MMAT 5322 – Fall 2009
Homework 3– XRD
Due Friday, Oct 30, at the start of class
44 points total

Question 1 10 points (2 points each column for dspacing, 2theta, SC, BCC, and FCC)

Complete the following table for an incident wavelength of 0.71 Angstroms (Molybdenum K_{alpha}) and a cubic unit cell of 3.4 Angstroms. Note the question asks to **determine 2*theta, not theta—calculate this <u>in degrees</u>**. For primitive (simple cubic), BCC, and FCC, simply note whether the reflexions are allowed or forbidden.

Figure out hkl in your head.
Get the d-spacing from:
Get 2theta from the Bragg equation

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

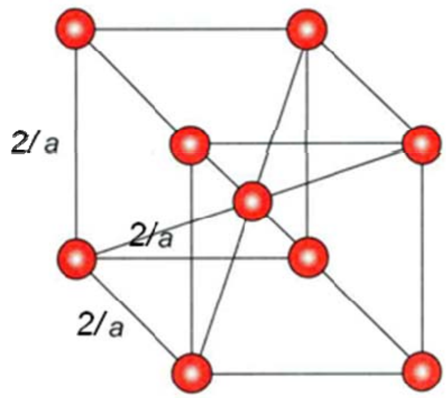
$$n\lambda = 2d(\sin\theta)$$

Figure out the allowed/disallowed visually or mathematically.

h^2+k^2+l^2	h	k	l	d spacing	2theta°	h+k+l	SC	BCC	FCC
1	1	0	0	3.40	11.99	1	Ok	forbidden	Forbidden
2	1	1	0	2.40	16.98	2	Ok	Ok	Forbidden
3	1	1	1	1.96	20.84	3	Ok	Forbidden	Ok
4	2	0	0	1.70	24.11	2	Ok	Ok	Ok
5	2	1	0	1.52	27.00	3	Ok	Forbidden	Forbidden
6	2	1	1	1.39	29.64	4	Ok	Ok	Forbidden
7	-	-	-	1.29	32.07	-	Ok	-	-
8	2	2	0	1.20	34.35	4	Ok	Ok	Ok

Question 2 4 points
Draw the 3-d reciprocal lattice for an FCC crystal. You may ignore h^2+k^2+l^2>8 (you may find useful part of your answer from question 1).

Based on the last column in Fig 1, the reciprocal lattice for an FCC crystal looks exactly like a BCC structure, with allowed reciprocal lattice points at 000, 200, 020, 002, and 111 (and 220, 202, 022, and 222 by symmetry).



Question 3   10 points

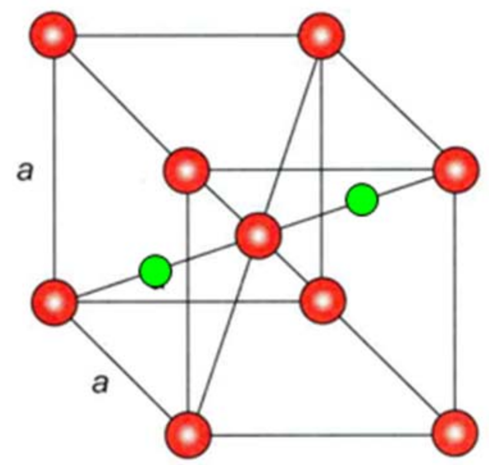
Consider the following hypothetical crystal:

Large red dots at (0, 0, 0)

Large red dots at (½, ½, ½)

Small light green dots at (¼, ¼, ¼)   (ie. different atoms from the dots)

Small light green dots at (¾, ¾, ¾)   (ie. different atoms from the dots)



a. Calculate the structure factor. 4 points
b. Determine the basic rules for diffracting planes (e.g. for even and odd variations of hkl planes, etc). 4 points
c. Identify which rules are for strong, weak, or forbidden reflexions. 2 points

Hard way: solve structure for each atom position.

Easy way: notice that this is a BCC lattice, with large red dot atoms at a basis of (000), (which includes the body center since this is a BCC lattice) and small light green dot atoms at (¼, ¼, ¼).

$$F_{\text{hom}\,ework} = \frac{F_{BCC}}{f_n}\left\{ f_{red}\exp\left[2\pi i(0h+0k+0l)\right] + f_{green}\exp\left[2\pi i\left(\frac{1}{4}h+\frac{1}{4}k+\frac{1}{4}l\right)\right]\right\}$$

$$= \frac{F_{BCC}}{f_n}\left\{ f_{red} + f_{green}\exp\left[\pi i\left(\frac{h}{2}+\frac{k}{2}+\frac{l}{2}\right)\right]\right\}$$

$$= \frac{F_{BCC}}{f_n}\left\{ f_{red} + f_{green}\cos\left[\left(\frac{h+k+l}{2}\right)\pi\right] + i\sin\left[\left(\frac{h+k+l}{2}\right)\pi\right]\right\}$$

$$AND \quad because \quad f_{BCC} = \begin{matrix} 2f_n & if \quad h+k+l = even \\ 0 & if \quad h+k+l = odd \end{matrix}$$

$$F_{\text{hom}\,ework} = \left\{\begin{matrix} 0 & if \quad h+k+l = odd \\ f_{red} + f_{green}\cos\left[\left(\frac{h+k+l}{2}\right)\pi\right] + i\sin\left[\left(\frac{h+k+l}{2}\right)\pi\right] & if \quad h+k+l = even \end{matrix}\right\}$$

$$= \left\{\begin{matrix} 0 & if \quad h+k+l = odd \\ f_{red} + f_{green}\cos\left[(odd)\pi\right] + i\sin\left[(odd)\pi\right] & if \quad \frac{h+k+l}{2} = odd \\ f_{red} + f_{green}\cos\left[(even)\pi\right] + i\sin\left[(even)\pi\right] & f \quad \frac{h+k+l}{2} = even \end{matrix}\right\}$$

$$= \left\{\begin{matrix} 0 & if \quad h+k+l = odd & forbidden \\ f_{red} - f_{green} & if \quad \frac{h+k+l}{2} = odd & weak \\ f_{red} + f_{green} & if \quad \frac{h+k+l}{2} = even & strong \end{matrix}\right\}$$

Question 4 **Question not graded**

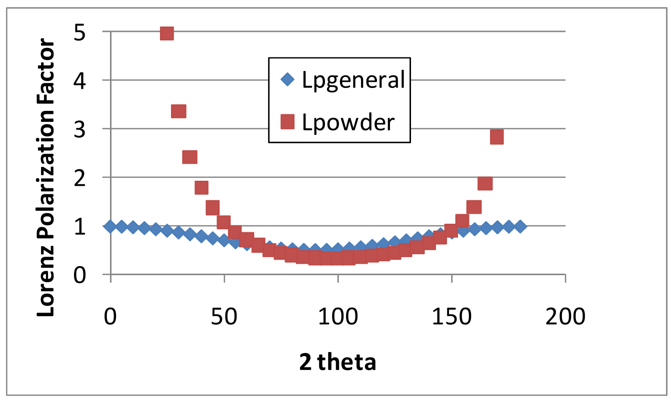
a. Plot the general Lorentz polarization factor vs. 2*theta, and overlay the Lorentz polarization factor for a powder diffraction pattern.

b. What are the diffraction angles (2theta), and multiplicity factors (P), **for a simple cubic crystal**? You should already have the angles from Q1. **Only consider up to h^2+k^2+l^2=4.**

c. Ignoring other common terms in the diffraction intensity equation (specifically assume k=1, A=1, B=0), plot the predicted diffraction peak angles and intensities as a function of 2*theta. Again, part of your answer to Q1 may be useful, as will be the answer from Q4a.

a. Both cases are plotted below.
i) Use the simple eq. for the general lorentzian polarization factor
ii) Use the slightly more complicated eq. for the lorentzian polarization factor for powder diffraction patterns.

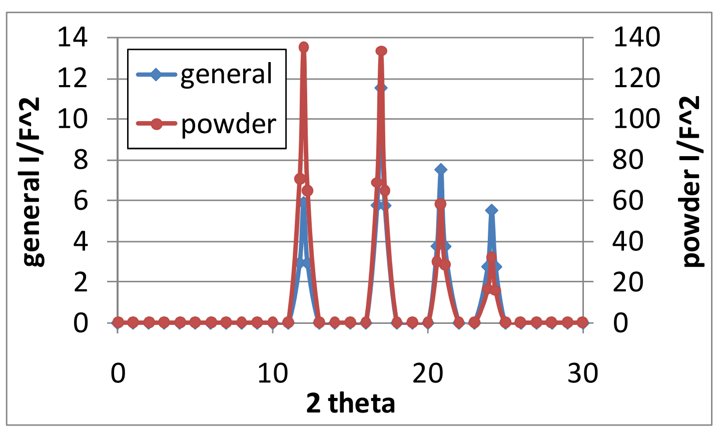
$$LP_{general} = \frac{1+\cos^2 2\theta}{2} \qquad LP_{powder} = \frac{1+\cos^2 2\theta}{8\sin^2\theta \cdot \cos\theta}$$



b. Angles and multiplicity factors are as follows:

h^2+k^2+l^2	h	k	l	2theta°	Multiplicity
1	1	0	0	11.99	6
2	1	1	0	16.98	12
3	1	1	1	20.84	8
4	2	0	0	24.11	6

c. The predicted peaks are as follows, solved for both general, and powder samples (either is fine for full credit). These are based on the generalized XRD equation, simplified as in the instructions, along with the multiplicity factors, allowed angles, and LP terms from parts a and b:



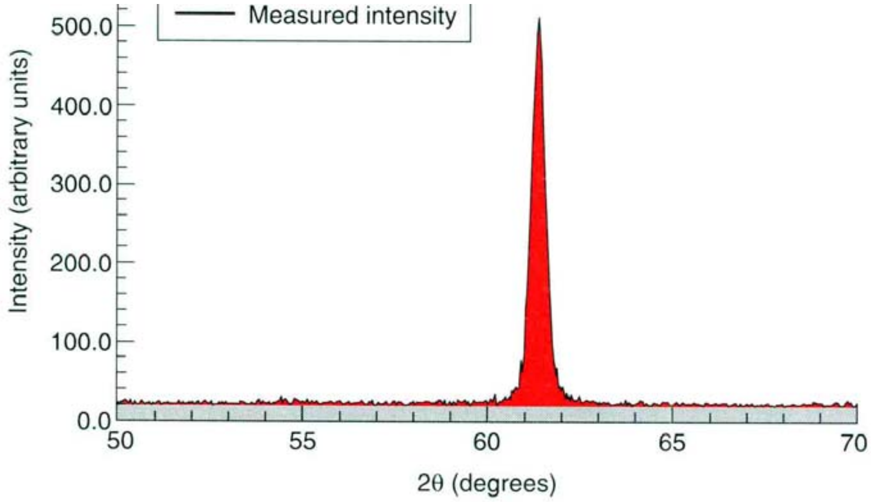
$$I = k \cdot \left|F^2\right| \cdot LP \cdot M \cdot A(\theta) \cdot \exp\left(-2\frac{B\sin^2\theta}{\lambda^2}\right)$$

$$I = 1 * \left|F^2\right| \cdot LP \cdot M \cdot 1 \cdot 1$$

Question 5 8 points

For the following peak at 61.5 degrees of 2theta, with an approximate FWHM of 0.7 degrees, and assuming an incident wavelength of 0.71 Angstroms (Mo Kalpha):

a. Describe two ways in which this peak pattern will change as temperature increases. 2 points
b. Assuming this peak breadth is due to diffraction domain size (i.e. grains, particles, etc), what is the volume weighted size? 3 points



c. Assuming the peak breadth is due to strain, how much strain is there? 3 points

a. i) With temperature, the peak position will shift. This is because the lattice parameter and hence d-spacing will change due to thermal expansion, generally increasing as T increases. This will cause the peak angle to change as well, generally decreasing with increasing T since angle is inversely proportional to d-spacing.
ii) With temperature, the peak may broaden due to increased entropy, and hence randomness, around the atomic sites. Defect densities will increase as well, also broadening the peak.

b. Using the simple eq. at right, FWHM in radians is 0.0122, theta (not 2theta) is 30.75 degrees, and thus d_v=60.86 Angstroms (6.086 nm).

$$d_v = \frac{0.9\lambda}{FWHM|_{radians} \cos\theta_{diffraction}}$$

c. Using the simple eq. at right, strain= 0.005

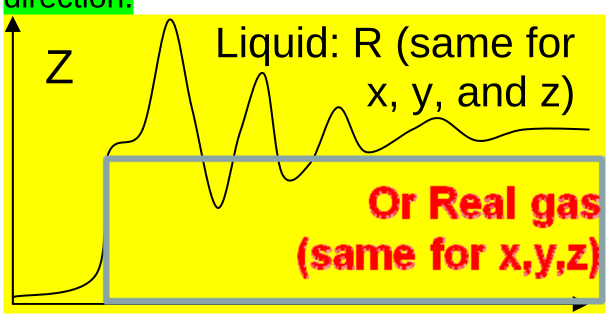
$$\varepsilon = \frac{FWHM|_{radians}}{4\tan\theta_{diffraction}}$$

Question 6 12 points (3 each, as long exhibit main features as identified below)

Following are several images of pumpkins. Assuming the pumpkins are actually atoms, sketch approximate distribution functions (not the transforms, just the real-space functions) **in plane (x, and also y if different), and out of plane (z)**? Ignore pumpkin details, dimples, coloring, stems, faces, etc.—i.e., a pumpkin is a pumpkin is a pumpkin.

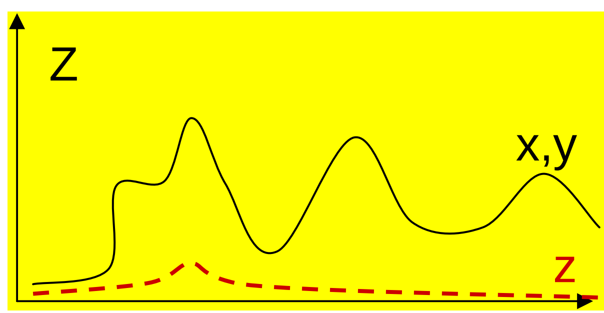
a. (random 3-d pile of pumpkins)

Some initial peaks, dying out with increasing distance, identical for each direction.



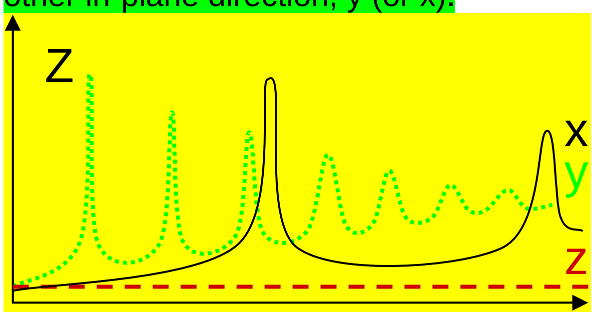
b. (single layer of pumpkins on the ground, some ordering)

Initial peaks, broad and dying out, basically same in x and y, but basically nothing in z (or a tiny peak as shown here indicating the possibility of a few pumpkins stacked—can't really tell either way, of course).



c. (varying periodicities, ignore image distortion near top from wide angle lens)

No staking in z, so no signal for z. Consistent peaks in x (or y), and consistent peaks with a larger period in the other in-plane direction, y (or x).



d. (some ordering in all directions)

Consistent peaks for x and y. Peaks in z, but with weird periodicity—details of weirdness not crucial…