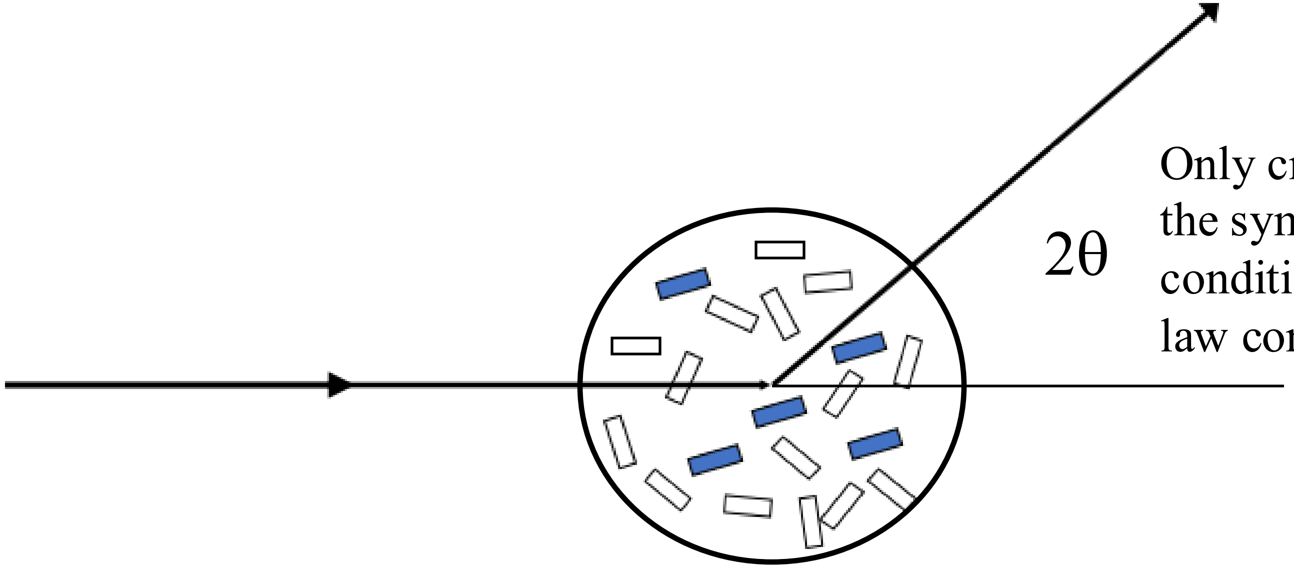
Lecture

X-Ray Powder Diffraction

What is a powder?

- In the context of powder diffraction, a powder is a sample that consists of many small crystallites with a wide range of different orientations in space.
    - Ideally, a random and uniform distribution of orientations
- Only some small fraction of the crystallites in the sample are in the correct orientation to contribute to the diffracted intensity in a given peak



Only crystallites that are in the symmetrical reflection condition and fulfill Bragg’s law contribute to diffraction

What is X-ray Powder Diffraction (XRD)

- X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.
- In other methods a single crystal is required whose size is much larger than microscopic dimensions. However, in the powder method as little as 1 mg of the material is sufficient for the study.
- The analyzed material is finely ground, homogenized, and average bulk composition is determined

History

- Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice.
- The powder method was devised independently by Debye and Scherrer in Germany and by Hull in America at about the same time.

Fundamental Principles of X-ray Powder Diffraction (XRD)

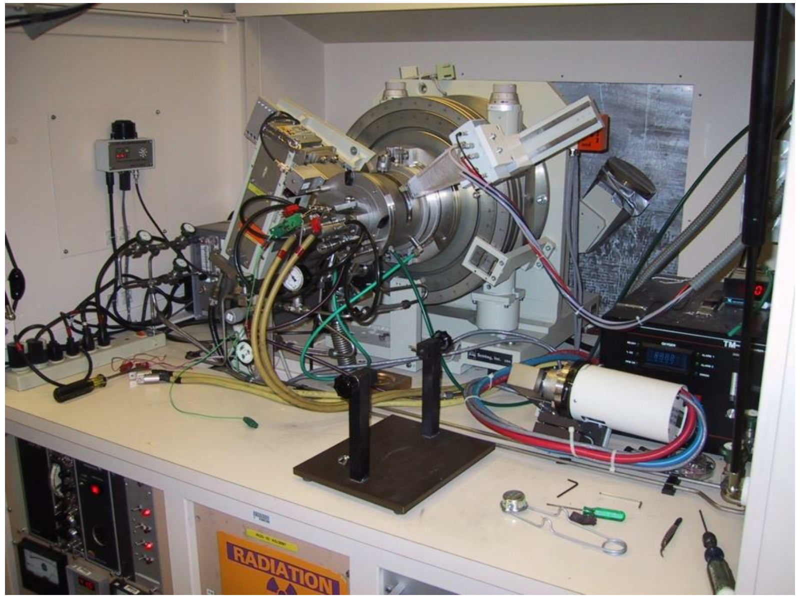
- X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample.
- These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample.
- For every set of crystal planes , one or more crystals will be in the correct orientation to give the correct Bragg angle to satisfy Bragg's equation.
- Each diffraction line is made up of a large number of small spots, each from a separate crystal.
- Each spot is so small as to give the appearance of a continuous line. Every crystal plane is thus capable of diffraction.

- The powdered sample generates the concentric cones of diffracted X-rays because of the random orientation of crystallites in the sample.
- Hence, instead of the sample generating only single diffraction spots, it generates cones of diffracted X-rays, with the point of all of the cones at the sample.
- The powder diffracts the x-rays in accordance with Bragg’s law to produce cones of diffracted beams.
- These cones intersect a strip of photographic film located in the cylindrical camera to produce a characteristic set of arcs on the film.
- When the film is removed from the camera, flattened and processed, it shows the diffraction lines and the holes for the incident and transmitted beams.
- The x-ray pattern of a pure crystalline substance can be considered as a “fingerprint” with each crystalline material having, within limits, a unique diffraction pattern

Electronic 1D detectors

- 1D position sensitive detectors based on many different types of technology are available.
  - Fast data collection, but not as efficient as a 2D detector
  - But access to high 2θ by curving the detector

INEL curved detector at Cal Tech



Braun linear PSD at ORNL/HTML

THE POWDER METHOD

$$\lambda = 2dSin\theta$$

Cubic crystal

$$(h^2 + k^2 + l^2) = \frac{4a^2}{\lambda^2}\sin^2\theta$$

$$a^2 = \frac{\lambda^2}{4\sin^2\theta}(h^2 + k^2 + l^2)$$

$$\boxed{(h^2 + k^2 + l^2) \propto \sin^2\theta}$$

The experimental arrangement of powder crystal method is shown in fig.1. its main feature are outlined as below: A is a source of X-rays which can be made monochromatic by a filter Allow the X-ray beam to fall on the powdered specimen P through the slits S1 and S2.

The function of these slits is to get a narrow pencil of X-rays. Fine powder, P, struck on a hair by means of gum is suspended vertically in the axis of a cylindrical camera.

This enables sharp lines to be obtained on the photographic film which is surrounding the powder crystal in the form of a circular arc.

Applications Identification

- The most common use of powder (polycrystalline) diffraction is chemical analysis. This can include phase identification (search/match) X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds).
- Other applications include: identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically

- Determination of unit cell dimensions. measurement of sample purity .
- Most useful for cubic crystal. Used for determining the complex structure of metals and alloys.
- Useful to make distinction between the allotropic modifications of the same substance.

• Strengths and Limitations of X-ray Powder Diffraction (XRD)?

- **Strengths** :- Powerful and rapid (< 20 min) technique for identification of an unknown mineral.

- In most cases, it provides a clear structural determination. XRD units are widely available. Data interpretation is relatively straight forward

Limitations:-

- Homogeneous and single phase material is best for identification of an unknown.
- Requires tenths of a gram of material which must be ground into a powder.
- For mixed materials, detection limit is ~ 2% of sample. Peak overlay may occur and worsens for high angle 'reflections’ .
- For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated

Insert the values into a table and compute sinθ and $\sin^2\theta$.
Since the lowest value of $\sin^2\theta$ is 3A and the next is 4A the first
Entry in the Calc. $\sin^2\theta$ column is (0.10854/3)*4 *etc.*

d/Å	Sinθ	$\sin^2\theta$	Calc. $\sin^2\theta$	(h, k, l)
2.338	0.32945	0.10854		(1,1,1)
2.024	0.38056	0.14482	0.14472	(2,0,0)
1.431	0.53826	0.28972	0.28944	(2,2,0)
1.221	0.63084	0.39795	0.39798	(3,1,1)
1.169	0.65890	0.43414	0.43416	(2,2,2)
1.0124	0.76082	0.57884	0.57888	(4,0,0)
0.9289	0.82921	0.68758	0.68742	(3,3,1)
0.9055	0.85063	0.72358	0.72360	(4,2,0)

The reflections have now been indexed.

Calculation of a

For the first reflection (for which $h^2 + k^2 + l^2 = 3$)

$\sin^2\theta = 3A = 3 (\lambda^2 / 4a^2)$

$a^2 = 3\lambda^2 / 4\sin^2\theta$

$a = 4.04946$ Å $= 4.04946 \times 10^{-8}$ cm.

Calculation of the density of aluminium

$a^3 = 66.40356$ Å^3 $= 66.40356 \times 10^{-24}$ cm^3.

If the density of aluminium is ρ (g. cm.$^{-3}$), the mass of the unit cell is

$\rho \times 66.40356 \times 10^{-24}$ g.

The unit cell of aluminium contains 4 atoms.

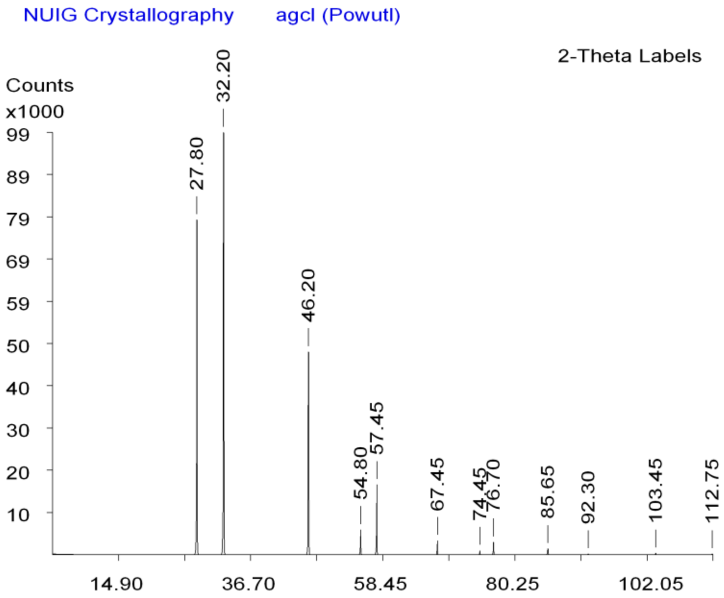
The weight of one aluminium atom is $26.98/(6.022 \times 10^{23}) = 4.48024 \times 10^{-23}$ and the weight of four atoms (the content of the unit cell) is 179.209×10^{-24}.

$\rho \times 66.40356 \times 10^{-24} = 179.209 \times 10^{-24}$

$p = 2.6988$ g.cm^{-3}.

Example

The X-ray powder diffraction pattern of AgCl obtained using radiation of wavelength 1.54Å is shown below. The peaks are labelled with 2θ values



Answer **each** of the following.

On the basis that the structure is cubic and of either the NaCl or CsCl type

1. Index the first six reflections.
2. Calculate the unit cell parameter
3. Calculate the density of AgCl.

(Assume the following atomic weights: Ag, 107.868; Cl, 35.453; and Avogadro's number is 6.022 x 1023)

Since θ values are available $\sin^2\theta$ values can be calculated and inserted in a table.

2θ	θ	$\mathrm{Sin}^2\theta$
27.80	13.90	0.0577
32.20	16.10	0.0769
46.20	23.10	0.1539
54.80	27.40	0.2118
57.45	28.73	0.2310
67.45	33.73	0.3083

Calc. $\mathrm{Sin}^2\theta$
0.07693
0.1539
0.2116
0.2308
0.3077

From $\mathrm{Sin}^2\theta = A(h^2 + k^2 + l^2)$ the possible values are:

1. for a face centred lattice 3A, 4A , 8A, 11A, 12A and 16A
2. for a primitive lattice 1A, 2A, 3A, 4A, 5A and 6A

The second option is not possible as the first 2 are not in the ratio of 1:2.
To test the first option, divide the first by 3 and multiply the result by 4, 8 *etc.*

Density of AgCl

Since $\sin^2\theta = \lambda^2(h^2 + k^2 + l^2)/4a^2$

$a^2 = (1.54)^2.(16)/4(0.3083)$ using the largest (most accurate) 2θ

$a^2 = 30.7692$

$a = 5.547\text{Å}$ ($1\text{Å} = 10^{-8}$ cm)

Formula wt. of unit cell = 4AgCl = 573.284g

This is the weight of 4 moles of AgCl.

The weight of 4 molecules is $573.284 / (6.02 \times 10^{23})$

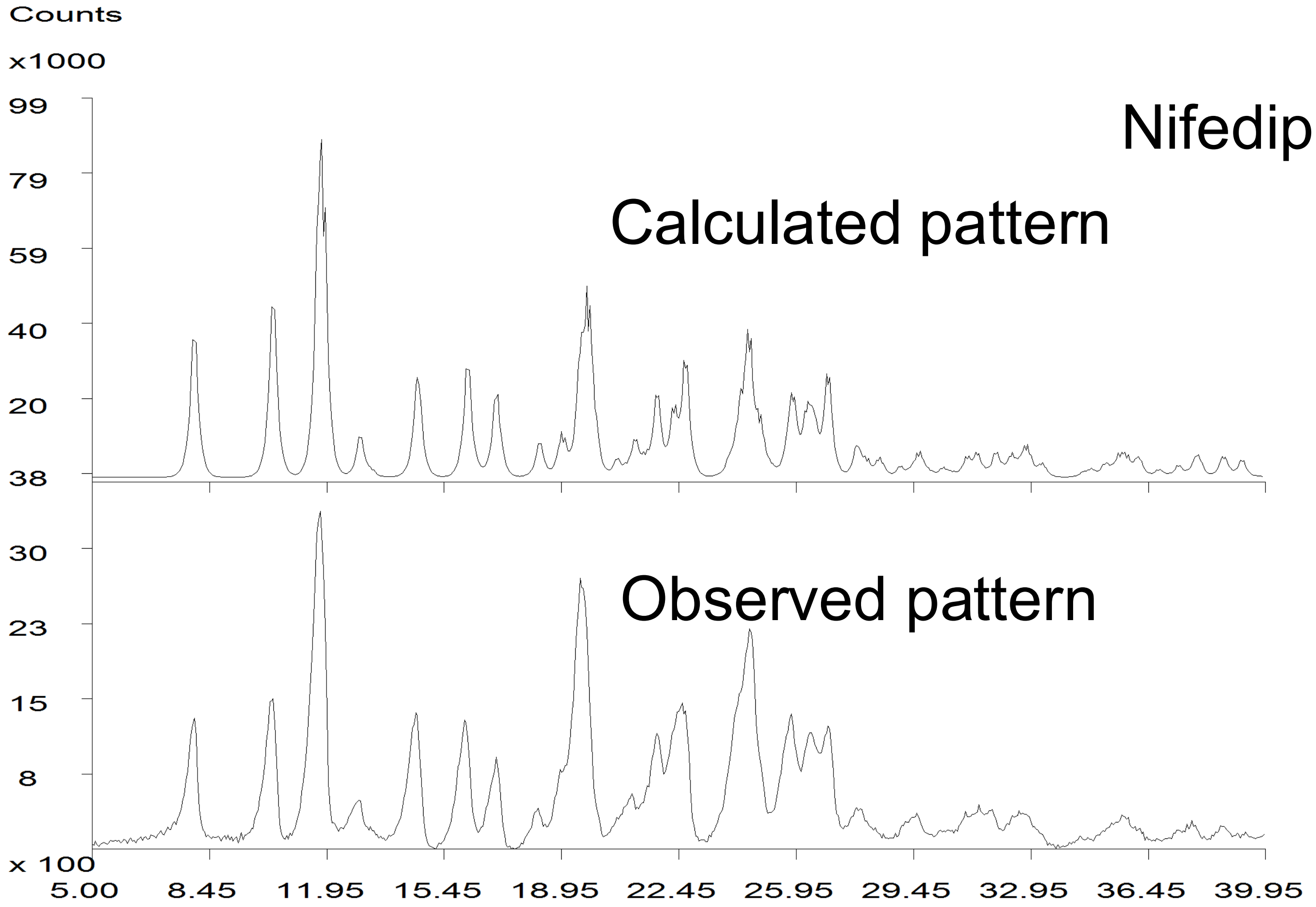
Density = $573.284 / (6.02 \times 10^{23})(5.547 \times 10^{-8})^3$

A is in Å thus the answer should be multiplied by $1 / 10^{-24}$

Density = 5.580 g/cm^3

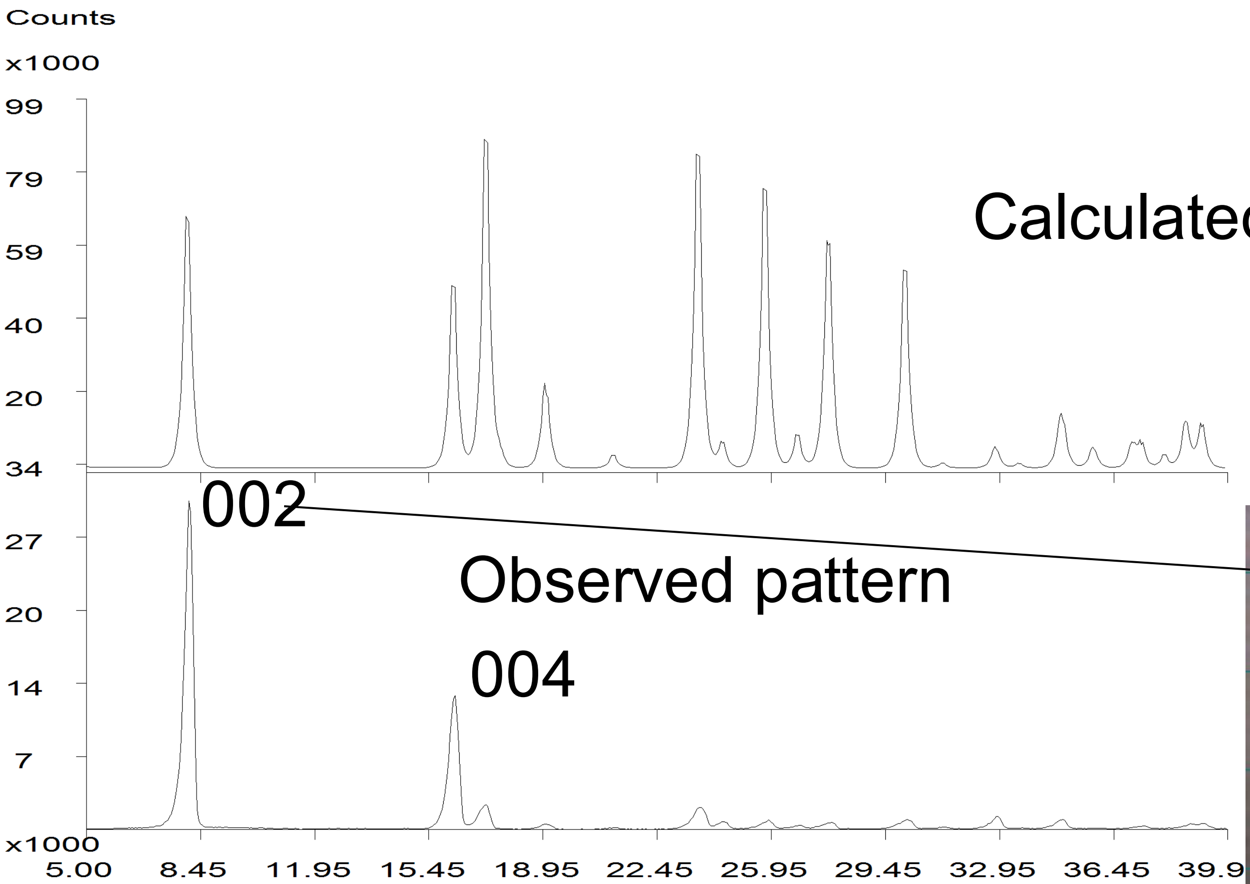
Preferred Orientation Effects in X-ray Powder Diffraction Patterns

It is possible to calculate the theoretical diffraction pattern if the crystal structure is known.



There are no preferred orientation effects here as all reflections have their expected intensity.

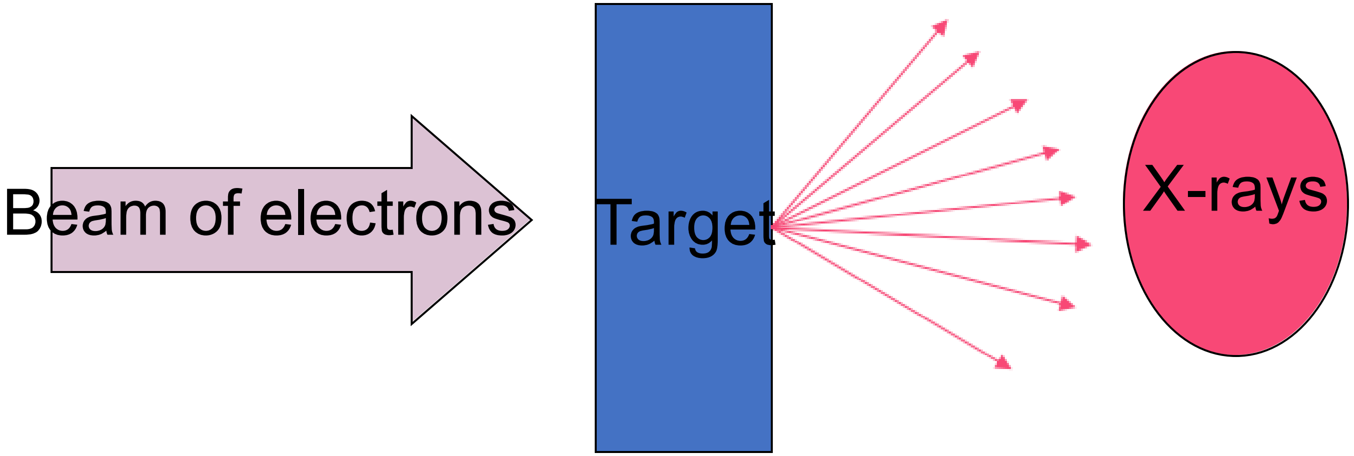
Benzoic acid



There is clear preferred orientation here. The 002 is the flat face exposed when the needles lie down on a flat plate.

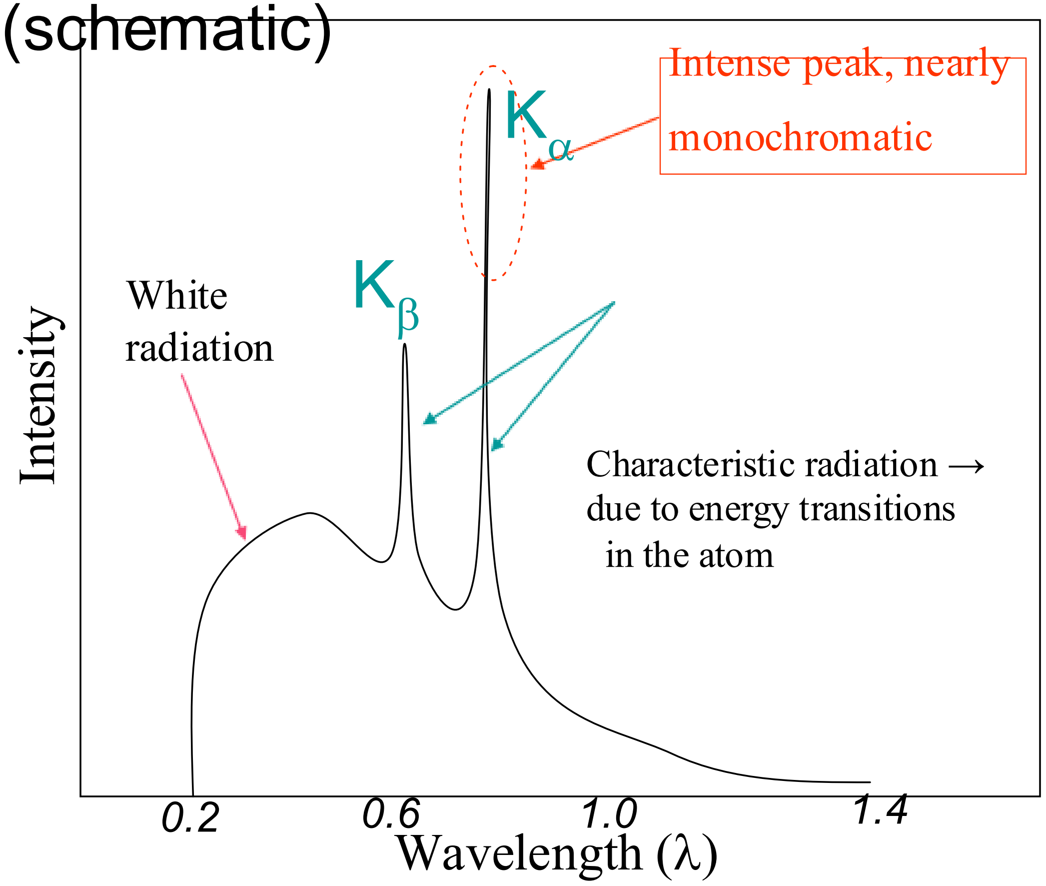
Lecture : X-ray Diffraction (XRD)

- For electromagnetic radiation to be diffracted the spacing in the grating should be of the same order as the wavelength.
- In crystals the typical interatomic spacing ~ 2-3 Å** → so the suitable radiation for the diffraction study of crystals is X-rays.
- Hence, X-rays are used for the investigation of crystal structures.
- Neutrons and Electrons are also used for diffraction studies from materials.



An accelerating (or decelerating) charge radiates electromagnetic radiation

Mo Target impacted by electrons accelerated by a 35 kV potential shows the emission spectrum as in the figure below (schematic)



Intense peak, nearly monochromatic

White radiation

Characteristic radiation → due to energy transitions in the atom

X-ray sources with different λ for doing XRD studies

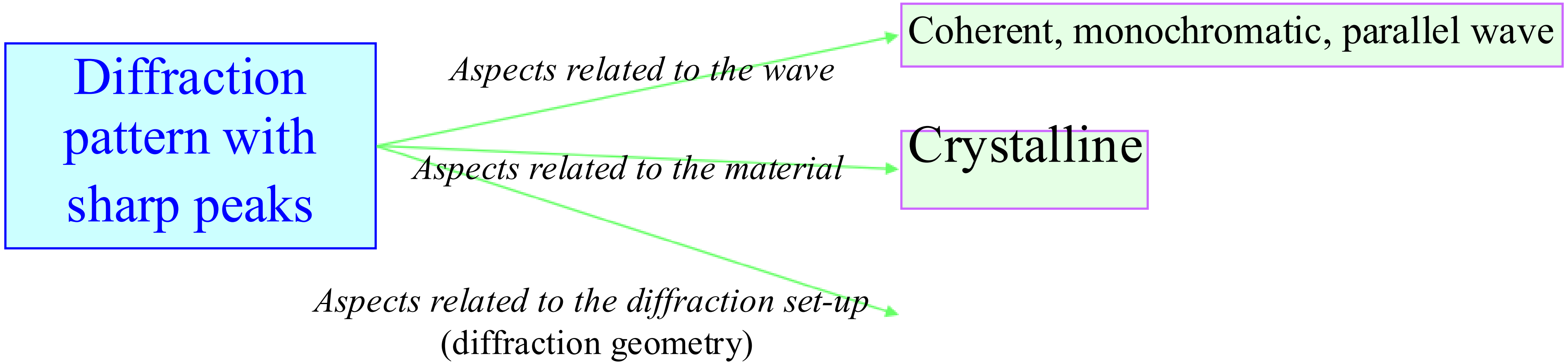
Target Metal	**λ Of K_α radiation (Å)**
Mo	0.71
Cu	1.54
Co	1.79
Fe	1.94
Cr	2.29

The high intensity nearly monochromatic K_α x-rays can be used as a radiation source for

X-ray diffraction (XRD) studies ➢ a monochromator can be

Diffraction

- Now we shall consider the important topic as to how X-rays interact with a crystalline array (of atoms, ions etc.) to give rise to the phenomenon known as X-ray diffraction (XRD).
- Let us consider a special case of diffraction → a case where we get '*sharp diffraction peaks*'.
- Diffraction (*with sharp peaks*) requires two important conditions to be satisfied:
  - Coherent, monochromatic, parallel waves (with wavelength λ).
  - Crystalline array of scatterers* with spacing of the order of (~) λ.



Diffraction pattern with sharp peaks

Aspects related to the wave

Coherent, monochromatic, parallel wave

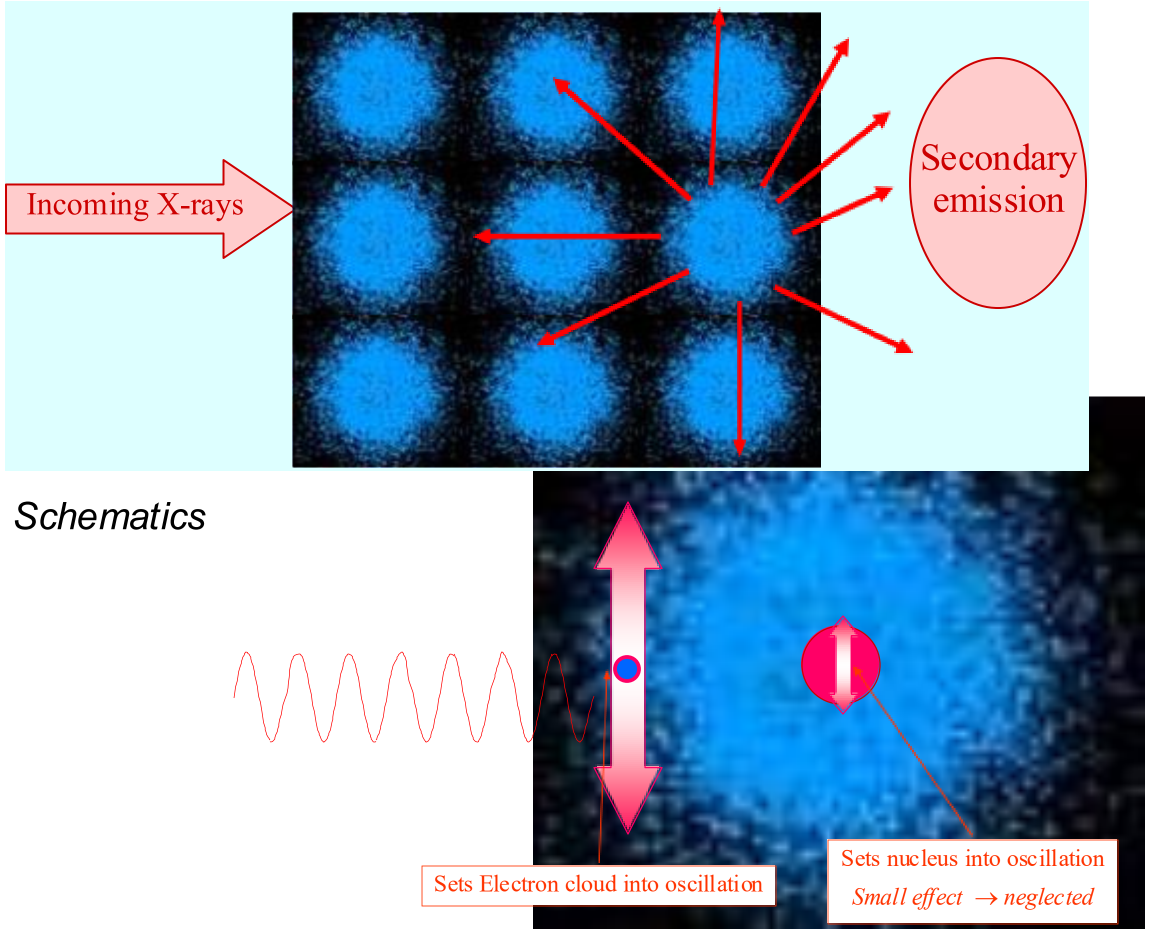
Aspects related to the material

Crystalline

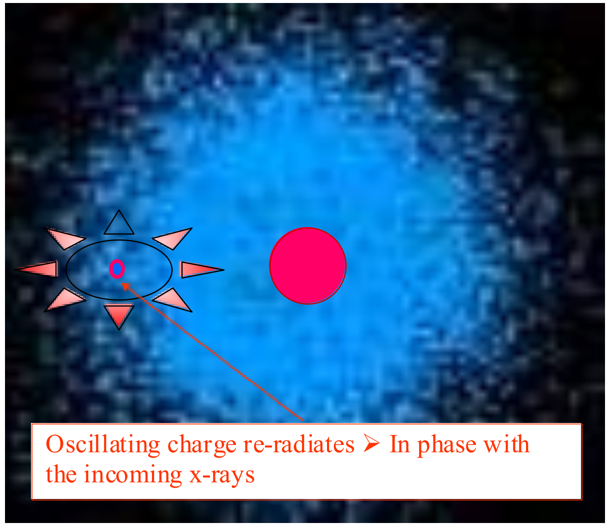
Aspects related to the diffraction set-up
(diffraction geometry)

XRD → the first step

- A beam of X-rays directed at a crystal interacts with the electrons of the atoms in the crystal.
- The electrons oscillate under the influence of the incoming X-Rays and become secondary sources of EM radiation.
- The secondary radiation is in all directions.
- The waves emitted by the electrons have the same frequency as the incoming X-rays ⇒ *coherent.*
- The emission can undergo constructive or destructive interference.

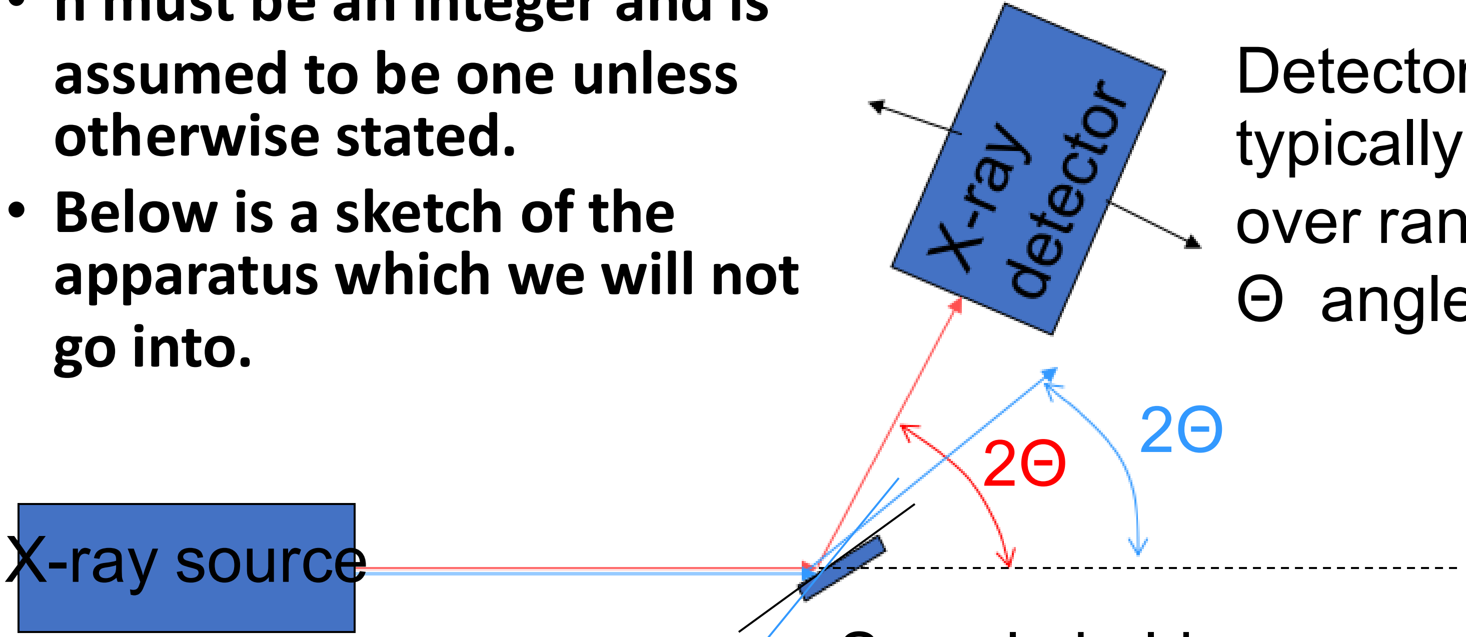


Schematics



Bragg Equation

- $n \lambda = 2 d \sin\Theta$
  - **n must be an integer and is assumed to be one unless otherwise stated.**
  - **Below is a sketch of the apparatus which we will not go into.**



Detector typically moves over range of 2 Θ angles

Typically a Cu or Mo target
1.54 or 0.8 Å wavelength

Sample holder

Orientation of diffracting planes

Planes in Lattices and Bragg's Law

We are interested in the planes in a crystal lattice in the context of X-ray diffraction because of Bragg's Law:

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

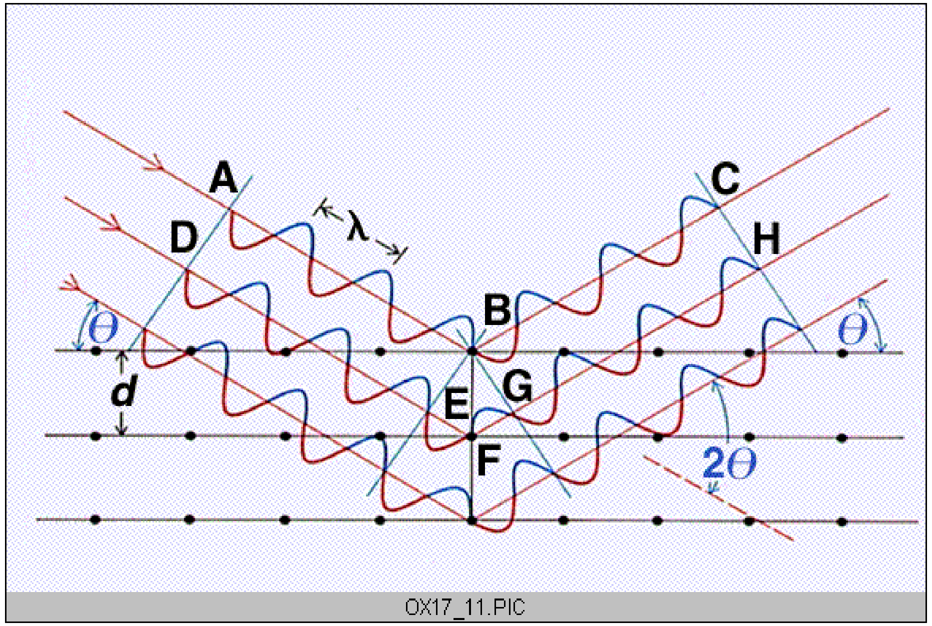
Where:

n is an integer

λ is the wavelength of the X-rays

d is distance between adjacent *planes* in the lattice

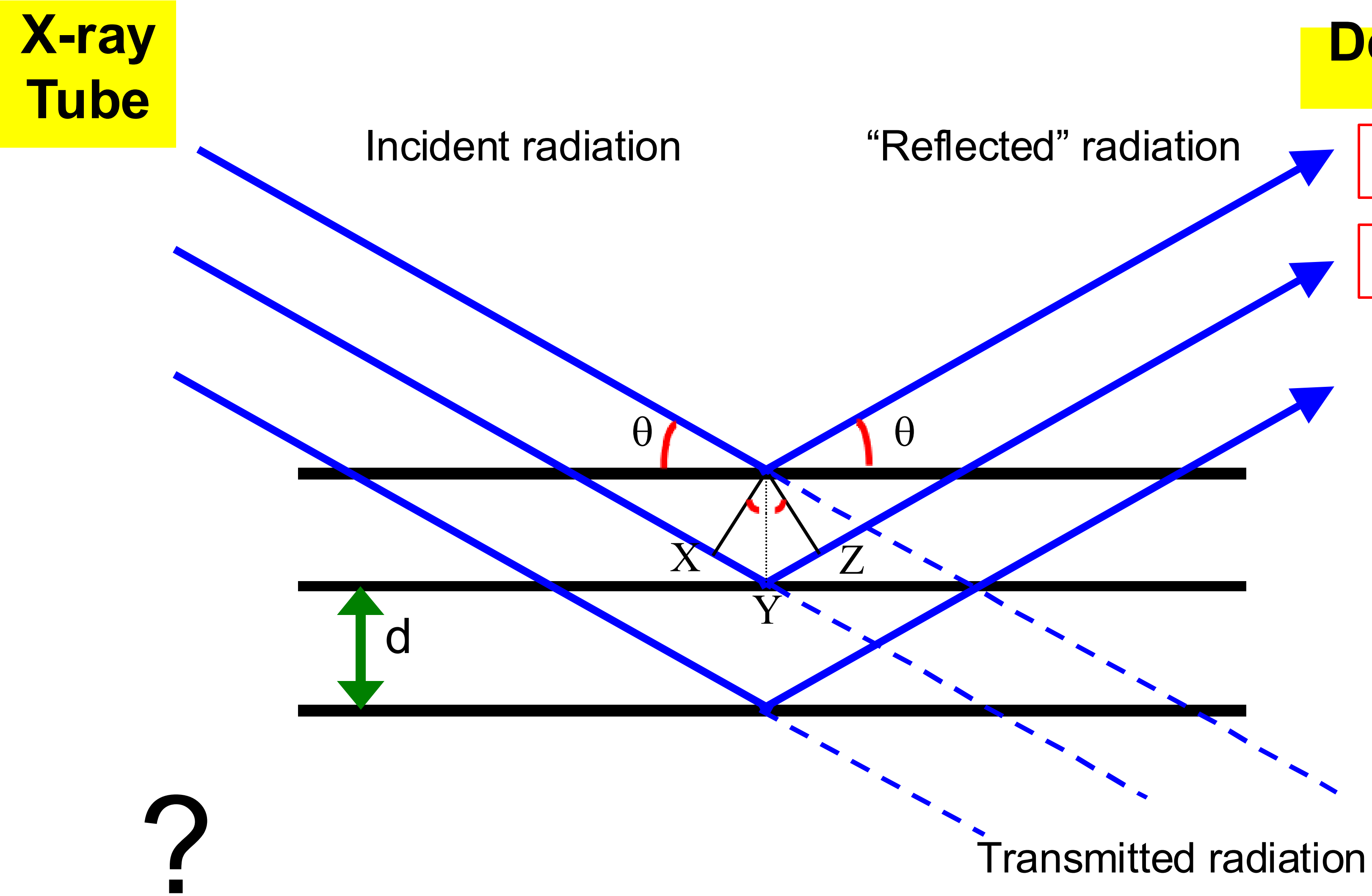
θ is the incident angle of the X-ray beam



Bragg's law tells us the conditions that must be met for the reflected X-ray waves to be in phase with each other (constructive interference). If these conditions are not met, destructive interference reduces the reflected intensity to zero!

W.H.Bragg and son W.L.Bragg were awarded the Nobel prize in 1915.

Diffraction from crystals



X-ray Tube

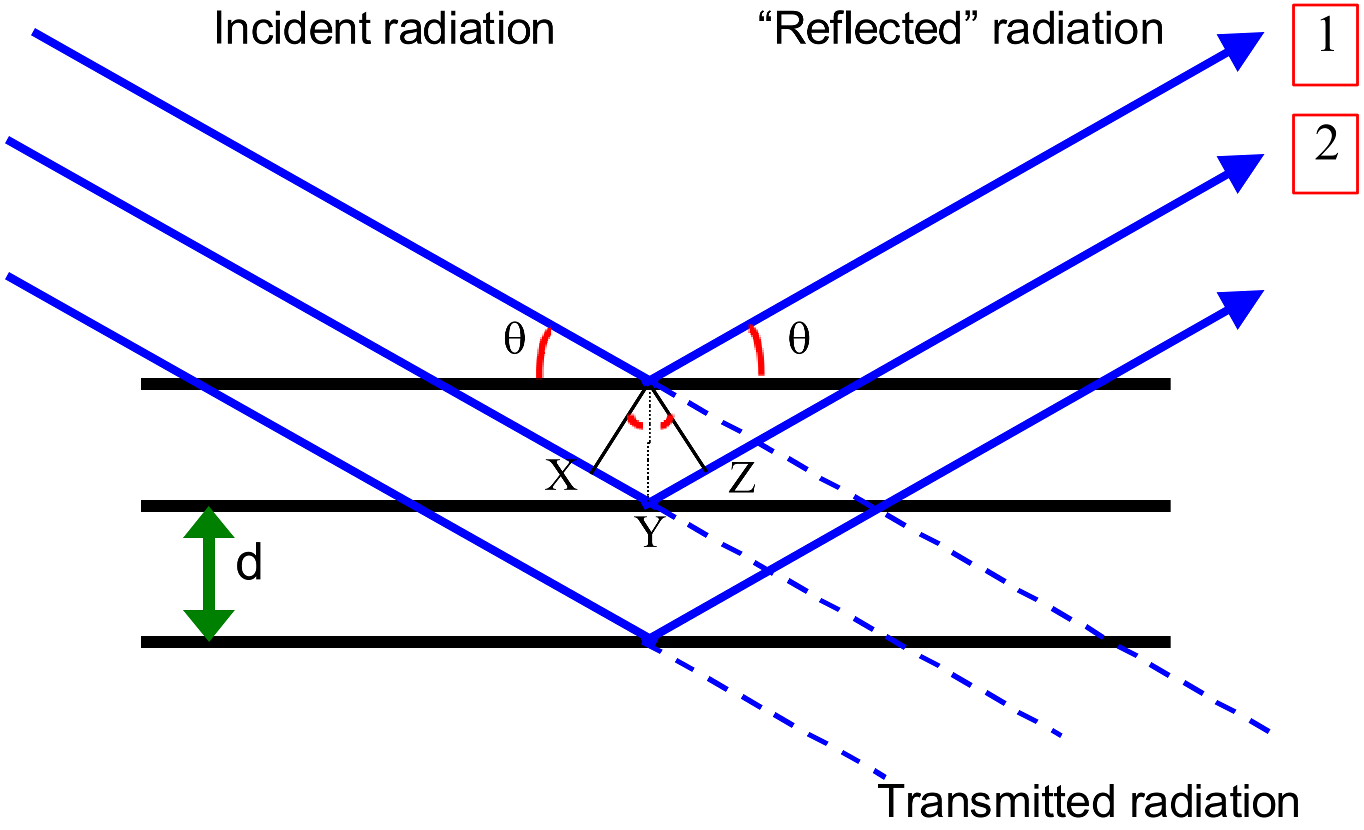
Detector

Incident radiation

“Reflected” radiation

Transmitted radiation

?



Beam 2 lags beam 1 by XYZ = $2d \sin \theta$

so $$2d \sin \theta = n\lambda$$ **Bragg’s Law**

Examples for Bragg Equation

If the wavelength striking a crystal at a 38.3° angle has a wavelength of 1.54 Å, what is the distance between the two layers. Recall we assume n = 1.

You will need your calculator to determine the sine of the angle.

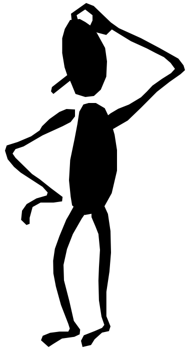
$$\mathbf{n\,\lambda = 2\,d\,\sin\,\theta}$$

$1.54\ \text{Å} = 2\ d\ \sin 38.3°$

this can be rearranged to $d = \lambda / (2\ \text{Sin}\ \theta_B)$

SO

$= 1.54\ \text{Å} / (\,2 * \text{Sin}\ 38.3\,) \rightarrow = 1.24\ \text{Å}$



X rays of wavelength 0.154 nm are diffracted from a crystal at an angle of 14.17^0. Assuming that $n = 1$, what is the distance (in pm) between layers in the crystal?

The given information is $n\,\lambda = 2\,d \sin\theta$

$n = 1$

$\theta = 14.17^0$

$\lambda = 0.154 \text{ nm} = 154 \text{ pm}$

$$d = \frac{n\,\lambda}{2\sin\theta} = \frac{1 \times 154 \text{ pm}}{2 \times \sin 14.17} = \underline{\mathbf{314.54\ \ pm}}$$

X-rays with wavelength 1.54Å are reflected from planes with d=1.2Å. Calculate the Bragg angle, θ, for constructive interference?

$\lambda = 1.54 \times 10^{-10}$ m, $d = 1.2 \times 10^{-10}$ m, $\theta = ?$

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

$$\theta = \sin^{-1}\left(\frac{n\lambda}{2d}\right)$$

n=1 : $\theta = 39.9^\circ$

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

We normally set n=1 and adjust Miller indices, to give

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

Use Bragg's law and the d-spacing equation to solve a wide variety of problems

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

or

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

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Combining Bragg and d-spacing equation

X-rays with wavelength 1.54 Å are "reflected" from the (1 1 0) planes of a cubic crystal with unit cell **a** = 6 Å. Calculate the Bragg angle, θ, for all orders of reflection, n.

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{1+1+0}{6^2} = 0.056$$

$$d^2 = 18 \quad \Rightarrow \quad \text{d} = 4.24\ \text{Å}$$

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

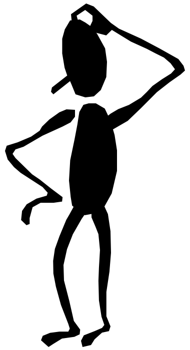
$$\theta = \sin^{-1}\left(\frac{n\lambda}{2d}\right)$$

n = 1 : θ = 10.46° = (1 1 0)

n = 2 : θ = 21.30° = (2 2 0)

It’s Importance

- The Bragg equation enables us to find the dimensions of a unit cell. This gives us accurate values for the volume of the cell.
- As you will see in the following on unit cells and the equations, this is how density is determined accurately.



When silver crystallizes, it forms face-centered cubic cells. The unit cell edge length is 408.7 pm. Calculate the density of silver. Though not shown here, the edge length was determined by the Bragg Equation.

$$d = \frac{m}{V} \qquad V = a^3 = (408.7\ \text{pm})^3 = \underline{\mathbf{6.83 \times 10^{-23}\ cm^3}}$$

Remember that there are 4 atoms/unit cell in a face-centered cubic cell

$$m = 4\ \text{Ag}\ \cancel{\text{atoms}} \times \frac{107.9\ \text{g}}{\cancel{\text{mole}}\ \text{Ag}} \times \frac{1\ \cancel{\text{mole}}\ \text{Ag}}{6.022 \times 10^{23}\ \cancel{\text{atoms}}} = \underline{\mathbf{7.17 \times 10^{-22}\ g}}$$

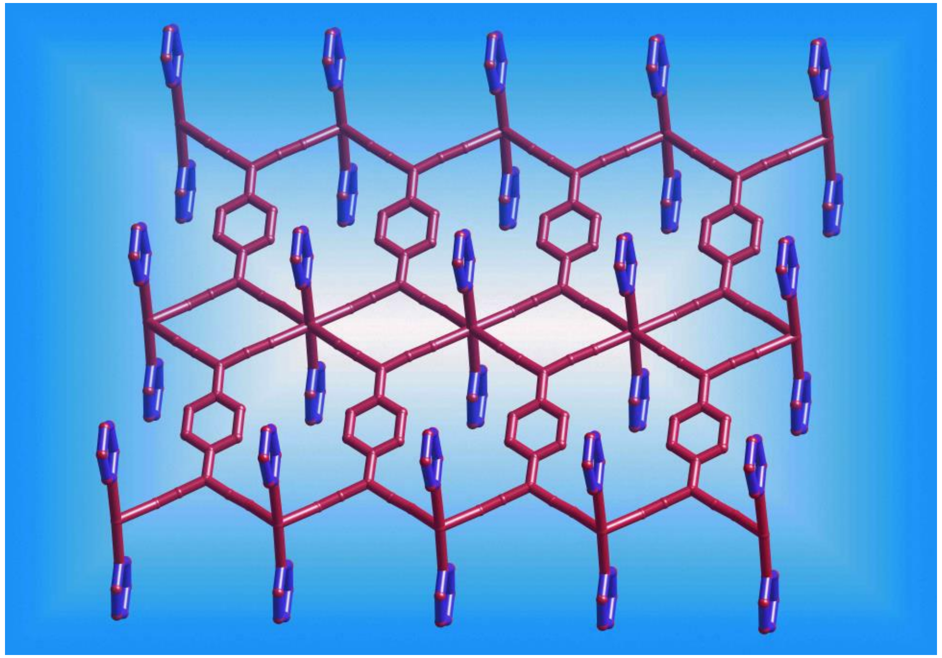
$$d = \frac{m}{V} = \frac{7.17 \times 10^{-22}\ \text{g}}{6.83 \times 10^{-23}\ \text{cm}^3} = \underline{\mathbf{10.5\ g/cm^3}}$$

This is a pretty standard type of problem to determine density from edge length.

Lecture (optional)

X-ray Crystallography (continued)

- The reciprocal lattice and Laue symmetry
- Data collection
- Space group determination
- Structure solution
- Powder X-ray diffraction



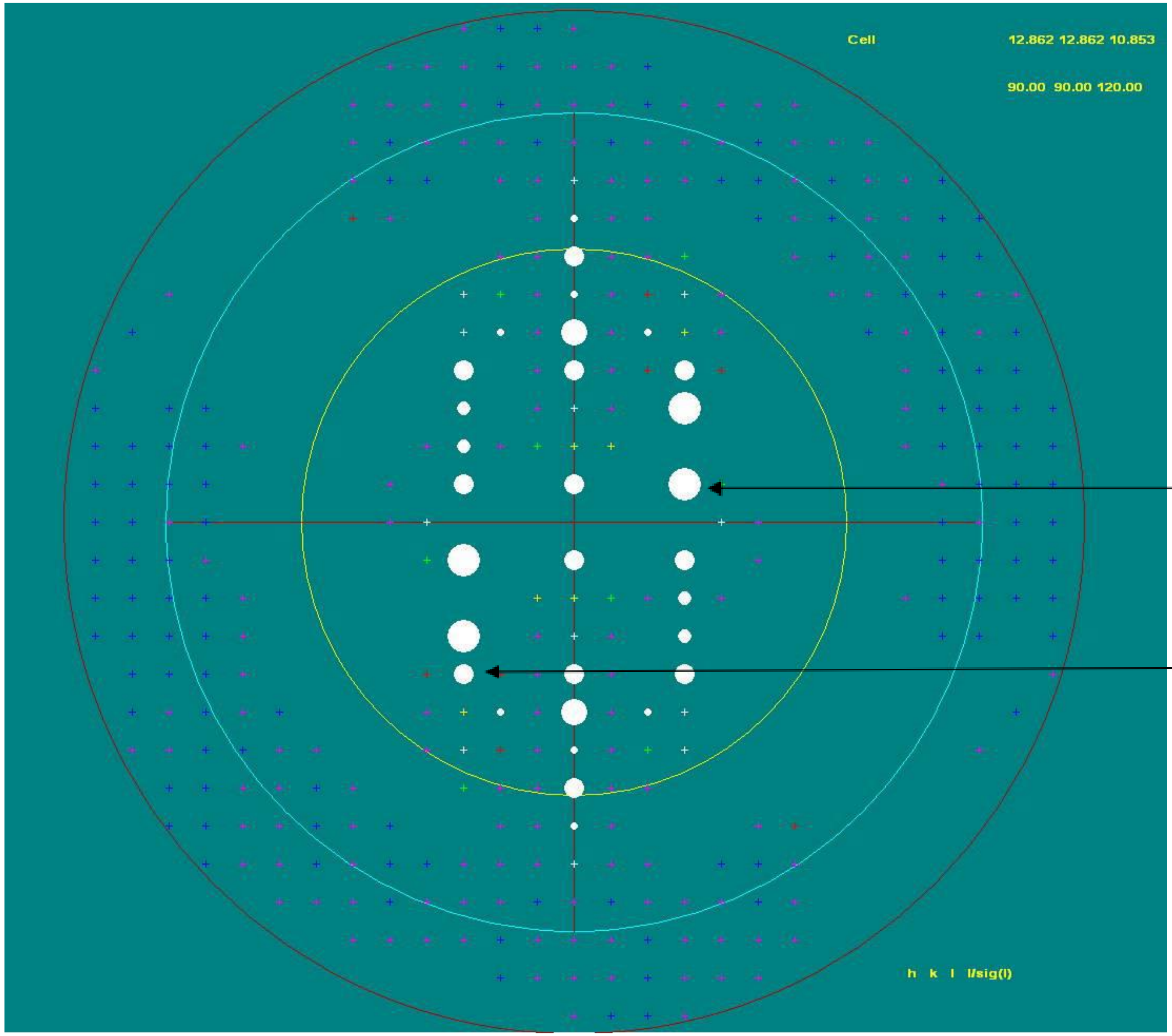
Reciprocal lattice and Laue symmetry

Through a geometrical construction it is possible to obtain a lattice with points corresponding to individual reflections.

This lattice is known as the reciprocal lattice, so called because of the reciprocal nature of the relationship between the axes in the real lattice and the reciprocal lattice.

For example, a long *b* cell length in the crystal corresponds to a small separation between lattice points in the reciprocal lattice (in the corresponding direction).

A reciprocal lattice plane (*h 0 l* plane); *h* horizontal, *l* vertical



In this representation spot size is related to X-ray intensity.

3 0 1

-3 0 -4

The symmetry with respect to reflection intensity in a reciprocal lattice is related to the symmetry in the real crystal.

For example in a monoclinic crystal the diffraction (or Laue) symmetry is 2/*m* i.e. 2-fold axis parallel to *k* and mirror plane in the *h*-*l* plane.

Therefore the reflection 4 5 6 is symmetry related to (i.e. will have the same intensity as):

4 -5 6; -4 5 -6; -4 -5 -6.

By considering the equivalency between reflections we can determine the Laue symmetry.

If a crystal is orthorhombic then it is has Laue symmetry of *mmm*.

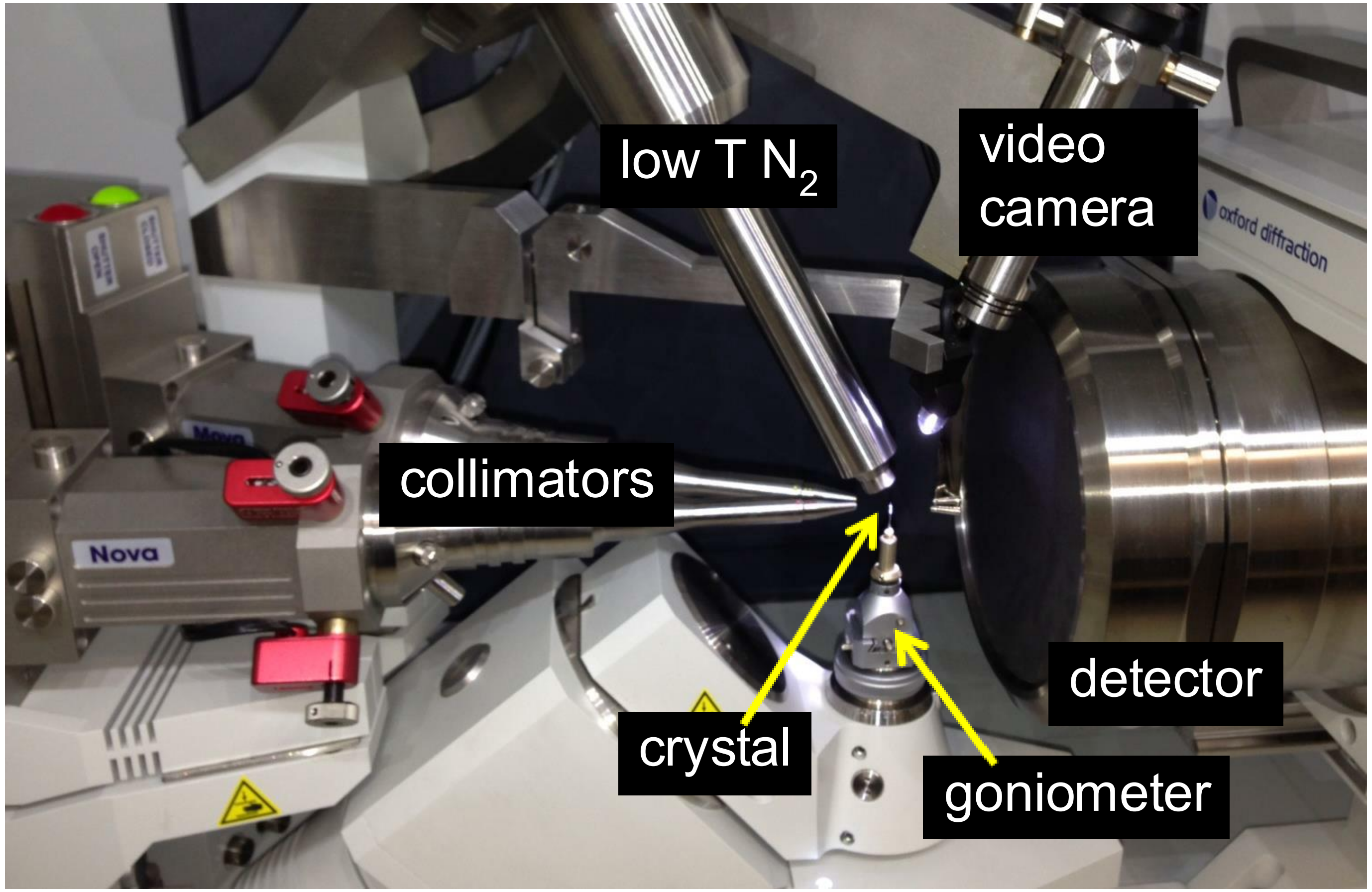
Therefore the reflection 4 5 6 will be equivalent to:

-4 5 6
-4 -5 6
4 -5 6
4 -5 -6
4 5 -6
-4 -5 -6

If a crystal is tetragonal then it may have 4/*m* or 4/*mmm* Laue symmetry.

Determining the Laue symmetry helps to narrow down the choice of space groups.

Data collection on a modern diffractometer



Once a suitable crystal has been found it is mounted normally on the tip of a glass fibre that is attached to a goniometer.

Determining the unit cell and crystal class

First step involves determination of the unit cell.

X-rays are directed towards the crystal and the diffraction spots are measured.

The diffractometer allows reflections to be measured over a number of orientations over a range of angles.

This process of measuring the position of almost random reflections allows the diffractometer computer to calculate the *reciprocal cell* for the crystal.

From the reciprocal cell the direct cell may be calculated.

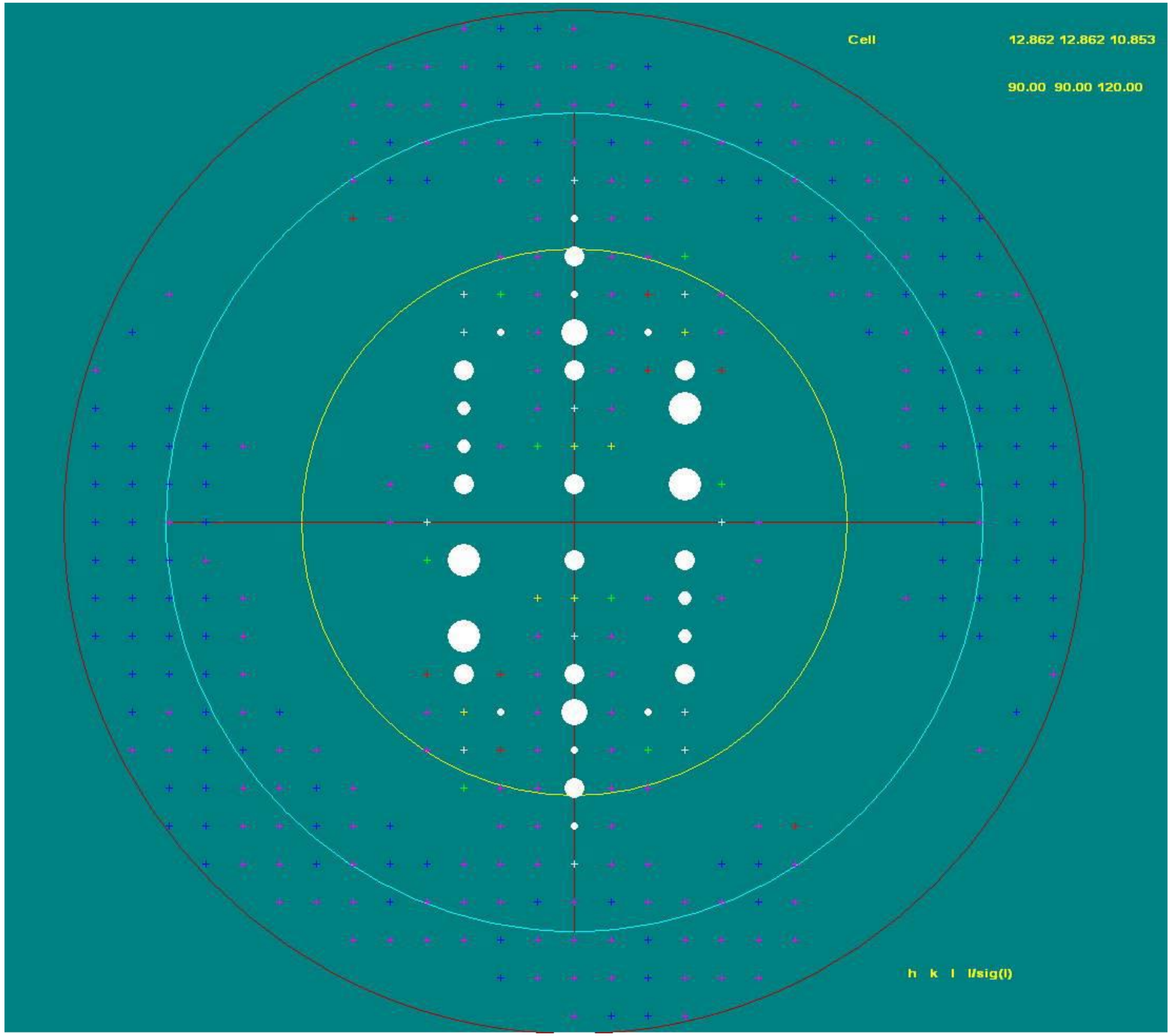
Once the reciprocal cell is obtained then it is possible to calculate the position of every reflection in the reciprocal lattice.

Measuring every reflection in the full reciprocal lattice may take an unnecessarily long period of time.

We can take advantage of the Laue symmetry in the diffraction pattern and measure only a fraction of the reflections.

Consider the case where a monoclinic cell is indicated.

The reciprocal lattice has Laue symmetry of $2/m$ and therefore we only need to collect 1/4 of the full sphere of reflections.



Note the symmetry in the reciprocal lattice –

we don’t have to collect every reflection

At this point the crystallographer aided by the computer software will then select a data collection strategy.

This involves choosing appropriate exposure times and ensuring that enough data is collected.

It is normal practice to collect some symmetry related reflections in order to gauge the quality of the crystal and help in the identification of the correct Laue symmetry.

Typically a data collection might run between 0.5 and 8 hours.

Space group determination

Once the reflection data has been collated we are then in a position to decide upon the space group.

The first step involves determining the Laue symmetry.

At this point we look for *systematic absences* in the data.

The presence of certain symmetry operations in a crystal can result in some reflections suffering from complete destructive interference.

Consider the following selected reflections from a monclinic crystal.

h 0 l	*I*	σ(*I*)	*0 k 0*	*I*	σ(*I*)
1 0 1	28.3	25.0	0 1 0	22.4	18.0
1 0 2	987.0	41.0	0 2 0	496.0	21.0
1 0 3	24.1	16.9	0 3 0	9.0	16.2
1 0 4	633.4	27.2	0 4 0	787.0	20.6
2 0 1	17.6	20.5	0 5 0	31.0	19.1
2 0 2	1445.1	52.6	0 6 0	145.6	15.1
2 0 3	5.2	14.3	0 7 0	6.1	14.8

I is the intensity
σ(*I*) is the standard uncertainty

Note that for reflections of the type *h* 0 *l* the reflection is absent when *l* is an odd integer.

This *systematic absence* arises because of the presence of *c*-glides.

For reflections of the type 0 *k* 0 the reflection is absent when *k* is odd.

This *systematic absence* arises because of the presence of *2-fold screws*.

Thus if the Laue symmetry was shown to be 2/*m* the systematic absences indicate that the space group is $P2_1/c$.

While analysis of systematic absences can narrow down the choice of space groups it does not always lead to a single space group.

In many cases a number of space groups will have the same systematic absences.

At this point it may be necessary to try to solve the structure in a number of different space groups.

In such situations it is often possible to solve the structure in more than one space group.

Under these circumstances we generally choose the highest symmetry space group that provides a sensible solution.

Structure solution

In order to solve a crystal structure we need, for each reflection,

Reflection position (indicated by the Miller indices)
Intensity (measured by the detector)
Phase angle

The phase angle for a reflection is the shift in the wave relative to the origin in the unit cell.

While the reflection position and intensity are measured with relative ease we cannot measure the phase angle.

This is known as the *phase problem*.