Lecture 2-3 : Crystal lattices; from real space to reciprocal lattice

- See slides for a summary of crystal lattices:

Solid o crystal: Any structure that is made up from a well defined unit structure infinitelly repeated following a fixed geometrical rule (periodicity).

Bravais Lattice : describes the periodic arrangement of the repeated units of a crystal

BL: All points defined by $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

n_1, n_2, n_3 integers

$\vec{a}_{1,2,3}$ → primitive lattice vectors

- $\vec{R}$ → Translational symmetry
- infinite repetition ($N \sim 10^{23}$, bulk properties are independent of surfaces)
- Each lattice point can have a simple or complex structural unit at each latice point

simple → 1 atom

complex → set of atoms, molecule...

structural unit → basis

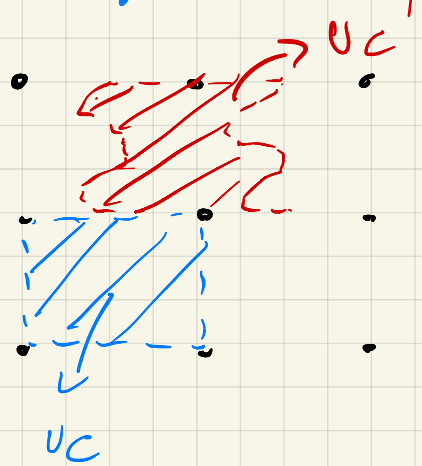
crystal structure = Bravais lattice + basis

Def : Primitive Unit cell

→ a region in space associated with a lattice point that when translated with all lattice vectors $\vec{R}$ will fill the whole space without overlapping & voids.

· No unique choice

2D



Th : Volume of a primitive unit cell : $v = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$

$V_c = \frac{V}{N}$ independent of the choice of U.C

V: Vol of crystal

N: # of lattice points

1 cell contains 1 lattice point → primitive

Def : Conventional unit cell : Fills the full space with translations but can contain more than 1 lattice point

One can describe the fcc or BCC lattice as a simple cubic (SC) + basis. This would be a conventional U.C.

fcc $\rightarrow$ SC + 4 pts $V = 4 \times V_p$

BCC $\rightarrow$ SC + 2 pts $V = 2 \times V_p$

fcc # of points in SC cell: 8 corners $\left(\times \frac{1}{8}\right)$ + 6 faces $\left(\frac{1}{2}\right)$
$= 4$; $V_p = \frac{1}{4} a^3$

BCC : # points : 8 corners $\left(\times \frac{1}{8}\right) + 1 = 2$

$V_p = \frac{1}{2} a^3$

<u>Def</u> : Wigner-SEITZ Primitive cell

$\rightarrow$ Region of space that is closer to a lattice point than any other lat. point.

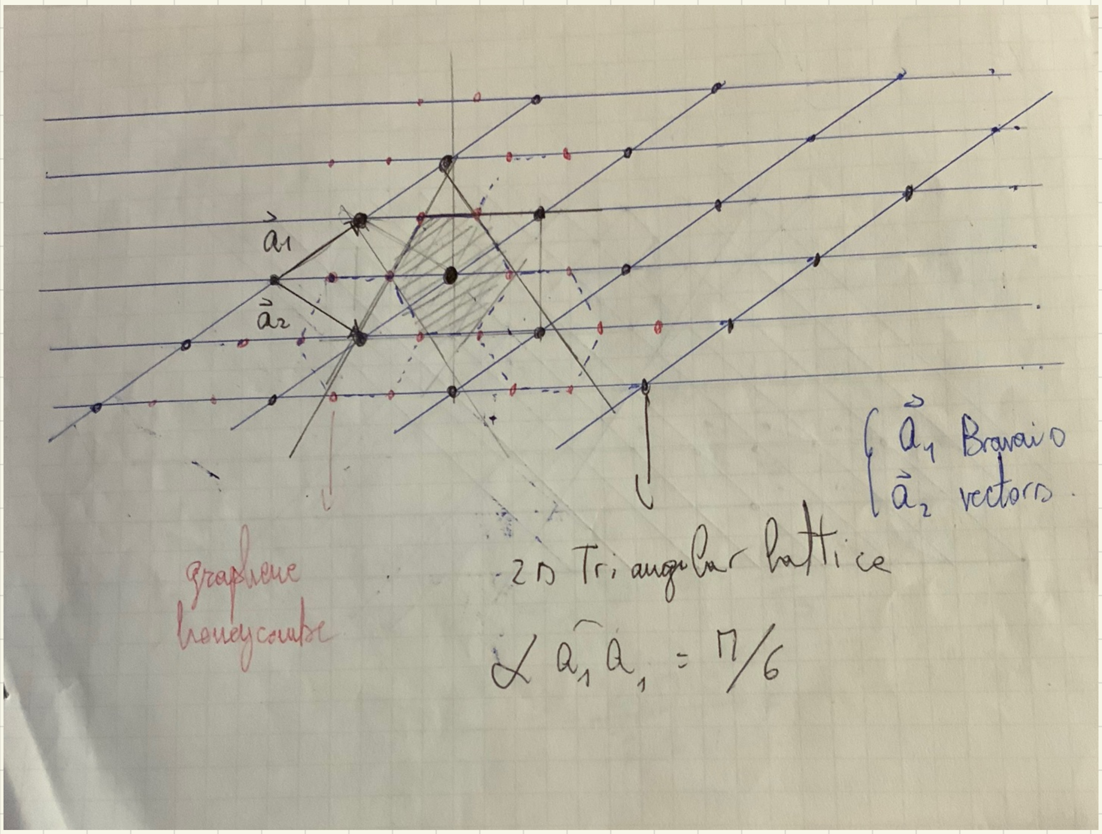
near neigh.

- 1.- Draw lines from origin to all NN lattice points
- 2.- Draw $\perp$ bisector planes
- 3.- Smallest Vol enclosed $\Rightarrow$ WS cell.

Crystal structure : Bravais lattice + Basis

$\Rightarrow$ Honey-Comb lattice : 2D bravais $\angle$ + 2 atom basis

Triangular lattice.



Examples of crystal structures :

hcp : simple hexagonal lattice + basis of 2 atoms at $\vec{0}$ & $\frac{1}{3}\vec{a}_1 + \frac{1}{3}\vec{a}_2 + \frac{1}{2}\vec{a}_3$

$|a_1| = |a_2| = a$; $|a_3| = c$; for hard spheres $c/a = \sqrt{8/3}$

$\begin{cases} \text{ABAB} \ldots \ \underline{\text{hcp}} \rightarrow \text{Ru, Cd, Re, Y, Hf, Gd} \\ \text{ABC ABC} \ldots \ \underline{\text{fcc}} \end{cases}$

Examples of lattices + non trivial basis (different species)

1.- Zinc Blende (ZnS)

Bravais lattice: fcc ; 2 atom basis $\begin{cases} Zn\ (0,0,0) \\ S\ (1,1,1)\, a/4 \end{cases}$

→ Replace Zn & S by C ⇒ Diamond

Coordination # 4 ⇒ sp_3 hybridization, Tetragonal coordination

2.- NaCl

BL: fcc with basis $\begin{cases} Na\ (0,0,0) \\ Cl\ (1/2, 1/2, 1/2)\, a \end{cases}$

3.- CsCl

BL = SC + basis $\begin{cases} Cl\ (0,0,0) \\ Cs: \frac{a}{2}(1,1,1) \end{cases}$

Replace Cl by Cs → BCC Cs

Coordination # is 8

→ Def: (Atomic) Packing factor

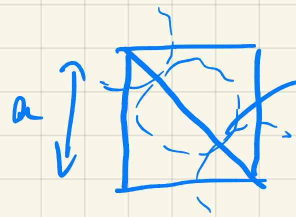
$$APF = \frac{N_{at} \cdot V_{at}}{V_{cell}}$$

N_{at} = # atoms in unit cell

$V_{at} = \frac{4}{3}\pi r_{at}^3$

V_{cell} → related to r_{at}

Ex: BCC



→ diagonal (volume)

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

$$APF = \frac{2 \cdot 4/3\, \pi r^3}{\left(4r/\sqrt{3}\right)^3} = \frac{\pi\sqrt{3}}{8} \approx 0.68 \qquad r = \sqrt{3}\,a/4$$

HCP → $a = 2r$, APF = 0.74

FCC → HCP → 0,74

SC → 0,34

Reciprocal Lattice

$\Rightarrow$ Set of PW vectors with the periodicity of a Bravais lat.

$$e^{ik(\vec{R}+\vec{r})} = e^{i\vec{k}\vec{r}} \Rightarrow e^{i\vec{K}\vec{R}} = 1$$

condition for $\vec{K}$ a R.L.V

Reciprocal lattice

$$\vec{R}\cdot\vec{K} = 2\pi n$$

direct lattice

Th: The R.L is a Bravais lattice

$\longrightarrow$ D.L (direct lattice) $\vec{a}_i$; $i=1,2,3$

$\longrightarrow$ RL (Reciprocal lattice) $\vec{b}_i$, $i=1,2,3$

$$\boxed{\vec{b}_i\cdot\vec{a}_j = 2\pi\delta_{ij}}$$

$$b_i = 2\pi\frac{a_j\times a_k}{\underbrace{\vec{a}_i\cdot(\vec{a}_j\times\vec{a}_k)}_{V_P}} \quad \text{for } j,k\neq i$$

any vector in the R.L can be written as

$\vec{K} = k_1\vec{b}_1 + k_2\vec{b}_2 + k_3\vec{b}_3$, k_1, k_2, k_3 integers because $\vec{K}\cdot\vec{R} = 2\pi\underbrace{(k_1 n_1 + k_2 n_2 + k_3 n_3)}_{\text{integer}}$

Th: The reciprocal of the Reciprocal lattice is the direct lattice.

Examples:

1.- C.L $\Rightarrow$ Trivial, the reciprocal is also C.L

$a_1 = (a,0,0)$ $a_2 = (0,a,0)$ $a_3 = (0,0,a)$

$b_1 = \frac{2\pi}{a}(1,0,0)$; $b_2 = \frac{2\pi}{a}(0,1,0)$ $b_3 = \frac{2\pi}{a}(0,0,1)$

2.- FCC: RL is a BCC with $a = \frac{4\pi}{a}$ $(a = a_{cubic})$

$a_1 = \frac{a}{2}(0,1,1)$; $a_2 = \frac{a}{2}(1,0,1)$; $a_3 = \frac{a}{2}(1,1,0)$

$b_1 = 2\pi \frac{a^2/4}{a^3/4}(-1,1,1) = \frac{2\pi}{a}(-1,1,1)$;

$b_2 = \frac{2\pi}{a}(1,-1,1)$; $b_3 = \frac{2\pi}{a}(1,1,-1)$

$\Bigg\}\ \frac{4\pi}{a}\vec{a}_i^{\,bcc}$

$\vec{a}_i^{\,bcc} = \frac{1}{2}\begin{cases}(-1,1,1)\\(1,-1,1)\\(1,1,-1)\end{cases}$

3.- BCC: RL is an fcc with $a^{cubic} = \frac{4\pi}{a}$

(prove applying the Theorem above).

4. RL of hexagonal lattice is a H.L rotated by 30°

Th: V_R = Vol of reciprocal cell $= \frac{(2\pi)^3}{V_p}$ (obvious!)

Def: First Brillouin zone = Wigner-Seitz primitive cell of the Reciprocal lattice

→ Hence 1s BZ of FCC = Wigner-Seitz cell of BCC and viceversa.

* Lattice planes & Miller Indices

• The BL can also be seen or constructed from a family of lattice planes: → set of parallel & equally spaced planes which together contain all the points in the lattice. The choice of planes family is not unique (but it is finite!)

Th: If there is a family of (lattice) planes, with spacing d and normal $\vec{n}$, then $\boxed{K = 2\pi \frac{\vec{n}}{d}}$ is a R.L.V, and the shortest along the $\vec{n}$ direction.

$$\Longrightarrow \vec{K} = 2\pi \frac{\vec{n}}{d} = \sum_i \overbrace{l_i}^{\text{integers}} \vec{b}_i$$, where l_i have no common factors

→ Exercise: prove This!

→ The converse of This Theorem:

for any $\vec{K}$ (RLV) There is a family of planes (lattice planes) $\perp \vec{K}$. If $\vec{K}$ is The shortest vector along The $\hat{K}$ direction ($K = \sum_i l_i b_i$, l_i no common factor)

Then The spacing between planes is $d = \frac{2\pi}{K}$

$\Rightarrow$ equations for These planes: $\vec{K} \cdot \vec{r} = 2\pi N$

each value of N corresponds to one plane

$N = (-\infty \ldots -1, 0, 1 \ldots \infty)$

→ Exercise: prove This

Miller Indices of a Lattice plane

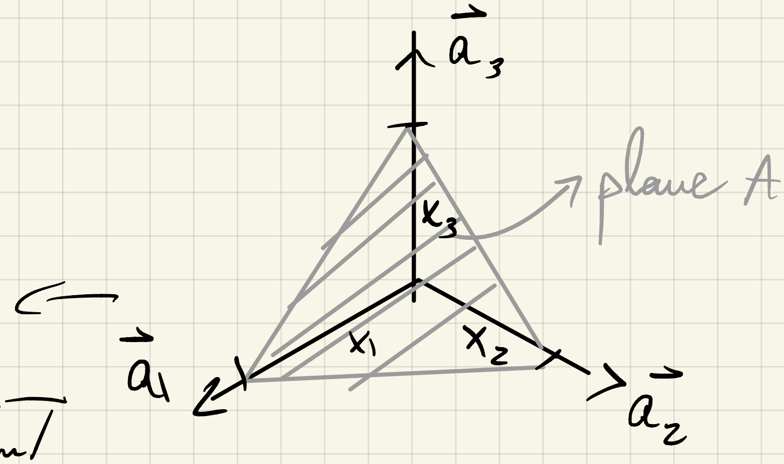
We know That families of lattice planes are associated To unique R.L. vectors $\vec{K}$. The Miller indices of The plane are The coordinates of The shortest R.L.V $\perp$ To a family of planes. The coordinates of The miller planes are given in a basis of a specific set of primitive reciprocal vectors. So a plane with miller indices h, k, l is $\perp$ To The RLV $\vec{K} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$

Say a plane $A \perp \vec{K} = \sum_i l_i \vec{b}_i$, (l_i's no common factors)

$d\,|A_N - A_{N+1}| = \frac{2\pi}{K}$; The Miller indices for $A = (l_1, l_2, l_3)$

→ Geometrical meaning

A intercepts the axis $\{\vec{a}_i\}$ at x_1, x_2, x_3



⇒ eq for A : $\vec{K}\cdot\vec{r} = \text{constant}$

$$\vec{K}(x_1\vec{a}_1) = \vec{K}(x_2\vec{a}_2) = \vec{K}(x_3\vec{a}_3) = 2\pi l_1 x_1 = 2\pi l_2 x_2 = 2\pi l_3 x_3$$

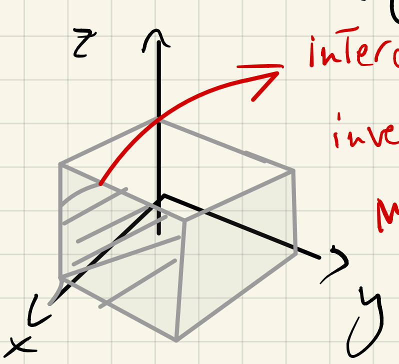
$$l_1 x_1 = l_2 x_2 = l_3 x_3 = \text{const}$$

$$\text{Miller indices} \equiv (l_1, l_2, l_3) \propto \left(\frac{1}{x_1}, \frac{1}{x_2}, \frac{1}{x_3}\right)$$

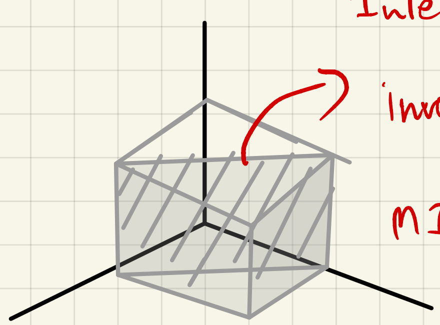
How to : Determine x_1, x_2, x_3 ⇒ where the plane intercepts the axis; take $\frac{1}{x_i}$; multiply by a common factor to obtain the smallest integers

Conventions to specify directions

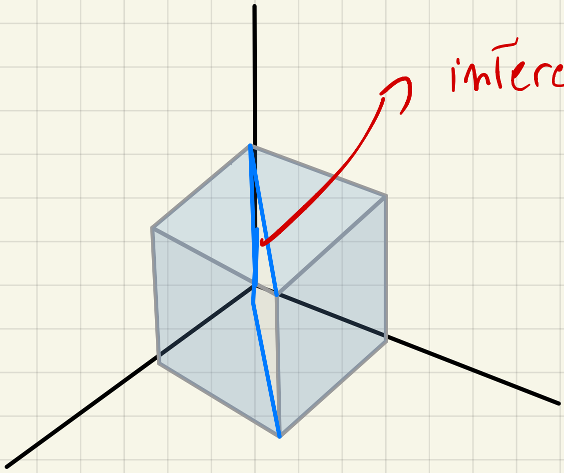
1.- Usually (for cubic lattices) they are given WRT the conventional unit cell.



intercepts $(1, \infty, \infty)$
inverse $(1, 0, 0)$
MI (100)



Intercepts $(1, 1, \infty)$
inverse $(1, 1, 0)$
MI (110)



intercepts $(0,0,0)$? $\Rightarrow$ we need to take a // plane of the same family

ex $(1,-1,0)$ or $(-1,+1,0)$

MI $(1,\bar{1},0)$ or $(\bar{1},1,0)$

Notations : (100) a lattice plane

$$(0\,-1\,0) \equiv (0\bar{1}0)$$

$\{100\} = (100), (\bar{1}00), (010)$ etc

$[100] \equiv$ direction along a_1

$[xyz] \to$ direction along $x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3$

$\langle 100\rangle \equiv [100], [\bar{1}00]\, [010] \ldots$

Uses (for many things!)

ex: cleavage : cut crystal along a face; different faces have different cleavage energies which depend on the atomic density of the planes

· Low indices planes $(100)\,(111)\,(010)$ are relevant because they represent the more common cleavage planes for certain crystals (semiconductors specially)

GaAs (110) Si (111)

Which surface is the cleavage surface depends on surface energy.

Ex: Cleavage energy of Diamond

C-C bond strength $\sim 5.8 \cdot 10^{-19}$ J $\quad a = 3.57$ Å

Which is the cleavage surface? $\begin{cases} (111) \rightarrow |K| = \frac{2\pi}{a}\sqrt{3} \\ (100) \rightarrow |K| = 2\pi/a \\ (110) \quad |K| = \frac{2\pi}{a}\sqrt{2} \end{cases}$

(111) → lattice plane spacing d

$$d = \frac{2\pi}{|K|} = \frac{2\pi}{2\pi \cdot \sqrt{3}/a} = \frac{a}{\sqrt{3}}$$

- density of lattice points $= \frac{N_p}{V_p} = \frac{4}{a^3} = \rho$ (for fcc)
- Surface density of bonds in (111) plane $\quad \sigma = \rho \cdot d = \frac{4}{\sqrt{3}} \frac{1}{a^2} \approx \frac{2.3}{a^2}$

(110) $\rightarrow d = \frac{a}{\sqrt{2}} \quad ; \sigma = \frac{2\sqrt{2}}{a^2} \sim \frac{2.8}{a^2}$

(100) $d = a \quad \sigma = \frac{4}{a^2}$

So (111) is the surface with the lowest density of bonds

$E = \frac{4}{\sqrt{3}} \frac{1}{a^2} * 5.8 \cdot 10^{-19}$ J $= 10.5$ J/m^2 (exp one $= 12$ J/m^2)