



# Analytical Methods for Materials

## Laboratory Module #2

### Crystal Structure Determination for Non-Cubic Crystals

#### Suggested Reading

1. **Pages 116 and 117 in Waseda.**
2. **Chapter 14 in Pecharsky and Zavalij (“Very useful!”).**
3. C. Suryanarayana and M.G. Norton, *X-ray Diffraction A Practical Approach*, (Plenum Press, New York, 1998), pages 97-152.
4. B.D. Cullity and S.R. Stock, *Elements of X-ray Diffraction, 3<sup>rd</sup> edition*, (Prentice Hall, Upper Saddle River, NJ, 2001), Ch. 10, pages 295-315.
5. H.P. Klug and L.E. Alexander, *X-ray Diffraction Procedures For Polycrystalline and Amorphous Materials, 2<sup>nd</sup> Edition*, (John Wiley & Sons, 1974) pp. 446-465.

# Methodology

- Indexing a scan/pattern
  - All powder patterns can be indexed by comparing observed *d-spacing's* with those computed using the appropriate formulas.
  - All powder patterns can be indexed by comparing **observed values of  $\sin^2\theta$**  and theoretical values of  $\sin^2\theta$ .
  - Methods are not necessarily successful due to the possibility of peak/line superposition.
  - These methods tend to be more successful with hexagonal, tetragonal crystals rather than more complex orthorhombic, monoclinic, or triclinic crystals.

# Methodology - cont'd

- Sometimes XRD patterns do not have all of the peaks that they should.
  - Is specimen textured?
  - What is the particle size?
  - Think! How you process or handle a material can make this happen.
- This can make it tricky to index patterns correctly.

# Recall/Remember

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

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

$$\sin^2 \theta = \frac{\lambda^2}{4d^2} = \frac{\lambda^2}{4} \frac{1}{d^2}$$

# Interplanar Spacing

CUBIC: 
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

HEXAGONAL: 
$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

TETRAGONAL: 
$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

RHOMBOHEDRAL: 
$$\frac{1}{d^2} = \frac{(h^2 + hk + k^2) \sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2 (1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}$$

ORTHORHOMBIC: 
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

MONOCLINIC: 
$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$

TRICLINIC\*: 
$$\frac{1}{d^2} = \frac{1}{V^2} (S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

\*See Appendix 1 in the text for a complete listing and definitions of symbols

For cubic crystals

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

For tetragonal crystals

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

# Problem with tetragonal symmetry

- Lower symmetry
- Results are dependent on  $c/a$  ratio (and  $b/a$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ ). There are no general tables.
- Nonequivalent indices
  - $001 \neq 100$ , etc...
- Similar problems with hexagonal crystals.

# Indexing Hexagonal Structures

- Plane spacing equation:

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

# Indexing Hexagonal Structures

- Combine with Bragg's law ( $\lambda = 2d\sin\theta$ ):

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} = \frac{4\sin^2 \theta}{\lambda^2}$$

# Indexing Hexagonal Structures

- Rewrite as:

$$\sin^2 \theta = \frac{\lambda^2}{4} \left[ \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \right]$$

OR

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} \left[ \frac{4}{3} (h^2 + hk + k^2) + \frac{l^2}{(c/a)^2} \right]$$

# Indexing Hexagonal Patterns

- We need to know the  $c/a$  ratio.
- We can determine this graphically as was done in the 'old days.'
- We can do this mathematically using the full power of modern calculators or computers.

Skip  
graphical  
method



# MATHEMATICAL METHOD

## Hexagonal

## Recall

$$\begin{aligned}\sin^2 \theta &= \frac{\lambda^2}{4a^2} \left[ \frac{4}{3} (h^2 + hk + k^2) + \frac{l^2}{(c/a)^2} \right] \\ &= \frac{\lambda^2}{4a^2} [A] + \frac{\lambda^2}{4a^2} [B]\end{aligned}$$

The parameters highlighted in red are constant for any given diffraction pattern.

We can now index a pattern by considering the parameters  $[A]$  and  $[B]$  individually.

$$\frac{4}{3}(h^2 + hk + k^2) \dots\dots\dots[A]$$

and

$$\frac{l^2}{(c/a)^2} \dots\dots\dots[B]$$

[A] depends only upon  $h$  and  $k$ .

We can calculate allowable values of term [A] by modulating  $h$  and  $k$  as is illustrated on the following viewgraph.

We can calculate the values of term  $[A]$  by modulating  $h$  and  $k$  as is illustrated below.\*

**STEP 1: Prepare list for term  $[A]$  and sort in increasing order**

Due to symmetry relationships,  $h$  and  $k$  are interchangeable

List		
h	k	$4/3(h^2+hk+k^2)$
0	0	0.000
1	0	1.333
2	0	5.333
3	0	12.000
0	1	1.333
1	1	4.000
2	1	9.333
3	1	17.333
0	2	5.333
1	2	9.333
2	2	16.000
3	2	25.333
0	3	12.000
1	3	17.333
2	3	25.333
3	3	36.000

Sorted List		
h	k	$4/3(h^2+hk+k^2)$
0	0	0.000
1	0	1.333
0	1	1.333
1	1	4.000
2	0	5.333
0	2	5.333
2	1	9.333
1	2	9.333
3	0	12.000
0	3	12.000
2	2	16.000
3	1	17.333
1	3	17.333
3	2	25.333
2	3	25.333
3	3	36.000

\* You could also have used your chart of quadratic forms of the Miller indices to generate the appropriate list.

Term  $[B]$  can be determined by substituting in the known  $c/a$  ratio as is illustrated below for zinc ( $c/a = 1.8562$ ).

**STEP 2: assume a  $c/a$  ratio and prepare a list for term  $[B]$**

let  $c/a = 1.8562$

$l$	$l^2/(c/a)^2$
0	0.0000
1	0.2902
2	1.1609
3	2.6121
4	4.6438
5	7.2559
6	10.4485

The next step is to add terms [A] and [B] together, to sort them in increasing order, and to eliminate the combinations of  $hkl$  that yield a structure factor of zero

**Step 3: add terms [A] and [B] together and sort in increasing order.**

Initial List			
$h$	$k$	$l$	[A] + [B]
0	0	1	0.290
0	0	2	1.161
0	0	3	2.612
0	0	4	4.644
0	0	5	7.256
0	0	6	10.448
1	0	0	1.333
1	0	1	1.624
1	0	2	2.494
1	0	3	3.945
1	0	4	5.977
1	0	5	8.589
1	0	6	11.782

0	1	0	1.333
0	1	1	1.624
0	1	2	2.494
0	1	3	3.945
0	1	4	5.977
0	1	5	8.589
0	1	6	11.782
1	1	0	4.0000
1	1	1	4.2902
1	1	2	5.1609
1	1	3	6.6121
1	1	4	8.6438
1	1	5	11.2559
1	1	6	14.4485

2	0	0	5.333
2	0	1	5.624
2	0	2	6.494
2	0	3	7.945
2	0	4	9.977
2	0	5	12.589
2	0	6	15.782
2	1	0	9.333
2	1	1	9.624
2	1	2	10.494
2	1	3	11.945
2	1	4	13.977
2	1	5	16.589
2	1	6	19.782

The next step is to add terms [A] and [B] together, to sort them in increasing order, and to eliminate the combinations of  $hkl$  that yield a structure factor of zero

**Step 3: add terms [A] and [B] together and sort in increasing order.**

Sorted List			
$h$	$k$	$l$	[A] + [B]
<del>0</del>	<del>0</del>	<del>1</del>	<del>0.290</del>
0	0	2	1.161
1	0	0	1.333
0	1	0	1.333
1	0	1	1.624
0	1	1	1.624
1	0	2	2.494
0	1	2	2.494
<del>0</del>	<del>0</del>	<del>3</del>	<del>2.612</del>
1	0	3	3.945
0	1	3	3.945
1	1	0	4.000
<del>1</del>	<del>1</del>	<del>1</del>	<del>4.290</del>

0	0	4	4.644
1	1	2	5.161
2	0	0	5.333
2	0	1	5.624
1	0	4	5.977
0	1	4	5.977
2	0	2	6.494
<del>1</del>	<del>1</del>	<del>3</del>	<del>6.612</del>
<del>0</del>	<del>0</del>	<del>5</del>	<del>7.256</del>
2	0	3	7.945
1	0	5	8.589
0	1	5	8.589
1	1	4	8.644
2	1	0	9.333

2	1	1	9.624
2	0	4	9.977
0	0	6	10.448
2	1	2	10.494
<del>1</del>	<del>1</del>	<del>5</del>	<del>11.256</del>
1	0	6	11.782
0	1	6	11.782
2	1	3	11.945
2	0	5	12.589
2	1	4	13.977
1	1	6	14.448
2	0	6	15.782
2	1	5	16.589
2	1	6	19.782

# RECALL!!!

For hexagonal crystals,

$$F_{hkl}^2 = \begin{cases} 0 & \text{when } h + 2k = 3n \text{ and } l = \text{odd} \\ f_i^2 & \text{when } h + 2k = 3n \pm 1 \text{ and } l = \text{even} \\ 3f_i^2 & \text{when } h + 2k = 3n \pm 1 \text{ and } l = \text{odd} \\ 4f_i^2 & \text{when } h + 2k = 3n \text{ and } l = \text{even} \end{cases}$$

**THUS**

**IF  $l$  is odd**, see whether or not  $h + 2k = 3n$ .

If  **$h + 2k = 3n$  and  $l$  is odd**, then there is **no XRD peak!**

Several values for the bracketed quantities are listed below. I have subtracted forbidden peaks and eliminated equivalent ones.

**Step 4: Eliminate equivalent planes/reflections**

Due to symmetry relationships,  $h$  and  $k$  are interchangeable because  $a = b$ .

Sorted List			
$h$	$k$	$l$	$[A] + [B]$
0	0	2	1.161
1	0	0	1.333
1	0	1	1.624
1	0	2	2.494
1	0	3	3.945
1	1	0	4.000
0	0	4	4.644
1	1	2	5.161
2	0	0	5.333
2	0	1	5.624
1	0	4	5.977
2	0	2	6.494
2	0	3	7.945

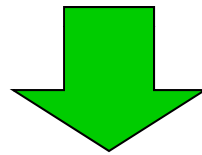
1	0	5	8.589
1	1	4	8.644
2	1	0	9.333
2	1	1	9.624
2	0	4	9.977
0	0	6	10.448
2	1	2	10.494
1	0	6	11.782
2	1	3	11.945
2	0	5	12.589
2	1	4	13.977
1	1	6	14.448
2	0	6	15.782
2	1	5	16.589

Now we can assign specific  $hkl$  values for each of the peaks in the hexagonal XRD pattern. The sequence of peaks on the pattern will be the same as indicated in the table.

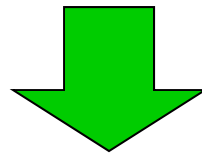
# Lattice Parameters - 1

We can calculate  $a$  by substituting  $l = 0$  into:

$$\sin^2 \theta = \left( \frac{\lambda^2}{4a^2} \right) \left[ \frac{4}{3} (h^2 + hk + k^2) + \frac{l^2}{(c/a)^2} \right]$$



$$\sin^2 \theta = \left( \frac{\lambda^2}{4a^2} \right) \left[ \frac{4}{3} (h^2 + hk + k^2) + 0 \right]$$



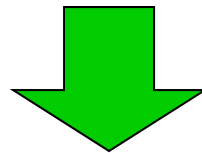
$$a = \frac{\lambda}{\sqrt{3} \sin \theta} \sqrt{h^2 + hk + k^2}$$

This corresponds to peaks with  $hk0$  type indices (e.g., 110, 210, ...)

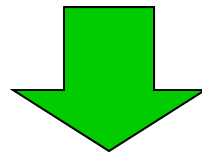
## Lattice Parameters - 2

We can calculate  $c$  by substituting  $h = k = 0$  into:

$$\sin^2 \theta = \left( \frac{\lambda^2}{4a^2} \right) \left[ \frac{4}{3} (h^2 + hk + k^2) + \frac{l^2}{(c/a)^2} \right]$$



$$\sin^2 \theta = \left( \frac{\lambda^2}{4a^2} \right) \left[ \frac{4}{3} (0) + \frac{l^2}{(c/a)^2} \right]$$



$$c = \frac{\lambda}{2 \sin \theta} l$$

This corresponds  
to peaks with  $00l$   
type indices  
(e.g., 002, 004, ...)

2q	sin <sup>2</sup> θ	h	k	l	$\frac{4}{3}(h^2+hk+k^2)+l^2/(c/a)^2$	a	c
36.33	0.097	0	0	2	1.161		4.942 ← 00l
39.07	0.112	1	0	0	1.333	2.660 ← hk0	
43.29	0.136	1	0	1	1.624		
54.35	0.209	1	0	2	2.494		
70.09	0.330	1	0	3	3.945		
70.65	0.334	1	1	0	4.000		
77.05	0.388	0	0	4	4.644		4.947 ← 00l
82.11	0.431	1	1	2	5.161		
83.77	0.446	2	0	0	5.333	2.664 ← hk0	
86.57	0.470	2	0	1	5.624		
89.91	0.499	1	0	4	5.977		
94.91	0.543	2	0	2	6.494		
109.15	0.664	2	0	3	7.945		
115.75	0.717	1	0	5	8.589		
116.33	0.722	1	1	4	8.644		
average						2.662	4.944
standard deviation						0.003	0.004

c/a ratio = 1.857

This order matches the ICDD card for Zn (#00-004-0831).  
 Now you can calculate *a* and *c* from *hk0* and *00l* type peaks, respectively.

## NOTE:

You don't need to know the  $c/a$  ratio in order to index a pattern.

You can assume an initial value for  $c/a$ , calculate lattice parameters and see if they yield the assumed  $c/a$  ratio.

If not

iterate the assumed  $c/a$  ratio until your calculated  $c/a$  ratio matches your guess.

## Worked Example #2 - HCP powder pattern

**STEP 1:** Solve  $(4/3) \times (h^2 + hk + k^2)$  for allowed reflections

I will tell you  
what this  
powder is in  
a few  
viewgraphs

		k			
		0	1	2	3
h	0	0.000	1.333	5.333	12.000
	1	1.333	4.000	9.333	17.333
	2	5.333	9.333	16.000	25.333
	3	12.000	17.333	25.333	36.000

**STEP 2:** Solve  $l^2/(c/a)^2$  for allowed reflections

### ITERATION #1

UNKNOWN (c/a)  
Guess (c/a) = 1.4000

l	l <sup>2</sup>	l <sup>2</sup> /(c/a) <sup>2</sup>
0	0	0.000
1	1	0.510
2	4	2.041
3	9	4.592
4	16	8.163
5	25	12.755
6	36	18.367

MATHEMATICAL METHOD FOR NON-CUBIC MATLS.

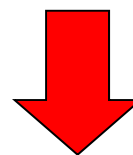
**STEP 3:** Add results from steps 1 and 2 together. Establishes order of allowed reflections

<i>hkl</i>	Pt.1+Pt.2
002	2.041
100	1.333
101	1.844
102	3.374
103	5.925
110	4.000
004	8.163
112	6.041
200	5.333
201	5.844
104	9.497
202	7.374
203	9.925
105	14.088
114	12.163
210	9.333
211	9.844
204	13.497
006	18.367
212	11.374
106	19.701
213	13.925
300	12.000
205	18.088
302	14.041

**ITERATION #1**

UNKNOWN (c/a)  
Guess (c/a) = 1.4000

**STEP 4:** Re-arrange results from step 3 in increasing order. Establishes the order of reflections in the XRD pattern



**Use this order to index the collected pattern**

<i>hkl</i>	Pt.1+Pt.2
100	1.333
101	1.844
002	2.041
102	3.374
110	4.000
200	5.333
201	5.844
103	5.925
112	6.041
202	7.374
004	8.163
210	9.333
104	9.497
211	9.844
203	9.925
212	11.374
300	12.000
114	12.163
204	13.497
213	13.925
302	14.041
105	14.088
205	18.088
006	18.367
106	19.701

MATHEMATICAL METHOD FOR NON-CUBIC MATLS.

$\lambda$									
1.5406	Peak	$l/lo$	$\sin^2\theta$	$d$ (nm)	$hkl$	$a$	$c$	$h^2+hk+k^2$	$P$
	35.275	21	0.091805	2.5423	100	2.936		1	
	38.545	18	0.108941	2.3338	101				
	40.320	100	0.118779	2.2351	002		4.470		4
	53.115	16	0.199895	1.7229	102				
	63.095	11	0.273744	1.4723	110	2.945		3	
	70.765	9	0.335278	1.3303	200	3.072		4	
	74.250	10	0.36428	1.2763	201				
	76.365	8	0.382132	1.2461	103				
	77.500	14	0.39178	1.2307	112				
	82.360	2	0.433526	1.1699	202				
	86.940	2	0.473309	1.1197	004		4.479		16
	92.900	10	0.525296	1.0628	210	3.247		7	
	<b>AVG</b>					<b>2.943</b>	<b>4.674</b>	<b><math>c/a = 1.588</math></b>	
						<b>0.125</b>	<b>0.004</b>		

**ITERATION #1**

UNKNOWN ( $c/a$ )  
 Guess ( $c/a$ ) = 1.4000

**STEP 5:** Insert  $hkl$  according to order established in step 4.

**STEP 6:** Use  $hk0$  reflections to calculate  $a$ .

**STEP 7:** Use  $00l$  reflections to calculate  $c$ .

**The calculated value is larger than guess. NEED TO REVISE GUESS.**

## Worked Example #2 - HCP powder pattern

**STEP 1:** Solve  $(4/3) \times (h^2 + hk + k^2)$  for allowed reflections

		k			
		0	1	2	3
h	0	0.000	1.333	5.333	12.000
	1	1.333	4.000	9.333	17.333
	2	5.333	9.333	16.000	25.333
	3	12.000	17.333	25.333	36.000

**STEP 2:** Solve  $l^2 / (c/a)^2$  for allowed reflections

### ITERATION #2

UNKNOWN  $(c/a)$   
 Guess  $(c/a) = 1.5000$

$l$	$l^2$	$l^2 / (c/a)^2$
0	0	0.000
1	1	0.444
2	4	1.778
3	9	4.000
4	16	7.111
5	25	11.111
6	36	16.000

MATHEMATICAL METHOD FOR NON-CUBIC MATLS.

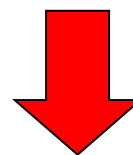
**STEP 3:** Add results from steps 1 and 2 together. Establishes order of allowed reflections

<i>hkl</i>	Pt.1+Pt.2
002	1.778
100	1.333
101	1.778
102	3.111
103	5.333
110	4.000
004	7.111
112	5.778
200	5.333
201	5.778
104	8.444
202	7.111
203	9.333
105	12.444
114	11.111
210	9.333
211	9.778
204	12.444
006	16.000
212	11.111
106	17.333
213	13.333
300	12.000
205	16.444
302	13.778

**ITERATION #2**

UNKNOWN (*c/a*)  
Guess (*c/a*) = 1.5000

**STEP 4:** Re-arrange results from step 3 in increasing order. Establishes the order of reflections in the XRD pattern



**Use this order to index the collected pattern**

<i>hkl</i>	Pt.1+Pt.2
100	1.333
002	1.778
101	1.778
102	3.111
110	4.000
103	5.333
200	5.333
112	5.778
201	5.778
004	7.111
202	7.111
104	8.444
203	9.333
210	9.333
211	9.778
114	11.111
212	11.111
300	12.000
204	12.444
105	12.444
213	13.333
302	13.778
006	16.000
205	16.444
106	17.333

MATHEMATICAL METHOD FOR NON-CUBIC MATLS.

$\lambda$									
1.5406	Peak	Intensity	$\sin^2\theta$	$d$ (nm)	$hkl$	$a$	$c$	$h^2+hk+k^2$	$P$
	35.275	21	0.091805	2.5423	100	2.936		1	
	38.545	18	0.108941	2.3338	002		4.668		4
	40.320	100	0.118779	2.2351	101				
	53.115	16	0.199895	1.7229	102				
	63.095	11	0.273744	1.4723	110	2.945		3	
	70.765	9	0.335278	1.3303	103				
	74.250	10	0.36428	1.2763	200	2.947		4	
	76.365	8	0.382132	1.2461	112				
	77.500	14	0.39178	1.2307	201				
	82.360	2	0.433526	1.1699	004		4.680		16
	86.940	2	0.473309	1.1197	202				
	92.900	10	0.525296	1.0628	104				
					<b>AVG</b>	<b>2.943</b>	<b>4.674</b>	<b><math>c/a = 1.588</math></b>	
						<b>0.002</b>	<b>0.006</b>		

**ITERATION #2**

UNKNOWN ( $c/a$ )  
 Guess ( $c/a$ ) = 1.5000

**STEP 5:** Insert  $hkl$  according to order established in step 4.

**STEP 6:** Use  $hk0$  reflections to calculate  $a$ .

**STEP 7:** Use  $00l$  reflections to calculate  $c$ .

**The calculated value is still larger than guess. NEED TO REVISE GUESS.**

## Worked Example #2 - HCP powder pattern

**STEP 1:** Solve  $(4/3) \times (h^2 + hk + k^2)$  for allowed reflections

		<i>k</i>			
		0	1	2	3
<i>h</i>	0	0.000	1.333	5.333	12.000
	1	1.333	4.000	9.333	17.333
	2	5.333	9.333	16.000	25.333
	3	12.000	17.333	25.333	36.000

**STEP 2:** Solve  $l^2/(c/a)^2$  for allowed reflections

### ITERATION #3

UNKNOWN (c/a)  
Guess (c/a) = 1.6000

<i>l</i>	<i>l</i> <sup>2</sup>	<i>l</i> <sup>2</sup> /(c/a) <sup>2</sup>
0	0	0.000
1	1	0.391
2	4	1.563
3	9	3.516
4	16	6.250
5	25	9.766
6	36	14.063

MATHEMATICAL METHOD FOR NON-CUBIC MATLS.

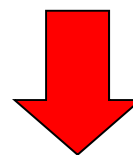
**STEP 3:** Add results from steps 1 and 2 together. Establishes order of allowed reflections

<i>hkl</i>	Pt.1+Pt.2
002	1.563
100	1.333
101	1.724
102	2.896
103	4.849
110	4.000
004	6.250
112	5.563
200	5.333
201	5.724
104	7.583
202	6.896
203	8.849
105	11.099
114	10.250
210	9.333
211	9.724
204	11.583
006	14.063
212	10.896
106	15.396
213	12.849
300	12.000
205	15.099
302	13.563

**ITERATION #3**

UNKNOWN (*c/a*)  
Guess (*c/a*) = 1.6000

**STEP 4:** Re-arrange results from step 3 in increasing order. Establishes the order of reflections in the XRD pattern



**Use this order to index the collected pattern**

<i>hkl</i>	Pt.1+Pt.2
100	1.333
002	1.563
101	1.724
102	2.896
110	4.000
103	4.849
200	5.333
112	5.563
201	5.724
004	6.250
202	6.896
104	7.583
203	8.849
210	9.333
211	9.724
114	10.250
212	10.896
105	11.099
204	11.583
300	12.000
213	12.849
302	13.563
006	14.063
205	15.099
106	15.396

MATHEMATICAL METHOD FOR NON-CUBIC MATLS.

$\lambda$									
1.5406	Peak	$l/l_0$	$\sin^2\theta$	$d$ (nm)	$hkl$	$a$	$c$	$h^2+hk+k^2$	$P$
	35.275	21	0.091805	2.5423	100	2.936		1	
	38.545	18	0.108941	2.3338	002		4.668		4
	40.320	100	0.118779	2.2351	101				
	53.115	16	0.199895	1.7229	102				
	63.095	11	0.273744	1.4723	110	2.945		3	
	70.765	9	0.335278	1.3303	103				
	74.250	10	0.36428	1.2763	200	2.947		4	
	76.365	8	0.382132	1.2461	112				
	77.500	14	0.39178	1.2307	201				
	82.360	2	0.433526	1.1699	004		4.680		16
	86.940	2	0.473309	1.1197	202				
	92.900	10	0.525296	1.0628	104				
					AVG	2.943	4.674	c/a = 1.588	
						0.002	0.006		

**ITERATION #3**

UNKNOWN (c/a)  
Guess (c/a) = 1.6000

**STEP 5:** Insert  $hkl$  according to order established in step 4.

**STEP 6:** Use  $hk0$  reflections to calculate  $a$ .

**STEP 7:** Use  $00l$  reflections to calculate  $c$ .

Calculated value is now smaller than guess.  
**REVISE GUESS DOWN.**

## Worked Example #2 - HCP powder pattern

**STEP 1:** Solve  $(4/3) \times (h^2 + hk + k^2)$  for allowed reflections

		k			
		0	1	2	3
h	0	0.000	1.333	5.333	12.000
	1	1.333	4.000	9.333	17.333
	2	5.333	9.333	16.000	25.333
	3	12.000	17.333	25.333	36.000

**STEP 2:** Solve  $l^2/(c/a)^2$  for allowed reflections

### ITERATION #4

UNKNOWN (c/a)

Guess between 1.5 and 1.6

My guess (c/a) = 1.5871

*This powder is Ti of unknown purity.*

*I've intentionally selected the ICDD c/a values for Ti.*

l	l <sup>2</sup>	l <sup>2</sup> /(c/a) <sup>2</sup>
0	0	0.000
1	1	0.397
2	4	1.588
3	9	3.573
4	16	6.352
5	25	9.926
6	36	14.292

MATHEMATICAL METHOD FOR NON-CUBIC MATLS.

**STEP 3:** Add results from steps 1 and 2 together. Establishes order of allowed reflections

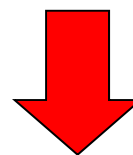
<i>hkl</i>	Pt.1+Pt.2
002	1.588
100	1.333
101	1.730
102	2.921
103	4.906
110	4.000
004	6.352
112	5.588
200	5.333
201	5.730
104	7.685
202	6.921
203	8.906
105	11.258
114	10.352
210	9.333
211	9.730
204	11.685
006	14.292
212	10.921
106	15.625
213	12.906
300	12.000
205	15.258
302	13.588

**ITERATION #4**

UNKNOWN (*c/a*)  
Guess (*c/a*) = 1.5871

*This is the c/a ratio from the ICDD card*

**STEP 4:** Re-arrange results from step 3 in increasing order. Establishes the order of reflections in the XRD pattern



**Use this order to index the collected pattern**

<i>hkl</i>	Pt.1+Pt.2
100	1.333
002	1.588
101	1.730
102	2.921
110	4.000
103	4.906
200	5.333
112	5.588
201	5.730
004	6.352
202	6.921
104	7.685
203	8.906
210	9.333
211	9.730
114	10.352
212	10.921
105	11.258
204	11.685
300	12.000
213	12.906
302	13.588
006	14.292
205	15.258
106	15.625

MATHEMATICAL METHOD FOR NON-CUBIC MATLS.

$\lambda$									
1.5406	Peak	$l/lo$	$\sin^2\theta$	$d$ (nm)	$hkl$	$a$	$c$	$h^2+hk+k^2$	$P$
	35.275	21	0.091805	2.5423	100	2.936		1	
	38.545	18	0.108941	2.3338	002		4.668		4
	40.320	100	0.118779	2.2351	101				
	53.115	16	0.199895	1.7229	102				
	63.095	11	0.273744	1.4723	110	2.945		3	
	70.765	9	0.335278	1.3303	103				
	74.250	10	0.36428	1.2763	200	2.947		4	
	76.365	8	0.382132	1.2461	112				
	77.500	14	0.39178	1.2307	201				
	82.360	2	0.433526	1.1699	004		4.680		16
	86.940	2	0.473309	1.1197	202				
	92.900	10	0.525296	1.0628	104				
<b>ITERATION #4</b>						2.943	4.674	c/a = 1.588	

UNKNOWN (c/a)  
Guess (c/a) = 1.5871

**STEP 5:** Insert  $hkl$  according to order established in step 4.

**STEP 6:** Use  $hk0$  reflections to calculate  $a$ .

**STEP 7:** Use  $00l$  reflections to calculate  $c$ .

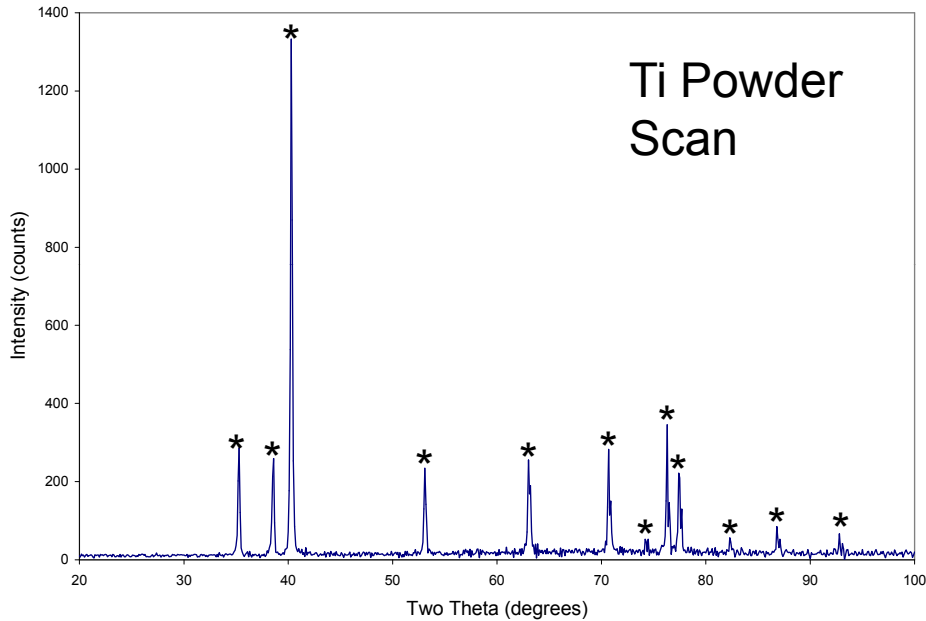
**PRETTY GOOD!**  
The ICDD value  
is 1.5871 nm

We could refine this further by calculating  $2\theta$  values for each reflection using our guessed  $c/a$  ratios and comparing them to the observed ones. This means assuming values for  $c$  and  $a$ .

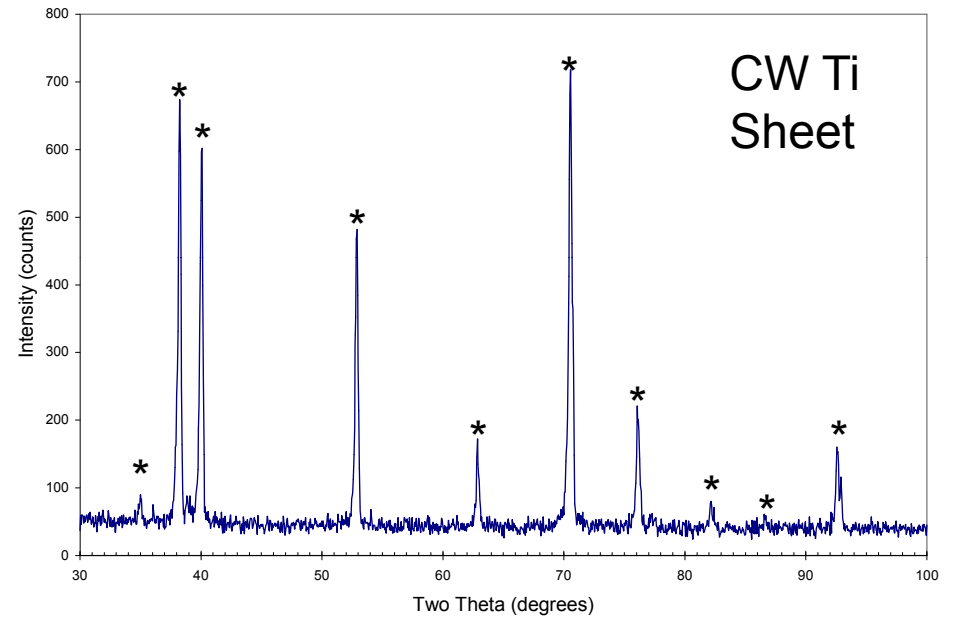
If the difference is a small fraction of the FWHM for the observed reflections then we can consider our result to be accurate.

# What if material is missing xrd peaks?

Makes misinterpretation of peaks possible.



12 XRD peaks



10 XRD peaks

Same material so why are peaks be missing and why are peak intensities different?



# ANALYTICAL METHOD Hexagonal

Works for all patterns whether or not  
peaks are missing.

# Recall

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} \left[ \frac{4}{3} (h^2 + hk + k^2) + \frac{l^2}{(c/a)^2} \right]$$

$a$  and  $c/a$  are constant for any pattern.

Thus, we can write

$$\sin^2 \theta = A (h^2 + hk + k^2) + Cl^2$$

$$A = \frac{\lambda^2}{3a^2}$$

$$C = \frac{\lambda^2}{4c^2}$$

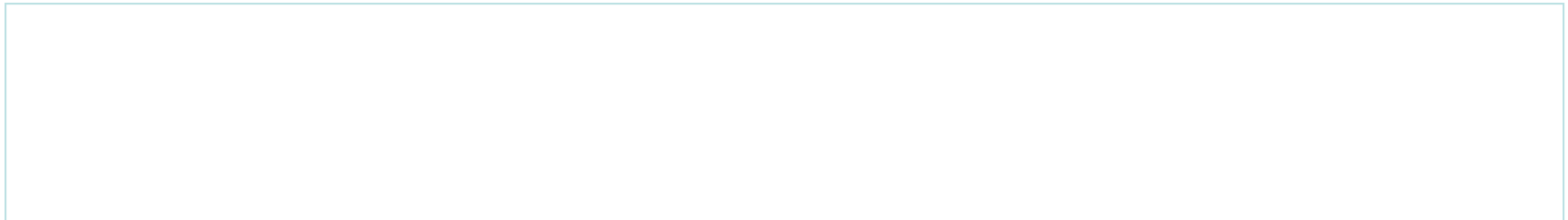


Since  $h$   $k$  and  $l$  are always integers:

$$h^2 + hk + k^2 \equiv 0, 1, 3, 4, 7, 9, 12, \dots$$

$$l^2 \equiv 0, 1, 4, 9, \dots$$

1. Calculate  $\sin^2\theta$  for each peak
2. Divide each  $\sin^2\theta$  value by integers 3, 4, 7, 9, 12, ...  
(from  $h^2+hk+k^2$  allowed by the structure factor)
3. Look for lowest common quotient\*.



Since  $h$   $k$  and  $l$  are always integers:

$$h^2 + hk + k^2 \equiv 0, 1, 3, 4, 7, 9, 12, \dots$$

$$l^2 \equiv 0, 1, 4, 9, \dots$$

4. Let lowest common quotient =  $A$ .
5. Peaks with the lowest common quotient are  $hk0$  type peaks. Assign allowed  $hk0$  indices to those peaks.

Steps to success:

1. Calculate  $\sin^2\theta$  for each peak
2. Divide each  $\sin^2\theta$  value by integers 3, 4, 7...  
(from  $h^2+hk+k^2$  allowed by the structure factor)
3. Look for lowest common quotient.
4. Let lowest common quotient = A.
5. Peaks with lowest common quotient are  $hk0$  type peaks.  
Assign allowed  $hk0$  indices to peaks.

For this part of the problem

$$\frac{\sin^2 \theta}{n} = \frac{\sin^2 \theta}{(h^2 + hk + k^2)}$$

Quadratic form  
of Miller indices



Peak	l/lo	$\sin^2\theta$	$(\sin^2\theta)/3$	$(\sin^2\theta)/4$	$(\sin^2\theta)/7$	$(\sin^2\theta)/9$	$(\sin^2\theta)/12$	hkl	$(\sin^2\theta)/A$
35.100	25.5	<b>0.0909</b>	0.0303	0.0227	0.0130	0.0101	0.0076	<b>100</b>	<b>1.0</b>
38.390	25.6	0.1081	0.0360	0.0270	0.0154	0.0120	0.0090		1.2
40.170	100	0.1179	0.0393	0.0295	0.0168	0.0131	0.0098		1.3
53.000	12.8	0.1991	0.0664	0.0498	0.0284	0.0221	0.0166		2.2
62.940	13.4	<b>0.2725</b>	<b>0.0908</b>	0.0681	0.0389	0.0303	0.0227	<b>110</b>	<b>3.0</b>
70.650	13	0.3343	0.1114	0.0836	0.0478	0.0371	0.0279		3.7
74.170	1.8	<b>0.3636</b>	0.1212	<b>0.0909</b>	0.0519	0.0404	0.0303	<b>200</b>	<b>4.0</b>
76.210	13.1	0.3808	0.1269	0.0952	0.0544	0.0423	0.0317		4.2
77.350	9.3	0.3905	0.1302	0.0976	0.0558	0.0434	0.0325		4.3
82.200	1.7	0.4321	0.1440	0.1080	0.0617	0.0480	0.0360		4.8
86.740	2.1	0.4716	0.1572	0.1179	0.0674	0.0524	0.0393		5.2
92.680	1.8	0.5234	0.1745	0.1308	0.0748	0.0582	0.0436		5.8
102.350	4.4	0.6069	0.2023	0.1517	0.0867	0.0674	0.0506		6.7
105.600	1.4	<b>0.6345</b>	0.2115	0.1586	<b>0.0906</b>	0.0705	0.0529	<b>210</b>	<b>7.0</b>
109.050	8.3	0.6632	0.2211	0.1658	0.0947	0.0737	0.0553		7.3
114.220	5.4	0.7051	0.2350	0.1763	0.1007	0.0783	0.0588		7.8
119.280	2.7	0.7445	0.2482	0.1861	0.1064	0.0827	0.0620		8.2

A = **0.0908**

Indices correspond to:  
 $h^2+hk+k^2 = 1, 3, 4, 7...$   
 or  
 $hk = 10, 11, 20, 21$

## Rearrange equation to find $C$

$$\sin^2 \theta = A(h^2 + hk + k^2) + Cl^2$$



$$Cl^2 = \sin^2 \theta - A(h^2 + hk + k^2)$$

6. Subtract  $(h^2 + k^2 + l^2) \cdot A$  from  $\sin^2 \theta$  for each peak (i.e.,  $A, 3A, 4A, 7A, \dots$ )
7. Look for the lowest common quotient from Step 6.
8. Identify values of  $\sin^2 \theta$  that increase by factors of  $l^2$  (i.e.,  $l^2 = 1, 4, 9, \dots$ ). These correspond to  $00l$  peaks.

6. Subtract from each  $\sin^2\theta$  value  $3A, 4A, 7A\dots$   
 (from  $h^2+hk+k^2$  allowed by the structure factor);

7. Look for lowest common quotient (LCQ). From this you can identify  $00l$ -type peaks. The first allowed peak for hexagonal systems is 002. Determine  $C$  from the equation:

$$C \times l^2 = \sin^2\theta - (h^2+hk+k^2)A$$

Since  $h=0$  and  $k=0$ , then:

$$C = LCQ/l^2 = \sin^2\theta/l^2;$$

8. Look for values of remainders that increase by factors of 1, 4, 9, 16...  
 (because  $l = 1,2,3,4\dots, l^2=1,4,9,16\dots$ ). The peaks exhibiting these characteristics are allowed  $00l$ -type peaks (e.g., 002, 004...).

- We identify the 4th peak as 102 because we observe the LCQ for  $\sin^2\theta-1A$ . Recall that the 1 comes from the quadratic form of Miller indices (i.e.,  $h^2+hk+k^2=1$ ).
- We identify the 8th peak as 112 because we observe the LCQ for  $\sin^2\theta-3A$ . Recall that the 1 comes from the quadratic form of Miller indices (i.e.,  $h^2+hk+k^2=3$ ).
- We identify the 11th peak as ...
- etc...

$\lambda$		$A = 0.0908$											
1.54062	$h^2+hk+k^2$	0	1	3	4	7							
Peak	$l/lo$	$\sin^2\theta$	$\sin^2\theta-A$	$\sin^2\theta-3A$	$\sin^2\theta-4A$	$\sin^2\theta-7A$	$\sin^2\theta/LCQ$	$h$	$k$	$l$	$C=LCQ/l^2$	$l^2=LCQ/C$	
35.100	25.5	0.0909						1	0	0			
38.390	25.6	0.1081	0.0173				1.0	0	0	2	0.0270	4.0	
40.170	100	0.1179	0.0271				1.1						
53.000	12.8	0.1991	0.1083				1.8	1	0	2	0.0271		
62.940	13.4	0.2725	0.1817	0.0001				1	1	0			
70.650	13	0.3343	0.2435	0.0618			3.1						
74.170	1.8	0.3636	0.2728	0.0911	0.0003			2	0	0			
76.210	13.1	0.3808	0.2900	0.1083	0.0175		3.5	1	1	2	0.0271		
77.350	9.3	0.3905	0.2997	0.1180	0.0272		3.6						
82.200	1.7	0.4321	0.3413	0.1597	0.0688		4.0	0	0	4	0.0270	16	
86.740	2.1	0.4716	0.3807	0.1991	0.1083		4.4	2	0	2	0.0271		
92.680	1.8	0.5234	0.4326	0.2509	0.1601		4.8						
102.350	4.4	0.6069	0.5161	0.3345	0.2436		5.6						
105.600	1.4	0.6345	0.5436	0.3620	0.2711			2	1	0			
109.050	8.3	0.6632	0.5724	0.3907	0.2999	0.0274	6.1						
114.220	5.4	0.7051	0.6143	0.4326	0.3418	0.0693	6.5						
119.280	2.7	0.7445	0.6537	0.4721	0.3812	0.1087	6.9						

$LCQ = 0.1083$

9. Peaks that are not  $hk0$  or  $00l$  can be identified using combinations of A and C values. This is accomplished by considering:

$$\sin^2 \theta = Cl^2 + A(h^2 + hk + k^2)$$

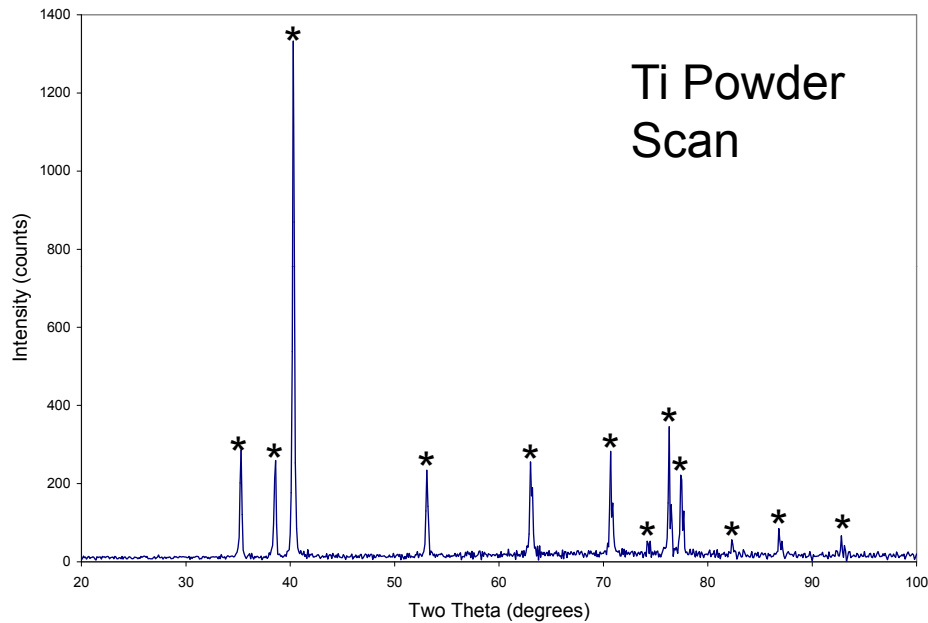
Cycle through allowed values for  $h$   $k$  and  $l$ , and compare  $\sin^2\theta$  value to the labeled peaks. They are the  $hkl$  peaks!

A	C					
0.0908	0.0270					
Peak	l/lo	sin <sup>2</sup> θ	h	k	l	sin <sup>2</sup> θ = $C \times l^2 + A \times (h^2 + hk + k^2)$ Calculated
35.100	25.5	0.0909	1	0	0	0.0908
38.390	25.6	0.1081	0	0	2	0.1081
40.170	100.0	0.1179	1	0	1	0.1179
53.000	12.8	0.1991	1	0	2	0.1989
62.940	13.4	0.2725	1	1	0	0.2725
70.650	13.0	0.3343	1	0	3	0.3341
74.170	1.8	0.3636	2	0	0	0.3633
76.210	13.1	0.3808	1	1	2	0.3806
77.350	9.3	0.3905	2	0	1	0.3903
82.200	1.7	0.4321	0	0	4	0.4324
86.740	2.1	0.4716	2	0	2	0.4714
92.680	1.8	0.5234	1	0	4	0.5232
102.350	4.4	0.6069	2	0	3	0.6065
105.600	1.4	0.6345	2	1	0	0.6358
109.050	8.3	0.6632	2	1	1	0.6628
114.220	5.4	0.7051	1	1	4	0.7049
119.280	2.7	0.7445	2	1	2	0.7439

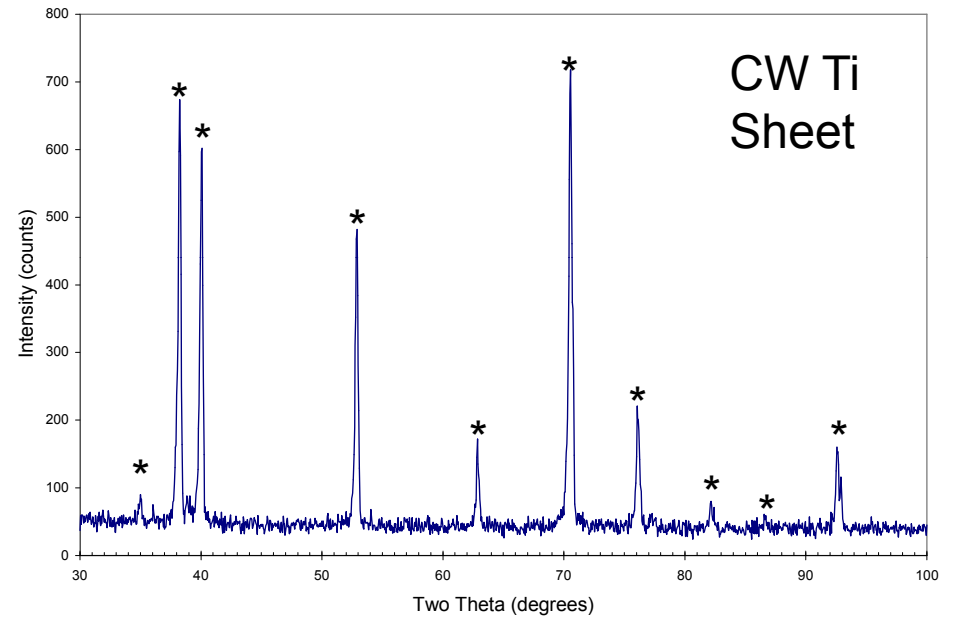
10. Now that we know  $A$  and  $C$ , we can calculate lattice parameters.

$$\begin{array}{c} \text{Red Arrow} \\ \downarrow \\ a = \frac{\lambda}{\sqrt{3A}} \end{array}
 \quad
 \begin{array}{c} \text{Red Arrow} \\ \rightarrow \\ c = \frac{\lambda}{\sqrt{4C}} \end{array}
 \quad
 \begin{array}{c} \text{Red Arrow} \\ \rightarrow \\ \begin{array}{|c|c|c|} \hline \mathbf{a} & \mathbf{c} & \mathbf{c/a} \\ \hline 2.951 & 4.686 & 1.588 \\ \hline \end{array} \end{array}$$

Before we finish, let's consider the application of the analytical method to both of these experimental XRD patterns.



12 XRD peaks



10 XRD peaks

Will it work?

# Practice Exercises

1. The XRD data listed to the right was collected for a hexagonal crystal.  $\text{CuK}_\alpha$  radiation was used.

1. Determine the  $c/a$  ratio.
2. Index the diffraction data/pattern.

Peak #	$2\theta$
1	32.16
2	34.38
3	36.60
4	47.80
5	57.36
6	63.05
7	67.30
8	68.61
9	70.00
10	72.46
11	77.83
12	81.51
13	90.42
14	94.31
15	96.83
16	99.21
17	104.29
18	104.56
19	108.24
20	112.49

# Practice Exercises

1. The XRD data listed to the right was collected for a tetragonal crystal.  $\text{CuK}_\alpha$  radiation was used.

1. Determine the  $c/a$  ratio.
2. Index the diffraction data/pattern.

Peak #	$2\theta$
1	23.73
2	39.23
3	46.36
4	56.69
5	62.31
6	71.10
7	76.15
8	84.35
9	89.20
10	97.29
11	102.21
12	110.63
13	115.90