Examples of Calculating the Distance Between Planes (d) and Calculating the Lattice Constant (a_0) in a Cubic System

Example (1) : Calculate the distance between the planes in a cubic system to plane (**100**), when the lattice constant equal **4Å** .

The answer :

As: plane (100)   So: h= 1 , k= 0 , l = 0 a_0= 4Å

$d_{hkl} = a_0 / \sqrt{h^2 + k^2 + l^2}$
$d_{100} = 4 / \sqrt{(1)^2 + (0)^2 + (0)^2}$
$\quad\quad = 4 / \sqrt{1}$
$\quad\quad = 4\text{Å}$

....

Example (2) : Calculate the distance between the planes, when the wavelength to X-ray equal (154pm) and the value of (θ) is 22.5^0 , (n=1) .

The answer :

As: 1 pm = 1×10^{-12} m $\theta = 22.5^0$ n = 1

λ = 154 pm = 154×10^{-12} m = 1.54×10^{-10} m

$n\lambda = 2\, d \sin\theta$
$1 \times 1.54 \times 10^{-10} = 2 \times d \times \sin 22.5^0$
$d = 1 \times 1.54 \times 10^{-10} / 2 \times \sin 22.5^0$
$\quad = 1.54 \times 10^{-10} / 2 \times 0.382$
$\quad = 1.54 \times 10^{-10} / 0.764$
$\quad = 2.015 \times 10^{-10}$ m

....

Example (3) : A reflection from the (**111**) plane of a cubic crystal was observed at a glancing angle of **11.2^0** when CuK_α X-ray of wavelength (**154pm**) were used. What is the length of the side of the unit cell (lattice constant), n=1.

The answer : As : h=1, k/=1, l=1 , n=1 , θ=11.2^0 , λ = 154 pm = 154×10^{-12} m = 1.54×10^{-10} m , a_0=?

$d_{111} = \lambda / 2 \sin\theta$ .... (1) $d_{111} = a_0 / \sqrt{h^2 + k^2 + l^2}$ .... (2)

The two equations are equal to (1, 2)

$\lambda / 2 \sin\theta = a_0 / \sqrt{h^2 + k^2 + l^2}$
$1.54 \times 10^{-10} \text{m} / 2 \times \sin 11.2^0 = a_0 / \sqrt{(1)^2 + (1)^2 + (1)^2}$
$1.54 \times 10^{-10} \text{m} / 0.388 = a_0 / \sqrt{3}$
$3.969 \times 10^{-10} \text{m} = a_0 / 1.732$
$a_0 = 3.969 \times 10^{-10} \text{m} \times 1.732$
$a_0 = 6.874 \times 10^{-10} \text{m}$
$a_0 = 6.874\text{Å}$

or : $d_{111} = \lambda / 2 \sin\theta$
$$= 1.54 \times 10^{-10}m \ / \ 2 \sin 11.2^0$$
$$= 1.54 \times 10^{-10}m \ / \ 0.388$$
$$= 3.969 \times 10^{-10}m$$

$d_{111} = a_0 / \sqrt{h^2 + k^2 + l^2}$
$3.969 \times 10^{-10}m = a_0 / \sqrt{(1)^2 + (1)^2 + (1)^2}$
$3.969 \times 10^{-10}m = a_0 / \sqrt{3}$
$3.969 \times 10^{-10}m = a_0 / 1.732$
$a_0 = 3.969 \times 10^{-10}m \times 1.732$
$a_0 = 6.874 \times 10^{-10}m$
$a_0 = 6.874 \text{Å}$

Homework (1) : Calculate the d-value of the planes (**226**) and (**132**) in a cubic system, if the value of (**a_0**) is **10Å** .

Homework (2) : Calculate the distance between the planes in **metres**, when the wavelength to X-ray equal (**1.54Å**) and the value of (**θ**) is **30.3^0** , (**n=1**) .

Homework (3) : It was found that the reflection of the plane (**223**) of a cubic crystal has the angle of reflection at **40.6^0** when the wavelength used for CuK_α X-ray was (**1.54Å**). What is the side length of a unit cell (lattice constant), **n=1**.

Scherrer equation

The **Scherrer equation**, in X-ray diffraction and crystallography, is a formula that relates the size of sub-micrometre crystallites in a solid to the broadening of a peak in a diffraction pattern. It is often referred to, incorrectly, as a formula for particle size measurement or analysis. It is named after Paul Scherrer.[1][2] It is used in the determination of size of crystals in the form of powder.

The Scherrer equation can be written as:

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

where:

- L is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, which may be smaller or equal to the particle size;
- K is a dimensionless **shape factor**, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite;
- λ is the X-ray wavelength;
- β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as $\Delta(2\theta)$;
- θ is the Bragg angle.

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Applicability

The Scherrer equation is limited to nano-scale crystallites, or more-strictly, the coherently scattering domain size, which can be smaller than the crystallite size (due to factors mentioned below). It is not applicable to grains larger than about 0.1 to 0.2 μm, which precludes those observed in most metallographic and ceramographic microstructures.

The Scherrer Equation was published in 1918

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

- **Peak width (B) is inversely proportional to crystallite size (L)**

- P. Scherrer, "Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen," *Nachr. Ges. Wiss. Göttingen* **26** (1918) pp 98-100.

- J.I. Langford and A.J.C. Wilson, "Scherrer after Sixty Years: A Survey and Some New Results in the Determination of Crystallite Size," *J. Appl. Cryst.* **11** (1978) pp 102-113.

The Laue Equations describe the intensity of a diffracted peak from a single parallelopipeden crystal

$$I = I_e F^2 \frac{\sin^2(\pi/\lambda)(s-s_o) \bullet N_1 a_1}{\sin^2(\pi/\lambda)(s-s_o) \bullet a_1} \frac{\sin^2(\pi/\lambda)(s-s_o) \bullet N_2 a_2}{\sin^2(\pi/\lambda)(s-s_o) \bullet a_2} \frac{\sin^2(\pi/\lambda)(s-s_o) \bullet N_3 a_3}{\sin^2(\pi/\lambda)(s-s_o) \bullet a_3}$$

- N_1, N_2, and N_3 are the number of unit cells along the a_1, a_2, and a_3 directions
- When N is small, the diffraction peaks become broader
- The peak area remains constant independent of N
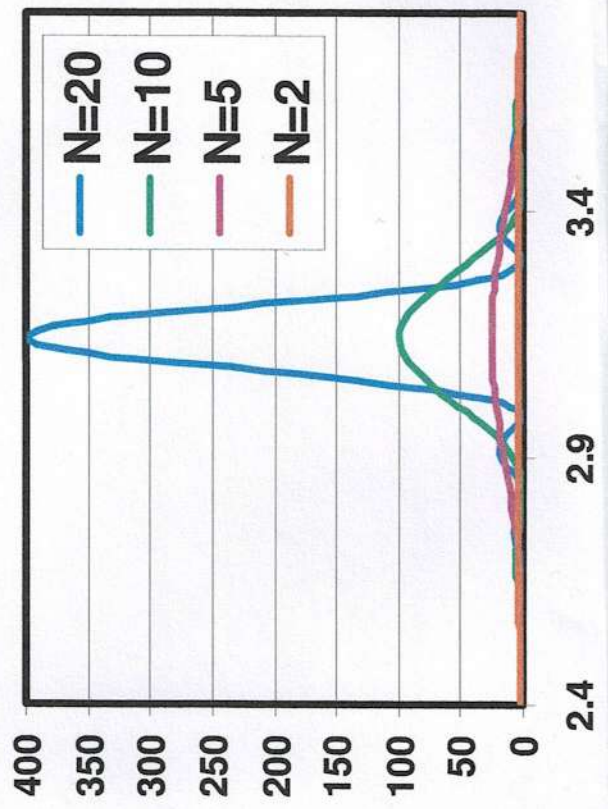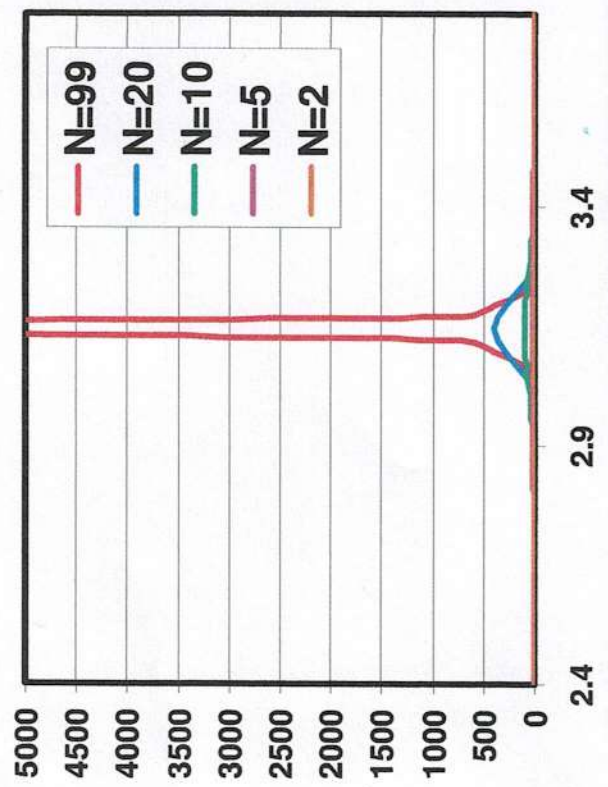
Which of these diffraction patterns comes from a nanocrystalline material?
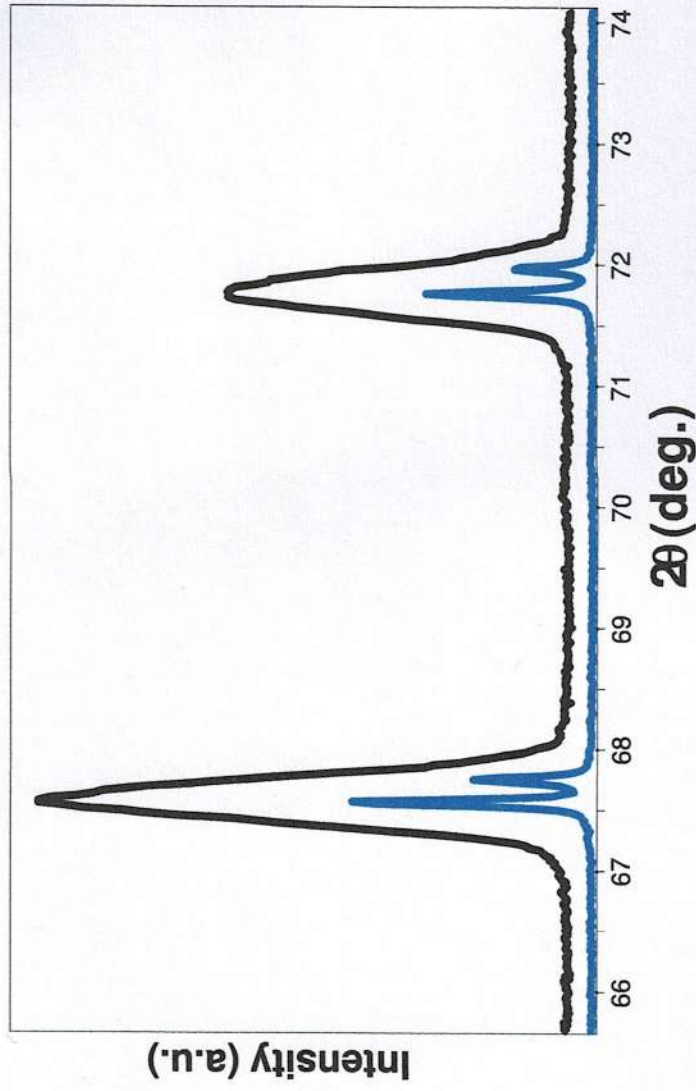
- These diffraction patterns were produced from the **exact same sample**
- Two different diffractometers, with different optical configurations, were used
- *The apparent peak broadening is due solely to the instrumentation*

Many factors may contribute to the observed peak profile

- Instrumental Peak Profile
- Crystallite Size
- Microstrain
  - Non-uniform Lattice Distortions
  - Faulting
  - Dislocations
  - Antiphase Domain Boundaries
  - Grain Surface Relaxation
- Solid Solution Inhomogeneity
- Temperature Factors

- *The peak profile is a convolution of the profiles from all of these contributions*

Instrument and Sample Contributions to the Peak Profile must be Deconvoluted

- In order to analyze crystallite size, we must deconvolute:
  - Instrumental Broadening FW(I)
    - also referred to as the Instrumental Profile, Instrumental FWHM Curve, Instrumental Peak Profile
  - Specimen Broadening FW(S)
    - also referred to as the Sample Profile, Specimen Profile

- We must then separate the different contributions to specimen broadening
  - Crystallite size and microstrain broadening of diffraction peaks

Contributions to Peak Profile

1. Peak broadening due to crystallite size

2. Peak broadening due to the instrumental profile

3. Which instrument to use for nanophase analysis

4. Peak broadening due to microstrain

   - the different types of microstrain

   - Peak broadening due to solid solution inhomogeneity and due to temperature factors

Crystallite Size Broadening

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

- Peak Width due to crystallite size varies inversely with crystallite size
  - as the crystallite size gets smaller, the peak gets broader
- The peak width varies with 2θ as $\cos\theta$
  - The crystallite size broadening is most pronounced at large angles 2Theta
    - However, the instrumental profile width and microstrain broadening are also largest at large angles 2theta
    - peak intensity is usually weakest at larger angles 2theta
  - If using a single peak, often get better results from using diffraction peaks between 30 and 50 deg 2theta
    - below 30deg 2theta, peak asymmetry compromises profile analysis

The Scherrer Constant, K

$$B(2\theta) = \frac{K\lambda}{L\cos\theta} \qquad B(2\theta) = \frac{0.94\lambda}{L\cos\theta}$$

- The constant of proportionality, K (the Scherrer constant) depends on the how the width is determined, the shape of the crystal, and the size distribution
  - the most common values for K are:
    - 0.94 for FWHM of spherical crystals with cubic symmetry
    - 0.89 for integral breadth of spherical crystals w/ cubic symmetry
    - 1, because 0.94 and 0.89 both round up to 1
  - K actually varies from 0.62 to 2.08

- For an excellent discussion of K, refer to JI Langford and AJC Wilson, "Scherrer after sixty years: A survey and some new results in the determination of crystallite size," *J. Appl. Cryst.* **11** (1978) p102-113.

Factors that affect K and crystallite size analysis

- how the peak width is defined
- how crystallite size is defined
- the shape of the crystal
- the size distribution