Indexing, Lattice Parameter Determination

<u>Some references</u>

A.R. West, *Solid State Chemistry and Its Applications*, (John Wiley & Sons, New York, 1984).

M.F.C. Ladd, R.A. Palmer, *Structure Determination by X-ray Crystallography*, 3rd ed., (Plenum Press, New York, 1993).

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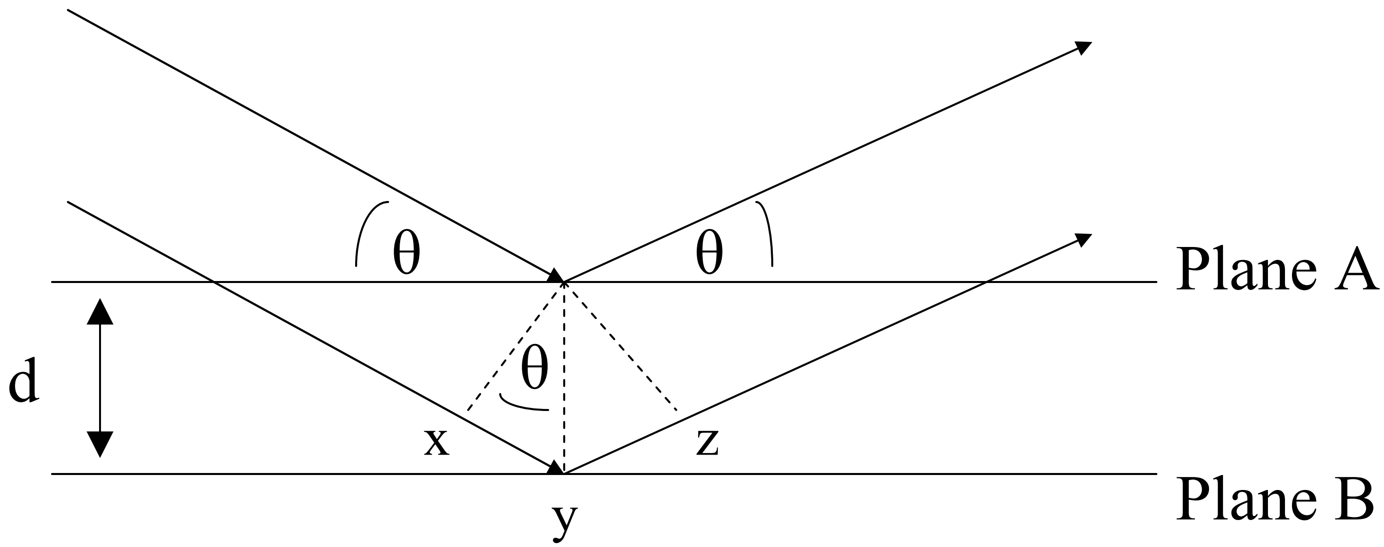
Bragg's Law



$$xy = yz = d \sin \theta$$

$$xyz = 2d \sin \theta$$

$$xyz = n\lambda$$

$$\boxed{n\lambda = 2d \sin \theta}$$

Bragg's Law $n\lambda = 2d \sin\theta$

Cubic

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

Tetragonal

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

Orthorhombic

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

Hexagonal

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

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

$$\frac{1}{d^2} = \frac{1}{V^2}\begin{pmatrix} h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta + l^2a^2b^2\sin^2\gamma \\ + 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma) \\ + 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha) \\ + 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta) \end{pmatrix}$$

$$V = abc\left(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma\right)^{1/2}$$

Primitive cubic example

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

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

		a	3.905	angstroms				
	lambda		1.5406	angstroms				
h	k	l	h2+k2+l2	1/d2	d	sin(Theta)	Theta (rad)	2Theta (deg)
1	0	0	1	0.0656	3.9050	0.1973	0.1986	22.7536
1	1	0	2	0.1312	2.7613	0.2790	0.2827	32.3972
1	1	1	3	0.1967	2.2546	0.3417	0.3487	39.9566
2	0	0	4	0.2623	1.9525	0.3945	0.4055	46.4721
2	1	0	5	0.3279	1.7464	0.4411	0.4568	52.3465
2	1	1	6	0.3935	1.5942	0.4832	0.5043	57.7875
2	2	0	8	0.5246	1.3806	0.5579	0.5919	67.8263
3	0	0	9	0.5902	1.3017	0.5918	0.6333	72.5669
2	2	1	9	0.5902	1.3017	0.5918	0.6333	72.5669
3	1	0	10	0.6558	1.2349	0.6238	0.6736	77.1870
3	1	1	11	0.7214	1.1774	0.6542	0.7132	81.7237
2	2	2	12	0.7869	1.1273	0.6833	0.7523	86.2086
3	2	0	13	0.8525	1.0831	0.7112	0.7912	90.6704
3	2	1	14	0.9181	1.0437	0.7381	0.8302	95.1362

Limiting conditions/Systematic absences

Type	Limiting conditions
P	none
C	$h + k = 2n$
I	$h + k + l = 2n$
F	$h + k = 2n$, $k + l = 2n$, and $h + l = 2n$

The limiting conditions are the conditions where reflections *can* occur.
Systematic absences are the conditions where reflections *cannot* occur.

The limiting conditions exist because of the structure factor, $\mathbf{F_{hkl}}$, for the given unit cell type.

Body-centered cubic example

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

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

$$h + k + l = 2n$$

		a	3.905	angstroms
	lambda		1.5406	angstroms

h	k	l	$h^2+k^2+l^2$	$1/d^2$	d	sin(Theta)	Theta (rad)	2Theta (deg)
1	0	0	1	0.0656	3.9050	0.1973	0.1986	22.7536
1	1	0	2	0.1312	2.7613	0.2790	0.2827	32.3972
1	1	1	3	0.1967	2.2546	0.3417	0.3487	39.9566
2	0	0	4	0.2623	1.9525	0.3945	0.4055	46.4721
2	1	0	5	0.3279	1.7464	0.4411	0.4568	52.3465
2	1	1	6	0.3935	1.5942	0.4832	0.5043	57.7875
2	2	0	8	0.5246	1.3806	0.5579	0.5919	67.8263
3	0	0	9	0.5902	1.3017	0.5918	0.6333	72.5669
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3	1	0	10	0.6558	1.2349	0.6238	0.6736	77.1870
3	1	1	11	0.7214	1.1774	0.6542	0.7132	81.7237
2	2	2	12	0.7869	1.1273	0.6833	0.7523	86.2086
3	2	0	13	0.8525	1.0831	0.7112	0.7912	90.6704
3	2	1	14	0.9181	1.0437	0.7381	0.8302	95.1362

Going the other way: Indexing

1. Calculate the d-spacings and convert to $1/d^2$

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

2Theta (deg)
27.4344
30.1790
36.0710
39.1885
41.2390
44.0389
56.6232
62.7525
64.0439
68.9969

Before you index, are you sure these peak positions are correct? There are peak finding programs (e.g., Xfit) that can help you determine if a broad peak is composed of two or more peaks.

Indexing

2. Find any common multiples and divide by that common divisor

2Theta (deg)	d	1/d2
27.4344	3.2484	0.0948 ←
30.1790	2.9590	0.1142
36.0710	2.4880	0.1615
39.1885	2.2970	0.1895 ←
41.2390	2.1874	0.2090
44.0389	2.0546	0.2369
56.6232	1.6242	0.3791 ←
62.7525	1.4795	0.4569
64.0439	1.4527	0.4738 ←
68.9969	1.3600	0.5406

Indexing

3. Try to find other common multiples or similar differences between numbers

2Theta (deg)	d	1/d2	/ 0.0948
27.4344	3.2484	0.0948	1.0000
30.1790	2.9590	0.1142	1.2052
36.0710	2.4880	0.1615	1.7047
39.1885	2.2970	0.1895	2.0001
41.2390	2.1874	0.2090	2.2055
44.0389	2.0546	0.2369	2.4998
56.6232	1.6242	0.3791	4.0001
62.7525	1.4795	0.4569	4.8209
64.0439	1.4527	0.4738	5.0001
68.9969	1.3600	0.5406	5.7049

multiply by 2?

Indexing

4. Try to find corresponding *hkl*'s.

2Theta (deg)	d	1/d2		- common
27.4344	3.2484	0.0948	2.0000	
30.1790	2.9590	0.1142	2.4104	0.4104
36.0710	2.4880	0.1615	3.4094	1.4094
39.1885	2.2970	0.1895	4.0001	
41.2390	2.1874	0.2090	4.4110	0.4110
44.0389	2.0546	0.2369	4.9996	
56.6232	1.6242	0.3791	8.0002	
62.7525	1.4795	0.4569	9.6418	1.6418
64.0439	1.4527	0.4738	10.0002	
68.9969	1.3600	0.5406	11.4098	1.4098

Lattice parameters

5. Estimate the lattice parameters

2Theta (deg)	d	1/d2		- common	hkl
27.4344	3.2484	0.0948	2.0000		110
30.1790	2.9590	0.1142	2.4104	0.4104	111
36.0710	2.4880	0.1615	3.4094	1.4094	?
39.1885	2.2970	0.1895	4.0001		200
41.2390	2.1874	0.2090	4.4110	0.4110	201
44.0389	2.0546	0.2369	4.9996		210
56.6232	1.6242	0.3791	8.0002		220
62.7525	1.4795	0.4569	9.6418	1.6418	222
64.0439	1.4527	0.4738	10.0002		310
68.9969	1.3600	0.5406	11.4098	1.4098	?

It looks tetragonal, so we'll use $$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

a=b = 4.594 Å and c = ~7.17 Å, but 2 peaks are not indexed

Indexing and lattice parameters

Try to re-index the peaks.

2Theta (deg)	d	1/d2		- common	hkl
27.4344	3.2484	0.0948	2.0000		110
30.1790	2.9590	0.1142	2.4104	2.4104	001
36.0710	2.4880	0.1615	3.4094	2.4094	101
39.1885	2.2970	0.1895	4.0001		200
41.2390	2.1874	0.2090	4.4110	2.4110	111
44.0389	2.0546	0.2369	4.9996		210
56.6232	1.6242	0.3791	8.0002		220
62.7525	1.4795	0.4569	9.6418	9.6418	002
64.0439	1.4527	0.4738	10.0002		310
68.9969	1.3600	0.5406	11.4098	2.4098	301

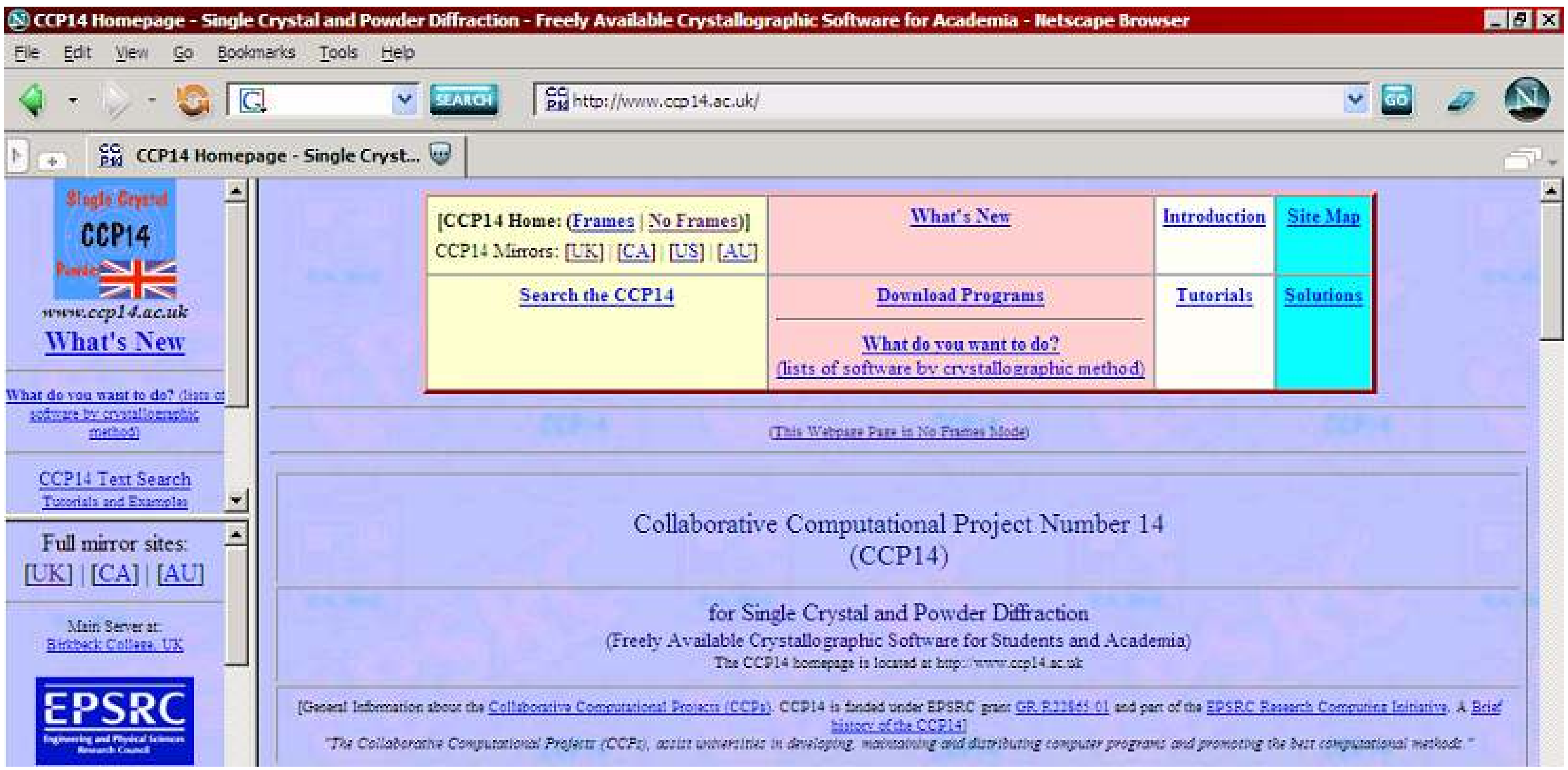
a=b = 4.594 Å and c = 2.959 Å, and all the peaks are indexed.

The sample is pure, and appears to have a primitive unit cell.
It was the rutile phase ($P4_2/mnm$) of TiO_2.

There must be an easier way to index

0. Use a program

Free programs available at www.ccp14.ac.uk.



Programs

Crysfire program

• DOS program

• creates and runs (!) setup files for many indexing programs: DICVOL, ITO12, TREOR, etc.

• These programs typically give you a figure of merit, M or F, of their results.

• so what can go wrong?

Zero point error and impurities: the bane of students who are indexing

	DicVol	TREOR
Ideal	Hex (a = 5.066Å, c = 5.404Å)	Hex (a = 5.066Å, c = 5.404Å)
Random errors	Mono (a = 5.062Å, b = 5.4031Å, c = 5.054Å, β = 119.8°)	Orth (a = 8.7799Å, b = 5.3994Å, c = 5.0547Å)
0.1° error	Mono (a = 5.0914Å, b = 5.4108Å, c = 5. 0791Å, β = 119.56°)	Hex (a = 8.786Å, c = 5.416Å)
0.2° error	Mono (a = 5.0926Å, b = 5.0769Å, c = 5. 4214Å, β = 119.76°)	Mono (a = 5.1098Å, b = 5.4249Å, c = 5.0918Å, β = 119.56°)
2 impurity peaks	Mono (a = 8.789Å, b = 5.403Å, c = 2.697Å, β = 93.11°)	Hex (a = 5.066Å, c = 10.807Å)