1. (a). Upon forming Schottky defects, atoms (ions) move out of its original place, forming vacancy (out of the interior ~~of~~ to the surface of a crystal). Therefore there are less number of atoms consisting the crystal so that the crystal becomes less dense upon Schottky defect.

(b), simply, V_{Ca}'' ($\because Ca^{2+}$) and $V_F^{\bullet}$ ($\because F^-$) so that for Schottky pair, reaction is.

$$\underline{\text{null} \rightleftarrows V_{Ca}'' + 2V_F^{\bullet}}$$

(c) (b) Excess holes. – At $M_{1-x}S$ (metal deficient) state, Usually S (non-metallic) is missing number of electrons compared to M (Metals). Therefore, there are missing (less) electrons compared to positive charge that the nucleus have. Therefore, it is (can be thought as) <u>excess holes</u>

(d) $Sn^{2+}Ti^{4+}O_3^{2-}$, $h^{\bullet}$, e' → localized to Ti atom.

① Oxygen vacancy : $V_O^{\bullet\bullet}$

② Anti-site : Ti_{Sr}'' and $Sr_{Ti}^{\bullet\bullet}$

③ Hole on Ti site : $Ti_{Ti}^{\bullet}$

④ Substitute Ti^{4+} with Fe^{3+} : Fe_{Ti}'

⑤ 〃 Ti^{4+} 〃 Nb^{5+} : $Nb_{Ti}^{\bullet}$

2. (a) We already know that

$$Y_2O_3 \rightleftarrows 2Y_{Zr}' + 3O_O^{\times} + V_O^{\bullet\bullet} \quad (1)$$

also it is straight forward to have

$$\text{null} \rightleftarrows 2V_O^{\bullet\bullet} + O_2 + 4Zr_{Zr}' \quad (2)$$

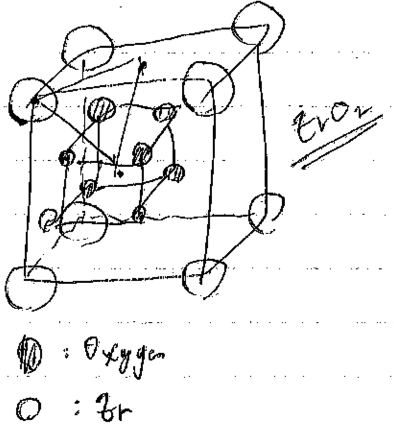
→ answer

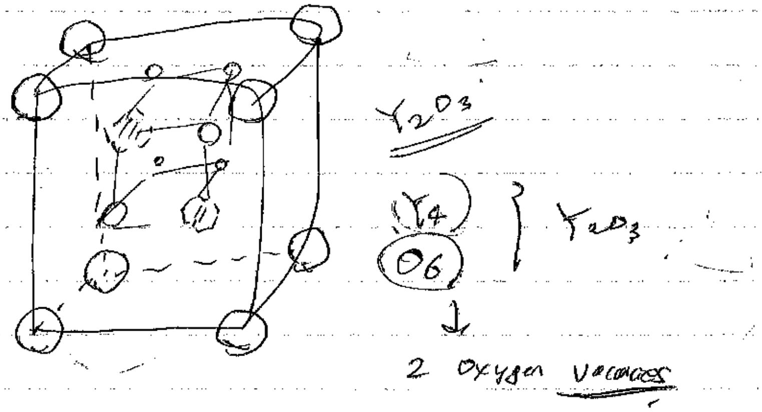
$$\Rightarrow 4Zr_{Zr}^{\times} + 2O_O^{\times} \rightleftarrows 2V_O^{\bullet\bullet} + O_2 + 4Zr_{Zr}'$$

Combining (1) and (2),

$$Y_2O_3 \rightleftarrows 2Y_{Zr}' + 3O_O^{\times} + 3V_O^{\bullet\bullet} + O_2(g) + 4Zr_{Zr}'.$$

satisfies charge neutrality.





(b) $G = 1500\,kJ/mol \quad (T = 1000K)$

$$\Delta H - T\Delta S = \Delta G \Rightarrow \Delta G = -RT\ln K \Rightarrow K = \exp\left(\frac{-\Delta G}{RT}\right)$$

$$\Rightarrow K = \frac{pO_2 \cdot [V_O^{\bullet\bullet}]^2 \cdot [Zr_{Zr}']^4}{[O_O^{\times}]^2 \, (Zr_{Zr}^{\times})^4} \quad (3)$$

Also, from $Y_{0.2}Zr_{0.8}O_{1.9-\delta}$. must be balanced in charge,

$$\Rightarrow 0.2\cdot 3 + 0.8\cdot 4 + (1.9-\delta)(-2) \rightarrow \boxed{\delta = 0}$$

$R = 8.314 \cdot J/mol\cdot K.$
$= 8.314\cdot 10^{-3}\ kJ/mol\cdot K.$

0.2 mol Y
0.8 mol Zr
1.9 mol $O_O^{\times}$
0.1 mol $V_O^{\bullet\bullet}$

$$\Rightarrow K = \frac{pO_2 \cdot (0.1)^2 \cdot (0.1)^4}{1.9^2 \cdot \underbrace{0.7^4}_{=(0.8-0.1)}}$$

$$\Rightarrow pO_2 = \underline{3.83 \cdot 10^{-73}}, \rightarrow \text{very low compared to } 10^{-30}$$

3. a) ① $V_O^{\bullet\bullet}$ and Ti_{Ti}' pair.

start from $\underline{2Ti_{Ti}^{\times} + O_O^{\times} \rightleftarrows \frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2Ti_{Ti}'}$ — (1)

② O_i'' and. $Ti_{Ti}^{\bullet}$ pair.

start from.

$Ti_{Ti}^{\times} + \frac{1}{2}O_2 \rightleftarrows O_i'' + Ti_{Ti}^{\bullet}$ to match charge, (∵ charge neutrality)

⇒ $\underline{2Ti_{Ti}^{\times} + \frac{1}{2}O_2(g) \rightleftarrows O_i'' + 2Ti_{Ti}^{\bullet}}$ —— (2)

③ V_{Ti}'''' and. $Ti_{Ti}^{\bullet}$ pair..

$4Ti_{Ti}^{\times} \rightleftarrows 4Ti_{Ti}'$

⇒ $2V_O^{\bullet\bullet} + 4Ti_{Ti}^{\times} + O_2 \rightleftarrows 4Ti_{Ti}^{\bullet} + 2O_O^{\times}$

but we know that

null $\rightleftarrows V_{Ti}'''' + 2V_O^{\bullet\bullet}$ so we add on both sides.

⇒ $\underline{V_{Ti}'''' + 2V_O^{\bullet\bullet} + 4Ti_{Ti}^{\times} + O_2(g) \rightleftarrows V_{Ti}'''' + 4Ti_{Ti}^{\bullet} + 2O_O^{\times}}$ —— (3)

④ $Ti_I^{\bullet\bullet\bullet\bullet}$ and Ti_{Ti}' pair.

$Ti_{Ti}^{\times} + (\;) \rightleftarrows Ti_I^{\bullet\bullet\bullet\bullet} + 4Ti_{Ti}' + V_{Ti}''''$

⇒ $Ti_{Ti}^{\times} + 2O_O^{\times} \rightleftarrows Ti_I^{\bullet\bullet\bullet\bullet} + 4Ti_{Ti}' + V_{Ti}'''' + 2V_O^{\bullet\bullet} + O_2(g)$.

⇒ $\underline{5Ti_{Ti}^{\times} + 2O_O^{\times} \rightleftarrows Ti_I^{\bullet\bullet\bullet\bullet} + 4Ti_{Ti}' + V_{Ti}'''' + 2V_O^{\bullet\bullet} + O_2(g)}$. — (4)

We have two more equations

$2Ti_{Ti}^{\times} \rightleftarrows Ti_{Ti}^{\bullet} + Ti_{Ti}'$ —— (5)

null $\rightleftarrows V_{Ti}'''' + 2V_O^{\bullet\bullet}$ — (6).

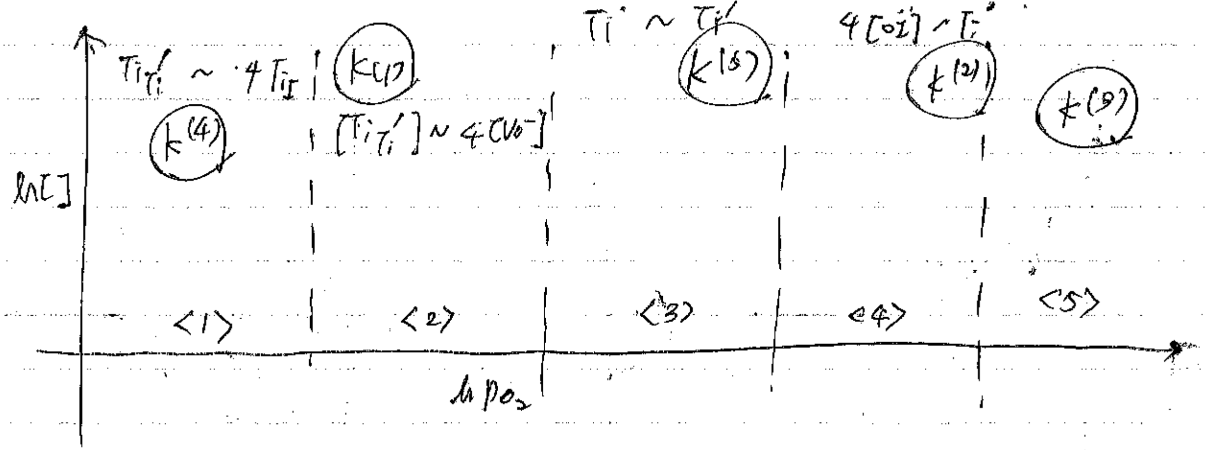
3. b) $K^{(1)} = [pO_2]^{1/2} [V_O^{\bullet\bullet}] \cdot [Ti_{Ti}']^2$

$$k^{(2)} = \frac{[O_I''] [Ti_{Ti}^{\bullet}]^2}{[pO_2]^{1/2}}$$

$$k^{(3)} = \frac{[Ti_{Ti}^{\bullet}]^4 \cdot \cancel{[O_O^X]^2} \cdot \cancel{[V_{Ti}'''']}}{[PO_2] \cdot [V_O^{\bullet\bullet}]^2 \cancel{[V_{Ti}'''']}} - \frac{[Ti_{Ti}^{\bullet}]^4}{[pO_2] [V_O^{\bullet\bullet}]^2}$$

$$k^{(4)} = [Ti_I^{\bullet\bullet\bullet\bullet}] [Ti_{Ti}']^4 [V_{Ti}''''] [V_O^{\bullet\bullet}]^2 [pO_2].$$

$$k^{(5)} = [Ti_{Ti}^{\bullet}] [Ti_{Ti}']$$



In <1> $k^{(4)}$ dominates. $[Ti_{Ti}'] \sim [pO_2]^{-1/5}$

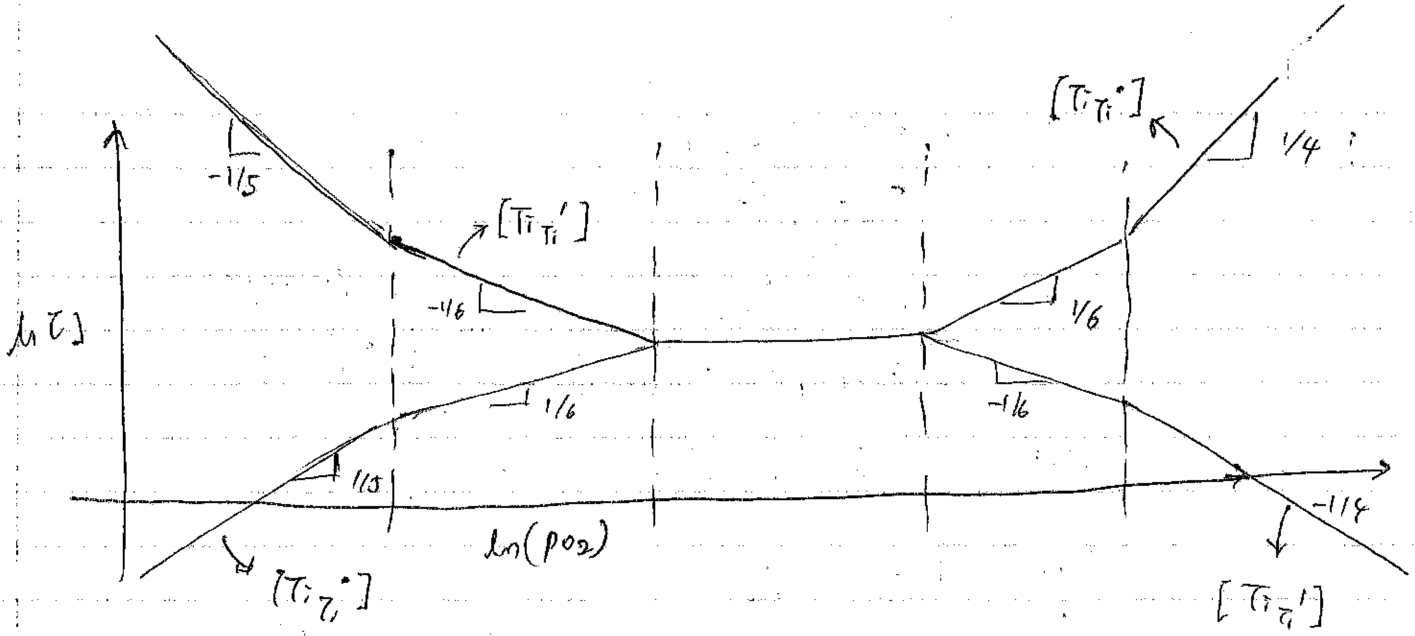
In <2>, $k^{(1)}$ " $\Rightarrow K^{(1)} = [pO_2]^{1/2} \cdot \frac{1}{4} [Ti_{Ti}']^3.$

$\Rightarrow \underline{[Ti_{Ti}'] \sim [pO_2]^{-1/6}}.$

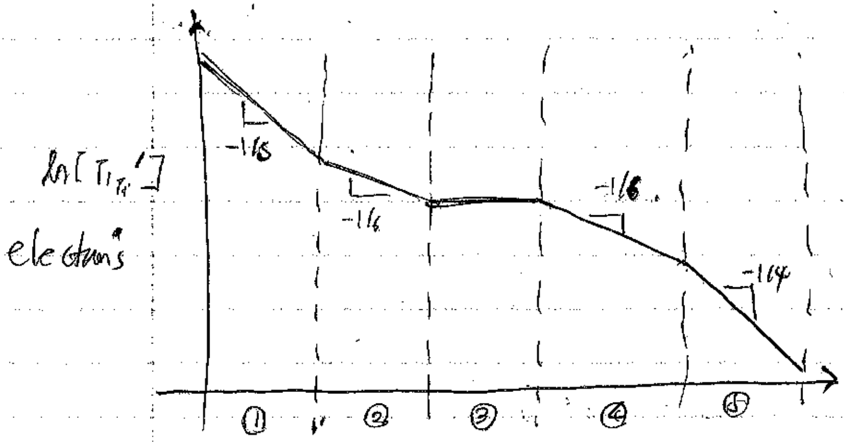
In <3>, $[Ti_{Ti}'] \approx [Ti_{Ti}^{\bullet}] = \sqrt{k^{(5)}}$

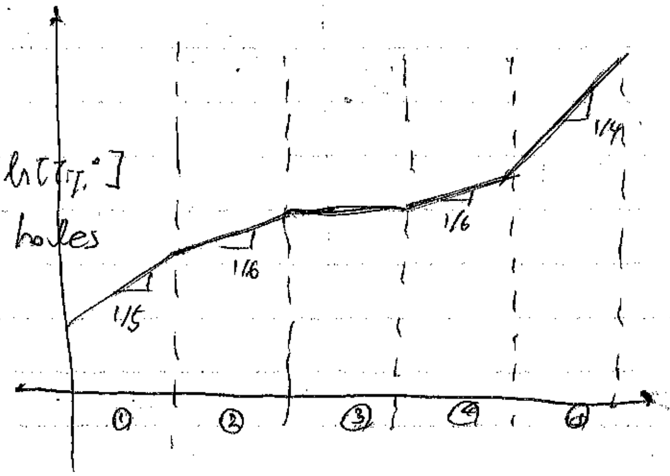
In <4>, $[Ti_{Ti}^{\bullet}]^3 \sim [pO_2]^{1/2} \Rightarrow \underline{[Ti_{Ti}^{\bullet}] \sim [pO_2]^{1/6}}$

In <5>, $[Ti_{Ti}^{\bullet}]^4 [O_O^X]^2 / [pO_2] \sim k^{(3)} \Rightarrow [Ti_{Ti}^{\bullet}] \sim [pO_2]^{1/4}$



Thus,





Where

① : $[Ti'] \cong 4[Ti_I^{\bullet\bullet\bullet\bullet}]$

② $[Ti'] \simeq 4[V_O^{\bullet\bullet}]$

③ $[Ti'] \approx [Ti^{\bullet}]$

④ $4[O_I''] \approx [Ti_{Ti}^{\bullet}]$

⑤ $4[V_{Ti}'''']\approx [Ti_{Ti}^{\bullet}]$

4. (a) Using chain law,

$$\partial D/\partial p = \partial D/\partial(\Delta G_V) \cdot \partial(\Delta G_V)/\partial p.$$ is satisfied.

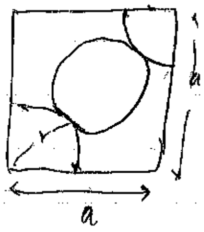
$$\Rightarrow \partial D/\partial p = \partial D/\partial(\Delta G_V) \cdot V \Big|_{T=\text{constant}}.$$

since we already know info about $\partial D/\partial(\Delta G_V)$ fromm the equation.

$$D = k a_0^2 \cdot \nu \cdot \exp\left[-\frac{\Delta G_V}{RT}\right] \exp\left[-\frac{\Delta G_M}{RT}\right].$$

Therefore, if you know diffusion coefficient vs. hydraulic pressure. $(\partial D/\partial p)$,, we can obtain the formation volume.

(b). Ag, Au, Cu are FCC structure and Li, Na are BCC structure.
Volume fraction of FCC is.

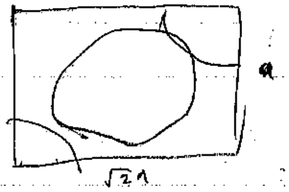


$$4r = \sqrt{2}a \Rightarrow r = \frac{\sqrt{2}}{4} \cdot a.$$

$$4 \text{ atoms} \rightarrow V_{atoms} = 4 \cdot \frac{4}{3}\pi \cdot \left(\frac{\sqrt{2}}{4}\right)^3 \cdot a^3.$$

$$\Rightarrow V.F. = V_{atoms}/a^3 = 4 \cdot \frac{4}{3}\pi \cdot \left(\frac{\sqrt{2}}{4}\right)^3 \cdot = \sqrt{2}\pi/6 \sim \boxed{74\%}$$

Volume fraction of BCC is.



$$4r = \sqrt{3}a \Rightarrow r = \sqrt{3}/4 \cdot a$$

$$2 \text{ atoms} \rightarrow V_{atoms} = 2 \cdot \frac{4}{3}\pi \cdot \left(\frac{\sqrt{3}}{4}\right)^3 \cdot a^3$$

$$\Rightarrow V.F. = V_{atoms}/a^3 = 2 \cdot \frac{4}{3}\pi \cdot \left(\frac{\sqrt{3}}{4}\right)^3 \cdot = \frac{2\sqrt{3}}{8}\pi. \boxed{\sim 56\%}.$$

Since (Ag Au Cu) has ~~more~~ less space to move around. solid self diffusion does not happen as frequently as BCC (Li, Na).
Therefore, V_{SD} of Ag Au Cu is larger than Li Na, making it harder to self-diffuse.

(c) Since the size of C or N is much smaller than that of Fe or V, so that it can freely move → more interstitial occur, so that small measured volume (SD). → Easy for small atoms to go through large atoms.

5. $\chi_v = \exp\left(-\frac{\Delta g_v}{kT}\right)$

(a) It will <u>decrease</u> — Intuitively, pressure decreases and vacancy forms. There are two approaches.

① By Cai–Nix book, we know that

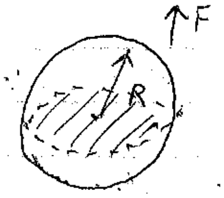
$$\frac{\chi_v}{\chi_0} = \exp\left(\frac{-P_{ext}\cdot\Delta V_v}{k_B T}\right)$$ because

$$\chi = \exp\left(-\Delta g_v/(k_B T)\right) = \exp\left(-\frac{\Delta h_v - T\Delta s_v}{k_B T}\right) = \exp\left(\frac{\Delta s_v}{k_B}\right)\cdot\exp\left(-\frac{\Delta h_v}{k_B T}\right)$$

$$= \exp\left(\Delta s_v/k_B\right)\cdot\exp\left(-\frac{\Delta e_v + P_{ext}\,\Delta V_v}{k_B T}\right) = \underbrace{\exp\left(\frac{\Delta s_v}{k_B}\right)\cdot\exp\left(-\frac{\Delta e_v}{k_B T}\right)}_{=\chi_0}\exp\left(\frac{-P_{ext}\cdot\Delta V_v}{k_B T}\right) \quad \text{— ①}$$

$\therefore \chi_v/\chi_0 = \exp\left(\frac{-P_{ext}\cdot\Delta V}{k_B T}\right)$ ⇒ If we increase P_{ext}, vacancy site fraction χ <u>decreases</u>.

(b)



We just need to know how much is $-P_{ext}\cdot\Delta V$ is. since from equation ①. the term $\exp\left(\frac{-P_{ext}\cdot\Delta V}{k_B T}\right)$ affects the vacancy site fraction.

⇒ When we place the particle back, surface energy exerts,

$$F = -\gamma\cdot(2\pi R) \quad \text{(along circumference)}$$

where effective area is πR^2 so the pressure P_{ext} is.

$$P_{ext} = F/(\pi R^2) = -2\gamma/R$$

Plugging into equation ①,

$$\chi_V = \exp\left(-\frac{\Delta g_v - (-2\gamma/R)\cdot\Delta V}{k_B T}\right) = \underline{\exp\left(-\frac{\Delta g_v + (2\gamma/R)\Delta V}{k_B T}\right)} \quad \#$$

<u>Different approach</u> is

$\gamma\cdot\Delta A$ = work done where $\Delta A = 4\pi(r+\Delta r)^2 - 4\pi r^2 \sim 2\cdot 4\pi\cdot r\cdot\Delta r$.

$\Delta V = 4\pi\cdot r^2\cdot\Delta r$ so that $\Delta A = 2/R$ ⇒ $\gamma\Delta A = \boxed{2\gamma/R}$ – same as above.

Note : edge dislocation : line $\perp \vec{b}$ ⇒ may slip only one plane,
screw " : line $\parallel \vec{b}$ ⇒ may slip within plane.

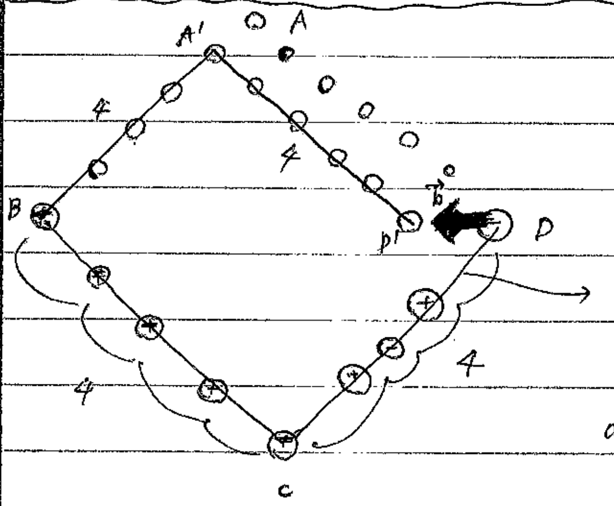
1. (a) Edge dislocation used climb to overcome the obstacle where it moves perpendicular to glide plane (slip plane).

(b). Yes. this is because at high temperature. more vacancies and interstitials are formed so that it's easier to form climb.

(c) For screw dislocations, unlike edge dislocations it can move (slip) in any plane that contains the burger's vector so that it is more flexible at overcome obstacles by just glide..

2.

(a)



line direction $[0 0 \bar{1}]$

clockwise burgers circuit.

Burger's circuit is

D → C → B → A' → D'

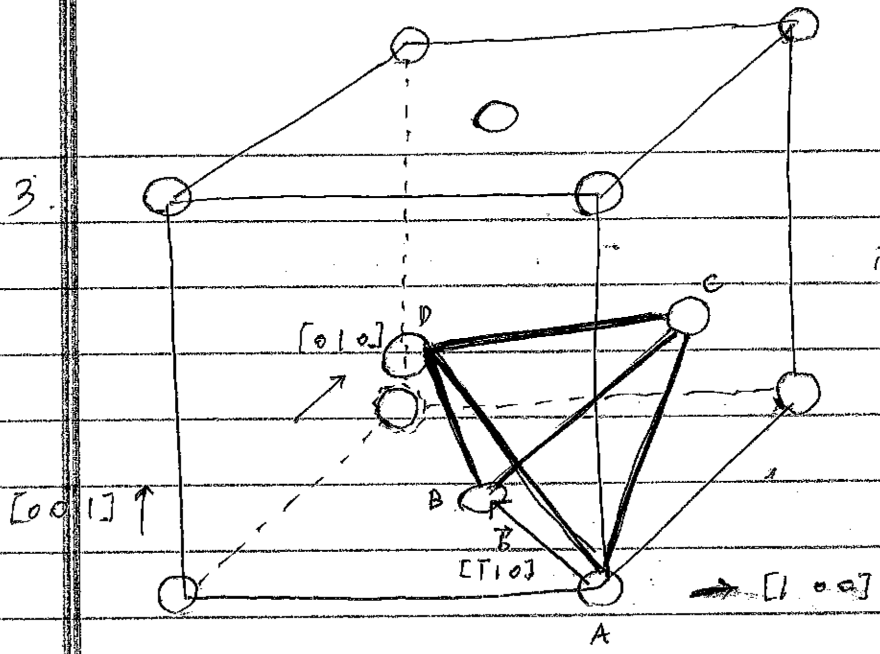
and the burgers vector is $\overrightarrow{D'D}$.

in [110] direction. (SF convention)

(b) Note that in order to form (edge) dislocation, you need vacancies of negative charged atoms elsewhere to fill in excessive negative charged atoms around (inside) dislocation region. Therefore, in full length, there also exists excessive positively charged atoms which results in total charge neutrality.

→ We move charged atoms

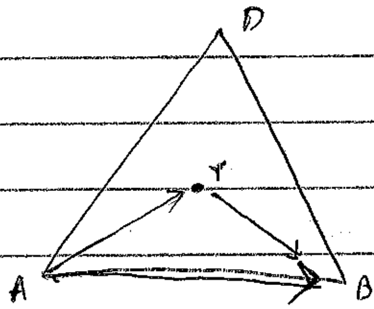
3.



Focus on tetrahedron ABCD
in fact this is called
Thompson's tetrahedron.

$\vec{b_1} = \vec{AB} = \frac{1}{2}a\,[\bar{1}\,1\,0]$

(a) Since we are looking from plane (1 1 1), which is plane 'ABD.'
we can draw plane ABD (plane (111))



$\vec{b_1} = [\bar{1}\,1\,0]\frac{a}{2}$

We know $\vec{AB} = \vec{A\gamma} + \vec{\gamma B}$

① $\vec{A\gamma} = \frac{2}{3}\cdot\frac{1}{2}\cdot(\vec{AB}+\vec{AD}) = \frac{1}{3}(\vec{AB}+\vec{AD})$

$= \frac{1}{3}([\bar{1}\,1\,0]+[\bar{1}\,0\,1])\cdot\frac{a}{2}$

$= \underline{\frac{a}{6}[\bar{2}\,1\,1]}$

Similarly, $\vec{\gamma B} = \frac{2}{3}\cdot\frac{1}{2}\cdot(\vec{DB}+\vec{AB}) = \frac{1}{3}([0\,1\,\bar{1}]+[\bar{1}\,1\,0])\cdot\frac{a}{2}$

$= \underline{\frac{a}{6}[\bar{1}\,2\,\bar{1}]}$

Check $\vec{A\gamma} + \vec{\gamma B} = \frac{a}{6}\{[\bar{3}\,3\,0]\} = \frac{a}{2}[\bar{1}\,1\,0] = \vec{b_1}$

$$\boxed{\begin{array}{l}\therefore\ \vec{b_2} = \frac{a}{6}[\bar{2}\,1\,1] \text{ and } \vec{b_3} = \frac{a}{6}[\bar{1}\,2\,\bar{1}] \\ \text{and } \vec{b_2} + \vec{b_3} = \frac{a}{6}[\bar{3}\,3\,0] = \frac{a}{2}[\bar{1}\,1\,0] = \vec{b_1}\end{array}}$$

3-(b) We have

$$\vec{b_1} = \frac{a}{2}[\bar{1}\,1\,0] = \vec{b_2} + \vec{b_3} = \frac{a}{6}\left([\bar{2}\,1\,1] + [\bar{1}\,2\,\bar{1}]\right)$$

Energy of LHS $\propto \|\vec{b_1}\|^2 = \frac{1}{4}a^2 \cdot 2 = \frac{1}{2}a^2$

Energy of RHS $\propto \|\vec{b_2}\|^2 + \|\vec{b_3}\|^2 = \frac{a^2}{36}\cdot(6+6) = \frac{1}{3}a^2$.

Since $\frac{1}{2}a^2 > \frac{1}{3}a^2 \Rightarrow E(\vec{b_1}) > E(\vec{b_2}$ and $\vec{b_3})$

∴ splitting reaction is energetically favorable.

3-(c) Previously (before dislocations), the layers are

$$\cdots \text{ A B C A B C A B C } \cdots \quad (\text{stacked periodically}).$$

$$\text{A } \boxed{\text{B C B C}} \text{ A B C}$$

or,

A B C A B C A B C . . .   there exists a stacking fault (CACA layer).

$\text{A B } \boxed{\text{C A C A}} \text{ B C} \cdots$ due to imperfection caused by the partial dislocations $\vec{b_2} + \vec{b_3}$.

In our case, B layer is replaced by C layer due to $\vec{b_1} = \vec{b_2} + \vec{b_3}$ dislocation

so that $\text{A B C A B C} \rightarrow \text{A B } \underbrace{\boxed{\text{C A C A}}}_{\text{stacking fault occur.}} \text{ B C}$

This is a ②D defect. (occur within planes).

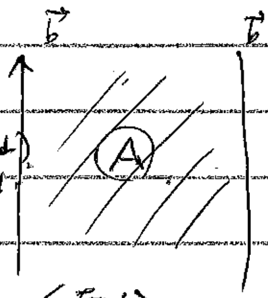
Note : $\Delta G = \gamma_{SF} \cdot A$. ($\gamma_{SF}$ is stacking fault energy — material property).

Therefore, in figure 1, A (or distance) between two dislocations differ by materials. For example,

Si : High γ_{SF} → ⇒ ⇈ (almost ~~merged~~ Merged)

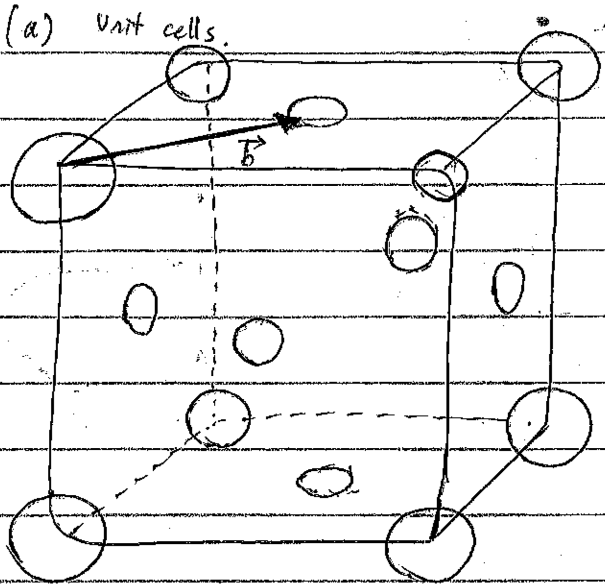
Ni : Medium γ_{SF} ⇒ ↑////↑

Cu : Small γ_{SF} ⇒ ↑/////////////////↑



<Fig 1>

4. (a) Unit cells.



Most likely burgers vector is drawn as left.

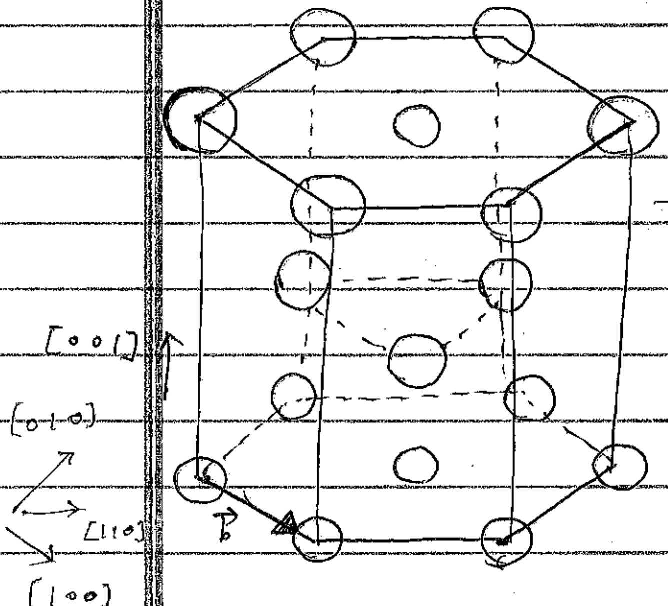
$\vec{b} = \frac{a}{2}[\bar{1}\ 1\ 0]$

(closest atom)

($a \simeq 4.05$ Å)

as long as it's on (111) plane

Al (FCC)



There are ONE most likely burger's vectors

~~a[$\bar{1}\bar{2}$10], a[0100], and a[1100]~~

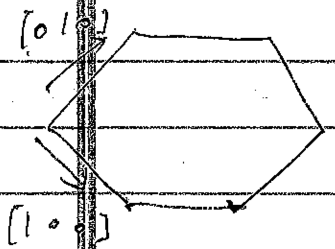
~~a[1 0 0], a[0 1 0] → this one.~~

~~which connects to closest atoms~~ (a<c)

~~(a ≃ 3.21 Å and c ≃ 5.21 Å)~~

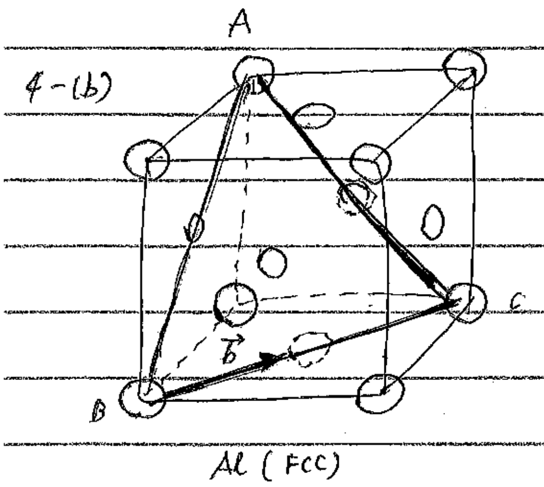
[1 0 0] is the most likely.

Mg (HCP)



→ This is convention

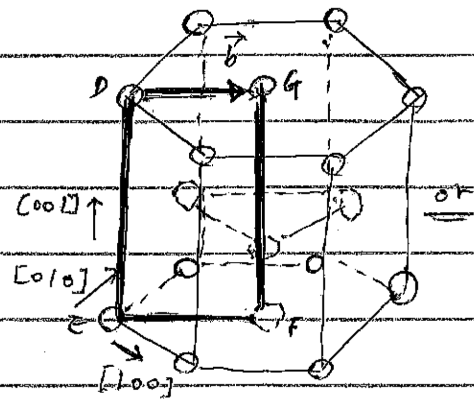
4-(b)



Al (FCC)

$\vec{b} = \frac{1}{2}a\ [1\ 1\ 0]$

Plane ABC is one example.
which is, $(1\ \bar{1}\ 1)$
(Note : 3 atoms in a plane)



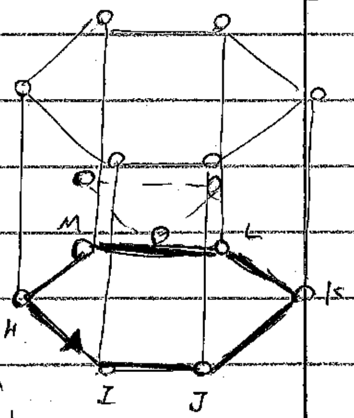
Mg (HCP)

$\vec{b} = a\ [1\ 1\ 0]$

Plane DEFG is one example
which is, $\{1\ \bar{1}\ 0\}$
(Note, 4 atoms in a plane)

or

This is more likely



or you can also
$\vec{b} = a\ [1, 0\ 0]$
plane (001)

4-(c) For Al, we have 4 slip planes $(1\ \bar{1}\ 1)$, $(1\ \bar{1}\ \bar{1})$, $(1\ 1\ \bar{1})$, $(\bar{1}\ \bar{1}\ \bar{1})$
which each has 3 burger's vectors → $\boxed{\text{12 slip system}}$.
(we want to know "distinct" so that these planes form a tetrahedron)
Infact, there are 5 independent slip systems (FCC, Al)

For Mg, 3 slip planes, (001), if we only consider (001) plane systems,
even if 3 slip planes contain. Basal (001), prismatic, and pyramidal,
we only care (0 0 1) plane in this case. Then, [1 0 0], [0 1 0] can happen.
Note that also [1 1 0] can happen but it is equivalent as [1 0 0] + [0 1 0].
Therefore, only $\boxed{\text{3 independent}}$ slip systems (HCP. Mg)
You can also say for (001) plane, [1 0 0] [0 1 0], [1 1 0] forms 3 independent
two
∴ Mg cracks, Al crumbles (safer)

5. (a) There are more "solute" atoms below the half plane compared to C_o because it is where θ is $\pi < \theta < 2\pi$.

Thus, $\sin(\theta) < 0$ at $\pi < \theta < 2\pi \Rightarrow \exp\left(-\frac{\beta \sin\theta}{rkT}\right) > 1$

$\therefore$ $C > C_o$ at below $(\pi < \theta < 2\pi)$

Also, at region above, there are less solute atoms compared to C_o because $0 < \theta < \pi \Rightarrow \sin(\theta) > 0 \Rightarrow \exp\left(-\frac{\beta \sin\theta}{rkT}\right) < 1$

$\therefore$ $C < C_o$ at above $(0 < \theta < \pi)$

(b) C/C_o is maximized when $\theta = 3\pi/2$ so that $\sin(\theta) = -1$ (below)

$$\Rightarrow C/C_o = \exp\left(\frac{\beta}{rkT}\right).$$

$$\beta = \frac{\mu b e}{3\pi} \frac{1+\nu}{1-\nu} \cdot (V_s - V_a) = \frac{(40\,GPa)\cdot(0.3\,nm)}{3\pi} \frac{1+0.3}{1-0.3} \cdot (1.1 - 1.0)(0.3\,nm)^3$$

$$= \frac{1}{3\pi}\left(\frac{1.3}{0.7}\right)\cdot(0.1)\cdot \underbrace{(40\cdot10^9\cdot Pa)\cdot(0.3\cdot10^{-9}\,m)^3}_{\text{This is units of } J} \cdot (0.3\,nm).$$

$$= 2.1281 \cdot 10^{-20}\,J \cdot (0.3\,nm)$$

Thus, $C/C_o = \exp\left(\frac{2.1281\cdot10^{-20}\,J\cdot(0.3\,nm)}{(1\,nm)\cdot(1.3806\cdot10^{-23}\,J/K)\cdot(300\,K)}\right) \cong 4.67$

$\therefore$ 4.67 times enhancement

6. (a) There are two approaches

(1) As θ is small, $D = b/\theta$ is very large. Thus, dislocations are very far apart from each other. Hence, the dislocations do not interact each other. Thus the energy (total) does not have correlation term → $E_{total} \sim (\text{length of dislocation})^2$.

Here we want to know boundary energy per unit area.

$$\therefore \quad E \cancel{\propto} (D)^2/D \left(= \frac{\text{Energy of dislocation}}{\underline{\text{length}} \cdot \cancel{\text{depth}}} \right) \quad \text{(per unit } \cancel{\text{area}}\text{)}$$

$\propto D$.

$$\Rightarrow E \propto D = b/\theta$$

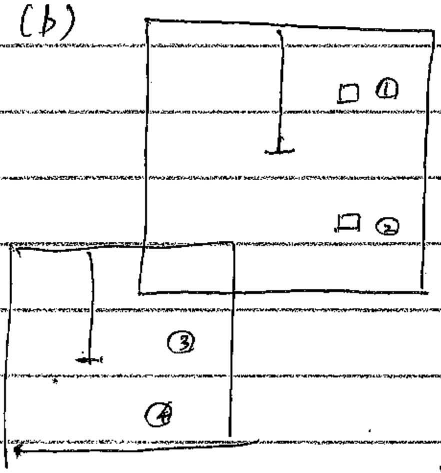
Since b is constant, as θ increases as θ is very small the boundary energy per unit area decreases $\therefore$ $E_{bound} \sim 1/\theta$.

(2) Without interaction between dislocations, $\Delta G = \Delta H - T\Delta S$ (const. temperature)

ΔH does not change much as θ is small, however, there exists imperfections that elevates the entropy of a solid. ⇒ ΔS increases.

Therefore, ΔG decreases as θ increases which can be interpreted as decrease of boundary energy ⇒ $E_{bound} \cancel{\propto} \Delta G \sim 1/\theta$.

(b)



Element on half space as dislocation line experiences compression whereas the other half plane goes through tension. When two dislocations get near as R gets smaller the compression region ③ and tensile region ② gets closer and cancels stress each other. Therefore, when two dislocations get closer (R decrease), the energy (boundary energy) decreases.

⇒ As R in $E(edge) = \frac{Gb^2}{4\pi(1-\nu)} \cdot \ln(R/r_0)$ decreases, energy decreases.

so that it makes less expensive

1. (a) This is because amorphous silicon forms network with <u>specific bond angles</u>. However, we cannot represent these specific bond angles when we use dense random packed model. (

(b) $G(r) = J(r)/r$ → <u>Number density</u> can be obtained

(linear # density in this case)

(c) (i) No, it will have almost no change

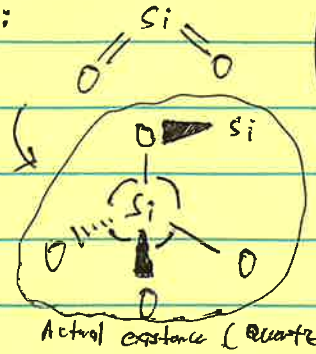
(ii) Yes, it will be broader (presence of long range order)

In crystalline structures atoms are well structured and periodic., thus hard to move around / expand. On the other hand, amorphous structures are disordered so that disorder affects longer range atom more ⇒ Second nearest peak to be broader than the first nearest neighbor.

(d) Average coordination number (# of neighboring atoms).

(e) Oxygen atoms constrain the angle firmly at SiO_2

Details :



Actual existence (Quartz)

4 Si-O bond stretch constraints

5 " angle bend constraints.

(9 total, 5 independent)

Total # of freedom = 9 (3 per atom)

Total # of constraints = 9.

∴ For SiO_2, it is well constrained. so it is difficult to change bond angles where for $SiSi_4$ it is easier to change bond angles (tetrahedrals)

⇒ Spread in tetrahedrals$^{(Si)}$ are greater than SiO_2

2. (a) Warren says crystalline hypothesis leads to a very small size crystalline particles, and since there are no small angle scattering, glass should be continuous medium without discrete particles. However, this means. only partially the material has form of crystobalite and hence.

Another argument against the crystalline hypothesis is that Vit silica has large peak with whereas crystobalite has narrower width. which implies that particle size should be extremely small and approximately constant, which X-ray analysis says (proves) that the major part of the material cannot be in this cristobalite form.

(b) This is because in liquids, a molecule does not have permanent neighbors. Since all the molecules move around, they will constantly find few neighbors approximately in contact (not exact always) so that the dip does not come down all the way to zero for monatomic liquids (liquid Na & water).

(c) According to X-ray analysis, liquid Na has a structure, and the existence of it implies atoms are closely packed similar to solids ⇒ Dense Random Packing.

(d) $O-H$ length ~ 95.7 pm = 0.957 Å

$O-O$ 〃 ~ 2.76 Å

∴ $O-H$ bond will yield first/nearest neighbor peaks around (1 Å)

(e) Oxygen atoms are larger than the hydrogen atoms so they scatter X-rays more. Therefore, the scattering effect caused by $H-O$ (hydrogens) will be neglected compared to that by oxygen atoms. (This is connected to (similar to) the Born-oppenheimer. approximation theory) since oxygen is larger, it ~~diffracts~~ X-ray more. hence we observe more (many) neighboring atoms (tetrahedral).

because of crystal structure (of BCC)

3. (a) The net ray scattered by the entire primitive cell is the sum of individual rays, will have amplitude of

$$S_K = \sum_{j=1}^{2} \cdot e^{jK d_j} \qquad d_j = \begin{cases} 0 \\ \frac{a}{2}(\hat{x}+\hat{y}+\hat{z}) \end{cases}$$

for BCC. (AgI).
— basis

$$\Rightarrow S_K = 1 + \exp\left(j \cdot K \cdot \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})\right)$$

$$= 1 + \exp\left(j\, \frac{2\pi}{a} \cdot (n_1\hat{x} + n_2\hat{y} + n_3\hat{z}) \cdot (\hat{x}+\hat{y}+\hat{z})\right)$$

$$\left(\because K = 2\pi/a \left(n_1\hat{x} + n_2\hat{y} + n_3\hat{z}\right)\right)$$

$$\Rightarrow S_K = 1 + 0 + (-1)^{n_1+n_2+n_3}$$

$$= 1 + (-1)^{n_1+n_2+n_3} = \begin{cases} 2 & n_1+n_2+n_3 = \text{even} \\ 0 & n_1+n_2+n_3 = \text{odd} \end{cases}$$

only peaks formed where $n_1+n_2+n_3$ = even (can be checked in figure).

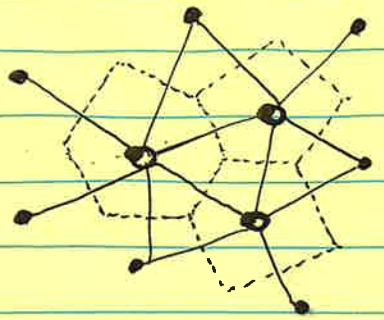
These peaks are formed by interference of waves scattered. (constructive interference)
destructive

(b) Zallen says split second is key characteristic of RDF of amorphous solids which is absent in liquid solids (metals).

From the figure, the second peak does not have split second peak, so that Ag-sublattice is liquid like.

(Intuitively, amorphous are very disordered, when liquid has somewhat order.).

4. (a)



○ : atoms of interest ● : atoms in background.

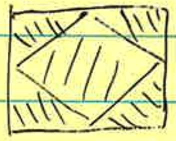
— : Geometric neighbors connected with real line

- - - : Wigner-Seitz cells is constructed in dotted lines.

Γ : bonding site

(b) ① No — Tetrahedrons form icosahedron, which cannot be closed only with tetrahedrons.

② Tetrahedral and Octahedral



tetrahedral : octahedral = 2 : 1

⇒ ~~(not larger than tetrahedral)~~

$8 \cdot 1 = 8$ / unitcell $\frac{1}{4} 12 + 1 = 4$ / unit cell. Octahedrals are larger than tetrahedrals.

③ (1) Surface energy.

Icosahedron is the lowest surface energy structure for 13 atom cluster system. So when # of atoms decrease to 13, it tends to contribute more.

As volume gets larger, atomistic interaction plays larger role than surface energy (note that surface energy scales with $\sim 4\pi r^2$ and volume scales with $4\pi r^3/3$.) So as r decreases (scales down), for instance, Au_{13}, surface energy dominates.

⇒ Icosahedron is a structure to minimize the surface energy. So it (Au_{13}) tends to remain at Icosahedron, rather than FCC.

5. (a) Silicones are diamond cubic structure. (DC).

Bond length $d = \frac{\sqrt{3}}{4} \cdot a$ (a = lattice constant).

In a single lattice box there are ⑧ atoms

$\therefore$ Density $\rho \propto \frac{8 \cdot M_{Si}}{a^3} = \frac{8 \cdot M_{Si}}{\left(\frac{4}{\sqrt{3}} \cdot d\right)^3} \propto 1/d^3$

Recall that ~~difference~~ between bond lengths between c-Si and a-Si is

$\left(d_a/d_c - 1\right) \sim \frac{2.355}{2.350} - 1 \sim 0.0021 \cong \underset{\sim}{0.2\%}$

$$\begin{array}{cc} \text{c-Si} & \text{a-Si} \\ \downarrow & \downarrow \\ d_c & d_a \end{array}$$

$\Rightarrow$ Assume $d_a/d_c - 1 \cong 0.002 \Rightarrow \underset{\sim\sim\sim}{d_a/d_c = 1.002}$

Then, $\rho_a/\rho_c \sim d_c^3/d_a^3 \sim 0.9940$

$\Rightarrow |\rho_c/\rho_a - 1| \sim 0.6\%$ difference. (amorphous has lower density).

(b) ✓① Dangling Bonds : At the surface of a-Si, the periodicity is broken so that surface atoms rearrange to minimize the energy (free energy G). These non-bonding sp orbitals are called dangling bonds, causes loss of density at the long range compared to dense packed structure.

✓② Disordered arrangements : Of course disorder in arrangements lower the density especially at long ranges also

(c) Adding hydrogen (hydrogen passivation) can break Si-H bond, rather inserts H (hydrogen) into a Si-Si bond. which prohibits the formation of the dangling bonds on the surface (mostly) of a-Si. Thus, adding hydrogen reduces dangling bond defect density. for application, I fat Hydrogen attaches to the dangling bonds to decrease dangling bond.