Analytical Methods for Materials

Laboratory Module #2

Crystal Structure Determination for Non-Cubic Crystals

Suggested Reading

1. Y. Waseda, E. Matsubara, and K. Shinoda, *X-ray Diffraction Crystallography*, (Springer, New York, NY, 2011), Ch. 4, pages 116-117, 131-1139.
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, 3rd 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, 2nd 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: $$\frac{1}{d^2}=\frac{\left(h^2+hk+k^2\right)\sin^2\alpha+2\left(hk+kl+hl\right)\left(\cos^2\alpha-\cos\alpha\right)}{a^2\left(1-3\cos^2\alpha+2\cos^3\alpha\right)}$$

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*: $$\frac{1}{d^2}=\frac{1}{V^2}\left(S_{11}h^2+S_{22}k^2+S_3l^2+2S_{12}hk+2S_{23}kl+2S_{13}hl\right)$$

*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, α, β, γ). 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

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

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

GRAPHICAL METHOD
Hexagonal

Graphical Method for Indexing Hexagonal Patterns

- We need to know the c/a ratio.

- The Hull-Davey chart will tell us the c/a ratio
  and
  provide us with peak identification (i.e., proper Miller indices).

Indexing With Hull-Davey Charts

- Rewrite the following equation:

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

- In the following form

$$2\log d=2\log a-\log\left[\frac{4}{3}\left(h^2+k^2+l^2\right)+\frac{l^2}{(c/a)^2}\right]$$

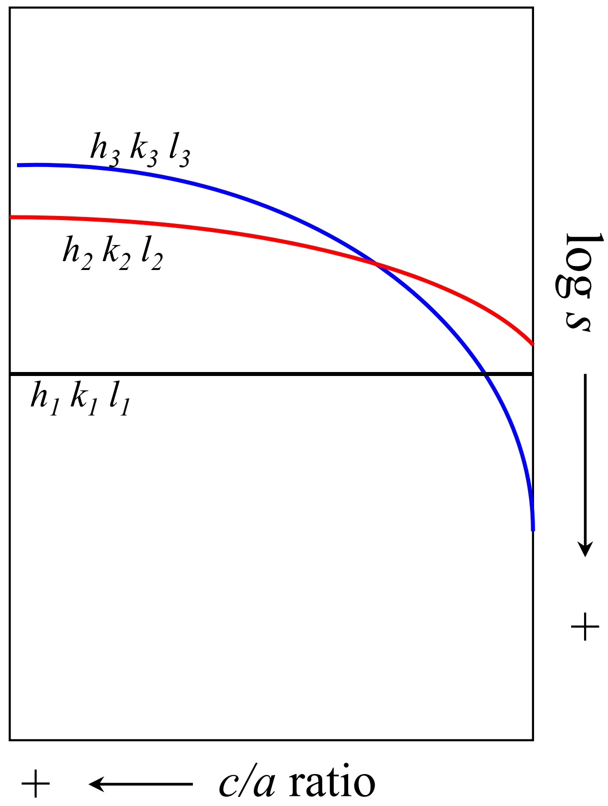
Hull-Davey Charts cont'd

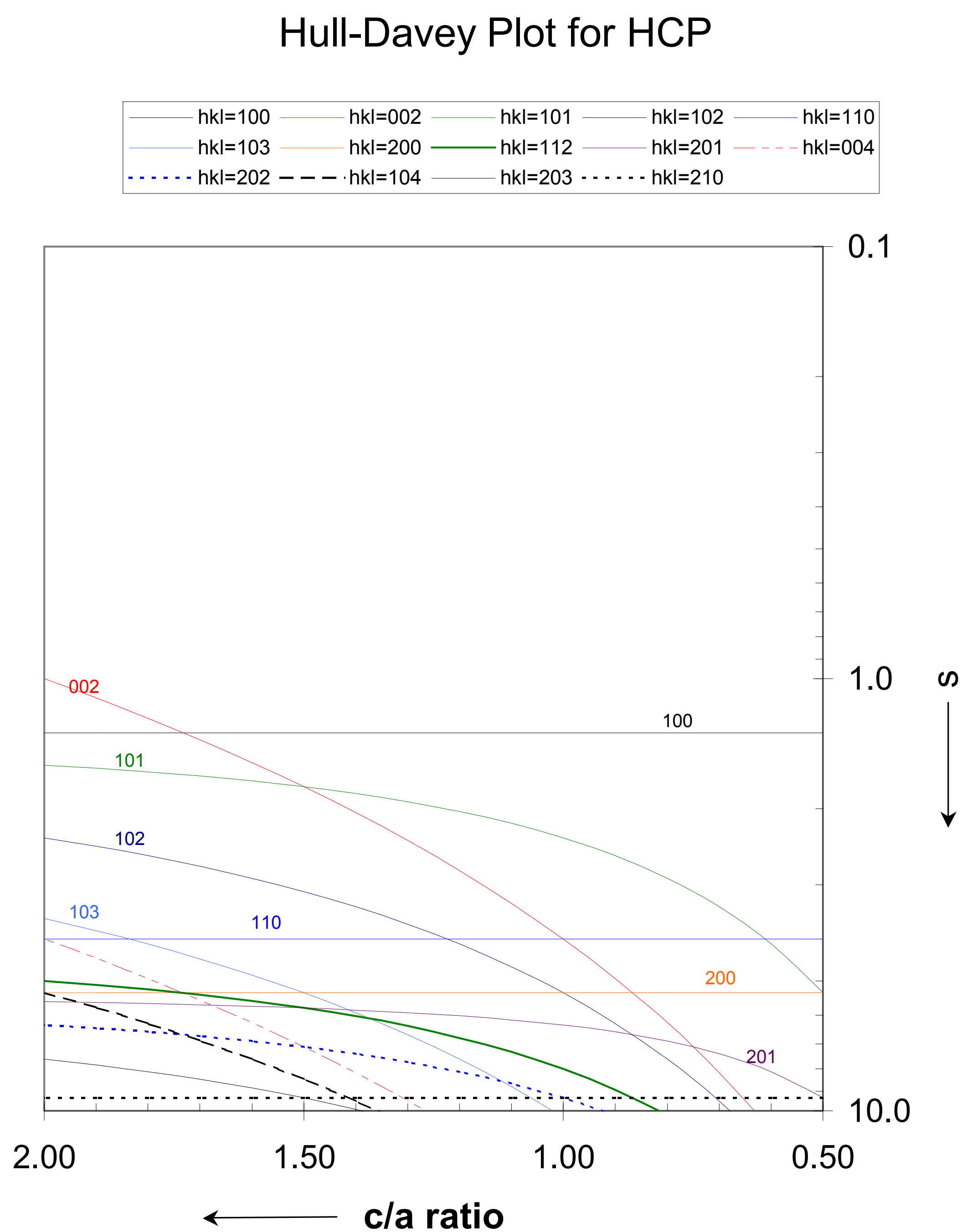
$$2\log d = 2\log a - \log\left[\frac{4}{3}\left(h^2 + k^2 + l^2\right) + \frac{l^2}{(c/a)^2}\right]$$

$$2\log d = 2\log a - \log[s]$$

Hull-Davey Charts cont'd

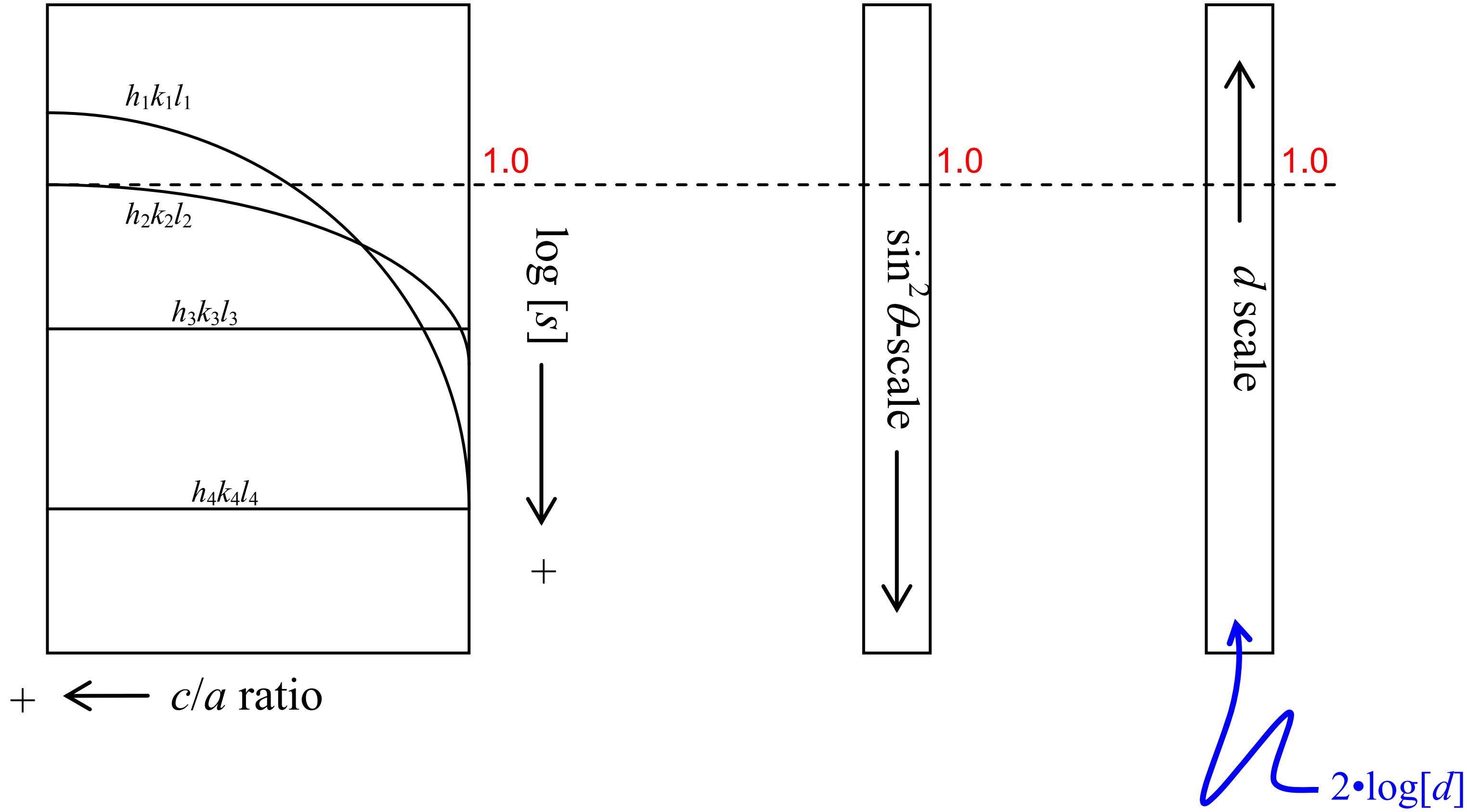
- Now plot the variation of log [*s*] with *c/a*





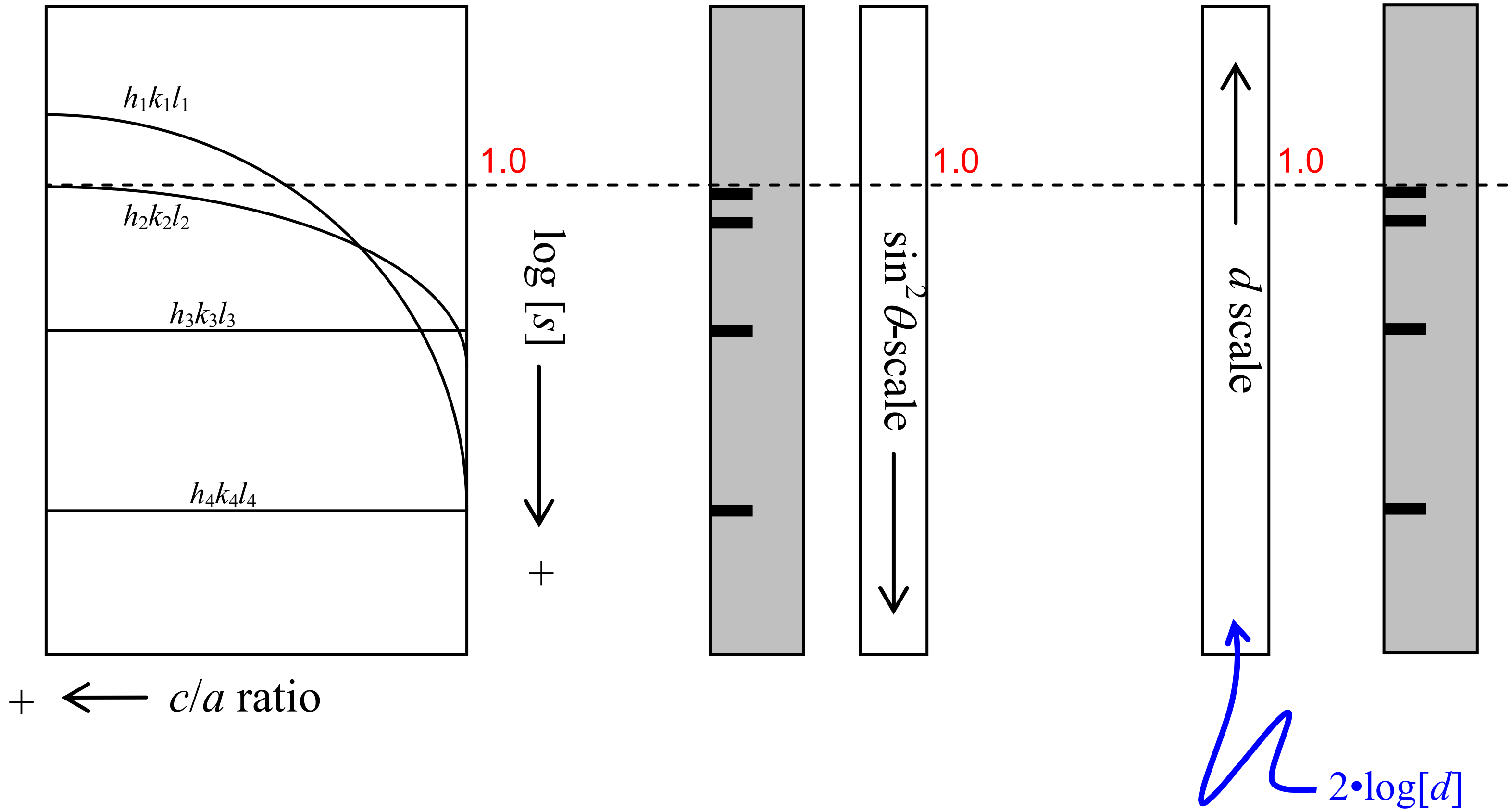
- To determine the *c*/*a* ratio: (i) collect an XRD pattern, (ii) identify the XRD peak locations in terms of the Bragg angle, (iii) calculate the *d*-spacing for each peak, and (iv) construct a single range *d*-spacing scale (2·log *d*) that is the same size as the logarithmic [*s*] scale (you can use $\sin^2\theta$ instead if you prefer).

- See the diagrams on the next couple of pages for guidance.

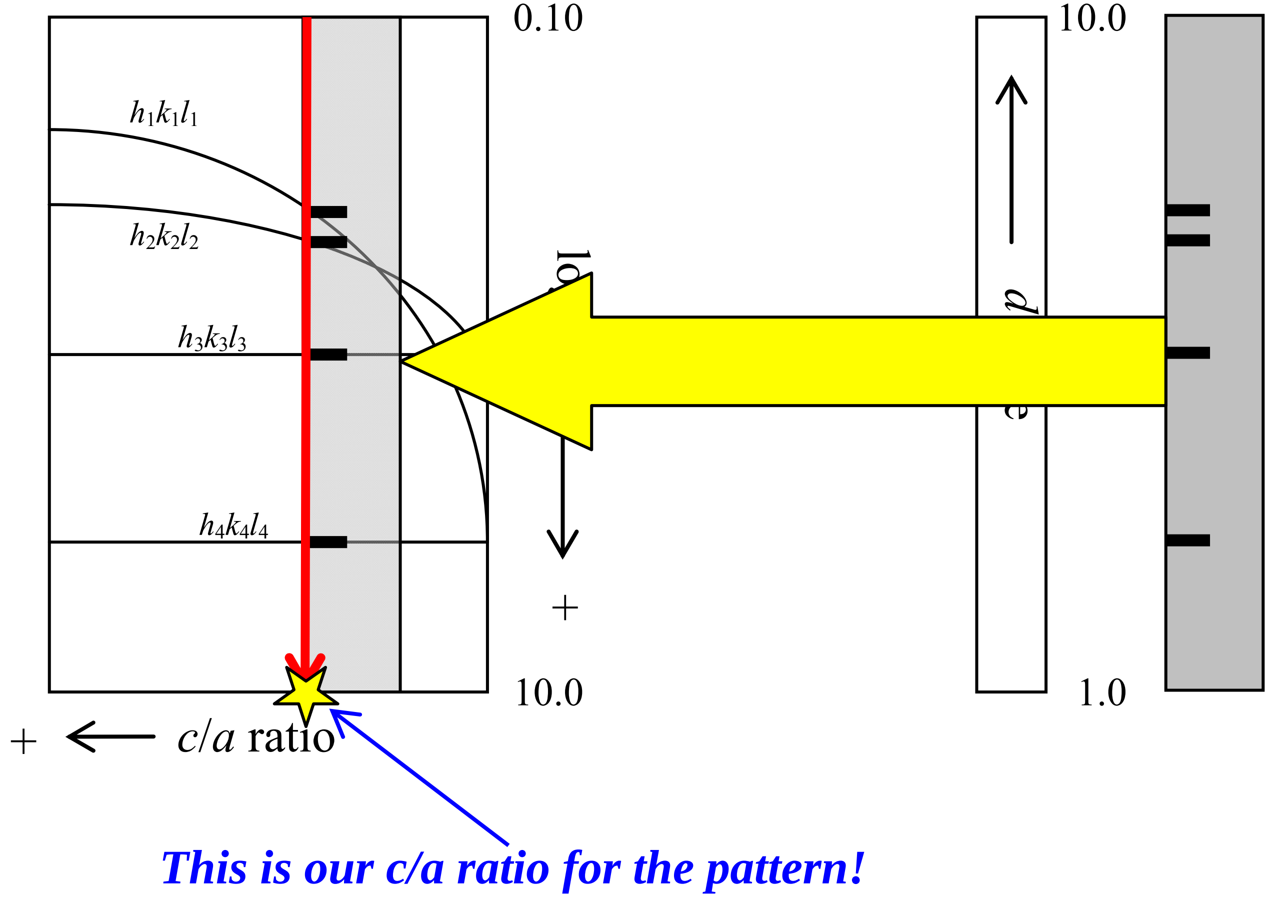


Plot 2·log[*d*] on the same axis as–log[*s*] with both starting at the same origin

(*i.e.*, log [1] = 0 should line up for each)

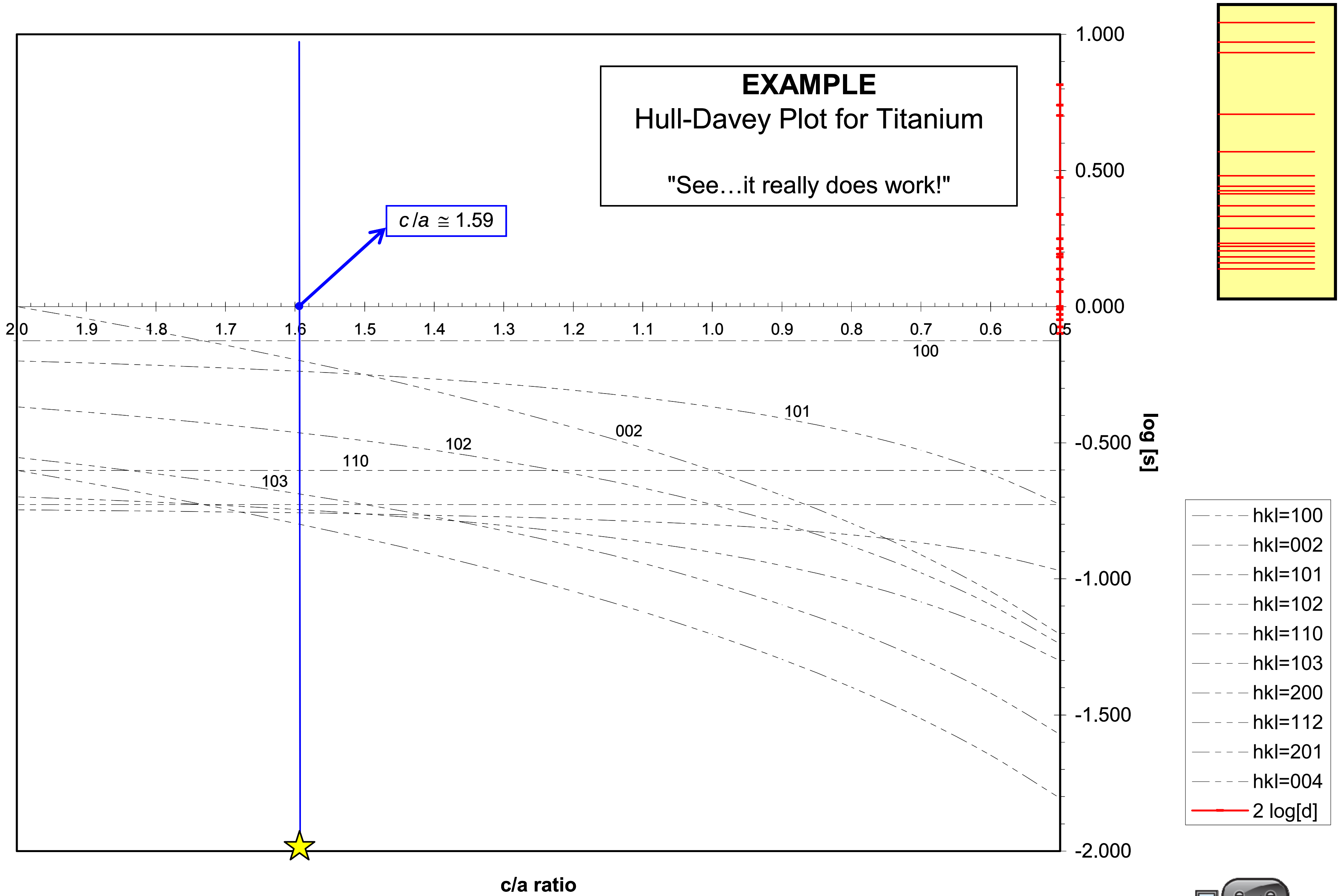


Calculate the d-spacing or $\sin^2\theta$ values for the observed peaks and mark them on a strip laid along side the appropriate d- or $\sin^2\theta$ - scale



The strip should be moved horizontally and vertically across the log [*s*] – *c*/*a* plot until a position is found where each mark on your strip coincides with a line on the chart.

This is the *c*/*a* ratio


EXAMPLE
Hull-Davey Plot for Titanium
"See…it really does work!"
c/a ≅ 1.59
c/a ratio
log [s]
1.000
0.500
0.000
-0.500
-1.000
-1.500
-2.000
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
100
101
002
102
110
103
hkl=100
hkl=002
hkl=101
hkl=102
hkl=110
hkl=103
hkl=200
hkl=112
hkl=201
hkl=004
2 log[d]

Final note on graphical methods

- The graphical methods work, but are tedious. They aren't really used that much anymore.

- Modern computers allow one to determine c/a ratios more rapidly via an iterative process.

Indexing and Lattice Parameter Calculations

- Mathematical method
  - Limitations if peaks are missing from your XRD pattern.

- Analytical method
  - Works for any material, no matter how many peaks you have (or don't have).

- The following will demonstrate the use of each.

Go back to graphical method

MATHEMATICAL METHOD
Hexagonal

Recall

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

$$= \frac{\lambda^2}{4a^2}[A] + \frac{\lambda^2}{4a^2}[B]$$

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.

$$\frac{4}{3}\left(h^2 + hk + k^2\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [A]$$

and

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

[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]*
~~0~~	~~0~~	~~1~~	~~0.290~~
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
~~0~~	~~0~~	~~3~~	~~2.612~~
1	0	3	3.945
0	1	3	3.945
1	1	0	4.000
~~1~~	~~1~~	~~1~~	~~4.290~~
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
~~1~~	~~1~~	~~3~~	~~6.612~~
~~0~~	~~0~~	~~5~~	~~7.256~~
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
~~1~~	~~1~~	~~5~~	~~11.256~~
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* + 2*k* = 3*n*.

If *h* + 2*k* = 3*n* 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:

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

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

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

This corresponds to peaks with *hk*0 type indices (e.g., 110, 210, …)

Lattice Parameters - 2

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

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

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

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

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

2q	$\sin^2\theta$	*h*	*k*	*l*	$4/3(h^2+hk+k^2)+l^2/(c/a)^2$	*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 ***hk*0** and **00*l*** 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^2	$l^2/(c/a)^2$
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

hkl	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

hkl	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

λ								
1.5406								
Peak	**I/Io**	**sin²θ**	***d* (nm)**	***hkl***	***a***	***c***	***h*²+*hk*+*k*²**	***l*²**
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	
				AVG	**2.943**	**4.674**	**c/a = 1.588**	
					0.125	**0.004**		

ITERATION #1

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

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

STEP 6: Use *hk*0 reflections to calculate *a*.

STEP 7: Use 00*l* 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

hkl	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

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

hkl	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

ITERATION #2

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

λ
1.5406

Peak	Intensity	$\sin^2\theta$	*d* (nm)	*hkl*	*a*	*c*	h^2+hk+k^2	l^2
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 #2

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

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

STEP 6: Use *hk*0 reflections to calculate *a*.

STEP 7: Use 00*l* 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

		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 #3

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

l	l^2	$l^2/(c/a)^2$
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

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

hkl	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

hkl	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

λ
1.5406

Peak	I/Io	$\sin^2\theta$	*d* (nm)	*hkl*	*a*	*c*	h^2+hk+k^2	l^2
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 *hk*0 reflections to calculate *a*.

STEP 7: Use 00*l* 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^2	$l^2/(c/a)^2$
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

hkl	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

hkl	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

λ								
1.5406								
Peak	**I/Io**	**sin²θ**	***d* (nm)**	***hkl***	***a***	***c***	***h²+hk+k²***	***l²***
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				
					2.943	**4.674**	**c/a = 1.588**	

ITERATION #4

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

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

STEP 6: Use *hk*0 reflections to calculate *a*.

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

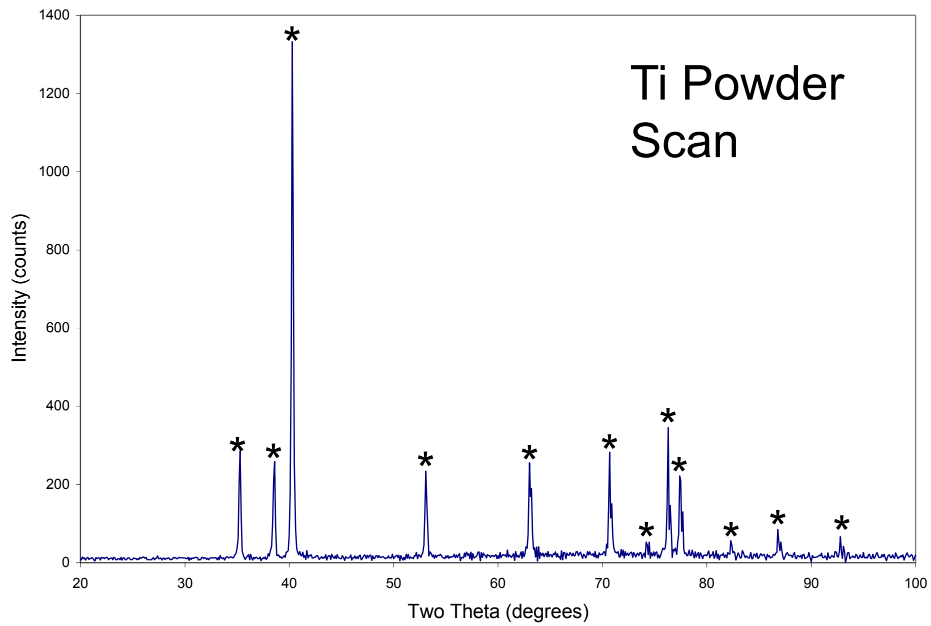
We could refine this further by calculating 2θ values for each reflection using our guessed c/a ratios and comparing them to the observed ones. This means assuming values for c and a.

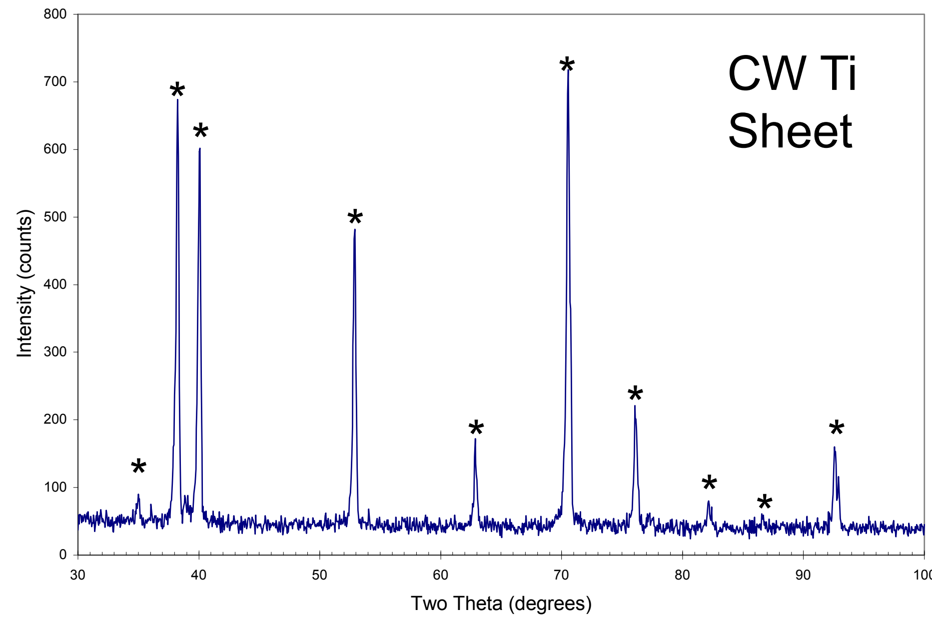
If the difference is a small fraction of the FWHM for the observed reflections then we can consider our result to be accurate.

PRETTY GOOD!
The ICDD value is 1.5871 nm

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

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

a and c/a are constant for any pattern.

Thus, we can write

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

$$A = \frac{\lambda^2}{3a^2} \qquad C = \frac{\lambda^2}{4c^2}$$

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

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

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

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:

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

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

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 sin2θ for each peak
2. Divide each sin2θ 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

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

Quadratic form of Miller indices

Peak	I/Io	$\sin^2\theta$	$(\sin^2\theta)/3$	$(\sin^2\theta)/4$	$(\sin^2\theta)/7$	$(\sin^2\theta)/9$	$(\sin^2\theta)/12$	*hkl*	$(\sin^2\theta)/A$
35.100	25.5	**0.0909**	0.0303	0.0227	0.0130	0.0101	0.0076	**100**	**1.0**
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	**0.2725**	**0.0908**	0.0681	0.0389	0.0303	0.0227	**110**	**3.0**
70.650	13	0.3343	0.1114	0.0836	0.0478	0.0371	0.0279		3.7
74.170	1.8	**0.3636**	0.1212	**0.0909**	0.0519	0.0404	0.0303	**200**	**4.0**
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	**0.6345**	0.2115	0.1586	**0.0906**	0.0705	0.0529	**210**	**7.0**
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*

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

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

6. Subtract $(h^2 + k^2 + l^2)\cdot A$ from $\sin^2\theta$ for each peak (i.e., A, $3A$, $4A$, $7A$,…)
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., $l^2 = 1, 4, 9, \ldots$). These correspond to 00*l* peaks.

6. Subtract from each sin2θ value 3*A*, 4*A*, 7*A*…
   (from h^2+hk+k^2 allowed by the structure factor);

7. Look for lowest common quotient (LCQ). From this you can identify 00*l*-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..., l^2=1,**4**,**9**,16...). The peaks exhibiting these characteristics are <u>allowed</u> 00*l*-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...

λ					A =	0.0908						
1.54062	h^2+hk+k^2	0	1	3	4	7						
Peak	**I/Io**	**$\sin^2\theta$**	**$\sin^2\theta$-*A***	**$\sin^2\theta$-3*A***	**$\sin^2\theta$-4*A***	**$\sin^2\theta$-7*A***	**$\sin^2\theta$/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 *hk*0 or 00*l* can be identified using combinations of A and C values. This is accomplished by considering:

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

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

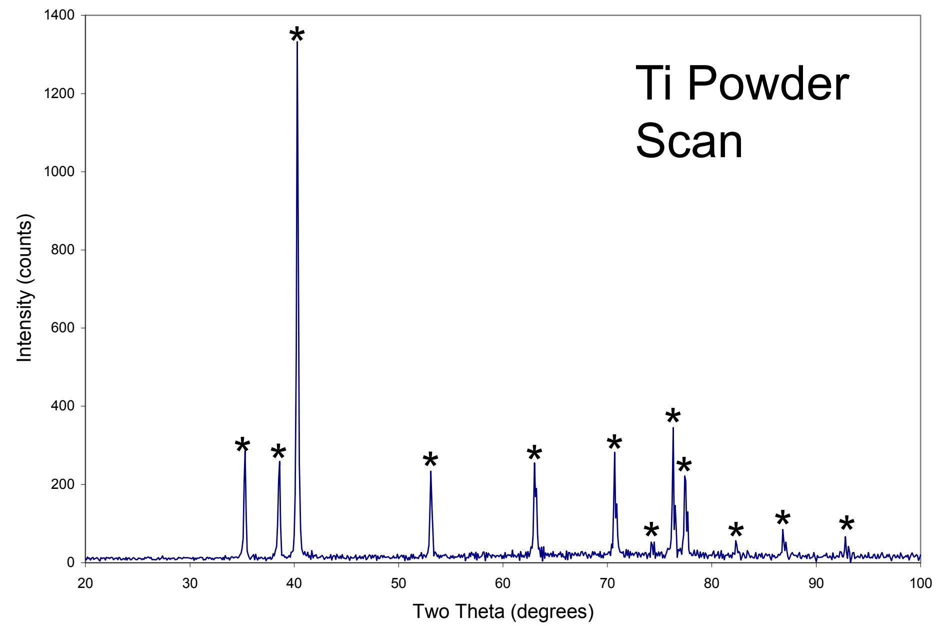
Peak	I/Io	$\sin^2\theta$	*h*	*k*	*l*	$\sin^2\theta$ Calculated $= C\times l^2 + A\times(h^2+hk+k^2)$
35.100	25.5	0.0909	1	0	0	0.0908
38.390	25.6	0.1081	0	0	2	0.1081
40.170	100.0	0.1179	1	0	1	0.1179
53.000	12.8	0.1991	1	0	2	0.1989
62.940	13.4	0.2725	1	1	0	0.2725
70.650	13.0	0.3343	1	0	3	0.3341
74.170	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

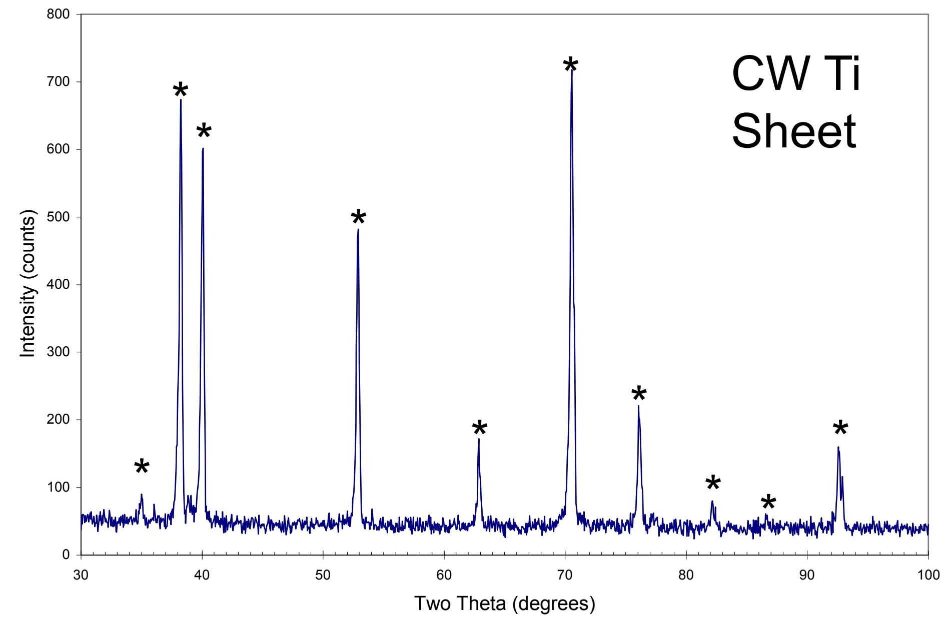
10. Now that we know *A* and *C*, we can calculate lattice parameters.

$$a = \frac{\lambda}{\sqrt{3A}} \qquad c = \frac{\lambda}{\sqrt{4C}}$$

a	c	c/a
2.951	4.686	1.588

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?

Ti Powder Pattern

$\sin^2\theta/A = h^2+hk+k^2$
Must match pattern
$h^2+hk+k^2 = 1, 3, 4, 7...$
for *hk* = 10, 11, 20, 21...

	$\sin^2\theta$	$\sin^2\theta/3$	$\sin^2\theta/4$	$\sin^2\theta/7$	$\sin^2\theta/9$	$\sin^2\theta/12$	$\sin^2\theta/A$			
2θ	**1**	**3**	**4**	**7**	**9**	**12**	***A***	***h***	***k***	***l***
35.23	0.0916	0.0305	0.0229	0.0131	0.0102	0.0076	1.0	1	0	0
38.52	0.1088	0.0363	0.0272	0.0155	0.0121	0.0091	1.2			
40.15	0.1178	0.0393	0.0295	0.0168	0.0131	0.0098	1.3			
52.99	0.1990	0.0663	0.0498	0.0284	0.0221	0.0166	2.2			
62.8	0.2715	0.0905	0.0679	0.0388	0.0302	0.0226	3.0	1	1	0
70.52	0.3333	0.1111	0.0833	0.0476	0.0370	0.0278	3.7			
74.15	0.3634	0.1211	0.0909	0.0519	0.0404	0.0303	4.0	2	0	0
76.26	0.3812	0.1271	0.0953	0.0545	0.0424	0.0318	4.2			
77.19	0.3891	0.1297	0.0973	0.0556	0.0432	0.0324	4.3			
82.09	0.4312	0.1437	0.1078	0.0616	0.0479	0.0359	4.7			
86.65	0.4708	0.1569	0.1177	0.0673	0.0523	0.0392	5.2			
			A=	**0.0910**						

		$\sin^2\theta$-A	$\sin^2\theta$-3A	$\sin^2\theta$-4A	$\sin^2\theta$-7A					
2θ	**$\sin^2\theta$**	**1**	**3**	**4**	**7**	***h***	***k***	***l***	**$\sin^2\theta$/LCQ**	***C=$\sin^2\theta/l^2$***
35.23	0.0916	0.0006	-0.1813	-0.2723	-0.5452	1	0	0	0.8	
38.52	0.1088	0.0178	-0.1641	-0.2551	-0.5280	0	0	2	1.0	0.0272
40.15	0.1178	0.0268	-0.1551	-0.2461	-0.5190				1.1	
52.99	0.1990	0.1080	-0.0739	-0.1649	-0.4378				1.8	
62.8	0.2715	0.1805	-0.0015	-0.0924	-0.3654	1	1	0	2.5	
70.52	0.3333	0.2423	0.0603	-0.0306	-0.3036				3.1	
74.15	0.3634	0.2725	0.0905	-0.0005	-0.2734	2	0	0	3.4	
76.26	0.3812	0.2903	0.1083	0.0173	-0.2556				3.5	
77.19	0.3891	0.2982	0.1162	0.0252	-0.2477				3.6	
82.09	0.4312	0.3402	0.1583	0.0673	-0.2056	0	0	4	4.0	0.0269
86.65	0.4708	0.3798	0.1979	0.1069	-0.1660				4.4	
92.3	0.5201	0.4291			-0.1168				4.8	
			LCQ	**0.1080**						

This suggests (001), but 001 is not allowed in HCP. (002) is first.

Divide $\sin^2\theta$ by *LCQ* and look for a pattern of integers that increases 1,4,9,16...

(002), (004), (006), (008) ...

Ti Powder Pattern

		A	C	calculated				
	Observed	0.0910	0.0271	$\sin^2\theta$				**Difference**
2θ	**$\sin^2\theta$**	**(h^2+hk+k^2)**	**(l^2)**	**X+Y**	***h***	***k***	***l***	***obs-calc***
35.23	0.0916	1	0	0.0910	1	0	0	0.0006
38.52	0.1088	0	4	0.1083	0	0	2	0.0005
40.15	0.1178	1	1	0.1180	1	0	1	-0.0002
52.99	0.1990	1	4	0.1993	1	0	2	-0.0003
62.8	0.2715	3	0	0.2729	1	1	0	-0.0015
70.52	0.3333	1	9	0.3347	1	0	3	-0.0014
74.15	0.3634	4	0	0.3639	2	0	0	-0.0005
76.26	0.3812	3	4	0.3812	1	1	2	0.0000
77.19	0.3891	4	1	0.3910	2	0	1	-0.0018
82.09	0.4312	0	16	0.4332	0	0	4	-0.0020
86.65	0.4708	4	4	0.4722	2	0	2	-0.0014
92.3	0.5201	1	16	0.5242	1	0	4	-0.0041

a =	2.949
c =	4.681
c/a=	1.587

Values for *hk* come from the list of allowed indices (determined from structure factor calculation).

Look for combinations of hkl where observed $\sin^2\theta$ values nearly equal calculated values. This tells you the indices for each peak.

Ti Foil Pattern

	$\sin^2\theta$	$\sin^2\theta/3$	$\sin^2\theta/4$	$\sin^2\theta/7$	$\sin^2\theta/9$	$\sin^2\theta/12$	$\sin^2\theta/A$			
2θ	**1**	**3**	**4**	**7**	**9**	**12**	***A***	***h***	***k***	***l***
35.044	0.0906	0.0302	0.0227	0.0129	0.0101	0.0076	1.0	1	0	0
38.22	0.1072	0.0357	0.0268	0.0153	0.0119	0.0089	1.2			
40.05	0.1173	0.0391	0.0293	0.0168	0.0130	0.0098	1.3			
52.83	0.1979	0.0660	0.0495	0.0283	0.0220	0.0165	2.2			
62.86	0.2719	0.0906	0.0680	0.0388	0.0302	0.0227	3.0	1	1	0
70.53	0.3333	0.1111	0.0833	0.0476	0.0370	0.0278	3.7			
76.04	0.3794	0.1265	0.0948	0.0542	0.0422	0.0316	4.2			
82.07	0.4310	0.1437	0.1078	0.0616	0.0479	0.0359	4.7			
86.58	0.4702	0.1567	0.1175	0.0672	0.0522	0.0392	5.2			
92.5	0.5218	0.1739	0.1305	0.0745	0.0580	0.0435	5.7			
			A=	**0.0906**						

$\sin^2\theta/A = h^2+hk+k^2$
Must match pattern
$h^2+hk+k^2 = 1, 3, 4, 7...$
for *hk* = 10, 11, 20, 21...

		$\sin^2\theta-A$	$\sin^2\theta-3A$	$\sin^2\theta-4A$	$\sin^2\theta-7A$					
2θ	**$\sin^2\theta$**	**1**	**3**	**4**	**7**	***h***	***k***	***l***	**$\sin^2\theta$/LCQ**	
35.044	0.0906	-0.0003	-0.1823	-0.2733	-0.5462	1	0	0	0.85	
38.22	0.1072	0.0162	-0.1657	-0.2567	-0.5296	0	0	2	1.00	0.0268
40.05	0.1173	0.0263	-0.1557	-0.2466	-0.5196				1.10	
52.83	0.1979	0.1069	-0.0750	-0.1660	-0.4389				1.85	
62.86	0.2719	0.1809	-0.0010	-0.0920	-0.3649	1	1	0	2.55	
70.53	0.3333	0.2424	0.0604	-0.0306	-0.3035				3.12	
76.04	0.3794	0.2884	0.1065	0.0155	-0.2574				3.56	
82.07	0.4310	0.3400	0.1581	0.0671	-0.2058	0	0	4	4.04	0.0269
86.58	0.4702	0.3792	0.1973	0.1063	-0.1666				4.41	
92.5	0.5218	0.4308	0.2489	0.1579	-0.1150				4.89	
			LCQ	**0.1067**						

This suggests (001), but 001 is not allowed in HCP. (002) is first.

Divide $\sin^2\theta$ by *LCQ* and look for a pattern of integers that increases 1,4,9,16...

(002), (004), (006), (008) ...

Ti Foil Pattern

		A	C	calculated				
	Observed	0.0906	0.0269	$\sin^2\theta$				Difference
2θ	$\sin^2\theta$	(h^2+hk+k^2)	(l^2)	X+Y	*h*	*k*	*l*	*obs-calc*
35.044	0.0906	1	0	0.0906	1	0	0	0.0000
38.22	0.1072	0	4	0.1075	0	0	2	-0.0003
40.05	0.1173	1	1	0.1175	1	0	1	-0.0003
52.83	0.1979	1	4	0.1981	1	0	2	-0.0002
62.86	0.2719	3	0	0.2719	1	1	0	0.0000
70.53	0.3333	1	9	0.3324	1	0	3	0.0009
76.04	0.3794	3	4	0.3794	1	1	2	0.0000
82.07	0.4310	0	16	0.4299	0	0	4	0.0012
86.58	0.4702	4	4	0.4700	2	0	2	0.0001
92.5	0.5218	1	16	0.5205	1	0	4	0.0013

a =	2.954
c =	4.699
c/a=	1.591

Values for *hk* come from the list of allowed indices (determined from structure factor calculation).

Look for combinations of hkl where observed $\sin^2\theta$ values nearly equal calculated values. This tells you the indices for each peak.

LOOKS LIKE THE METHOD STILL WORKS!

Practice Exercises

1. The XRD data listed to the right was collected for a hexagonal crystal. CuK_α radiation was used.

   1. Determine the *c*/*a* ratio.

   2. Index the diffraction data/pattern.

Peak #	2θ
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. CuK_{α} radiation was used.

    1. Determine the *c*/*a* ratio.

    2. Index the diffraction data/pattern.

Peak #	2θ
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