

Homework #8

solution outlines

22. X-rays are used to determine the structures of crystalline materials because they have wavelengths on the order of 10^{-10} m, which is the size scale of interatomic bonds and distances. The diffraction of x-rays from planes of atoms within a crystalline lattice provides information about the atomic arrangement. Gamma rays have wavelengths on the order of 10^{-12} to 10^{-11} m; they are too small to be diffracted by crystals.

23. Information about the structures of crystalline materials can be gleaned from the diffraction of light by planes of atoms in the sample. Since interatomic spacings are on the order of 10^{-10} m (equal to 100 pm or 1 Å), light of this wavelength must be used to satisfy the diffraction condition described by the Bragg equation. Visible light, with wavelengths around 10^{-7} m, cannot be used.

25. Assuming $n=1$, the Bragg equation can be rearranged to $d = \frac{\lambda}{2\sin\theta}$

For a given set of planes in a crystal, d will be constant. If λ decreases, such as when replacing a copper source with a molybdenum source, the factor $2\sin\theta$ must also decrease. This requires a decrease in the scattering angle θ .

26. Assuming $n=1$, the Bragg equation can be rearranged to $d = \frac{\lambda}{2\sin\theta}$

For a given (constant) wavelength, a larger scattering angle, θ , results in a larger spacing in the diffraction pattern. From the above expression, the larger spacing in the diffraction pattern of crystal A implies that its interatomic spacing, d , is smaller than that of crystal B.

*81. Use the Bragg equation to calculate the diffraction angle:

$$2d \sin \theta = n\lambda \longrightarrow \theta = \sin^{-1} \frac{n\lambda}{2d}$$

For $n = 1$, $\lambda = 154$ pm, and using the d spacings given, the diffraction angles are: Mg 17.2° , Zn 18.2° , and Ni 20.9° .

82. To find the d spacing of the Mg planes, use the Bragg equation for first-order diffraction:

$$2d \sin \theta = n\lambda \longrightarrow d = \frac{n\lambda}{2\sin \theta} = \frac{(1)(154 \text{ pm})}{2\sin(17.23^\circ)} = 260 \text{ pm}$$

The d spacing of the Ni planes is:

$$d = \frac{n\lambda}{2\sin \theta} = \frac{(1)(154 \text{ pm})}{2\sin(20.88^\circ)} = 216 \text{ pm}$$

$$1. (a) \quad \bar{v} = \frac{1}{\lambda} = \frac{5}{36}(74 - 7.4)^2 R \Rightarrow \lambda = 1.476 \times 10^{-10} \text{ m}$$

This is FCC with a value of $V_{\text{molar}} = 19.9 \text{ cm}^3$

$$\therefore \frac{4}{a^3} = \frac{N_{\text{Av}}}{V_{\text{molar}}} \Rightarrow a = \left(\frac{4 \times 19.9}{6.02 \times 10^{23}} \right)^{1/3} = 5.095 \times 10^{-8} \text{ cm}$$

$$\lambda = 2d \sin \theta \quad d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

4th reflection in FCC: 111; 200; 220; **311**; 222

$$h^2 + k^2 + l^2 = 11$$

$$\lambda_{\theta} = \frac{2a \sin \theta}{\sqrt{h^2 + k^2 + l^2}} \Rightarrow \sin^{-1} \left(\frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2a} \right) = \sin^{-1} \left(\frac{1.476 \sqrt{11}}{2 \times 5.095} \right) = 28.71^\circ$$

$$(b) \quad \lambda_{\text{neutrons}} = \lambda_{\text{x-rays}}$$

$$\lambda_{\text{neutrons}} = \frac{h}{p} = \frac{h}{mv}, \quad \therefore v = \frac{h}{m\lambda} = \frac{6.6 \times 10^{-34}}{1.675 \times 10^{-27} \times 1.476 \times 10^{-10}} = 2.68 \times 10^3 \text{ m/s}$$

2. Follow the procedure suggested in lecture:

Step 1 Start with 2θ values and generate a set of $\sin^2 \theta$ values.

Step 2 Normalize the $\sin^2 \theta$ values by generating $\sin^2 \theta_n / \sin^2 \theta_1$.

Step 3 Clear fractions from "normalized" column.

Step 4 Speculate on the hkl values that would seem as $h^2 + k^2 + l^2$ to generate the sequence of the "clear fractions" column.

Step 5 Compute for each θ the value of $\sin^2 \theta / (h^2 + k^2 + l^2)$ on the basis of the assumed hkl values. If each entry in this column is identical, then the entire process is validated.

(a) For the data set in question, it is evident from the hkl column that the crystal structure is FCC (see table below).

$$(b) \quad \frac{\lambda^2}{4a^2} = \frac{\sin^2 \theta}{h^2 + k^2 + l^2} = 0.0358, \quad \lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}, \quad \therefore a = \frac{1.5418}{(4 \times 0.0358)^{1/2}} = 4.07 \text{ \AA}$$

$$(c) \quad \text{In FCC, } \sqrt{2}a = 4r, \quad \therefore r = \frac{\sqrt{2}}{4} \times 4.07 \text{ \AA} = 1.44 \text{ \AA}$$

(d) $\rho = \frac{m}{V}$ Here we'll use atomic mass and atomic volume.

$$\frac{4 \text{ atoms}}{a^3} = \frac{N_{\text{Av}} \text{ atoms}}{V_{\text{molar}}}, \quad \therefore V_{\text{molar}} = \frac{6.02 \times 10^{23}}{4} \times (4.07 \times 10^{-8} \text{ cm})^3 = 10.15 \text{ cm}^3$$

$$\therefore \rho = \frac{66.6 \text{ g/mol}}{10.15 \text{ cm}^3/\text{mol}} = 6.56 \text{ g/cm}^3$$

Data Reduction of Debye-Scherrer Experiment:

2θ	$\sin^2\theta$	normalized	clear fractions	(hkl)?	$\frac{\sin^2\theta}{h^2+k^2+l^2}$
38.40	0.108	1.00	3	111	0.0360
44.50	0.143	1.32	4	200	0.0358
64.85	0.288	2.67	8	220	0.0359
77.90	0.395	3.66	11	311	0.0358
81.85	0.429	3.97	12	222	0.0358
98.40	0.573	5.31	16	400	0.0358
111.20	0.681	6.31	19	331	0.0358

3. Same approach as described in the answer to Problem 2.

(a) See table below. It is evident that the crystal structure is BCC. Look at the hkl column.

(b) $\frac{\lambda^2}{4a^2} = \frac{\sin^2\theta}{h^2+k^2+l^2} = 7.53 \times 10^{-3}$, $\lambda_{Ag_{K\alpha}} = 0.574 \text{ \AA}$, $\therefore a = \frac{0.574}{(4 \times 7.53 \times 10^{-3})^{1/2}} = 3.31 \text{ \AA}$

(c) In BCC, $\sqrt{3}a = 4r$

$$\therefore r = \frac{\sqrt{3}}{4} \times 3.31 \text{ \AA} = 1.43 \text{ \AA}$$

(d) $\lambda = 2 d_{hkl} \sin\theta$ $d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} = \frac{a}{\sqrt{2}} \therefore \theta = \sin^{-1} \left\{ \lambda / \left(2 \times \frac{a}{\sqrt{2}} \right) \right\}$

$$\lambda_{L\alpha} \text{ given by } \bar{\nu} = \lambda^{-1} = \frac{5}{36} R(Z - 7.4)^2 = \frac{5}{36} \times 1.1 \times 10^7 (47 - 7.4)^2 = 2.40 \times 10^9 \text{ m}^{-1}$$

$$\Rightarrow \lambda = 4.17 \text{ \AA} \quad \therefore \theta = \sin^{-1} \left(\frac{4.17}{2 \times 3.31 / \sqrt{2}} \right) = 63.0^\circ$$

Data Reduction of Diffractometer Experiment: incident x-ray, $Ag_{K\alpha}$ for which $\lambda = 0.574 \text{ \AA}$

2θ	$\sin^2\theta$	normalize d	clear fractions	try again	hkl	$10^3 \frac{\sin^2\theta}{h^2+k^2+l^2}$
14.10	0.0151	1.00	1	2	110	7.550
19.98	0.0301	1.99	2	4	200	7.525
24.54	0.0452	2.99	3	6	211	7.533
28.41	0.0602	3.99	4	8	220	7.525
31.85	0.0753	4.99	5	10	310	7.530
34.98	0.0903	5.98	6	12	222	7.525
37.89	0.1054	6.98	7	14	321	7.529
40.61	0.1204	7.97	8	16	400	7.525

4. The longest wavelength capable of 1st order diffraction in Pt can be identified on the basis of the Bragg equation: $\lambda = 2d \sin \theta$. λ_{\max} will diffract on planes with maximum interplanar spacing (in compliance with the selection rules): {111} at the maximum value θ (90°); we determine a for Pt, and from it obtain $d_{\{111\}}$. Pt is FCC with a value of atomic volume or $V_{\text{molar}} = 9.1 \text{ cm}^3/\text{mole}$.

$$V_{\text{molar}} = \frac{N_{\text{Av}}}{4} a^3; a = \sqrt[3]{\frac{9.1 \times 10^{-6} \times 4}{N_{\text{Av}}}} = 3.92 \times 10^{-10} \text{ m}$$

If we now look at 2nd order diffraction we find $2\lambda = 2d_{\{111\}} \sin 90$

$$\therefore \lambda_{\max} = d_{\{111\}} = \frac{a}{\sqrt{3}} = \frac{3.92 \times 10^{-10}}{\sqrt{3}} = 2.26 \times 10^{-10} \text{ m}$$

5. We first determine the wavelength of particle waves (λ_p) required for diffraction and then the voltage to be applied to the electrons:

$$\lambda = 2d_{\{220\}} \sin \theta = 2 \frac{a}{\sqrt{8}} \sin 5$$

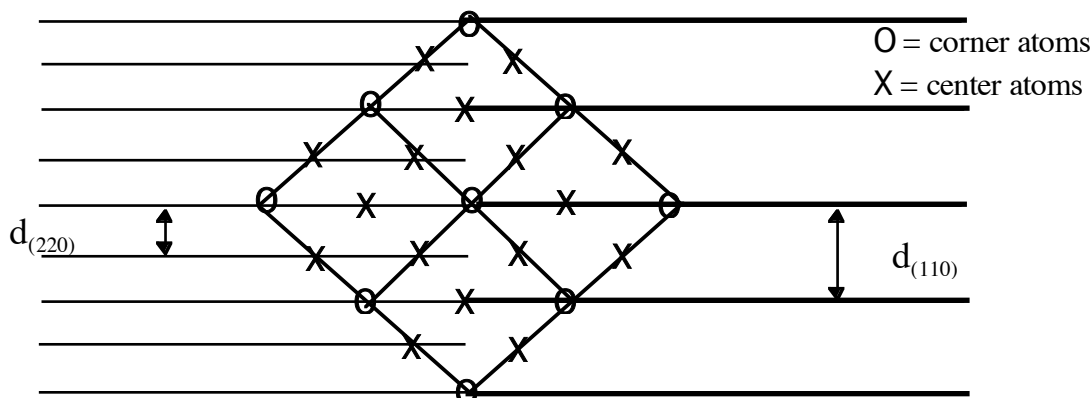
$$a_{\text{Au}} = \sqrt[3]{\frac{4 \times 10.2 \times 10^{-6}}{6.02 \times 10^{23}}} = 4.08 \times 10^{-10} \text{ m}$$

$$\lambda = \frac{2 \times 4.08 \times 10^{-10}}{\sqrt{8}} \sin 5 = \frac{4.08 \times 10^{-10}}{\sqrt{2}} \times 0.087 = 0.25 \times 10^{-10} \text{ m} = \lambda_p$$

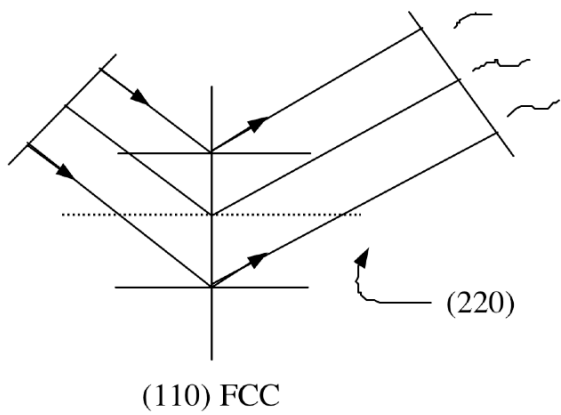
$$eV = \frac{mv^2}{2}, \quad \therefore v = \sqrt{2eV/m}$$

$$\lambda_p = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}, \quad \therefore V = \frac{h^2}{2\lambda^2 me} = 2415 \text{ V}$$

6. {110} planes of Pd cannot be used to isolate K_{α} radiation from the x-rays emitted by a tube with a Cu target. Pd has FCC structure and any reflection on {110} planes are destructively interfered with by corresponding {220} planes, composed of “center” atoms.



$$d_{\{220\}} = \frac{1}{2} d_{\{110\}}$$



Δx for $\{220\}$ reflections

$$= \frac{1}{2} \Delta x \text{ for } \{110\} \text{ reflections!!}$$