CME 300 Properties of Materials

ANSWERS Homework 2 October 5, 2011

Problems from Callister p. 78

3.57 Using the data for aluminum in Table 3.1, compute the interplanar spacing for the (110) set of planes.

r = 1.431 Å so a = 2√2 r = 4.048 Å
d$_{(110)}$ = a/√2 = 2r = 2.862Å

3.58 Determine the expected diffraction angle for the first-order reflection from the (310) set of planes for BCC chromium when monochromatic radiation of wavelength 0.0711 nm is used.

d$_{(310)}$ = a/√10 and a = 4r/√3 = 4 1.249/√3 Å = 2.884
d$_{(310)}$ = 0.912 Å
d = λ/(2sinθ) so 2θ = 2 asin(λ/2d) = 45.9°

3.59 Using the data for α-iron in Table 3.1, compute the interplanar spacings for the (111) and (211) sets of planes.

r = 1.241 Å a = 4r/√3 = 2.866Å
d$_{(111)}$ = a/√3 = 1.655Å
d$_{(211)}$ = a/√6 = 1.170Å

3.60 The metal rhodium has an FCC crystal structure. If the angle of diffraction for the (311) set of planes occurs at 36.12° (first-order reflection) when monochromatic x-radiation having a wavelength of 0.0711 nm is used, compute **(a)** the interplanar spacing for this set of planes, and **(b)** the atomic radius for a rhodium atom.

a) d$_{(311)}$ = λ/(2sinθ) = 0.711Å/(2sin(18.06°)) = 1.147Å
b) r = a/(2√2) for FCC
a = d$_{(311)}$ √(11) = 3.803Å
r = 3.803Å/(2√2) = 1.345Å

3.61 The metal niobium has a BCC crystal structure. If the angle of diffraction for the (211) set of planes occurs at 75.99° (first-order reflection) when monochromatic x-radiation having a wavelength of 0.1659 nm is used, compute **(a)** the interplanar spacing for this set of planes, and **(b)** the atomic radius for the niobium atom.

a) $d_{(211)} = \lambda/(2\sin\theta) = 1.659\text{Å}/(2\sin(37.95°)) = 1.347\text{Å}$
b) For BCC $r = \sqrt{3}a/4$
$a = d_{(211)} \sqrt{(6)} = 3.301\text{Å}$
$r = \sqrt{3}\ 3.301\text{Å}/4 = 1.429\text{Å}$

3.62 For which set of crystallographic planes will a first-order diffraction peak occur at a diffraction angle of 44.53° for FCC nickel when monochromatic radiation having a wavelength of 0.1542 nm is used?

$d_{(hkl)} = a/\sqrt{(h^2+k^2+l^2)} = \lambda/(2\sin\theta) = 1.542\text{Å}/(2\sin(22.26°)) = 2.035\text{Å}$
$r = 1.246\text{Å}$ for Nickel FCC so $a = 1.246\ \text{Å}\ 2\sqrt{2} = 3.524\text{Å}$
For FCC the first 6 reflections are (111), (200), (220), (311), (222), (400) so by trial and error we find this is the (111) reflection.

3.63 Figure 3.21 shows an x-ray diffraction pattern for lead taken using a diffractometer and monochromatic x-radiation having a wavelength of 0.1542 nm; each diffraction peak on the pattern has been indexed. Compute the interplanar spacing for each set of planes indexed; also determine the lattice parameter of Pb for each of the peaks.

Figure 3.21
Diffraction pattern for powdered lead. (Courtesy of Wesley L. Holman.)
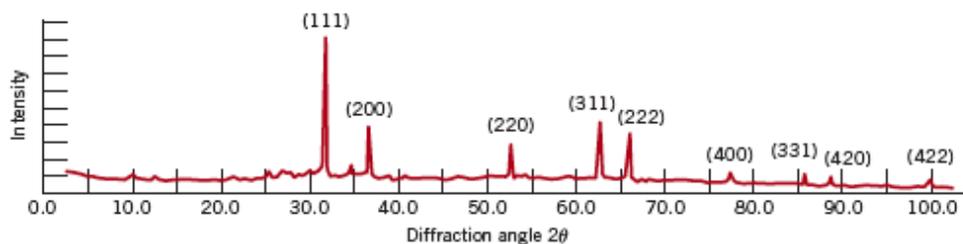
Need to measure the peak positions from the plots,

| Plane	2θ	$d = \lambda/(2\sin\theta)$	$a = d\ \sqrt{(h^2+k^2+l^2)}$
(111)	32°	2.80Å	4.84Å
(200)	37°	2.43Å	4.88Å
(220)	53°	1.73Å	4.89Å
(311)	63.5°	1.47Å	4.86Å

(222) 66°   1.42Å   4.90Å
(400) 77.2° 1.24Å   4.94Å
(331) 86°   1.13Å   4.93Å
(420) 89°   1.10Å   4.92Å
(422) 99.8° 1.01Å   4.94Å

The higher angle values are probably better for "a" since there is less relative error in the angle at higher values.

3.64 The diffraction peaks shown in Figure 3.21 are indexed according to the reflection rules for FCC (i.e., h, k, and l must all be either odd or even). Cite the h, k, and l indices of the first four diffraction peaks for BCC crystals consistent with $h + k + l$ being even.

(110), (200), (211), (220), (310), (222) for BCC
The following diagram shows how the peaks are spaced for BCC, basically evenly spaced peaks.

Figure 10-2 Calculated diffraction patterns for various lattices $s = (h^2 + k^2 + l^2)$.
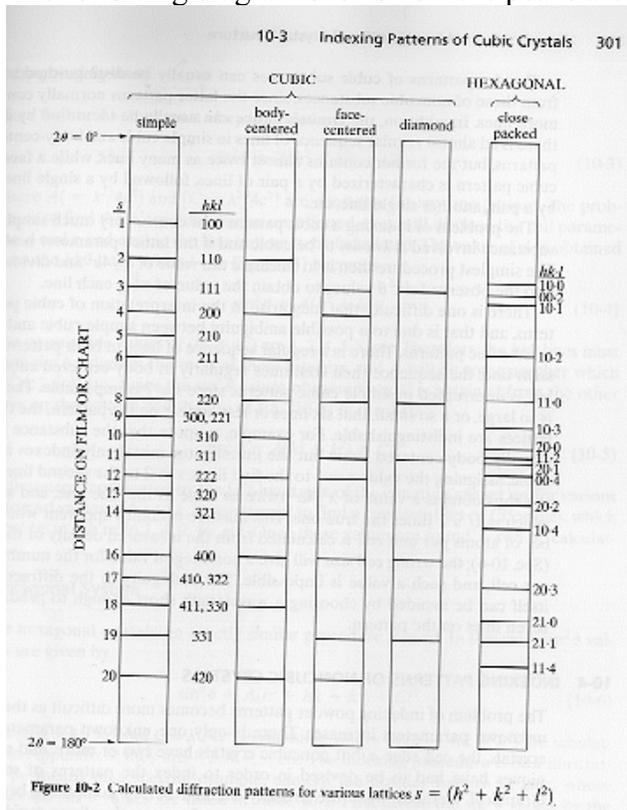
Compare the FCC in this diagram to the spacing's of the peaks in Figure 3.21 above, i.e. 2: 1: 2 signature.

3.65 Figure 3.24 shows the first five peaks of the x-ray diffraction pattern for tungsten, which has a BCC crystal structure; monochromatic x-radiation having a wavelength of 0.1542 nm was used.

(a) Index (i.e., give h, k, and l indices) for each of these peaks.

(b) Determine the interplanar spacing for each of the peaks.

(c) For each peak, determine the atomic radius for W and compare these with the value presented in Table 3.1.

(a) At a glance you can see that the spacing's are even so it is likely a BCC crystal if it is a metal. For BCC the first 5 peaks are (110), (200), (211), (220), (310). (Indexing a diffraction pattern is usually a bit more involved than this. Many diffractometers have a search procedure that will solve the composition of the sample for you.)

(b) $d = \lambda/(2\sin\theta)$ θ: (110) 40.2° , (200) 58°, (211) 73°, (220) 83.5°, (310) 101°

$d(110) = 2.24$Å
$d(200) = 1.59$Å
$d(211) = 1.29$Å
$d(220) = 1.16$Å
$d(310) = 1.00$Å

(c) $a = d\sqrt{(h^2+k^2+l^2)}$ $r = \sqrt{3}a/4$

$a(110) = 3.17$Å   1.37Å
$a(200) = 3.18$Å   1.38Å
$a(211) = 3.16$Å   1.37Å
$a(220) = 3.28$Å   1.42Å
$a(310) = 3.16$Å   1.37Å

Reported value for r is: 1.36Å
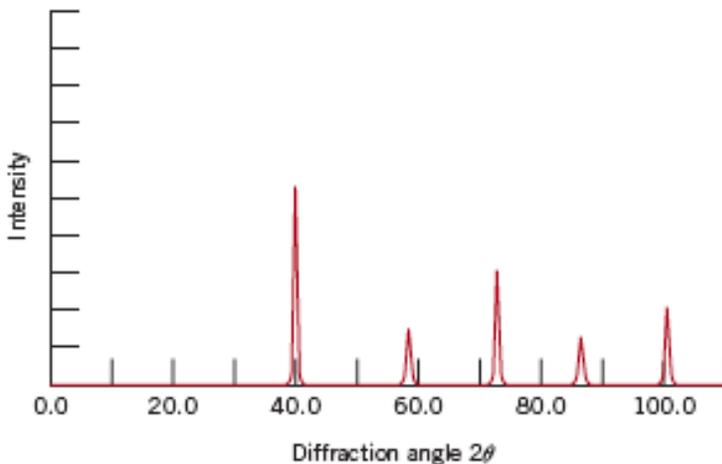
Figure 3.24 Diffraction pattern for powdered tungsten. (Courtesy of Wesley L. Holman.)

Intensity

Diffraction angle 2θ

4

Table 3.1 Atomic Radii and Crystal Structures for 16 Metals

| Metal	Crystal Structure[a]	Atomic Radius[b] (nm)	Metal	Crystal Structure	Atomic Radius (nm)
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	FCC	0.1442	Titanium (α)	HCP	0.1445
Iron (α)	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

[a] FCC = face-centered cubic; HCP = hexagonal close-packed; BCC = body-centered cubic.

[b] A nanometer (nm) equals 10^{-9} m; to convert from nanometers to angstrom units (Å), multiply the nanometer value by 10.

3.66 Would you expect a material in which the atomic bonding is predominantly ionic in nature to be more or less likely to form a noncrystalline solid upon solidification than a covalent material? Why? (See Section 2.6.)

This question is vague since there are two possibilities for covalent materials, generally covalent materials crystallize as a molecular unit such as napthylene or polyethylene so the covalent bonds are not particularly important in deciding the crystal structure, the crystalline structure is decided by weaker interactions such as hydrogen bonding and van der Waals interactions. For these materials the formation of a glass is quite common depending on the rate of crystallization. I believe that Callister is referring to materials like diamond and graphite where the crystal is composed of 3-d covalent bonds. In this case the formation of the crystal is like a chemical synthesis of an organic material and it is very difficult to form a glass since the bonding needs to be tetrahedral in diamond and there is little room for misplacement of bonds. For ionic materials like NaCl it is also difficult to form a glass since the simple ionic structure and strong ionic nature forces the material to crystallize and misplaced units carry a high energy penalty. For other ionic materials such as SiO_2, glass formation is common. This material has a combination of tetrahedral bonding and ionic bonds so formation of the structure is quite complex and misplaced atoms are common. The system can be locked into a disordered structure or a glass. If the glass is annealed it can crystallize. The tendency to form a glass is also related to the kinetics, particularly the viscosity of the melt. NaCl has a low viscosity in the melt while SiO_2 has a high viscosity melt. So issues involved in glass formation are the complexity of the crystalline structure, the viscosity of the melt, generally the difficulty of moving the atoms or molecules into a crystalline lattice, the more difficult the more likely it is that a glass will form.

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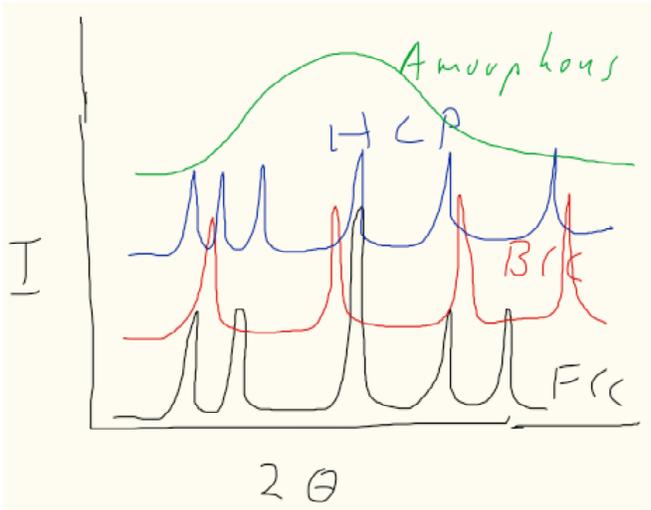
The peak position for the amorphous halo is associated with the root mean square separation distance for the atoms, $d_{RMS} = \lambda/(2\sin\theta)$

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

Two such X-rays are shown here, where the spacing between the atomic planes occurs over the distance, d. Ray 1 reflects off of the upper atomic plane at an angle q equal to its angle of incidence. Similarly, Ray 2 reflects off the lower atomic plane at the same angle q. While Ray 2 is in the crystal, however, it travels a distance of 2a farther than Ray 1. If this distance 2a is equal to an integral number of wavelengths (nl), then Rays 1 and 2 will be in phase on their exit from the crystal and constructive interference will occur.
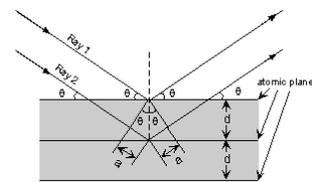
If the distance 2a is not an integral number of wavelengths, then destructive interference will occur and the waves will not be as strong as when they entered the crystal. Thus, the condition for constructive interference to occur is

$$nl = 2a$$

but, from trigonometry, we can figure out what the distance 2a is in terms of the spacing, d, between the atomic planes.

$$a = d \sin q$$

$$or\ 2a = 2\ d \sin q$$

$$thus,\ nl = 2d \sin q$$

This is known as **Bragg's Law** for X-ray diffraction.

What it says is that if we know the wavelength ,l , of the X-rays going in to the crystal, and we can measure the angle q of the diffracted X-rays coming out of the crystal, then we know the spacing (referred to as **d-spacing**) between the atomic planes.

$$d = nl\ /2 \sin q$$

Again it is important to point out that this diffraction will only occur if the rays are in phase when they emerge, and this will only occur at the appropriate value of n (1, 2, 3, etc.) and q.

In theory, then we could re-orient the crystal so that another atomic plane is exposed and measure the d-spacing between all atomic planes in the crystal, eventually leading us to determine the crystal structure and the size of the unit cell.

13) What can the breadth of a diffraction peak indicate? That is, for two copper samples if one displays a broad diffraction peak while the other displays a sharp peak what is the difference between the two samples? What about for two aluminum samples.

The breadth of a diffraction peak can be related to small crystalline grains, residual stress in the crystals or thermal vibrations. For a typical copper sample the most likely source for peak broadening is residual stress. For a typical aluminum sample the most likely source for peak broadening is thermal vibrations. This has to do with the ability of atoms to move in the crystal

structure in aluminum. To see broadening due to small crystallite size the crystals or grains need to be much less than a micron in size, i.e. nano-size crystals show broadening.

14) 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.
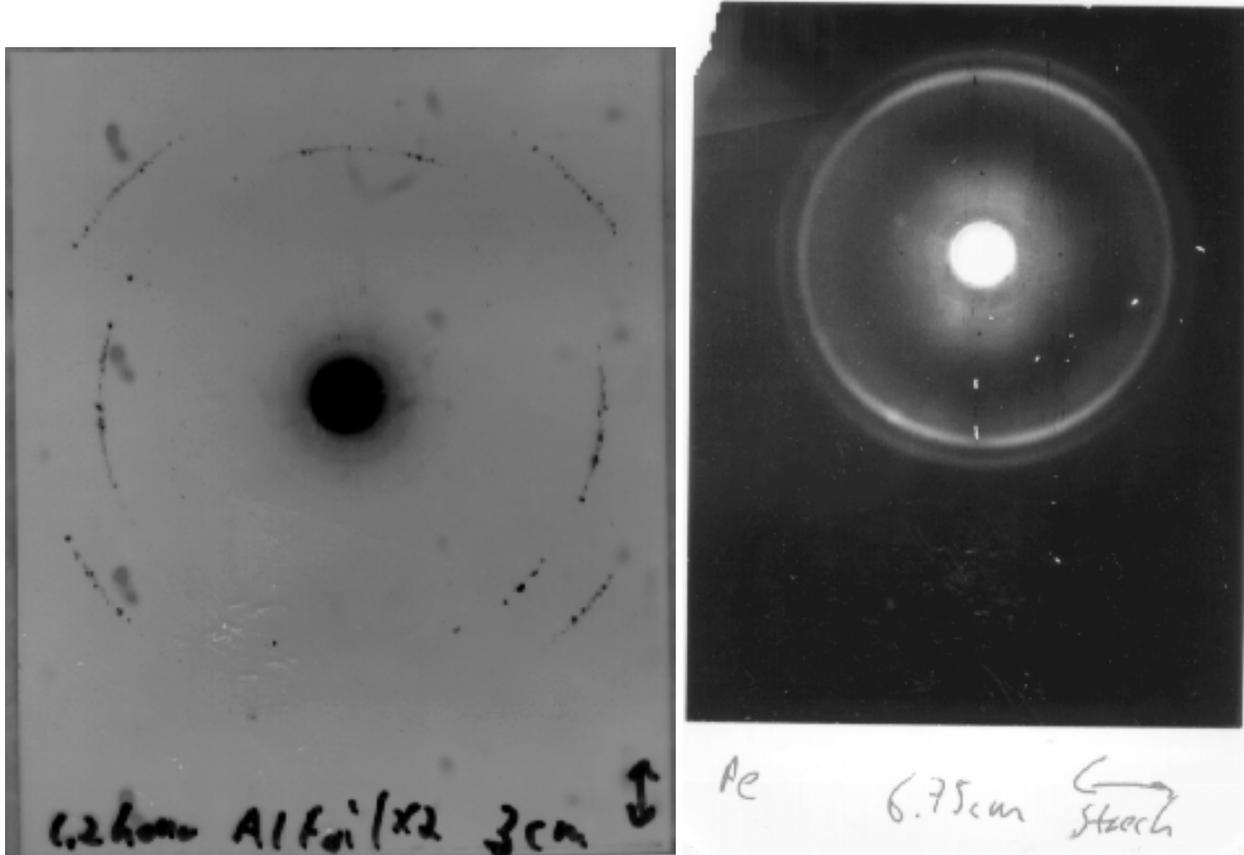
The aluminum sample has rather large crystals or grains that are oriented in a drawn foil sample. The grains are so large that in the x-ray beam (20μm by 1 cm) there are only about 50-100 grains in the beam so each grain yields a spot for a given reflection if the planes are aligned property for diffraction 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 brighness 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.