

Structure of Crystalline Solids

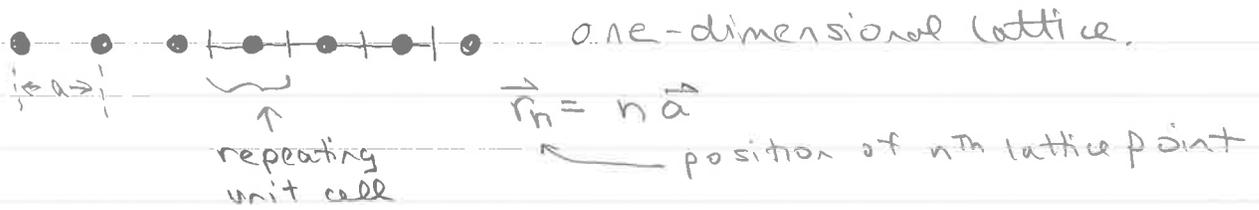
When atoms and molecules are brought together by attractive forces into a solid, they pack together in a structure with the lowest free energy.

The lowest free energy structure is a crystal, where the atoms and molecules are arranged periodically in 3 dimensions.

Any periodic pattern can be described by a repeating unit cell and an algorithm for how to repeat it.

lattice

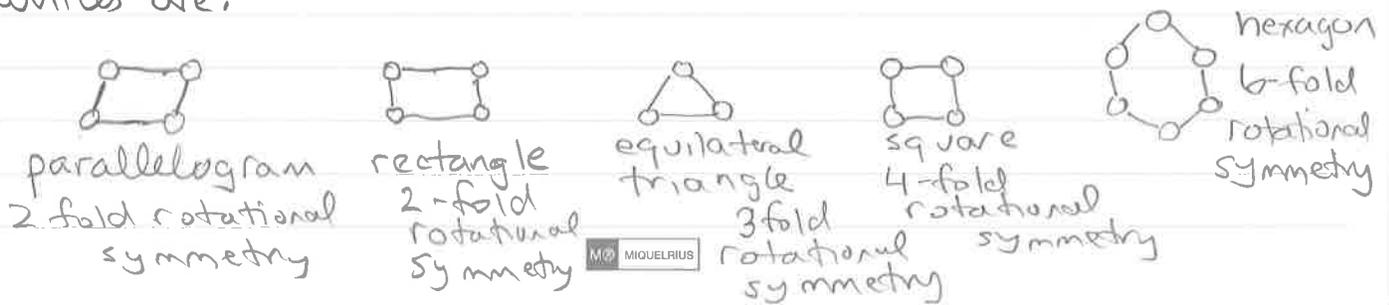
any lattice point can be reached from any other lattice point by an integer number of unit cell translations.



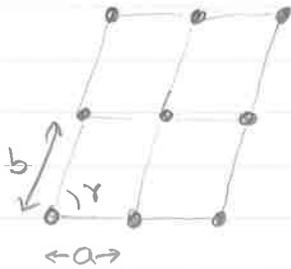
A lattice is a mathematical concept. It can represent an atom, a molecule, or the space between atoms and molecules.

Repeating unit cells that fill space with no gaps create a Bravais lattice.

In two dimensions the repeating unit cells that create Bravais lattices are:



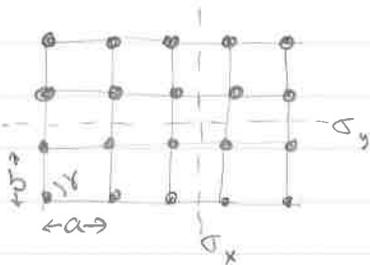
The most general and least symmetric 2D lattice is
The Oblique lattice ①



$$a \neq b \text{ and } \gamma \neq 90^\circ$$

This lattice is invariant (identical) after
a 180° rotation in the plane
(2 fold symmetry)

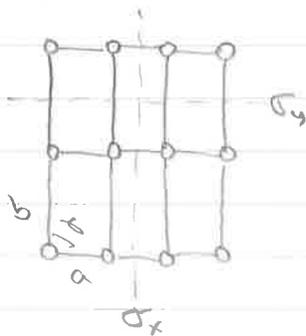
If $\gamma = 90^\circ$ and $a = b$ we have a square lattice ②



$$a = b, \text{ and } \gamma = 90^\circ$$

This lattice is identical after 90° rotation
in the plane. (4 fold symmetry)
Also invariant after two mirror (σ)
operations shown.

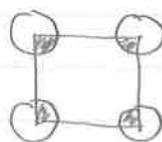
if $\gamma = 90^\circ$ but $a \neq b$, we have a rectangular lattice



primitive rectangular lattice ③

has 2 fold rotation symmetry, and σ_x, σ_y mirror
symmetry

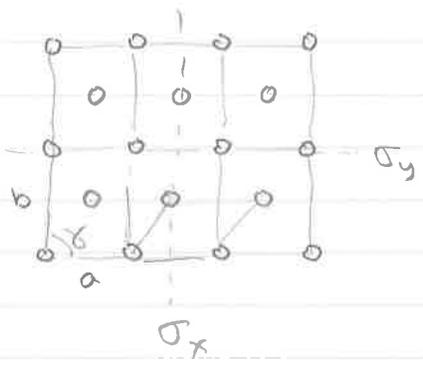
A primitive lattice contains only one
lattice point inside the unit cell.



inside unit cell is $1/4$ of
each lattice point, so
 $4(1/4) = 1$ lattice point
inside.

So, oblique and square lattices are also primitive lattices

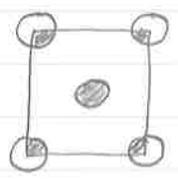
A centered Rectangular lattice is a special case that you might think is an oblique lattice, but it actually has a higher symmetry.



Centered Rectangular lattice (4)

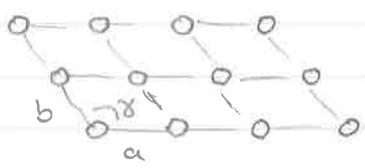
$a \neq b, \gamma = 90^\circ$

has 2 fold rotation and $\sigma_x \neq \sigma_y$ symmetry.



Centered Rectangular lattice is not a primitive lattice. It has $4(1/4) + 1 = 2$ lattice points inside unit cell.

Finally, if $a = b$ and $\gamma = 120^\circ$ we have the hexagonal lattice (5)



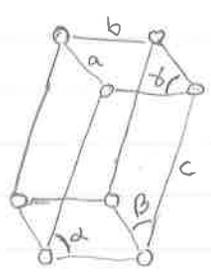
$a = b$ and $\gamma = 120^\circ$

has 3 fold rotation symmetry.

Summary: There are five Bravais lattices in two-dimensions.

In three dimensions there are 14 Bravais lattices.

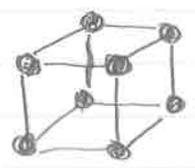
The oblique lattice in 2D corresponds to the Triclinic lattice in 3D



Convention: lattice vectors are labeled a, b, c and angles are given by Greek letter corresponding to lattice vector not spanning the angle. i.e., angle between a and c is β .

$a \neq b \neq c, \alpha \neq \beta \neq \gamma$ Triclinic (1)

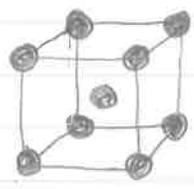
Primitive Cubic (2)



$a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$ Cubic P

8 corners and each corner has $1/8$ lattice point inside unit cell, so $8(1/8) = 1 \leftarrow$ primitive

Body Centered Cubic (3)

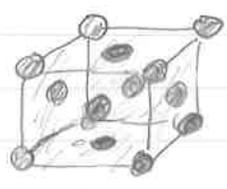


$a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$ Cubic I

8 corners with each having $1/8$ lattice point
 $8(1/8) + 1 = 2$ lattice points inside
not primitive

Face Centered Cubic (4)

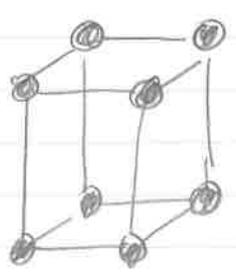
harder to draw, see text.



$a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$ Cubic F

8 corners each having $1/8$ lattice pt.
+ 6 faces each having $1/2$ lattice pt.
so $8(1/8) + 6(1/2) = 4$ lattice pts inside

Primitive Tetragonal (5)



$a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$ Tetragonal P

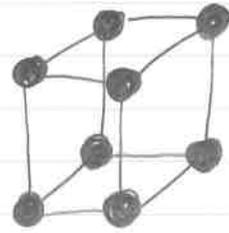
Also, Body Centered Tetragonal (6) (not drawn)

with $a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$ Tetragonal I

but no face centered tetragonal. why? Can be expressed in terms of others by choosing a different unit cell.

Primitive Orthorhombic (7)

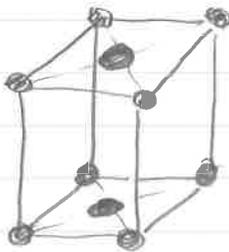
$a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$



Orthorhombic P

Side Centered Orthorhombic (8)

$a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ Orthorhombic C



lattice point on top and bottom face of unit cell.

$8(1/8) + 2(1/2) = 2$ lattice points inside unit cell.

Body Centered Orthorhombic (9)

$a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ Orthorhombic I

not shown see text

$8(1/8) + 1 = 2$ lattice points inside

Face Centered Orthorhombic (10)

$a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$ Orthorhombic F

not shown see text

lattice points on each corner and on each face.

$8(1/8) + 6(1/2) = 4$ lattice pts inside

Primitive Monoclinic (11)

$a \neq b \neq c$
 $\alpha = \gamma = 90^\circ$
 $\beta \neq 90^\circ$

Monoclinic P

Side Centered Monoclinic (12)

$a \neq b \neq c$
 $\alpha = \gamma = 90^\circ$
 $\beta \neq 90^\circ$

Monoclinic C

Trigonal (13)

$$a=b=c \text{ and } \alpha=\beta=\gamma \neq 90^\circ$$

also is a primitive cell

see text
for drawing

Hexagonal (14)

$$a=b \neq c$$

$$\alpha=\beta=90^\circ$$

$$\gamma=120^\circ$$

also
primitive

see text
for drawing

Close Packing of Identical Atoms

Imagine identical atoms packed together in one layer on a surface.

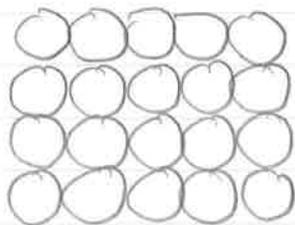


close packed
layer

this is
tightest packing,
Each atom touches
6 atoms around it

less void
space between
atoms

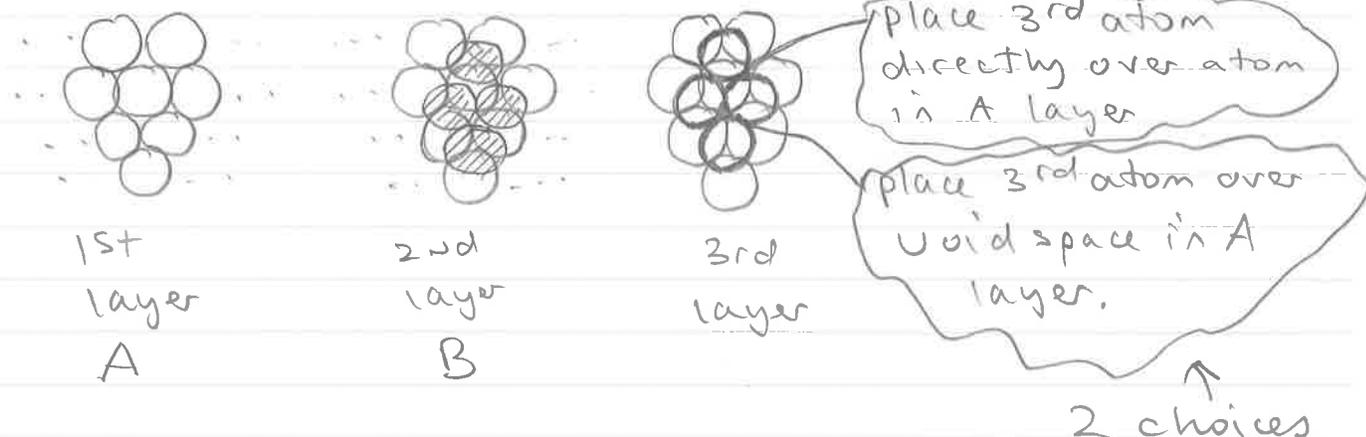
alternatively we could have found



square array

less tightly packed
than close packed,
more void space
between atoms

To build a closed packed structure in three dimensions, we need to stack another layer on top of the first



Placing 3rd layer directly over A layer is known as hexagonal close packing, (hcp)

layers are built as ABABAB...

Placing 3rd layer directly over void space in A layer is known as cubic close packing, (ccp) or face centered cubic

layers are built as ABCABCABC...

Close packing (hcp & ccp) is the most efficient use of space when packing equal diameter spheres.

74% of volume is occupied by the spheres.

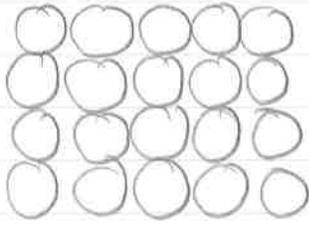
Each sphere has 6 nearest neighbors in same layer, and 3 nearest neighbor above and 3 below for a total coordination of 12.

many metals adopt close packed structures.

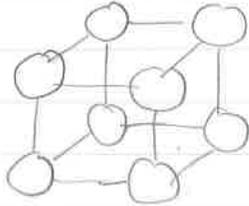
Be, Mg, Sc, Ti, Zr, Co, Zn → all take hcp

Ca, Sr, Ni, Cu, Pd, Ag, Pt, Au, Pb → all take ccp.

We can also build a 3D structure by stacking on top of the square array of atoms



One option is to place each atom of the next layer directly on top of an atom in the 1st layer.

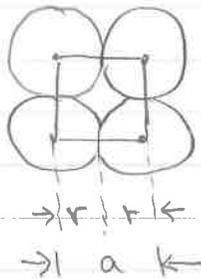


This will give us the primitive cubic lattice.

We can calculate the packing efficiency (PE)

$$PE = \frac{\text{Volume of spheres in unit cell}}{\text{Volume of unit cell}}$$

For primitive cubic



since spheres are touching we have $a = 2r$

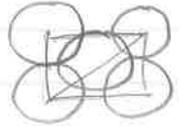
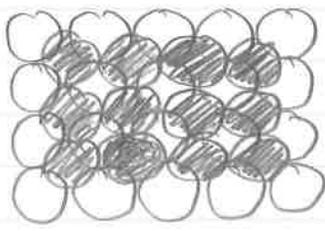
and inside primitive cubic is $8(1/8) = 1$ sphere

so

$$PE = \frac{\text{Vol of sphere}}{\text{Vol. of unit cell}} = \frac{4/3 \pi r^3}{a^3} = \frac{4/3 \pi r^3}{(2r)^3} = \frac{4/3 \pi}{8}$$

PE = 0.524
or 52.4%

Another option for stacking atop the square array leads to body centered cubic structure



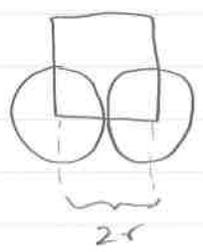
one can show that $a = \frac{4r}{\sqrt{3}}$

for face centered cubic $a = \sqrt{8} r$

Home work →

Calculate the packing efficiency of body centered cubic and face centered cubic.

A metal with atomic wt of 60.2 g crystallizes in a primitive cubic structure of length 3.18 \AA . Calculate the radius of the metal atom, and the density of the metal.



$$\frac{3.18 \text{ \AA}}{2} = 1.59 \text{ \AA}$$

$$\rho = \frac{m}{V}$$

$$\rho = \frac{1 \text{ atom}}{\text{unit cell}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{60.2 \text{ g}}{\text{mol}} \times \frac{1 \text{ \AA}^3}{(10^{-8} \text{ cm})^3}$$

$$= 3.1 \text{ g/cm}^3$$

Ionic Crystals

While close packing of equal diameter spheres is a good picture for understanding the structure, high coordination numbers (up to 12), and dense packing of metals (high density) when we consider ionic solids we quickly realize that our packing picture becomes more complicated.

1st: Cations and Anions are charged, so repulsive and attractive forces are much stronger.

2nd: Cations and Anions are have different diameters.
Even if we found a cation and anion with equal diameters, we cannot have a closed packed structure with coordination numbers of 12 because we could not maintain charge neutrality with such higher coordination numbers.

Thus, ionic solids are less dense than metals.

A simple idea that extends the close packing picture to ionic solids is to put the smaller cations into the empty space between close packed anions.

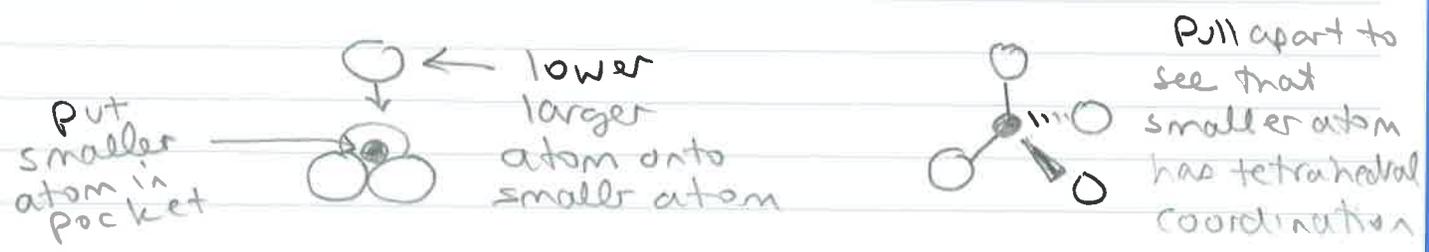
We could have also suggested putting anion into the empty spaces between close packed cations, but generally we find that anions are larger than cations.

Let's look closely at the space in between packed atoms

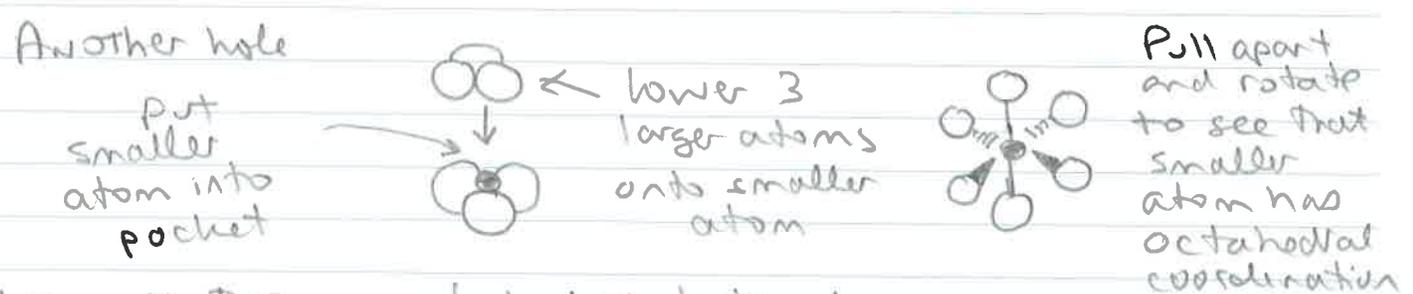


If we placed an atom on top of these holes we create an empty pocket called an interstitial void.

Imagine a smaller diameter atom with just the right size to fit inside this interstitial void.

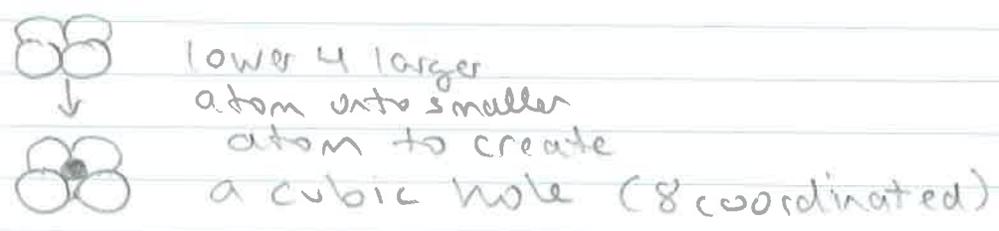


We call this a tetrahedral hole in a close packed structure.



We call this an octahedral hole in a close packed structure

Similarly, in a cubic lattice,



The holes may not be the right size for the smaller atom, but the structure of ionic compounds can often be guessed by looking at the radius ratio

radius ratio	$\frac{r_{\text{small ion}}}{r_{\text{large ion}}}$	ratio	CN	hole	Example
		0.225 - 0.414	4	Td	ZnS
		0.414 - 0.732	6	Oh	NaCl
		0.732 - 1.000	8	Cubic	CsCl