PHY369: CHARACTERIZATION OF MATERIALS XRD

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Structure of crystalline solids

- Simple cubic crystal structure
    - $a = 2R$
    - $n_{eff} = 1$
    - (u v w) = (000)
    - CN = 6
    - APF = 0.52

- Body centered cubic crystal structure
    - $a = 2\sqrt{2}R$
    - $n_{eff} = 2$
    - CN = 8
    - APF = 0.68
    - (u v w) = (000) and $\left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$

- Face centered cubic crystal structure
    - $a = \frac{4}{\sqrt{3}}R$
    - ($n_{eff} = 4$)
    - CN = 12
    - APF = 0.74
    - (u v w) = (000), $\left(0\frac{1}{2}\frac{1}{2}\right)$, $\left(\frac{1}{2}0\frac{1}{2}\right)$ and $\left(\frac{1}{2}\frac{1}{2}0\right)$

$$APF = \frac{volume\ of\ atoms\ in\ unit\ cell}{volume\ of\ unit\ cell}$$

where, a is lattice constant, R is radius of atom, n_{eff} is effective number of lattice points, (u v w) are atomic positions, APF is atomic packing fraction and CN is coordination number.
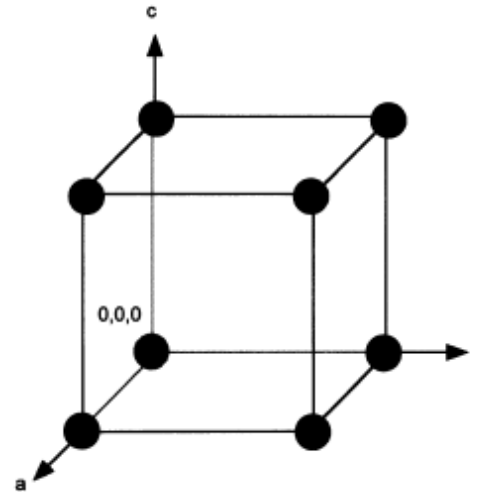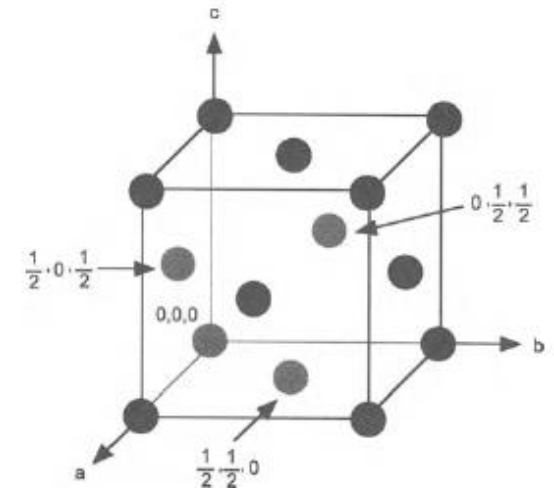
Simple cubic structure

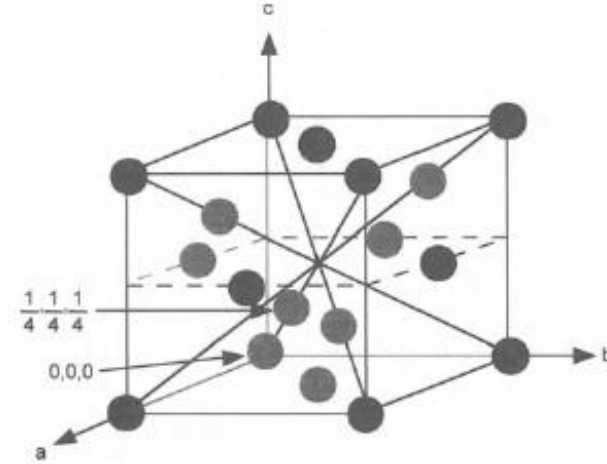**Body centered cubic structure**

Face centered cubic structure

Structure of crystalline solids

- Diamond cubic crystal structure

  $n_{eff} = 8$

  $(u\ v\ w) = (000),\ \left(0\frac{1}{2}\frac{1}{2}\right),\ \left(\frac{1}{2}0\frac{1}{2}\right),\ \left(\frac{1}{2}\frac{1}{2}0\right),\ \left(\frac{1}{4}\frac{1}{4}\frac{1}{4}\right),\ \left(\frac{3}{4}\frac{3}{4}\frac{1}{4}\right),$
  $\left(\frac{3}{4}\frac{1}{4}\frac{3}{4}\right)$ and $\left(\frac{1}{4}\frac{3}{4}\frac{3}{4}\right)$

Diamond cubic structure

LINEAR AND PLANAR DENSITIES

- Linear density (LD) is defined as the ratio of number of atoms centered on direction vector to the length of direction vector.

-Example: $LD_{[110]}$ = 2 atoms/4R = 1 atom/2R

$$LD_{[110]} = \frac{2\ atoms}{4R} = \frac{1\ atom}{2R}$$

(a)

(b)

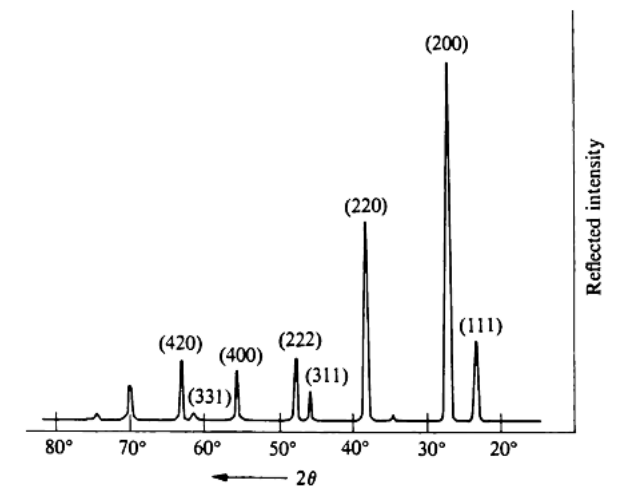- Planar density (PD) is the number of atoms per unit area that are centered on a particular plane.

-Example:

$$PD_{(110)} = \frac{2\ atoms}{8\sqrt{2}R^2} = \frac{1\ atom}{4\sqrt{2}R^2}$$
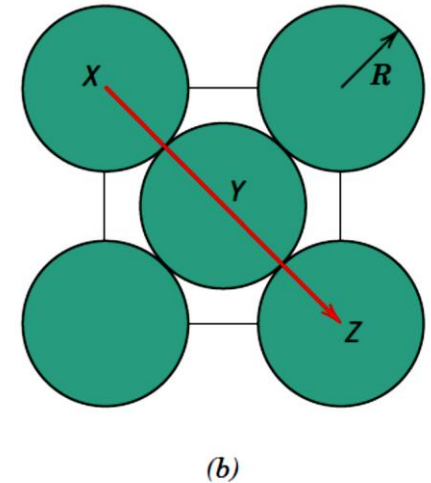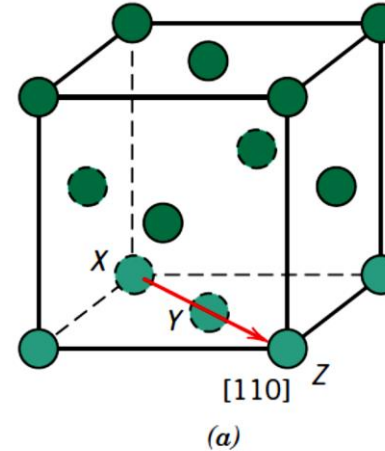
Crystal structure determination:

X ray diffraction
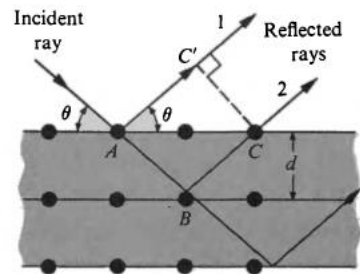
X-ray diffraction

- Diffraction is possible if the wavelength of electromagnetic radiation is same order as the spacing in the grating (here, crystal size).

- The typical crystal size lies in the range of 2-3 Å which is close to the X-rays ($\lambda \sim$ 0.7 to 3 Å).

- Thus, X-rays can be used to investigate crystal structures.

- Bragg's condition:

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

where, θ, λ, n and d_{hkl} are angle of incidence, wavelength of incident x-ray, order of reflection and interplanar distance.

For cubic crystals,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$
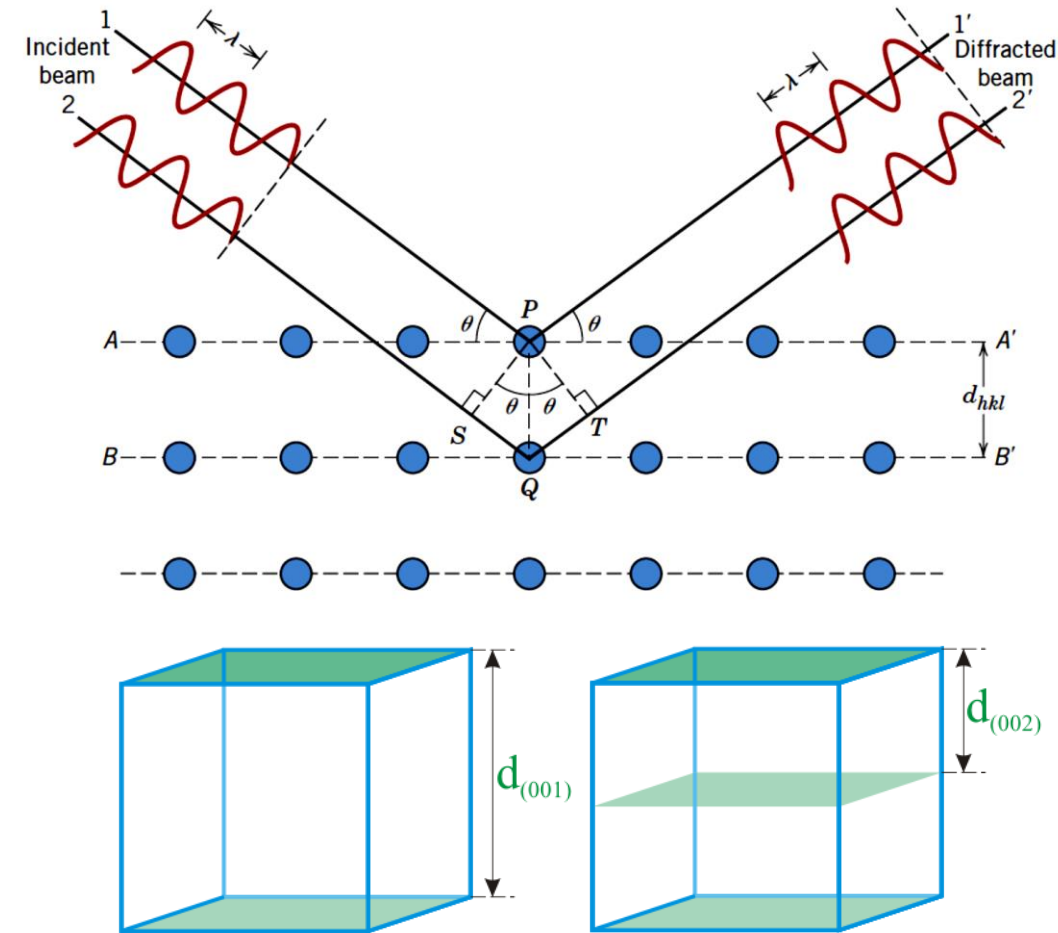
$$d_{nhnknl} = \frac{d_{hkl}}{n}$$

Problem 1

For BCC iron, compute (a) the interplanar spacing and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm. Also, assume that monochromatic radiation having a wavelength of 0.1790 nm is used, and the order of reflection is 1.

- d = 0.1013 nm

- Diffraction angle: 124.26°

Intensity of diffracted x-ray

The intensity of diffracted (scattered) x-ray consists of three types scattering factors:

    1) scattering from electrons

    2) scattering from an atom

    3) scattering from a unit cell

- The intensity is proportional to the square of structure factor which is resultant wave scattered by all atoms of the unit cell.

- Structure factor (F_{hkl}) dependent on the position of the atoms/ions etc. within the cell

$$F_{hkl} = f_a \sum_j e^{i2\pi(hu_j + kv_j + lw_j)}$$

where,

    f_a = atomic scattering factor

    (hkl) = Miller indices

    (u_j, v_j, w_j) = atomic position

Selection / Extinction Rules

- *As we have noted before even if Bragg's equation is satisfied, 'reflections may go missing'* → *this is due to the presence of additional atoms in the unit cell.*
- *The reflections present and the missing reflections due to additional atoms in the unit cell are listed in the table below.*

Bravais Lattice	Allowed Reflections
SC	All
BCC	$(h + k + l)$ even
FCC	h, k and l unmixed
DC	h, k and l are all odd *or* all are even & *(h + k + l) divisible by 4*

Allowed reflections in SC*, FCC*, BCC* & DC crystals

$h^2 + k^2 + l^2$	SC	FCC	BCC	DC
1	100			
2	110		110	
3	111	111		111
4	200	200	200	
5	210			
6	211		211	
7				
8	220	220	220	220
9	300, 221			
10	310		310	
11	311	311		311
12	222	222	222	
13	320			
14	321		321	
15				
16	400	400	400	400
17	410, 322			

Crystal structure determination methods

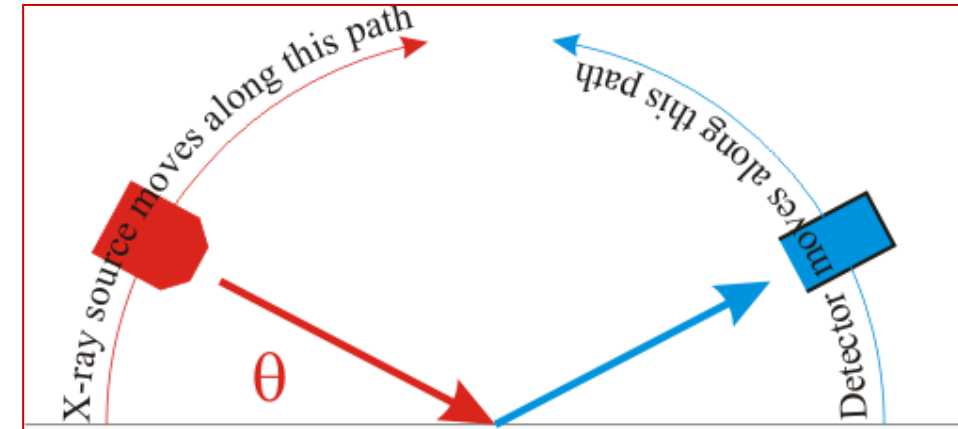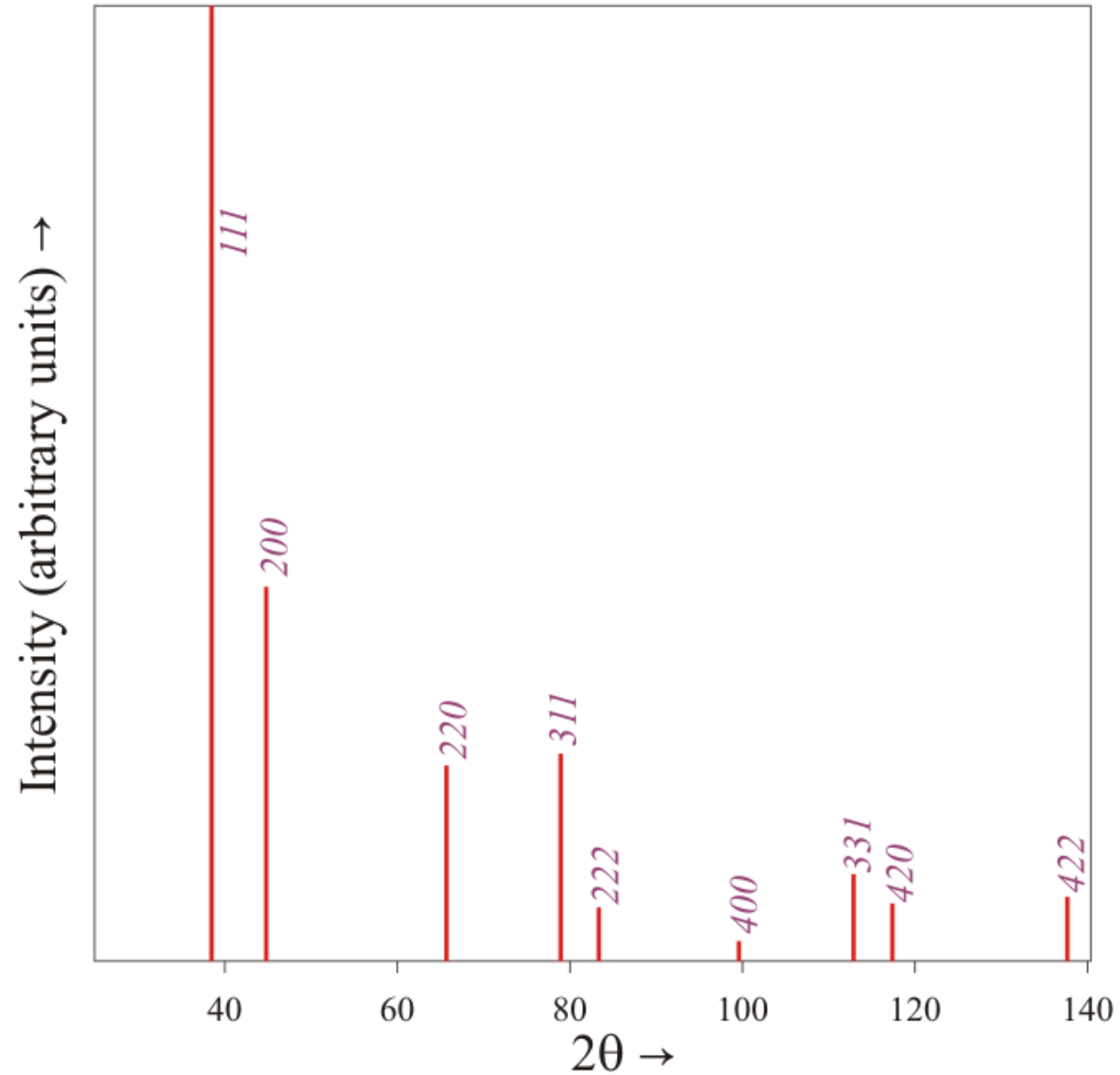| Monochromatic X-rays →	Many θs (orientations) Powder specimen	POWDER METHOD	$\lambda \rightarrow$ fixed $\theta \rightarrow$ variable
Panchromatic X-rays →	Single θ	LAUE TECHNIQUE	$\lambda \rightarrow$ variable $\theta \rightarrow$ fixed
Monochromatic X-rays →	θ Varied by rotation	ROTATING CRYSTAL METHOD	$\lambda \rightarrow$ fixed $\theta \rightarrow$ rotated
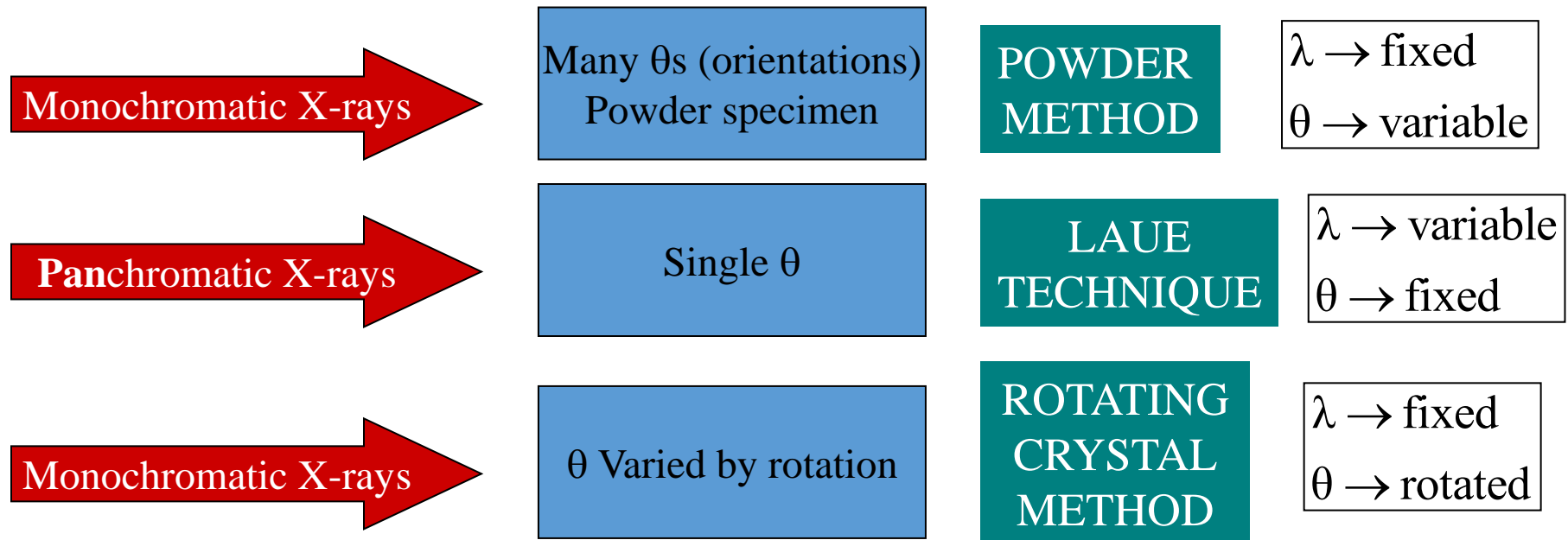
Only the powder method (which is commonly used in materials science) will be considered in this text.

Powder method

- In the powder sample there are crystallites in different 'random' orientations (a polycrystalline sample too has grains in different orientations)
- The coherent x-ray beam is diffracted by these crystallites at various angles to the incident direction
- All the diffracted beams (called 'reflections') from a single plane, but from different crystallites lie on a cone.
- Depending on the angle there are forward and back reflection cones.
- A diffractometer can record the angle of these reflections along with the intensities of the reflection
- The X-ray source and diffractometer move in arcs of a circle- maintaining the Bragg 'reflection' geometry.

X-ray source moves along this path

moves along this path

X-ray source moves along this path

Detector

θ

Powder diffraction pattern from Al

Radiation: Cu Kα, λ = 1.54 Å

Determination of Crystal Structure (lattice type) from 2θ versus Intensity Data

Let us assume that we have the 2θ versus intensity plot from a diffractometer
  ➢ *To know the lattice type we need only the position of the peaks (as tabulated below)*

#	2θ	θ	Sinθ	Sin² θ	ratio	Index	d
1	38.52	19.26	0.33	0.11	*3*	111	2.34
2	44.76	22.38	0.38	0.14	*4*	200	2.03
3	65.14	32.57	0.54	0.29	*8*	220	1.43
4	78.26	39.13	0.63	0.40	*11*	311	1.22
5	82.47	41.235	0.66	0.43	*12*	222	1.17
6	99.11	49.555	0.76	0.58	*16*	400	1.01
7	112.03	56.015	0.83	0.69	*19*	331	0.93
8	116.60	58.3	0.85	0.72	*20*	420	0.91
9	137.47	68.735	0.93	0.87	*24*	422	0.83
10	163.78	81.89	0.99	0.98	*27*	333	0.78

From the ratios in column 6 we conclude that ➡ **FCC**

Note
$$(h^2 + k^2 + l^2) \propto \sin^2 \theta$$

Using $\lambda = 2d \, Sin\theta$ $\quad 1.54 = 2 d_{111} \, Sin\theta_{111} = 2 \dfrac{a}{\sqrt{3}} 0.33$

$a = 4.04 \, \overset{o}{\text{Å}} \to Al$ We can get the lattice parameter → which correspond to that for Al

Note: Error in d spacing decreases with θ → so we should use high angle lines for lattice parameter calculation

Applications of XRD

Bravais lattice determination

Lattice parameter determination

already seen these applications

Determination of secondary phase

Long range order

Crystallite size and Strain

Determine if the material is amorphous or crystalline

Crystallite size

Crystallite : a set of planes oriented along one direction in a crystal.
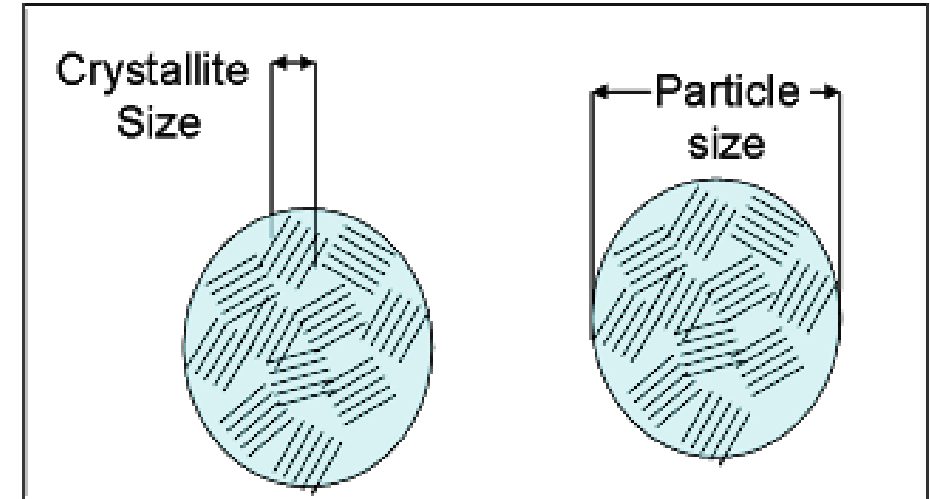
The size of the crystallite is determined using XRD
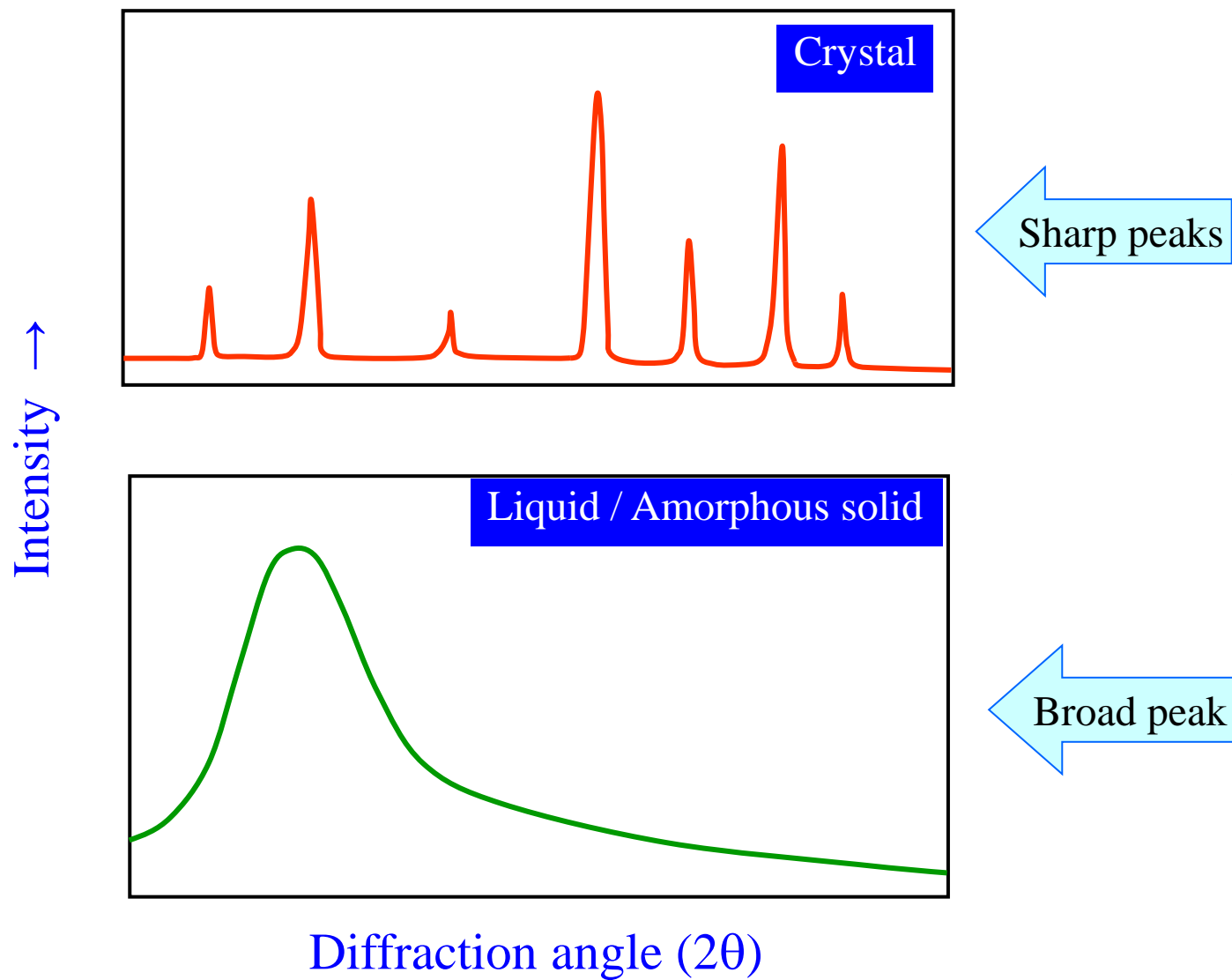
$$D = \frac{0.94\lambda}{\beta \cos \theta}$$

where λ is the X-ray wavelength, β is the full width at half maximum (FWHM) and θ is the Bragg angle.

Lattice strain:

$$\varepsilon = \frac{\beta}{4 \tan \theta}$$

Schematic of difference between
the diffraction patterns of various phases

References

Text Books:

❑ **CALLISTER'S MATERIAL SCIENCE AND ENGINEERING**, R. Balasubramaniam, *Wiley*, 1st Edition, (2016).

Further Readings:

❑ **CONCEPTS OF MODERN PHYSICS,** Arthur Beiser, *McGraw-Hill Higher Education, Sixth Edition*, (2003).