# Analytical Methods for Materials

## Laboratory Module #3

## Precise Lattice Parameter Determination

## Suggested Reading

- C. Suryanarayana and M.G. Norton, *X-ray Diffraction A Practical Approach*, (Plenum Press, New York, 1998), pages 153-166.
- B.D. Cullity and S.R. Stock, *Elements of X-ray Diffraction, 3rd Edition*, (Prentice-Hall, Upper Saddle River, NJ, 2001), Ch. 13, pages 363-383.
- Y. Waseda, E. Matsubara, and K. Shinoda, *X-ray Diffraction Crystallography*, (Springer, New York, NY, 2011), Ch. 4, pages 120-121, 145-152.

# Learning Objectives

- Upon completion of this module you will understand how to determine lattice parameters precisely for polycrystalline materials using X-ray diffraction methods.

# Introduction

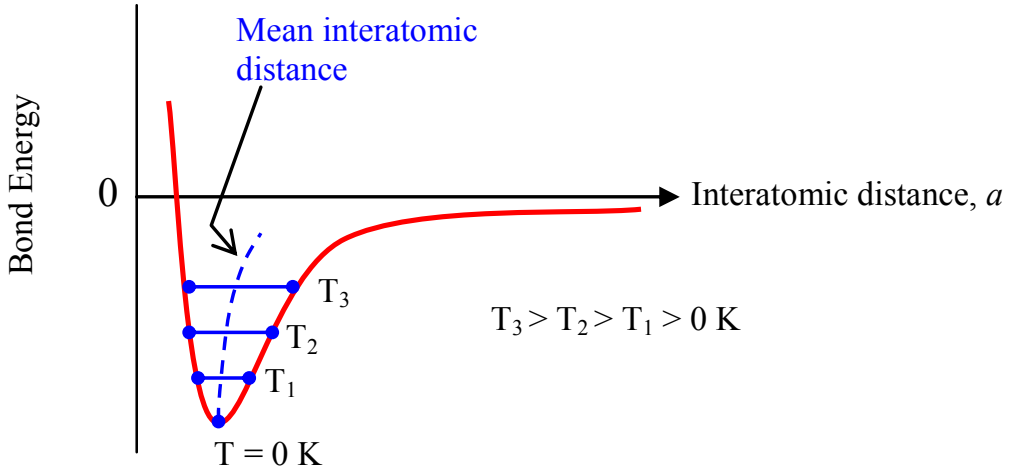
- Many scientific/engineering applications require precise knowledge of lattice parameters for a material.

- The majority of these applications involve solid solutions because the lattice parameter of a solid solution varies with concentration of the solute.

- Thus, one can use accurate and precise lattice parameter measurements to calculate composition.

# Introduction

- One can also determine thermal expansion coefficients ($\alpha \sim 10^{-6}\ °C^{-1}$) from accurate and precise lattice parameter measurements.




Recall Morse curves. Thermal vibrations cause slight changes in interatomic spacing and corresponding changes in *d*-spacing.

$$\alpha_{Al} = 23.6 \times 10^{-6}/°C$$

- At 25°C, ***a*** = 4.049 Å; at 50°C, ***a*** = 4.051 Å
- An accuracy of at least 0.06% is required to detect such a small change in ***a***

# Precision Lattice Parameter Determination

- Accuracy
  –
- Precision / reproducibility
  –
- Systematic errors
  – leads to inaccurate results
  – “precision without accuracy”

# Accuracy is critical!

To determine the lattice parameter to within

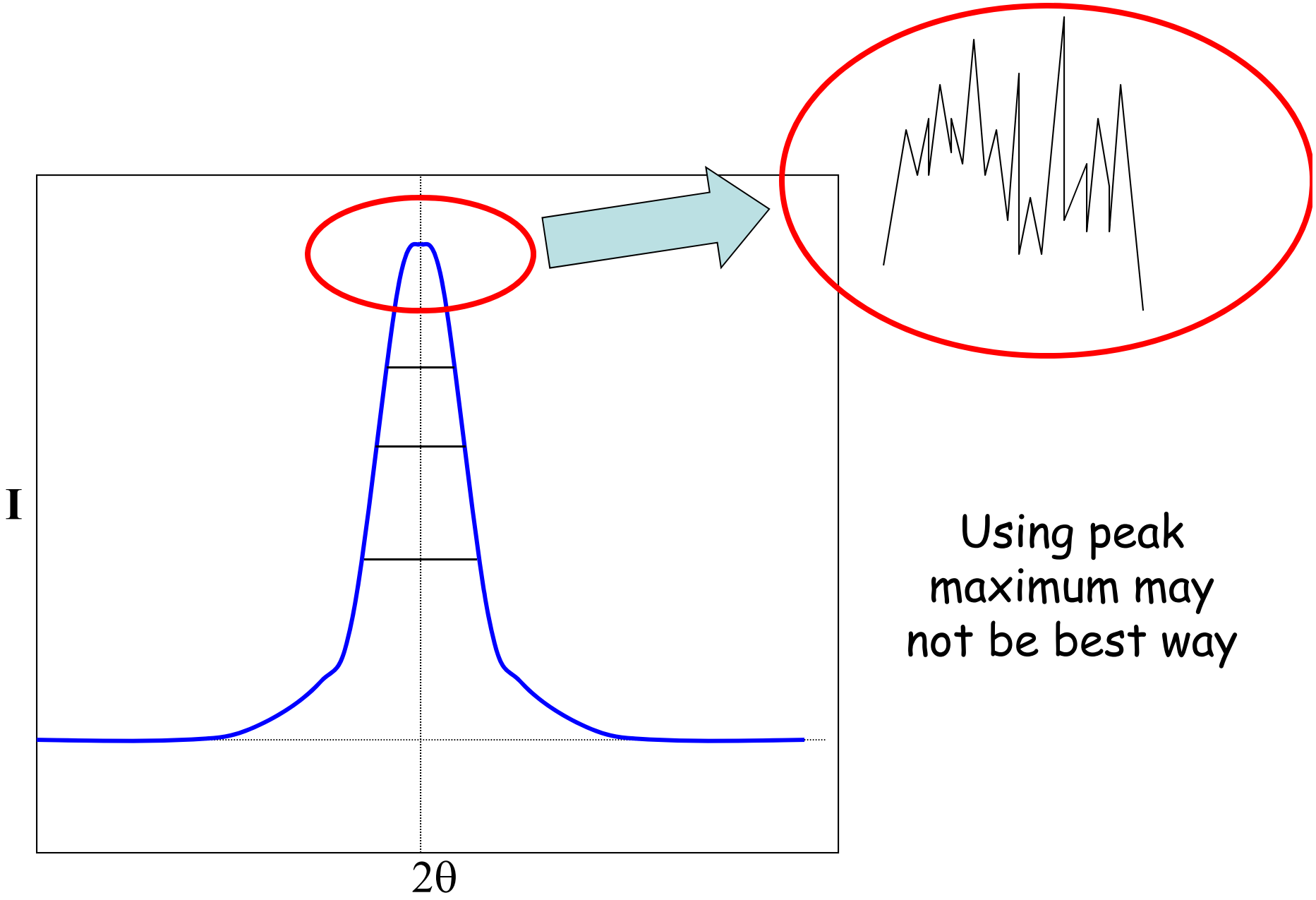
$1 \times 10^{-5}$ nm,

Must know the peak position to within

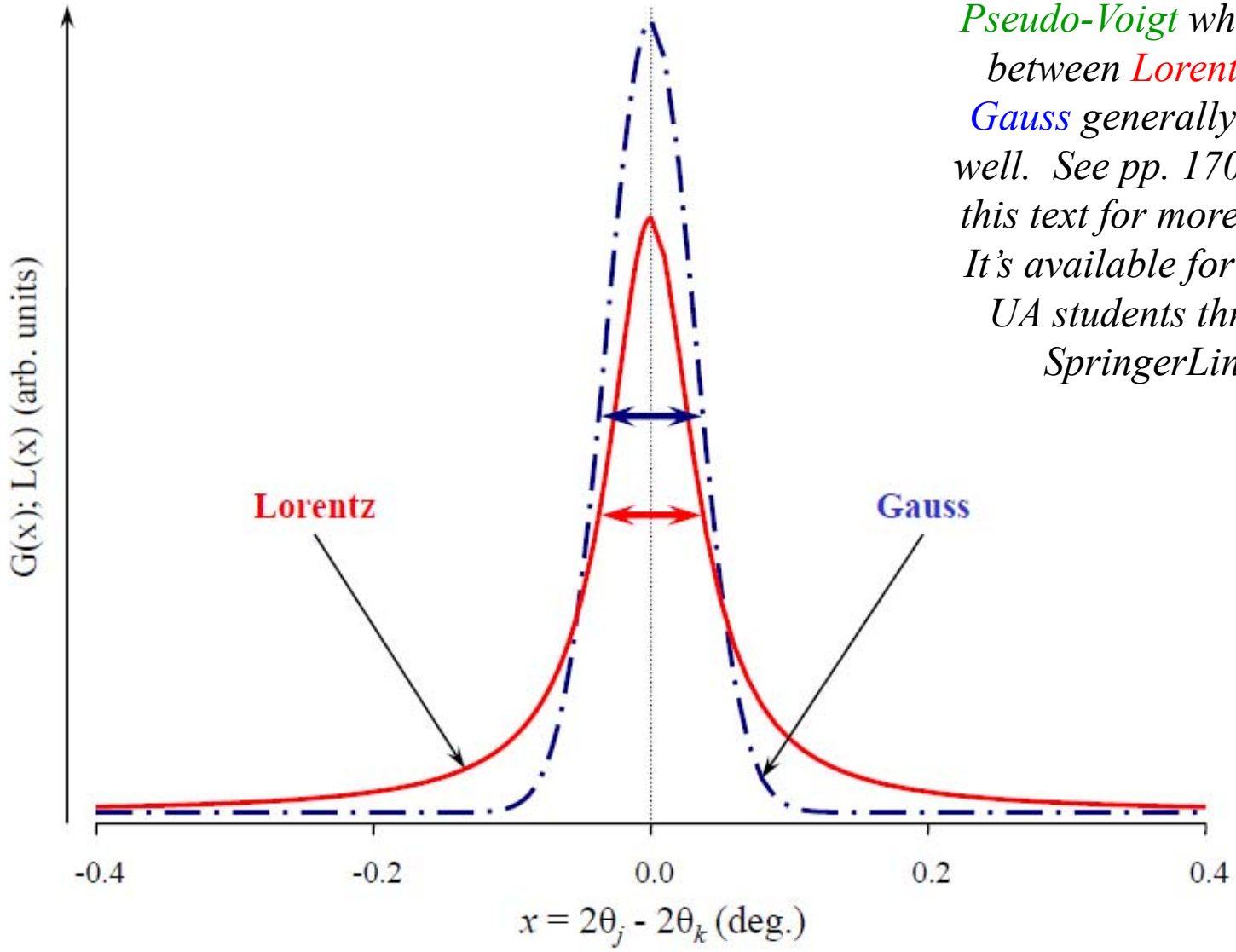
$0.02^{o}$ at $2\theta = 160^{o}$

# Peak Position

- Methods for determination
  - maximum intensity
  - center of gravity
  - projection
  - Gaussian
  - Lorentzian




Using peak maximum may not be best way




*Pseudo-Voigt which lies between Lorentz and Gauss generally works well. See pp. 170-178 in this text for more detail. It's available for free to UA students through SpringerLink.*

# Lattice parameter measurement is a very indirect process

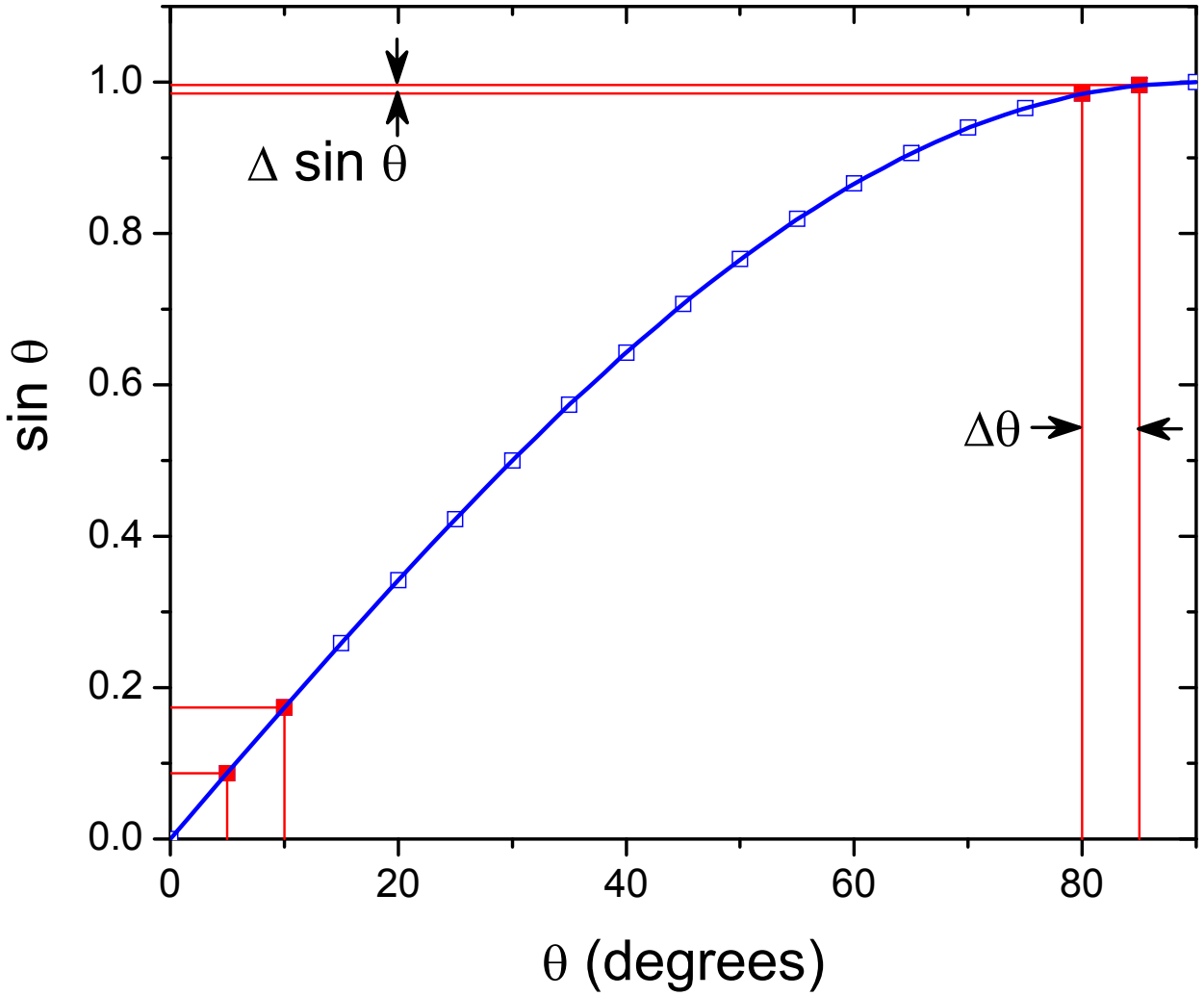
- For a cubic material:

$$a = d\sqrt{h^2 + k^2 + l^2}$$

- $d$-spacing is measured from Bragg's law.

$$\lambda = 2d\sin\theta$$

- Precision in measurement of $a$ or $d$ depends on precision in derivation of $\sin\theta$.




Error in the measurement of sin θ decreases as the value of θ increases.

- Differentiation of the Bragg equation with respect to $\theta$ provides us with the same result.

$$\lambda = 2d\sin\theta$$

- Take partial derivative of the Bragg equation:

$$0 = 2\Delta d\sin\theta + 2d\cos\Delta\theta$$

$$\frac{\Delta d}{d} = -\frac{\cos\theta}{\sin\theta}\Delta\theta = -\cot\theta\Delta\theta$$

- For a cubic system:

$$a = d\cdot\sqrt{h^2 + k^2 + l^2}$$

- Therefore:

$$\Delta a = \Delta d \cdot \sqrt{h^2 + k^2 + l^2}$$

$$\frac{\Delta a}{a} = \frac{\Delta d}{d} = -\cot\theta \Delta\theta$$

- The term $\Delta a/a$ (or $\Delta d/d$) is the fractional error in $a$ (or $d$) caused by a given error in $\theta$.

- The fractional error approaches zero as $\theta$ approaches 90°.

**The key to high precision in parameter measurements lies in the use of back reflected beams having 2θ values as near to 180° as possible!**

**It is impossible to reach 180°!**

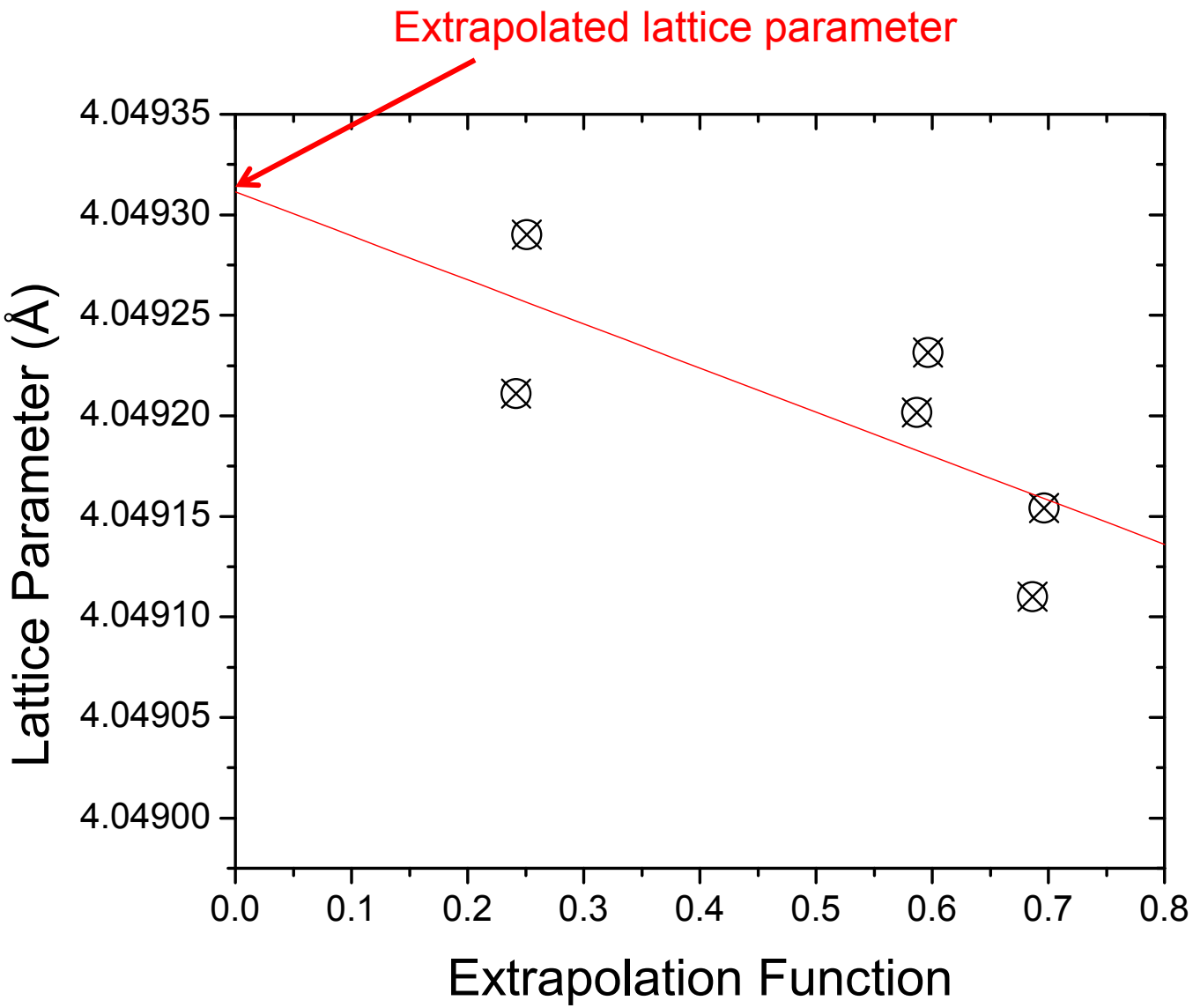
- Values of $a$ will approach the true value as we approach $2\theta = 180°$ (i.e., $\theta = 90°$).

- We can't measure $\boldsymbol{a}$ values at $2\theta = 180°$

- We must plot measured values and extrapolate to $2\theta = 180°$ versus some function of $\theta$.

Make sure that the functions of $\theta$ produce data that can be fit with a straight line.

This allows for extrapolation with higher confidence.


Extrapolated lattice parameter
Lattice Parameter (Å)
4.04935
4.04930
4.04925
4.04920
4.04915
4.04910
4.04905
4.04900
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Extrapolation Function

# Extrapolation Functions

- There are different types of extrapolation functions for different types of systematic error in ***a*** (or ***d***).

- Naturally there are different types of systematic errors associated with different x-ray instruments.

# Systematic errors in diffractometers

1. Misalignment of the instrument.

   The center of the diffracted beam must intersect the diffractometer axis at the 0° position of the detector slit.

2. Use of a flat specimen instead of a curved one to correspond to the diffractometer circle.

   Minimized by reducing horizontal divergence of the incident beam.

3. Absorption of the specimen.

   Select specimen thickness to get reflections with maximum intensity possible (little absorption).

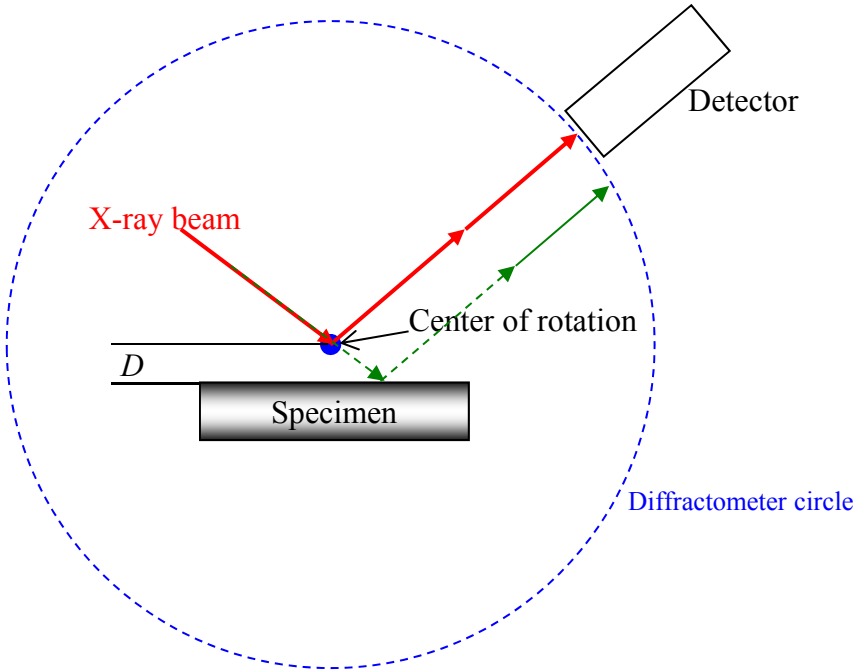
# Diffractometers

## 4. Displacement of specimen from the diffractometer axis must be minimized.

This is generally the largest source for error in $d$.

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

$D$ = specimen displacement parallel to the reflecting plane normal
$R$ = diffractometer radius.




## 5. Vertical divergence of the incident beam.

This error is minimized by reducing the vertical width of the receiving slit.

# Which Extrapolation Functions to Use

For error types (2) and (3):

$$\frac{\Delta d}{d} \propto \cos^2\theta \;\; \therefore \quad \text{SYSTEMATIC ERROR} \propto \cos^2\theta$$

For errors of type (4):

$$\frac{\Delta d}{d} \propto \frac{\cos^2\theta}{\sin\theta} \;\; \therefore \quad \text{SYSTEMATIC ERROR} \propto \frac{\cos^2\theta}{\sin\theta}$$

For errors of type (5):

$$\frac{\Delta d}{d} \propto \frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta} \;\; \therefore \quad \text{SYSTEMATIC ERROR} \propto \frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}$$

# General Information

At low $2\theta$, $\sin\theta \rightarrow 0$, which causes $\dfrac{\Delta d}{d} \Rightarrow \infty$

(Bad idea to use low$2\theta$)

What can we do?
USE HIGH ANGLES!

If we want to know $a_o$ to $\pm 0.0001$ Å, we need to know $2\theta$ to $\pm 0.02^o$ at $2\theta = 160^o$.

# How are precise lattice parameters measured?

- Carefully align the diffractometer;
- Make sure the specimen is flat and on axis;
- Use small slits (fixed in most instruments);
- Extrapolate peak positions to high 2θ using a method/function that minimizes the influence of systematic errors;
- Determine peak positions by maximum intensity or by proper curve fitting.

# Which extrapolation functions should be used

- Bradley-Jay function*
  - Only valid when θ>60°.

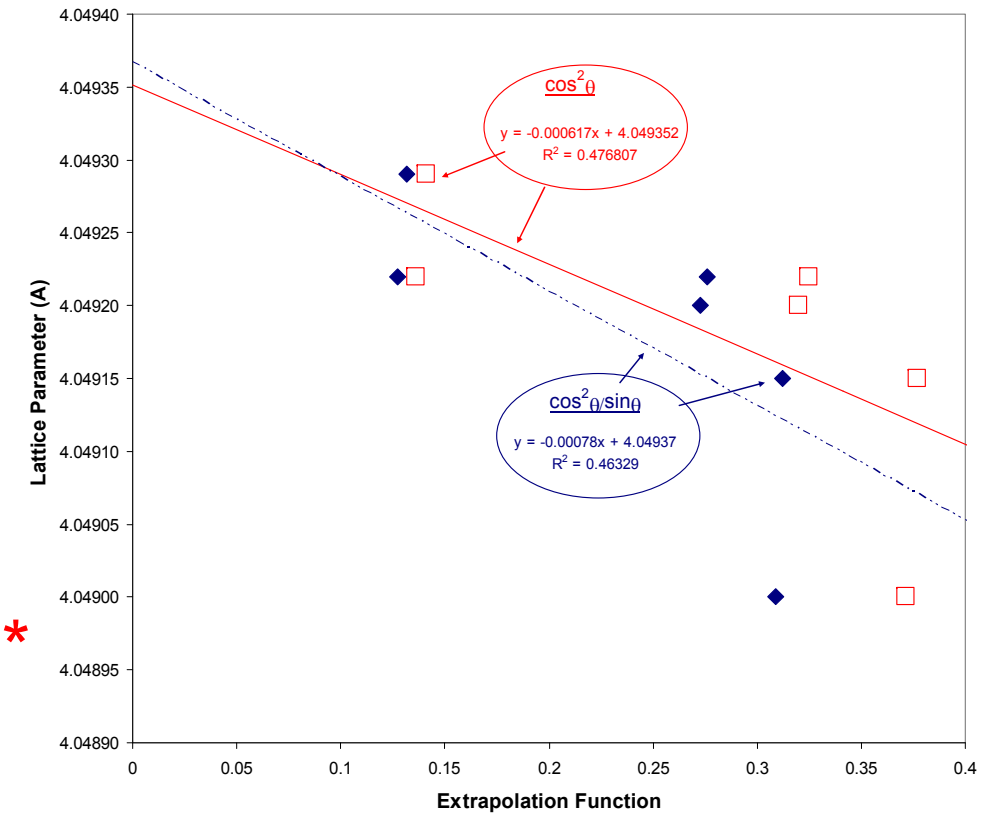
$$\cos^2\theta$$

- Nelson-Riley function**

$$\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}$$

- Specimen misalignment***

$$\frac{\cos^2\theta}{\sin\theta}$$




* Greater range of linearity

** More appropriate for Debye-Scherrer cameras

*** Largest source of error in diffractometer data

# Procedure

1. Carefully align instrument.
2. Adjust specimen surface to coincide with diffractometer axis
3. Extrapolate the calculated lattice parameter against $\cos^2\theta$ and $\frac{\cos^2\theta}{\sin\theta}$ out to $\theta = 90°$ and see which function yields the better straight-line fit.

This is the best way to decide which error is more significant

# Additional Notes

- Regardless, you need to have as many peaks as possible in the high-angle region of the diffraction pattern.
- If peaks can be resolved into $\alpha_1$ and $\alpha_2$ components, there will be more lattice parameter points for each *hkl* value.
- Increased resolution can be achieved by enlarging the $2\theta$ scale.
- Decreasing $\lambda$ increases the number of peaks.

# Cohen's Method

Analytical method that minimizes random errors.

For cubic systems, recall the Bragg equation: $\lambda = 2d\sin\theta$

Square the equation, rearrange it, and take logarithms of both sides:

$$\lambda^2 = 4d^2\sin^2\theta$$

*or*

$$\sin^2\theta = \lambda^2 / 4d^2$$

$$\log\left(\sin^2\theta\right) = \log\left(\frac{\lambda^2}{4}\right) - 2\log d$$

Differentiate

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

Assume that systematic errors are of the form:

$\frac{\Delta d}{d} = K\cos^2\theta$ and substitute it back into the equation above.

This gives,

$$\frac{\Delta \sin^2\theta}{\sin^2\theta} = -2K\cos^2\theta.$$

which can be re-written as:

$$\Delta \sin^2\theta = -2K\cos^2\theta\sin^2\theta = D\sin^2 2\theta.$$

where $D$ = constant.

- This equation only works when the $\cos^2\theta$ extrapolation function is valid.

Recall that 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 that we wish to find

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

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

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

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

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

$\sin^2\theta$ and $\alpha$ are known from indexing the diffraction pattern and from $\delta$.

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

We combine Cohen's method with the least square method to minimize observational errors.

Rewriting:

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

we find that

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

# IMPLEMENTING THE LEAST SQUARES METHOD:

$$\sum (e)^2 = \sum \left[ A\alpha + C\delta - \sin^2 \theta (observed) \right]^2$$

The best values of the coefficients $A$ and $C$ are those for which the sum of the squares of the random observational errors is a minimum.

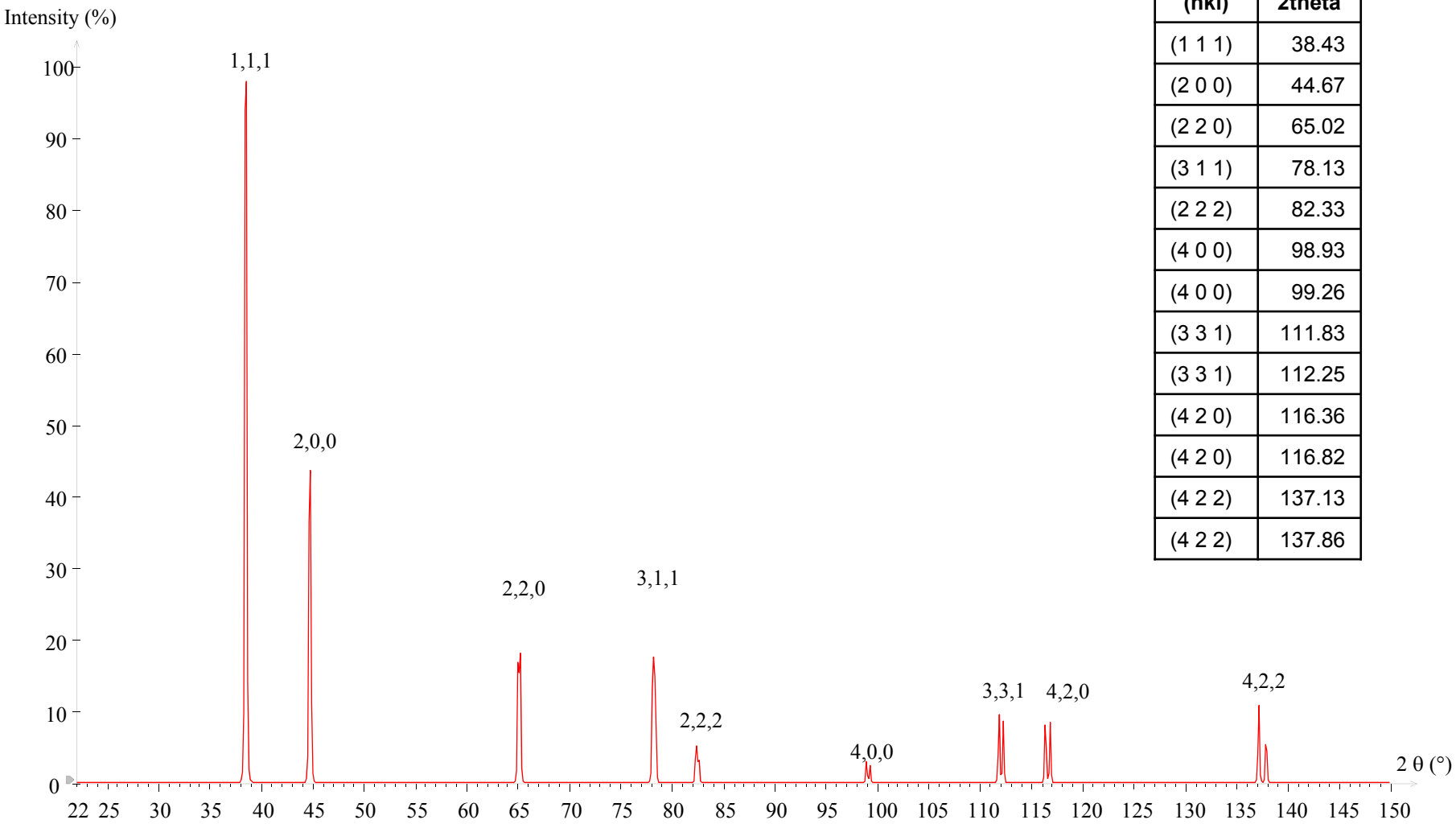
$$\boxed{\begin{aligned} \sum \alpha \sin^2 \theta &= A \sum \alpha^2 + C \sum \alpha\delta \\ \sum \delta \sin^2 \theta &= A \sum \alpha\delta + C \sum \delta^2 \end{aligned}}$$

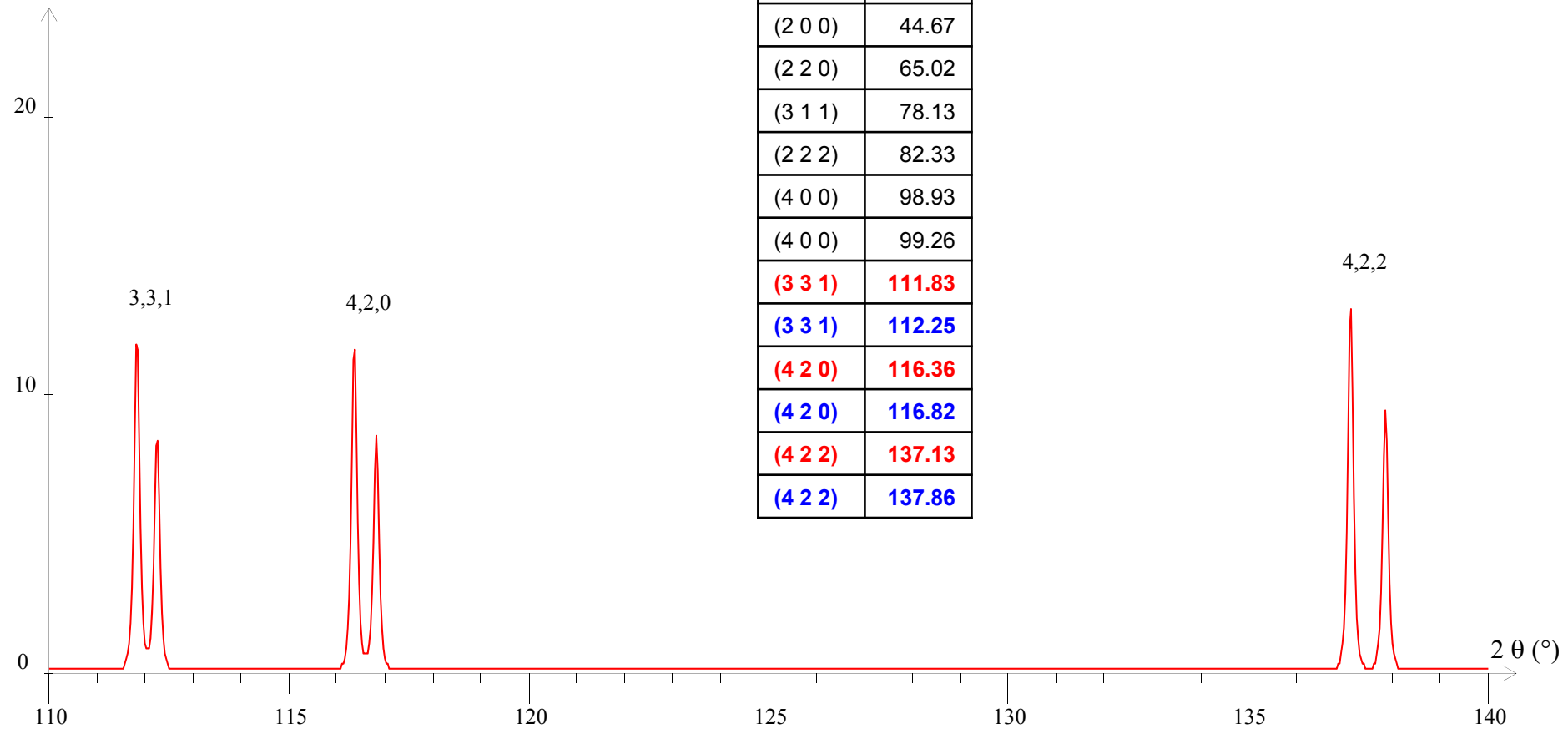
By solving these two equations, we determine $A$ from which we can determine $a_o$.

# 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 |






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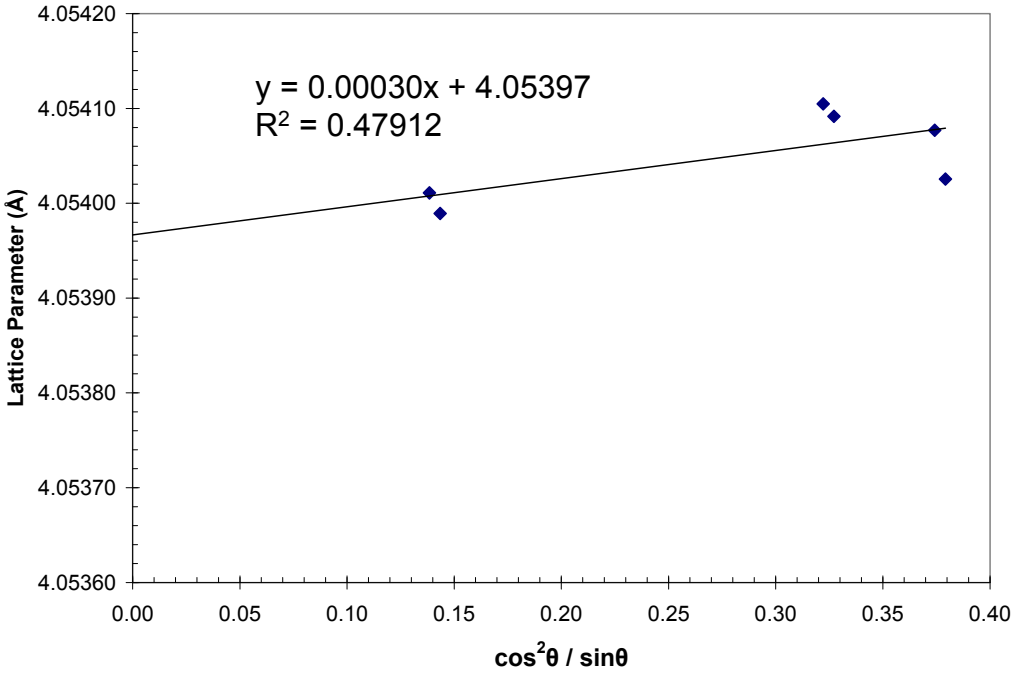
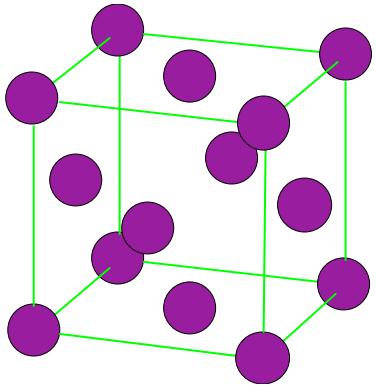
| (3 1 1) | 78.13 |
| (2 2 2) | 82.33 |
| (4 0 0) | 98.93 |
| (4 0 0) | 99.26 |
| **(3 3 1)** | **111.83** |
| **(3 3 1)** | **112.25** |
| **(4 2 0)** | **116.36** |
| **(4 2 0)** | **116.82** |
| **(4 2 2)** | **137.13** |
| **(4 2 2)** | **137.86** |

| $K\alpha_1$ | $K\alpha_2$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 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 |

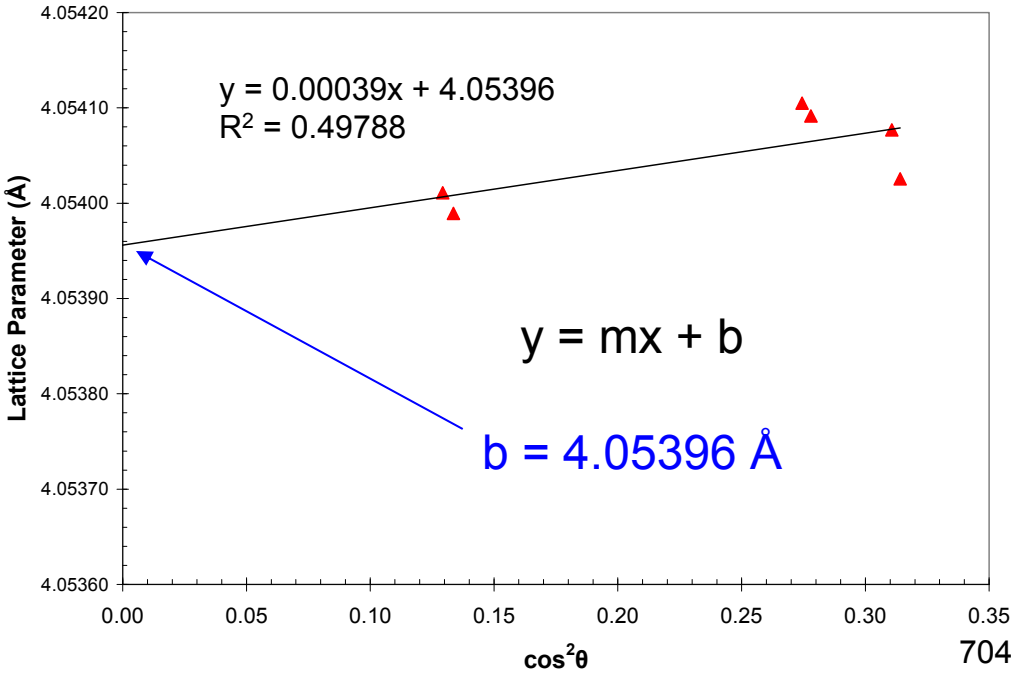
$$\sin^2\theta_{K\alpha 1(\mathrm{adj})} = \sin^2\theta_{K\alpha 2}\left(\frac{\lambda^2_{K\alpha 1}}{\lambda^2_{K\alpha 2}}\right)$$




From the plotted data, the second correlation function (i.e., $\cos^2\theta$) provides a better fit (i.e., $R^2$ is greater) suggesting a lattice parameter of 4.05396 Å.



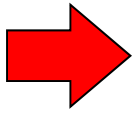
Actual lattice parameter was 4.054 Å.



| Peak | θ | $\sin^2\theta$ | adjusted $\sin^2(\theta)$ | *h* | *k* | *l* | α | δ | $\alpha^2$ | αδ | $\delta^2$ | $\alpha\sin^2(\theta)$ | $\delta\sin^2(\theta)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 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** |

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

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



$$2674A + 865.5C = 96.53435$$

$$865.5A + 317.21C = 31.24421$$

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

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

# Example – cont'd

| COHEN'S METHOD | | | | adjusted | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Peak | | $\theta$ | $\sin^2\theta$ | $\sin^2(\theta)$ | *h* | *k* | *l* | $\alpha$ | $\delta$ | $\alpha^2$ | $\alpha\delta$ | $\delta^2$ | $\alpha\sin^2(\theta)$ | $\delta\sin^2(\theta)$ |
| 1 | 111.83 | 55.92 | 0.6859 | 0.68593 | 3 | 3 | 1 | 19 | 8.6 | 361 | 163.7 | 74.26 | 13.03261 | 5.91080 |
| 2 | 112.25 | 56.13 | 0.6893 | 0.68591 | 3 | 3 | 1 | 19 | 8.6 | 361 | 162.8 | 73.38 | 13.03228 | 5.87567 |
| 3 | 116.36 | 58.18 | 0.7220 | 0.72200 | 4 | 2 | 0 | 20 | 8.0 | 400 | 160.6 | 64.46 | 14.44010 | 5.79665 |
| 4 | 116.82 | 58.41 | 0.7256 | 0.72200 | 4 | 2 | 0 | 20 | 8.0 | 400 | 159.3 | 63.43 | 14.44000 | 5.75021 |
| 5 | 137.13 | 68.57 | 0.8664 | 0.86645 | 4 | 2 | 2 | 24 | 4.6 | 576 | 111.1 | 21.42 | 20.79479 | 4.01044 |
| 6 | 137.86 | 68.93 | 0.8708 | 0.86644 | 4 | 2 | 2 | 24 | 4.5 | 576 | 108.0 | 20.26 | 20.79457 | 3.90042 |
| | | | | | | | | | $\Sigma$ | **2674** | **865.5** | **317.21** | **96.534353** | **31.24421** |

**Substituting values into equation:**

2674*A + 865.5*C=96.53435

865.5*A + 317.21C=31.24421

**Solve equations:**

C = -6.66E-05

A = 0.03612

$a = \lambda/(2*\mathrm{sqrt}(A))$

$a$ = 4.0530

# Final Comments

- Need to have as many peaks in the high-angle region of the diffraction pattern.
- This will yield many points and will allow you to draw the best straight line.
- Helps if $\alpha_1$ and $\alpha_2$ peaks can be resolved.