

Röntgenbeugung-Intensität (II):

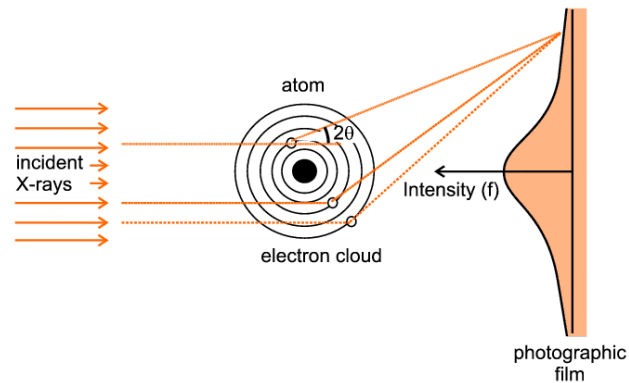
Application to powder method:

There are six factors affecting the relative intensity (I) of the diffraction lines on a powder pattern:

- Polarization factor
- Structure factor
- Multiplicity factor
- Lorenz factor
- Absorption factor
- Temperature factor

6.1 Polarization factor:

$$I \propto \frac{1}{2} (1 + \cos^2 2\theta)$$



6.2 Structure factor

$$I \propto |F_{hkl}|^2$$

6.3 Multiplicity factor (p):

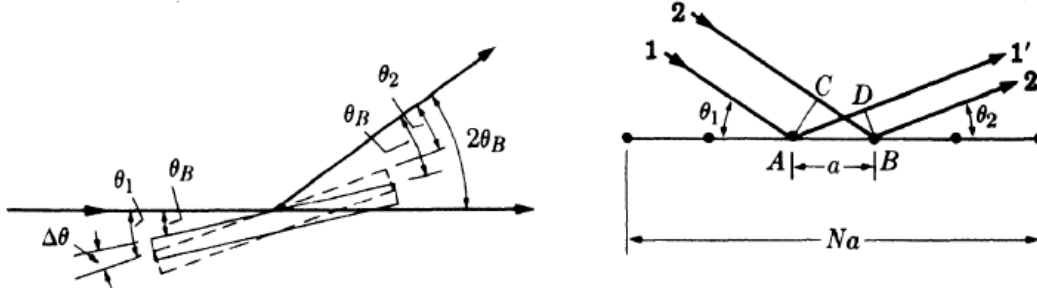
- The relative proportion of planes contributing to the same reflection enters the intensity equation as the quantity p, the **multiplicity factor**.
→ the number of different planes in a form having the same spacing.
- The value of p depends on the crystal system: in the tetragonal crystal, the (100) and (001) planes do not have the same spacing → p for {100} is 4 and for {001} is 2
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Multiplicity factors for the powder method								
Flächen-Häufigkeitszahlen von Netzebenen bei Debye-Scherrer Aufnahmen (R.Glocker)								
Cristal system	Indices							
	(hkl)	(hhl)	(h0l) (0kl)	(hk0)	(hh0)	(hhh)	(h00) (0k0)	(00l)
rhombisch	8	8	4	7	4	8	2	2
tetragonal	16	8	8	8	4	8	4	2
kubisch	48	24	24	24	12	8	6	6

6.4 Lorenz factor (Geometry dependence of the intensity)

6.4.1 first geometry factor:

- The integrated intensity of a reflection depends on the particular value of θ_B involved via the maximum intensity and the breadth.
- The value of $I_{\max}$ of the curve depends on the angular range ($\Delta\theta$) of crystal rotation over which the energy diffracted in the direction $2\theta_B$ is appreciable.



- $\Delta\theta = \frac{\lambda}{2Na\sin\theta}$, where a is atom spacing in the plane and Na the total length of the plane $\rightarrow$ this Eq. gives the maximum angular range of crystal rotation over which appreciable energy will be diffracted in the direction $2\theta_B$.
- $I_{\max}$ depends on this range $\rightarrow I_{\max} \propto \frac{1}{\sin\theta}$
- B (breadth) $\propto \frac{1}{\cos\theta_B}$ (Scherrer Eq.)
- Integrated intensity $\propto I_{\max}B \rightarrow I \propto \frac{1}{\sin^2\theta_B}$
- The powder method is the equivalent of single-crystal rotation.

6.4.2. second geometry factor:

- In powder method a second geometry factor arises
 $\rightarrow$ Integrated intensity depends on the number of crystals oriented at or near Bragg angle
- $\frac{\Delta N}{N} = \frac{\Delta\theta \cos\theta_B}{2}$, where ΔN is number of the crystals and N the total number
 $\rightarrow$ number of crystals oriented at or near Bragg angle $\propto \cos\theta_B$

6.4.3. third geometry factor:

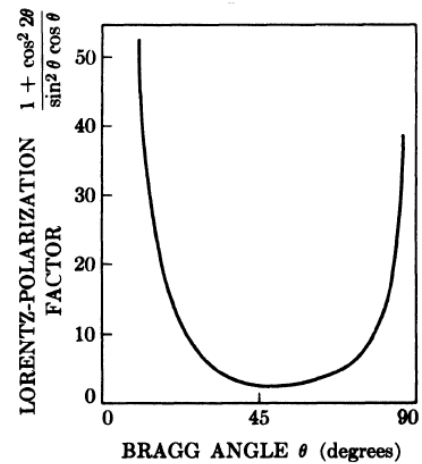
- In assessing relative intensities, we do not compare the total diffracted energy in one cone of rays with that in another but rather the integrated intensity per unit length of one diffraction line with that of another
 $\rightarrow$ the relative intensity per unit length of line $\propto \frac{1}{\sin^2\theta_B}$
- The three geometry factors are combined in one

$$\rightarrow \text{Lorentz factor} = \frac{1}{\sin 2\theta_B} \cdot \cos \theta_B \cdot \frac{1}{\sin 2\theta_B} = \frac{1}{4\sin^2 \theta \cos \theta}$$

→ **Lorentz factor + polarization factor** → **Lorentz-**

$$\text{polarization factor} = \frac{1 + \cos^2 \theta}{\sin^2 \theta \cos \theta}$$

- The overall effect of these geometry factor
→ decrease of the intensity of reflection at intermediate angles compared to those in forward or backward directions



Lorentz-polarization factor

(B. D. CULLITY 1977)

6.5 Absorption factor (A)

- The calculation of A depends on the geometry of the diffraction method involved.

6.6 Temperature factor

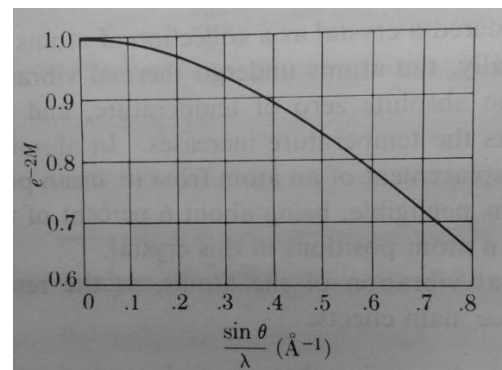
- Atoms vibrate about their mean position even at absolute zero.

Thermal vibration effects:

- The unit cell expands → plane spacing d changes → change in 2θ position of the diffraction lines
- The intensity of the diffraction lines decreases
- The intensity of the background scattering between lines decreases

Variations in intensity with 2θ at constant temperature.

- Thermal agitation decrease the intensity → the reinforcement is not perfect
- The thickness of the platelike “planes” in which the vibrating atoms lie is (on the average) 2u
→ u is the average displacement of an atom from mean position
- T increases → u/d increases → reinforcement become more imperfect
- High- θ reflection involve planes of low d**
→ thermal vibration causes a greater decrease in the reflected intensity at high angles than at low angles.
- In intensity calculation we allow for this effect by introducing the temperature factor e^{-2M} → e^{-2M} decreases as 2θ increases



Temperature factor e^{-2M} of iron at 20°C as a function of $(\sin \theta)/\lambda$ (B. D. CULLITY 1977)

- The quantity M depends on both the amplitude u of thermal vibration and the scattering angle 2θ

$$\rightarrow M = 2\pi^2 \left(\frac{\overline{u^2}}{d^2} \right) = 8\pi^2 \overline{u^2} \left(\frac{\sin\theta}{\lambda} \right)^2 = B \left(\frac{\sin\theta}{\lambda} \right)^2$$

The $\overline{u^2}$ is the mean square displacement of the atom in a direction normal to the reflecting planes.

Debye has given the following expression:

$$\rightarrow M = \frac{6h^2T}{mk\Theta^2} \left[\phi(x) + \frac{x}{4} \right] \left(\frac{\sin\theta}{\lambda} \right)^2$$

Where h is Planck's constant, T the absolute temperature, m the mass of vibrating atom, k Boltzmann's constant, Θ the Debye characteristic temperature of the substance in K,

$x = \frac{\Theta}{T}$, and $[\phi(x)]$ is a function tabulated, along with values of Θ . In Appendix 15.

Because $m = A/N$, where A = Atomic weight and N = Avogadro's number, the coefficient of the bracket terms above becomes

$$\frac{6h^2T}{mk\Theta^2} = \frac{6(6.02 \times 10^{26})(6.63 \times 10^{-34})^2T}{A\Theta^2(1.38 \times 10^{-23})(10^{-20})} = \frac{1.15 \times 10^4 T}{A\Theta^2}$$

if λ is in Å. This equation is approximate and applied only to elements with cubic crystal structure.

- **The temperature effect and absorption effect depends on angles in opposite ways
→ to a first approximation, cancel each other in Debye-Scherrer method**

7. Intensity of powder pattern lines:

- The relative intensity of powder pattern lines:

Debye-Scherrer Camera:

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

Where I = relative integrated intensity (arbitrary units), F = structure factor, p = multiplicity factor. And θ = Bragg angle.

- Omission of the temperature and absorption factors means that this Eq. is valid only for lines fairly close together on the pattern.
- This Eq. gives relative integrated intensity, i.e., the relative area under the curve of intensity vs. 2θ

$$I = |F|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) A(\theta) e^{-2M}, \text{ (Exact expression)}$$