# Session #18: Homework Solutions

## Problem #1

(a) In a diffractometer experiment a specimen of thorium (Th) is irradiated with tungsten (W) $L_\alpha$ radiation. Calculate the angle, $\theta$, of the $4^{th}$ reflection.

(b) Suppose that the experiment described in part (a) is repeated but this time the incident beam consists of neutrons instead of x-rays. What must the neutron velocity be in order to produce reflections at the same angles as those produced by x-rays in part (a)?

## Solution

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

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

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

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

4th reflection in FCC: 111; 200; 220; **311** $\rightarrow h^2 + k^2 + l^2 = 11$

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

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

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

## Problem #2

A Debye-Scherrer powder diffraction experiment using incident copper (Cu) $K_\alpha$ radiation gave the following set of reflections expressed as $2\theta$ : 38.40°; 44.50°; 64.85°; 77.90°; 81.85°; 98.40°; 111.20°.

(a) Determine the crystal structure.

(b) Calculate the lattice constant, a.

(c) Assume that the crystal is a pure metal and on the basis of the hard-sphere approximation calculate the atomic radius.

(d) Calculate the density of this element which has an atomic weight of 66.6 g/mol.

**Solution**

Follow the procedure suggested in lecture:

(1) Start with $2\theta$ values and generate a set of $\sin^2\theta$ values.
(2) Normalize the $\sin^2\theta$ values by generating $\sin^2\theta_n/\sin^2\theta_1$.
(3) Clear fractions from the "normalized" column.
(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.
(5) Compute for each $\theta$ 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) $\frac{\lambda^2}{4a^2} = \frac{\sin^2\theta}{h^2+k^2+l^2} = 0.0358,$

$\lambda_{CuK_\alpha} = 1.5418$ Å, $\therefore$ $a = \frac{1.5418}{(4\times 0.0358)^{1/2}} = 4.07$ Å

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

(d) Here we'll use atomic mass and atomic volume.

$$\rho = \frac{m}{V}; \ \frac{4\text{ atoms}}{a^3} = \frac{N_A\text{ atoms}}{V_{molar}} \ \therefore \ V_{molar} = \frac{6.02\times 10^{23}}{4}\times(4.07\times 10^{-8}\text{ cm})^3 = 10.15\text{ cm}^3$$

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

**Data Reduction of Debye-Scherrer Experiment:**

| $2\theta$ | $\sin^2\theta$ | 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 |

**Problem #3**

The following diffractometer data (expressed as $2\theta$ ) were generated from a specimen irradiated with silver (Ag) $K_\alpha$ radiation: 14.10°; 19.98°; 24.57°; 28.41°; 31.85°; 34.98°; 37.89°; 40.61°.

(a) Determine the crystal structure.

(b) Calculate the lattice constant, a.

(c) Assume that the crystal is a pure metal and on the basis of the hard-sphere approximation calculate the atomic radius.

(d) At what angle $\theta$ would we find the first reflection if, instead of $K_\alpha$ radiation, we used silver $L_\alpha$ radiation to illuminate the specimen?

**Solution**

We follow the 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) $\frac{\lambda^2}{4a^2} = \frac{\sin^2\theta}{h^2+k^2+l^2} = 7.53\times10^{-3}$, $\lambda_{Ag_{K_\alpha}} = 0.574$ Å $\therefore$ $a = \frac{0.574}{\sqrt{4\times7.53\times10^{-3}}} = 3.31$ Å

(c) In BCC, $\sqrt{3}a = 4r$ $\therefore$ $r = \frac{\sqrt{3}}{4}\times3.31$ Å $=1.43$ Å

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

$\lambda_{L_\alpha}$ given by: $\bar{\nu} = \lambda^{-1} = \frac{5}{36}R(Z - 7.4)^2 = \frac{5}{36}\times1.1\times10^7(47 - 7.4)^2 = 2.40\times10^9\ m^{-1}$

$\rightarrow$ $\lambda = 4.17$ Å $\therefore$ $\theta = \sin^{-1}\left(\frac{4.17}{\sqrt{2}\times3.31}\right) = 63.0°$

**Data Reduction of Diffractometer Experiment**: incident x-ray $Ag_{K_\alpha}$ $\rightarrow$ $\lambda = 0.574$ Å

| $2\theta$ | $\sin^2\theta$ | 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 |

**Problem #4**

What is the maximum wavelength ($\lambda$) of radiation capable of second order diffraction in platinum (Pt)?

**Solution**

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

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

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

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

**Problem #5**

What acceleration potential V must be applied to electrons to cause electron diffraction on {220} planes of gold (Au) at $\theta = 5°$?

**Solution**

We first determine the wavelength of particle waves ($\lambda_p$) required for diffraction and then the voltage to be applied to the electrons:

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

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

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

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

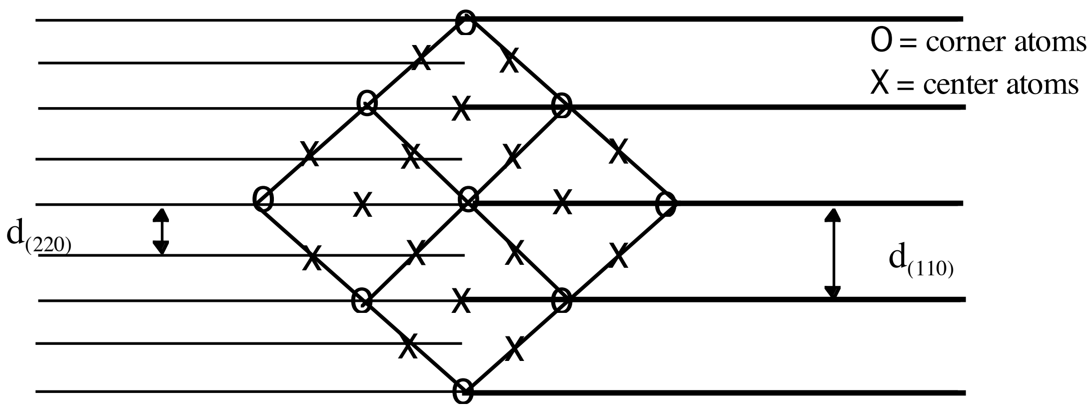
$$\lambda_P = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}, \quad \therefore\ V = \frac{h^2}{2\lambda^2 me} = 2415\ V$$

**Problem #6**

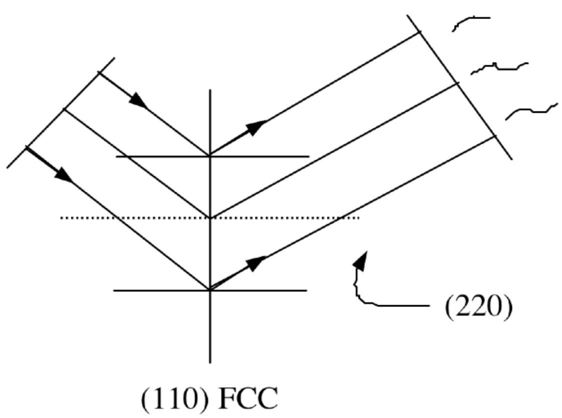
How can diffraction on {110} planes of palladium (Pd) be used to isolate $K_\alpha$ radiation from the "white" spectrum of x-rays emitted by an x-ray tube with a copper (Cu) target? Rationalize your answer and provide an appropriate schematic drawing.

**Solution**

{110} planes of Pd cannot be used to isolate $K_\alpha$ 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.




$$d_{\{220\}} = \frac{1}{2} d_{\{110\}} \rightarrow \Delta x \text{ for } \{220\} \text{ reflections} = \frac{1}{2} \Delta x \text{ for } \{110\} \text{ reflections}$$



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