

chem 5390

Advanced X-ray Analysis



LECTURE 18

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Application of Diffraction Data

XRD can be used for:

- Bravais lattice determination – phase determination (crystalline phases and orientation)**
- Lattice parameter determination**
- Determination of solvus line in phase diagrams (order-disorder transformation)**
- Long range order**
- Crystallite size and Strain**
- Temperature factor – thermal diffuse scattering (thermal expansion)**
- Thickness measurements of thin films and multilayers**

Application of Diffraction Data

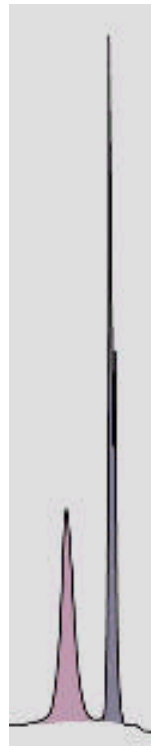
XRD can be used for:

- Bravais lattice determination – phase determination (crystalline phases and orientation)
- Lattice parameter determination
- Determination of solvus line in phase diagrams (order-disorder transformation)
- Long range order (Texture Analysis)
- Crystallite size and Strain**
- Temperature factor – thermal diffuse scattering (thermal expansion)
- Thickness measurements of thin films and multilayers

Application of Diffraction Data

XRD can be used for:

to determine the crystallite size of a material and also measure stress or strain within a crystalline structure.



The position (2θ) and broadness of the peak are influenced by size and strain.

Application of Diffraction Data

Crystallite Size

Crystallite (Grain) size in materials has an effect on the material's properties, i.e., strength, hardness, etc...

When size of the individual crystals is less than $\sim 0.1 \mu\text{m}$ (1000 \AA) the term "particle size" or "crystallite size" is used.

The widths of the peaks in a particular pattern provide an indication of the average crystallite size.

Large crystallites give rise to sharp peaks, while the peak width increases as crystallite size decreases.

Application of Diffraction Data

Crystallite Size

This peak broadening can be used to quantify the average crystallite size of nanoparticles.

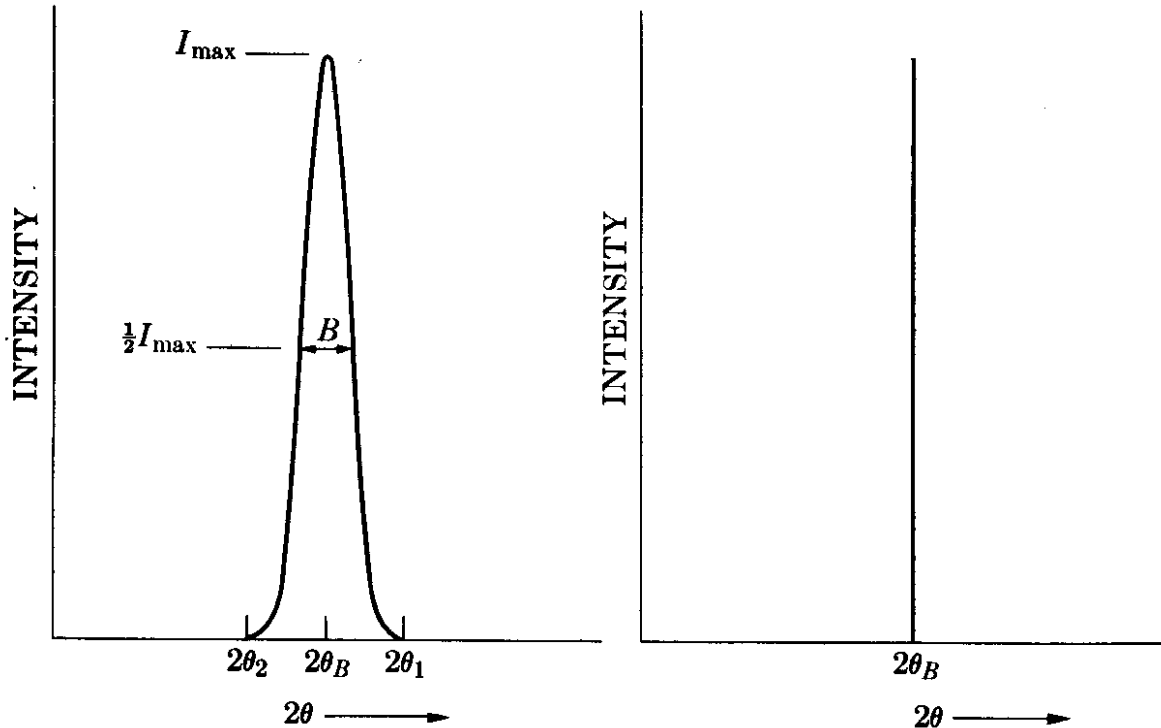
There are several methods for determining crystallite size:

- Scherrer equation (assume no strain present)
- Williamson-Hall plot
- Warren Averbach calculation

(typically must know the contribution of the instrument to the peak width – this is called instrumental broadening)

Application of Diffraction Data

Scherrer equation



Crystallite size can be calculated using the Scherrer Formula

$$t = \frac{0.9\lambda}{B \cos \theta_B}$$

Instrumental broadening must be subtracted

Application of Diffraction Data

Scherrer equation

$$\tau = \frac{K\lambda}{\beta_{\tau} \cos \theta}$$

Where

τ is the mean crystallite dimension,
 K is the shape factor (typically about 0.9),
 λ is the wavelength,
 θ is the peak position

and

β_{τ} is the line broadening

(equal to the $\beta_{\text{exp}} - \beta_i$

β_{exp} - the breadth of the observed diffraction line at its half-intensity maximum, and β_i - instrumental broadening)

Application of Diffraction Data

Crystallite Size

Scherrer equation

$$\tau = \frac{K\lambda}{\beta_{\tau} \cos \theta}$$

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.

Application of Diffraction Data

Crystallite Size

The peak width varies with 2θ as $\cos \theta$

The crystallite size broadening is most pronounced at large angles of 2θ

However, the instrumental profile width and microstrain broadening are also largest at large 2θ angles

Peak intensity is usually weakest at larger angles

If using a single peak, often get better results from using diffraction peaks between 30° and 50° deg 2θ

below 30° 2θ , peak asymmetry compromises profile analysis

Application of Diffraction Data

Crystallite Size

In order to analyze crystallite size, we must deconvolute:
**Instrumental Broadening from Sample (Experimental)
Broadening**

We must then separate the different contributions to sample broadening:

Crystallite size and microstrain (if present) broadening of diffraction peaks

Application of Diffraction Data

Crystallite Size

Instrument broadening is the line width shown by a standard sample diffraction peak from a sample with large crystallite size $\sim > 1 \mu\text{m}$.

It is a characteristic of the individual XRD instrument (setup, optics, etc...) used to make the measurements and not related to the sample (when the sample crystallite size is large).

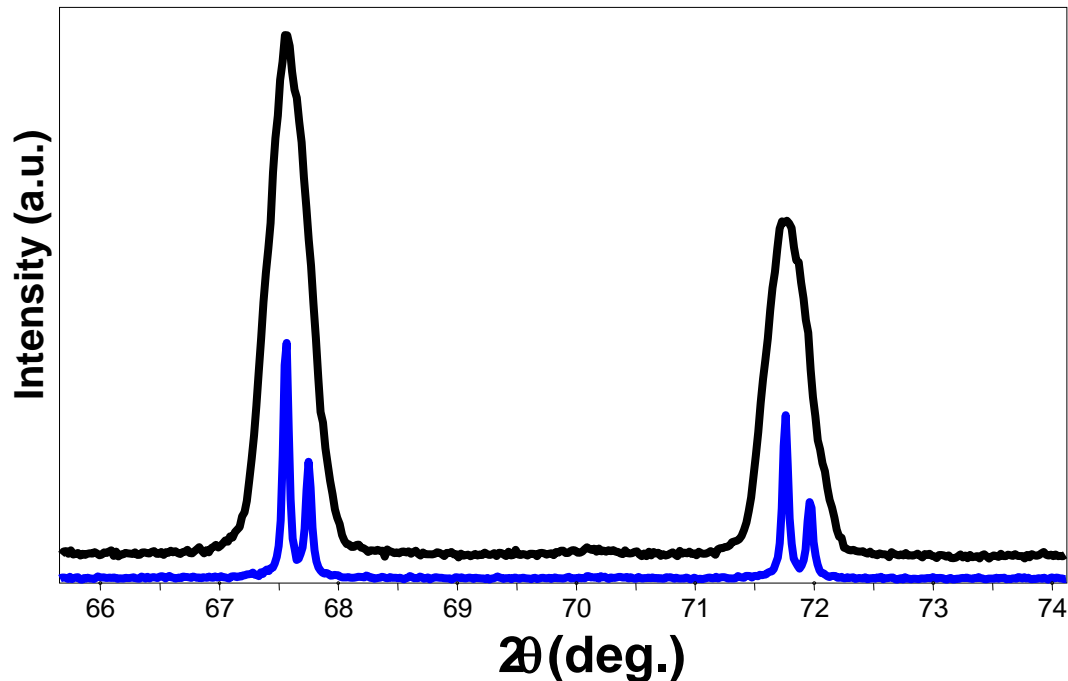
Crystallite or particle size broadening is related to deviation of crystallite size from ideal.

Broadening related to crystallite size is measurable in the nm region (typically below 100-300 nm).

Application of Diffraction Data

Instrumental broadening related to XRD setup

Which of these diffraction patterns comes from a nanocrystalline material?



- These diffraction patterns were produced from the exact same sample
- The apparent peak broadening is due solely to the instrumentation
0.0015° slits vs. 1° slits

Application of Diffraction Data

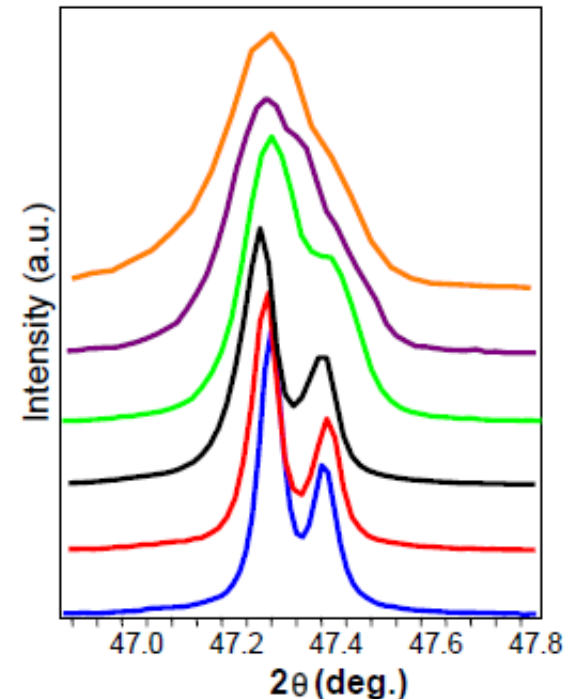
The peak width from the instrumental broadening are due to:

–X-ray Source Profile

- Wavelength widths of $K\alpha_1$ and $K\alpha_2$ lines
- Size of the X-ray source
- Superposition of $K\alpha_1$ and $K\alpha_2$ peaks

–Goniometer Optics

- Divergence and Receiving Slit widths
- Imperfect focusing
- Beam size
- Penetration into the sample



Patterns collected from the same sample with different instruments and configurations at MIT

Application of Diffraction Data

To get an instrumental broadening curve:

- Collect data from a standard using the exact instrument and configuration as for the sample
 - same optical configuration of diffractometer
 - same sample preparation geometry
 - You need a separate calibration curve for every different instrument and instrument configuration
 - Even a small change, such as changing the divergence slit from $\frac{1}{2}$ to $\frac{1}{4}^\circ$ aperture, will change the instrument profile
 - calibration curve should cover the 2θ range of interest for the sample diffraction pattern
 - do not extrapolate the calibration curve
- Profile fit the diffraction peaks from the standard
- Find the FWHM of the peak widths ($\beta_i - \beta_{\text{instrumental}}$)
- Use calibration peaks (β_i) that are in the same 2θ range as your sample (β_{exp})

Application of Diffraction Data

How do you pick the standard?

Standard should share characteristics with the nanocrystalline specimen

- Similar linear absorption coefficient
- similar mass absorption coefficient
- similar atomic weight
- similar packing density

The standard should not contribute to the diffraction peak profile

- macrocrystalline: crystallite size larger than 500 nm (I prefer μm range, ie. 325 mesh)
- particle size less than 10 microns
- defect and strain free

Application of Diffraction Data

How do you pick the standard?

There are several calibration techniques

- Internal Standard
- External Standard of same composition
- External Standard of different composition

Application of Diffraction Data

Internal Standard Method for Calibration

- **Mix a standard in with your nanocrystalline specimen, a NIST certified standard is preferred, use a standard with similar mass absorption coefficient**
 - **NIST 640c Si**
 - **NIST 660a LaB6**
 - **NIST 674b CeO2**
 - **NIST 675 Mica**

standard should have few, and preferably no, overlapping peaks with the specimen

overlapping peaks will greatly compromise accuracy of analysis

Application of Diffraction Data

Internal Standard Method for Calibration

Advantages:

- know that standard and specimen patterns were collected under identical circumstances for both instrumental conditions and sample preparation conditions
- the linear absorption coefficient of the mixture is the same for standard and specimen

Disadvantages:

- difficult to avoid overlapping peaks between standard and broadened peaks from very nanocrystalline materials
- the specimen becomes contaminated
- only works with a powder specimen

Application of Diffraction Data

External Standard Method for Calibration

If internal calibration is not an option, then use external calibration

Run calibration standard separately from specimen, keeping as many parameters identical as is possible

The best external standard is a macrocrystalline specimen of the same phase as your nanocrystalline specimen

– How can you be sure that macrocrystalline specimen does not contribute to peak broadening?

Application of Diffraction Data

How can you be sure that macrocrystalline specimen does not contribute to peak broadening?

- select the potential macrocrystalline standard powder
 - if needed possibly anneal it to allow crystallites to grow and to allow defects to heal
- use internal calibration to validate that macrocrystalline powder as an appropriate standard
 - mix macrocrystalline standard with appropriate NIST SRM
 - compare FWHM curves for macrocrystalline specimen and NIST standard
 - if the macrocrystalline FWHM curve is similar to that from the NIST standard, than the macrocrystalline specimen is suitable
 - collect the XRD pattern from pure sample of you macrocrystalline specimen
 - do not use the FWHM curve from the mixture with the NIST SRM

Application of Diffraction Data

External Calibration with a Standard of the Same Composition

Advantages:

- will produce better calibration curve because mass absorption coefficient, density, molecular weight are the same as your sample
- can duplicate a mixture in your nanocrystalline specimen
- might be able to make a macrocrystalline standard for thin film samples

Disadvantages:

- time consuming
- need a different calibration standard for every different nanocrystalline phase and mixture
- macrocrystalline standard may be hard/impossible to produce
- calibration curve will not compensate for discrepancies in instrumental conditions or sample preparation conditions between the standard and the sample (user error)

Application of Diffraction Data

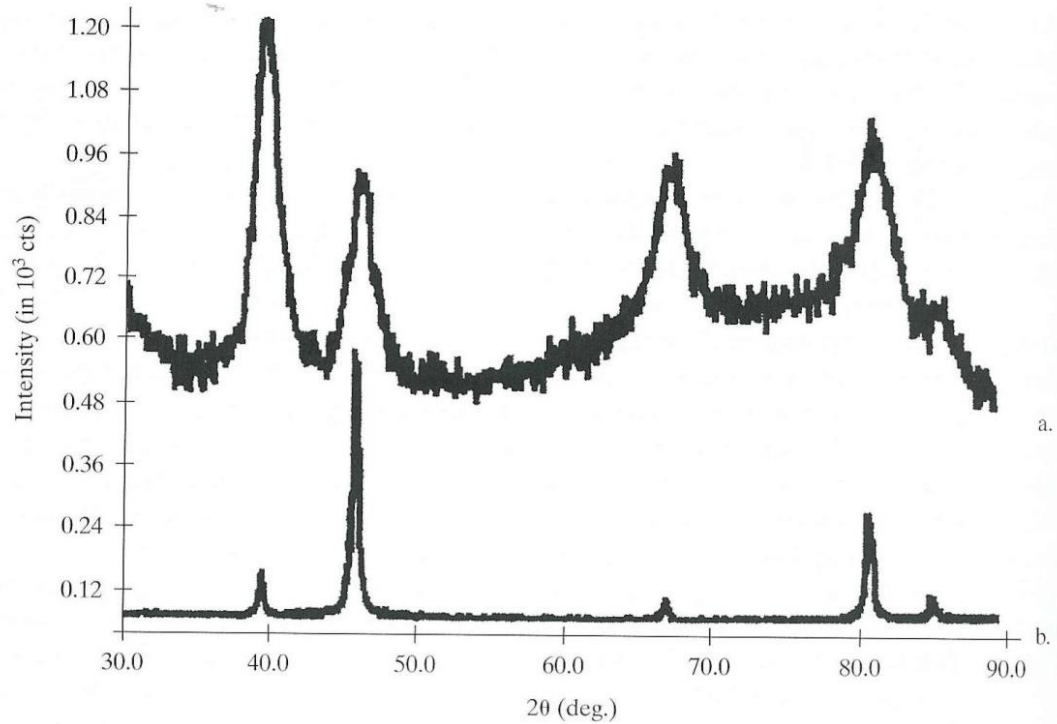


Figure 14-2 Comparison of θ - 2θ diffraction patterns for platinum nanoparticles in a silica matrix [14.1] (top) and rolled platinum sheet showing strong preferred orientation (bottom).

TABLE 14.1

hkl	FWHM ($^{\circ}2\theta$)	t (\AA)
111	1.9	50
200	1.7	55
220	2.1	50
311	2.5	45-50

Application of Diffraction Data

External Standard Method of Calibration using a NIST Standard

As a last resort, use an external standard of a composition that is different than your nanocrystalline specimen

- This is actually the most common method used
- Also the least accurate method

Use a certified NIST standard to produce instrumental FWHM calibration curve

- Use the standard that has the most similar linear absorption coefficient

Application of Diffraction Data

External Standard Method of Calibration using a NIST Standard

Advantages

- only need to build one calibration curve for each instrumental configuration
- NIST standard diffraction patterns for each instrument and configuration available for download from literature/database
- know that the standard is high quality if from NIST
- neither standard nor sample are contaminated

• Disadvantages

- The standard may behave significantly different in diffractometer than your sample
 - different mass absorption coefficient
 - different depth of penetration of X-rays
- NIST standards are expensive
- cannot duplicate exact conditions for thin films

Application of Diffraction Data

Calibration error more likely for crystallite sizes approaching the instrumental broadening limit of the diffractometer.

FWHM of
Instrumental Profile
at $48^\circ 2\theta$ is
0.061 deg

Crystallite Size	B (2theta) (rad)	FWHM (deg)
100 nm	0.0015	0.099
50 nm	0.0029	0.182
10 nm	0.0145	0.871
5 nm	0.0291	1.745

For a very small crystallite size, the sample broadening dominates over instrumental broadening

But need the most exacting (careful) calibration when the sample broadening is small and approaches instrumental broadening

Application of Diffraction Data

The instrumental profile determines the upper limit of crystallite size that can be evaluated

- if the Instrumental peak width is much larger than the broadening due to crystallite size, then cannot accurately determine size
- For analyzing larger nanocrystallites, it is important to use the instrument with the smallest instrumental peak width

Very small nanocrystallites produce weak signals

- the sample broadening will be significantly larger than the instrumental broadening
- the signal:noise ratio is more important than the instrumental profile
- long experimental runs may be needed to improve S/N

Application of Diffraction Data

Comparison of Peak Widths at $47^\circ 2\theta$ for Instruments

Configuration	FWHM (deg)
185mm radius, 0.5° DS, diffracted-beam monochromator, point detector	0.124
240mm radius, 0.25° DS, beta-filter, linear PSD	0.060
240mm radius, 0.5° DS, beta-filter, linear PSD	0.077
240mm radius, 0.5° DS, diffracted-beam monochromator, linear PSD	0.073
Gobel mirror, 0.09° Parallel Beam Collimator	0.175
Gobel mirror, 0.27° Parallel Beam Collimator	0.194

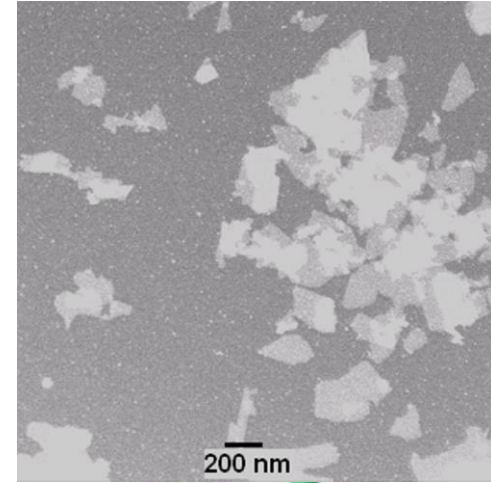
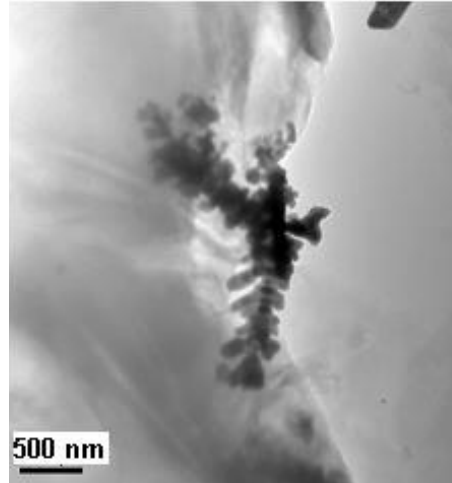
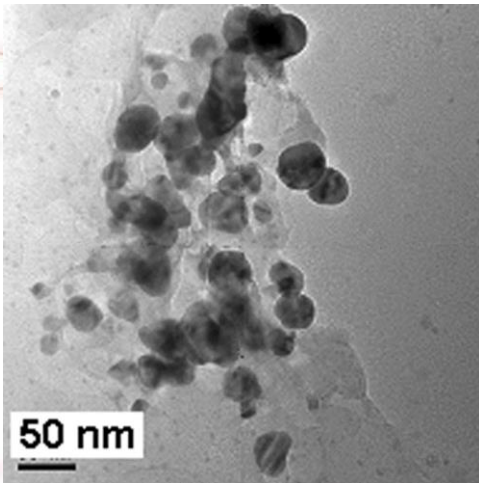
Application of Diffraction Data

Crystallite Shape (the K value)

$$\tau = \frac{K\lambda}{\beta_{\tau} \cos \theta}$$

Though the shape of crystallites is usually irregular, we can often approximate them as:

- sphere, cube, tetrahedra, or octahedra
- parallelepipeds such as needles or plates
- prisms or cylinders



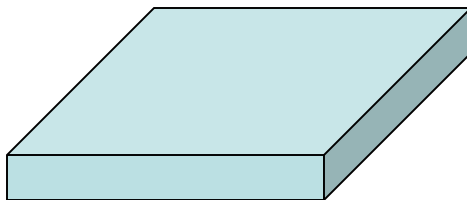
Application of Diffraction Data

Crystallite Shape (the K value)

$$\tau = \frac{K\lambda}{\beta_{\tau} \cos \theta}$$

Most applications of Scherrer analysis assume spherical crystallite shapes
If we know the average crystallite shape from another analysis, we can select the proper value for the Scherrer constant K

Anisotropic peak shapes can be identified by anisotropic peak broadening
-if the dimensions of a crystallite are $2x * 2y * 200z$, then (h00) and (0k0) peaks will be more broadened than (00l) peaks.



Application of Diffraction Data

Crystallite Size

The constant of proportionality, K (the Scherrer constant) depends on 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 with cubic symmetry, and 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 ,

Jl 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.

Application of Diffraction Data

K actually varies from 0.62 to 2.08

- Values of K from Langford and Wilson, *J. Appl. Cryst* (1978) 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
- Assuming the Scherrer definition of crystallite size, values of K listed in the Help for HighScore Plus are:

Crystallite Shape	FWHM	Integral Breadth
Spheres	0.89	1.07
Cubes	0.83 - 0.91	1.00 – 1.16
Tetrahedra	0.73 - 1.03	0.94 – 1.39
Octahedra	0.82 - 0.94	1.04 – 1.14

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.

Application of Diffraction Data

Example: Analysis Using Different Values of K

For the typical values of $0.81 < K < 1.03$

- The precision of XRD analysis is never better than ± 1 nm
- The size is reproducibly calculated as 2-3 nm (10%)

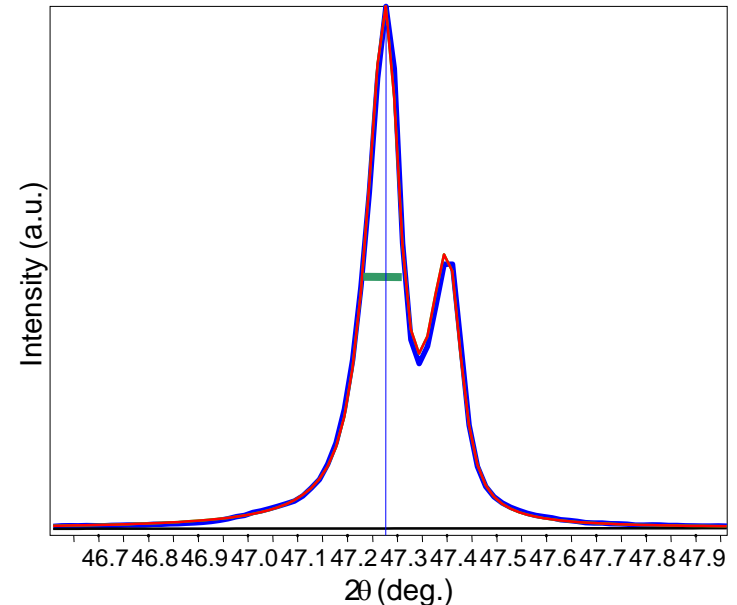
2θ	0.62	0.81	0.89	0.94	1	1.03	2.08	K
28.6	19	24	27	28	30	31	60	
32.9	19	24	27	28	30	31	60	
47.4	17	23	25	26	28	29	56	
56.6	15	19	22	23	24	25	48	
69.3	21	27	30	32	34	35	67	
77.8	14	18	20	21	22	23	44	
88.6	18	23	26	27	29	30	58	
95.4	17	22	24	25	27	28	56	
Avg	17	22	25	26	28	29	56	

Application of Diffraction Data

Broadening is at FWHM

Methods used to Define Peak Width

Full Width at Half Maximum (FWHM)
-the width of the diffraction peak,
in radians, at a height half-way
between background and the
peak maximum



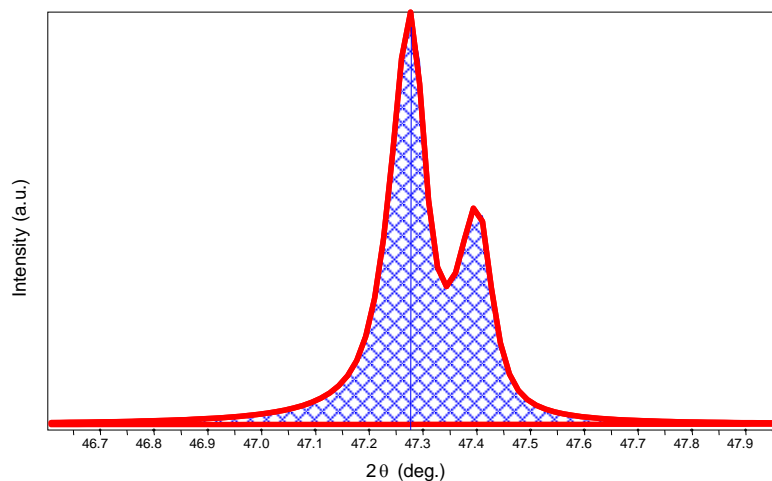
Application of Diffraction Data

Broadening is at FWHM

Methods used to Define Peak Width

Integral Breadth

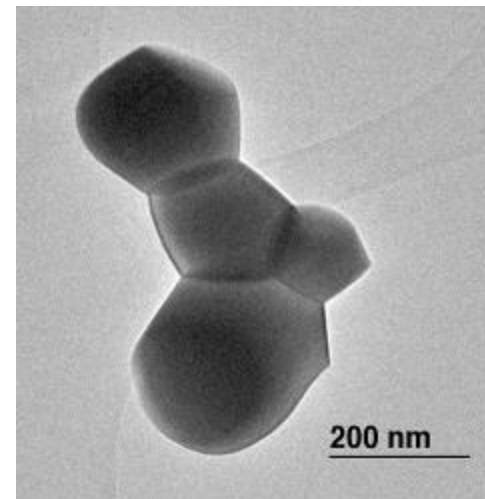
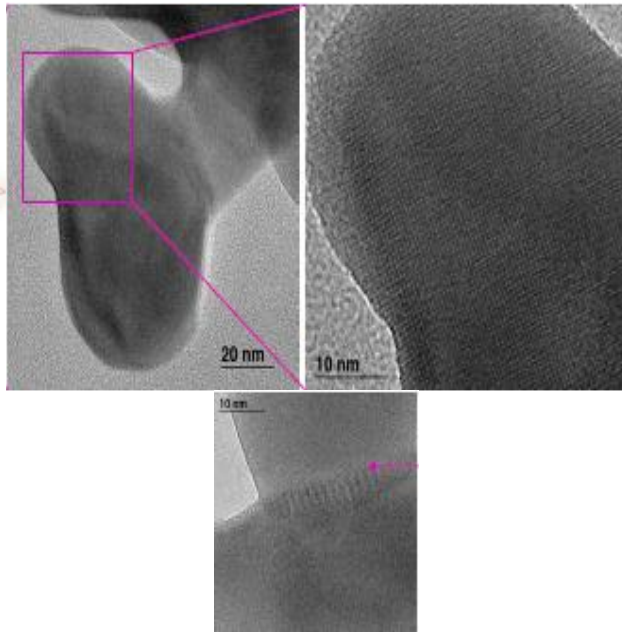
- the total area under the peak divided by the peak height
- the width of a rectangle having the same area and the same height as the peak
- requires very careful evaluation of the tails of the peak and the background



Application of Diffraction Data

Remember, Crystallite Size is Different than Particle Size

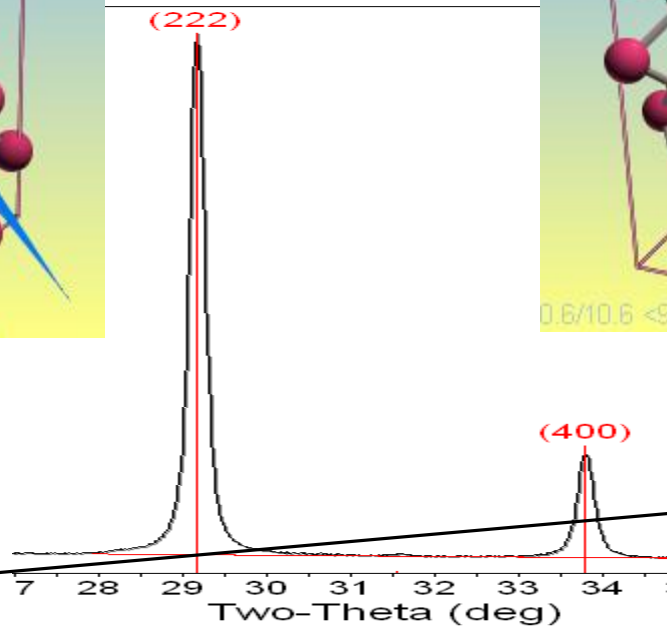
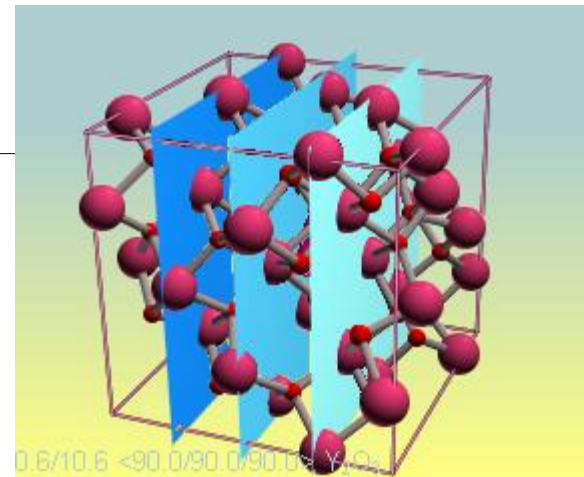
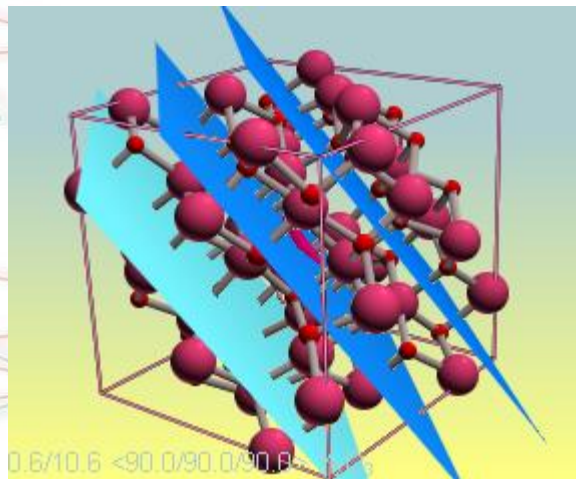
- A particle may be made up of several different crystallites
- Crystallite size often matches grain size, but there are exceptions



Application of Diffraction Data

Crystallite Size – Anisotropic Size Broadening

-The broadening of a single diffraction peak is the product of the crystallite dimensions in the direction perpendicular to the planes that produced the diffraction peak.



Use 111 and 222 peaks

Use 200 and 400 peaks

To determine aspect ratios



Application of Diffraction Data

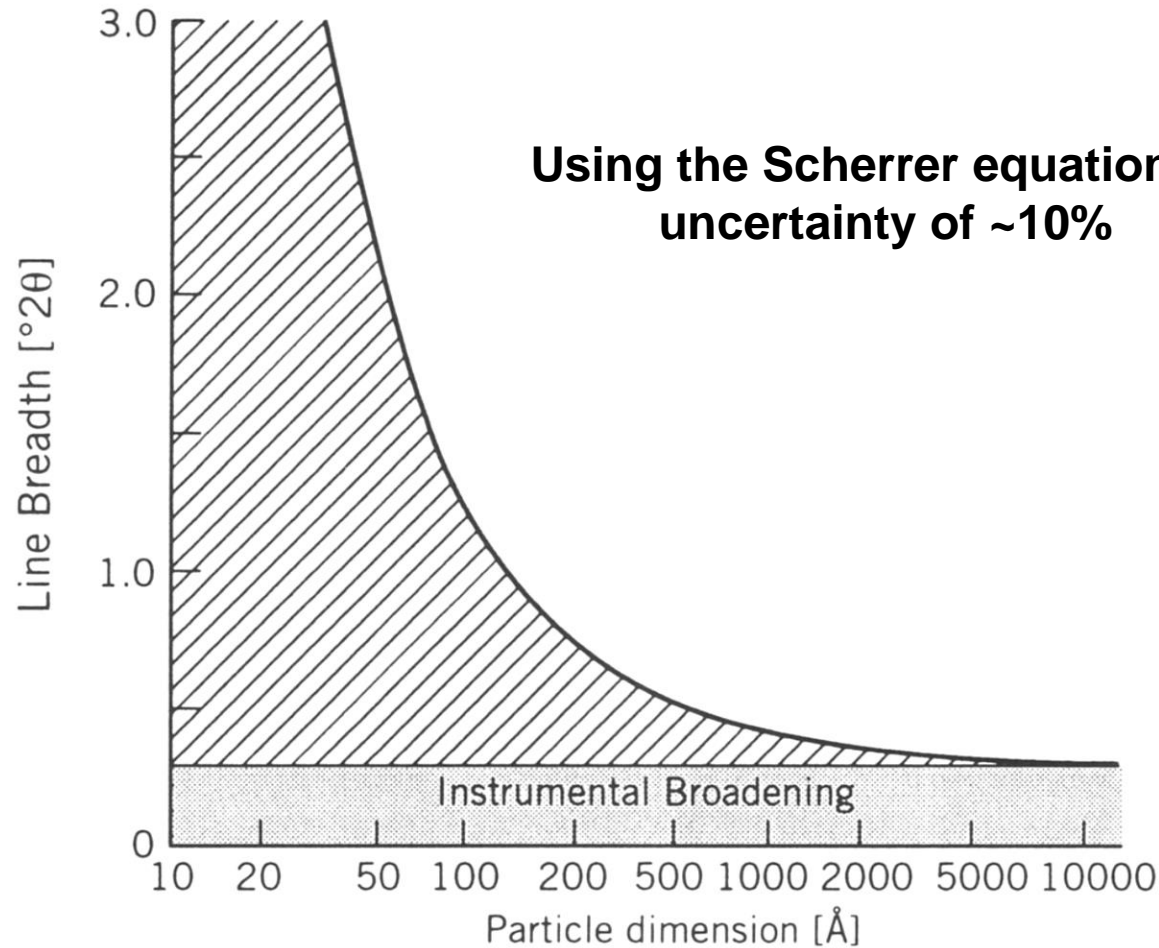
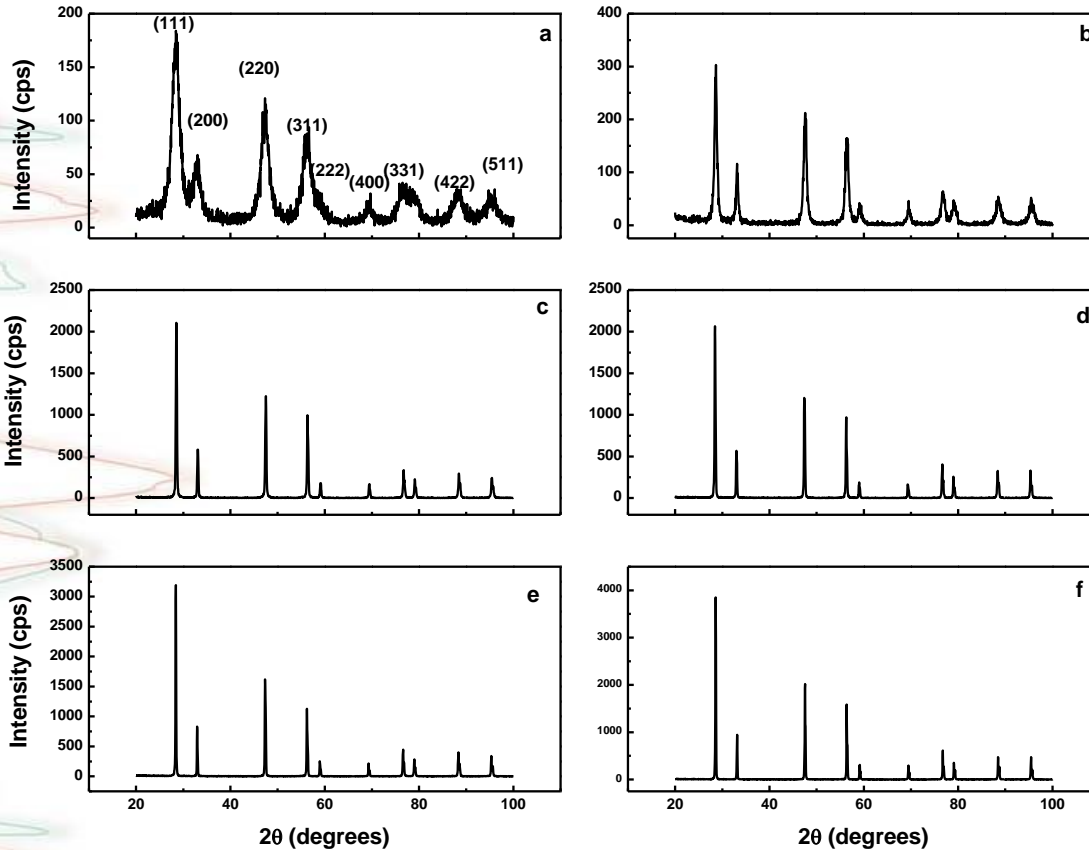


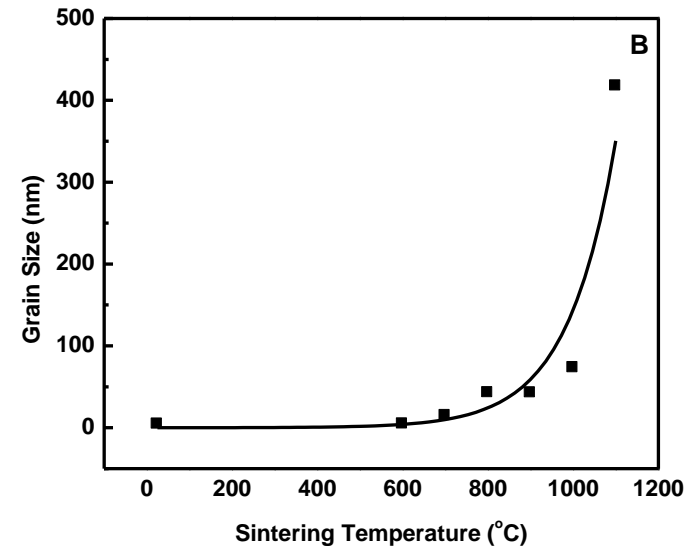
Figure 3.21. Line width as a function of particle dimension.

Application of Diffraction Data

Sintering your sample to make standards



A



Application of Diffraction Data

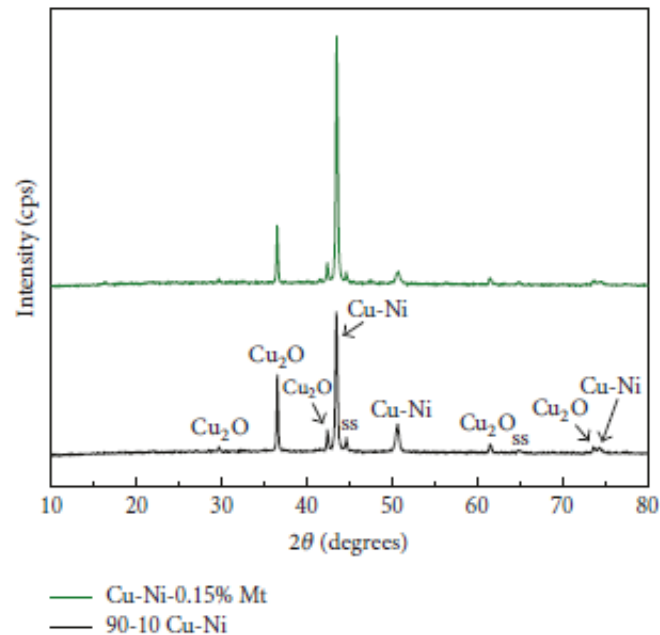


FIGURE 8: X-ray diffraction scans of the 90-10 Cu-Ni and Cu-Ni-0.15% Mt coatings after soaking in the simulated seawater for 30 days to determine the corrosion products (ss: steel substrate).

TABLE 3: Film thickness measured by a profilometer of the pure 90-10 Cu-Ni and Cu-Ni-Mt composite coatings deposited to 30 Coulombs of charge. Crystallite sizes of the pure 90-10 Cu-Ni and Cu-Ni-Mt composite coatings calculated from the Scherrer equation using X-ray diffraction data.

Coatings	Film thickness (μm) ($n = 3$)	Crystallite size (nm) ($n = 3$)
Cu-Ni	6.12 ± 0.04	58 ± 5
Cu-Ni-0.05% Mt	6.17 ± 0.03	19 ± 3
Cu-Ni-0.10% Mt	6.20 ± 0.05	16 ± 4
Cu-Ni-0.15% Mt	6.24 ± 0.07	12 ± 3

Application of Diffraction Data

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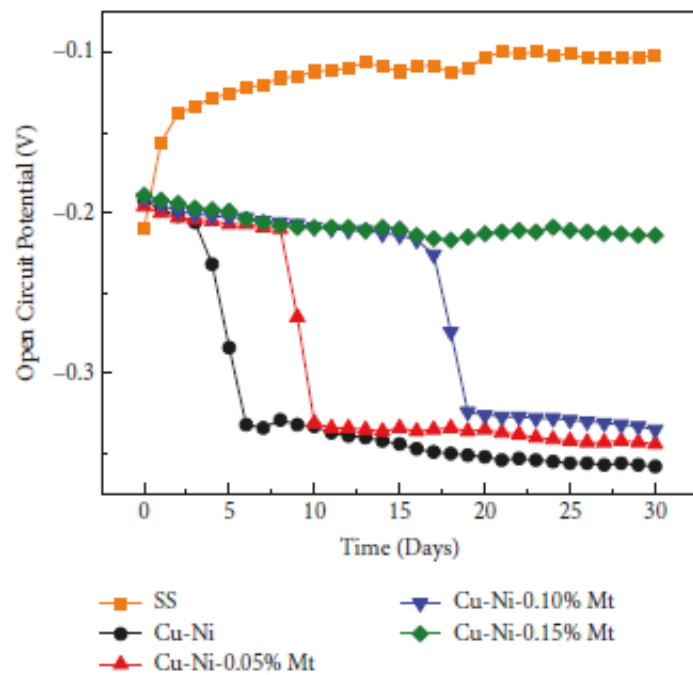


FIGURE 6: Plot of the immersion test for the 90-10 Cu-Ni and Cu-Ni-Mt nanocomposite coatings measured by OCP versus time for 30 days in Burkholder's Formula B solution.

Application of Diffraction Data

Several other factors can contribute to peak broadening.

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

Homework Assignment: Precise Lattice Parameters

Due 12-3-24

Homework Assignment: Determination Crystallite Size and Lattice Strain

Due 12-5-24

Reading Assignment:

Read Chapter 8 from:

-X-ray Diffraction Procedures by Klug and Alexander

Read Chapter 3-7, 9-11 and 13 from:

-Introduction to X-ray powder

Diffraction by Jenkins and Synder

Read Chapter 3, 4, 6, 13, and 14 from

-Elements of X-ray Diffraction

by Cullity and Stock

Read Chapter 2 from Norton