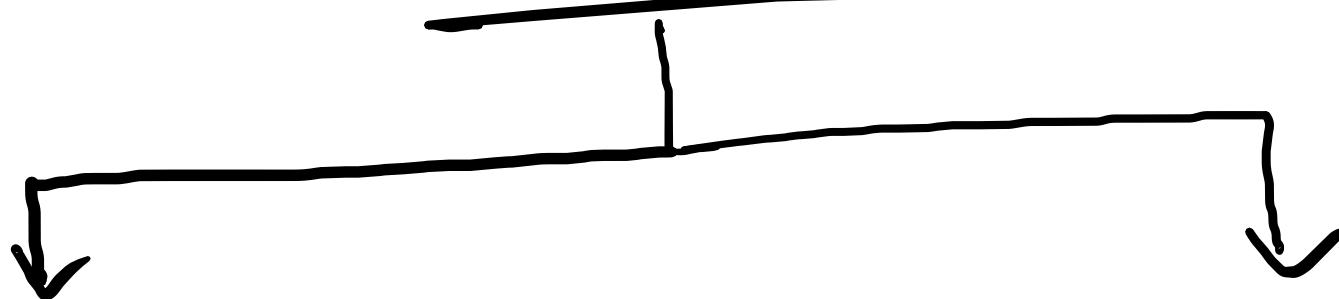


Unit 1 → Solid State Physics
Crystal Structure.

Solids → On the basis of internal structure.



Crystalline Solids

Amorphous Solids

Crystalline Solid

① Regular arrangement of atoms (ordered arrangement) structure

Low energy state

This is because energy released during the formation of ordered structure is more than the energy released during the formation of disordered structure.
Stable state.

Amorphous Solids

① Irregular arrangement of atoms (disordered structure)

High energy state.

Disordered structure

Metastable state

③ Crystalline solids are true solids

④ Proper cutting
Cutting along plane.

⑤ Melting point

Sharp Melting point

Due to Regularity of
Arrangement we need same
Thermal Energy to break bonds

③ Amorphous solids are
pseudo solids or Supercooled
solids

④ Improper cut.

⑤ Melt at different
temperatures (Temp Range)

→ Lattice
→ Basis
→ Crystal Structure

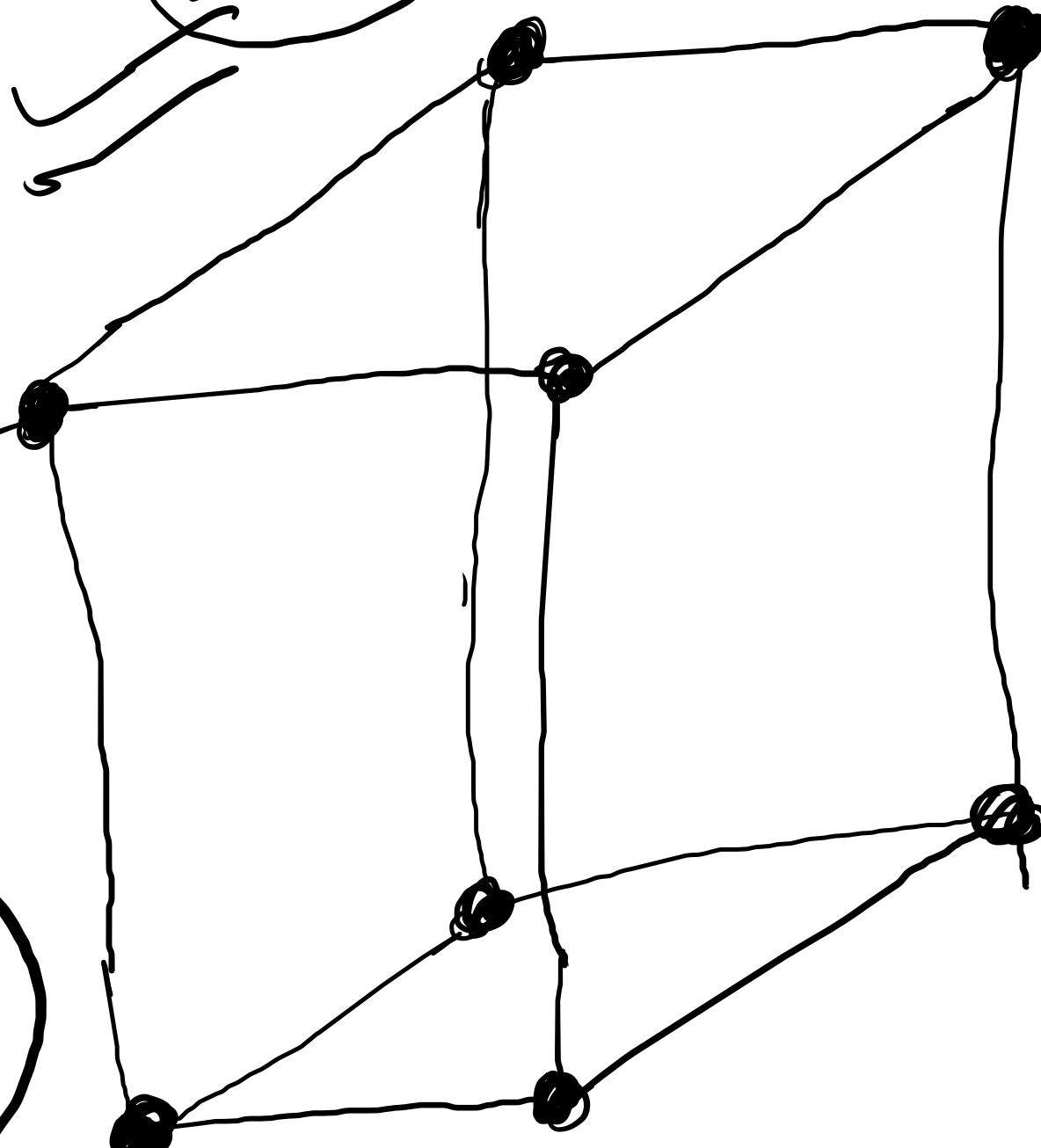
Unit cell

Lattice → Regular arrangement

of points

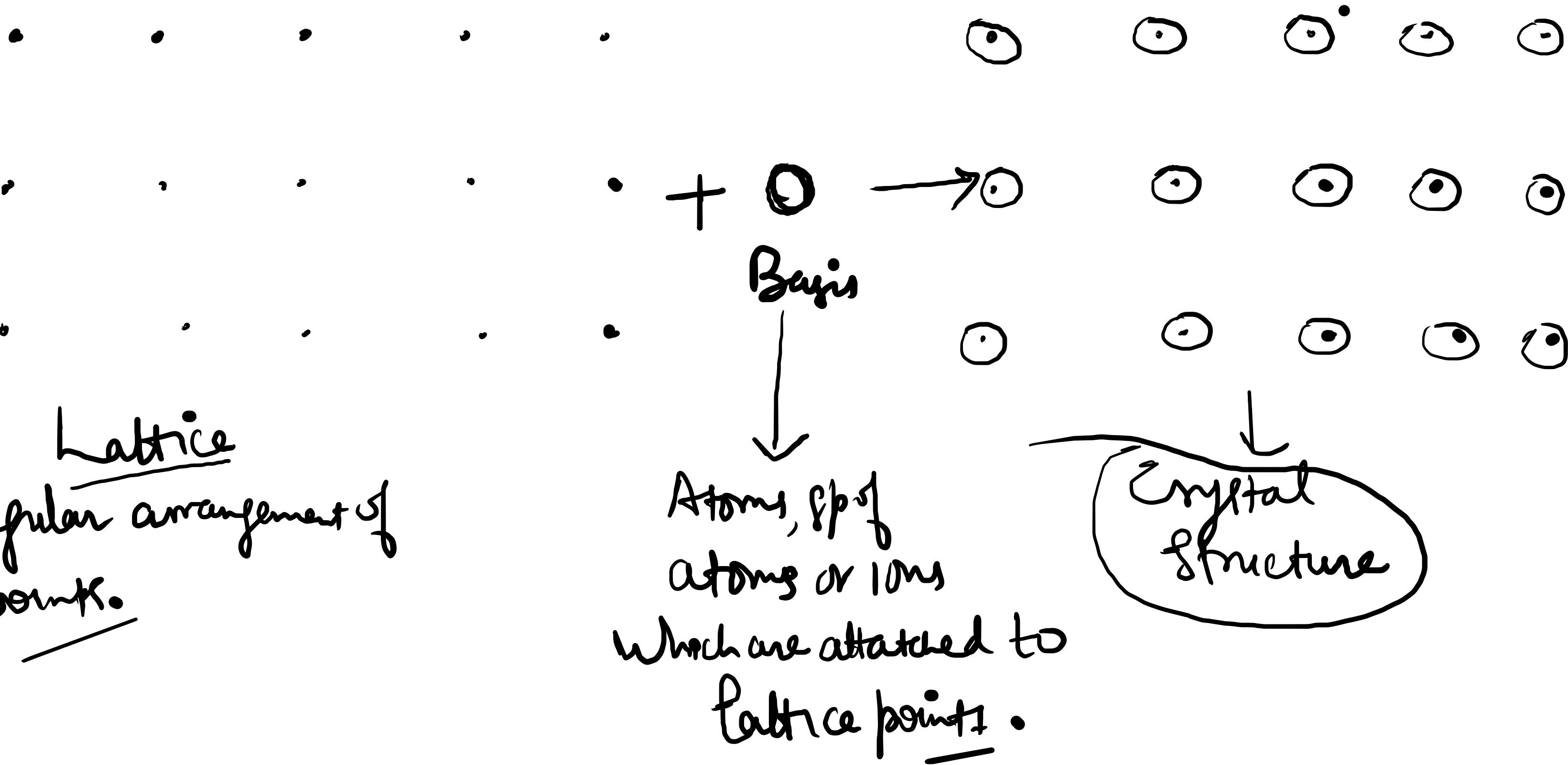
in space is
called lattice

atoms,
grp of atoms
or
ions



Lattice + Basis = Crystal
Structure

Lattice
Regular arrangement of
points.



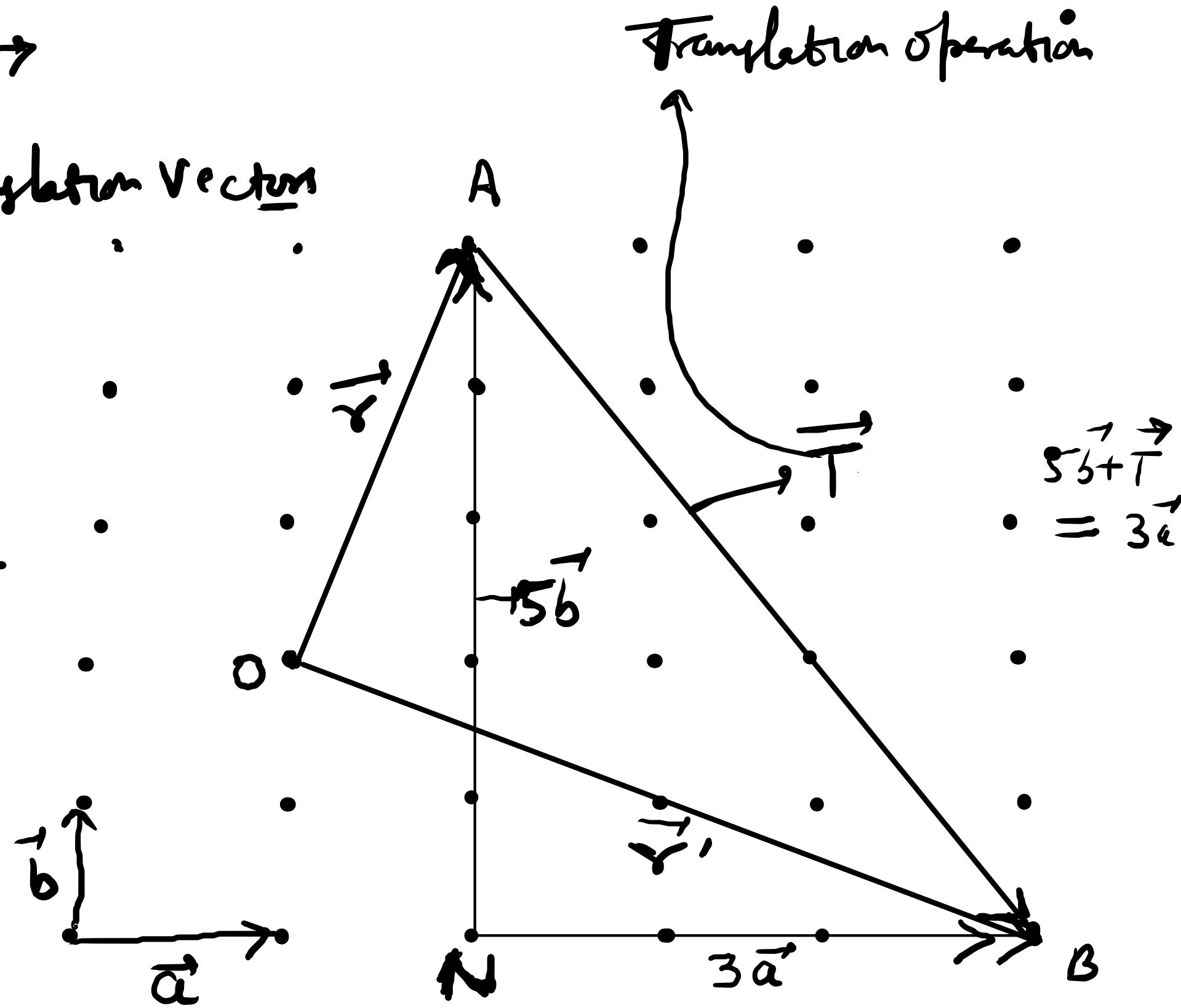
25/11/2020

Translation Vector →

$\vec{a}, \vec{b} \rightarrow$ Fundamental Translation Vectors

To understand the concept
of translation vector,

Draw a two dimension lattice
having fundamental translation
vectors \vec{a} and \vec{b} as
shown in the diagram.

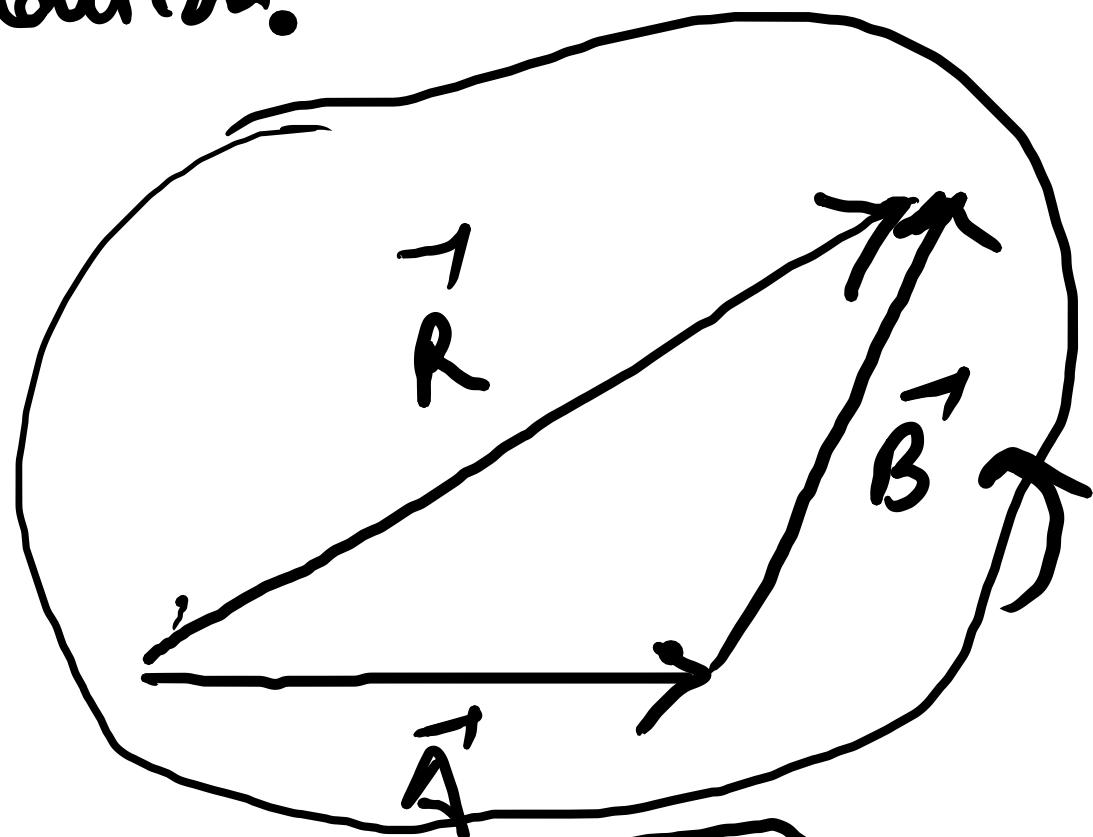


Choose any lattice point be origin O. Consider other two lattice
points defined by position vectors \vec{r} and \vec{r}' :

From $\triangle OAB$, by Δ law of vector addition.

$$\vec{r} + \vec{t} = \vec{r}' \quad \text{--- } ①$$

Find \vec{t} in terms of \vec{a} and \vec{b} .



From $\triangle ANB$. by Δ law of vector

addition

$$5\vec{b} + \vec{t} = 3\vec{a}$$

$$\Rightarrow \vec{t} = 3\vec{a} - 5\vec{b}$$

Put in eq. ① $\boxed{\vec{r}' = \vec{r} + 3\vec{a} - 5\vec{b}}$

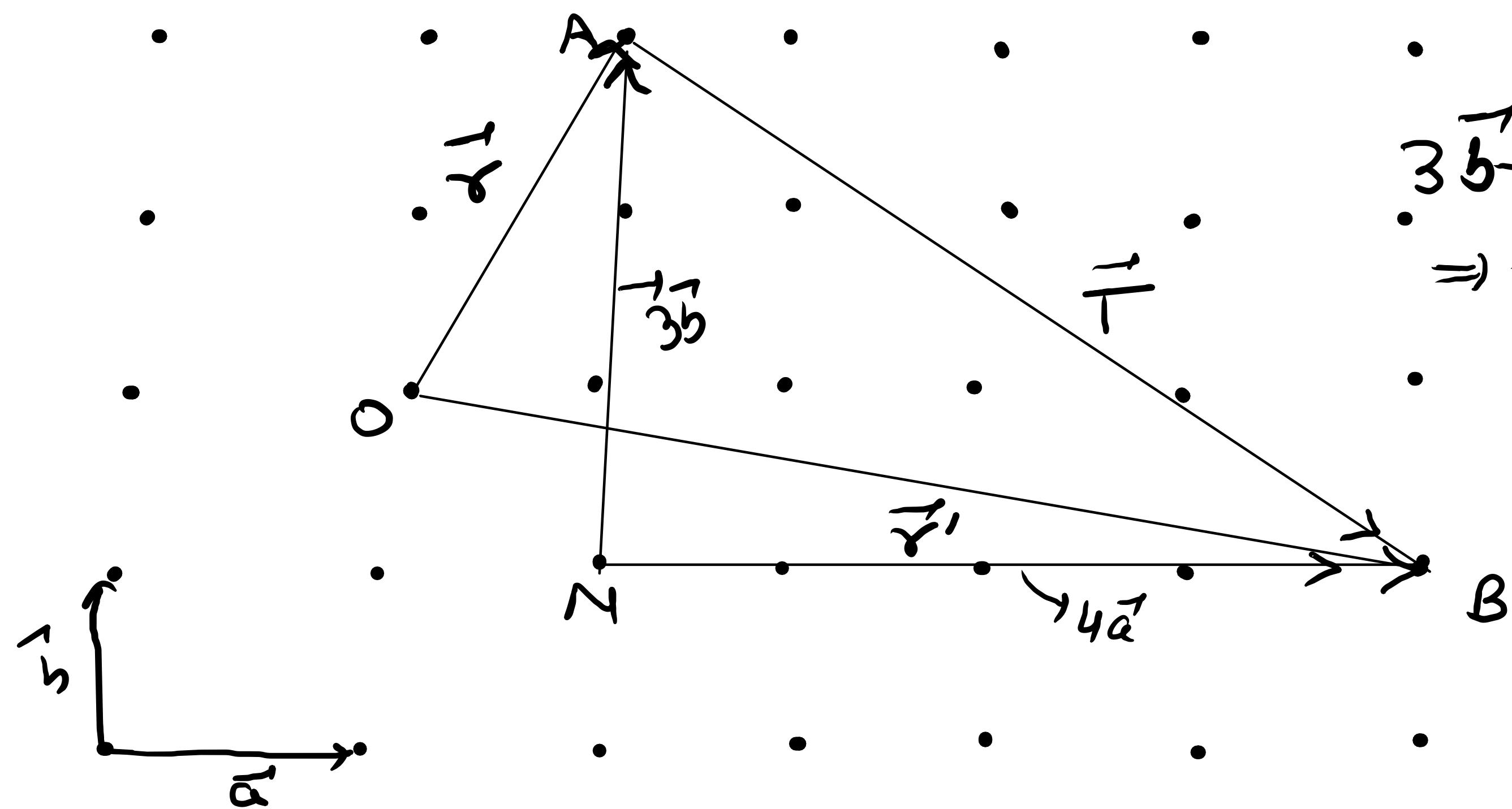
In general in two dimensions

$$\vec{r}' = \vec{r} + n_1 \vec{a} + n_2 \vec{b}$$

In three dimensions

$$\vec{r}' = \vec{r} + n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$

With the help of translation vectors we can translate or reach any lattice point to other.



$$\vec{r} + \vec{T} = \vec{r}'$$

$$\vec{T} = 4\vec{a} + 3\vec{b}$$

$$4\vec{a} + 3\vec{b}$$

$$4\vec{a} - 3\vec{b}$$

$$3\vec{b} + \vec{T} = 4\vec{a}$$

$$\Rightarrow \vec{T} = 4\vec{a} - 3\vec{b}$$

Unit cell →

Unit cell is the smallest block of the crystal which when repeated again and again regularly to form a crystal.

Types → Two types

↓
Primitive Unit cell

→ A minimum volume unit cell in which the atoms are present only at corners of unit cell.
ie Effective no of atoms → 1

↓
Non Primitive Unit cell

→ Effective no. of atoms in case of cubic unit cell

$$N_{\text{eff}} = \frac{N_c}{8} + \frac{N_f}{2} + N_b$$

$N_c \rightarrow$ No. of atoms at corners of unit cell

$N_f \rightarrow$ No. of atoms at face centred position.

$N_b \rightarrow$ No. of atoms at body centred position

For Simple Cubic ✓

$$N_{eff} = \frac{8}{8} + \frac{0}{2} + 0 = 1 \quad \checkmark$$

✓ For BCC ✓

$$N_{eff} = \frac{8}{8} + \frac{0}{2} + 1 = 2 \quad \checkmark$$

✓ For FCC ✓

$$N_{eff} = \frac{8}{8} + \frac{6}{2} + 0 = 4 \quad \checkmark$$

26/11/2020

Packing Fraction for Simple cubic Structure →

$$\text{Packing Fraction} = \frac{\sqrt{\text{Volume of atoms in the Unit cell}}}{\text{Volume of Unit cell.}}$$

$$\text{Packing Fraction} = \frac{\text{Effective no. of atoms per Unit cell} \times \text{Volume of one atom}}{\text{Volume of Unit cell}}$$

$$\text{Packing Efficiency} = \frac{\text{Effective no. of atoms per Unit cell} \times \text{Volume of one atom}}{\text{Volume of Unit cell}} \times 100$$

In Simple Cubic unit cell there
are 8 atoms at corners.

So effective no. of atoms per unit

$$\text{cell} = \frac{1}{8} \times 8 + \frac{0}{2} + 0 = 1$$

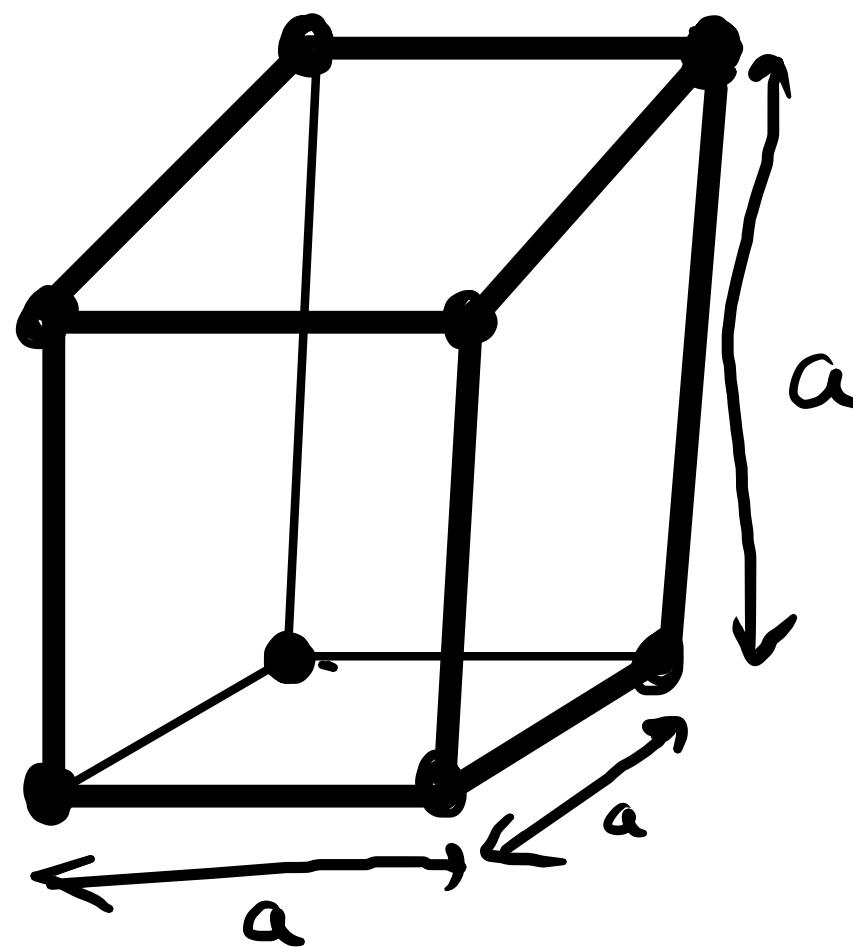
Let a be lattice constant

So Volume of unit cell will be

$$= a^3$$

Let r be the radius of atom, then Volume of one atom will be

$$= \frac{4}{3} \pi r^3$$



So Packing fraction will be = $\frac{1 \times \frac{4}{3}\pi r^3}{a^3}$
 (PF)

$$PF = \frac{\frac{4}{3}\pi r^3}{a^3} \quad \text{--- } \textcircled{1}$$

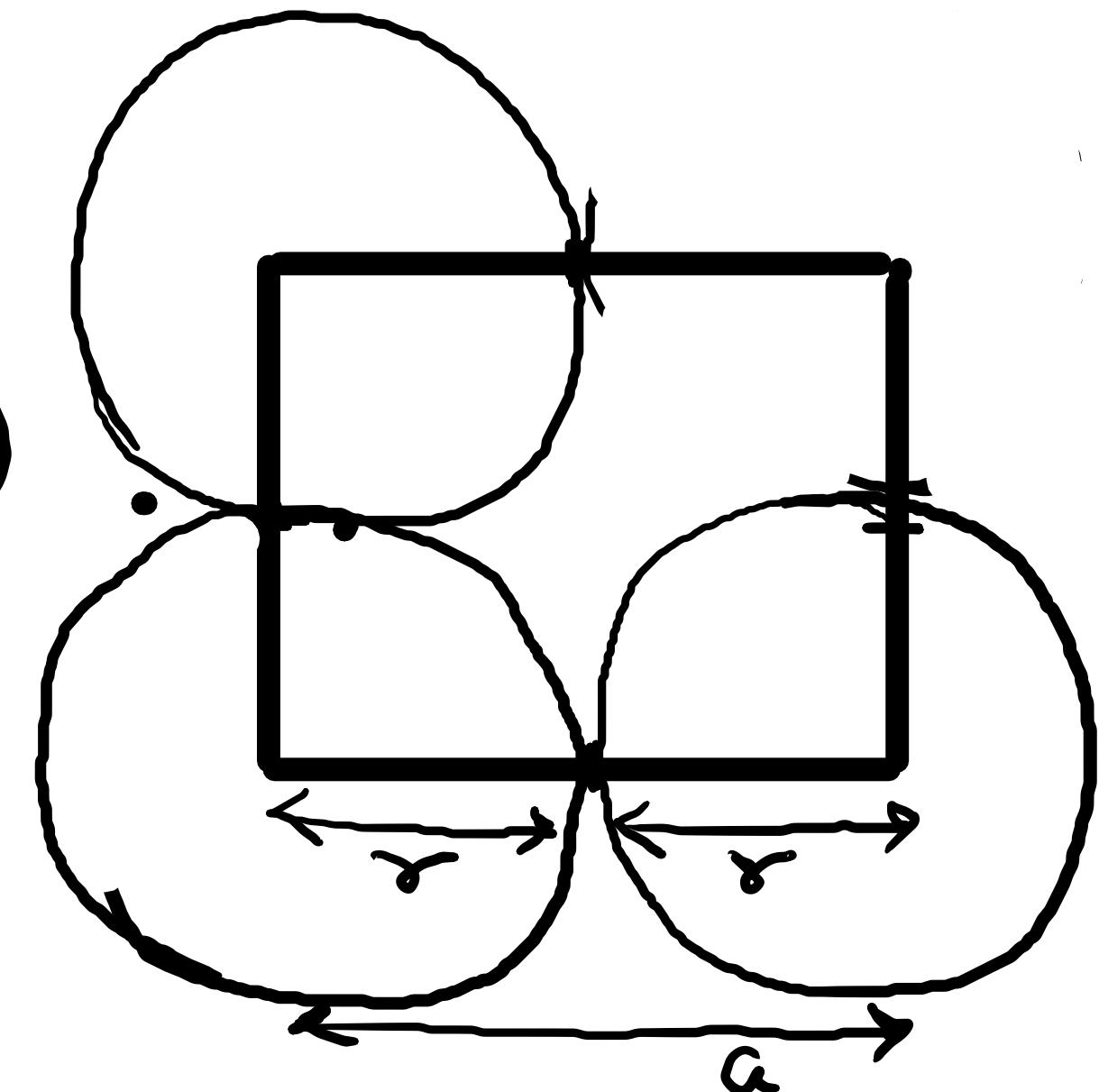
Relation b/w \textcircled{a} and \textcircled{r} .

From Diagram $a = 2r$

Put the value of $a = 2r$ in eq. $\textcircled{1}$

we get

$$PF = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6} = \frac{3.14}{6} = 0.52$$



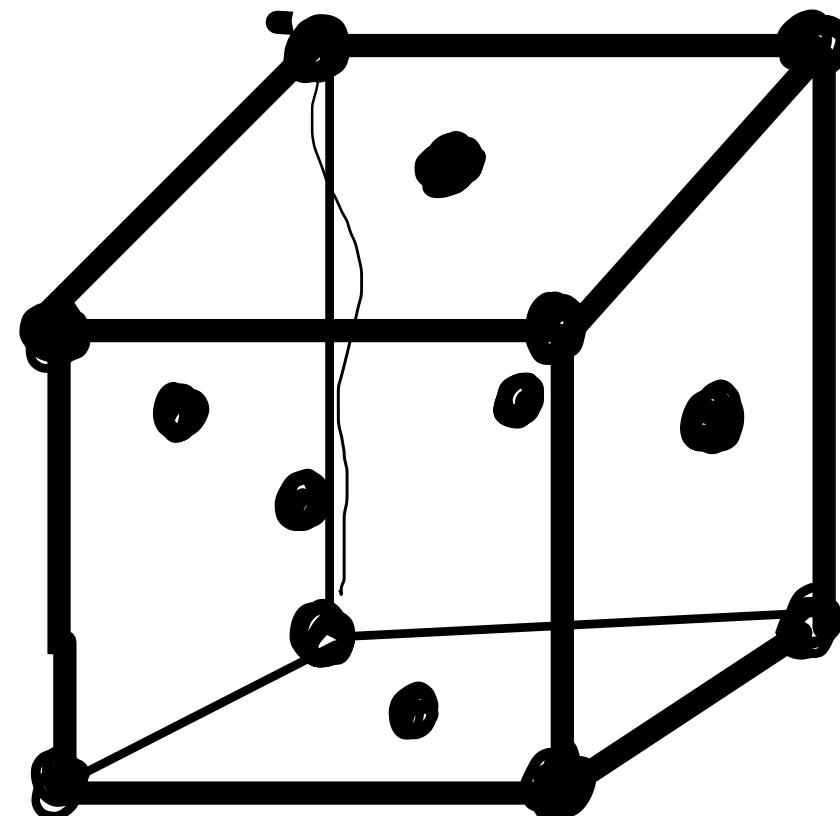
$$\text{Packing Efficiency} = 0.52 \times 100 = \boxed{52\%}$$

$$\text{Void space will be} = 100 - 52 = 48\%$$

So in case of Simple Cubic Unit cell 52% of the Space is occupied by atoms and rest is empty.

Packing Efficiency of Face centred cubic unit cell (FCC)

So in FCC unit cell there are eight atoms at the corners of unit cell and six atoms are at face centered positions as shown in the diagram.



So effective no. of atoms per unit cell in FCC will be = $\frac{8}{8} + \frac{6}{2} + 0 = 4$

Let a be the lattice constant and r be the atomic radius
So volume of unit cell will be = a^3

Volume of one atom will be = $\frac{4}{3} \pi r^3$

Packing fraction = $\frac{\text{Effective no. of atoms per unit cell} \times \text{Volume of one atom}}{\text{Volume of unit cell}}$

$$PF = \frac{4 \times \frac{4}{3} \pi r^3}{a^3}$$

$$PF = \frac{\frac{16}{3} \pi r^3}{a^3} \longrightarrow ①$$

Relation between a and $4r$ →

From $\triangle ABC$ applying Pythagoras theorem

$$(AC)^2 = (AB)^2 + (BC)^2$$

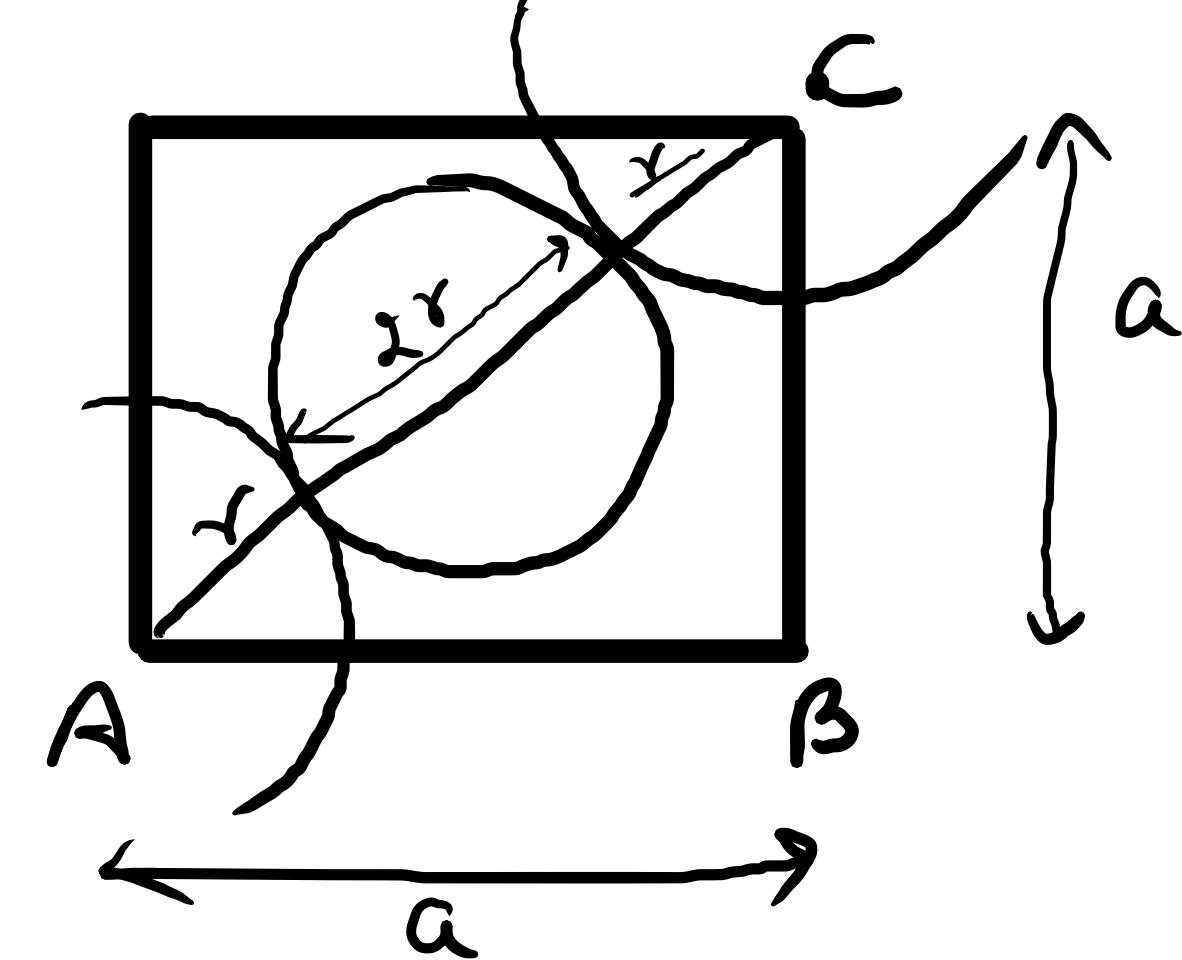
$$(4r)^2 = a^2 + a^2$$

$$(4r)^2 = 2a^2$$

$$\Rightarrow 4r = \sqrt{2} a$$

$$a = \frac{4r}{\sqrt{2}} \times \frac{\sqrt{2}}{\sqrt{2}} = \frac{4\sqrt{2}r}{2} = 2\sqrt{2}r$$

$$AC = 4r$$



Put in eq. ① we get

$$\rho_F = \frac{\pi}{3\sqrt{2}} = 0.74$$

Packing Efficiency = 74%

Void space = 26%

Packing Factor for Body Centered Cubic Structure

27/11/2020

In body centered cubic unit cell there are eight atoms at corners and one atom in the body centered position.

So effective no of atoms per unit cell will be

$$= \cdot \frac{8}{8} + \frac{1}{2} + 1 = 2$$

Now packing fraction = $\frac{\text{Effective no. of atoms per unit cell} \times \text{Volume of one atom}}{\text{Volume of unit cell}}$

Let a be the lattice constant and r be the radius of atom. Then Volume of unit cell will be $= a^3$

and Volume of one atom will be $= \frac{4}{3} \pi r^3$

$$PF = 2 \times \frac{4}{3} \pi r^3 - \textcircled{1}$$

Relation between a and r

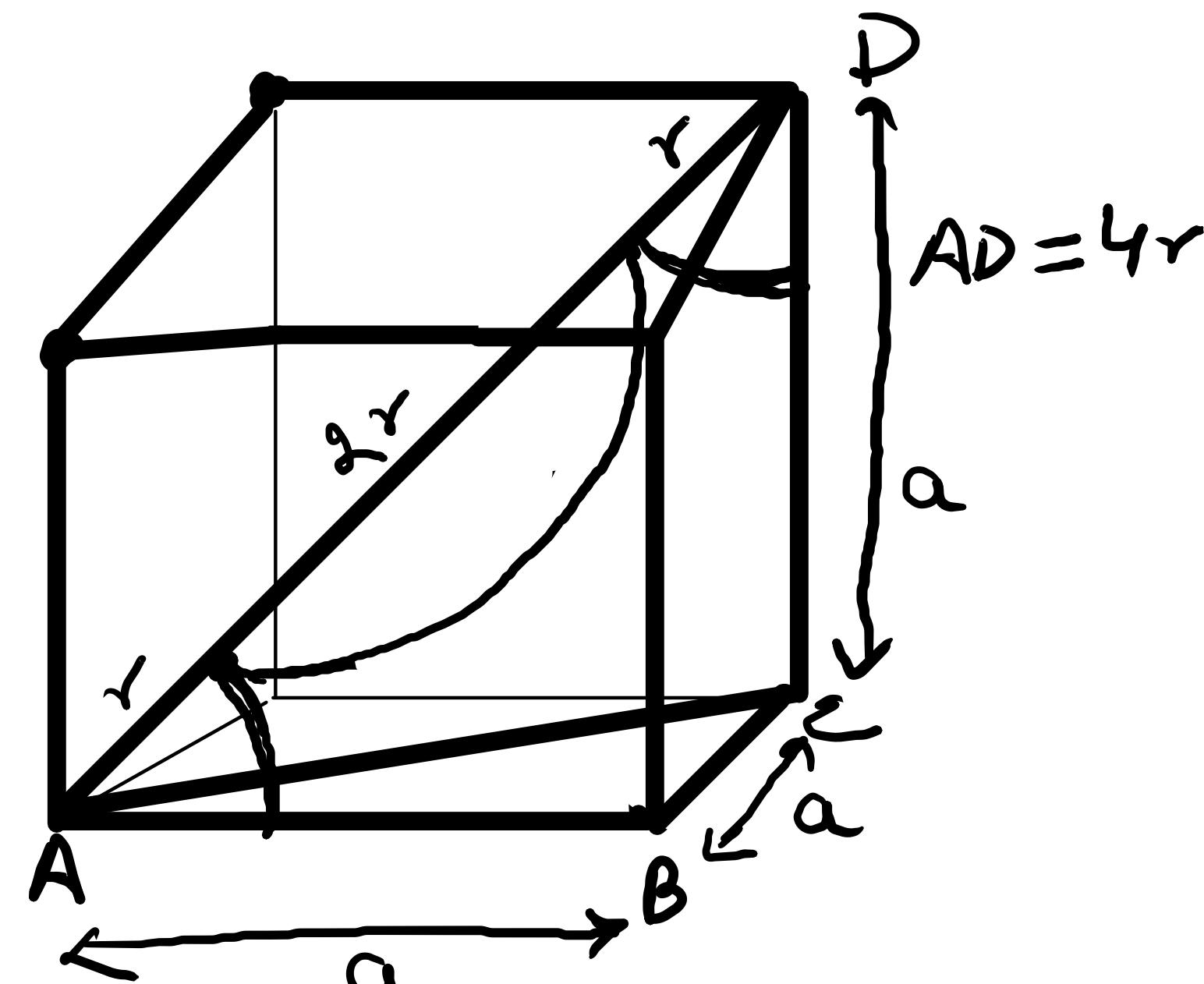
Now from $\triangle ACD$, applying Pythagoras theorem.

$$(AD)^2 = (AC)^2 + (DC)^2$$

$$(4r)^2 = (AC)^2 + a^2 - \textcircled{1}$$

From $\triangle ABC$, applying Pythagoras theorem

$$(AC)^2 = (AB)^2 + (BC)^2 = a^2 + a^2 = 2a^2$$



Put the value of $(AL)^2$ in eq. ① we get

$$(4r)^2 = 2a^2 + a^2$$

$$\Rightarrow (4r)^2 = 3a^2.$$

Taking square root on both sides

$$4r = \sqrt{3} a \Rightarrow a = \frac{4r}{\sqrt{3}}$$

$$\rho_F = \frac{2 \times \frac{4}{3} \pi r^3}{a^3} = \frac{\frac{8}{3} \pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{\frac{8}{3} \pi r^3}{\frac{64 r^3}{3\sqrt{3}}} = \frac{8\pi r^3}{64 r^3}$$

$$\Rightarrow \rho_F = \frac{\cancel{\frac{8}{3} \pi r^3} \times \cancel{3\sqrt{3}}}{\cancel{8.64 r^3}} = \frac{\pi \sqrt{3}}{8} = 0.68$$

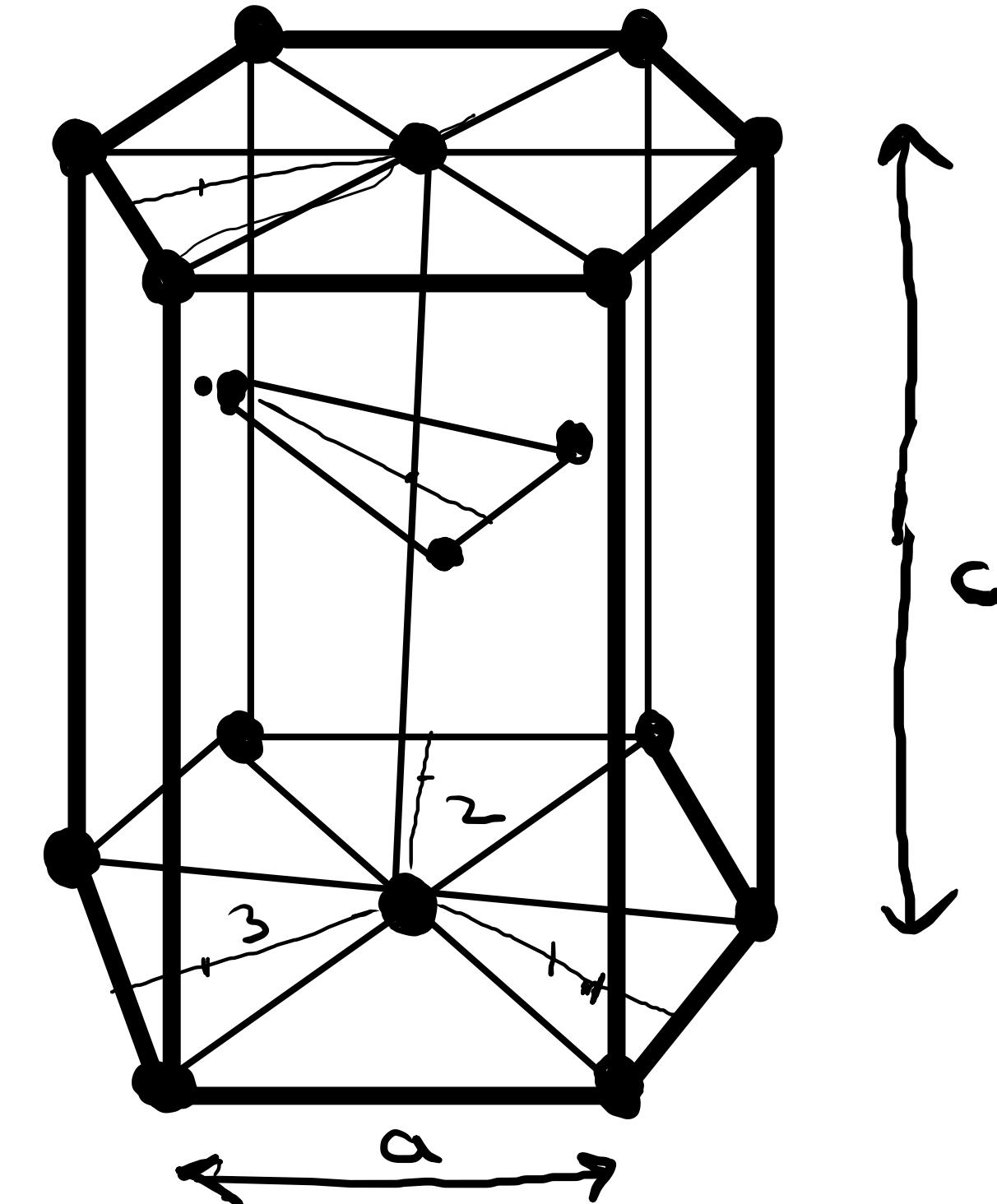
Packing efficiency = $0.68 \times 100 = 68\%$, Void space = 32%

Packing Fraction or efficiency of Hexagonal closed packed structures

(B) HCP
Yours

HCP unit cell is as shown in the diagram.

- There are 12 corner atoms, 6 on each hexagonal face.
- There are two atoms at face centred positions. One each on hexagonal face.
- And there are three atoms at body centred position



Now effective no. of atoms per unit cell

$$= 12 \times \frac{1}{8} + 2 \times \frac{1}{2} + 3 = 6$$

Corner atoms

face centred

body centred

Let a be lattice constant and r be the atomic radius.

Packing fraction = $\frac{\text{Effective no. of atoms per unit cell} \times \text{Volume of one atom}}{\text{Volume of unit cell.}}$

$$PF = \frac{6 \times \frac{4}{3} \pi r^3}{\text{Volume of unit cell}} \quad \text{--- ①}$$

Volume of unit cell → hexagon

Volume of unit cell = Area of Base × height

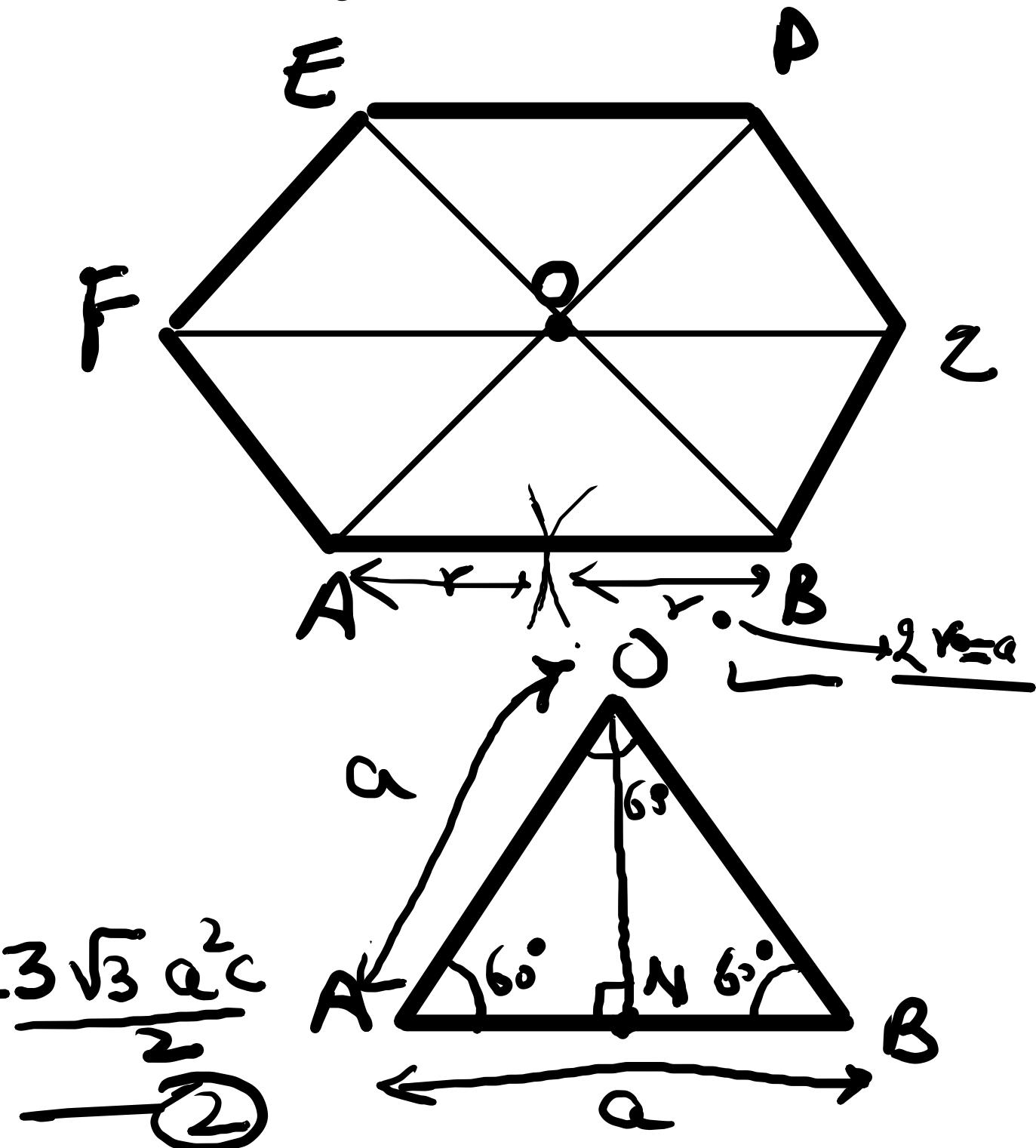
$$= 6 \times \text{Area of } \triangle AOB \times \text{height}$$

$$= 6 \times \frac{1}{2} AB \times \text{ON} \times \text{height}$$

Volume of unit cell = $3 a^2 \text{ON} \times c$

Given $\triangle AON$
 $\frac{ON}{AO} = \sin 60^\circ$
 $ON = a \frac{\sqrt{3}}{2}$

Volume of unit cell = $3 a \times a \frac{\sqrt{3}}{2} \times c = \frac{3\sqrt{3} a^2 c}{2}$

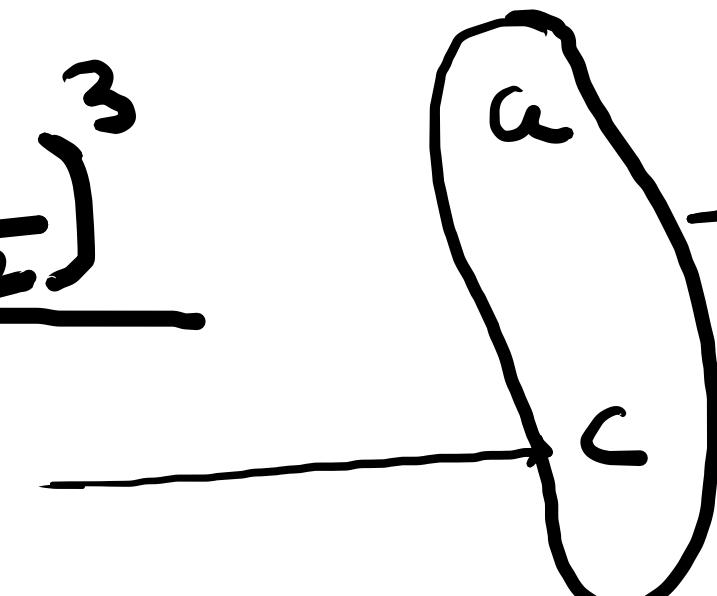


8 marks
15

$$PF = \frac{6 \times \frac{4}{3} \pi r^3}{\frac{3\sqrt{3}a^2c}{2}} \quad \text{--- } ③$$

Here $a = 2r$ or $r = \frac{a}{2}$

$$\sqrt{PF} = \frac{6 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{\frac{3\sqrt{3}a^2c}{2}}$$

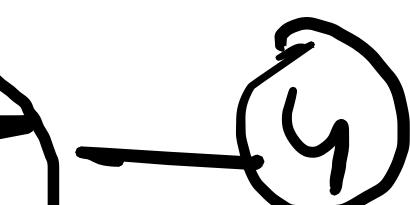


Relation b/w
@ and c

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

Separate
Questions

$$\rho_F \approx \frac{6 \times \frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{\frac{3 \sqrt{3} a^2 c}{2}}$$

$$\rho_F = \frac{\frac{24 \pi a^3}{24}}{\frac{3 \sqrt{3} a^2 c}{2}} = \frac{\frac{\pi a^3}{3 \sqrt{3} a c}}{\frac{2}{2}} = \frac{\pi a}{3 \sqrt{3} c}$$


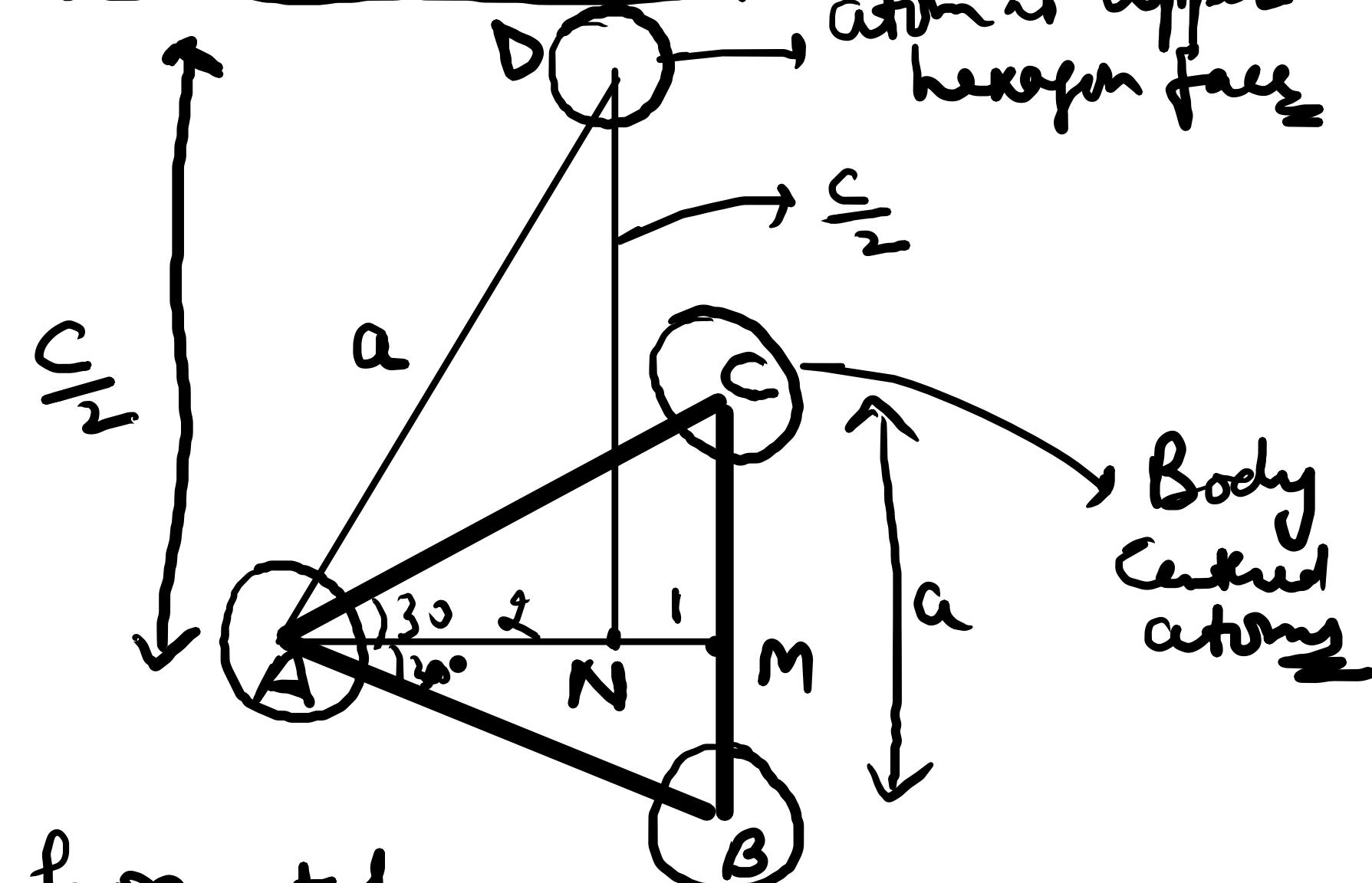
Calculation of $\frac{c}{a}$ ratio OR

$$\text{Prove } \frac{c}{a} = \sqrt{\frac{8}{3}}$$

Now in ΔAND , applying Pythagoras theorem,

$$(AD)^2 = (AN)^2 + (ND)^2$$

$$a^2 = (AN)^2 + \left(\frac{c}{2}\right)^2 - ⑤$$



The three body atoms lie in a horizontal plane at height $\frac{c}{2}$ from the centroids of alternate equilateral triangles in base or upper face
So the atoms at face centred position will lies above or below

Centroid of $\triangle \underline{ABC}$ made by three body atoms.

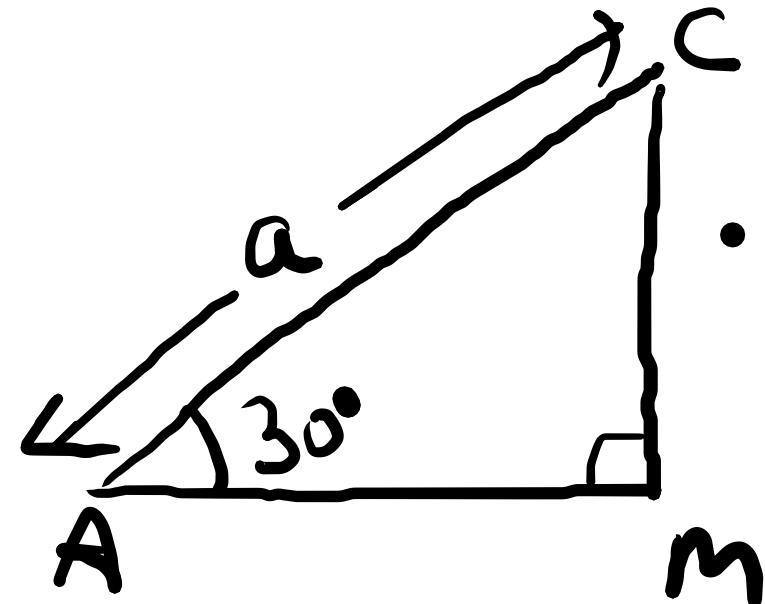
So from diagram

$$AN = \frac{2}{3} AM$$

From $\triangle AMC$

$$\frac{AM}{AC} = \cos 30^\circ$$

$$\Rightarrow AM = a \cos 30^\circ$$



$$\Rightarrow AN = \frac{2}{3} \times a \cos 30^\circ = \frac{2}{3} a \frac{\sqrt{3}}{2} = \frac{a\sqrt{3}}{3} \times \frac{\sqrt{3}}{\sqrt{3}} = \frac{3a}{3\sqrt{3}}$$

$$\Rightarrow AN = \frac{a}{\sqrt{3}}$$

Put the value of AN in eq. 5

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

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

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

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

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

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

$$\frac{2\sqrt{2}}{\sqrt{2}} = 2$$
$$\frac{2 \times 1.414}{1.414} = 1.6$$

Put $\frac{c}{a} = \sqrt{\frac{8}{3}}$ in equation no. ④

$$PF = \frac{\frac{\pi a}{3\sqrt{3}c}}{\frac{2}{2}} = \frac{\pi \sqrt{3}}{3\sqrt{3}\sqrt{8}} = \frac{\pi}{3\sqrt{2}\frac{x}{\pi}} = \frac{\pi}{3\sqrt{2}}$$

$$PF = \frac{\pi}{3\sqrt{2}} = 0.74$$

OR Packing Efficiency = 74%

Void space = 26%.

03/12/2020

✓ Point Defects in Solids →

Defect → Any deviation of crystal from perfect periodicity is called defect in crystal.

All the defects found in real crystals can be classified into three categories.

① Point Defect ② Line Defect ③ Surface Defect

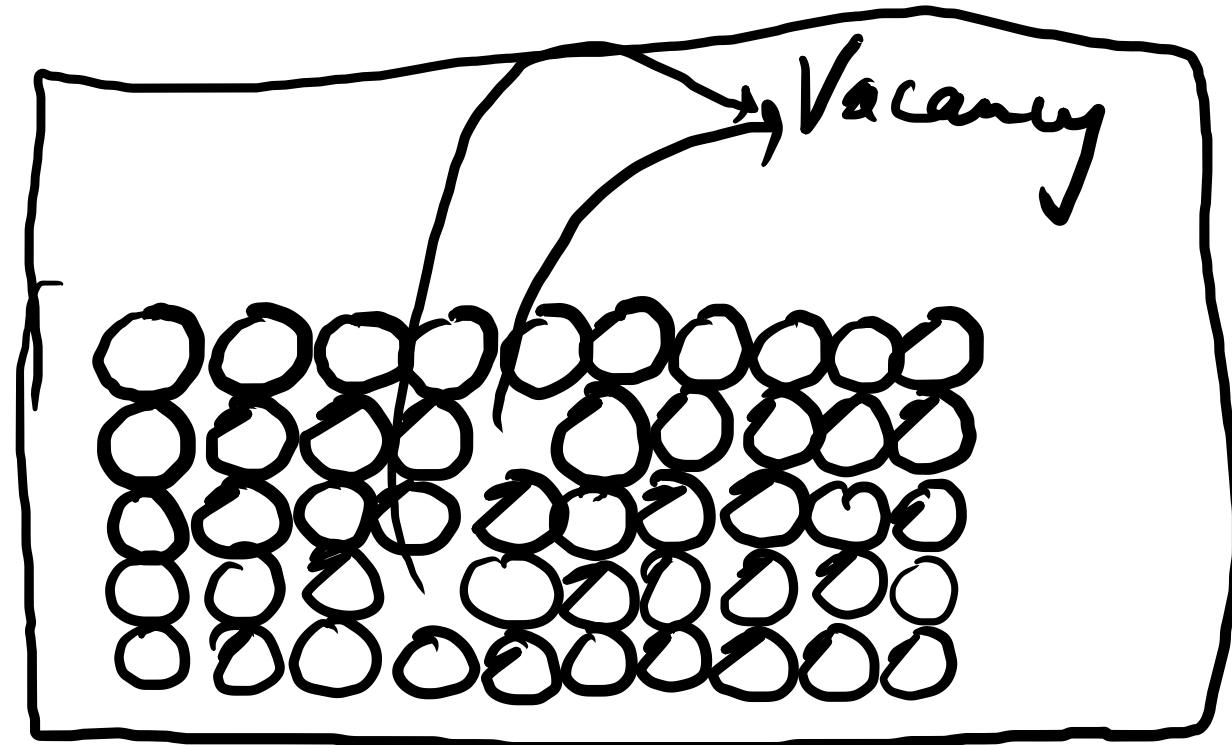
Point Defect →

[When the deviation from regular arrangement is localized only around few atoms than that type of defect is called point defect.]
→ A point defect produces strain in a very small region of a

Crystal around a defect.
Types of point defect →

① Vacancy defect

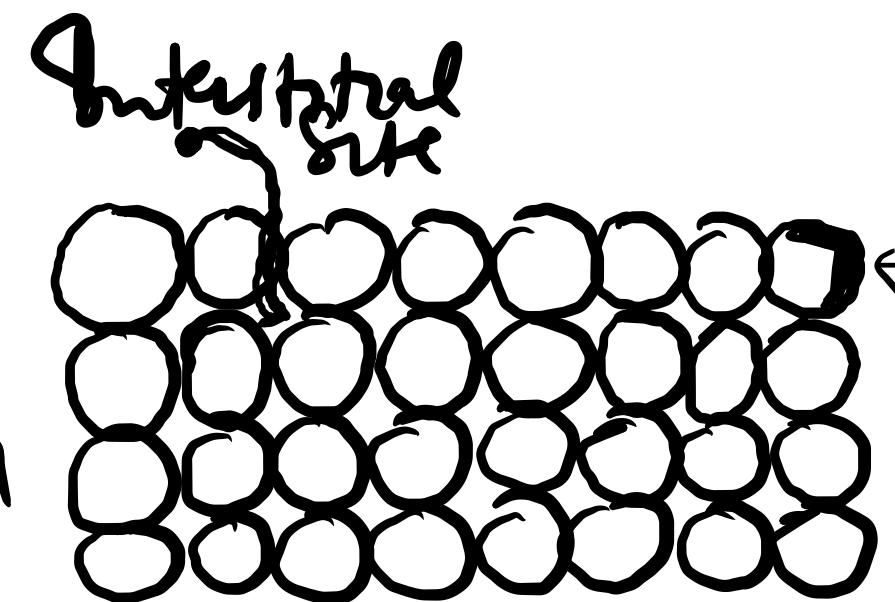
This type of defect arises due to missing of atom from its regular site.



This type of defect arises due to improper packing during the formation of crystal or due to thermal energy.

② Interstitial defect →

There may be a possibility that an extra atom may be introduced in the crystal



If the size of foreign element is equal to the size of Interstitial site then that element can occupy that site. Such type of defect is called Interstitial defect.

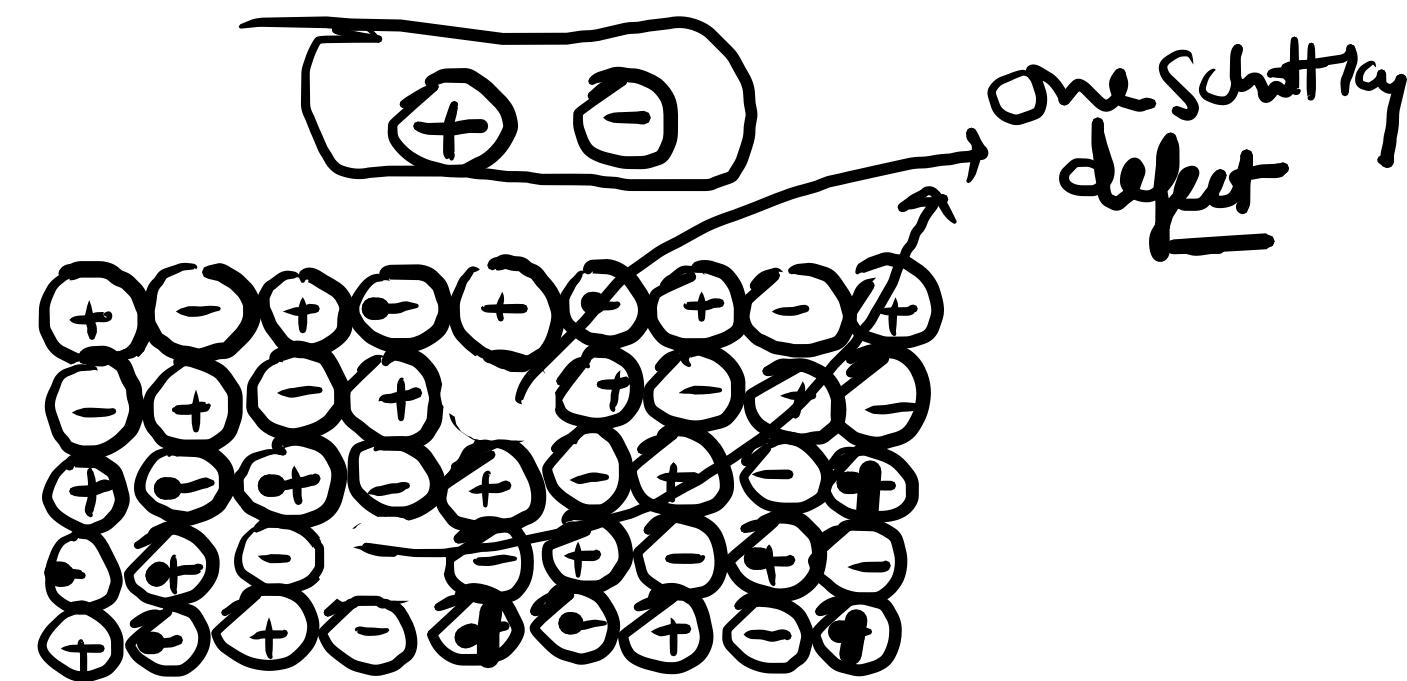
③

Schottky defect →

Such types of defects are found commonly in ionic crystals.

When a pair of cation and anion misses from its regular site and leaves the crystal then we have one Schottky defect.

For n Schottky defects we have n -cation vacancies and n anion Vacancies.



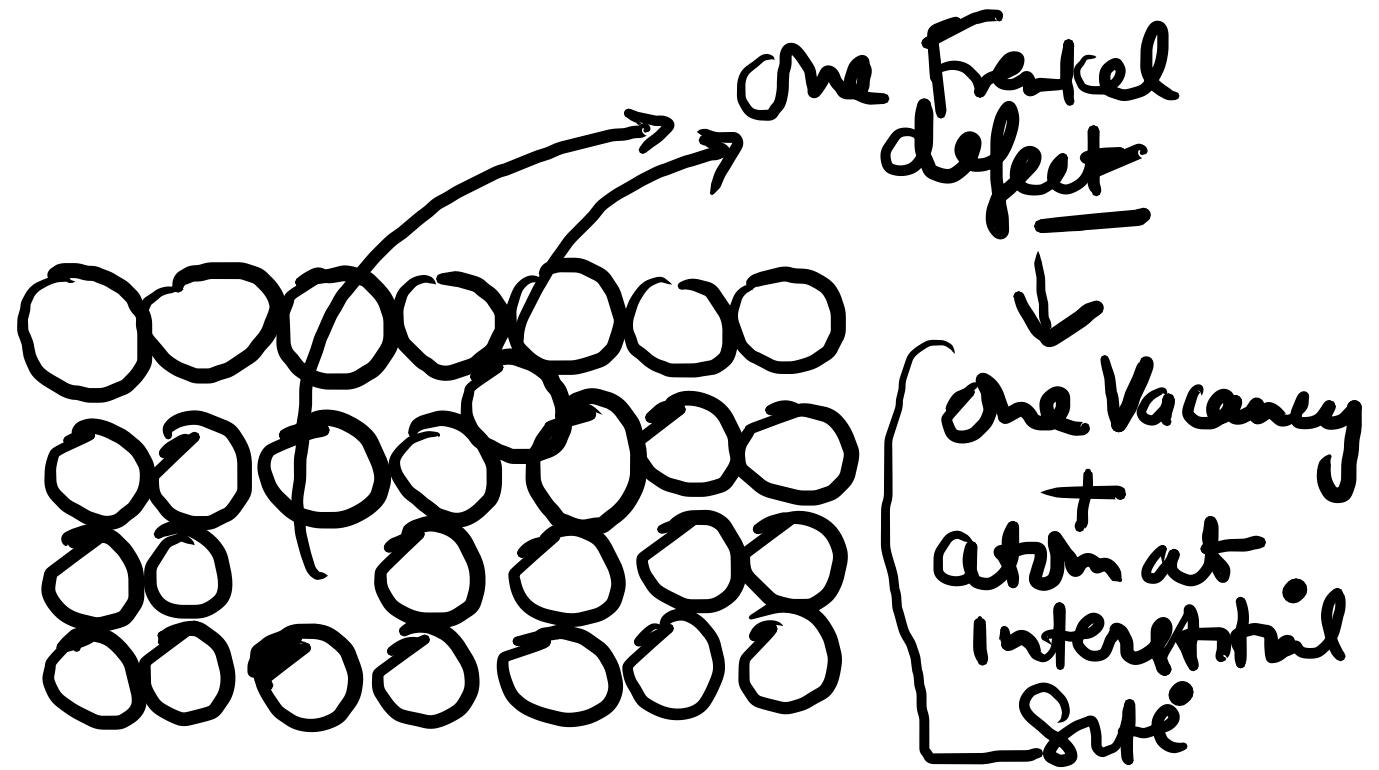
{ n - Schottky defects
 ↓
 $n \rightarrow$ Cation Vacancies
 $n \rightarrow$ Anion Vacancies

→ Density of crystal decreases but charge neutrality is maintained.

④ Frenkel Defect ✓

In this type of defect an atom or ion is transferred from its lattice position to an interstitial site. Then that defect is called Frenkel defect.

one Frenkel defect consists of one Vacancy and one atom at Interstitial Site.



n - Frenkel defect
↓
 n Vacancies +
 n atoms at Interstitial Sites

→ Density remains same and charge neutrality is maintained.

04/12/2020

Concentration of Schottky defect

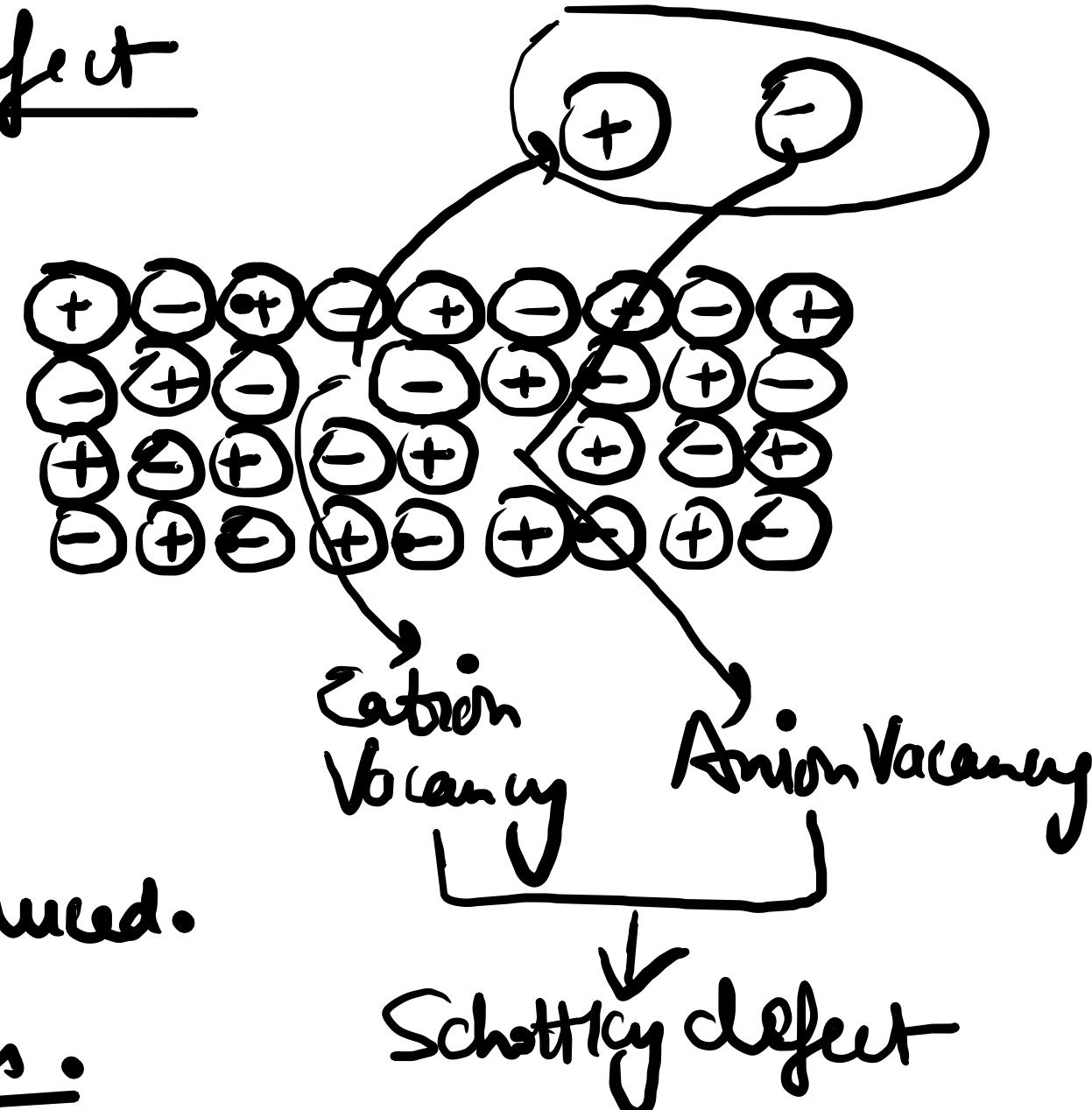
Consider a crystal consisting of equal number of cations and anions.

Let there are N cation and anion pairs ie there are N cations and N anions.

Let n Schottky defects are to be produced.
ie $n \rightarrow$ Cation Vacancies and $n \rightarrow$ Anion Vacancies.

Total number of ways such that n Cation Vacancies can be created will be = N_{Cn}

Now total no of ways such that n anion Vacancies can be created will be
= N_{An}



Now total no of ways such that n Schottky defects can be created will be Compound probability given by

$$W = N_{C_n} \times N_{C_n}$$

$$W = [N_{C_n}]^2 = \left[\frac{N!}{n!(N-n)!} \right]^2 = ①$$

Now degree of disorder ie entropy of the system will be given by

$$S = K_B \log W$$

Boltzmann Constant

Statistical Interpretation
Entropy

$$S = K_B \log \left[\frac{N!}{n!(N-n)!} \right]^2 \longrightarrow \textcircled{2}$$

Let \bar{E}_s be the average energy required to produce one Schottky defect. Then energy required to produce n Schottky defect will be $= n\bar{E}_s$

This change in internal energy produces a change in free energy given by

$$F = \bar{E} - TS \xrightarrow{\text{Temperature}} \\ F = n\bar{E}_s - K_B T \log \left[\frac{N!}{n!(N-n)!} \right]^2 \longrightarrow \textcircled{3}$$

$$\log \left[\frac{N!}{n!(N-n)!} \right]^2$$

Thus can be solved by using Stirling formula

$$\log x! = x \log x - x$$

$$\begin{aligned} \log \left[\frac{N!}{n!(N-n)!} \right]^2 &= 2 \log \left[\frac{N!}{n!(N-n)!} \right] \\ &= 2 \left[\log N! - \log(n!(N-n)!) \right] \\ &= 2 \left[\log N! - \log(N-n)! - \log n! \right] \end{aligned}$$

$$\log m^n = n \log m$$

$$\log \frac{m}{n} = \log m - \log n$$

$$\log mn = \log m + \log n$$

$$= 2 \left[\log N! - \underbrace{\log(N-n)!}_{\text{Apply Stirling formula.}} - \log n! \right]$$

$$\log x! = K \log x - x$$

$$= 2 \left[N \log N - N - \left\{ (N-n) \log(N-n) - (N-n) \right\} - \left\{ n \log n - n \right\} \right]$$

$$= 2 \left[N \log N - \cancel{N} - (N-n) \log(N-n) + \cancel{N-n} - n \log n + \cancel{n} \right]$$

$$= 2 \left[N \log N - (N-n) \log(N-n) - n \log n \right]$$

Put in eq. no. ③ we get

$$F = n \bar{E}_s - 2 K_B T [N \log N - (N-n) \log(N-n) - n \log n]$$

At thermal equilibrium the free energy is constant
then

$$\left. \frac{\partial F}{\partial n} \right|_T = 0$$

$$\Rightarrow \frac{\partial}{\partial n} \left[n \bar{E}_s - 2 k_B T \left(N \underbrace{\log N}_{1} - (N-n) \log(N-n) - \underbrace{n \log n}_{1} \right) \right] = 0$$

$$\Rightarrow \bar{E}_s - 2 k_B T \left[0 - \left\{ \frac{(N-n)(-1)}{(N-n)} + \log(N-n)(-1) \right\} - \left\{ \frac{n}{N} + \log n \cdot 1 \right\} \right] = 0$$

$$\Rightarrow \bar{E}_s - 2 k_B T \left[T + \log(N-n) - \cancel{1 - \log n} \right] = 0$$

$$\bar{E}_s - 2k_B T \left[\underbrace{\log(N-n) - \log n}_{\text{}} \right] = 0$$

$$\Rightarrow \bar{E}_s - 2k_B T \log \left(\frac{N-n}{n} \right) = 0$$

$$\Rightarrow \bar{E}_s = 2k_B T \log \left(\frac{N-n}{n} \right)$$

$$\Rightarrow \log \left(\frac{N-n}{n} \right) = \frac{\bar{E}_s}{2k_B T}$$

$$\Rightarrow \frac{N-n}{n} = e^{\frac{\bar{E}_s}{2k_B T}}$$

$$\text{Now } N \gg n \Rightarrow N-n \approx N$$

$$\Rightarrow \frac{N}{n} \approx e^{\frac{-\bar{E}_s}{2k_B T}} \Rightarrow n = N e^{\frac{-\bar{E}_s}{2k_B T}}$$

Concentration of Schottky defect at thermal equilibrium.

07/12/2020

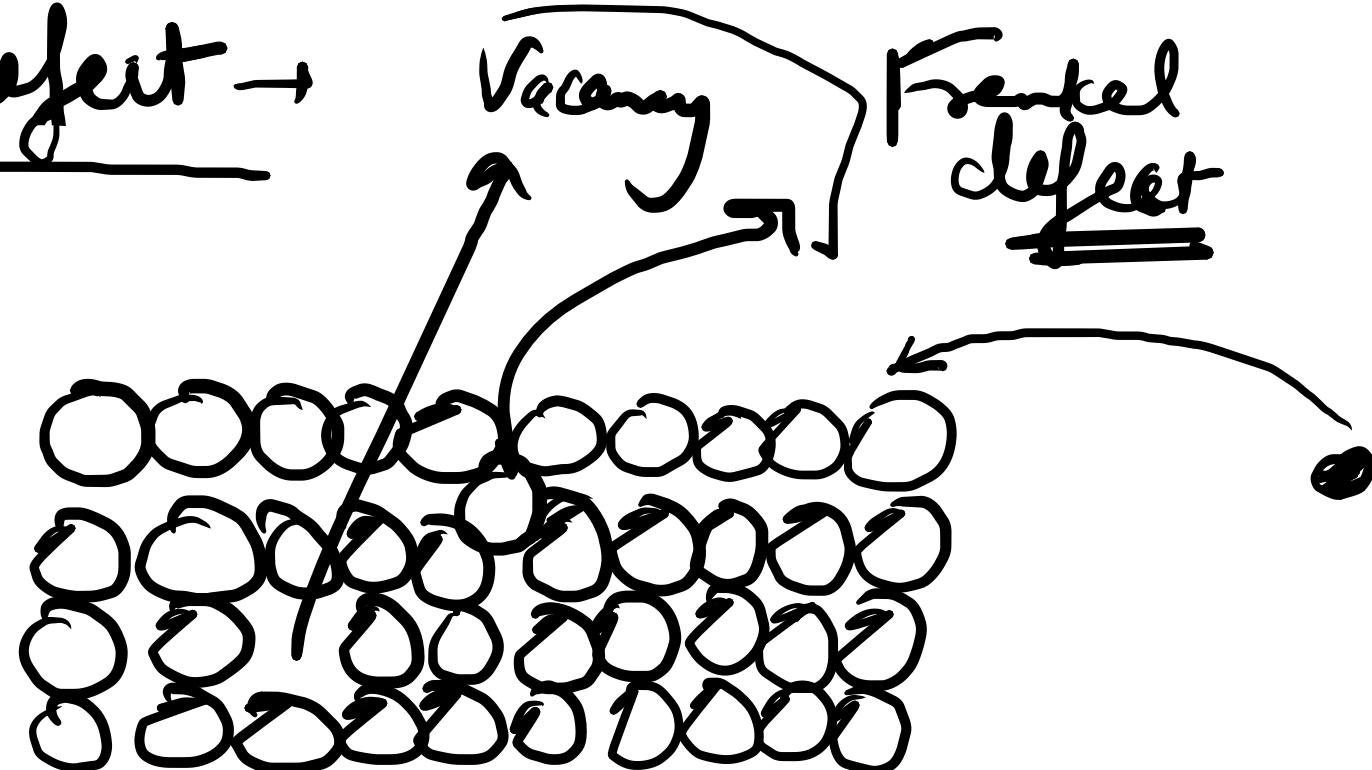
Concentration of Frankel defect →

In this defect an atom or ion is transferred from its regular site to interstitial position.

Then pair of vacancy and atom at interstitial site is called Frankel defect.

Let there are N ion pairs or atoms, and let there are n - Frankel defects. i.e. there are n Vacancies and n parent atoms at interstitial sites.

Let there are N_i number of interstitial sites.



Now total number of ways such that \textcircled{n} Vacancies can be created will be given by $= N_{C_n}$

Total no. of ways such that \textcircled{n} Intersitial positions will be occupied atoms will occupy $= N_{iC_n}$

Now total no. of ways such that \textcircled{n} Frenkel defects can be created will be given

$$W = N_{C_n} \times N_{iC_n}$$

Now entropy will be $S = k_B \log W$

$$\Rightarrow S = k_B \log [N_{C_n} \times N_{iC_n}] - \textcircled{1}$$

Let \bar{E}_F be energy required to produce one Frankel defect
 then $n\bar{E}_F$ will be the energy required to produce n Frankel defects.

so Free energy change will be

$$F = E - TS$$

$$\Rightarrow F = n\bar{E}_F - T k_B \lg [N_{C_n} N_{iC_n}]$$

$$F = n\bar{E}_F - k_B T \lg \left[\frac{N!}{n!(N-n)!} \cdot \frac{N_i!}{n_i!(N_i-n_i)!} \right]$$

$$\begin{aligned}
 \log \left[\frac{N!}{n!(N-n)!} \cdot \frac{N_i!}{n_i!(N_i-n)!} \right] &= \log \left[\frac{N!}{n!(N-n)!} \right] + \log \left[\frac{N_i!}{n_i!(N_i-n)!} \right] \\
 &= \log N! - \log [n!(N-n)!] + \log N_i! - \log [n_i!(N_i-n)!] \\
 &= \cancel{\log N!} - \cancel{\log n!} - \log(N-n)! + \cancel{\log N_i!} - \cancel{\log n_i!} - \cancel{\log(N_i-n)!}
 \end{aligned}$$

Now applying Stirling formula ie $\log x! = x \log x - x$

$$\begin{aligned}
 \log \left[\frac{N!}{n!(N-n)!} \frac{N_i!}{n_i!(N_i-n)!} \right] &= N \log N - N - 2\{n \log n - n\} - \{(N-n) \log(N-n) - (N-n)\} \\
 &\quad + N_i \log N_i - N_i - \{(N_i-n) \log(N_i-n) - (N_i-n)\} \\
 &= N \cancel{\log N} - \cancel{N} - 2n \log n + \cancel{2n} - (N-n) \log(N-n) + \cancel{N} \cancel{-n} \\
 &\quad + N_i \cancel{\log N_i} - \cancel{N_i} - (N_i-n) \log(N_i-n) + \cancel{N_i} \cancel{-n} \\
 &= N \log N - 2n \log n - (N-n) \log(N-n) + N_i \log N_i \\
 &\quad - (N_i-n) \log(N_i-n)
 \end{aligned}$$

Put in eq. ② we get.

$$F = n \bar{E}_f - k_B T \left[N \log N - 2n \log n - (N-n) \log(N-n) + N_i \log N_i - (N_i-n) \log(N_i-n) \right]$$

At thermal equilibrium Free energy is constant so

$$\frac{\partial F}{\partial n} \Big|_T = 0$$

$$\frac{\partial}{\partial n} \left[n \bar{E}_f - k_B T \left\{ N \log N - \sum_{\text{I}} n \log n - (N-n) \log(N-n) + N_i \log N_i - (N_i-n) \log(N_i-n) \right\} \right] = 0$$

$$\Rightarrow \bar{E}_f - k_B T \left[0 - 2 \left\{ \frac{n}{n} + \log n \right\} - \left\{ \frac{(N-n)}{(N-n)} (-1) + \log(N-n) (-1) \right\} + 0 - \left\{ \frac{N_i-n}{N_i-n} (-1) + \log(N_i-n) (-1) \right\} \right] = 0$$

$$\Rightarrow \bar{E}_f - k_B T \left[-2 \log n + 1 + \log(N-n) + 1 + \log(N_i-n) \right] = 0$$

$$\bar{E}_f = k_B T \left[\underbrace{\log(N-n) + \log(N_i-n)}_{\log m + \log n} - 2 \log n \right] = \frac{\log m + \log n}{\log n}$$

$$\bar{E}_f = k_B T \left[\underbrace{\log(N-n)(N_i-n)}_{\log m^2} - \underbrace{2 \log n}_{\log n^2} \right]$$

$$\Rightarrow \bar{E}_f = k_B T \log \left[\frac{(N-n)(N_i-n)}{n^2} \right] = \frac{\log m^2 - \log n^2}{\log n^2} = \frac{\log \frac{m^2}{n^2}}{\log \frac{n^2}{n^2}}$$

$$\Rightarrow \frac{\log \left[\frac{(N-n)(N_i-n)}{n^2} \right]}{\log \frac{n^2}{n^2}} = \frac{\bar{E}_f}{k_B T}$$

$$\Rightarrow \frac{(N-n)(N_i-n)}{n^2} = e^{\frac{\bar{E}_f}{k_B T}}$$

$$N \gg n, N_i \gg n$$

$$\text{So } N-n \approx N$$

$$N_i \cdot n \approx N_i$$

$$\Rightarrow \frac{N_n}{n^2} = e^{\frac{-E_f}{k_B T}}$$

$$\Rightarrow n^2 = \frac{N_n}{e^{E_f/k_B T}}$$

$$\Rightarrow n = \frac{(N_n)^{\frac{1}{2}}}{e^{E_f/2k_B T}}$$

$$\boxed{n = (N_n)^{\frac{1}{2}} e^{-\frac{E_f}{2k_B T}}}$$

or

Concentration of Frenkel defects.

8/12/2020

Assignment-I

Submission date 15/12/2020

- 1 Bravais lattices in two and three dimensions. ✓
 - 2 Discuss Various types of bonding in Solids. ✓ 10+1, 10+L Chemistry
 - 3 Structures of NaCl, S₈Cl, Zns and Diamond.
- Nitin.applied@piet.co.in

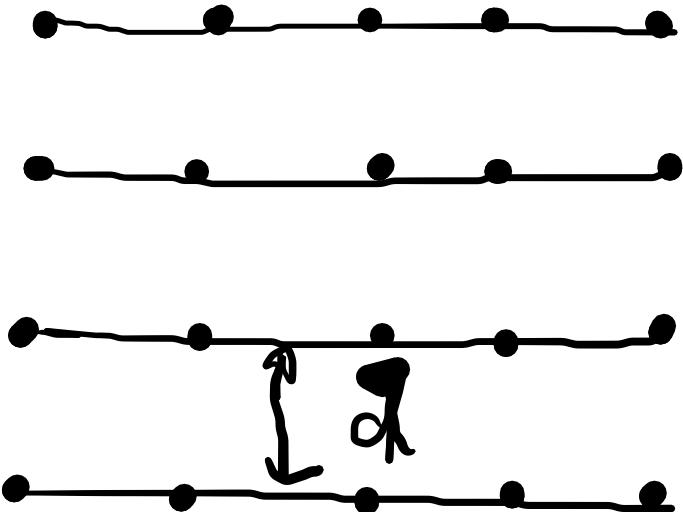
V. Sank

Crystal lattice planes and Miller Indices

000
010

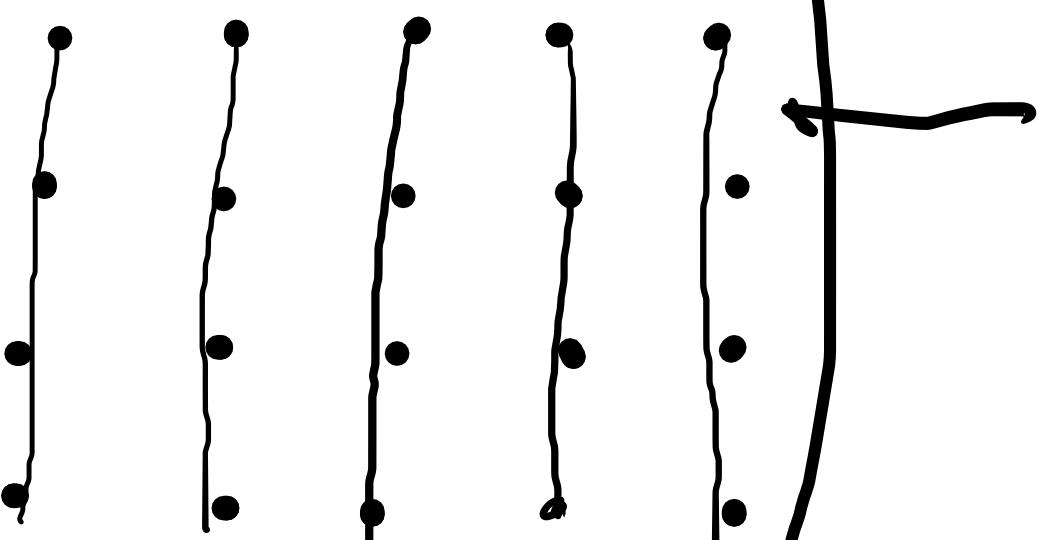
6a
4b
x
y

3c
3
z



To draw planes in single unit cell.

① 6a 4b 3c
 $\frac{6a}{a} = 6$ $\frac{4b}{b} = 4$ $\frac{3c}{c} = 3$
 $\frac{1}{6} \times 12 = 2$ $\frac{1}{4} \times 12 = 3$ $\frac{1}{3} \times 12 = 4$



(2 3 4) → Miller Indices

→ What are Miller Indices. Write down the steps to find Miller Indices.
A crystal lattice may be considered as an aggregate
of a set of parallel equidistant planes passing through
the lattice points.

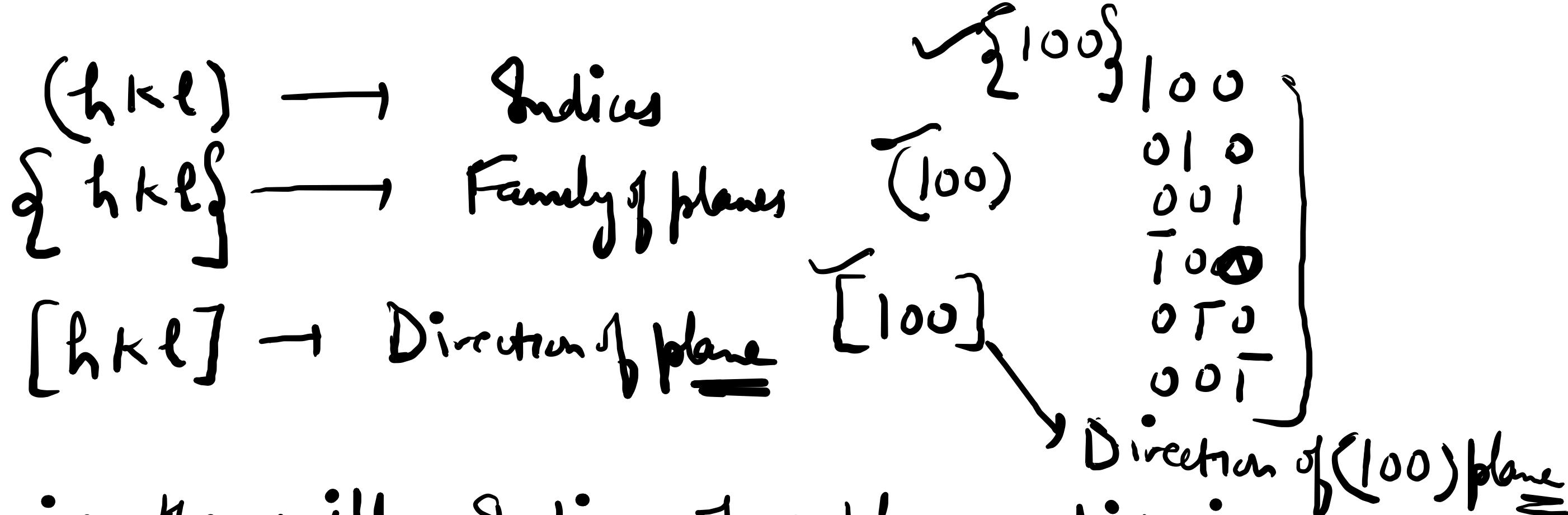
These planes are called lattice planes.

There is method to design these planes in a single
Unit cell, called the method of Miller Indices.

It is very difficult to design those planes with the
help of intercepts. So Miller gave a method to design
those planes with in a Unit cell.

Steps to find Miller Indices

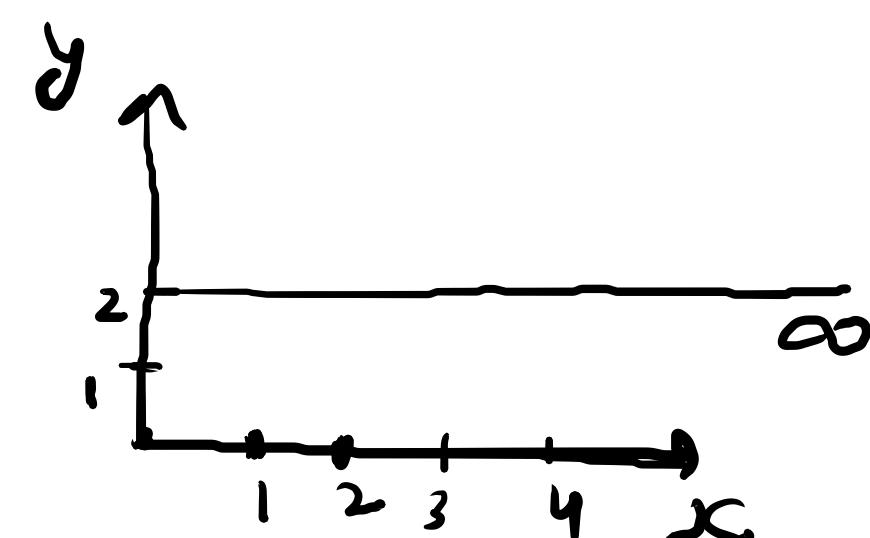
- 1 Write down the intercepts made by the plane along coordinate axes X, Y and Z.
- 2 Divide those intercepts with respective translation vector. After that we will get numbers.
- 3 Take reciprocal of these numbers.
- 4 If fraction arises, then convert them into smallest possible set of integers.
- 5 Put the resulting integers say h, k, l in to parenthesis as $\underline{(h k l)}$



Q-1 Determine the miller Indices of a plane which is parallel to x -axis and cuts intercepts of $2b$ and $\frac{c}{2}$ respectively along y and z -axis

Ans

- | | | | |
|---|------------------------|--------------------|------------------------------|
| ① | ∞ | $2b$ | $\frac{c}{2}$ |
| ② | $\frac{\infty}{a} = 0$ | $\frac{2b}{b} = 2$ | $\frac{c}{2c} = \frac{1}{2}$ |
| ③ | $\frac{1}{a} = 0$ | $\frac{1}{2}$ | 2 |
| ④ | 0 | 1 | 4 |
- (0 1 4)



→ Miller Indices are reciprocal of intercepts, made by the plane on axes when reduced to smallest possible integers.
 { By taking reciprocals, we bring all the planes in [a single unit cell]

Q. Find Miller Indices of a plane making intercepts of $\infty, -6b, \frac{c}{2}$ on the respective axes. where a, b, c are lattice parameters.

Sol

$$(i) \quad \infty \quad -6b \quad \frac{c}{2}$$

$$(ii) \quad \frac{\infty}{a} = \infty \quad -\frac{6b}{b} = -6 \quad \frac{c}{2c} = \frac{1}{2}$$

$$(iii) \quad \frac{1}{\infty} = 0 \quad -\frac{1}{6}$$

$$(iv) \quad 0 \quad -1 \quad 12 \quad (0\bar{1}12)$$

Q Determine the Miller Indices of a plane that makes intercepts of 2 \AA , 3 \AA , 4 \AA on the coordinate axes with $a:b:c = 4:3:2$.

Sol

(i)

2

3

4

111

$$\frac{2}{4} = \frac{1}{2}$$

$$\frac{3}{3} = 1$$

$$\frac{4}{2} = 2$$

(ii)

2

1

$$\frac{1}{2}$$

(iv)

4

2

1

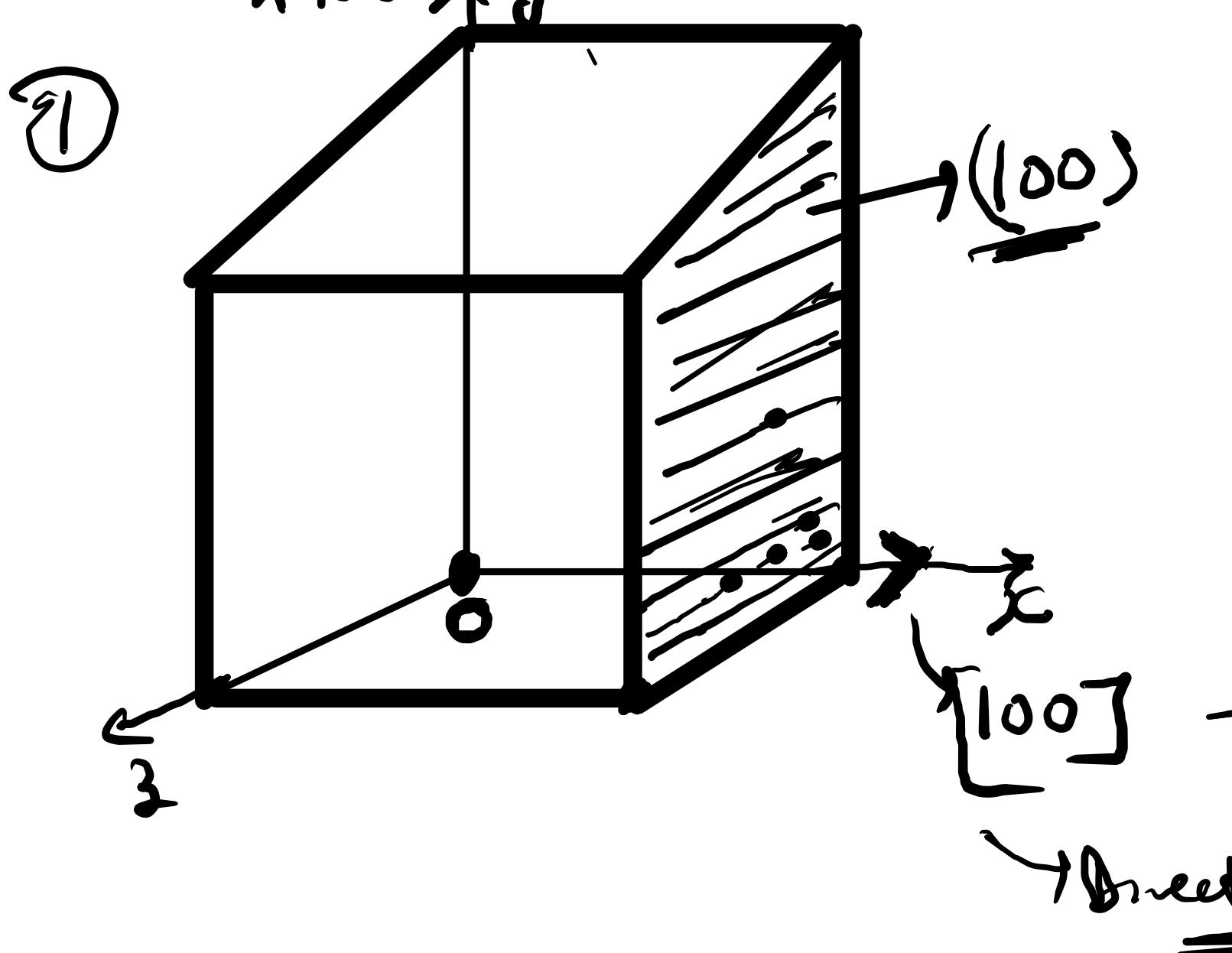
(v)

(4 2 1)

Representation of Planes of known Miller Indices

Q_ Draw planes having Miller Indices

(100) , (010) , (001)



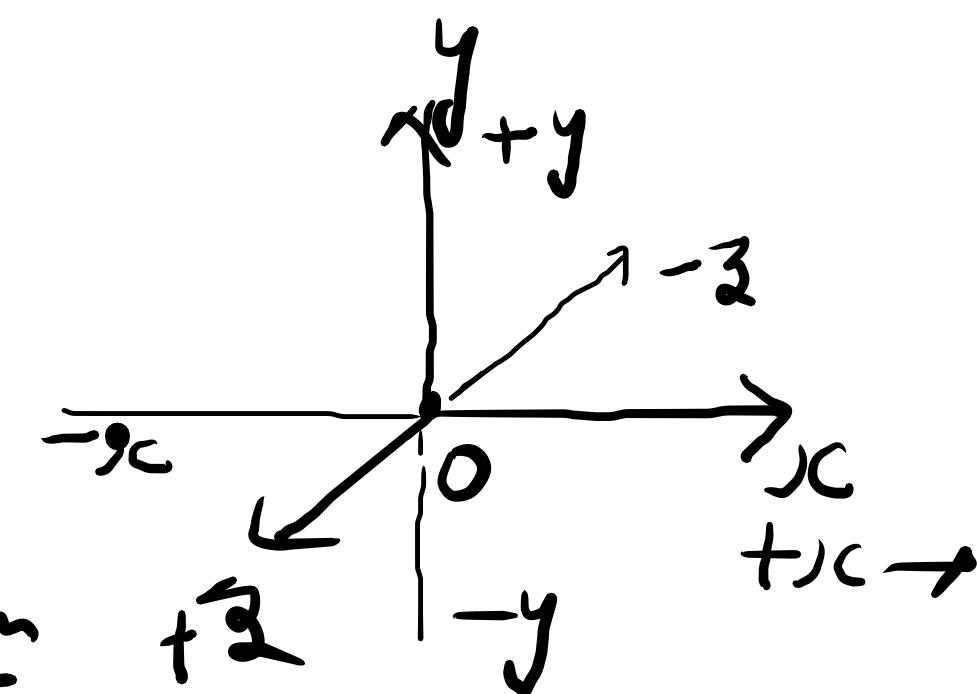
① draw unit cell

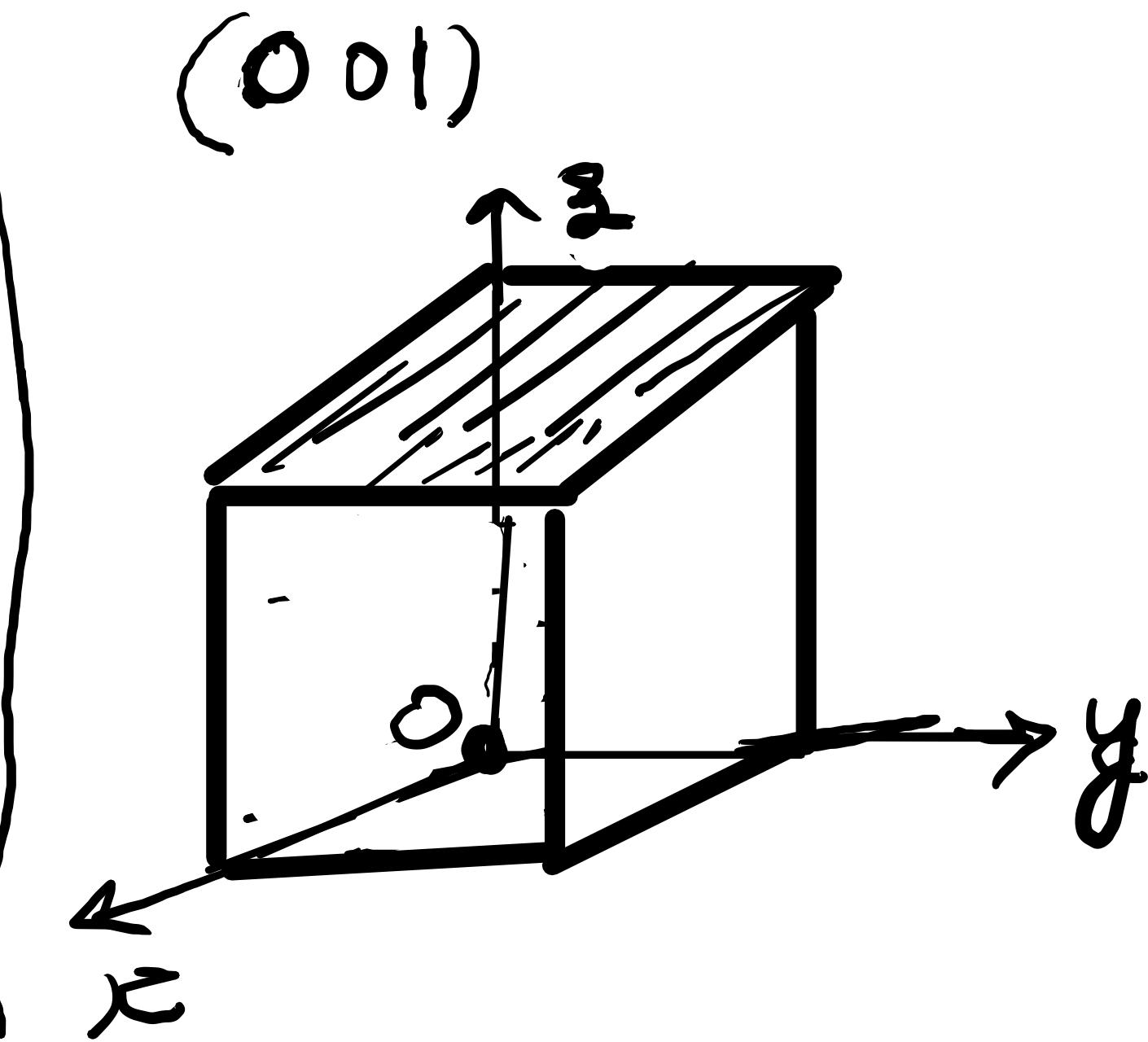
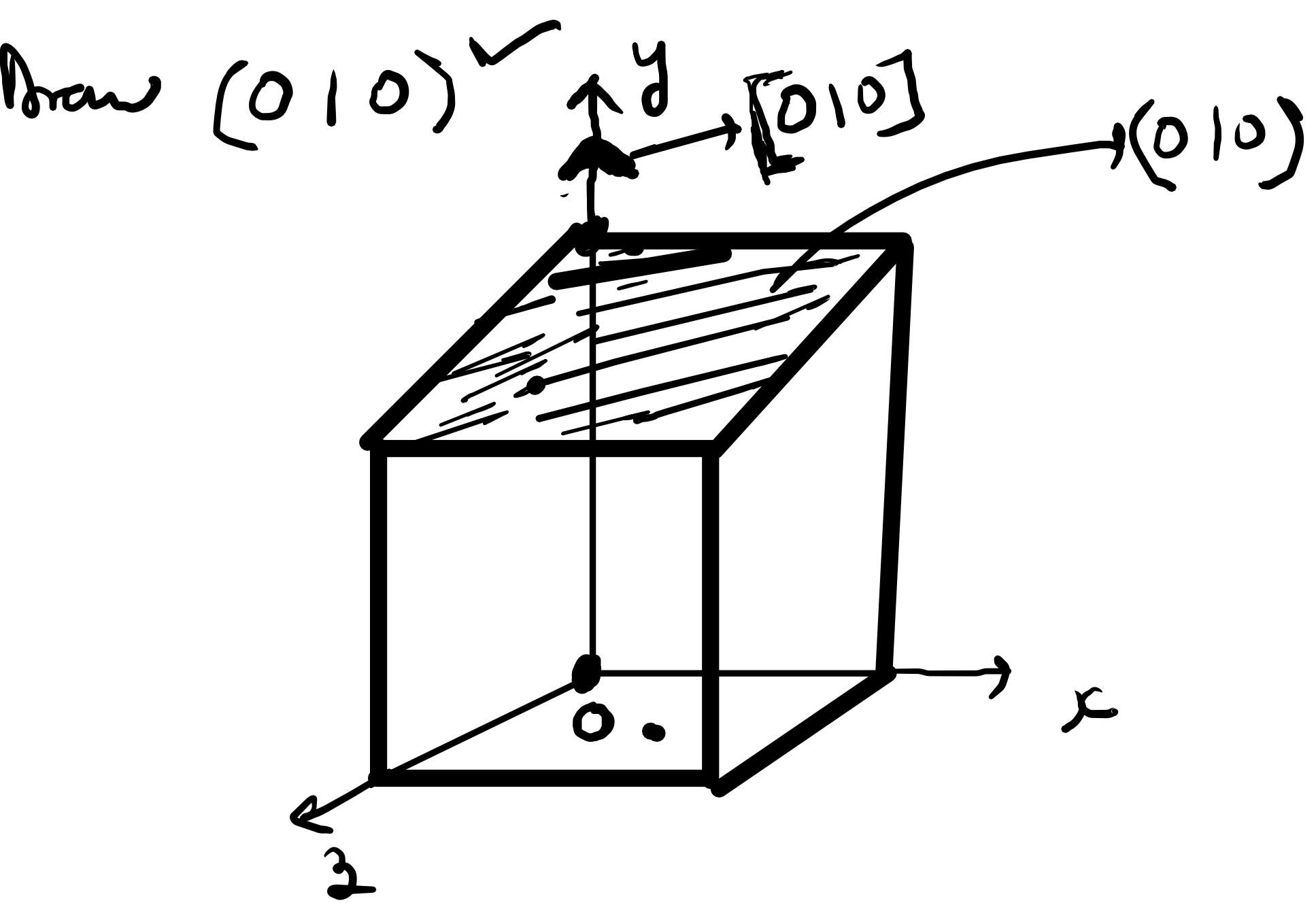
② choose origin and mark as O.

③ choose axes

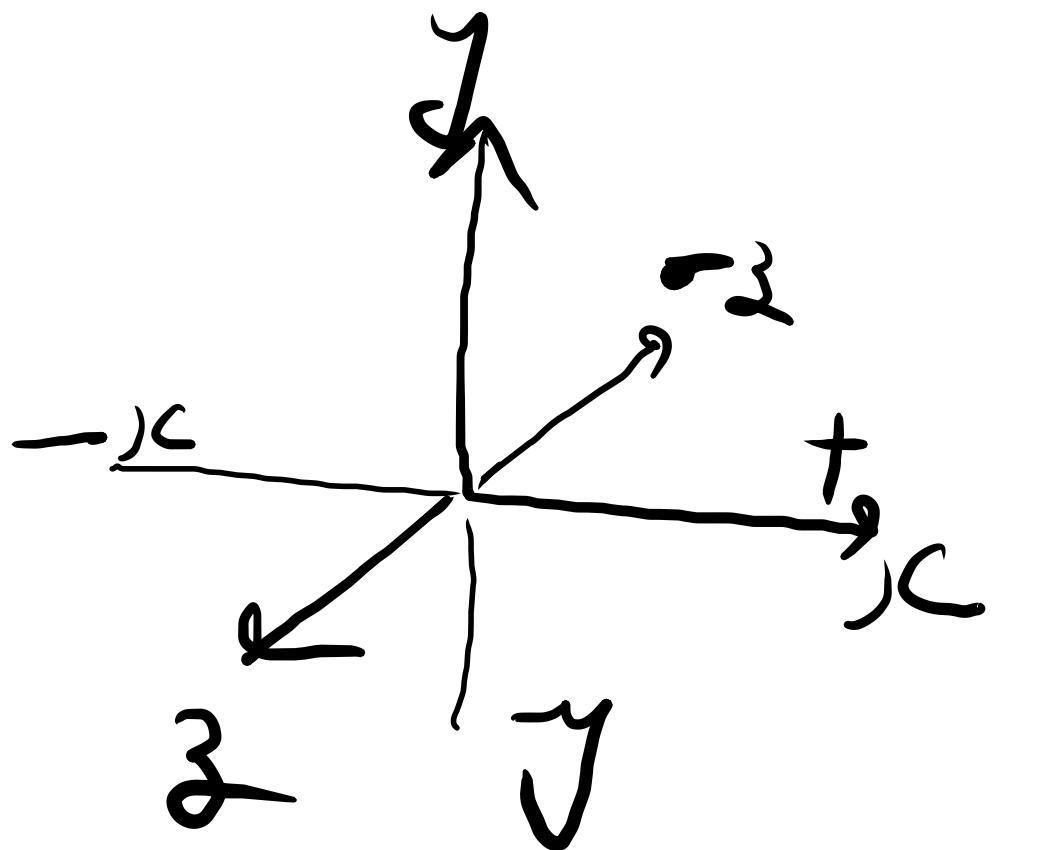
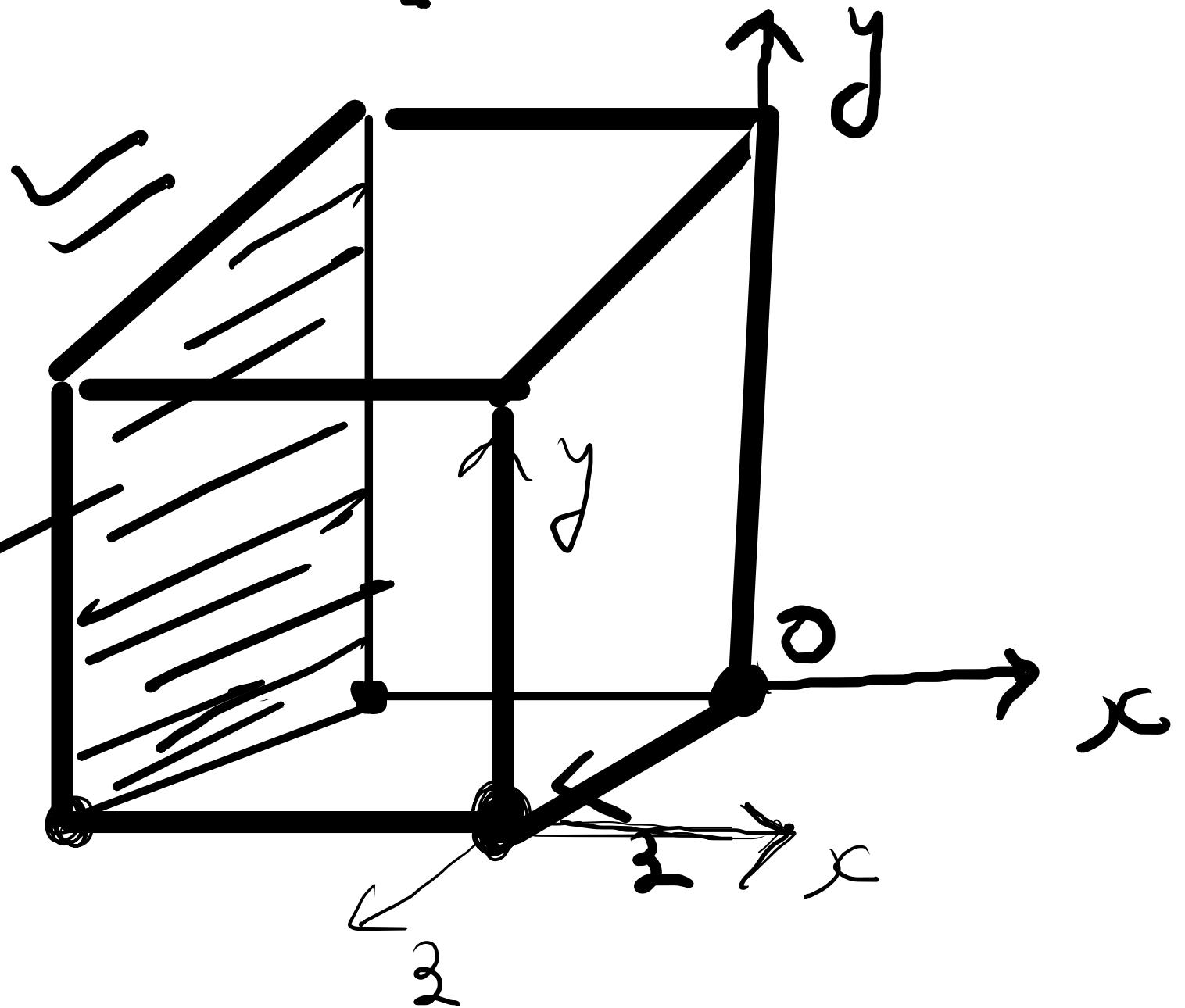
→ OR draw direction $\underline{[100]}$

Direction



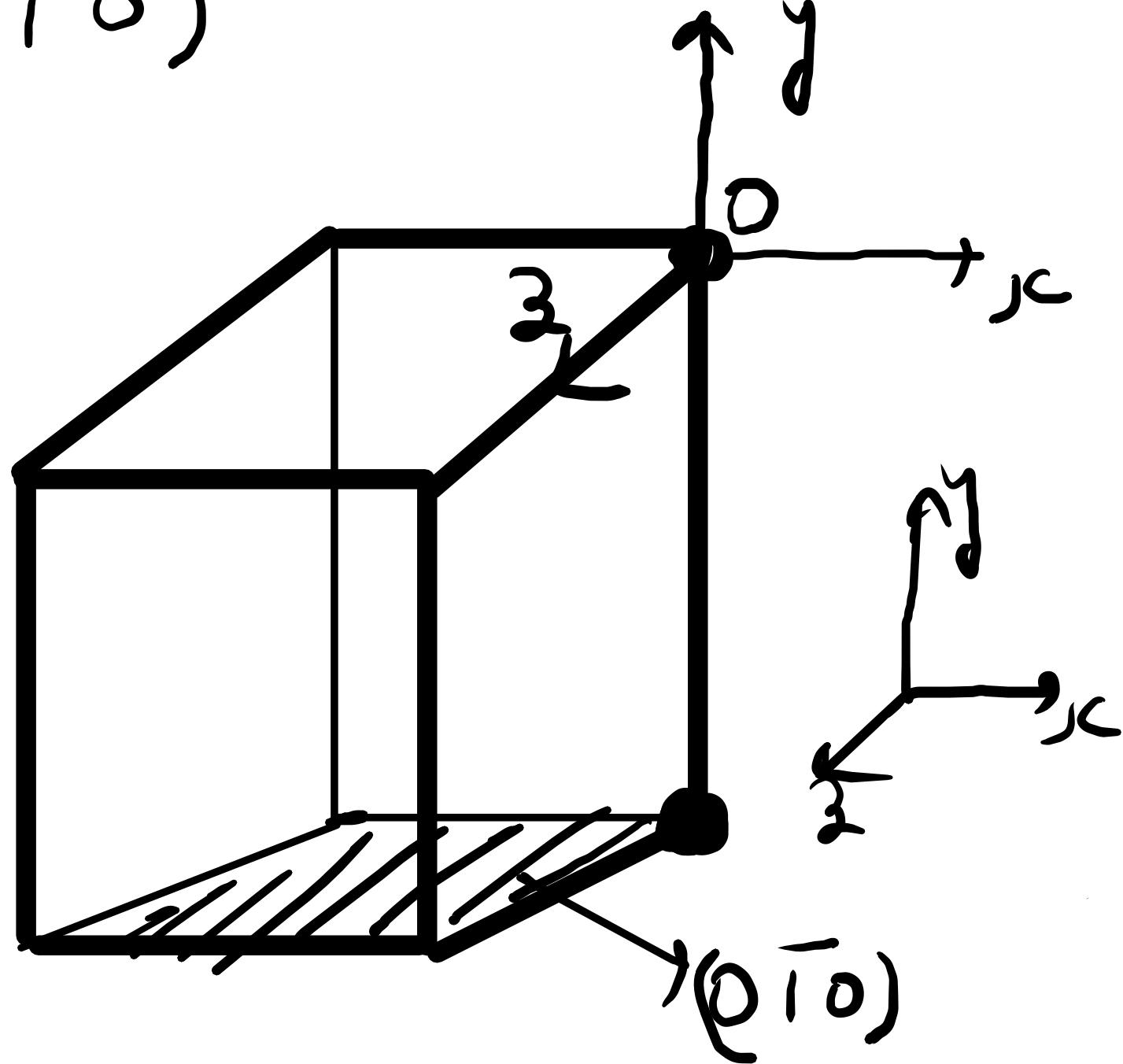


Draw planes $\{\bar{1}00\}, (0\bar{1}0), (00\bar{1})$

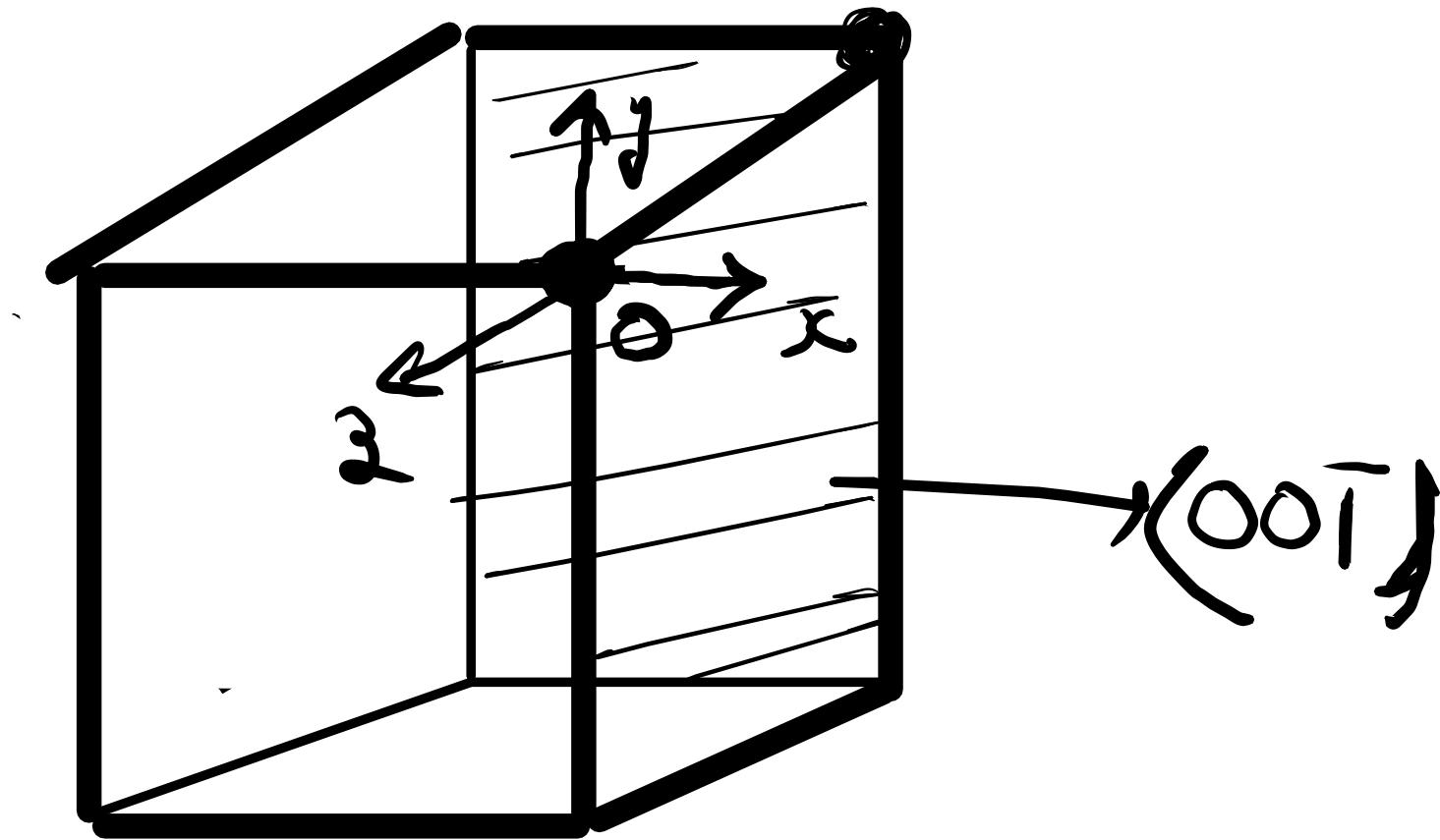


Home work

$(0\bar{1}0)$

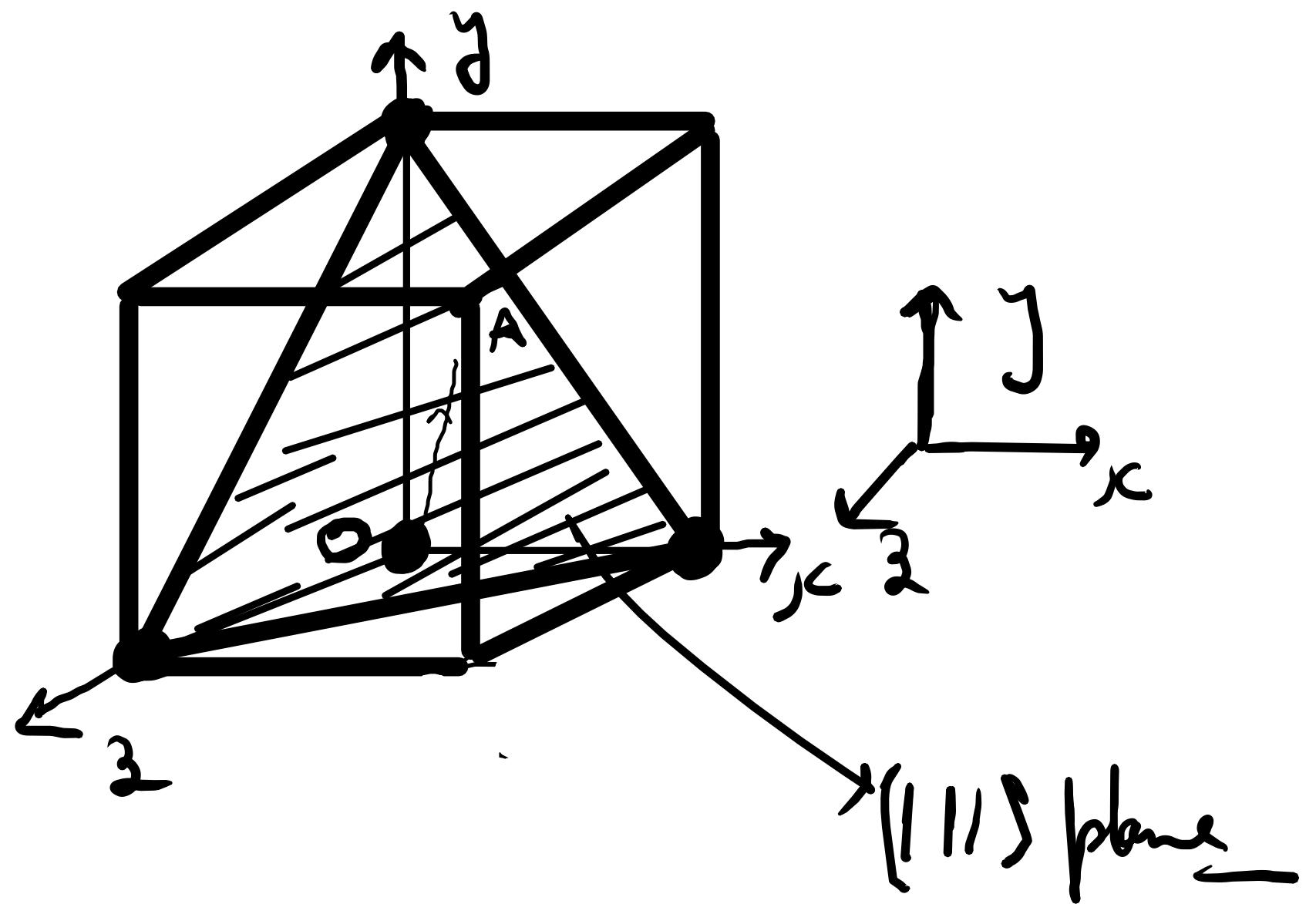


$(00\bar{1})$

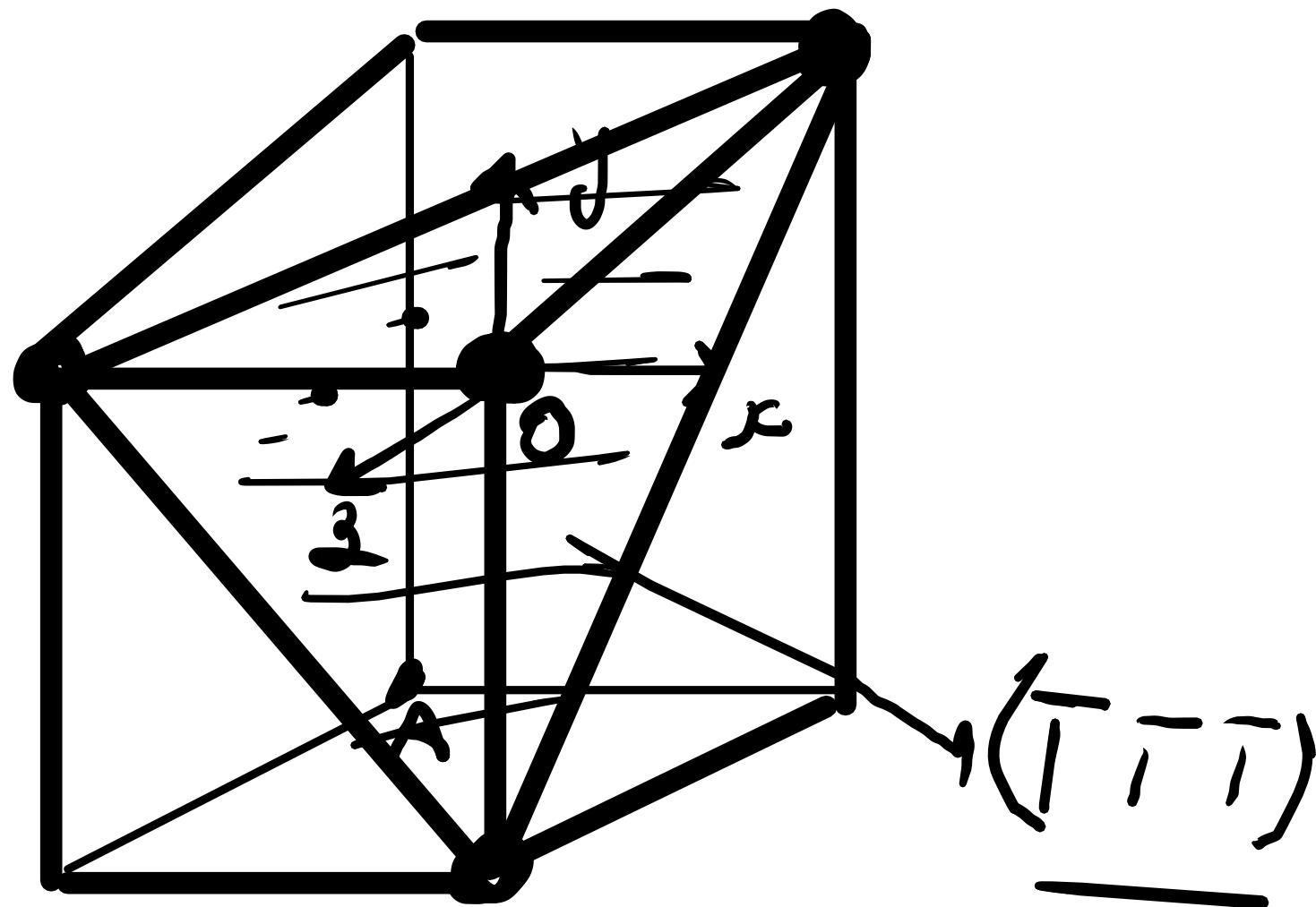


$\checkmark \underline{(111)} \checkmark \underline{(\bar{1}\bar{1}\bar{1})}$

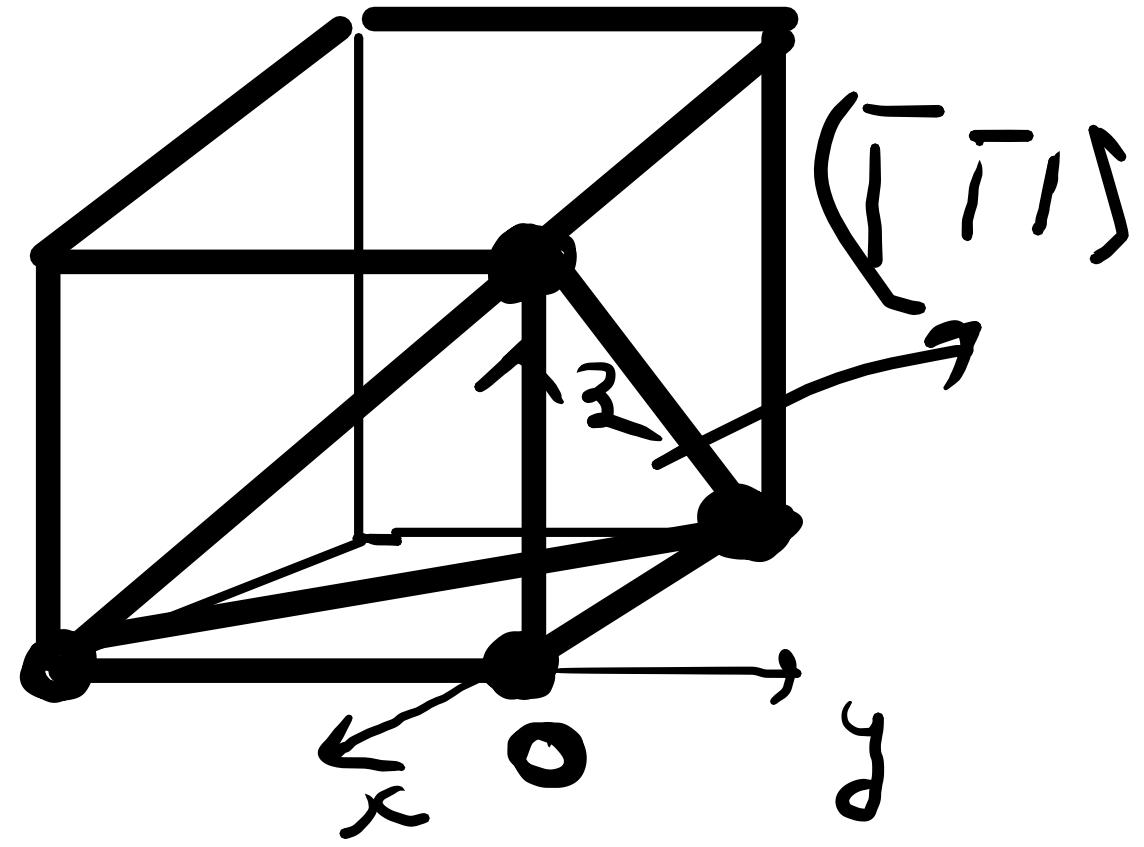
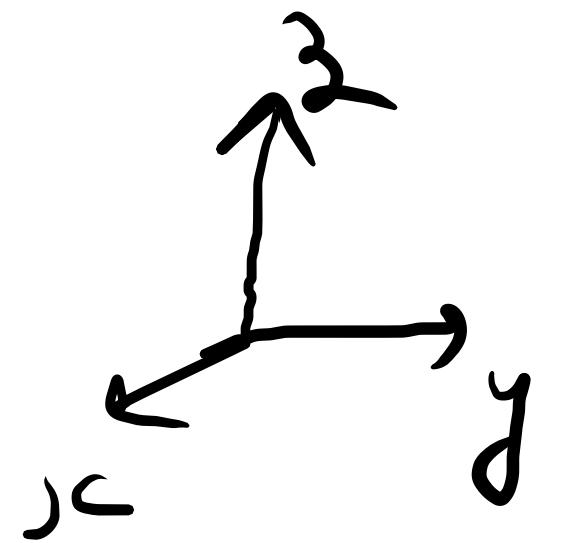
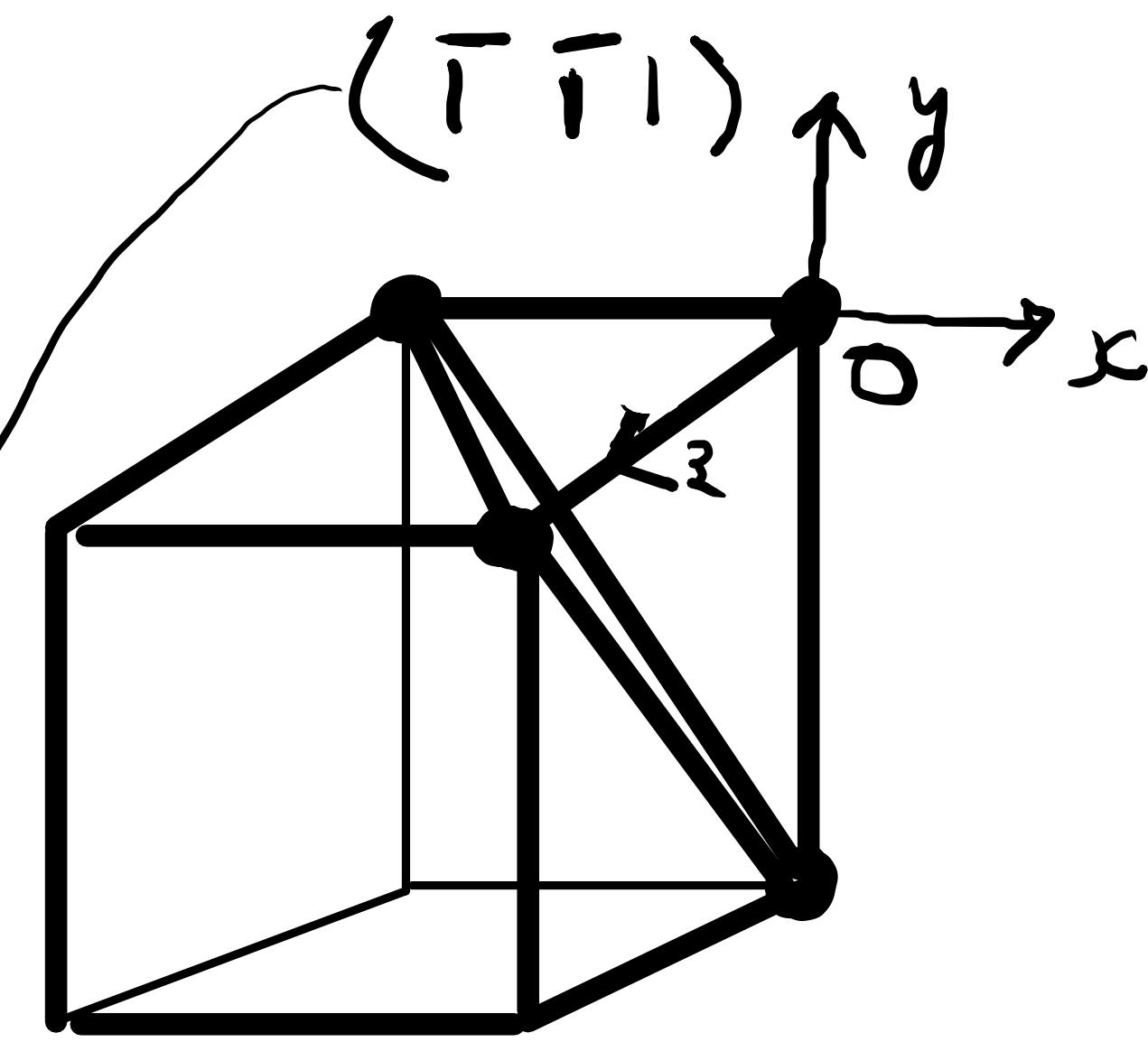
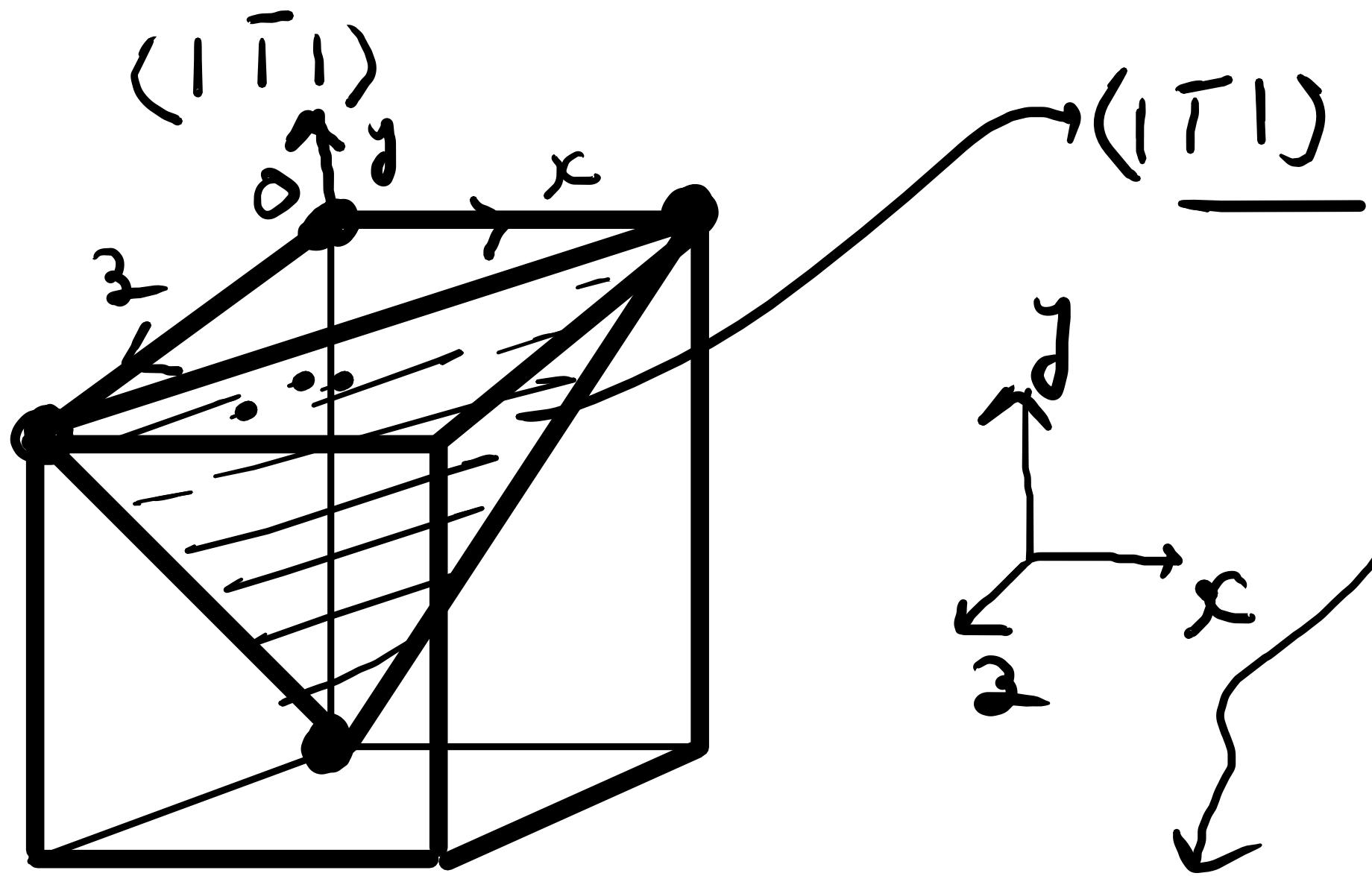
$(1\ 1\ 1)$



$(\bar{1}\ \bar{1}\ \bar{1})$

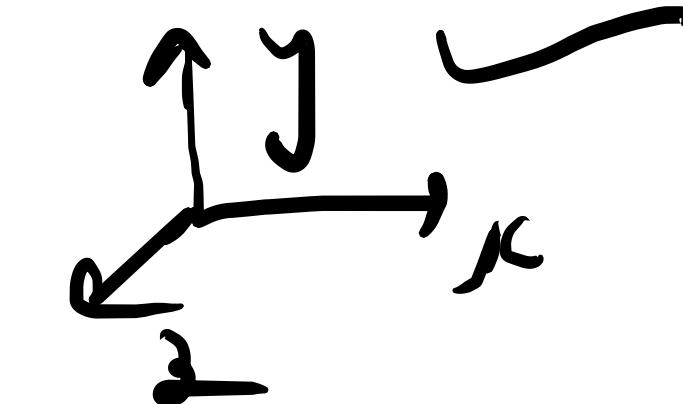
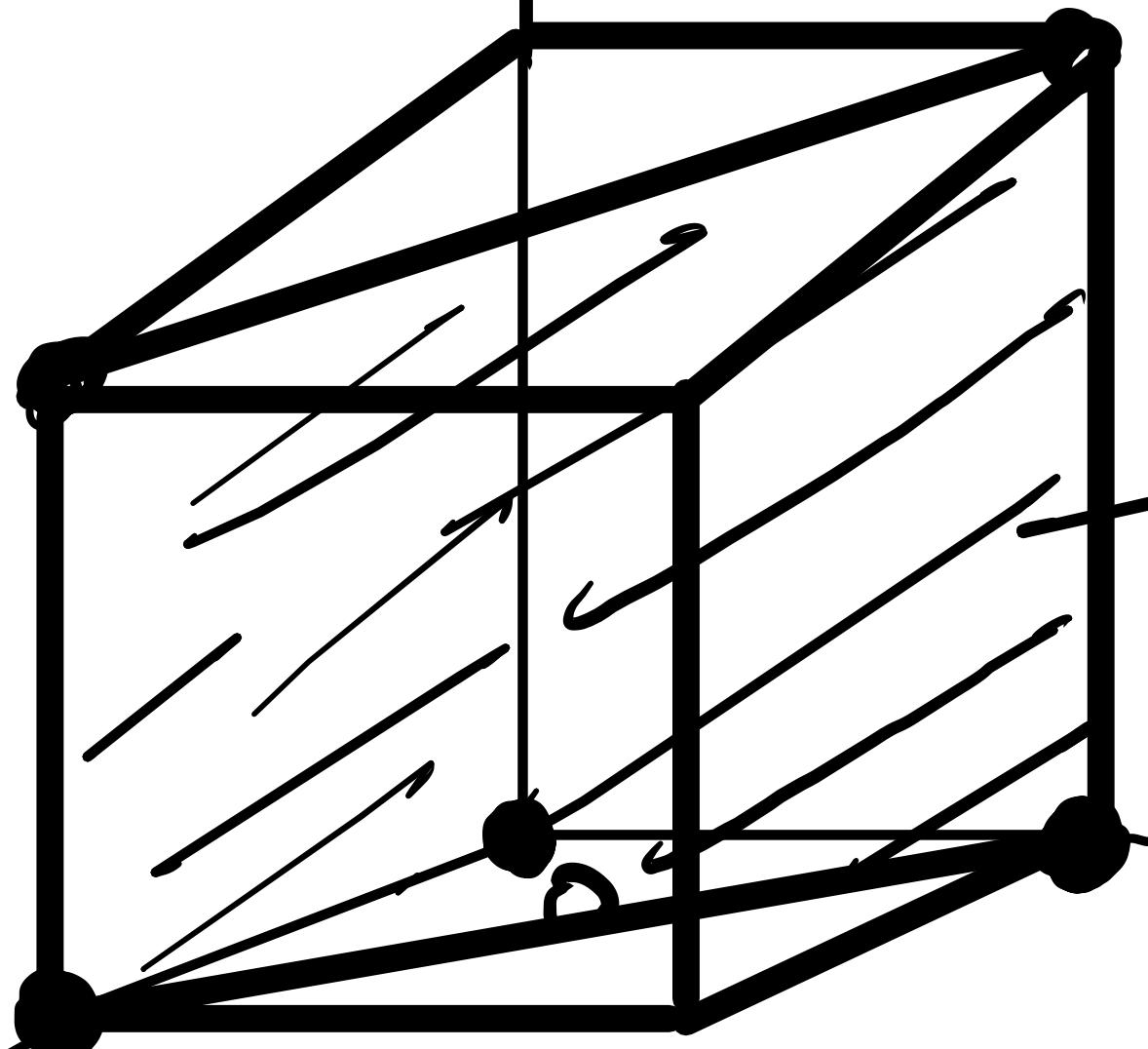


$(1\ \bar{1}\ 1)$

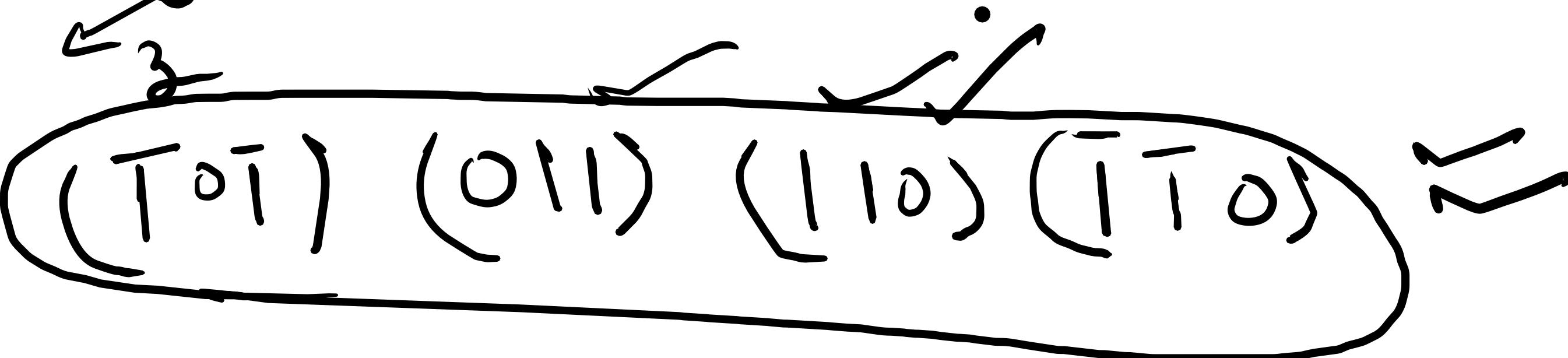


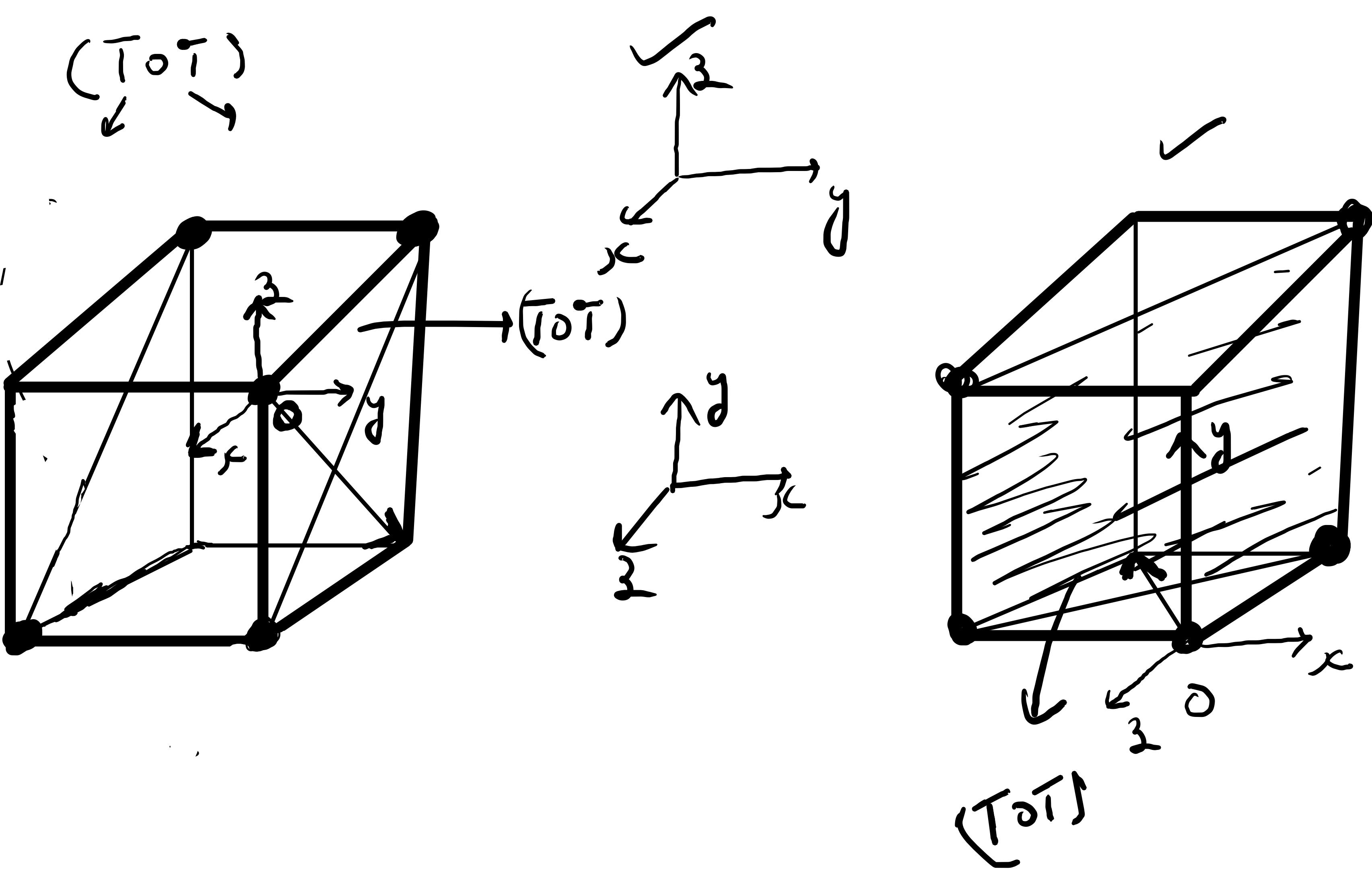
$(10\bar{1})$

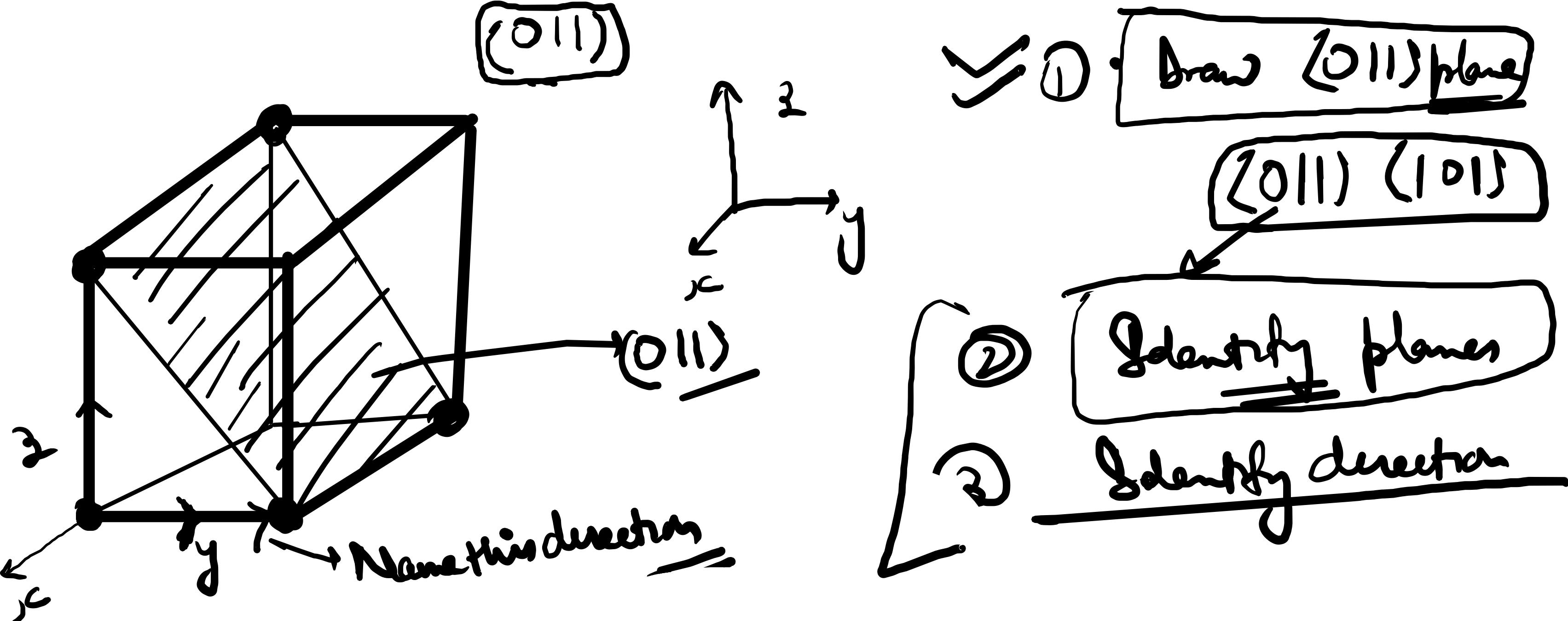
y

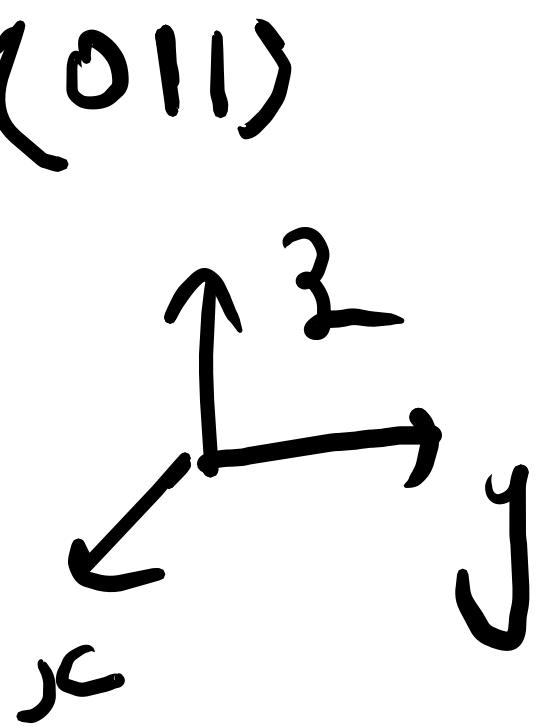
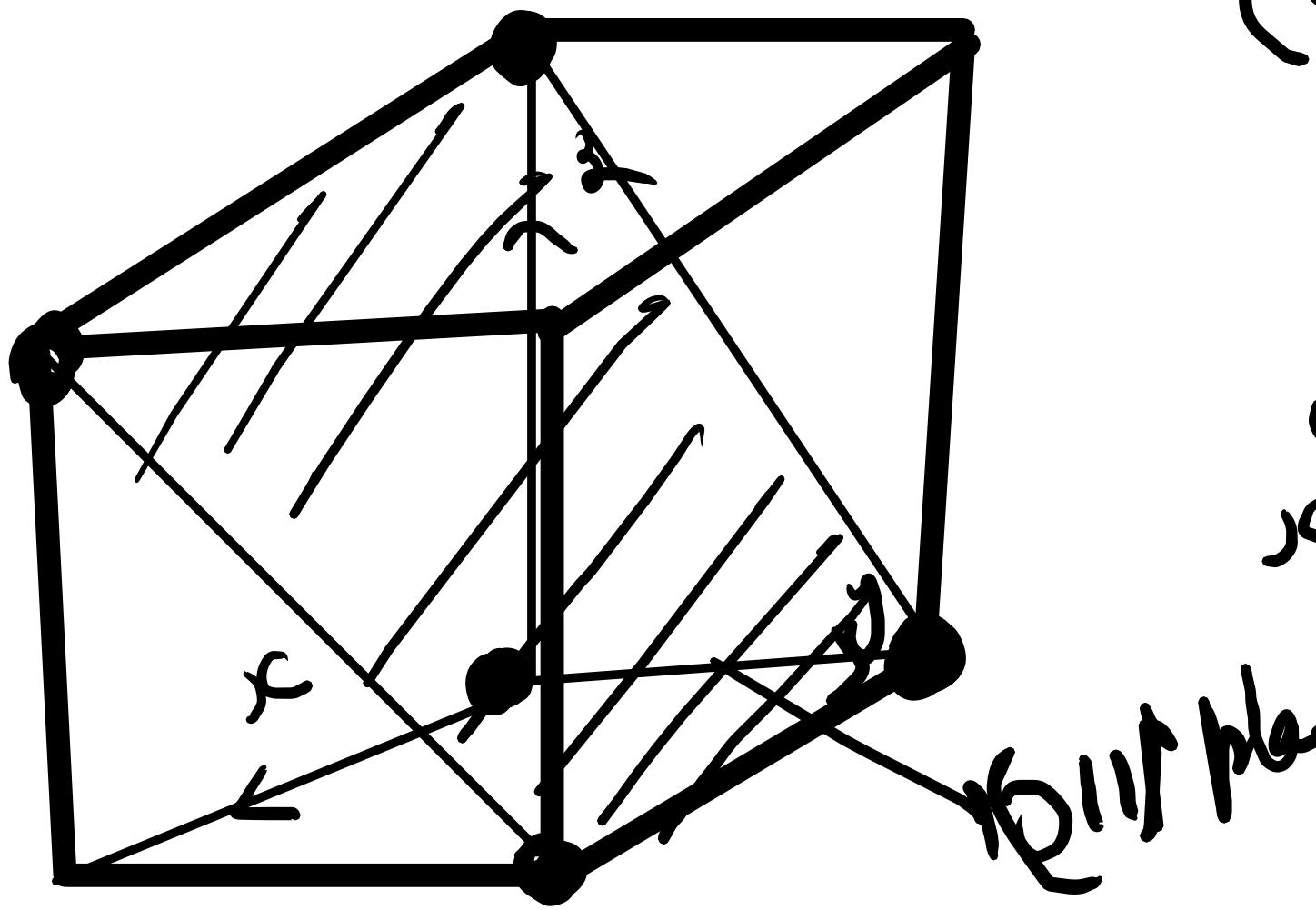


(101) plane

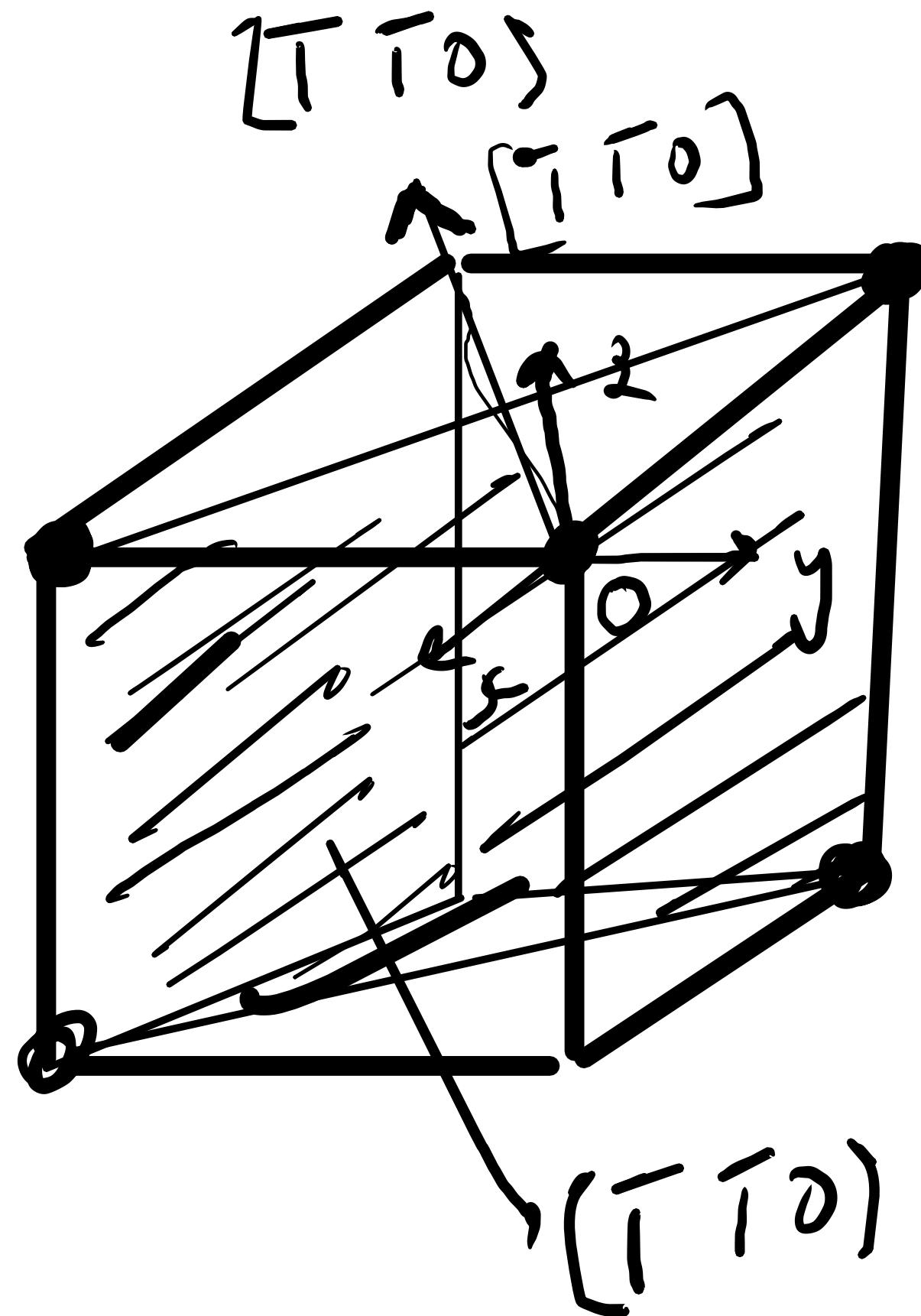


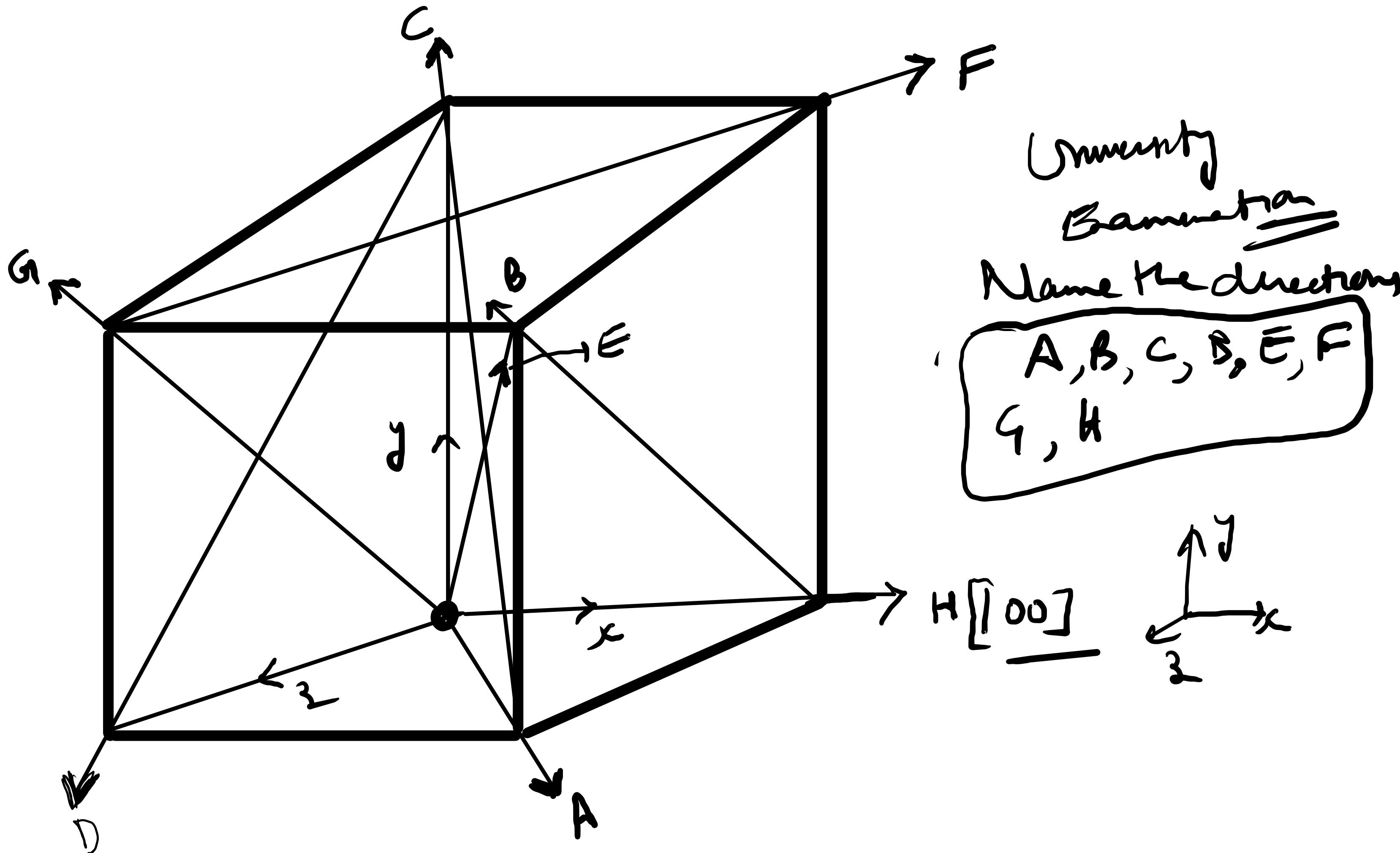


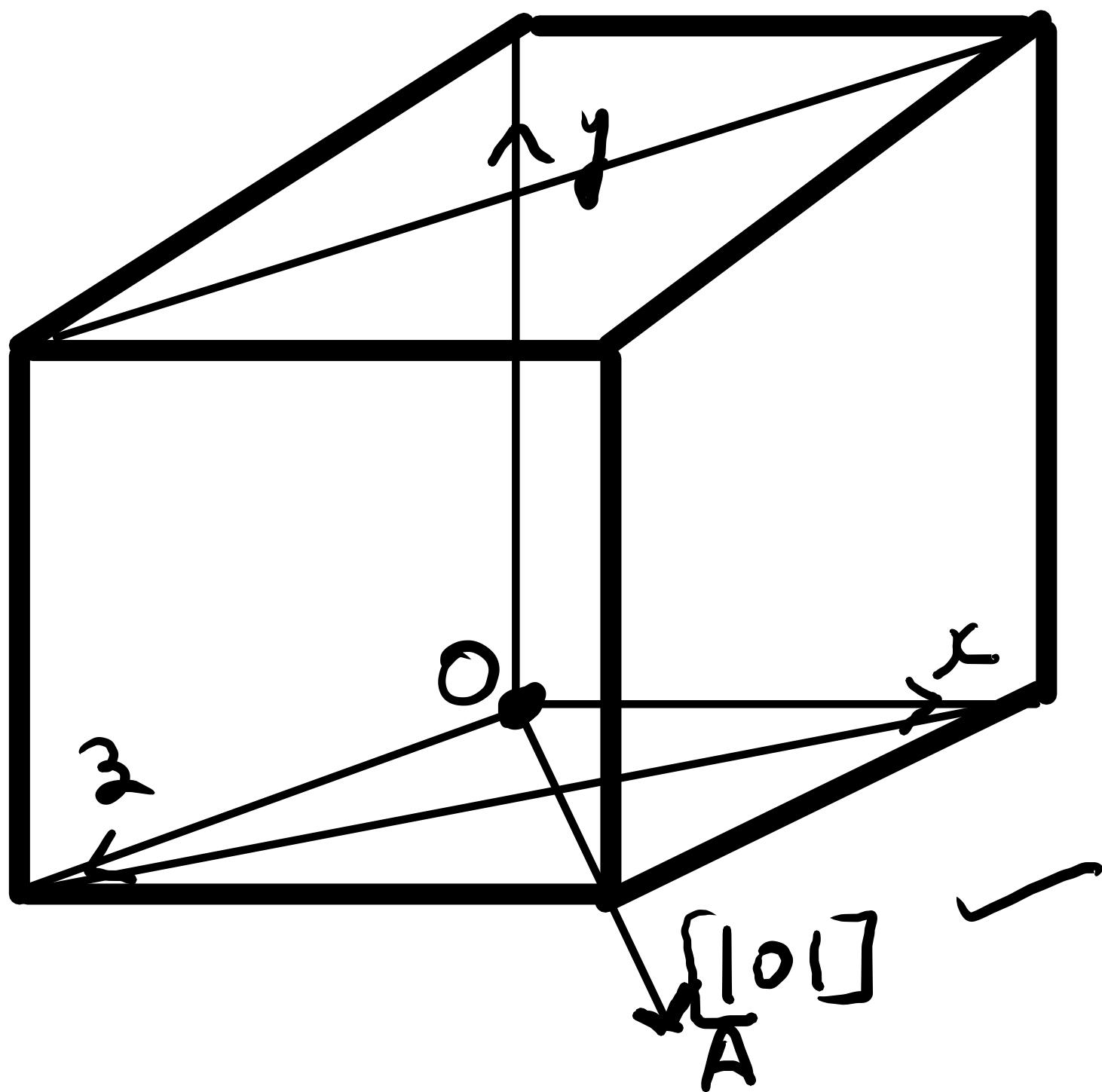




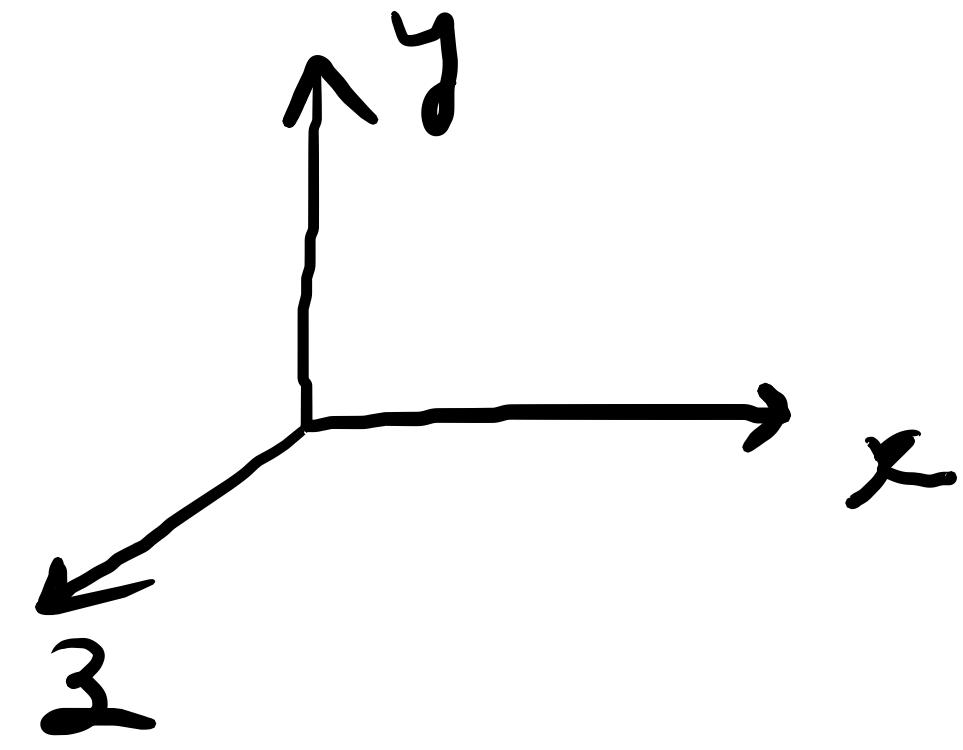
(011)

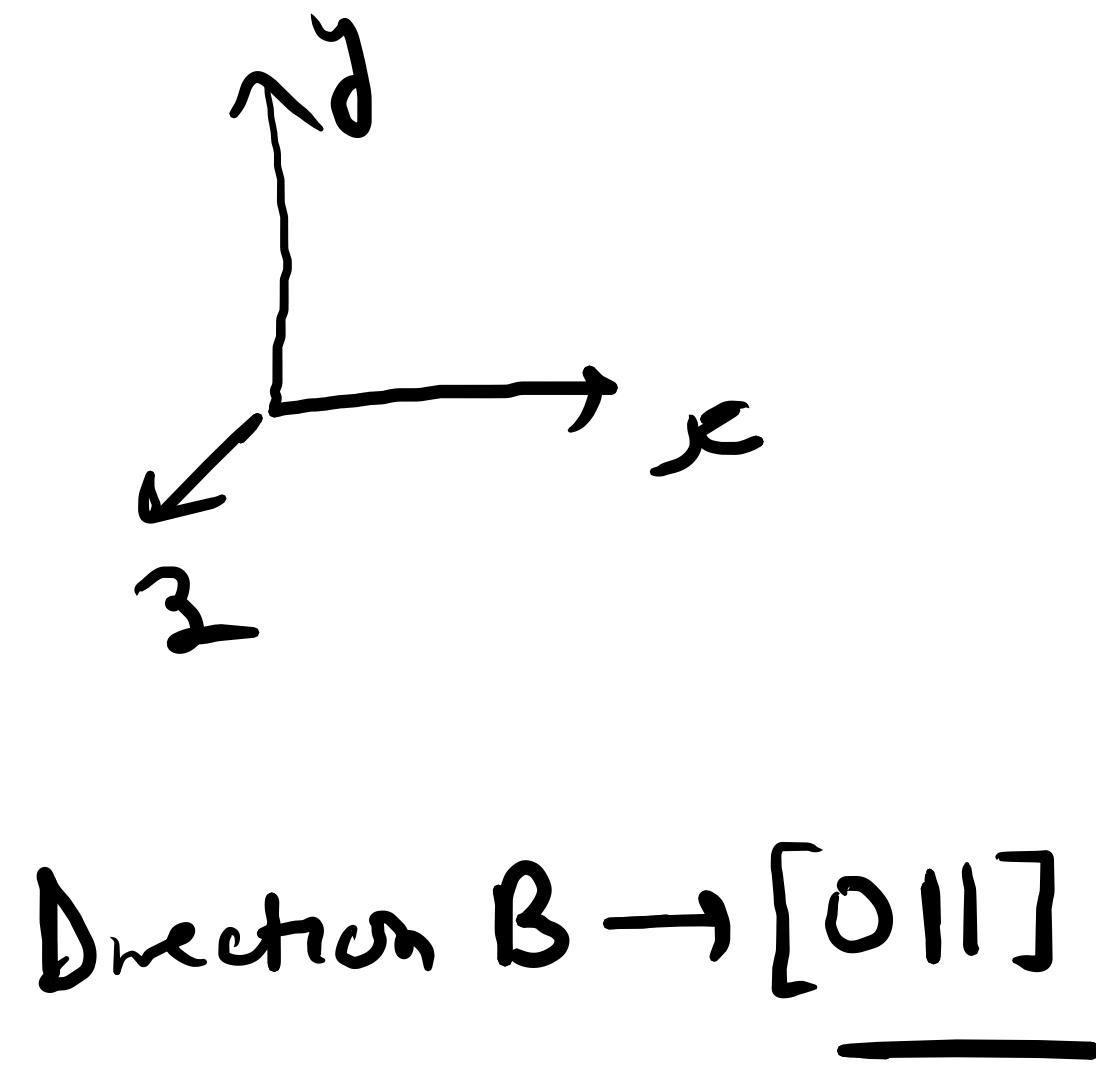
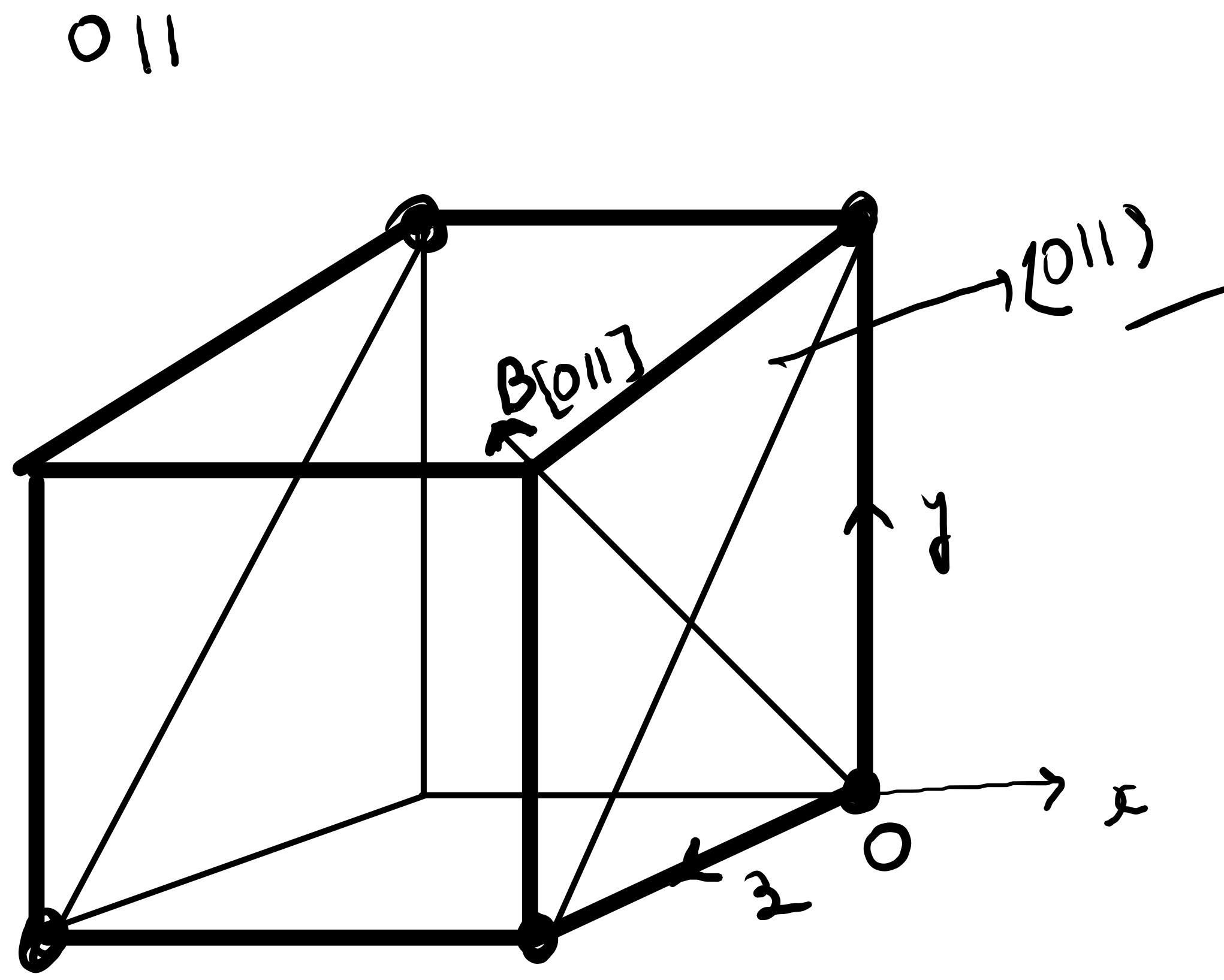


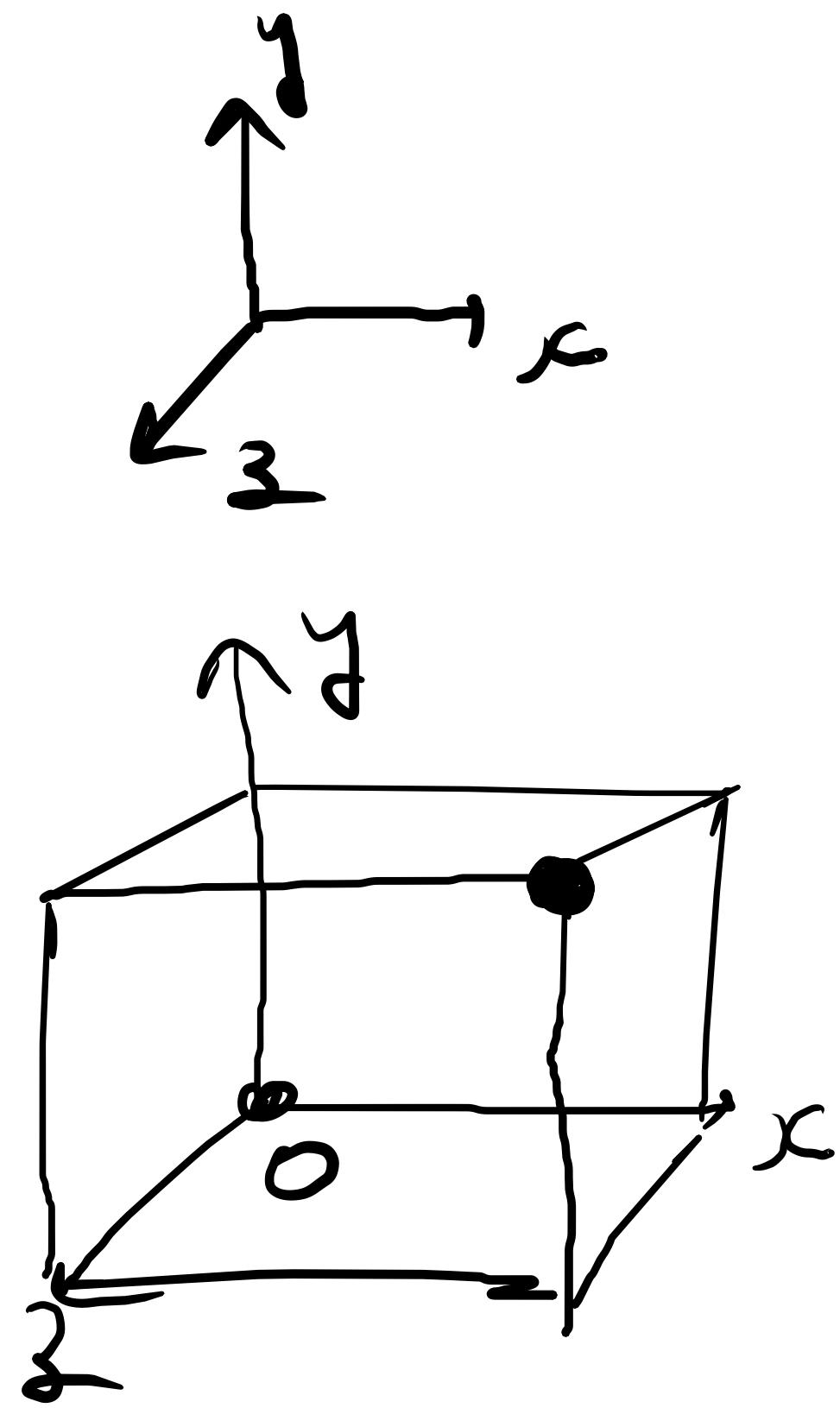
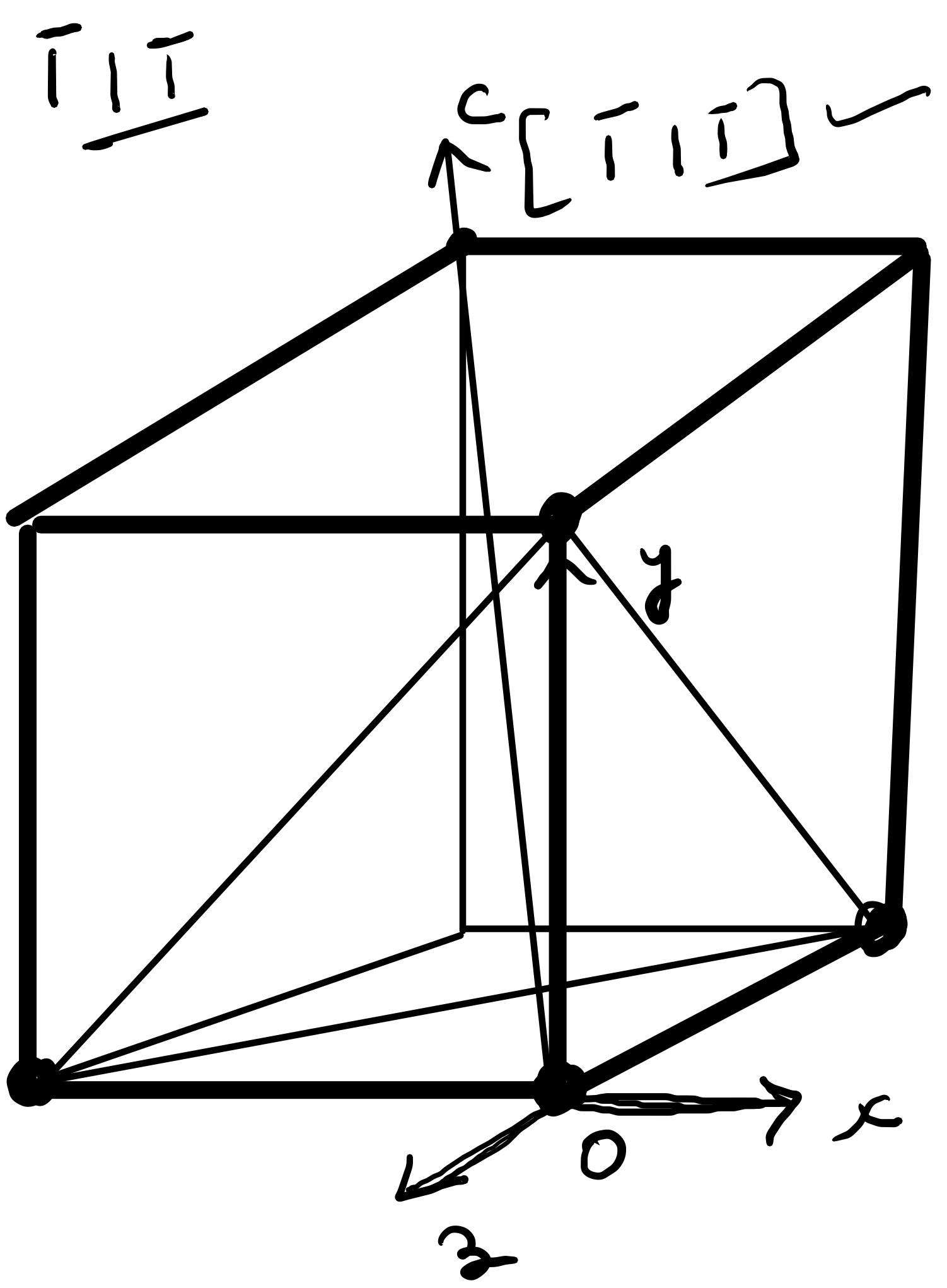


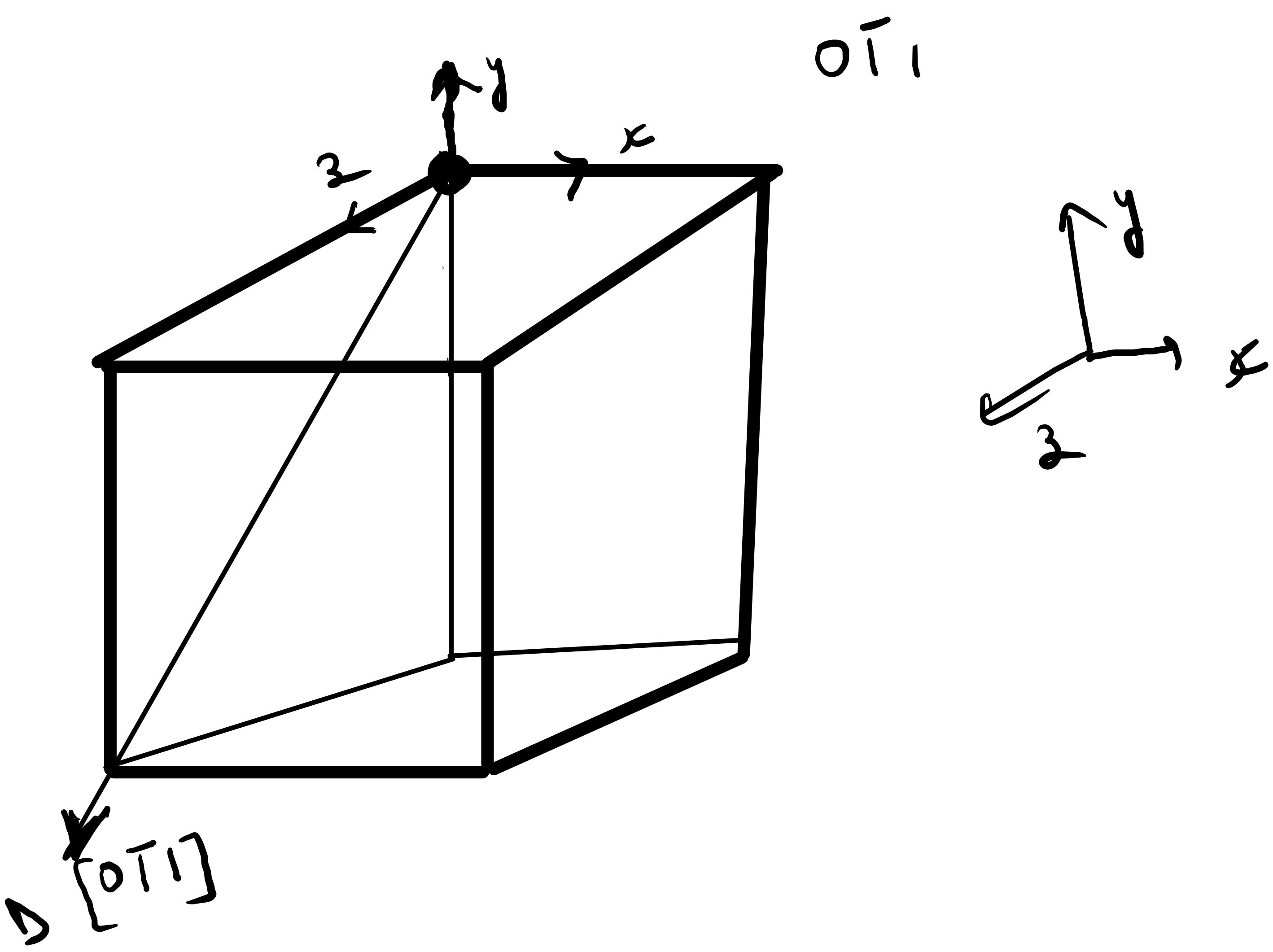


Direction A $\rightarrow [101]$

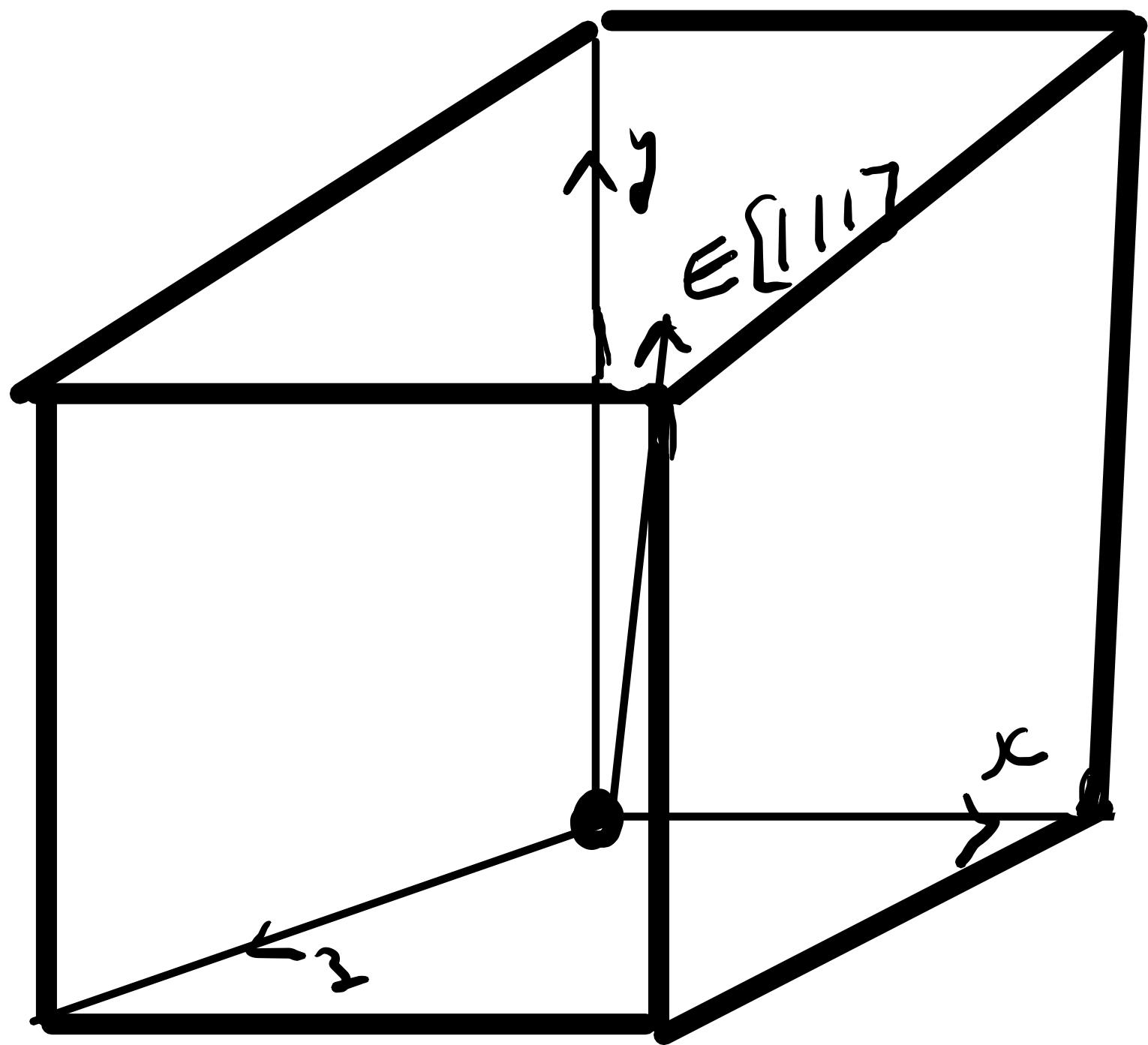




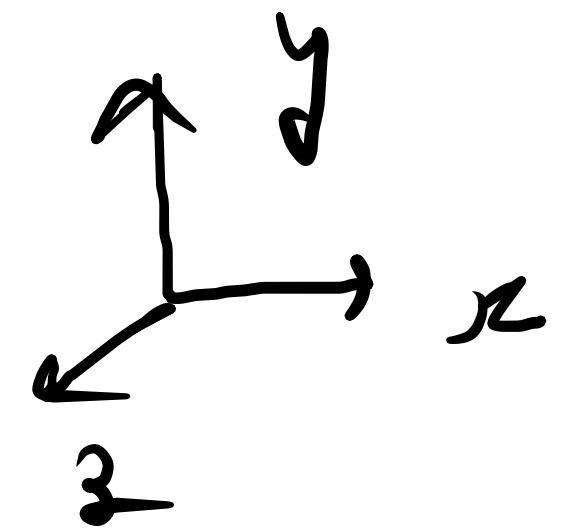


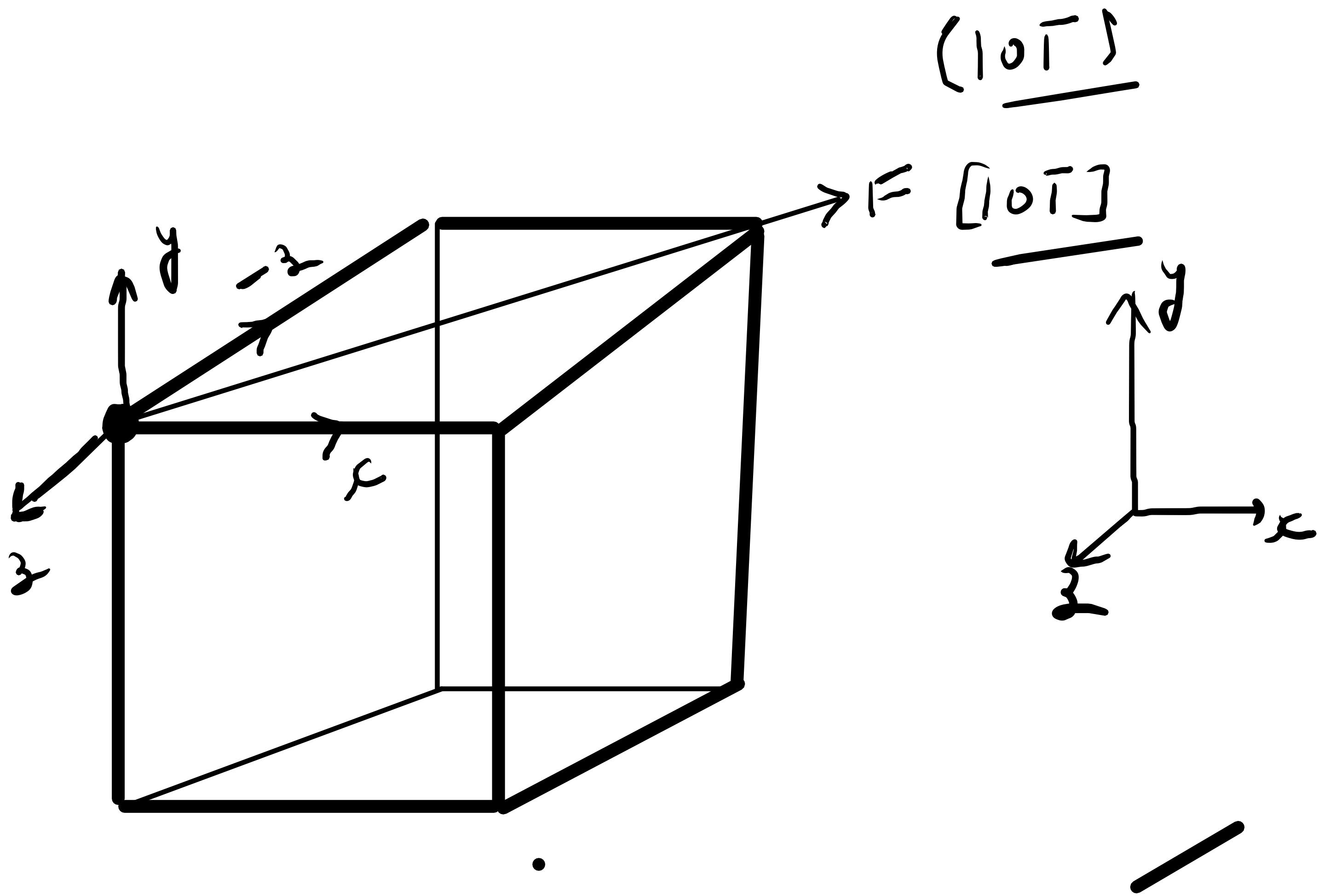


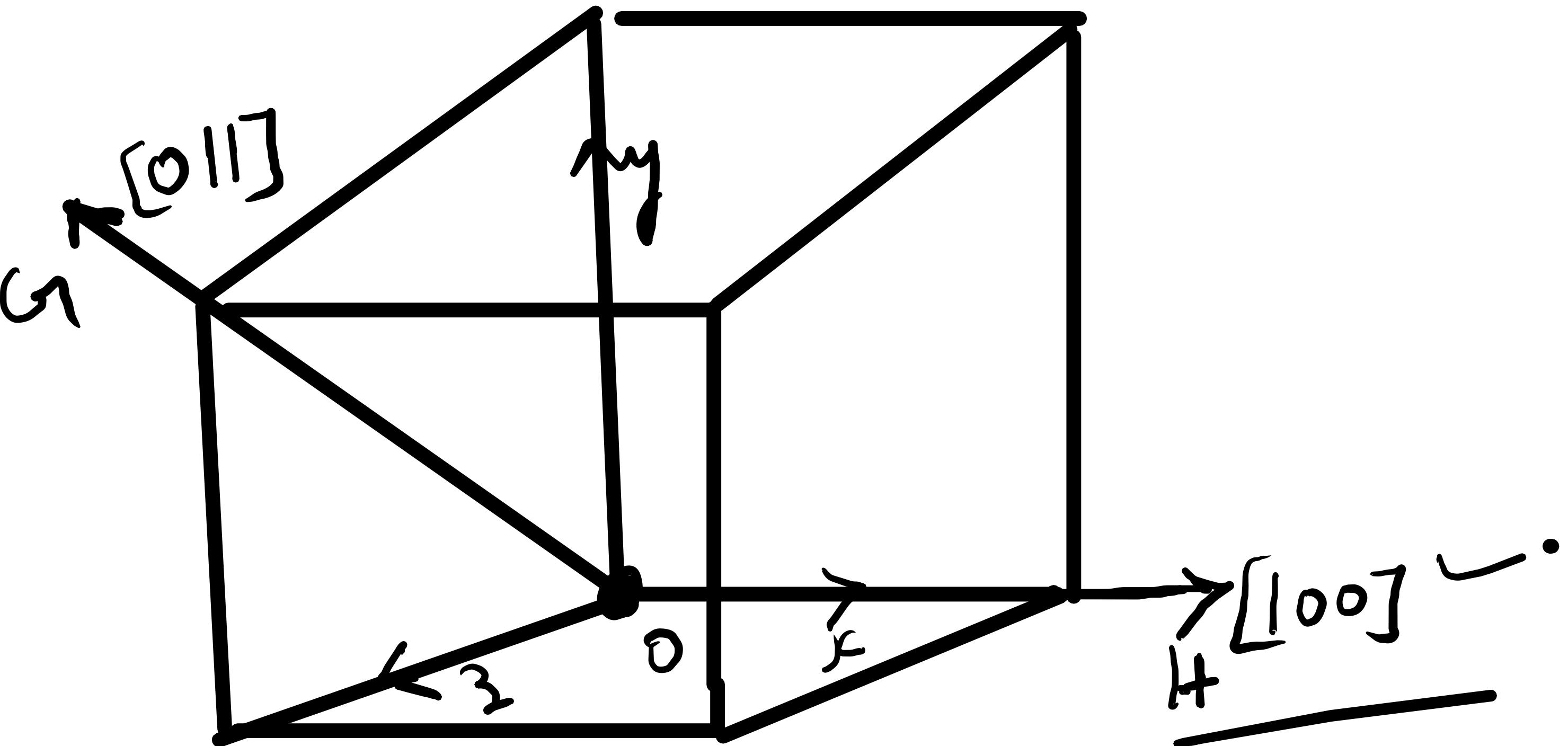
111 011 $\bar{1}01$



$E \rightarrow [111]$





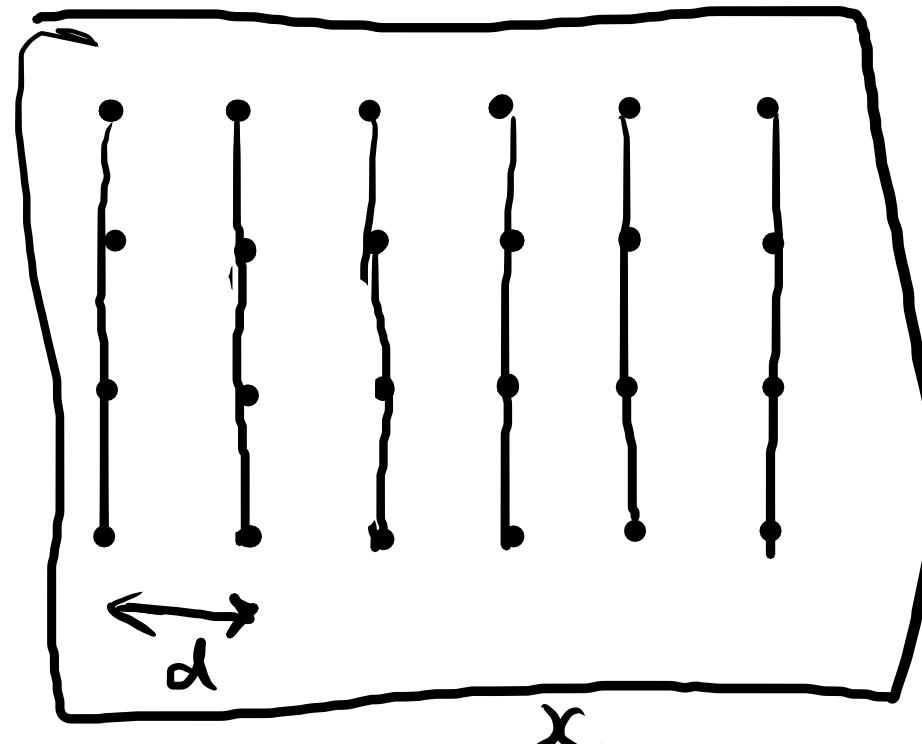
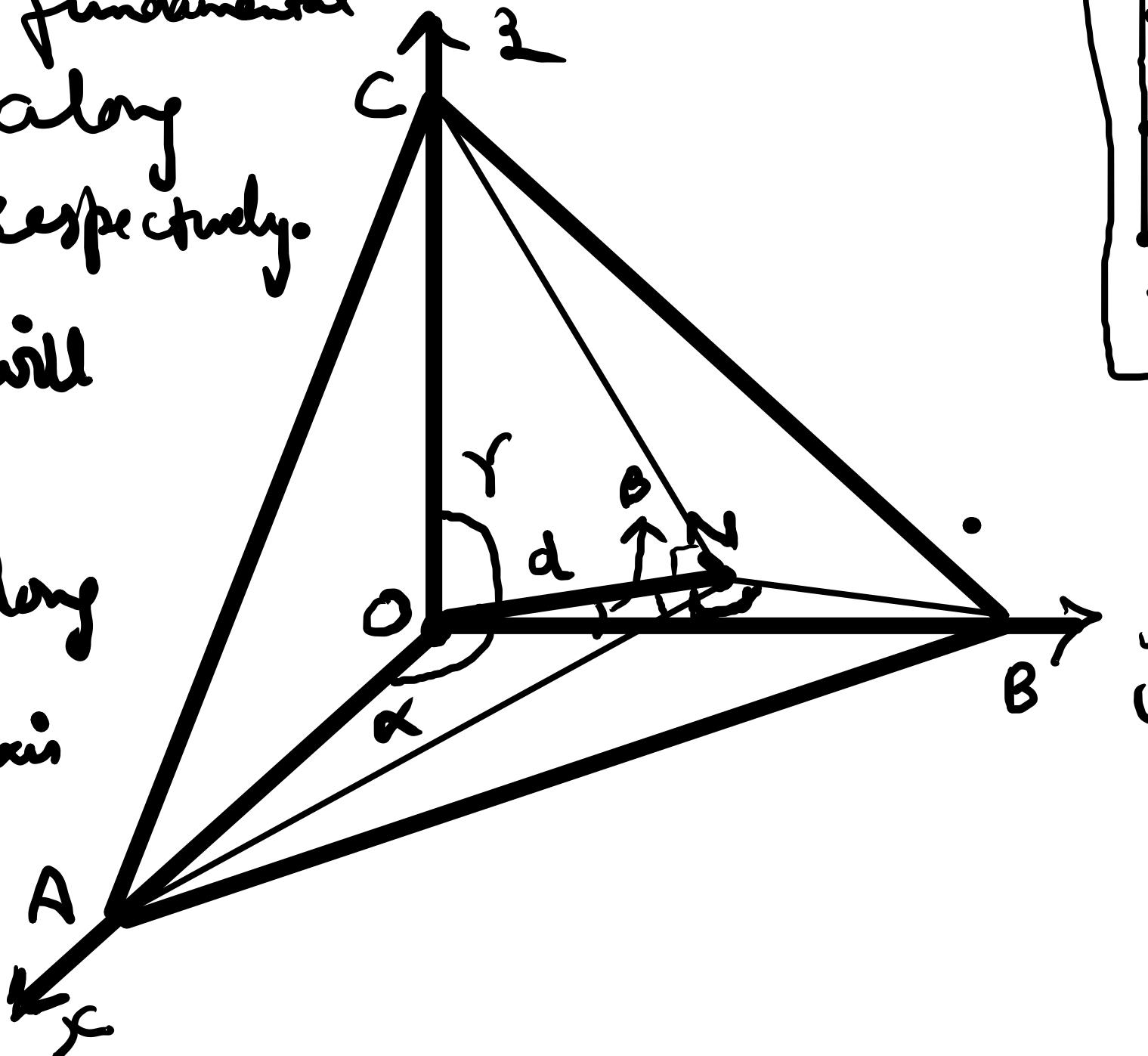


Interplanar Spacing (d)

Consider a family of planes $\{h \bar{k} l\}$.

Let $\vec{a}, \vec{b}, \vec{c}$ are fundamental translation vectors along x, y and z axes respectively.

The plane $\{h \bar{k} l\}$ will make intercepts of $\frac{a}{h}, \frac{b}{k}$ and $\frac{c}{l}$ along x -axis, y -axis and z -axis respectively.



$$\begin{aligned}
 & \text{Given: } 2a = \frac{a}{h} \\
 & \text{Simplifying: } 2 = \frac{1}{h} \\
 & \text{Intercept along } x \text{-axis: } \frac{a}{h}, \frac{c}{l}
 \end{aligned}$$

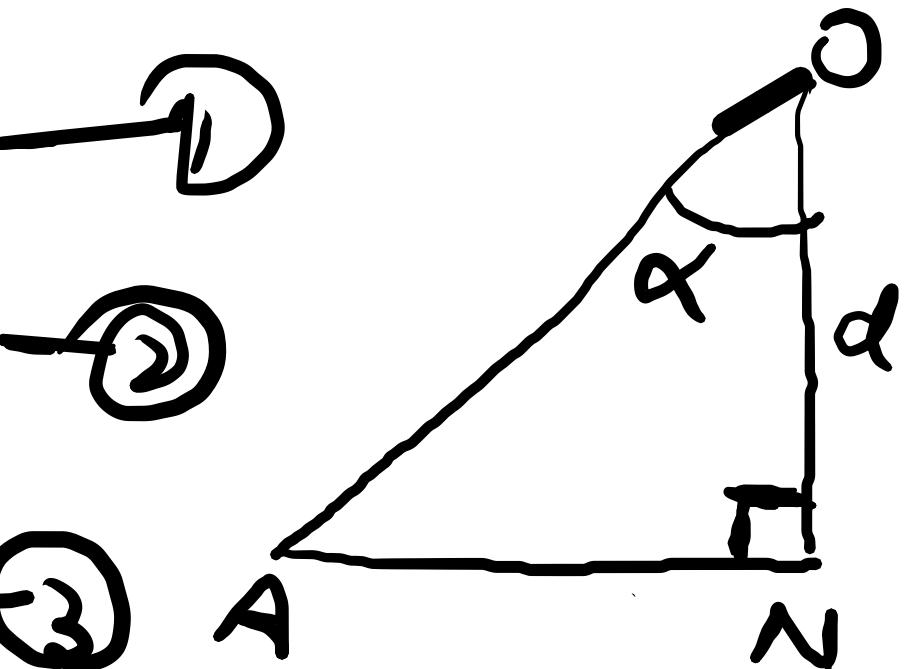
Draws normal on the nearest plane (hlc l) ie $ON = d$.
 Let α, β and γ are the angles between ON and respective axes in x, y and z .

From Δ 's ONA, ONB and ONC

$$\cos\alpha = \frac{ON}{OA} = \frac{d}{a/h} \quad \textcircled{1}$$

$$\cos\beta = \frac{ON}{OB} = \frac{d}{b/k} \quad \textcircled{2}$$

$$\cos\gamma = \frac{ON}{OC} = \frac{d}{c/l} \quad \textcircled{3}$$



According to the property of direction cosines

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1 \quad \textcircled{4}$$

Put eq. ① ② and ③ in eq. ④

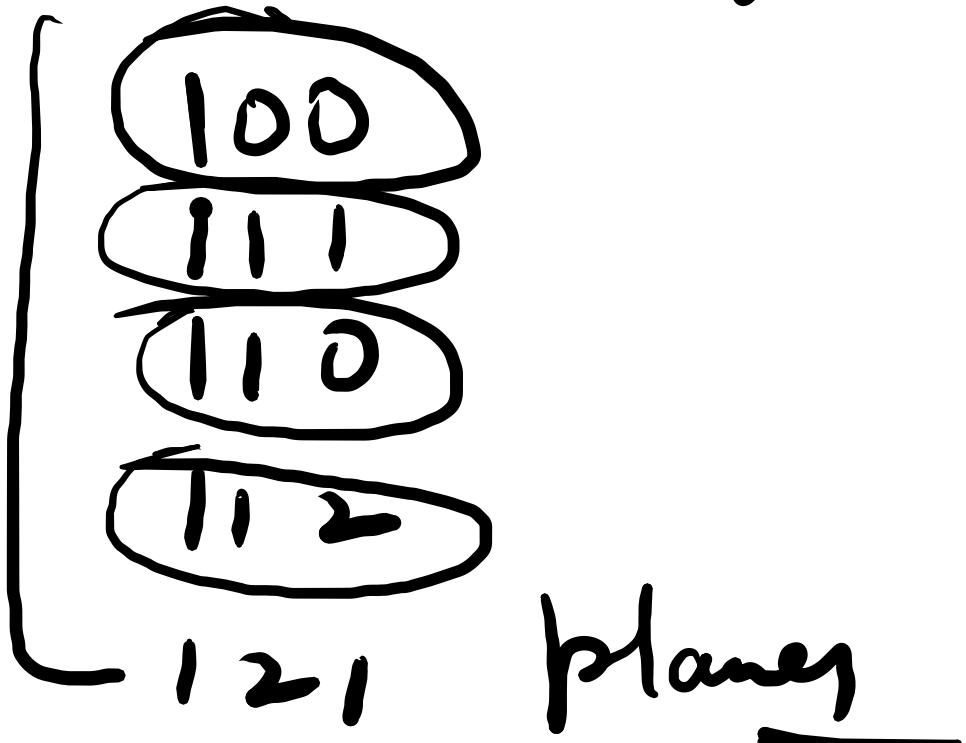
$$\left(\frac{d}{a/h}\right)^2 + \left(\frac{d}{b/k}\right)^2 + \left(\frac{d}{c/l}\right)^2 = 1$$

$$\Rightarrow \frac{h^2 d^2}{a^2} + \frac{k^2 d^2}{b^2} + \frac{l^2 d^2}{c^2} = 1$$

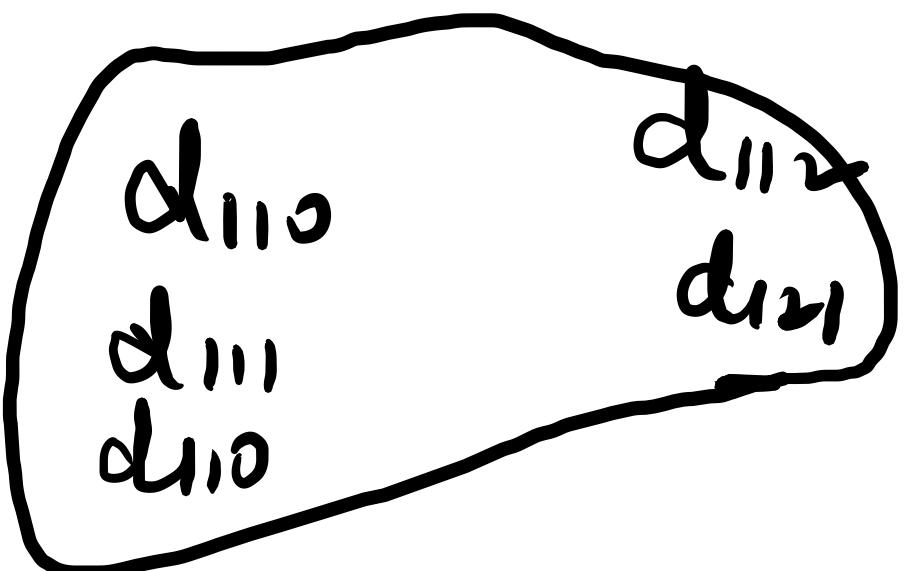
$$\Rightarrow d_{hkl} = \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}$$

For cubic $a=b=c \Rightarrow d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$

Q. The lattice constant of a cubic lattice is a . Find Spacing between



$$\text{Ans} \quad d_{\text{lattice}} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$



Unit I → Completed