chem 5390

Advanced X-ray Analysis

LECTURE 15

Dr. Teresa D. Golden
University of North Texas
Department of Chemistry

Diffraction Theory

Diffraction Methods

What can we learn from the diffractometer experiments?

- **Phase Analysis**
- **Texture Analysis**
- **Lattice Parameters**
- **Crystallite Size**
- **Stress Analysis**
- **Strain Analysis**

Quantitative Methods

Precise Lattice Parameter Measurements

Practical applications for lattice parameter measurements:

-determine composition (stoichiometry) of the sample

-determine thermal expansion coefficient

Quantitative Methods

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.

Quantitative Methods

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^{o}C, a_{Al} = 4.049 Å and at 50^{o}C, a_{Al} = 4.051 Å.

thermal expansion coefficient, α_{Al} = 23.6 x 10^{-6}/^{o}C

Quantitative Methods

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) .

Quantitative Methods

Precise Lattice Parameter Measurements

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

Example: At θ = 45º, there is a 1.7% error for sinθ.
At θ = 85º, there is a 0.15% error for sinθ.

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

Quantitative Methods

Precise Lattice Parameter Measurements

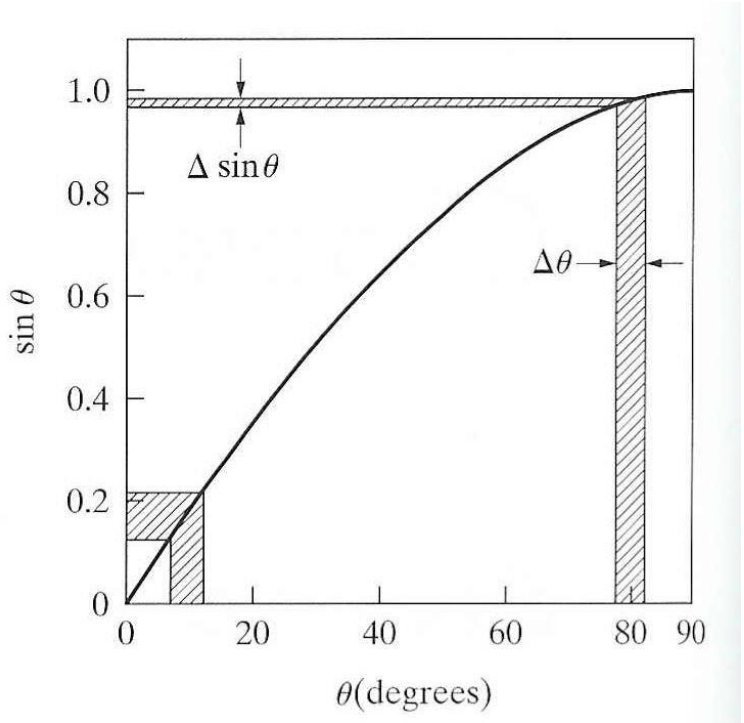


Figure 13-1 The variation of sin θ with θ. The error in sin θ caused by a given error in θ decreases as θ increases ($\Delta\theta$ exaggerated).

Quantitative Methods

Precise Lattice Parameter Measurements

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

Quantitative Methods

Precise Lattice Parameter Measurements

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.

Quantitative Methods

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.

Quantitative Methods

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.
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.

Quantitative Methods

Precise Lattice Parameter Measurements

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

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.

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

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

Quantitative Methods

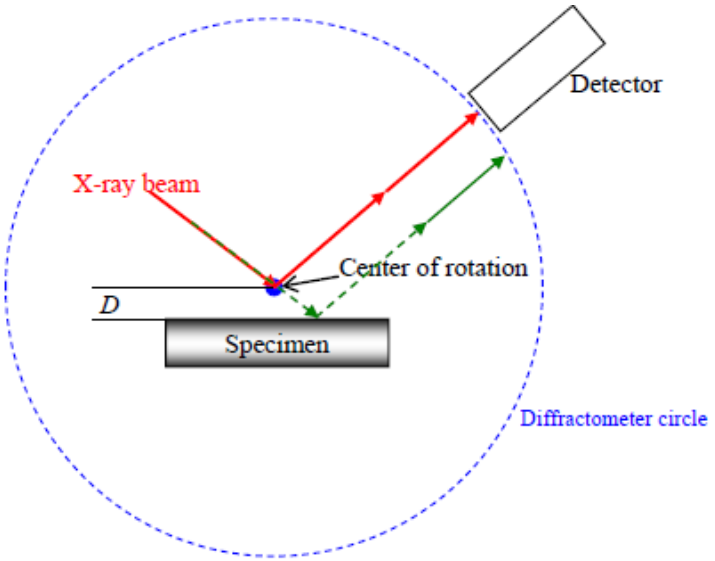
Precise Lattice Parameter Measurements

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.



Quantitative Methods

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.

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

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

Quantitative Methods

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 $\theta = 90^o$

Quantitative Methods

Precise Lattice Parameter Measurements

What you need to do to get the best answer:

1. **Use the actual λ value in your calculations.**
   Cu Kα1 = 1.540562 Å.
2. **Obtain as many reflections as possible in the high-angle region.**
   Can decrease the l of radiation by using Mo Kα instead of Cu Kα.
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.

Quantitative Methods

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:

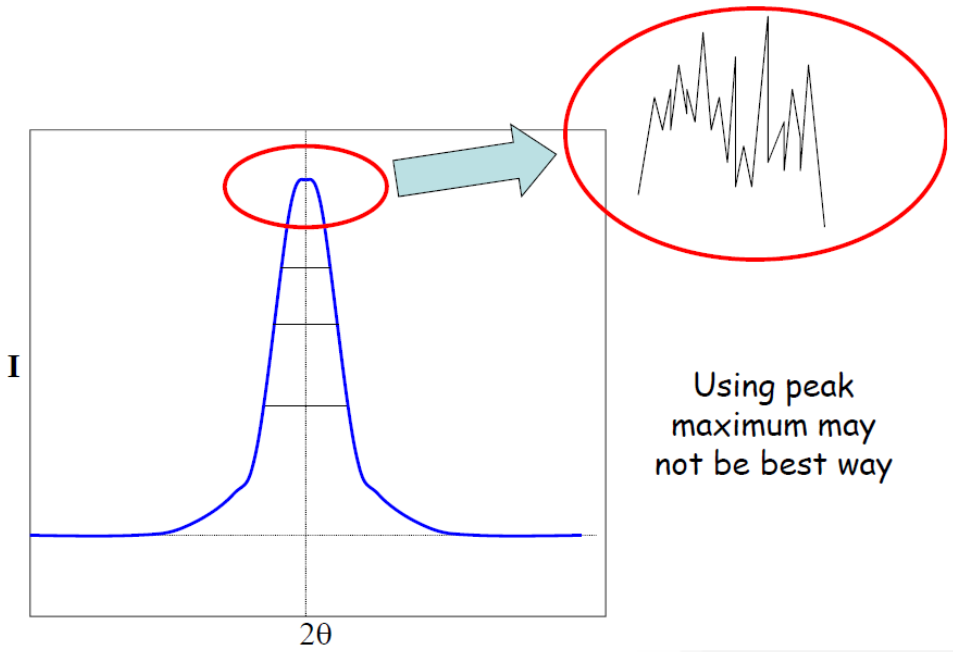
1. **Maximum intensity**
2. **Center of gravity**
3. **Projection**
4. **Gaussian**
5. **Lorentzian**

Quantitative Methods

Precise Lattice Parameter Measurements

Methods for determining peak position:

1. **Maximum intensity**



Using peak maximum may not be best way

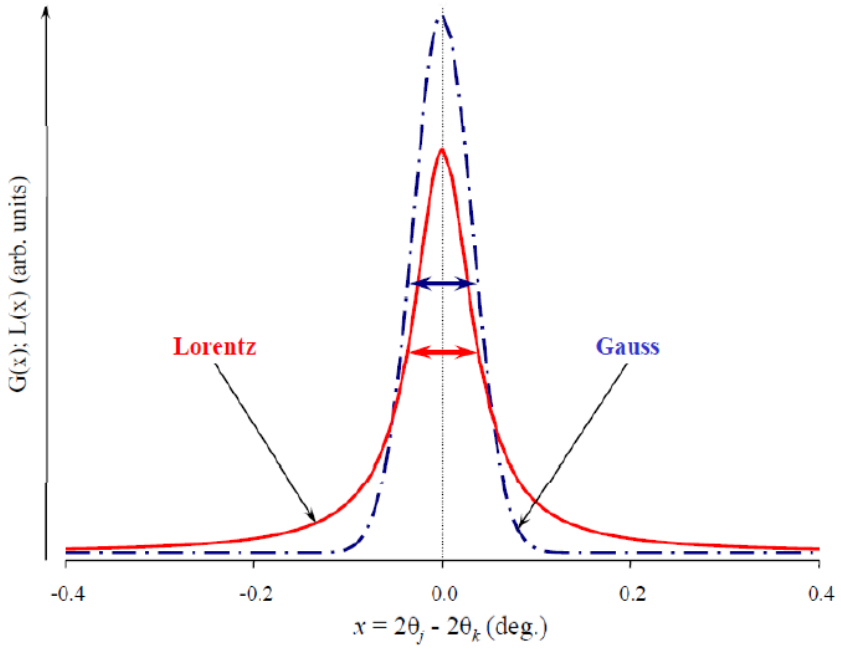
Quantitative Methods

Precise Lattice Parameter Measurements

Methods for determining peak position:

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

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



Quantitative Methods

Precise Lattice Parameter Measurements

Methods for determining peak position:

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

Quantitative Methods

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.

Quantitative Methods

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.

Quantitative Methods

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.

Quantitative Methods

Precise Lattice Parameter Measurements

Cohen method

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

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

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

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

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

Quantitative Methods

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.

Quantitative Methods

Precise Lattice Parameter Measurements

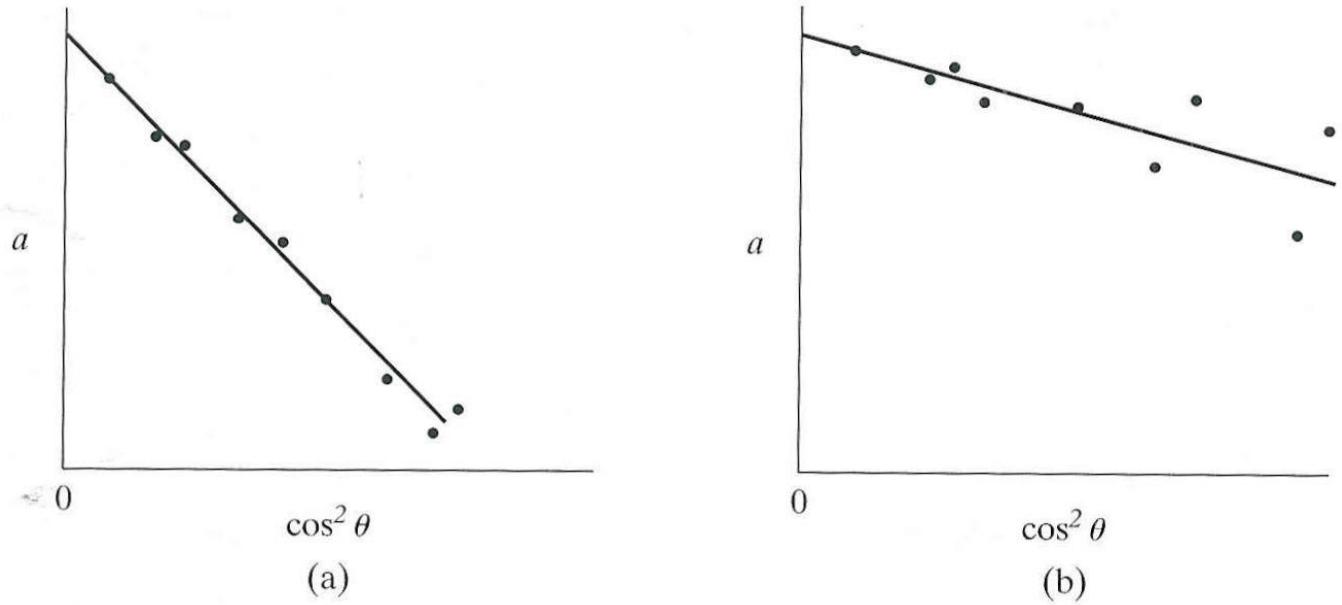


Figure 13-3 Extreme forms of extrapolation curves (schematic): (a) large systematic errors, small random errors; (b) small systematic errors, large random errors.

Quantitative Methods

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.

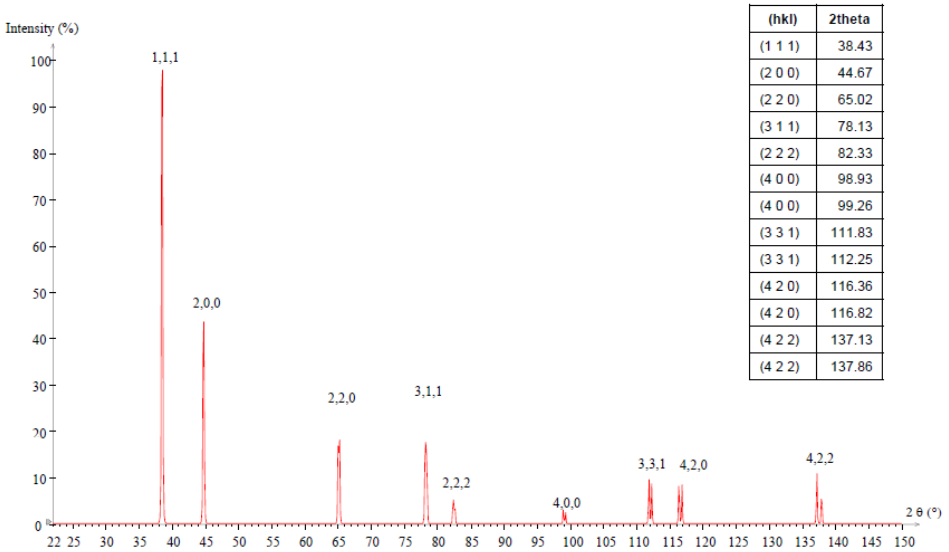
Random errors in a also decrease in magnitude as θ increases.

Quantitative Methods

Precise Lattice Parameter Measurements

XRD Pattern for Al

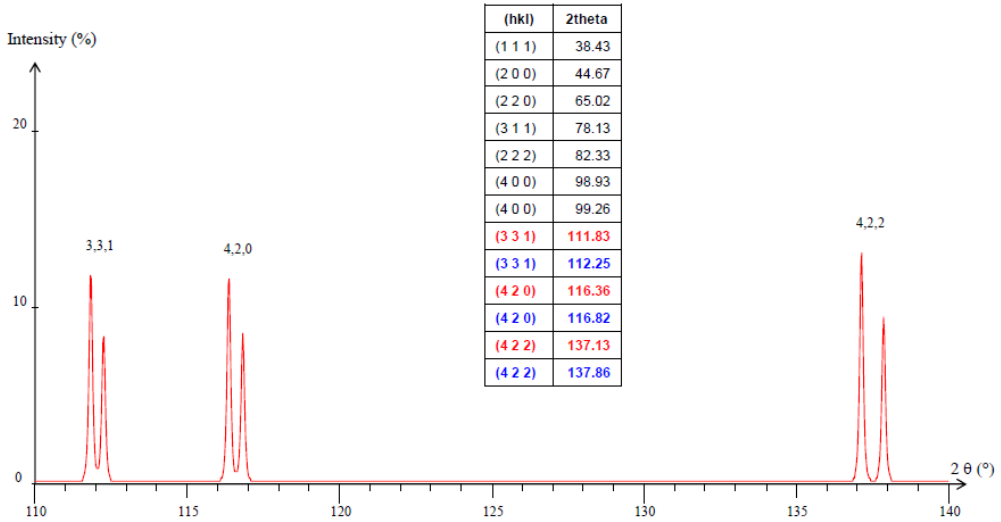
CuKα



(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

Quantitative Methods

Precise Lattice Parameter Measurements



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Quantitative Methods

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

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

Quantitative Methods

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**

$$A\sum\alpha^2 + C\sum\alpha\delta = \sum\alpha\sin^2\theta \quad \Rightarrow \quad 2674A + 865.5C = 96.53435$$

$$A\sum\alpha\delta + C\sum\delta^2 = \sum\delta\sin^2\theta \quad \Rightarrow \quad 865.5A + 317.21C = 31.24421$$

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

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

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Quantitative Methods

Precise Lattice Parameter Measurements

Can use lattice parameters for phase diagram determinations also.

Phase diagrams establish what phases are present at different temperatures, pressures, and compositions of an alloy system.

Phase diagrams can be very complex.

Quantitative Methods

Precise Lattice Parameter Measurements

Common terms associated with phase diagrams:

- **Continuous solid solution**

  Complete mixing of components. Components must have the same crystal structure. Crystal structure does not change through solubility range.

- **Primary (terminal) solid solution**

  Partial solubility of components in each other. Depends upon atomic size. Go beyond solubility limit for α and β will precipitate. α has different crystal structure than β.

- **Intermediate solid solution or Intermediate phase**

  Intermediate solid solution or phase almost always has different crystal structure than the phases on either side of it.

Quantitative Methods

Precise Lattice Parameter Measurements

To determine a phase diagram with X-ray diffraction:

For a binary systems (procedures for ternary systems are similar)

1. **Prepare alloys at definite composition intervals from pure elemental constituents.**
2. **Equilibrate alloy at the desired temperatures.**
3. **Collect and index XRD patterns.**
4. **Look at how the calculated lattice parameters vary with composition and temperature.**

Quantitative Methods

Precise Lattice Parameter Measurements

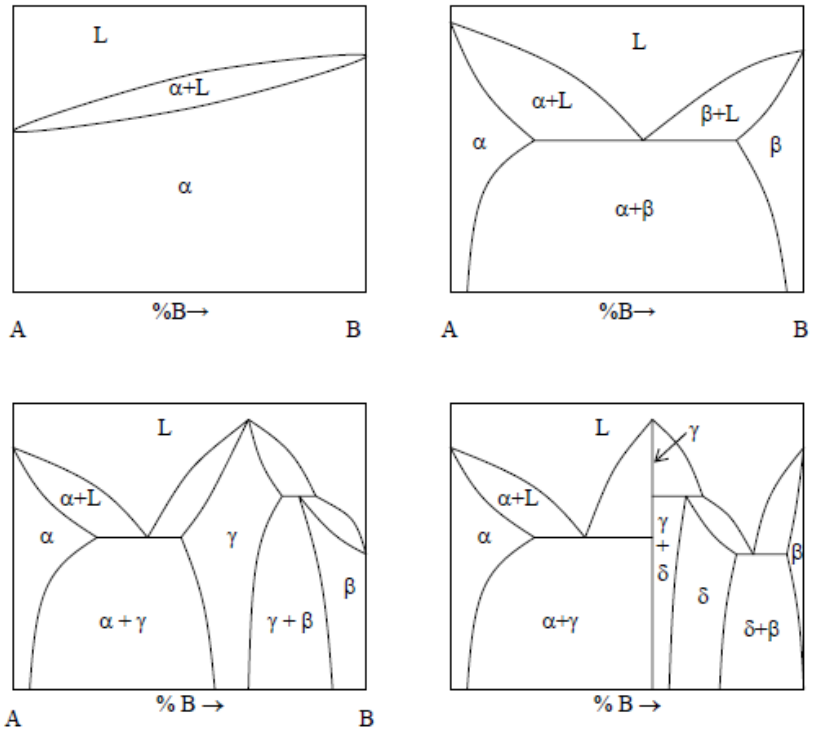


Figure 1: Representative examples of phase diagrams showing (a) complete solid solubility, (b) partial solid solubility, (c) and (d) partial solid solubility along with the formation of an intermediate phases.

Quantitative Methods

Precise Lattice Parameter Measurements

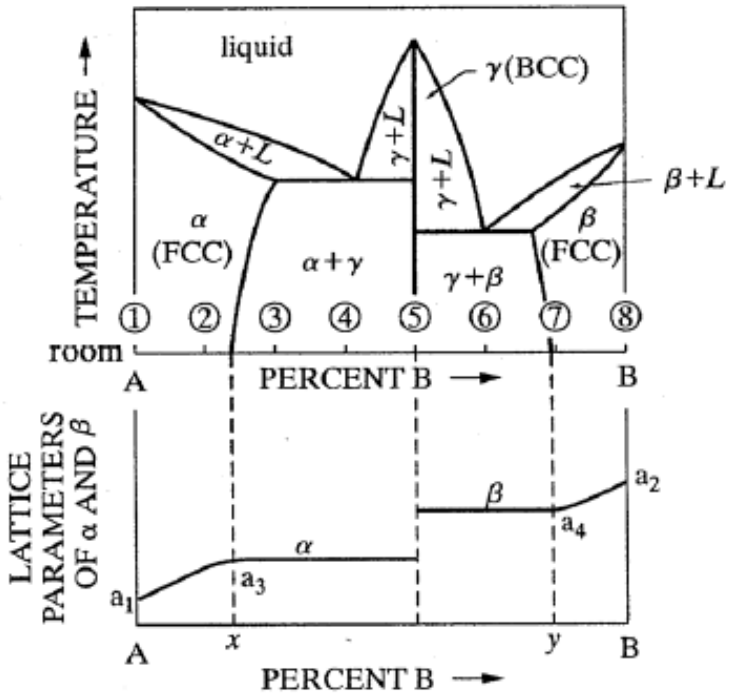


Figure 2: Phase diagram and lattice constants of a hypothetical alloy system. Adapted from Cullity and Stock, Elements of X-ray Diffraction, 3rd Edition (Prentice Hall, Upper Saddle River, NJ) p. 334.

Quantitative Methods

Precise Lattice Parameter Measurements

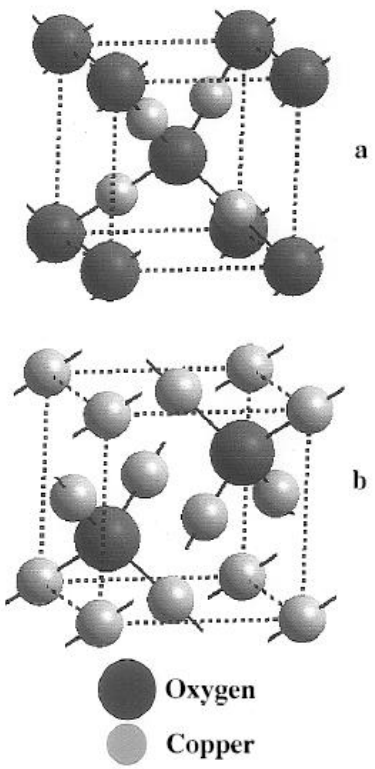


Figure 6. Cuprite structure for Cu_2O. Copper atoms are represented by small light spheres and oxygen atoms are represented by large dark spheres. (a) Copper special positions at (0.25, 0.25, 0.25); (0.75, 0.75, 0.25); (0.75, 0.25, 0.75); (0.25, 0.75, 0.75) and oxygen special positions at (0, 0, 0);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

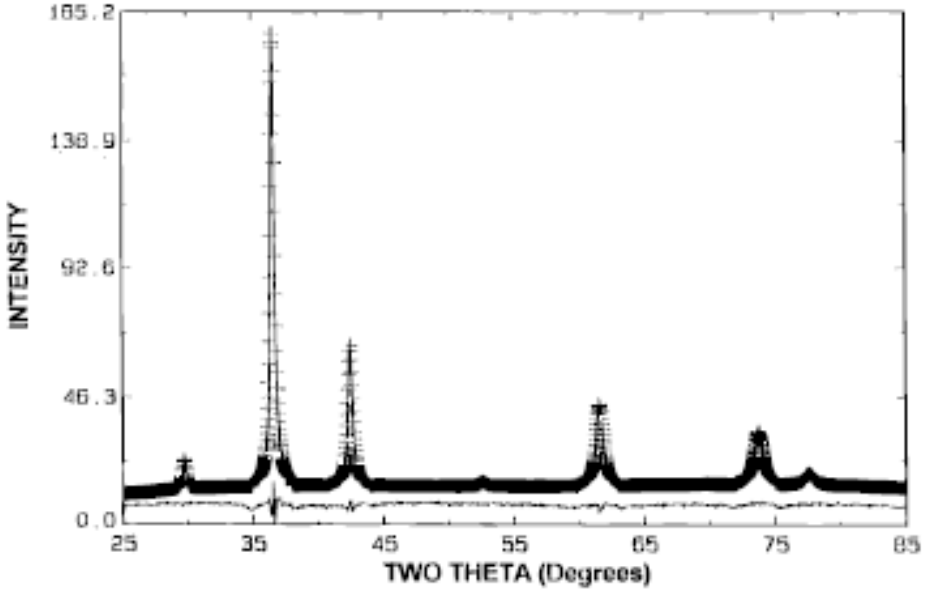
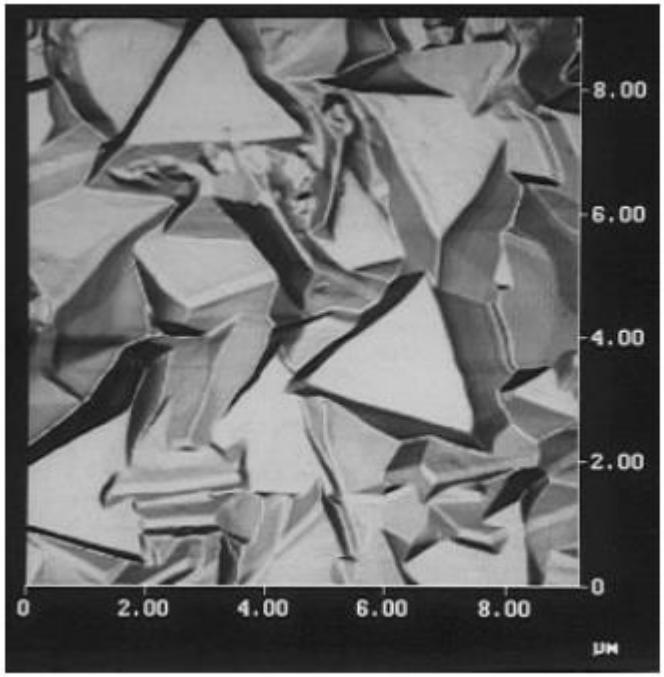
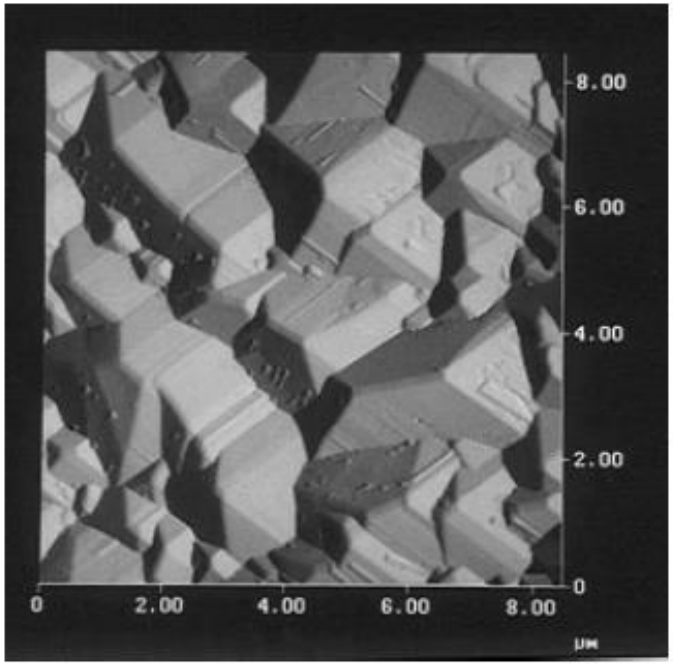


Figure 5. Rietveld analysis for powder produced by grinding several films deposited at 65 °C and $E = -0.45$ V. Powder X-ray data (solid line), Rietveld fit (crosses) and difference pattern (solid line shown below data) are shown for Cu_2O.

Quantitative Methods

Precise Lattice Parameter Measurements





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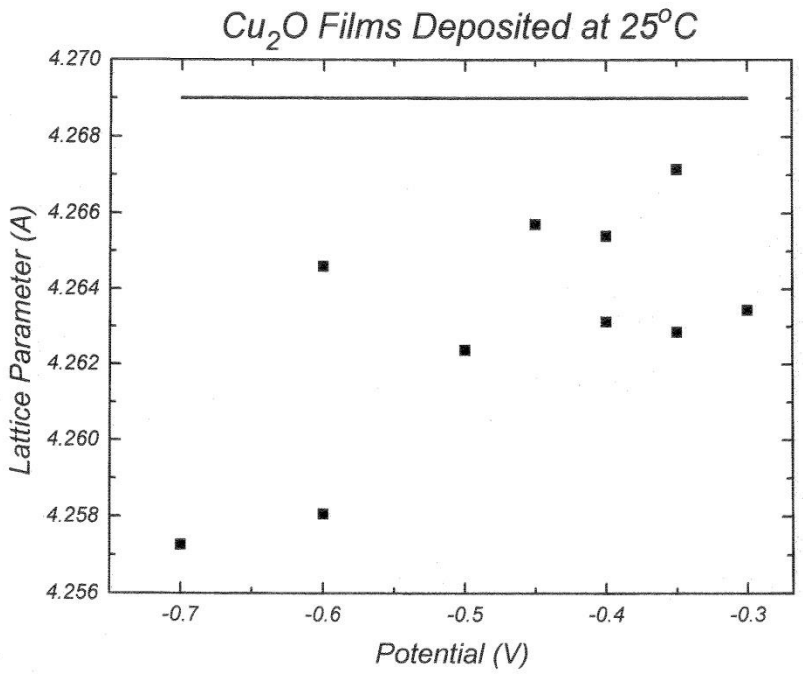
Quantitative Methods

Precise Lattice Parameter Measurements



Quantitative Methods

Precise Lattice Parameter Measurements

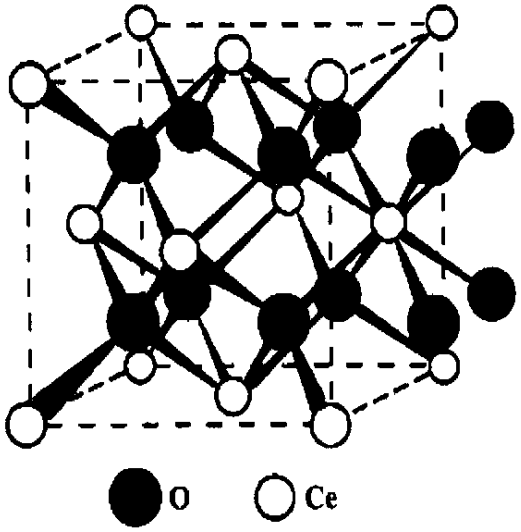
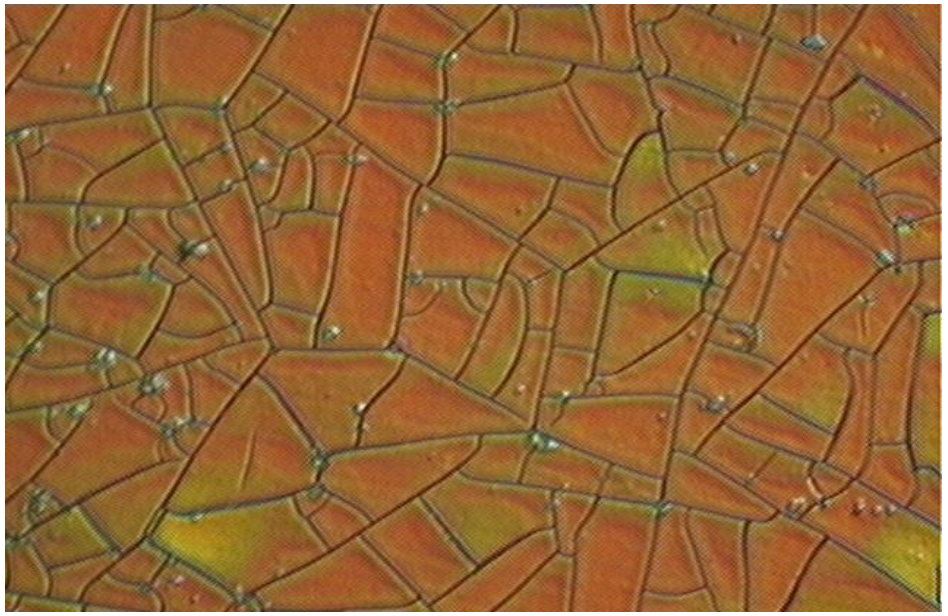


FIG. 1. The fcc cell of CeO_2 with the fluorite structure.



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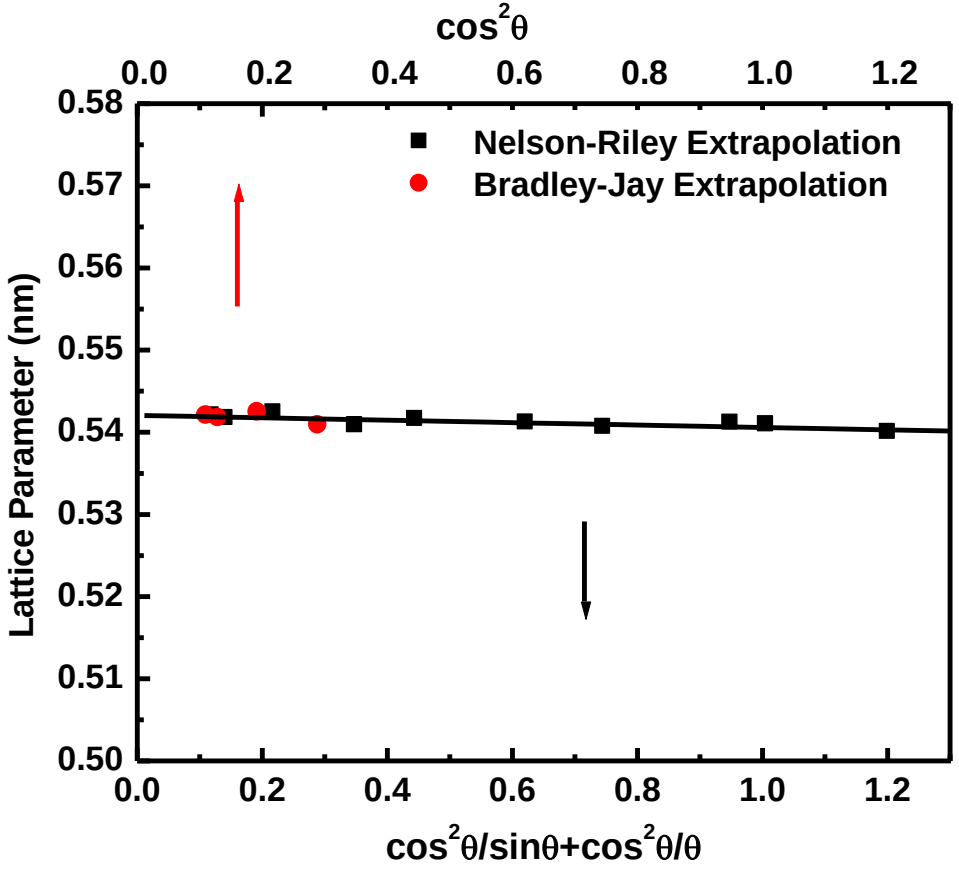
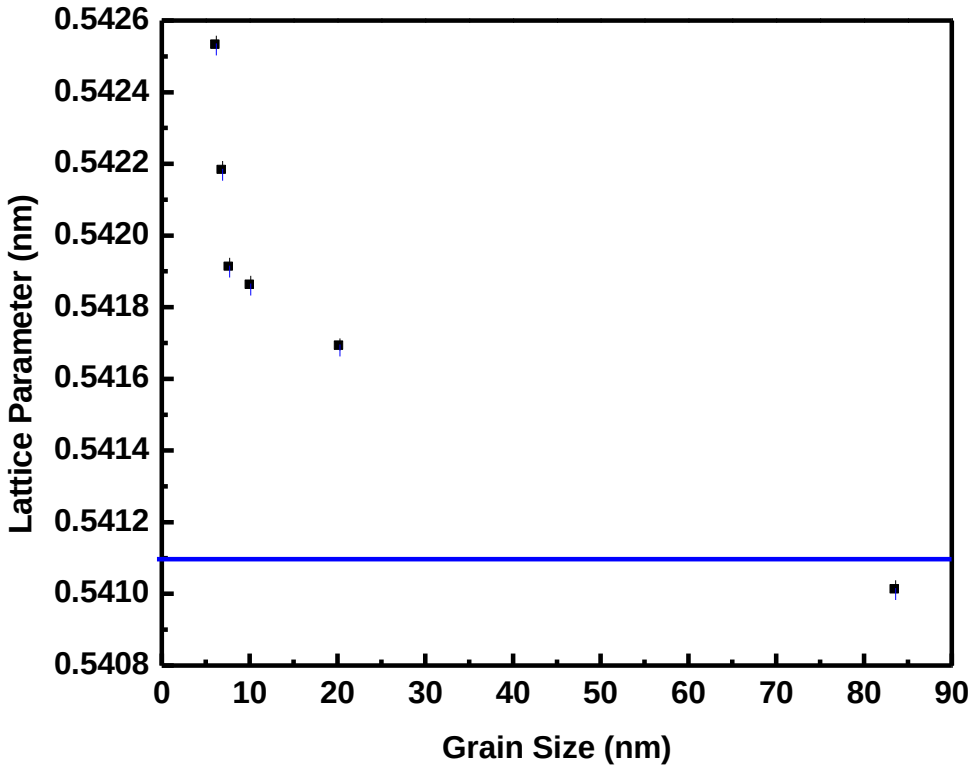
Quantitative Methods

Precise Lattice Parameter Measurements



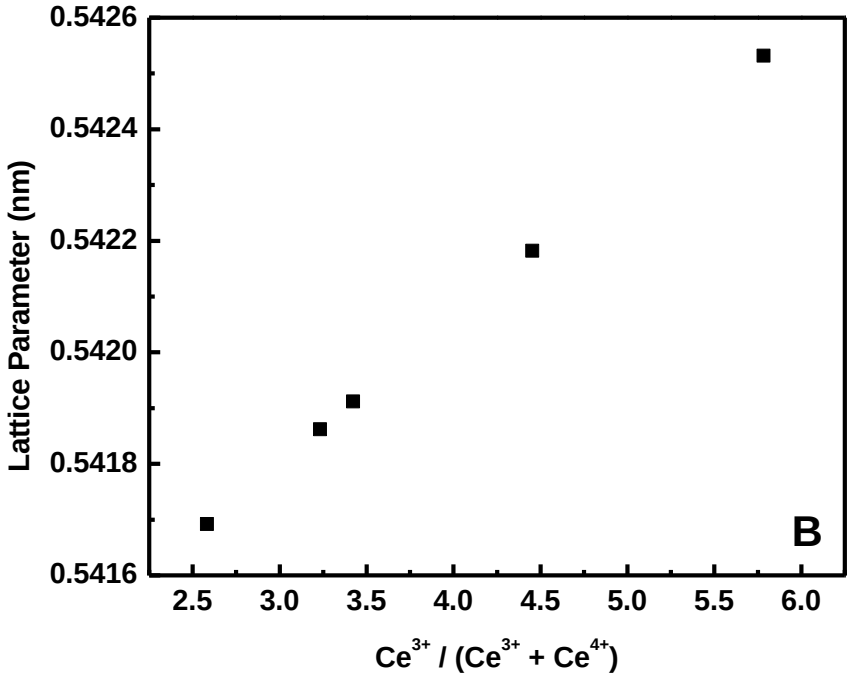
Quantitative Methods

Precise Lattice Parameter Measurements



Quantitative Methods

Precise Lattice Parameter Measurements



Lab 4 – Due today

Lab 5 – Due 11-30-21

Reading Assignment:

Read Chapter 8 from:

-X-ray Diffraction Procedures by Klug and Alexander

Read Chapter 13 from:

-Elements of X-ray Diffraction, 3rd edition, by Cullity and Stock