Crystal Lattices

→ until now, we have largely ignored the underlying structure of the materials, i.e. (+) ions in the material provide charge balance.

→ a complete model of $\bar{e}$'s in a solid-state material requires consideration of the arrangements of the atoms in the solid.

→ periodic positioning of ions modifies the $\bar{e}$ states of the system

→ importantly, movement of the ions & their interaction w/ $\bar{e}$'s must be considered

↳ coupled motion of the ions ⇒ phonons...

→ like most of Physics, symmetry plays a huge role.

Solid-state materials:

→ elemental solids (e.g. C) exist in a crystalline state.

↳ includes metals! metals are crystals

→ also many ionic (eg. salts) & covalent (eg. ceramics, H_2O) compounds.

→ alternative to crystalline is amorphus solid: e.g. glass, wax, many plastics (polymers).

→ IRL most crystalline materials are polycrystalline i.e. many single crystals bonded together.

crystal lattice: highly ordered structure consisting of a repeating group of atom(s) which extends in all directions.

Mathematical formulation: Bravais Lattice

1) A 3-D Bravais Lattice consits of all points w position $\bar{R}$ where:

$$\bar{R} = n_1 \bar{a}_1 + n_2 \bar{a}_2 + n_3 \bar{a}_3$$

where n_i = integer, and $\bar{a}_i$ are 3-vectors not all in same plane.

equiv.

2) Infinite set of points w arrangement & orientation exactly the same, from whichever pt. the set is viewed.

→ the Bravais lattice is the mathematical construction used to describe real crystals. It is infinite

→ real crystal would occupy some finite volume of it's B-L.

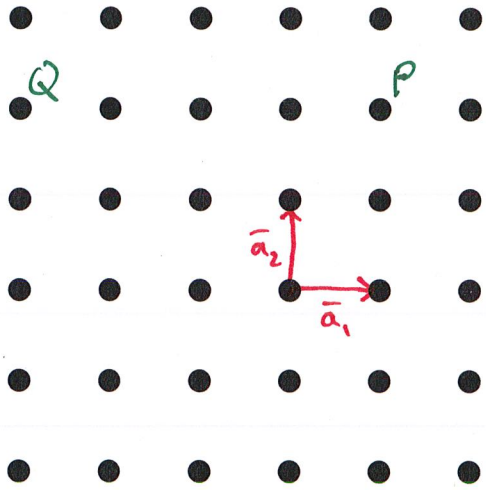
→ not all periodic structures correspond to a B-L

↳ BUT, they can be represented by one

→ the B-L represents fundamental symmetries of the structure:

in 2-D: 5 unique B-L

3-D: 14 unique B-L.

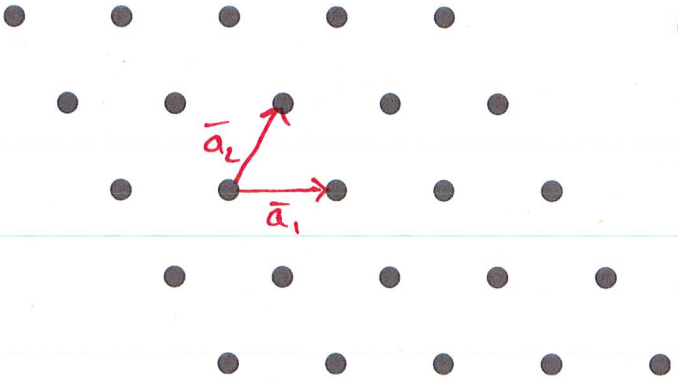


2D Bravais lattice (square)

primitive vectors $\bar{a}_1$ & $\bar{a}_2$

e.g. $\bar{P} = \bar{a}_1 + 2\bar{a}_2$

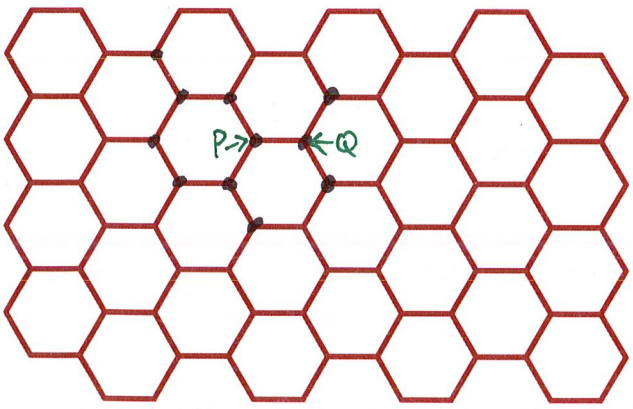
$\bar{Q} = -3\bar{a}_1 + 2\bar{a}_2$



arbitrary 2D lattice

Bravais Lattice (no particular sym)

$\bar{a}_1$ & $\bar{a}_2$ span lattice



Honeycomb lattice, pts @ vertex.

→ periodic/repeating

→ NOT Bravais Lattice

e.g. P & Q do not share same "view"

→ they are mirrored.

→ will learn to treat this later.

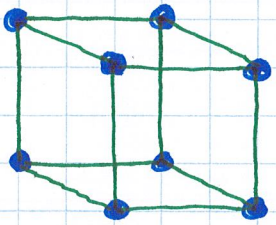
$$\bar{R} = n_1 \bar{a}_1 + n_2 \bar{a}_2 + n_3 \bar{a}_3$$

$\bar{a}_1, \bar{a}_2, \bar{a}_3$ → primitive lattice vectors
→ "span" or "generate" the array.

→ choice of $\bar{a}_i$ not unique — infinite choices!

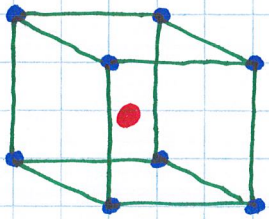
→ identifying a Bravais lattice & appropriate primitive lattice vectors can be challenging.

Cubic structures

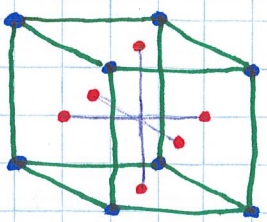


"primitive cubic"

simple cubic (sc)



body-centered cubic (bcc)



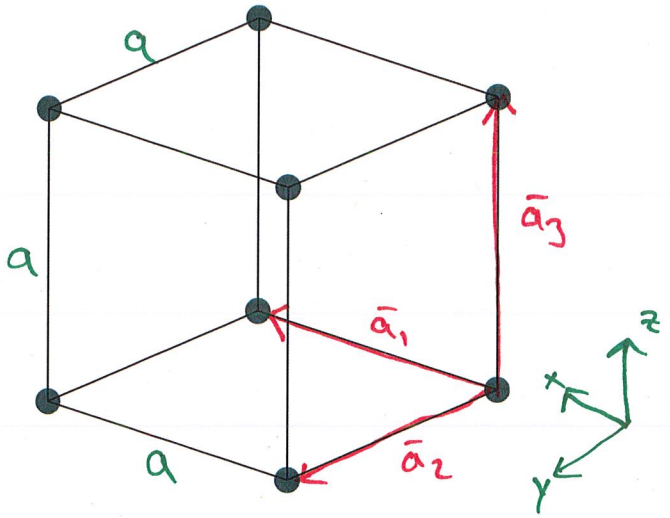
face-centered cubic (fcc)

→ see tables 4.1 & 4.2 for elements w bcc or fcc crystal structures

→ many ionic salts have simple cubic structure e.g. NaCl

Coordination Number: # of nearest neighbours

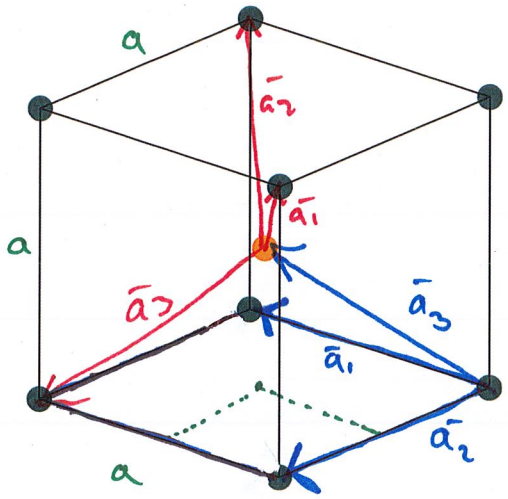
simple cubic: 6
body centered cubic: 8
face centered cubic: 12



sc (primitive cubic)

primitive vectors

$\bar{a}_1 = a\hat{x} \quad \bar{a}_2 = a\hat{y} \quad \bar{a}_3 = a\hat{z}$



bcc

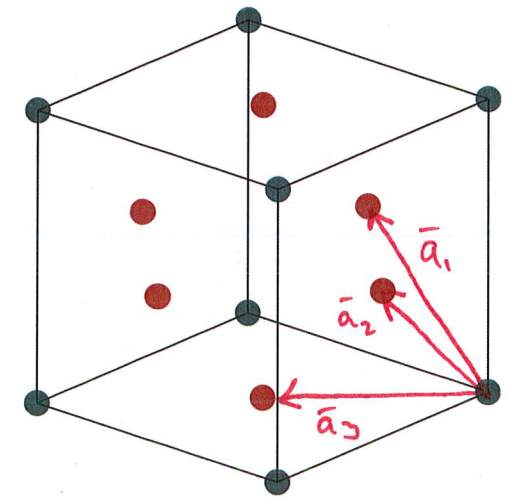
$\bar{a}_1 = a\hat{x} \quad \bar{a}_2 = a\hat{y} \quad \bar{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$

OR

$\bar{a}_1 = \frac{a}{2}(\hat{y}+\hat{z}-\hat{x})$

$\bar{a}_2 = \frac{a}{2}(\hat{z}+\hat{x}-\hat{y})$

$\bar{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}-\hat{z})$



fcc

$\bar{a}_1 = \frac{a}{2}(\hat{y}+\hat{z})$

$\bar{a}_2 = \frac{a}{2}(\hat{z}+\hat{x})$

$\bar{a}_3 = \frac{a}{2}(\hat{x}+\hat{y})$

Unit cell: fundamental repeating unit of lattice

e.g. the cubes of sc, bcc, or fcc

Primitive unit cell: smallest (in volume) unit cell

→ must fill all space when translated via primitive vectors $\bar{a}_i$

→ can not overlap when translated via $\bar{a}_i$

→ must contain precisely one lattice pt.

→ just like choice of $\bar{a}_i$, there are ∞ possible primitive unit cells.

Volume of primitive cell:

if the density of lattice points is n_L $\Rightarrow$ pts/volume
and the volume of the primitive cell is V_{pc} $\Rightarrow$ Vol/cell

then: $n_L V_{pc} = 1$ $\qquad \frac{\text{pts}}{V} \cdot \frac{V}{\text{cell}} = \frac{\text{pts}}{\text{cell}} = 1$

$$V_{pc} = \frac{1}{n_L}$$

Aside: n_L is related to, but not necessarily, the # density of $\bar{e}$'s.

Note: n_L does not change w/ choice of $\bar{a}_i$ or prim. cell.

i.e. all primitive unit cells for given B.L. have the same volume.

One choice of primitive cell is the parallelepiped formed by the primitive unit vectors, $\bar{a}_i$'s

volume given by triple product:

$$V_o = \bar{a}_1 \cdot (\bar{a}_2 \times \bar{a}_3)$$

e.g. simple cubic (trivial): $V_{sc} = a^3$

fcc: $\bar{a}_1 = \frac{a}{2}(\hat{y} + \hat{z})$

$\bar{a}_2 = \frac{a}{2}(\hat{z} + \hat{x})$

$\bar{a}_3 = \frac{a}{2}(\hat{x} + \hat{y})$

$$\bar{a}_2 \times \bar{a}_3 = (0-0)\hat{x} + \left(\frac{a^2}{4} - 0\right)\hat{y} + \left(\frac{a^2}{4} - 0\right)\hat{z}$$

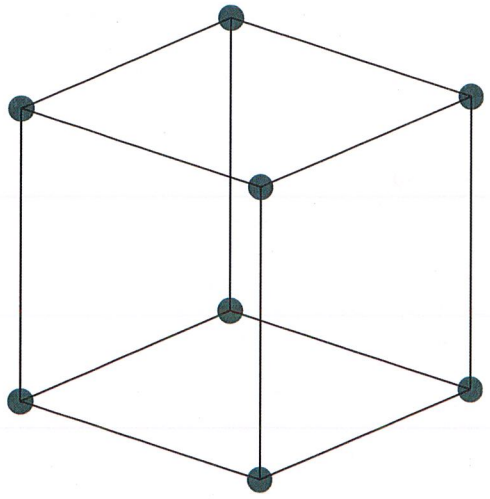
$$= \frac{a^2}{4}(\hat{y} + \hat{z})$$

$$\bar{a}_1 \cdot (\bar{a}_2 \times \bar{a}_3) = \frac{a}{2}\left(\frac{a^2}{4} + \frac{a^2}{4}\right) = \frac{a^3}{4}$$

∴ Volume of fcc prim. cell is $\frac{1}{4}$ that of the sc unit cell.

⇒ There is any easier way...

Count # of points in sc. unit cell.



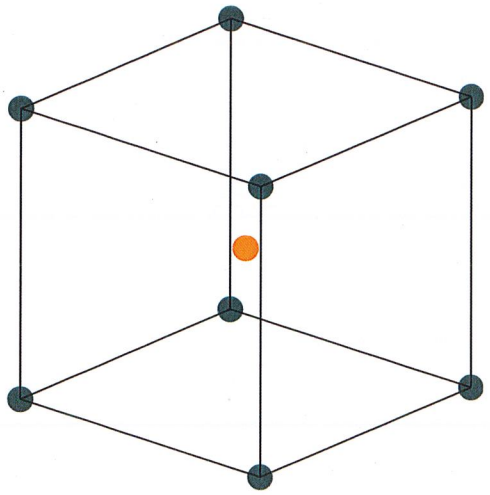
Simple cubic

$V_0 = a \times a \times a = a^3$

points:

each corner → $\frac{1}{8}$ of a pt.

$\therefore 8 \times \frac{1}{8} = 1$ pt. (of course)



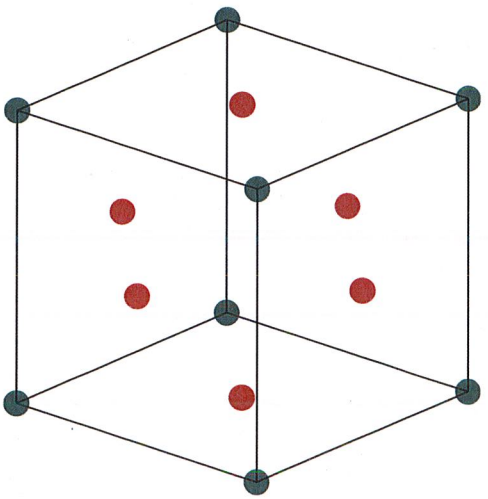
bcc

corners: $8 \times \frac{1}{8} = 1$

center: $1 \times 1 = 1$

$\therefore$ 2 pts per unit cell

$\therefore V_0 = \frac{a^3}{2}$ ⇒ primitive volume



fcc

Corners: $8 \times \frac{1}{8} = 1$

faces: $6 \times \frac{1}{2} = 3$

$\therefore$ 4 pts per unit cell

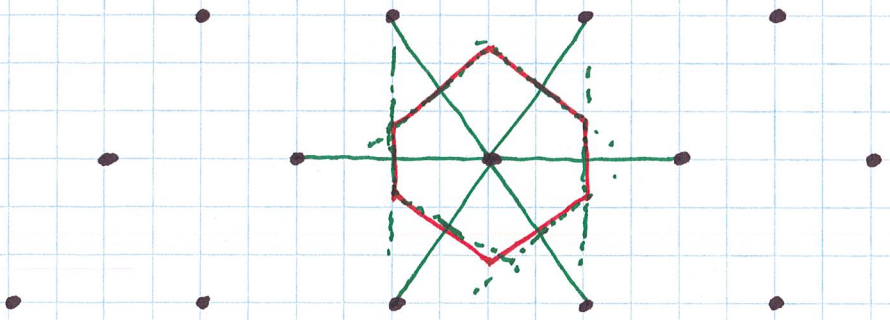
$V_0 = \frac{a^3}{4}$ ⇒ confirmed by $\bar{a}_1 \cdot (\bar{a}_2 \times \bar{a}_3)$

Wigner - Seitz Primitive Cell

→ a primitive unit cell which has the full symmetry of the B.L.

→ defined by the of space closest to a given lattice pt.

→ constructed by bisecting lines joining nearest neighbours



FCC → rhombic dodecahedron

BCC → truncated octahedron

SC → cube

Lattice w/ a basis

→ some periodic arrays are not a Bravais lattice e.g. honeycomb.

→ we can group lattice pts together such that the "group" forms a Bravais Lattice

→ the position of each pt. in the group is defined by the basis

→ we can envision this in the context of molecular crystals

→ each molecule may serve as a lattice pt. in a Bravais lattice

→ each atom in the molecule forms a basis point.

→ other Bravais lattices can be described using a basis:

e.g.: bcc is a SC B.L. w/ a 2pt. basis

basis pts: 0, $\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$

fcc is a sc, B.L. w/ 4 pt. basis:

: 0, $\frac{a}{2}(\hat{x}+\hat{y})$, $\frac{a}{2}(\hat{y}+\hat{z})$, $\frac{a}{2}(\hat{z}+\hat{x})$

→ very useful in describing complex crystals

Close-packed structures

→ for uniform spheres of constant volume, what structure maximizes density?

→ "cannonball problem"

Two basic repeating patterns in 3D:

Hexagonal close-packed (hcp): ABABAB...

Cubic close-packed (ccc): ABCABCABC...
↳ is the same as fcc!!

HCP lattice: $\bar{a}_1 = a\hat{x}$

$$\bar{a}_2 = \frac{a}{2}\hat{x} + \frac{\sqrt{3}}{2}a\hat{y}$$

$$\bar{a}_3 = c\hat{z}$$

Simple hexagonal B.L. w/ basis pt. @:

$$0, \quad \frac{1}{3}(\bar{a}_1 + \bar{a}_2 + \bar{a}_3)$$