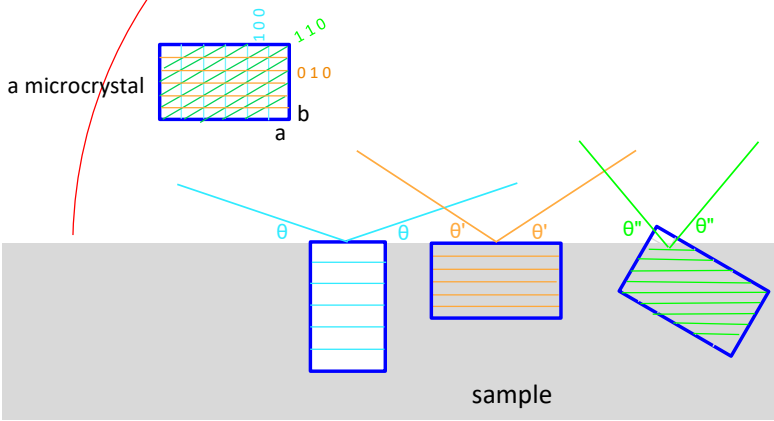


Synchrotron Diffractometer (ESRF ID22)
in transmission geometry - sample in capillary



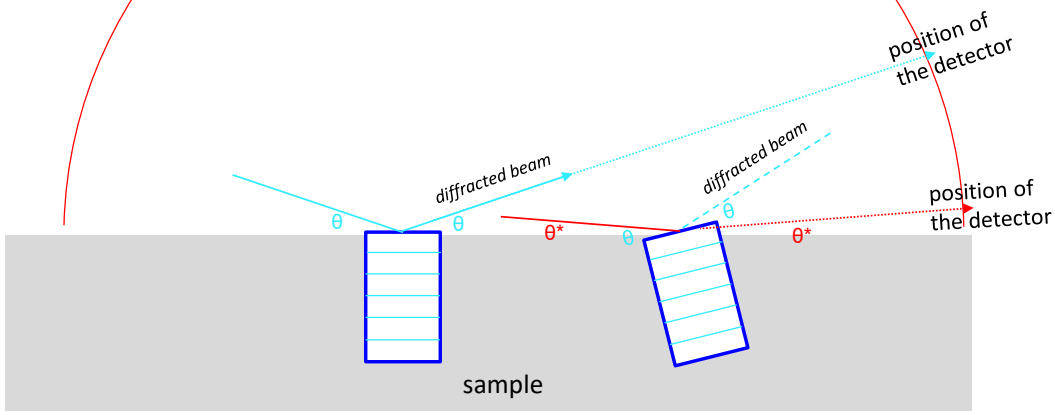
Reflection (Bragg-Brentano) geometry - flat sample

In reflection geometry the sample is packed onto a surface that lies in the focusing plane. In this geometry the incident beam and the detector synchronously rotate in the same circle and form the same theta angle with the sample surface. Only the diffraction effects of atomic planes parallel to the surface can be measured (at the proper angles). Therefore it is important that on the surface of the sample there is a large number of randomly oriented microcrystals in order to equally represent all the atomic planes.

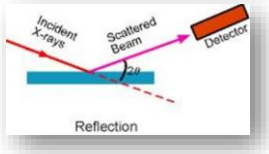


Reflection (Bragg-Brentano) geometry - flat sample

In reflection geometry the sample is packed onto a surface that lies in the focusing plane. In geometry the incident beam and the detector synchronously rotate in the same circle and the same theta angle with the sample surface. Only the diffraction effects of atomic planes parallel to the surface can be measured (at the proper angles). Therefore it is important that on the surface of the there is a large number of randomly oriented crocrystals in order to equally represent all the atomic planes.

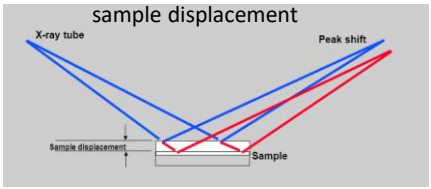


Reflection (Bragg-Brentano) geometry - flat sample

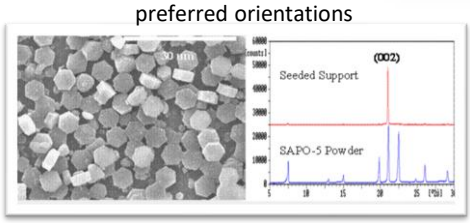


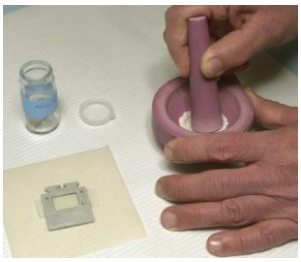
In reflection geometry the sample preparation is very simple but it is prone to introduce systematic errors, such as preferred orientations and sample displacement

sample displacement



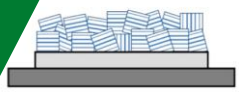
preferred orientations

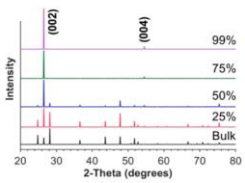




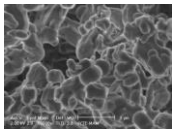
Preferred Orientations

Ex. metals soaps

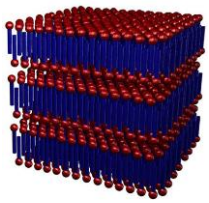




C.F. Holder, R.E. Shaak, ACS Nano 2019, 13, 7359



S. Ozturk et al. Ind. Eng. Chem. Res. 2010, 49, 1732



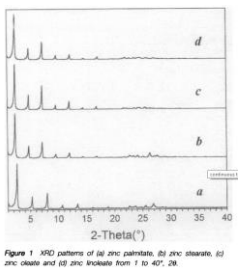
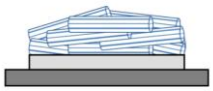
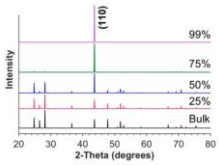


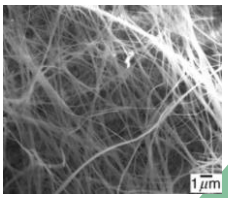
Figure 1 XRD patterns of (a) zinc palmitate, (b) zinc stearate, (c) zinc oleate and (d) zinc linoleate from 1 to 40°, 2θ.

L. Robinet, M.-C. Corbeil, Studies in Conservation , 2003, 48, 23

Ex. cerium phosphate



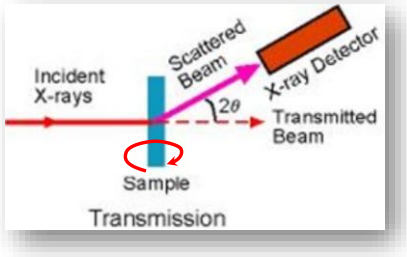




Chengchun Tang et al. Angew. Chem. 117, 582-585.

Transmission geometry - capillary sample

In transmission geometry the sample is generally packed into a capillary tube (0.5-0.3 mm) placed in the focusing spot. In this geometry the incident beam is fixed and the detector rotates in the 2theta circle. The capillary rotates around its axis to improve data statistics. This geometry is not affected by a sample displacement error, and reduces preferred orientation effects. However it is more difficult to set up and can present statistics problems due to the small amount of sample inside the capillary.



Setup of an X-ray diffraction data collection

In powder diffraction the 3D information is compressed in one dimension, and it is sometimes very difficult to extract information suitable for our needs from a diffractogram. A correct and accurate data collection is essential for any use.

Depending on several factors:

- the kind of sample
- what is the target of the experiment
- how much money and time is available
- what kind of instrument is available

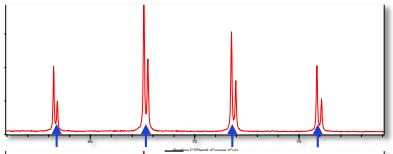
we must define:

- the sample preparation
- the instrument, geometry, optics and sample environment
- the 2theta angular interval, 2theta scan step, and the acquisition time per each step

Powder X-ray Diffraction Pattern - information that can be extracted

QUALITATIVE
- Identification of the crystalline phases

Useful data: 2theta position and number of peaks



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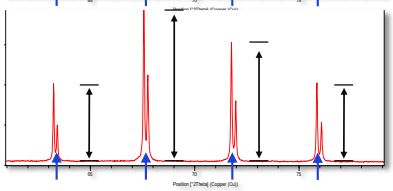
QUANTITATIVE
- Weigth % of each crystalline phase
- Amorphous phase content

Useful data: intensity and 2theta position and number of peaks



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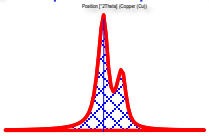
MICROSTRUCTURAL
- Size of crystallites
- Lattice deformations
- Dislocations, stacking defects

Useful data: peak profile (broadening)



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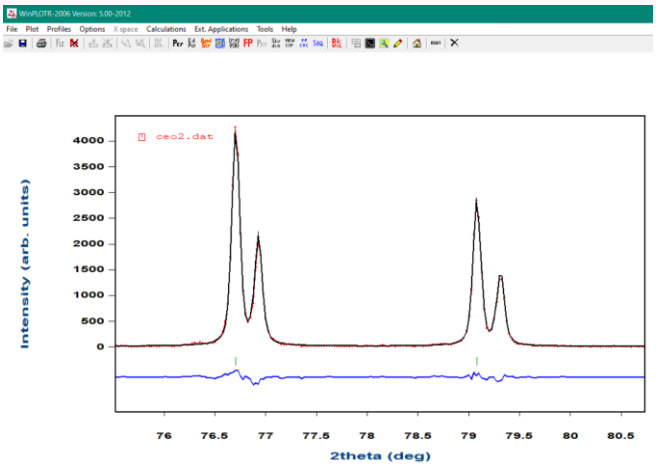
COMPLETE STRUCTURE
- Lattice parameters (crystalline system)
- Symmetry properties (lattice type, space group)
- atomic coordinates, thermal factors, occupancy

Useful data: everything

everything

=

Recommended a dedicated software



Powder X-ray Diffraction - Qualitative Analysis - Peak Positions

The 2theta position of diffraction peaks of a single phase depends on its unit cell parameters, while the total number of peaks also depends on space group.

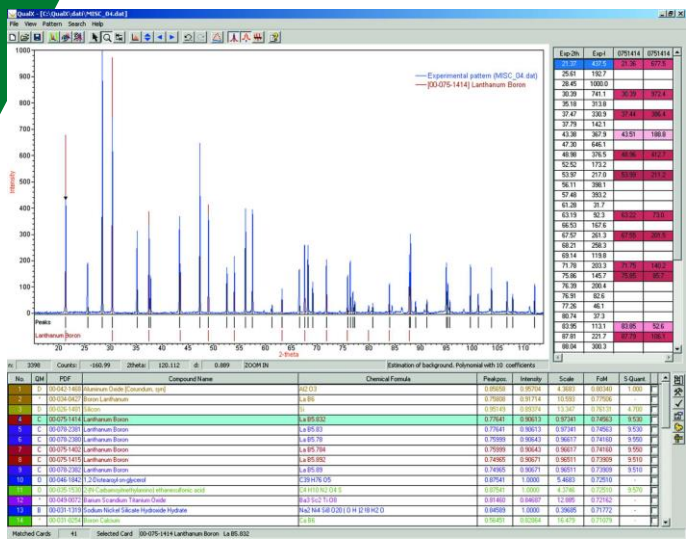
The diffraction pattern is a fingerprint of a crystal phase →
Qualitative analysis - Search and Match software (QUALX) linked with a database (PDF, COD)

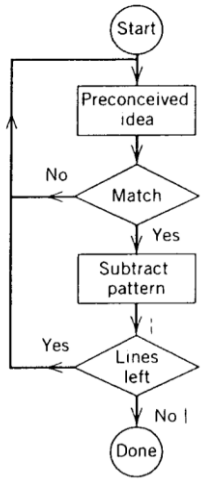
ICDD PDF4 ($$$) - 480.000 entries
https://www.icdd.com/pdf-4/

COD Crystallography Open Database

Free - 495.000 entries
http://www.crystallography.net/cod/

Powder X-ray Diffraction - Qualitative Analysis (QUALX→ 47-48)





Qualitative Analysis (QUALX)

$$FoM = \sqrt{\frac{FoM_{db} \cdot (w_\theta \cdot FoM_\theta + w_I \cdot FoM_I + w_{ph} \cdot FoM_{ph})}{w_\theta + w_I + w_{ph}}}$$

$$FoM_\theta = 1 - \frac{\sum_i^{N_{db}^{ass}} |2\theta_i^{\exp} - 2\theta_i^{db}|}{N_{db}^{ass} \cdot \Delta}$$

contribution coming from the 2ϑ, differences between the experimental and the associated database peaks

$$FoM_{ph} = \sqrt{\sum_{i=1}^{N_{\exp}^{ass}} I_i^{\exp} \cdot \frac{N_{\exp}^{ass}}{N_{\exp}} \Big/ \sum_{i=1}^{N_{\exp}} I_i^{\exp}}$$

contribution due to the differences between the intensities of the experimental and the associated database peaks

$$FoM_I = 1 - \frac{\sum_i^{N_{\exp}^{ass}} |I_i^{\exp} - I_i^{db}|}{N_{\exp}^{ass}}$$

contribution due to the differences between the intensities of the experimental and the associated database peaks

$$FoM_{db} = \sqrt{\sum_{i=1}^{N_{db}^{ass}} I_i^{db} \cdot \frac{N_{db}^{ass}}{N_{db}} \Big/ \sum_{i=1}^{N_{db}} I_i^{db}}$$

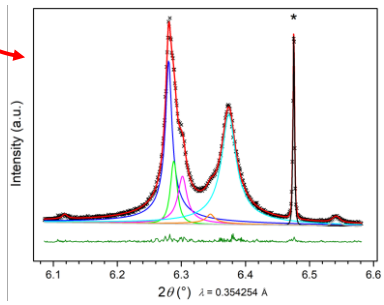
contribution due to the intensities of the associated database peaks and their percentage

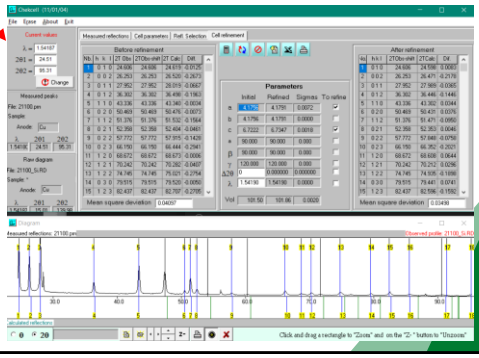
Altomare et al., *J. Appl. Cryst. (2015)*. **48**, 598

Refinement of Unit Cell Parameters (→ 21100)

Sometimes we know only approximately the unit cell parameters of a crystalline phase and their accurate values can give us precious informations on phase composition (→ Vegard's law) or for identification purposes.

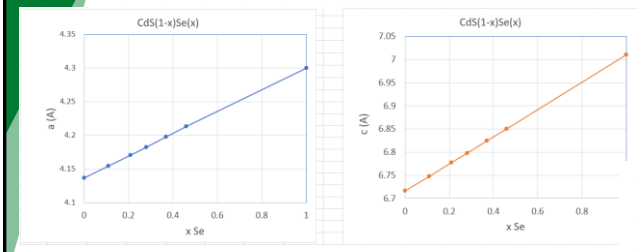
The refinement of unit cell parameters can be done by least square methods.
The accurate estimation of peak positions is needed first.
Single or cluster peak fit by a dedicated software: Fullprof, XFit, etc.
Then " Chekcell " or " Celref "





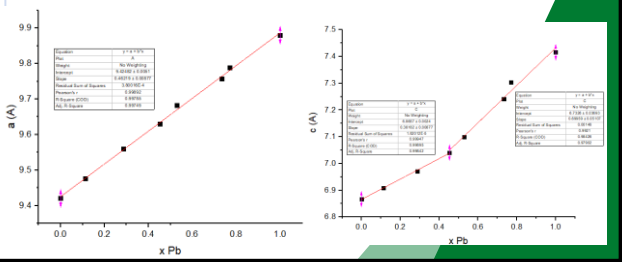
The Vegard's law

The Vegard's law is not a true "law", but only an empirical rule.
It states that in a two-component solid solution the unit cell parameters are generally linearly correlated with the composition. Useful i soe cases to find the composition from simple diffractometric measurements
Ex. $Cd_{(1-x)}Zn_xS$, $CdS_{(1-x)}Se_x$, Pb-Hydroxylapatite, many metal oxides



$CdS_{(1-x)}Se_x$

$(Pb_xCa_{1-x})_5(PO_4)_3OH$



EXPO

The software EXPO2014* is able to carry out the full pathway of the crystal structure solution process: indexing, space group determination, estimation of the integrated intensities, ab-initio and non ab-initio structure solution, Rietveld refinement. → EXPO

*A. Altomare, et al., J. Appl. Cryst. (2013). 46, 1231

Quantitative Analysis

The intensity of each *hkl* reflection, per each crystalline phase α is proportional to the volume fraction x_α of that phase in the mixture

$$I_{(hkl)\alpha} = \frac{1}{2}\frac{K_e K_{(hkl)\alpha} x_\alpha}{\mu_m}$$

$$K_e = \frac{I_0 \lambda^3 l_{fend}}{32\pi R_{gon}} \frac{e^2}{m_e c^2}$$

$$K_{(hkl)\alpha} = \frac{\left|F_{(hkl)\alpha}\right|^2 m_{(hkl)\alpha} Lp_{(hkl)\alpha}}{V_{c,\alpha}^2}$$

$$F_{(hkl)} = \sum_{j=1}^{N} f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

- K_e = experimental constant
- $K_{(hkl)}$ = constant specific of the structure of phase α
- x_α = Volume fraction of phase α
- μ_m= linear absorption coefficient of the mixture
- m_{hkl} = multiplicity of the hkl reflection
- V_α = Unit cell volume
- *Lp* = Lorentz - polarization factor
- $F_{(hkl)\alpha}$ = Structure factor

Quantitative Analysis

When the linear absorption coefficient μ_m is converted into the mass absorption coefficient μ_m*, and the volume fraction x_α is converted into the mass fraction w_α, the densities ρ_a , ρ_M of phase α and the matrix, respectively, must be introduced. While the density of phase α can be obtained, that of the matrix can be calculated if its composition is known.

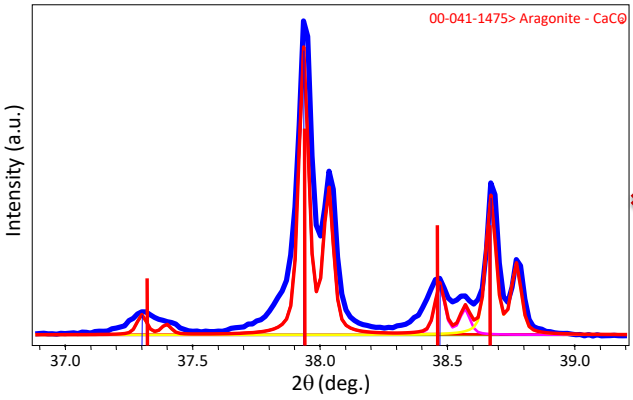
$$I_{(hkl)\alpha} = \frac{K_\alpha w_\alpha}{\rho_\alpha\left[w_\alpha\left(\mu_\alpha^* - \mu_M^*\right) + \mu_M^*\right]}$$

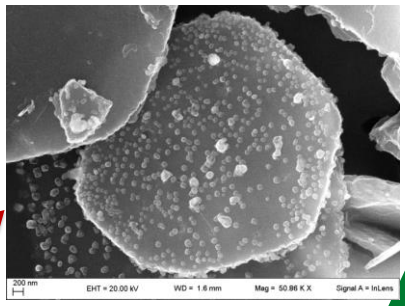
Furthermore, the intensity of an hkl peak can be affected by systematic errors due to preferred orientations.

→ **Quantitative analysis based on the measurement of the intensity one or a few peaks is not recommended**

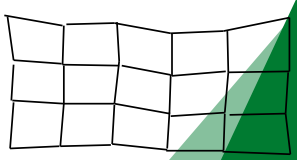
Rietveld Refinement Method

Peak Profile and Microstructure





CRYSTAL SIZE

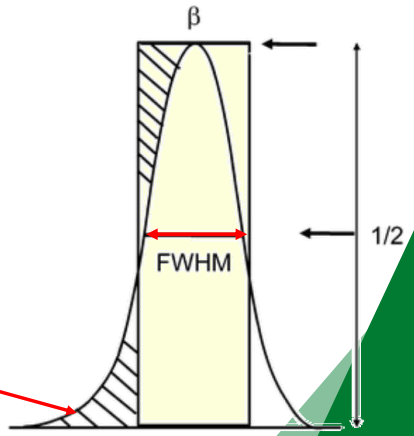


MICROSTRAIN

Peak Profile and Microstructure

Full Width at Half Maximum (FWHM)
the width of the diffraction peak, in radians, at a height half-way between background and the peak maximum

Integral Breadth
the total area under the peak divided by the peak height. Is the width of a rectangle having the same area and the same height as the peak
requires very careful evaluation of the tails of the peak and the background



Peak Profile and Microstructure

CRYSTAL SIZE

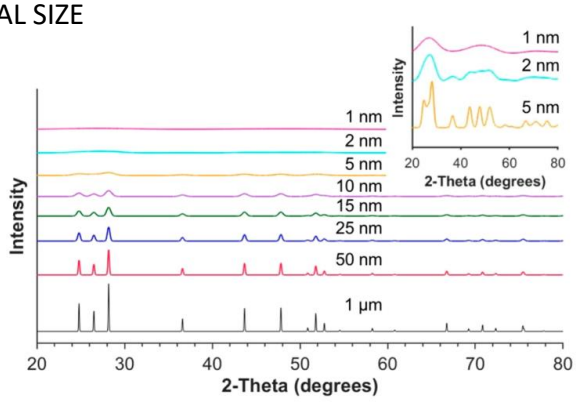
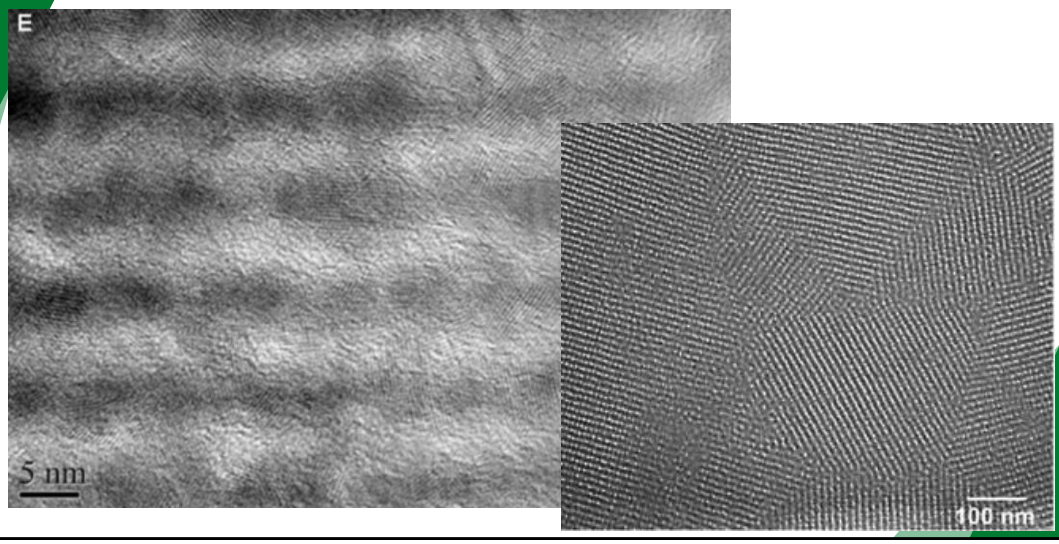


Figure 2. Simulated powder X-ray diffraction patterns for wurtzite CdS spherical particles of different sizes that range from 1 μm to 1 nm. The inset shows the 1, 2, and 5 nm XRD patterns on an expanded *y*-axis scale for clarity.

C.F. Holder, R.E. Shaak, ACS Nano 2019, 13, 7359

In powder diffraction CRYSTAL SIZE should be interpreted as "average dimension of coherent diffraction domains". It is generally indicated as *Dv* (or *S*)



Peak Profile and Microstructure

Size Broadening - The Scherrer Equation (1918)

$$\beta = \frac{K\lambda}{S\cos\theta}$$

β = contribution to the width of diffraction peaks, in radians 2theta

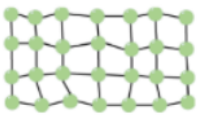
S = crystal size

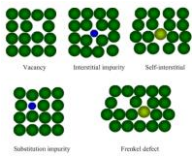
K = constant which depends on crystallite morphology

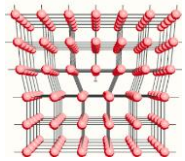
K = (0.87 ÷ 1.0)

Peak Profile and Microstructure

Microstrain is the is the set of lattice defects that lead to strain and disorder within the crystal and tends to and tends to broaden the amplitude of the diffraction peaks







point defects, plane defects, etc.

Strain Broadening - and Wilson (1944) $\beta = 4\varepsilon\tan\theta$

β = Contribution to the width of diffraction peaks

ε = Average strain

$$\varepsilon = \left\langle \frac{\Delta d}{d} \right\rangle$$

Profile Functions

Gaussian $$G(\Delta\vartheta,\Gamma)=\sqrt{\frac{4\ln 2}{\pi\Gamma^2}}\cdot e^{\frac{-4\ln 2(\Delta\vartheta)^2}{\Gamma^2}}$$

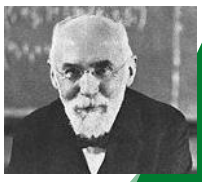
Lorentzian $$L(\Delta\vartheta,\gamma)=\frac{2}{\pi\gamma}\frac{1}{1+\left(\frac{2\Delta\vartheta}{\gamma}\right)^2}$$

Pseudo-Voigt $$P(\Delta\vartheta,\Gamma,\gamma)=\eta L+(1-\eta)G$$

$$\eta=A+B(2\vartheta)$$

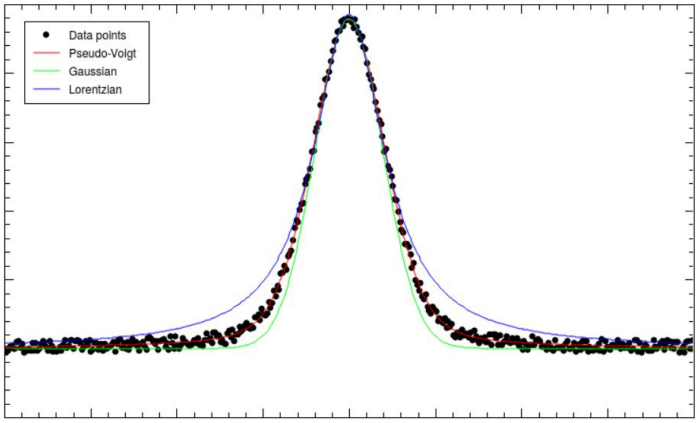
Γ = Gaussian FWHM γ = Lorentzian FWHM

Johann Carl Friedrich Gauss
(1777-1855)



Hendrik Lorentz
(1853-1928)

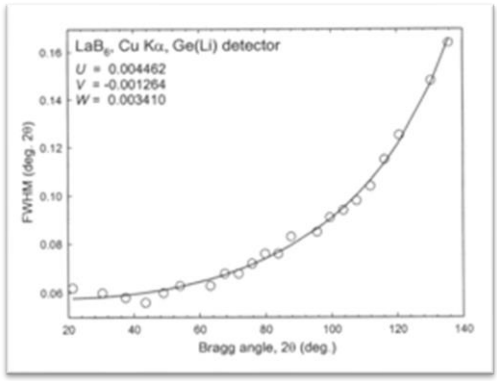
Gaussian and Lorentzian



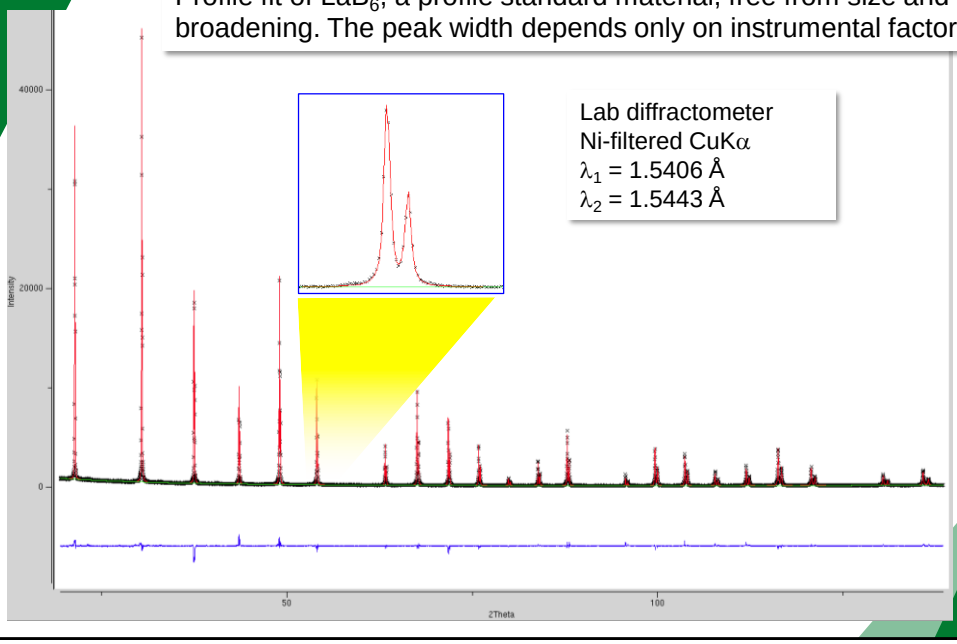
Gaussian FWHM

$$\Gamma = (U \tan^2 \theta + V \tan \theta + W)^{1/2}$$

Principally due to instrumental effects (optical aberrations)

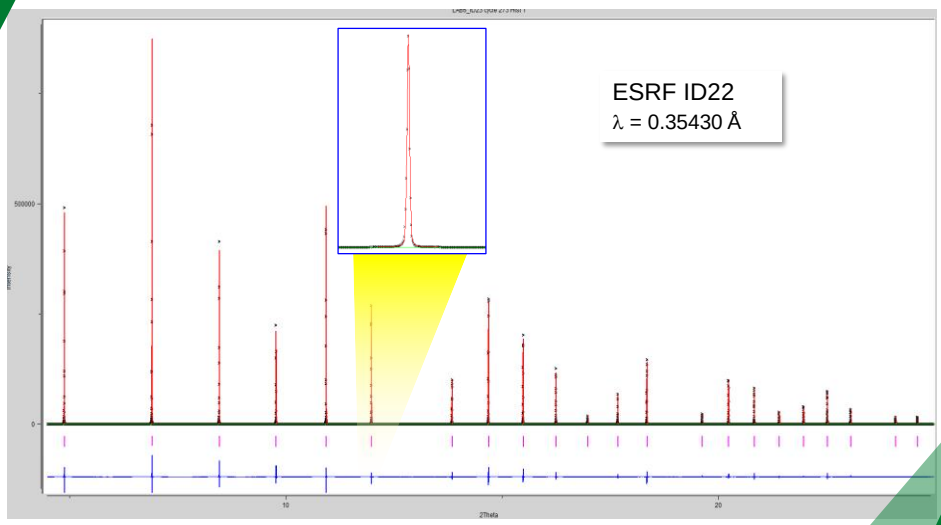


Profile fit of LaB_6, a profile standard material, free from size and strain broadening. The peak width depends only on instrumental factors

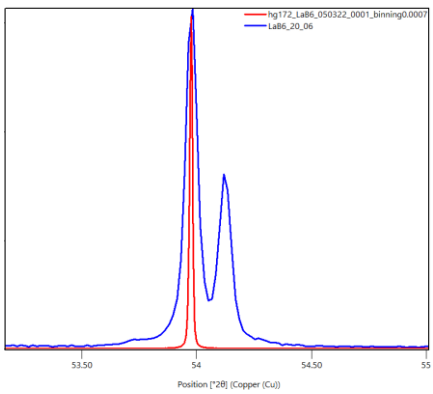


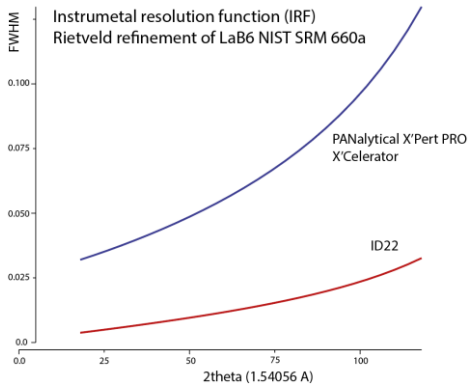
Lab diffractometer
Ni-filtered CuKα
λ_1 = 1.5406 Å
λ_2 = 1.5443 Å

Profile fit of LaB_6, a profile standard material, free from size and strain broadening. The peak width depends only on instrumental factors

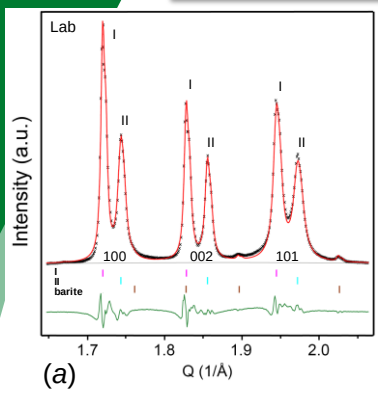


Comparison of the instrumental resolution functions (IRF) of a Lab diffractometer and ESRF ID22 beamline



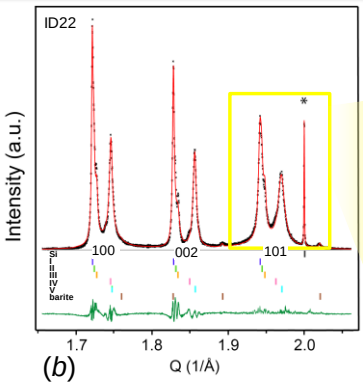


Comparison between XRD patterns of a CdSSe sample taken with a lab diffractometer (*a*) and ESRF-ID22 (*b* and *c*)



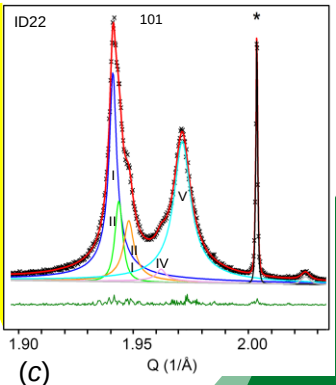
(*a*)

$CdS_{(1-x)}Se_x$ I) x = 0.54(1) II) x = 0.19(1)



(*b*)

$CdS_{(1-x)}Se_x$ I) x = 0.561(2) II) x = 0.528(2) III) x = 0.474(2) IV) x = 0.242(4) V) x = 0.185(2)



(*c*)

Lorentzian FWHM

$$\gamma = \frac{X}{\cos\vartheta} + Y\tan\vartheta$$

Principally due to sample microstructure

given: size *(Scherrer)* $\beta = \frac{K\lambda}{S\cos\theta}$

and Strain *(Stokes and Wilson)* $\beta = 4\varepsilon\tan\theta$

and setting: $X = \frac{K\lambda}{S}$ and $Y = 4\varepsilon$

we obtain: $\boxed{\gamma = \frac{X}{\cos\vartheta} + Y\tan\vartheta = \beta_{size} + \beta_{strain}}$

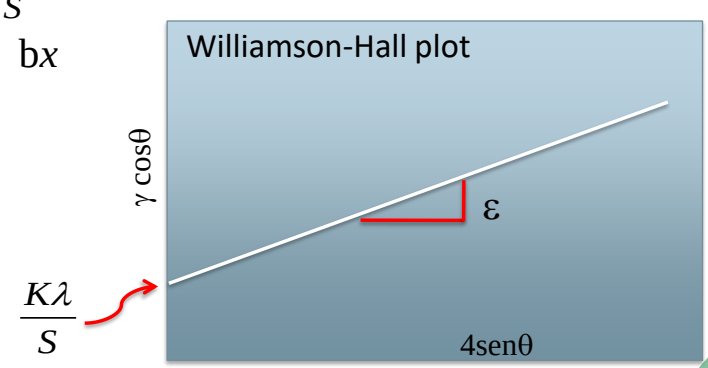
Total Width

β_{Tot} = integral breadth = $\beta_{instr} + \beta_{sample} = \Gamma + \gamma$

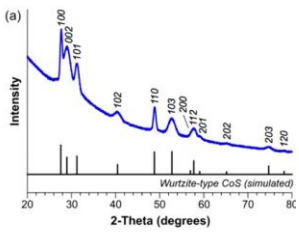
$$\beta_{sample} = \beta_{size} + \beta_{strain} = \gamma = \frac{K\lambda}{S\cos\vartheta} + 4\varepsilon\tan\vartheta$$

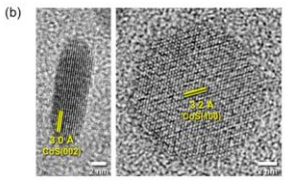
$$\gamma\cos\vartheta = \frac{K\lambda}{S} + 4\varepsilon \cdot sen\vartheta$$

$y = a + bx$



Anisotropic Broadening





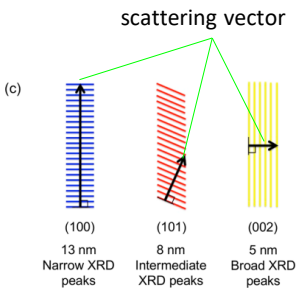


Figure 6. (a) Experimental and simulated powder XRD patterns for platelet-shaped wurtzite CoS nanoparticles. (b) High-resolution transmission electron microscope images of a CoS nanoplatelet viewed from the (left) side and (right) top. (c) Representation of the different effective thicknesses (*i.e.*, crystalline domain sizes) in different directions of the nanoplates, which correlate with different peak widths in the experimental XRD pattern. Adapted from ref 8. Copyright 2016 American Chemical Society.

Anisotropic Broadening

To take into account the anisotropic broadening there are different approaches. One simple method introduces two further parameters in the profile function, that are modulated by the angle ϕ between the scattering vector of the hkl reflection and the vector that defines the direction of the anisotropic broadening:

from: $$\gamma = \frac{X}{\cos\vartheta} + Y\tan\vartheta$$

to: $$\gamma = \frac{X + X_e\cos\varphi}{\cos\vartheta} + (Y + Y_e\cos\varphi)\tan\vartheta$$

Indexing of an XRPD pattern

The determination of unit cell parameters from the positions of diffraction peaks is called indexing procedure, because the problem is to assign the proper Miller indices to each reflection.
The procedure is not trivial because the problem does not have a unique solution. Try-and-error computational procedures are often used, however different programs use different strategies. For this reason the use of various programs is recommended (ex. Treor, Dicvol, Ito, McMaille, etc.), and the obtained solutions should be evaluated using statistical parameters.

Possible interplanar distances in a unit cell:

$Q = (1/d_{hkl})^2 = h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2kl\, b^*c^*\cos\alpha^* + 2hl\, a^*c^*\cos\beta^* + 2hk a^*b^*\cos\gamma^*$

where:

$$a^* = \frac{b\times c}{V};\quad \cos\alpha^* = \frac{\cos\beta\,.\cos\gamma - \cos\alpha}{\sin\beta\,.\sin\gamma}$$

$$b^* = \frac{c\times a}{V};\quad \cos\beta^* = \frac{\cos\alpha\,.\cos\gamma - \cos\beta}{\sin\alpha\,.\sin\gamma}$$

$$c^* = \frac{a\times b}{V};\quad \cos\gamma^* = \frac{\cos\alpha\,.\cos\beta - \cos\gamma}{\sin\alpha\,.\sin\beta}$$

REDUCED FORMULAS

Cubic:
$1/d^2 = (h^2 + k^2 + l^2)/a^2$

Tetragonal:
$1/d^2 = \{(h^2 + k^2)/a^2\} + (l^2/c^2)$

Orthorhombic:
$1/d^2 = (h^2/a^2) + (k^2/b^2) + (l^2/c^2)$

Hexagonal:
$1/d^2 = (4/3)\{(h^2 + hk + k^2)/a^2\} + (l^2/c^2)$

Monoclinic:
$1/d^2 = (1/\sin^2\beta)\{(h^2/a^2) + (k^2\sin^2\beta/b^2) + (l^2/c^2) - (2hl\cos\beta/ac)\}$

Indexing of an XRPD pattern

$$Q = (1/d_{hkl})^2 = h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2kl\, b^*c^*\cos\alpha^* + 2hl\, a^*c^*\cos\beta^* + 2hk a^*b^*\cos\gamma^*$$

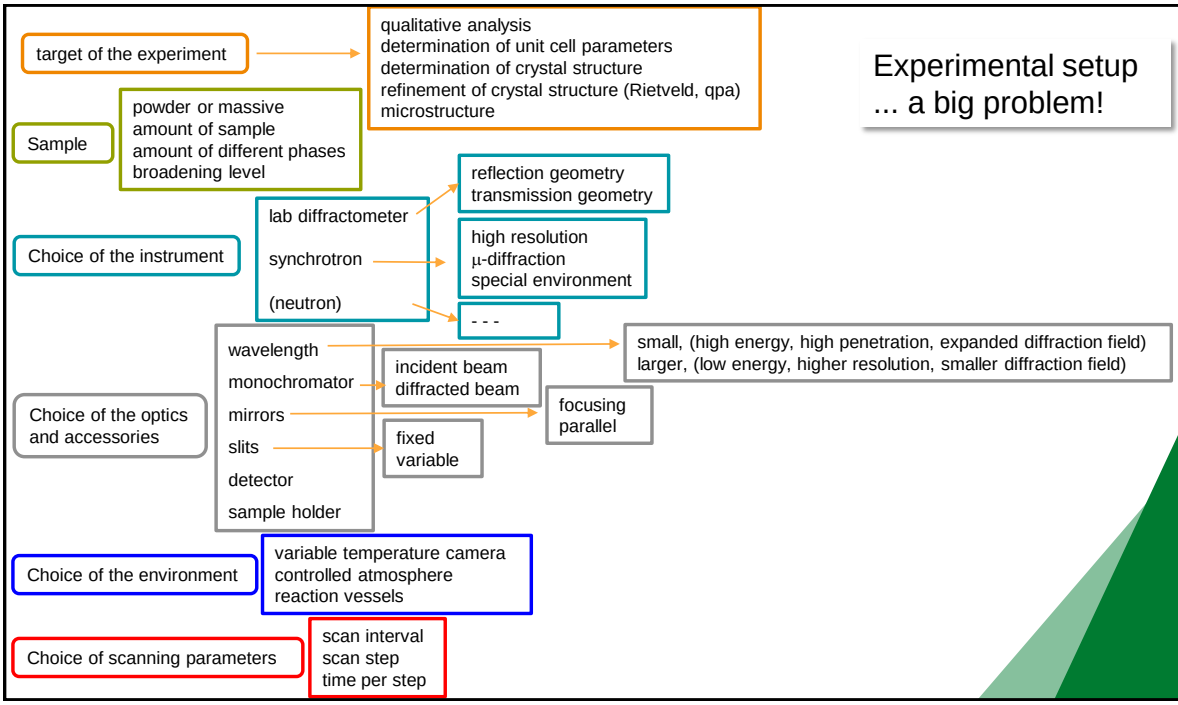
Some figures of merit can estimate the statistical relevance of the solution.
For example the M(20) by De Wolff: when M(20)>20 and all the first 20 reflections are indexed, it is strongly probable that the solution is correct.

De Wolff figure of merit: $M_{20} = Q_{20}/(2N_{20}|\Delta Q|_{avg})$

- Q_{20} is the Q value of the 20th peak observed & indexed
- N_{20} is the number of theoretical reflections with $Q < Q_{20}$
- $|\Delta Q|_{avg}$ is the average of the differences between each Q_{obs} and the nearest Q_{calc}.

$M_{20} > 20$ is typically a good indicator for a correct indexing

Experimental setup ... a big problem!



USEFUL FREE SOFTWARE (for academics)

Crystal Structure visualization
VESTA (https://jp-minerals.org/vesta/en/)
Ortep3 - https://www.chem.gla.ac.uk/~louis/software/ortep/index.html
Avogadro - https://avogadro.cc/
Mercury - https://www.ccdc.cam.ac.uk/Community/csd-community/freemercury/
Powdercell - http://mill2.chem.ucl.ac.uk/ccp/web-mirrors/powdcell/a_v/v_1/powder/e_cell.html

Powder diffraction data handling
Kalvados - https://www.fzu.cz/~knizek/kalvados/download.html
ATEX - http://www.atex-software.eu/
FullProf - https://www.ill.eu/sites/fullprof/index.html

Search and match
QualX - http://www.ba.ic.cnr.it/softwareic/qualx/
Profex-BGMN - https://www.profex-xrd.org/

Peak fitting
Fityk - https://fityk.nieto.pl/
Kalvados
XFIT - Ask (tutorial: http://ccp14.cryst.bbk.ac.uk/tutorial/xfit-95/xfit.htm)
GSAS - GSAS II - https://subversion.xray.aps.anl.gov/trac/EXPGUI
EXPO2014 - http://www.ba.ic.cnr.it/softwareic/expo/
FullProf - https://www.ill.eu/sites/fullprof/index.html
Profex-BGMN - https://www.profex-xrd.org/
Powdercell

Indexing
TREOR90 - NTREOR - ask
DICVOL14-Predict - https://www.icdd.com/predict/
McMAILLE - http://www.cristal.org/McMaille/

Unit cell refinement and space group search
GSAS - GSAS II
EXPO2014
Chekcell - Celref - http://ccp14.cryst.bbk.ac.uk/ccp/web-mirrors/lmgp-laugier-bochu/

Crystal structure solution
FOX - https://fox.vincefn.net/
EXPO2014
GSAS - GSAS II
DASH - from this year!

Rietveld refinement - Quantitative analysis
Quanto - http://www.ba.ic.cnr.it/softwareic/
GSAS-GSAS II
EXPO
MAUD - http://maud.radiographema.com/
FullProf
Profex-BGMN
JANA2020 - http://jana.fzu.cz/

Powder data conversion
PowDLL - http://users.uoi.gr/nkourkou/powdll/
Kalvados
Profex-BGMN

THE END

THANK YOU