
Intensity of X-ray Diffraction

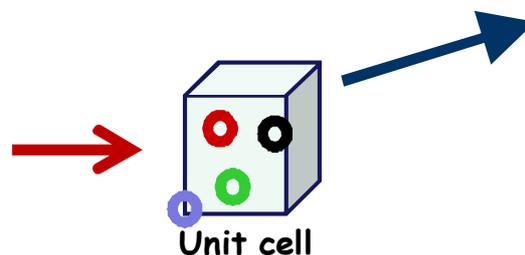
Crystal Structure Analysis
Materials Science & Engineering
Seoul National University
CHANPARK

Cullity Chapter 4

1 CHANPARK, MSE, SNU Spring-2019 Crystal Structure Analyses

Intensity

- How much Intensity a single electron will coherently scatter?
- Interference effects due to electrons being distributed in space around atoms
- Atoms are not stationary --- vibrate
- Intereference effects caused by scattering from atoms in different regions of the unit cell



2 CHANPARK, MSE, SNU Spring-2019 Crystal Structure Analyses

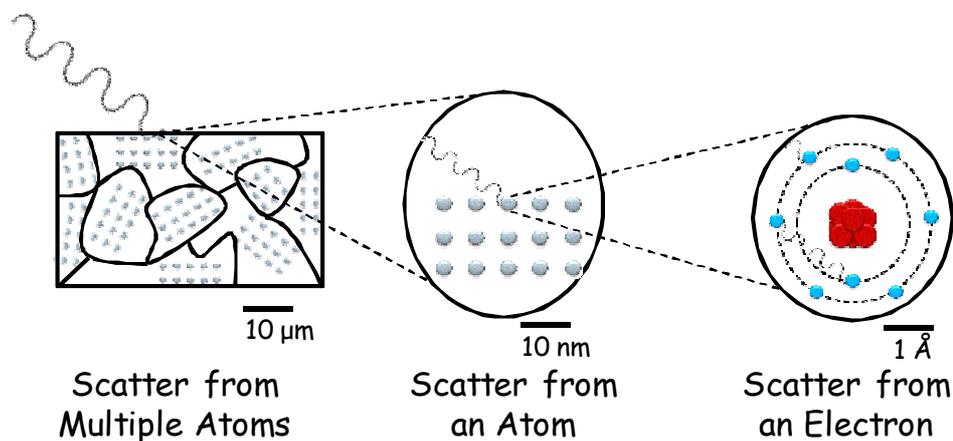
Factors affecting the relative intensity of Bragg reflections

- Structure factor
- Polarization factor
- Multiplicity factor
- Lorentz factor
- Absorption factor
- Temperature factor

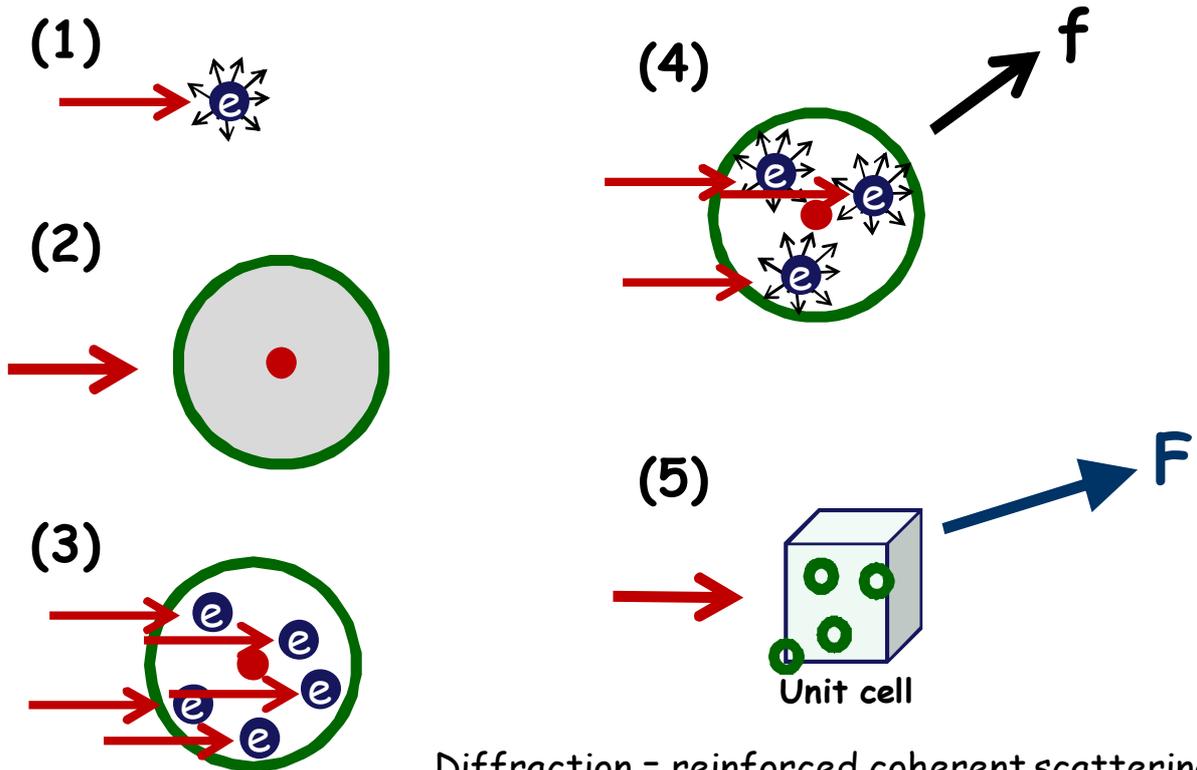
3 CHANPARK, MSE, SNU Spring-2019 Crystal Structure Analyses

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

- Scattering from a single electron
- Scattering from a single atom $\rightarrow f$
- Scattering from a unit cell $\rightarrow F$



4 CHANPARK, MSE, SNU Spring-2019 Crystal Structure Analyses



Diffraction = reinforced coherent scattering
Read Cullity Ch 4-3

Intensity of XRD

- 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

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

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

How much Intensity a single e' will coherently scatter?

→ 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

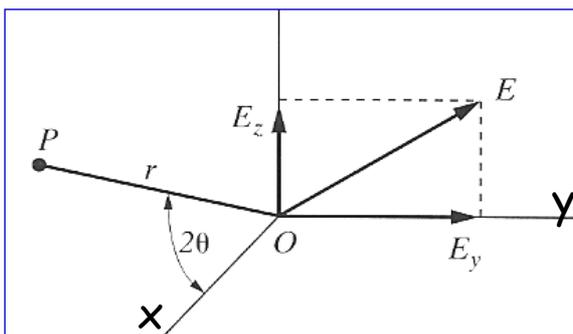
J.J. Thomson

$$I = I_0 \left(\frac{\mu_0}{4\pi} \right)^2 \left(\frac{e^4}{m^2 r^2} \right) \sin^2 \alpha = I_0 \frac{K}{r^2} \sin^2 \alpha$$

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

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

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



$$E^2 = E_y^2 + E_z^2$$

$$E_y^2 = E_z^2 = \frac{1}{2} E^2$$

$$I_{Oy} = I_{Oz} = \frac{1}{2} I_0$$

Read Cullity page 123 ~ 144

Total scattered intensity @ P

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

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

$$= \frac{K}{r^2} \left(\frac{I_0}{2} + \frac{I_0}{2} \cos^2 2\theta \right)$$

$$= I_0 \frac{K}{r^2} \left(\frac{1 + \cos^2 2\theta}{2} \right)$$

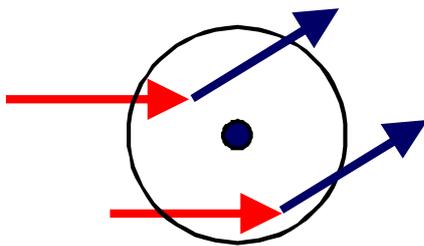
Thomson equation for the scattering of x-ray beam by a single electron

Polarization factor

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

→ atomic scattering factor

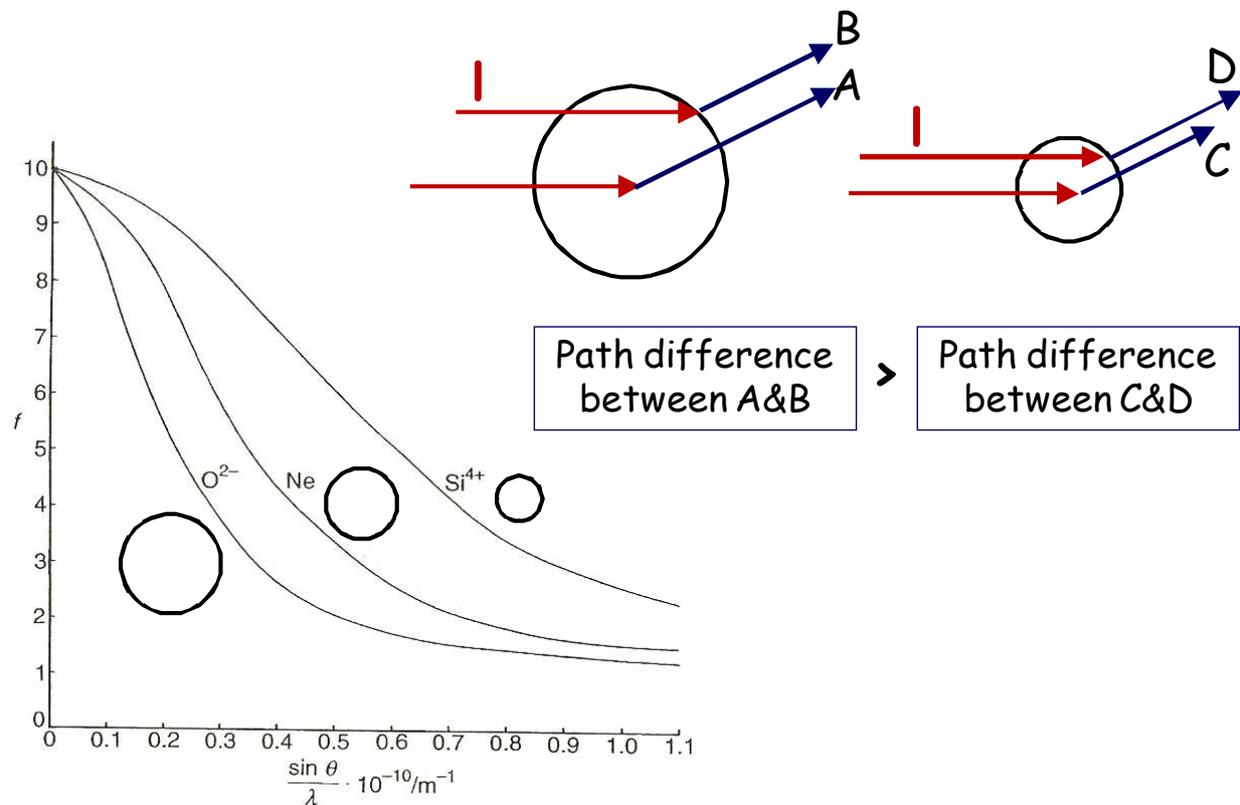
- Interference ← scattering from different regions of the e' cloud
- Takes into account the influence of the atom specific e' shell on the scattering of X-rays
- Normalized in units of the amount of scattering occurring from a single e'



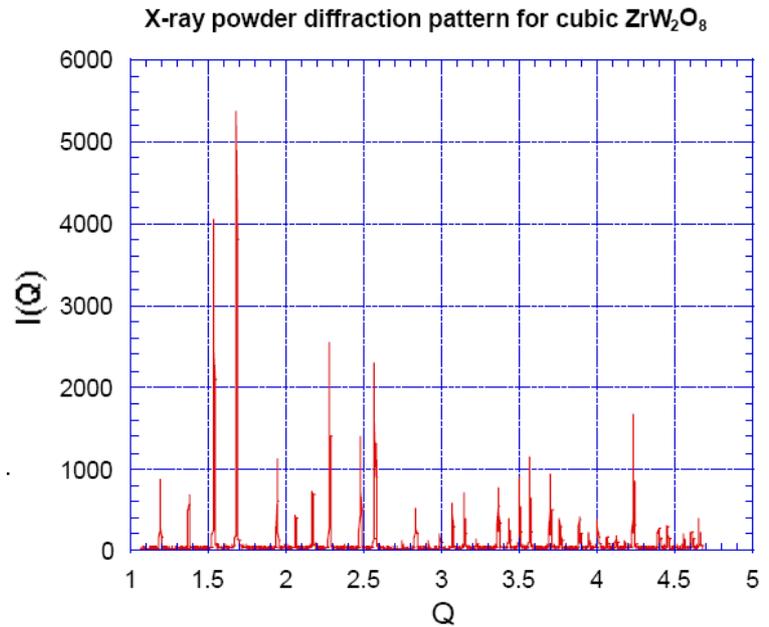
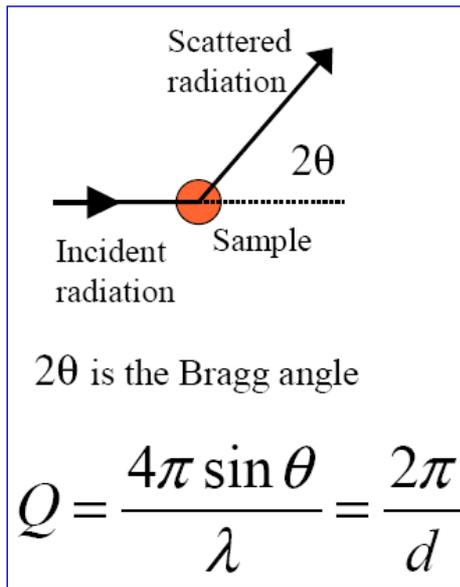
$$f = \frac{\text{amplitude scattered by an atom}}{\text{amplitude scattered by a single electron}}$$

$$f = F(\vartheta) \quad f(0^\circ) = Z$$

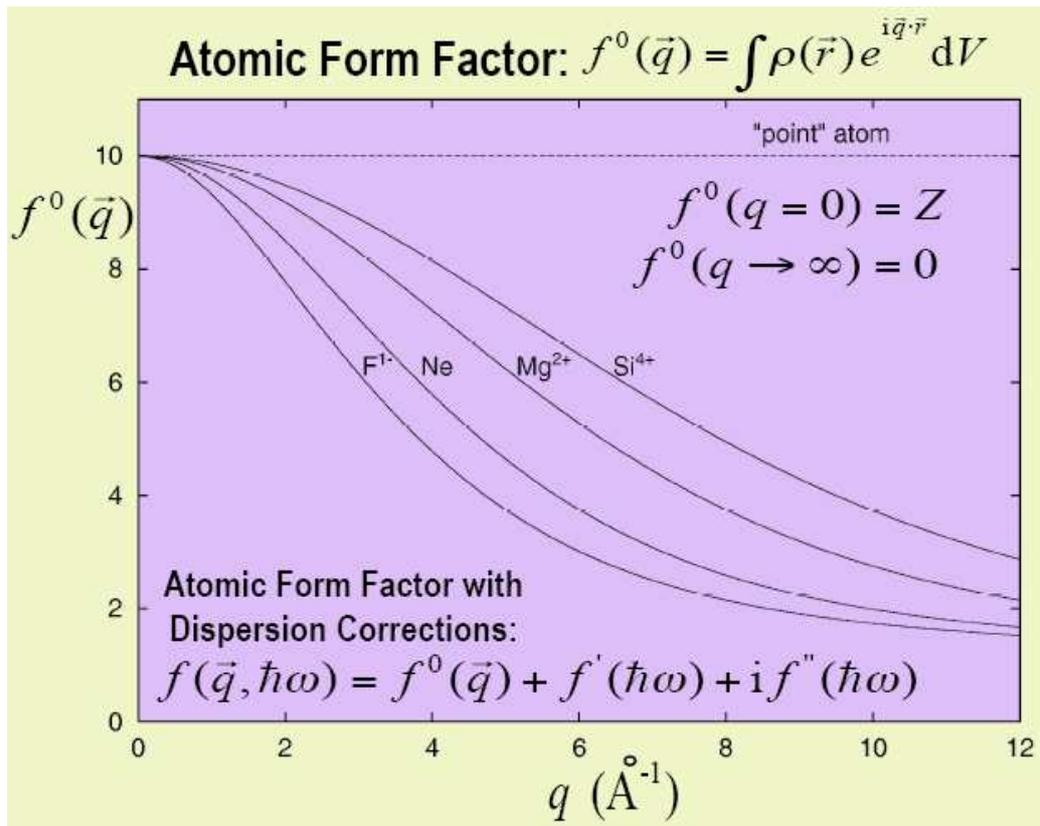
Atomic scattering factor (form factor)



XRPD pattern



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12 CHANPARK, MSE, SNU Spring-2019 Crystal Structure Analyses

Atomic scattering factor

		$\frac{\sin\theta}{\lambda} (\text{\AA}^{-1})$												
		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	

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Atomic scattering factor

	$\frac{\sin\theta}{\lambda} (\text{\AA}^{-1})$				
	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

Atomic scattering factor

$\frac{\sin\theta}{\lambda} (\text{\AA}^{-1})$	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
...

Factors affecting the intensity of the scattering from an atom (f)

➤ Anomalous scattering (anomalous dispersion)

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

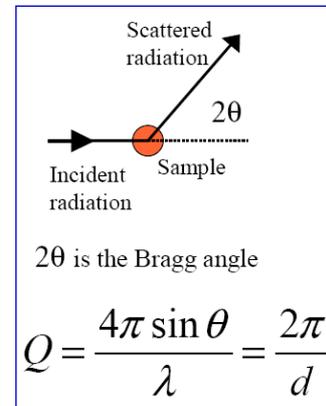
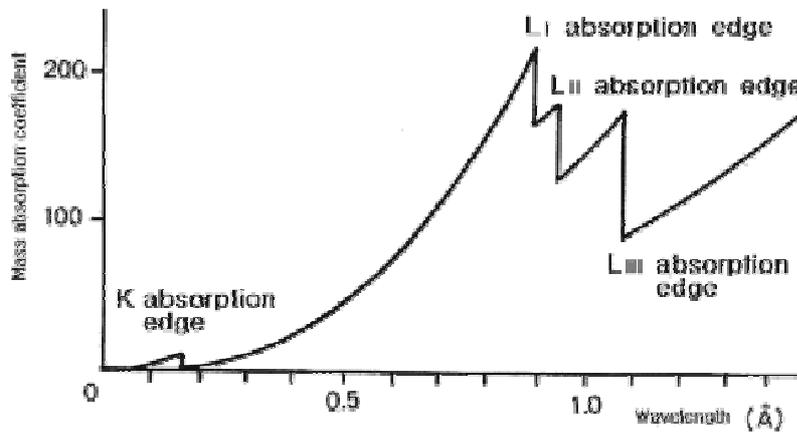
➤ Thermal motion

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

Anomalous scattering (anomalous dispersion)

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

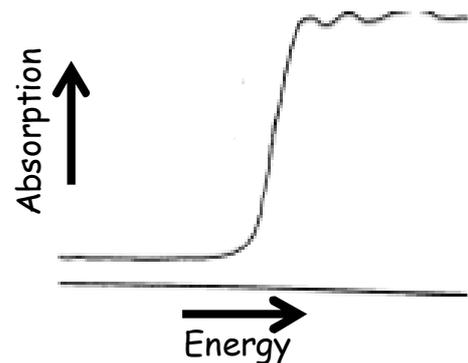
$$f(E, Q) = f_0(Q) + f'(E) + if''(E)$$



Absorption & anomalous scattering

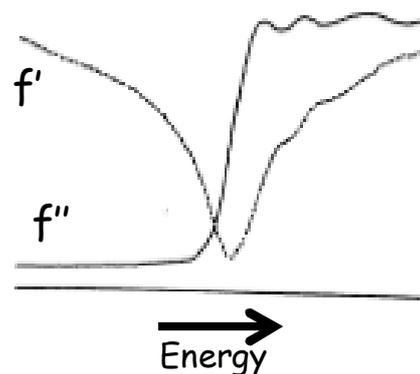
f' is intimately related to the absorption coefficient

$$f'(E) = \left(\frac{2}{\pi} \right) \int_0^\infty \frac{E f''(E)}{(E_0^2 - E^2)} dE$$



f'' "mirrors" the absorption coefficient

$$f''(E) = \left(\frac{2\pi mc \epsilon_0}{e^2 h} \right) E \mu_a$$



- Structure factor
- Polarization factor
- Multiplicity factor
- Lorentz factor
- Absorption factor
- **Temperature factor**

Temperature factor

Thermal motion

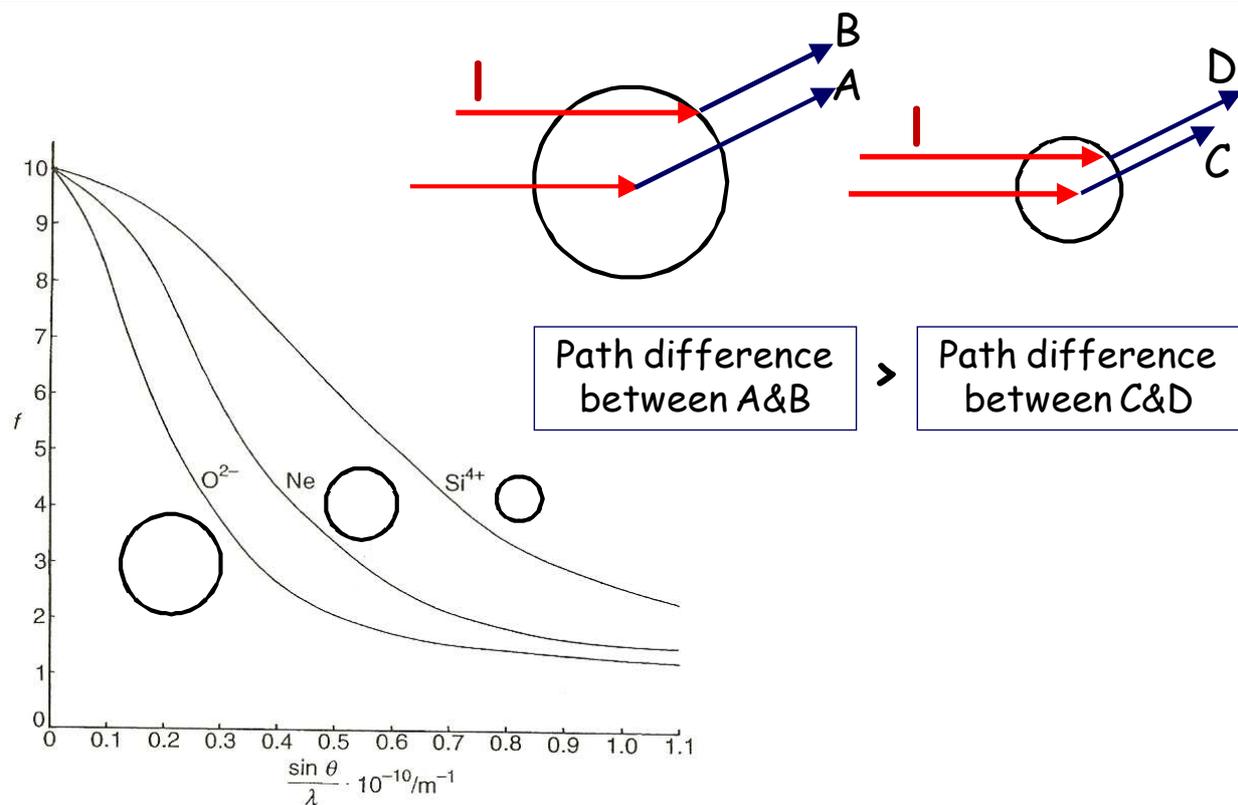
➤ Thermal vibration of atoms →

- ✓ 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

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Atomic scattering factor (form factor)



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Temperature factor

- Atomic vibration → effective size of atom is larger → interference effects larger

Debye-Waller temperature factor B

Mean-square displacement of atom vibration U^2

Mean displacement = 0

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

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

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

Thermal motion

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

Isotropic temp factor B, U_{iso}

Anisotropic temp factor $B_{ij} & U_{ij}$

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

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

$$f = f_0 \exp\left[-\frac{1}{4}(B_{11} h^2 \mathbf{a}^{*2} + B_{22} k^2 \mathbf{b}^{*2} + B_{33} l^2 \mathbf{c}^{*2} + 2B_{12} h k \mathbf{a}^* \mathbf{b}^* + 2B_{13} h l \mathbf{a}^* \mathbf{c}^* + 2B_{23} k l \mathbf{b}^* \mathbf{c}^*)\right].$$

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

$$2\pi^2 U_{ij} = \beta_{ij}$$

Temp factor: $B, U_{iso}, B_{ij}, U_{ij}, \beta_{ij}$

Thermal motion

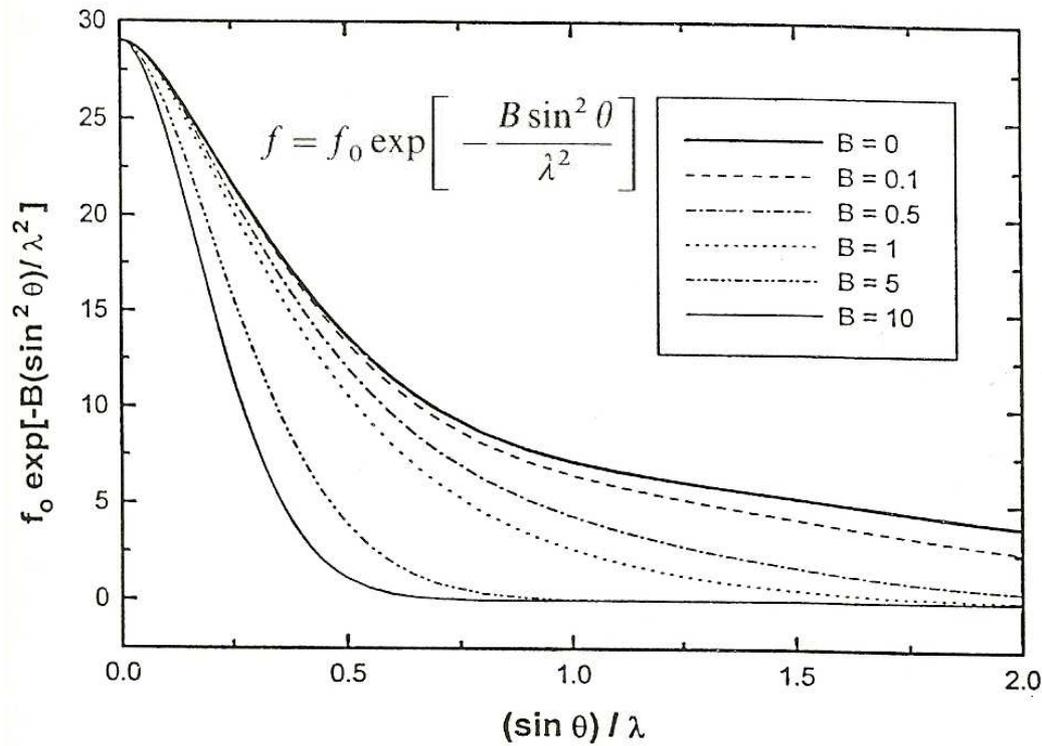
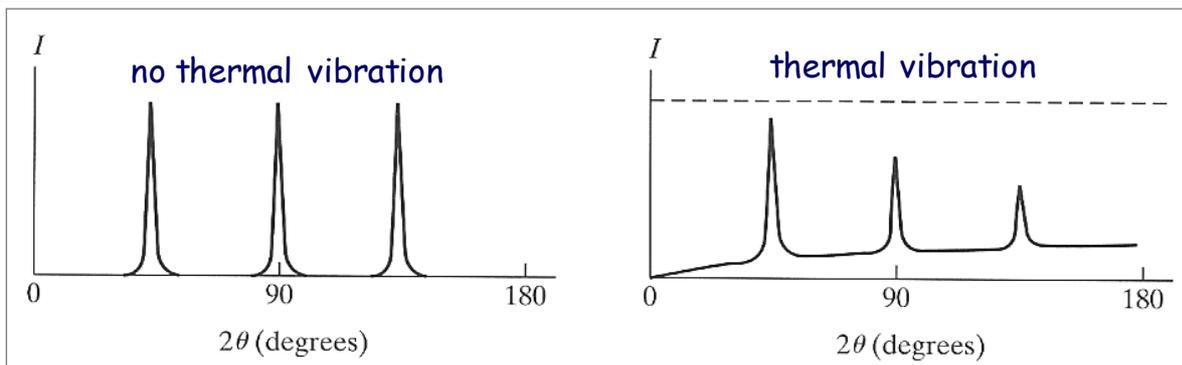


Figure 3.14. The effect of atomic thermal motion on the copper scattering factor.

Temperature factor



➤ Thermal vibration of atoms

➔ decrease of intensity of diffraction lines

✓ Effect increases with $2q$

➔ thermal diffuse scattering

✓ Thermal vibration causes general coherent scattering in all directions

✓ Contributes to background (BKG)

✓ BKG intensity increases with $2q$

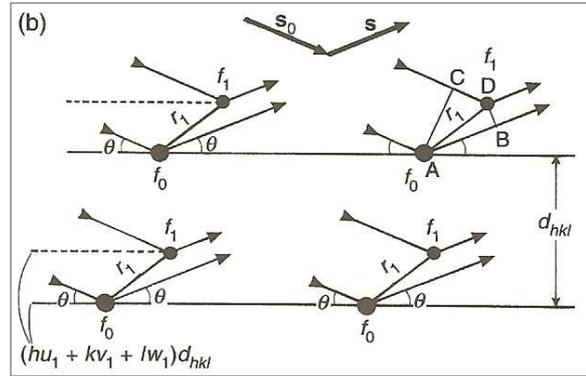
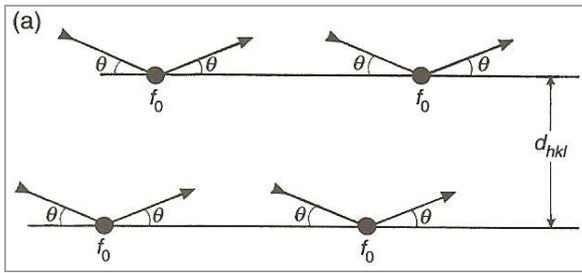
- Structure factor
- Polarization factor
- Multiplicity factor
- Lorentz factor
- Absorption factor
- Temperature factor

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

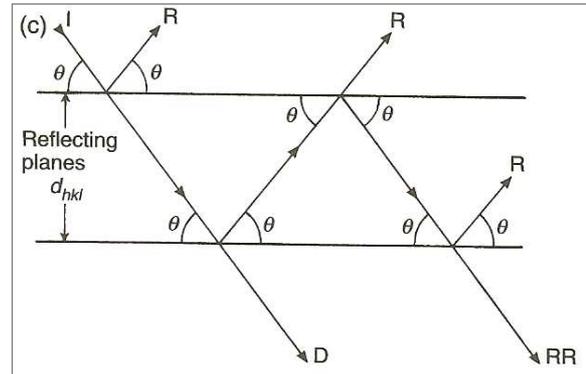
$$\text{P.D.} = AB - CD = \mathbf{r}_1 \cdot \mathbf{s} - \mathbf{r}_1 \cdot \mathbf{s}_0 = \mathbf{r}_1 \cdot (\mathbf{s} - \mathbf{s}_0)$$

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

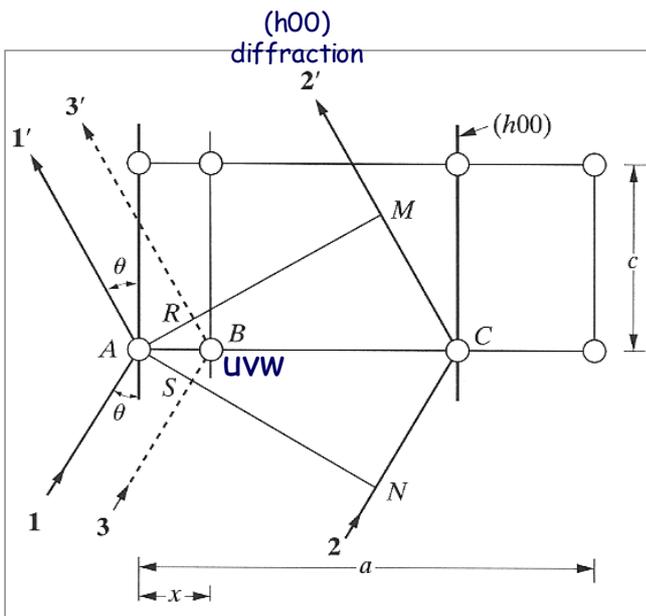
$$\text{P.D.} = \lambda(u_1\mathbf{a} + v_1\mathbf{b} + w_1\mathbf{c}) \cdot (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$$

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

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



Structure factor



Path difference b/w 2' & 1'

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

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

The effect of 3' on 1' & 2' ?

Path difference b/w 3' & 1'

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

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

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

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

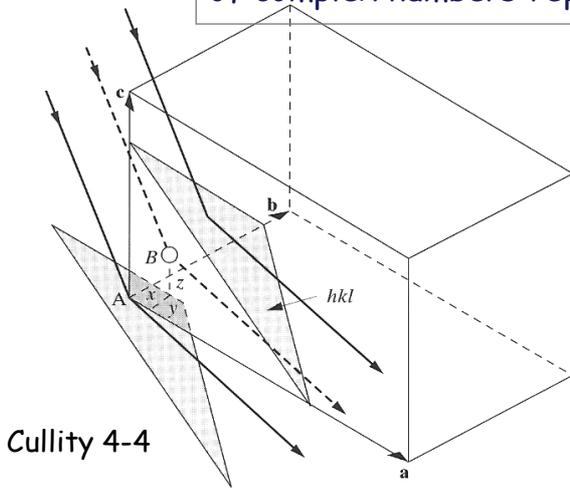
Position of atom B, $uvw \rightarrow \phi = 2\pi(hu + kv + lw) \rightarrow$

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

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 \rightarrow addition of complex numbers representing amplitudes and phase of each wave



Cullity 4-4

Any scattered wave from hkl reflection & atom in uvw

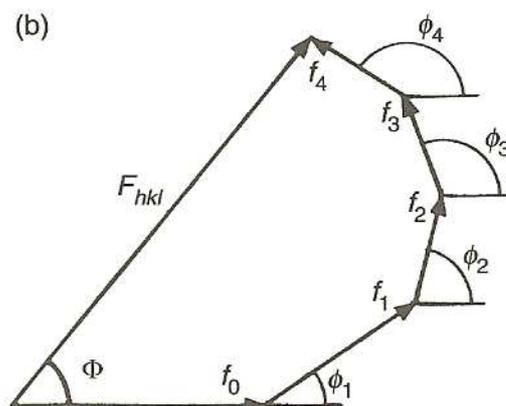
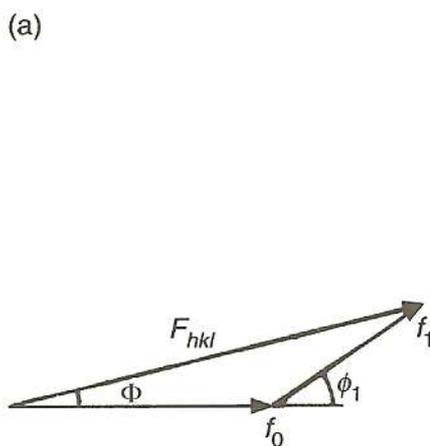
$$Ae^{i\phi} = fe^{2\pi i(hu + kv + lw)}$$

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

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

F contains info on both amplitude and phase of the resultant wave

Vector phase diagram for obtaining F_{hkl}



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

Structure Factor

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

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

Intensity of any hkl reflection from a knowledge of atomic positions can be calculated

$u_n, v_n, w_n, f_n \rightarrow F_{hkl}$ can be obtained \rightarrow can get I_{hkl}

Positions of atoms in unit cell, atomic scattering factors (kind of atoms) $\rightarrow F$ & I

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

33 CHANPARK, MSE, SNU Spring-2019 Crystal Structure Analyses

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

➤ Positions of atoms in unit cell, atomic scattering factors

$$\rightarrow F_{hkl} \text{ \& } I_{hkl} \quad I_{hkl} \sim |F_{hkl}|^2$$

➤ I_{hkl} from several sets of planes \rightarrow atom positions ;
crystal structure determination

➤ $F \rightarrow I$ vs. $I \rightarrow F$

✓ $F \rightarrow I$ (structure \rightarrow diff pattern); $I \rightarrow F$ (D pattern \rightarrow structure)

➤ Phase info in going from F_{hkl} to I_{hkl} is lost

\rightarrow phase problem

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

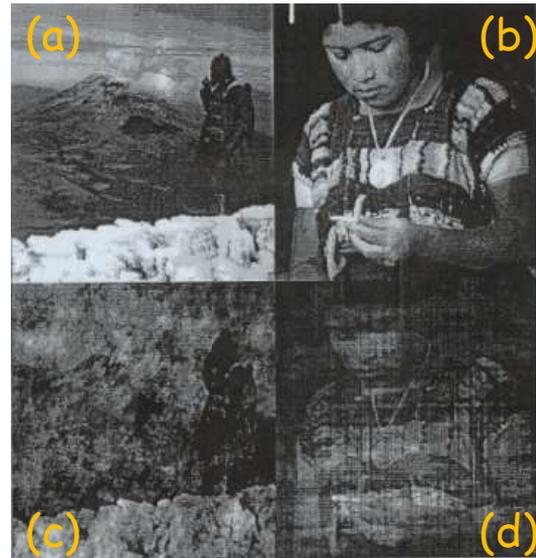
34 CHANPARK, MSE, SNU Spring-2019 Crystal Structure Analyses

Read Hammond Chap 9.1, 9.2, 9.3

Phase problem

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

A graphic illustration of phase problem



(a) & (b) : the original images.

(c) : Fourier reconstruction which has the Fourier phases of (a) and Fourier amplitude of (b).

(d) : reconstruction with the phase of (b) and the amplitude of (a).

Fourier transform

$$\text{➤ } F_{hkl} = \int_{xyz} \exp(2\pi i(hx+ky+lz)) dV$$

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

$$\text{➤ } r_{xyz} = (1/V) \sum_h \sum_k \sum_l F_{hkl} \exp(-2\pi i(hx+ky+lz))$$

- **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 (rdf)
- r space = real space diffraction space = reciprocal space
- Reciprocal space always has centrosymmetry even though there is no centrosymmetry in real space
- Diffraction pattern always gives Laue group pattern

Inverse Transform

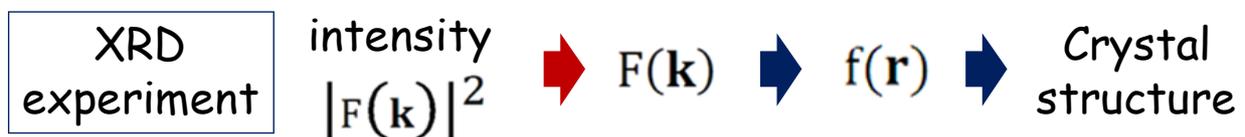
$$\text{Diffraction pattern } F(\mathbf{k}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}$$

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

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

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

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



$f(\mathbf{r})$ 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

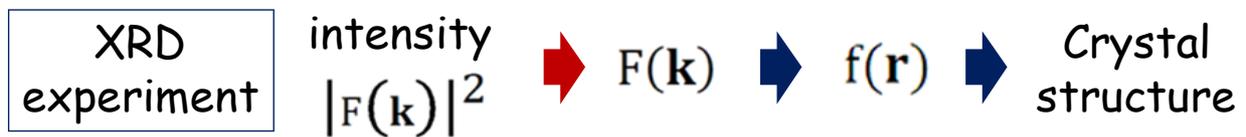
The act of diffraction = taking Fourier transform of the obstacle

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

Experimental Limitation

- 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



real space vs. reciprocal space

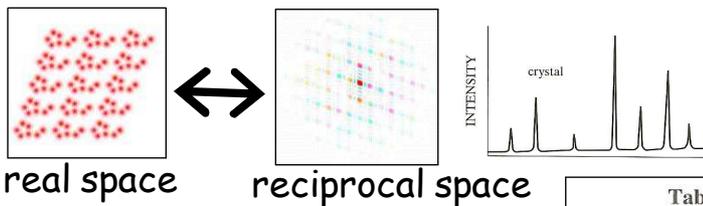


Table 9.1 The eleven Laue point groups or crystal classes

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

Friedel's law

- 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

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

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

Base-centered
cell 000 & $\frac{1}{2}\frac{1}{2}0$

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

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

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

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

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

$$F^2 = 0.$$

Body-centered cell
000 & $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

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

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

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

$$F = 4f^2.$$

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

$$F^2 = 0.$$

Read Cullity Chap 4.6

Cullity page 138

Structure factor

face-centered cell
000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$ & $0\frac{1}{2}\frac{1}{2}$

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

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

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

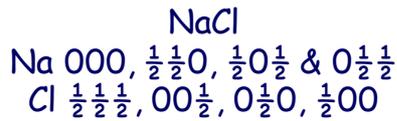
$$F = 4f \quad \text{for unmixed indices;}$$

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

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

$$F^2 = 0$$

Structure factor



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

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

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

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

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

$$F = 0 \quad \text{for mixed indices;} \\ F^2 = 0. \\ F = 4[f_{\text{Na}} + f_{\text{Cl}} e^{\pi i(h+k+l)}]. \\ F = 4(f_{\text{Na}} + f_{\text{Cl}}) \quad \text{if } (h+k+l) \text{ is even;} \\ F^2 = 16(f_{\text{Na}} + f_{\text{Cl}})^2. \\ F = 4(f_{\text{Na}} - f_{\text{Cl}}) \quad \text{if } (h+k+l) \text{ is odd;} \\ F^2 = 16(f_{\text{Na}} - f_{\text{Cl}})^2.$$

Structure Factor - CsCl

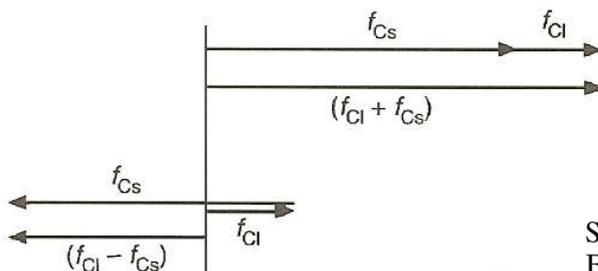


$$F_{hkl} = \sum_{n=0}^{n=N} f_n \exp 2\pi i(hu_n + kv_n + lw_n)$$

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

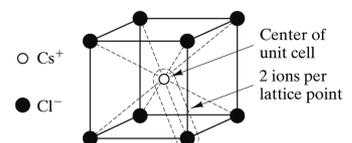
$$F_{hkl} = f_{\text{Cl}} + f_{\text{Cs}} \quad (h+k+l) = \text{even}$$

$$F_{hkl} = f_{\text{Cl}} - f_{\text{Cs}} \quad (h+k+l) = \text{odd}$$



➤ caesium iodide (CsI)
 ✓ basis I⁻: 0,0,0 Cs⁺: $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

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



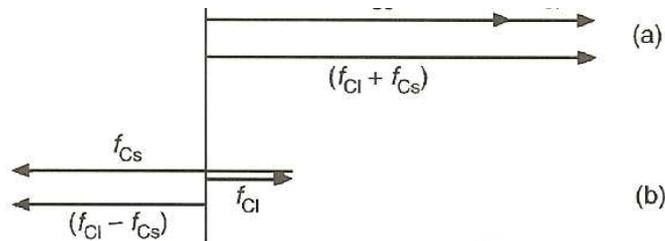
Structure Factor - CsCl

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

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 $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ for Cs, atomic scattering factor f_{Cs} . Substituting these two terms in the equation:

$$\begin{aligned} F_{hkl} &= f_{\text{Cl}} \exp 2\pi i(h0 + k0 + l0) + f_{\text{Cs}} \exp 2\pi i(h\frac{1}{2} + k\frac{1}{2} + l\frac{1}{2}) \\ &= f_{\text{Cl}} + f_{\text{Cs}} \exp \pi i(h + k + l). \end{aligned}$$

Two situations may be identified: when $(h + k + l) = \text{even integer}$, $\exp \pi i$ (even integer) = 1, hence $F_{hkl} = f_{\text{Cl}} + f_{\text{Cs}}$ and when $(h + k + l) = \text{odd integer}$, $\exp \pi i$ (odd integer) = -1, hence $F_{hkl} = f_{\text{Cl}} - f_{\text{Cs}}$. 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.



Structure Factor - hcp

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

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

$$[(h + 2k)/3 + l/2] = g \quad F = f(1 + e^{2\pi ig})$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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 $(\frac{1}{3}\frac{2}{3}\frac{1}{2})$ (the B layer atoms). Substituting these two terms in the equation:

Structure Factor hcp

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

$$= f(1 + \exp 2\pi i(h\frac{1}{3} + k\frac{2}{3} + l\frac{1}{2})).$$

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).

$$F_{002} = f(1 + \exp 2\pi i) = 2f$$

$$F_{100} = f(1 + \exp \frac{2}{3}\pi i) = f(1 + \cos \frac{2}{3}\pi + i \sin \frac{2}{3}\pi) = f(0.5 + i0.866)$$

$$F_{101} = f(1 + \exp 2\pi i(\frac{1}{3} + \frac{1}{2})) = f(1 + \cos \frac{5}{3}\pi + i \sin \frac{5}{3}\pi) = f(1.5 - i0.866).$$

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

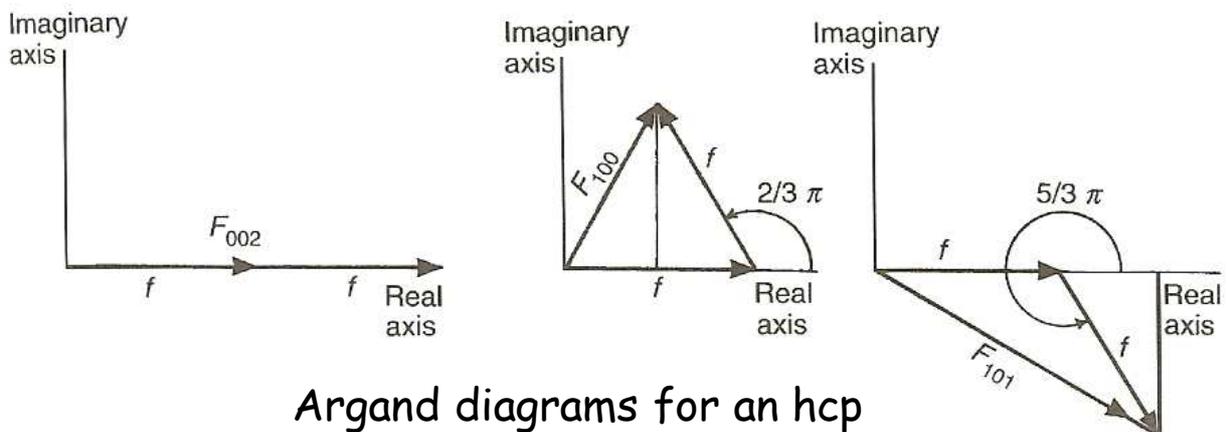
Hammond Chap 9

Structure Factor - hcp

$$F_{002} = f(1 + \exp 2\pi i) = 2f$$

$$F_{100} = f(1 + \exp \frac{2}{3}\pi i) = f(1 + \cos \frac{2}{3}\pi + i \sin \frac{2}{3}\pi) = f(0.5 + i0.866)$$

$$F_{101} = f(1 + \exp 2\pi i(\frac{1}{3} + \frac{1}{2})) = f(1 + \cos \frac{5}{3}\pi + i \sin \frac{5}{3}\pi) = f(1.5 - i0.866).$$



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:

$$\begin{aligned} F_{hkl} &= f \exp 2\pi i(hu + kv + lw) + f \exp 2\pi i(h\bar{u} + k\bar{v} + l\bar{w}) \\ &= f \exp 2\pi i(hu + kv + lw) + f \exp -2\pi i(hu + kv + lw). \end{aligned}$$

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.

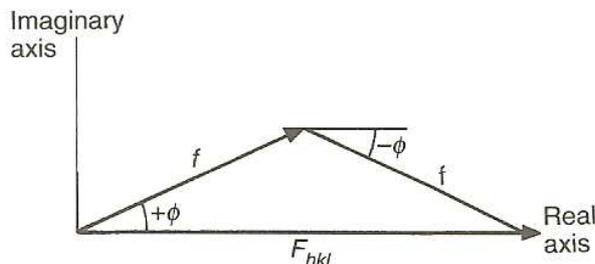


Fig. 9.6. The Argand diagram for a centrosymmetric crystal. The phase angle $+\phi$ for the atom at (uvw) is equal and opposite to the phase angle $-\phi$ for the atom at $(\bar{u}\bar{v}\bar{w})$, hence F_{hkl} is real.

Friedel's law

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

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

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

$$F_{hkl} = F_{\bar{h}\bar{k}\bar{l}}^* \text{ and } F_{hkl}^* = F_{\bar{h}\bar{k}\bar{l}}, \text{ hence } I_{hkl} = I_{\bar{h}\bar{k}\bar{l}}$$

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

- 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 absence (extinction)

- The condition that structure factor becomes zero due to a systematic symmetry condition
- Presence of reflections with zero intensity caused by the space group (symmetry) of unit cell
- Arise from centering of unit cell and/or the presence of translational symmetry elements - screw axes, glide planes
 - ✓ Can get info on these elements from the extinction of peaks

Structure factor & Extinction conditions

Body-centered
cell
 000 & $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

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

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

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

$$F = 4f^2.$$

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

$$F^2 = 0.$$

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

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

Systematic absence (extinction)

H, K, L; primitive
h, k, l; fcc unit cell

FCC

$$\mathbf{A} = \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b} + 0\mathbf{c}$$

$$H = \frac{1}{2}h + \frac{1}{2}k + 0l$$

$$2H = h + k$$

$$\mathbf{B} = \frac{1}{2}\mathbf{a} + 0\mathbf{b} + \frac{1}{2}\mathbf{c}$$

$$K = \frac{1}{2}h + 0k + \frac{1}{2}l \quad \text{or} \quad 2K = h + l$$

$$\mathbf{C} = 0\mathbf{a} + \frac{1}{2}\mathbf{b} + \frac{1}{2}\mathbf{c}$$

$$L = 0h + \frac{1}{2}k + \frac{1}{2}l$$

$$2L = k + l.$$

$$(000), (\frac{1}{2}\frac{1}{2}0), (\frac{1}{2}0\frac{1}{2}), (0\frac{1}{2}\frac{1}{2}).$$

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

$$F_{hkl} = f(1 + \cos 2\pi(h+k) + \cos 2\pi(h+l) + \cos 2\pi(k+l)).$$

hkl ; h, k, l mixed even and odd

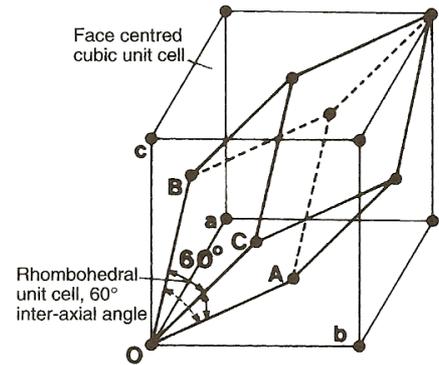


Fig. A6.1.

BCC

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

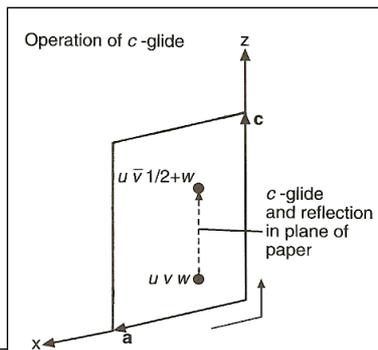
$$= f(1 + \cos \pi(h+k+l)).$$

Hence when $(h+k+l) = \text{even integer}$ $F_{hkl} = 2f$ and when $(h+k+l) = \text{odd integer}$ $F_{hkl} = 0$.

hkl ; $h+k+l = \text{odd}$

Systematic absence (extinction)

monoclinic $c \perp b$ $h0l$: $l = \text{odd}$



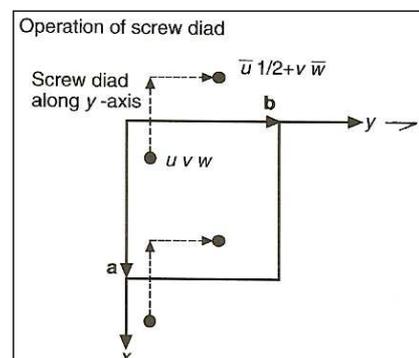
$$F_{hkl} = f \exp 2\pi i(hu + kv + lw) + f \exp 2\pi i(hu + kv + l(\frac{1}{2} + w)).$$

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

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

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

monoclinic $2_1 \parallel b$ $0k0$: $k = \text{odd}$



$$F_{hkl} = f \exp 2\pi i(hu + kv + lw) + f \exp 2\pi i(hu + k(\frac{1}{2} + v) + lw)$$

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

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

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

Table A6.1 Extinction criteria for lattices and symmetry elements

Systematic absence
(extinction)

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		$h + l = 2n$
			h, k, l
centred on all faces	F		all = n (odd) or all = $2n$ (even)
rhombohedral, obverse	R		$-h + k + l = 3n$
rhombohedral, reverse	R		$h - k + l = 3n$
Glide plane \parallel (001)	a b n d	$hk0$	$h = 2n$ $k = 2n$ $h + k = 2n$ $h + k = 4n$
Glide plane \parallel (100)	b c n d	$0kl$	$k = 2n$ $l = 2n$ $k + l = 2n$ $k + l = 4n$
Glide plane \parallel (010)	a c d n	$h0l$	$h = 2n$ $l = 2n$ $h + l = 2n$ $h + l = 4n$
Glide plane \parallel (110)	c n d	hhl	$l = 2n$ $h + k = 2n$ $2h + l = 4n$
Screw axis \parallel c	$2_1, 4_2, 6_3$ $3_1, 3_2, 6_2, 6_4$ $4_1, 4_2$ $6_1, 6_5$	$00l$	$l = 2n$ $l = 3n$ $l = 4n$ $l = 6n$
Screw axis \parallel a	$2_1, 4_2$ $4_1, 4_3$	$h00$	$h = 2n$ $h = 4n$
Screw axis \parallel b	$2_1, 4_2$ $4_1, 4_3$	$0k0$	$k = 2n$ $k = 4n$
Screw axis \parallel [110]	2_1	$hh0$	$h = 2n$

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 $\pm h, \pm k, \pm l$ 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
 - ✓ $(100), (010), (001), (-100), (0-10), (00-1) \rightarrow 6$
 - ✓ $(111), (-111), (1-11), (11-1), (1-1-1), (-11-1), (-1-11), (-1-1-1) \rightarrow 8$
 - ✓ (Intensity of 111) $\times 3 =$ (Intensity of 100) $\times 4$, when other things are equal
- Tetragonal
 - ✓ $(100), (010), (-100), (0-10) \rightarrow 4$
 - ✓ $(001), (00-1) \rightarrow 2$
 - ✓ $(111), (-111), (1-11), (11-1), (1-1-1), (-11-1), (-1-11), (-1-1-1) \rightarrow 8$
 - ✓ (Intensity of 111) = (Intensity of 100) $\times 2$, when other things are equal
 - ✓ (Intensity of 111) = (Intensity of 001) $\times 4$, when other things are equal

Multiplicity

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*
h01	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

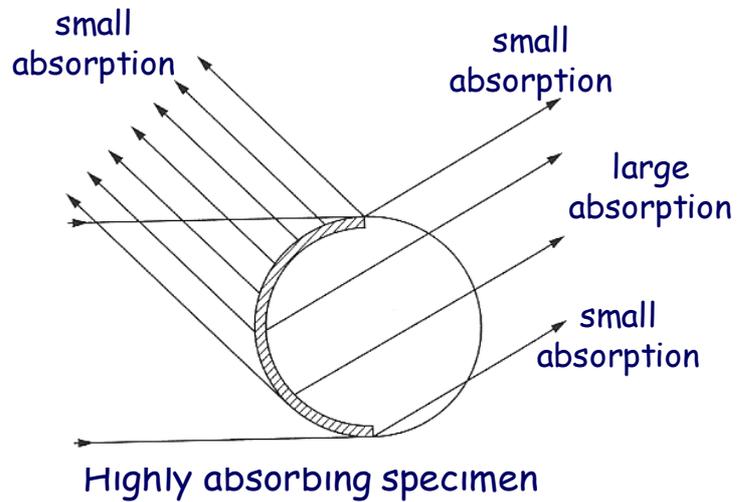
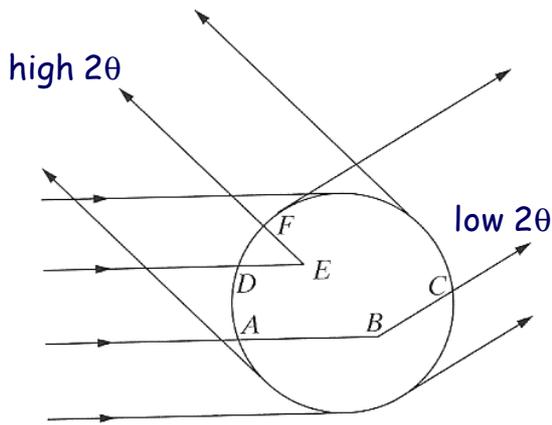
Note: For some space groups within the crystal systems, indexes marked with * are half the indicated values. A complete listing may be found in Table 3.5.1 in the *International Tables for X-Ray Crystallography*, Vol. 1, pp. 32–33.

CONTINUED		No. 14		$P2_1/c$	
Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3)					
Positions					
Multiplicity	Wyckoff letter	Coordinates	Reflection conditions		
Site symmetry					
4	e	Positions	Multiplicity	Coordinates	
2	d	Multiplicity	Number of equivalent points in a unit cell		
2	c	Wyckoff letter			
2	b	Site symmetry			
2	a	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	$\bar{1}$	$0, 0, 0$	$0, \frac{1}{2}, \frac{1}{2}$	

- Structure factor
- Polarization factor
- Multiplicity factor
- Lorentz factor
- **Absorption factor**
- Temperature factor

Absorption

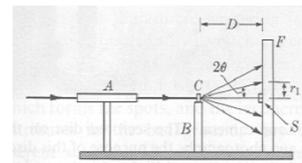
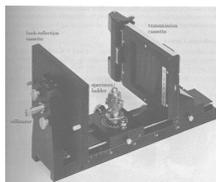
Absorption factor > Hull/Debye-Scherrer



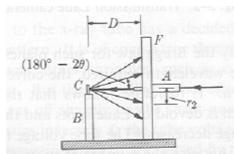
➤ Absorption is larger for low θ reflection

Absorption factor > Diffractometer, Camera

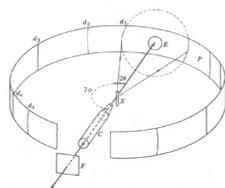
Transmission & back-reflection (Laue camera)



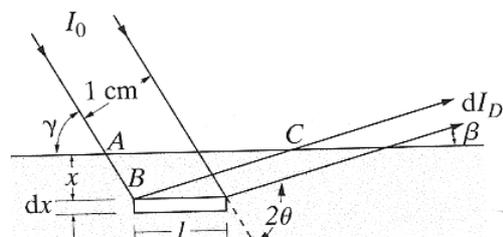
Transmission (Laue camera)



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

Extinction

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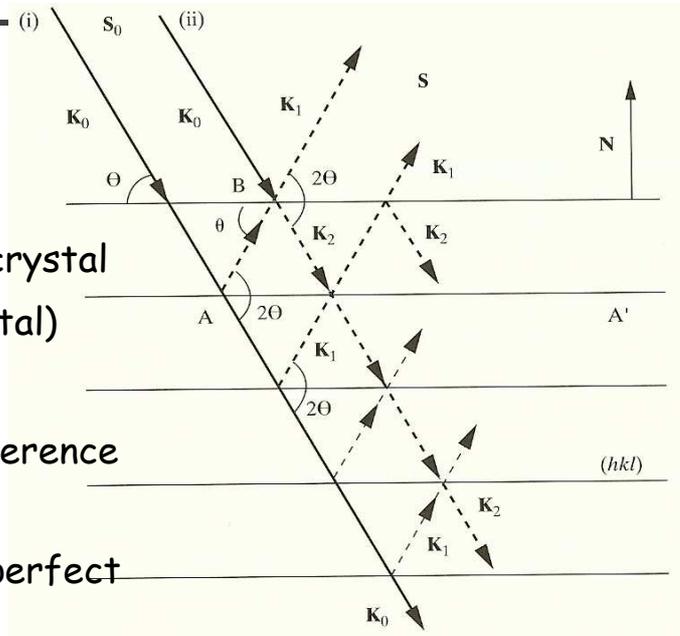
Extinction

- Diffracted intensity; perfect xtal << ideally imperfect xtal
- Decrease in intensity as the crystal becomes more perfect (large mosaic blocks, oriented)
- Ideally imperfect crystal 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

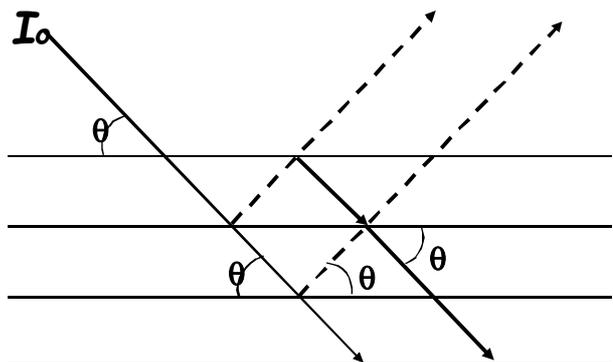
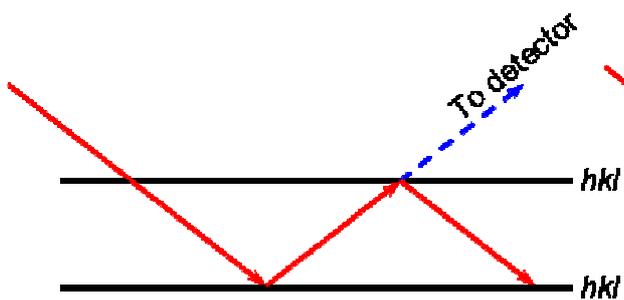
Primary Extinction

- Diffraction from highly perfect crystal
- I (perfect xtal) \ll I (imperfect xtal)
- $\phi(K_0/K_1) = p/2$
- $\phi(K_0/K_2) = p \rightarrow$ destructive interference \rightarrow lower intensity
- Depends on the degree of being perfect

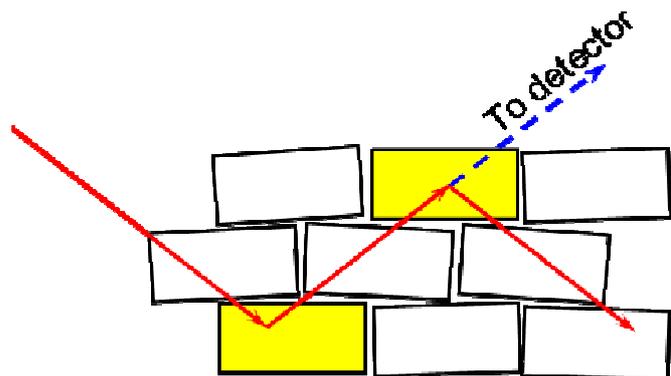


- Does not kill the reflection but lower intensity
- How to avoid? - give some stress (increase mosaicity by e.g. LN2 quenching, heat & quenching, etc.)

Primary Extinction

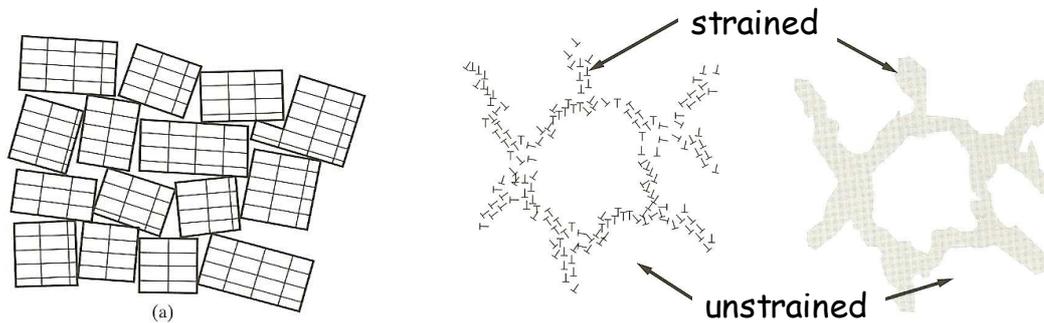


Secondary extinction



Mosaic structure

- Not perfectly regular lattice → collection of tiny blocks each slightly disoriented one from the other
- Angle of disorientation between the blocks is ϵ (< 1 degree) → diffraction occurs at all angles between θ_B and $\theta_B + \epsilon$
- Increases the integrated intensity relative to that obtained (or calculated) for an ideally perfect crystal ← strains & strain gradients associated with the groups of dislocations

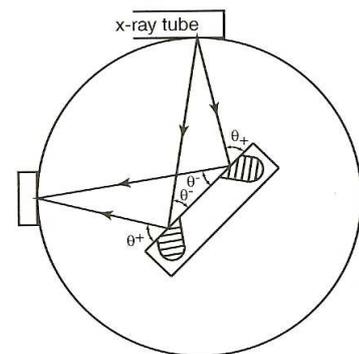
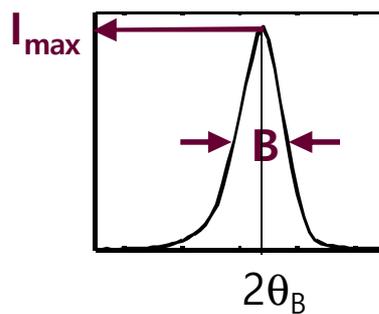
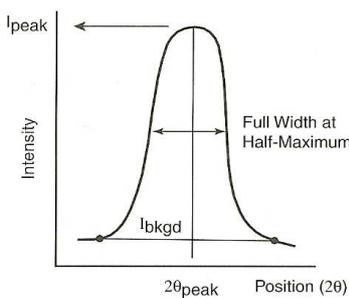


Factors affecting the relative intensity of Bragg reflections

- Structure factor
- Polarization factor
- Multiplicity factor
- Lorentz factor
- Absorption factor
- Temperature factor

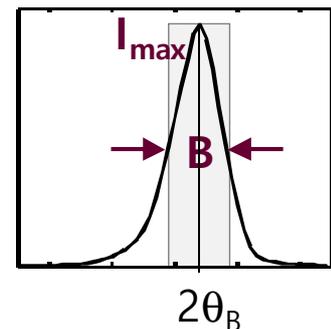
Lorentz Factor

A measure of the amount of time that a point of the reciprocal lattice remains on the reflection sphere during the measuring process



➤ Diffraction occurs over a range of angles

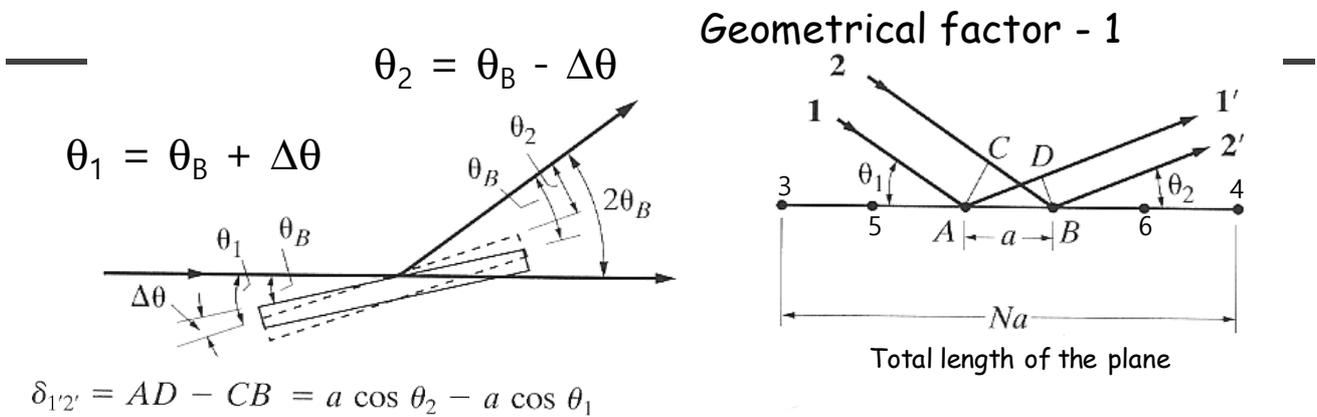
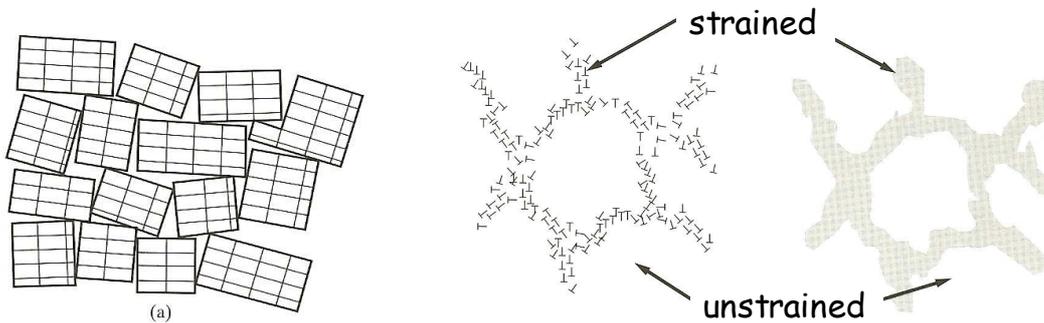
- ✓ Incident X-ray is not perfectly collimated
 - Angular divergence of the incident x-ray leads to diffraction from particles with slightly different orientations
- ✓ Incident X-ray is not purely monochromatic
- ✓ Crystals can have mosaic structure



I_{max} & $B \rightarrow$ integrated intensity

Mosaic structure

- Not perfectly regular lattice → collection of tiny blocks each slightly disoriented one from the other
- Angle of disorientation between the blocks is ε (< 1 degree) → diffraction occurs at all angles between θ_B and $\theta_B + \varepsilon$
- Increases the integrated intensity relative to that obtained (or calculated) for an ideally perfect crystal ← strains & strain gradients associated with the groups of dislocations

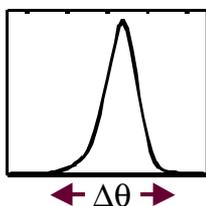


$$\delta_{1'2'} = AD - CB = a \cos \theta_2 - a \cos \theta_1$$

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

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

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

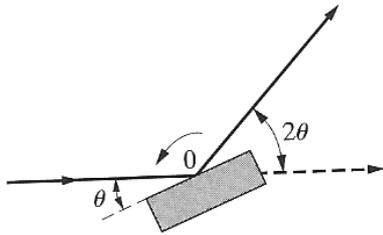


$$\boxed{\Delta\theta = \frac{\lambda}{2Na \sin \theta_B}}$$

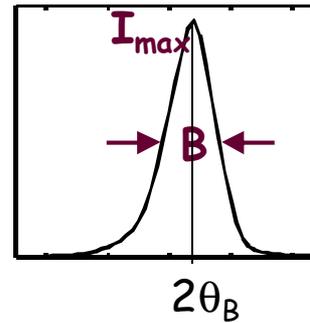
Max angular range of the peak

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

Geometrical factor - 1



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



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

Size & strain broadening

Integrated Intensity

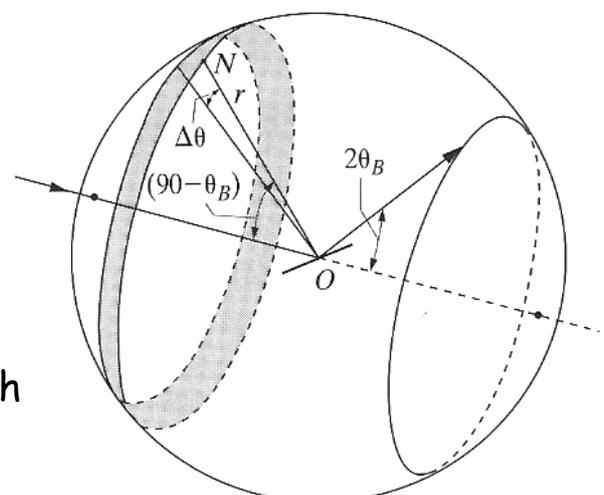
$$\propto I_{\max} B \propto (1/\sin \theta_B)(1/\cos \theta_B) \propto \frac{1}{\sin 2\theta}$$

(1)

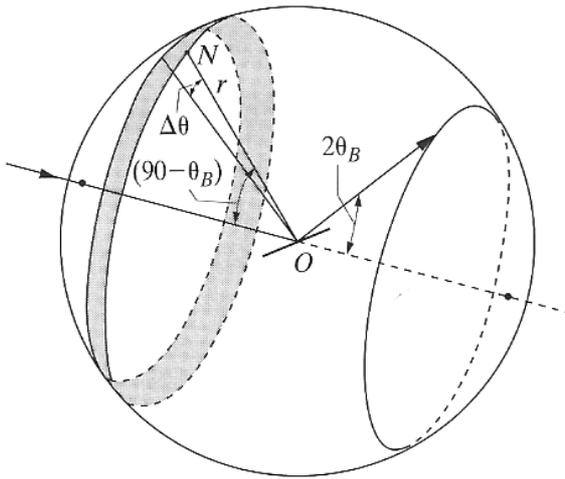
Geometrical factor - 2

- Intensity of a reflection at θ_B depends on the # of crystals oriented at or near θ_B
- 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
- Dq; 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

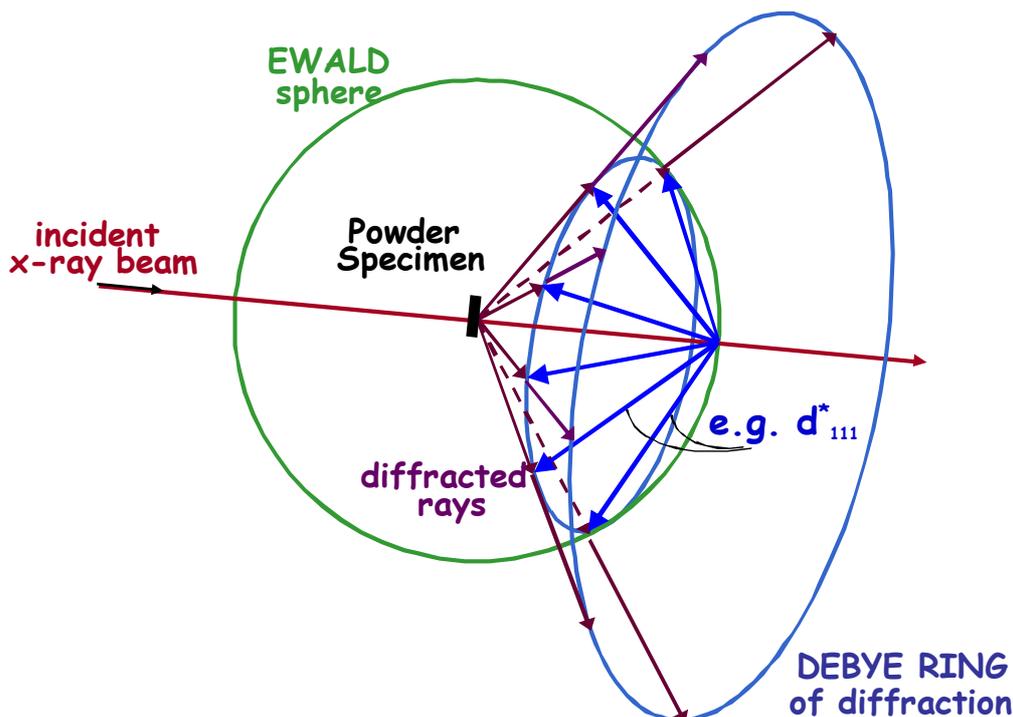
$$\frac{\Delta N}{N} = \frac{r\Delta\theta \cdot 2\pi r \sin(90^\circ - \theta_B)}{4\pi r^2} = \frac{\Delta\theta \cos \theta_B}{2}$$

- Number of crystals favorably oriented for diffraction

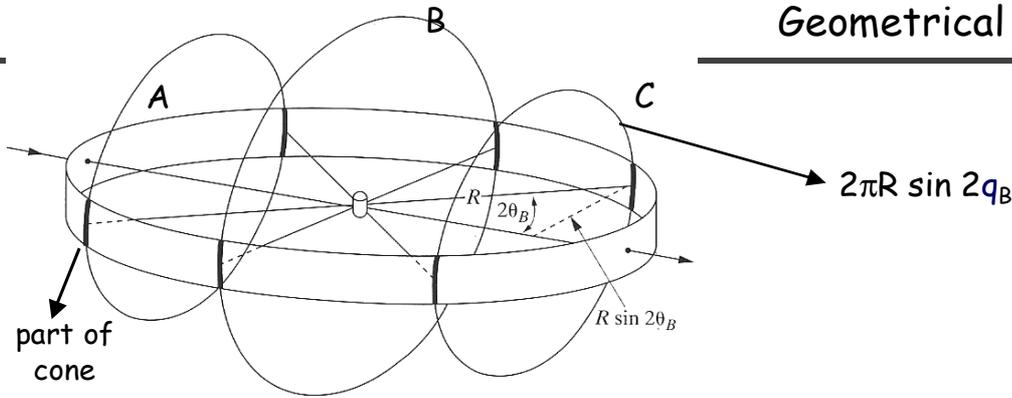
$$\Delta N \propto \cos \theta_B$$

(2)

Origin of powder diffraction pattern



Geometrical factor - 3



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

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 ($2\theta \ll 90^\circ$ or $2\theta \gg 90^\circ$)
- Smaller proportion of cone when $2\theta \sim 90^\circ$

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

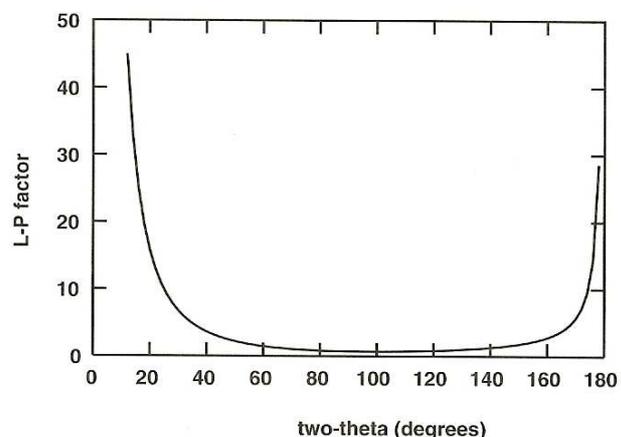
Lorentz-polarization factor (Lp factor)

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

(1) (2) (3) Lorentz factor

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

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



- 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

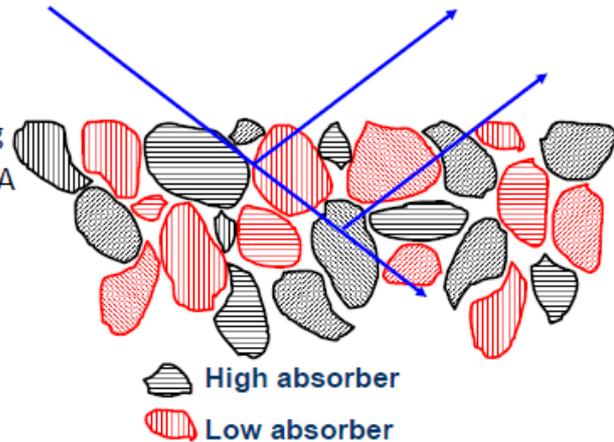
-
- In powder technique, accurate sampling & homogeneous mixing are critical
 - Factors affecting observed intensity to depart from the theoretical one (important in quantitative phase analysis)
 - ✓ Preferred orientation (texture)
 - ✓ Microabsorption
 - ✓ Extinction

Microabsorption

- Mixture of α & β
 - When $\mu_\alpha \approx \mu_\beta$, and particle size of α & β is different → microabsorption can make $I(\text{calculated})$ deviate from $I(\text{observed})$
 - If $\mu_\alpha \gg \mu_\beta$, or particle size of $\alpha \gg$ size of β → Intensity diffracted from a crystals will be much less than 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-estimated – low QPA
- Low absorbers
 - Beam penetrates further into grain
 - Greater likelihood of 'volume diffraction' occurring
 - Intensity over-estimated – high QPA



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
 - $\mu D =$ (linear absorption coefficient X particle diameter)
- Fine powders
 - $\mu D < 0.01$ – negligible micro-absorption, no correction necessary
- Medium powders
 - $0.01 < \mu D < 0.1$ – micro-absorption present, normal Brindley model applies
 - 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**
 - 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

- 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

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

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

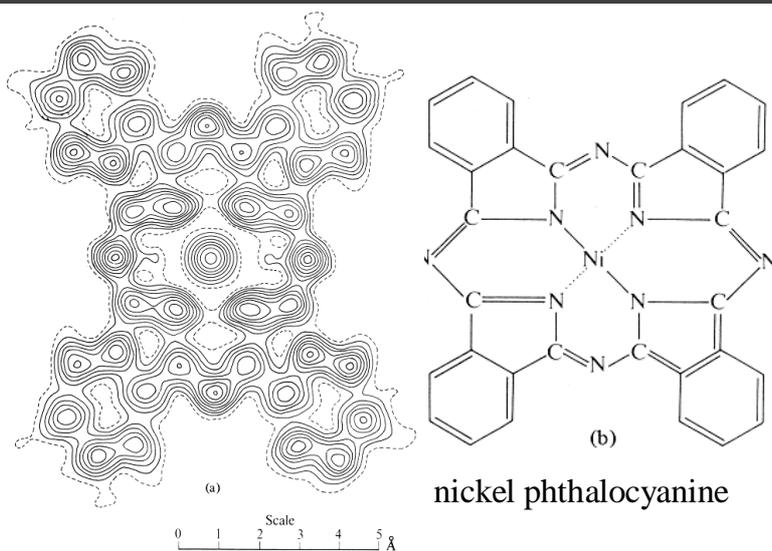
Intensity diffracted by a single phase powder specimen in a diffractometer

$$I(hkl) = \left(\frac{I_0 A \lambda^3}{32 \pi r} \right) \left[\left(\frac{\mu_o}{4\pi} \right)^2 \frac{e^4}{m^2} \right] \left(\frac{1}{v^2} \right) \left[|F(hkl)|^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) \right] \left(\frac{e^{-2M}}{2\mu} \right)$$

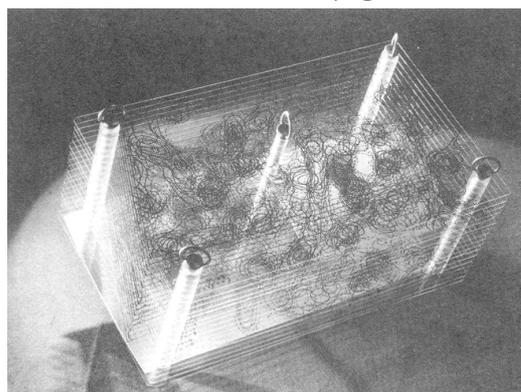
- $I(hkl)$ = integrated intensity per unit length of diffraction line
- I_0 = intensity of incident beam
- A = crosssectional area of incident beam
- r = radius of diffractometer circle
- V = volume of unit cell
- $F(hkl)$ = structure factor
- p = multiplicity factor
- e^{-2M} ; temperature factor
- μ = linear absorption coefficient

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Electron density distribution

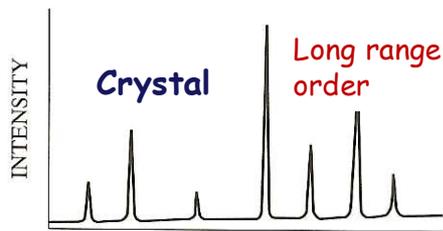


Protein myoglobin

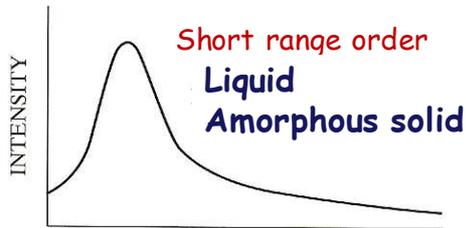


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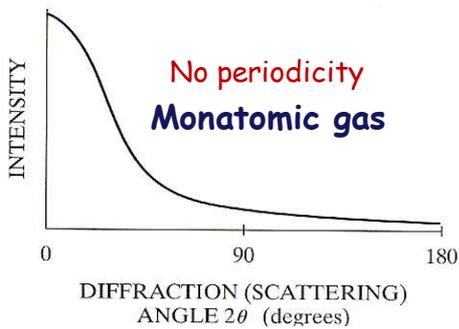
Amorphous & partially crystalline samples



- A single atom scatters incident X-ray beam in all directions



- Large # of atoms arranged in a perfectly periodic array in 3-D to form a crystal, scatters x-rays in a few directions



- Crystal imperfection → diffraction @ non-Bragg angles → diffraction occurs in a narrow angular range with center @ θ_B