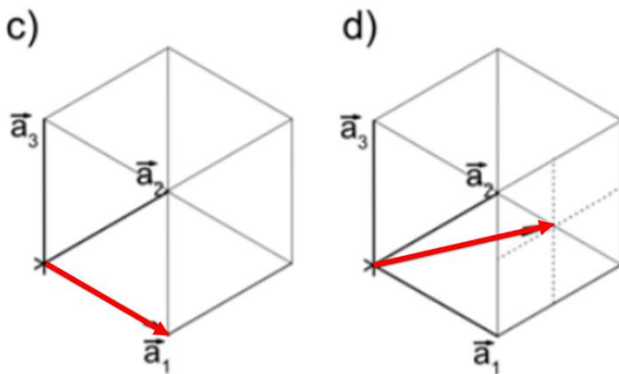


Assignment 2 Solutions:

Solution 1

For cubic systems

- a) We can see that the end of the vector is located at $\frac{1}{2}a_1 + 1a_2 + \frac{1}{4}a_3$.
- b) We can convert this to a crystallographic direction by multiplying through by 4 to get rid of the fractions while preserving the ratios.
The direction shown in a) is therefore [241].
- c) the end of the vector is located at $1a_2 + 1a_3$, which is represented as [011].
- c, d) Finally, the [100] (overlapping with a_1 axis) and [211] directions are shown below:



For hexagonal systems

Determine 3-axis system [xyz] and then convert to 4-index [uvw] system where

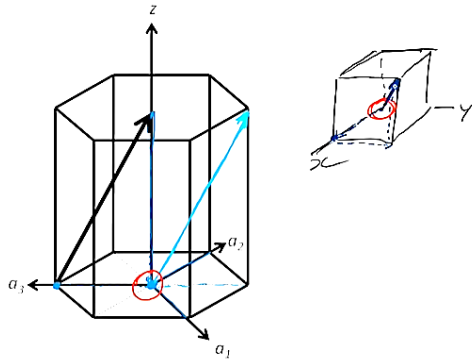
$$u = \frac{1}{3}(2x - y)$$

$$v = \frac{1}{3}(2y - x)$$

$$t = -(x + y)$$

$$w = z$$

- a) First translate the vector to origin, (or translate the origin).



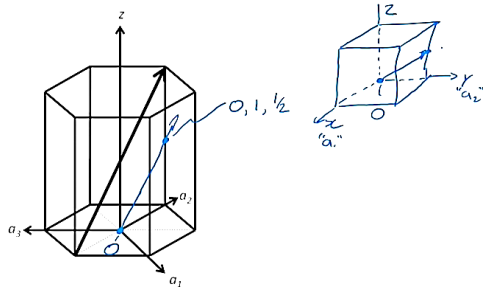
Now, $[xyz] = [111]$

Then,

$$u = \frac{1}{3}, v = \frac{1}{3}, t = -\frac{2}{3}, w = 1$$

$$[uvtw] = [11\bar{2}3]$$

First translate the vector to origin, (or translate the origin).



Now, $[xyz] = [021]$

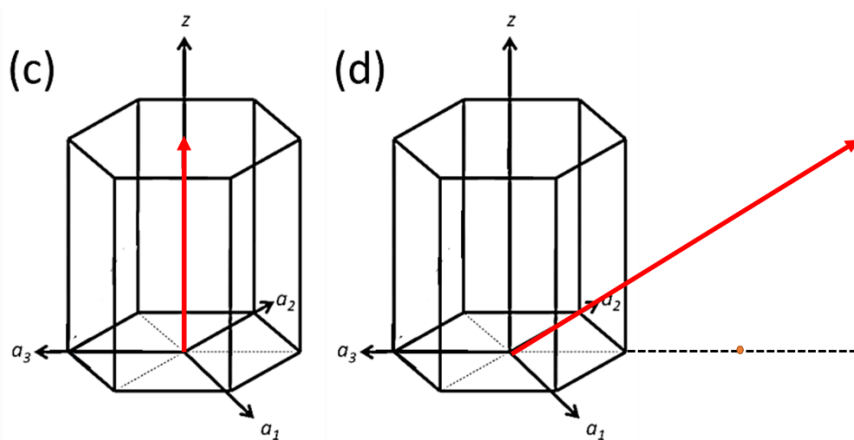
Then,

$$u = -\frac{2}{3}, v = \frac{4}{3}, t = -\frac{2}{3}, w = 1$$

$$[uvtw] = [\bar{2}4\bar{2}3]$$

c, d) $[0001]$, $[11\bar{2}1]$ directions are shown below.

Same can be achieved by converting into 3-axis system and then plotting.



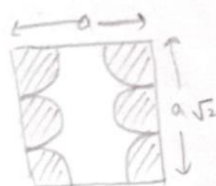
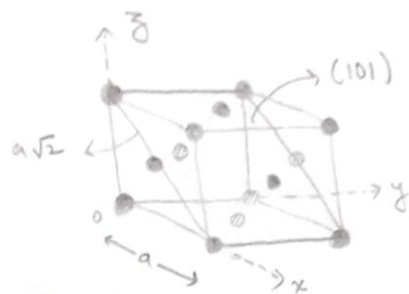
Solution 2

- (i) $n\lambda = 2d\sin\theta$
 $n = 1, \theta = 14.35^\circ, \lambda = 0.071\text{nm}$
 $h^2 + k^2 + l^2 = 8$ is possible only for $(hkl) = (220)$
 $d = n\lambda/2\sin\theta$
 $d = 0.071/2\sin(14.35^\circ) = 0.071/0.4957 = 0.1432\text{ nm}$

 $d = a/(\sqrt{h^2+k^2+l^2})$
 $a = 0.1432*(2.828) = 0.405\text{ nm} = 0.405*(10^{-9})\text{ m}$
- (ii) Reflections for smaller angle means large d and larger d means smaller $h^2+k^2+l^2$
 (hkl) smaller than (220) are (200) - all even and (111) - all odd
This means that the structure is FCC.
- (iii) Forbidden reflection for FCC is mixed odd and even.

Solution 3

Ans 3
(i)



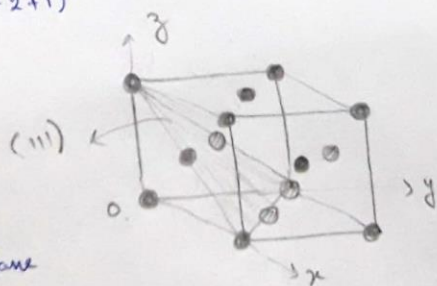
→ for correctly drawing plane
(2 marks)

Plane has $\frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{2} + \frac{1}{2}$
atoms = 2 atoms. (2 marks)

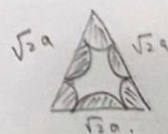
Area of plane = $a(a\sqrt{2}) = \sqrt{2}a^2$ (2 marks)

→ for correctly calculated
p. density (5 marks).
(2+2+1)

∴ planar density = $\frac{2}{\sqrt{2}a^2} = \frac{\sqrt{2}}{a^2}$ atoms/nm²
(1 mark) where 'a' is in nm



→ 2 marks for plane



atoms = $\frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{2} + \frac{1}{2}$
= 2 atoms. (2 marks)

→ 5 for p. density.
(2+2+1)

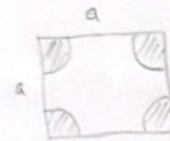
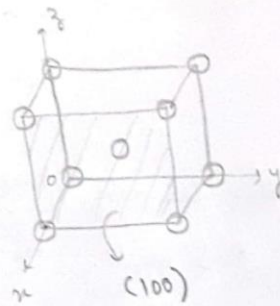
area of plane = $\frac{\sqrt{3}}{4}(\sqrt{2}a)^2 = \frac{\sqrt{3}}{2}a^2$
(2 marks)

$$\Rightarrow \text{planar density} = \frac{2}{\sqrt{3}/2 a^2} = \frac{4}{\sqrt{3} a^2} \frac{\text{atoms}}{\text{nm}^2}$$

(if 'a' is in nm).

(1 mark).

Ans 3
(ii)



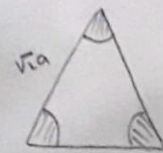
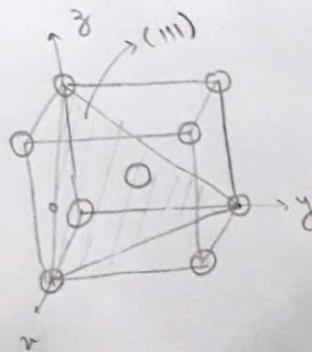
$$\text{no. of atoms} = \frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4}$$

$$= 1$$

$$\text{area} = a^2$$

$$\text{planar density} = \frac{1}{a^2} \frac{\text{atoms}}{\text{nm}^2}$$

(if 'a' is in nm).



$$\text{no. of atoms} = \frac{1}{6} + \frac{1}{6} + \frac{1}{6} = \frac{1}{2}$$

$$\text{area} = \frac{\sqrt{3}}{4} (\sqrt{3}a)^2 = \frac{\sqrt{3}}{2} a^2$$

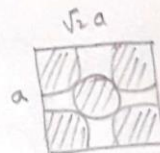
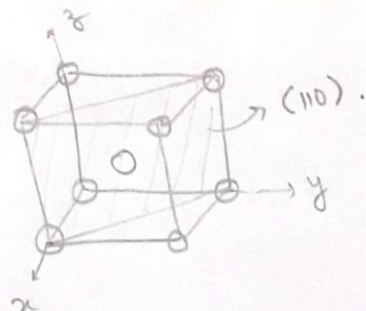
$$\text{Planar density} = \frac{1/2}{\sqrt{3}/2 a^2} = \frac{1}{\sqrt{3} a^2} \frac{\text{atoms}}{\text{nm}^2}$$

(if 'a' is in nm).

→ Follow marking scheme as in previous part.

Previous

3 (iii). α -Fe is BCC \rightarrow (0.5 marks).



marks

\rightarrow for correctly drawing BCC unit cell \rightarrow 0.5 marks.

\rightarrow for correctly drawing plane \rightarrow 1 mark.

$$\text{no. of atoms} = 2 \quad (0.5)$$

$$\text{area} = \sqrt{2} a^2 \quad (0.5)$$

$$\begin{aligned} \text{Planar density} &= \frac{2}{\sqrt{2} a^2} \\ &= \frac{\sqrt{2}}{a^2} \text{ atoms/nm}^2 \end{aligned}$$

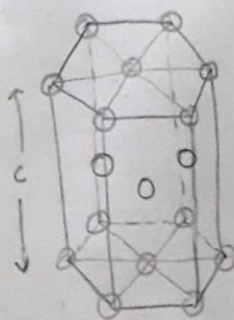
(0.5)

$$\text{for } a = 0.287 \text{ nm}$$

$$\text{Planar density} = \frac{\sqrt{2}}{(0.287)^2} = 17.169 \text{ atoms/nm}^2$$

(1.5 marks).

Ans 4



(1 mark for drawing).

$$\text{i) effective no. of atoms per unit HCP cell} = \left(12 \times \frac{1}{6}\right) + \left(2 \times \frac{1}{2}\right) +$$

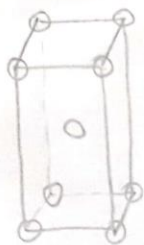
(3 marks for answer)

$$(3 \times 1) = 2 + 1 + 3$$

$$= 6$$

→ If someone hasn't explained & simply written answer - deduct 1 mark for that.

4 ii).



(1 mark for drawing & showing parallelepiped unit cell)

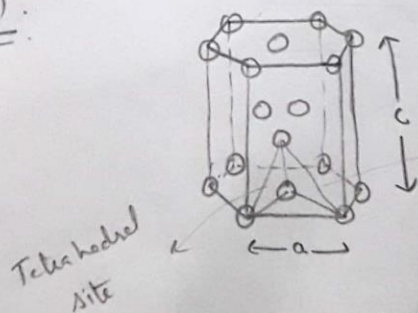
↓
Hexagonal primitive cell is $\frac{1}{3}$ of prism, containing 8 corner atoms & 1 atom inside cell

i effective no. of atoms in parallelepiped unit

cell of HCP = $6 \times \frac{1}{3} = \underline{2}$. (2 marks for right answer)

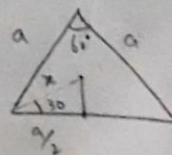
→ if explanation missing → deduct 1 mark.

4(iii):



$$\Rightarrow h^2 + x^2 = a^2 \quad \text{--- (i)}$$

where $h = \frac{c}{2}$.



$$\cos 30^\circ = \frac{a/2}{x}$$

$$x = \frac{a/2}{\sqrt{3}/2}$$

$$x = \frac{a}{\sqrt{3}}$$

from equation (i)

$$\Rightarrow \left(\frac{c}{2}\right)^2 + \left(\frac{a}{\sqrt{3}}\right)^2 = a^2$$

$$\frac{c^2}{4} + \frac{a^2}{3} = a^2$$

$$\frac{c^2}{4} = \frac{2}{3} a^2$$

$$\frac{c^2}{a^2} = \frac{8}{3}$$

$$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633.$$

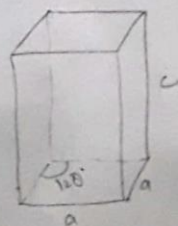
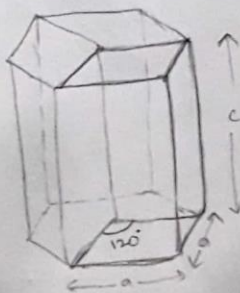
→ 5 marks for the complete answer.

4) iv). atomic packing fraction of HCP crystal =

$$\frac{\text{volume of atoms per unit cell}}{\text{volume of unit cell}}$$

→ no. of atoms in parallelepiped = 2 (as calculated earlier).

→ Volume of parallelepiped



$$\text{volume} = a \times a \times \sin(120) \times c$$

$$= a^2 \cdot \frac{\sqrt{3}}{2} \cdot c$$

$$= a^2 \cdot \frac{\sqrt{3}}{2} \cdot \sqrt{\frac{8}{3}} a = \sqrt{2} a^3$$

here $\gamma = \frac{9}{2}$

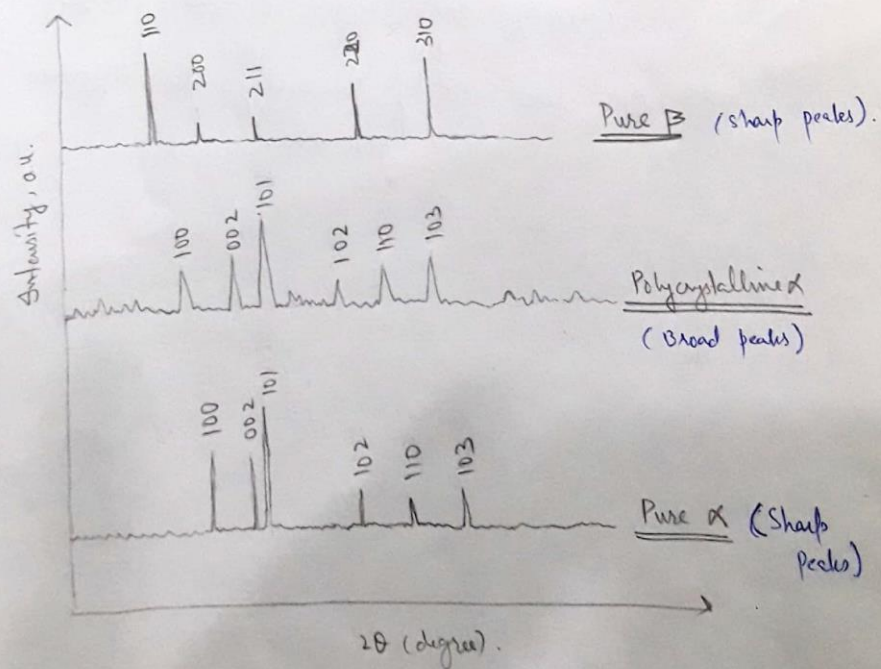
$$\therefore \text{Volume} = \sqrt{2} a^3 = \sqrt{2} (8\gamma^3) = 8\sqrt{2} \gamma^3$$

$$\therefore \text{packing fraction} = \frac{2 \times \frac{4}{3} \pi \gamma^3}{8\sqrt{2} \gamma^3} = \frac{\pi}{\sqrt{2} \cdot 3} = \underline{\underline{0.74}}$$

→ 3 marks for the question.

Note: Students may have calculated it differently. That is fine as long as they are doing it correctly.

Ans 6:

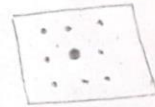


→ Polycrystalline material gives ring patterns while single crystal samples yield 2-D array of spots.



Polycrystalline

In XRD Sharp peaks for single crystal are seen while as in polycrystalline broader peaks are there.



Single crystal

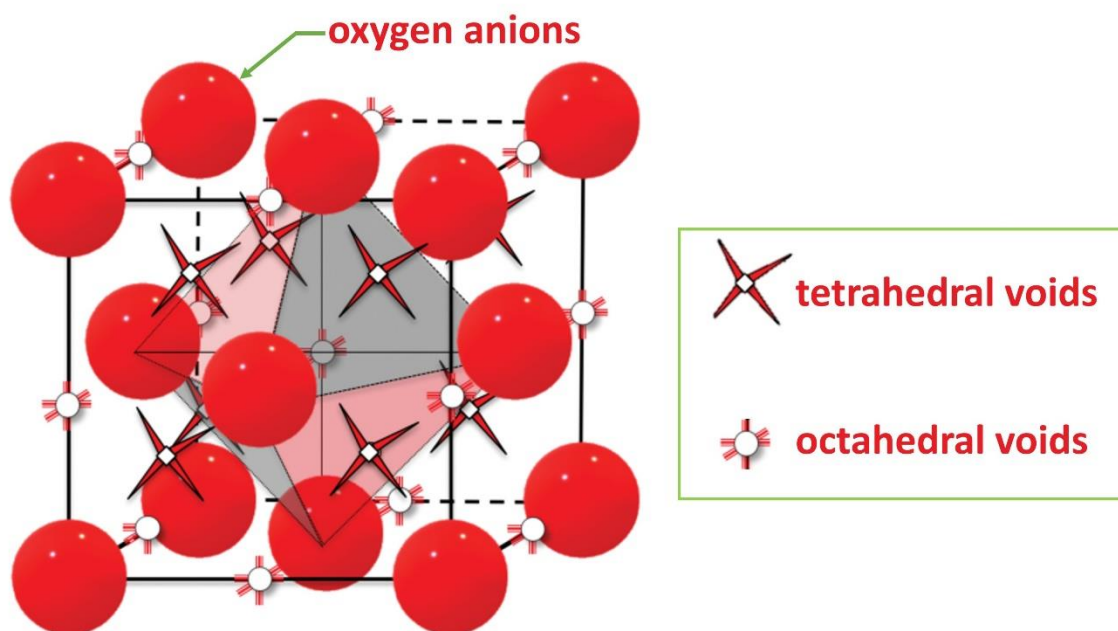
→ α -Ti is HCP while β -Ti is BCC, so they will have different peaks in XRD.

⇒ ~~0 marks~~ 1.5 marks for drawing correctly XRD pattern & indexing correctly each type (total 4.5).

⇒ 0.5 for correctly highlighting the difference b/w polycrystalline & single crystal specimens.

Solution 5

In a cubic closed packing arrangement (CCP) of oxygen anions, we have



(a) No. of tetrahedral sites/unit cell = $1 \times 8 = 8$

No. of octahedral sites/unit cell = $\left(\frac{1}{4} \times 12 \text{ edge centres}\right) + (1 \times 1 \text{ body centre}) = 4$

(b) In a CCP arrangement of atoms, the number of octahedral sites is always equal to the number of atoms, while the number of tetrahedral sites is always double the number of atoms.

Here, the oxygen anions are in CCP arrangement. Thus the effective number of

oxygen ions/unit cell = $\left(\frac{1}{2} \times 6 \text{ face centres}\right) + \left(\frac{1}{8} \times 8 \text{ cube corners}\right) = 4$

Therefore, the ratio of (octahedral sites : oxygen ions) = $4:4 \equiv 1:1$

and, the ratio of (tetrahedral sites : oxygen ions) = $8:4 \equiv 2:1$

(c) If one-half of the octahedral sites are filled with A,

then effective number of A/unit cell = $\left(\frac{1}{2} \times 4 \text{ octahedral voids}\right) = 2$

and since we already have 4 oxygen/unit cell, the stoichiometry of the oxide would be of the type $A_2O_4 \equiv AO_2$

If two-thirds of the octahedral sites are filled with A,

$$\text{then effective number of A/unit cell} = \left(\frac{2}{3} \times 4 \text{ octahedral voids}\right) = \frac{8}{3}$$

which is not a whole number. Hence, filling two-thirds of octahedral sites in a CCP arrangement is not possible.

[**Hint:** The $2/3^{\text{rd}}$ occupancy in octahedral sites is only possible with hexagonal close-packed systems]

If all of the octahedral sites are filled with A,

$$\text{then effective number of A/unit cell} = (1 \times 4 \text{ octahedral voids}) = 4$$

and since we already have 4 oxygen/unit cell, the stoichiometry of the oxide would be of the type $A_4O_4 \equiv AO$

(d) The coordinates of all the tetrahedral sites are:

$$\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right) \left(\frac{3}{4}, \frac{1}{4}, \frac{1}{4}\right) \left(\frac{1}{4}, \frac{3}{4}, \frac{1}{4}\right) \left(\frac{3}{4}, \frac{3}{4}, \frac{1}{4}\right) \left(\frac{1}{4}, \frac{1}{4}, \frac{3}{4}\right) \left(\frac{3}{4}, \frac{1}{4}, \frac{3}{4}\right) \left(\frac{1}{4}, \frac{3}{4}, \frac{3}{4}\right) \left(\frac{3}{4}, \frac{3}{4}, \frac{3}{4}\right)$$

Assuming a cation 'M' to be filled into the tetrahedral sites. Filling all the tetrahedral sites, we have then

$$\text{effective number of M/unit cell} = (1 \times 8 \text{ tetrahedral voids}) = 8$$

and since we already have 4 oxygen/unit cell, the stoichiometry of the oxide would be of the type $M_8O_4 \equiv M_2O$ (**Antifluorite structure**)

In order to preserve the charge neutrality, the effective charge of the crystal should be nullified. Hence, $2x + 1(-2) = 0 \Rightarrow x = +1$

Therefore, the cation M has to be monovalent, e.g. Li^+ , Na^+ , K^+ , Rb^+

(e) The coordinates of all the octahedral sites are:

$$\begin{aligned} &\left(\frac{1}{2}, 0, 0\right) \left(0, \frac{1}{2}, 0\right) \left(1, \frac{1}{2}, 0\right) \left(\frac{1}{2}, 1, 0\right) \\ &\left(\frac{1}{2}, 0, 1\right) \left(0, \frac{1}{2}, 1\right) \left(1, \frac{1}{2}, 1\right) \left(\frac{1}{2}, 1, 1\right) \\ &\left(0, 0, \frac{1}{2}\right) \left(0, 1, \frac{1}{2}\right) \left(1, 0, \frac{1}{2}\right) \left(1, 1, \frac{1}{2}\right) \text{ AND } \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right) \end{aligned}$$

Assuming a cation 'M' to be filled into the octahedral sites. Filling all the octahedral sites, we have then

$$\text{effective number of M/unit cell} = (1 \times 4 \text{ octahedral voids}) = 4$$

and since we already have 4 oxygen/unit cell, the stoichiometry of the oxide would be of the type $\text{M}_4\text{O}_4 \equiv \text{MO}$ (**Rock salt structure**)

In order to preserve the charge neutrality, the effective charge of the crystal should be nullified. Hence, $1(x) + 1(-2) = 0 \Rightarrow x = +2$

Therefore, the cation M has to be divalent, e.g. Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}