chem 5390

Advanced X-ray Analysis

LECTURE 17

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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

Precise Lattice Parameter Measurements

Practical applications for lattice parameter measurements:

-determine composition (stoichiometry) of the sample

-determine thermal expansion coefficient

Application of Diffraction Data

Precise Lattice Parameter Measurements

Practical applications for lattice parameter measurements:

-determine composition (stoichiometry) of the sample

Since the samples are solids, the lattice parameter of a solid solution varies with concentration of the solute.

So you can use accurate and precise lattice parameter measurements to calculate composition.

Application of Diffraction Data

Precise Lattice Parameter Measurements

Practical applications for lattice parameter measurements:

-determine thermal expansion coefficient

Thermal vibrations cause slight changes in interatomic spacing and corresponding changes in d-spacing.

Example: At 25°C, a_{Al} = 4.049 Å and at 50°C, a_{Al} = 4.051 Å.

thermal expansion coefficient, $\alpha_{Al} = 23.6 \times 10^{-6}/^{o}C$

Application of Diffraction Data

Precise Lattice Parameter Measurements

High precision is possible at higher angles (θ).

Example: For cubic system a $\propto$ d-spacing

Precision in a or d-spacing depends on precision in sinθ (derived from Bragg's law) not θ (a measured quantity) .

Application of Diffraction Data

Precise Lattice Parameter Measurements

The error in sinθ decreases as the value of θ increases.

Example: At $\theta = 45^o$, there is a 1.7% error for sinθ.
At $\theta = 85^o$, there is a 0.15% error for sinθ.

For this reason, precise lattice parameter measurements are done at 2θ values above 100^o.

Application of Diffraction Data

Precise Lattice Parameter Measurements

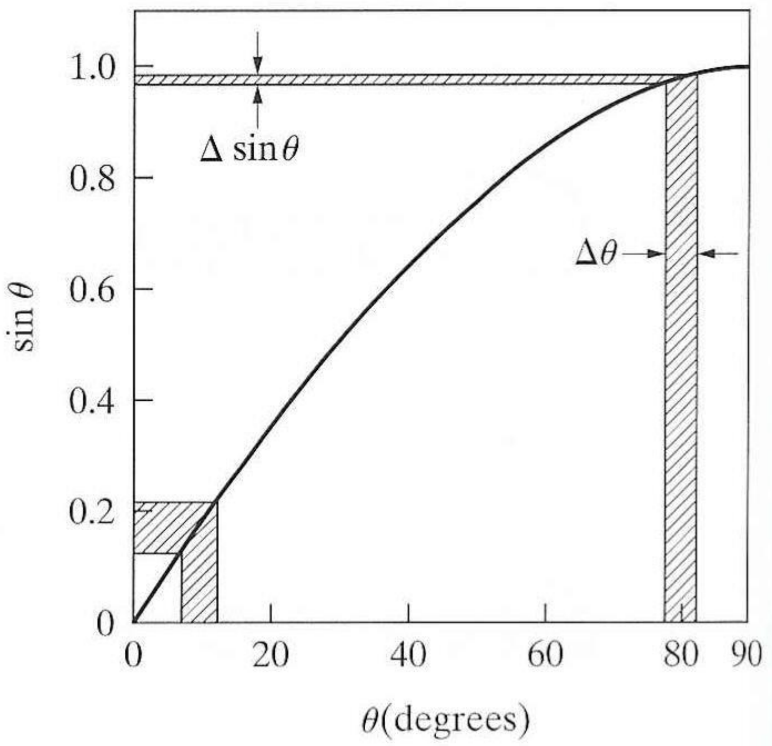

Figure 13-1 The variation of $\sin\theta$ with θ. The error in $\sin\theta$ caused by a given error in θ decreases as θ increases ($\Delta\theta$ exaggerated).

Application of Diffraction Data

Without any extrapolation or attention to good experimental techniques, a precision of 0.01 Å can be reached when measuring at angles above 100º 2θ.

However, with good experimental techniques and use of various extrapolation functions, a precision of 0.001 Å can be obtained.

The actual λ value used must be explicitly stated.

Cu $K_{\alpha 1}$ = 1.540562 Å.

Application of Diffraction Data

In measurement of precise lattice parameters, must be aware of systematic and random errors.

<u>Systematic error</u> – varies in a regular manner with some particular parameter and always is the same sign.

<u>Random error</u> – ordinary chance errors and do not vary in any regular manner with position of 2θ and may be positive or negative.

Application of Diffraction Data

Precise Lattice Parameter Measurements

In order to find the right extrapolation function, must know which effects are leading to error in the measurement of 2θ.

(Later we will discuss the different extrapolation techniques used)

Application of Diffraction Data

The most common sources of systematic error in measuring d-spacings and precise lattice parameters are:

1. **Misalignment of the instrument.**

   The center of the incident beam must intersect the diffractometer axis and the 0° position of the detector slit.

2. **Use of a flat sample instead of curved to conform to the focusing circle.**

   Minimized by decreasing the irradiation width of the sample.

3. **Absorption in the sample.**

   Samples of low absorption should be made as thin as possible.

4. **Displacement of the sample from the diffractometer axis.**

   Usually the largest source of error.

5. **Vertical divergence of the incident beam.**

   Minimize by decreasing the vertical opening of the detector slit.

Application of Diffraction Data

Precise Lattice Parameter Measurements

The most common sources of systematic error in measuring d-spacings are:

1. Misalignment of the instrument.

   The center of the incident beam must intersect the diffractometer axis and the 0^o position of the detector slit.

Obviously any measurement will be invalid if the instrument is not in alignment.

Always run standards before beginning any major measurements.

Application of Diffraction Data

Precise Lattice Parameter Measurements

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Application of Diffraction Data

Precise Lattice Parameter Measurements

2. **Use of a flat sample instead of curved to conform to the focusing circle. - Flat sample error**

The surface of the sample is flat, while the focusing circle is curved, this causes an asymmetric broadening in the diffraction peak.

The edges of the sample lie on a different focusing circle, giving a negative systematic error in the maximum of 2θ.

This also causes asymmetric broadening of the peak profile on the low 2θ side.

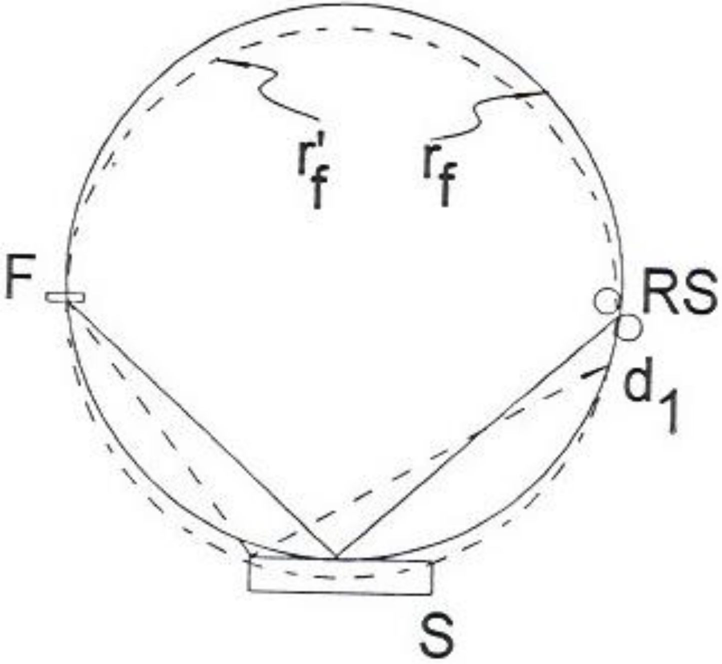
Minimized by decreasing the irradiation width of the sample.

Application of Diffraction Data

Precise Lattice Parameter Measurements

2. Use of a flat sample instead of curved to conform to the focusing circle. - Flat sample error

Flat sample error increases with increasing 2θ, since the radius of the focusing circle decreases with increasing Bragg angle.



Application of Diffraction Data

Precise Lattice Parameter Measurements

2. Use of a flat sample instead of curved to conform to the focusing circle. - Flat sample error

   Minimized by decreasing the irradiation width of the sample.

   Divergent slit opening can be decreased to expose less of the sample. (decreases intensity)

Application of Diffraction Data

Precise Lattice Parameter Measurements

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3. **Absorption in the sample.**

   Samples of low absorption should be made as thin as possible.

4. **Displacement of the sample from the diffractometer axis.**

   Usually the largest source of error.

5. **Vertical divergence of the incident beam.**

   Minimize by decreasing the vertical opening of the detector slit.

Application of Diffraction Data

Precise Lattice Parameter Measurements

3. Absorption in the sample.

Occurs because the incident x-ray beam penetrates a measurable depth into the sample, part of the diffraction beam is then below the focusing circle.

This increases with decreasing absorption of x-rays by the sample, i.e. organic materials have a large transparency error.

Depth of penetration depends on:

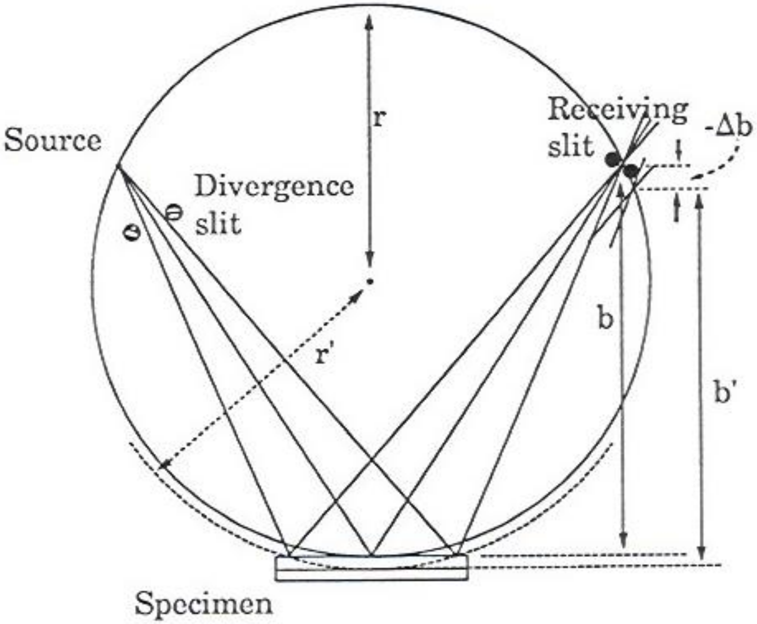
- the mass absorption coefficient of your sample
- the incident angle of the X-ray beam

Application of Diffraction Data

Precise Lattice Parameter Measurements

3. **Absorption in the sample.**

This error leads to angular errors as much as 0.1 of a degree with asymmetric peak profiles.



Application of Diffraction Data

Precise Lattice Parameter Measurements

3. Absorption in the sample.

Samples of low absorption should be made as thin as possible.

Thin specimens

- **Yield the best angular measurements (i.e. most accurate peak positions)**
- **Do not yield accurate intensity measurements (because of bad particle statistics)**
- **Tend to be more susceptible to preferred orientation effects**

***To decrease transparency error, use thin slices (films) of material on a zero-background holder.**

$\Delta d/d$ varies as $\cos^2\theta$ for #2 and 3.

$\cos^2\theta$ is Bradley-Jay function (only valid for diffraction peaks with $\theta > 60^o$).

Application of Diffraction Data

Precise Lattice Parameter Measurements

The most common sources of systematic error in measuring d-spacings are:

1. **Misalignment of the instrument.**

   The center of the incident beam must intersect the diffractometer axis and the 0° position of the detector slit.
2. **Use of a flat sample instead of curved to conform to the focusing circle.**

   Minimized by decreasing the irradiation width of the sample.
3. **Absorption in the sample.**

   Samples of low absorption should be made as thin as possible.
4. **Displacement of the sample from the diffractometer axis.**

   Usually the largest source of error.
5. **Vertical divergence of the incident beam.**

   Minimize by decreasing the vertical opening of the detector slit.

Application of Diffraction Data

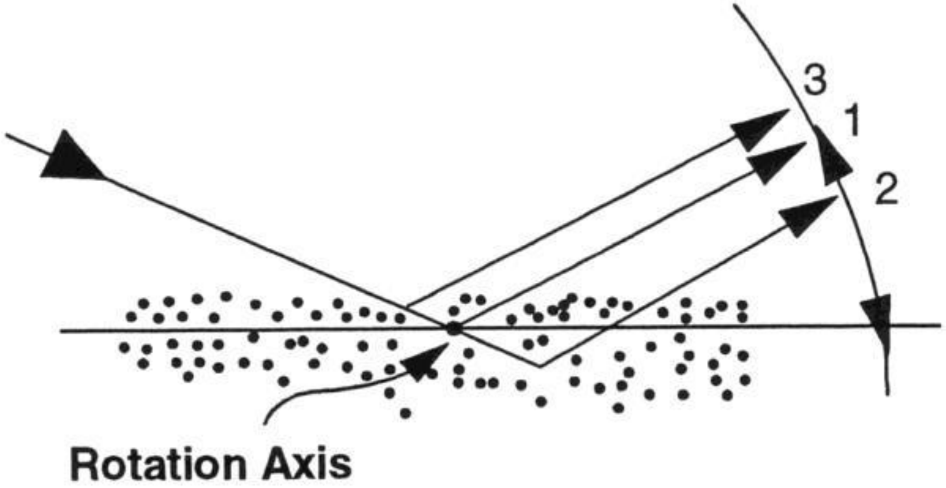
Precise Lattice Parameter Measurements

The most common sources of systematic error in measuring d-spacings are:

4. Displacement of the sample from the diffractometer axis.

   Usually the largest source of error.

   This is an experimental error due to operator error.



Application of Diffraction Data

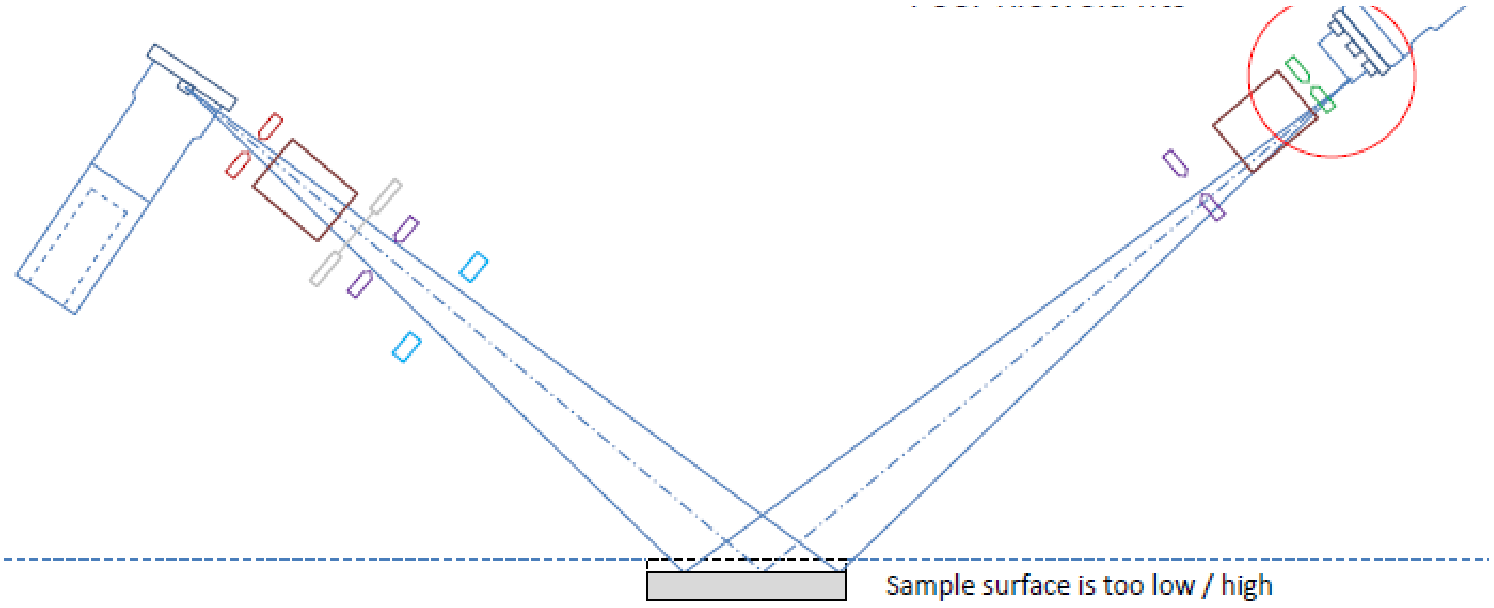
Precise Lattice Parameter Measurements

The most common sources of systematic error in measuring d-spacings are:

4. Displacement of the sample from the diffractometer axis.

Causes an asymmetric broadening of the peak profile on the low 2θ side and gives a peak shift in 2θ position of 0.01° 2θ for every 15 mm displacement.

This error is larger than all the others, therefore sample preparation is critical.



Application of Diffraction Data

Precise Lattice Parameter Measurements

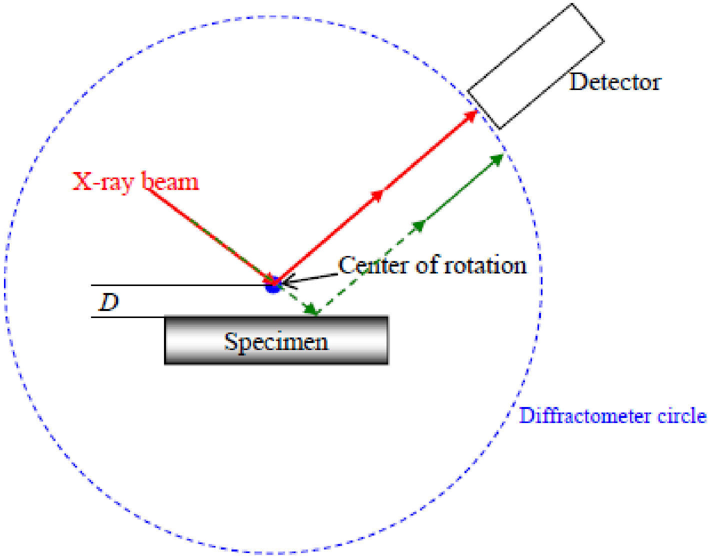
The most common sources of systematic error in measuring d-spacings are:

4. **Displacement of the sample from the diffractometer axis.**
   Usually the largest source of error.

$$\frac{\Delta d}{d} = -\frac{D\cos^2\theta}{R\sin\theta}$$

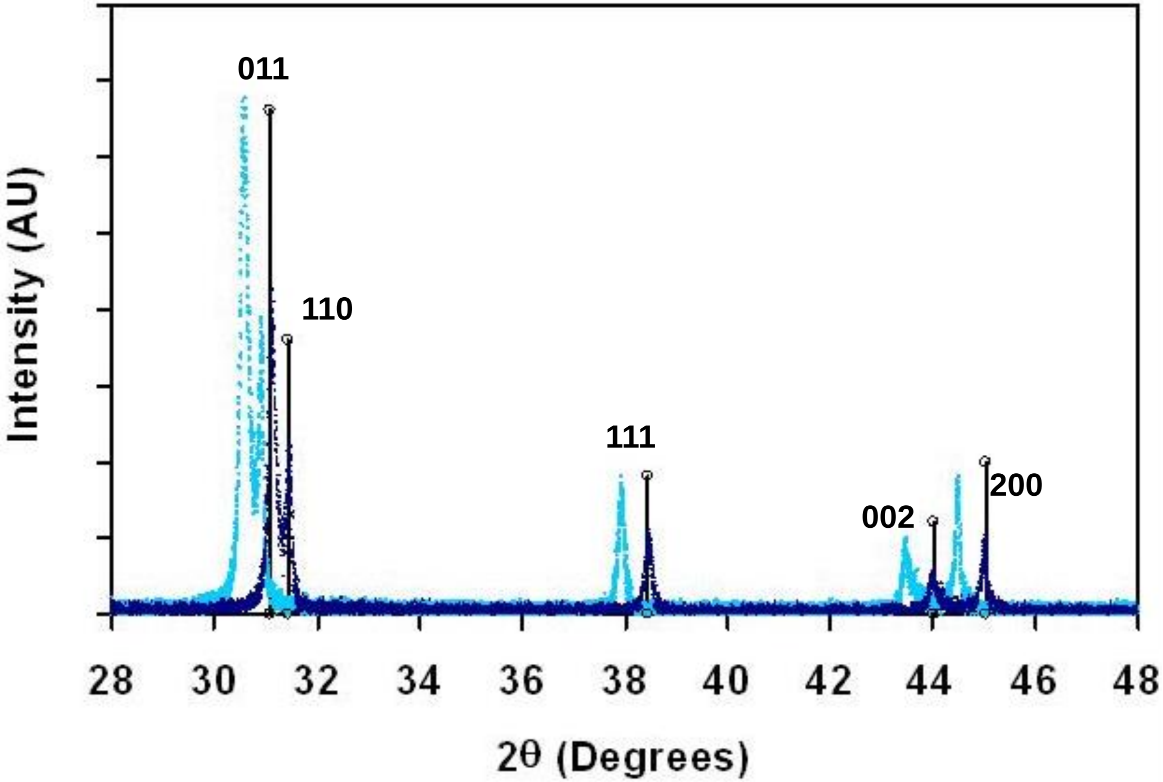
D = specimen displacement parallel to the reflecting plane normal

R = diffractometer radius.



Z-Displacements

- Tetragonal PZT
  - a=4.0215Å
  - b=4.1100Å



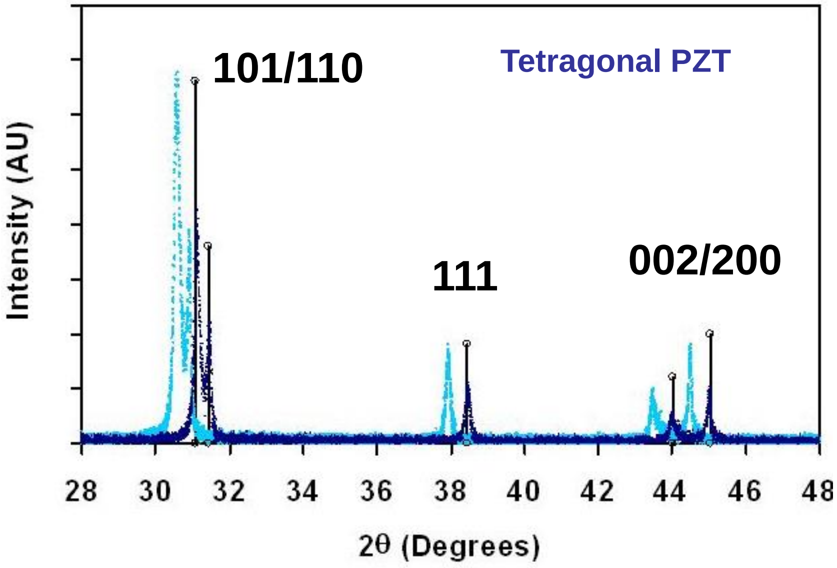
$$\frac{\Delta d}{d_{Actual}} = \frac{Disp \times \cos^2\theta}{R_{Detector} \times \sin\theta}$$

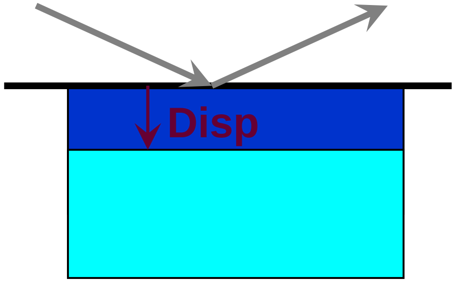
$$d_{Actual} = \frac{d_{Measured}}{1 + \frac{Disp \times \cos^2\theta}{R_{Detector} \times \sin\theta}}$$

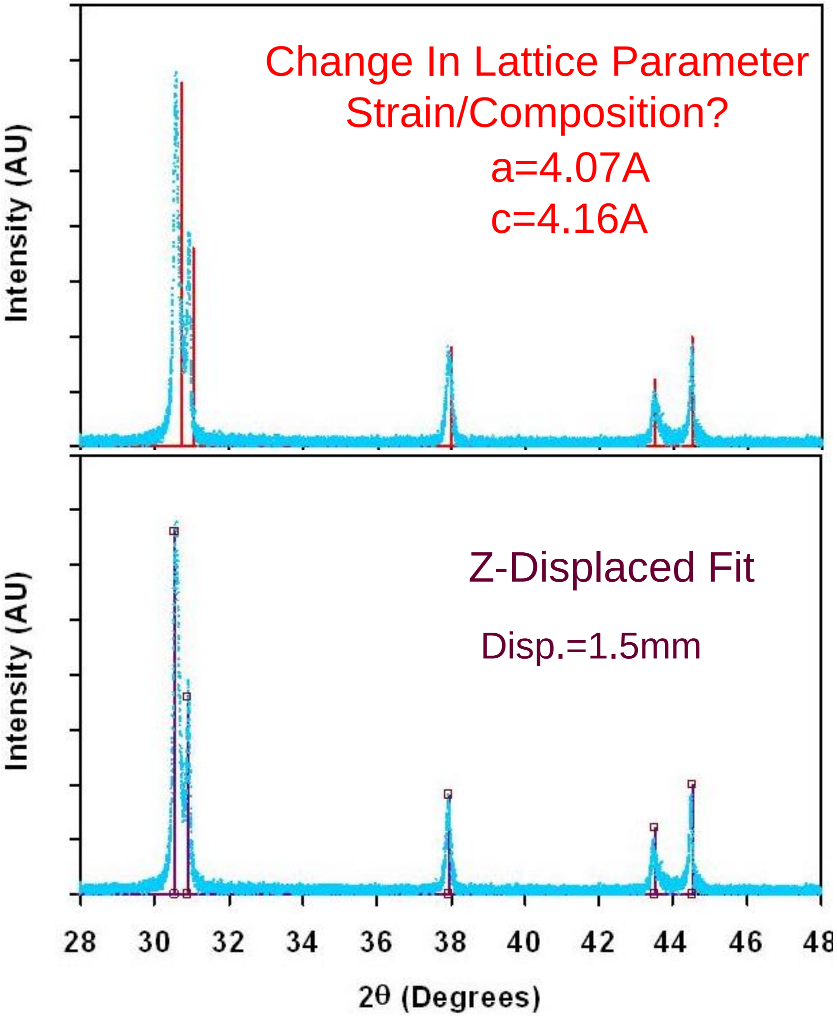
It is important that your sample be at the correct height

Z-Displacements vs. Change in Lattice Parameter

- Lattice Parameters
  - **a=4.0215 Å**
  - **c=4.1100 Å**







Change In Lattice Parameter
Strain/Composition?
a=4.07A
c=4.16A

Z-Displaced Fit

Disp.=1.5mm

Shifts due to z-displacements are systematically different and differentiable from changes in lattice parameter

Application of Diffraction Data

Precise Lattice Parameter Measurements

The most common sources of systematic error in measuring d-spacings are:

4. Displacement of the sample from the diffractometer axis.
   Usually the largest source of error.

Ways to compensate for sample displacement:

-use an internal calibration standard especially for publication quality data

-minimize by using a zero background sample holder

-of course take time to do good sample preparation

$\Delta d/d$ varies as $\cos^2\theta/\sin\theta$ for #4.

Application of Diffraction Data

Precise Lattice Parameter Measurements

The most common sources of systematic error in measuring d-spacings are:

1. **Misalignment of the instrument.**

   The center of the incident beam must intersect the diffractometer axis and the 0° position of the detector slit.
2. **Use of a flat sample instead of curved to conform to the focusing circle.**

   Minimized by decreasing the irradiation width of the sample.
3. **Absorption in the sample.**

   Samples of low absorption should be made as thin as possible.
4. **Displacement of the sample from the diffractometer axis.**

   Usually the largest source of error.
5. **Vertical divergence of the incident beam.**

   Minimize by decreasing the vertical opening of the detector slit.

Application of Diffraction Data

Precise Lattice Parameter Measurements

The most common sources of systematic error in measuring d-spacings are:

5. **Vertical divergence of the incident beam.**
   Minimize by decreasing the vertical opening of the detector slit.

$\Delta d/d$ varies as $[\cos^2\theta/\sin\theta + \cos^2\theta/\theta]$ for #5.

$[\cos^2\theta/\sin\theta + \cos^2\theta/\theta]$ is Nelson–Riley function for Hull/Debye-Scherrer camera

Application of Diffraction Data

Precise Lattice Parameter Measurements

Bradley-Jay method

Plot of lattice parameter versus $\cos^2\theta$

Nelson-Riley method

Plot of lattice parameter versus $\cos^2\theta/\sin\theta + \cos^2\theta/\theta$

Extrapolate plot to $\theta = 90^o$

Application of Diffraction Data

Precise Lattice Parameter Measurements

What you need to do to get the best answer:

1. **Use the actual λ value in your calculations.**

   Cu $K\alpha 1 = 1.540562$ Å.

2. **Obtain as many reflections as possible in the high-angle region.**

   Can decrease the λ of radiation by using Mo $K\alpha$ instead of Cu $K\alpha$.

3. **When α_1 and α_2 are resolved, use both points in your graph.**
4. **Obtain line positions as precisely as possible.**

   Use step scanning mode. Find the centroid.

Application of Diffraction Data

Precise Lattice Parameter Measurements

What you need to do to get the best answer:

4. **Obtain line positions as precisely as possible.**
   Use step scanning mode. Find the centroid.

Methods for determining peak position:

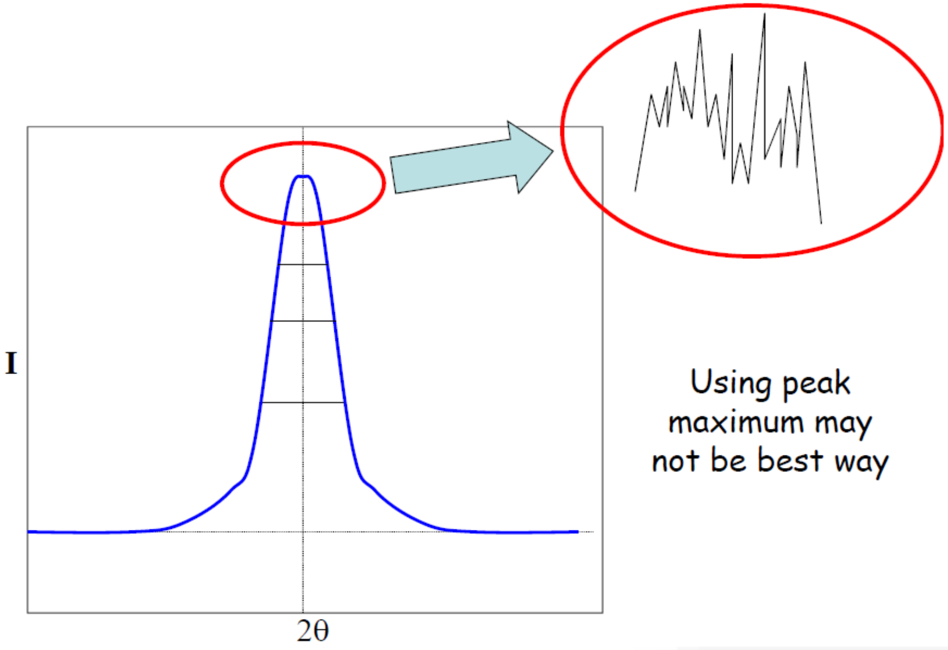
1. **Maximum intensity**
2. **Center of gravity**
3. **Projection**
4. **Gaussian**
5. **Lorentzian**

Application of Diffraction Data

Precise Lattice Parameter Measurements

Methods for determining peak position:

1. **Maximum intensity**



Using peak maximum may not be best way

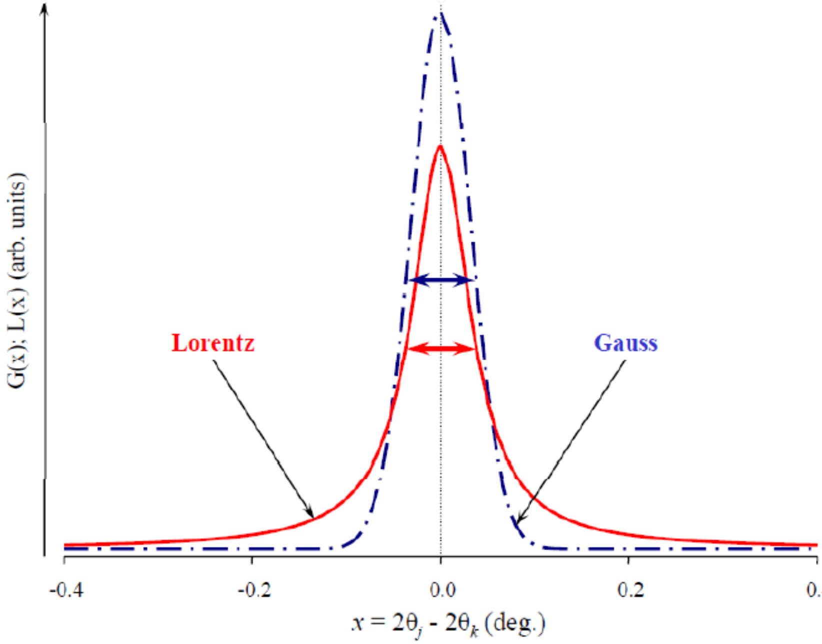
Application of Diffraction Data

Precise Lattice Parameter Measurements

Methods for determining peak position:

4. **Gaussian**
5. **Lorentzian**

Pseudo-Voigt which lies between gaussian and lorentzian generally works well.



Application of Diffraction Data

Precise Lattice Parameter Measurements

Methods for determining peak position:

Accuracy is critical, to know the lattice parameter to within 1×10^{-5} nm, must know the peak position to within 0.02^{o} at $2\theta = 160^{o}$.

Application of Diffraction Data

Precise Lattice Parameter Measurements

Noncubic crystals are more difficult.

Example: For hexagonal or tetragonal, the hkl represents the lattice parameters a and c.

However can use hk0 line to find value of a only.

Alternatively, the best method is the Cohen analytical method.

Application of Diffraction Data

Precise Lattice Parameter Measurements

Bradley-Jay and Nelson-Riley are designed for systematic errors.

For random errors, the Cohen method can be used for cubic and noncubic systems.

The Cohen method is a least-squares method.

Application of Diffraction Data

Precise Lattice Parameter Measurements

Cohen method

For cubic system combining Bragg equation and d-spacing equation, for any diffraction peak:

$$\sin^2\theta(true) = \frac{\lambda^2}{4a_o^2}\left(h^2 + k^2 + l^2\right)$$

a_o is the true lattice parameter.

Application of Diffraction Data

Precise Lattice Parameter Measurements

Cohen method

$$\sin^2\theta(observed) - \sin^2\theta(true) = \Delta\sin^2\theta$$

$$\sin^2\theta(observed) - \underbrace{\frac{\lambda^2}{4a_o^2}}_{}\underbrace{\left(h^2 + k^2 + l^2\right)}_{} = D\sin^2 2\theta$$

$$\sin^2\theta(observed) = A\alpha + C\delta$$

Drift constant. Fixed for every diffraction pattern. Best precision when D is small.

$C = D/10$ and $\delta = 10\sin^2 2\theta$

Application of Diffraction Data

Precise Lattice Parameter Measurements

Cohen method

$\sin^2\theta$ and α are known from indexing the diffraction pattern and from δ.

A and C are determined by solving two simultaneous equations for the observed reflections. The true value of the lattice parameter can then be calculated.

Combine Cohen's method with the least squares method to minimize observational errors.

Application of Diffraction Data

Precise Lattice Parameter Measurements

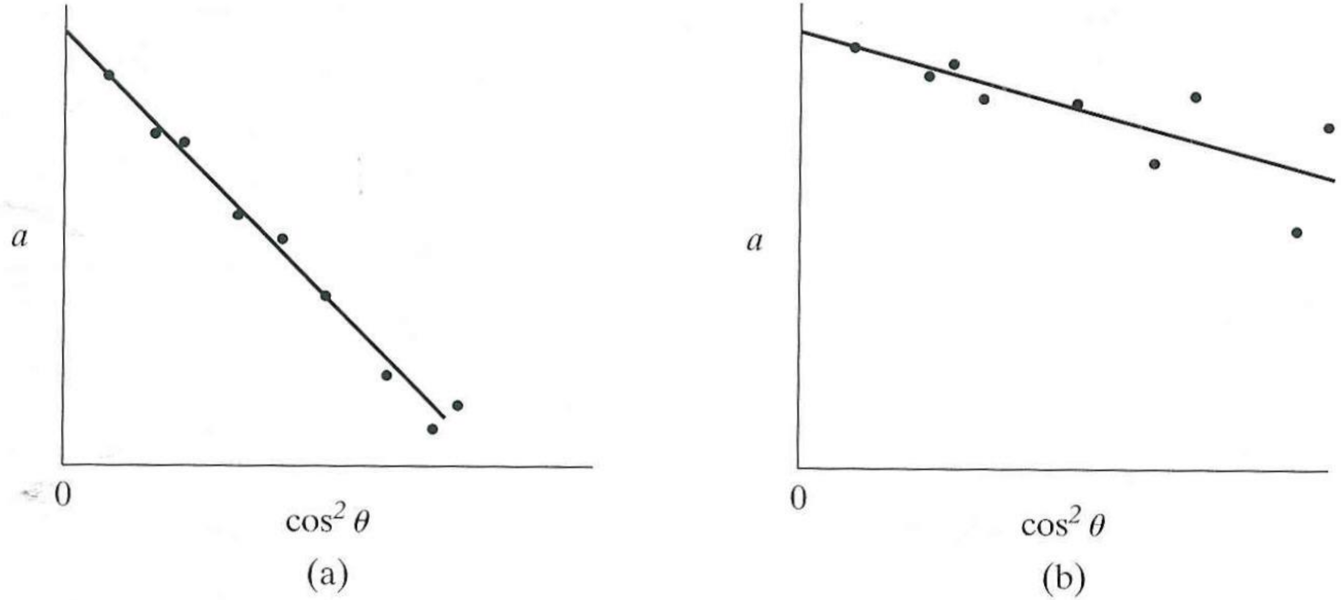


Figure 13-3 Extreme forms of extrapolation curves (schematic): (a) large systematic errors, small random errors; (b) small systematic errors, large random errors.

Application of Diffraction Data

Precise Lattice Parameter Measurements

Systematic errors in a (lattice parameter) approach zero as θ approaches 90^{o}, and are eliminated with extrapolation.

Magnitude of error $\propto$ slope of line.

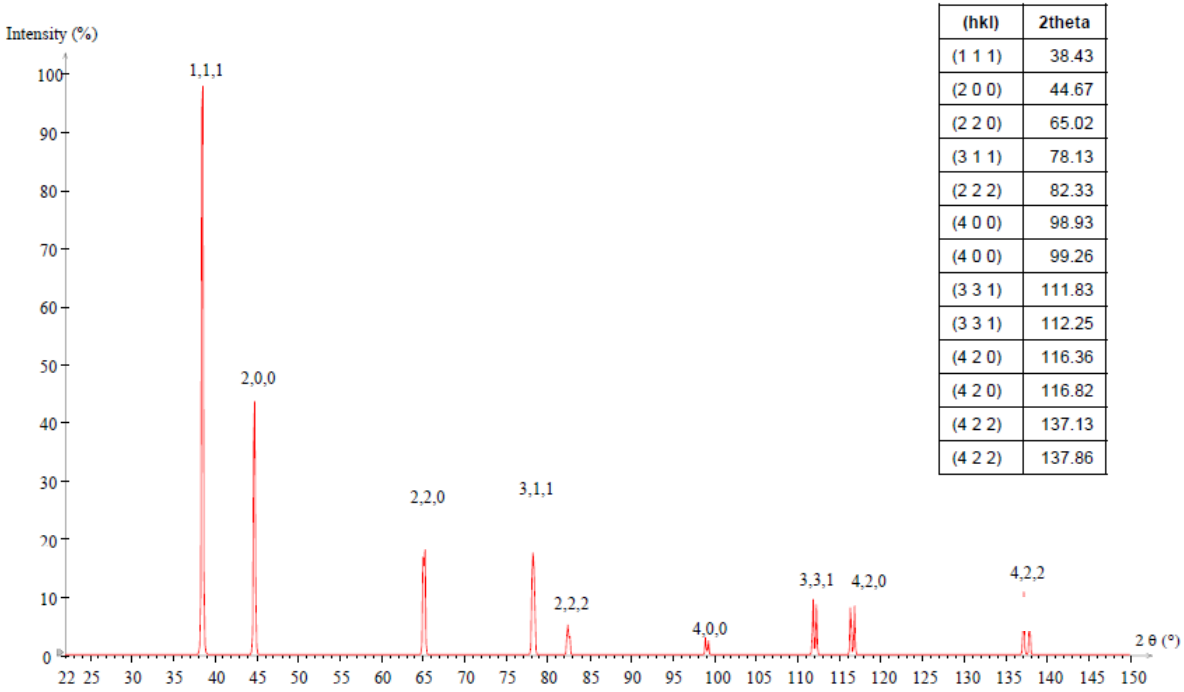
Small errors lead to flat lines.

Random errors in a also decrease in magnitude as θ increases.

Application of Diffraction Data

Precise Lattice Parameter Measurements

XRD Pattern for Al

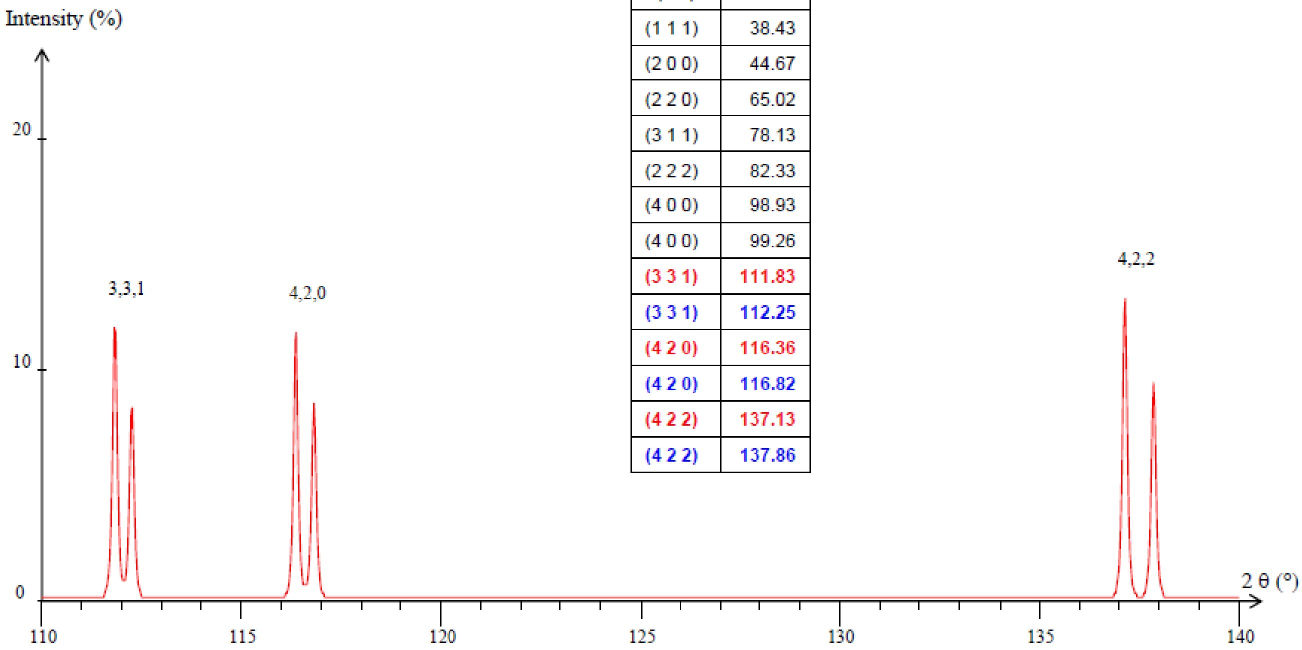


CuKα

(hkl)	2theta
(1 1 1)	38.43
(2 0 0)	44.67
(2 2 0)	65.02
(3 1 1)	78.13
(2 2 2)	82.33
(4 0 0)	98.93
(4 0 0)	99.26
(3 3 1)	111.83
(3 3 1)	112.25
(4 2 0)	116.36
(4 2 0)	116.82
(4 2 2)	137.13
(4 2 2)	137.86

Application of Diffraction Data

Precise Lattice Parameter Measurements



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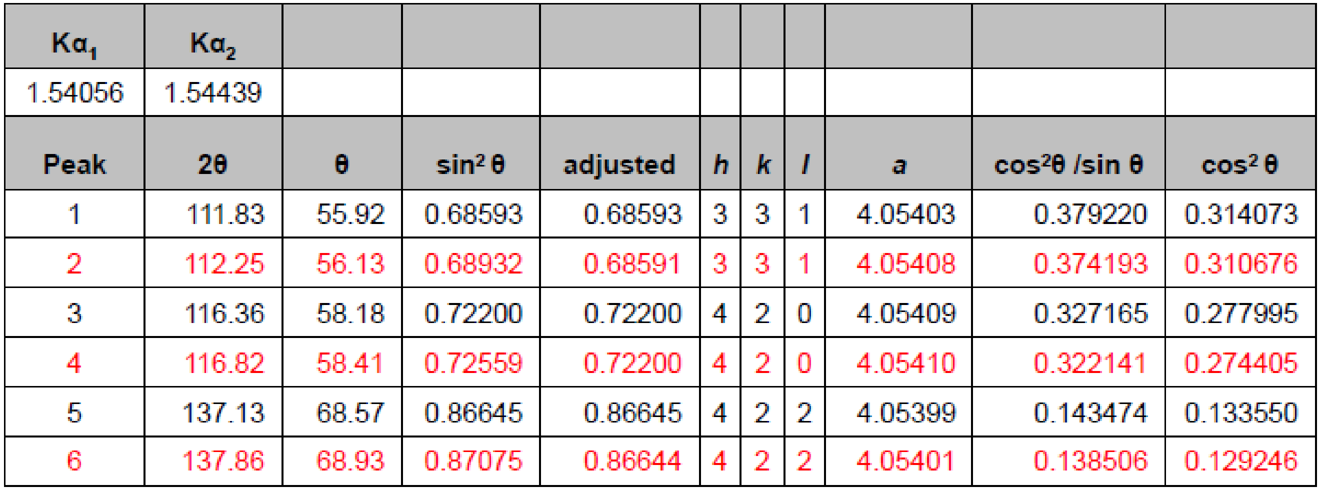
Application of Diffraction Data

Precise Lattice Parameter Measurements



$K\alpha_1$	$K\alpha_2$									
1.54056	1.54439									
Peak	**2θ**	**θ**	**$\sin^2\theta$**	**adjusted**	***h***	***k***	***l***	***a***	**$\cos^2\theta/\sin\theta$**	**$\cos^2\theta$**
1	111.83	55.92	0.68593	0.68593	3	3	1	4.05403	0.379220	0.314073
2	112.25	56.13	0.68932	0.68591	3	3	1	4.05408	0.374193	0.310676
3	116.36	58.18	0.72200	0.72200	4	2	0	4.05409	0.327165	0.277995
4	116.82	58.41	0.72559	0.72200	4	2	0	4.05410	0.322141	0.274405
5	137.13	68.57	0.86645	0.86645	4	2	2	4.05399	0.143474	0.133550
6	137.86	68.93	0.87075	0.86644	4	2	2	4.05401	0.138506	0.129246

$$\sin^2\theta_{K\alpha 1(\mathrm{adj})} = \sin^2\theta_{K\alpha 2}\left(\frac{\lambda^2_{K\alpha 1}}{\lambda^2_{K\alpha 2}}\right)$$

Application of Diffraction Data

Precise Lattice Parameter Measurements

Peak	θ	sin²θ	adjusted sin²(θ)	*h*	*k*	*l*	α	δ	α²	αδ	δ²	αsin²(θ)	δsin²(θ)
1	55.92	0.68593	0.68593	3	3	1	19	8.6	361	163.7	74.26	13.03261	5.91080
2	56.13	0.68932	0.68591	3	3	1	19	8.6	361	162.8	73.38	13.03228	5.87567
3	58.18	0.72200	0.72200	4	2	0	20	8.0	400	160.6	64.46	14.44010	5.79665
4	58.41	0.72559	0.72200	4	2	0	20	8.0	400	159.3	63.43	14.44000	5.75021
5	68.57	0.86645	0.86645	4	2	2	24	4.6	576	111.1	21.42	20.79479	4.01044
6	68.93	0.87075	0.86644	4	2	2	24	4.5	576	108.0	20.26	20.79457	3.90042
								Σ	**2674**	**865.5**	**317.21**	**96.53435**	**31.24421**

$$A\sum \alpha^2 + C\sum \alpha\delta = \sum \alpha \sin^2\theta$$

$$A\sum \alpha\delta + C\sum \delta^2 = \sum \delta \sin^2\theta$$

$$2674A + 865.5C = 96.53435$$

$$865.5A + 317.21C = 31.24421$$

$$\alpha = h^2 + k^2 + l^2$$

$$\delta = 10\sin^2 2\theta$$

Application of Diffraction Data

Precise Lattice Parameter Measurements

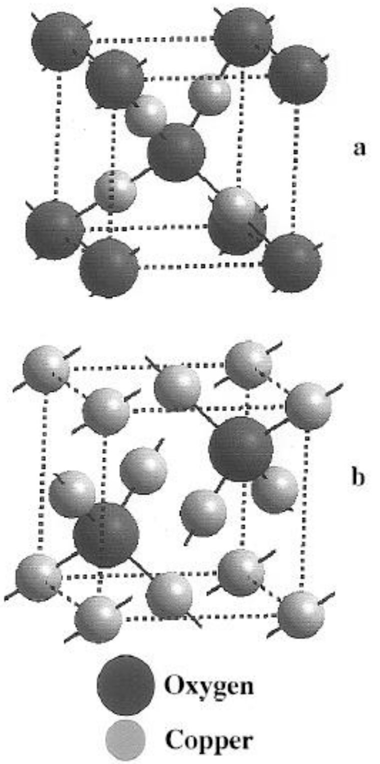


Figure 6. Cuprite structure for Cu_2O. Copper atoms are represented by small light spheres and oxygen atoms are represented by large dark spheres. (a) Copper special positions at (0.25, 0.25, 0.25); (0.75, 0.75, 0.25); (0.75, 0.25, 0.75); (0.25, 0.75, 0.75) and oxygen special positions at (0, 0, 0); (0.5, 0.5, 0.5). (b) Copper special positions at (0, 0, 0); (0.5, 0.5, 0); (0.5, 0, 0.5); (0, 0.5, 0.5) and oxygen special positions at (0.75, 0.75, 0.75); (0.25, 0.25, 0.25).

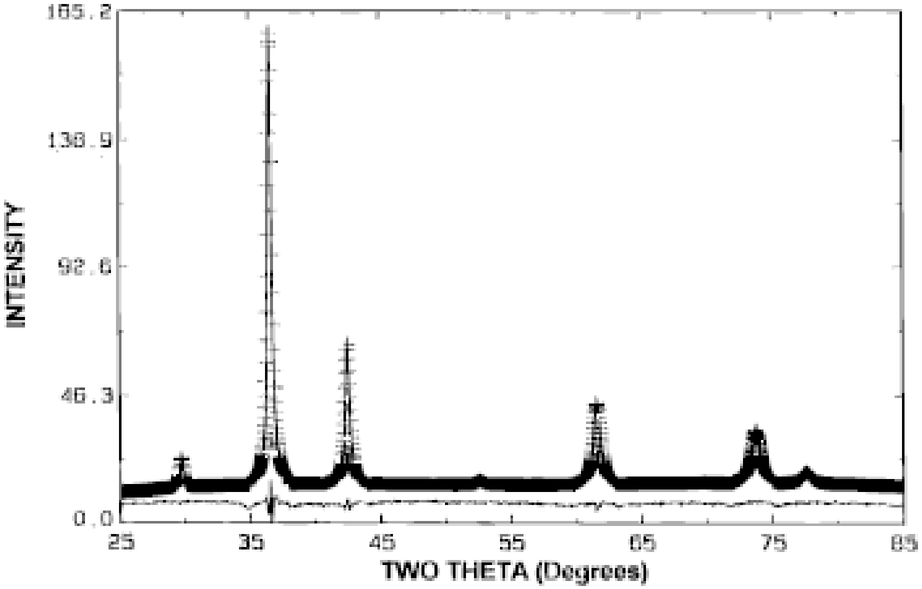
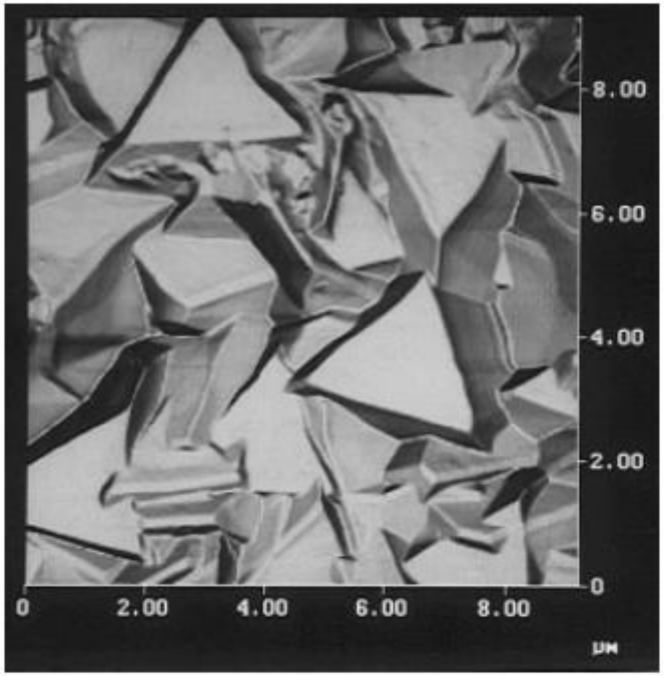
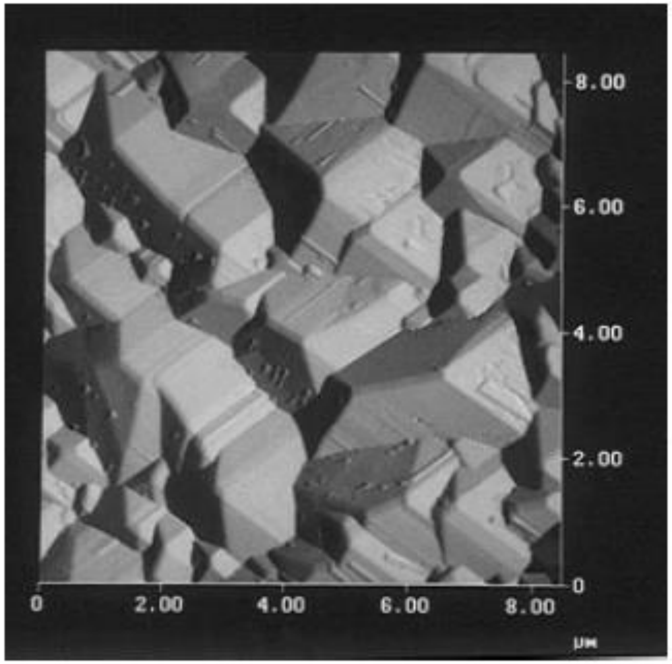


Figure 5. Rietveld analysis for powder produced by grinding several films deposited at 65 °C and $E = -0.45$ V. Powder X-ray data (solid line), Rietveld fit (crosses) and difference pattern (solid line shown below data) are shown for Cu_2O.

Application of Diffraction Data

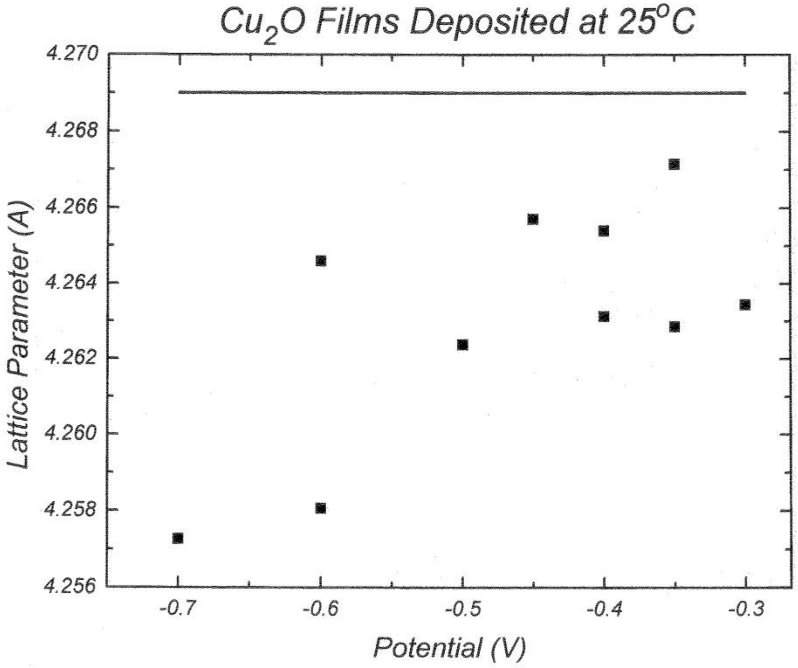
Precise Lattice Parameter Measurements





Application of Diffraction Data

Precise Lattice Parameter Measurements



Application of Diffraction Data

Precise Lattice Parameter Measurements

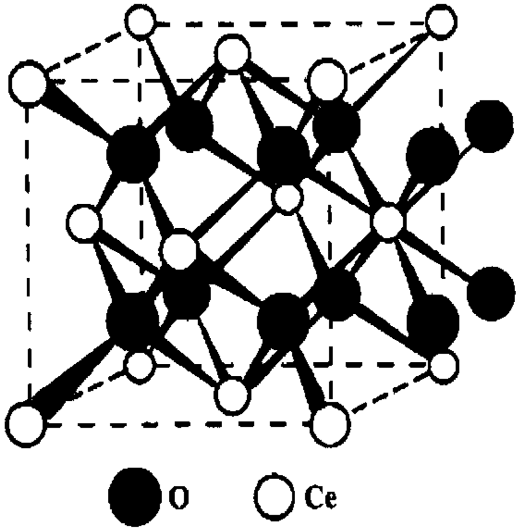
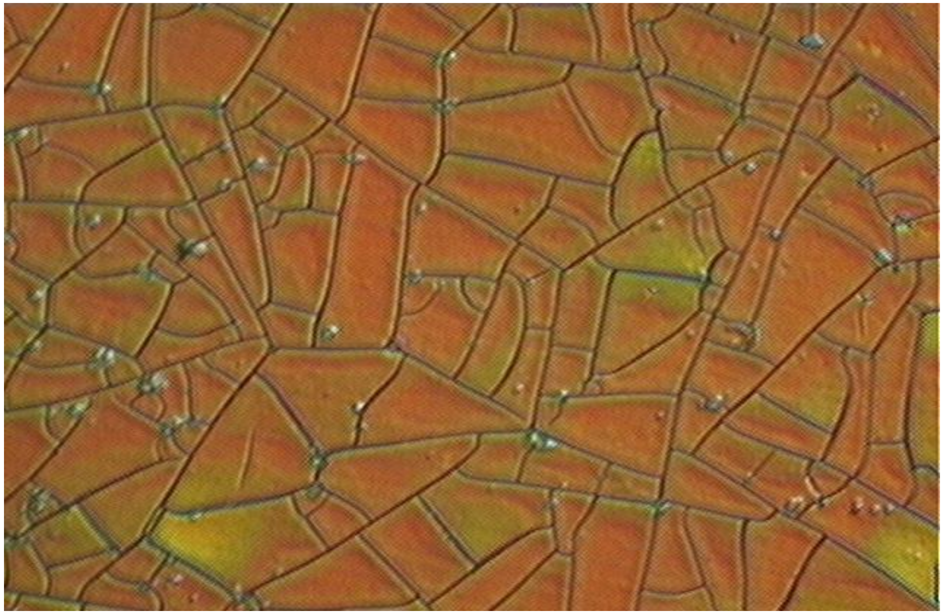


FIG. 1. The fcc cell of CeO_2 with the fluorite structure.



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Advanced X-ray Analysis

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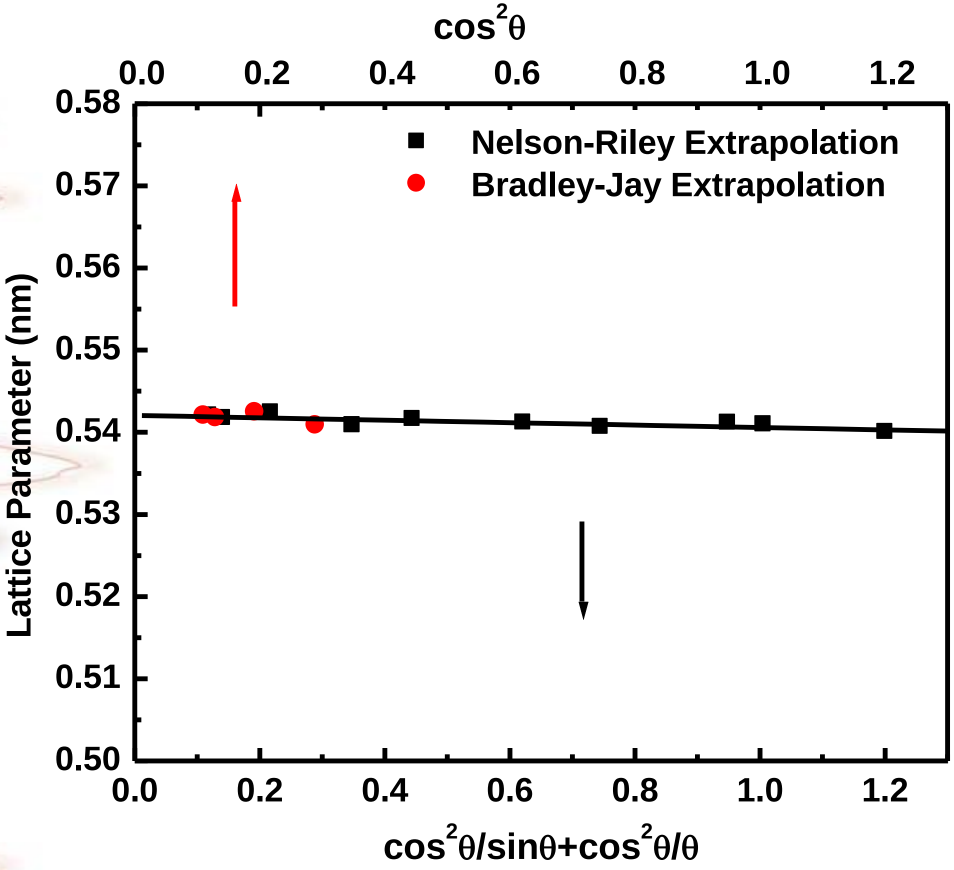
Application of Diffraction Data

Precise Lattice Parameter Measurements



Precise calculated lattice parameter of (6.22 nm) cerium oxide is 0.54268, 0.54264 and 0.54253 nm using Cohen’s, B-J, and N-R method, respectively.

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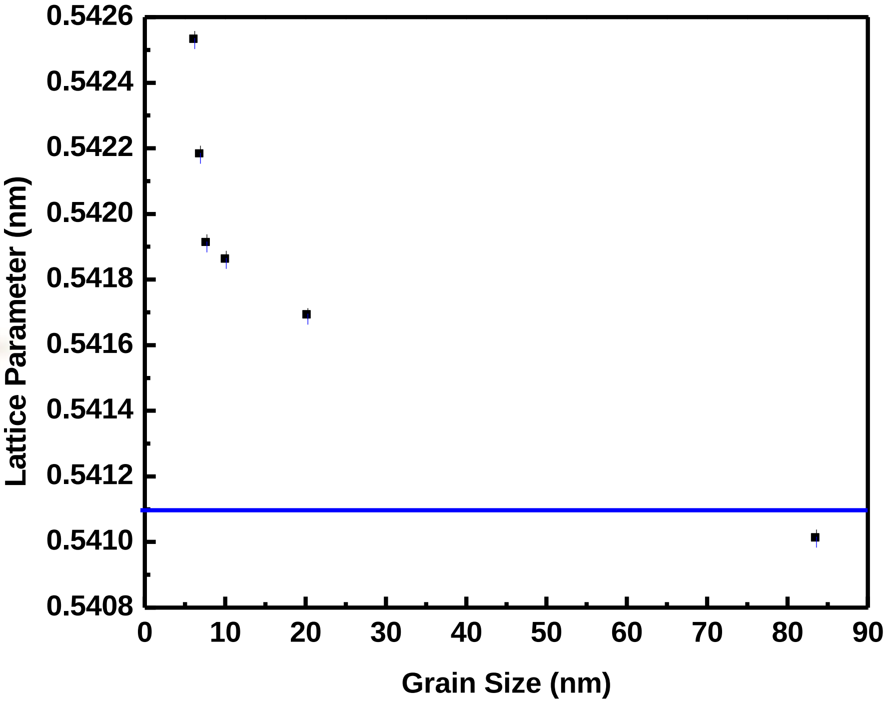
Application of Diffraction Data

Precise Lattice Parameter Measurements



Lattice parameter increases with decreasing particle size of cerium oxide.
Blue line represents the theoretical lattice parameter
for stoichiometric FCC CeO_2 .

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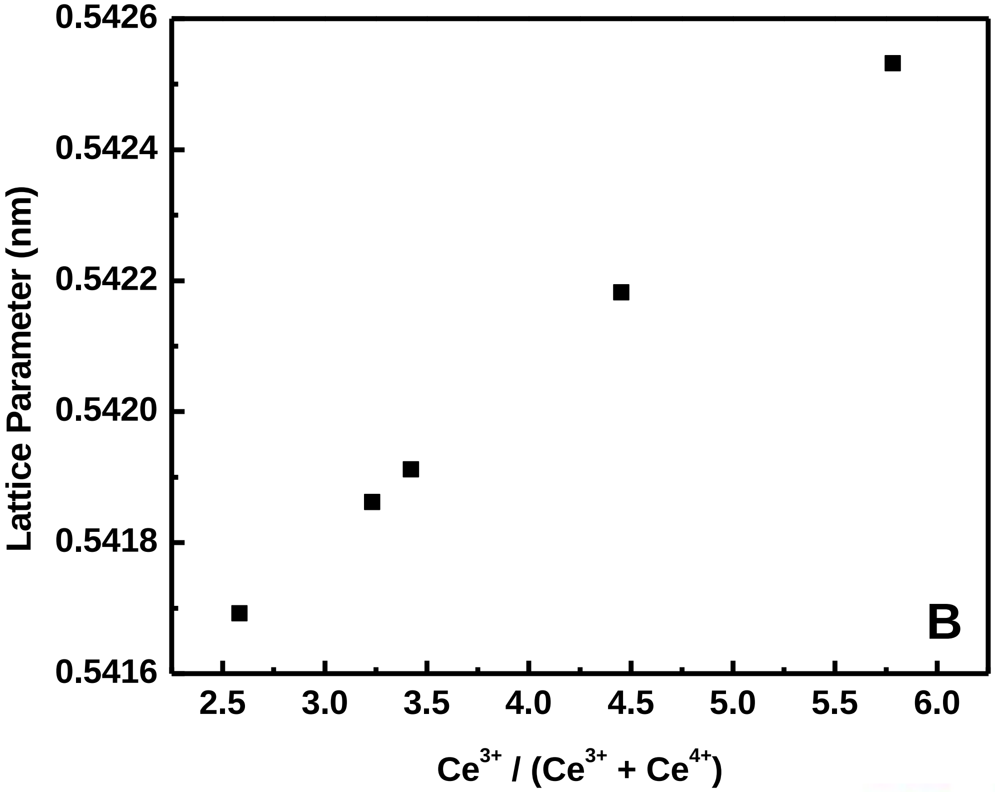
Application of Diffraction Data

Precise Lattice Parameter Measurements



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Application of Diffraction Data

Precise Lattice Parameter Measurements

Estimation of Ce^{3+} percentage and oxygen vacancies in electrosynthesized nanosized CeO_y

Grain Size (nm)	Lattice Parameter (nm)	Ce^{3+} / (Ce^{4+} +Ce^{3+}) (%)		Oxygen Vacancies (%)		y in CeO_y	
		M's	*T's*	*M's*	*T's*	*M's*	*T's*
6.21752	*0.54253*	*5.787*	*7.418*	*2.8935*	*3.7091*	*1.9710*	*1.9629*
6.91599	*0.54218*	*4.457*	*5.710*	*2.2285*	*2.8551*	*1.9777*	*1.9714*
7.72579	*0.54191*	*3.429*	*4.392*	*1.7145*	*2.1962*	*1.9829*	*1.9780*
10.10909	*0.54186*	*3.238*	*4.148*	*1.6190*	*2.0742*	*1.9838*	*1.9793*
20.30101	*0.54169*	*2.591*	*3.319*	*1.2955*	*1.6593*	*1.9870*	*1.9834*

Note: M's refers the results calculated using the method established by McBride and colleagues. T's refers the results calculated using the method suggested by Tsunekawa and colleagues. Grain sizes and lattice parameters are measured by XRD.

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Homework Assignment: Phase Diagram Calculations

Due Today

Homework Assignment: Precise Lattice Parameters

Due 12-3-24

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 Diffractometry 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