Analytical Methods for Materials

Lesson 19

Intensity of the Diffracted Beam

<u>Suggested Reading</u>

Chapter 3 in Waseda, all

Chapter 4 in Cullity & Stock

Chapter 2 in Brandon & Kaplan

Intensity of the Diffracted Beam

- The INTENSITY, I of the diffracted beam is proportional to F_{hkl}

$$\boxed{I \approx \left|F_{hkl}\right|^2 p \left(\frac{1+\cos^2 2\theta}{\sin^2\theta \cdot \cos\theta}\right) e^{-2M}}$$

$p =$ multiplicity factor

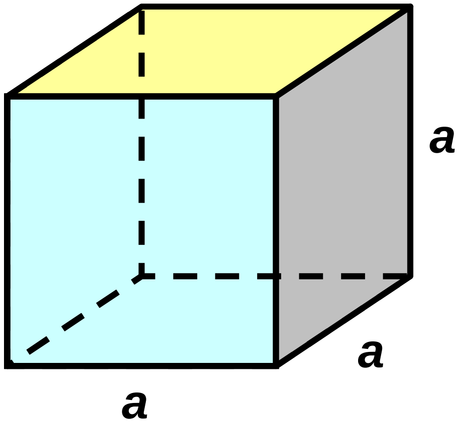
$e^{-2M} =$ temperature factor

$$\left(\frac{1+\cos^2 2\theta}{\sin^2\theta \cdot \cos\theta}\right) = \text{Lorenz-polarization factor (LPF)}$$

Multiplicity Factor

- Takes into account the <u>relative number of planes contributing to the same reflection</u> (i.e., the number of different planes in a form having the same spacing).

- <u>Cubic crystal</u>



e.g., $\{100\}$ planes in cubic crystal:

$$(100),(010),(010),(\bar{1}00),(0\bar{1}0),(00\bar{1})$$

$$p = 6$$

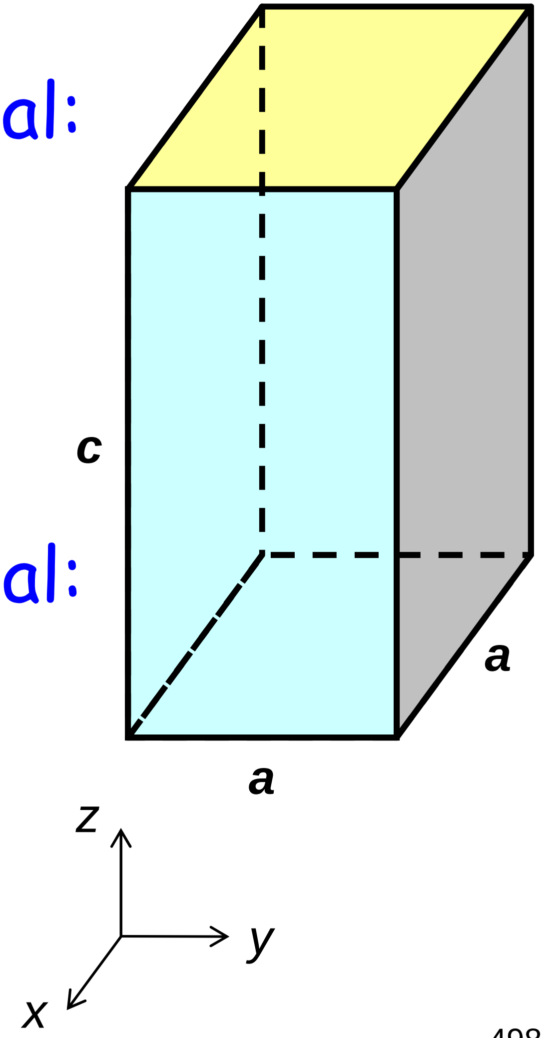
Multiplicity Factor

- Tetragonal crystal

e.g., $\{100\}$ planes in tetragonal crystal:

$(100),(010),(\bar{1}00),(0\bar{1}0)$

$p = 4$



e.g., $\{001\}$ planes in tetragonal crystal:

$(001),(00\bar{1})$

$p = 2$

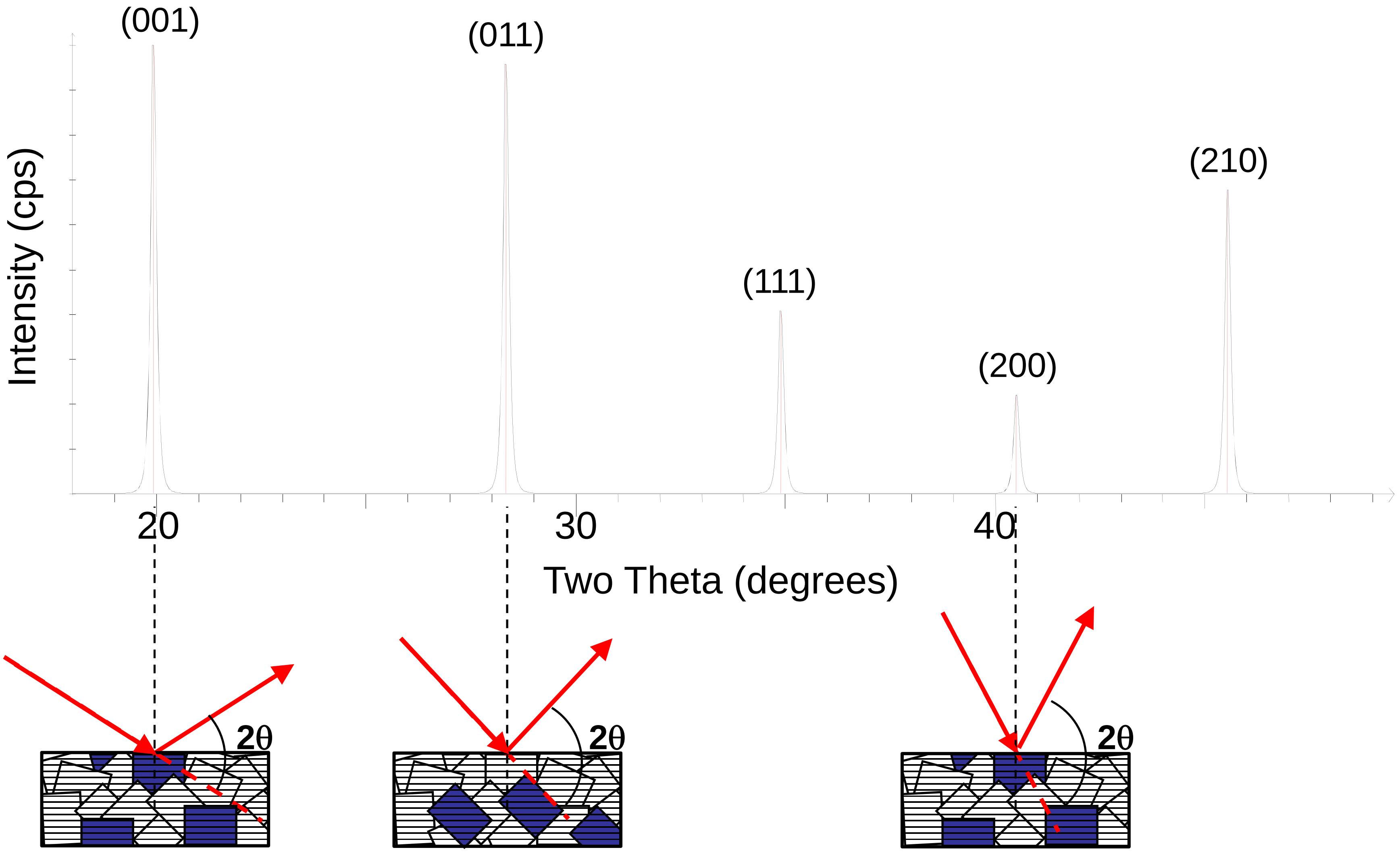
Cubic	$\frac{hkl}{48^*}$	$\frac{hhl}{24}$	$\frac{0kl}{24^*}$	$\frac{0kk}{12}$	$\frac{hhh}{8}$	$\frac{00l}{6}$	
Hexagonal/Rhombohedral	$\frac{hk\bullet l}{48^*}$	$\frac{hh\bullet l}{12^*}$	$\frac{0k\bullet l}{12^*}$	$\frac{hk\bullet 0}{12^*}$	$\frac{hh\bullet 0}{6}$	$\frac{0k\bullet 0}{6}$	$\frac{00\bullet l}{2}$
Tetragonal	$\frac{hkl}{16^*}$	$\frac{hhl}{8}$	$\frac{0kl}{8}$	$\frac{hkl}{8^*}$	$\frac{hh0}{4}$	$\frac{0k0}{4}$	$\frac{00l}{2}$
Orthorhombic	$\frac{hkl}{8}$	$\frac{0kl}{4}$	$\frac{h0l}{4}$	$\frac{hk0}{4}$	$\frac{h00}{2}$	$\frac{0k0}{2}$	$\frac{00l}{2}$
Monoclinic	$\frac{hkl}{4}$	$\frac{h0l}{2}$	$\frac{0k0}{2}$				
Triclinic	$\frac{hkl}{2}$						

[*] Denotes fact that some crystals have indices comprising two forms with the same lattice spacing but different structure factor and multiplicity. E.g.: in AuBe, (123) is not equivalent to (321).

Lorenz Factor

- Takes into account geometrical factors related to the *orientation of the reflecting planes* in the crystal that also affect the intensity of the diffracted beam.
- Accounts for the fact that crystals can still diffract strongly at angles that diverge from Bragg angle.
- Small deviations from the Bragg angle leads to broadening of peaks and reduced intensity.

Crystals can still diffract at angles that diverge from the Bragg angle



Polarization Factor

- Accounts for fact that the incident X-ray beam is not polarized.
- The that X-ray beam scatters differently in different directions actually onto conical surfaces w/ tops at the center of the Ewald sphere (i.e., it is polarized).
- In powder diffraction, we collect/measure a small part of the total diffracted intensity.
- The total intensity is the sum of the intensities of each component. (depends on 2θ).

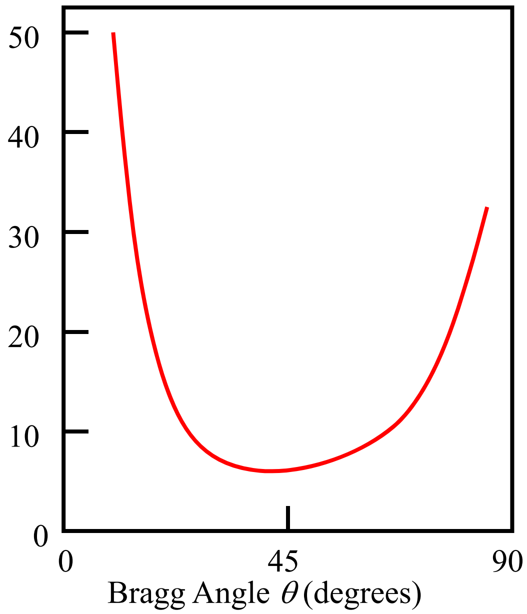
Lorenz-Polarization Factor

$$\mathrm{LPF} = \frac{1 + \cos^2 2\theta}{\sin^2\theta\cos\theta}$$

You can look it up or calculate it

- We typically combine the Lorenz and polarization factors. They account for the time required to scan through the Ewald sphere.

$$\mathrm{LPF} = \frac{1 + \cos^2 2\theta}{\sin^2\theta\cos\theta}$$



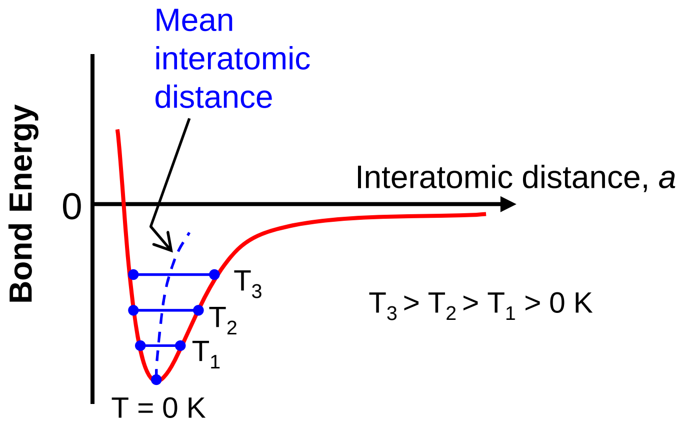
These factors are geometrical in nature.

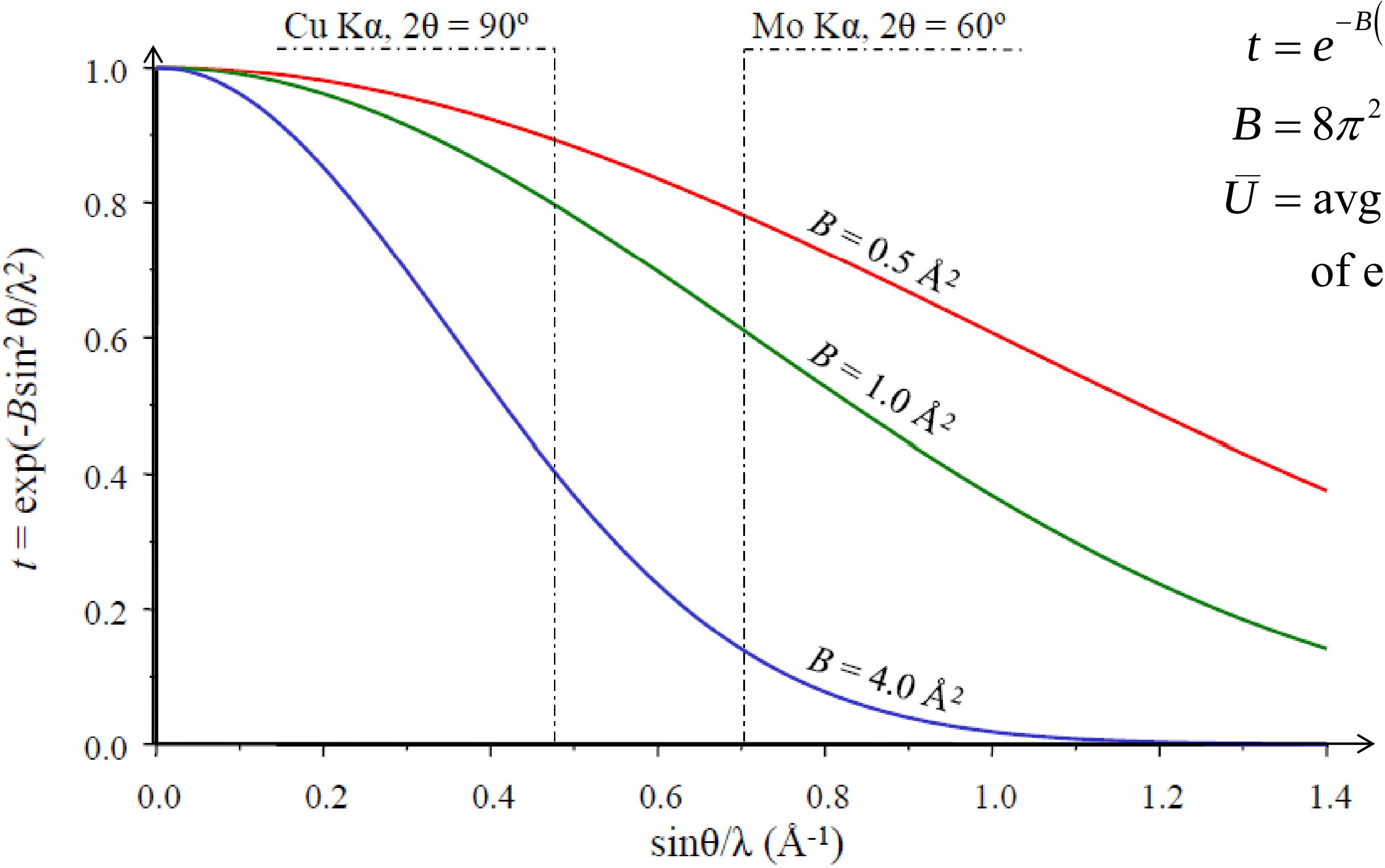
They decrease the intensity of reflections at intermediate angles relative to those in forward or backward directions

Temperature Factor

- Takes into account the fact that the atoms in all crystals vibrate about their equilibrium positions when temperature is varied.
- As T increases:
  - The unit cell expands which causes changes in *d*-spacing and 2θ values.
  - Thus, intensity of the diffraction lines decreases.
  - Intensity of background scattering between lines increases.

Recall Morse curves. Thermal vibrations cause slight changes in interatomic spacing <u>and</u> corresponding changes in *d*-spacing.





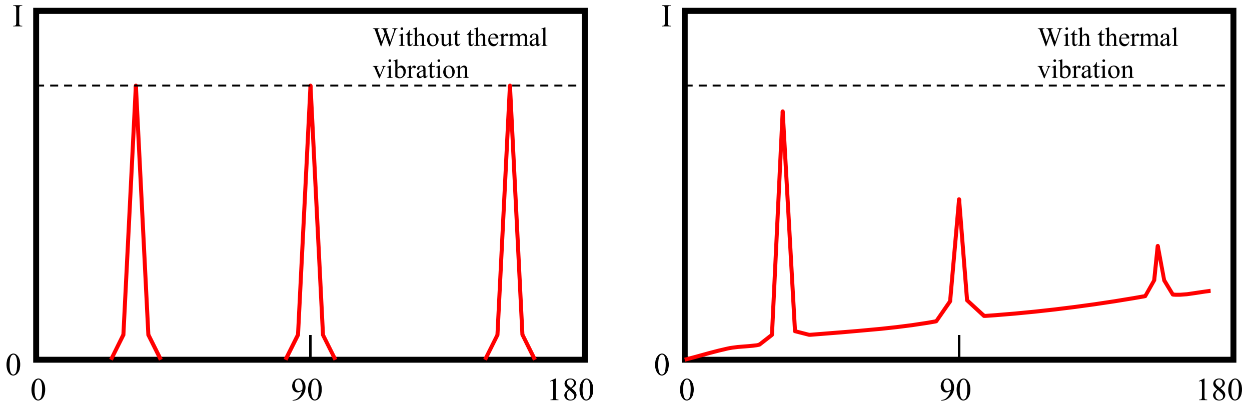
$$t = e^{-B\left(\sin^2\theta/\lambda^2\right)}$$

$$B = 8\pi^2\bar{U}^2$$

$\bar{U}$ = avg. displ. of each atom

Fig. 9.2 Temperature factor as a function of sinθ/λ for several different atomic displacement parameters (*B*). The two vertical dash-dotted lines correspond to two commonly used upper limits of the Bragg angle in diffraction experiments using CuKα and MoKα radiation. From V.K. Pecharsky and P.Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, 2nd Edition, (Springer, NY, 2008)

Effect of Thermal Vibrations on Diffraction Patterns



- Lines decrease in intensity by a factor $e^{-B\left(\sin^2\theta/\lambda^2\right)}$ and are superimposed on a background of thermal diffuse scattering.
- The significance of thermal diffuse scattering increases at higher temperatures resulting in reduced intensity and increased background.

Absorption Factor

- In practice, there is also another factor, the Absorption Factor (A).
- It accounts for absorption by the specimen. It is a number that we multiply the calculated intensity by.
- It depends on the geometry of the diffraction method used.

Sample Problem

- Calculate the relative intensities of the diffraction lines for Cu collected with a powder diffractometer using CuKα radiation. Ignore temperature and absorption effects.

Line	1	2	3	4	5	6	7	8
hkl	111	200	220	311	222	400	331	420
$h^2+k^2+l^2$	3	4	8	11	12	16	19	20

Solution

- **In** the **absence of temperature and absorption effects**, the equation for intensity becomes:

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

- All of the relevant parameters can be determined from tables of data and the resulting XRD (i.e., peak location) results.
- This is best done using a spreadsheet (as you will do in homework and lab assignments).

- To begin, we must determine the allowable XRD peaks. Since Cu is FCC, diffraction peaks occur when *hkl* are unmixed. The allowable diffraction peaks are listed above as indices and in their proper quadratic forms.

$$\sin^2\theta = \frac{\lambda^2}{4a^2}\left(h^2+k^2+l^2\right),$$

$$\lambda = 1.54056\ \text{Å}$$

$$a = 3.615\ \text{Å}$$

- The necessary parameters read from tables and/or calculated.
- Typical results are shown on the next page.

Intensity calculation for Copper

$\sin^2\theta = \frac{\lambda^2}{4a^2}\left(h^2+k^2+l^2\right)$, λ=1.54056 Å, and a=3.615 Å

NOTE: Waseda uses a slightly different equation for LPF.

From Appendix 3 in Waseda

From structure factor calculation $F^2=16f_{Cu}^2$

From this set of notes

Calculated

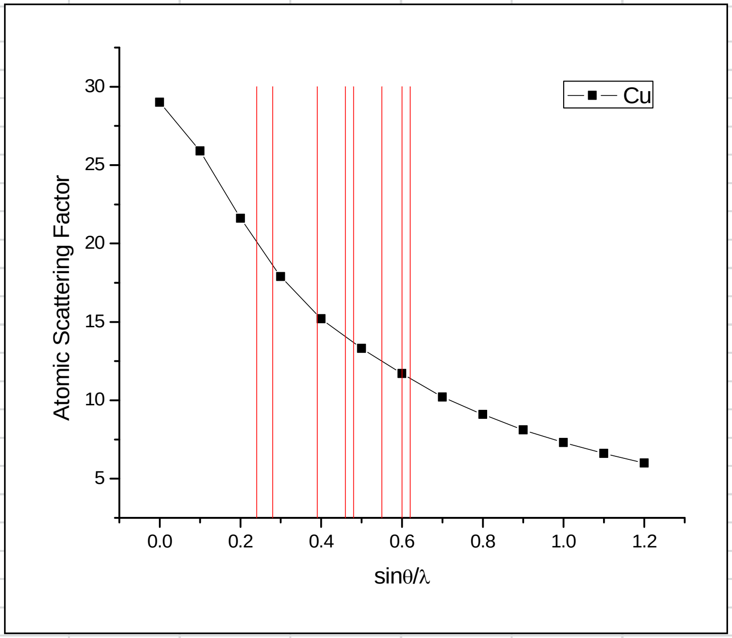
Line	*h*	*k*	*l*	$h^2+k^2+l^2$	$\sin^2\theta$	sinθ	θ	2θ	sinθ/λ	f_{Cu}	F^2	*p*	*LPF*	Intensity	*Rel. Int.*	*ICDD Card 4-0836*
1	1	1	1	3	0.136	0.369	21.7	43.3	0.24	20.2	6528.64	8	12.08	6.31E+05	100	100
2	2	0	0	4	0.182	0.426	25.2	50.5	0.28	18.7	5595.04	6	8.55	2.87E+05	46	46
3	2	2	0	8	0.363	0.603	37.1	74.2	0.39	15.5	3844	12	3.71	1.71E+05	27	20
4	3	1	1	11	0.499	0.707	45.0	90.0	0.46	14.1	3180.96	24	2.83	2.16E+05	34	17
5	2	2	2	12	0.545	0.738	47.6	95.2	0.48	13.7	3003.04	8	2.74	6.59E+04	10	5
6	4	0	0	16	0.726	0.852	58.5	117.0	0.55	12.4	2460.16	6	3.18	4.69E+04	7	3
7	3	3	1	19	0.863	0.929	68.3	136.6	0.60	11.7	2190.24	24	4.78	2.51E+05	40	9
8	4	2	0	20	0.908	0.953	72.4	144.8	0.62	11.3	2043.04	24	6.07	2.97E+05	47	8

Reasonable agreement up to here!

Calculated from data

From Appendix 3 in Waseda

sinθ/λ	f_{Cu}
0	29
0.1	25.9
0.2	21.6
0.3	17.9
0.4	15.2
0.5	13.3
0.6	11.7
0.7	10.2
0.8	9.1
0.9	8.1
1	7.3
1.1	6.6
1.2	6

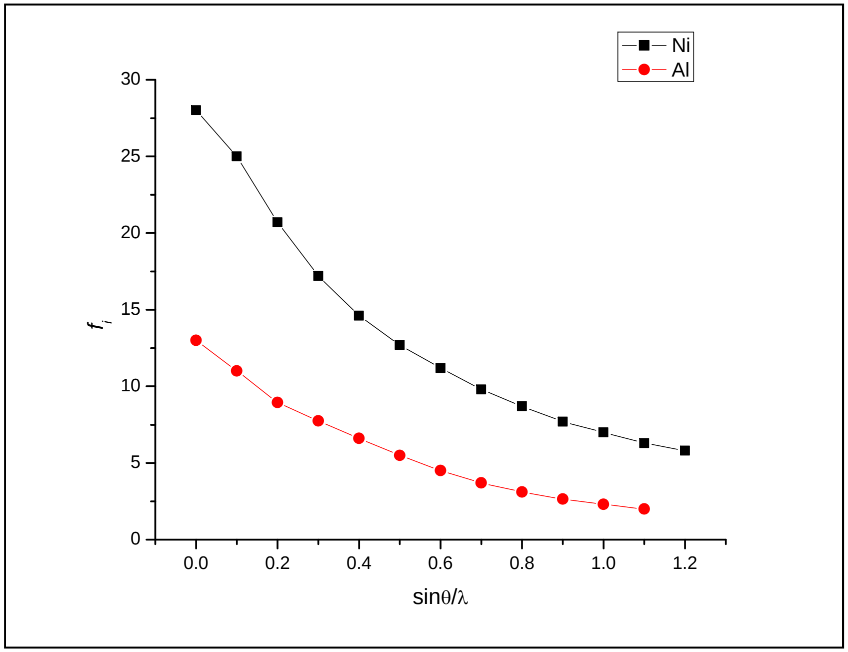


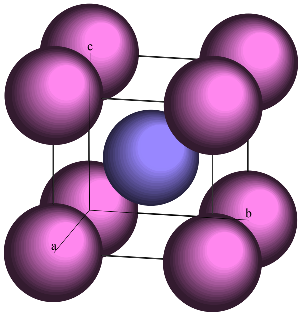
This is the plot that I used to determine the actual values of f_{Cu}

Intensity calculation for NiAl

Line	h	k	l	$h^2+k^2+l^2$	$\sin^2\theta$	$\sin\theta$	θ	2θ	$\sin\theta/\lambda$	f_{Ni}	f_{Al}	F	F^2	*p*	LPF	Intensity	Relative	ICDD
1	1	0	0	1	0.0711	0.2667	15.469	30.938	0.173	21.90	9.50	-12.40	153.76	6	25.32	23355.4	23	15
2	1	1	0	2	0.1423	0.3772	22.160	44.320	0.245	19.00	8.40	27.40	750.76	12	11.47	103368.3	100	100
3	1	1	1	3	0.2134	0.4620	27.514	55.028	0.300	17.20	7.75	-9.45	89.30	8	7.02	5014.5	5	5
4	2	0	0	4	0.2846	0.5334	32.238	64.476	0.346	15.82	7.14	22.96	527.16	6	4.93	15581.4	15	23
5	2	1	0	5	0.3557	0.5964	36.612	73.225	0.387	14.90	6.75	-8.15	66.42	24	3.79	6048.6	6	5
6	2	1	1	6	0.4268	0.6533	40.793	81.585	0.424	14.08	6.30	20.38	415.34	24	3.16	31508.3	30	46
7	2	2	0	8	0.5691	0.7544	48.972	97.945	0.490	12.70	5.50	18.20	331.24	12	2.73	10843.4	10	16
8	2	2	1	9	0.6402	0.8002	53.145	106.290	0.519	12.35	5.18	-7.17	51.41	24	2.81	3465.7	3	3
8	3	0	0	9	0.6402	0.8002	53.145	106.290	0.519	12.35	5.18	-7.17	51.41	6	2.81	866.4	1	
9	3	1	0	10	0.7114	0.8434	57.505	115.009	0.547	11.95	4.96	16.91	285.95	24	3.08	21166.5	20	32

$\sin\theta/\lambda$	Ni	Al
0	28	13
0.1	25	11
0.2	20.7	8.95
0.3	17.2	7.75
0.4	14.6	6.6
0.5	12.7	5.5
0.6	11.2	4.5
0.7	9.8	3.7
0.8	8.7	3.1
0.9	7.7	2.65
1	7	2.3
1.1	6.3	2
1.2	5.8	





Exercises

- Calculate the relative intensities of the diffraction lines for NiAl and Ru. Assume you are collecting your data on a powder diffractometer using CuKα radiation. Ignore temperature and absorption effects.

- Print out and compare your results with the appropriate ICDD card.