



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).

Quadratic Forms of Miller Indices

| $h^2+k^2+l^2$ | h | k | l | hkl | | | | h^2+hk+k^2 | h | k |
|---------------|-----|-----|-----|----------|---------------|---------------|---------|--------------|-----|-----|
| | | | | Simple | Face-Centered | Body-Centered | Diamond | | | |
| 1 | 1 | 0 | 0 | 100 | | | | 1 | 1 | 0 |
| 2 | 1 | 1 | 0 | 110 | | 110 | | 2 | | |
| 3 | 1 | 1 | 1 | 111 | 111 | | 111 | 3 | 1 | 1 |
| 4 | 2 | 0 | 0 | 200 | 200 | 200 | | 4 | 2 | 0 |
| 5 | 2 | 1 | 0 | 210 | | | | 5 | | |
| 6 | 2 | 1 | 1 | 211 | | 211 | | 6 | | |
| 7 | - | - | - | --- | --- | --- | --- | 7 | 2 | 1 |
| 8 | 2 | 2 | 0 | 220 | 220 | 220 | 220 | 8 | | |
| 9 | 3 | 0 | 0 | 300, 221 | | | | 9 | 3 | 0 |
| 9 | 2 | 2 | 1 | | | | | 9 | | |
| 10 | 3 | 1 | 0 | 310 | | 310 | | 10 | | |
| 11 | 3 | 1 | 1 | 311 | 311 | | 311 | 11 | | |
| 12 | 2 | 2 | 2 | 222 | 222 | 222 | | 12 | 2 | 2 |
| 13 | 3 | 2 | 0 | 320 | | | | 13 | 3 | 1 |
| 14 | 3 | 2 | 1 | 321 | | 321 | | 14 | | |
| 15 | - | - | - | --- | --- | --- | --- | 15 | | |
| 16 | 4 | 0 | 0 | 400 | 400 | 400 | 400 | 16 | 4 | 0 |
| 17 | 4 | 1 | 0 | 410, 322 | | | | 17 | | |
| 17 | 3 | 2 | 2 | | | | | 17 | | |
| 18 | 4 | 1 | 1 | 411, 330 | | 411, 330 | | 18 | | |
| 18 | 3 | 3 | 0 | | | | | 18 | | |
| 19 | 3 | 3 | 1 | 331 | 331 | | 331 | 19 | 3 | 2 |
| 20 | 4 | 2 | 0 | 420 | 420 | 420 | | 20 | | |
| 21 | 4 | 2 | 1 | 421 | | | | 21 | 4 | 1 |
| 22 | 3 | 3 | 2 | 332 | | 332 | | 22 | | |
| 23 | - | - | - | --- | --- | --- | --- | 23 | | |
| 24 | 4 | 2 | 2 | 422 | 422 | 422 | 422 | 24 | | |
| 25 | 5 | 0 | 0 | 500 | | | | 25 | 5 | 0 |
| 25 | 4 | 3 | 0 | 433 | | | | 25 | | |

(See Appendix 9 in Cullity for a more complete list)

F_{hkl} for Simple Cubic

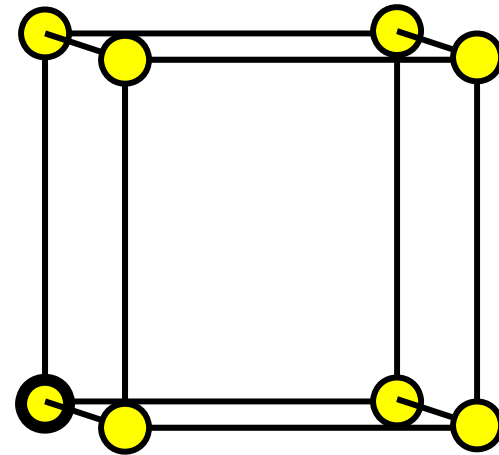
- Atom coordinate(s) u, v, w :

– 0,0,0

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

$$I \propto F^2 = f^2$$

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



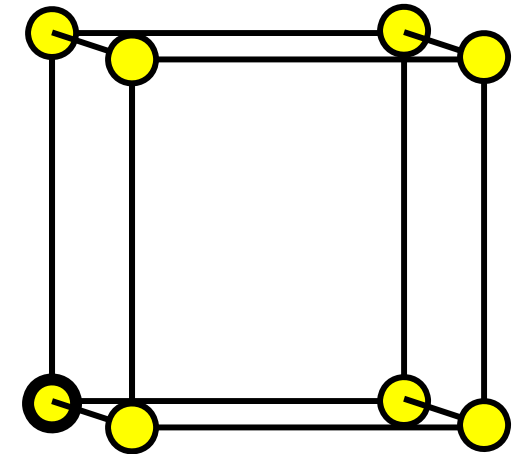
No matter what atom coordinates or plane indices you substitute into the structure factor equation for simple cubic crystals, the solution is always non-zero.

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

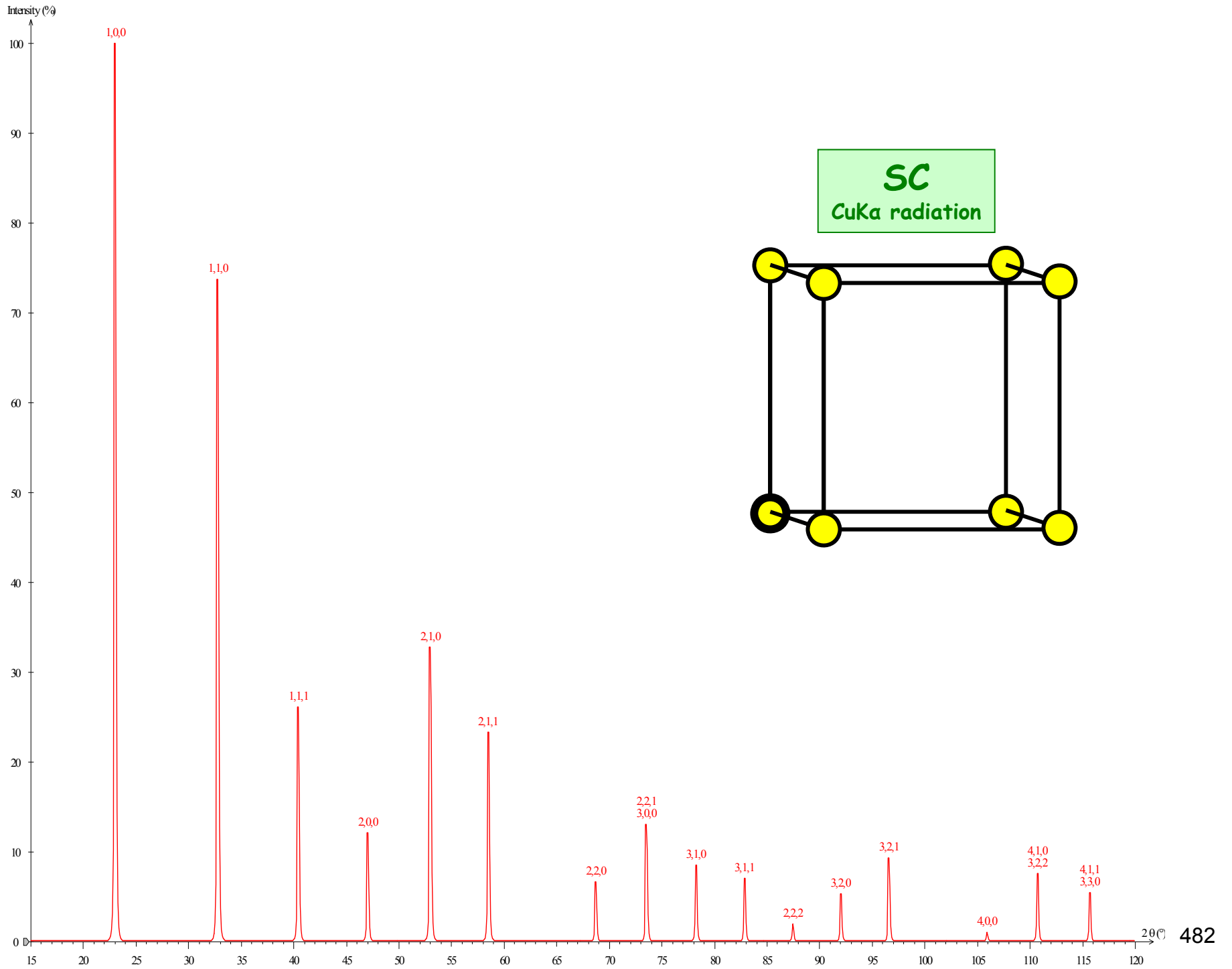
F_{hkl} for Simple Cubic

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

| | | |
|---------|----------|----------------------|
| (1 0 0) | $S = 1$ | $F_{hkl} = f(1) = f$ |
| (1 1 0) | $S = 2$ | $F_{hkl} = f(1) = f$ |
| (1 1 1) | $S = 3$ | $F_{hkl} = f(1) = f$ |
| (2 0 0) | $S = 4$ | $F_{hkl} = f(1) = f$ |
| (2 1 0) | $S = 5$ | $F_{hkl} = f(1) = f$ |
| (2 1 1) | $S = 6$ | $F_{hkl} = f(1) = f$ |
| (2 2 0) | $S = 8$ | $F_{hkl} = f(1) = f$ |
| (2 2 1) | $S = 9$ | $F_{hkl} = f(1) = f$ |
| (3 0 0) | $S = 9$ | $F_{hkl} = f(1) = f$ |
| (3 1 0) | $S = 10$ | $F_{hkl} = f(1) = f$ |
| (3 1 1) | $S = 11$ | $F_{hkl} = f(1) = f$ |
| (2 2 2) | $S = 12$ | $F_{hkl} = f(1) = f$ |



$$(S = h^2 + k^2 + l^2)$$



F_{hkl} for Body Centered Cubic

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

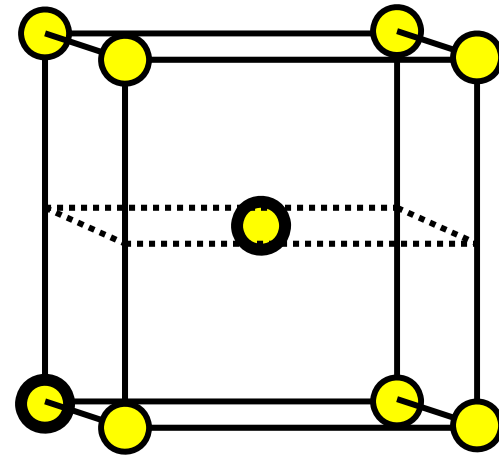
- 0,0,0;
- $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

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

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

\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.

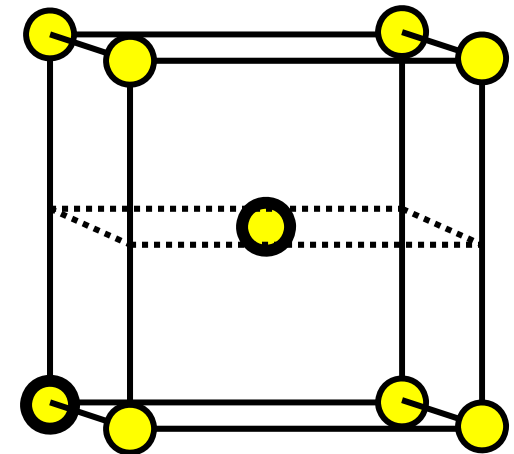
When $h+k+l$ is odd $F_{hkl} = 0 \rightarrow$ no reflection.

See next slide for explanation

F_{hkl} for Body Centered Cubic

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

| | | |
|---------|----------|-------------------------|
| (1 0 0) | $S = 1$ | $F_{hkl} = f(1-1) = 0$ |
| (1 1 0) | $S = 2$ | $F_{hkl} = f(1+1) = 2f$ |
| (1 1 1) | $S = 3$ | $F_{hkl} = f(1-1) = 0$ |
| (2 0 0) | $S = 4$ | $F_{hkl} = f(1+1) = 4f$ |
| (2 1 0) | $S = 5$ | $F_{hkl} = f(1-1) = 0$ |
| (2 1 1) | $S = 6$ | $F_{hkl} = f(1+1) = 2f$ |
| (2 2 0) | $S = 8$ | $F_{hkl} = f(1+1) = 2f$ |
| (2 2 1) | $S = 9$ | $F_{hkl} = f(1-1) = 0$ |
| (3 0 0) | $S = 9$ | $F_{hkl} = f(1-1) = 0$ |
| (3 1 0) | $S = 10$ | $F_{hkl} = f(1+1) = 2f$ |
| (3 1 1) | $S = 11$ | $F_{hkl} = f(1-1) = 0$ |
| (2 2 2) | $S = 12$ | $F_{hkl} = f(1+1) = 2f$ |



$$(S = h^2 + k^2 + l^2)$$

F_{hkl} for Body Centered Cubic

Consider the previous body-centered unit cell containing two atoms of the same kind located at origin, $uvw=000$ and $uvw=1/2, 1/2, 1/2$ basis. ($S = h^2+k^2+l^2$)

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

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

Selection
rules for hkl
reflections

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

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

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

$$F^2 = 0$$

$S = 2 \quad 4 \quad 6 \quad \text{etc.}$

$(110) \quad (200) \quad (211) \quad \text{etc.}$

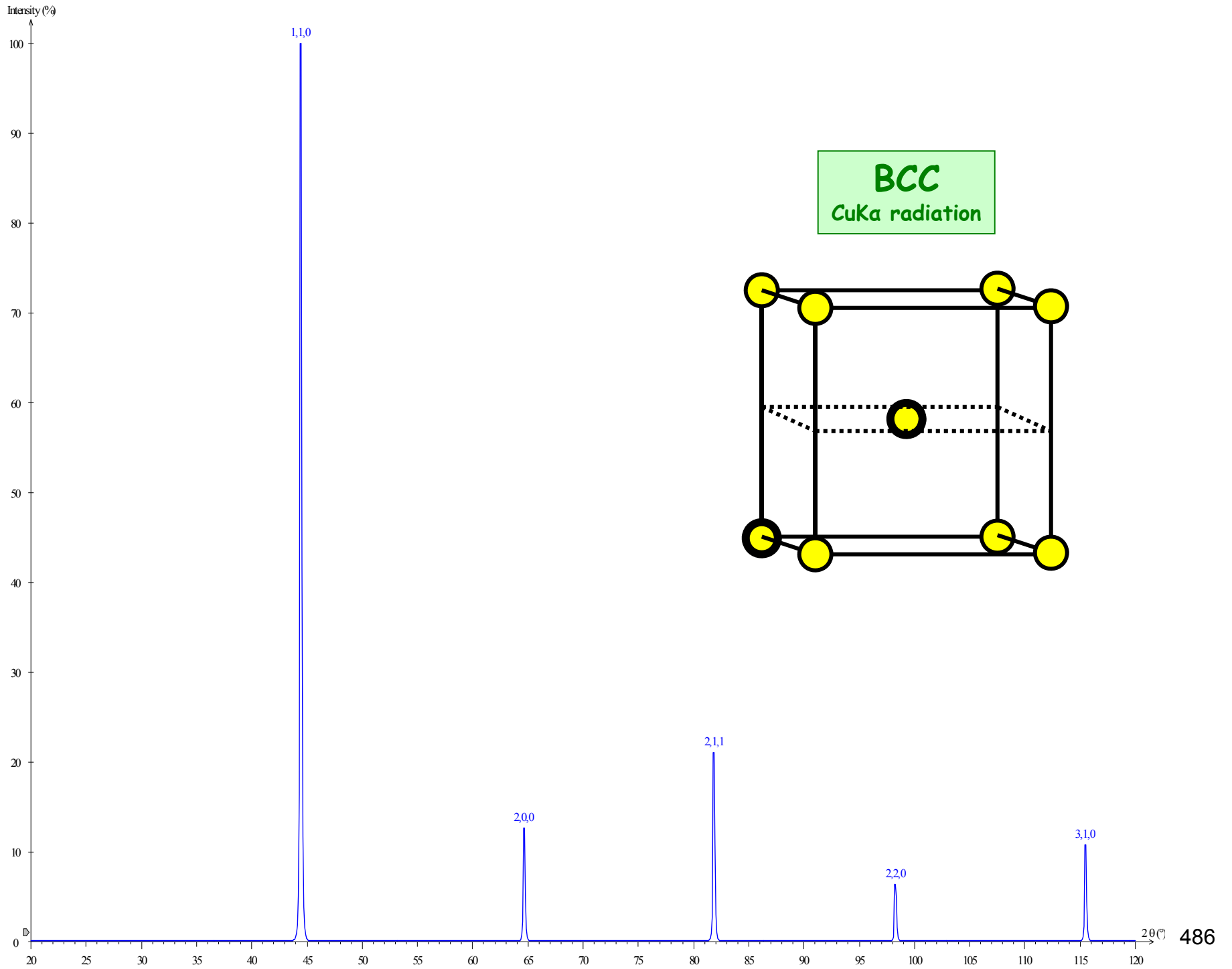
are allowed

$S = 1 \quad 3 \quad 5 \quad \text{etc.}$

$(100) \quad (111) \quad (210) \quad \text{etc.}$

are not allowed

(001) planes are out of phase and cancel whereas (002) planes are allowed.

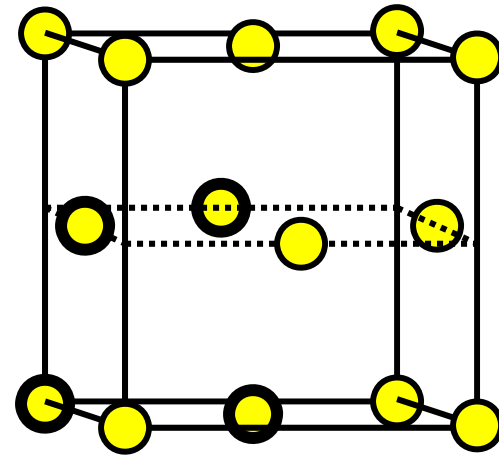


F_{hkl} for Face Centered Cubic

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

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

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



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

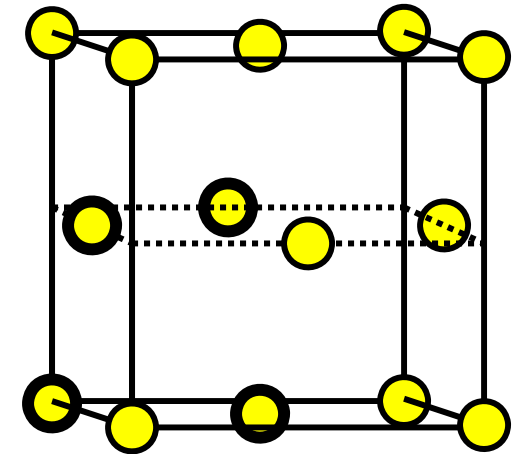
\therefore

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

F_{hkl} for Face Centered Cubic

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

| | | |
|---------|----------|-----------------------------|
| (1 0 0) | $S = 1$ | $F_{hkl} = f(1-1-1+1) = 0$ |
| (1 1 0) | $S = 2$ | $F_{hkl} = f(1+1-1-1) = 0$ |
| (1 1 1) | $S = 3$ | $F_{hkl} = f(1+1+1+1) = 4f$ |
| (2 0 0) | $S = 4$ | $F_{hkl} = f(1+1+1+1) = 4f$ |
| (2 1 0) | $S = 5$ | $F_{hkl} = f(1-1+1-1) = 0$ |
| (2 1 1) | $S = 6$ | $F_{hkl} = f(1+1-1-1) = 0$ |
| (2 2 0) | $S = 8$ | $F_{hkl} = f(1+1+1+1) = 4f$ |
| (2 2 1) | $S = 9$ | $F_{hkl} = f(1+1-1-1) = 0$ |
| (3 0 0) | $S = 9$ | $F_{hkl} = f(1-1-1+1) = 0$ |
| (3 1 0) | $S = 10$ | $F_{hkl} = f(1+1-1-1) = 0$ |
| (3 1 1) | $S = 11$ | $F_{hkl} = f(1+1+1+1) = 4f$ |
| (2 2 2) | $S = 12$ | $F_{hkl} = f(1+1+1+1) = 4f$ |



$$(S = h^2 + k^2 + l^2)$$

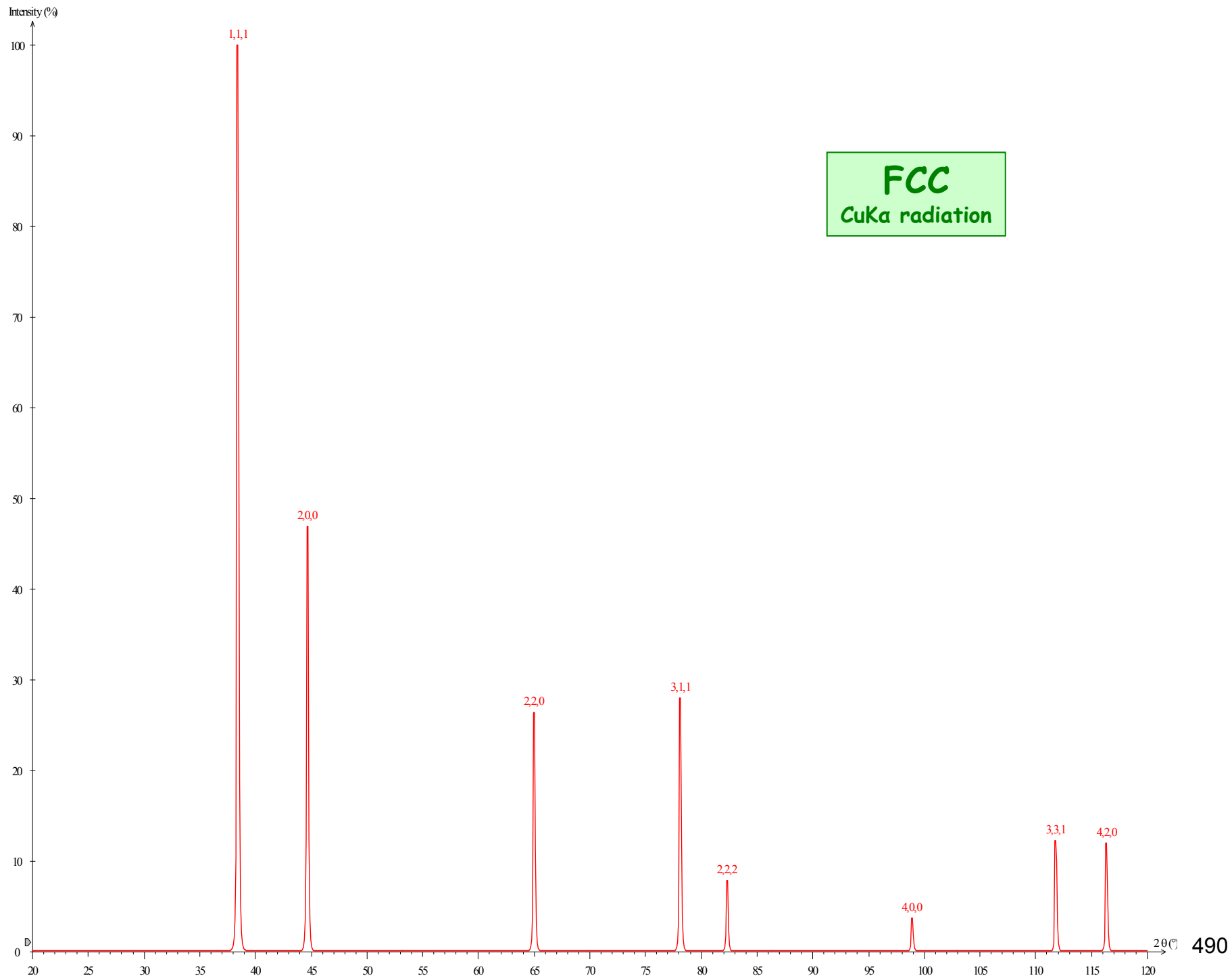
F_{hkl} for Face Centered Cubic

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

- Substitute in a few values of hkl and you will find the following:

Selection rules for hkl reflections

- 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 NaCl Structure

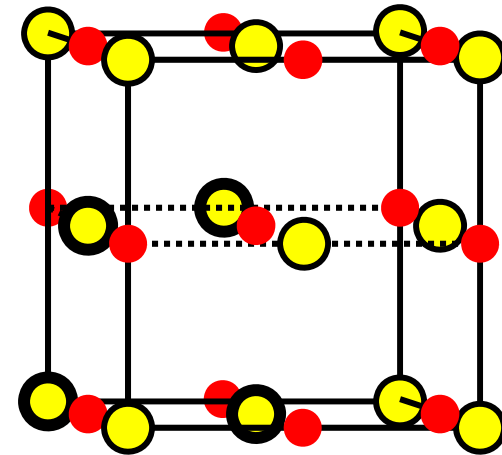
- Atom coordinate(s) u, v, w :

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

- – 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 $F_{hkl} = 4(f_{Na} + f_{Cl})$

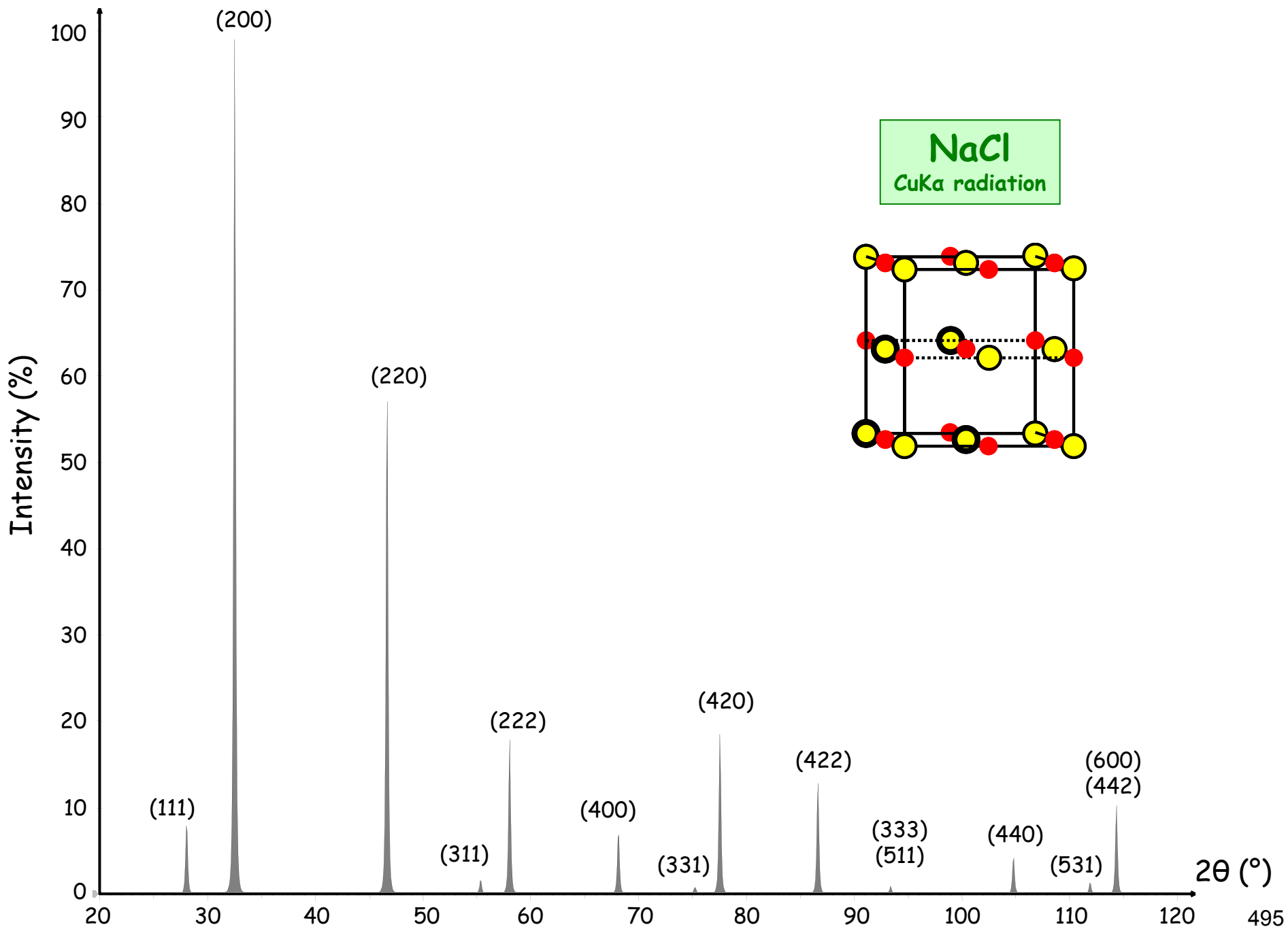
Primary reflections

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

Superlattice reflections

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

No reflections

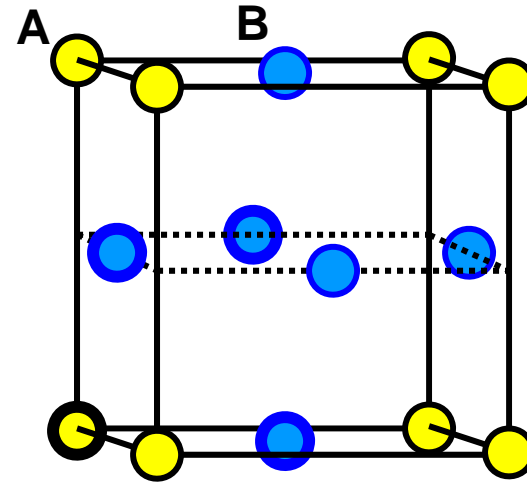


F_{hkl} for $L1_2$ Crystal Structure

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

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

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



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

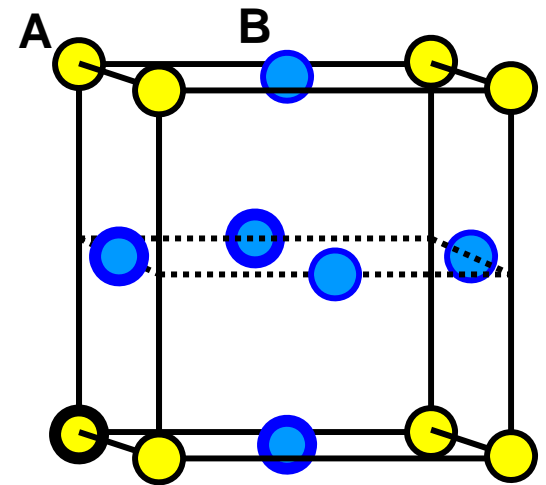
\therefore

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

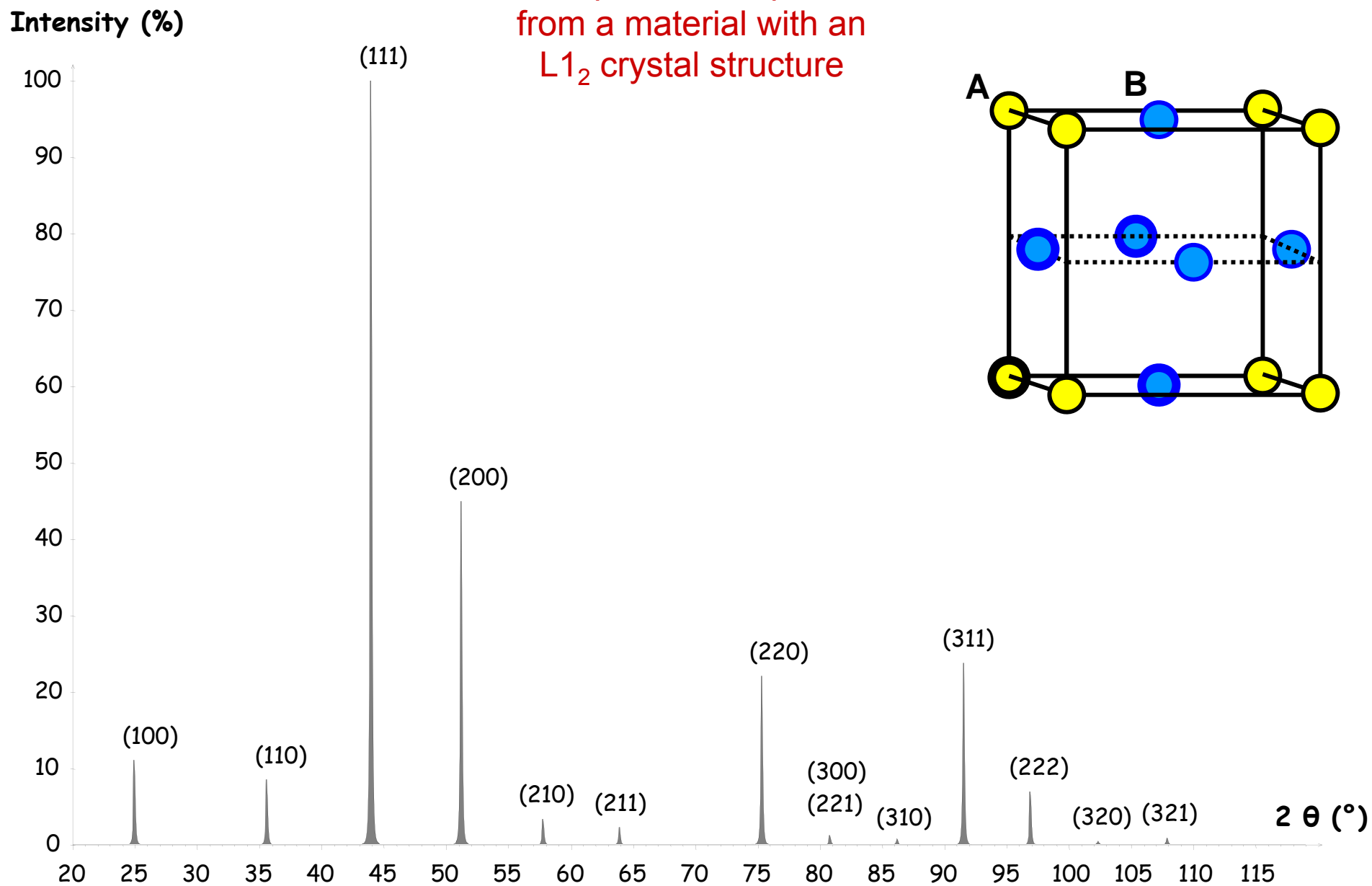
F_{hkl} for $L1_2$ Crystal Structure

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

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



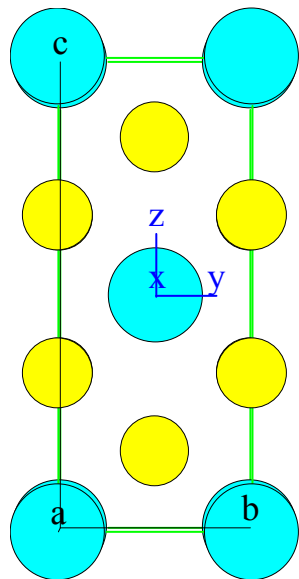
Example of XRD pattern from a material with an $L1_2$ crystal structure



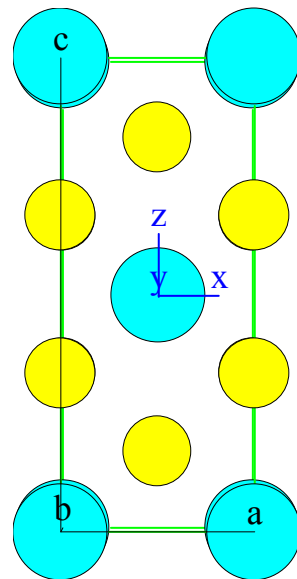
F_{hkl} for MoSi_2

- Atom positions:**

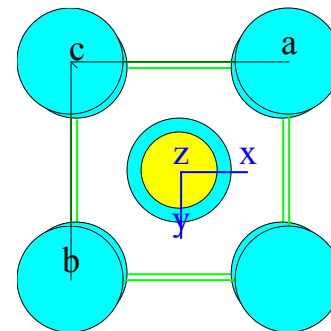
- Mo atoms at $0,0,0$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$
- Si atoms at $0,0,\bar{z}$; $0,0,z$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}+z$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}-z$; $z=\frac{1}{3}$
- MoSi_2 is actually body centered tetragonal with $a = 3.20 \text{ \AA}$ and $c = 7.86 \text{ \AA}$



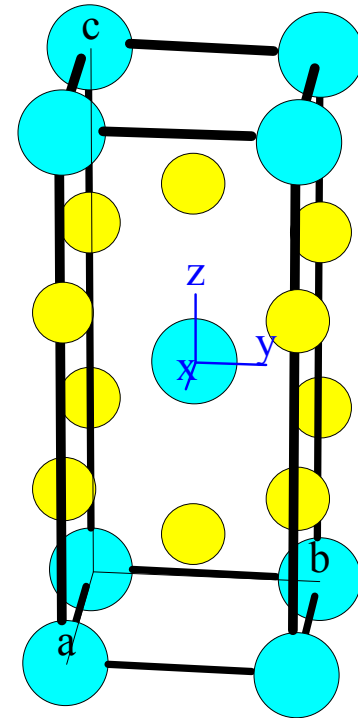
Viewed down x-axis



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 $h k l = 0 0 1$

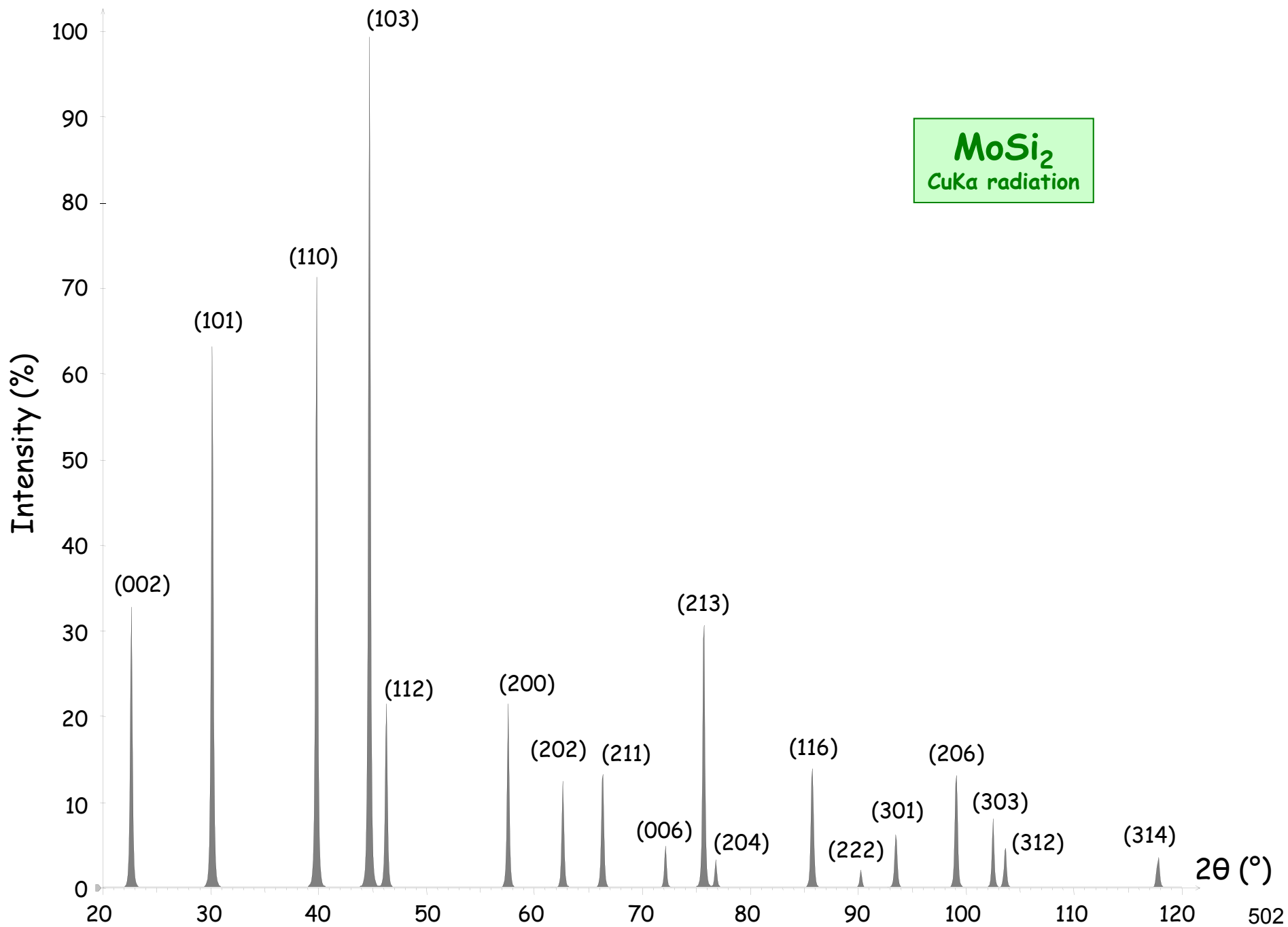
$$\begin{aligned} F_{hkl} &= f_{\text{Mo}} \left(e^0 + e^{\pi i(0+0+1)} \right) + f_{\text{Si}} \left(e^{2\pi i(\frac{1}{3})} + e^{-2\pi i(\frac{1}{3})} + e^{\pi i(0+0+\frac{5(1)}{3})} + e^{\pi i(0+0+\frac{(1)}{3})} \right) \\ &= f_{\text{Mo}} (1 + e^{\pi i}) + f_{\text{Si}} (2\text{COS}(\frac{2\pi}{3})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

- For $h k l = 1 1 0$

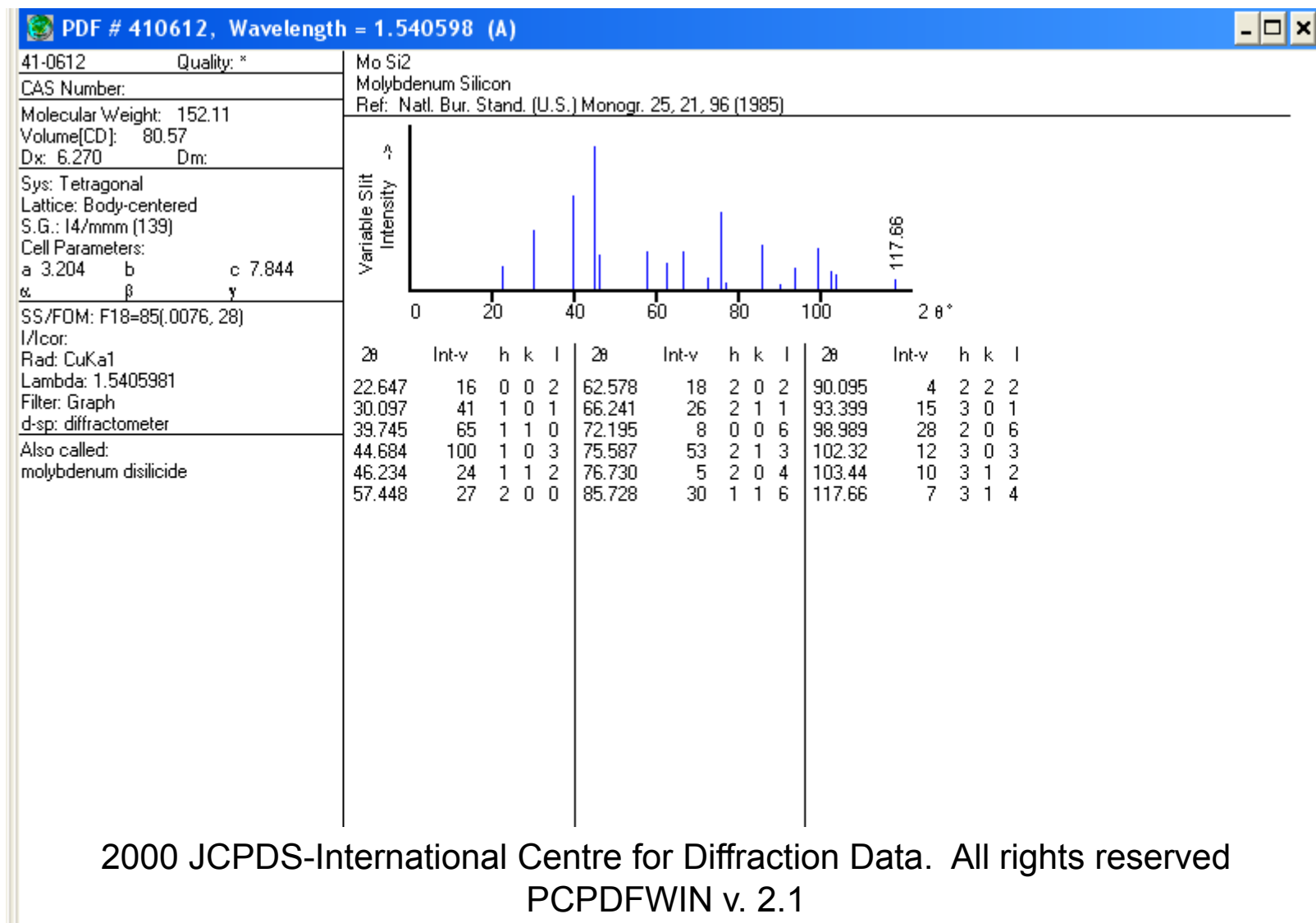
$$\begin{aligned} F_{hkl} &= f_{\text{Mo}} \left(e^0 + e^{\pi i(1+1+0)} \right) + f_{\text{Si}} \left(e^{2\pi i(0)} + e^{-2\pi i(0)} + e^{\pi i(1+1+0)} + e^{\pi i(1+1+0)} \right) \\ &= f_{\text{Mo}} (1 + e^{2\pi i}) + f_{\text{Si}} (e^{(0)} + e^{(0)} + e^{2\pi i} + e^{2\pi i}) \\ &= f_{\text{Mo}} (2)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

- 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 the following expression:

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

- It is possible for g to be a fraction which keeps F_{hkl} complex.

- Since F_{hkl} represents a wave, we can multiply it by its complex conjugate.

This gives us the square of absolute value of wave w/ amplitude F :

$$\begin{aligned} F_{hkl}^2 &= |F_{hkl}|^2 = f_i^2 (1 + e^{2\pi ig})(1 + e^{-2\pi ig}) \\ &= f_i^2 (2 + e^{2\pi ig} + e^{-2\pi ig}) \\ &= f_i^2 (2 + 2\cos(2\pi g)) \\ &= f_i^2 (2 + 2(\cos^2(\pi g) - 1)) \\ &= f_i^2 (4\cos^2(\pi g)) \end{aligned}$$

- Now, if we substitute g into the preceding, where

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

we get:

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

- Zero is obtained from this equation when:

$$(h + 2k) = \text{multiple of } 3$$

$$l = \text{odd}$$

- The table on the next page summarizes structure factor values for HCP crystals.

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.

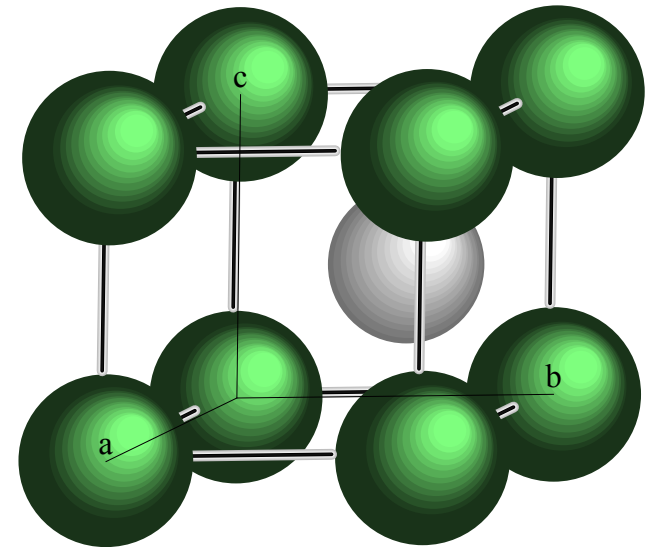
HINT: It might save you some time if you already had the ICDD card for Ru.

Structure Factor (F_{hkl}) for δ -WC

- Now let's consider a slightly more complicated structure.
- Tungsten carbide:
 - SG: 187 ($P\bar{6}m2$)
 - Pearson: $hP2$
 - Atom Coordinates:

| Element | Wyckoff Symbol | Symmetry | x | y | z | Occ. | CN |
|---------|----------------|-------------|-----|-----|-----|------|----|
| W | $1d$ | $\bar{6}m2$ | 0 | 0 | 0 | 1 | 6 |
| C | $1a$ | $\bar{6}m2$ | 1/3 | 2/3 | 1/2 | 1 | 6 |

- The crystal structure is drawn to the right.
- This structure is similar to HCP, but contains two distinct equipoints (i.e., C and W).
- Therefore, the structure factor becomes:



$$\begin{aligned}
 F_{hkl} &= f_W e^{2\pi i(0)} + f_C e^{2\pi i\left(\frac{h}{3} + \frac{2k}{3} + \frac{l}{2}\right)} \\
 &= f_W + f_C e^{2\pi ig}
 \end{aligned}$$

- As before, we can multiply F_{hkl} by its complex conjugate which gives us:

$$\begin{aligned}
F_{hkl}^2 &= |F_{hkl}|^2 \\
&= (f_W + f_C e^{2\pi i g})(f_W + f_C e^{-2\pi i g}) \\
&= f_W^2 + f_W f_C e^{-2\pi i g} + f_W f_C e^{2\pi i g} + f_C^2 (e^{2\pi i g} e^{-2\pi i g}) \\
&= f_W^2 + f_C^2 + f_W f_C (e^{2\pi i g} + e^{-2\pi i g}) \\
&= f_W^2 + f_C^2 + f_W f_C (2 \cos(2\pi g)) \\
&= f_W^2 + f_C^2 + f_W f_C 2(2 \cos^2(\pi g) - 1) \\
&= f_W^2 + f_C^2 + 4 f_W f_C \cos^2(\pi g) - 2 f_W f_C \\
&= (f_W - f_C)^2 + 4 f_W f_C (\cos^2(\pi g))
\end{aligned}$$

- Now, if we substitute g into the preceding, where

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

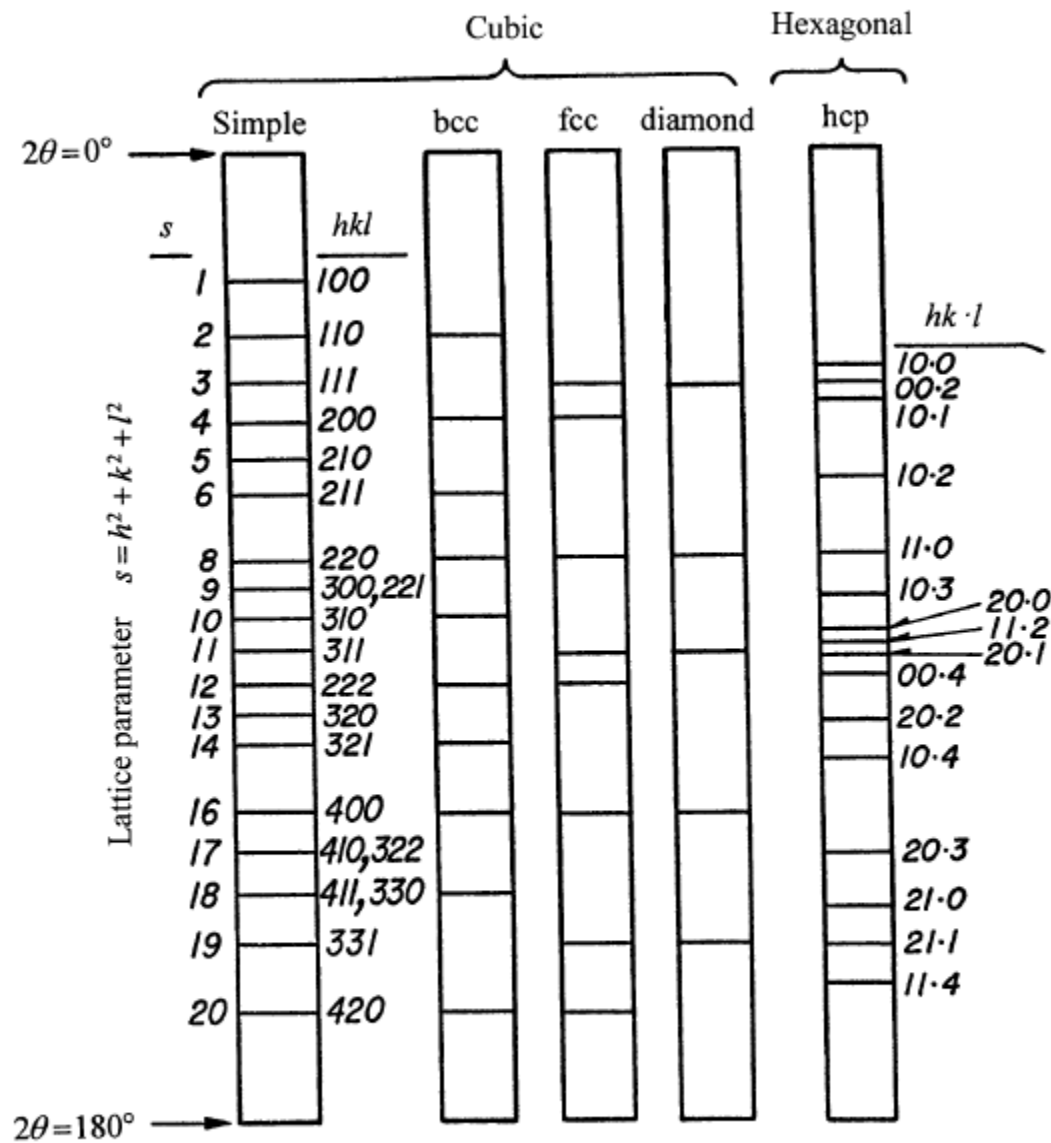
we will find the selection rules to be:

$$F_{hkl}^2 = \begin{cases} (f_W + f_C)^2 & \text{when } h + 2k = 3n \text{ and } l = \text{even} \\ (f_W - f_C)^2 + f_W f_C & \text{when } h + 2k = 3n \pm 1 \text{ and } l = \text{even} \\ (f_W - f_C)^2 & \text{when } h + 2k = 3n \text{ and } l = \text{odd} \\ (f_W - f_C)^2 + 3f_W f_C & \text{when } h + 2k = 3n \text{ and } l = \text{odd} \end{cases}$$

- I urge you to try it out.

Selection Rules for Common Crystals

| Crystal Type | Bravais Lattice | Reflections Present for | Reflections Absent for |
|------------------------|------------------|--|---|
| 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 |



(From Leng)

Fig. 4.5 Characteristic sequence of diffraction peaks of four common cubic lattice types together with a hexagonal close-packed lattice

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