3.091 Fall Term 2002

Homework #7

Solutions

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

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

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

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

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

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

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

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

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

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) $\frac{\lambda^2}{4a^2} = \frac{\sin^2\theta}{h^2 + k^2 + l^2} = 0.0358$, $\lambda_{CuK\alpha} = 1.5418$ 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) $\rho = \frac{m}{V}$ Here we'll use atomic mass and atomic volume.

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

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

Data Reduction of Debye-Scherrer Experiment:

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

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

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

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

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

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

Data Reduction of Diffractometer Experiment: incident x-ray, Ag_{K_α} for which $\lambda = 0.574$ Å

2θ	$\sin^2\theta$	normalized	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 $V_{molar} = 9.1\text{ cm}^3/\text{mole}$.

$$V_{molar} = \frac{N_{Av}}{4} a^3 \; ; \; a = \sqrt[3]{\frac{9.1\times10^{-6}\times4}{N_{Av}}} = 3.92 \times 10^{-10}\text{ m}$$

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

$$\therefore \lambda_{max} = d_{(111)} = \frac{a}{\sqrt{3}} = \frac{3.92\times10^{-10}}{\sqrt{3}} = 2.26\times10^{-10}\text{ m}$$

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

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

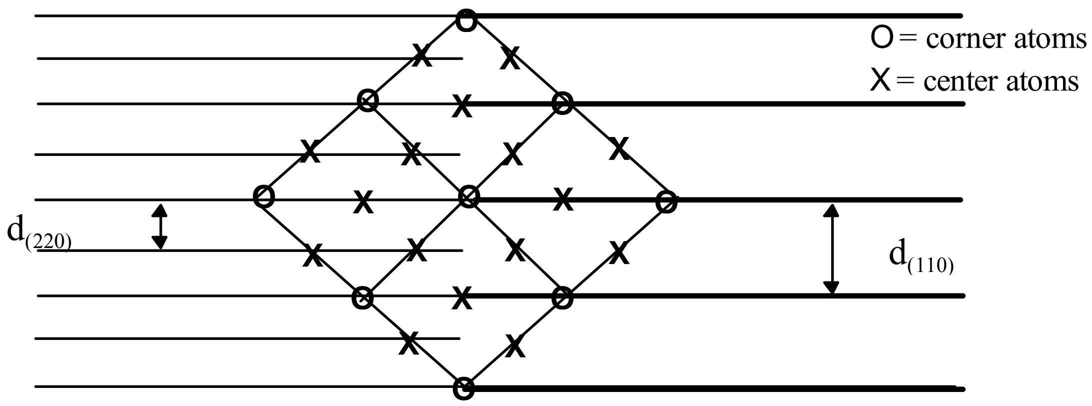
$$a_{Au} = \sqrt[3]{\frac{4\times10.2\times10^{-6}}{6.02\times10^{23}}} = 4.08\times10^{-10}\text{ m}$$

$$\lambda = \frac{2\times4.08\times10^{-10}}{\sqrt{8}}\sin 5 = \frac{4.08\times10^{-10}}{\sqrt{2}}\times0.087 = 0.25\times10^{-10}\text{ m} = \lambda_p$$

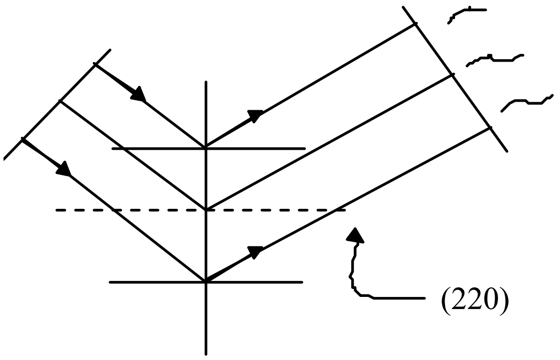
$$eV = \frac{mv^2}{2}, \qquad \therefore v = \sqrt{2eV/m}$$

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

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.



$$d_{(220)} = \frac{1}{2}\, d_{(110)}$$



(110) FCC

Δx for {220} reflections

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

7. $n_V/N = 3.091 \times 10^{-5}$ at 1234°C = 1507 K

$= 5.26 \times 10^{-3}$ at mp = 2716 K

$$\frac{n_V}{N} = A \exp\left(-\frac{\Delta H_V}{RT}\right)$$

$$3.091 \times 10^{-5} = A \exp -\frac{\Delta H_V}{1507\,R} \qquad (1)$$

$$5.26 \times 10^{-3} = A \exp -\frac{\Delta H_V}{2716\,R} \qquad (2)$$

$$(1)/(2) = 5.876 \times 10^{-3} = \exp\left(-\frac{\Delta H_V}{1507\ \ R} + \frac{\Delta H_V}{2716\ \ R}\right)$$

Taking the logarithm of both sides gives

$$-5.137 = \frac{\Delta H_V}{R}\left(-\frac{1}{1507} + \frac{1}{2716}\right) = -2.954 \times 10^{-4}\,\frac{\Delta H_V}{R} \Rightarrow \Delta H_V = 1.497 \times 10^{5}\ \text{J/mol}$$

2θ	**$\sin^2\theta$**	**normalized**	**clear fractions**	**(hkl)?**	$\frac{\sin^2\theta}{h^2+k^2+l^2}$
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8. All we need to know is the temperature dependence of the vacancy density:

$\frac{n_v}{N} = Ae^{-\frac{\Delta H_v}{RT}}$ where T is in Kelvins and the m.p. of Al is 660ºC

$\frac{0.08}{100} = Ae^{-\Delta H_v/RT_1}$, where $T_1 = 923K$; $\frac{0.01}{100} = Ae^{-\Delta H_v/RT_2}$, where $T_2 = 757K$

Taking the ratio:

$$\frac{8\times10^{-4}}{1\times10^{-4}} = \frac{Ae^{-\Delta H_v/RT_1}}{Ae^{-\Delta H_v/RT_2}} = e^{-\frac{\Delta H_v}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} \qquad \therefore \ln 8 = -\frac{\Delta H_v}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$\therefore \Delta H_v = -\frac{R\times\ln 8}{\frac{1}{923}-\frac{1}{757}} = -\frac{8.314\times\ln 8}{\frac{1}{923}+\frac{1}{757}} = 7.28\times10^4 \text{ J/mole vac}$$

$$\therefore \Delta H_v = \frac{7.28\times10^4}{6.02\times10^{23}} = 1.21\times10^{-19} \text{ J/vac} = 0.755 \text{ eV/vac}$$

9.(a) We need to know the temperature dependence of the vacancy density:

$$\frac{1}{10^4} = Ae^{-\frac{\Delta H_v}{kT_1}} \quad \text{and} \quad \frac{1}{10^3} = Ae^{-\frac{\Delta H_v}{kT_x}}$$

From the ratio: $\frac{\frac{1}{10^4}}{\frac{1}{10^3}} = \frac{10^3}{10^4} = \frac{Ae^{-\Delta H_v/kT_1}}{Ae^{-\Delta H_v/kT_x}}$ we get $-\ln 10 = -\frac{\Delta H_v}{k}\left(\frac{1}{T_1}-\frac{1}{T_x}\right)$

$$\therefore \left(\frac{1}{T_1}-\frac{1}{T_x}\right) = \frac{k\ln 10}{\Delta H_v}$$

$$\frac{1}{T_x} = \frac{1}{T_1} - \frac{k\ln 10}{\Delta H_v} = \frac{1}{1073} - \frac{1.38\times10^{-23}\times\ln 10}{2\times1.6\times10^{-19}} = 8.33\times10^{-4}$$

$T_x = 1200$ K = 928°C

(b) repeat the calculation following the method given above but with $\Delta H_v = 1.0$ eV to find that T_x = 1364 K = 1091ºC

NOTE: the change in ΔH_v from 2.0 eV to 1.0 eV resulted in a change in ΔT from 128 K to 291 K.

10. Cu is FCC; example: $(111)\ [10\bar{1}]$; $(111)\ [\bar{1}01]$; $(\overline{111})\ [0\bar{1}1]$; $(\bar{1}1\bar{1})\ [\bar{1}01]$

11.

Defect	Type	Improved Materials Properties	Adversely Affected Materials Properties
	Vacancy f(T)	– diffusivity	– electron mobility

		– color centers – ionic conductivity	– carrier lifetime
Point Defect	Substitutional	– conductivity (dopant) – strength (hardness) – characteristic T (like T_M)	– conductivity (impurities) – ductility – characteristic T
	Interstitial	– strength – characteristic T – electrical properties	– ductility – characteristic T – electrical properties
Line Defect	Dislocation	– ductility (malleability) – strength (at high dislocation density)	– strength – yield stress – optical properties – lasing action
Planar Defect	Grain Boundaries	– strength	– creep resistance – electrical properties – magnetic properties

12. $\frac{n_v}{N} = A \exp - \frac{\Delta H_v}{k_B T}$, $\Delta H_v = 1.5\, eV$ $\frac{n_v}{N} = \frac{1}{10^6}$ at 888°C

need first to solve for value of A -- use data at 888°C

$$A = \frac{\frac{n_v}{N}}{\exp - \frac{\Delta H_v}{k_B T}} = \frac{10^{-6}}{\exp - \frac{1.5 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times (888 + 273)}} = 3.203$$

calculate $\frac{n_v}{N}$ at m.p. of Pd, 1825K

$$\therefore \frac{n_v}{N} = 3.203 \times \exp\left(- \frac{1.5 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 1825} \right) = 2.328 \times 10^{-4} < 10^{-3}$$

$\therefore$ it is **not** possible to achieve a vacancy fraction of 10^{-3} by simply raising temperature.