The intensity of the diffraction peaks are determined by the arrangement of atoms in the entire crystal

$$I_{hkl} \propto |F_{hkl}|^2$$
$$F_{hkl} = \sum_{j=1}^m N_j f_j \exp\left[2\pi i \left(hx_j + ky_j + lz_j\right)\right]$$

- The structure factor F_{hkl} sums the result of scattering from all of the atoms in the unit cell to form a diffraction peak from the (hkl) planes of atoms
- The amplitude of scattered light is determined by:
 - where the atoms are on the atomic planes
 - this is expressed by the fractional coordinates x_i y_i z_i
 - what atoms are on the atomic planes
 - the scattering factor f_j quantifies the efficiency of X-ray scattering at any angle by the group of electrons in each atom
 - The scattering factor is equal to the number of electrons around the atom at 0° θ, the drops off as θ increases
 - N_j is the fraction of every equivalent position that is occupied by atom j

Crystal Structure factor calculations

(A) X-Ray Scattering by an Atom

- □ The *conventional* UC has lattice points as the vertices
- □ There may or may not be atoms located at the lattice points
- The shape of the UC is a parallelepiped in 3D
- There may be additional atoms in the UC due to two reasons:
 The chosen UC is non-primitive
 - \succ The additional atoms may be part of the motif

Scattering by the Unit cell (uc)

- Coherent Scattering
- Unit Cell (UC) is representative of the crystal structure
- Scattered waves from various atoms in the UC interfere to create the diffraction pattern



The wave scattered from the middle plane is out of phase with the ones scattered from top and bottom planes



Extending to 3D $\varphi = 2\pi (h x' + k y' + l z') \longrightarrow$ Independent of the shape of UC

Note: R_1 is from corner atoms and R_3 is from atoms in additional positions in UC

 $\varphi = 2\pi (h x' + k y' + l z')$ In complex notation $E = Ae^{i\varphi} = fe^{i[2\pi (h x' + k y' + l z')]}$

- If atom B is different from atom A → the amplitudes must be weighed by the respective atomic scattering factors (f)
- The resultant amplitude of all the waves scattered by all the atoms in the UC gives the scattering factor for the unit cell
- The unit cell scattering factor is called the Structure Factor (F)

Scattering by an unit cell = f(position of the atoms, atomic scattering factors)

 $F = Structure Factor = \frac{Amplitude of wave scattered by all atoms in uc}{Amplitude of wave scattered by an electron}$

$$I \propto F^2$$

$$F_n^{hkl} = \sum_{j=1}^n f_j \quad e^{i\varphi_j} = \sum_{j=1}^n f_j \quad e^{i[2\pi(h x'_j + k y'_j + l z'_j)]} \quad F_n^{hkl} = \sum_{j=1}^n f_j \quad e^{i\varphi_j} = \sum_{j=1}^n f_j \quad e^{i[2\pi(h x'_j + k y'_j + l z'_j)]} \quad F_n^{hkl} = \sum_{j=1}^n f_j \quad e^{i\varphi_j} = \sum_{j=1}^n f_j \quad e^{i\varphi_j} = \sum_{j=1}^n f_j \quad e^{i(2\pi(h x'_j + k y'_j + l z'_j))}$$

For <mark>n</mark> atoms in the UC

Structure factor is independent of the *shape* and *size* of the unit cell

If the UC distorts so do the planes in it !!



$$\Rightarrow$$
 F is independent of the scattering plane (h k l)

 $F^{2} = f^{2}$

Atom at (0,0,0) & $(\frac{1}{2}, \frac{1}{2}, 0)$ and equivalent positions

C- centred Orthorhombic



e.g. (100), (101), (102); (031), (032), (033)

 \Rightarrow F is independent of the 'l' index

B



C-Centred Orthorhombic lattice [001] projection



To form a translationally equivalent set of planes (passing through all lattice points) the red set of planes have to be drawn

- If the blue planes are scattering in phase then on C- centering the red planes will scatter out of phase (with the blue planes- as they bisect them) and hence the (210) reflection will become extinct
- This analysis is consistent with the extinction rules: (h + k) odd is absent

Simple Orthorhombic lattice [001] projection



These (310) planes form a translationally equivalent set: pass through all lattice points

C-Centred Orthorhombic lattice [001] projection



No new planes are to be added to form a translationally equivalent set of planes on C-centering

- In case of the (310) planes no new translationally equivalent planes are added on lattice centering ⇒ this reflection cannot go missing.
- This analysis is consistent with the extinction rules: (h + k) even is present



e.g. (100), (001), (111); (210), (032), (133)



Two odd and one even (e.g. 112); two even and one odd (e.g. 122)

Mixed indices

Two odd and one even (e.g. 112); two even and one odd (e.g. 122)

Mixed indices	CASE	h	k	1
	А	0	0	e
	В	0	e	e

CASE A:
$$[1 + e^{i\pi(e)} + e^{i\pi(o)}] = [1 + 1 - 1 - 1] = 0$$

CASE B: $[1 + e^{i\pi(o)} + e^{i\pi(e)} + e^{i\pi(o)}] = [1 - 1 + 1 - 1] = 0$
(h, k, l) mixed $F = 0 \longrightarrow F^2 = 0$ e.g. (100), (211); (210), (032), (033)

Unmixed indices

All odd (e.g. 111); all even (e.g. 222)

Unmixed indices	CASE	h	k	1
	А	0	0	0
	В	e	e	e

CASE A: $[1 + e^{i\pi(e)} + e^{i\pi(e)} + e^{i\pi(e)}] = [1 + 1 + 1 + 1] = 4$

CASE B:
$$[1 + e^{i\pi(e)} + e^{i\pi(e)} + e^{i\pi(e)}] = [1 + 1 + 1 + 1] = 4$$

k, I) unmixed
$$F = 4f \longrightarrow F^2 = 16f^2$$

e.g. (111), (200), (220), (333), (420)

$$\begin{split} \mathbf{F} & = \mathbf{M}_{Na^{+}} \operatorname{tr} (0,0,0) + \operatorname{Face Centering Translations} \rightarrow (\%, \%, 0), (\%, 0, \%), (0, \%, \%) \\ \mathbf{C}^{+} \operatorname{at} (\%, 0, 0) + \operatorname{FCT} \rightarrow (0, \%, 0), (0, 0, \%), (\%, \%, \%) \\ \mathbf{F} & = f_{Na^{+}} \left[e^{i[2\pi(0)]} + e^{i[2\pi(\frac{h+k}{2})]} + e^{i[2\pi(\frac{k+l}{2})]} + e^{i[2\pi(\frac{k+l}{2})]} + e^{i[2\pi(\frac{k+k+l}{2})]} \right] + \\ f_{Cl^{-}} \left[e^{i[2\pi(\frac{h}{2})]} + e^{i[2\pi(\frac{k}{2})]} + e^{i[2\pi(\frac{l}{2})]} + e^{i[2\pi(\frac{h+k+l}{2})]} \right] \\ \mathbf{F} & = f_{Na^{+}} \left[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(l+h)} \right] + \\ f_{Cl^{-}} \left[e^{i\pi(h)} + e^{i\pi(k)} + e^{i\pi(k+l)} + e^{i\pi((h+k+l))} \right] \\ \end{array} \\ \hline \mathbf{F} & = f_{Na^{+}} \left[1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi((h+k))} \right] + \\ f_{Cl^{-}} \left[e^{i\pi(h+k+l)} \left[e^{i\pi(-k-l)} + e^{i\pi(-l-h)} + e^{i\pi(-h-k)} + 1 \right] \right] \\ \hline \mathbf{F} & = \left[f_{Na^{+}} + f_{Cl^{-}} e^{i\pi(h+k+l)} \right] \left[1 + e^{i\pi(h+k)} + e^{i\pi((k+l))} + e^{i\pi((k+l))} + e^{i\pi((k+l))} \right] \\ \end{split}$$

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

$$F = [Term - 1][Term - 2]$$

Zero for mixed indices

	Mixed indices	CASE	h	k	1
ivitxed indices		А	Ο	0	e
		В	0	e	e

CASE A: $Term - 2 = [1 + e^{i\pi(e)} + e^{i\pi(o)} + e^{i\pi(o)}] = [1 + 1 - 1 - 1] = 0$ CASE B: $Term - 2 = [1 + e^{i\pi(o)} + e^{i\pi(e)} + e^{i\pi(o)}] = [1 - 1 + 1 - 1] = 0$

(h, k, l) mixed
$$F = 0 \longrightarrow F^2 = 0$$
 e.g. (100), (211); (210), (032), (033)

U	Inm	ixed	ind	ices
U	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	INCU	mu	ICC3

Unmixed indices	CASE	h	k	1
	А	0	0	0
	В	e	e	e

CASE A:
$$Term - 2 = [1 + e^{i\pi(e)} + e^{i\pi(e)} + e^{i\pi(e)}] = [1 + 1 + 1 + 1] = 4$$

CASE B: $Term - 2 = [1 + e^{i\pi(e)} + e^{i\pi(e)} + e^{i\pi(e)}] = [1 + 1 + 1 + 1] = 4$

(h, k, l) unmixed

$$F = 4[f_{Na^{+}} + f_{Cl^{-}} e^{i\pi(h+k+l)}]$$
e.g. (111), (222); (133), (244)

$$F = 4[f_{Na^{+}} + f_{Cl^{-}}] \longrightarrow \text{ If (h + k + l) is even } \longrightarrow F^{2} = 16[f_{Na^{+}} + f_{Cl^{-}}]^{2}$$
e.g. (222),(244)

$$F = 4[f_{Na^{+}} - f_{Cl^{-}}] \longrightarrow \text{ If (h + k + l) is odd } \longrightarrow F^{2} = 16[f_{Na^{+}} - f_{Cl^{-}}]^{2}$$
e.g. (111), (133)

⇒ Presence of additional atoms/ions/molecules in the UC can alter the intensities of some of the reflections



Click here to know more about ordered structures

$$F = f_{Al} \quad e^{i[2\pi(h\cdot 0+k\cdot 0+l\cdot 0)]} + f_{Ni} \quad e^{i[2\pi(h\cdot \frac{1}{2}+k\cdot \frac{1}{2}+l\cdot \frac{1}{2})]}$$

$$= f_{Al} e^{0} + f_{Ni} e^{i[2\pi(\frac{h+k+l}{2})]} = f_{Al} + f_{Ni} e^{i\pi[h+k+l]}$$
Read
$$F = f_{Al} + f_{Ni} e^{i\pi[h+k+l]}$$

$$F = f_{Al} - f_{Ni} + F^{2} = (f_{Al} - f_{Ni})^{2}$$

$$e.g. (100), (111), (210), (032), (133)$$

$$F = f_{Al} - f_{Ni} + F^{2} = (f_{Al} - f_{Ni})^{2}$$

$$e.g. (100), (111), (210), (032), (133)$$

$$F = f_{Al} - f_{Ni} + F^{2} = (f_{Al} - f_{Ni})^{2}$$

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$$F = f_{Al} - f_{Ni} + F^{2} = (f_{Al} - f_{Ni})^{2}$$

$$F = f_{Al} - f_{Ni} + F^{2} = (f_{Al} - f_{Ni})^{2}$$

$$F = f_{Al} - f_{Al} + F^{2} +$$

e.g. (110), (200), (211); (220), (310)



e.g. (100), (111), (210), (032), (133)



e.g. (111), (200), (220), (333), (420) $F^2 = (f_{Al} + 3f_{Ni})^2$ <u>ī</u>11 \vec{b}_2^* $F^2 = (f_{Al} - f_{Ni})^2$ • 110 $\vec{b_1}^*$ Superlattice reflection Fundamental reflection

e.g. (100), (211); (210), (032), (033)

Selection / Extinction Rules

Bravais Lattice Reflection may be		ons which present	Reflections necessarily absent		
Simple	all		None		
Body centred	(h+k+1) even		(h+k+l) even		(h + k + l) odd
Face centred	h, k and l	unmixed	h, k and l mixed		
End centred	h and k unmixed <i>C centred</i>		h and k mixed <i>C centred</i>		
Bravais Latt	ice	Allowed Reflections			
SC		All			
BCC		(h + k + l) even			
FCC		h, k and l unmixed			
			and 1 are all odd		
DC		Or			
		all are even			
		& & (h + k + l) divisible by 4			

$h^2 + k^2 + l^2$	SC	FCC	BCC	DC
1	100			
2	110		110	
3	111	111		111
4	200	200	200	
5	210			
6	211		211	
7				
8	220	220	220	220
9	300, 221			
10	310		310	
11	311	311		311
12	222	222	222	
13	320			
14	321		321	
15				
16	400	400	400	400
17	410, 322			
18	411, 330		411, 330	
19	331	331		331

Relative intensity of peaks in powder patterns

- □ We have already noted that absolute value of intensity of a peak (which is the area under a given peak) has no significance w.r.t structure identification.
- □ The relative value of intensities of the peak gives information about the motif.
- One factor which determines the intensity of a hkl reflection is the structure factor.
- □ In powder patterns many other factors come into the picture as in the next slide.
- □ The multiplicity factor relates to the fact that we have 8 {111} planes giving rise to single peak, while there are only 6 {100} planes (and so forth). Hence, by this very fact the intensity of the {111} planes should be more than that of the {100} planes.
- A brief consideration of some these factors follows. The reader may consult Cullity's book for more details.



Multiplicity factor

Actually only 3 planes !

Lattice	Index	Multiplicity	Planes
Cubic	(100)	6	[(100) (010) (001)] (× 2 for negatives)
(with highest symmetry)	(110)	12	$[(110) (101) (011), (\overline{1}10) (\overline{1}01) (0 \overline{1}1)] (\times 2 \text{ for negatives})$
	(111)	12	$[(111) (11 \ \overline{1}) (1 \ \overline{1}1) (\ \overline{1}11)] (\times 2 \text{ for negatives})$
	(210)	24*	$(210) \rightarrow 3!$ Ways, $(\overline{210}) \rightarrow 3!$ Ways, $(2\overline{10}) \rightarrow 3!$ Ways, $(\overline{2}\overline{10}) \rightarrow 3!$ Ways
	(211)	24	$(211) \rightarrow 3 \text{ ways, } (21 \ \overline{1}) \rightarrow 3! \text{ ways,} (\ \overline{2}11) \rightarrow 3 \text{ ways}, (21 \ \overline{1}) \rightarrow 3! \text{ ways,} $
	(321)	48*	
Tetragonal	(100)	4	[(100) (010)] (× 2 for negatives)
(with highest symmetry)	(110)	4	[(110) ($\overline{110}$)] (× 2 for negatives)
	(111)	8	$[(111) (11 \ \overline{1}) (1 \ \overline{1}1) (\ \overline{1}11)] (\times 2 \text{ for negatives})$
	(210)	8*	$(210) = 2$ Ways, $(\overline{2}10) = 2$ Ways, $(2\ \overline{1}0) = 2$ Ways, $(\overline{2}\ \overline{1}0) = 2$ Ways
	(211)	16	[Same as for $(210) = 8$] × 2 (as l can be +1 or -1)
	(321)	16*	Same as above (as last digit is anyhow not permuted)

* Altered in crystals with lower symmetry

Multiplicity factor

Cubic	hkl	hhl	hk0	hh0	hhh	h00	
Cubic	48^{*}	24	24*	12	8	6	
Havaganal	hk.l	hh.l	h0.1	hk.0	hh.0	h0.0	00.1
nexagonai	24^{*}	12*	12*	12*	6	6	2
	hkl	hhl	h01	hk0	hh0	h00	001
Tetragonal	16*	8	8	8^*	4	4	2
Outhouhomhio	hkl	hk0	h01	0kl	h00	0k0	001
Orthornombic	8	4	4	4	2	2	2
Manaalinia	hkl	h01	0k0				
Monoclinic	4	2	2				
Trialinia	hkl						
Iriclinic	2						

* Altered in crystals with lower symmetry (of the same crystal class)



Intensity of powder pattern lines (*ignoring Temperature & Absorption factors*)

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

- Valid for Debye-Scherrer geometry
- I → Relative **Integrated** *"Intensity"*
- $F \rightarrow$ Structure factor
- $p \rightarrow$ Multiplicity factor

POINTS

- As one is interested in relative (integrated) intensities of the lines constant factors are omitted
 - Volume of specimen m_e , e (1/dectector radius)
- \blacktriangleright Random orientation of crystals \rightarrow in a material with *Texture* relative intensities are modified
- I is really diffracted energy (as Intensity is *Energy/area/time*)
- > Ignoring Temperature & Absorption factors \Rightarrow valid for lines close-by in pattern