

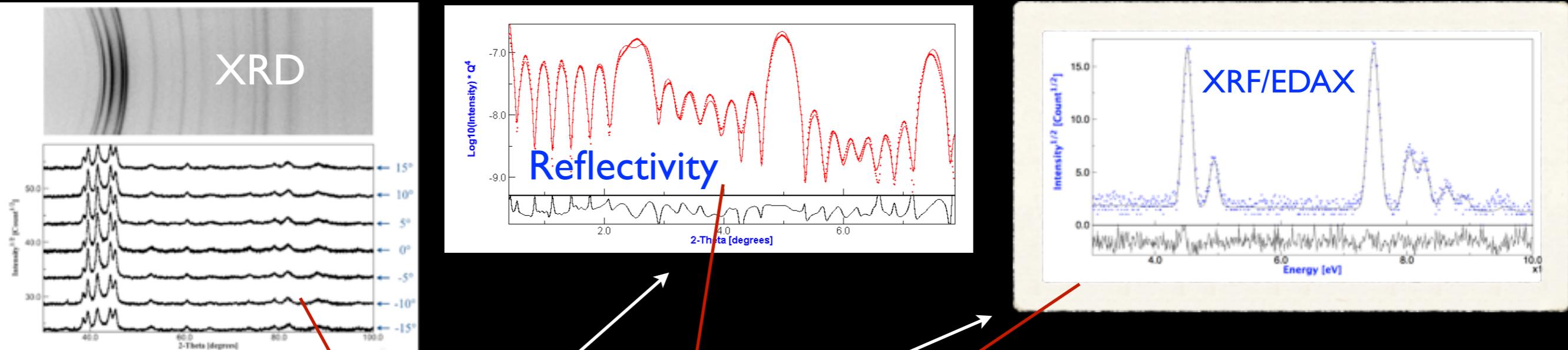
Introduction to Crystallography & Diffraction Techniques

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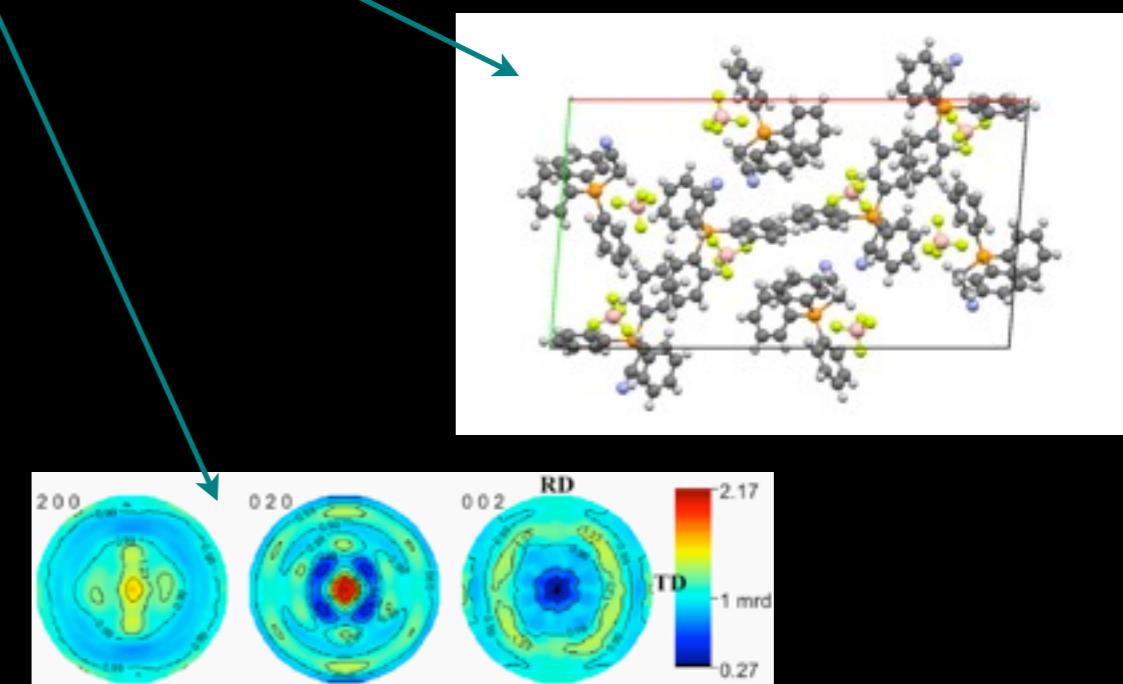
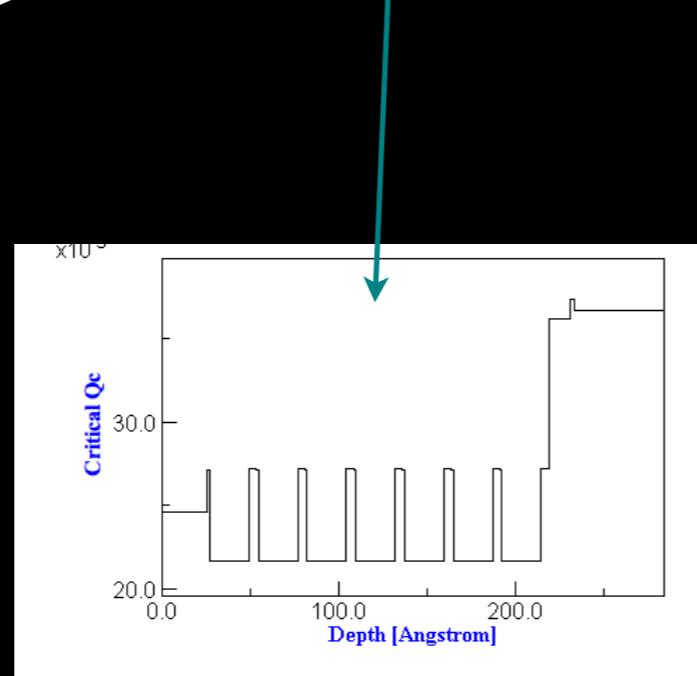
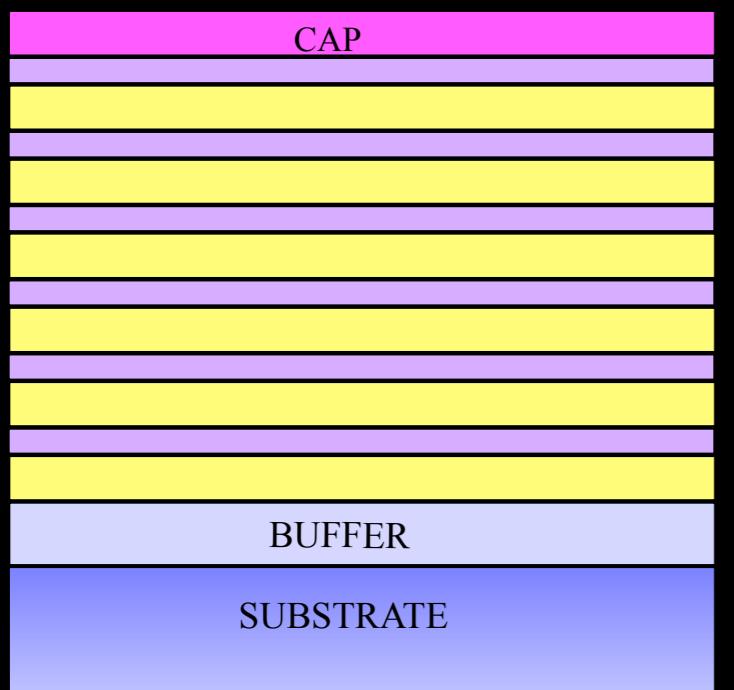
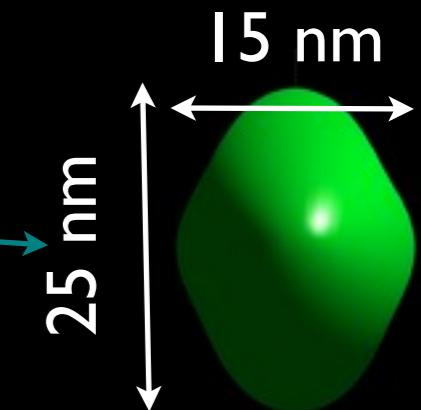


Combined techniques analysis

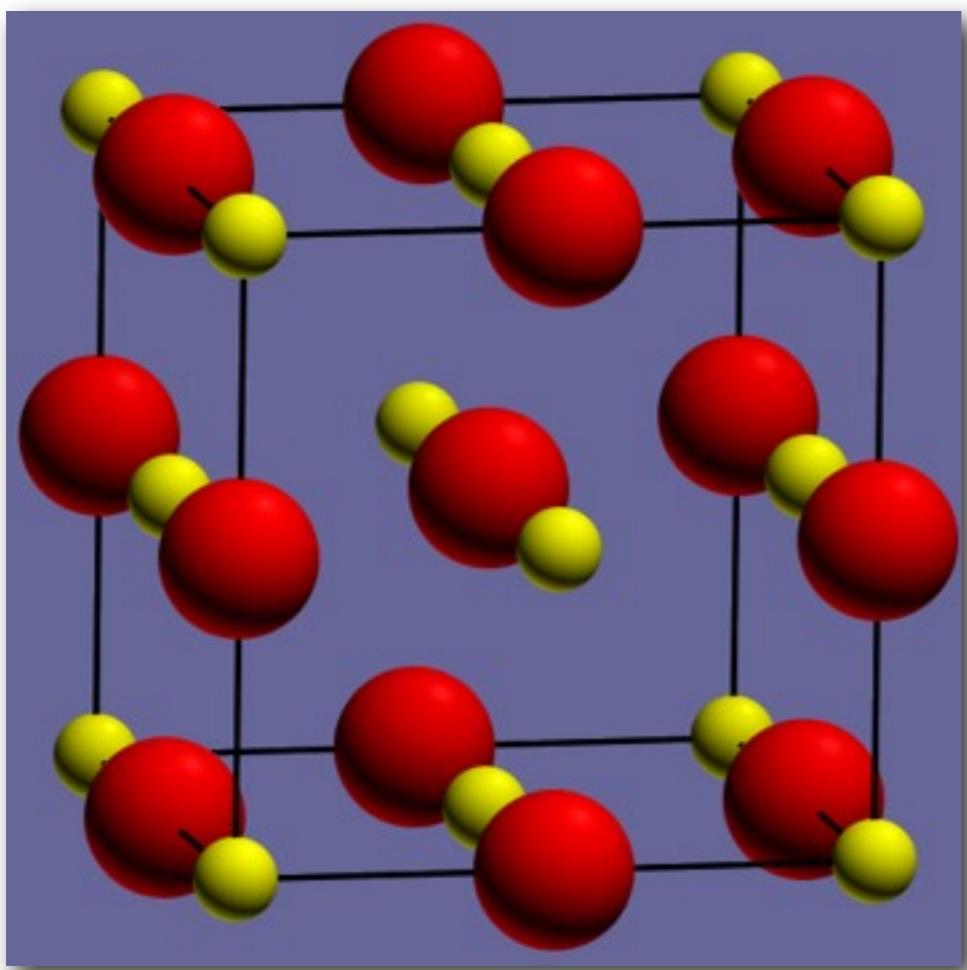


$$WSS = \sum_{t=1}^{N_{\text{Techniques}}} \sum_{i=1}^{N_t} \left[w_{i,t} \left(I_{i,t}^{\exp} - I_{i,t}^{\text{calc}} \right) \right]^2,$$

$$w_{i,t} = \frac{1}{\sqrt{I_{i,t}^{\exp}}}$$

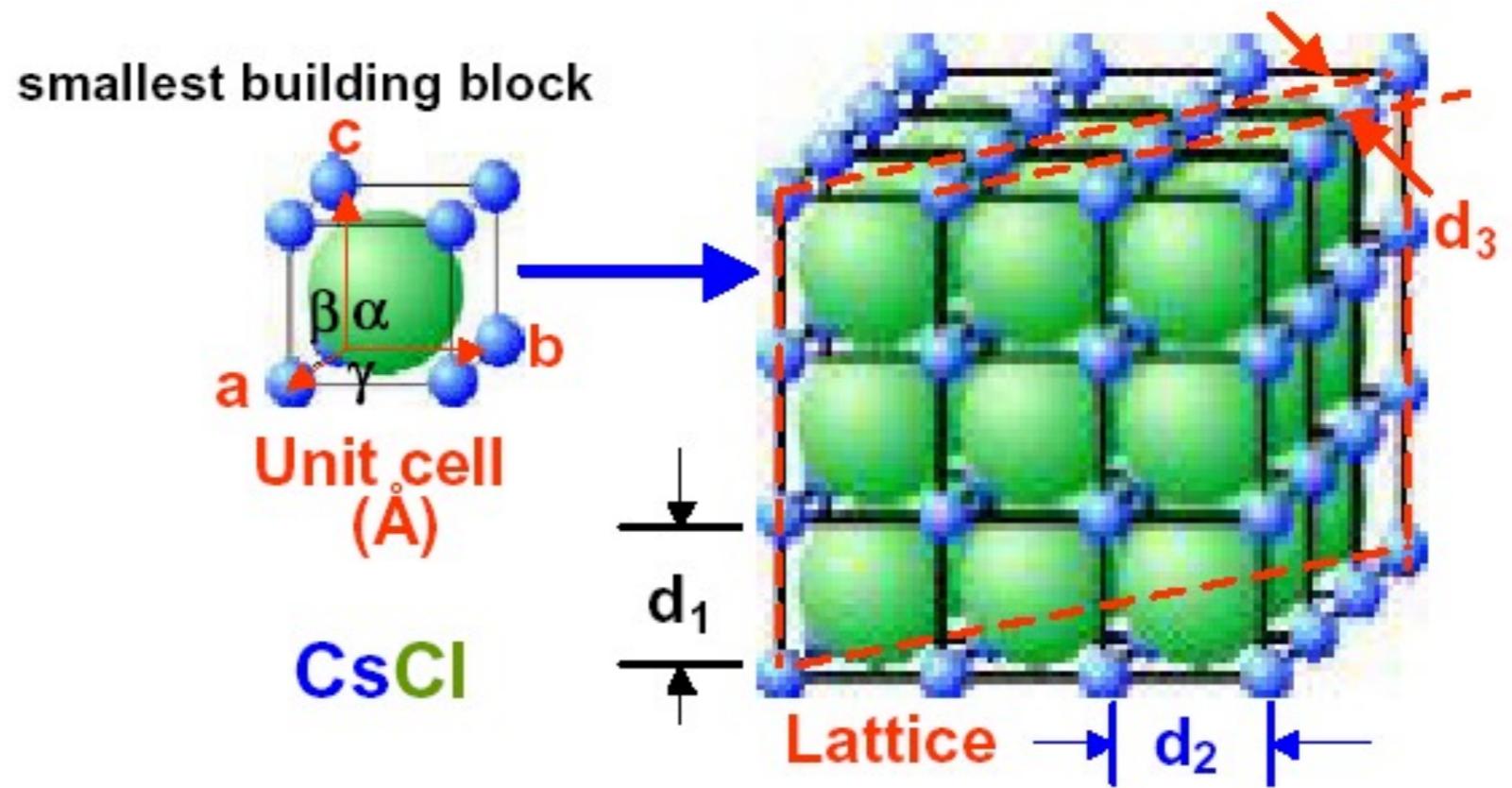
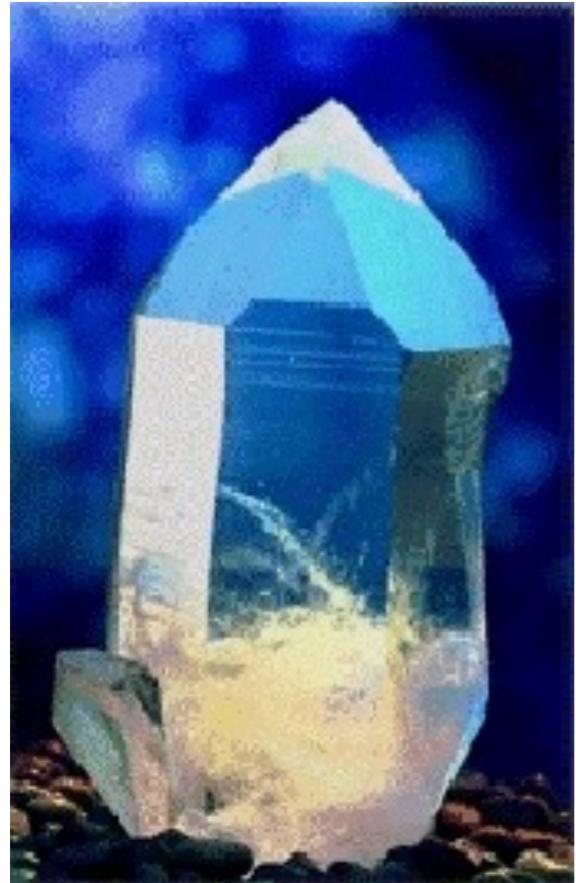


X-Ray Diffraction is used to study crystalline materials



- X-rays scatter off of the atoms in a sample
- If those atoms are systematically ordered, the scattered X-rays tell us:
 - what atoms are present
 - how they are arranged

Crystallography basics

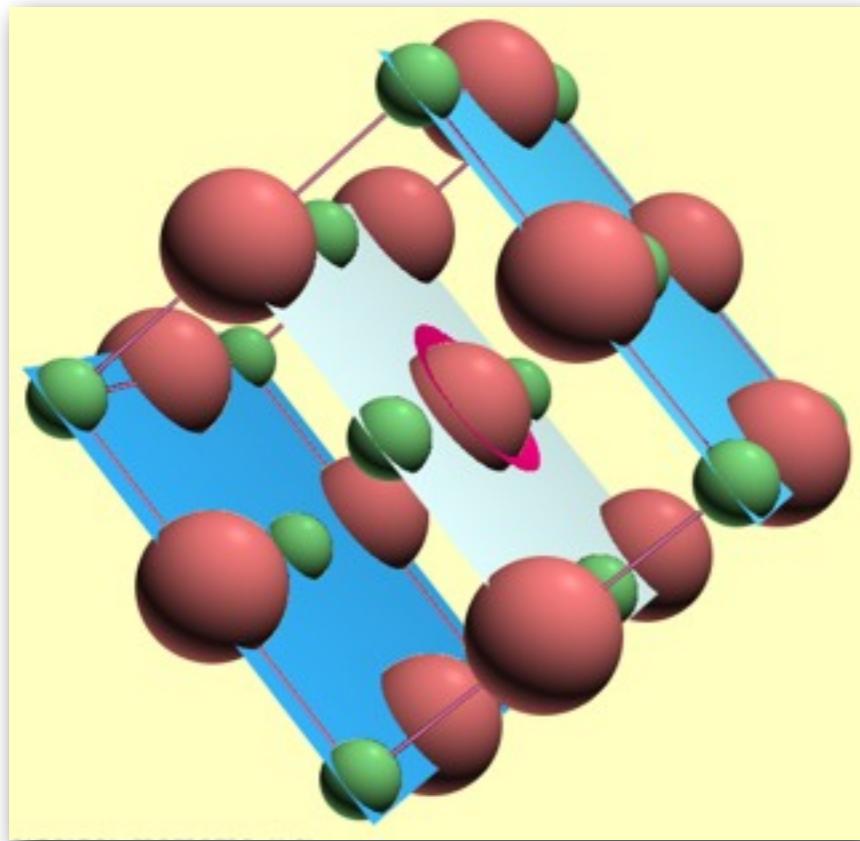


A crystal consists of a periodic arrangement of the unit cell into a lattice. The unit cell can contain a single atom or atoms in a fixed arrangement.

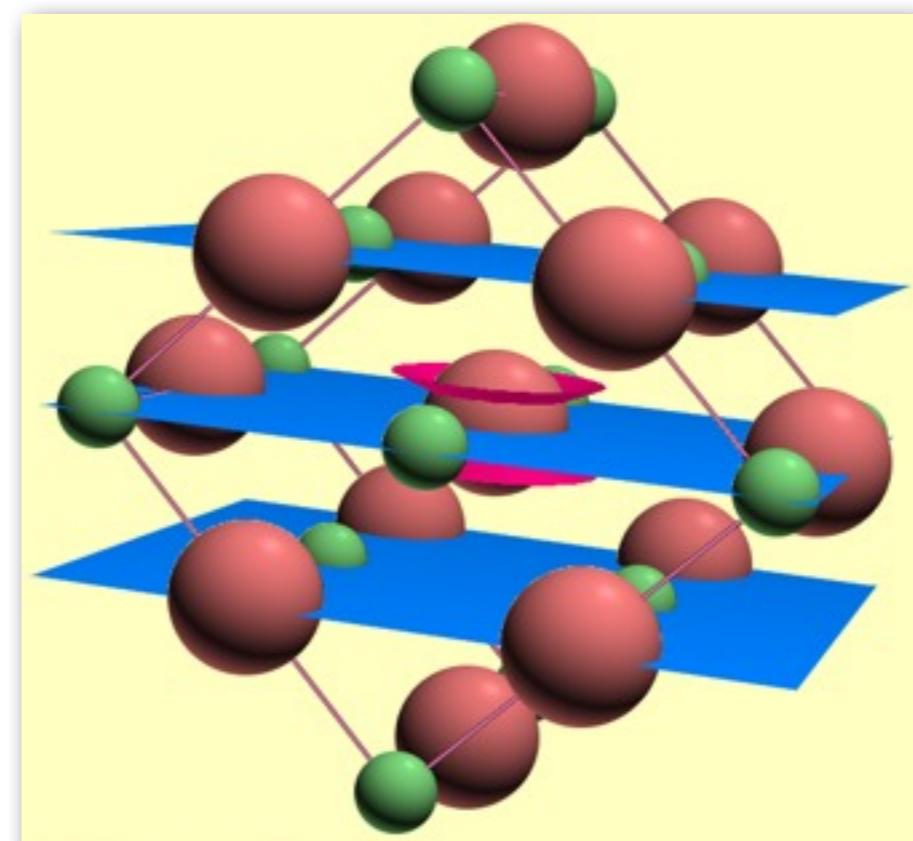
a, b and c (length) and α , β and γ angles between a, b and c are lattice constants or parameters which can be determined by XRD.

Crystalline materials are characterized by the orderly periodic arrangements of atoms

The (200) planes of atoms in NaCl



The (220) planes of atoms in NaCl



- Parallel planes of atoms intersecting the unit cell are used to define directions and distances in the crystal.
 - These crystallographic planes are identified by **Miller** indices.

Examples of Miller Planes

$h=1, k=-1$

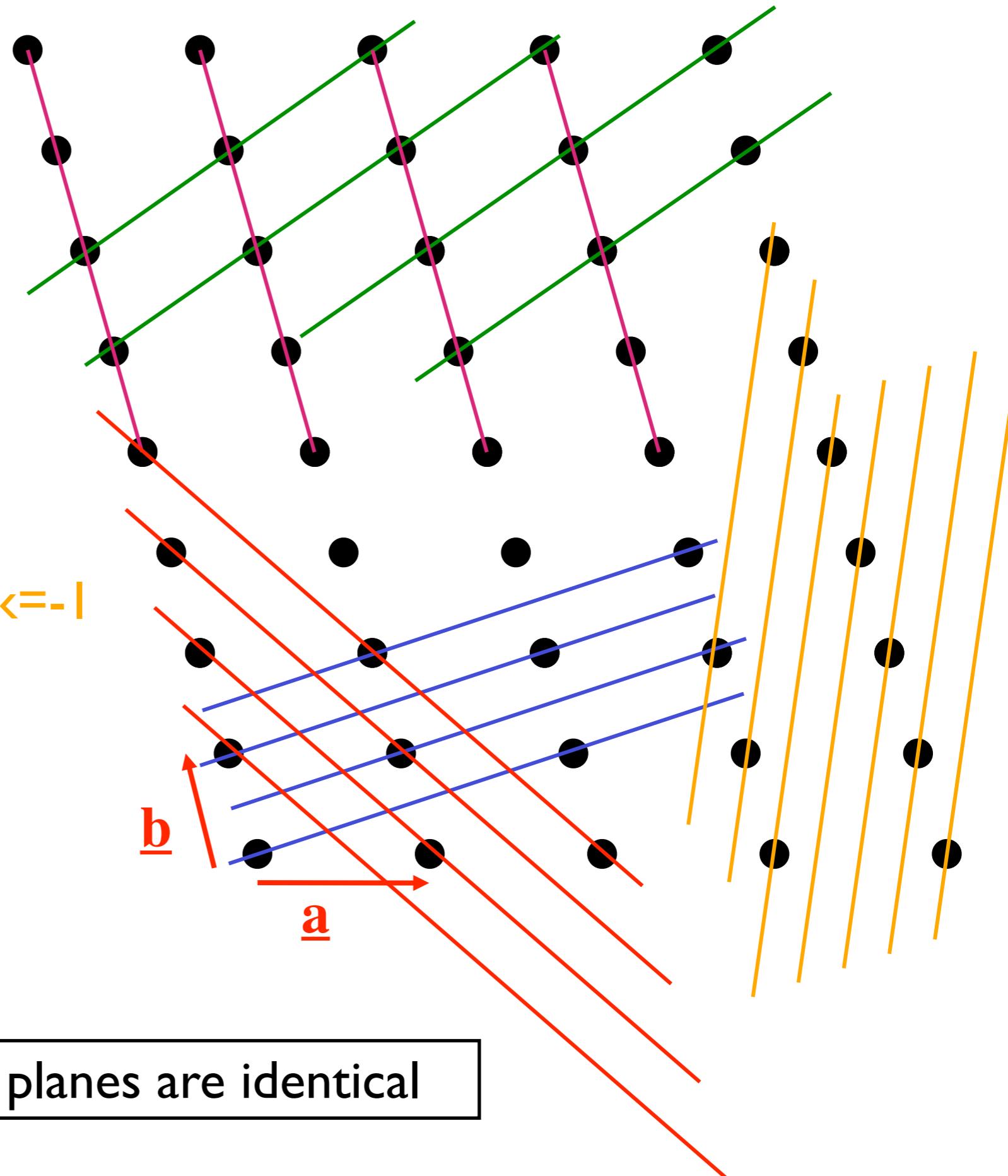
$h=1, k=0$

$h=4, k=-1$

$h=1, k=-2$

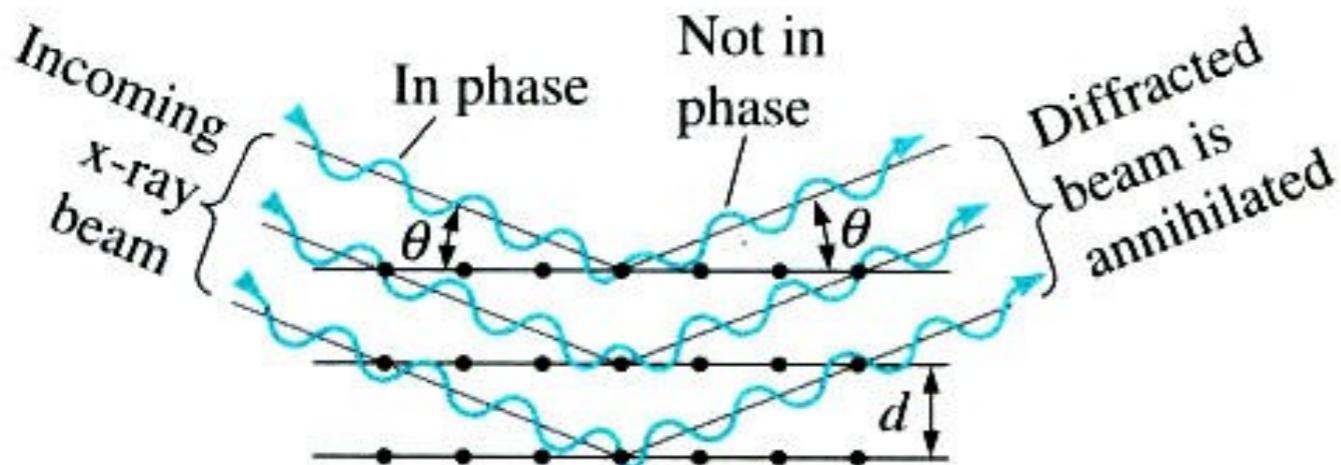
$h=2, k=1$

\underline{a}
 \underline{b}



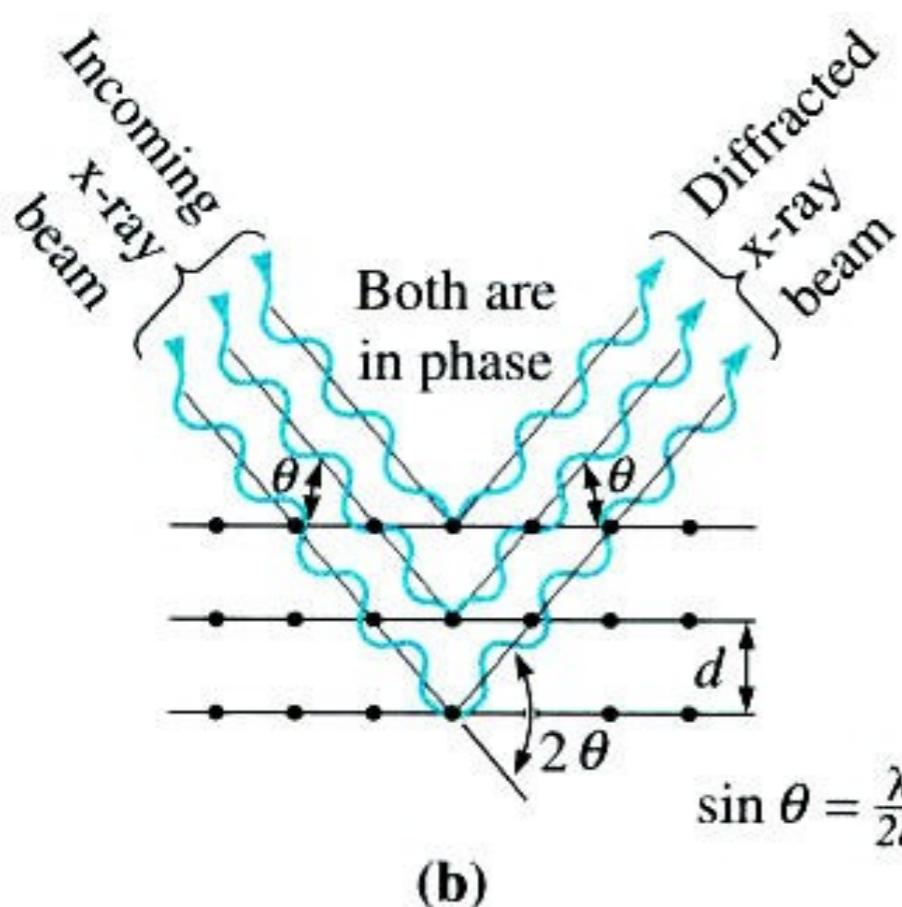
Note that the 2, 2 and -2, -2 planes are identical

Bragg's law



$$\sin \theta \neq \frac{\lambda}{2d}$$

(a)



$$\sin \theta = \frac{n\lambda}{2d}$$

Figure 3-43

(a) Destructive and (b) reinforcing interactions between x-rays and the crystalline material. Reinforcement occurs at angles that satisfy Bragg's law.

The diffraction process occurs when the Bragg's law (condition) is satisfied. It is expressed as:

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

Where λ is the wavelength of x-rays
d is the interplanar spacing
 θ is the x-ray angle
n is an integer

Lattices

- In 1848, Auguste Bravais demonstrated that in a 3-dimensional system there are fourteen possible lattices
- A Bravais lattice is an infinite array of discrete points with identical environment
- seven crystal systems + four lattice centering types = 14 Bravais lattices
- Lattices are characterized by translation symmetry

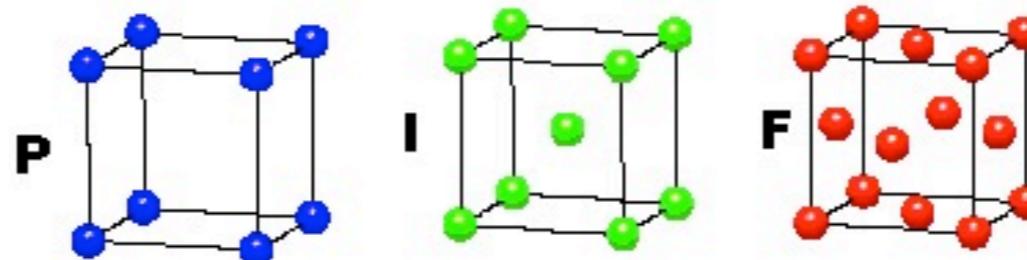
Auguste Bravais
(1811-1863)



Categories of Space Groups

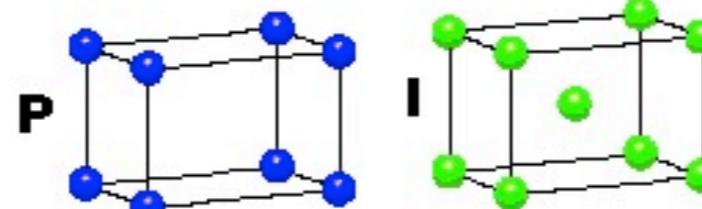
CUBIC

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



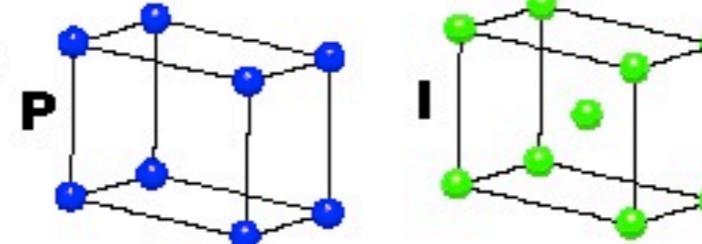
TETRAGONAL

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



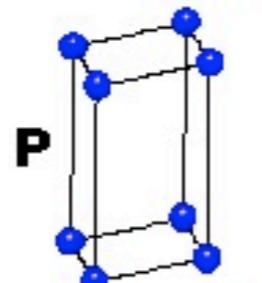
ORTHORHOMBIC

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



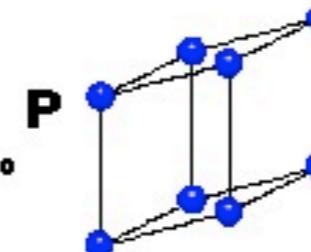
HEXAGONAL

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



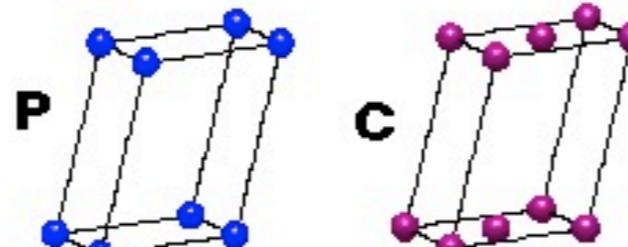
TRIGONAL

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



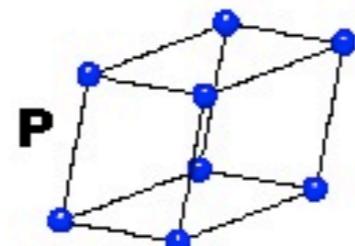
MONOCLINIC

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



TRICLINIC

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



4 Types of Unit Cell

P = Primitive

I = Body-Centred

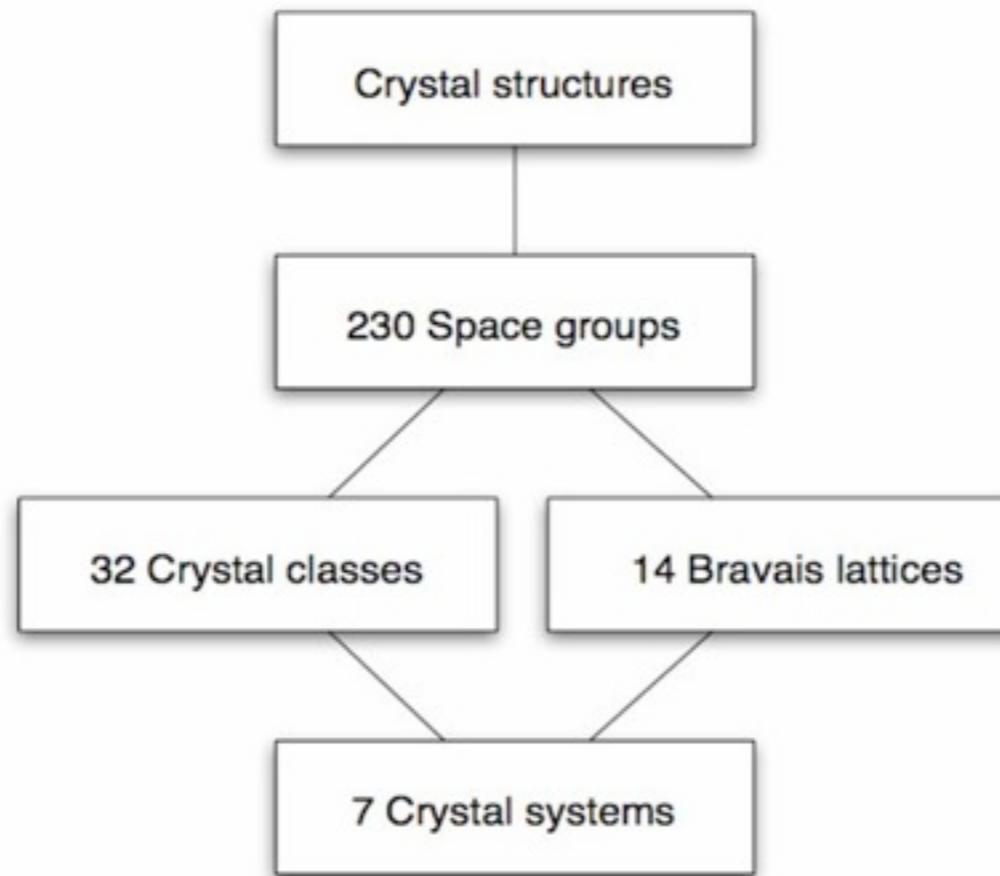
F = Face-Centred

C = Side-Centred

+

7 Crystal Classes

→ 14 Bravais Lattices



The combination of all available symmetry operations (32 point groups), together with translation symmetry, within the all available lattices (14 Bravais lattices) lead to 230 Space Groups that describe the only ways in which identical objects can be arranged in an infinite lattice. The International Tables list those by symbol and number, together with symmetry operators, origins, reflection conditions, and space group projection diagrams.

An interactive tutorial on Space Groups can be found on-line in Bernhard Rupp's Crystallography 101 Course: <http://www-structure.llnl.gov/Xray/tutorial/spcgrps.htm>

Generating a Crystal Structure from its Crystallographic Description

Using the space group information contained in the International Tables we can do many things. One powerful use is to generate an entire crystal structure from a brief description.

Let us consider the description of the crystal structure of NaCl.

Space Group = Fm $\bar{3}m$

$a = 5.44 \text{ \AA}$

Atomic Positions

Cl

1:(0.0,0.0,0.0), 2:(0.5,0.5,0.0),
3:(0.5,0.0,0.5), 4:(0.0,0.5,0.5)

Na

1:(0.5,0.5,0.5), 2:(0.0,0.0,0.5),
3:(0.0,0.5,0.0), 4:(0.5,0.0,0.0)

Using the face centering generators $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$, $(0,\frac{1}{2},\frac{1}{2})$ together with the coordinates of each Wyckoff site we can generate the fractional coordinates of all atoms in the unit cell.

Summary:

With no knowledge of the symmetry diagram we can identify the crystal system from the space group symbol.

- Cubic – The secondary symmetry symbol will always be either 3 or -3 (i.e. $Ia3$, $Pm3m$, $Fd3m$)
- Tetragonal – The primary symmetry symbol will always be either 4, (-4), 4_1 , 4_2 or 4_3 (i.e. $P4_12_12$, $I4/m$, $P4/mcc$)
- Hexagonal – The primary symmetry symbol will always be a 6, ($\bar{6}$), 6_1 , 6_2 , 6_3 , 6_4 or 6_5 (i.e. $P6mm$, $P6_3/mcm$)
- Trigonal – The primary symmetry symbol will always be a 3, ($\bar{3}$), 3_1 or 3_2 (i.e. $P3_1m$, $R3$, $R3c$, $P3_12$)
- Orthorhombic – All three symbols following the lattice descriptor will be either mirror planes, glide planes, 2-fold rotation or screw axes (i.e. $Pnma$, $Cmc2_1$, $Pnc2$)
- Monoclinic – The lattice descriptor will be followed by either a single mirror plane, glide plane, 2-fold rotation or screw axis or an axis/plane symbol (i.e. Cc , $P2$, $P2_1/n$)
- Triclinic – The lattice descriptor will be followed by either a l or a (\bar{l}).

Wyckoff Sites

- The Wyckoff positions tell us where the atoms in a crystal can be found.
- Wyckoff position denoted by a number and a letter. Number is called multiplicity of the site and letter is called Wyckoff site.
- Multiplicity tells us how many atoms are generated by symmetry if we place a single atom at that position.
- The letter is simply a label and has no physical meaning. They are assigned alphabetically from the bottom up.
- The uppermost Wyckoff position (with highest multiplicity), corresponding to an atom at an arbitrary position never resides upon any symmetry elements. This Wyckoff position is called the general position. All of the remaining Wyckoff positions are called special positions. They correspond to atoms which lie upon one or more symmetry elements, because of this they always have a smaller multiplicity than the general position.

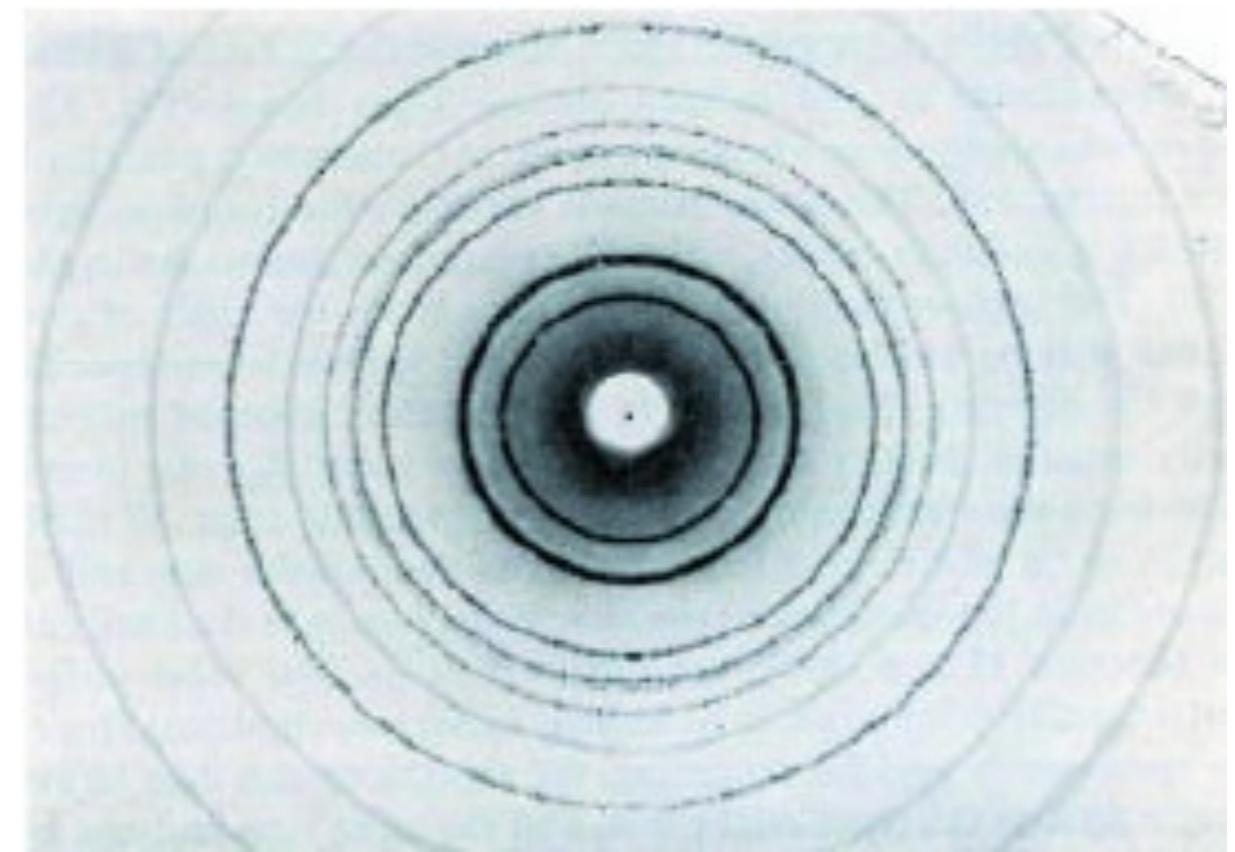
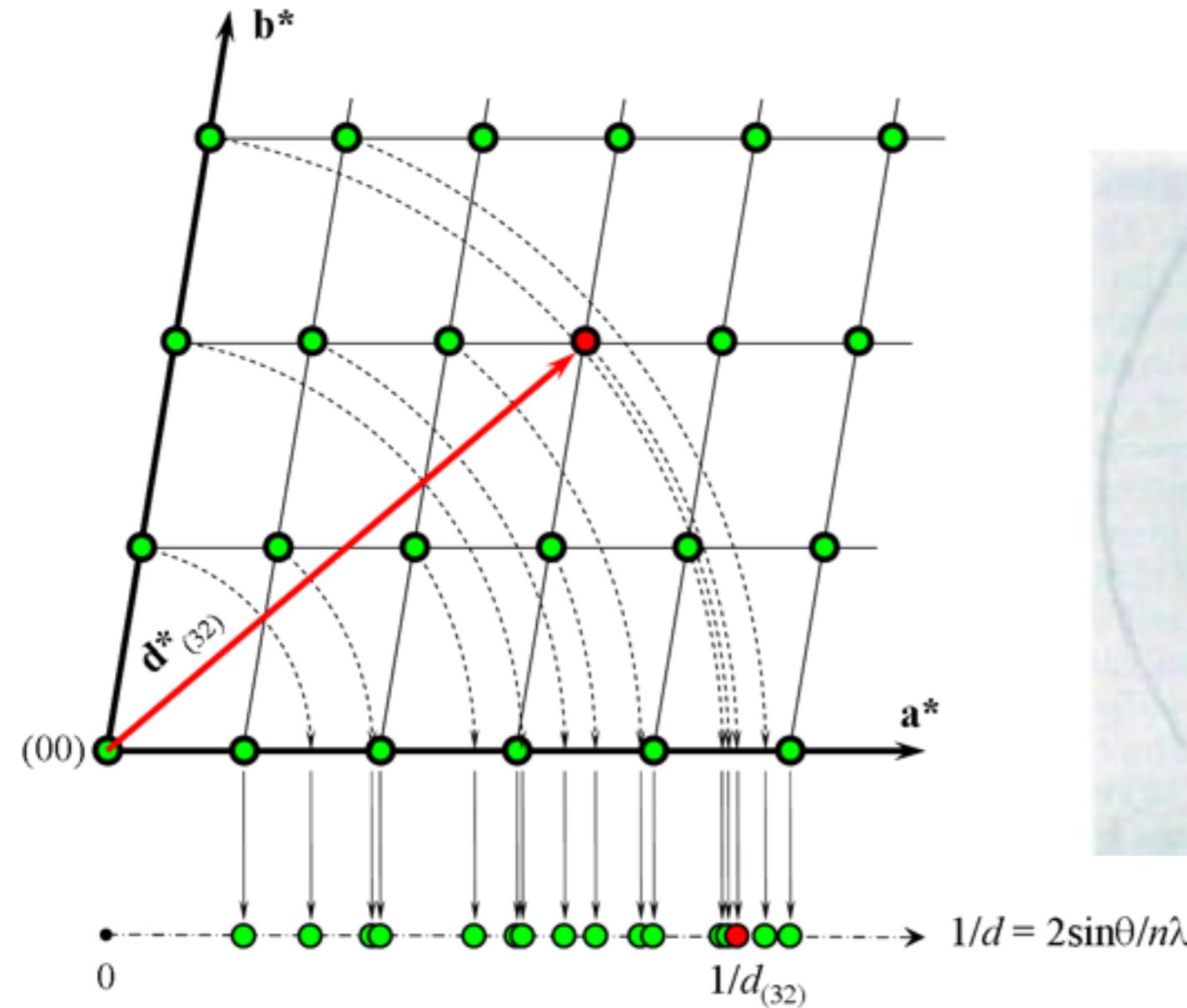
The Powder Diffraction Pattern

Powders (i.e., polycrystalline aggregates) are billions of tiny crystallites in all possible orientations.

When placed in an x-ray beam, all possible interatomic planes will be seen

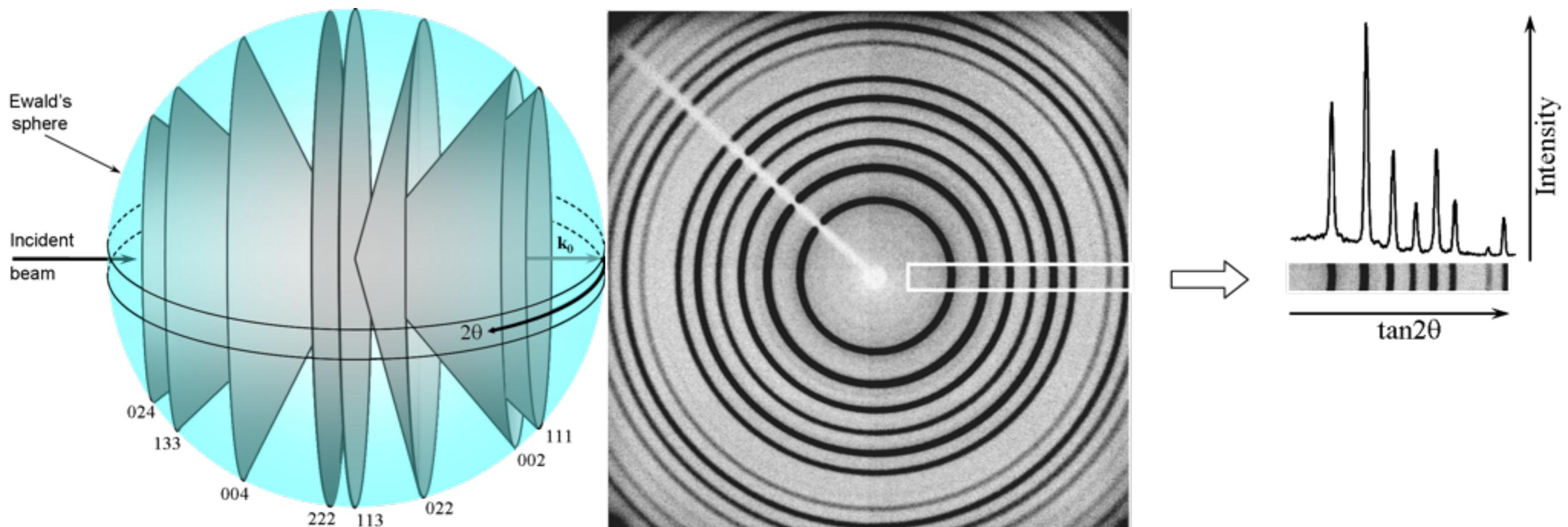
By systematically changing the experimental angle, we will produce all possible diffraction peaks from the powder

Geometric relationship between the 2D reciprocal lattice [d*(hk') vector] and its 1D projection $|d^*| = 2\sin\theta/\lambda$



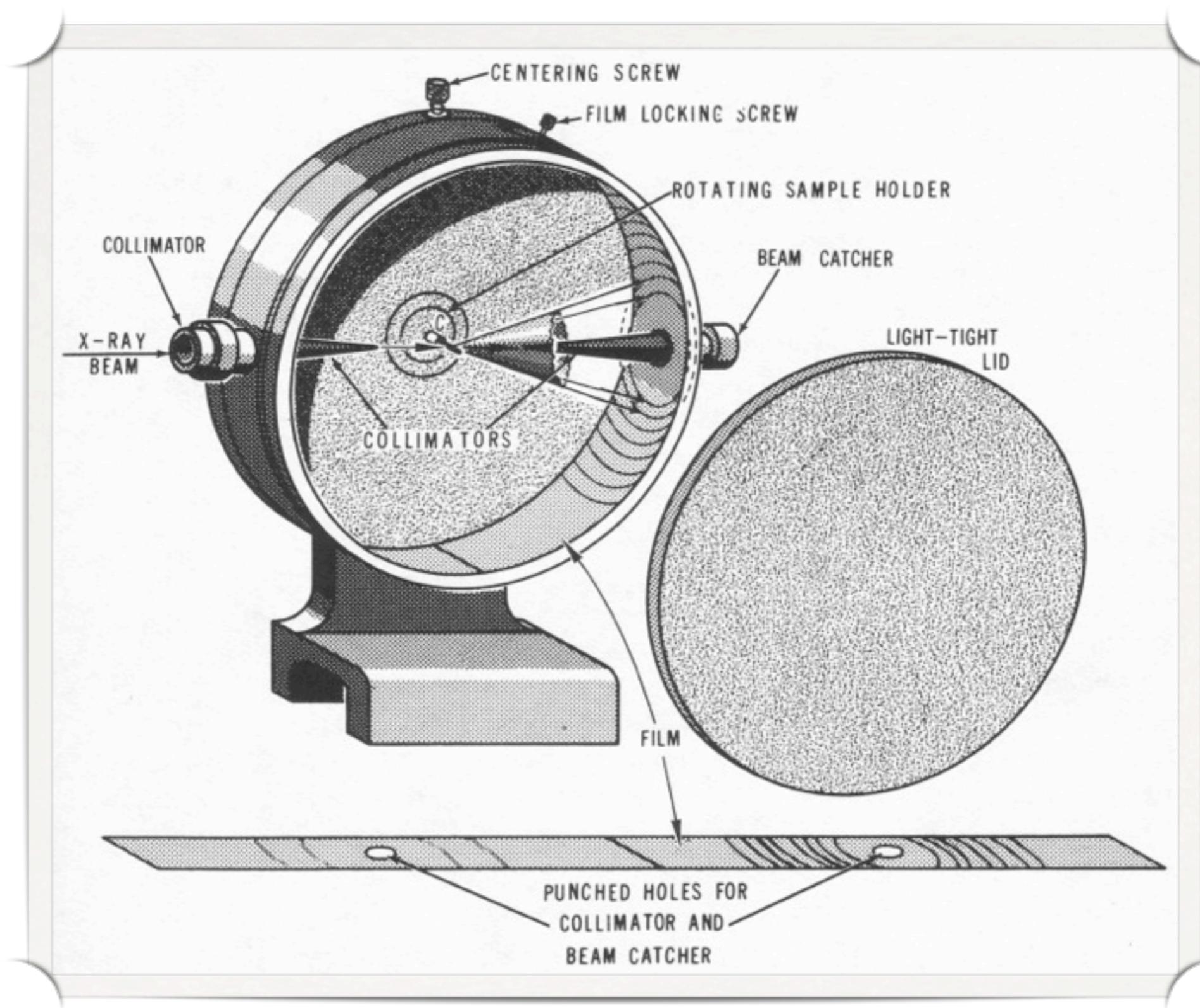
Indexing: Determination of hkl indices for each peak and lattice parameters evaluation, i.e., reconstruction of the 3-D geometry

We do not need to collect the rings from cones but just the ring intersection on an “equatorial” film

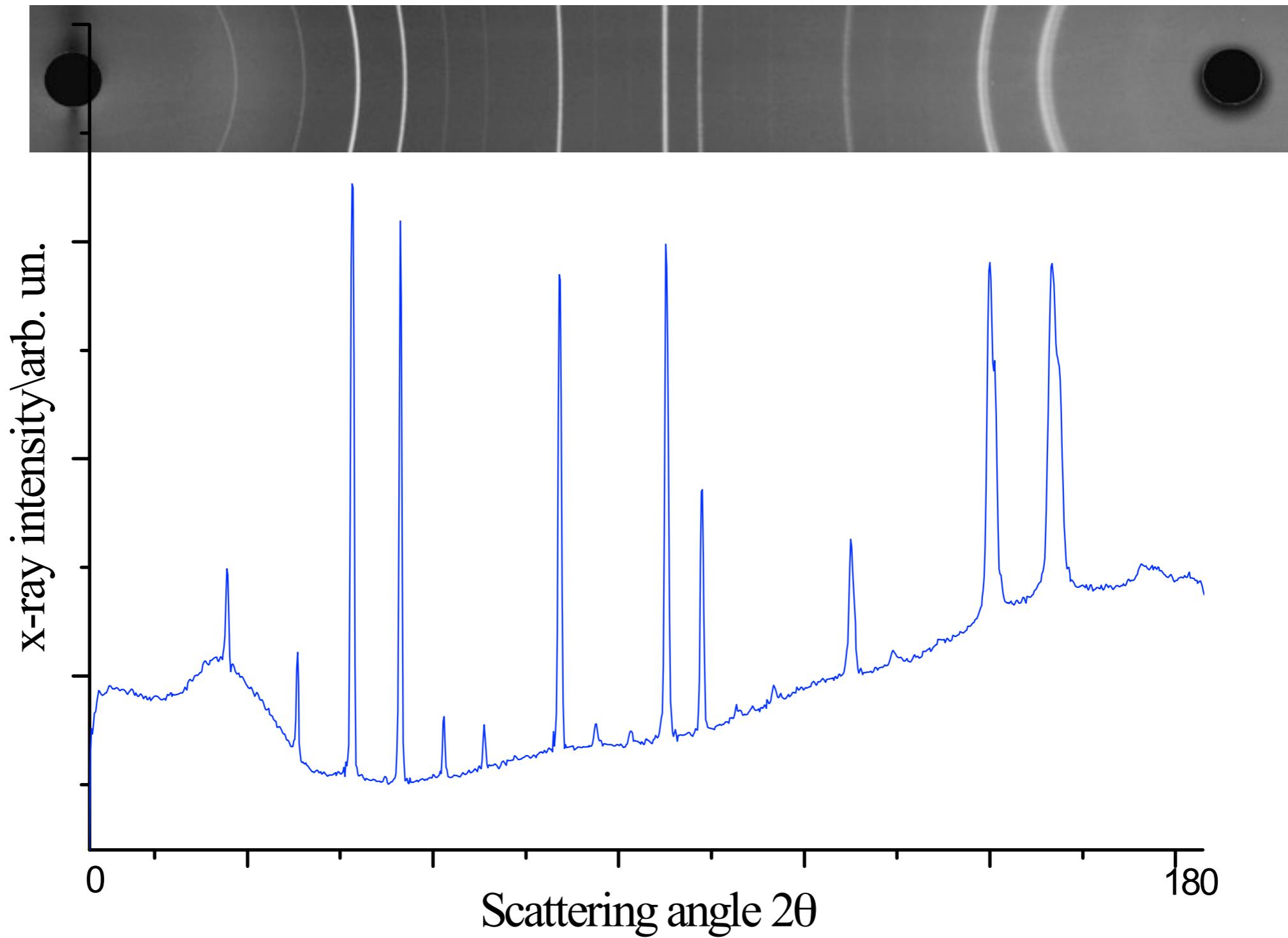


If the scattering power is low, the integration of intensity in the cones may be required.

In the “early times” this was done with a Debye-Scherrer camera

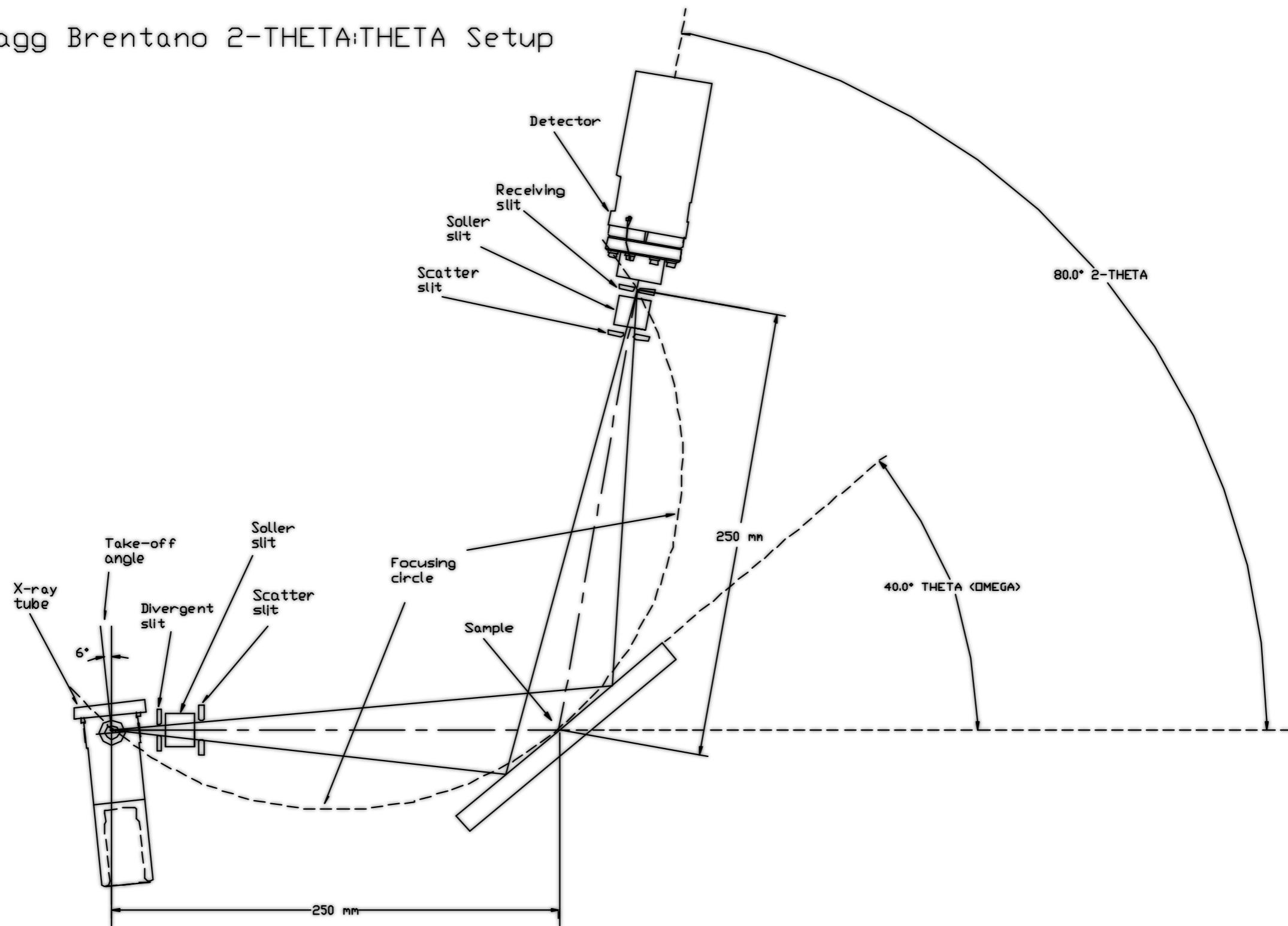


From film to powder diffraction pattern



....But for better angular resolution of peaks,
a modern diffractometer is more suitable

Bragg Brentano 2-THETA:THETA Setup



Which Wavelength to Use in the home lab?

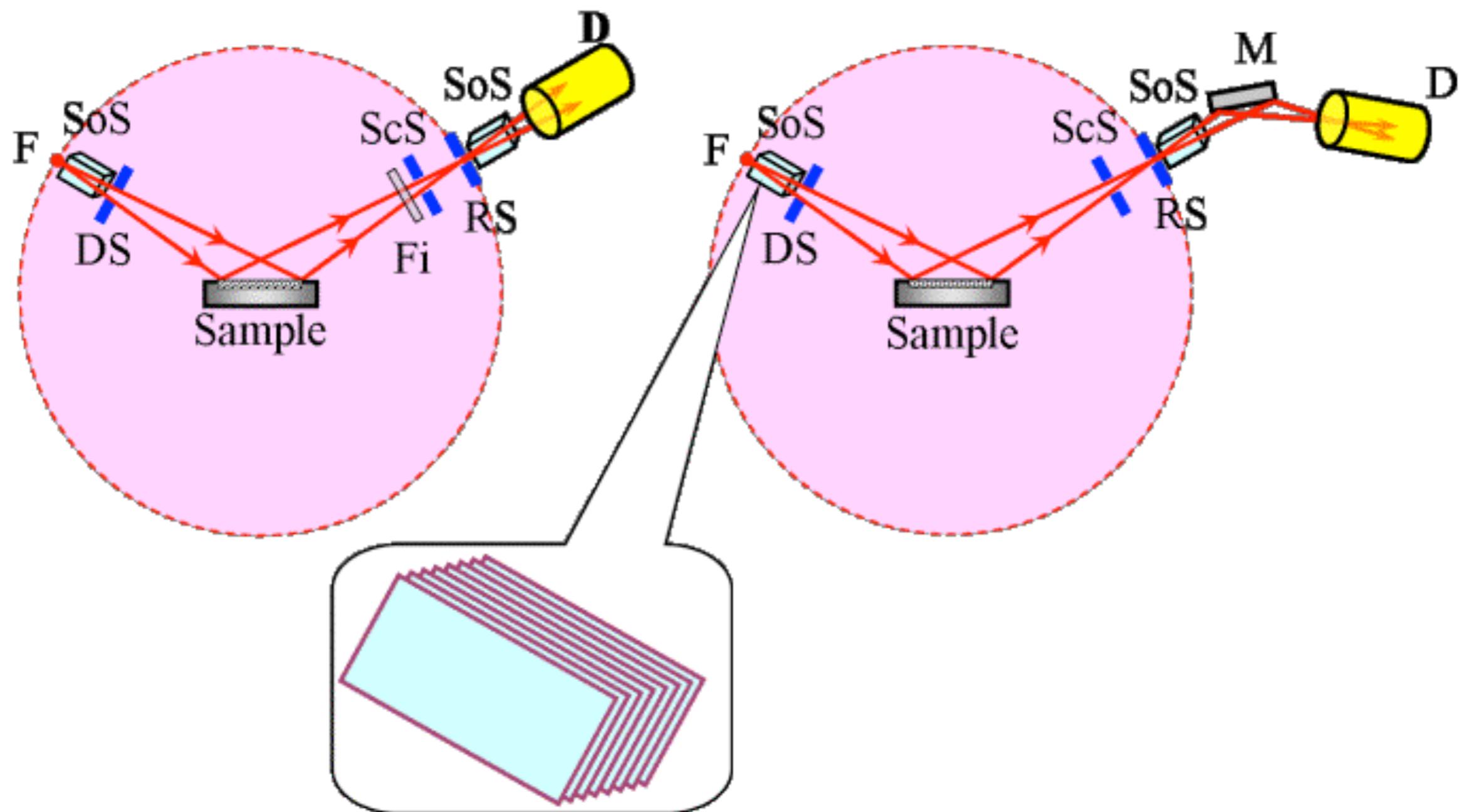
Generally use Cu 1.5418Å or Mo 0.71073Å

The longer the wavelength the farther apart the diffraction spots (lines) are in space. For large unit cells like macromolecules biologists should prefer Cu.

Cu produces x-rays efficiently and the detectors have a higher efficiency in measuring them.

Mo is not as absorbed as Cu. Best for heavy element problems. However metals have in general small unit cells.

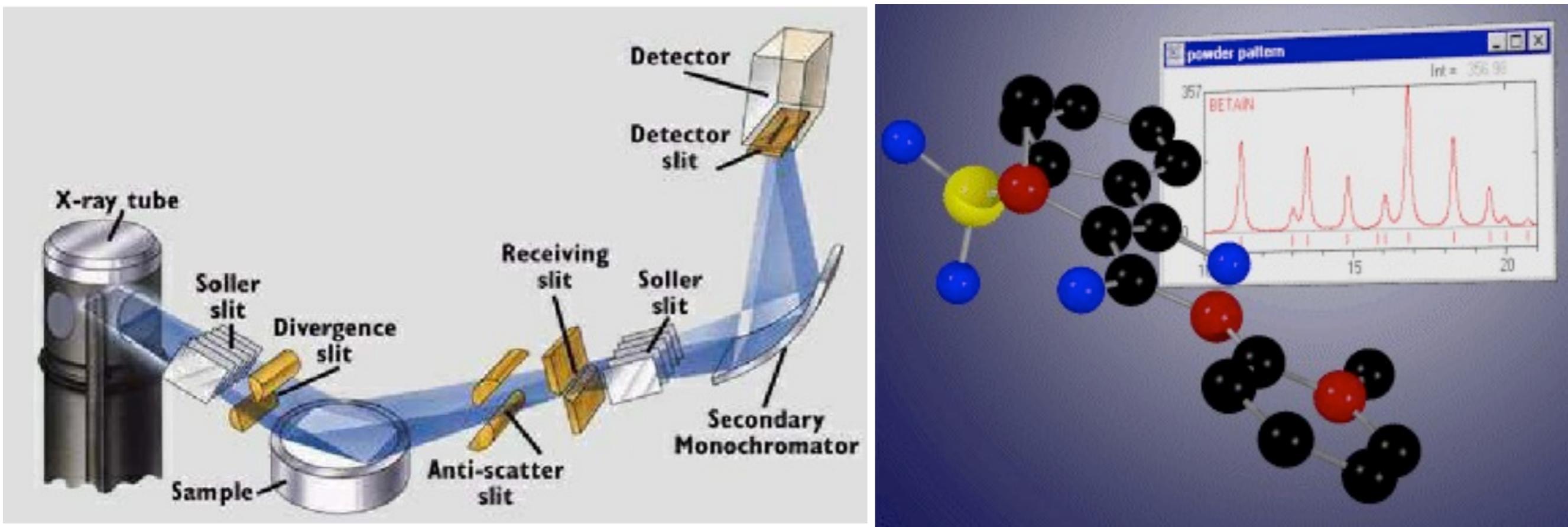
- Powder diffractometers working in the Bragg-Brentano ($\theta/2\theta$) geometry utilize a parafocussing geometry to increase intensity and angular resolution



Powder diffractometer operation

- proper choice of slits
 - divergence slit – small enough so that the beam does not “spill off” the sample, but large enough for adequate intensity (sometimes a “θ-compensating” slit is used)
 - receiving slit – large enough to receive entire Debye ring, but not too large to degrade resolution
 - Soller slits – improve resolution by decreasing vertical divergence
- errors
 - axial divergence:
$$\Delta 2\theta \propto \frac{k_1 \cot 2\theta + k_2 \cosec 2\theta}{3R^2}$$
 - flat specimen:
$$\Delta 2\theta \propto -\alpha^2 \cot \theta$$
 - specimen transparency:
$$\Delta 2\theta \propto \sin 2\theta / 2\mu R$$
 - sample displacement:
$$\Delta 2\theta \propto \frac{-2s \cos \theta}{R}$$

Reciprocity rules and atoms in the unit cell

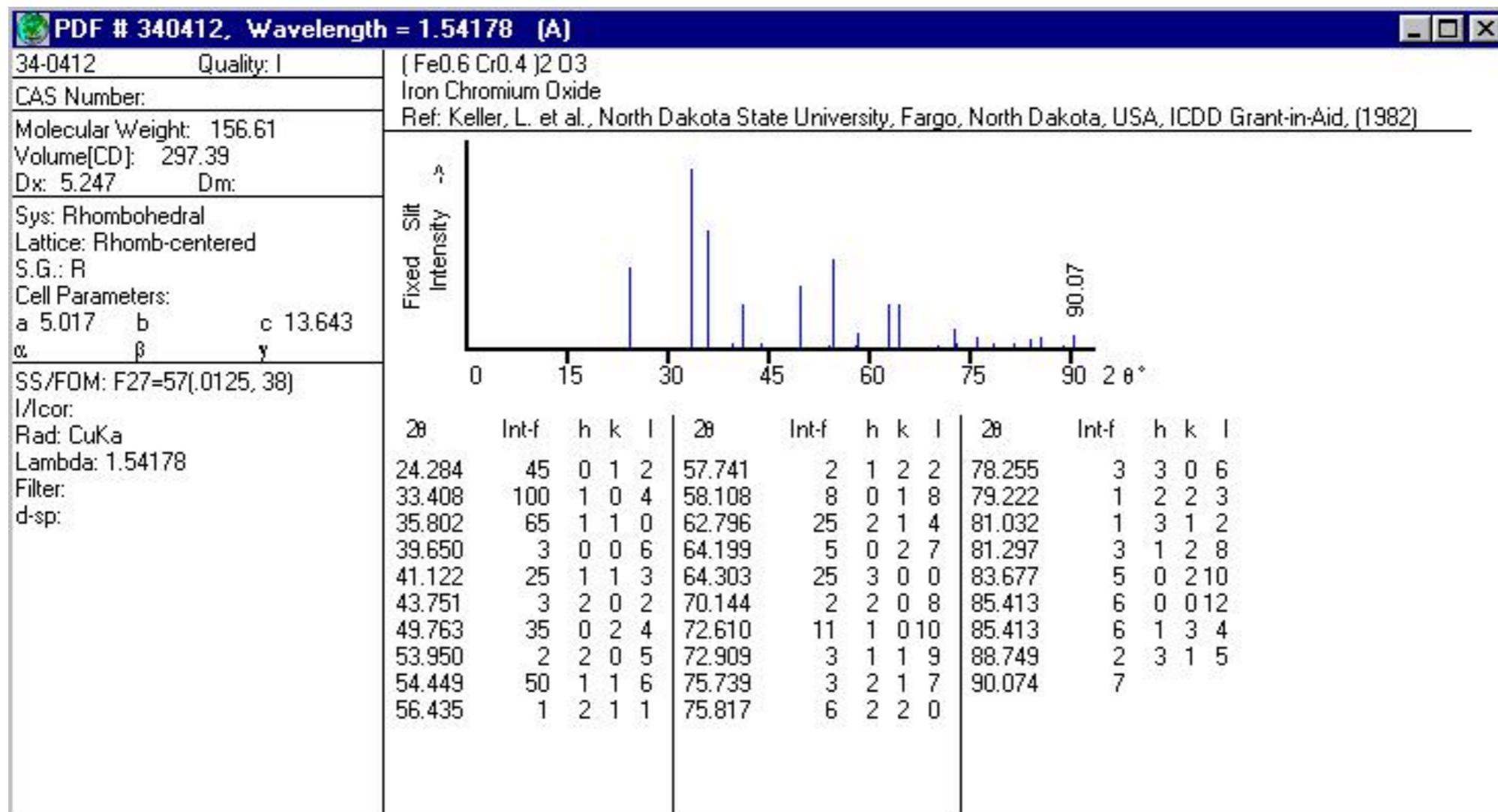


- The lattice symmetry determines the diffraction peaks sequence.
- The elementary cell size determines peak densification in the diffraction space (according to reciprocity laws, small dimension determines large separation)
- Atom position within the unit cell affects the relative peak intensities
- Small crystallite size and large lattice strain affect the peak broadening

Diffraction analyses

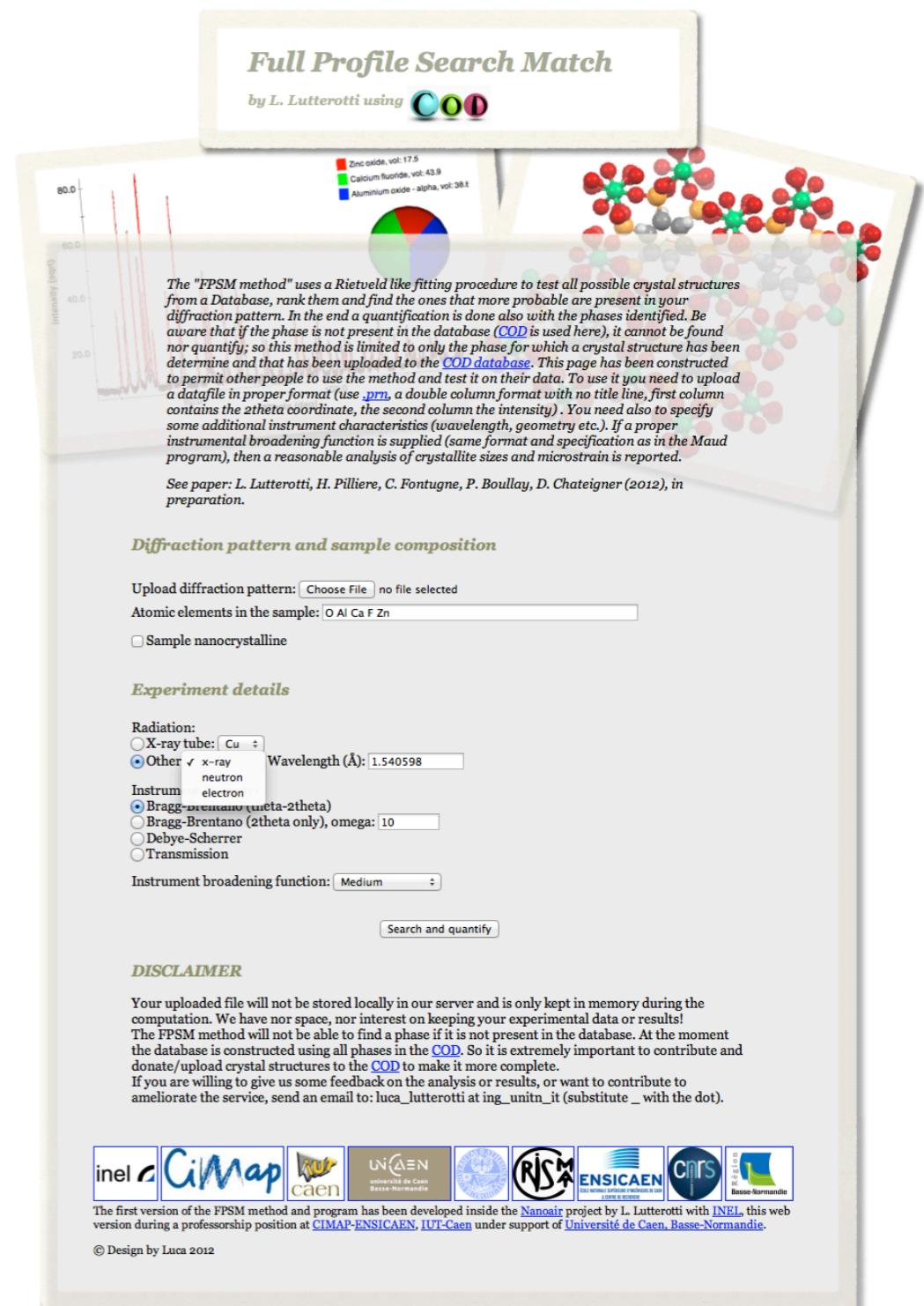
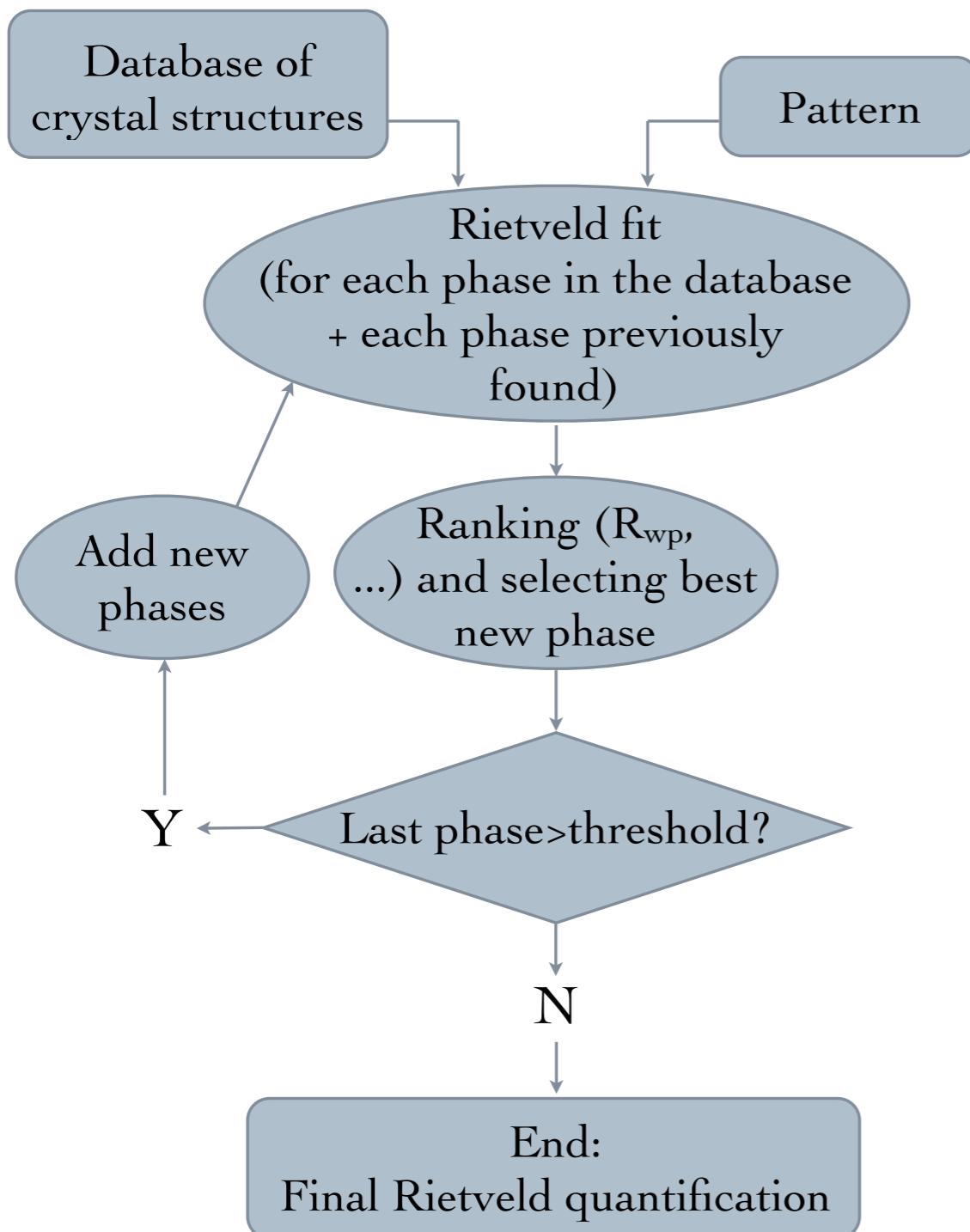
- Phase identifications (crystalline and amorphous)
- Crystal structure determination
- Crystal structure refinements
- Quantitative phase analysis (and crystallinity determination)
- Microstructural analyses (crystallite sizes - microstrain)
- Texture analysis
- Residual stress analysis
- Order-disorder transitions and compositional analyses
- Thin films

Search match



- Peaks search
- Search in the PDF database using the identified peaks (higher intensity or longer d-space etc.). Use of composition necessary in certain cases.
- Validating manually the phases found to determine the correct ones.

Full Profile Search Match



- <http://cod.iutcaen.unicaen.fr> (<http://fpsm.iutcaen.unicaen.fr>)
- <http://nanoair.ing.unitn.it:8080/sfpm/>

Structure solution: when?

- First use the search-match
- Check for every similar compound
- Check literature and structural databases
- Repeat the experiment in case
- If nothing similar is found then go for the ab initio structure solution
- After indexing better to do the search again

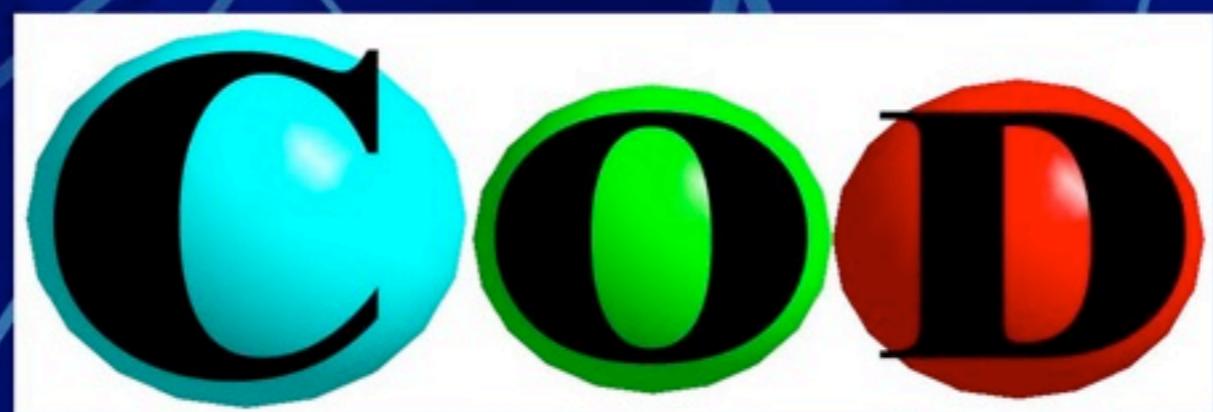
OPEN DATA and Crystallography Databases

- Open access on the Web :
 - PDB (proteins)
 - NDB (nucleic acids)
 - AMCSd (minerals)
 - COD (small/medium crystal structures, based on donations)
- Toll databases :
 - CSD (organic, organometallic)
 - ICSD (inorganic, minerals)
 - CRYSTMET (metals, intermetallics)
 - ICDD (powder patterns)

Other structure Databases

- For all metallic/intermetallic phases: The Pearson books (in paper format)
- For some simple structures: Wyckoff, Crystal Structures (book)
- Literature: all IUCr journals like Acta Cryst., J. Appl. Cryst. etc.

Crystallographers join the Crystallography Open Database



www.crystallography.net



Deposit your crystal data
in the Public Domain
Thanks !



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Searching the COD

<http://www.crystallography.net/>

Crystallography Open Database

COD Crystallography Open Database



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Search

(Output limited to 300 entries maximum, see the [hints and tips](#))

Search by COD ID:

Enter SMILES or SMARTS:

Note: substructure search by SMARTS is currently available in a subset of COD containing 50 000 structures.

text (1 or 2 words)	<input type="text"/>
journal	<input type="text"/>
year	<input type="text"/>
volume	<input type="text"/>
issue	<input type="text"/>
1 to 8 elements	<input type="checkbox"/> <input type="checkbox"/>
NOT these elements	<input type="text"/>
volume min and max	<input type="text"/> <input type="text"/>
number of distinct elements min and max	<input type="text"/> <input type="text"/>
filters	<input type="checkbox"/> has F_{obs}
Reset	<input type="button" value="Send"/>

a (min - max)	<input type="text"/>
b	<input type="text"/>
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beta	90 <input type="text"/> 90
gamma	90 <input type="text"/> 90
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Reset	<input type="button" value="Send"/>

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Searching the COD

Crystallography Open Database

COD Crystallography Open Database

Search Results

Result : There are 43 entries in the selection

You can download the COD numbers of the selection as a text file
You can download all files as a single ZIP archive

Searching elements including Al, O number of elements between 2 and 2

COD ID: 1000017

CIF file Formula: - Al₂O₃ -
Comments: Tsirelson, V G; Antipin, M Y; Gerr, R G; Ozerov, R P; Struchkov, Y T Ruby structure peculiarities derived from X-ray data. Localization of chromium atoms and electron deformation density Physica Status Solidi, Sectio A: Applied Research 87 (1985) 425-433
Space group: R-3 c :H
Cell volume: 255
Cell parameters: 4.7606; 4.7606; 12.994; 90; 90; 120;

COD ID: 1000032

CIF file Formula: - Al₂O₃ -
Comments: Lutterotti, L; Scardi, P Simultaneous structure and size-strain refinement by the Rietveld method Journal of Applied Crystallography 23 (1990) 246-252
Space group: R-3 c :H
Cell volume: 255.1
Cell parameters: 4.7605; 4.7605; 12.9956; 90; 90; 120;

COD ID: 1000059

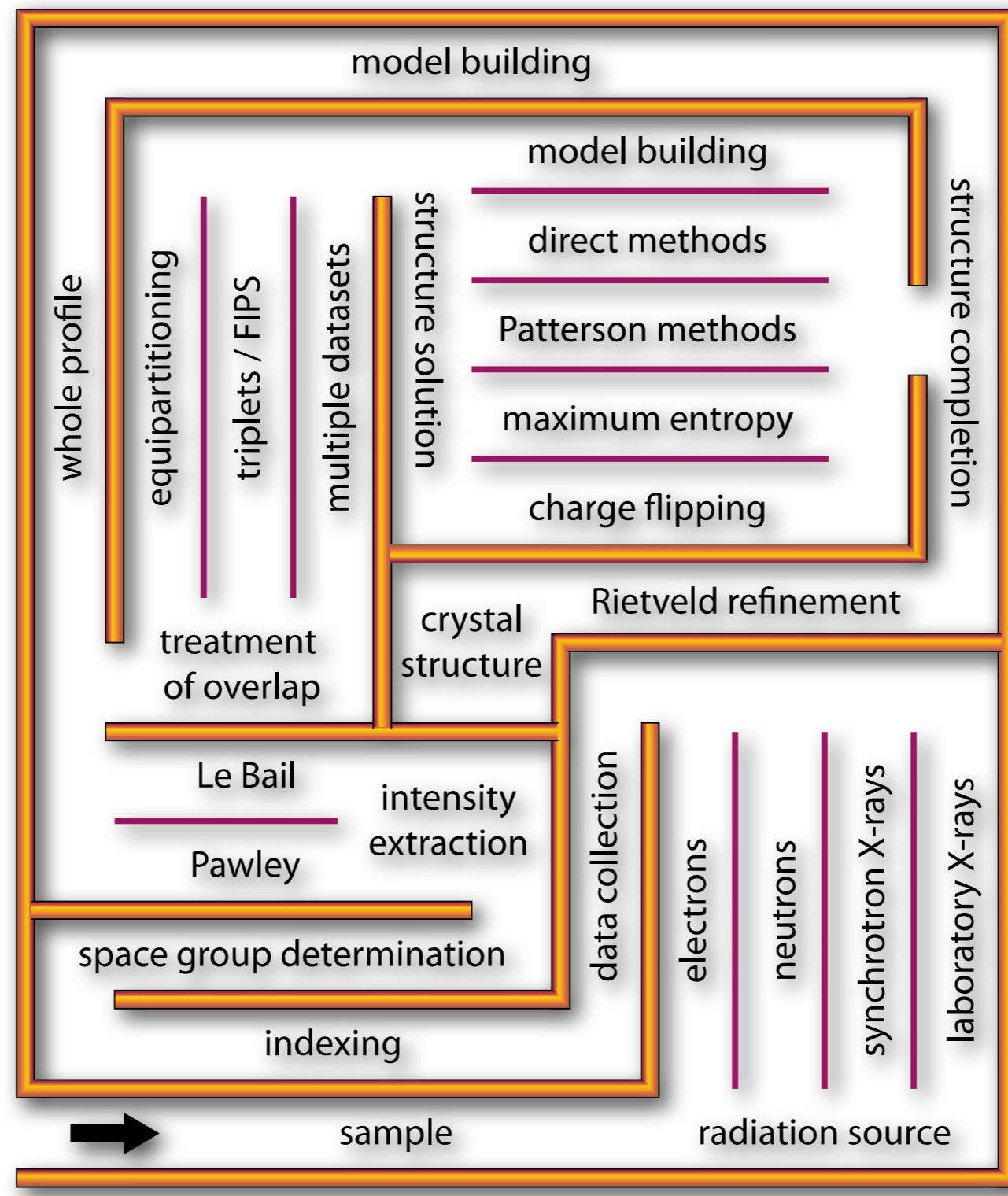
CIF file Formula: - Al₂O₃ -
Comments: Wang, X - L; Hubbard, C R; Alexander, K B; Becher, P F Neutron diffraction measurements of the residual stresses in Al₂O₃ - ZrO₂ (CeO₂) ceramic composites Journal of the American Ceramic Society 77(6) (1994) 1569-1575
Space group: R-3 c :H
Cell volume: 254.4
Cell parameters: 4.7554; 4.7554; 12.991; 90; 90; 120;

COD ID: 1000442

CIF file Formula: - Al₂O₃ -
Comments: Ollivier, B; Retoux, R; Lacorre, P; Massiot, D; Ferey, G Crystal structure of S-kappa-alumina: an X-ray powder diffraction, TEM and NMR study Journal of Materials Chemistry 7(6) (1997) 1049-1056
Space group: Pn a 21
Cell volume: 361.3

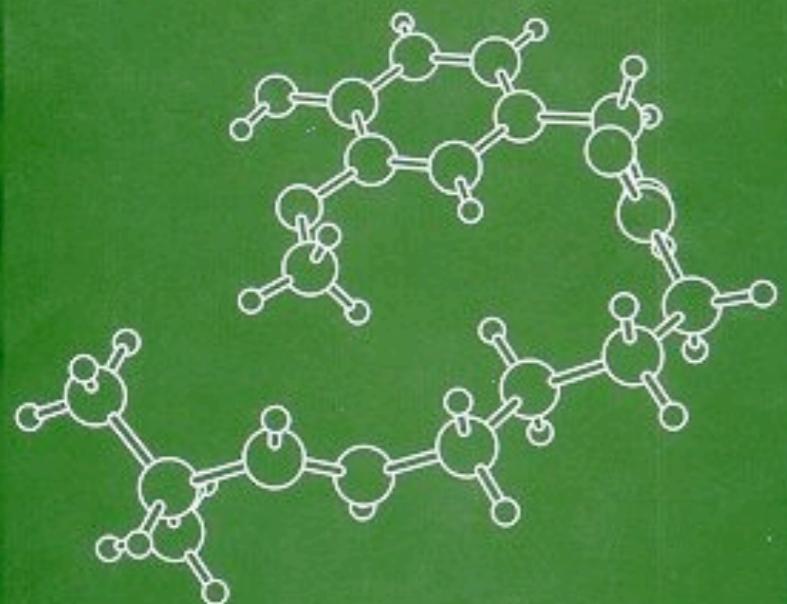
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_atom_site_aniso_U_13
_atom_site_aniso_U_22
_atom_site_aniso_U_23
_atom_site_aniso_U_33
Al1 0.0022(2) 0.0011 0. 0.0022(2) 0. 0.0012(3)
01 0.0021(71) 0.0017 0.00035 0.0034(149) 0.0007(54) 0.0019(3)
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_attached_hydrogens
_atom_site_calc_flag
Al1 Al3+ 12 c 0. 0. 0.35216(3) 1. 0 d
01 02- 18 e 0.30668(16) 0. 0.25 1. 0 d
loop_
_atom_type_symbol
_atom_type_oxidation_number
Al3+ 3.000
02- -2.000

Solving the crystal structure: McCusker maze



Structure Determination from Powder Diffraction Data

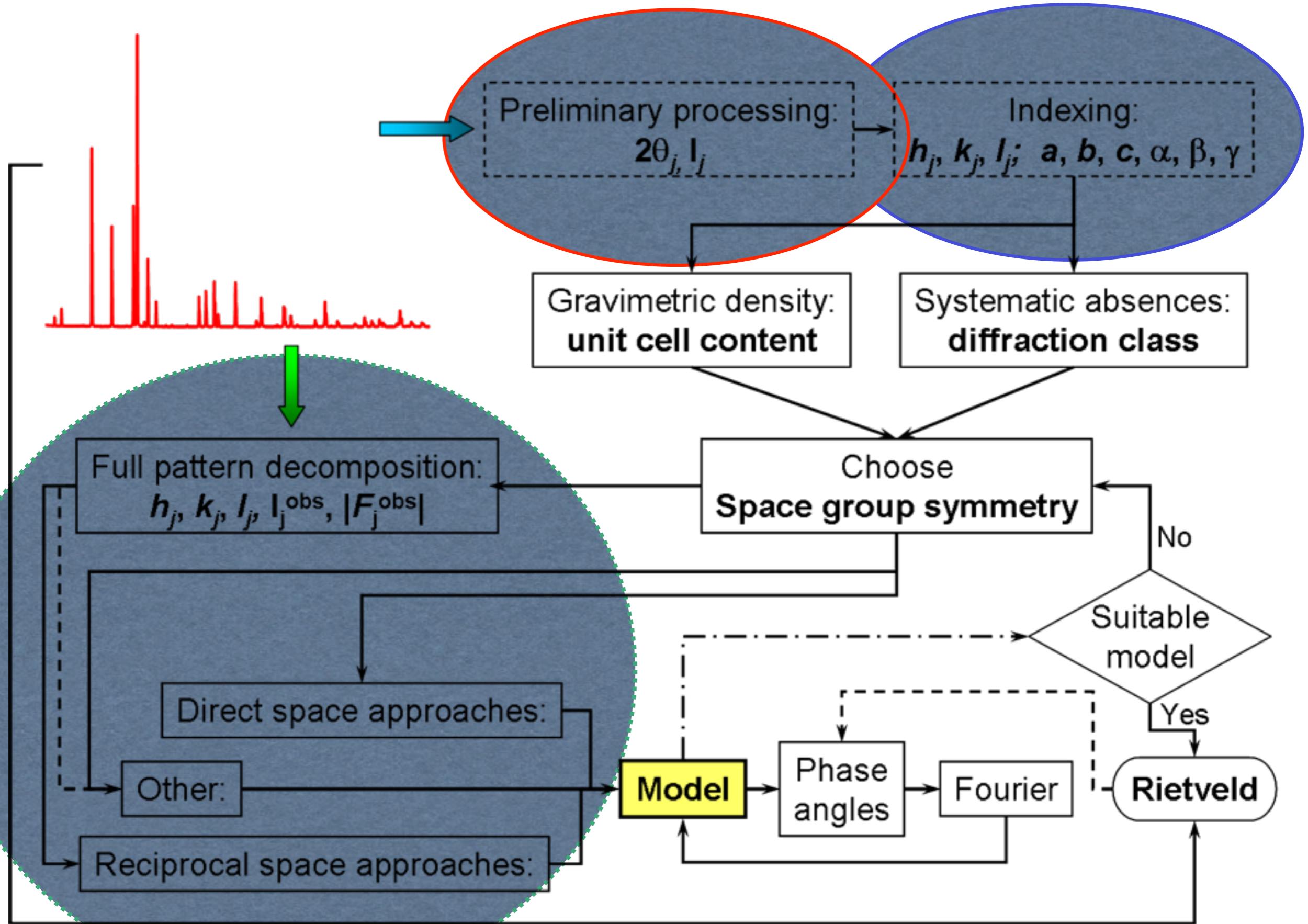
Edited by
W. I. F. David, K. Shankland,
L. B. McCusker, and Ch. Baerlocher



The issue of indexing and
solving a crystal structure
from powder pattern
was treated in a monograph

2002

By the International
Union of Crystallography



In Maud

- Ab initio structure solution
 - Indexing
 - Structure solution
- Structure databases
 - Search match
 - Crystal structure databases

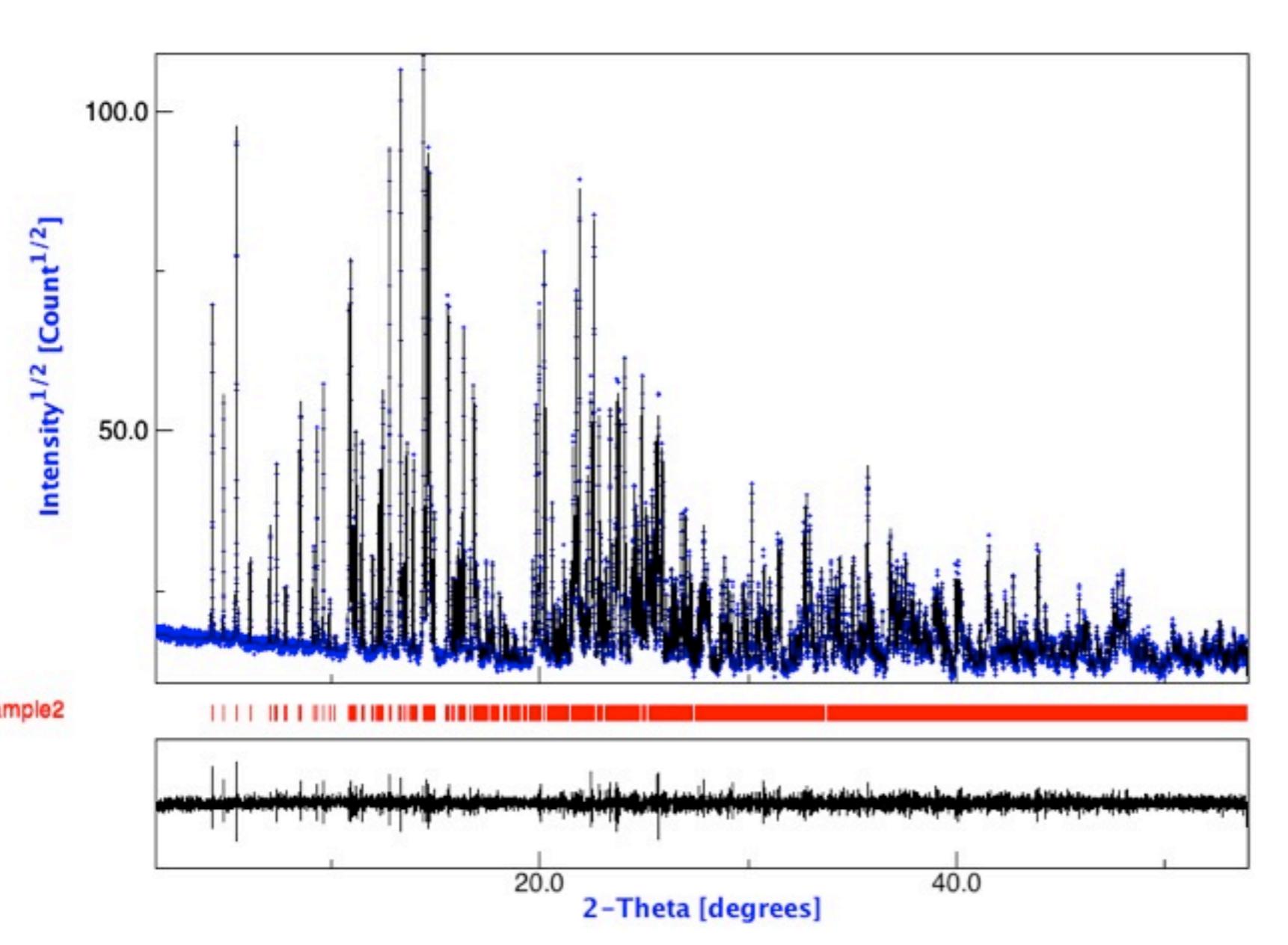
Indexing and solution in Maud

- Indexing:
 - smoothing, background subtraction and peak locations
 - peak list export for classical indexing programs (Dicvol, Treor etc.)
 - or genetic indexing or full pattern indexing (when no one else program succeed)
- Dicvol indexing results import and space group sorting (space group identification)
- Le Bail fitting for cell refinement and structure intensities extraction (with export for structure solution programs)
- Structure solutions:
 - Genetic algorithm
 - Electron density maps
 - Export to other programs (superflip, sir20xx, shelx....)

ab-initio structure solution

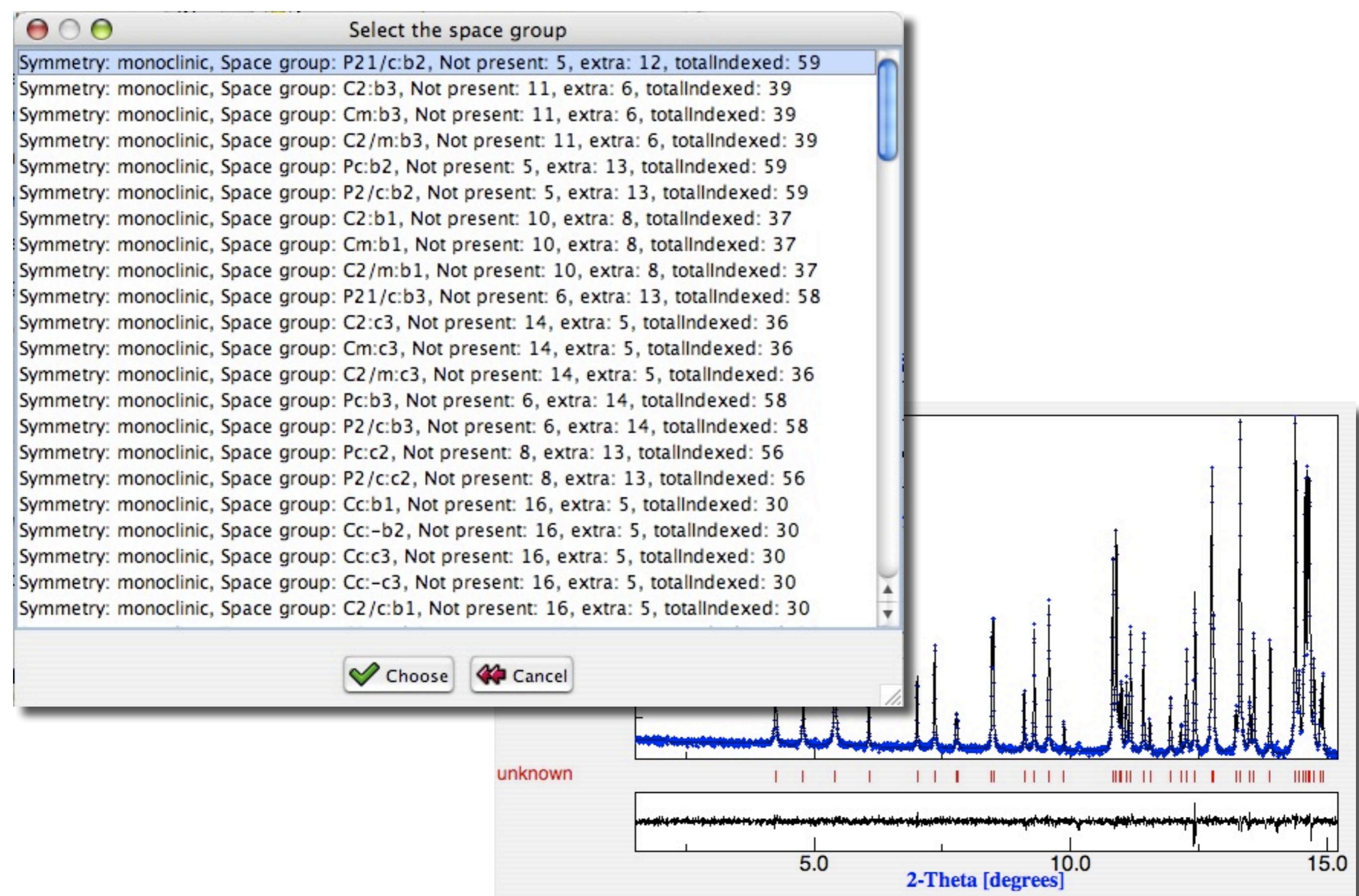
- Collection of a very good experimental pattern
 - accurate peak positions
 - low noise, good intensities, sharp peaks
- Indexing (to determine symmetry, cell parameters and possible space groups)
- Atoms location
 - usual:
 - structure factors extraction
 - structure solving by specialized programs
 - direct:
 - atoms location from fitting
- Structure refinement (Rietveld)
- Structure validation (Platon?)

Le Bail or Pawley fitting



- monoclinic
- $R_w(\%)=7.5$
- $a=19.87820(5)$
- $b=8.19454(2)$
- $c=11.24154(3)$
- $\beta=106.0656(2)$

Space groups sorting



Atom locations

- Direct methods (Shelx, Sir2004...):
 - Some algorithms are used to solve the phase problem
 - They work best with single crystal structure factors
- Electron density maps, difference electron density maps and Patterson maps
 - using Fourier transform or maximum entropy methods
 - from electron density maps atom should then be located (not easy)
- Charge flipping algorithm: special technique to obtain electron density maps, as for the previous lot of reflections are required (ex. superflip)
- Direct atom locations:
 - genetic algorithms
 - simulated annealing
 - Montecarlo methods
- Special methods were developed for particular cases: envelopes, energy principles....

Databases in Maud

- Maud has a small structure database that can be expanded by the user
- Phases, Instruments can be stored in the databases in CIF format
- The CIF format is the Crystallographic Information Format developed by the IUCr
- Maud can import from any file containing phases or instruments in CIF format
- A special function can submit a solved or refined structure directly to the COD database online