The Structure Factor

Suggested Reading

Pages 303-312 in DeGraef & McHenry

Pages 59-61 in Engler and Randle

Structure Factor (F_{hkl})

$$F_{hkl} = \sum_{i=1}^{N} f_i e^{2\pi i(hu_i + kv_j + lw_i)}$$

- Describes how atomic arrangement (*uvw*) influences the intensity of the scattered beam.
- It tells us which reflections (i.e., peaks, *hkl*) to expect in a diffraction pattern.

Structure Factor (F_{hkl})

- The amplitude of the resultant wave is given by a ratio of amplitudes:

$$|F_{hkl}| = \frac{\text{amplitude of the wave scattered by all atoms of a UC}}{\text{amplitude of the wave scattered by one electron}}$$

- The intensity of the diffracted wave is proportional to $|F_{hkl}|^2$.

Some Useful Relations

$$e^{\pi i} = e^{3\pi i} = e^{5\pi i} = \ldots = -1$$

$$e^{2\pi i} = e^{4\pi i} = e^{6\pi i} = \ldots = +1$$

$e^{n\pi i} = (-1)^n$, where n is any integer

$e^{n\pi i} = e^{-n\pi i}$, where n is any integer

$$e^{ix} + e^{-ix} = 2\cos x$$

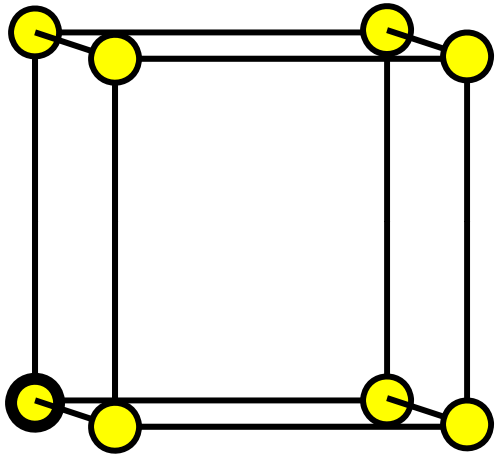
Needed for structure factor calculations

F_{hkl} for Simple Cubic

$$F_{hkl} = \sum_{i=1}^{N} f_i e^{2\pi i(hu_i + kv_j + lw_i)}$$

- Atom coordinate(s) u,v,w:
  - 0,0,0

$$F_{hkl} = fe^{2\pi i(0\cdot h + 0\cdot k + 0\cdot l)} = f$$



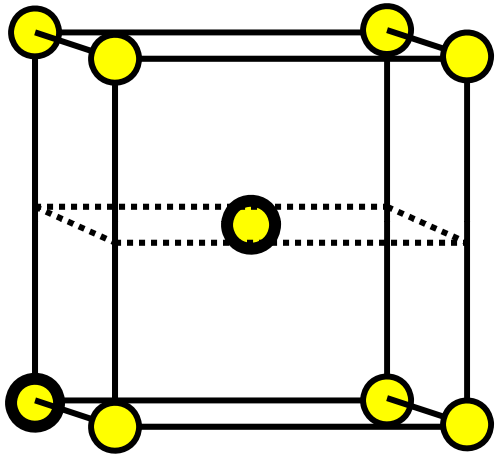
No matter what atom coordinates or plane indices you substitute into the structure factor equation for simple cubic crystals, the solution is always non-zero.

Thus, all reflections are allowed for simple cubic (primitive) structures.

F_{hkl} for Body Centered Cubic

$$F_{hkl} = \sum_{i=1}^{N} f_i e^{2\pi i(hu_i + kv_j + lw_i)}$$

- Atom coordinate(s) u,v,w:
  - 0,0,0;
  - ½, ½, ½.



$$F_{hkl} = fe^{2\pi i(0)} + fe^{2\pi i\left(\frac{h}{2}+\frac{k}{2}+\frac{l}{2}\right)}$$

$$\therefore$$

$$F_{hkl} = f\left(1 + e^{\pi i(h+k+l)}\right)$$

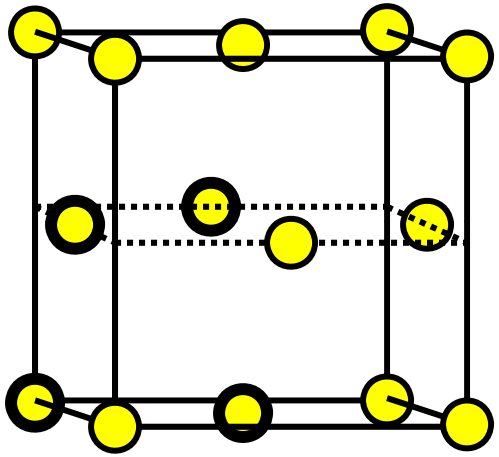
When $h+k+l$ is even F_{hkl} = non-zero → reflection.

When $h+k+l$ is odd $F_{hkl} = 0$ → no reflection.

F_{hkl} for Face Centered Cubic

$$F_{hkl} = \sum_{i=1}^{N} f_i e^{2\pi i(hu_i + kv_j + lw_i)}$$

- Atom coordinate(s) u,v,w:
  - 0,0,0;
  - ½,½,0;
  - ½,0,½;
  - 0,½,½.



$$F_{hkl} = fe^{2\pi i(0)} + fe^{2\pi i\left(\frac{h}{2}+\frac{k}{2}\right)} + fe^{2\pi i\left(\frac{h}{2}+\frac{l}{2}\right)} + fe^{2\pi i\left(\frac{k}{2}+\frac{l}{2}\right)}$$

$$\therefore$$

$$F_{hkl} = f\left(1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\right)$$

F_{hkl} for Face Centered Cubic

$$F_{hkl} = f\left(1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\right)$$

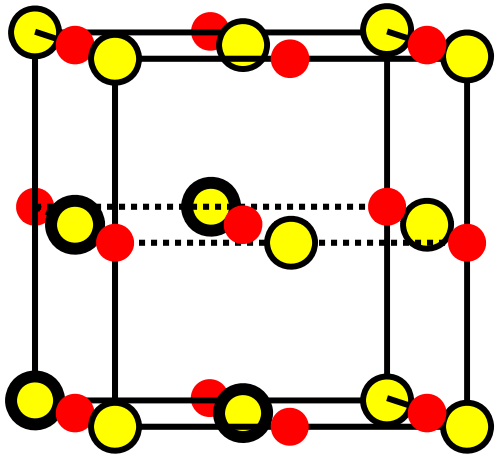
- Substitute in a few values of *hkl* and you will find the following:
  - When *h*,*k*,*l* are unmixed (i.e. all even or all odd), then F_{hkl} = 4*f*. [NOTE: zero is considered even]
  - F_{hkl} = 0 for mixed indices (i.e., a combination of odd and even).

F_{hkl} for NaCl Structure

$$F_{hkl} = \sum_{i=1}^{N} f_i e^{2\pi i(hu_i + kv_j + lw_i)}$$

- Atom coordinate(s) u,v,w:
  - Na at 0,0,0 + FC transl.;
    - 0,0,0;
    - ½,½,0;
    - ½,0,½;
    - 0,½,½.

    This means these coordinates (u,v,w)



  - Cl at ½,½,½ + FC transl.
    - ½,½,½; → ½,½,½
    - 1,1,½; → 0,0,½
    - 1,½,1; → 0,½,0
    - ½,1,1. → ½,0,0

    The re-assignment of coordinates is based upon the equipoint concept in the international tables for crystallography

- Substitute these u,v,w values into F_{hkl} equation.

F_{hkl} for NaCl Structure – cont'd

$$F_{hkl} = \sum_{i=1}^{N} f_i e^{2\pi i(hu_i + kv_j + lw_i)}$$

- For Na:

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

$$f_{Na}\left(1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\right)$$

- For Cl:

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

$$f_{Cl}\left(e^{\pi i(h+k+l)} + e^{\pi i(2h+2k+\boldsymbol{l})} + e^{\pi i(2h+\boldsymbol{k}+2l)} + e^{\pi i(\boldsymbol{h}+2k+2l)}\right) \cong$$

$$f_{Cl}\left(e^{\pi i(h+k+l)} + e^{\pi i(\boldsymbol{l})} + e^{\pi i(\boldsymbol{k})} + e^{\pi i(\boldsymbol{h})}\right)$$

These terms are all positive and even. ∴ Whether the exponent is odd or even depends solely on the remaining ***h***, ***k***, and ***l*** in each exponent.

F_{hkl} for NaCl Structure – cont'd

- Therefore F_{hkl}:

$$F_{hkl} = \sum_{i=1}^{N} f_i e^{2\pi i(hu_i + kv_j + lw_i)}$$

$$F_{hkl} = f_{Na}\left(1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\right) + f_{Cl}\left(e^{\pi i(h+k+l)} + e^{\pi i(\boldsymbol{l})} + e^{\pi i(\boldsymbol{k})} + e^{\pi i(\boldsymbol{h})}\right)$$

which can be simplified to*:

$$F_{hkl} = \left(f_{Na} + f_{Cl} e^{\pi i(h+k+l)}\right)\left(1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\right)$$

F_{hkl} for NaCl Structure

When *hkl* are even $F_{hkl} = 4(f_{Na} + f_{Cl})$

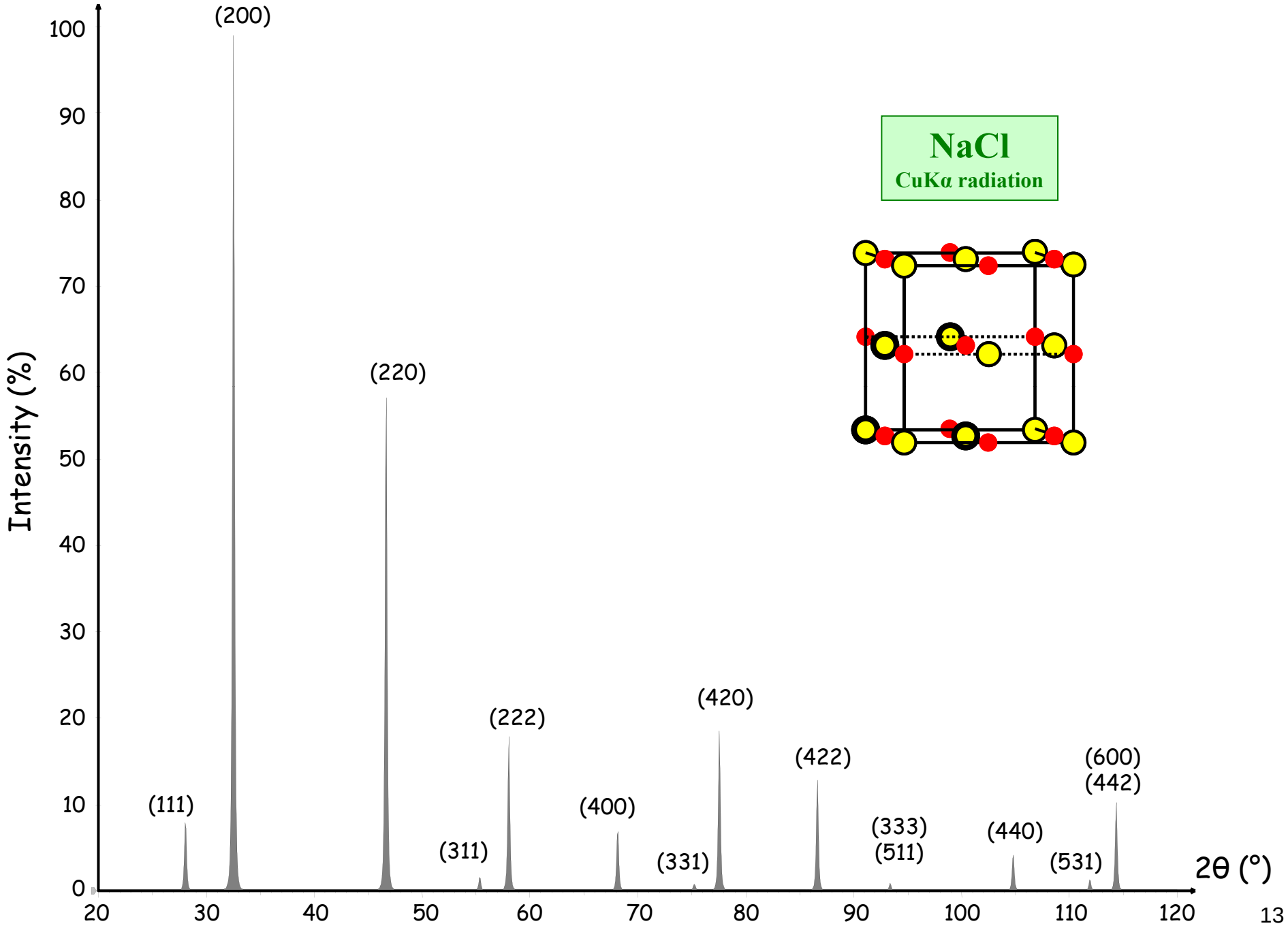
Primary reflections

When *hkl* are odd $F_{hkl} = 4(f_{Na} - f_{Cl})$

Superlattice reflections

When *hkl* are mixed $F_{hkl} = 0$

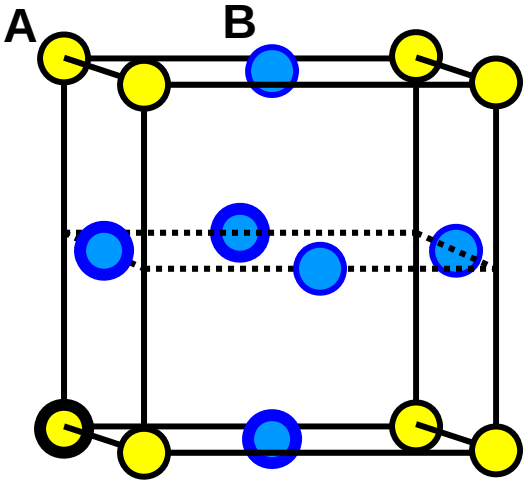
No reflections


NaCl
CuKα radiation
Intensity (%)
2θ (°)
(200)
(220)
(111)
(311)
(222)
(400)
(331)
(420)
(422)
(333)
(511)
(440)
(531)
(600)
(442)

F_{hkl} for $L1_2$ Crystal Structure

$$F_{hkl} = \sum_{i=1}^{N} f_i e^{2\pi i(hu_i + kv_j + lw_i)}$$

- Atom coordinate(s) u,v,w:
  - – 0,0,0;
  - – ½,½,0;
  - – ½,0,½;
  - – 0,½,½.



$$F_{hkl} = f_A e^{2\pi i(0)} + f_B e^{2\pi i\left(\frac{h}{2}+\frac{k}{2}\right)} + f_B e^{2\pi i\left(\frac{h}{2}+\frac{l}{2}\right)} + f_B e^{2\pi i\left(\frac{k}{2}+\frac{l}{2}\right)}$$

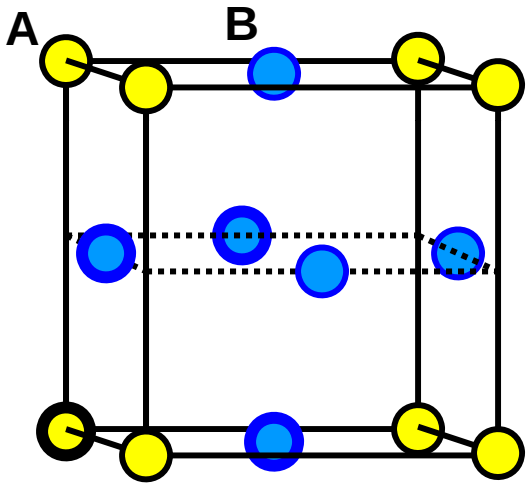
$$\therefore$$

$$F_{hkl} = f_A + f_B\left(e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\right)$$

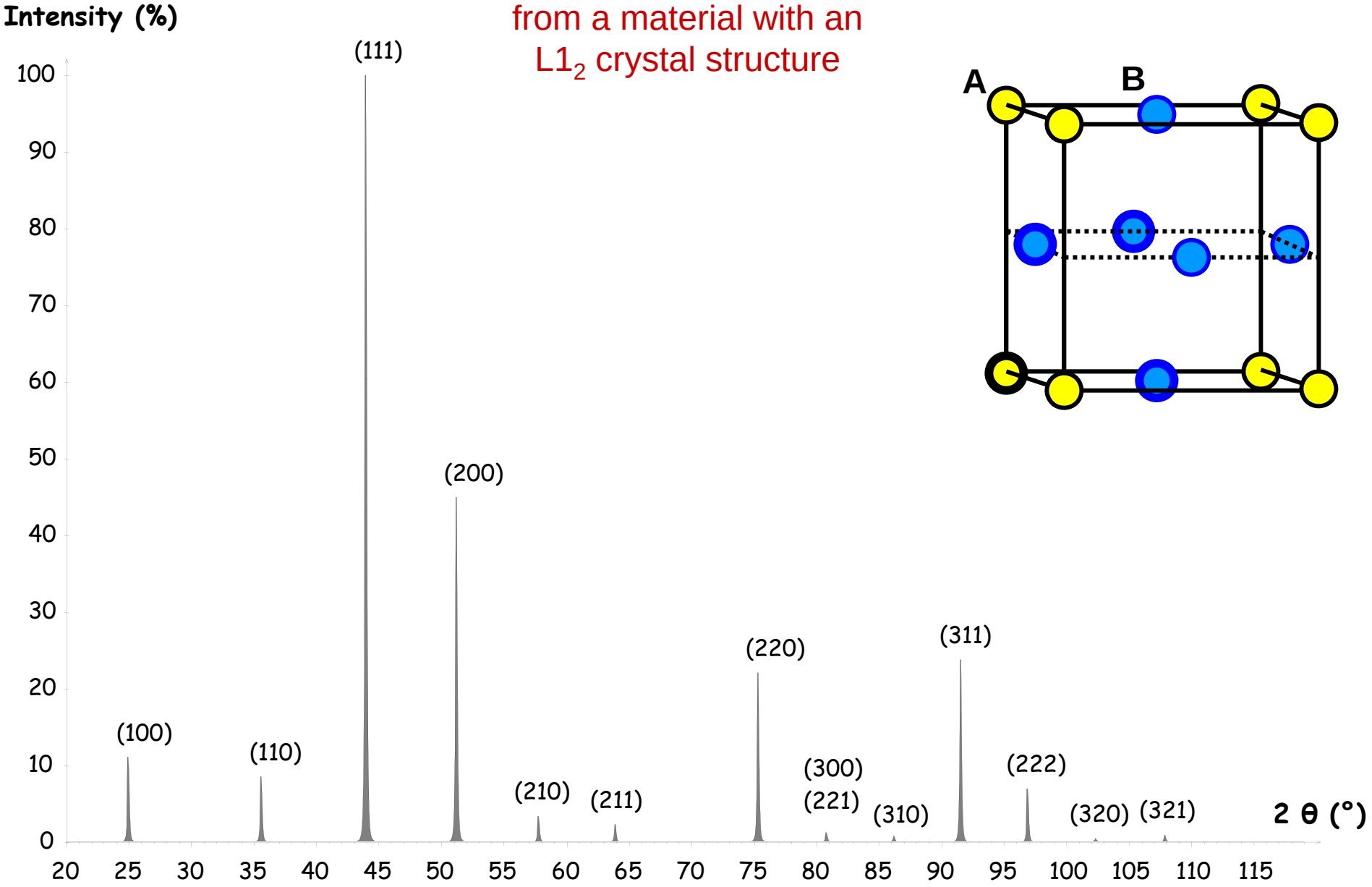
F_{hkl} for $L1_2$ Crystal Structure

$$F_{hkl} = f_A + f_B\left(e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}\right)$$

(1 0 0)	$F_{hkl} = f_A + f_B(-1-1+1) = f_A - f_B$
(1 1 0)	$F_{hkl} = f_A + f_B(1-1-1) = f_A - f_B$
(1 1 1)	$F_{hkl} = f_A + f_B(1+1+1) = f_A + 3\,f_B$
(2 0 0)	$F_{hkl} = f_A + f_B(1+1+1) = f_A + 3\,f_B$
(2 1 0)	$F_{hkl} = f_A + f_B(-1+1-1) = f_A - f_B$
(2 2 0)	$F_{hkl} = f_A + f_B(1+1+1) = f_A + 3\,f_B$
(2 2 1)	$F_{hkl} = f_A + f_B(1-1-1) = f_A - f_B$
(3 0 0)	$F_{hkl} = f_A + f_B(-1-1+1) = f_A - f_B$
(3 1 0)	$F_{hkl} = f_A + f_B(1-1-1) = f_A - f_B$
(3 1 1)	$F_{hkl} = f_A + f_B(1+1+1) = f_A + 3\,f_B$
(2 2 2)	$F_{hkl} = f_A + f_B(1+1+1) = f_A + 3\,f_B$

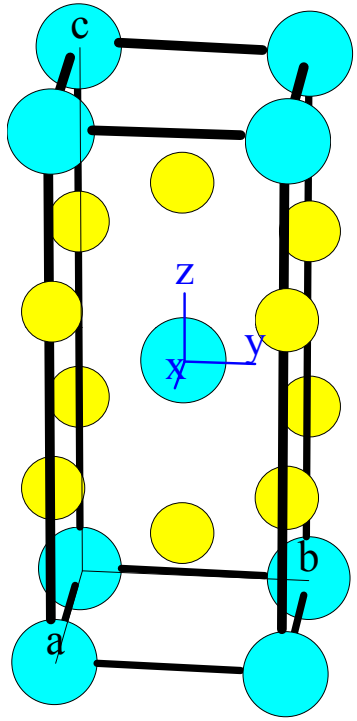


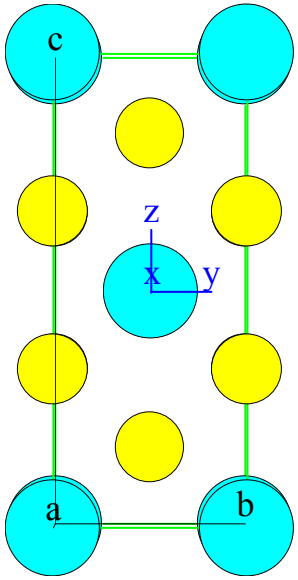
Example of XRD pattern from a material with an $L1_2$ crystal structure



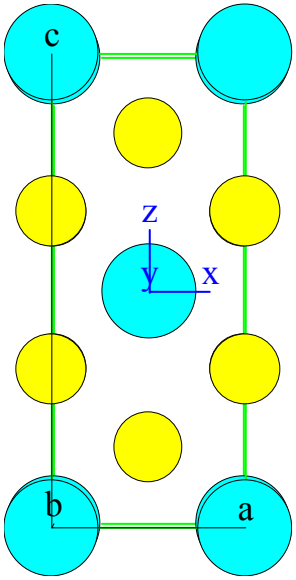
F_{hkl} for $MoSi_2$

- **Atom positions:**
  - Mo atoms at 0,0,0; ½,½,½
  - Si atoms at 0,0,$\bar{z}$; 0,0,z; ½,½,½+z; ½,½,½-z; z=1/3
  - $MoSi_2$ is actually body centered tetragonal with a = 3.20 Å and c = 7.86 Å

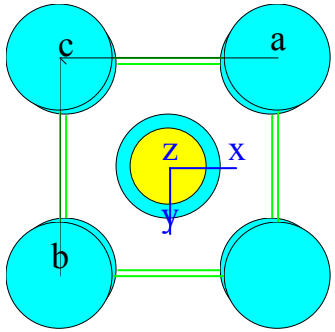




Viewed down x-axis



Viewed down y-axis



Viewed down z-axis

F_{hkl} for $MoSi_2$

$$F_{hkl} = \sum_{i=1}^{N} f_i e^{2\pi i(hu_i + kv_j + lw_i)}$$

Substitute in atom positions:

- Mo atoms at 0,0,0; ½,½,½
- Si atoms at 0,0, ; 0,0,$\bar{z}$; ½,½,½+z; ½,½,½-z; z=1/3

$$F_{hkl} = \left(f_{Mo} e^{2\pi i(0)} + f_{Mo} e^{2\pi i\left(\frac{h}{2}+\frac{k}{2}+\frac{l}{2}\right)} \right) + \left(f_{Si} e^{2\pi i(\frac{l}{3})} + f_{Si} e^{-2\pi i(\frac{l}{3})} + f_{Si} e^{2\pi i\left(\frac{h}{2}+\frac{k}{2}+\frac{5l}{6}\right)} + f_{Si} e^{2\pi i\left(\frac{h}{2}+\frac{k}{2}+\frac{l}{6}\right)} \right)$$

$$F = f_{Mo}\left(1 + e^{\pi i(h+k+l)}\right) + f_{Si}\left(e^{2\pi i(\frac{l}{3})} + e^{-2\pi i(\frac{l}{3})} + e^{\pi i\left(h+k+\frac{5l}{3}\right)} + e^{\pi i\left(h+k+\frac{l}{3}\right)} \right)$$

Now we can plug in different values for *h k l* to determine the structure factor.

- For *h k l* = 1 0 0

$$F_{hkl} = f_{Mo}\left(1 + e^{\pi i(1+0+0)}\right) + f_{Si}\left(e^{2\pi i(\frac{(0)}{3})} + e^{-2\pi i(\frac{(0)}{3})} + e^{\pi i\left(1+0+\frac{5(0)}{3}\right)} + e^{\pi i\left(1+0+\frac{(0)}{3}\right)} \right)$$

$$= f_{Mo}(1-1) + f_{Si}(1+1-1-1) = 0$$

$$\therefore \qquad F_{hkl}^2 = 0$$

F_{hkl} for $MoSi_2$ – cont'd

Now we can plug in different values for *h k l* to determine the structure factor.

- For *h k l* = 0 0 1

$$F_{hkl} = f_{Mo}\left(e^{0} + e^{\pi i(0+0+1)}\right) + f_{Si}\left(e^{2\pi i(\frac{1}{3})} + e^{-2\pi i(\frac{1}{3})} + e^{\pi i\left(0+0+\frac{5(1)}{3}\right)} + e^{\pi i\left(0+0+\frac{(1)}{3}\right)}\right)$$

$$= f_{Mo}(1+e^{\pi i}) + f_{Si}(2COS(\tfrac{2\pi}{3}) + e^{2\pi i})$$

$$= f_{Mo}(1-1) + f_{si}(-1+1) = 0$$

$$\therefore$$

$F_{hkl}^2 = 0$ NO REFLECTION!

- For *h k l* = 1 1 0

$$F_{hkl} = f_{Mo}\left(e^{0} + e^{\pi i(1+1+0)}\right) + f_{Si}\left(e^{2\pi i(0)} + e^{-2\pi i(0)} + e^{\pi i(1+1+0)} + e^{\pi i(1+1+0)}\right)$$

$$= f_{Mo}(1+e^{2\pi i}) + f_{Si}(e^{(0)} + e^{(0)} + e^{2\pi i} + e^{2\pi i})$$

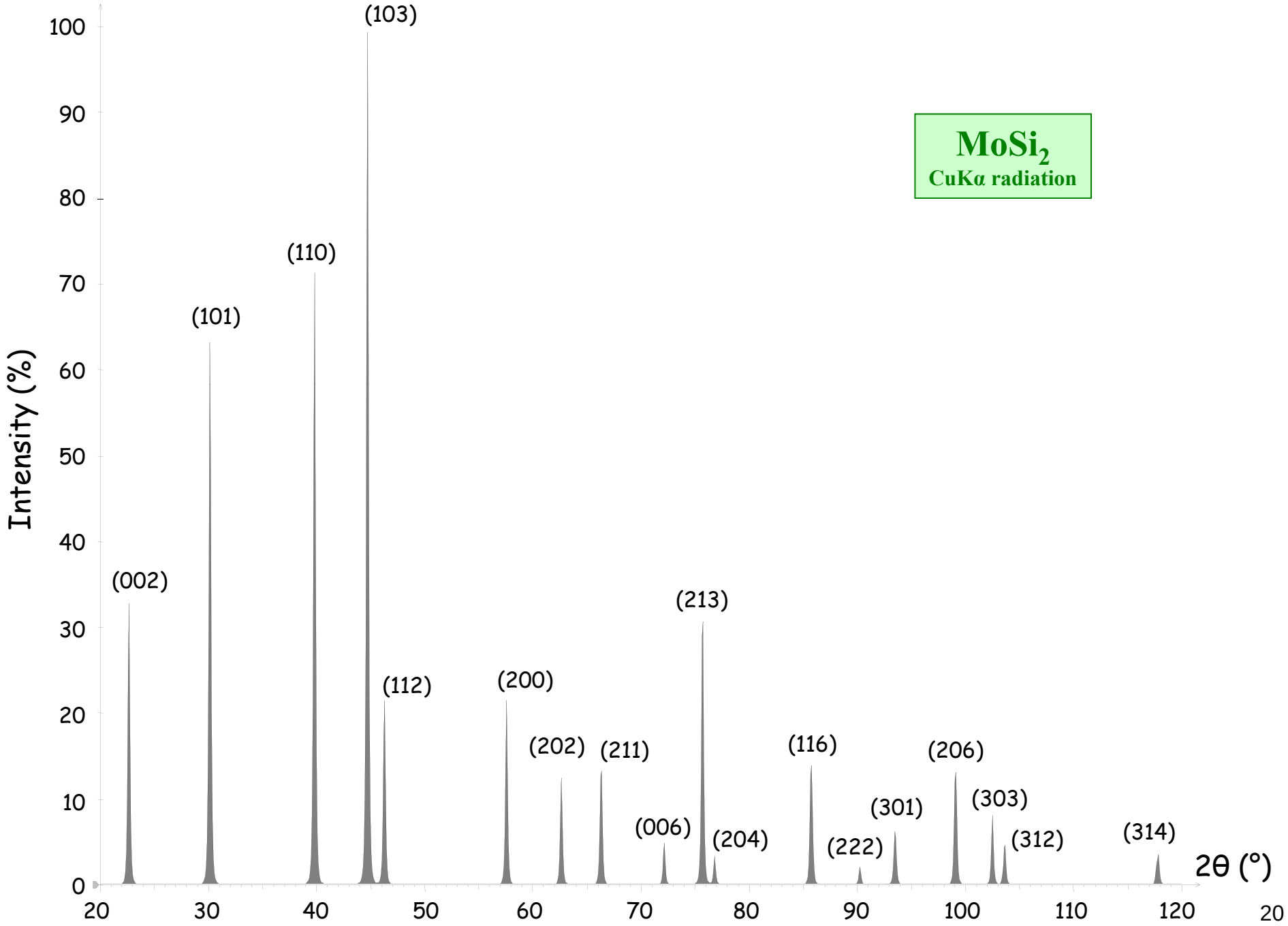
$$= f_{Mo}(2) + f_{si}(4)$$

$$\therefore$$

F_{hkl}^2 = POSITIVE! YOU WILL SEE A REFLECTION

- If you continue for different *h k l* combinations… trends will emerge… this will lead you to the rules for diffraction…

  ***h + k + l* = even**


MoSi2
CuKα radiation
Intensity (%)
2θ (°)
(002)
(101)
(110)
(103)
(112)
(200)
(202)
(211)
(006)
(213)
(204)
(116)
(222)
(301)
(206)
(303)
(312)
(314)

F_{hkl} for $MoSi_2$ – cont'd

PDF # 410612, Wavelength = 1.540598 (A)

41-0612 Quality: *

CAS Number:

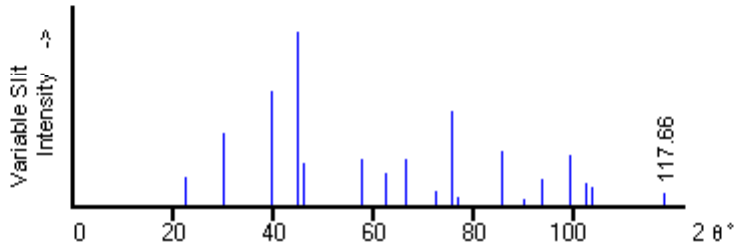
Molecular Weight: 152.11
Volume[CD]: 80.57
Dx: 6.270 Dm:

Sys: Tetragonal
Lattice: Body-centered
S.G.: I4/mmm (139)
Cell Parameters:
a 3.204 b c 7.844
α β γ

SS/FOM: F18=85(.0076, 28)
I/Icor:
Rad: CuKa1
Lambda: 1.5405981
Filter: Graph
d-sp: diffractometer

Also called:
molybdenum disilicide

Mo Si2
Molybdenum Silicon
Ref: Natl. Bur. Stand. (U.S.) Monogr. 25, 21, 96 (1985)



2θ	Int-v	h	k	l	2θ	Int-v	h	k	l	2θ	Int-v	h	k	l
22.647	16	0	0	2	62.578	18	2	0	2	90.095	4	2	2	2
30.097	41	1	0	1	66.241	26	2	1	1	93.399	15	3	0	1
39.745	65	1	1	0	72.195	8	0	0	6	98.989	28	2	0	6
44.684	100	1	0	3	75.587	53	2	1	3	102.32	12	3	0	3
46.234	24	1	1	2	76.730	5	2	0	4	103.44	10	3	1	2
57.448	27	2	0	0	85.728	30	1	1	6	117.66	7	3	1	4

Structure Factor (F_{hkl}) for HCP

$$F_{hkl} = \sum_{i=1}^{N} f_i e^{2\pi i(hu_i + kv_j + lw_i)}$$

- Describes how atomic arrangement (*uvw*) influences the intensity of the scattered beam.

i.e.,

- It tells us which reflections (i.e., peaks, *hkl*) to expect in a diffraction pattern from a given crystal structure with atoms located at positions *u*,*v*,*w*.

- In HCP crystals (like Ru, Zn, Ti, and Mg) the lattice point coordinates are:

  – 0 0 0

  – $\frac{1}{3}\ \frac{2}{3}\ \frac{1}{2}$

- Therefore, the structure factor becomes:

$$F_{hkl} = f_i \left\{ 1 + e^{2\pi i\left(\frac{h}{3}+\frac{2k}{3}+\frac{l}{2}\right)} \right\}$$

- We simplify this expression by letting:

$$g = \frac{h + 2k}{3} + \frac{1}{2}$$

which reduces the structure factor to:

$$F_{hkl} = f_i \left\{ 1 + e^{2\pi i g} \right\}$$

- We can simplify this once more using:

from which we find:

$$e^{ix} + e^{-ix} = 2\cos x$$

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

Selection rules for HCP

$$F_{hkl}^2 = \begin{cases} 0 & \text{when } h+2k = 3n \text{ and } l = \text{odd} \\ f_i^{\,2} & \text{when } h+2k = 3n \pm 1 \text{ and } l = \text{even} \\ 3\,f_i^{\,2} & \text{when } h+2k = 3n \pm 1 \text{ and } l = \text{odd} \\ 4\,f_i^{\,2} & \text{when } h+2k = 3n \text{ and } l = \text{even} \end{cases}$$

For your HW problem, you will need these things to do the structure factor calculation for Ru.

HINT: It might save you some time if you already had the ICDD card for Ru.

List of selection rules for different crystals

Crystal Type	Bravais Lattice	Reflections Present	Reflections Absent
Simple	Primitive, P	Any *h*,*k*,*l*	None
Body-centered	Body centered, I	$h+k+l$ = even	$h+k+l$ = odd
Face-centered	Face-centered, F	*h*,*k*,*l* unmixed	*h*,*k*,*l* mixed
NaCl	FCC	*h*,*k*,*l* unmixed	*h*,*k*,*l* mixed
Zincblende	FCC	Same as FCC, but if all even and $h+k+l \neq 4N$ then absent	*h*,*k*,*l* mixed and if all even and $h+k+l \neq 4N$ then absent
Base-centered	Base-centered	*h*,*k* both even or both odd	*h*,*k* mixed
Hexagonal close-packed	Hexagonal	$h+2k=3N$ with *l* even $h+2k=3N\pm1$ with *l* odd $h+2k=3N\pm1$ with *l* even	$h+2k=3N$ with *l* odd

What about solid solution alloys?

- If the alloys lack long range order, then you must average the atomic scattering factor.

$$f_{\text{alloy}} = x_A f_A + x_B f_B$$

where x_n is an atomic fraction for the atomic constituent

Exercises

- For CaF_2 calculate the structure factor and determine the selection rules for allowed reflections.