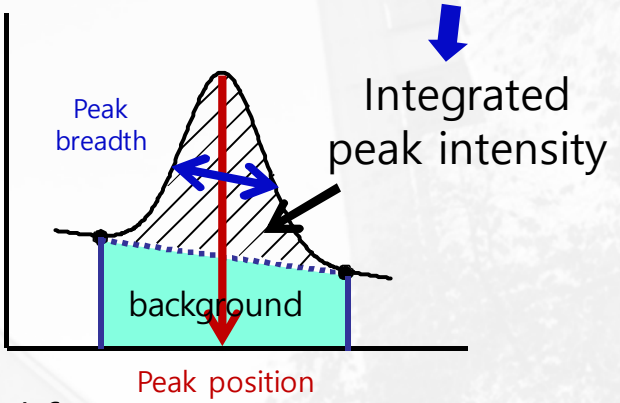
XRD-3 Intensity



XRD-3 READ

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

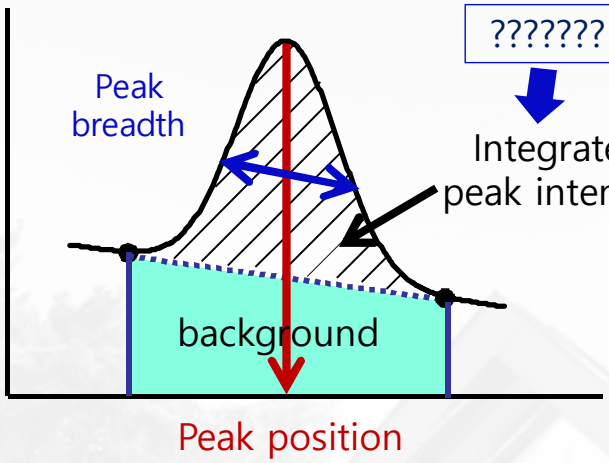
Krawitz Chapter 5, p132 ~ p143

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 (except 7.5)

Intensity



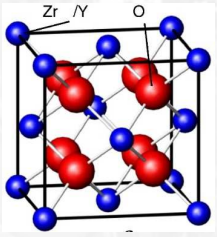
?????? Atom type/Arrangement

Integrated
peak intensity

Crystal Structure of "cubic" "ZrO2"

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

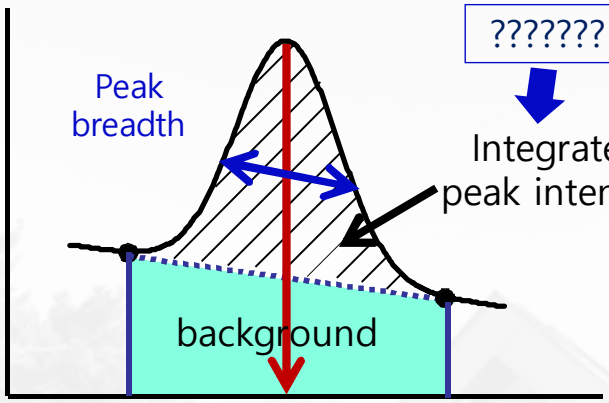
Atom	x	y	z	B_{iso}	occupancy
Zr	0	0	0	1.14	1
O	0.25	0.25	0.25	2.4	1



Factor affecting the Relative Intensity of Bragg Reflections

- Structure sensitive
  - ✓ Atomic scattering factor
  - ✓ Structure factor
  - ✓ Polarization
  - ✓ Multiplicity
  - ✓ Temperature
- Sample sensitive
  - ✓ Absorption
  - ✓ Degree of crystallinity
  - ✓ Particle orientation
- Instrument sensitive
  - ✓ Absolute intensities
    - Source intensity
    - Diffractometer efficiency
    - Take-off angle of tube
    - Receiving slit width
    - Axial divergence allowed
  - ✓ Relative intensities
    - Divergence slit aperture
    - Detector dead-time
- Measurement sensitive
  - ✓ Method of peak area measurement
  - ✓ Method of background subtraction
  - ✓ α2 stripping or not
  - ✓ Degree of data smoothing employed

Intensity



?????? Atom type/Arrangement

Integrated peak intensity

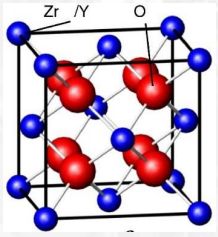
complicated

- ✓ 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



Intensity

Intensity diffracted by a single phase powder specimen in a diffractometer

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

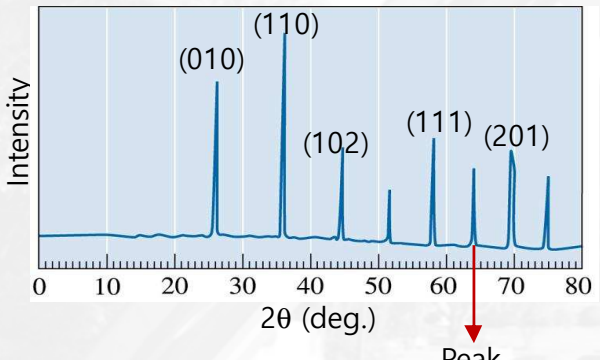
I(hkl) = integrated intensity per unit length of diffraction line

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

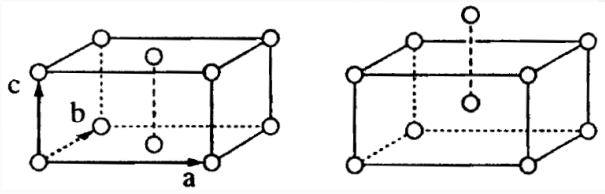


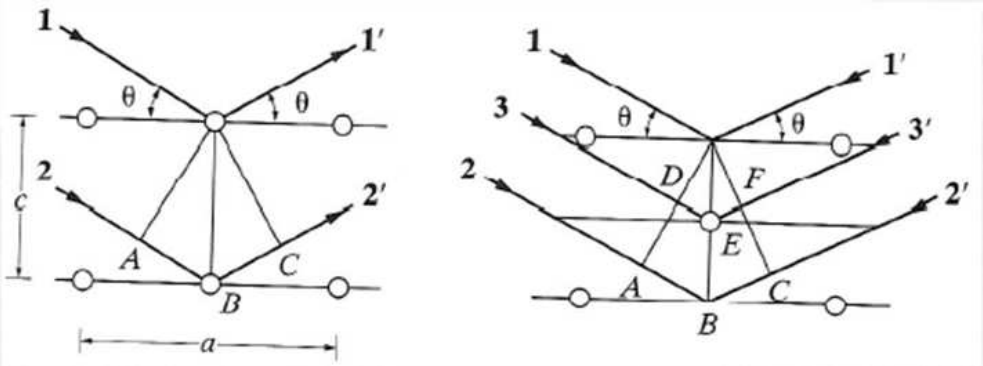
Relative intensity

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

Bragg's law $\lambda = 2d\sin\theta$

Diffraction from (001) planes of scatterers





(a) base-centered orthorhombic lattice

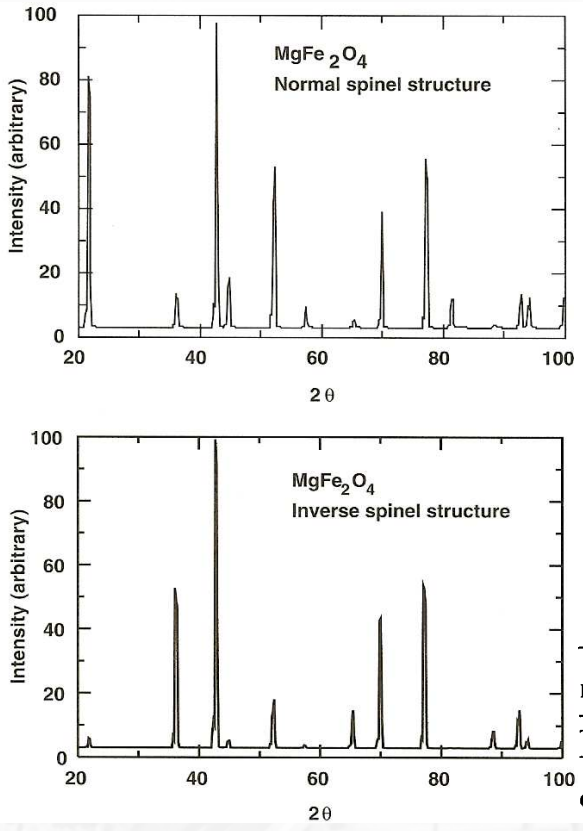
(b) body-centered orthorhombic lattice

atom position ⟷ intensity

relation

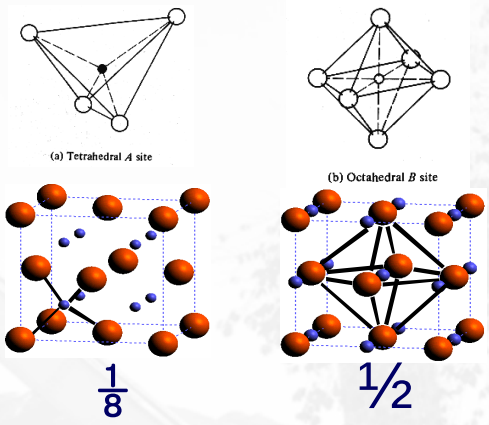
Cullity page 124

Intensity from "atom type/position"



Spinel AB_2O_4

Oxygen; cubic close packing



MFe_2O_4

Kind of site	Number available	Number occupied	Occupants: Normal spinel	Occupants: 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+}

Read (can be skipped)

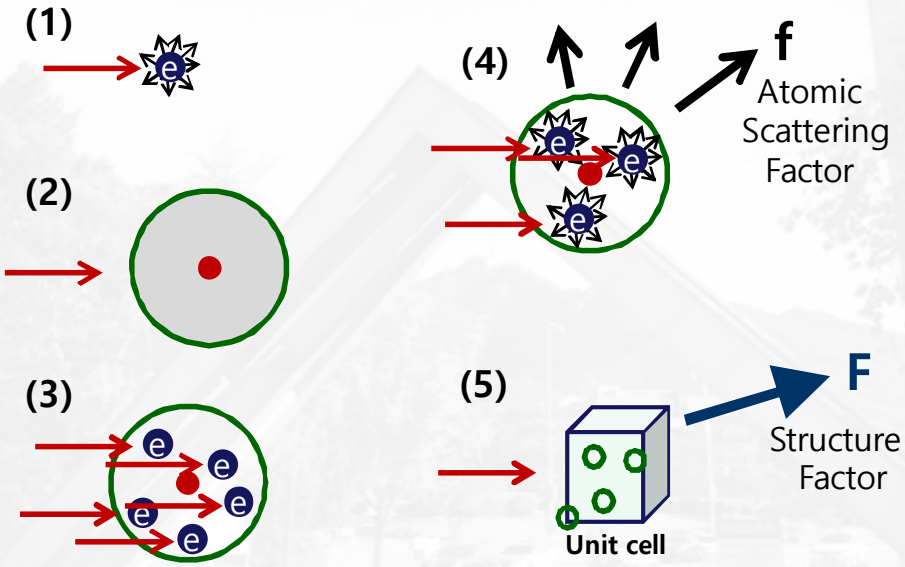
- J.J. Thomson equation
- Polarization factor
- Compton effect
- Compton modified radiation
- Anomalous dispersion

Scattering & diffraction

- Coherent scattering (unmodified scattering)
  - ✓ Tightly bound electrons
- Incoherent scattering (modified scattering)
  - ✓ loosely bound electrons
  - → background
- Diffraction = reinforced coherent scattering

Atomic scattering factor (f) & Structure factor (F)

- Scattering from a single electron
- ⇩
- Scattering from a single atom
- ⇩
- Scattering from a unit cell



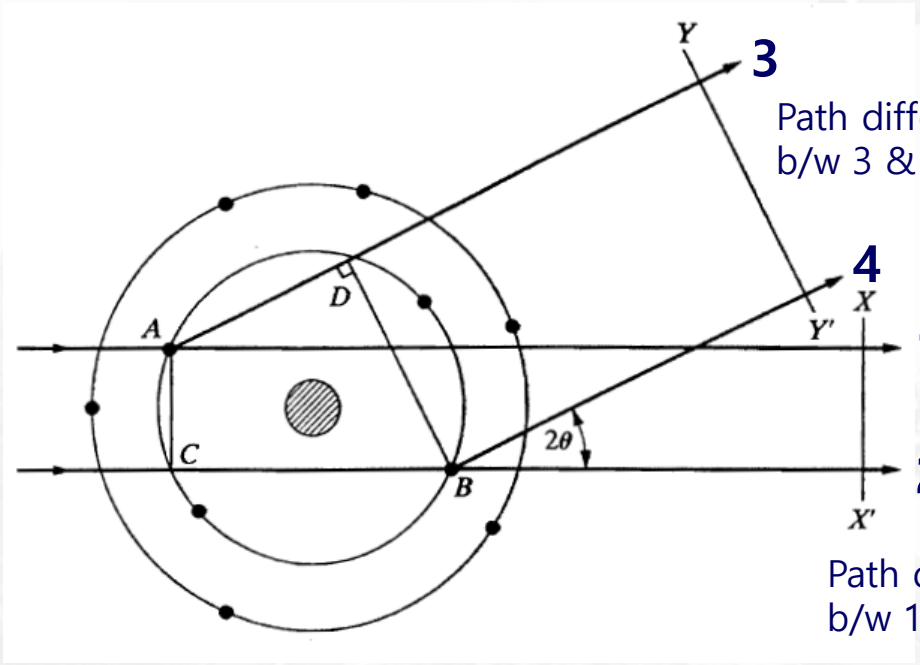
Intensity of XRD

- Scattering amplitude of a single electron
  - ✓ How much Intensity a single electron will coherently scatter?
- Scattering amplitude of a single atom → **f (atomic scattering factor)**
  - ✓ Interference effects due to electrons being distributed in space around atoms
- Scattering amplitude of a unit cell → **F (structure factor)**
  - ✓ Interference effects caused by scattering from atoms in different regions of unit cell

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

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

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



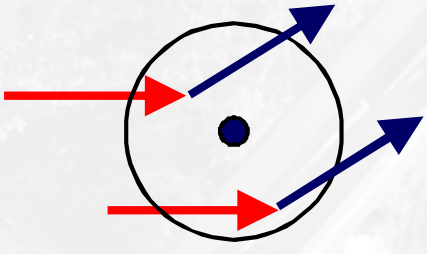
f (atomic scattering factor)
= efficiency of scattering of an atom in a given direction

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

→ atomic scattering factor (form 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'

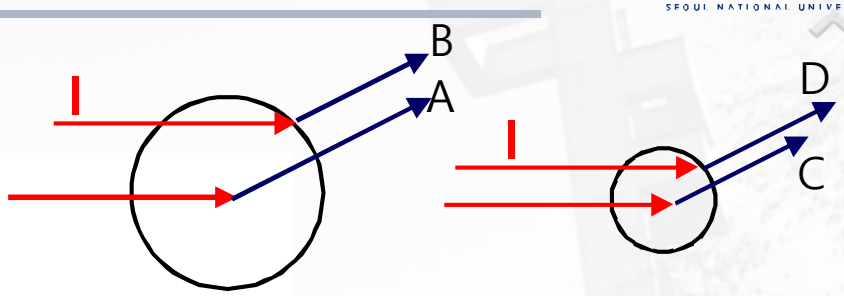
$$f = \frac{\text{amplitude scattered by an atom}}{\text{amplitude scattered by a single electron}}$$



$$f = F(\vartheta) \qquad f(0^o) = Z$$

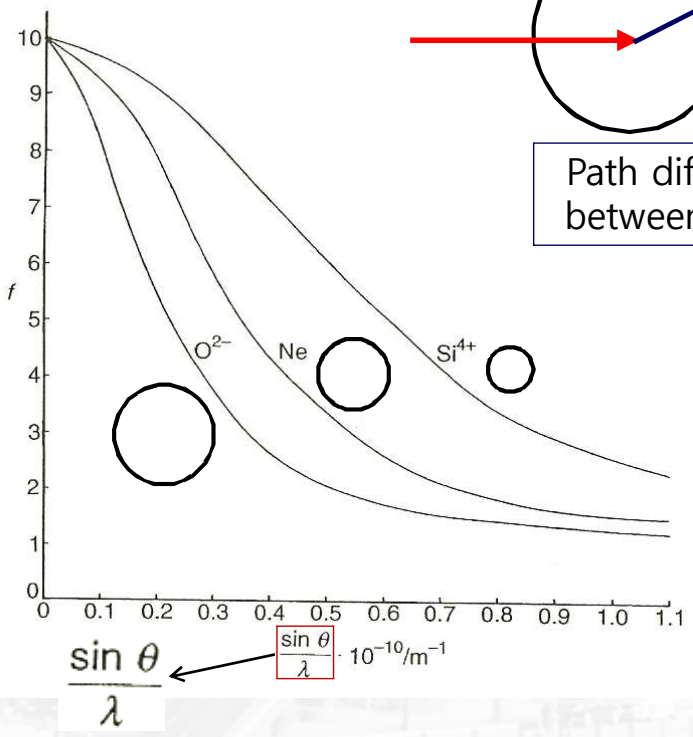
f'n(sinθ/λ)

Atomic scattering factor (form factor)



Path difference between A & B > Path difference between C & D

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



Hammond Chapter 9
Cullity 4-3

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

$\frac{\sin\theta}{\lambda}$ (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

Factors affecting f

Factors affecting the intensity of the scattering from an atom

- Anomalous scattering (anomalous dispersion)

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

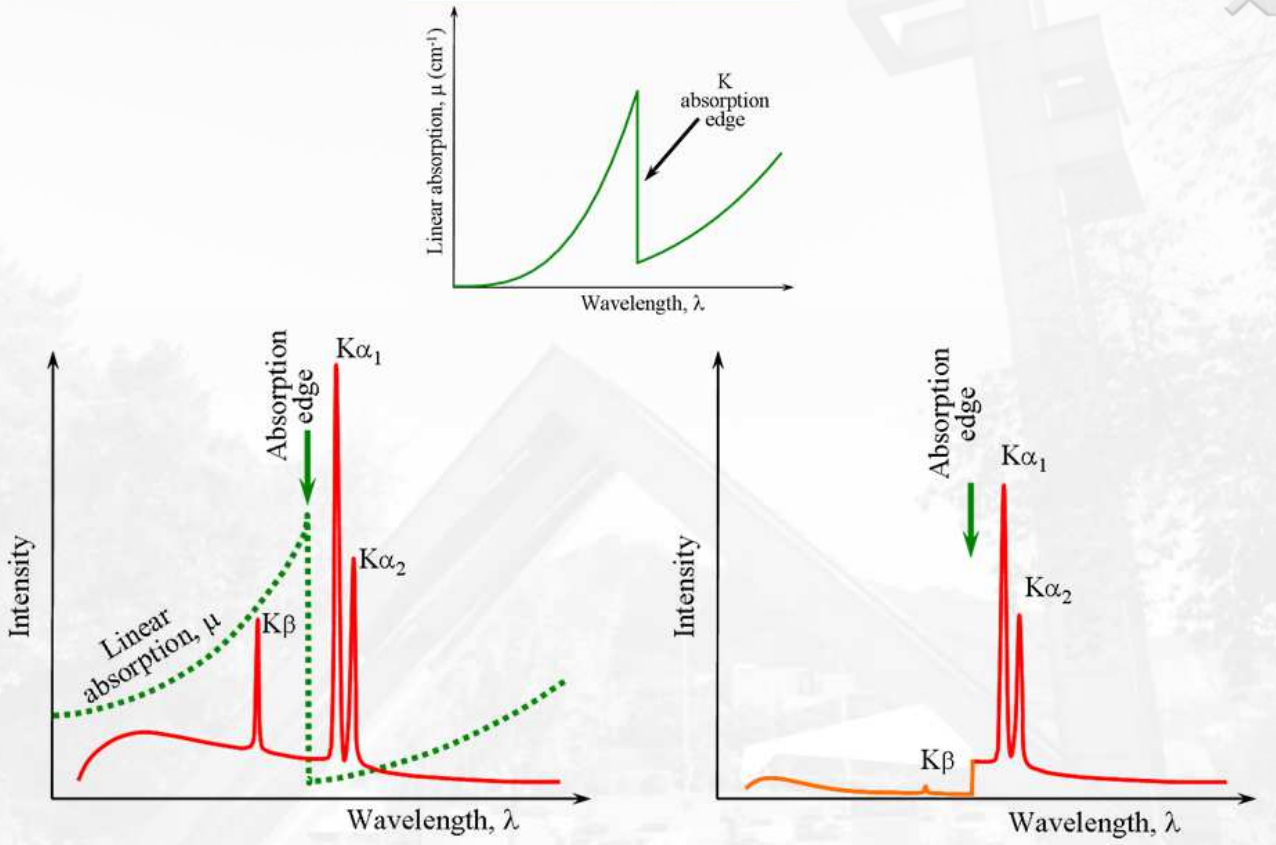
- Thermal motion

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

Sherwood & Cooper 9.8

Cullity 4-11

β-filter

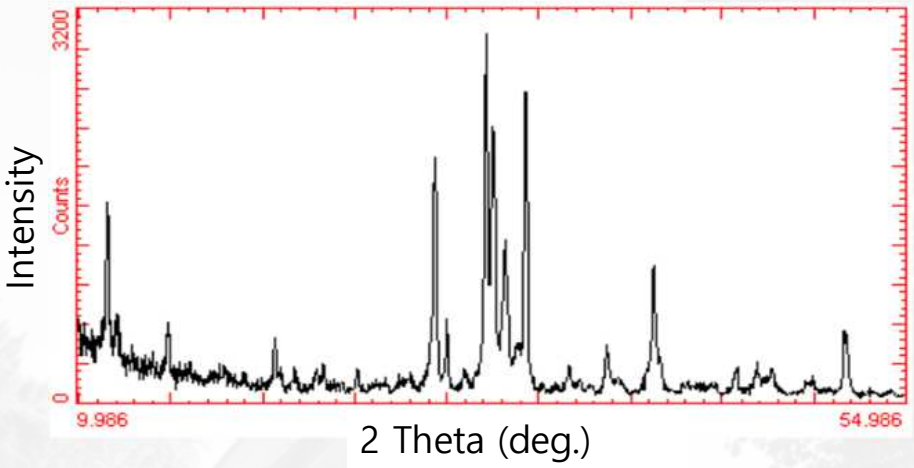


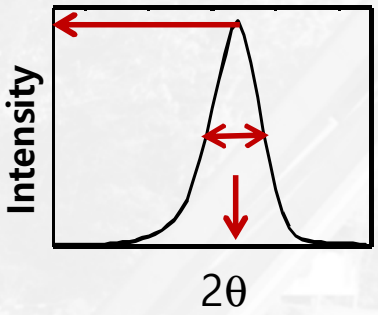
Pecharsky

Factors affecting the relative intensity of Bragg reflections

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

θ – 2θ XRD pattern

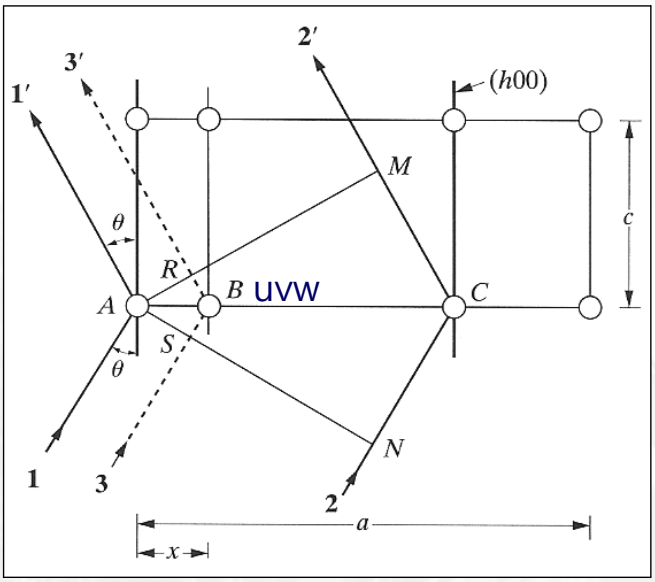




- Positions, **intensities**, shapes → crystal structure, physical state, etc.

Structure factor

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 B on the intensity in that direction ?

Path difference b/w 3′ & 1′

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

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

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

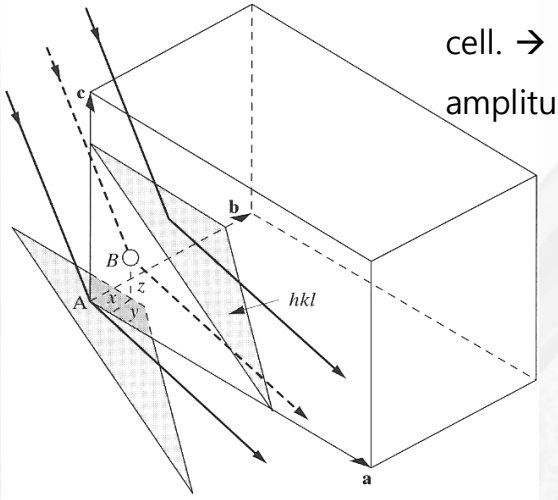
Position of atom B, u = x/a → $\phi_{3'1'} = 2\pi hu$

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

Structure factor

Phase difference b/w waves scattered by B and that scattered by A at origin, for the 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 amplitude and phase of each wave

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 (structure factor) = resultant wave scattered by all the atoms in the unit cell

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

Structure Factor

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

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

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

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

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

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

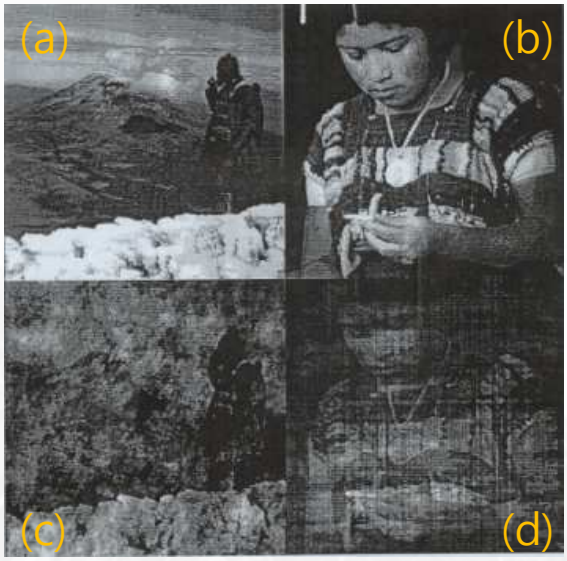
Phase problem

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

Source unknown

A graphic illustration of the phase problem

(a) (b) original images



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

Fourier transform

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

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

- 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.

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 & ½½0

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

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

$F = 2f$ for h and k unmixed;

$F^2 = 4f^2.$

$F = 0$ for h and k mixed;

$F^2 = 0.$

Structure factor of bcc

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

Body-centered cell
000 & ½½½

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

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

$F = 2f$ when $(h + k + l)$ is even;

$F = 4f^2.$

$F = 0$ when $(h + k + l)$ is odd;

$F^2 = 0.$

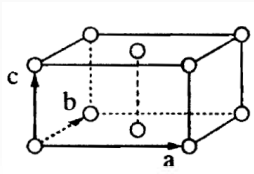
Systematic extinction (absence)

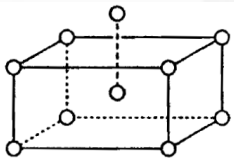
- The condition that structure factor becomes zero due to a systematic symmetry condition
- Presence of reflections with zero intensity caused by the space group (symmetry) of unit cell
- Translational symmetry inside unit cell, screw axes, glide planes can introduce systematic extinctions.

Hammond Appendix 6

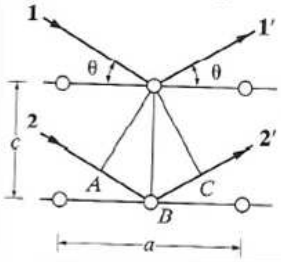
Diffraction from (001) planes of scatterers

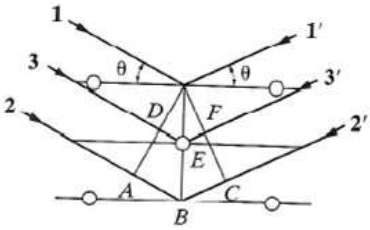
base-centered orthorhombic lattice





body-centered orthorhombic lattice





$F = 2f$ for h and k unmixed; $F^2 = 4f^2$.	$F = 0$ when $(h + k + l)$ is odd; $F^2 = 0$.

atom position ⟷ intensity

relation

Cullity page 124

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

$F = 0$ for h and k mixed;

$F^2 = 0$.

Jenkins & Snyder
Cullity page 140

CONTINUED **No. 25** ***Pmm*2**

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) $\bar{x},y,z$
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	$mm2$	$0,0,z$			

General position

Special position

Reflection conditions

General:
no conditions

Special: 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

International Tables for X-ray Crystallography

① CONTINUED No. 35 *Cmm2*

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				Reflection conditions
		$(0,0,0)+$	$(\frac{1}{2},\frac{1}{2},0)+$			General:
8	f 1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $x,\bar{y},z$	(4) $\bar{x},y,z$	hkl : $h+k=2n$ $0kl$: $k=2n$ $h0l$: $h=2n$ $hk0$: $h+k=2n$ $h00$: $h=2n$ $0k0$: $k=2n$
4	e m . .	$0,y,z$				Special: as above, plus
4	d . m .	$x,0,z$				no extra conditions
4	c . . 2	$\frac{1}{2},\frac{1}{2},z$				no extra conditions
2	b m m 2	$0,\frac{1}{2},z$				hkl : $h=2n$
2	a m m 2	$0,0,z$				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 **Symmetry of special projections**

Along [001] $c2mm$
$\mathbf{a}' = \mathbf{a}$ $\mathbf{b}' = \mathbf{b}$
Origin at $0,0,z$

Along [100] $p1m1$
$\mathbf{a}' = \frac{1}{2}\mathbf{b}$ $\mathbf{b}' = \mathbf{c}$
Origin at $x,0,0$

Along [010] $p11m$
$\mathbf{a}' = \mathbf{c}$ $\mathbf{b}' = \frac{1}{2}\mathbf{a}$
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)+

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

$$F = fe^{2\pi i(0)} + fe^{2\pi i(h/2+k/2)} + fe^{2\pi i(k/2+l/2)} + fe^{2\pi i(h/2+l/2)}$$
$$= f\left[1 + e^{\pi i(h+k)} + e^{\pi i(k+l)} + e^{\pi i(h+l)}\right].$$

$F = 4f$ for unmixed indices;

$F^2 = 16f^2$

$F = 0$ 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

Structure factor of NaCl

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

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

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

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

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

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

Structure factor of NaCl (continued)

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

$F = 0$ for mixed indices;

$F^2 = 0.$

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

For unmixed indices

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

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

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

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

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

FCC

$F = 4f$ for unmixed indices;

$F^2 = 16f^2$

$F = 0$ for mixed indices;

$F^2 = 0$

Friedel's law

- Diffraction pattern from a centrosymmetric crystal is centrosymmetric.
- Diffraction pattern from a non-centrosymmetric crystal is centrosymmetric.
  → 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

- 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.

Hammond page 220
Sherwood Chap 9.11
Hammond Chap 9

11 Laue group

- 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

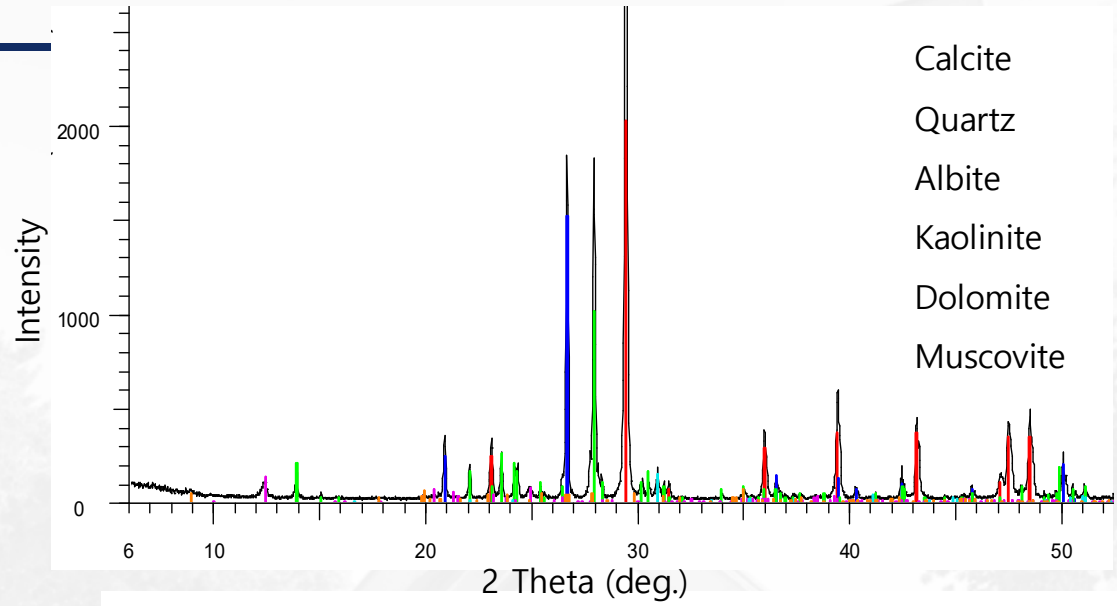
Hammond Table 9.1

Qualitative phase analysis (Phase ID)

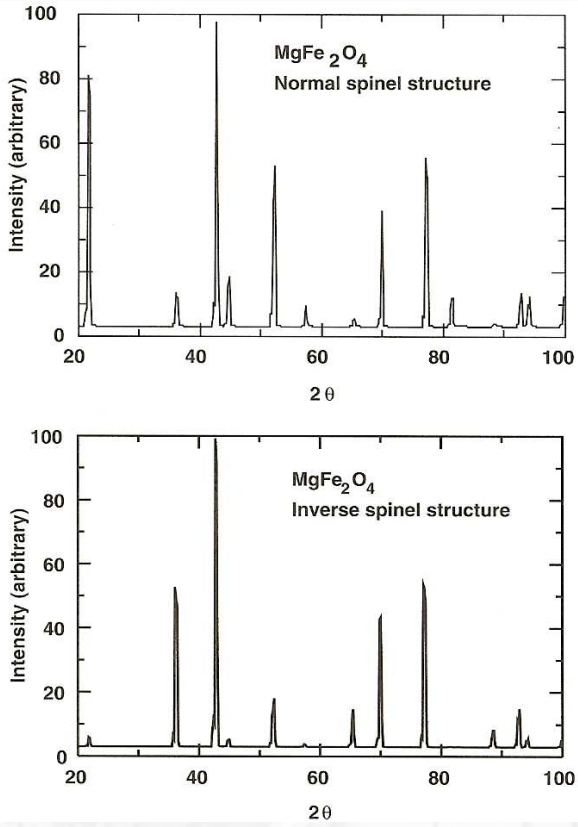
Cullity Chap 9

Krawitz Chap 8

Jenkins & Snyder Chap 12

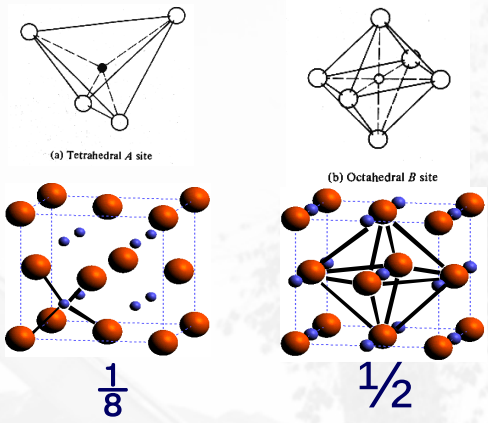


File: B14-Mischung.raw - Type: 2Th/Th locked - Start: 6.000 ° - End: 70.0
05-0586 (*) - Calcite, syn - CaCO3
46-1045 (*) - Quartz, syn - SiO2
09-0466 (*) - Albite, ordered - NaAlSi3O8
80-0886 (C) - Kaolinite - Al2(Si2O5)(OH)4
73-2361 (C) - Dolomite - CaMg(CO3)2
72-1503 (C) - Muscovite - KAl2(Si3Al)O10(OH)2



Spinel AB_2O_4

Oxygen; cubic close packing



MFe_2O_4

Kind of site	Number available	Number occupied	Occupants: Normal spinel	Occupants: 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+}

ICDD & PDF

ICDD - International Centre for Diffraction Data

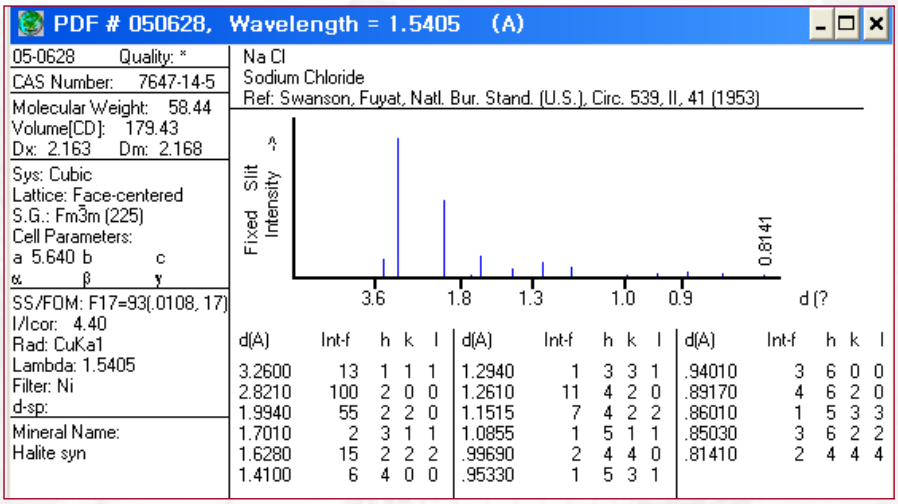
- A non-profit organization
- Collect, edit, publish, and distribute powder diffraction data
- Joint Committee for Chemical Analysis by Powder Diffraction Methods (founded in 1941)
- Joint Committee on Powder Diffraction Standards (JCPDS) (established in 1969)
- Renamed to ICDD in 1978

PDF (Powder Diffraction File)

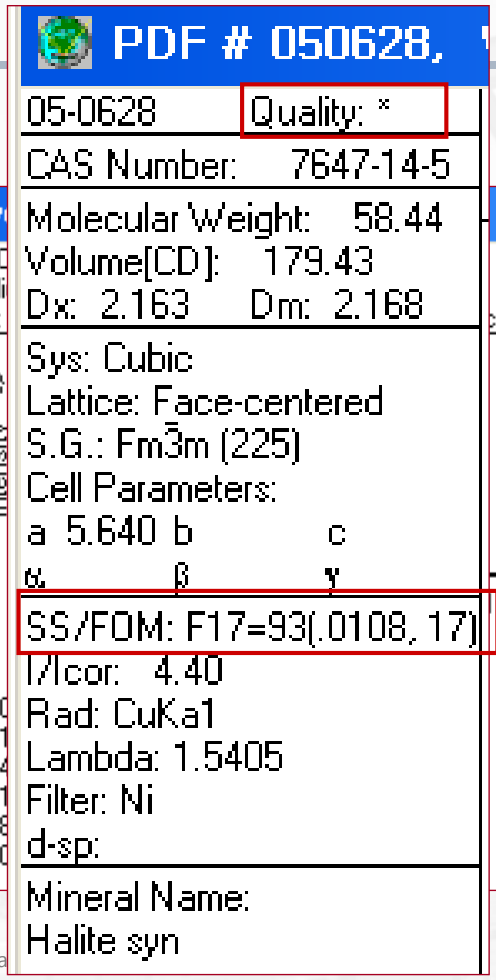
- A collection of single-phase X-ray powder diffraction patterns
- Interplanar spacings (d's), corresponding relative intensities (I's) and other pertinent physical and crystallographic properties

PDF - powder diffraction file

- a collection of single-phase X-ray powder diffraction patterns in the form of tables of characteristic interplanar spacings and corresponding relative intensities along with other pertinent physical and crystallographic properties
- a collection of single-phase X-ray powder diffraction patterns in the form of tables of characteristic d's & I's along with other pertinent physical and crystallographic properties



PDF



PDF card (in the past)

Quality mark
* Highest quality
i reasonable quality
o low quality
blank quality lower than o
c calculated data
r d's from Rietveld refinement

Set number
Add 1950 → year

Chemical formula
Chemical name
Mineral name

Experimental info
Types of X-ray
Wavelength
Monochromator/filter
Method of d measurement
Max measurable d-spacing
Method of I measurement
I/I(corundum)
Literature source

Physical data
Xtal system
International tables space group symbol
Axial lengths
Axial ratios
Interaxial angles
Number of chemical formulas in unit cell
Melting point
Literature source
X-ray density
Measured density
Figure of Merit

5- 628 ★

NaCl

Sodium Chloride

Halite, syn

Rad. CuKα$_1$ λ 1.5405 **Filter** Ni **d-sp**
Cutoff **Int.** Diffractometer **I/I$_{cor}$**: 4.40
Ref. Swanson, Fuyai, *Natl. Burl. Stand. (U.S.), Circ. 539, II 41 (1953)*

Sys. Cubic **S.G.** Fm3m(225)
A 5.6402 **b** **c** **AC**
α β γ **Z** 4 **mp** 804
Ref. Ibid.
D$_x$ 2.16 **D$_m$** 2.17 **SS/FOM F$_{17}$**=93(.011,17)
εα ηωβ 1.542 εγ **Sign** **2V**
Ref. *Dana's System of Mineralogy, 7th Ed.*, II 4

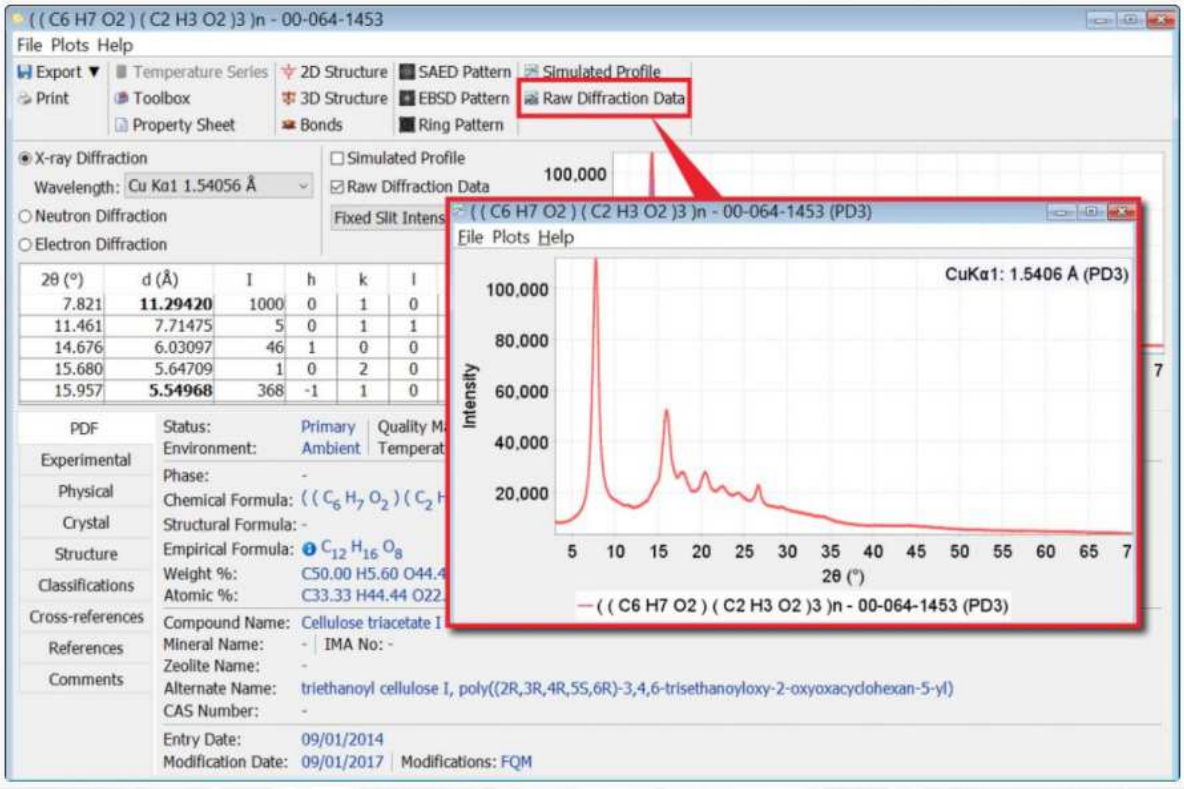
Color Colorless
Pattern taken at 26 C. CAS#: 7647-14-5. An ACS reagent grade sample recrystallized twice from hydrochloric acid. Halite group, halite subgroup. PSC: cF8.

d Å	Int	h k l	d Å	Int	h k l
3.26	13	111			
2.821	100	200			
1.994	55	220			
1.701	2	311			
1.628	15	222			
1.410	6	400			
1.294	1	331			
1.261	11	420			
1.1515	7	422			
1.0855	1	511			
0.9969	2	440			
0.9533	1	531			
0.9401	3	600			
0.8917	4	620			
0.8601	1	533			
0.8503	32	622			
0.8141	2	444			

General comments

D's, I's and Miller indices

PDF card (2021)



SEOUL NATIONAL UNIVERSITY

ICDD® 2022 Product Summary

Data Entry Source	PDF-4+ 2022 PDF-4+/Web 2022	PDF-4/ Axiom 2022	PDF-4/ Minerals 2022	PDF-4/ Organics 2022	PDF-2 2022
00- ICDD	122,611	36,257	12,805	43,162	122,611
01- FIZ	84,354	13,448	13,987	17,378	194,077
02- CCDC	0	0	0	444,125	0
03- NIST	2,862	412	229	283	10,067
04- MPDS	250,258	51,856	22,819	0	0
05- ICDD Crystal Data	869	0	75	55,247	869
Total No. of Entries	460,954	101,973	49,915	560,195	327,624
Subfile Distribution:					
Inorganic	438,726	92,727	49,861	324,259	305,502
Organic	51,414	11,978	732	548,959	49,726
New Entries	16,187	4,184	969	12,900	10,804
Rietveld—No. with atomic coordinates	353,330	71,560	41,376	156,107	0
Reference Intensity Ratio (RIR)—I/I_c	358,223	73,144	38,387	525,705	224,922
Experimental Digital Patterns	17,053	7,535	169	9,167	0

All ICDD databases combine the power of both powder diffraction and crystal structure reference data. We are the only crystallographic database in the world with quality marks and quality review processes that are ISO certified. Each PDF® database includes our integrated data mining software.

https://www.icdd.com/assets/files/2022-Product-Summary.pdf

WHICH ICDD DATABASE IS RIGHT FOR YOU?

https://www.icdd.com/assets/files/2022-Which-Database-Flyer.pdf

	PDF-4+ 2022	PDF-4+/ WEB 2022	PDF-4/ AXIOM 2022	PDF-4/ MINERALS 2022	PDF-4/ ORGANICS 2022	PDF-2 2022
I WORK PRIMARILY WITH INORGANIC COMPOUNDS	✔	✔	✔			✔
I WORK PRIMARILY WITH ORGANIC COMPOUNDS					✔	
I WORK PRIMARILY WITH MINERALS				✔		
I WORK WITH ELECTRON DIFFRACTION/SYNCHROTRON	✔	✔		✔	✔	
I NEED TO WORK AT THE OFFICE AND HOME		✔				
I NEED TO DO QUANTITATIVE ANALYSIS						
RIETVELD	✔ *	✔ *	✔ *	✔ *	✔ *	
REFERENCE INTENSITY RATIO (RIR)	✔ †	✔ †	✔ *	✔ †	✔ †	✔ †
PATTERN FITTING	✔ *	✔ *	✔ *	✔ *	✔ *	
I NEED A DATABASE WITH ATOMIC COORDINATES	✔	✔	✔	✔	✔	
HOW MANY ENTRIES ARE IN THE DATABASE?	460,954	460,954	101,973	49,915	560,195	327,624
HOW MANY ENTRIES ARE NEW?	16,821	16,821	4,184	969	12,900	10,804
I am using vendor software for my analysis. Which databases will work with my vendor software? Global software vendors provide search/match software that interfaces with our databases. Please check with your software vendor for compatibility.	✔	✔	✔	✔	✔	✔
WHAT IS THE LICENSE TERM FOR THE DATABASE?	1 YEAR	1 YEAR	3 YEAR	1 YEAR	1 YEAR	5 YEAR
MULTI-YEAR LICENSE AVAILABLE	✔	✔		✔	✔	
SITE LICENSE AVAILABLE	✔	✔			✔	✔

* Using diffraction equipment manufacturer or vendor software.
† Using Sleve or Sleve+, diffraction equipment manufacturer or vendor software.
NEW- Extended multi-year license terms – let us know what you need!

PDF-4+ 2021

PDF-4+ Purchase Options

https://www.icdd.com/assets/files/2021-Purchase-Options.pdf

PDF-4+ 2021	DVD CODE	USB CODE	2020 –2021 LIST $	2020 –2021 ACADEMIC $
New - Single License	F4D21	F4S21	$8,910	$5,925
Renewal from 2020 to 2021	F4RD21	F4RS21	$1,960	$1,250
PDF-4+ and JADE Pro Bundle*				
New - Single License	BUJPF4D21	BUJPF4S21	$15,648	$10,986
*Purchase a new license for PDF-4+ and JADE Pro				
PDF-4+ 2021 Multi-year License*				
Renewal - 3 year license	F4D22MR24	F4S22MR24	$5,290	$3,375
Renewal - 5 year license	F4D22MR26	F4S22MR26	$8,330	$5,315
PDF-4+Scholar 2021 (10-Year License Package)*				
PDF-4+ New – Single License	F4D21	F4S21	NA	$5,925
Sleve+ – New Single License	SWS421N	SWS421N	NA	$500
Scholar Multi-year	F4SPD22MR26	F4SPS22MR26	NA	$6,125
				$12,550
Save Money! Take advantange of ICDD's Combo Site License – Request a quote today!				
PDF-4+ 2021 Site License*				
New Master License	F4D21M	F4S21M	$8,910	$5,925
New - additional licenses, each	F4D21C	F4S21C	$1,960	$1,250
Renewal - Yearly Master License	F4RD21M	F4RS21M	$1,960	$1,250
Renewal - additional licenses, each	F4RD21C	F4RS21C	$750	$495
PDF-4+ 2021 Site/Multi-year License*				
Renewal - 3 year Master Site License	F4D22MR24M	F4S22MR24M	$5,290	$3,375
Renewal - 3 year additional licenses, each	F4D22MR24C	F4S22MR24C	$2,250	$1,485
Renewal - 5 year Master Site License	F4D22MR26M	F4S22MR26M	$8,330	$5,315
Renewal - 5 year additional licenses, each	F4D22MR26C	F4S22MR26C	$3,750	$2,475
PDF-2 to PDF-4+ Conversion				
PDF-2 2020 to PDF-4+ 2021	F2420RDU21	F2420RSU21	$1,960	$1,250
PDF-2 2019 to PDF-4+ 2021	F2419RDU21	F2419RSU21	$3,920	$2,500
PDF-2 2018 to PDF-4+ 2021	F2418RDU21	F2418RSU21	$5,880	$3,750
PDF-2 2016 to PDF-4+ 2021	F2416RDU21	F2416RSU21	$7,840	$5,000

PDF - Quality Mark & Figure of Merit

Quality Mark

- * highest quality - average Δ2θ < 0.03 degree, all lines were indexed, I measured quantitatively
- **i** reasonable quality - average Δ2θ < 0.06 degree, indexed with no more than two lines being unaccounted for, I measured quantitatively
- **o** low quality - low precision, poorly characterized, no unit cell data
- **blank** quality lower than o
- **c** calculated data
- **r** d's from Rietveld refinement
- h (hypothetical)

www.icdd.com/resources/webpdf/explain.htm
"Evaluating Data Quality" from ICDD

Figure of Merit

- To quantify better the quality of a given set of d-spacings
- To judge the credibility and worth of the results
- To evaluate the quality of d measurements
- The higher, the better

< 20 → poor quality

SS/FOM

(Smith & Snyder FOM)

$$F_N = \frac{1}{|\Delta 2\theta|} \frac{N_{obs}}{N_{poss}}$$

F_N = Figure of merit
$\Delta 2\theta$ = The average error in 2θ
N_{obs} = The number of lines observed
N_{poss} = Number of lines possible

Jenkins & Snyder page 315

Quality Mark of PDF

- A reliability index used in Powder Diffraction File (PDF)
- Plays an important role in interpreting search match results.
- Data validation and the assignment of the quality mark are the most important steps in the editorial process of PDF.
- The criteria for the assignment of the quality marks differ between patterns obtained experimentally and those determined from the crystal structure (calculated patterns).
- Editorial comments describing the quality of the pattern are extremely useful in evaluating and eventually accepting the search/match results.

"Evaluating Data Quality" from ICDD

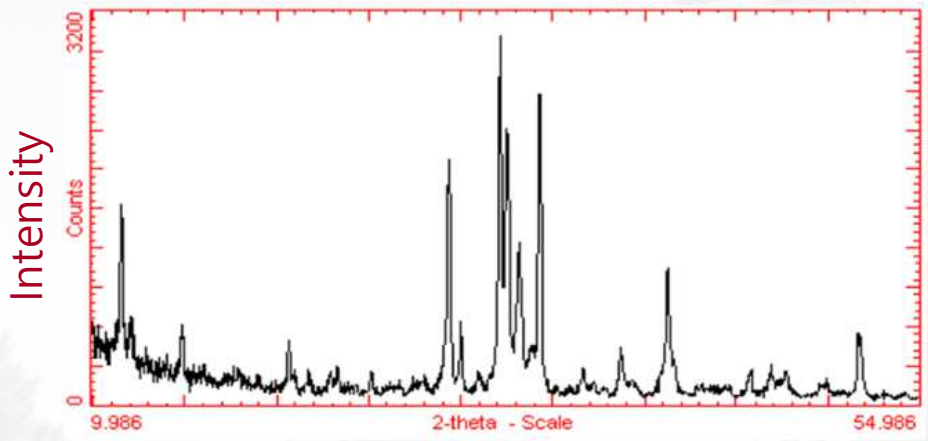
Standard Reference Materials (SRMs)

- Powder Line Position + Line Shape Std for Powder Dif
  - ✓ **Silicon (SRM 640f)**; $745/7.5g
- Line position - Fluorophlogopite mica (SRM 675); $809/7.5g
- Line profile - **LaB_6 (SRM 660c)**; $907/6g
- Intensity
  - ✓ ZnO, TiO_2 (rutile), Cr_2O_3, CeO_2 (SRM 674b); out of stock
- Quantitative phase analysis
  - ✓ Al_2O_3 (SRM 676a); out of stock, Silicon Nitride (SRM 656); $580/ 20g
- Instrument Response Std
  - ✓ Alumina plate (SRM 1976c); $721/1 disc

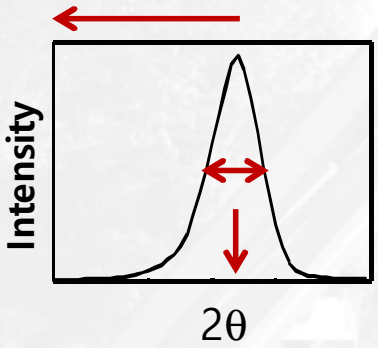
Prices; 2021-06-17
www.nist.gov/srm/index.cfm

Gold
$58.66 / gram
(2021-06-17)
goldprice.org

θ – 2θ X-ray diffraction pattern



2 Theta (deg.)



- **Positions**, **intensities**, shapes → crystal structure, physical state, etc.

- 2theta
  - ✓ **size & shape** - Geometry (crystal system, lattice parameter)
- Intensity
  - ✓ Atom type
  - ✓ Arrangement
  - ✓ Orientation, etc
- Shape of diffraction lines
  - ✓ Instrument broadening
  - ✓ Particle dimension
  - ✓ Strain

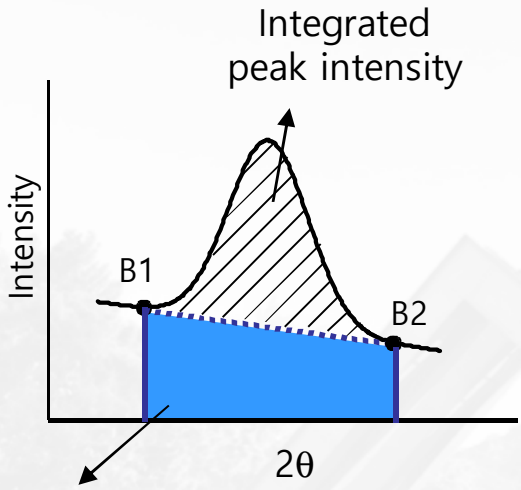
D-spacing accuracy

- Diffractometer misalignment
- Specimen displacement error
- Problems in establishing true peak position
- Background
- Kα2
- ---

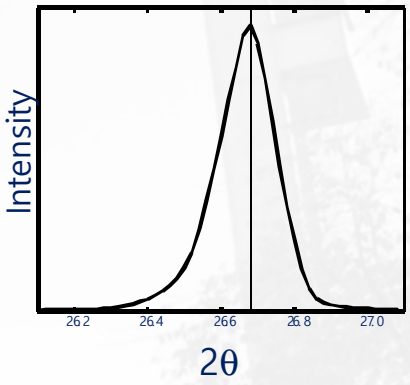
Intensity

- Structure sensitive
  - ✓ Atomic scattering factor
  - ✓ Structure factor
  - ✓ Polarization
  - ✓ Multiplicity
  - ✓ Temperature
- Sample sensitive
  - ✓ Absorption
  - ✓ Crystallite size
  - ✓ Degree of crystallinity
  - ✓ Particle orientation
- Instrument sensitive
  - ✓ Absolute intensities
    - Source intensity
    - Diffractometer efficiency
    - Take-off angle of tube
    - Receiving slit width
    - Axial divergence allowed
  - ✓ Relative intensities
    - Divergence slit aperture
    - Detector dead-time
- Measurement sensitive
  - ✓ Method of peak area measurement
  - ✓ Method of background subtraction
  - ✓ α2 stripping or not
  - ✓ Degree of data smoothing employed

Integrated intensity



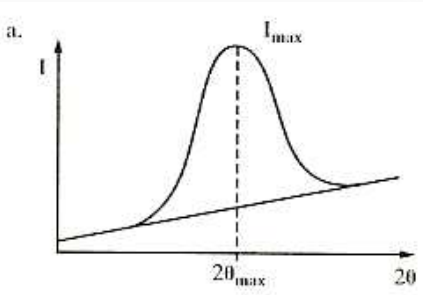
Integrated background intensity



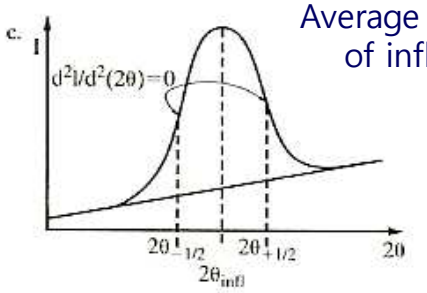
Asymmetric profile due to axial divergence

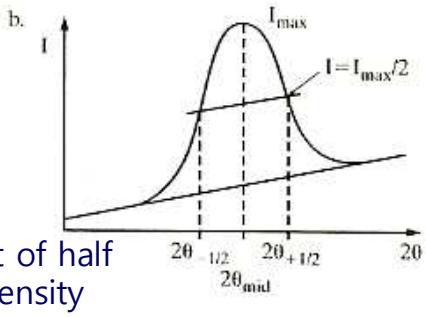
Methods of defining peak position

peak maximum

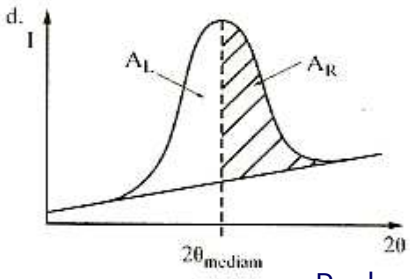


Average of points of inflection





Mid-point of half max intensity



Peak median
Peak centroid

$2\theta_{max}=d[I_{top}(2\theta)-I_{back}(2\theta)]/d(2\theta)$

$2\theta_{mid}=1/2[2\theta_{-1/2}+2\theta_{+1/2}]$

$2\theta_{infl}=1/2[2\theta'_{-1/2}+2\theta'_{+1/2}]$

$$<2\theta>=\frac{\int 2\theta \cdot I(2\theta)\cdot d(2\theta)}{\int I(2\theta)\cdot d(2\theta)}$$

Peak profile fitting

Crystal structure determination

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➢ Two step process

(1) Determination of the size & shape of the unit cell ← peak positions

(2) Determination of lattice type & distribution of the atoms in the structure ← intensities of the diffraction peaks

todos

SEOUL NATIONAL UNIVERSITY

➢XRD-3 READ

✓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

➢ XRD-3 Homework (due in 1 week)

✓ Hammond 9.4; 9.5

✓ Krawitz p5.2; p5.5; p5.6

✓ Cullity 4-4; 4-5; 4-6