



Analytical Methods for Materials

Lesson 18

The Structure Factor

Suggested Reading

Chapter 3 in Waseda, pp. 100-106

Chapters 3 and 4 in Cullity & Stock

Chapter 2 in Brandon & Kaplan

Pages 303-312 in DeGraef & McHenry

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.

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 .

Structure Factor (F_{hkl})

- The amplitude of the resultant wave is given by the 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 reflected wave is proportional to $|F_{hkl}|^2$.

Some Useful Relations

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

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

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

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

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

YOU WILL NEED THESE FOR STRUCTURE FACTOR
CALCULATIONS

The quadratic forms of the Miller Indices will also be
needed (Appendix 9 in Cullity).

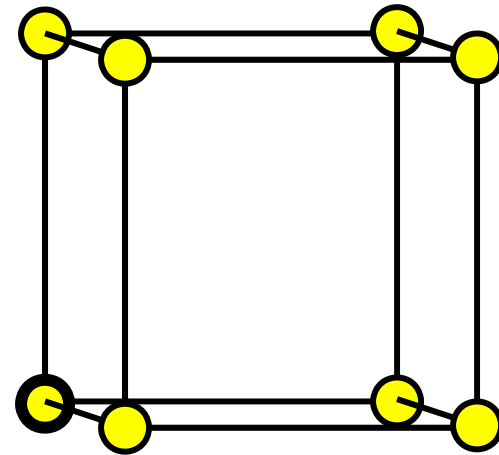
F_{hkl} for Simple Cubic

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

– 0,0,0

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

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



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.

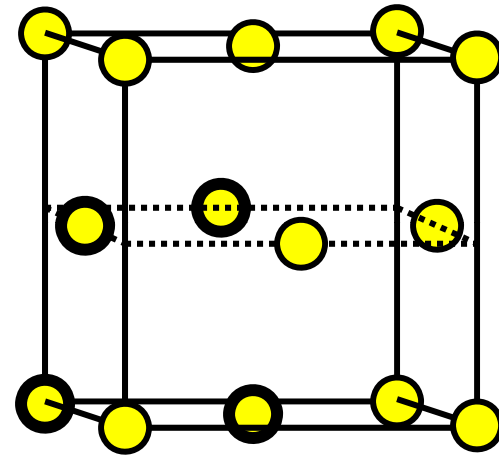
Thus, all reflections are allowed for simple cubic (primitive) structures.

F_{hkl} for Face Centered Cubic

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

- $0, 0, 0$;
- $\frac{1}{2}, \frac{1}{2}, 0$;
- $\frac{1}{2}, 0, \frac{1}{2}$;
- $0, \frac{1}{2}, \frac{1}{2}$.

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



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

\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 $F_{hkl} = 4f$. [NOTE: zero is considered even]
 - $F_{hkl} = 0$ for mixed indices (i.e., a combination of odd and even).

F_{hkl} for Body Centered Cubic

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

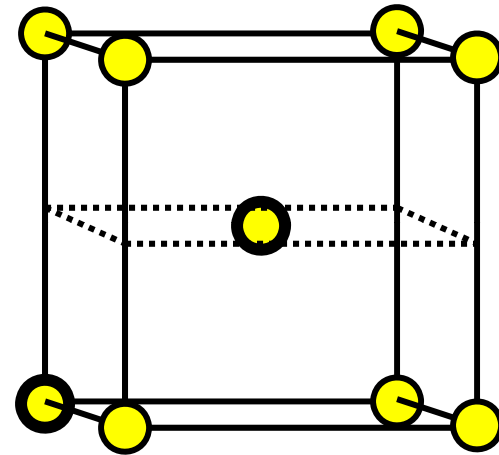
- 0,0,0;
- $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

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

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

\vdots

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



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

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

F_{hkl} for NaCl Structure

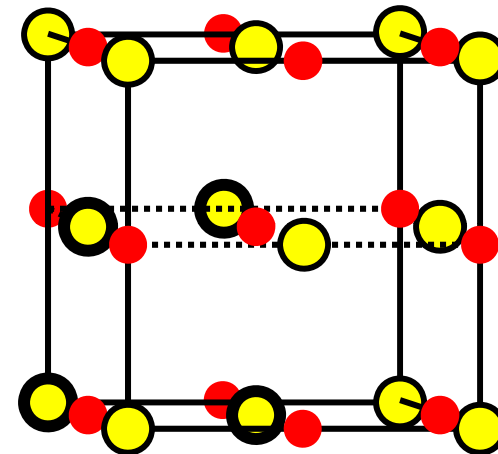
- Atom coordinate(s) u, v, w :

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

- – Na at $0,0,0$ + FC transl.;

- $0,0,0$;
- $\frac{1}{2}, \frac{1}{2}, 0$;
- $\frac{1}{2}, 0, \frac{1}{2}$;
- $0, \frac{1}{2}, \frac{1}{2}$.

This means these
coordinates
(u, v, w)



- – Cl at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ + FC transl.

- $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; → $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
- $1, 1, \frac{1}{2}$; → $0, 0, \frac{1}{2}$
- $1, \frac{1}{2}, 1$; → $0, \frac{1}{2}, 0$
- $\frac{1}{2}, 1, 1$. → $\frac{1}{2}, 0, 0$

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

- For Na:

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

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

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

- For Cl:

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

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

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

These terms are all positive and even.
 \therefore 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} :

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

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

which can be simplified to*:

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

* See pages 140-142 in Cullity and Stock for a little more detail on this.

F_{hkl} for NaCl Structure

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

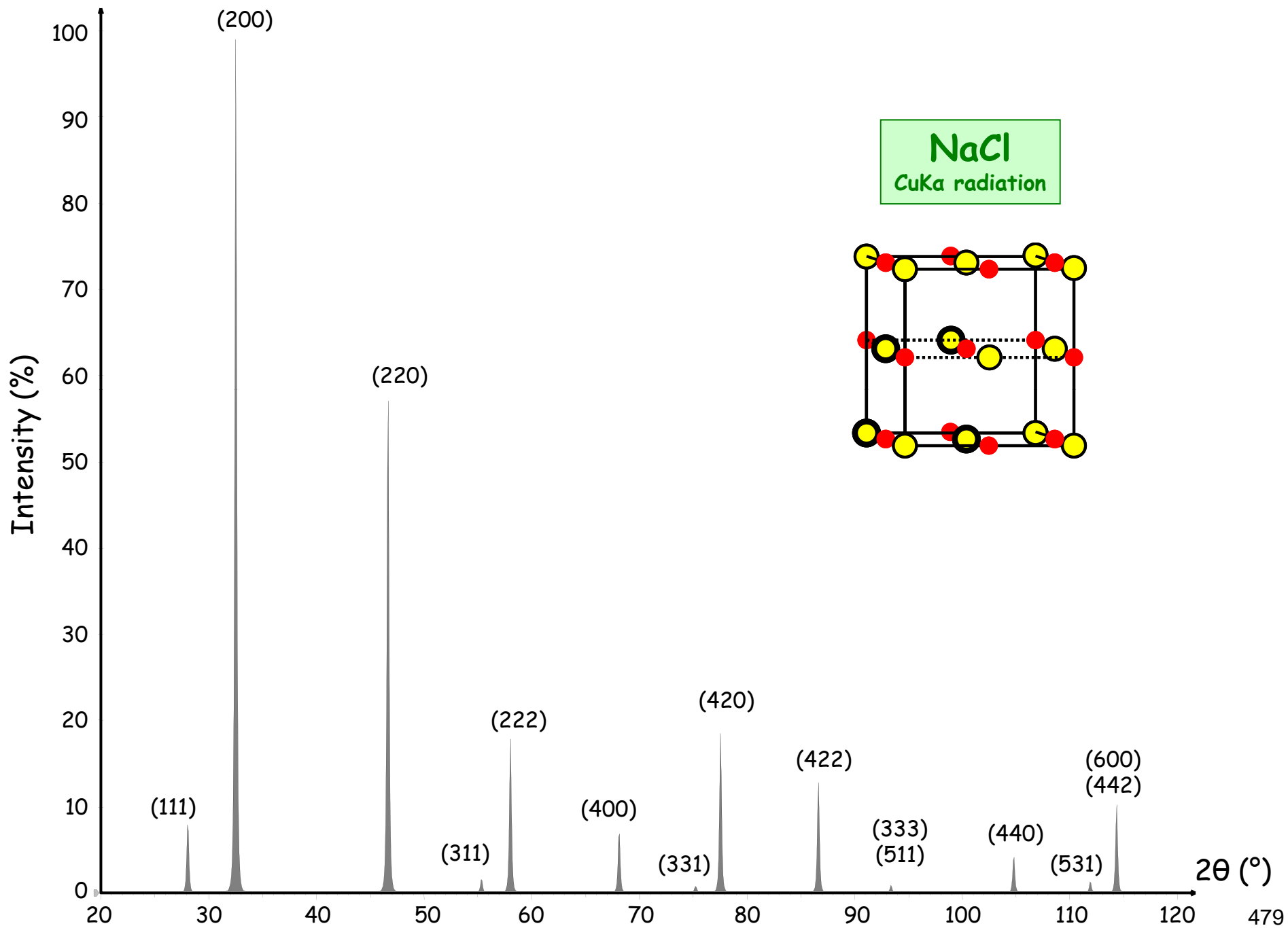
Primary reflections

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

Superlattice reflections

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

No reflections

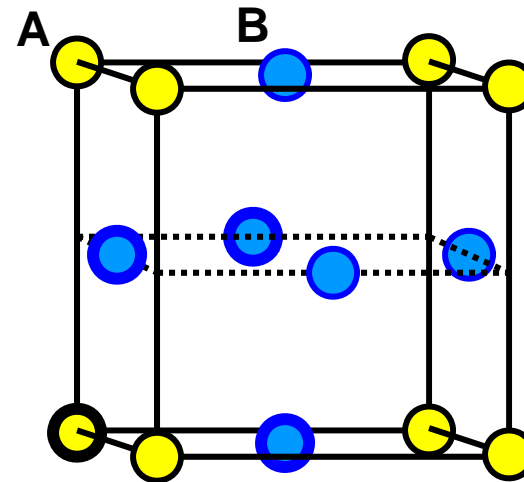


F_{hkl} for $L1_2$ Crystal Structure

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

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

- — $0, 0, 0$;
 - $\frac{1}{2}, \frac{1}{2}, 0$;
 - — $\frac{1}{2}, 0, \frac{1}{2}$;
 - $0, \frac{1}{2}, \frac{1}{2}$.



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

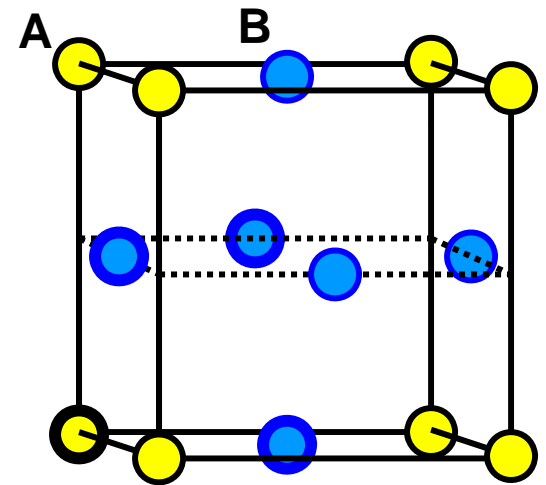
\therefore

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

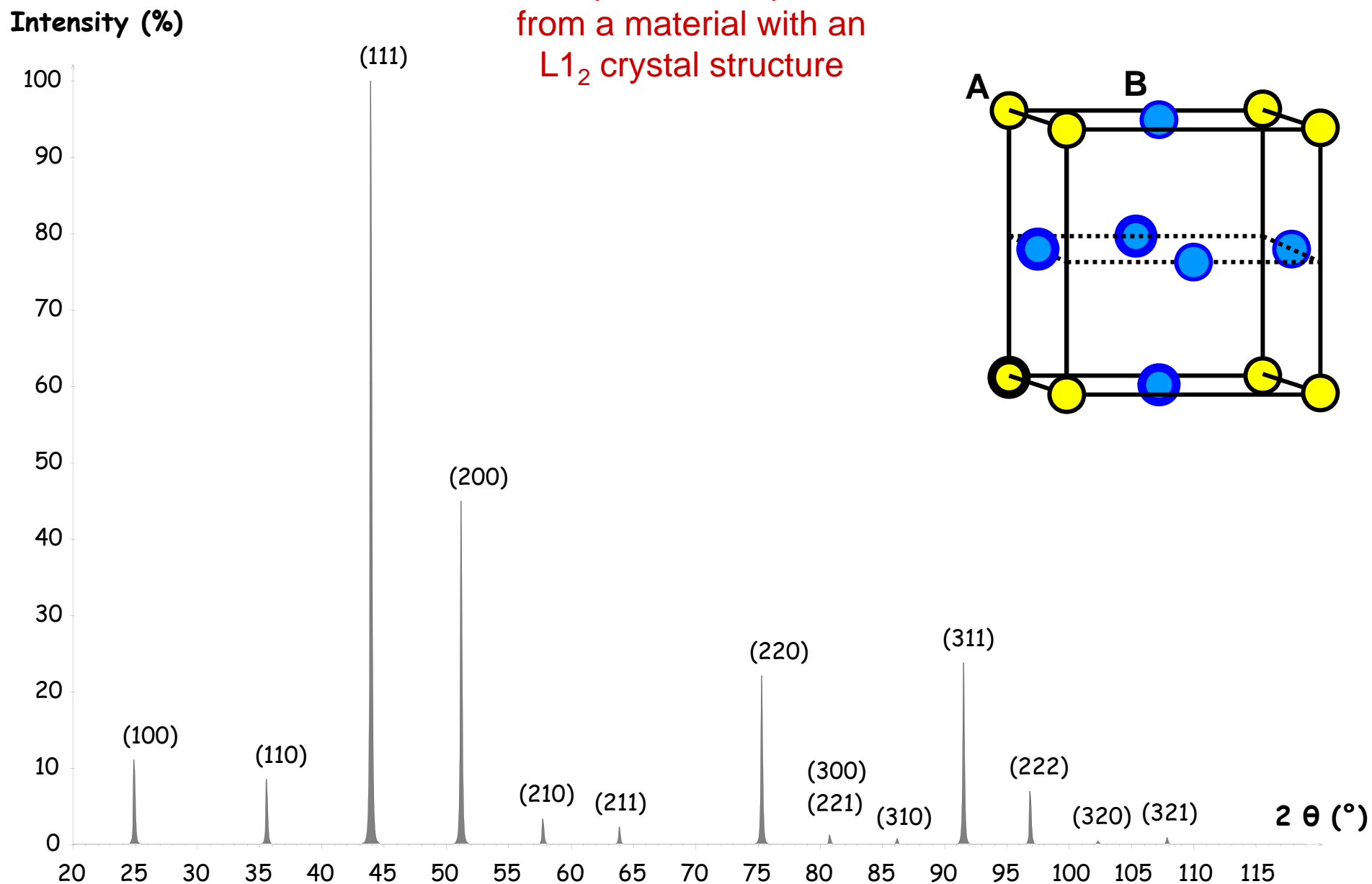
F_{hkl} for $L1_2$ Crystal Structure

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

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



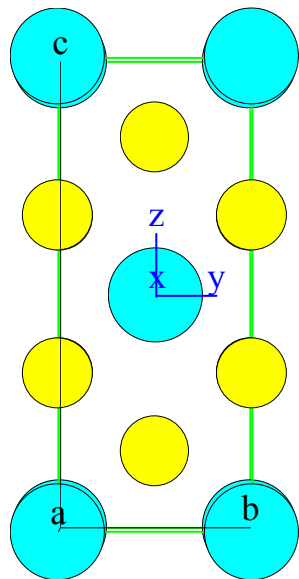
Example of XRD pattern from a material with an $L1_2$ crystal structure



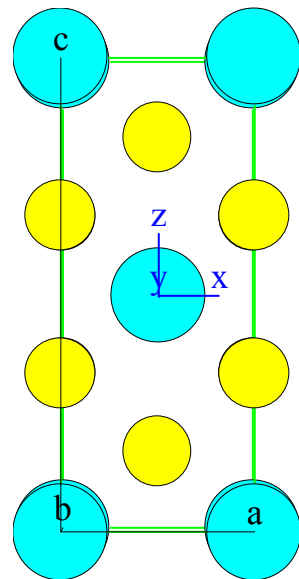
F_{hkl} for MoSi_2

- Atom positions:**

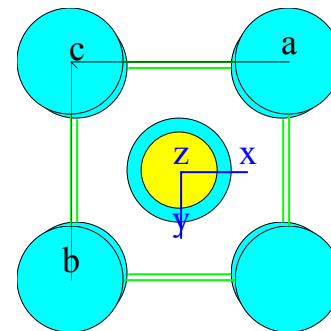
- Mo atoms at $0,0,0$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$
- Si atoms at $0,0,\bar{z}$; $0,0,z$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}+z$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}-z$; $z=\frac{1}{3}$
- MoSi_2 is actually body centered tetragonal with $a = 3.20 \text{ \AA}$ and $c = 7.86 \text{ \AA}$



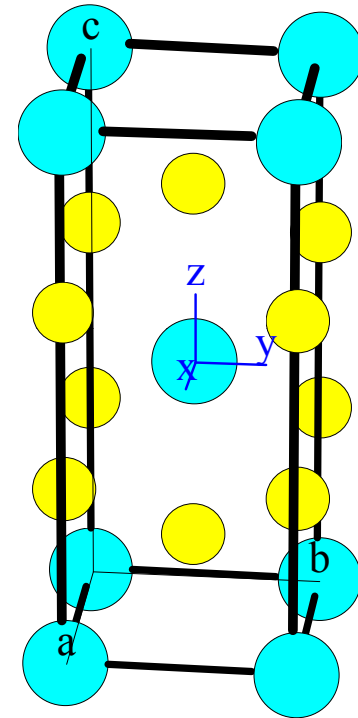
Viewed down x-axis



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 $0,0,0$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
- Si atoms at $0,0, \bar{z}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+z$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-z$; $z=1/3$

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

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

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

- For $h k l = 1 0 0$

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

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



F_{hkl} for MoSi_2 - cont'd

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

- For $h k l = 0 0 1$

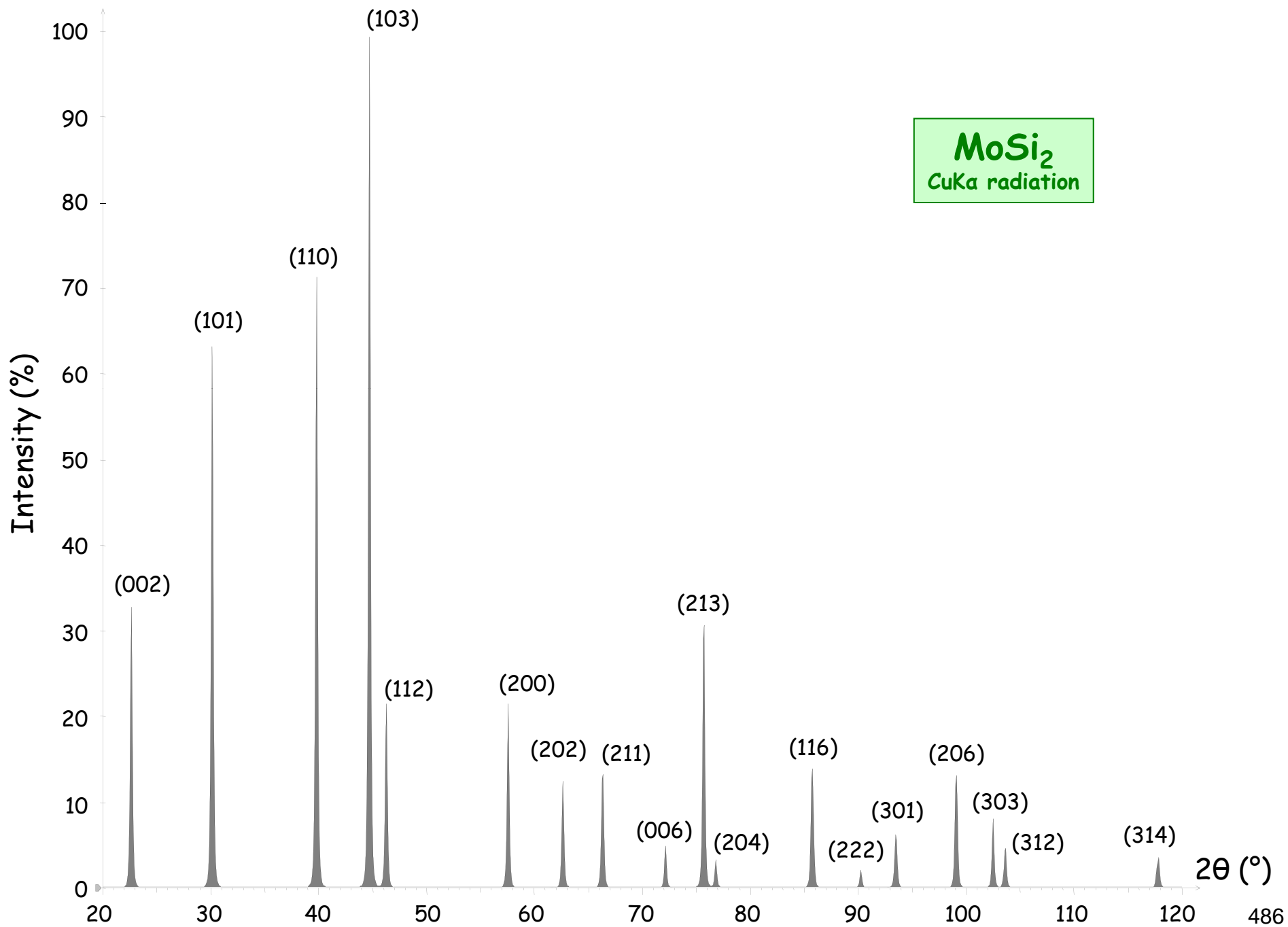
$$\begin{aligned} F_{hkl} &= f_{\text{Mo}} \left(e^0 + e^{\pi i(0+0+1)} \right) + f_{\text{Si}} \left(e^{2\pi i(\frac{1}{3})} + e^{-2\pi i(\frac{1}{3})} + e^{\pi i(0+0+\frac{5(1)}{3})} + e^{\pi i(0+0+\frac{(1)}{3})} \right) \\ &= f_{\text{Mo}} (1 + e^{\pi i}) + f_{\text{Si}} (2\text{COS}(\frac{2\pi}{3}) + e^{2\pi i}) \\ &= f_{\text{Mo}} (1 - 1) + f_{\text{Si}} (-1 + 1) = 0 \\ &\therefore \\ F_{hkl}^2 &= 0 \quad \text{NO REFLECTION!} \end{aligned}$$

- For $h k l = 1 1 0$

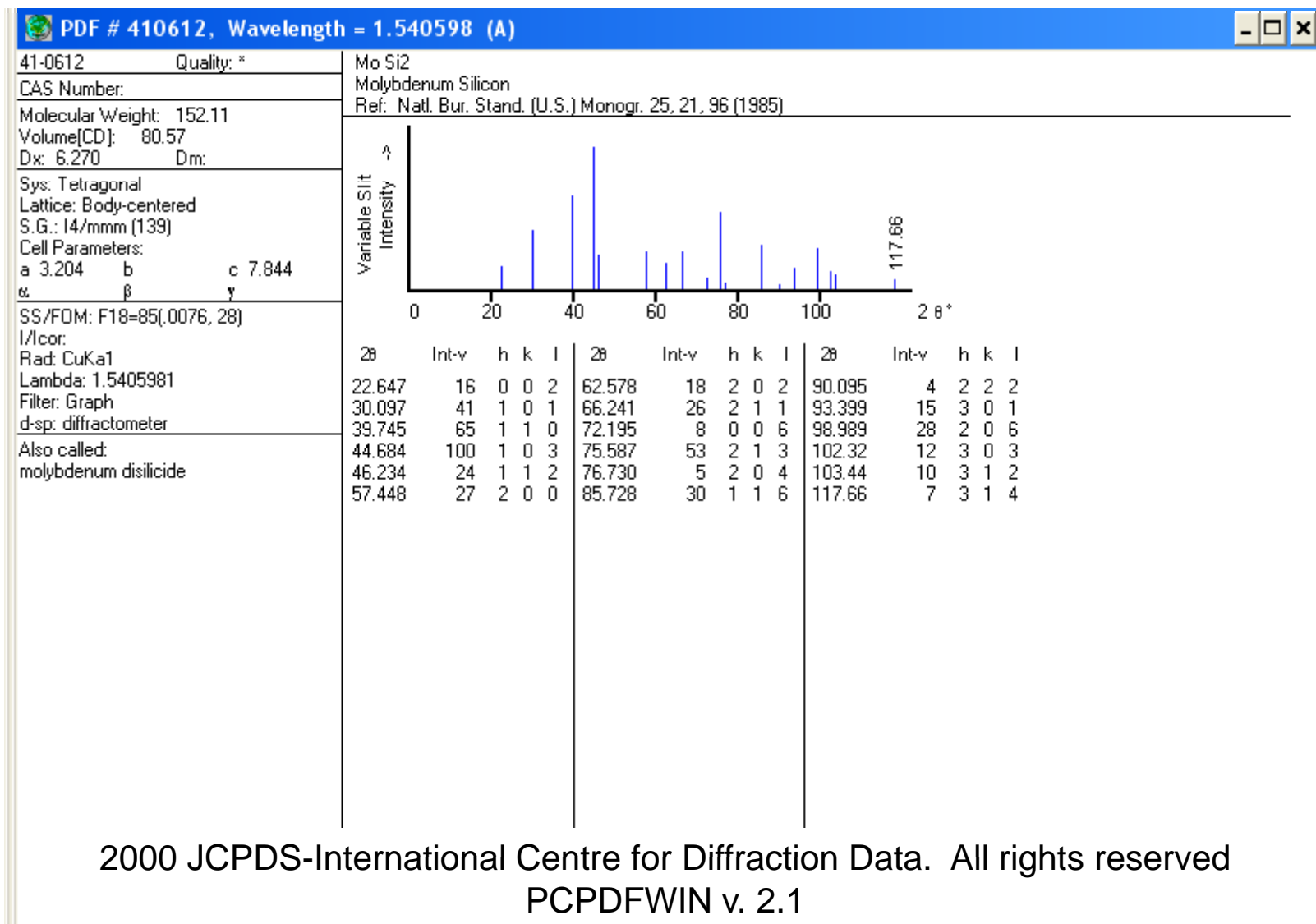
$$\begin{aligned} F_{hkl} &= f_{\text{Mo}} \left(e^0 + e^{\pi i(1+1+0)} \right) + f_{\text{Si}} \left(e^{2\pi i(0)} + e^{-2\pi i(0)} + e^{\pi i(1+1+0)} + e^{\pi i(1+1+0)} \right) \\ &= f_{\text{Mo}} (1 + e^{2\pi i}) + f_{\text{Si}} (e^{(0)} + e^{(0)} + e^{2\pi i} + e^{2\pi i}) \\ &= f_{\text{Mo}} (2) + f_{\text{Si}} (4) \\ &\therefore \\ F_{hkl}^2 &= \text{POSITIVE! YOU WILL SEE A REFLECTION} \end{aligned}$$

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

$h + k + l = \text{even}$



F_{hkl} for MoSi_2 - cont'd



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:

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

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:

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

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

Selection rules for HCP

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

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	$h+k+l = \text{even}$	$h+k+l = \text{odd}$
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 $h+2k=3N\pm 1$ with l odd $h+2k=3N\pm 1$ 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