Chapter five: The determination of crystal structure

5.1 Basic Principles of Crystal Structure Analysis

(1) The angular positions of diffracted peaks gives information on the properties (size and type) of the unit cell

(2) The intensities of diffracted peaks gives information on the positions and types of atoms within the unit cell

General procedure:

(1) "Index the pattern" → assign *hkl* values to each peak.

(2) Determine the number of atoms per unit cell (chemical composition, density, and size/shape of unit cell.

(3) Determine the positions of atoms in the unit cell from the measured intensities.

Only when these three steps have been accomplished is the structure determination complete. The third step is generally the most difficult, and there are many structures which are known only incompletely, in the sense that this final step has not yet been made. Nevertheless, knowledge of the shape and size of the unit cell, without any knowledge of atom positions, is in itself of very great value in many applications.

5.2 Indexing patterns of cubic crystals

For cubic unit cell:

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

so Bragg's law becomes:

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

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

$s = (h^2+k^2+l^2)$ is always integer and $\frac{\lambda^2}{4a^2}$ is a constant for any one pattern.

Therefore, the lattice parameters can be calculated from:

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

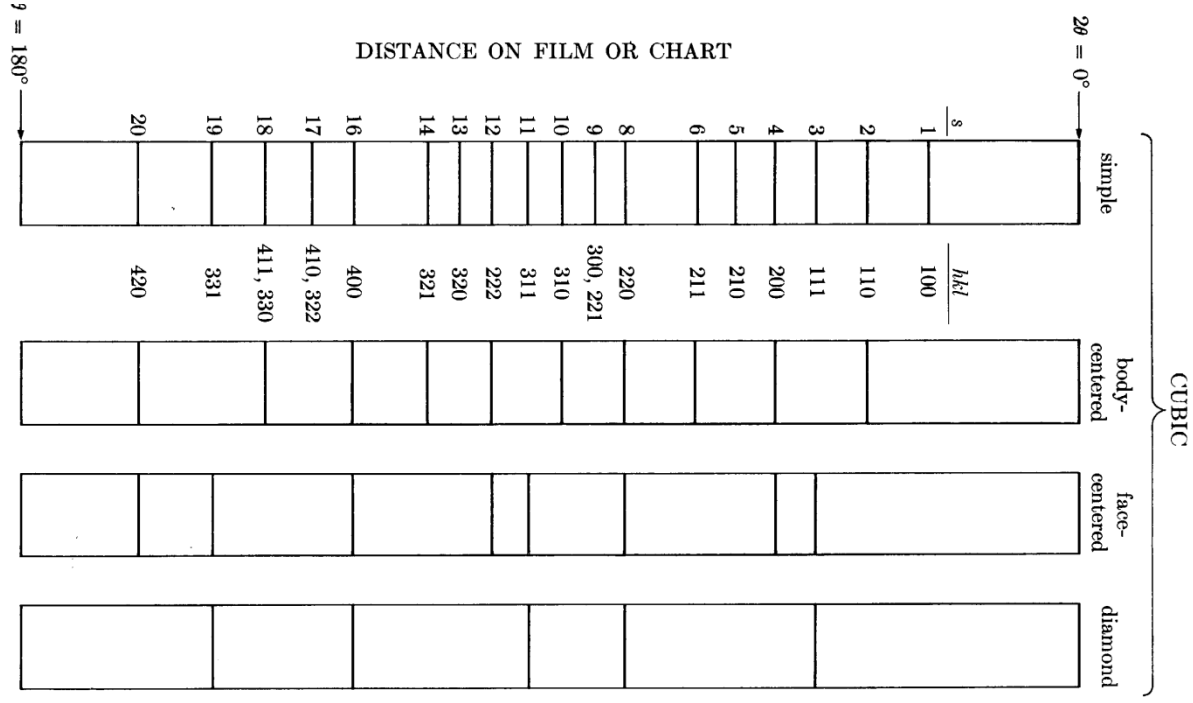
5.2.1 Characteristic line sequences in the cubic system:

(1) Simple cubic: 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, …

(2) Body-centered cubic: 2, 4, 6, 8, 10, 12, 14, 16, …

(3) Face-centered cubic: 3, 4, 8, 11, 12, 16, 19, 20,

(4) Diamond cubic: 3, 8, 11, 16, 19, …



5.2.2 Steps in indexing a cubic pattern:

(1) Identify the peaks.

(2) Determine $sin^2\theta$.

(3) Calculate the ratio $sin^2\theta$ /$sin^2\theta_{min}$ and multiply by the appropriate integers.

(4) Select the result from (3) that yields $(h^2 + k^2 + l^2)$ as an integer.

(5) Compare results with the sequences of $(h^2 + k^2 + l^2)$ values to identify the Bravais lattice.

(6) Calculate lattice parameters.

The following example will illustrate the steps involved in indexing the pattern of a cubic substance and finding its lattice parameter. In this particular example, CuKα radiation was used and eight diffraction lines were observed.

Peak no.	$sin^2\theta$	1× ($sin^2\theta$ /$sin^2\theta_{min}$)	2× ($sin^2\theta$ /$sin^2\theta_{min}$)	3× ($sin^2\theta$ /$sin^2\theta_{min}$)	$(h^2 + k^2 + l^2)$	hkl	aÅ
1	0.140	1.0	2.0	3.0	3	111	3.57
2	0.185	1.3	2.6	3.9	4	200	3.58
3	0.369	2.6	5.3	7.8	8	220	3.59
4	0.503	3.6	7.2	10.8	11	311	3.61
5	0.548	3.9	7.8	11.7	12	222	3.61
6	0.726	5.2	10.4	15.6	16	400	3.62
7	0.861	6.2	12.4	18.6	19	331	3.62
8	0.905	6.5	13.0	19.5	20	420	3.62

Our analysis of line positions therefore leads to the conclusion that the substance involved, copper in this case, is cubic in structure with a lattice parameter of 3.62Å and the Bravais lattice is Face-Centered Cubic.

5.3 Analytical Method for Non-Cubic Crystals

(1) *Tetragonal system*:

The plane-spacing equation for this system involves two unknown parameters, *a* and *c*:

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

Therefore, $sin^2\theta$ values can be given by:

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

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

Where $A = \frac{\lambda^2}{4a^2}$ and $C = \frac{\lambda^2}{4c^2}$ are constants for any pattern.

A can be found from *hk*0 indices:

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

$(h^2 + k^2)$ are 1, 2, 4, 5, 8,.....

then C can be found from other lines:

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

(2) *Hexagonal System*:

The plane-spacing equation for this system also involves two unknown parameters, *a* and *c*:

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

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

Suppose that, $A = \frac{\lambda^2}{3a^2}$ and $C = \frac{\lambda^2}{4c^2}$

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

(3) *Orthorhombic System*:

The plane-spacing equation for this system involves three unknown parameters, *a*, b and *c*:

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

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

Suppose that, $A = \frac{\lambda^2}{2a^2}$, $B = \frac{\lambda^2}{2b^2}$ and $C = \frac{\lambda^2}{2c^2}$

where *h, k* and *l* assume various integral values

5.4 Determination of the number of atoms in a unit cell

To find this number we use the fact that the volume of the unit cell, calculated from the lattice parameters, multiplied by the measured density of the substance equals the weight of all the atoms in the cell.

$$\sum A = \frac{\rho V}{1.66020}$$

where $\sum A$ is the sum of the atomic weights of the atoms in the unit cell, ρ is the density (gm/cm^3), and V is the volume of the unit cell (A^3)). If the substance is an element of atomic weight A, then

$$\sum A = n_1 A$$

where n_1 is the number of atoms per unit cell. If the substance is a chemical compound, or an intermediate phase whose composition can be represented by a simple chemical formula, then

$$\sum A = n_2 M$$

where n_2 is the number of "molecules" per unit cell and M the molecular weight. The number of atoms per cell can then be calculated from n_2 and the composition of the phase.

The following Table give the volume V of the unit cell:

Cubic	$V = a^3$
Tetragonal	$V = a^2 c$
Hexagonal	$V = \frac{\sqrt{3}a^2 c}{2} = 0.866 a^2 c$
orthorhombic	$V = abc$

5.5 Determination of Atomic Positions

We now have to find the positions of a known number of atoms in a unit cell of known shape and size. To solve this problem, we must make use of the observed relative intensities of the diffracted beams, since these intensities are determined by atom positions. There is no known general method of directly calculating atom positions from observed intensities. we must consider the two basic equations involved, namely,

$$I = |F|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right)$$

which gives the relative intensities of the reflected beams, and

$$F_{hkl} = \sum_{1}^{N} f_n e^{2\pi i (hu_n + kv_n + lw_n)}$$

which gives the value of the structure factor F for the hkl reflection in terms of the atom positions uvw. Since the relative intensity I, the multiplicity factor p, and the Bragg angle θ are known for each line on the pattern, we can find the value of $|F|$ for each reflection

Example CdTe

If the lattice parameter is 6.46Å and the density of the specimen is 5.82 gm/cm^3. We then find the atomic weights of the atoms in the unit cell:

$$\sum A = \frac{(5.82)(6.46)^3}{1.66020} = 948$$

Since the molecular weight of CdTe is 240.02, the number of "molecules" per unit cell is 948/240.02 = 3.94$\sim$ 4. At this point, we know that the unit cell of CdTe is cubic and that it contains 4 "molecules" of CdTe, i.e., 4 atoms of cadmium and 4 atoms of tellurium. We must now consider possible arrangements of these atoms in the unit cell.

Peak no.	$sin^2\theta$	hkl
1	0.0462	111
2	0.1198	220
3	0.1615	311
4	0.1790	222
5	0.234	400
6	0.275	331
7	0.346	422
8	0.391	511, 333
9	0.461	440
10	0.504	531
11	0.575	620
12	0.616	533
13	0.688	444
14	0.729	711, 551
15	0.799	642
16	0.840	731, 553

Since die indices of the observed lines (see above Table) are all unmixed, the Bravais lattice must be face-centered. The CdTe structure contains four molecules per unit cell, therefore, there is either the NaCl structure or the zinc-blende form of ZnS.

The next step is to calculate relative diffracted intensities for each structure and compare them with experiment, in order to determine whether or not one of these structures is the correct one. If CdTe has the NaCl structure, then its structure factor for unmixed indices is given by:

$F^2 = 16(f_{Cd} + f_{Te})^2$, if $(h + k + l)$ is even

$F^2 = 16(f_{Cd} - f_{Te})^2$, if $(h + k + l)$ is odd.

On the other hand, if the ZnS structure is correct, then the structure factor for unmixed indices is given by:

$|F|^2 = 16(f_{Cd}^2 + f_{Te}^2)$, if $(h + k + l)$ is odd.

$|F|^2 = 16(f_{Cd}^2 - f_{Te}^2)$, if $(h + k + l)$ is an odd multiple of 2

$|F|^2 = 16(f_{Cd}^2 + f_{Te}^2)$, if $(h + k + l)$ is an even multiple of 2.

We can therefore conclude that CdTe has the structure of the zinc blende form of ZnS.