Quiz 3 Properties of Materials CME 300
October 12, 2011

a) Small nano-crystals melt at a lower temperature than large crystals (see Figure 1 below). Obtain an expression for crystal size as a function of crystallization temperature that explains this behavior following the method of Gibbs-Thompson. (That is derive an equation for Radius as a function of Crystallization Temperature).

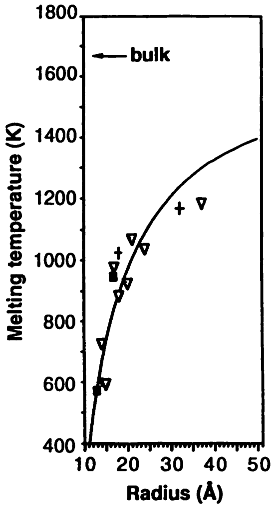


Figure 1. Melting Temperature versus crystal size for Cadmium Sulfide nano-crystals.
Goldstein AN, Echer CM, Alivisatos AP *Science* **256** 1425-7 (1992).

b) Sketch the diffraction pattern from FCC, BCC and HCP metals as well as the diffraction pattern from an amorphous solid. What does the peak position of the amorphous halo indicate?

c) Derive Bragg's Law using the specular reflection analogy.

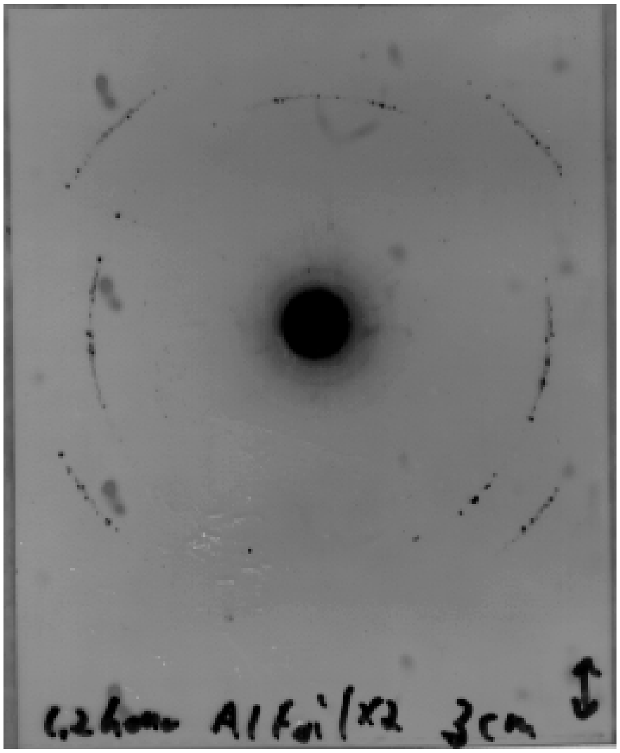
d) The following images are photographic diffraction patterns from aluminum foil and a polyethylene bag.

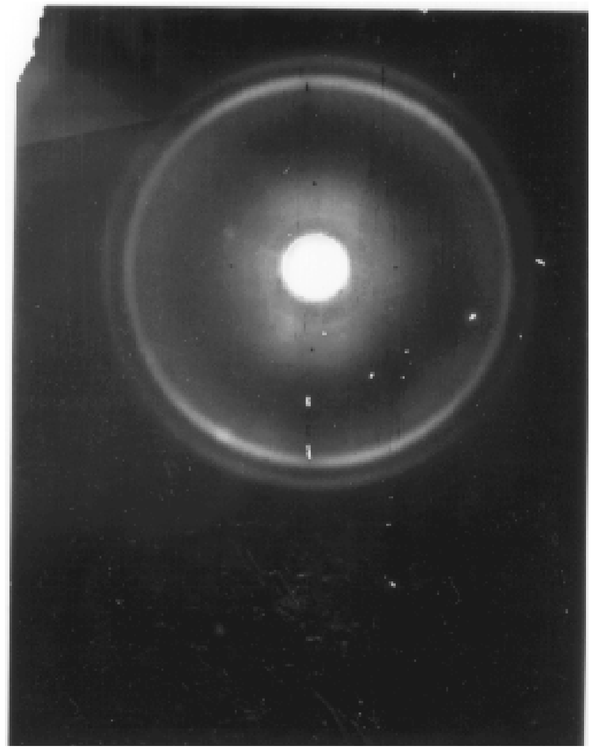
-Explain why the aluminum shows dots in the Debye-Scherer rings and the polymer does not.

-Explain why the polymer peaks are broader than those of aluminum.

-Explain why the aluminum pattern shows arcs rather than complete rings.

-Guess the unit cell for these two patterns and explain your choice.



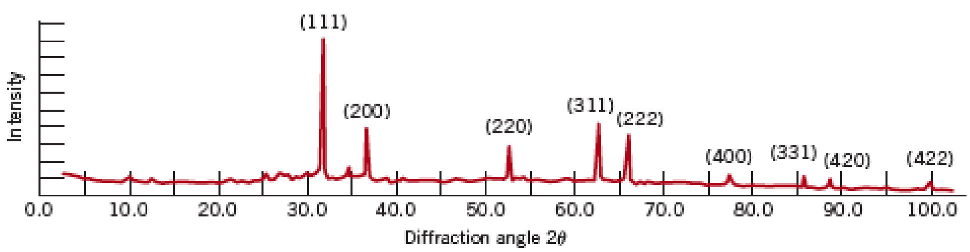


e) The following diffraction pattern was produced using $Cu_{K\text{-}\alpha}$ radiation (λ = 1.54Å).

-What is the unit cell for this crystal? Explain

-Calculate the lattice spacing for the (220) and (422) reflections.

Figure 3.21 Diffraction pattern for powdered lead. (Courtesy of Wesley L. Holman.)



Answers Quiz 3 CME 300 October 12, 2011

a)

The derivation is similar to that for the polymer crystal except that there are 6 surfaces to a cubic crystal compared with two high energy fold surfaces in a polymer crystal.

The Hoffman-Lauritzen equation for polymers is derived as follows:

Consider a crystal where t => ∞

$$\Delta G_{f,T_\infty} = 0 = \Delta H_f - T_\infty \Delta S_f$$

$$\Delta S_f = \frac{\Delta H_f}{T_\infty}$$

Consider a crystal where t is finite crystallized at $T_{m,t}$ (Gibbs Pseudo-Equilibrium Assumption)

$$V\Delta G_{f,T_\infty} = 0 = V\left(\Delta H_f - T_{m,\infty}\Delta S_f\right) - 2R^2\sigma_e$$

$$tR^2\Delta H_f\left(\frac{T_{m,\infty} - T_{m,t}}{T_{m,\infty}}\right) = 2R^2\sigma_e$$

$$t = \frac{2\sigma_e T_{m,\infty}}{\Delta H_f\left(T_{m,\infty} - T_{m,t}\right)}$$

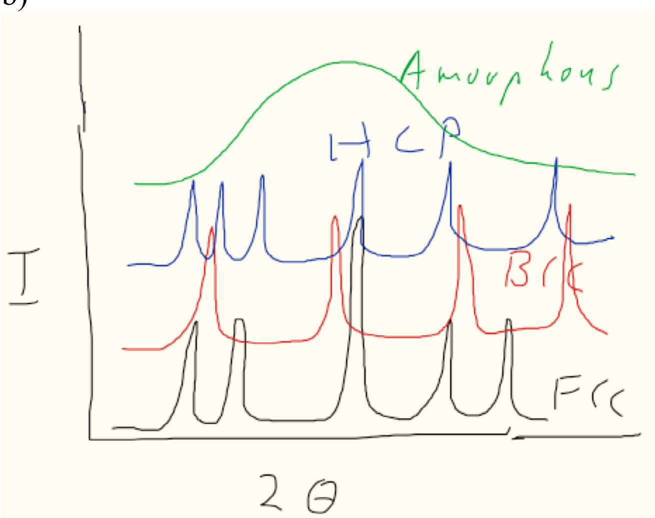
For cubic crystals the third equation becomes:

$$V\Delta G_{f,T_{m,t}} = 0 = V\left(\Delta H_f - T_{m,\infty}\Delta S_f\right) - 6R^2\sigma_e$$

so we have,

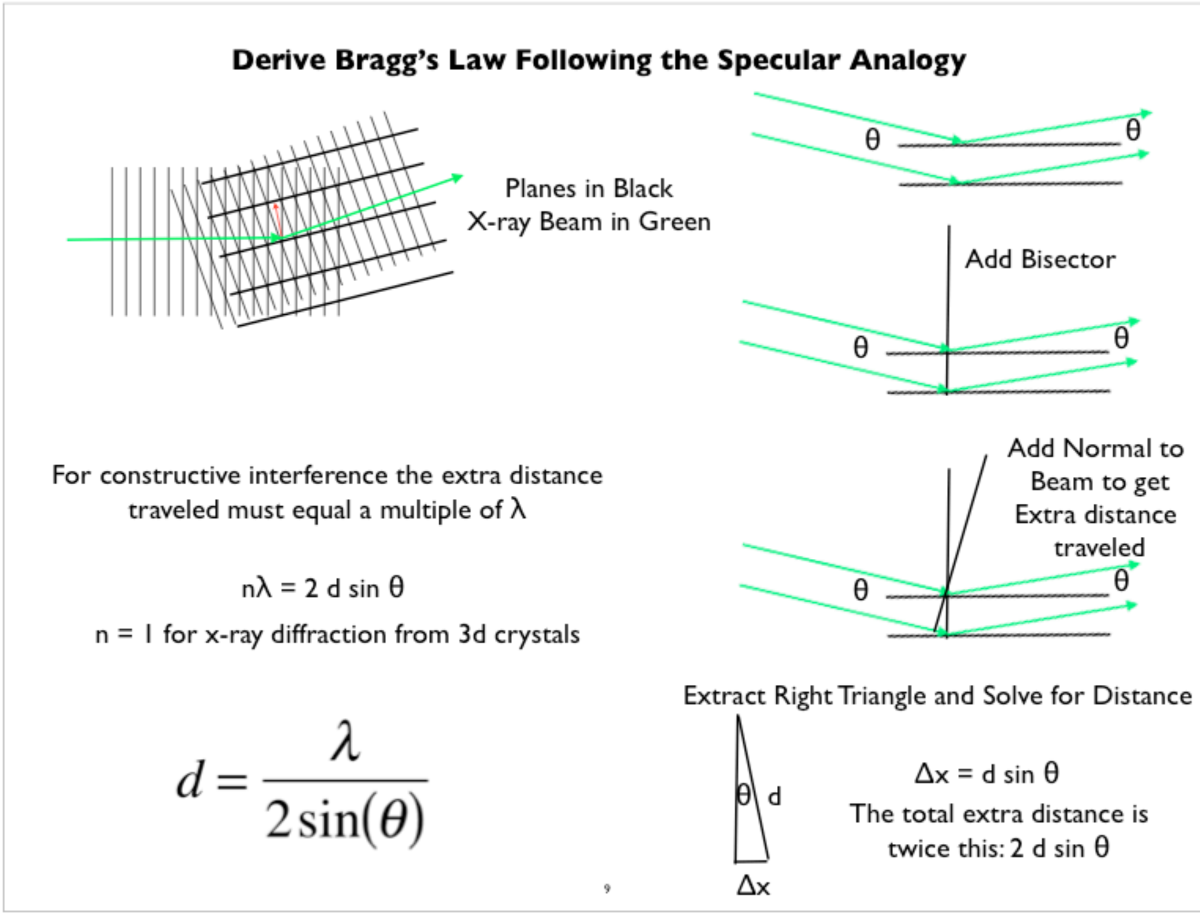
$$t = \frac{6\sigma_e T_{m,\infty}}{\Delta H_f\left(T_{m,\infty} - T_{m,t}\right)} \sim \text{Radius}$$

b)



The peak position for the amorphous halo is associated with the root mean square separation distance for the atoms, $d_{RMS} = \lambda/(2\sin\theta)$

c)



d) The aluminum sample has rather large crystals or grains that are oriented in a drawn foil sample. The grains are so large that in the x-ray beam (20μm by 1 cm) there are only about 50-100 grains in the beam so each grain yields a spot for a given reflection if the planes are aligned property for diffraction to occur. The grains have a preferred orientation relative to the draw direction so that reflections for a given plane show up as arcs centered on the preferred direction of orientation. The two Debye Scherer rings shown for this FCC structure are the (111) and (200) reflections.

For the polyethylene sample the crystal structure is orthorhombic with a central chain offset in orientation. The structure ends up looking something like an FCC structure so the diffraction pattern has a motif reminiscent of FCC, in that there are two prominent peaks at low-q. The polyethyelene sheet also displays some degree of orientation due to the brightness of the peaks at the top and bottom of the figure. The peaks are broad because these crystals have a thickness on the order of 100Å or 10 nm so they are nano-crystals. The broader the peak the smaller the crystalline thickness.

Both appear to be FCC from the shape of the patterns but the PE is orthorhombic with a structure reminiscent of FCC.

e) It is an FCC structure due to the shape of the pattern.

Need to measure the peak positions from the plot,

Plane	2θ	$d = \lambda/(2\sin\theta)$	$a = d\sqrt{(h^2+k^2+l^2)}$
(220)	53°	1.73Å	4.89Å
(422)	99.8°	1.01Å	4.94Å