Determination of crystal structure

Crystal structure		**Diffraction pattern**
Unit cell	←→	**Line positions**
Atom position	←→	**Line intensities**

- Structure determines the diffraction pattern→ it should be possible to determine the structure from the pattern (phase problem)
- **The determination of an unknown structure proceeds in three major steps:**

1. The **shape and size** of the unit cell are deduced from angular position of the diffraction lines (indexing the pattern).
2. The **number of the atoms per unit cell** is then computed from the shape and size of the unit cell, the chemical composition of the specimen, and its measured density.
3. The positions of the atoms within the unit cell are deduced from the relative intensities of the diffraction lines (most difficult step!).

1. Indexing pattern of cubic crystals

For cubic crystal →

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

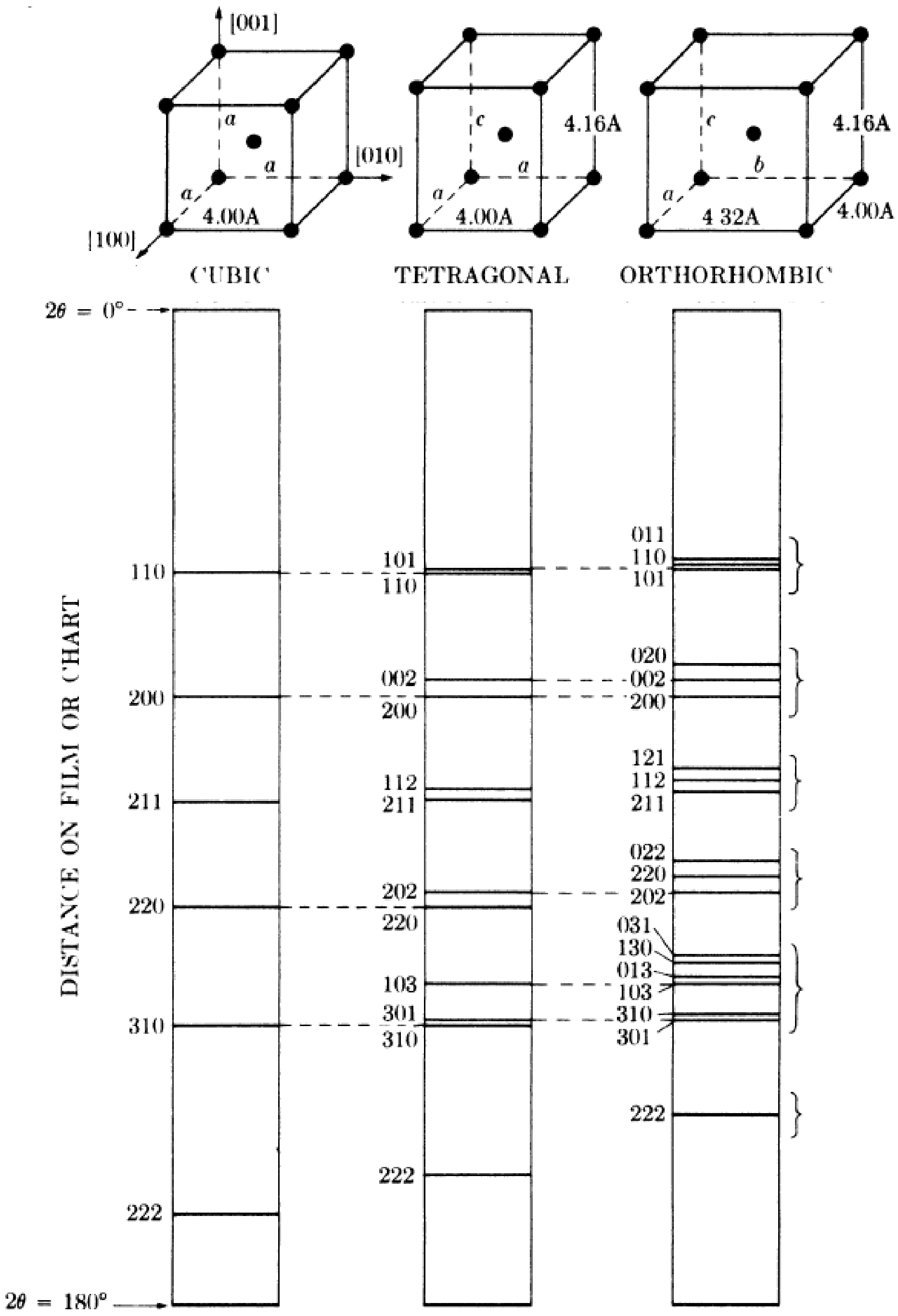
- Finding a **set of integers s** which will yield a constant quotient when divided one by one into the observed $sin^2\theta$ valuses (such as 7,15,23,38,31,… are impossible)
- Each of the four common cubic lattice types has a characteristic sequence of diffraction lines:
  Simple cubic: 1, 2, 3, 4, 5, 6, 8, 10, 11, 12, 13, 14, 16, …
  Body-center cubic: 2, 4, 6, 8, 10, 12, 14, 16, …
  Face-centered cubic: 3, 4, 8, 11, 12, 16, …
  Diamond cubic: 3, 8, 11, 16, …

Bravais lattice:

- There is almost regular sequence of lines in simple cubic and body centered cubic pattern, but the former contains almost twice as many lines, while a face centered cubic pattern is characterized by a pair of lines, followed by a single line, followed by a pair, another single line, etc.

1.1 The effect of cell distortion on the powder pattern:

Any distortion of the unit cell which decreases its symmetry will increase the number of lines on the powder pattern.



- **Left pattern:** calculated diffraction pattern of the bcc substance for a=4 Å and Cr kα radiation.

- If the cubic cell is distorted along only one axis→ then it becomes tetragonal→ its symmetry decreases and more diffraction lines are formed.
- **The center pattern shows the effect of stretching the cubic cell by 4 percent along its [001] axis→ c is 4.16Å**
- **Right pattern**: If tetragonal cell is now stretched by 8 % along its [010] axis, it becomes orthorhombic, with a=4.00Å, b=4.32Å, and c=4.16Å → all more line to the pattern.

The increase in the number of lines is due to introduction of new plane spacing caused by non-uniform distortion.

- ✓ (200), (020),(002) planes all have the same spacing→ one line is formed (200) line
- ✓ This line splits into two lines when the cell becomes tetragonal: (002) plane spacing differs from the other two.
- ✓ When cell become orthorhombic → all three spacing are different→ three line are formed

2. Determination of the number of atoms in the unit cell:

After establishing the shape and size of the unit cell → number of the atoms in the unit cell must be known before their position can be determined.

- **Volume of the unit cell × density of substance= weight of all atoms in unit cell**

$$\rho = \frac{\sum A/N}{V} = \frac{\sum A}{NV} = \frac{\sum A}{(6.02257 \times 10^{23})(V' \times 10^{-24})} = \frac{1.66042 \sum A}{V'}$$

Where ρ is in g/cm^3 and V' is the unit cell volume in Å^3

$\sum A$ = sum of the atomic weights of all the atoms in the unit cell, V = volume of unit cell (cm^3)

$$\sum A = \rho V'/1.66042$$

If the substance is an element of atomic weight A, → $\sum A = n_1 A$

n_1 is number of the atoms per unit cell.

3. Determination of Atom position

To find the position of a known number of atoms in a unit cell of known shape and size→ use of observed relative intensities of the diffracted beam, since these intensities are determined by atom positions.

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

gives the relative intensities of the reflected beams.

- $F_{hkl} = \sum_1^N f_n e^{2\pi i (hu_n + kv_n + lw_n)}$, N atoms of the unit cell

gives the value of the structure factor F for the hkl reflection in terms of the atom position $u\, v\, w$.

- p is multiplicity
- I , P and Bragg angle are known → $|F|$ can be found.
- But $|F|$ measures only the relative amplitude of the each reflection whereas we need value of F which measures both the **amplitude** and **phase** of one reflection relative to another. This “phase problem” is crux of the problem.