



# Analytical Methods for Materials

## Lesson 19

### Intensity of the Diffracted Beam

#### Suggested Reading

Chapter 3 in Waseda, all

Chapter 4 in Cullity & Stock

Chapter 2 in Brandon & Kaplan

# Intensity of the Diffracted Beam

- In a diffractometer, the INTENSITY,  $I$  of the diffracted beam is proportional to  $F_{hkl}$ :

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

$p$  = multiplicity factor

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

$$M = B(\sin^2 \theta / \lambda^2)$$

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

$\bar{U}$  = amplitude of thermal vibration

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



# Integrated Intensity

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

$I_o$  = intensity of incident beam ( $\text{J s}^{-1} \text{m}^{-2}$ );

$A$  = area of incident beam ( $\text{m}^2$ );

$\lambda$  = wavelength of incident beam (m);

$r$  = radius of diffractometer circle (m);

$\mu_o = 4\pi \times 10^{-1} \text{ (m kg C}^{-2}\text{)}$ ;

$e$  = charge of electron (C);

$\mu$  = linear absorption coefficient ( $\text{m}^{-1}$ )

$m$  = mass of electron (kg);

$V$  = volume of unit cell ( $\text{m}^3$ );

$F_{hkl}$  = structure factor for reflection;

$p$  = multiplicity factor

$\theta$  = Bragg angle;

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

This is the full equation.

This equation applies for single phase polycrystalline specimens with randomly oriented grains.

# Multiplicity Factor

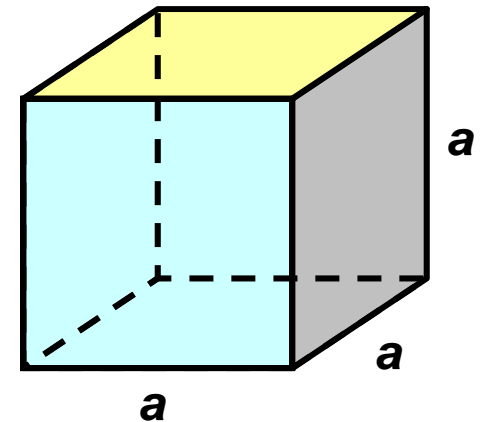
- Takes into account the relative number of planes contributing to the same reflection (i.e., the number of different planes in a form having the same spacing).

- Cubic crystal

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

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

$$p = 6$$



# Multiplicity Factor

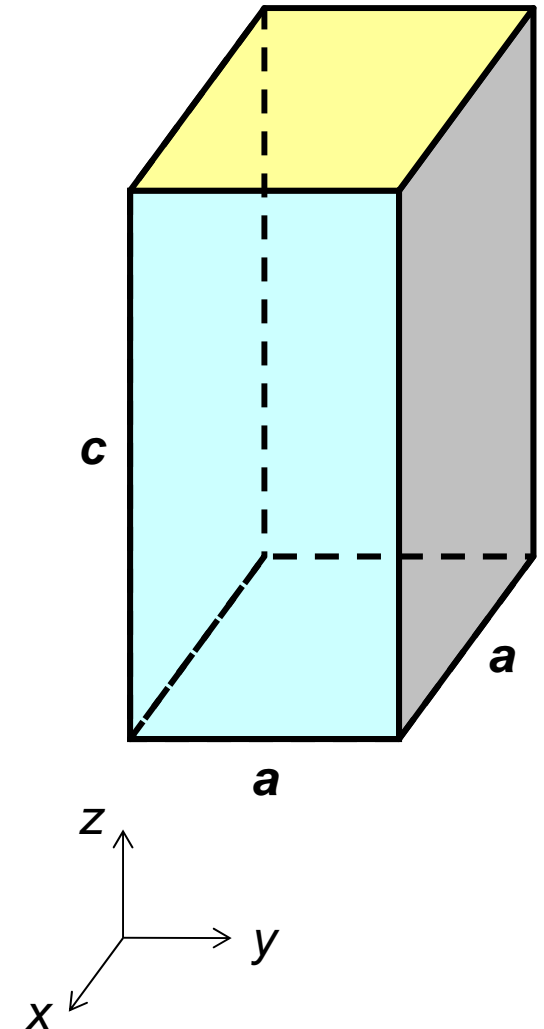
- Tetragonal crystal

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	$\frac{hk \cdot l}{48^*}$	$\frac{hh \cdot l}{12^*}$	$\frac{0k \cdot l}{12^*}$	$\frac{hk \cdot 0}{12^*}$	$\frac{hh \cdot 0}{6}$	$\frac{0k \cdot 0}{6}$	$\frac{00 \cdot l}{2}$
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).

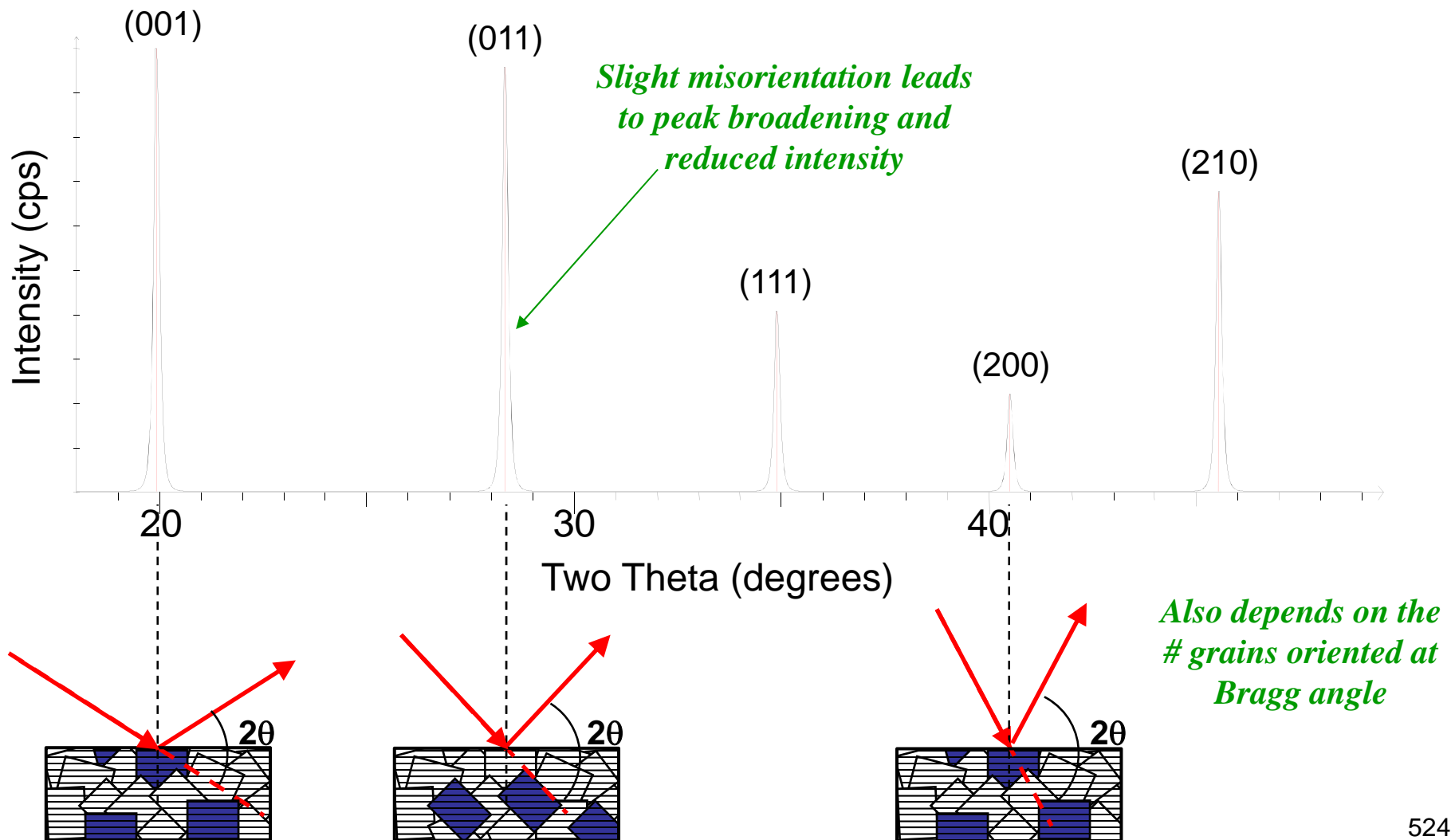
# Lorenz Factor

- 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.  
(see next page)

# Lorenz Factor

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

(X-rays will be collected by detector w/slight shift from Bragg)





# Polarization Factor

- Accounts for fact that the incident X-ray beam is not polarized.
- The X-ray beam scatters differently in different directions actually onto conical surfaces w/ tops at the center of the Ewald sphere (i.e., “the scattered wave 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  $2\theta$ ).

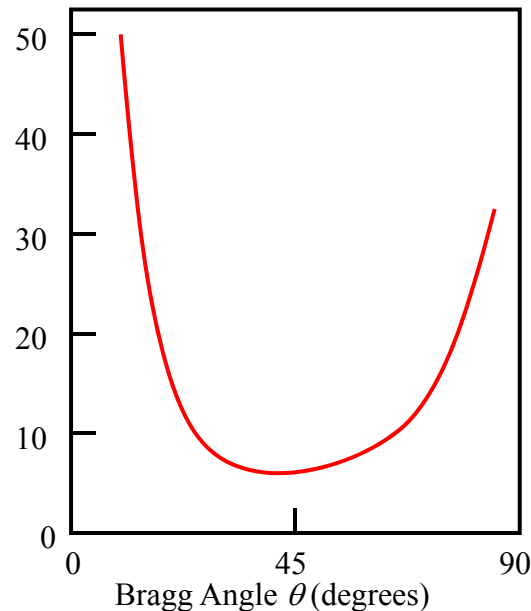
# Lorenz-Polarization Factor

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

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.

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



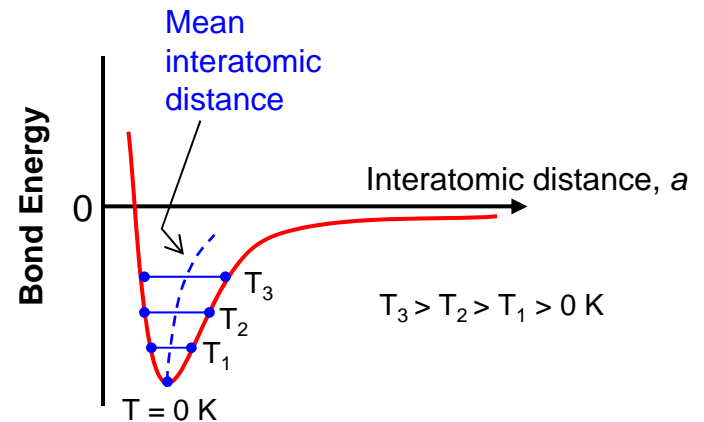
These factors are geometrical  
in nature.

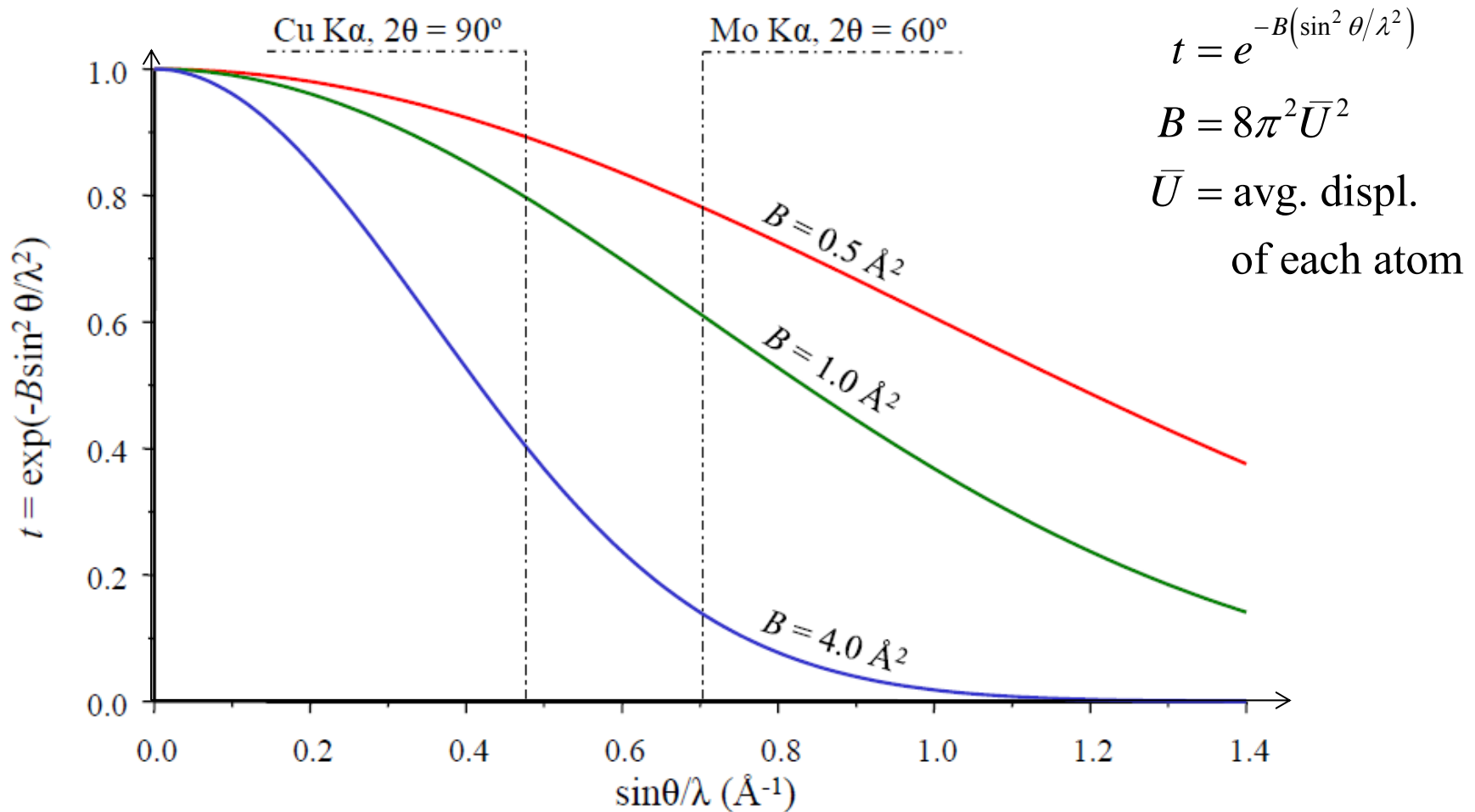
They decrease the intensity of  
reflections at intermediate  
angles relative to those in  
forward or backward directions

# Temperature Factor

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

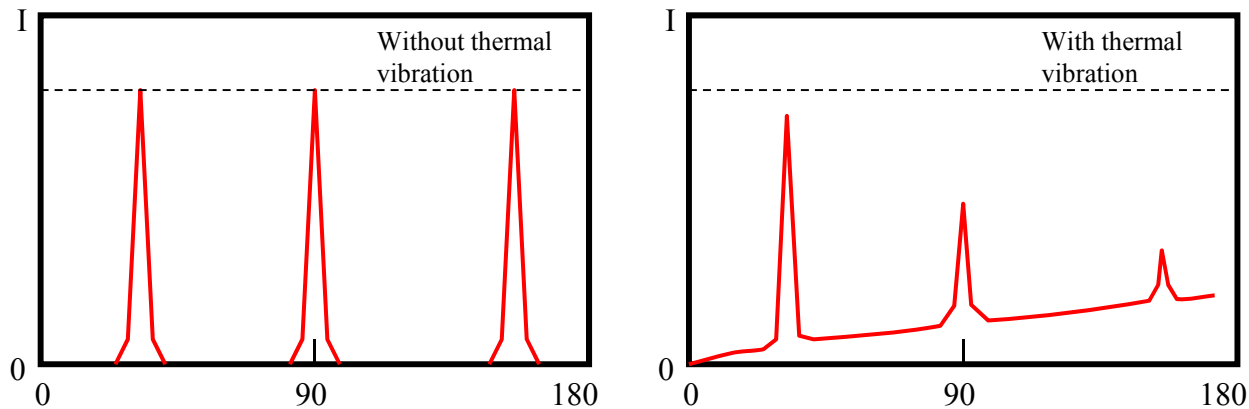
Recall Morse curves.  
Thermal vibrations cause slight changes in interatomic spacing and corresponding changes in  $d$ -spacing.





**Fig. 9.2** Temperature factor as a function of  $\sin\theta/\lambda$  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  $\text{CuK}\alpha$  and  $\text{MoK}\alpha$  radiation. From V.K. Pecharsky and P.Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, 2<sup>nd</sup> Edition, (Springer, NY, 2008)

# Effect of Thermal Vibrations on Diffraction Patterns



- Lines decrease in intensity by a factor  $e^{-B(\sin^2 \theta / \lambda^2)}$  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 copper (Cu) collected on a powder diffractometer using  $\text{CuK}\alpha$  radiation. Ignore temperature and absorption effects.

<b>Line</b>	1	2	3	4	5	6	7	8
<i>hkl</i>	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.

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

$$\lambda = 1.54056 \text{ \AA}$$

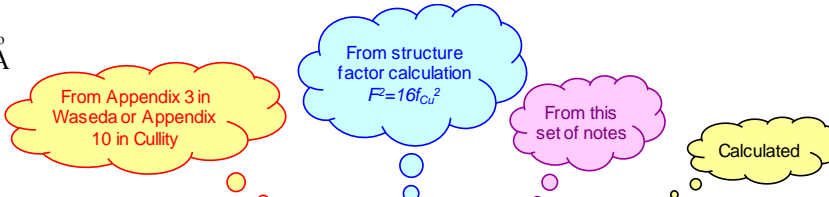
$$a = 3.615 \text{ \AA}$$

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

# Intensity calculation for Copper

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2), \lambda = 1.54056 \text{ \AA}, \text{ and } a = 3.615 \text{ \AA}$$

**NOTE:** Waseda uses a slightly different equation for LPF than Cullity.

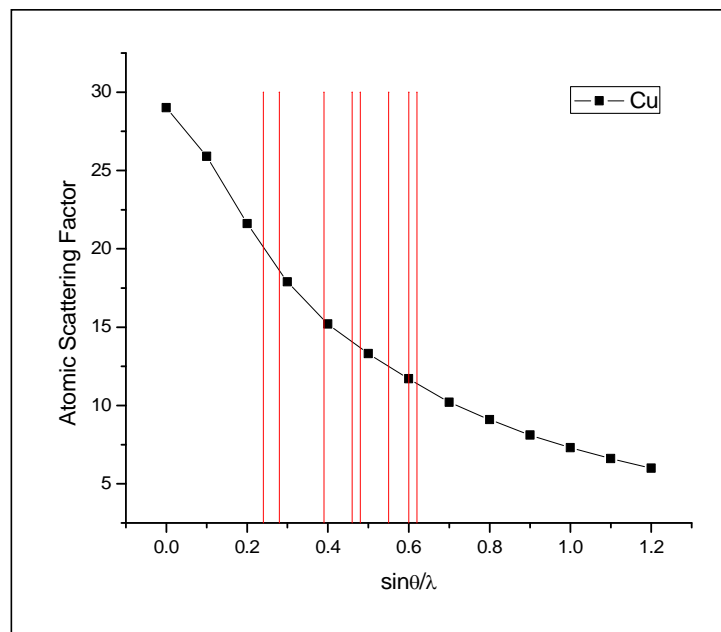


Line	<i>h</i>	<i>k</i>	<i>l</i>	$h^2+k^2+l^2$	$\sin^2\theta$	$\sin\theta$	$\theta$	$2\theta$	$\sin\theta/\lambda$	$f_{Cu}$	$F^2$	<i>p</i>	LPF	Rel. Int. Intensity	Rel. Int.	ICDD Card 4-0836
1	1	1	1	3	0.1362	0.369	21.7	43.3	0.24	20.2	6528.64	8	12.08	6.31E+05	100	100
2	2	0	0	4	0.1816	0.426	25.2	50.5	0.28	18.7	5595.04	6	8.55	2.87E+05	46	46
3	2	2	0	8	0.3632	0.603	37.1	74.2	0.39	15.5	3844	12	3.71	1.71E+05	27	20
4	3	1	1	11	0.4994	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	0.5448	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	0.7264	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	0.8626	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	0.9081	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!



$\sin\theta/\lambda$	$f_{Cu}$
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

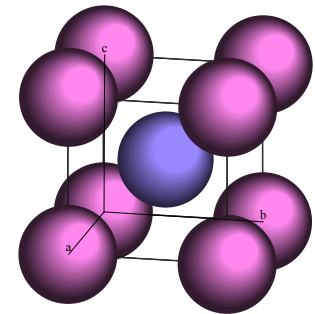
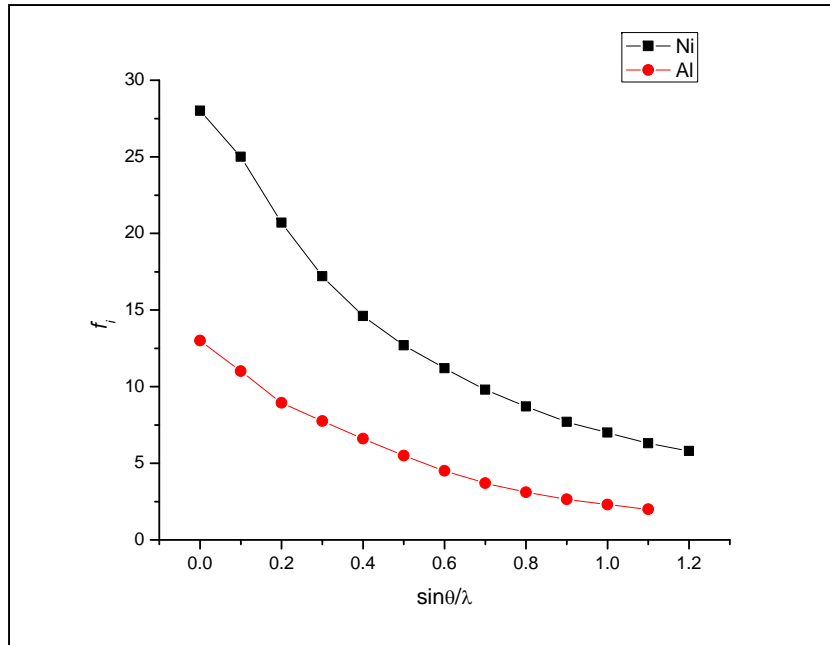


This is the plot that I used to determine the actual values of  $f_{Cu}$

# Intensity calculation for NiAl

Line	h	k	l	$h^2+k^2+l^2$	$\sin^2\theta$	$\sin\theta$	$\theta$	$2\theta$	$\sin\theta/\lambda$	$f_{Ni}$	$f_{Al}$	F	$F^2$	$\rho$	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  $\text{Ni}_3\text{Al}$  and Ru. Assume you are collecting your data on a powder diffractometer using  $\text{CuK}\alpha$  radiation. Ignore temperature and absorption effects.
- Print out and compare your results with the appropriate ICDD card.