

Materials Analysis MATSCI 162/172
Laboratory Exercise No. 1
Crystal Structure Determination – Pattern Indexing

Objectives:

To index the x-ray diffraction pattern, identify the Bravais lattice, and calculate the precise lattice parameters.

Complete determination of an unknown crystal structure consists of three steps:

1. Calculation of the size and shape of the unit cell from the angular positions of the diffraction peaks.
2. Computation of the number of atoms per unit cell from the size and shape of the unit cell, the chemical composition of the specimen, and its measured density.
3. Deduction of the atom positions within the unit cell from the relative intensities of the diffraction peaks.

We will do only step 1.

“Indexing pattern” involves assigning the correct Miller indices to each peak in the diffraction pattern.

For cubic unit cell:

$$d_{hkl} = \frac{a_o}{\sqrt{h^2 + k^2 + l^2}}$$

Bragg's law becomes:

$$\lambda^2 = 4d^2 \sin^2 \theta = \frac{4a_o^2}{(h^2 + k^2 + l^2)} \sin^2 \theta$$

so:

$$\frac{\sin^2 \theta}{(h^2 + k^2 + l^2)} = \frac{\sin^2 \theta}{s} = \frac{\lambda^2}{4a_0^2} \leftarrow \text{constant for a given crystal}$$

always equal
to an integer

In the cubic system, the first reflection in the diffraction pattern is due to diffraction from planes with Miller indices (100) for primitive cubic, (110) for body-centered cubic, and (111) for face-centered cubic lattices, so $h^2 + k^2 + l^2 = 1, 2, \text{ or } 3$, respectively.

Characteristic line sequences in the cubic system:

Simple cubic:	1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16, ...
Body-centered cubic:	2, 4, 6, 8, 10, 12, 14, 16, ...
Face-centered cubic:	3, 4, 8, 11, 12, 16, 19, 20, 24, 27, 32, ...
Diamond cubic:	3, 8, 11, 16, 19, 24, 27, 32, ...

If the diffraction pattern contains only six peaks and if the ratio of the $\sin^2\theta$ values is 1, 2, 3, 4, 5, and 6 for these reflections, then Bravais lattice may be either primitive cubic or body-centered cubic, it is not possible to unambiguously distinguish the two. But remember that the simple cubic structure is not very common and, therefore, in such a situation, you will probably be right if you had indexed the pattern as belonging to a material with the BCC structure.

Steps in indexing cubic pattern:

1. Measure sample & list angles 2θ .
2. Calculate $\sin^2\theta$.
3. Calculate $\sin^2\theta/s$.
4. Write characteristic line sequences for the cubic system.
5. Identify Bravais lattice.
6. Calculate the lattice parameter.
7. Compare the lattice parameter and crystal class to tabulated values for metals to determine the material.

EXAMPLE

1	2	3	4	5	6	7	8	9	10
FCC					SC		BCC		
Line	$\sin^2 \theta$	$s = (h^2 + k^2 + l^2)$	$\frac{\sin^2 \theta}{s} = \frac{\lambda^2}{4a^2}$	$a(\text{\AA})$	hkl	s	$\frac{\sin^2 \theta}{s}$	s	$\frac{\sin^2 \theta}{s}$
1	0.140	3	0.0467	3.57	111	1	0.140	2	0.0700
2	0.185	4	0.0463	3.59	200	2	0.093	4	0.0463
3	0.369	8	0.0461	3.59	220	3	0.123	6	0.0615
4	0.503	11	0.0457	3.61	311	4	0.123	8	0.0629
5	0.548	12	0.0457	3.61	222	5	0.110	10	0.0548
6	0.726	16	0.0454	3.62	400	6	0.121	12	0.0605
7	0.861	19	0.0453	3.62	331	8	0.108	14	0.0615
8	0.905	20	0.0453	3.62	420	9	0.101	16	0.0566

Measurement of the lattice parameter is indirect process.
For cubic material

$$\frac{1}{d^2} = \frac{a^2}{h^2 + k^2 + l^2} \quad d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

and

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

We are measuring θ not $\sin\theta$!

Differentiating Bragg's equation we get:

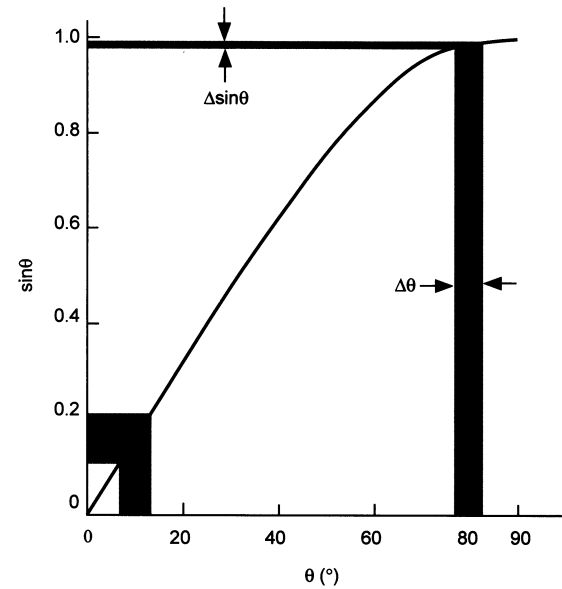
$$\frac{\Delta d}{d} = -\cot \theta \Delta \theta$$

$\cot\theta = 0$ when $\theta = 90^\circ$

The plot of lattice parameter vs θ is not linear.

Extrapolation of the lattice parameter against certain functions of θ will produce a straight line, which can then be extrapolated to the value corresponding to $\theta = 90^\circ$.

The function depends on the kind of equipment used to record XRD pattern.



Diffractometer

The general approach in finding an extrapolation function is to consider the various effects which can lead to errors in the measured values of θ , and to find out how these errors in θ vary with the angle θ itself.

Most important systematic errors:

1. Misalignment of the instrument.
2. Use of a flat specimen instead of a curved one.
3. Absorption in the specimen.
4. Displacement of the specimen from the diffractometer axis. Usually this is the largest source of error. It causes an error given by:

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

where D is the specimen displacement parallel to the diffraction-plane normal.
 R – diffractometer radius.

5. Vertical divergence of the beam.

No single extrapolation function can be completely satisfactory.

For (2) and (3) $\Delta d/d$ varies as $\cos^2 \theta$.

For (4) $\Delta d/d$ varies as $\cos^2 \theta / \sin \theta$.

Extrapolation against $\cos^2 \theta$ is best if the main error is the flat sample effect. It is valid for diffraction peaks with $\theta > 60^\circ$.

For cubic materials and if the sample has a displacement error, the Bradley-Jay extrapolation function can be used:

$$\frac{\Delta d}{d} = \frac{\Delta a}{a_0} = \frac{a - a_0}{a_0} = k_1 \frac{\cos^2 \theta}{\sin \theta},$$

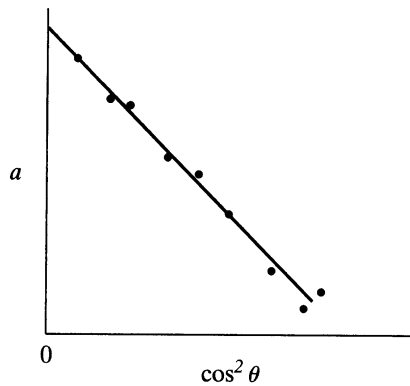
$$a = a_0 + a_0 k_1 \frac{\cos^2 \theta}{\sin \theta}.$$

If a Nelson-Riley extrapolation function is appropriate:

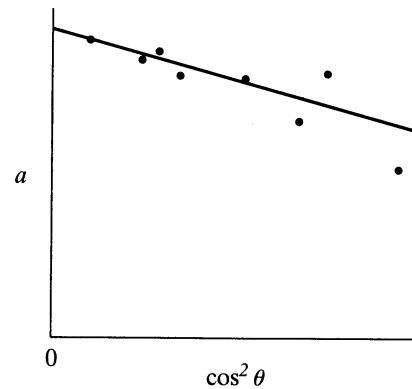
$$\frac{\Delta d}{d} = \frac{\Delta a}{a_0} = \frac{a - a_0}{a_0} = k_2 \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right),$$

$$a = a_0 + a_0 k_2 \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right).$$

Large systematic errors,
small random errors



Small systematic errors,
large random errors



- a) systematic errors are eliminated by selection of the proper extrapolation function
- b) Random errors are reduced using the least squares method devised by Cohen.

Cohen Method

Squaring the Bragg equation we get:

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

After differentiation:

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

Lets assume that combined systematic errors take the form:

$$\frac{2 \Delta d}{d} = K \cos^2 \theta$$

then combining equations we get:

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

D – a new constant.

The true value for $\sin^2 \theta$ is:

$$\sin^2 \theta_{true} = \frac{\lambda^2}{4a_0^2} (h^2 + k^2 + l^2)$$

a_0 – true lattice parameter

We rewrite:

$$\begin{aligned}\sin^2 \theta_{observed} - \sin^2 \theta_{true} &= \Delta \sin^2 \theta \\ \sin^2 \theta_{observed} - \frac{\lambda^2}{4a_0^2} (h^2 + k^2 + l^2) &= D \sin^2 2\theta \\ \sin^2 \theta_{observed} &= A\alpha + C\delta\end{aligned}$$

can be written for each reflection in the XRD pattern

where:

$$\begin{aligned}A &= \frac{\lambda^2}{4a_0^2} \\ \alpha &= (h^2 + k^2 + l^2) \\ C &= \frac{D}{10} \\ \delta &= 10 \sin^2 2\theta\end{aligned}$$

The procedure can be combined with the least squares principle to minimize the effect of random observational errors

$$A\alpha + C\delta - \sin^2 \theta_{observed} = \varepsilon$$

According to the theory of least squares, 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:

$$\sum (\varepsilon)^2 = \sum (A\alpha + C\delta - \sin^2 \theta_{observed})^2$$

By differentiating we get a pair of normal equations with respect to A and C and equating them to zero:

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

By solving these equations we determine A , and from this value of A the true lattice parameter a_0 can be determined.

Material: Aluminum					Radiation: Cu K α		
Peak #	α	δ	α^2	$\alpha\delta$	δ^2	$\alpha \sin^2 \theta^a$	$\delta \sin^2 \theta^a$
1	19	8.6	361	163.4	73.96	13.06402	5.91319
2	19	8.5	361	161.5	72.25	13.06497	5.84486
3	20	8.0	400	160.0	64.00	14.47700	5.79080
4	20	7.9	400	158.0	62.41	14.47500	5.71763
5	24	4.6	576	110.4	21.16	20.84280	3.99487
6	24	4.4	576	105.6	19.36	20.84760	3.82206
			$\Sigma \alpha^2 = 2674$	$\Sigma \alpha\delta = 858.9$	$\Sigma \delta^2 = 313.14$	$\Sigma \alpha \sin^2 \theta = 96.77139$	$\Sigma \delta \sin^2 \theta = 31.08341$

^aRemember to use the $\sin^2 \theta$ values adjusted to the K α_1 wavelength.