

STRUCTURE OF MATTER: X-RAY DIFFRACTION

Analysis of intensities

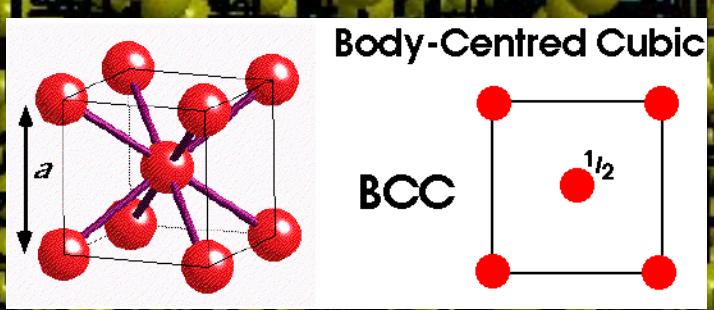
Fernando Aguado
Laboratorio de Física IV, Curso 2022-2023

General Objectives

- To apply your knowledge on the theory of X-ray diffraction by solids to gain structural information from diffraction patterns (including peak position and intensities).
- To determine the structure of simple crystalline solids using the powder x-ray diffraction technique.
- To understand the basis of the Rietveld method for full structural characterization of compounds, performing some simple refinements.

Long Range Order
Translational symmetry

Hierro
 $[Fe]^{86}$



Structural characterization

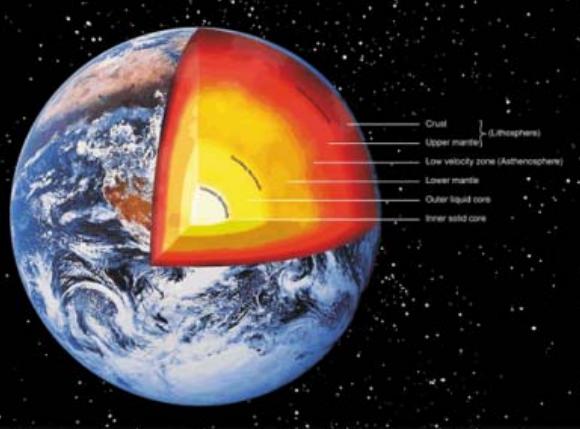
***Why do we need to determine
crystal structures ?***

- To **categorize unknown compounds**
- To **rationalize structures** / Understanding of bases
- To **establish correlations** between structure and properties

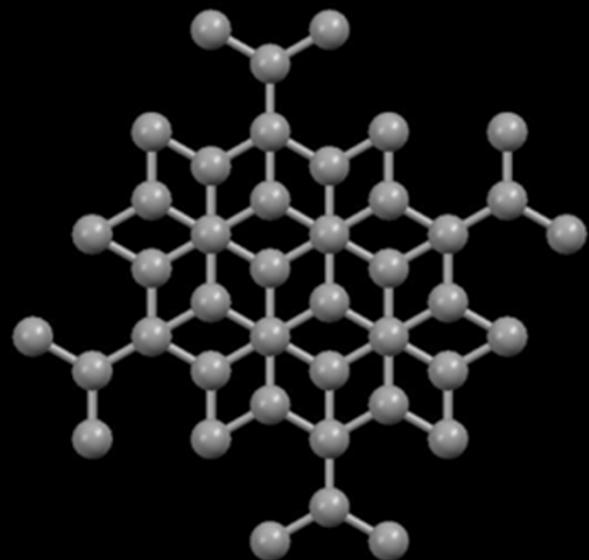
Formas alotrópicas del Carbono. Relación estructura-propiedades



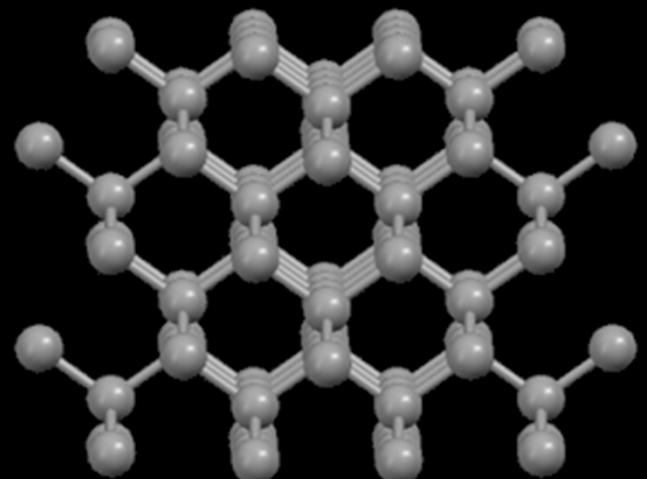
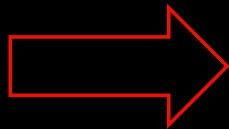
Grafito



Diamante

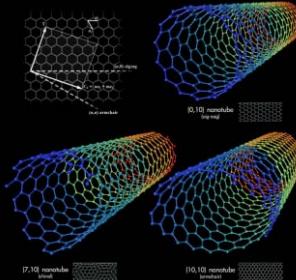
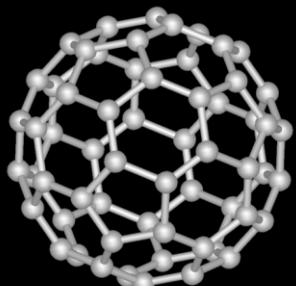


Alta Presión
Alta Temperatura



Fulerenos

Nanotubos



Structure Hexagonal

Space Group $P6_3mc$ (No. 186)

$a = 2.4700 \text{ \AA}$, $b = 2.4700 \text{ \AA}$, $c = 6.7900 \text{ \AA}$

$\alpha = \beta = 90.00^\circ$, $\gamma = 120.00^\circ$

$Z = 4$

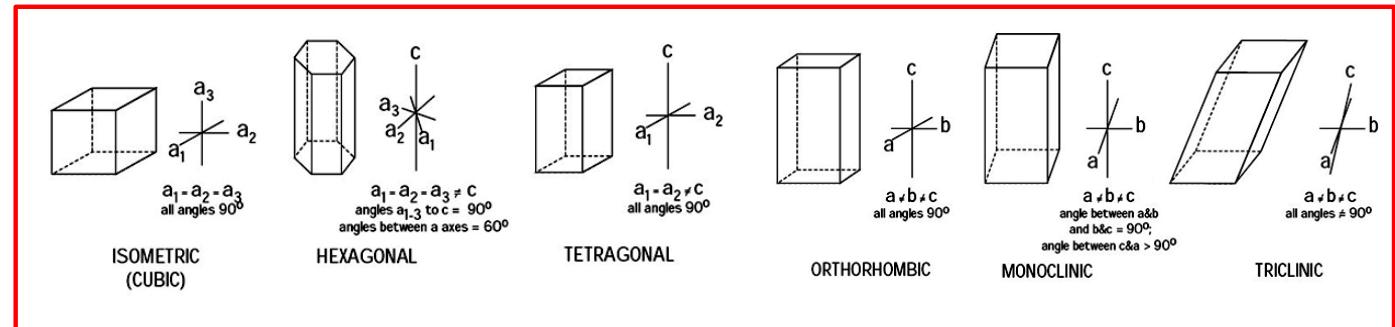
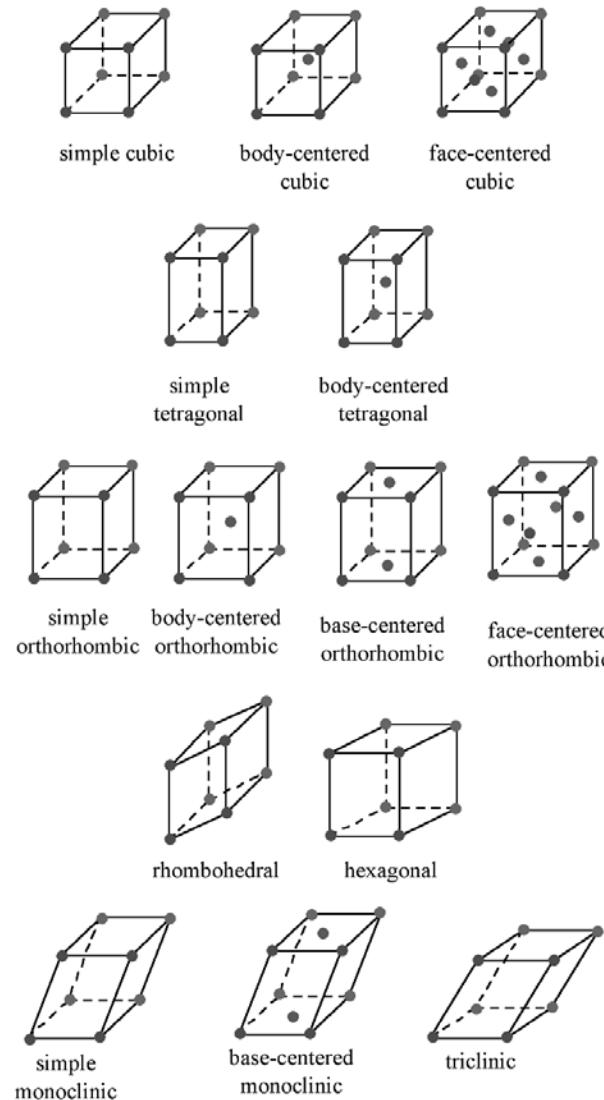
Structure Cubic

Space Group $Fd\bar{3}m$ (No. 227)

$a = 3.5668 \text{ \AA}$

$Z = 8$

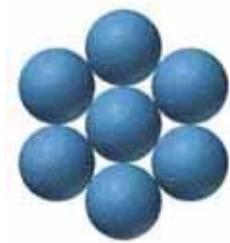
Crystal systems



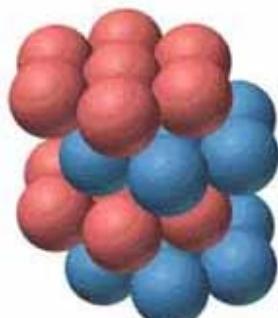
System	Defining symmetry	Unit cell geometry
Triclinic	Only translational	$a \neq b \neq c ; \alpha \neq \beta \neq \gamma$
Monoclinic	One diad parallel to [010] or/and one mirror plane perpendicular to [010]	$a \neq b \neq c ; \alpha = \gamma = 90^\circ ; \beta > 90^\circ$
Orthorhombic	Each axis should be parallel to a diad or/and perpendicular to a mirror plane	$a \neq b \neq c ; \alpha = \beta = \gamma = 90^\circ$
Trigonal	One triad parallel to [001]	$a = b \neq c ; \alpha = \beta = 90^\circ ; \gamma = 120^\circ$
Hexagonal	One hexad parallel to [001]	$a = b \neq c ; \alpha = \beta = 90^\circ ; \gamma = 120^\circ$
Tetragonal	One tetrad parallel to [001]	$a = b \neq c ; \alpha = \beta = \gamma = 90^\circ$
Cubic	Four triads parallel to <111>	$a = b = c ; \alpha = \beta = \gamma = 90^\circ$

Some simple structures

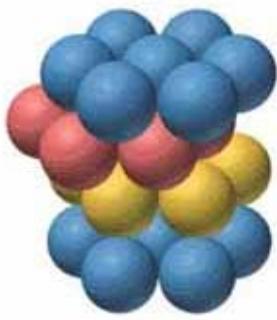
Closed Packing



Close-packed layer of spheres

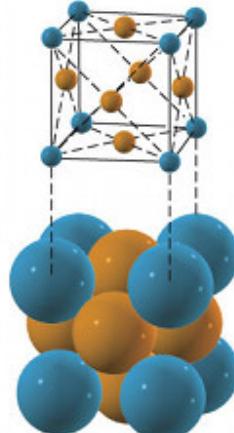
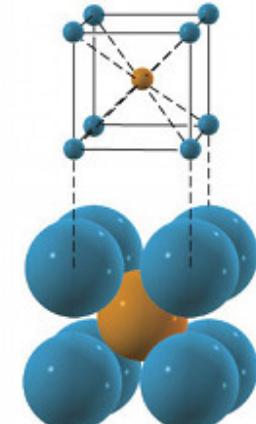
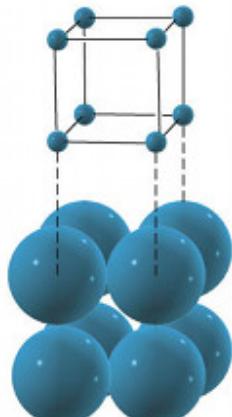


CCP



HCP

Cubic Bravais Lattices (P, I, F)

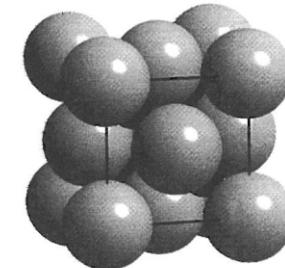


NaCl

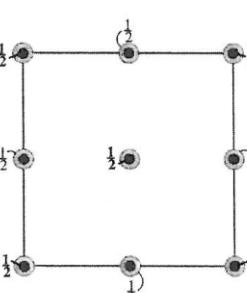
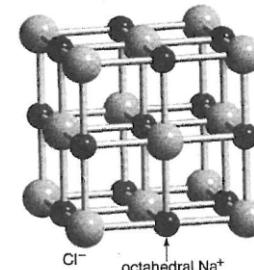
Space filling models:



ZnS (sphalerite)

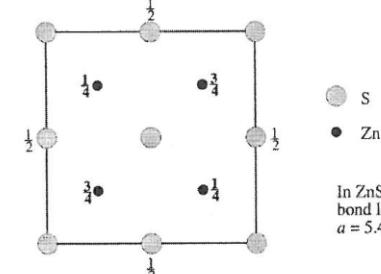
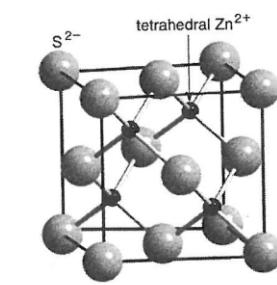
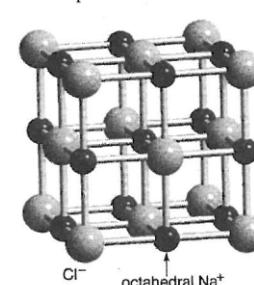


Ball and spoke models:



F Lattice

Motif: Cl: 0,0,0; Na: 0,0,1/2



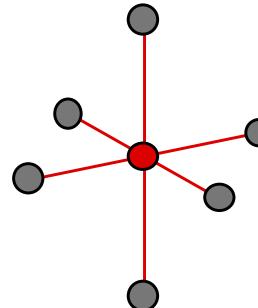
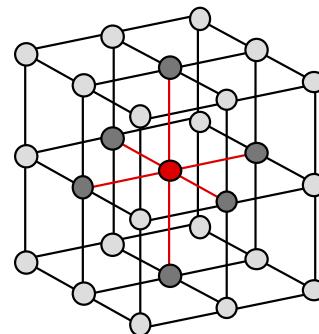
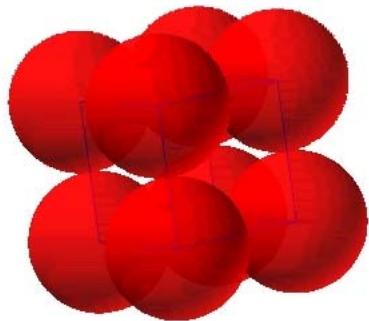
F Lattice

Motif: S: 0,0,0; Zn: 1/4,1/4,1/4

In NaCl, the Na-Cl bond length = 2.81 Å
 $a = 5.62 \text{ \AA}$

In ZnS, the Zn-S bond length = 2.34 Å
 $a = 5.41 \text{ \AA}$

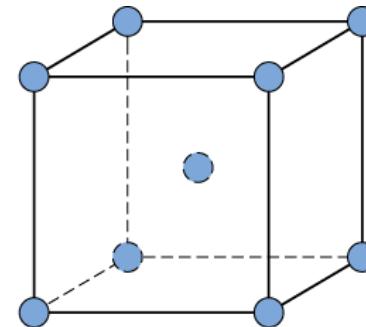
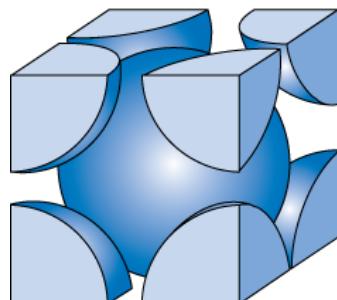
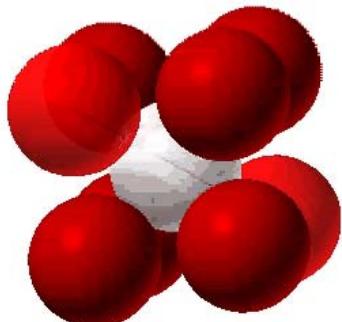
Simple Structures



SC

Coord: 6

Elements: only Po

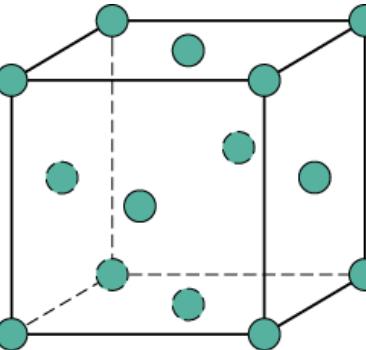
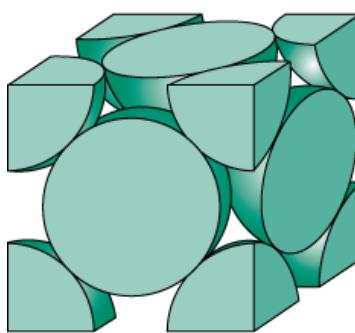
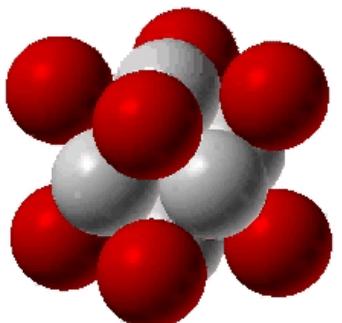


BCC

Coord: 8

Elements: Fe(a), Cr, Mo

Z=2



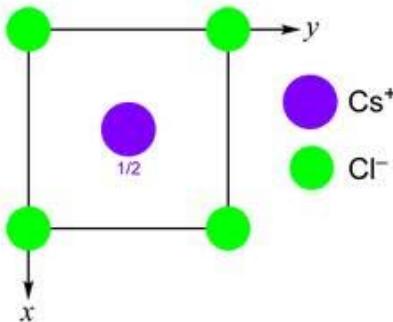
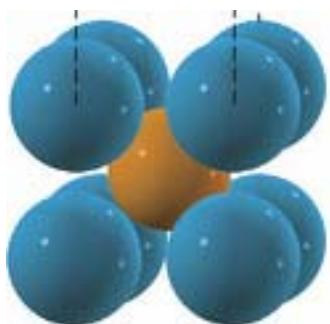
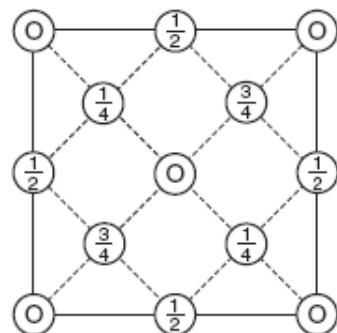
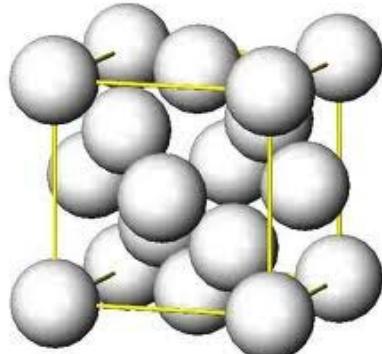
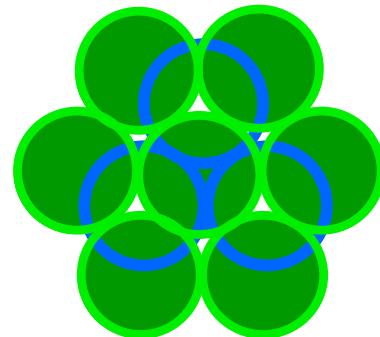
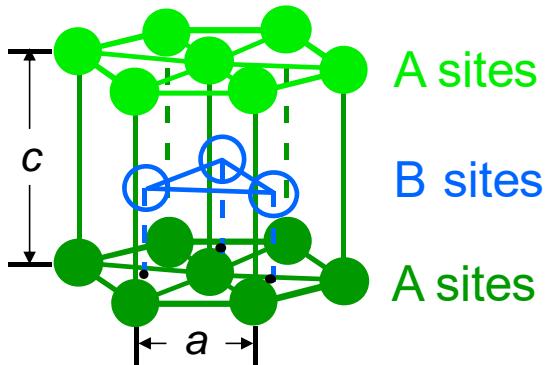
FCC

Coord: 12

Elements: Al, Cu, Au,...

Z=4

Simple Structures



HCP

Coord: 12

Elements: Mg, Ti, Zn,...

$Z=6$

Diamond

Coord: 4

Examples: Diamond

$Z=8$

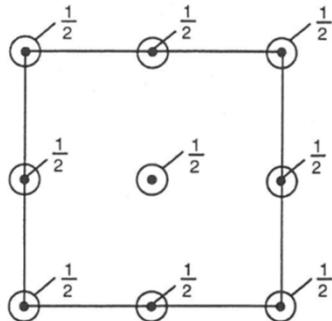
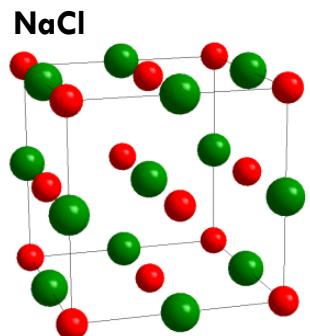
CsCl

Motif:

$\text{Cl} (0,0,0)$

$\text{Cs} (1/2,1/2, 1/2)$

Simple Structures

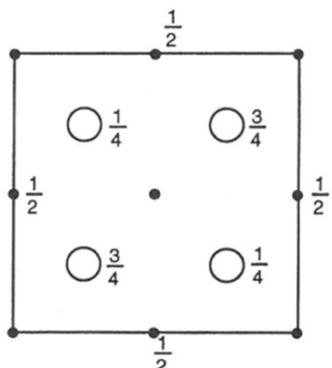
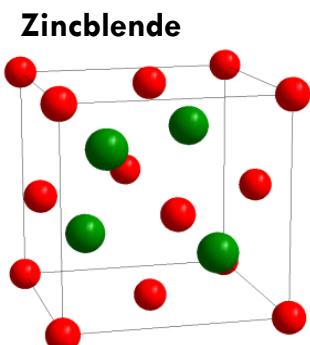


NaCl

Motif:

Na (0,0,0)

Cl (1/2,0,0)

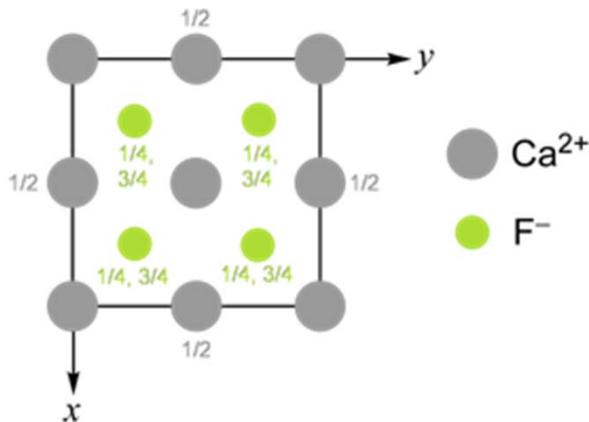
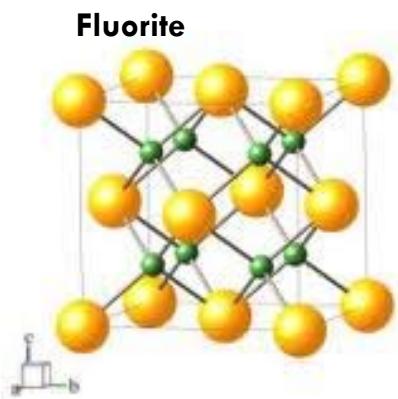


ZnS

Motif:

Zn (0,0,0)

S (1/4, 1/4, 1/4)



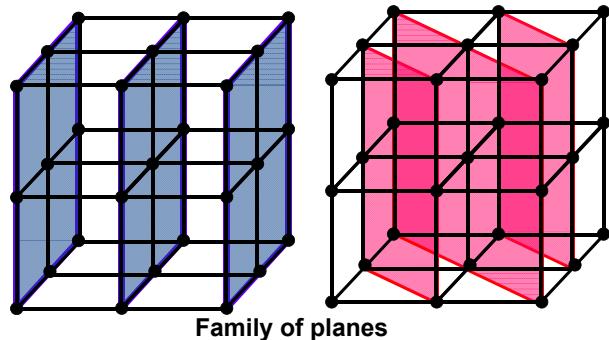
CaF₂

Motif:

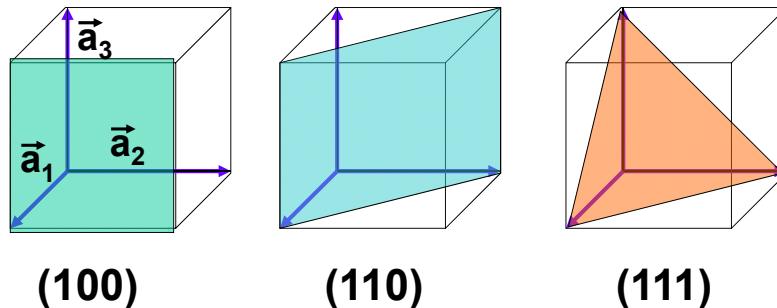
Ca (0,0,0)

F (1/4, 1/4, 1/4)

Crystal Planes -Miller indices



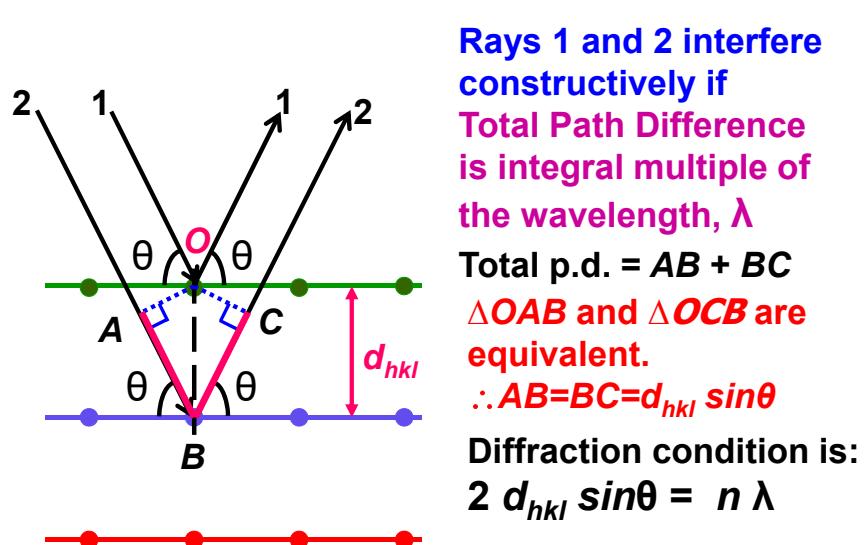
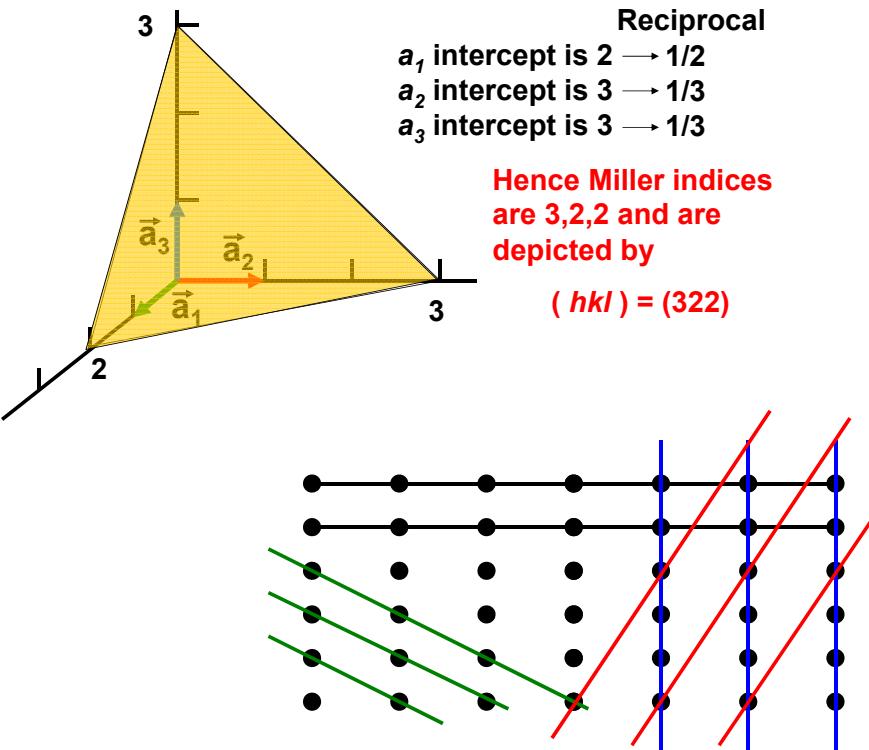
Crystal planes in cubic lattices



$$d_{hkl} = a$$

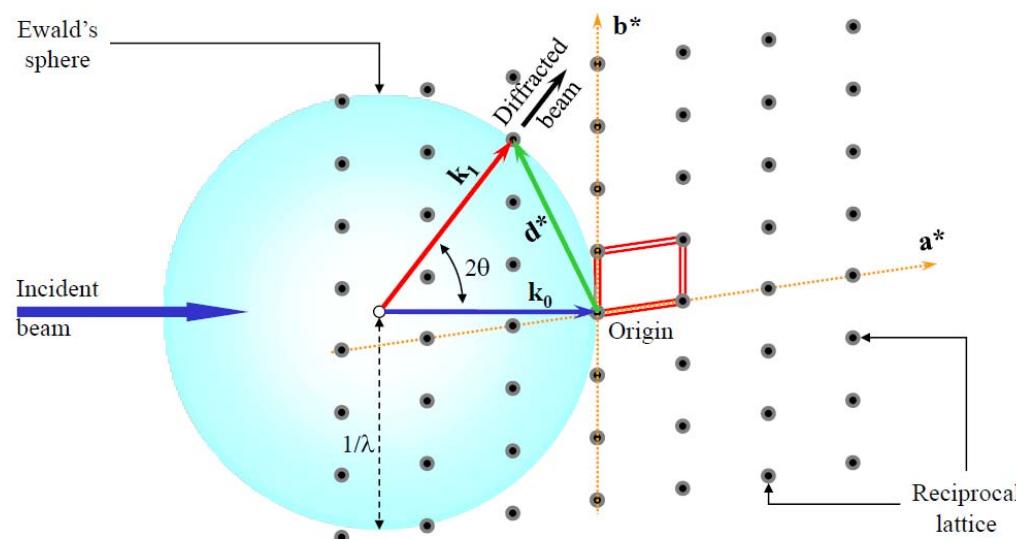
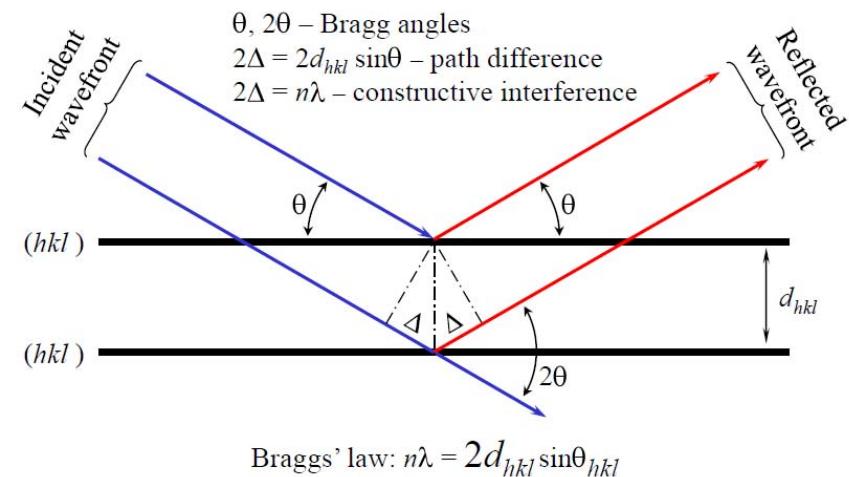
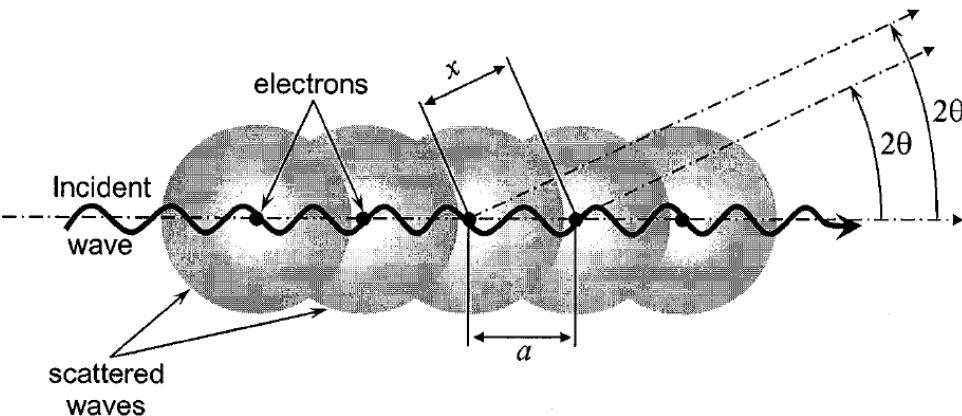
$$d_{hkl} = a/\sqrt{2}$$

$$d_{hkl} = a/\sqrt{3}$$



Fundamentals in diffraction

Diffraction condition: The Bragg's Law



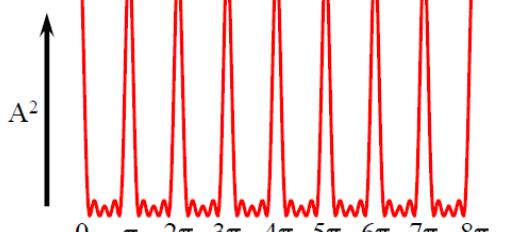
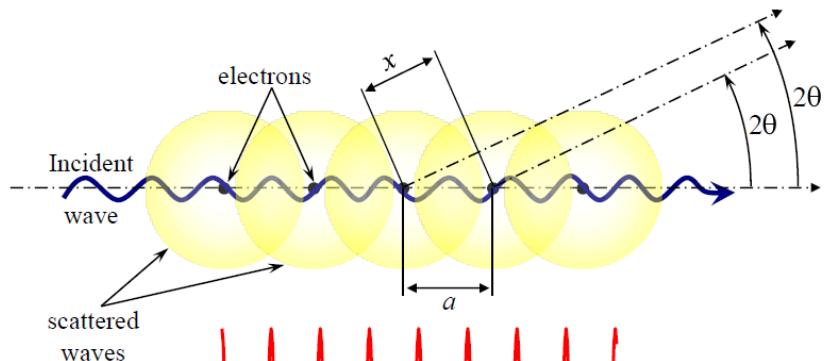
$$|\mathbf{k}_1| = |\mathbf{k}_0| = 1/\lambda$$

$$\mathbf{k}_1 = \mathbf{k}_0 + \mathbf{d}_{hkl}^*$$

$$|\mathbf{k}_1| \sin \theta = |\mathbf{k}_0| \sin \theta = \frac{|\mathbf{d}^*|}{2} \Rightarrow 2d \sin \theta = \lambda$$

Fundamentals in diffraction

Atomic Scattering

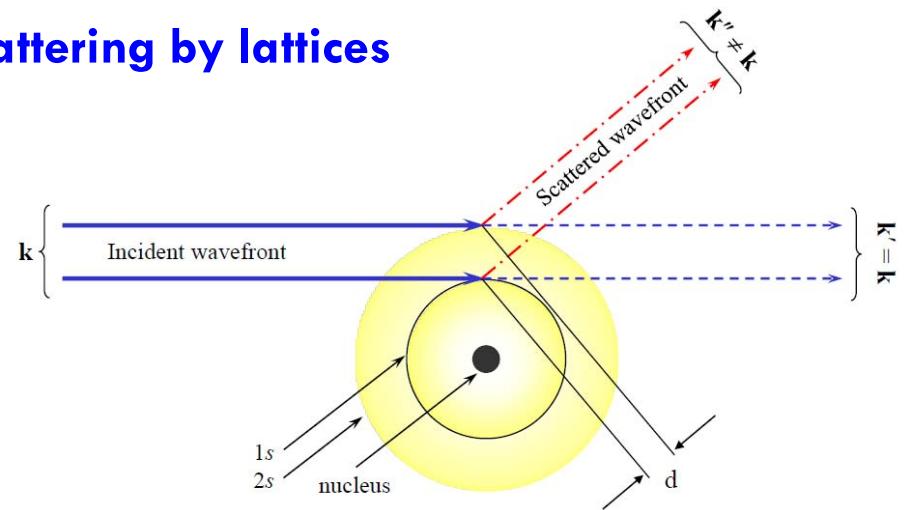


$$\phi = 2\pi \frac{a-x}{\lambda} = 2\pi \frac{a(1-\cos 2\theta)}{\lambda} = 4\pi \frac{a \sin^2 \theta}{\lambda}$$

$$I(\phi) \propto \frac{\sin^2 N\phi}{\sin^2 \phi} \quad \boxed{\rightarrow} \quad I(\phi) \propto f^2(\phi) \frac{\sin^2 N\phi}{\sin^2 \phi}$$

Interference function

Scattering by lattices

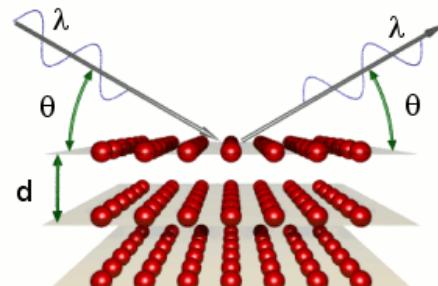


$$I(\phi) \propto f^2(\phi) \frac{\sin^2 N\phi}{\sin^2 \phi} = f^2(\phi) \frac{\sin^2 Nh\pi}{\sin^2 h\pi}$$

$$I(hkl) \propto F^2(hkl) \frac{\sin^2 U_1 h\pi}{\sin^2 h\pi} \frac{\sin^2 U_2 k\pi}{\sin^2 k\pi} \frac{\sin^2 U_3 l\pi}{\sin^2 l\pi}$$

$$I(hkl) = K \times G(\theta) \times F^2(hkl)$$

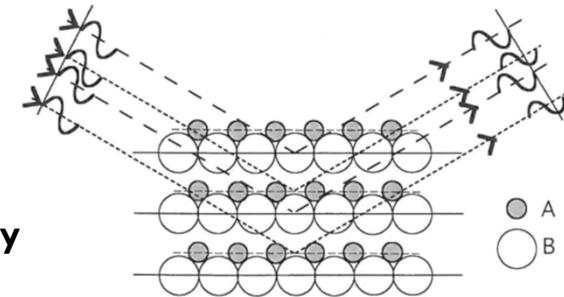
Basic information from XRD



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

Bragg's Law

Peaks Position



Peaks Intensity

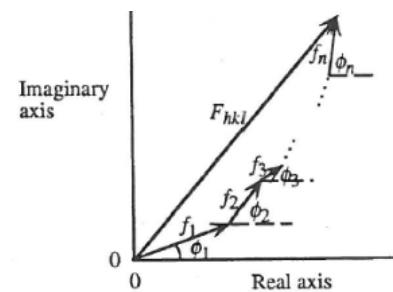
$$F = f_1 + f_2 = f_1(\cos \phi_1 + i \sin \phi_1) + f_2(\cos \phi_2 + i \sin \phi_2)$$

$$\begin{aligned} |F_{hkl}|^2 &= F_{hkl} F_{hkl}^* \\ &= F_{hkl} (\cos \phi_{hkl} + i \sin \phi_{hkl}) \cdot F_{hkl} (\cos \phi_{hkl} - i \sin \phi_{hkl}) \\ &= F_{hkl}^2 (\cos^2 \phi_{hkl} + i \cos \phi_{hkl} \sin \phi_{hkl} - i \cos \phi_{hkl} \sin \phi_{hkl} - i^2 \sin^2 \phi_{hkl}) \\ &= F_{hkl}^2 (\cos^2 \phi_{hkl} + \sin^2 \phi_{hkl}) \end{aligned}$$

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

Structure Factor

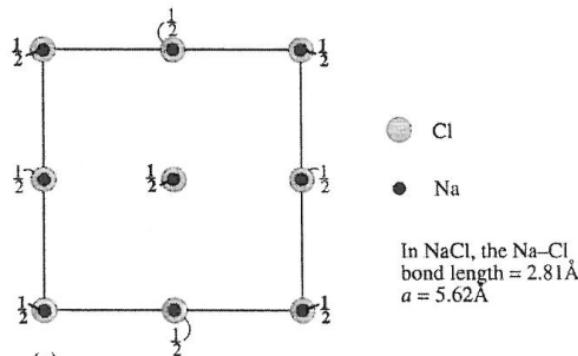
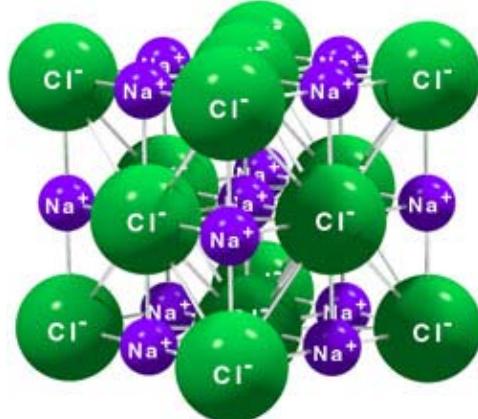
$$F_{hkl} = \sum_{j=1}^{j=n} f_j (\cos \phi_j + i \sin \phi_j)$$



Intensity

$$I_{hkl} \propto |F_{hkl}|^2 = F_{hkl} F_{hkl}^* = \left[\sum_{j=1}^{j=n} f_j \cos \phi_j \right]^2 + \left[\sum_{j=1}^{j=n} f_j \sin \phi_j \right]^2$$

Intensities in diffraction



F Lattice

Motif: Cl: 0,0,0; Na: 0,0,1/2

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

$$F_{hkl} = \sum_{j=1}^n f_j [\cos 2\pi(hx_j + ky_j + lz_j) + i \sin 2\pi(hx_j + ky_j + lz_j)]$$

Calculation of structure factor for the 331 reflection:

$$F_{hkl} = \sum_{j=1}^{j=n} f_j [\cos 2\pi(hx_j + ky_j + lz_j) + i \sin 2\pi(hx_j + ky_j + lz_j)]$$

$$F_{331} = 4f_{\text{Na}} [\cos 2\pi(3 \times 0 + 3 \times 0 + 1 \times \frac{1}{2}) + i \sin 2\pi(3 \times 0 + 3 \times 0 + 1 \times \frac{1}{2})]$$

$$+ 4f_{\text{Cl}} [\cos 2\pi(3 \times 0 + 3 \times 0 + 1 \times 0) + i \sin 2\pi(3 \times 0 + 3 \times 0 + 1 \times 0)]$$

$$= 4[f_{\text{Cl}} - f_{\text{Na}}]$$

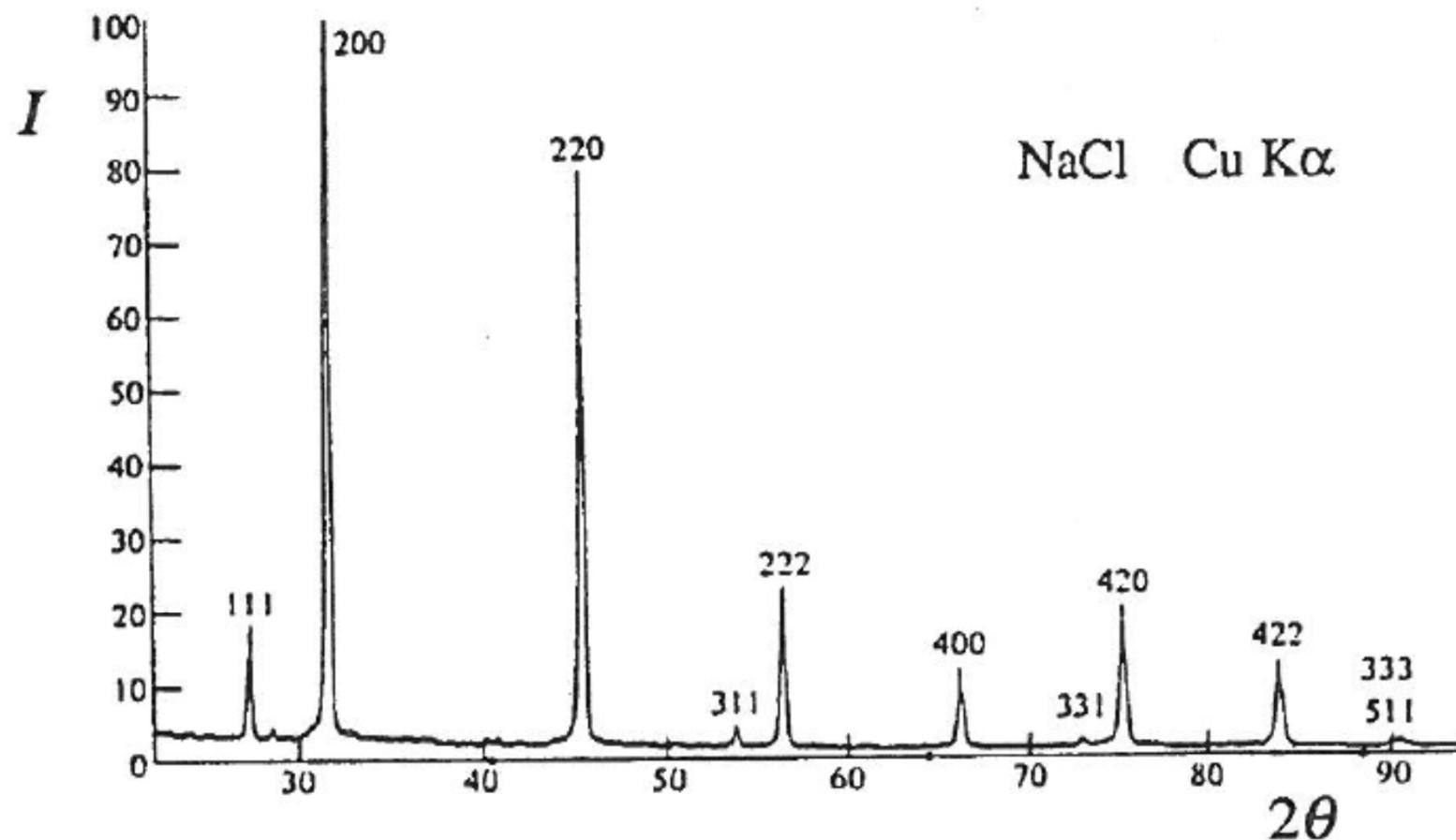
Multiplicity of 331 planes: $m_{331} = 24$

Calculation of intensity of 331 reflection:

$$I_{331} \propto G(\theta) \cdot m_{331} |F_{331}|^2 \propto 24 \times 16 [f_{\text{Cl}} - f_{\text{Na}}]^2$$

Intensities in diffraction

Experimental intensities in NaCl



Absences in diffraction patterns

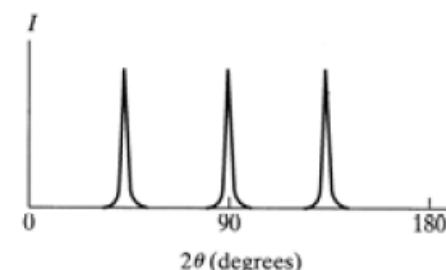
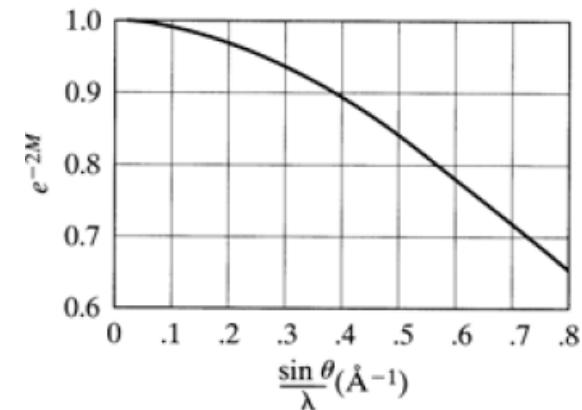
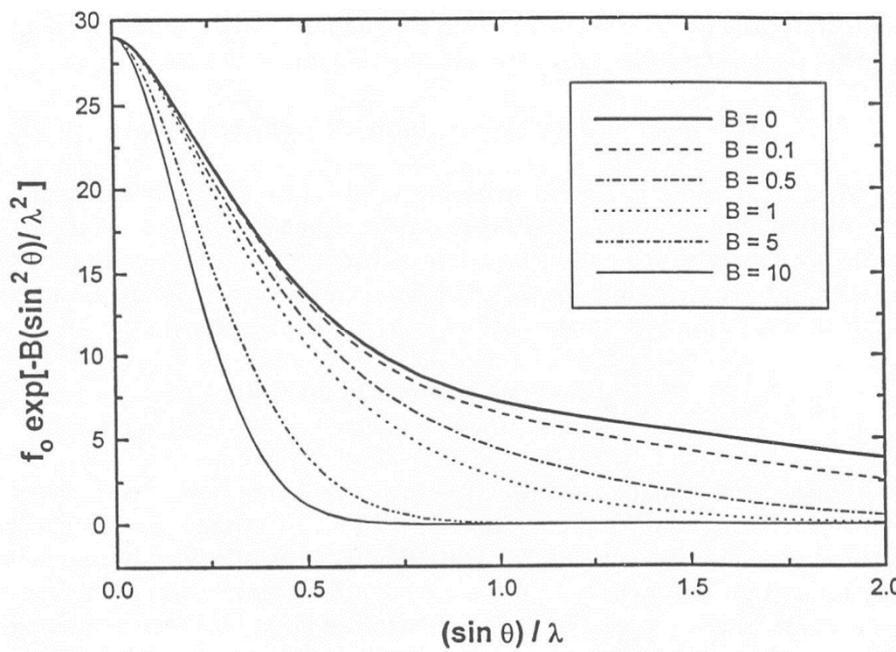
General rules for systematic absences due to lattice type (for all crystal systems)

Lattice	Restrictions on hkl
P	None
A	$(k + l)$ odd absent
B	$(h + l)$ odd absent
C	$(h + k)$ odd absent
I	$(h + k + l)$ odd absent
F	$h, k,$ and l not all odd or all even, absent

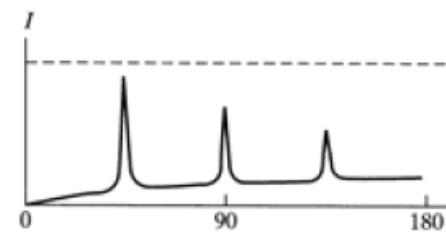
Warning: Some reflections may be missing for reasons not connected with lattice type. The opposite of systematic absence is not systematic presence!

Atomic Scattering Factors & DW

- The **atomic scattering factor** for X-ray decreases with the diffraction angle and is **proportional to the number of electrons**.
- The **temperature factor** (Debye-Waller, B) accelerates the decrease.



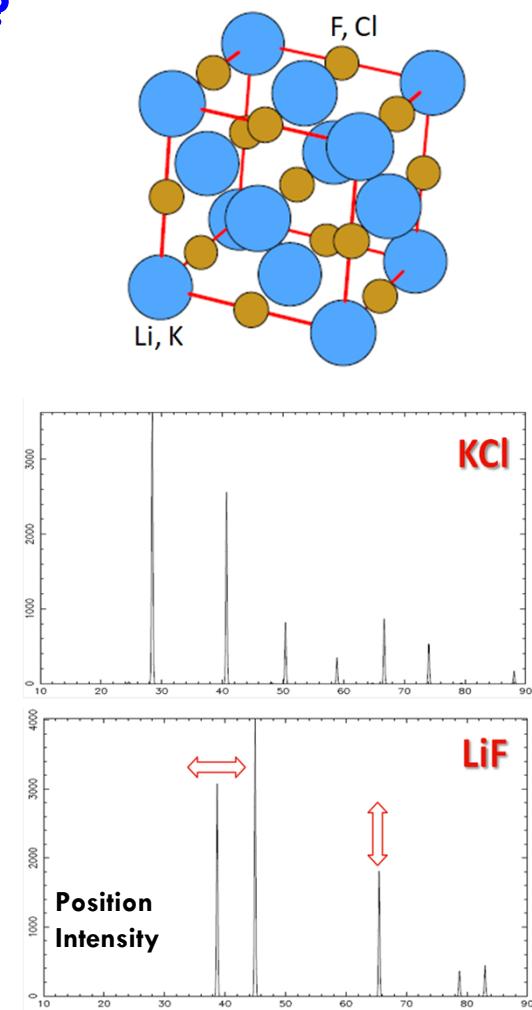
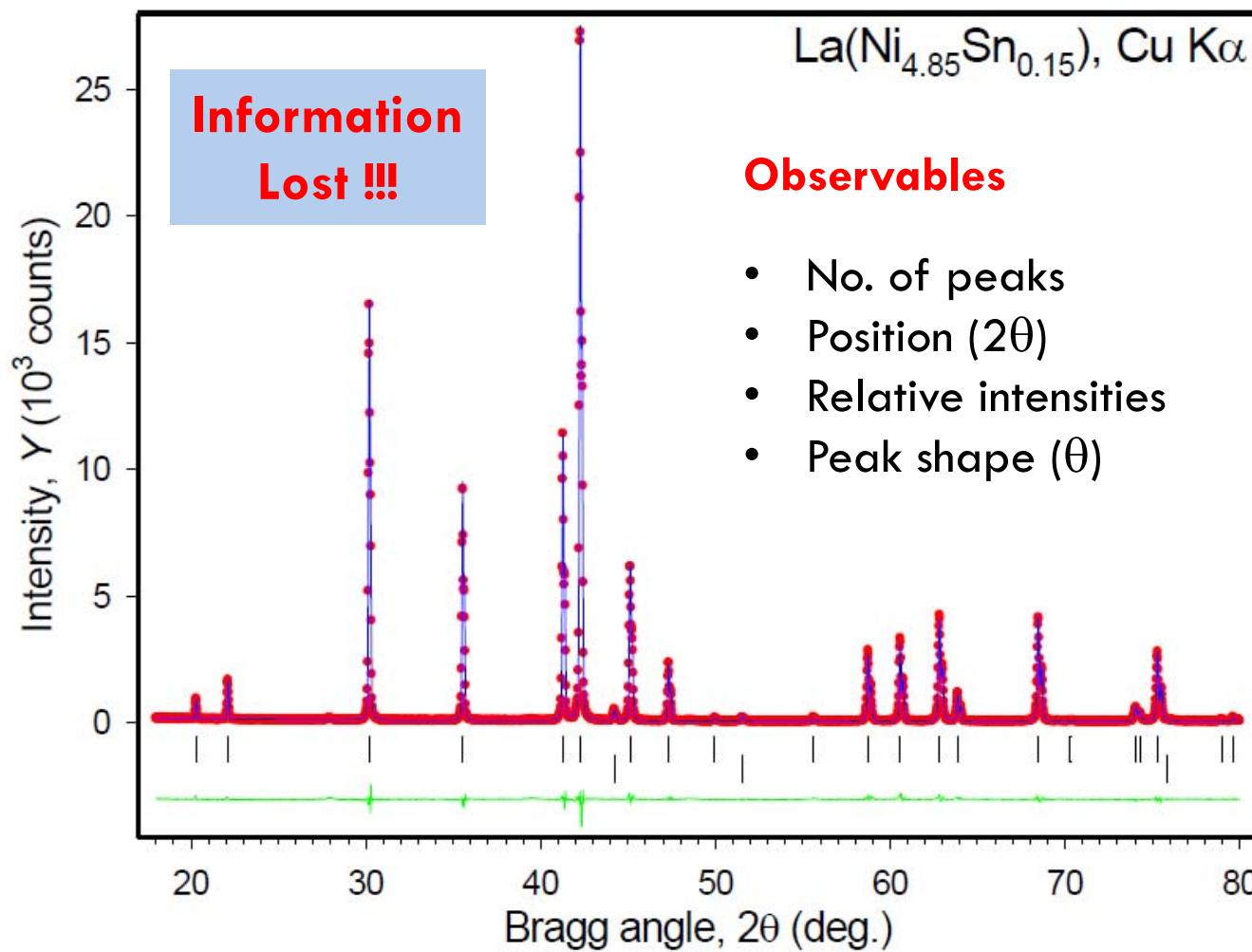
(a) No thermal vibration



(b) Thermal vibration

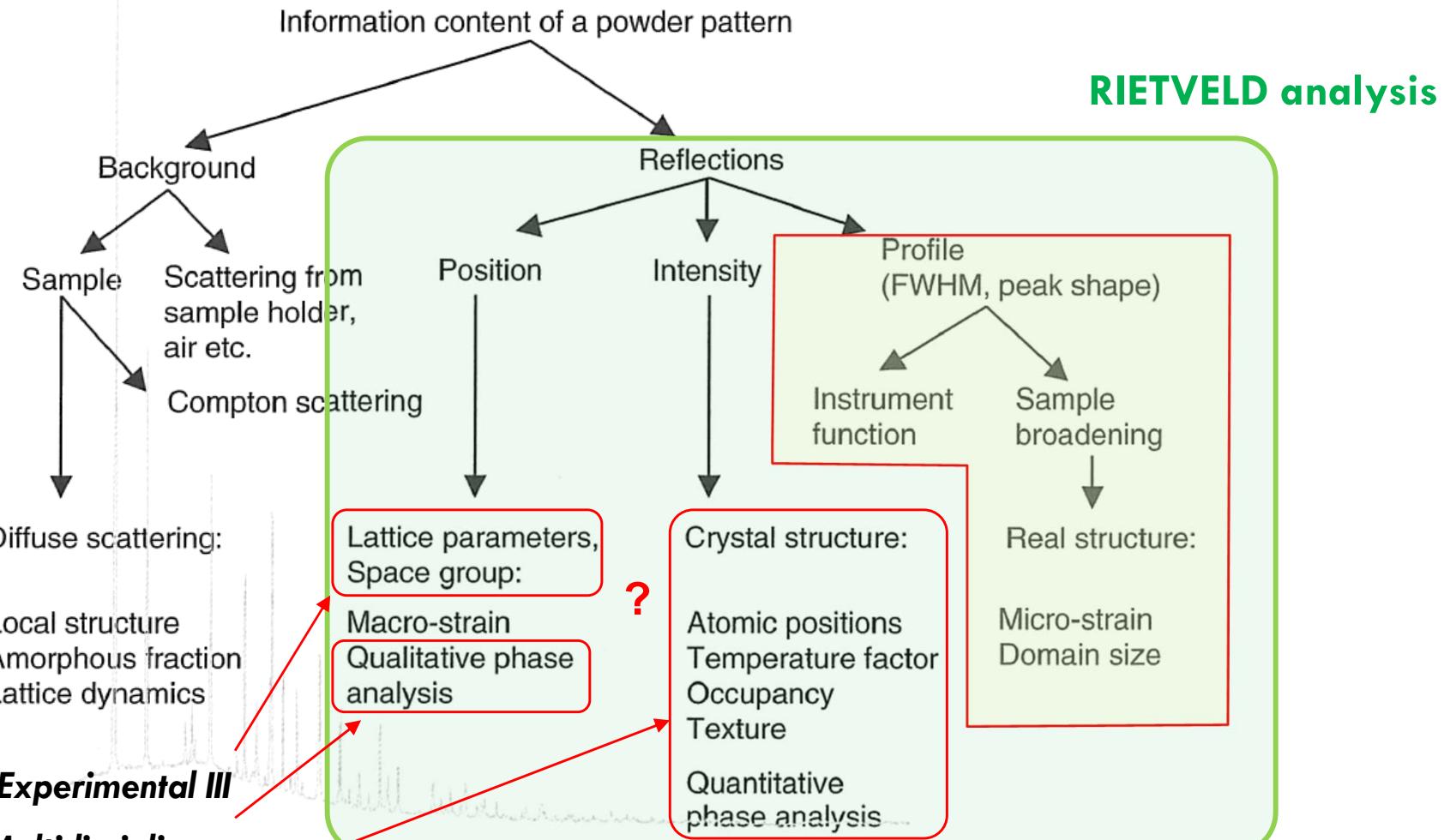
Information from powder XRD

What kind of information can be inferred from powder XRD?



Information from powder XRD

X-ray hitting condensed matter



Física Básica Experimental III

Laboratorio Multidisciplinar

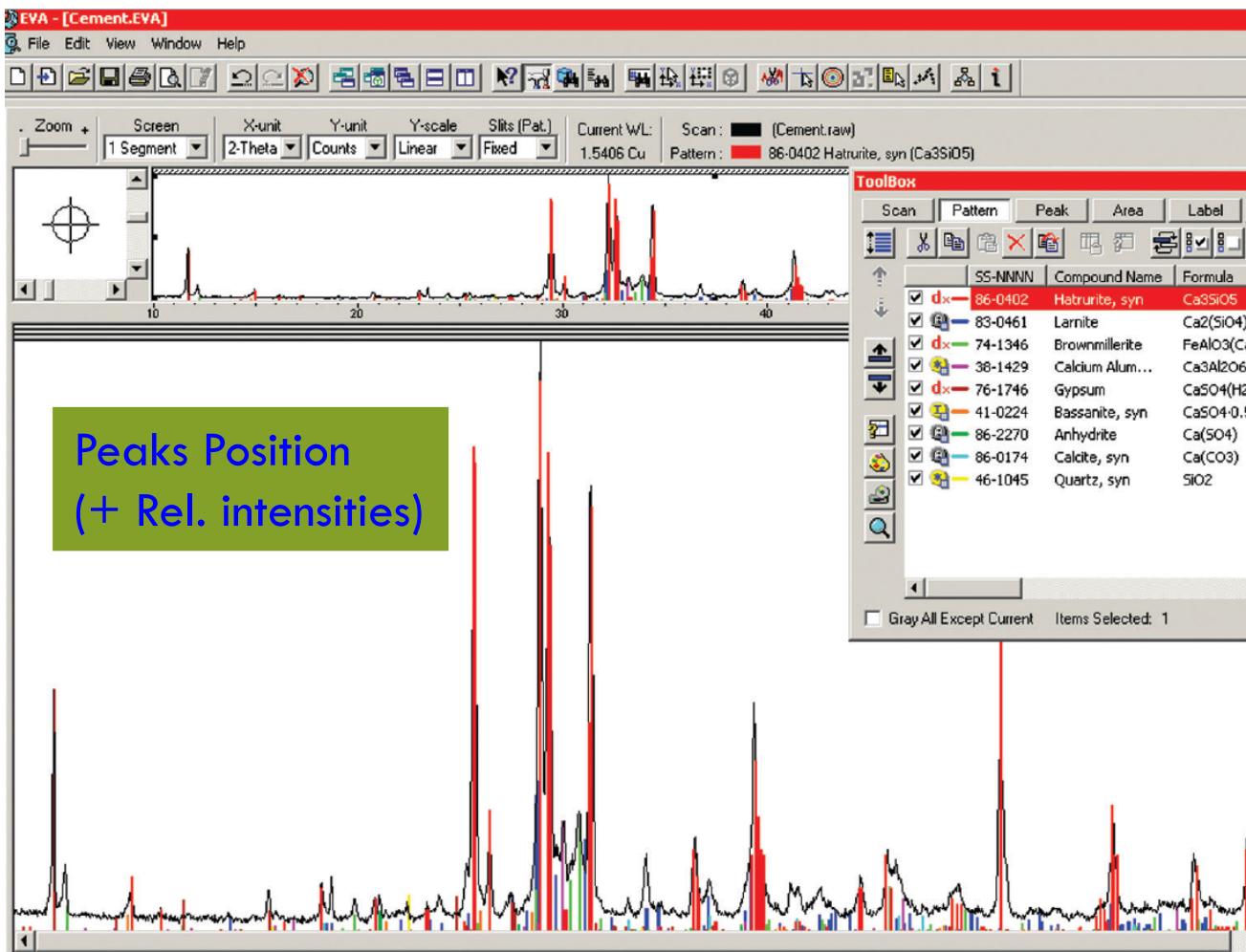
Laboratorio Física IV

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

$$F(\mathbf{h}) = \sum_{j=1}^n g^j t^j(s) f^j(s) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}^j)$$

What you have done so far

1st Course : Phase identification in natural samples (*Laboratorio multidisciplinar*)



Determination of known phases (e.g. quartz) in natural rock samples (local sand).



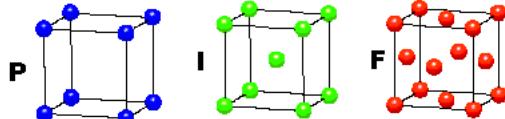
XRD as a probe for qualitative (or even quantitative) analysis.

What you have done so far

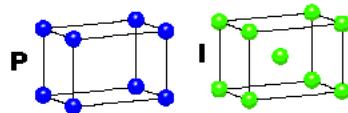
1st Course (*Física Básica Experimental 3*)

3rd Course (*F. Cuántica y Estr. de la Materia 2*)

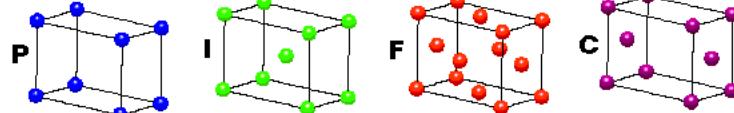
CUBIC
 $a=b=c$
 $\alpha=\beta=\gamma=90^\circ$



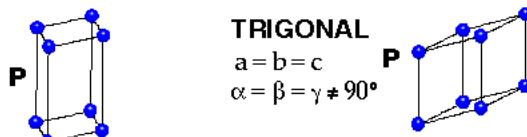
TETRAHEDRAL
 $a=b \neq c$
 $\alpha=\beta=\gamma=90^\circ$



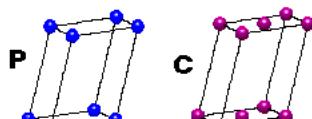
ORTHORHOMBIC
 $a \neq b \neq c$
 $\alpha=\beta=\gamma=90^\circ$



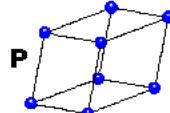
HEXAGONAL
 $a=b \neq c$
 $\alpha=\beta=90^\circ$
 $\gamma=120^\circ$



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

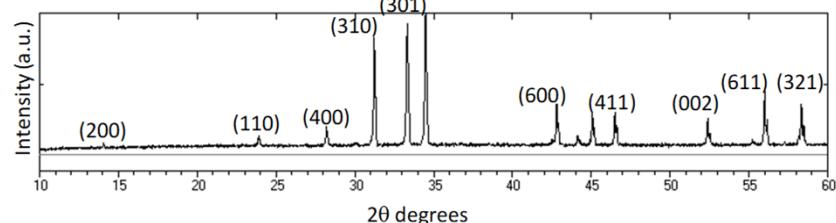
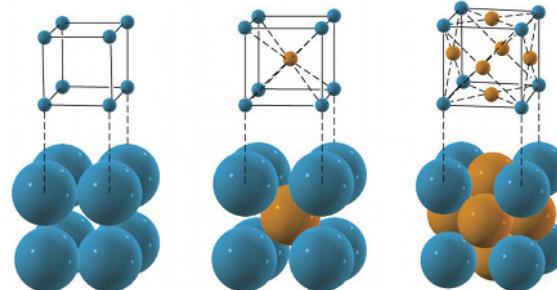


TRICLINIC
 $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$



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

Simple (cubic) structures

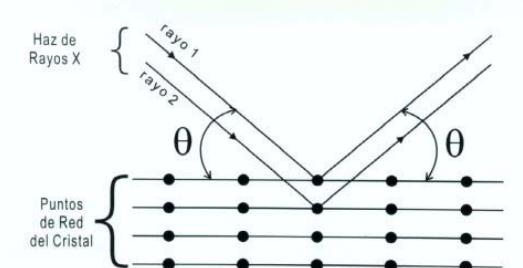


n	$2\theta(^{\circ})$	$\sin^2\theta(^{\circ})$	$\sin^2\theta_n/\sin^2\theta_1$	$3(\sin^2\theta_n/\sin^2\theta_1)$	N	hkl
1	28.35	0.0600	1	3	3	111
2	32.68	0.0800	1.333	3.999	4	200
3	47.13	0.1598	2.663	7.989	8	220
4	55.91	0.2198	3.663	10.989	11	311
5	58.61	0.2396	3.993	11.979	12	222
6	68.86	0.3197	5.328	15.984	16	400
7	76.07	0.3796	6.327	18.981	19	331
8	78.39	0.3994	6.657	19.971	20	420
9	87.62	0.4792	7.987	23.961	24	422

Information from powder XRD

Component	Structure	Property	Parameters
Peak Position	Cell Parameters (a, b, c, α , β , γ)	Absorption Porosity	Wavelength Alignment Diff. Geometry
Intensity	Atomic coordinates (x, y, z, B's, etc.)	P.O. Absorption Porosity	Lorentz, Polarization Geometry
Peak Shape	Crystallinity Disorder Defects	Grain Size <i>Strain</i> <i>Stress</i>	Radiation (purity) Geometry Beam condition

Peak Position (Bragg's Law)



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

$$I_{hkl} = K \times p_{hkl} \times L_\theta \times P_\theta \times A_\theta \times T_{hkl} \times E_{hkl} \times |F_{hkl}|^2$$

K: Scale Factor

P_{hkl} : Multiplicity

L_θ : Lorentz Factor

P_θ : Polarization

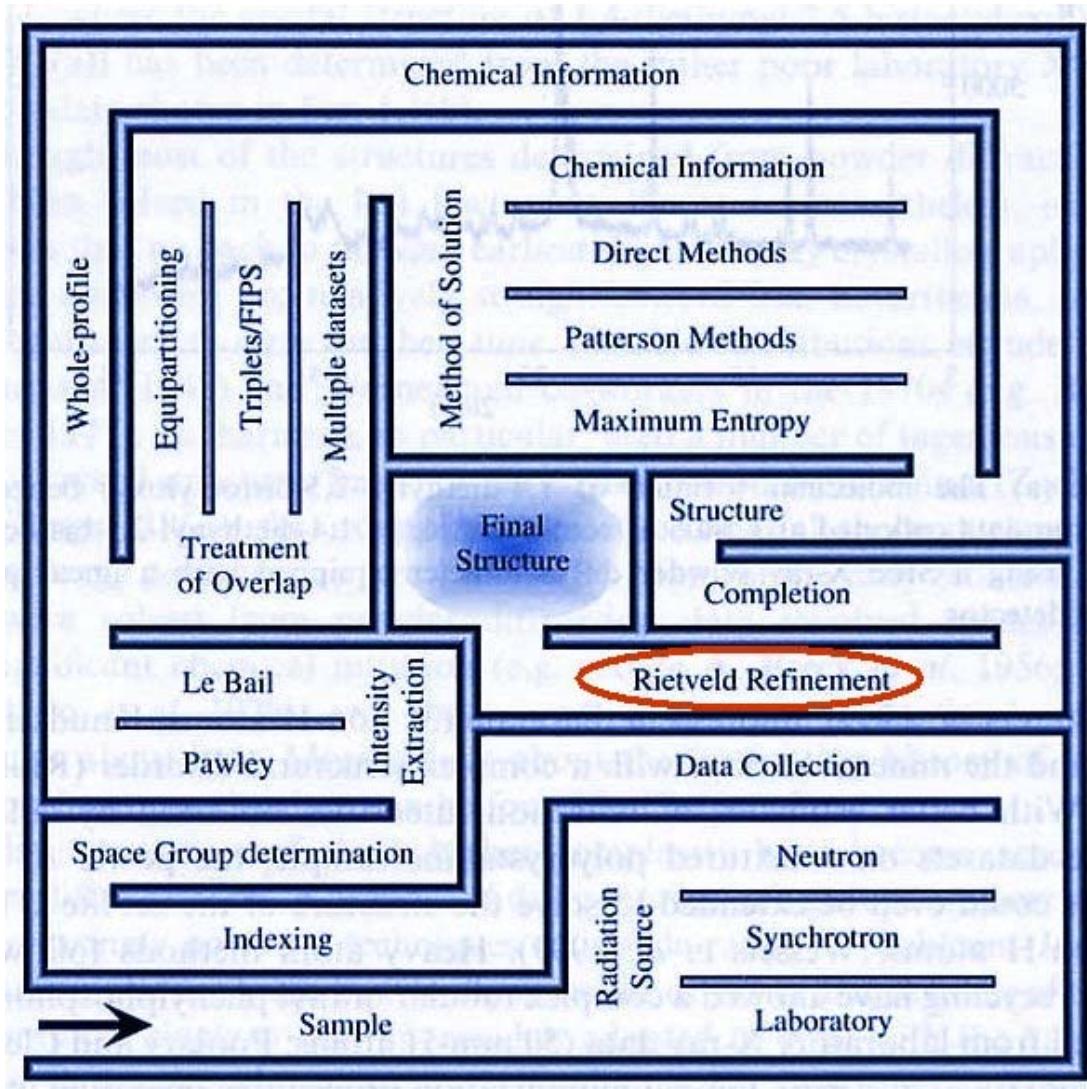
A_θ : Absorption

T_{hkl} : Preferred Orientation

E_{hkl} : Extinction factor

F_{hkl} : Structure Factor → Crystal Structure

Information from powder XRD



Structural solution stages from powder XRD (from scratch)

- Indexing. Space Group
- Intensity extraction:
 - Pawley
 - Le Bail
- Solution methods (several)
- Rietveld refinement

Experimental Tools: Diffraction

***Types of conventional
diffraction techniques for
structural analysis***

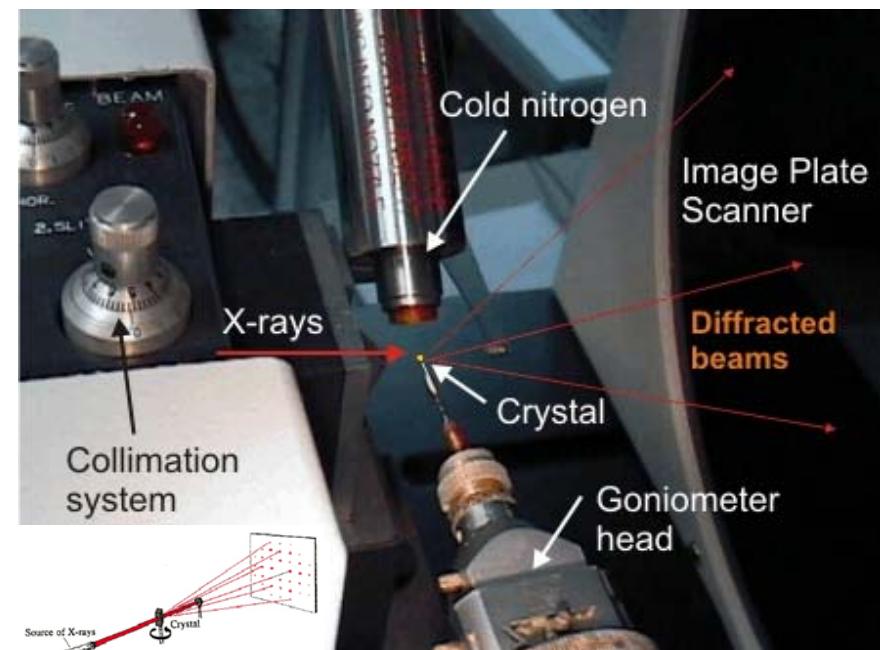
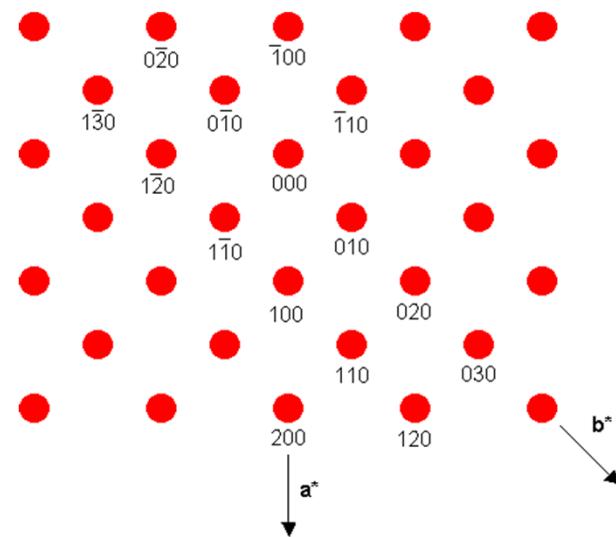
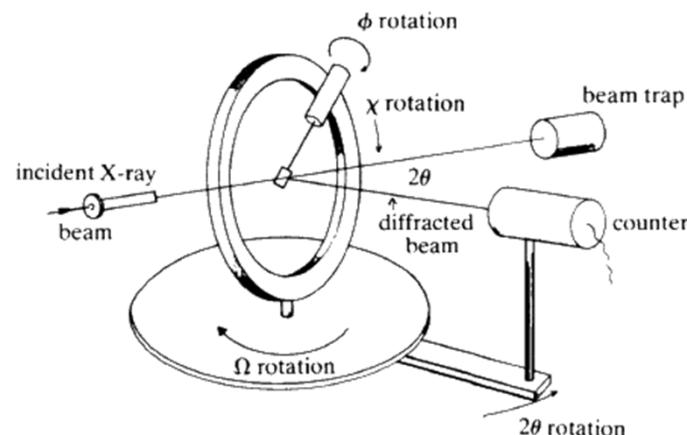
- Powder (polycrystalline samples)
 - Neutron Powder Diffraction (NPD)
 - X-ray diffraction (XRD)
 - Electron diffraction (ED)
- Single Crystal (All sources)

- Full determination of atomic structures
- Refinement of some structural parameters (lattice, atomic positions,...)
- Extra information (thermal parameters, particle size, strain...)

Information to be obtained from experiments

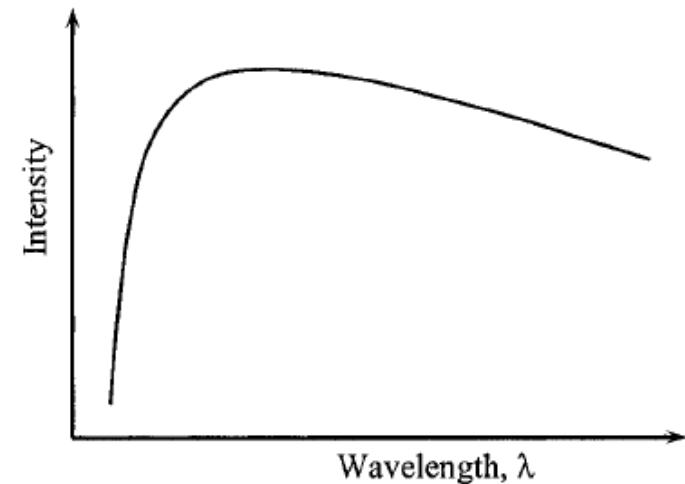
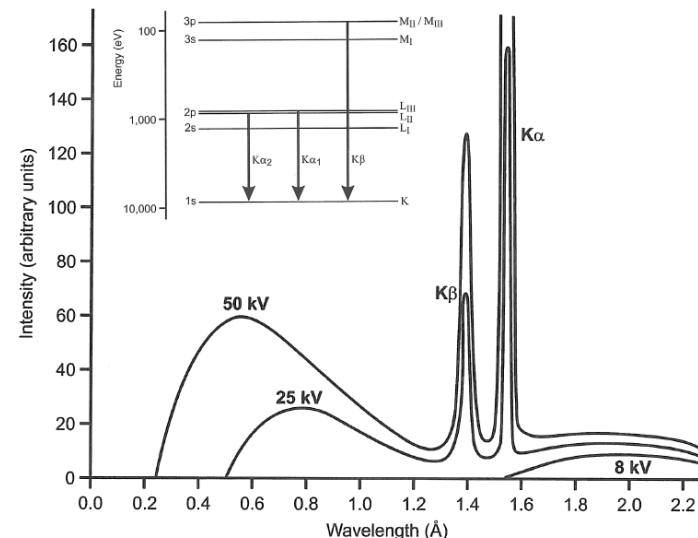
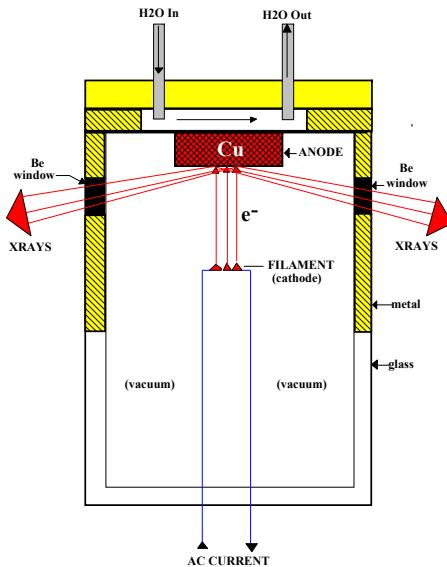
Experimental Tools: Diffraction

Single Crystal diffraction allows Full Structural Characterization



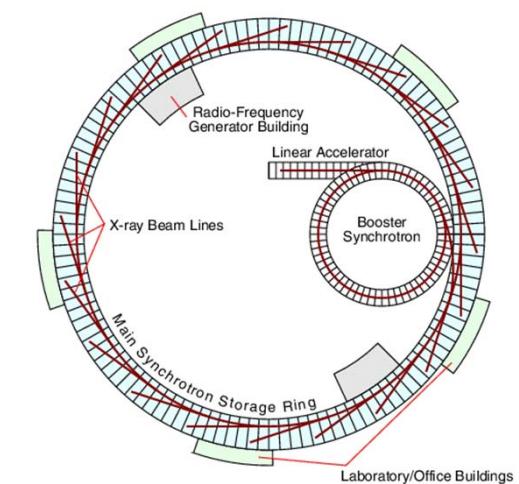
How to measure: Diffractometry

X-ray elements: Sources

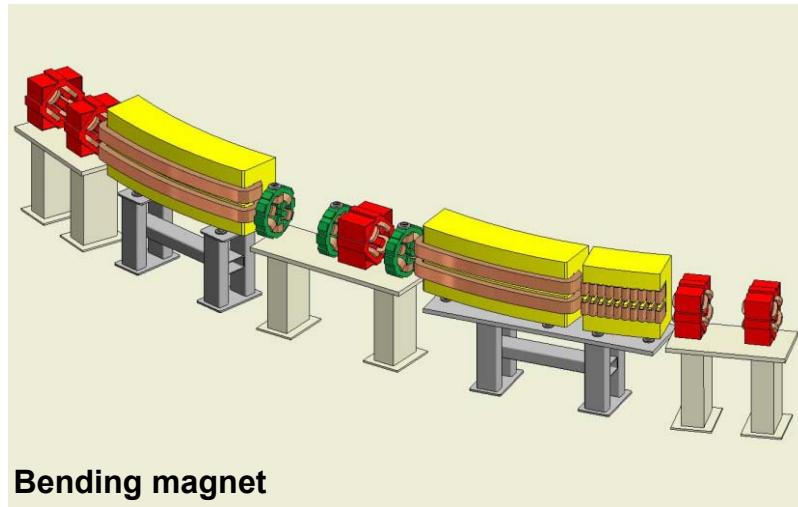


Metal	Wavelength (\AA)				β	K-absorption edge, (\AA)
	$K\alpha^a$	$K\alpha_1$	$K\alpha_2$	$K\beta$	filter	
Cr	2.29105	2.28975(3)	2.293652(2)	2.08491(3)	V	2.26921(2)
Fe	1.93739	1.93608(1)	1.94002(1)	1.75664(3)	Mn	1.896459(6)
Co	1.79030	1.78900(1)	1.79289(1)	1.62082(3)	Fe	1.743617(5)
Cu	1.54187	1.5405929(5)	1.54441(2)	1.39225(1)	Ni	1.488140(4)
Mo	0.71075	0.7093171(4)	0.71361(1)	0.63230(1)	Nb	0.653134(1)
					Zr	0.688959(3)

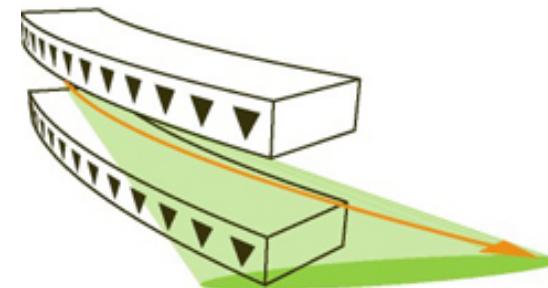
^a The weighted average value, calculated as $\lambda_{\text{average}} = (2\lambda_{K\alpha_1} + \lambda_{K\alpha_2})/3$.



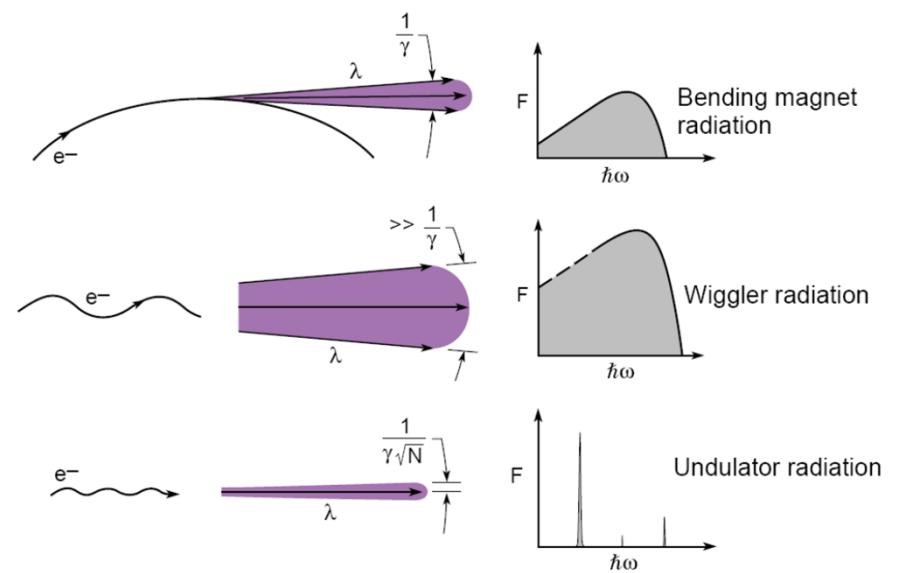
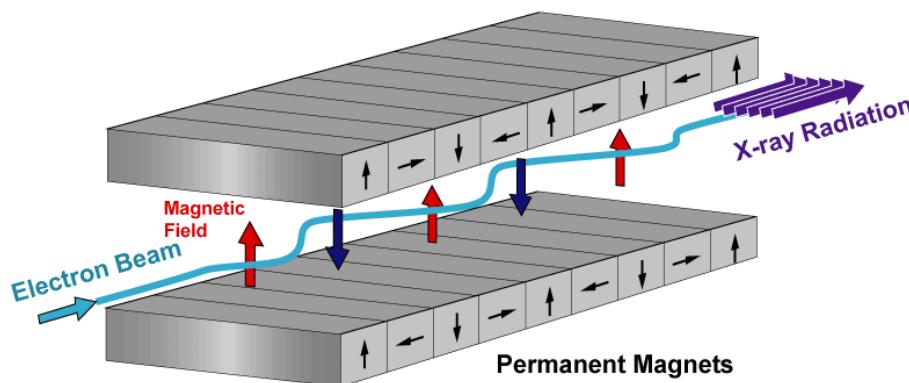
Synchrotron sources



Bending magnet

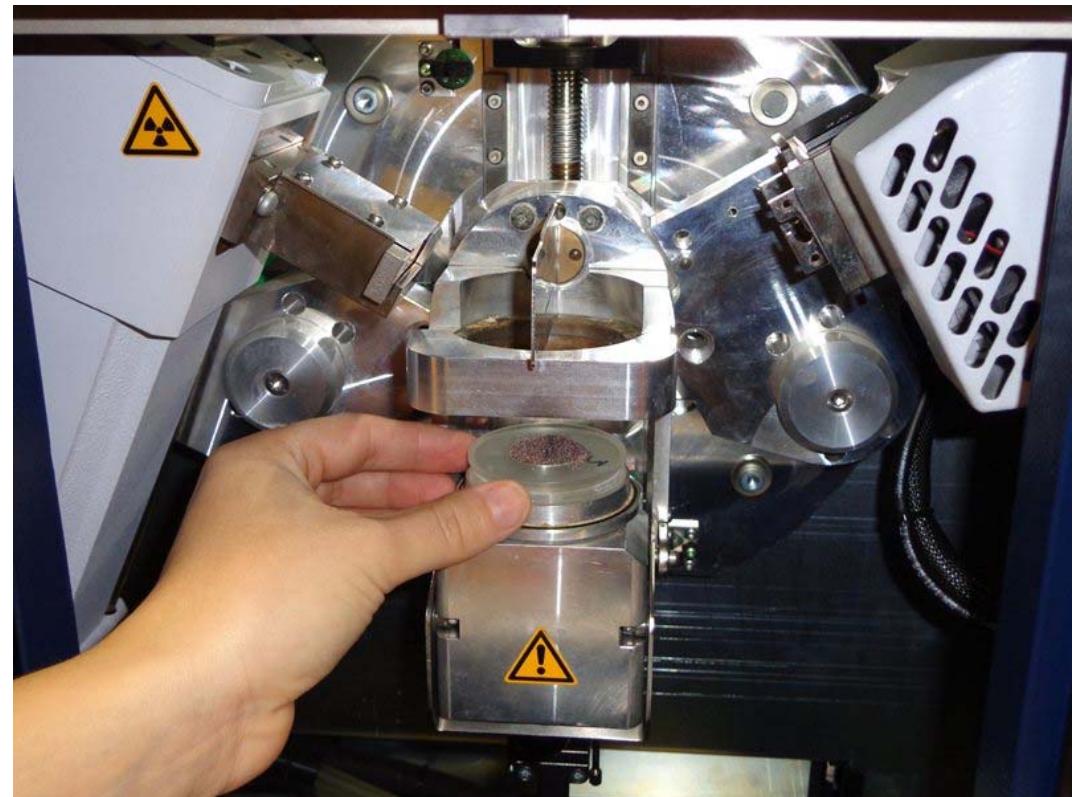
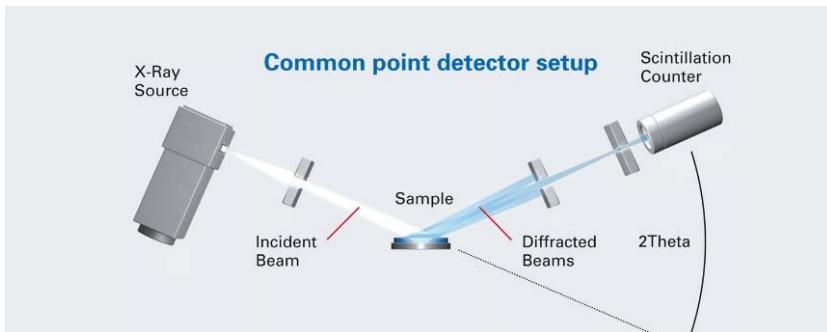


Undulator



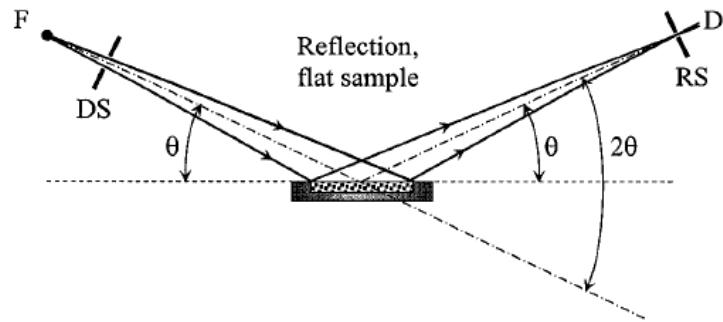
How to measure: Diffractometry

The experimental equipment: Bruker D2 Phaser



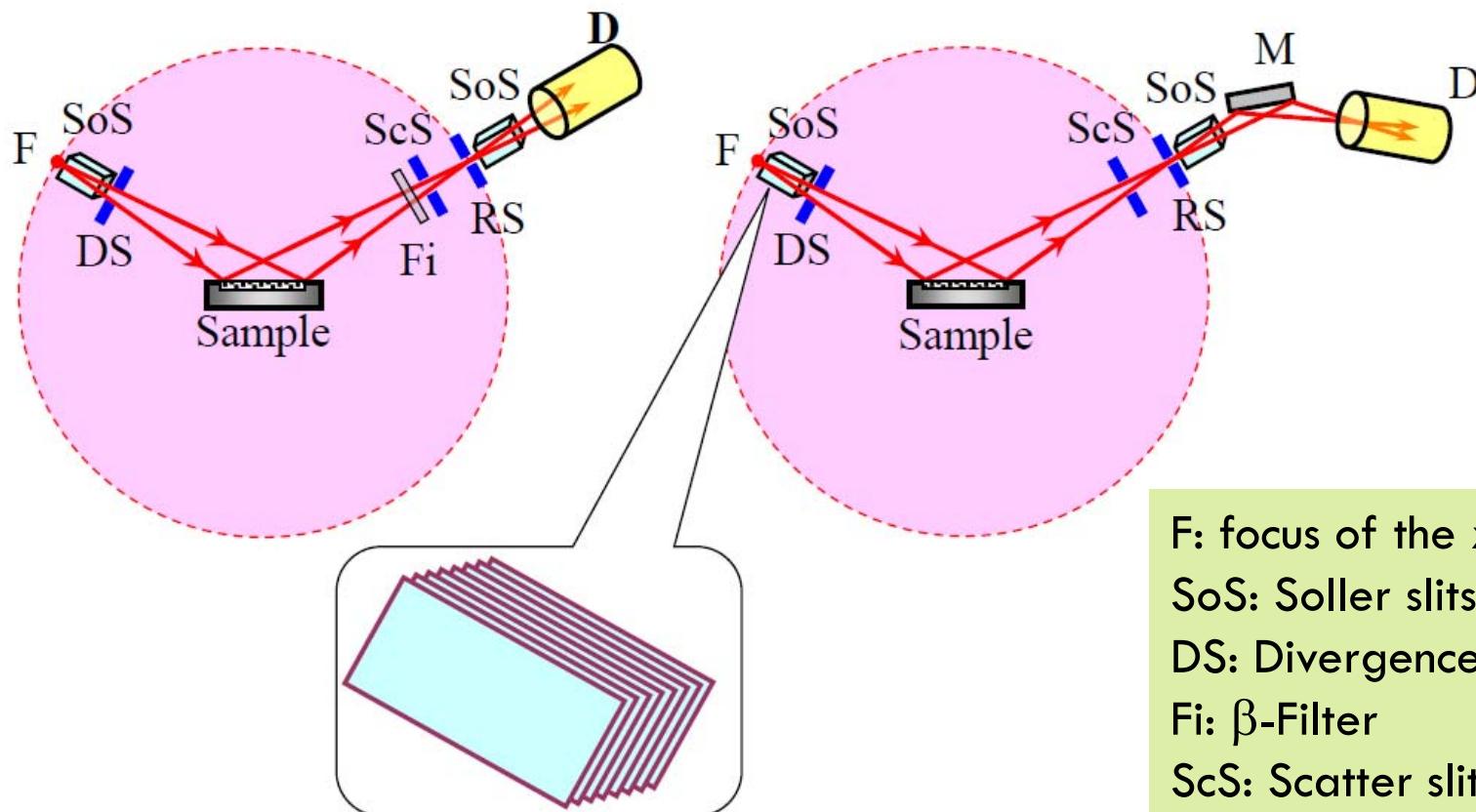
How to measure: Diffractometry

The experimental equipment: Bruker D8 Advance



How to measure: Diffractometry

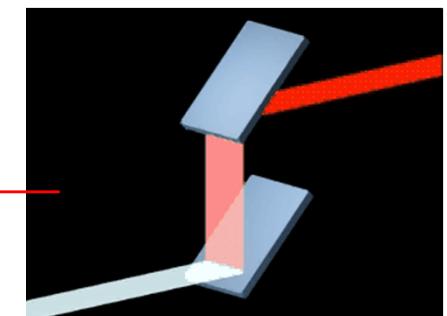
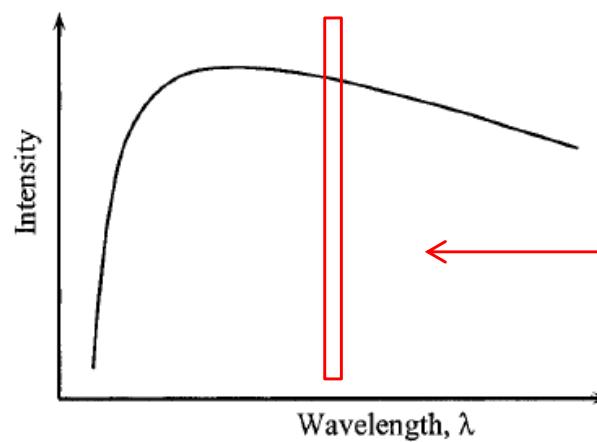
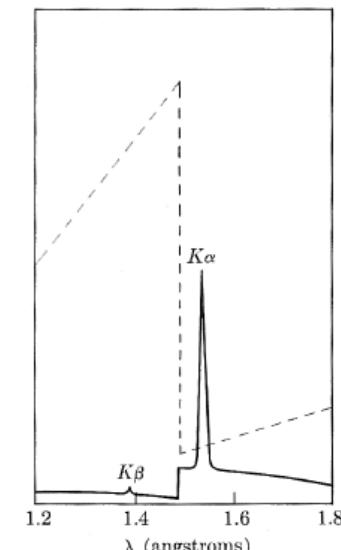
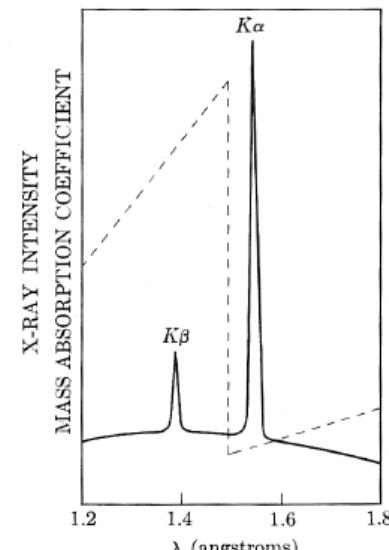
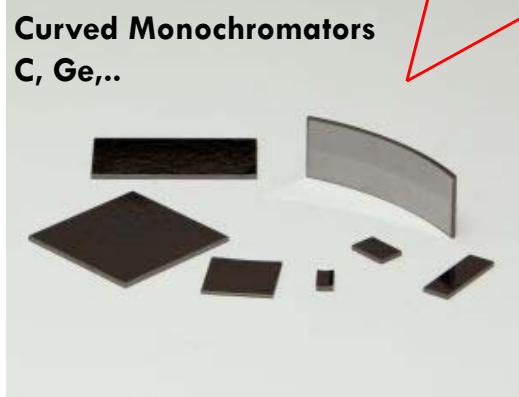
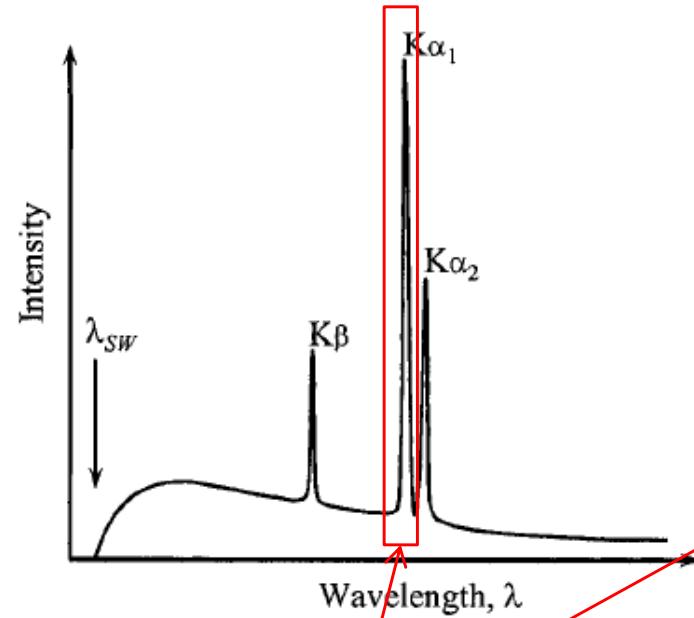
Typical focusing optics in modern diffractometers



F: focus of the x-ray source
SoS: Soller slits
DS: Divergence slit
Fi: β -Filter
ScS: Scatter slit (optional)
RS: Receiving slit
M: Monochromator
D: Detector

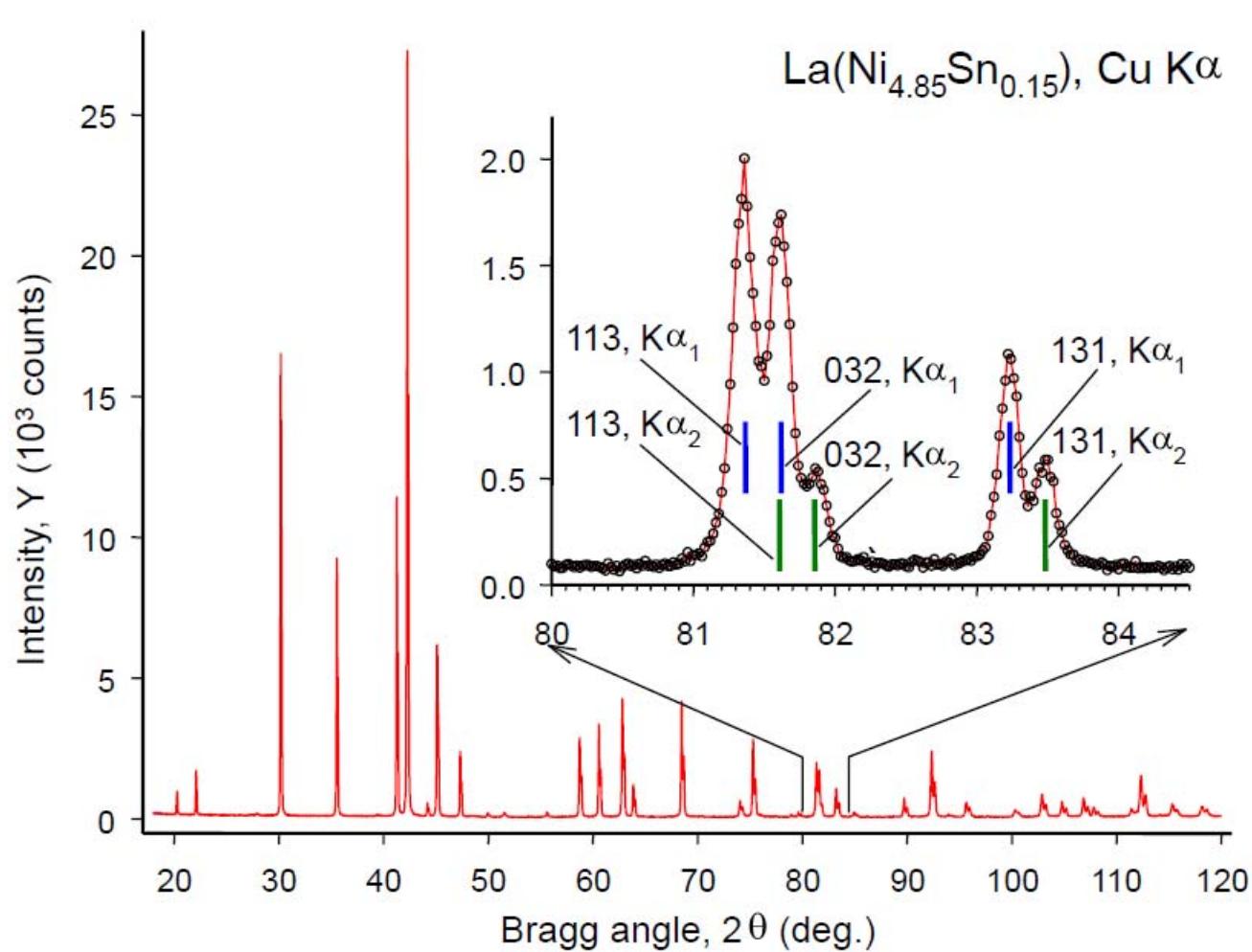
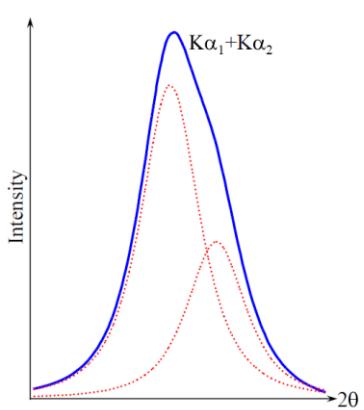
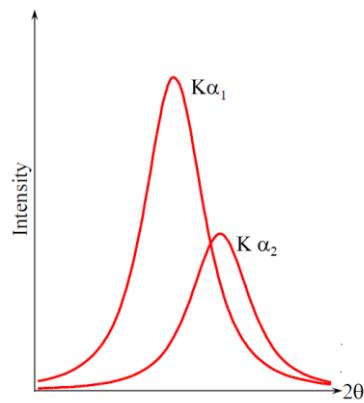
How to measure: Diffractometry

Optical devices: Monochromators



How to measure: Diffractometry

Copper Sources : $K\alpha_1 + K\alpha_2$ components



How to measure: Diffractometry

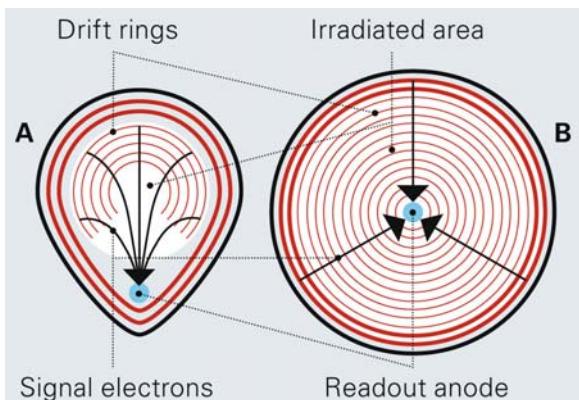
Detectors for conventional diffractometers

Table 2.5. Selected characteristics of the most common detectors using Cu K α radiation.

Detector \ Property	Linearity loss at 40,000 cps ^a	Proportionality	Resolution for Cu K α	Energy per event (eV)	No. of events ^b
Scintillation	<1%	Very good	45%	350	23
Proportional	<5%	Good, but fails at high photon flux	14%	26	310
Solid-state	Up to 50%	Pileup in mid-range	2%	3.7	2200

^a cps – counts per second.

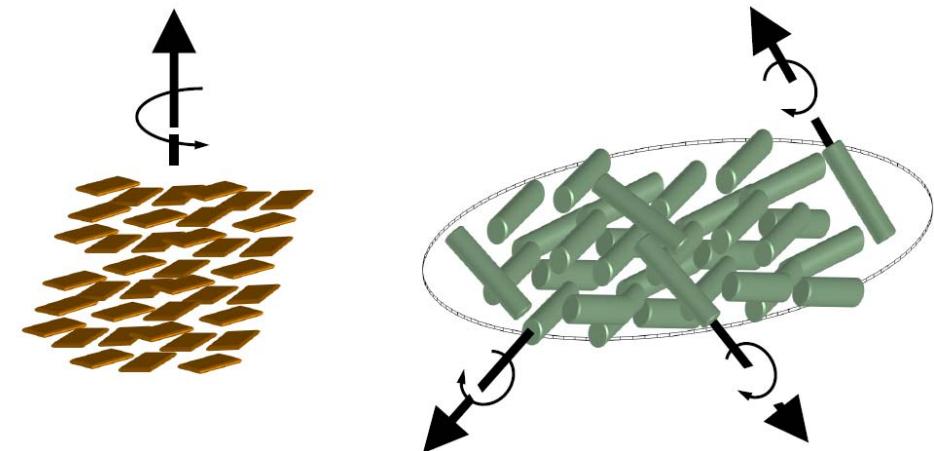
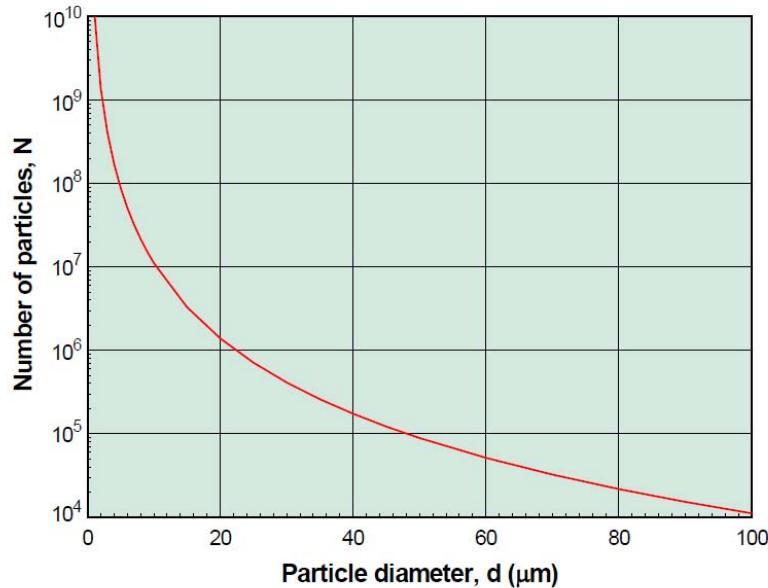
^b Approximate number of ion pairs or visible light photons resulting from a single x-ray photon assuming Cu K α radiation with photon energy of about 8 keV.



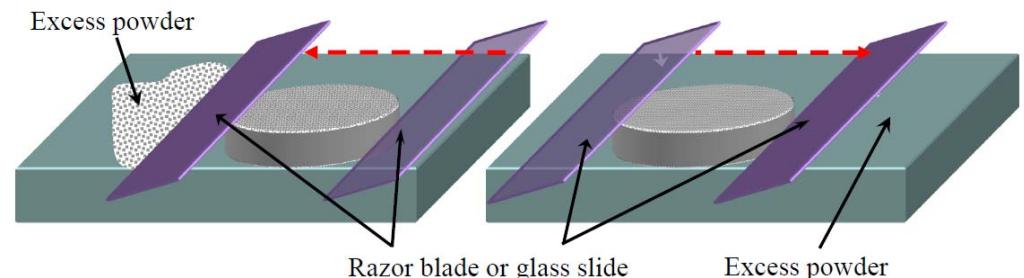
Specifications	
Detector type	XFlash Silicon Drift Detector maintenance-free
Active window size	30 mm ²
Energy resolution	<180 eV (CuK α) at 100,000 cps
Cooling	Electrical Peltier cooling
Maximum count rate	1,000,000 cps
Elemental range	K to Hf (~3 to 20 keV)
Operational conditions	Temperature: 0°C - 35°C Humidity: max. 90% rel. H.

How to measure: Diffractometry

Sample Preparation

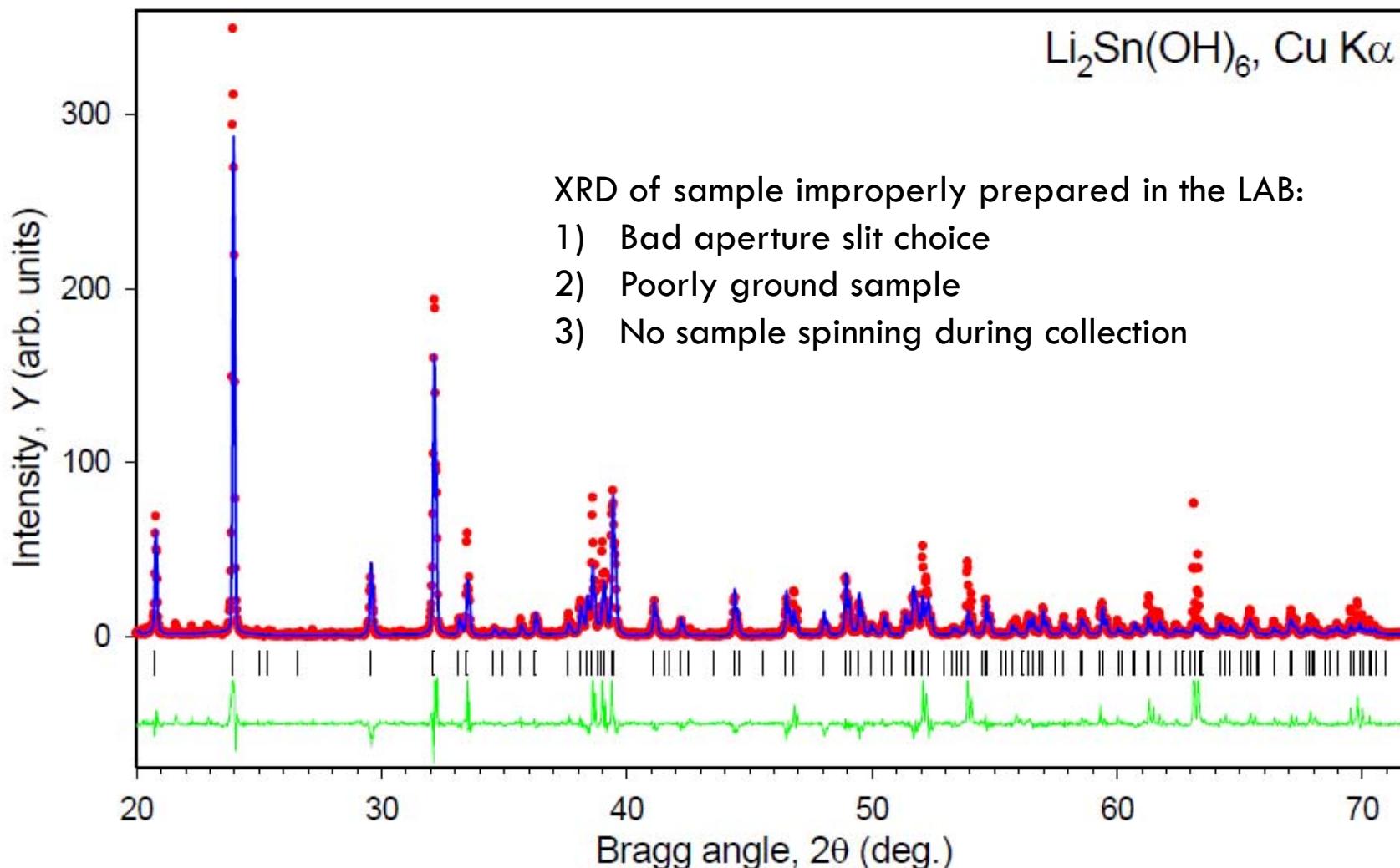


Sample needs to be carefully prepared for powder diffraction. Number of particles and homogeneous size are to be controlled by grinding



How to measure: Diffractometry

Sample Preparation



Software for powder XRD analysis

- **Fullprof suite**

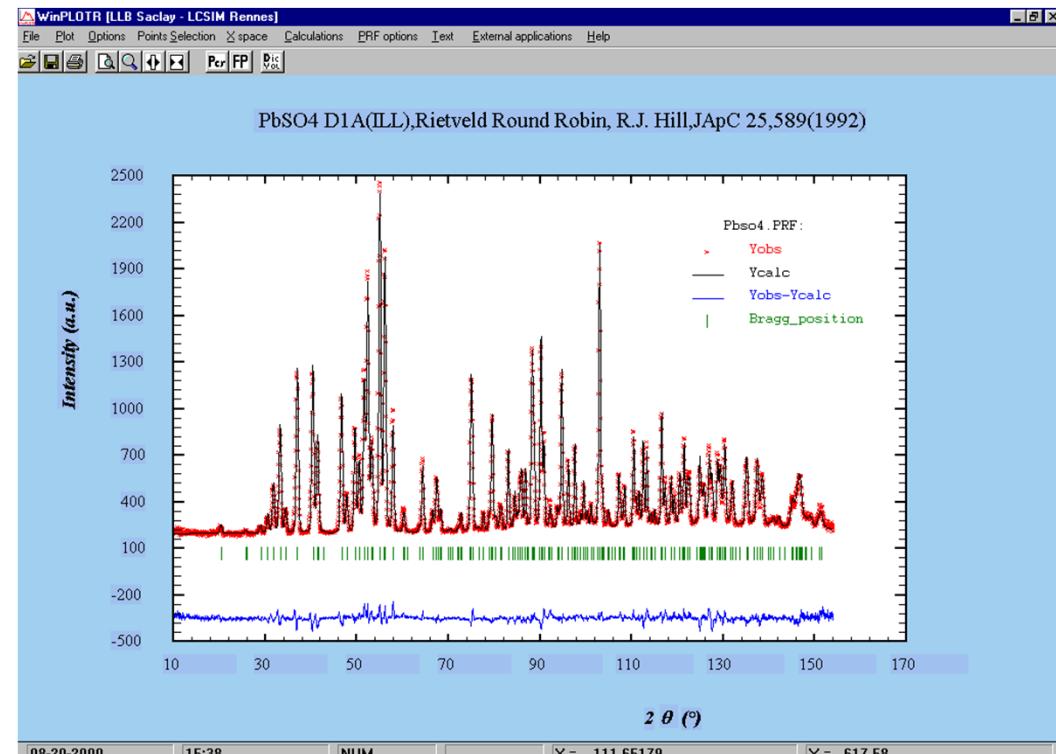
- Designed for PND data
- Many associated programs
- Difficult to input data (text)
- Not easy convergence (crashes)

- **GSAS**

- Widespread
- Consistent and friendly (GUI)
- Some features only in text mode
- Not as many features as others

- **TOPAS**

- Very user friendly
- Very consistent, powerful and fast
- Advanced features only in text mode
- Not free (commercial and academic)

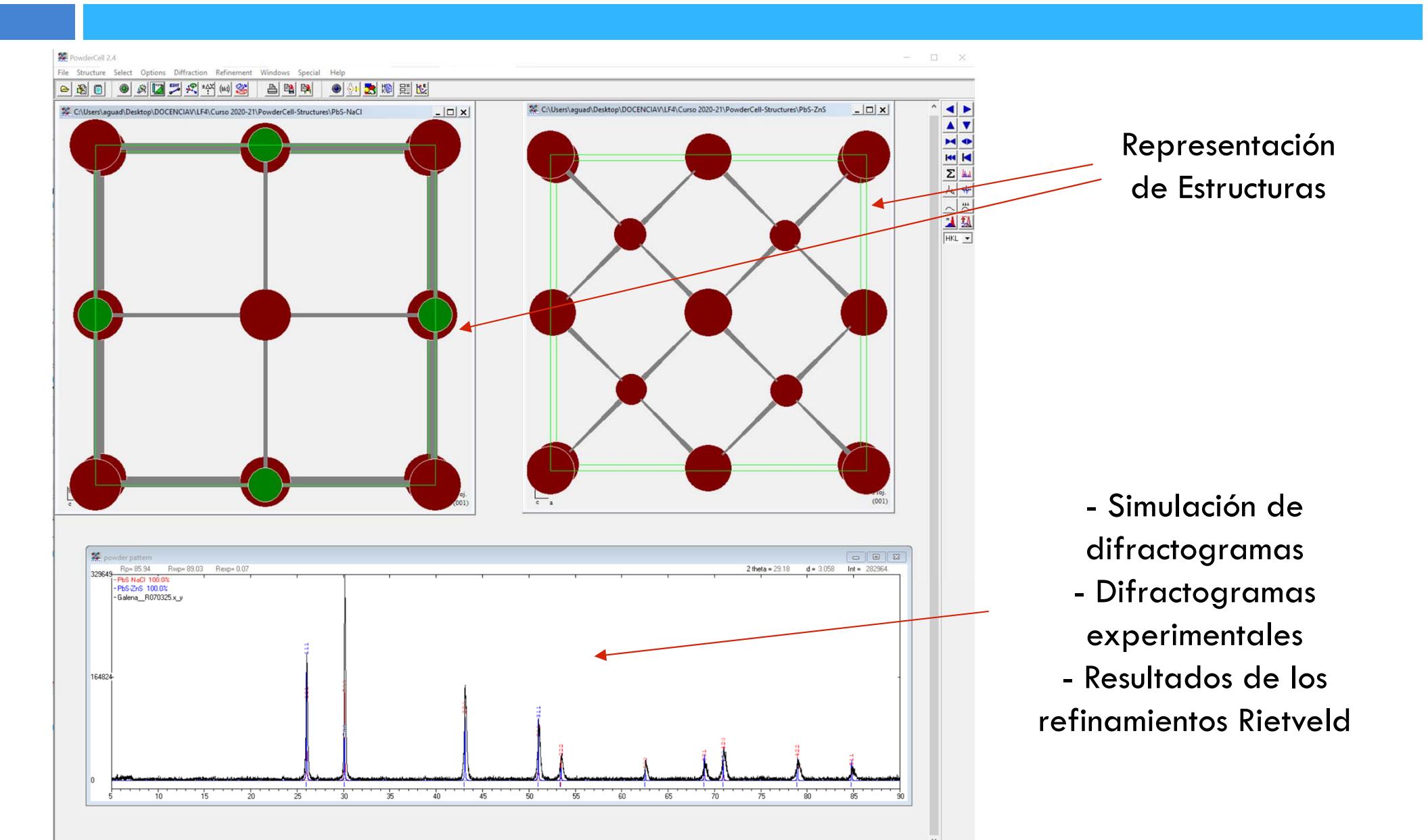


Fullprof graphic interface (Winplotr)

- **PowderCell**
- **Other Choices**

http://www.ccp14.ac.uk/solution/rietveld_software/index.html

PowderCell



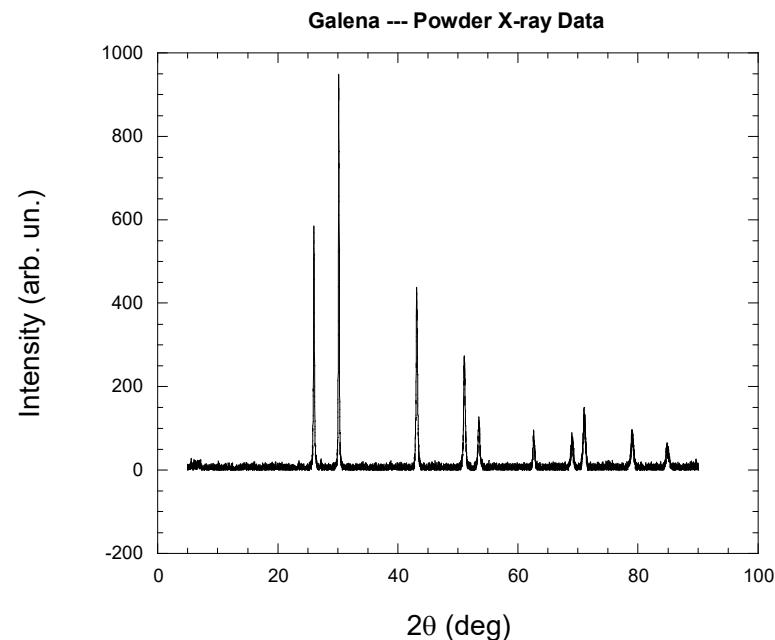


First task: Structural analysis of PbS



Objectives:

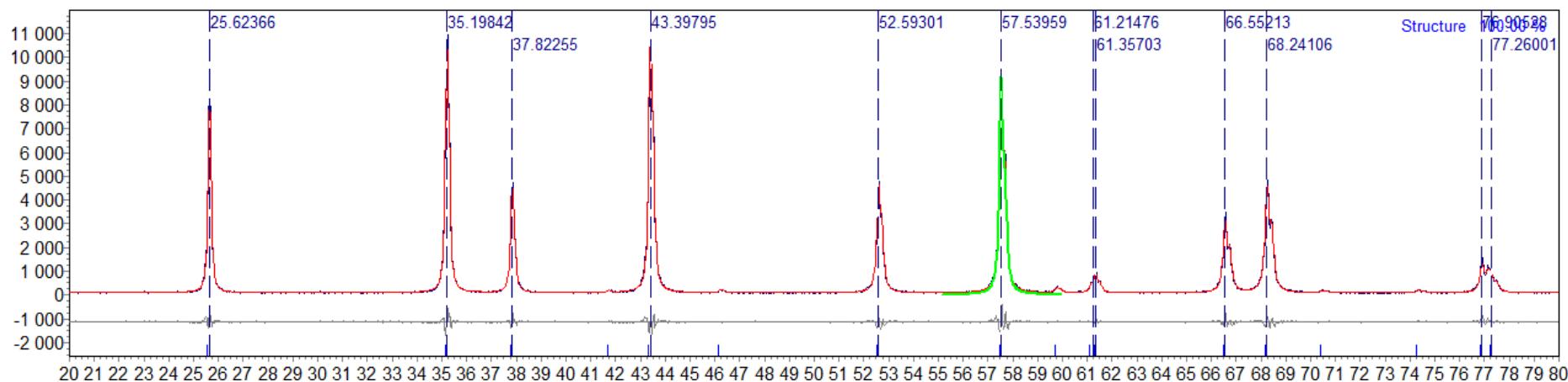
- To index the diffraction pattern of Galena sample (PbS) using *PowderCell* software for peak analysis when required.
- To determine the Lattice type (P, I or F) observing the systematic absences.
- To calculate the lattice constant using the methods you learned in previous courses.
- To determine the lattice type calculating different peak intensities.
- To get familiar with *PowderCell* software for structure and pattern analyses.
- To perform simple simulations and Rietveld refinements



Second task: Introduction to Rietveld

Objectives:

- To perform similar structural studies using *PowderCell* on some other samples of high symmetry: NaCl, ZnS or CsCl types.
- To discuss possible approaches for full structural solutions. Phase problem.
- To perform structural refinements of some samples, cubic and other low symmetry phases, working with structural (atomic positions and thermal parameters) as well as instrumental parameters.
- Introduction to indexing powder patterns. Different choices



Pattern indexing...

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

Cubic Structure

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

#p	2θ(°)	sin²θ(°)	sin²θ _n /sin²θ ₁
1	26.05	0.0508	1
2	30.14	0.0676	1.331
3	43.13	0.1351	2.660
4	51.05	0.1857	3.655
5	53.53	0.2028	3.993
6	62.62	0.2701	5.317
7	68.96	0.3205	6.310
8	71.02	0.3374	6.642
9	79.05	0.4050	7.974

Pattern indexing...

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

Cubic Structure

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

#p	2θ(°)	sin²θ(°)	sin²θ _n /sin²θ ₁	3(sin²θ _n /sin²θ ₁)	N
1	26.05	0.0508	1	3	3
2	30.14	0.0676	1.331	3.99	4
3	43.13	0.1351	2.660	7.98	8
4	51.05	0.1857	3.655	10.97	11
5	53.53	0.2028	3.993	11.98	12
6	62.62	0.2701	5.317	15.95	16
7	68.96	0.3205	6.310	18.93	19
8	71.02	0.3374	6.642	19.93	20
9	79.05	0.4050	7.974	23.92	24

Pattern indexing...

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

Cubic Structure

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

#p	2θ(°)	sin²θ(°)	sin²θ _n /sin²θ ₁	3(sin²θ _n /sin²θ ₁)	N	hkl
1	26.05	0.0508	1	3	3	(111)
2	30.14	0.0676	1.331	3.99	4	(200)
3	43.13	0.1351	2.660	7.98	8	(220)
4	51.05	0.1857	3.655	10.97	11	(311)
5	53.53	0.2028	3.993	11.98	12	(222)
6	62.62	0.2701	5.317	15.95	16	(400)
7	68.96	0.3205	6.310	18.93	19	(331)
8	71.02	0.3374	6.642	19.93	20	(420)
9	79.05	0.4050	7.974	23.92	24	(422)

Indexing all structures

n	symmetry	$Q(kh\bar{l};ABCDEF)$	short	relation to a, c, b
:1	<i>cubic</i>	$q^2 = [h^2+k^2+l^2].A$	$Q = [M^2].A$	$a = (2\pi)/\sqrt{A};$
:2:	<i>tetragonal</i> :	$q^2 = [h^2+k^2].A + [l^2].C$	$Q = [HK].A + [L^2].C$	$a = (2\pi)/\sqrt{A}; c = (2\pi)/\sqrt{C}$
:2:	<i>hexagonal</i> :	$q^2 = [h^2+k^2+h.k].A + [l^2].C$	$Q = [HK].A + [L^2].C$	$a = (4\pi)/\sqrt{(3A)}; c = (2\pi)/\sqrt{C}$
:3:	<i>orthorhombic</i> :	$q^2 = [h^2]A + [k^2]B + [l^2].C$		$a = (2\pi)/\sqrt{A}; b = (2\pi)/\sqrt{B}; c = (2\pi)/\sqrt{C}$
:4:	<i>monoclinic</i> :	$q^2 = [h^2]A + [k^2]B + [l^2].C + [h.l].D$		$a \cdot \sin\beta = (2\pi)/\sqrt{A};$ $b = (2\pi)/\sqrt{B};$ $c \cdot \sin\beta = (2\pi)/\sqrt{C};$ $\cos\beta = -D/2\sqrt{(AC)}$
:6:	<i>triclinic</i> :	$q^2 = [h^2]A + [k^2]B + [l^2].C + [h.l].D + [h.k].E + [k.l].F$		(see Cullity page 501)

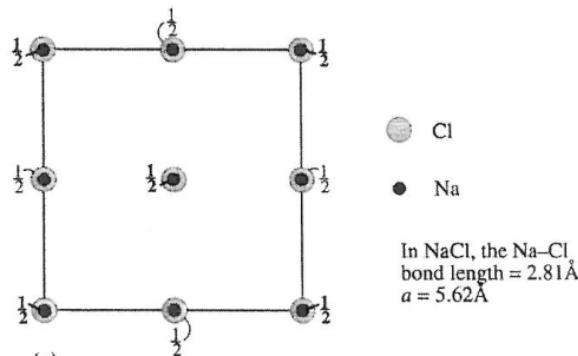
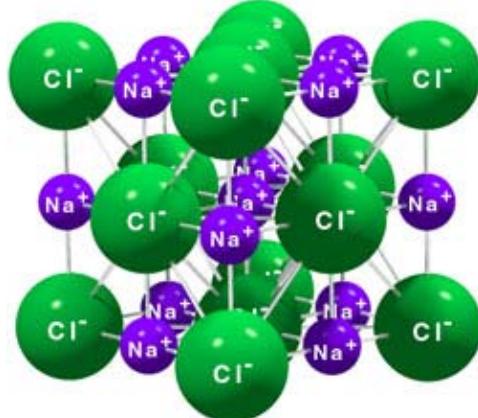
Absences in diffraction patterns

General rules for systematic absences due to lattice type (for all crystal systems)

Lattice	Restrictions on hkl
P	None
A	$(k + l)$ odd absent
B	$(h + l)$ odd absent
C	$(h + k)$ odd absent
I	$(h + k + l)$ odd absent
F	$h, k,$ and l not all odd or all even, absent

Warning: Some reflections may be missing for reasons not connected with lattice type. The opposite of systematic absence is not systematic presence!

Intensities in diffraction



F Lattice

Motif: Cl: 0,0,0; Na: 0,0,1/2

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

$$F_{hkl} = \sum_{j=1}^n f_j [\cos 2\pi(hx_j + ky_j + lz_j) + i \sin 2\pi(hx_j + ky_j + lz_j)]$$

Calculation of structure factor for the 331 reflection:

$$F_{hkl} = \sum_{j=1}^{j=n} f_j [\cos 2\pi(hx_j + ky_j + lz_j) + i \sin 2\pi(hx_j + ky_j + lz_j)]$$

$$F_{331} = 4f_{\text{Na}} [\cos 2\pi(3 \times 0 + 3 \times 0 + 1 \times \frac{1}{2}) + i \sin 2\pi(3 \times 0 + 3 \times 0 + 1 \times \frac{1}{2})]$$

$$+ 4f_{\text{Cl}} [\cos 2\pi(3 \times 0 + 3 \times 0 + 1 \times 0) + i \sin 2\pi(3 \times 0 + 3 \times 0 + 1 \times 0)]$$

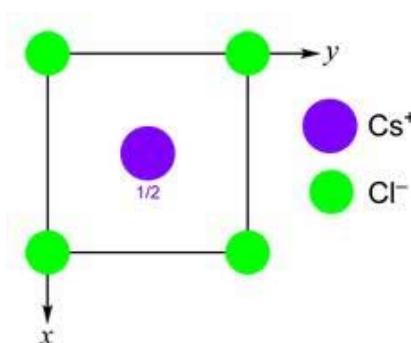
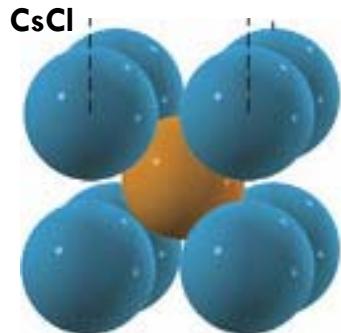
$$= 4[f_{\text{Cl}} - f_{\text{Na}}]$$

Multiplicity of 331 planes: $m_{331} = 24$

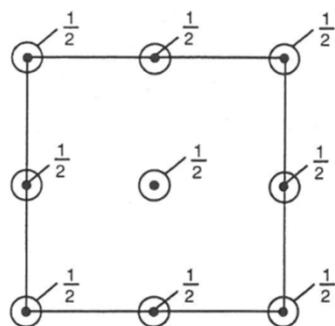
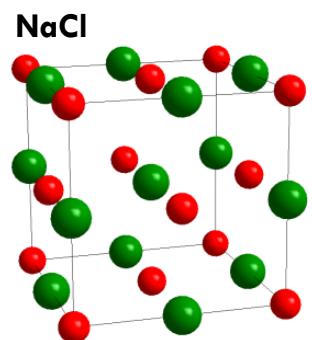
Calculation of intensity of 331 reflection:

$$I_{331} \propto G(\theta) \cdot m_{331} |F_{331}|^2 \propto 24 \times 16 [f_{\text{Cl}} - f_{\text{Na}}]^2$$

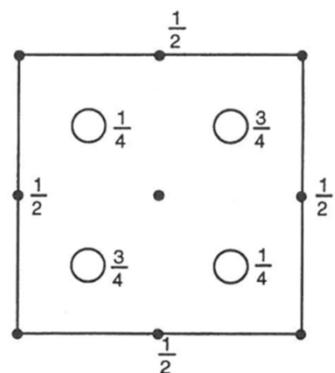
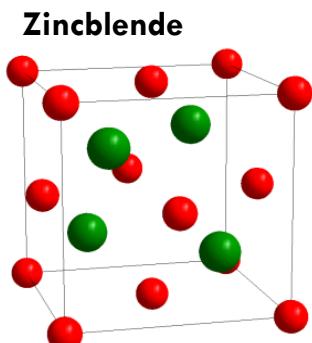
Simple Structures



CsCl
Motif:
 $\text{Cl} (0,0,0)$
 $\text{Cs} (1/2,1/2, 1/2)$

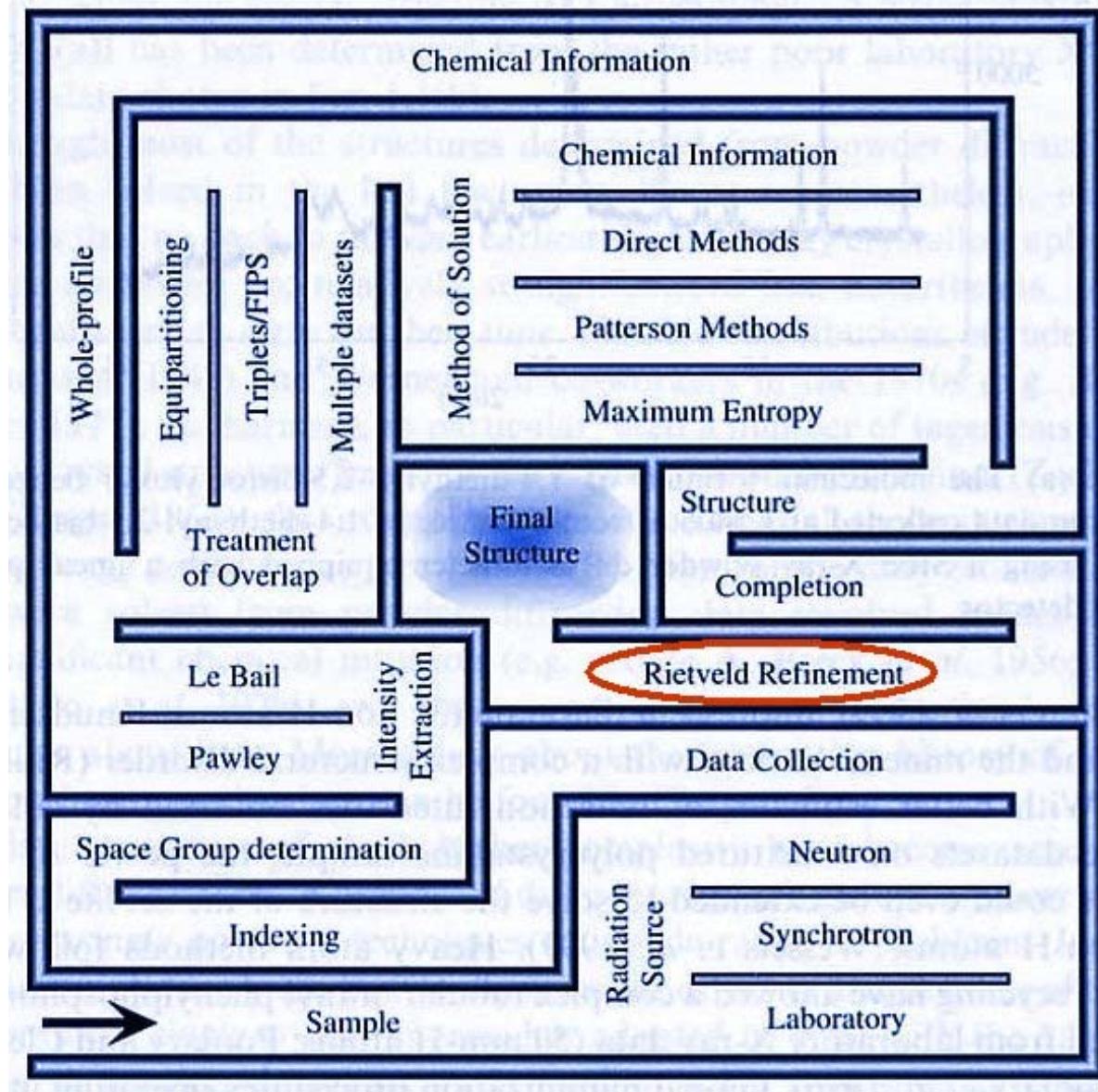


NaCl
Motif:
 $\text{Na} (0,0,0)$
 $\text{Cl} (1/2,0,0)$



ZnS
Motif:
 $\text{Zn} (0,0,0)$
 $\text{S} (1/4, 1/4, 1/4)$

Crystal structure determination



Additional tasks: Crystal representation

Objectives:

- To draw refined structures using the appropriate software for graphical representation.
- To determine different structural parameters (bond lengths and angles) using that software.
- To analyse different elements of symmetry in selected systems.

