Intensity of XRD peak

???????

Integrated peak intensity

Peak breadth

background

Peak position
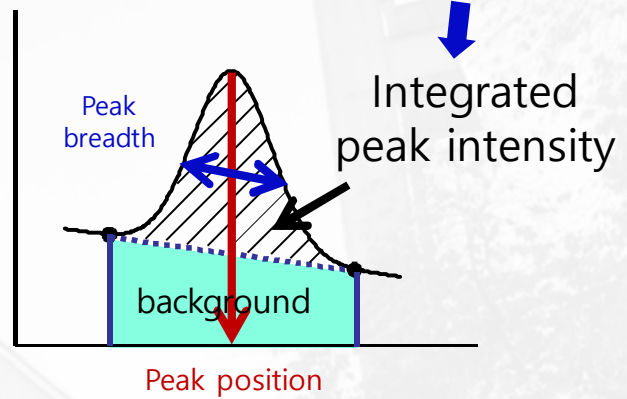
Cullity, Chapter 4-1, 4-2, 4-3, 4-4, 4-5, 4-6

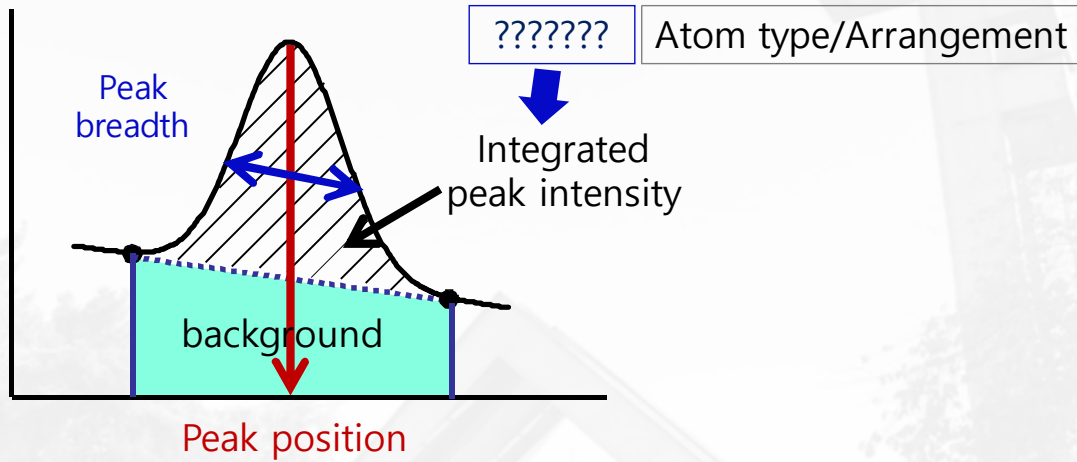Hammond Chapter 9.1, 9.2

Sherwood & Cooper, Chapter 4.13

Sherwood & Cooper, Chapter 4.11~4.12

Krawitz Chapter 5, p132 ~ p143


Reading recommendations

Read

➢ Sherwood & Cooper

  ✓ Chap 5 Fourier Transform & convolutions

  ✓ Chap 6 Diffraction

  ✓ Chap 7 Diffraction by one-dimensional obstacles

  ✓ Chap 8 Diffraction by 3-dimensional obstacles

  ✓ Chap 9 The contents of unit cell
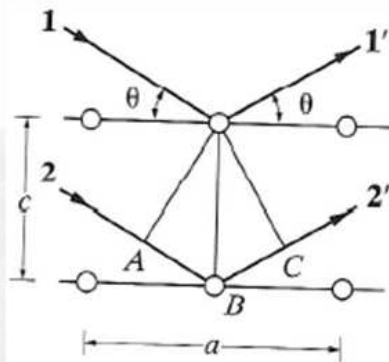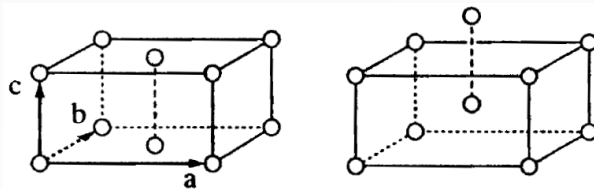
➢ Hammond, Chap 7 The diffraction of light

SEOUL NATIONAL UNIVERSITY

Peak breadth

??????? Atom type/Arrangement

Integrated peak intensity

background

Peak position

Crystal Structure of "cubic" "ZrO2"

Space Group Fm$\bar{3}$m (225)
→ cubic
Lattice Parameter a=5.11

Atom	x	y	z	B_{iso}	occupancy
Zr	0	0	0	1.14	1
O	0.25	0.25	0.25	2.4	1

Zr /Y   O

3

SEOUL NATIONAL UNIVERSITY
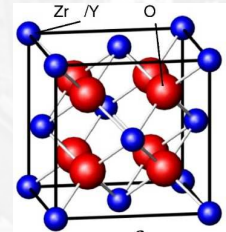
(a) base-centered orthorhombic lattice

(b) body-centered orthorhombic lattice

atom position ←——→ intensity

relation

Cullity page 124

4
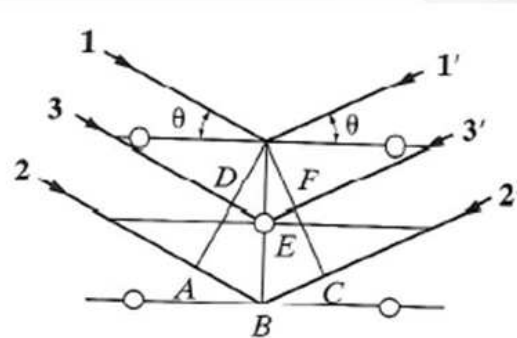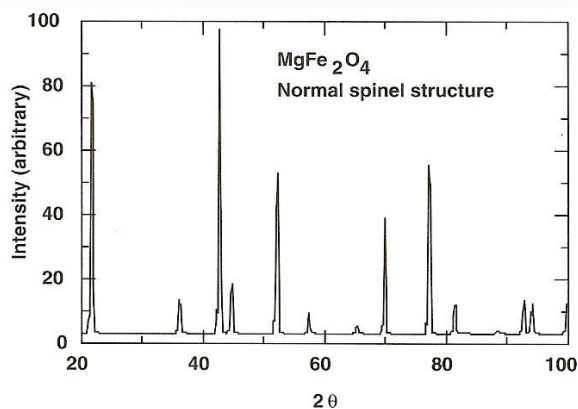
Spinel AB_2O_4

Oxygen; cubic close packing

MFe_2O_4
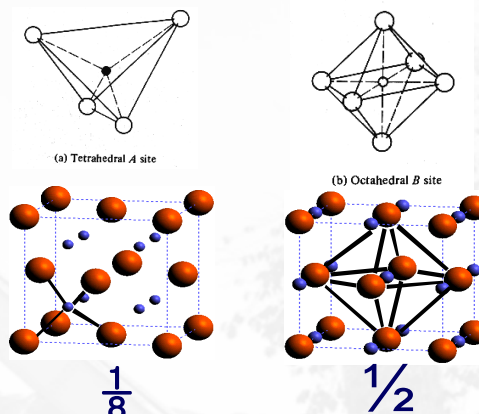
Kind of site	Number available	Number occupied	Occupants Normal spinel	Inverse spinel
Tetrahedral (A)	64	8	8 M^{2+}	8 Fe^{3+}
Octahedral (B)	32	16	16 Fe^{3+}	8 Fe^{3+} 8 M^{2+}

Factors affecting line intensities of XRPD peaks

factor	parameter	factor	parameter
Structure-sensitive	Atomic scattering factor	Sample-sensitive	Microabsorption
	Structure factor		Crystallite size
	Polarization		Degree of crystallinity
	Multiplicity		Residual stress
	Temperature		Degree of peak overlap
Instrument-sensitive (Absolute intensity)	Source intensity	Measurement-sensitive	Preferred orientation
	Diffractometer efficiency		Method of peak area measurement
	Voltage drift		Degree of peak overlap
	Takeoff angle of tube		Method of background subtraction
	Receiving slit width		Kα2 stripping or not
	Axial divergence allowed		Degree of data smoothing used
Instrument-sensitive (Relative intensity)	Divergence slit aperture		
	Detector dead time		

??????? → Integrated peak intensity

Atom type/Arrangement → complicated

✓ Structure factor
✓ Polarization
✓ Multiplicity
✓ Temperature
✓ Absorption
✓ Degree of crystallinity
✓ Particle orientation

Crystal Structure of "cubic" "ZrO2"

Space Group Fm$\bar{3}$m (225)
→ cubic
Lattice Parameter a=5.11

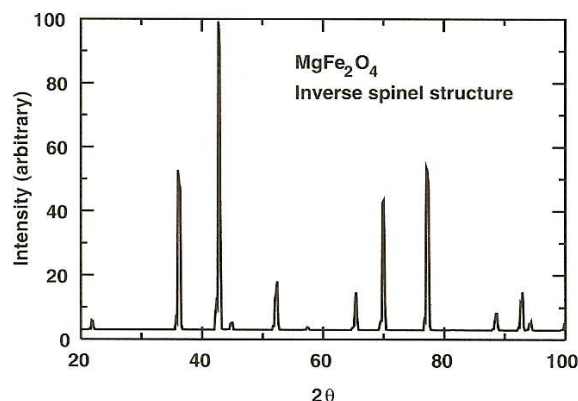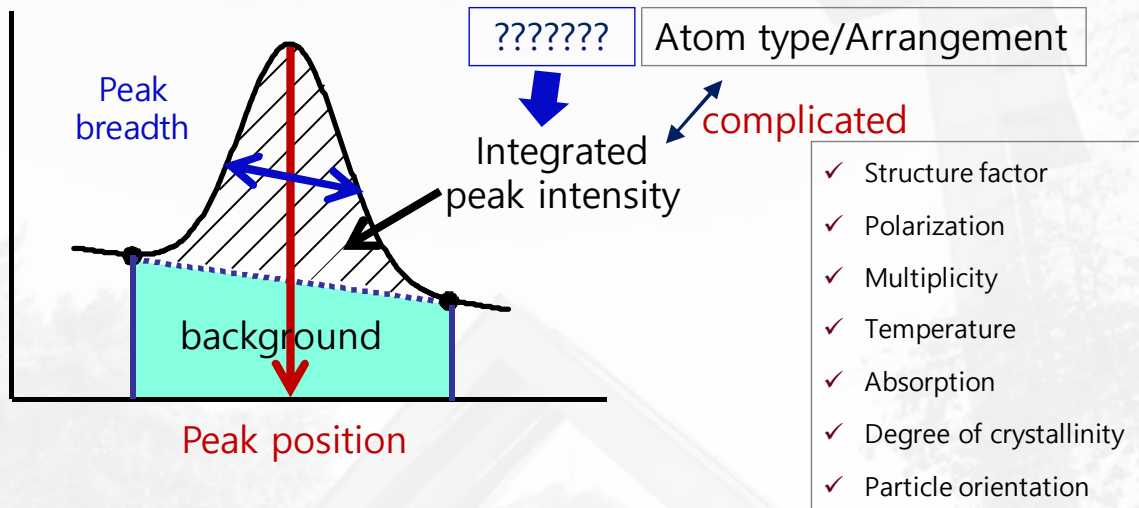| Atom	x	y	z	B_{iso}	occupancy
Zr	0	0	0	1.14	1
O	0.25	0.25	0.25	2.4	1

Zr /Y   O

Intensity diffracted by a single phase powder specimen in a diffractometer

$$I(hkl) = \left(\frac{I_oA\lambda^3}{32\pi r}\right)\left[\left(\frac{\mu_o}{4\pi}\right)^2\frac{e^4}{m^2}\right]\left(\frac{1}{v^2}\right)\left[|F(hkl)|^2 p\left(\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\right)\right]\left(\frac{e^{-2M}}{2\mu}\right).$$

I(hkl) = integrated intensity per unit length of diffraction line

I_0 = intensity of incident beam   A = cross-sectional area of incident beam

r = radius of diffractometer circle   V = volume of unit cell

F(hkl) = structure factor   p = multiplicity factor

e^{-2M} = temperature factor   μ = linear absorption coefficient

Relative intensity

d(A)	Int-f	h	k	l
3.2600	13	1	1	1
2.8210	100	2	0	0
1.9940	55	2	2	0
1.7010	2	3	1	1
1.6280	15	2	2	2
1.4100	6	4	0	0

Peak position ← Bragg's law

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

➢ How much Intensity <u>a single electron </u>will coherently scatter?

➢ <u>Interference</u> effects due to electrons being distributed in space around atoms

➢ Atoms are not stationary --- vibrate

➢ Intereference effects caused by <u>scattering from atoms in different regions of the unit cell</u>

Unit cell
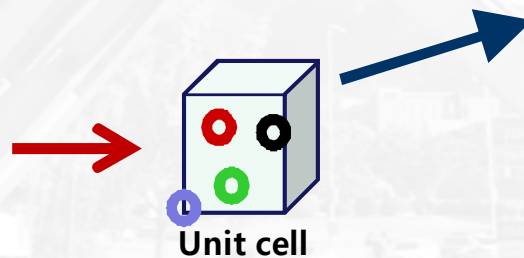
➢ Coherent scattering (unmodified scattering)

✓ Tightly bound electrons

➢ Incoherent scattering (modified scattering)

✓ loosely bound electrons
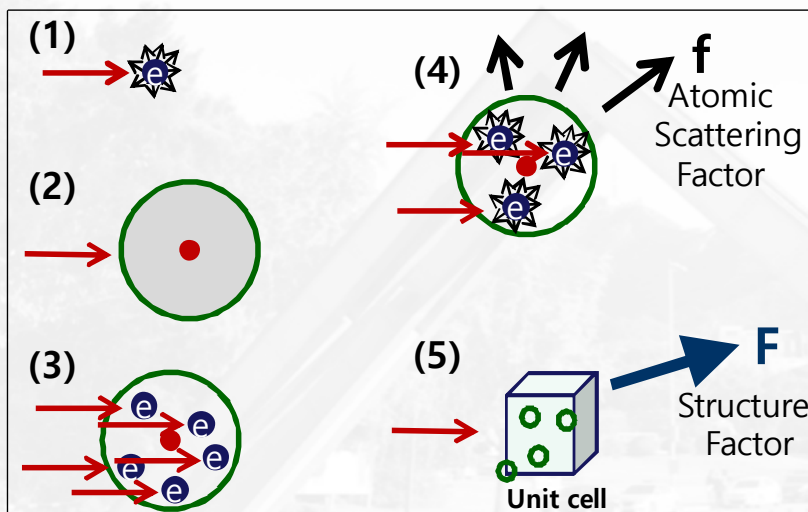
→ background

➢ Diffraction = reinforced coherent scattering

Read Cullity Chap 4-3

> Structure factor

> Polarization factor

> Multiplicity factor

> Lorentz factor

> Absorption factor

> Temperature factor

Atomic Scattering Factor (f), Structure Factor (F)

> Scattering from a single electron

> Scattering from a single atom → **f**

> Scattering from a unit cell → **F**

Scatter from
Multiple Atoms

Scatter from
an Atom

Scatter from
an Electron

10 μm

10 nm

1 Å

(1)

(2)

(3)

(4) **f**
Atomic
Scattering
Factor

(5) **F**
Structure
Factor

Unit cell

SEOUL NATIONAL UNIVERSITY
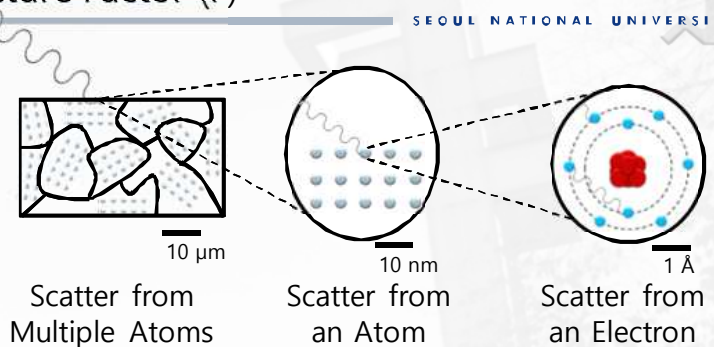
➢ Scattering amplitude of a single electron

  ✓ How much Intensity a single e′ will coherently scatter?

➢ Scattering amplitude of a single atom → **f** (atomic scattering factor)

  ✓ Interference effects due to coherent scatter of all the e′′s in an atom?

➢ Scattering amplitude of a unit cell → **F** (structure factor)

  ✓ Interference effects caused by scattering from all the atoms in different regions of the unit cell

$$\mathbf{f} = \frac{\text{amplitude scattered by an atom}}{\text{amplitude scattered by a single } e'}$$

$$\mathbf{F} = \frac{\text{amplitude scattered by all the atoms of a unit cell}}{\text{amplitude scattered by a single } e'}$$

SEOUL NATIONAL UNIVERSITY

→ polarization factor

➢ X-ray is electromagnetic radiation which can be seen, from a fixed point in space, as an oscillating electric field.

➢ This field can cause an e′ to oscillate (accelerate & decelerate). → cause an e′ to re-radiate the energy as a spherical wave.

➢ J.J. Thomson --- Intensity scattered from an e′

$$I = \frac{I_0}{r^2}\left[\frac{e^2}{m_e c^2}\right]^2 \frac{1 + \cos^2(2\theta)}{2}$$

➢ Incident X-ray is unpolarized.

➢ Process of scattering polarizes X-ray. → polarization factor

$$\frac{1 + \cos^2(2\theta)}{2}$$
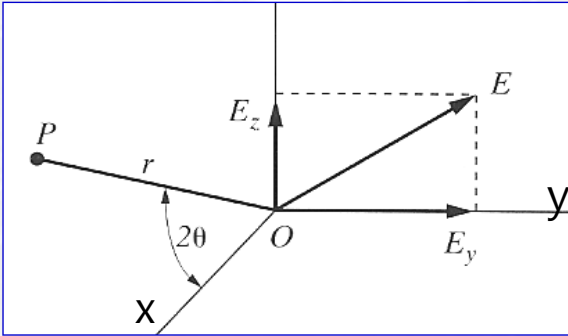
Scattering by a single electron

J.J. Thomson

$$I = I_O \left(\frac{\mu_O}{4\pi}\right)^2 \left(\frac{e^4}{m^2 r^2}\right) \sin^2 \alpha = I_O \frac{K}{r^2} \sin^2 \alpha$$

$$I_{Py} = I_{Oy} \frac{K}{r^2} \qquad \alpha = \sphericalangle yOP = \pi/2.$$

$$I_{Pz} = I_{Oz} \frac{K}{r^2} \cos^2 2\theta. \qquad \alpha = \pi/2 - 2\theta$$

α = angle b/w scattering direction & acceleration direction of e′

$$E^2 = E_y^2 + E_z^2$$
$$E_y^2 = E_z^2 = \tfrac{1}{2}E^2$$
$$I_{Oy} = I_{Oz} = \tfrac{1}{2}I_O$$

Read Cullity page 123 ~ 144

Total scattered intensity @ P

$$I_P = I_{Py} + I_{Pz}$$

$$= \frac{K}{r^2}(I_{Oy} + I_{Oz}\cos^2 2\theta)$$

$$= \frac{K}{r^2}\left(\frac{I_O}{2} + \frac{I_O}{2}\cos^2 2\theta\right)$$

$$= I_O \frac{K}{r^2}\left(\frac{1 + \cos^2 2\theta}{2}\right).$$

Thomson equation for the scattering of X-ray beam by a single electron

Polarization factor

X-ray scattering by an atom → f (atomic scattering factor)

3
Path difference b/w 3 & 4 ≠ 0

f'n(sinθ/λ)

4

1

2

Path difference b/w 1 & 2 = 0
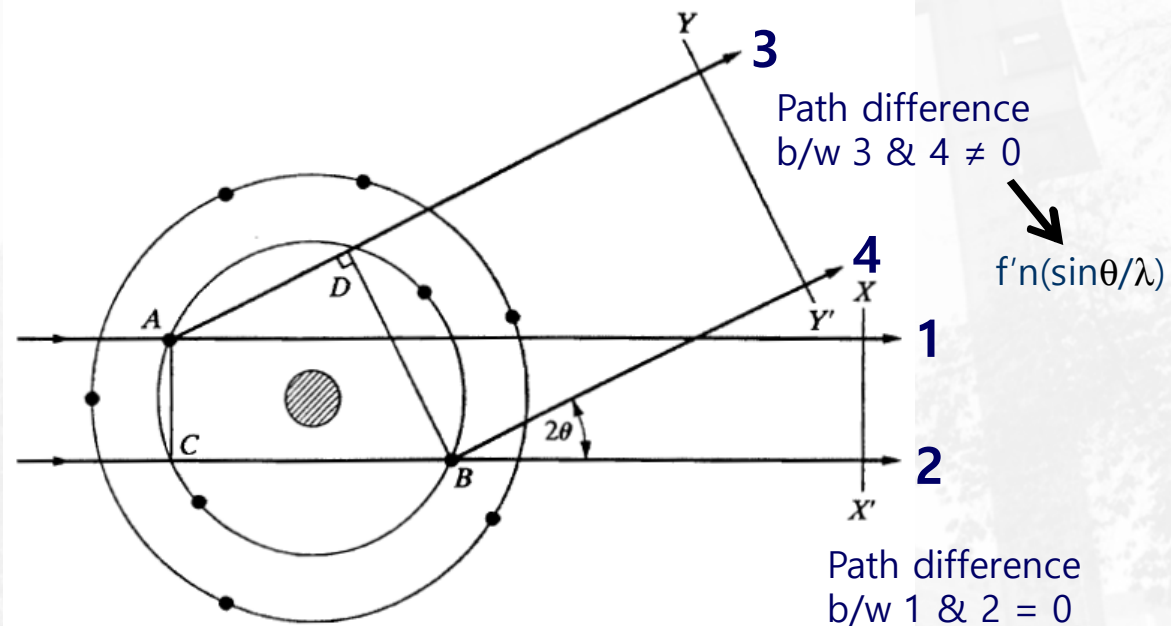
f (atomic scattering factor)
= efficiency of scattering of an atom in a given direction

Interference effect due to the e's distributed in space around atoms

→ atomic scattering factor

- Interference ← scattering from different regions of the e' cloud
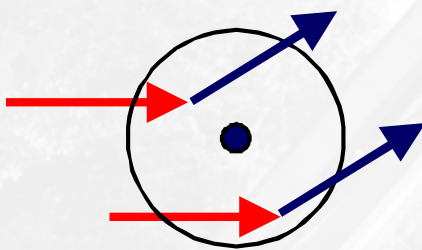- Takes into account the influence of the atom specific e' shell on the scattering of X-rays.
- Normalized in units of the amount of scattering occurring from a single e'.

$$f = \frac{\text{amplitude scattered by an atom}}{\text{amplitude scattered by a single electron}}$$

$$f = F(\vartheta) \qquad f(0^o) = Z$$
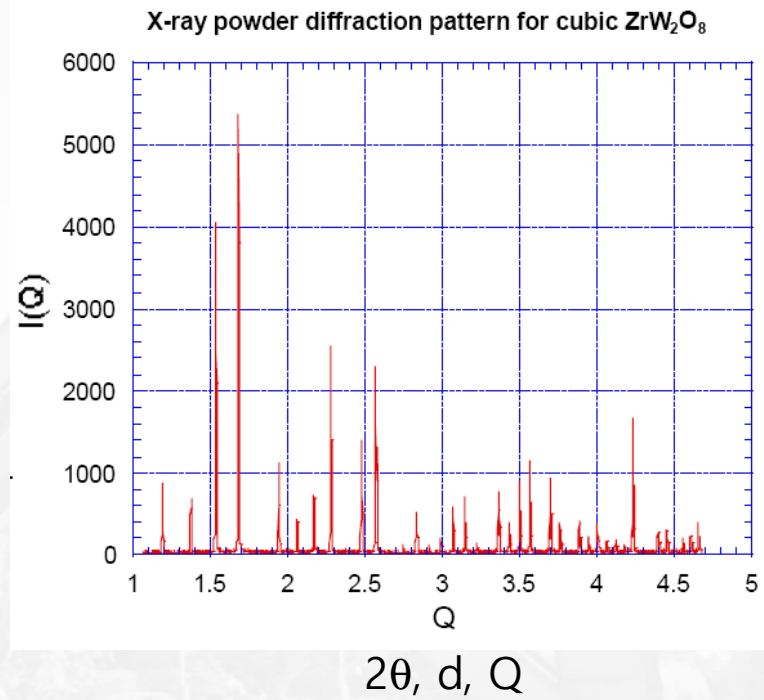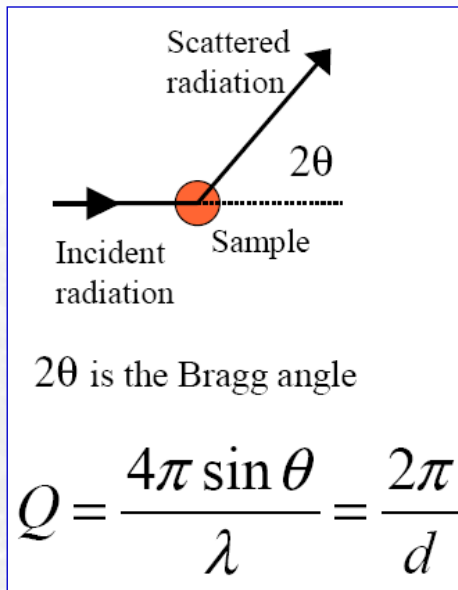$$f'n(\sin\theta/\lambda)$$

Atomic scattering factor (form factor)
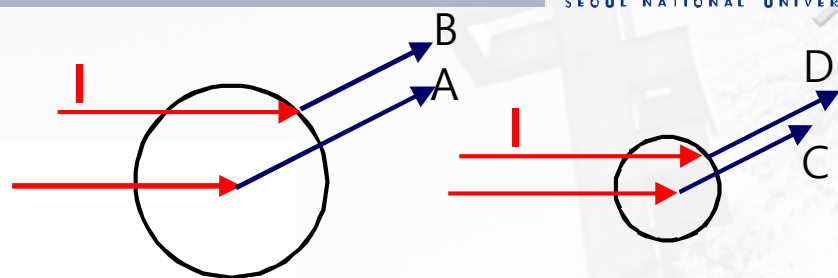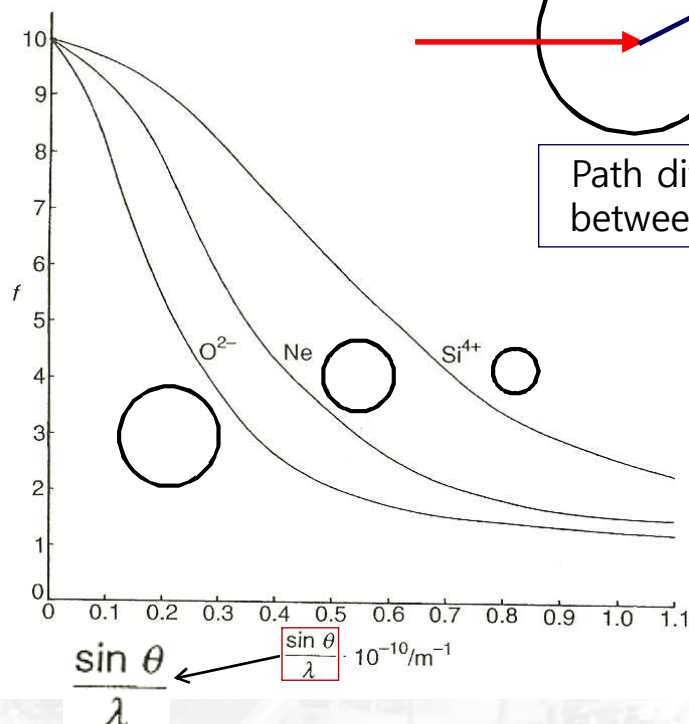
| Path difference between A & B | > | Path difference between C & D |

$$\phi = \frac{\delta}{\lambda}(2\pi)$$

$$\frac{\sin\theta}{\lambda} \quad \leftarrow \quad \boxed{\frac{\sin\theta}{\lambda}} \cdot 10^{-10}/\text{m}^{-1}$$

XRPD pattern

Scattered radiation

2θ

Sample

Incident radiation

2θ is the Bragg angle

$$Q = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{d}$$

X-ray powder diffraction pattern for cubic ZrW_2O_8

2θ, d, Q

Atomic scattering factor

$\frac{\sin\theta}{\lambda}$ (Å⁻¹)		0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
H	1	0.81	0.48	0.25	0.13	0.07	0.04	0.03	0.02	0.01	0.00	0.00		
He	2	1.88	1.46	1.05	0.75	0.52	0.35	0.24	0.18	0.14	0.11	0.09		
Li$^+$	2	1.96	1.8	1.5	1.3	1.0	0.8	0.6	0.5	0.4	0.3	0.3		
Li	3	2.2	1.8	1.5	1.3	1.0	0.8	0.6	0.5	0.4	0.3	0.3		
Be^{+2}	2	2.0	1.9	1.7	1.6	1.4	1.2	1.0	0.9	0.7	0.6	0.5		
Be	4	2.9	1.9	1.7	1.6	1.4	1.2	1.0	0.9	0.7	0.6	0.5		
B^{+3}	2	1.99	1.9	1.8	1.7	1.6	1.4	1.3	1.2	1.0	0.9	0.7		
B	5	3.5	2.4	1.9	1.7	1.5	1.4	1.2	1.2	1.0	0.9	0.7		
C	6	4.6	3.0	2.2	1.9	1.7	1.6	1.4	1.3	1.16	1.0	0.9		
N^{+5}	2	2.0	2.0	1.9	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.16		
N^{+3}	4	3.7	3.0	2.4	2.0	1.8	1.66	1.56	1.49	1.39	1.28	1.17		
N	7	5.8	4.2	3.0	2.3	1.9	1.65	1.54	1.49	1.39	1.29	1.17		
O	8	7.1	5.3	3.9	2.9	2.2	1.8	1.6	1.5	1.4	1.35	1.26		
O^{-2}	10	8.0	5.5	3.8	2.7	2.1	1.8	1.5	1.5	1.4	1.35	1.26		
F	9	7.8	6.2	4.45	3.35	2.65	2.15	1.9	1.7	1.6	1.5	1.35		
F$^-$	10	8.7	6.7	4.8	3.5	2.8	2.2	1.9	1.7	1.55	1.5	1.35		
Ne	10	9.3	7.5	5.8	4.4	3.4	2.65	2.2	1.9	1.65	1.55	1.5		
Na$^+$	10	9.5	8.2	6.7	5.25	4.05	3.2	2.65	2.25	1.95	1.75	1.6		
Na	11	9.65	8.2	6.7	5.25	4.05	3.2	2.65	2.25	1.95	1.75	1.6		
Mg^{+2}	10	9.75	8.6	7.25	5.95	4.8	3.85	3.15	2.55	2.2	2.0	1.8		
Mg	12	10.5	8.6	7.25	5.95	4.8	3.85	3.15	2.55	2.2	2.0	1.8		
Al^{+3}	10	9.7	8.9	7.8	6.65	5.5	4.45	3.65	3.1	2.65	2.3	2.0		
Al	13	11.0	8.95	7.75	6.6	5.5	4.5	3.7	3.1	2.65	2.3	2.0		
Si^{+4}	10	9.75	9.15	8.25	7.15	6.05	5.05	4.2	3.4	2.95	2.6	2.3		
Si	14	11.35	9.4	8.2	7.15	6.1	5.1	4.2	3.4	2.95	2.6	2.3		
P^{+5}	10	9.8	9.25	8.45	7.5	6.55	5.65	4.8	4.05	3.4	3.0	2.6		
P	15	12.4	10.0	8.45	7.45	6.5	5.65	4.8	4.05	3.4	3.0	2.6		
P^{-3}	18	12.7	9.8	8.4	7.45	6.5	5.65	4.85	4.05	3.4	3.0	2.6		
S^{+6}	10	9.85	9.4	8.7	7.85	6.85	6.05	5.25	4.5	3.9	3.35	2.9		
S	16	13.6	10.7	8.95	7.85	6.85	6.0	5.25	4.5	3.9	3.35	2.9		
S^{-2}	18	14.3	10.7	8.9	7.85	6.85	6.0	5.25	4.5	3.9	3.35	2.9		
Cl	17	14.6	11.3	9.25	8.05	7.25	6.5	5.75	5.05	4.4	3.85	3.35		
Cl$^-$	18	15.2	11.5	9.3	8.05	7.25	6.5	5.75	5.05	4.4	3.85	3.35		
A	18	15.9	12.6	10.4	8.7	7.8	7.0	6.2	5.4	4.7	4.1	3.6		
K$^+$	18	16.5	13.3	10.8	8.85	7.75	7.05	6.44	5.9	5.3	4.8	4.2		
K	19	16.5	13.3	10.8	9.2	7.9	6.7	5.9	5.2	4.6	4.2	3.7	3.3	
Ca^{+2}	18	16.8	14.0	11.5	9.3	8.1	7.35	6.7	6.2	5.7	5.1	4.6		
Ca	20	17.5	14.1	11.4	9.7	8.4	7.3	6.3	5.6	4.9	4.5	4.0	3.6	
Sc^{+3}	18	16.7	14.0	11.4	9.4	8.3	7.6	6.9	6.4	5.8	5.35	4.85		
Sc	21	18.4	14.9	12.1	10.3	8.9	7.7	6.7	5.9	5.3	4.7	4.3	3.9	
Ti^{+4}	18	17.0	14.4	11.9	9.9	8.5	7.85	7.3	6.7	6.15	5.65	5.05		
Ti	22	19.3	15.7	12.8	10.9	9.5	8.2	7.2	6.3	5.6	5.0	4.6	4.2	
V	23	20.2	16.6	13.5	11.5	10.1	8.7	7.6	6.7	5.9	5.3	4.9	4.4	
Cr	24	21.1	17.4	14.2	12.1	10.6	9.2	8.0	7.1	6.3	5.7	5.1	4.6	
Mn	25	22.1	18.2	14.9	12.7	11.1	9.7	8.4	7.5	6.6	6.0	5.4	4.9	

Cullity page 634, Appendix 10

Atomic scattering factor

$\frac{\sin\theta}{\lambda}(\text{Å}^{-1})$	0.0	0.1	0.2	0.3	0.4
H	1	0.81	0.48	0.25	0.13
He	2	1.88	1.46	1.05	0.75
Li^+	2	1.96	1.8	1.5	1.3
Li	3	2.2	1.8	1.5	1.3
Be^{+2}	2	2.0	1.9	1.7	1.6
Be	4	2.9	1.9	1.7	1.6
B^{+3}	2	1.99	1.9	1.8	1.7
B	5	3.5	2.4	1.9	1.7
C	6	4.6	3.0	2.2	1.9
N^{+5}	2	2.0	2.0	1.9	1.9
N^{+3}	4	3.7	3.0	2.4	2.0
N	7	5.8	4.2	3.0	2.3
O	8	7.1	5.3	3.9	2.9
O^{-2}	10	8.0	5.5	3.8	2.7
F	9	7.8	6.2	4.45	3.35

Cullity page 634, Appendix 10

Atomic scattering factor

$\frac{\sin\theta}{\lambda}(\text{Å}^{-1})$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
Fe	26	23.1	18.9	15.6	13.3	11.6	10.2	8.9	7.9	7.0	6.3	5.7	5.2
Co	27	24.1	19.8	16.4	14.0	12.1	10.7	9.3	8.3	7.3	6.7	6.0	5.5
Ni	28	25.0	20.7	17.2	14.6	12.7	11.2	9.8	8.7	7.7	7.0	6.3	5.8
Cu	29	25.9	21.6	17.9	15.2	13.3	11.7	10.2	9.1	8.1	7.3	6.6	6.0
Zn	30	26.8	22.4	18.6	15.8	13.9	12.2	10.7	9.6	8.5	7.6	6.9	6.3
Ga	31	27.8	23.3	19.3	16.5	14.5	12.7	11.2	10.0	8.9	7.9	7.3	6.7
Ge	32	28.8	24.1	20.0	17.1	15.0	13.2	11.6	10.4	9.3	8.3	7.6	7.0
As	33	29.7	25.0	20.8	17.7	15.6	13.8	12.1	10.8	9.7	8.7	7.9	7.3
Se	34	30.6	25.8	21.5	18.3	16.1	14.3	12.6	11.2	10.0	9.0	8.2	7.5
Br	35	31.6	26.6	22.3	18.9	16.7	14.8	13.1	11.7	10.4	9.4	8.6	7.8
Kr	36	32.5	27.4	23.0	19.5	17.3	15.3	13.6	12.1	10.8	9.8	8.9	8.1
Rb^+	36	33.6	28.7	24.6	21.4	18.9	16.7	14.6	12.8	11.2	9.9	8.9	
Rb	37	33.5	28.2	23.8	20.2	17.9	15.9	14.1	12.5	11.2	10.2	9.2	8.4
Sr	38	34.4	29.0	24.5	20.8	18.4	16.4	14.6	12.9	11.6	10.5	9.5	8.7
Y	39	35.4	29.9	25.3	21.5	19.0	17.0	15.1	13.4	12.0	10.9	9.9	9.0
Zr	40	36.3	30.8	26.0	22.1	19.7	17.5	15.6	13.8	12.4	11.2	10.2	9.3
Nb	41	37.3	31.7	26.8	22.8	20.2	18.1	16.0	14.3	12.8	11.6	10.6	9.7
Mo	42	38.2	32.6	27.6	23.5	20.8	18.6	16.5	14.8	13.2	12.0	10.9	10.0
Tc	43	39.1	33.4	28.3	24.1	21.3	19.1	17.0	15.2	13.6	12.3	11.3	10.3
Ru	44	40.0	34.3	29.1	24.7	21.9	19.6	17.5	15.6	14.1	12.7	11.6	10.6

SEOUL NATIONAL UNIVERSITY

X-rays

Scattered from electrons

➤Scattering proportional to Z

H	C	N	O	Al	Si	P	Ti	D
1	6	7	8	13	14	15	22	1

Neutrons

Scattered by nuclei

➤Scattering not proportional to Z

H	C	N	O	Al	Si	P	Ti	D
1	6	7	8	13	14	15	22	1

| -37.4 | 66.5 | 93.6 | 58.0 | 34.5 | 41.5 | 51.3 | -34.4 | 66.7 | $\times 10^{-14}$ |

SEOUL NATIONAL UNIVERSITY
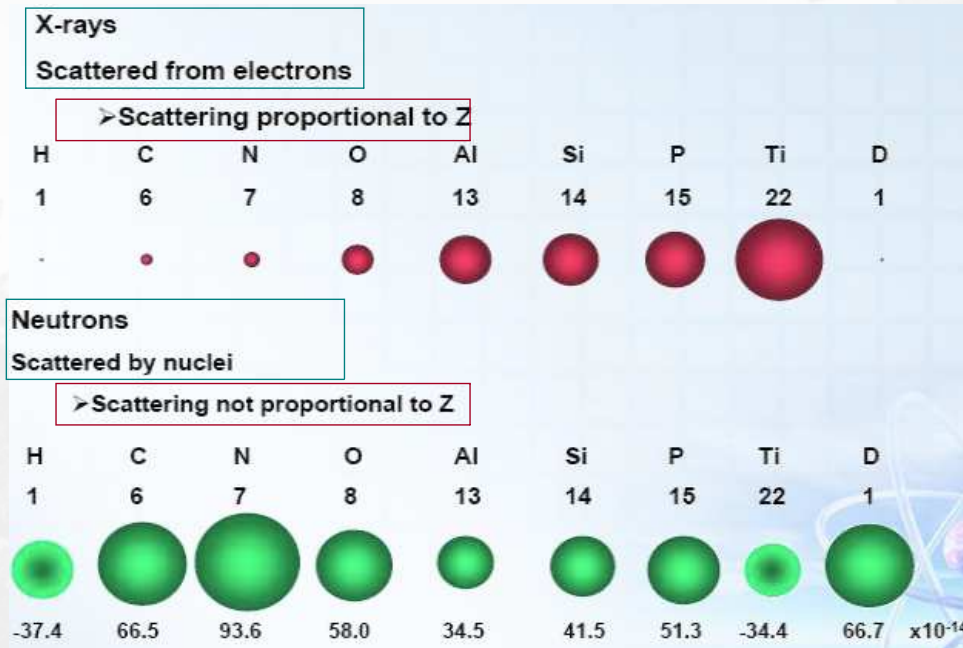
➤Anomalous scattering (anomalous dispersion)

$$|f|^2 = (f_0 + \Delta f')^2 + (\Delta f'')^2.$$

➤Thermal motion

$$f = f_0 \exp\left[-\frac{B \sin^2 \theta}{\lambda^2} \right]$$

Sherwood & Cooper 9.8

Cullity 4-11

$$|f|^2 = (f_0 + \Delta f')^2 + (\Delta f'')^2$$

$$f(E, Q) = f_o(Q) + f'(E) + i f''(E)$$

2θ is the Bragg angle

$$Q = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{d}$$
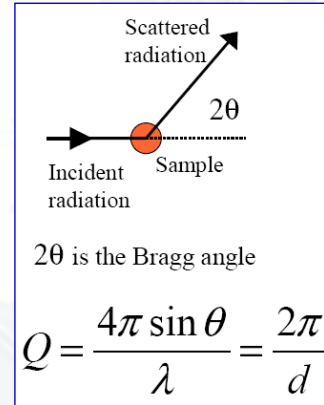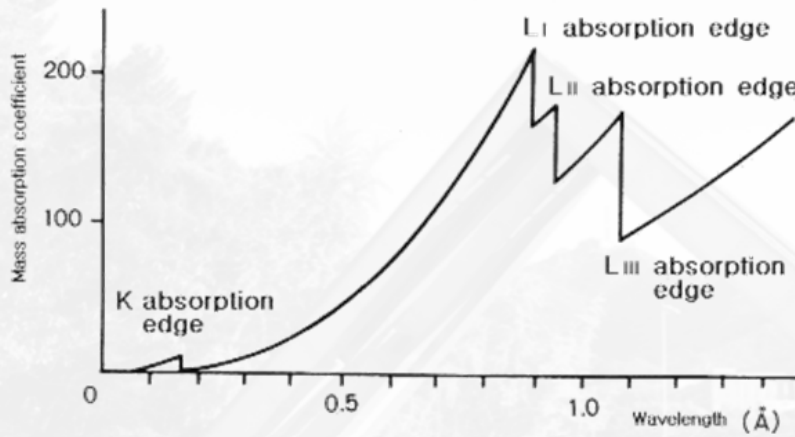
Atomic Form Factor: $f^0(\vec{q}) = \int \rho(\vec{r}) e^{i\vec{q}\cdot\vec{r}} \, dV$

$$f^0(q = 0) = Z$$
$$f^0(q \to \infty) = 0$$

Atomic Form Factor with Dispersion Corrections:
$$f(\vec{q}, \hbar\omega) = f^0(\vec{q}) + f'(\hbar\omega) + i f''(\hbar\omega)$$
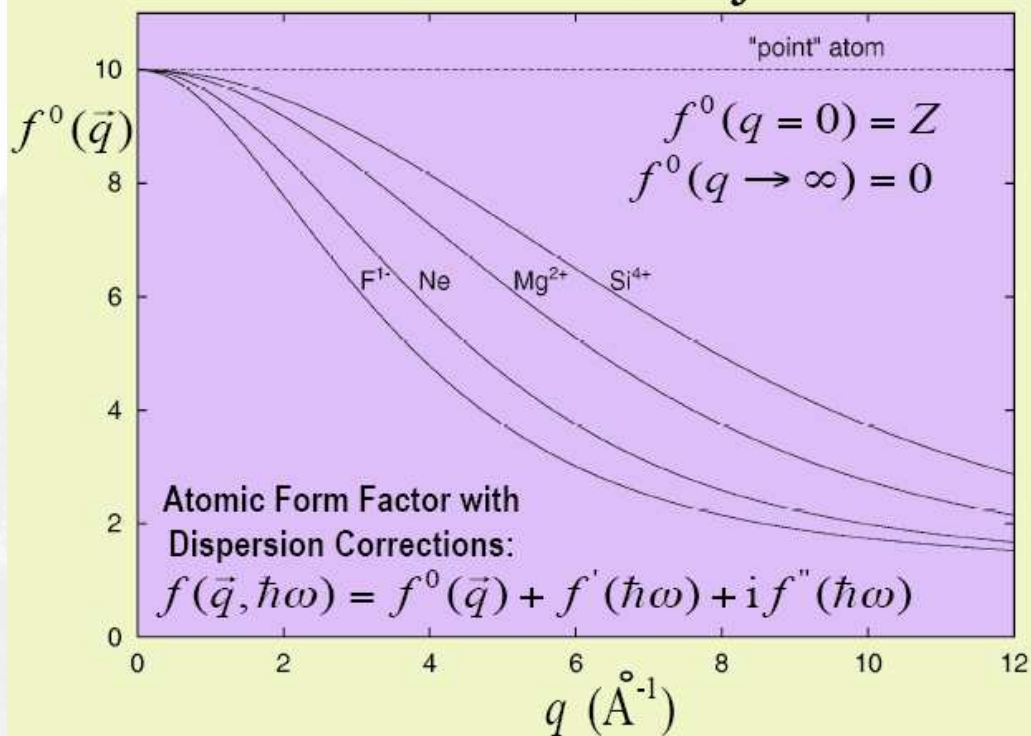
f′ is intimately related to the absorption coefficient.

$$f'(E) = \left(\frac{2}{\pi}\right) \int_{0}^{\infty} \frac{E f''(E)}{(E_0^{\,2} - E^2)} dE$$

Absorption

Energy
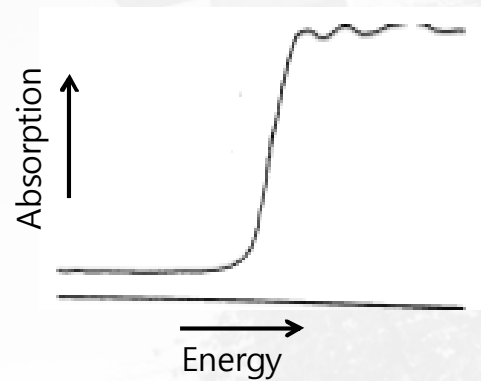
f″ "mirrors" the absorption coefficient.

$$f''(E) = \left(\frac{2\pi mc\,\varepsilon_0}{e^2 h}\right) E \mu_a$$
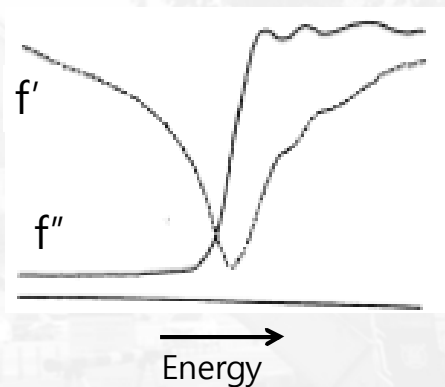
f′

f″

Energy

➢ Structure factor

➢ Polarization factor

➢ Multiplicity factor

➢ Lorentz factor

➢ Absorption factor

➢ Temperature factor

Temperature factor

Thermal motion

➤ Thermal vibration of atoms →

✓ Unit cell expands → Interplanar spacing (d) changes → 2θ position changes.

✓ Intensity of diffraction lines decreases.

▪ Degrades the periodicity of the lattice.

✓ Intensity of background scattering increases.

➤ Effective size of atom is larger. → Destructive interference increases with increasing 2θ.

Temperature factor

➢ Atomic vibration ↑ → effective size of atom ↑ → interference effect ↑

Debye-Waller temperature factor B
Mean-square displacement of atom vibration U^2
Mean displacement = 0

$$B = 8\pi^2 U^2$$

$$f = f_0 \exp\left[-\frac{B \sin^2 \theta}{\lambda^2} \right]$$

$$f = f_0 \exp\left[-\frac{B\mathbf{d}^{*2}}{4} \right];$$

Thermal motion

Isotropic temp factor B, U_{iso}
Anisotropic temp factor B_{ij} & U_{ij}

$$B = 8\pi^2 U^2$$

$$f = f_0 \exp\left[-\frac{B \sin^2 \theta}{\lambda^2} \right]$$

$$f = f_0 \exp\left[-\frac{B\mathbf{d}^{*2}}{4} \right];$$

$$f = f_0 \exp -\tfrac{1}{4}(B_{11}h^2\mathbf{a}^{*2} + B_{22}k^2\mathbf{b}^{*2} + B_{33}l^2\mathbf{c}^{*2}$$
$$+ 2B_{12}hk\mathbf{a}^*\mathbf{b}^* + 2B_{13}hl\mathbf{a}^*\mathbf{c}^* + 2B_{23}kl\mathbf{b}^*\mathbf{c}^*).$$

$$f = f_0 \exp -2\pi^2(U_{11}h^2\mathbf{a}^{*2} + U_{22}k^2\mathbf{b}^{*2} + U_{33}l^2\mathbf{c}^{*2}$$
$$+ 2U_{12}hk\mathbf{a}^*\mathbf{b}^* + 2U_{13}hl\mathbf{a}^*\mathbf{c}^* + 2U_{23}kl\mathbf{b}^*\mathbf{c}^*).$$

$2\pi^2 U_{ij} = \beta_{ij}$ Temp factor; B, U_{iso}, B_{ij}, U_{ij}, β_{ij}

Thermal motion

$$f = f_0 \exp\left[-\frac{B \sin^2 \theta}{\lambda^2}\right]$$

- B = 0
- B = 0.1
- B = 0.5
- B = 1
- B = 5
- B = 10
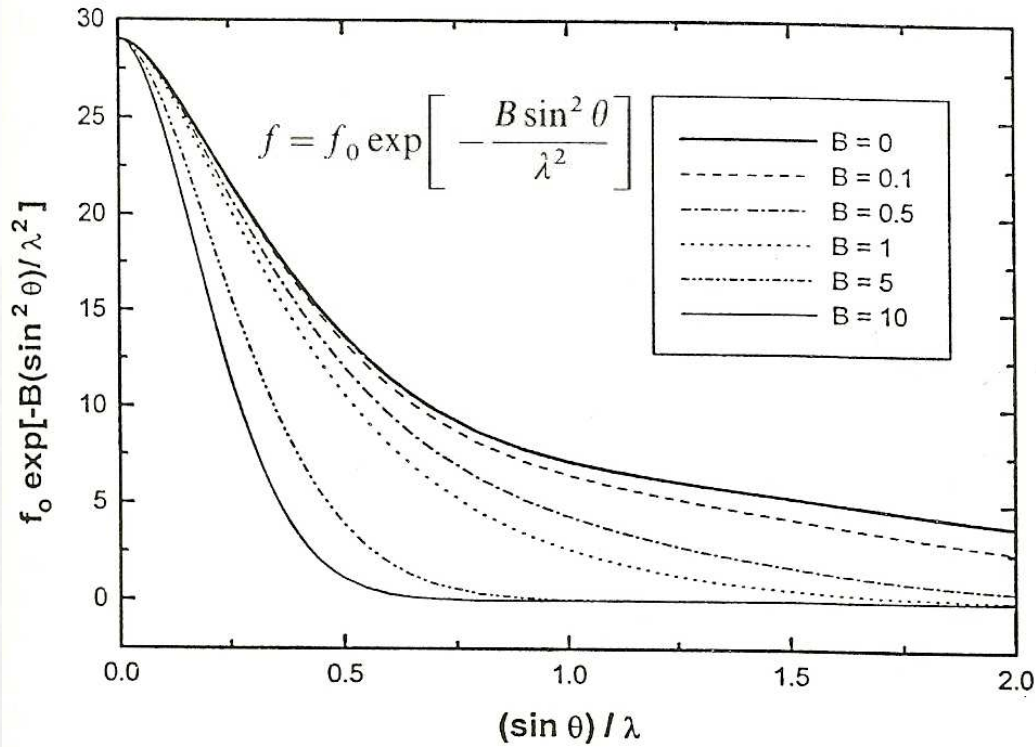
Figure 3.14. The effect of atomic thermal motion on the copper scattering factor.

Temperature factor

no thermal vibration
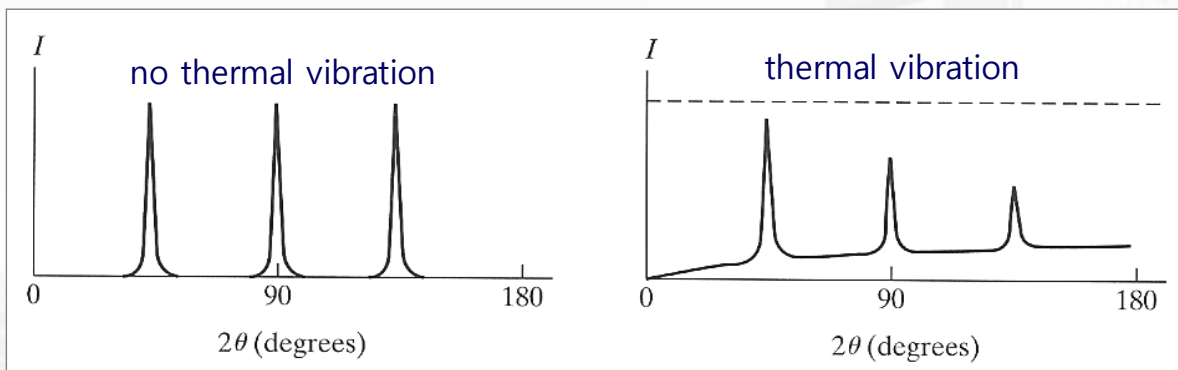
thermal vibration

➤ Thermal vibration of atoms

→ Decrease of <u>intensity</u> of diffraction lines

✓ Effect increases with 2θ.

→ <u>Thermal diffuse scattering</u>

✓ Thermal vibration causes general coherent scattering in all directions.

✓ Contributes to background (BKG).

✓ BKG intensity increases with 2θ.

➢ Structure factor

➢ Polarization factor

➢ Multiplicity factor

➢ Lorentz factor

➢ Absorption factor

➢ Temperature factor

Structure factor

Unpolarized incident X-ray becomes polarized after diffraction.

Every time a ray is diffracted, it undergoes a phase shift of $\pi/2$ relative to the incident beam.

Structure factor
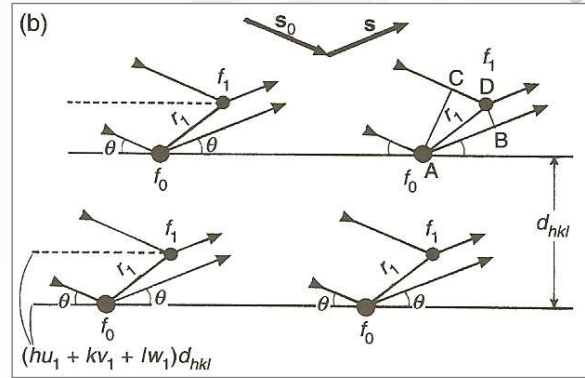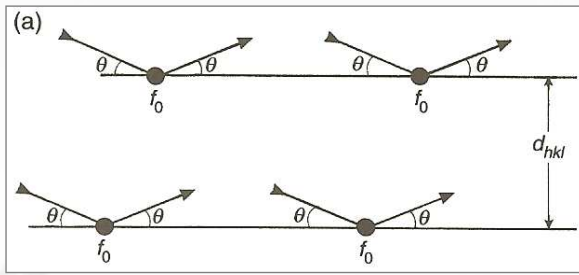
Path difference

$$\text{P.D.} = AB - CD = \mathbf{r}_1 \cdot \mathbf{s} - \mathbf{r}_1 \cdot \mathbf{s}_0 = \mathbf{r}_1 \cdot (\mathbf{s} - \mathbf{s}_0)$$

$$(\mathbf{s} - \mathbf{s}_0) = \lambda \mathbf{d}^*_{hkl} = \lambda(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*).$$

$$\text{P.D.} = \lambda(u_1\mathbf{a} + v_1\mathbf{b} + w_1\mathbf{c}) \cdot (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$$

$$\text{P.D.} = \lambda(hu_1 + kv_1 + lw_1).$$

$$\phi_1 = 2\pi(hu_1 + kv_1 + lw_1).$$
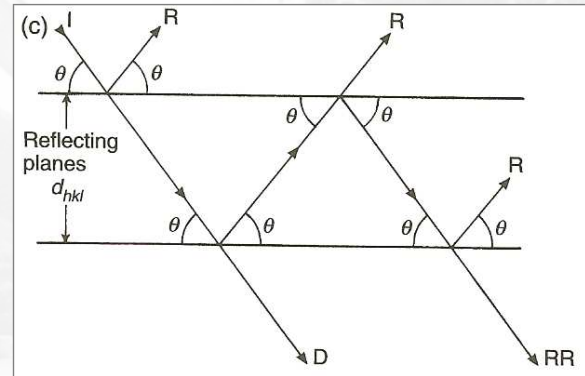
Structure factor

> What is the path difference b/w waves scattered by an atom @ origin (atom A) and another atom (atom B) @ x (in 1 dimension)?

Position of atom B, u = x/a → $\phi_{3'1'} = 2\pi hu$

Position of atom B, uvw → $\boxed{\phi = 2\pi(hu + kv + lw)}$

Path difference b/w 2' & 1'

$$\delta_{2'1'} = MCN = 2d_{h00}\sin\theta = \lambda$$

$$d_{h00} = AC = \frac{a}{h}$$

> The effect of atom B (@ uvw) on the intensity in that direction (1', 2')?

Path difference b/w 3' & 1'

$$\delta_{3'1'} = RBS = \frac{AB}{AC}(\lambda) = \frac{x}{a/h}(\lambda)$$

Phase difference ϕ $\phi = \frac{\delta}{\lambda}(2\pi)$

$$\phi_{3'1'} = \frac{\delta_{3'1'}}{\lambda}(2\pi) = \frac{2\pi hx}{a}$$

phase difference b/w waves scattered by B and that by A at origin, for the hkl reflection

Structure factor

Phase difference b/w waves scattered by B and that scattered by A at origin for hkl reflection

$$\phi = 2\pi(hu + kv + lw)$$

Add all the waves scattered by each atom in the unit cell. → addition of complex numbers representing amplitudes and phase of each wave

Cullity 4-4
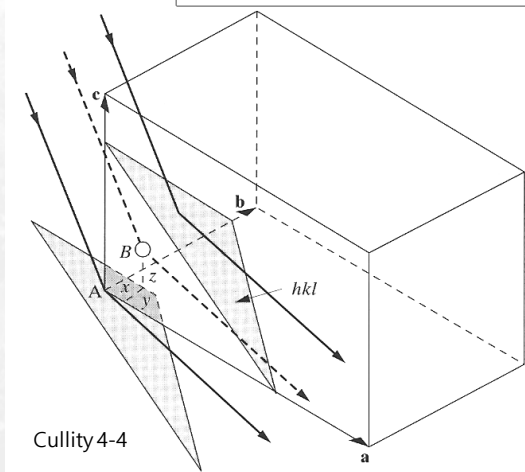
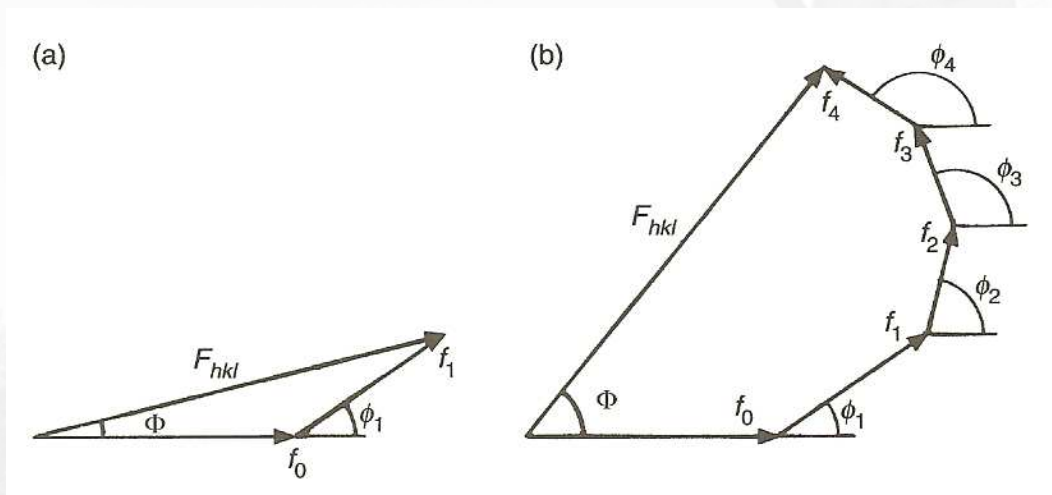Any scattered wave from hkl reflection & atom in uvw

$$Ae^{i\phi} = fe^{2\pi i(hu + kv + lw)}.$$

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

F = resultant wave scattered by all the atoms in the unit cell

F contains info on <u>both amplitude and phase</u> of the resultant wave.

Vector phase diagram for obtaining F$_{hkl}$

(a)

(b)

Atomic scattering factors are represented with phase angles with respect to a wave scattered from the origin.

$$|F| = \frac{\text{amplitude scattered by all the atoms of a unit cell}}{\text{amplitude scattered by a single electron}}$$

$$F_{hkl} = \sum_{n=0}^{n=N} f_n \exp 2\pi i(hu_n + kv_n + lw_n)$$

$$I_{hkl} \sim |F_{hkl}|^2$$

intensity of any hkl reflection ⬅ atomic positions

u_n, v_n, w_n, f_n → F_{hkl} can be obtained → can get I_{hkl}

Positions of atoms in unit cell, atomic scattering factors → F → I

Read Hammond Chap 9.1, 9.2, 9.3
Read Cullity Chap 4.4

$$F_{hkl} = \sum_{n=0}^{n=N} f_n \exp 2\pi i(hu_n + kv_n + lw_n)$$

➢ Positions of atoms in unit cell, atomic scattering factors → F_{hkl} & I_{hkl}

$$I_{hkl} \sim |F_{hkl}|^2$$

➢ I_{hkl} from several sets of planes → atom positions ; crystal structure determination

➢ F → I   vs.   I → F

  ✓ F → I (structure → Diff pattern); I → F (D pattern → structure)

➢ Phase info is lost in going from F_{hkl} to I_{hkl}. → <u>phase problem</u>

  ✓ We do not know in which direction the vector F_{hkl} points.

SEOUL NATIONAL UNIVERSITY

We would be better off if diffraction measured phase of scattering rather than amplitude! Unfortunately, nature did not oblige us.

Source unknown

(a) (b) original images

A graphic illustration of the phase problem
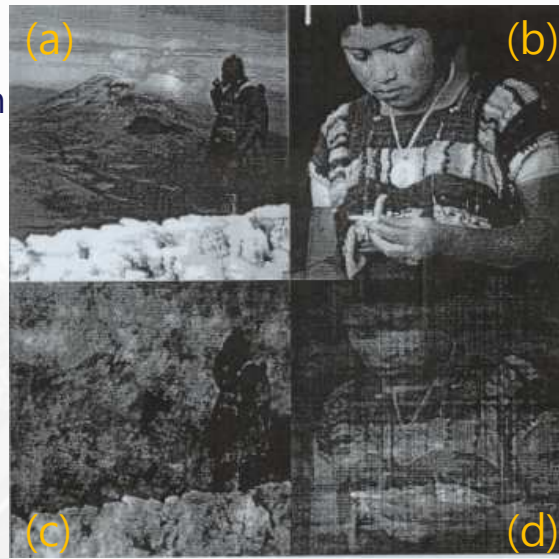
Fourier reconstruction with phase of (a) and amplitude of (b)

Fourier reconstruction with phase of (b) and amplitude of (a)

Picture by courtesy of D. Sivia   43

Fourier transform

SEOUL NATIONAL UNIVERSITY

$$F_{hkl} = \int_V \rho_{xyz} \exp[2\pi i(hx+ky+lz)]dV$$

$$F_{hkl} = \sum_{n=0}^{n=N} f_n \exp 2\pi i(hu_n + kv_n + lw_n)$$

$$\rho_{xyz} = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}| \exp[-2\pi i(hx+ky+lz)]$$

➢ e' density ← Fourier transform → diffraction pattern

  ✓ I is related to e' density through Fourier transform

➢ Xtal structure ← Fourier transform → diffraction pattern

  ✓ EXAFS pattern ← Fourier transform → radial distribution function

➢ ρ space = real space   diffraction space = reciprocal space = k space

➢ Reciprocal space always has centrosymmetry even though there is no centrosymmetry in real space. → 11 Laue groups (Hammond page 221)

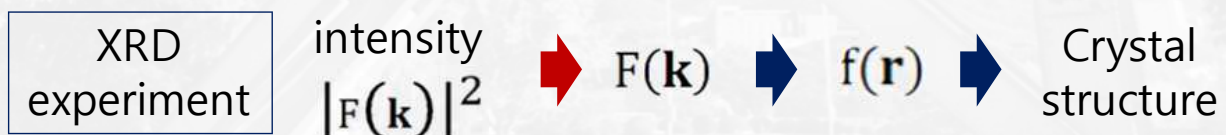➢ Diffraction pattern always gives Laue group pattern.

Sherwood & Cooper   44

Diffraction pattern $\quad F(\mathbf{k}) = \displaystyle\int_{\text{all } r} f(\mathbf{r}) e^{i\,\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}$

$F(\mathbf{k})$ is Fourier transform of $f(\mathbf{r})$.

Inverse transform $\quad f(\mathbf{r}) = \displaystyle\int_{\text{all } \mathbf{k}} F(\mathbf{k}) e^{-i\,\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{k}$

$F(\mathbf{k})$; contains info on the spatial distribution of diffraction pattern.

$f(\mathbf{r})$; contains info on the structure of obstacle.

| XRD experiment | intensity $\lvert F(\mathbf{k}) \rvert^2$ | ➡ | $F(\mathbf{k})$ | ➡ | $f(\mathbf{r})$ | ➡ | Crystal structure |

---

f($\mathbf{r}$) vs. F($\mathbf{k}$)

If the structure is known
→ f($\mathbf{r}$) is known.
→ diffraction pattern F($\mathbf{k}$) can be computed.

If the diffraction pattern is known
→ F($\mathbf{k}$) is known.
→ f($\mathbf{r}$) can be computed.

The act of diffraction = taking Fourier transform of the obstacle

Diffraction pattern of an obstacle described by f($\mathbf{r}$) is the Fourier transform of f($\mathbf{r}$), which is F(k).

➢ Information is contained in all space.

➢ It is impossible to scan all space to collect all the information.

→ some info is lost.

→ reconstruction of the obstacle from the diffraction data will be incomplete.

➢ PHASE PROBLEM

| XRD experiment | → | intensity $|F(k)|^2$ | ⮕ | $F(k)$ | ⮕ | $f(r)$ | ⮕ | Crystal structure |
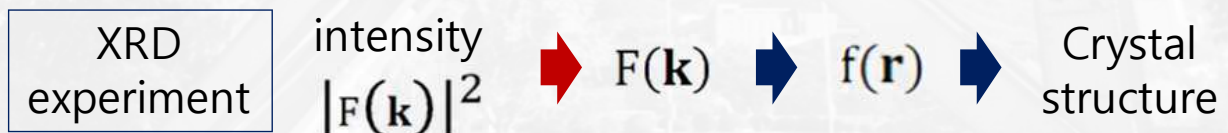
Real space vs. Reciprocal space   Friedel's law
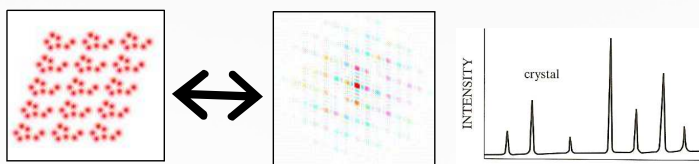
real space   reciprocal space

Table 9.1   The eleven Laue point groups or crystal classes

Crystal system	Laue point group and centrosymmetric point group	Non-centrosymmetric point groups belonging to the Laue point group		
Cubic	$m\bar{3}m$	432	$\bar{4}3m$	
(two Laue point groups)	$m\bar{3}$	23		
Tetragonal	$4/mmm$	422	$4mm$	$\bar{4}2m$
(two Laue point groups)	$4/m$	4	$\bar{4}$	
Orthorhombic	mmm	222	$mm2$	
Trigonal	$\bar{3}m$	32	$3m$	
(two Laue point groups)	$\bar{3}$	3		
Hexagonal	$6/mmm$	622	$6mm$	$\bar{6}m2$
(two Laue point groups)	$6/m$	6	$\bar{6}$	
Monoclinic	$2/m$	2	m	
Triclinic	$\bar{1}$	1		

➢ Diffraction pattern from a centrosymmetric crystal is centrosymmetric.

➢ Diffraction pattern from a non-centrosymmetric crystal is centrosymmetric. → Friedel's law

Structure factor

$$F_{hkl} = \sum_1^N f_n e^{2\pi i(hu_n + kv_n + lw_n)}$$

Unit cell with only one atom at 000

$$F = f e^{2\pi i(0)} = f$$

$$F^2 = f^2.$$

Base-centered cell 000 & ½½0

$$F = f e^{2\pi i(0)} + f e^{2\pi i(h/2 + k/2)}$$

$$= f\left[1 + e^{\pi i(h + k)}\right].$$

$$F = 2f \qquad \text{for } h \text{ and } k \text{ unmixed;}$$

$$F^2 = 4f^2.$$

$$F = 0 \qquad \text{for } h \text{ and } k \text{ mixed;}$$

$$F^2 = 0.$$

Body-centered cell 000 & ½½½

$$F = f e^{2\pi i(0)} + f e^{2\pi i(h/2 + k/2 + l/2)}$$

$$= f\left[1 + e^{\pi i(h + k + l)}\right].$$

$$F = 2f \qquad \text{when } (h + k + l) \text{ is even;}$$

$$F = 4f^2.$$

$$F = 0 \qquad \text{when } (h + k + l) \text{ is odd;}$$

$$F^2 = 0.$$

Read Cullity Chap 4.6

Structure factor of fcc

$$F_{hkl} = \sum_1^N f_n e^{2\pi i(hu_n + kv_n + lw_n)},$$

face-centered cell 000, ½½0, ½0½ & 0½½

$$F = f e^{2\pi i(0)} + f e^{2\pi i(h/2 + k/2)} + f e^{2\pi i(k/2 + l/2)} + f e^{2\pi i(h/2 + l/2)}$$

$$= f\left[1 + e^{\pi i(h + k)} + e^{\pi i(k + l)} + e^{\pi i(h + l)}\right].$$

$$F = 4f \qquad \text{for unmixed indices;}$$

$$F^2 = 16f^2$$

$$F = 0 \qquad \text{for mixed indices;}$$

$$F^2 = 0$$

	h	k	l	h+k	k+l	h+l	h+k+l
unmixed	e	e	e	e	e	e	e
mixed	e	e	o	e	o	o	o
mixed	e	o	o	o	e	o	e
unmixed	o	o	o	e	e	e	o

Structure factor is independent of size & shape of the unit cell

SEOUL NATIONAL UNIVERSITY

$$F_{hkl} = \sum_1^N f_n e^{2\pi i (hu_n + kv_n + lw_n)}$$

NaCl
Na 000, ½½0, ½0½ & 0½½
Cl ½½½, 00½, 0½0, ½00

$$F = f_{Na}e^{2\pi i(0)} + f_{Na}e^{2\pi i(h/2 + k/2)} + f_{Na}e^{2\pi i(h/2 + l/2)} + f_{Na}e^{2\pi i(k/2 + l/2)}$$

$$+ f_{Cl}e^{2\pi i(h/2 + k/2 + l/2)} + f_{Cl}e^{2\pi i(l/2)} + f_{Cl}e^{2\pi i(k/2)} + f_{Cl}e^{2\pi i(h/2)},$$

$$F = f_{Na}[1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}]$$

$$+ f_{Cl}[e^{\pi i(h+k+l)} + e^{\pi i l} + e^{\pi i k} + e^{\pi i h}].$$

$$F = f_{Na}[1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}]$$

$$+ f_{Cl}e^{\pi i(h+k+l)}[1 + e^{\pi i(-h-k)} + e^{\pi i(-h-l)} + e^{\pi i(-k-l)}]$$

$$F = [1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}][f_{Na} + f_{Cl}e^{\pi i(h+k+l)}]$$

$$F = 0 \qquad \text{for mixed indices;}$$

$$F^2 = 0.$$

For unmixed indices
$$F = 4[f_{Na} + f_{Cl}e^{\pi i(h+k+l)}].$$

$$F = 4(f_{Na} + f_{Cl}) \qquad \text{if } (h + k + l) \text{ is even;}$$

$$F^2 = 16(f_{Na} + f_{Cl})^2.$$

$$F = 4(f_{Na} - f_{Cl}) \qquad \text{if } (h + k + l) \text{ is odd;}$$

$$F^2 = 16(f_{Na} - f_{Cl})^2.$$

FCC	for unmixed indices		for mixed indices	
	$F = 4f$	$F^2 = 16f^2$	$F = 0$	$F^2 = 0$

NIVERSITY

$$\left(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}\right) \text{ for Cs} \qquad (000) \text{ for Cl}$$

$$F_{hkl} = \sum_{n=0}^{n=N} f_n \exp 2\pi i (hu_n + kv_n + lw_n)$$

$$F_{hkl} = f_{Cl} \exp 2\pi i(h0 + k0 + l0) + f_{Cs} \exp 2\pi i\left(h\tfrac{1}{2} + k\tfrac{1}{2} + l\tfrac{1}{2}\right)$$
$$= f_{Cl} + f_{Cs} \exp \pi i(h + k + l).$$

$$F_{hkl} = f_{Cl} + f_{Cs} \qquad (h + k + l) = \text{ even}$$

$$F_{hkl} = f_{Cl} - f_{Cs} \qquad (h + k + l) = \text{ odd}$$
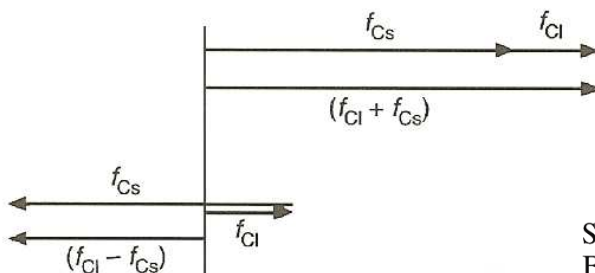
➢ caesium iodide (CsI)
  ✓ basis   I⁻: 0,0,0   Cs⁺:½,½,½

Structure: CsCl type
Bravais lattice: simple cubic
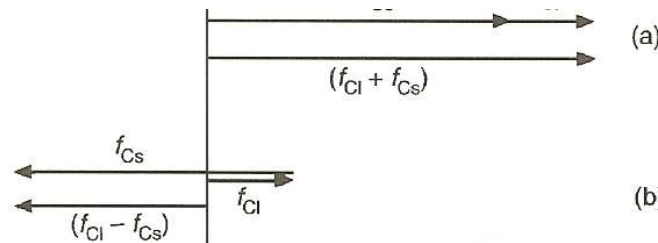Ions/unit cell: 1Cs⁺ + 1Cl⁻

○ Cs⁺
● Cl⁻

Center of unit cell
2 ions per lattice point
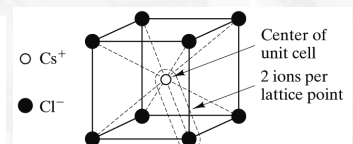
$$F_{hkl} = \sum_{n=0}^{n=N} f_n \exp 2\pi i(hu_n + kv_n + lw_n)$$

Example 1: CsCl structure (Fig. 1.12). The $(u_n\ v_n\ w_n)$ values are (000) for Cl, atomic scattering factor f_{Cl} and $\left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right)$ for Cs, atomic scattering factor f_{Cs}. Substituting these two terms in the equation:

$$F_{hkl} = f_{Cl} \exp 2\pi i(h0 + k0 + l0) + f_{Cs} \exp 2\pi i\left(h\frac{1}{2} + k\frac{1}{2} + l\frac{1}{2}\right)$$
$$= f_{Cl} + f_{Cs} \exp \pi i(h + k + l).$$

Two situations may be identified: when $(h + k + l)$ = even integer, $\exp \pi i$ (even integer) = 1, hence $F_{hkl} = f_{Cl} + f_{Cs}$ and when $(h + k + l)$ = odd integer, $\exp \pi i$ (odd integer) = -1, hence $F_{hkl} = f_{Cl} - f_{Cs}$. These two situations may be simply represented on the Argand diagram as shown in Fig. 9.4. Note that in both cases F_{hkl} is a real number; the imaginary component is zero. This arises because CsCl has a centre of symmetry at the origin, as explained below.

(a) $(f_{Cl} + f_{Cs})$

(b) f_{Cs} f_{Cl} $(f_{Cl} - f_{Cs})$

$(000) \left(\frac{1}{3}\frac{2}{3}\frac{1}{2}\right)$

$$F_{hkl} = \sum_{n=0}^{n=N} f_n \exp 2\pi i(hu_n + kv_n + lw_n)$$

$$F_{hkl} = f \exp 2\pi i(h0 + k0 + l0) + f \exp 2\pi i\left(h\frac{1}{3} + k\frac{2}{3} + l\frac{1}{2}\right)$$
$$= f\left(1 + \exp 2\pi i\left(h\frac{1}{3} + k\frac{2}{3} + l\frac{1}{2}\right)\right).$$

$[(h + 2k)/3 + l/2] = g$

$F = f(1 + e^{2\pi ig})$

$|F|^2 = f^2(1 + e^{2\pi ig})(1 + e^{-2\pi ig})$

$= f^2(2 + e^{2\pi ig} + e^{-2\pi ig}).$

$|F|^2 = f^2(2 + 2\cos 2\pi g)$

$= f^2[2 + 2(2\cos^2 \pi g - 1)]$

$= f^2(4\cos^2 \pi g)$

$= 4f^2 \cos^2 \pi \left(\frac{h + 2k}{3} + \frac{l}{2}\right)$

$= 0$ when $(h + 2k)$ is a multiple of 3 and l is odd.

When $(h + 2k)$ is a multiple of 3 and l is even

$\left(\frac{h + 2k}{3} + \frac{l}{2}\right) = n$, where n is an integer;

$\cos \pi n = \pm 1,$

$\cos^2 \pi n = 1,$

$|F|^2 = 4f^2.$

$h + 2k$	l	$|F|^2$
3 m	odd	0
3 m	even	$4f^2$
3 m $\pm$ 1	odd	$3f^2$
3 m $\pm$ 1	even	f^2

Read Cullity Chap 4.6

Structure Factor hcp

Example 2: hcp metal structure. We have a choice of unit cells (Fig. 5.8); it is best to refer to the primitive hexagonal cell, Fig. 5.8(a), which contains two identical atoms, atomic scattering factor f, with fractional coordinates (000) (the A layer atoms) and $\left(\frac{1}{3}\frac{2}{3}\frac{1}{2}\right)$ (the B layer atoms). Substituting these two terms in the equation:

$$F_{hkl} = f \exp 2\pi i(h0 + k0 + l0) + f \exp 2\pi i\left(h\tfrac{1}{3} + k\tfrac{2}{3} + l\tfrac{1}{2}\right)$$
$$= f\left(1 + \exp 2\pi i\left(h\tfrac{1}{3} + k\tfrac{2}{3} + l\tfrac{1}{2}\right)\right).$$

Now let us apply this to some particular (hkl) planes, e.g. $(002) \equiv (0002)$; $(100) \equiv (10\bar{1}0)$ and $(101) \equiv (10\bar{1}1)$.

$$F_{002} = f(1 + \exp 2\pi i) = 2f$$
$$F_{100} = f(1 + \exp \tfrac{2}{3}\pi i) = f\left(1 + \cos \tfrac{2}{3}\pi + i \sin \tfrac{2}{3}\pi\right) = f(0.5 + i0.866)$$
$$F_{101} = f(1 + \exp 2\pi i(\tfrac{1}{3} + \tfrac{1}{2})) = f\left(1 + \cos \tfrac{5}{3}\pi + i \sin \tfrac{5}{3}\pi\right) = f(1.5 - i0.866).$$

These results are shown graphically in Fig. 9.5. Note that F_{100} and F_{101} are complex numbers.

The intensities I_{hkl} of X-ray beams are proportional to their amplitudes squared, or F_{hkl} multiplied by its complex conjugate F^*_{hkl} (see Appendix 5). For the hcp metal examples above:

$$I_{002} = 2f \cdot 2f = 4f^2$$
$$I_{100} = f(0.5 + i0.866)f(0.5 - i0.866) = f^2$$
$$I_{101} = f(1.5 - i0.866)f(1.5 + i0.866) = 3f^2.$$

Read Cullity Chap 4.6

Structure Factor - hcp

$$F_{002} = f(1 + \exp 2\pi i) = 2f$$
$$F_{100} = f(1 + \exp \tfrac{2}{3}\pi i) = f\left(1 + \cos \tfrac{2}{3}\pi + i \sin \tfrac{2}{3}\pi\right) = f(0.5 + i0.866)$$
$$F_{101} = f(1 + \exp 2\pi i(\tfrac{1}{3} + \tfrac{1}{2})) = f\left(1 + \cos \tfrac{5}{3}\pi + i \sin \tfrac{5}{3}\pi\right) = f(1.5 - i0.866).$$
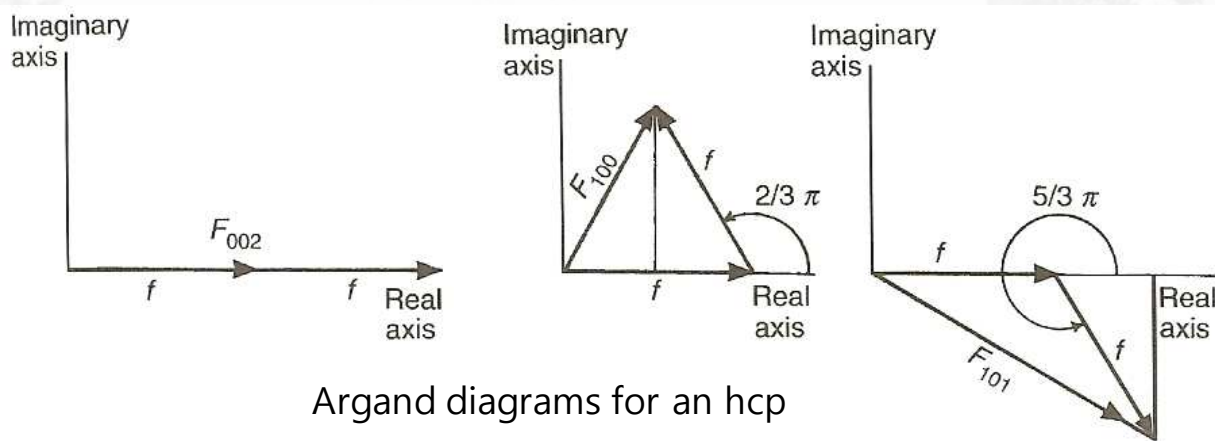
Argand diagrams for an hcp

Example 3: A crystal with a centre of symmetry at the origin. This is an important case because the structure factor for all reflections is real. For every atom with fractional coordinates (uvw) and phase angle $+\phi$ there will be an identical one on the *opposite* side of the origin with fractional coordinates $(\bar{u}\bar{v}\bar{w}$ and phase angle $-\phi$. For these two atoms:
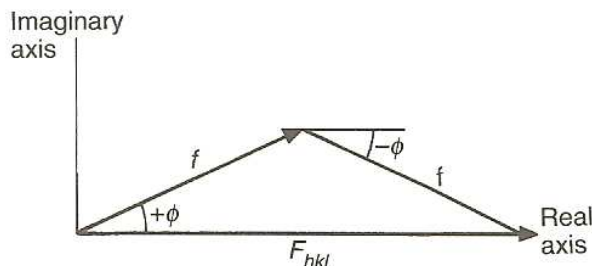
$$F_{hkl} = f \exp 2\pi i(hu + kv + lw) + f \exp 2\pi i(h\bar{u} + k\bar{v} + l\bar{w})$$
$$= f \exp 2\pi i(hu + kv + lw) + f \exp -2\pi i(hu + kv + lw).$$

The second term is the complex conjugate of the first, hence the sine terms cancel and

$$F_{hkl} = 2f \cos 2\pi(hu + kv + lw)$$

as shown graphically in Fig. 9.6.

Fig. 9.6. The Argand diagram for a centrosymmetric crystal. The phase angle $+\phi$ for the atom at (uvw) is equal and opposite to the phase angle $-\phi$ for the atom at $(\bar{u}\bar{v}\bar{w})$, hence F_{hkl} is real.

Friedel's law

> ➢ Diffraction pattern from a <u>centrosymmetric</u> crystal is <u>centrosymmetric.</u>
>
> ➢ Diffraction pattern from a <u>non-centrosymmetric</u> crystal is <u>centrosymmetric.</u>
>   → Friedel's law
>
> ➢ Laue group (Laue class)

$$I_{hkl} = F_{hkl} \cdot F_{hkl}^* = f \exp 2\pi i(hu + kv + lw) f \exp -2\pi i(hu + kv + lw)$$
$$= f \exp 2\pi i(hu + kv + lw) f \exp 2\pi i(\bar{h}u + \bar{k}v + \bar{l}w)$$

$$I_{\bar{h}\bar{k}\bar{l}} = F_{\bar{h}\bar{k}\bar{l}} \cdot F_{\bar{h}\bar{k}\bar{l}}^* = f \exp 2\pi i(\bar{h}u + \bar{k}v + \bar{l}w) f \exp -2\pi i(\bar{h}u + \bar{k}v + \bar{l}w)$$
$$= f \exp 2\pi i(\bar{h}u + \bar{k}v + \bar{l}w) f \exp 2\pi i(hu + kv + lw).$$

$F_{hkl} = F_{\bar{h}\bar{k}\bar{l}}^*$ and $F_{hkl}^* = F_{\bar{h}\bar{k}\bar{l}}$, hence $\boxed{I_{hkl} = I_{\bar{h}\bar{k}\bar{l}}}$ Friedel's law

> ➢ <u>Reciprocal space always has centrosymmetry even though there is no centrosymmetry in real space.</u> → <u>11 Laue groups</u> (Hammond page 221)
>
> ➢ <u>Diffraction pattern always gives Laue group pattern.</u>

Hammond page 220

➤ The presence of a center of symmetry in the diffraction pattern means that "non-centrosymmetric crystals cannot be distinguished from those with a center of symmetry".

➤ There are 11 centrosymmetric point groups and hence 11 symmetries which diffraction patterns can possess. These are called 11 Laue groups.

Table 9.1   The eleven Laue point groups or crystal classes

Crystal system	Laue point group and centrosymmetric point group	Non-centrosymmetric point groups belonging to the Laue point group		
Cubic	$m\bar{3}m$	432	$\bar{4}3m$	
(two Laue point groups)	$m\bar{3}$	23		
Tetragonal	$4/mmm$	422	$4mm$	$\bar{4}2m$
(two Laue point groups)	$4/m$	4	$\bar{4}$	
Orthorhombic	mmm	222	$mm2$	
Trigonal	$\bar{3}m$	32	$3m$	
(two Laue point groups)	$\bar{3}$	3		
Hexagonal	$6/mmm$	622	$6mm$	$\bar{6}m2$
(two Laue point groups)	$6/m$	6	$\bar{6}$	
Monoclinic	$2/m$	2	m	
Triclinic	$\bar{1}$	1		

Meaning of Laue index, Laue class, Laue group???

Table 9.1   The eleven Laue point groups or crystal classes

Crystal system	Laue point group and centrosymmetric point group	Non-centrosymmetric point groups belonging to the Laue point group		
Cubic	$m\bar{3}m$	432	$\bar{4}3m$	
(two Laue point groups)	$m\bar{3}$	23		
Tetragonal	$4/mmm$	422	$4mm$	$\bar{4}2m$
(two Laue point groups)	$4/m$	4	$\bar{4}$	
Orthorhombic	mmm	222	$mm2$	
Trigonal	$\bar{3}m$	32	$3m$	
(two Laue point groups)	$\bar{3}$	3		
Hexagonal	$6/mmm$	622	$6mm$	$\bar{6}m2$
(two Laue point groups)	$6/m$	6	$\bar{6}$	
Monoclinic	$2/m$	2	m	
Triclinic	$\bar{1}$	1		

➤ Non-centrosymmetric point groups cannot be distinguished from centrosymmetric groups from diffraction.

➤ 11 centrosymmetric point groups (Laue group) → diffraction pattern can have 11 symmetries.

Systematic absence (extinction)


Systematic extinction (absence)

➢ The condition that structure factor becomes zero <u>due to a systematic symmetry condition</u>

➢ Presence of reflections with zero intensity caused by the <u>space group (symmetry) of unit cell</u>

➢ Arise from <u>centering of unit cell</u> and/or the <u>presence of translational symmetry elements</u> – screw axes, glide planes.

  ✓ Can get info on these elements from the extinction of peaks.

  ✓ Translational symmetry inside unit cell, screw axes, glide planes can introduce systematic extinctions.

base-centered orthorhombic lattice
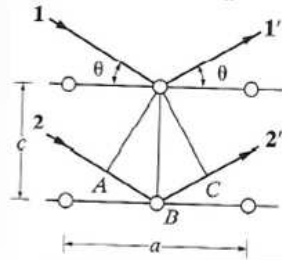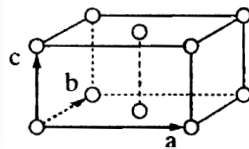
body-centered orthorhombic lattice
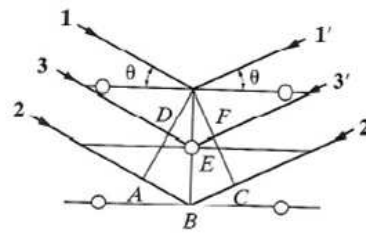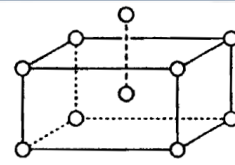
$$F = 2f \qquad \text{for } h \text{ and } k \text{ unmixed;}$$

$$F^2 = 4f^2.$$

$$F = 0 \quad \text{when } (h + k + l) \text{ is odd;}$$

$$F^2 = 0.$$

| atom position | ⟷ | intensity |

relation

$$F = fe^{2\pi i(0)} + fe^{2\pi i(h/2 + k/2)}$$

$$= f\left[1 + e^{\pi i(h + k)}\right].$$

$$F = 2f \qquad \text{for } h \text{ and } k \text{ unmixed;}$$

$$F^2 = 4f^2.$$

$$F = 0 \qquad \text{for } h \text{ and } k \text{ mixed;}$$

$$F^2 = 0.$$

Table 3.2. Example of Conditions for the Extinction of Reflections Due to Translational Symmetries

Symmetry	Extinction Conditions
P	none
C	hkl; $h + k = $ odd
I	hkl; $h + k + l = $ odd
F	hkl; h, k, l mixed even and odd
$2_1 \| b$	$0k0$: $k = $ odd
$c \perp b$	$h0l$: $l = $ odd

$$F = fe^{2\pi i(0)} + fe^{2\pi i(h/2 + k/2 + l/2)}$$

$$= f\left[1 + e^{\pi i(h + k + l)}\right].$$

$$F = 2f \qquad \text{when } (h + k + l) \text{ is even}$$

$$F = 4f^2.$$

$$F = 0 \qquad \text{when } (h + k + l) \text{ is odd;}$$

$$F^2 = 0.$$

Generators selected   (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$;   (2);   (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates

4   i 1   (1) x,y,z (2) $\bar{x},\bar{y},z$ (3) $x,\bar{y},z$ (4) $\bar{x},y,z$

General position

Reflection conditions

General:
no conditions

Special: no extra conditions

2   h m.. $\frac{1}{2},y,z$ $\frac{1}{2},\bar{y},z$

2   g m.. $0,y,z$ $0,\bar{y},z$

2   f .m. $x,\frac{1}{2},z$ $\bar{x},\frac{1}{2},z$

2   e .m. $x,0,z$ $\bar{x},0,z$

1   d $mm2$ $\frac{1}{2},\frac{1}{2},z$

1   c $mm2$ $\frac{1}{2},0,z$

1   b $mm2$ $0,\frac{1}{2},z$

1   a $mm2$ $0,0,z$

Special position

Table 3.2. Example of Conditions for the Extinction of Reflections Due to Translational Symmetries

Symmetry	Extinction Conditions
P	none
C	hkl; $h+k=$ odd
I	hkl; $h+k+l=$ odd
F	hkl; h, k, l mixed even and odd
$2_1 \parallel b$	$0k0$: $k=$ odd
$c \perp b$	$h0l$: $l=$ odd

---

② **Generators selected**   (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{2},\frac{1}{2},0)$; (2); (3)

③ **Positions**

Multiplicity, Wyckoff letter, Site symmetry	Coordinates

$(0,0,0)+$ $(\frac{1}{2},\frac{1}{2},0)+$

8   f 1   (1) x,y,z (2) $\bar{x},\bar{y},z$ (3) $x,\bar{y},z$ (4) $\bar{x},y,z$

Reflection conditions

General:

hkl : $h+k=2n$
$0kl$: $k=2n$
$h0l$: $h=2n$
$hk0$: $h+k=2n$
$h00$: $h=2n$
$0k0$: $k=2n$

Special: as above, plus

no extra conditions

no extra conditions

hkl : $h=2n$

no extra conditions

no extra conditions

Table 3.2. Example of Conditions for the Extinction of Reflections Due to Translational Symmetries

Symmetry	Extinction Conditions
P	none
C	hkl; $h+k=$ odd
I	hkl; $h+k+l=$ odd
F	hkl; h, k, l mixed even and odd
$2_1 \parallel b$	$0k0$: $k=$ odd
$c \perp b$	$h0l$: $l=$ odd

4   e m.. $0,y,z$

4   d .m. $x,0,z$

4   c ..2 $\frac{1}{4},\frac{1}{4},z$

2   b $mm2$ $0,\frac{1}{2},z$

2   a $mm2$ $0,0,z$

④ **Symmetry of special projections**

Along [001] $c2mm$ Along [100] $p1m1$ Along [010] $p11m$
$a'=a$ $b'=b$ $a'=\frac{1}{2}b$ $b'=c$ $a'=c$ $b'=\frac{1}{2}a$
Origin at $0,0,z$ Origin at $x,0,0$ Origin at $0,y,0$

⑤ **Maximal non-isomorphic subgroups**
I   [2] $C1m1$ (Cm, 8)   (1; 3)+
       [2] $Cm11$ (Cm, 8)   (1; 4)+
       [2] $C112$ ($P2$, 3)   (1; 2)+

Generators selected   (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity,   Coordinates
Wyckoff letter,
Site symmetry

4   e 1   (1) x,y,z (2) $\bar{x}, y+\frac{1}{2}, \bar{z}+\frac{1}{2}$ (3) $\bar{x},\bar{y},\bar{z}$ (4) $x, \bar{y}+\frac{1}{2}, z+\frac{1}{2}$

Reflection conditions

General:

$h0l$: $l = 2n$
$0k0$: $k = 2n$
$00l$: $l = 2n$

Special: as above, plus

2   d $\bar{1}$ $\frac{1}{2},0,\frac{1}{2}$ $\frac{1}{2},\frac{1}{2},0$ hkl : $k+l = 2n$

2   c $\bar{1}$ $0,0,\frac{1}{2}$ $0,\frac{1}{2},0$ hkl : $k+l = 2n$

2   b $\bar{1}$ $\frac{1}{2},0,0$ $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ hkl : $k+l = 2n$

2   a $\bar{1}$ $0,0,0$ $0,\frac{1}{2},\frac{1}{2}$ hkl : $k+l = 2n$

Symmetry of special projections

Along [001] $p2gm$ Along [100] $p2gg$ Along [010] $p2$
$a' = a_p$ $b' = b$ $a' = b$ $b' = c_p$ $a' = \frac{1}{2}c$ $b' = a$
Origin at $0,0,z$ Origin at $x,0,0$ Origin at $0,y,0$

Maximal non-isomorphic subgroups

I   [2] $P1c1$ (Pc, 7)   1; 4
        [2] $P12_11$ ($P2_1$, 4)   1; 2
        [2] $P\bar{1}$ (2)   1; 3

IIa   none

IIb   none

Maximal isomorphic subgroups of lowest index

IIc   [2] $P12_1/c1$ ($a' = 2a$ or $a' = 2a, c' = 2a + c$) ($P2_1/c$, 14); [3] $P12_1/c1$ ($b' = 3b$) ($P2_1/c$, 14)

Minimal non-isomorphic supergroups

I   [2] $Pnna$ (52); [2] $Pmna$ (53); [2] $Pcca$ (54); [2] $Pbam$ (55); [2] $Pccn$ (56); [2] $Pbcm$ (57); [2] $Pnnm$ (58); [2] $Pbcn$ (60);
        [2] $Pbca$ (61); [2] $Pnma$ (62); [2] $Cmce$ (64)

II   [2] $A12/m1$ ($C2/m$, 12); [2] $C12/c1$ ($C2/c$, 15); [2] $I12/c1$ ($C2/c$, 15); [2] $P12_1/m1$ ($c' = \frac{1}{2}c$) ($P2_1/m$, 11);
        [2] $P12/c1$ ($b' = \frac{1}{2}b$) ($P2/c$, 13)

Systematic absence (extinction)

monoclinic $c \perp b$ $h0l$: $l =$ odd

Operation of c-glide

c-glide and reflection in plane of paper
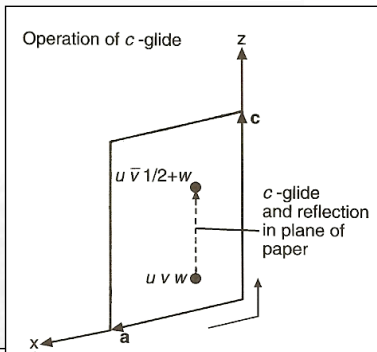
$$F_{hkl} = f \exp 2\pi i(hu + kv + lw) + f \exp 2\pi i\left(hu + k\bar{v} + l\left(\tfrac{1}{2} + w\right)\right).$$

Consider the $h0l$ reflections ($k = 0$):

$$F_{h0l} = f \exp 2\pi i(hu + lw) + f \exp 2\pi i(hu + lw) \exp 2\pi i \tfrac{1}{2} l$$
$$= f \exp 2\pi i(hu + lw)[1 + \exp \pi i l].$$

$F_{h0l} = 0$ when l = odd ;
systematic absence for h0l planes

monoclinic $2_1 \| b$ $0k0$: $k =$ odd

Operation of screw diad

Screw diad along y-axis
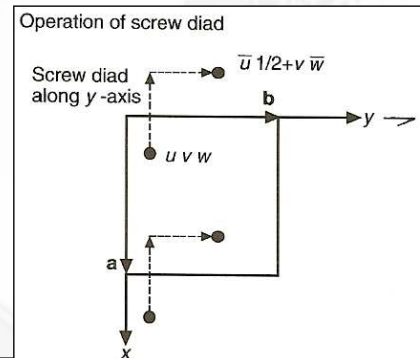
$$F_{hkl} = f \exp 2\pi i(hu + kv + lw) + f \exp 2\pi i\left(h\bar{u} + k\left(\tfrac{1}{2} + v\right) + l\bar{w}\right)$$

consider the $0k0$ reflections ($h = l = 0$)

$$F_{0k0} = f \exp 2\pi i(kv) + f \exp 2\pi i\left(k\tfrac{1}{2} + kv\right)$$
$$= f \exp 2\pi i(kv)[1 + \exp \pi i k].$$

$F_{0k0} = 0$ when k = odd ;
systematic absence for 0k0 planes

Systematic absence (extinction)

Table A6.1 Extinction criteria for lattices and symmetry elements

Lattice or symmetry element type	Symbol	Class of reflections	Condition for presence
Lattice type:		hkl	
primitive	P		none
body-centred	I		$h+k+l=2n$
centred on the C face	C		$h+k=2n$
centred on the A face	A		$k+l=2n$
centred on the B face	B		$h+l=2n$
centred on all faces	F		h,k,l all $=n$ (odd) or all $=2n$ (even)
rhombohedral, obverse	R		$-h+k+l=3n$
rhombohedral, reverse	R		$h-k+l=3n$
Glide plane ∥ (001)	a	$hk0$	$h=2n$
	b		$k=2n$
	n		$h+k=2n$
	d		$h+k=4n$
Glide plane ∥ (100)	b	$0kl$	$k=2n$
	c		$l=2n$
	n		$k+l=2n$
	d		$k+l=4n$
Glide plane ∥ (010)	a	$h0l$	$h=2n$
	c		$l=2n$
	d		$h+l=2n$
	n		$h+l=4n$
Glide plane ∥ (110)	c	hhl	$l=2n$
	n		$h+k=2n$
	d		$2h+l=4n$
Screw axis ∥ c	$2_1,4_2,6_3$	$00l$	$l=2n$
	$3_1,3_2,6_2,6_4$		$l=3n$
	$4_1,4_2$		$l=4n$
	$6_1,6_5$		$l=6n$
Screw axis ∥ a	$2_1,4_2$	$h00$	$h=2n$
	$4_1,4_3$		$h=4n$
Screw axis ∥ b	$2_1,4_2$	$0k0$	$k=2n$
	$4_1,4_3$		$k=4n$
Screw axis ∥ [110]	2_1	$hh0$	$h=2n$

($n=$ odd integer, $2n=$ even integer etc.)

Factors affecting the relative intensity of Bragg reflections

➤ Structure factor

➤ Polarization factor

➤ Multiplicity factor

➤ Lorentz factor

➤ Absorption factor

➤ Temperature factor

Multiplicity


Multiplicity

➢ # of permutations of position and sign of ±h, ±k, ±l for planes having same d and F^2 (Cullity)

➢ # of equivalent planes cutting a unit cell in a particular hkl family (Jenkins & Snyder)

➢ # of equivalent orientations that a unit cell can have for a given crystallographic direction (Krawitz)

➢ Cubic

✓ (100), (010), (001), (-100), (0-10), (00-1) → 6

✓ (111), (-111), (1-11), (11-1), (1-1-1), (-11-1), (-1-11), (-1-1-1) → 8

✓ (Intensity of 111) x 3 = (Intensity of 100) x 4, when other things are equal

➢ Tetragonal

✓ (100), (010), (-100), (0-10) → 4

✓ (001), (00-1) → 2

✓ (111), (-111), (1-11), (11-1), (1-1-1), (-11-1), (-1-11), (-1-1-1) → 8

✓ (Intensity of 111) = (Intensity of 100) x 2, when other things are equal

✓ (Intensity of 111) = (Intensity of 001) x 4, when other things are equal

Table 6.1. Multiplicities for the Seven Crystal Systems

Index	Triclinic	Monoclinic	Orthorhombic	Hexagonal Trigonal	Tetragonal	Cubic
hkl	2	4	8	24*	16*	48*
hhl	2	4	8	12*	8	24
hh0	2	4	8	6	4	12
0kk	2	4	8	12	8	12
hhh	2	4	8	12	8	8
hk0	2	4	8	12*	8*	24*
h0l	2	2	4	12*	8	24*
0kl	2	4	4	12*	8	24*
h00	2	2	2	6	4	6
0k0	2	2	2	6	4	6
001	2	2	2	2	2	6

Note: For some space groups within the crystal systems, indexes marked with * are half the indicated values. A complete listing may be found in Table 3.5.1 in the *International Tables for X-Ray Crystallography*, Vol. 1, pp. 32–33.

CONTINUED   No. 14 $P2_1/c$

TIONAL UNIVERSITY

Generators selected   (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates	Reflection conditions

4	e		
2	d		
2	c		
2	b		
2	a		

Positions

Multiplicity, Wyckoff letter, Site symmetry		Coordinates

Multiplicity
Number of equivalent points in a unit cell

4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$		
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$		
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$		
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$		

SEOUL NATIONAL UNIVERSITY

➢ Structure factor

➢ Polarization factor

➢ Multiplicity factor

➢ Lorentz factor

➢ Absorption factor

➢ Temperature factor

SEOUL NATIONAL UNIVERSITY

Absorption

Transmission & back-reflection (Laue camera)
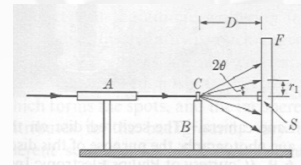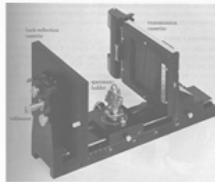
Transmission (Laue camera)
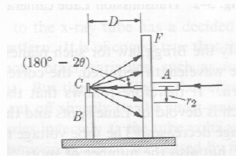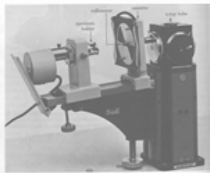
back-reflection (Laue camera)
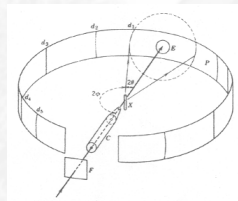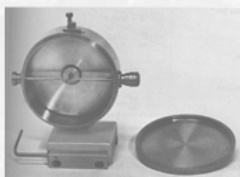
Hull/Debye-Scherrer camera
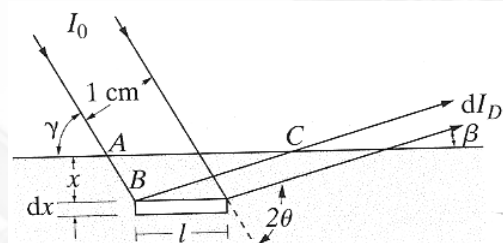
➢ Absorption is independent of θ. ← irradiated volume constant (fixed slit)

➢ No effect on the relative intensity ← decreases the intensities of all diffracted beams by the same factor.

---

high 2θ

low 2θ

small absorption

small absorption

large absorption

small absorption

Highly absorbing specimen

➢ Absorption is larger for low θ reflection.

Cullity page 150

Extinction

Extinction

> Diffracted intensity; <u>perfect xtal</u> << <u>ideally imperfect xtal</u>

> Decrease in intensity as the crystal becomes more perfect (large mosaic blocks, oriented).

> <u>Ideally imperfect crystal</u> consists of very small mosaic blocks, uniformly disoriented; no extinction.

> Kinematical theory/dynamical theory

> Powder specimens should be ground as fine as possible.

> Grinding → reduce crystal size, increase # of diffraction cones, decrease mosaic block size, disorient mosaic blocks, strain the crystals non-uniformly.

See Cullity 5-4 for mosaic structure

Cullity page 360

Primary Extinction

- Diffraction from highly perfect crystal
- I (perfect xtal) << I (imperfect xtal)
- $\phi(K_o/K_1) = \pi/2$
- $\phi(K_o/K_2) = \pi$ → destructive interference
  → lower intensity
- Depends on the degree of being perfect.
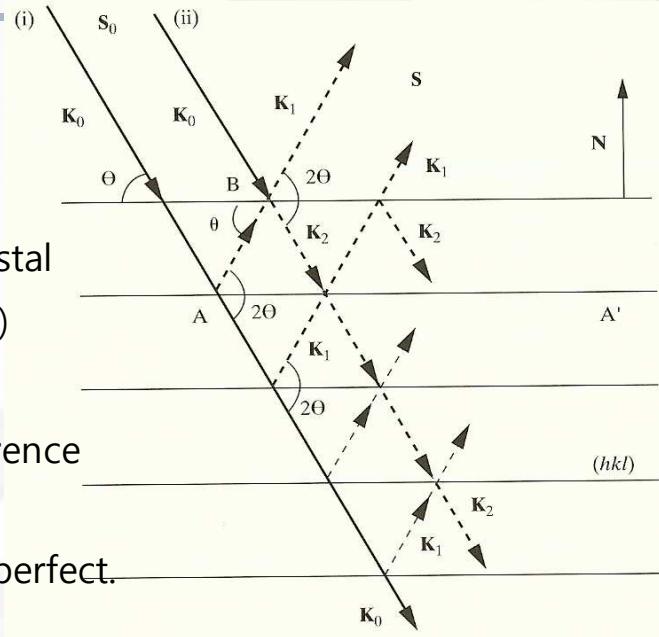
  - Does not kill the reflection but lower intensity.
  - How to avoid? – give some stress (increase mosaicity by e.g. LN2 quenching, heat & quenching, etc.).

Primary Extinction
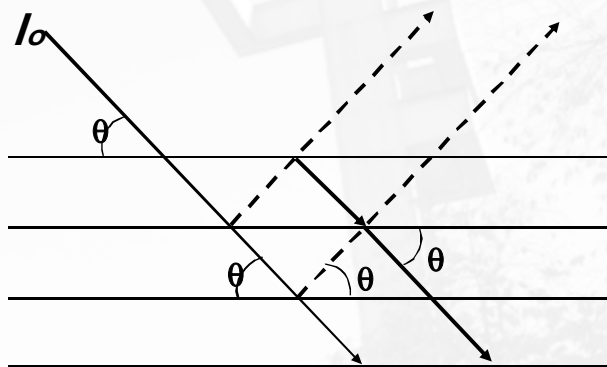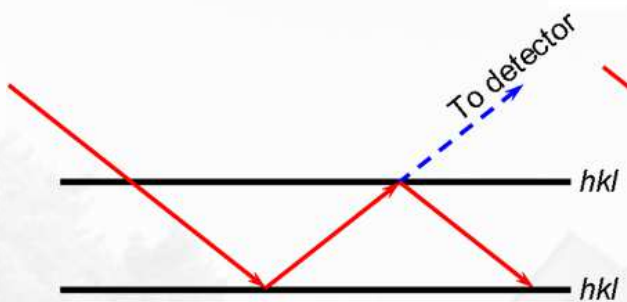
Secondary extinction
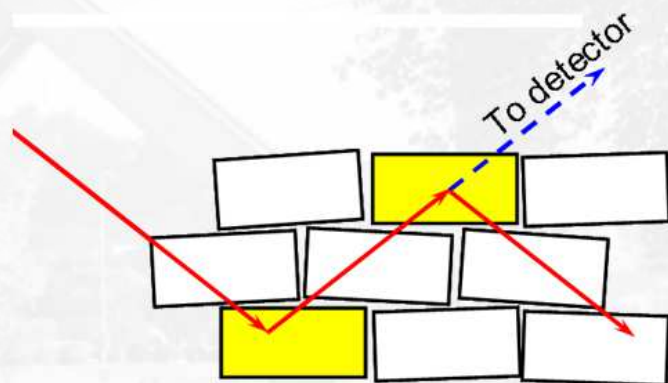
Mosaic structure, mosaic blocks

➤ Angle of disorientation between the tiny blocks is ε. → diffraction occurs at all angles between θ_B and $\theta_B \pm \varepsilon$.

➤ Increases the integrated intensity relative to that obtained (or calculated) for an <u>ideally perfect crystal</u>. ← strains & strain gradients associated with the groups of dislocations

A single xtal divided into 3 mosaic blocks

Boundaries are "walls" of edge dislocations.

strained

Sub-grain

Sub-grain boundary

unstrained

(a)
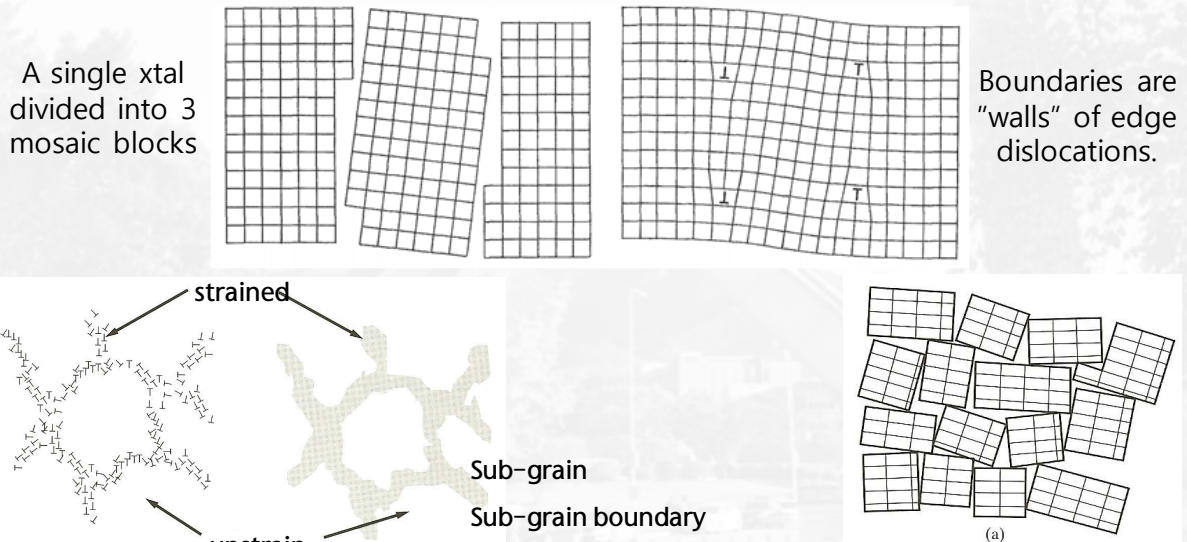
Mosaic spread

➤ Mosaicity is created by slight misorientations of different crystals as they nucleate and grow on the substrate. When the crystals join, they form boundaries.
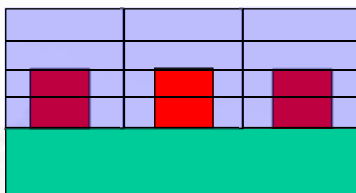
In an ideal case, each nuclei (red) is perfectly oriented.
When the crystals grow and meet, there is perfect bounding between the crystallites → no boundary.
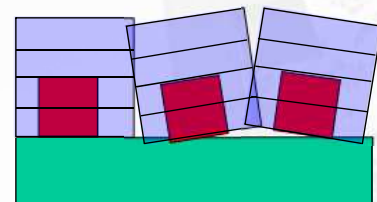
If the nuclei (red) are slightly misaligned, then boundaries will be formed.

Mosaic Spread - reciprocal space

- ➤ Mosaic spread can be quantified by measuring the broadening of the lattice point in reciprocal space.

- ➤ The amount of broadening of the reciprocal lattice point that is perpendicular to the reflecting plane normal can be attributed to mosaic spread.

- ➤ The peak broadening parallel to the interface can be attributed to lateral correlation length.
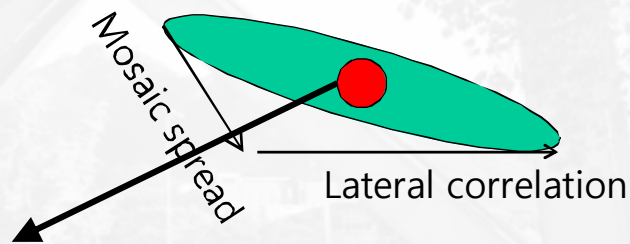
Ideally imperfect crystal

- ➤ Diffracted intensity; perfect xtal << ideally imperfect xtal

- ➤ Intensity is decreased as the crystal becomes more perfect (large mosaic blocks).

- ➤ Ideally imperfect crystal consists of very small mosaic blocks, uniformly disoriented. → no extinction

- ➤ Kinematical theory vs. dynamical theory

- ➤ Powder specimens should be ground as fine as possible.

- ➤ Grinding → reduce crystal size, increase # of diffraction cones, decrease mosaic block size, disorient mosaic blocks, strain the crystals non-uniformly.

Primary Extinction
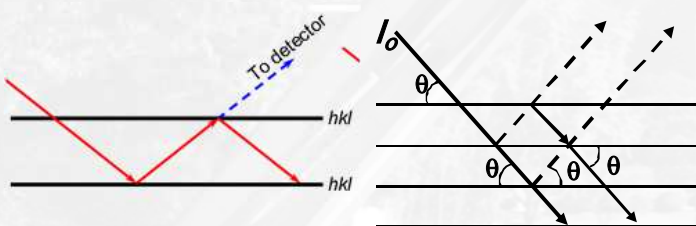
- ➤ Does not kill the reflection but lower intensity.

- ➤ How to avoid? – give some stress (increase mosaicity by e.g. LN2 quenching, heat & quenching, etc.)

SEOUL NATIONAL UNIVERSITY

➢ Structure factor

➢ Polarization factor

➢ Multiplicity factor

➢ Lorentz factor

➢ Absorption factor

➢ Temperature factor

SEOUL NATIONAL UNIVERSITY

Lorentz Factor

A measure of the amount of time that a point of the reciprocal lattice remains on the reflection sphere during the measuring process
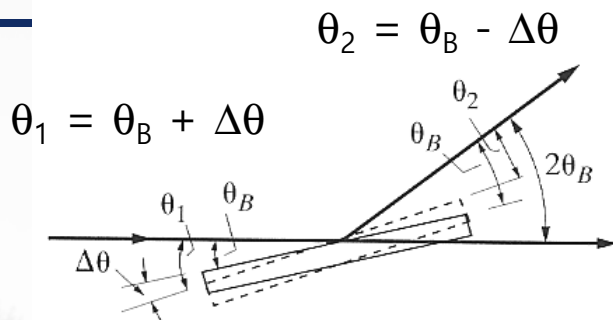
Cullity 4-9 (~ 4 pages)
Jenkins & Snyder page 76
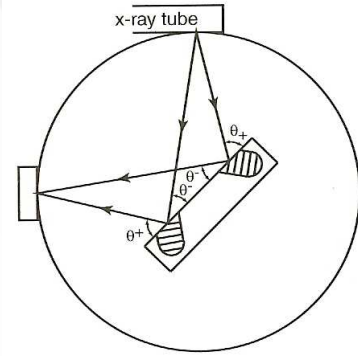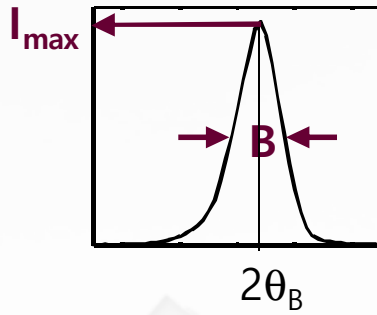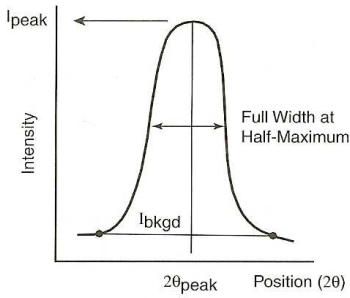
➤ Diffraction occurs over a range of angles.

  ✓ Incident X-ray is not perfectly collimated.

    ▪ Angular divergence of the incident x-ray leads to diffraction from particles with slightly different orientations.

  ✓ Incident X-ray is not purely monochromatic.

  ✓ Crystals can have mosaic structure.
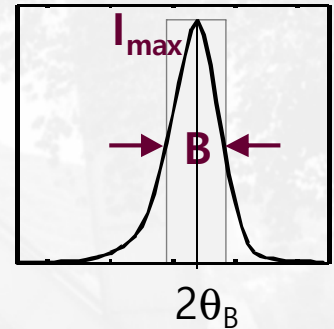
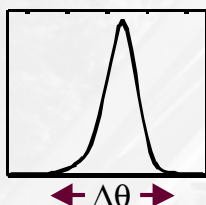I_{max} & B → integrated intensity

89

Geometrical factor - 1

$$\theta_2 = \theta_B - \Delta\theta$$

$$\theta_1 = \theta_B + \Delta\theta$$
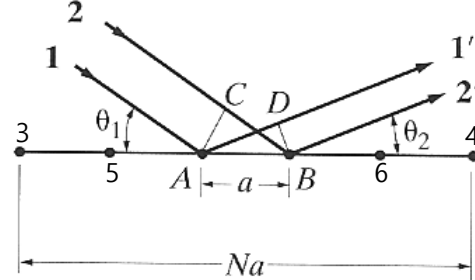
Total length of the plane

$\delta_{1'2'} = AD - CB = a\cos\theta_2 - a\cos\theta_1$

$\qquad = a[\cos(\theta_B - \Delta\theta) - \cos(\theta_B + \Delta\theta)].$

$\delta_{1'2'} = 2a\Delta\theta\sin\theta_B,$ → $2Na\,\Delta\theta\,\sin\theta_B$ Path difference b/w rays scattered by atoms at either end of the plane (3 & 4)

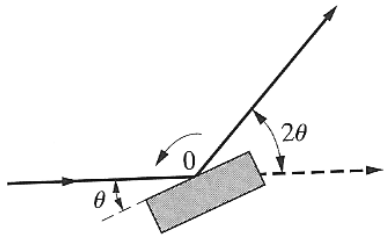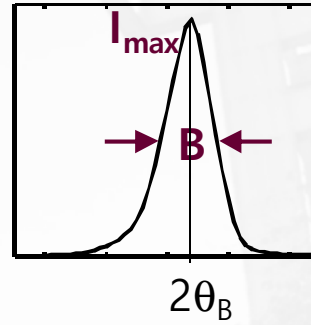Diffracted intensity = zero when $\boxed{2Na\,\Delta\theta\,\sin\theta_B = \lambda}$

$$\boxed{\Delta\theta = \frac{\lambda}{2\,Na\,\sin\theta_B}}$$

$I_{max} \propto 1/\sin\theta$

Max angular range of the peak

Cullity page 145~147   90

$$I_{max} \propto 1/\sin \theta_B$$

$$B \propto 1/\cos \theta_B$$

Size & strain broadening

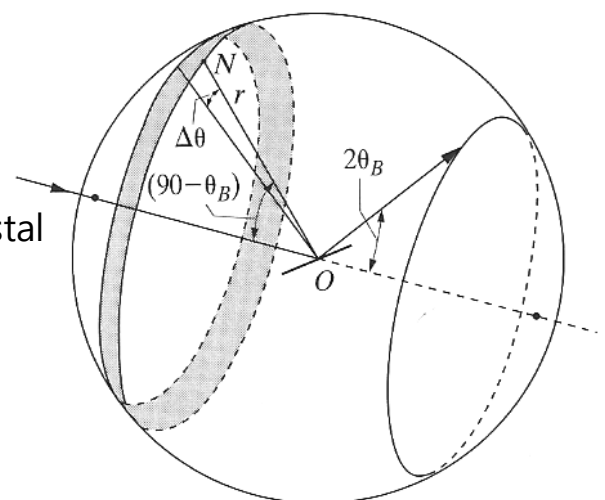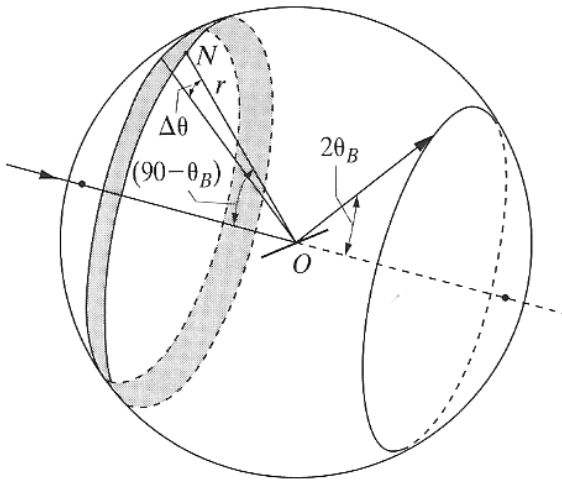| Integrated Intensity |
|---|

$$\propto I_{max} \, B \propto (1/\sin \theta_B)(1/\cos \theta_B) \propto \frac{1}{\sin 2\theta}$$

(1)

➢ Intensity of a reflection at θ_B depends on <u>the # of crystals oriented at or near θ_B.</u>

➢ This # is not constant even when the crystals are oriented completely at random.

➢ Powder specimen at O

➢ ON; normal to hkl plane in one crystal of the powder

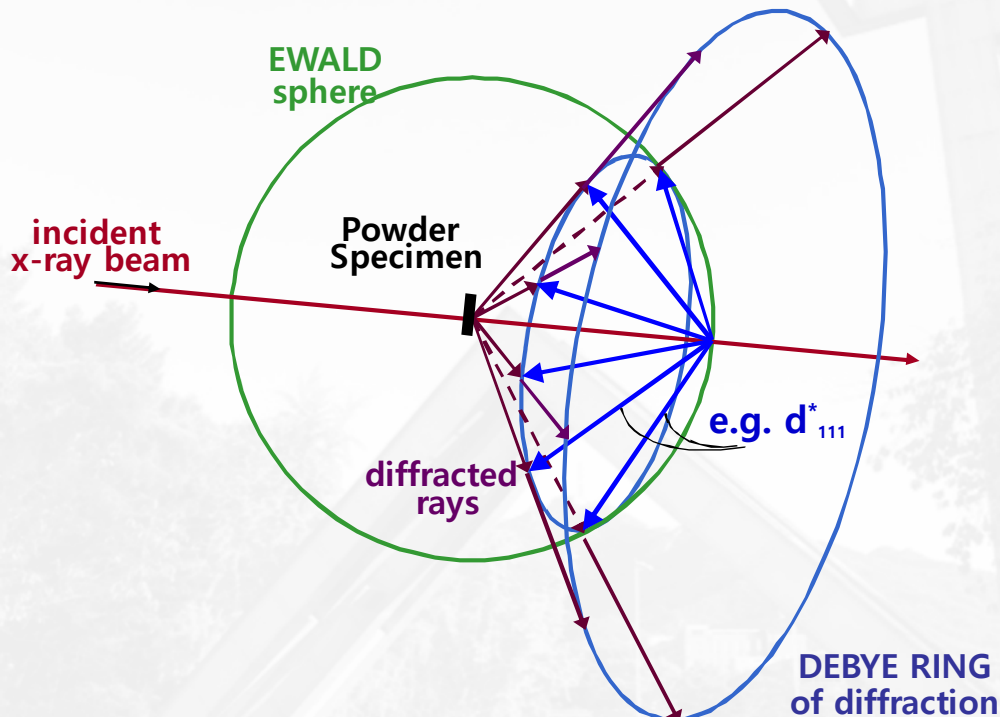➢ $\Delta\theta$; range of θ near θ_B over which diffraction is appreciable

Geometrical factor - 2

➢ Planes with ends of their normals lying in this band on the surface of the sphere, are diffracting.

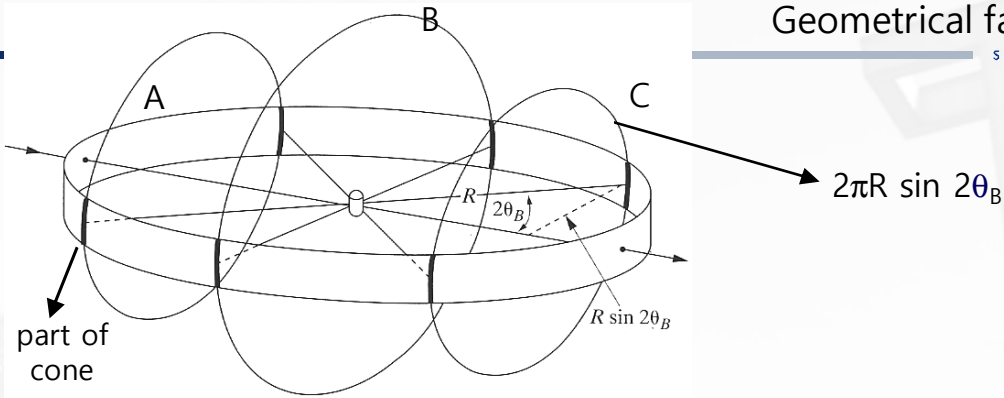➢ Fraction of crystals favorably oriented for reflection = ratio of strip area to area of the sphere.

$$\frac{\Delta N}{N} = \frac{r\Delta\theta \cdot 2\pi r \sin(90° - \theta_B)}{4\pi r^2} = \frac{\Delta\theta \cos\theta_B}{2}.$$

➢ Number of crystals favorably oriented for diffraction

$$\Delta N \propto \cos\theta_B$$
$$(2)$$

Origin of powder diffraction pattern

EWALD sphere

incident x-ray beam

Powder Specimen

diffracted rays

e.g. d^*_{111}

DEBYE RING of diffraction

Geometrical factor - 3

$2\pi R \sin 2\theta_B$

part of cone

$\dfrac{\text{Part of cone A}}{\text{Circumference A}} > \dfrac{\text{Part of cone B}}{\text{Circumference B}}$

A & C has larger proportion of diffraction cone than B on the film.

➢ Relative intensity → integrated intensity per unit line length of one diffraction line is compared with that of another.

➢ Can get larger proportion of diffraction cone when reflection is forward or backward direction ($2\theta << 90°$ or $2\theta >> 90°$).

➢ Smaller proportion of cone when $2\theta \sim 90°$.

$$\text{Relative intensity per unit length} \propto \frac{1}{\sin 2\theta} \quad (3)$$
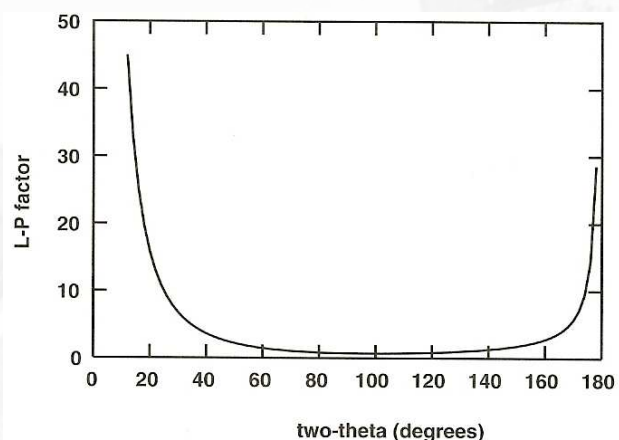
Cullity page 149

Lorentz-polarization factor (Lp factor)

$$\left(\frac{1}{\sin 2\theta}\right)(\cos \theta)\left(\frac{1}{\sin 2\theta}\right) = \frac{\cos \theta}{\sin^2 2\theta} = \frac{1}{4 \sin^2 \theta \cos \theta}.$$

(1)   (2)   (3)

Lorentz factor

polarization factor $\frac{1}{2}(1 + \cos^2 2\theta)$

Lp factor $\dfrac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}.$

➢ Geometrical factors decrease intensity of reflections @ intermediate angles compared to those in forward or backward directions.

➢ Lp factor decreases the intensity at intermediate 2θ angles.

➢ In powder technique, accurate sampling & homogeneous mixing are critical.

➢ Factors affecting observed intensity to depart from the theoretical one (important in quantitative phase analysis)

  ✓ Preferred orientation (texture)

  ✓ Microabsorption

  ✓ Extinction

Microabsorption

➢ Mixture of α & β

➢ When $\mu_\alpha \approx \mu_\beta$, and particle size of α & β is different. → microabsorption can make I(calculated) deviate from I(observed).

➢ If $\mu_\alpha >> \mu_\beta$, or particle size of α >> size of β → Intensity diffracted from a crystals will different from the calculated intensity.

➢ Can be negligible when (1) $\mu_\alpha \approx \mu_\beta$, and particle size of α & β is same, or (2) particle size of α & β is very small.

→ Powder samples should be finely ground.

Microabsorption

- Largest source of residual error in QPA by XRD due to microabsorption
- Occurs when sample contains a mix of low & highly absorbing phases
  - A disproportionate amount (more or less) of observed intensity comes from individual grains relative to what would be expected for the average absorption of the sample
- High absorbers
  - Beam absorbed in surface of grain
    - Only a fraction of the grain diffracting
  - Intensity under-overestimated – low QPA
- Low absorbers
  - Beam penetrates further into grain
    - Greater likelihood of 'volume diffraction' occurring
  - Intensity over-estimated – high QPA

High absorber
Low absorber
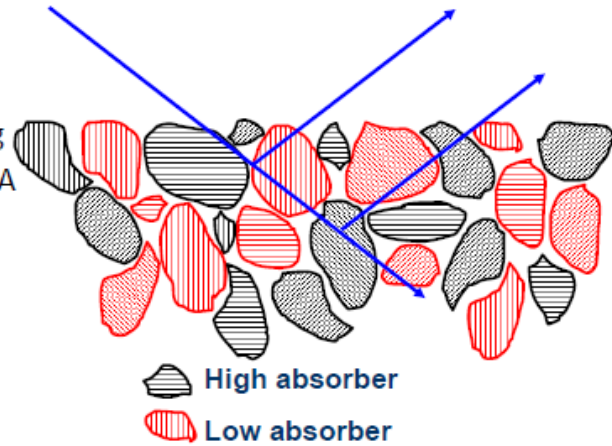
Microabsorption

- When dealing with a new sample, it is difficult to determine whether a correction for microabsorption is required without first obtaining additional information.
- The Brindley model is most frequently applied correction.
  - Requires knowledge of absorption contrast and particle sizes.
    - The latter is not easily achieved in 'real' samples.
- The Brindley model assumes spherical particles of uniform size.
  - Assumption is unrealistic in real samples.
  - Even when particle size is measured by e.g. laser-sizing or SEM, the best form of correction can still be unclear.
- Many applications suffer from unnecessary and/or excessive correction.
  - Largely overcorrected when addressed.
- **Better results achieved through care in sample preparation than in application of correction**
- Microabsorption is virtually absent for neutrons.
  - Neutron diffraction based results can act as a 'benchmark' for X-ray studies.

Sample Related Factors Affecting Accuracy
Microabsorption (cont'd)

- Brindley devised criteria for assessing whether microabsorption is likely to present a problem
  - μD = (linear absorption coefficient X particle diameter)

  - o Fine powders
    - $\mu D < 0.01$ – negligible micro-absorption, no correction necessary
  - o Medium powders
    - $0.01 < \mu D < 0.1$ – micro-absorption present, normal Brindley model applies
  - o Coarse powders
    - $0.1 < \mu D < 1.0$ – larger micro-absorption effect, use Brindley model to estimate effect – **provided μD is closer to the lower limit**
  - o Very coarse powders
    - $\mu D > 1.0$ – severe micro-absorption effect, beyond limits of model, concept of micro-absorption loses meaning

---

Intensities of diffraction peaks

SEOUL NATIONAL UNIVERSITY

- ➤ RELATIVE intensity (no absolute intensity)

- ➤ Factors constant for all lines are omitted.

> I; relative integrated intensity F; structure factor
> p; multiplicity factor   A; absorption factor
> e^{-2M}; temperature factor

Hull/Debye-Scherrer camera

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

Diffractometer

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

$$I(hkl) = \left(\frac{I_o A \lambda^3}{32\pi r} \right) \left[\left(\frac{\mu_o}{4\pi} \right)^2 \frac{e^4}{m^2} \right] \left(\frac{1}{v^2} \right) \left[|F(hkl)|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \right] \left(\frac{e^{-2M}}{2\mu} \right).$$
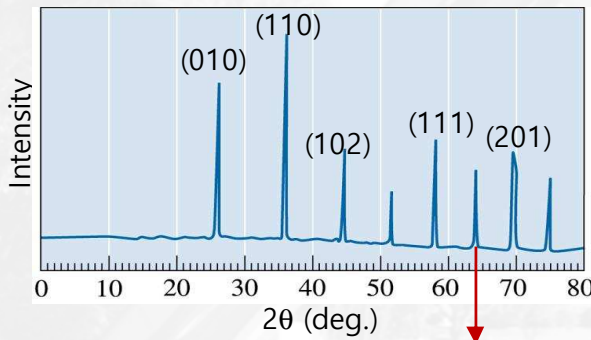
Intensity

Intensity diffracted by a single phase powder specimen in a diffractometer

$$I(hkl) = \left(\frac{I_o A \lambda^3}{32\pi r}\right)\left[\left(\frac{\mu_o}{4\pi}\right)^2 \frac{e^4}{m^2}\right]\left(\frac{1}{v^2}\right)\left[|F(hkl)|^2 p\left(\frac{1 + \cos^2 2\theta}{\sin^2\theta \cos\theta}\right)\right]\left(\frac{e^{-2M}}{2\mu}\right).$$

I(hkl) = integrated intensity per unit length of diffraction line

I_0 = intensity of incident beam   A = cross-sectional area of incident beam

r = radius of diffractometer circle   V = volume of unit cell

F(hkl) = structure factor   p = multiplicity factor

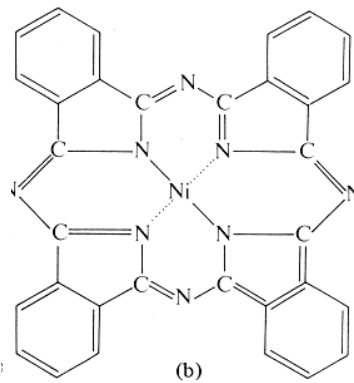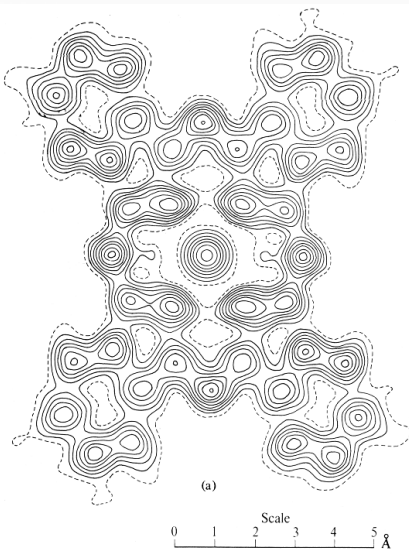e^{-2M} = temperature factor   μ = linear absorption coefficient

Relative intensity

d(A)	Int-f	h	k	l
3.2600	13	1	1	1
2.8210	100	2	0	0
1.9940	55	2	2	0
1.7010	2	3	1	1
1.6280	15	2	2	2
1.4100	6	4	0	0

Peak position

Bragg´s law $\lambda = 2d \sin\theta$

Electron density distribution

nickel phthalocyanine

Protein myoglobin