Materials Characterization

Interaction: Intensity of the Diffracted Beam

Reading Assignment
Chapter 4 in C&S
Chapter 2 in Brandon & Kaplan

Intensity of the Diffracted Beam

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

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

$p =$ multiplicity factor

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

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

Multiplicity Factor

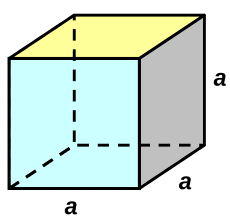
- Takes into account the relative number of planes contributing to the same reflection (i.e., the number of different planes in a form having the same spacing).

- Cubic crystal.

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

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

$p = 6$

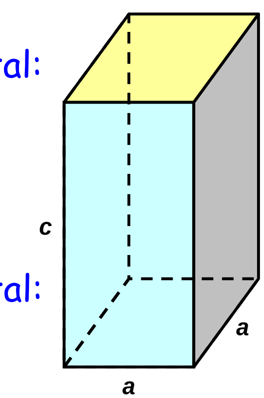


Multiplicity Factor

- Tetragonal crystal.

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

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



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.
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- SMALL DEVIATIONS FROM THE BRAGG ANGLE ARE ACCEPTABLE $\rightarrow$ broadening of peaks.

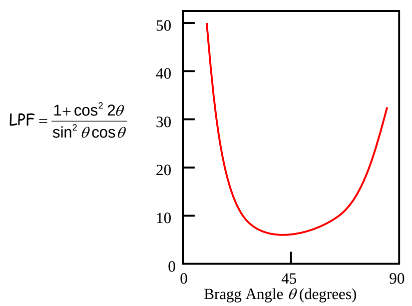
Polarization Factor

- Takes into account the fact that the incident X-ray beam is not polarized whereas the scattered X-ray beam is polarized. (i.e., it can be resolved into two components).
- The total intensity is the sum of the intensities of each component. (depends on 2θ).

Lorenz-Polarization Factor

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

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



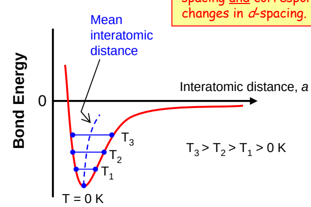
These factors are geometrical in nature.

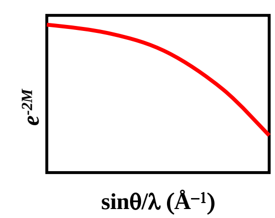
They decrease the intensity of reflections at intermediate angles relative to those in forward or backward directions

Temperature Factor

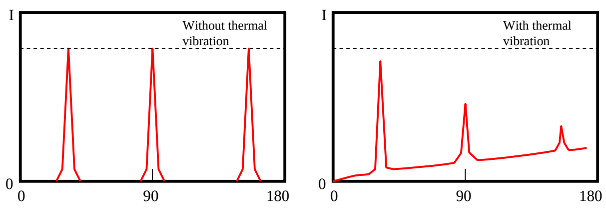
- Takes into account the fact that the atoms in all crystals vibrate about their equilibrium positions when temperature is varied.
- As T increases:
  - The unit cell expands which causes changes in *d*-spacing and 2θ values.
  - Thus, intensity of the diff-raction lines decreases.
  - Intensity of background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

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





Effect of Thermal Vibrations on Diffraction Patterns



- Lines decrease in intensity by a factor e^{-2M} 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.
- You can read pages 154-157 in Cullity's text for more details.

Absorption Factor

- In practice, there is also another factor, the Absorption Factor (A), which accounts for absorption within the specimen. It is a number that we multiply the calculated intensity by.
- It depends on the geometry of the diffraction method used. A detailed accounting can be found on pages 150-154 of Cullity's text.

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 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.

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

$$\lambda = 1.54056\ \text{Å}$$

$$a = 3.615\ \text{Å}$$

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

$\sin^2\theta = \frac{\lambda}{4a^2}\left(h^2+k^2+l^2\right)$, $\lambda=1.54056$ Å, and $a=3{,}615$ Å

From Appendix 10 in Cully (f_{Cu})

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

From Appendix 11 in Cullity (p)

From Appendix 12 in Cullity (LPF)

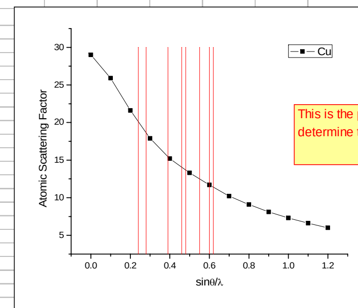
Line	h	k	l	$h^2+k^2+l^2$	$\sin^2\theta$	$\sin\theta$	θ	2θ	$\sin\theta/\lambda$	f_{Cu}	F^2	p	LPF	Intensity	Rel. Int.	ICDD Card 4-0836
1	1	1	1	3	0.136	0.369	21.7	43.3	0.24	20.2	6528.64	8	12.03	6.28E+05	100.0	100
2	2	0	0	4	0.182	0.426	25.2	50.5	0.28	18.7	5595.04	6	8.573	2.88E+05	45.8	46
3	2	2	0	8	0.363	0.603	37.1	74.2	0.39	15.5	3844	12	3.701	1.71E+05	27.2	20
4	3	1	1	11	0.499	0.707	45.0	90.0	0.46	14.1	3180.96	24	2.828	2.16E+05	34.4	17
5	2	2	2	12	0.545	0.738	47.6	95.2	0.48	13.7	3003.04	8	2.742	6.59E+04	10.5	5
6	4	0	0	16	0.726	0.852	58.5	117.0	0.55	12.4	2460.16	6	3.175	4.69E+04	7.5	3
7	3	3	1	19	0.863	0.929	68.3	136.6	0.60	11.7	2190.24	24	4.787	2.52E+05	40.0	9
8	4	2	0	20	0.908	0.953	72.4	144.8	0.62	11.3	2043.04	24	6.071	2.98E+05	47.4	8

Reasonable agreement up to here! (lines 1–6)

Calculated from data ($\sin\theta/\lambda$)

From Appendix 10 in Cullity (f_{Cu})

$\sin\theta/\lambda$	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}

Homework

- Calculate the relative intensities of the diffraction lines for Ag. 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.