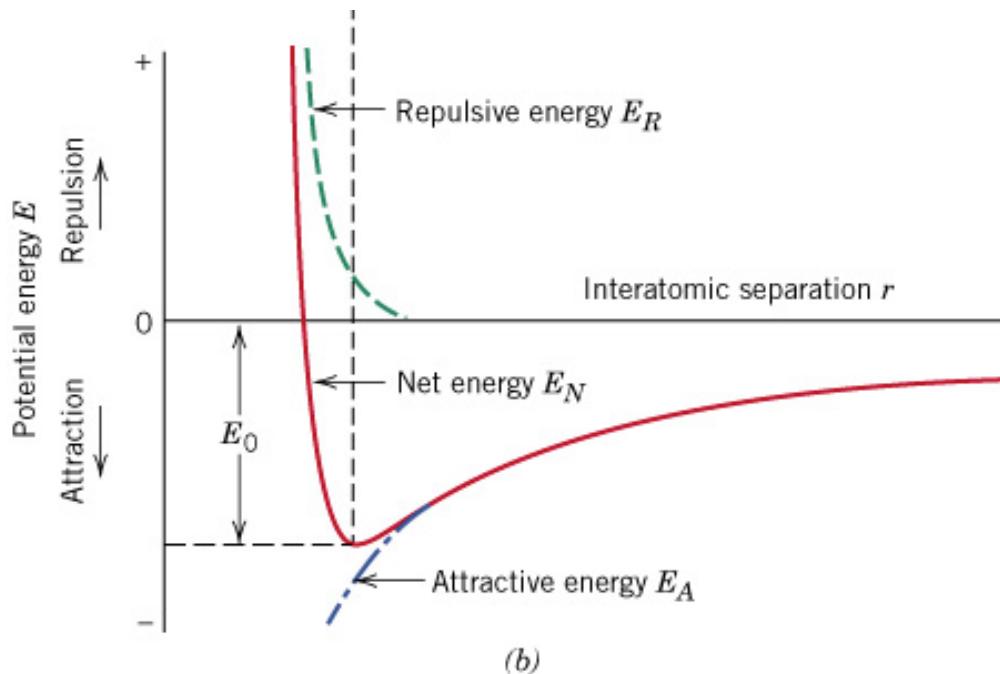


APS104S – Introduction to Materials & Chemistry

Lecture 4
January 12, 2016

- 1) Bonding energy
- 2) Ionic bonding (Madelung constant)

Bonding energy, attractive, repulsive



$$E_N = E_A + E_R = \frac{A}{r} + \frac{B}{r^n}$$

Attractive energy Repulsive energy

A, B, n = constants

At $r = r_0 \rightarrow dE/dr = 0 \quad \& \quad E = E_0$

r_0 = equilibrium separation distance (bond distance)

E_0 = Bond energy

$r_0 = r_{\text{cation}} + r_{\text{anion}}$

Example 2

- The potential energy between Mg^{2+} and O^{2-} ions in a MgO crystal can be estimated as

$$E = -\frac{A}{r} + \frac{B}{r^8}$$

- where $A = 1.61 \times 10^{-27} \text{ J m}$, $B = 3.87 \times 10^{-96} \text{ J m}^8$, r is the separation (between ion centers) in m, and E is the potential energy in J.
- Calculate the equilibrium separation between the ion centers.
- Calculate the bonding energy between the Mg and O ions at this equilibrium distance.
- If the ionic radius of Mg^{2+} is 0.072 nm, what is the ionic radius of O^{2-} ?

Example 2-solution

(a)

$$E = -\frac{A}{r} + \frac{B}{r^8}$$

at Equilibrium $\left.\frac{dE}{dr}\right|_{r=r_0} = 0$

$$\frac{dE}{dr} = \frac{A}{r^2} - \frac{8B}{r^9} = 0 \rightarrow Ar^7 = 8B \rightarrow r = \left(\frac{8B}{A}\right)^{1/7} = \left(\frac{8(3.87 \times 10^{-96})}{1.61 \times 10^{-27}}\right)^{1/7} = 2.12 \times 10^{-10} \text{ m}$$

$$1 \text{ m} = 10^{+10} \text{ Å} \rightarrow [2.12 \text{ Å}]$$

attraction energy
repulsion energy

$$E = -\frac{A}{r_0} + \frac{B}{r_0^8} = -\frac{1.61 \times 10^{-27}}{2.12 \times 10^{-10}} + \frac{3.87 \times 10^{-96}}{(2.12 \times 10^{-10})^8} = -6.65 \times 10^{-18} \text{ J}$$

We can convert to eV $\rightarrow 1.6 \times 10^{-19} \text{ J} = 1 \text{ eV}$

$$\rightarrow E = \frac{-6.65 \times 10^{-18}}{1.6 \times 10^{-19}} = -41.5 \text{ eV} \leftarrow \text{binding Energy}$$

(c) $r_0 = r_{O^{2-}} + r_{Mg^{2+}}$

$$r_0 = 2.12 \times 10^{-10} \text{ m}$$

$1 \text{ m} = 10^{+9} \text{ nm}$

$$\rightarrow 0.212 = r_{O^{2-}} + 0.072$$

$$[r_{O^{2-}} = 0.14] \text{ nm}$$

Ionic Bonding (example NaCl)

Bonding is described as electrostatic attraction between point charges.

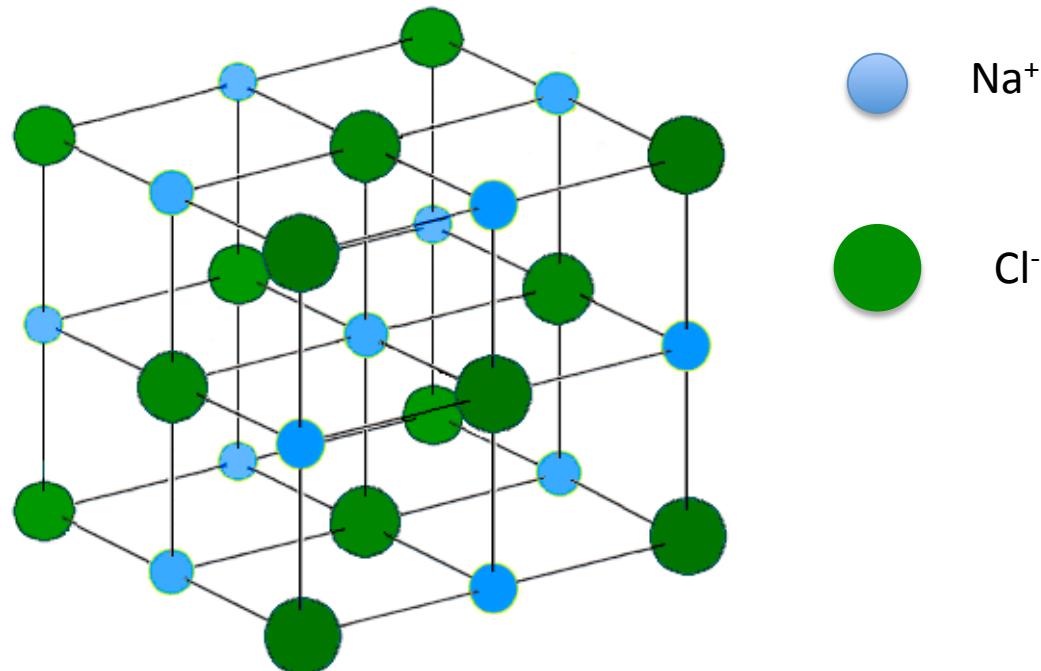
Example: NaCl

$$E = \frac{q_1 q_2}{4\pi\epsilon_0}$$

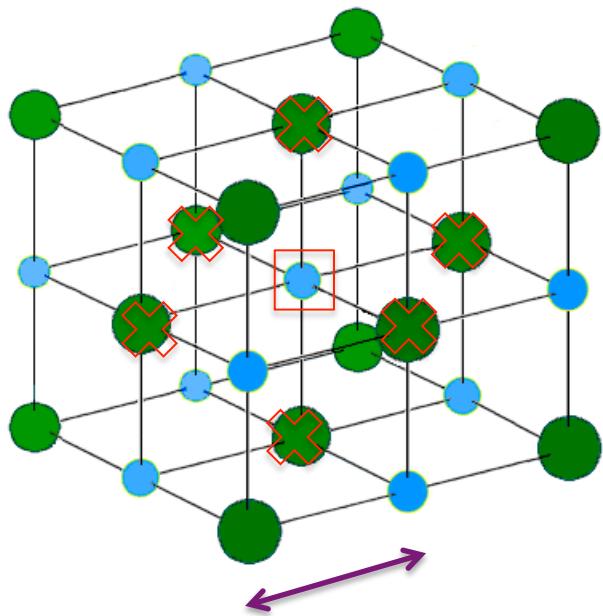
	Na ⁺	Cl ⁻
ionic radii (nm) (tabulated)	0.102	0.181

interatomic distance:

r_o = 0.28 nm (sum of ionic radii)



Ionic Bonding (example NaCl)



6 nearest neighbours @ $r = a$ (+ -)

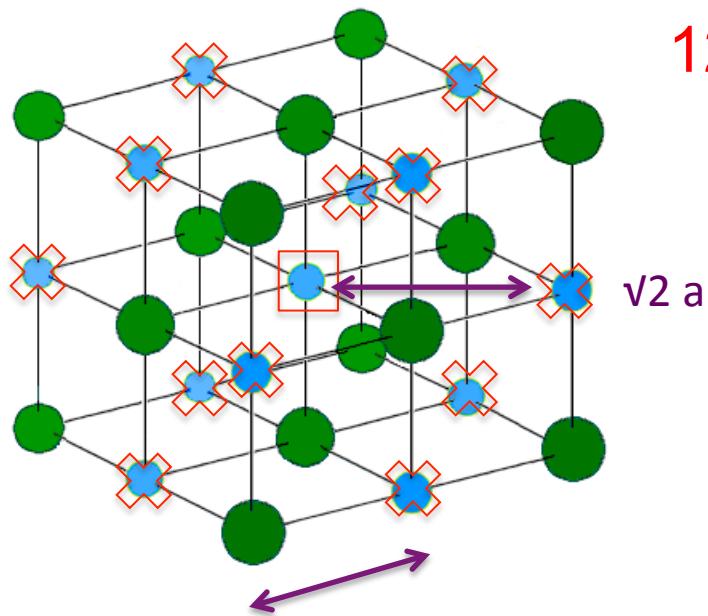
$$E = \frac{q_1 q_2}{4\pi\epsilon_0}$$

Let's call this "a"

$$a = r_0$$

$$E = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{6}{a}\right)$$

Ionic Bonding (example NaCl)

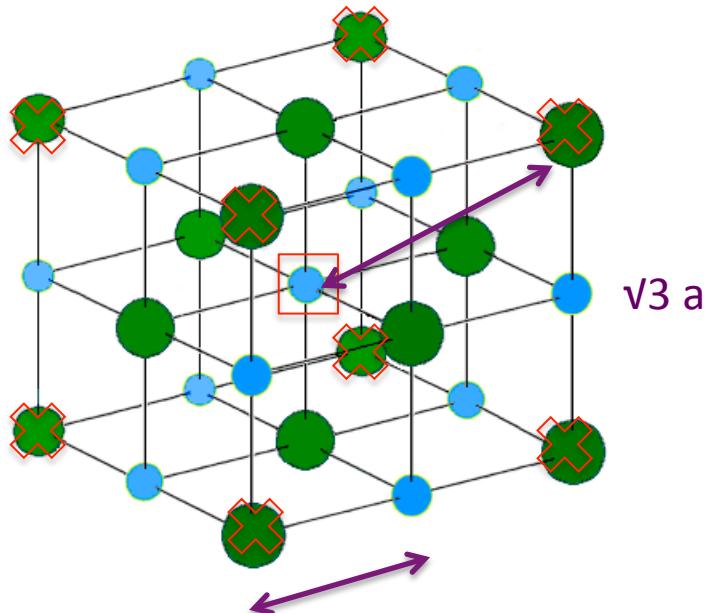


12 nearest neighbours @ $r = \sqrt{2} a (+ +)$

$$E = \frac{q_1 q_2}{4\pi\epsilon_0}$$

$$E = + \frac{e^2}{4\pi\epsilon_0} \left(\frac{12}{\sqrt{2}a} \right)$$

Ionic Bonding (example NaCl)



8 nearest neighbours @ $r = \sqrt{3} a (+ -)$

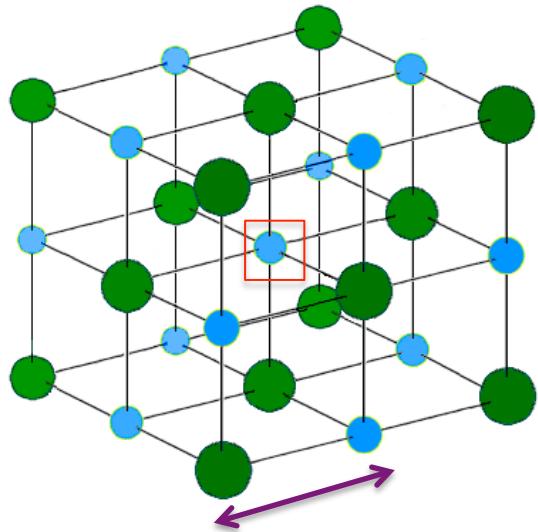
Let's call this "a"

$$a = r_0$$

$$E = \frac{q_1 q_2}{4\pi\epsilon_0}$$

$$E = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{8}{\sqrt{3}a}\right)$$

Ionic Bonding (example NaCl)



Let's call this "a"
 $a = r_0$

$$E = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{6}{a} - \frac{12}{a\sqrt{2}} + \frac{8}{a\sqrt{3}} - \dots \right)$$

$$E = -M \frac{e^2}{4\pi\epsilon_0} \frac{1}{a}$$

$$M = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \dots$$

M: Madelung constant

M depends on the geometry; for rock salt = 1.748

$$1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

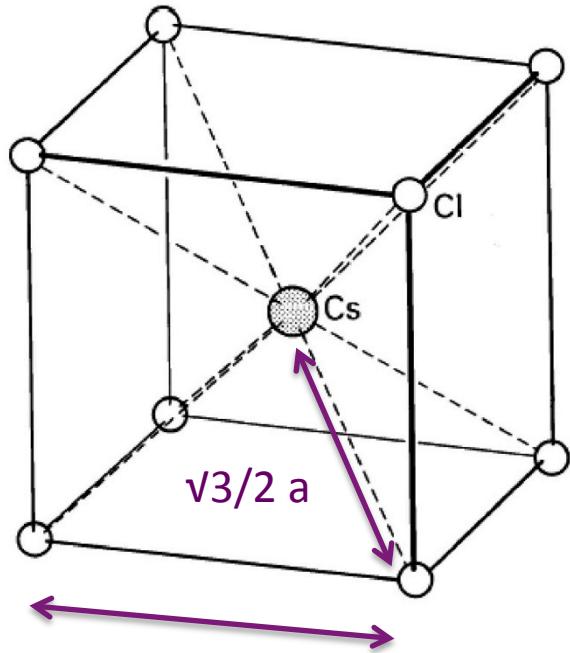
$$a = r_0 = 0.28 \text{ nm}$$

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2/(\text{Nm}^2)$$

$$E = -1.748 \times \frac{(1.602 \times 10^{-19})^2}{4\pi (8.854 \times 10^{-12})} \times \frac{1}{(0.28 \times 10^{-9} \text{ m})} = -1.43 \times 10^{-18} \text{ J}$$
$$E = \frac{-1.43 \times 10^{-18} \text{ J}}{1.6 \times 10^{-19} \text{ J}/\text{eV}} = -8.97 \text{ eV}$$

$$E = -8.97 \text{ eV/atom} \text{ (only 10% of the real value)}$$

Madelung constant for CsCl

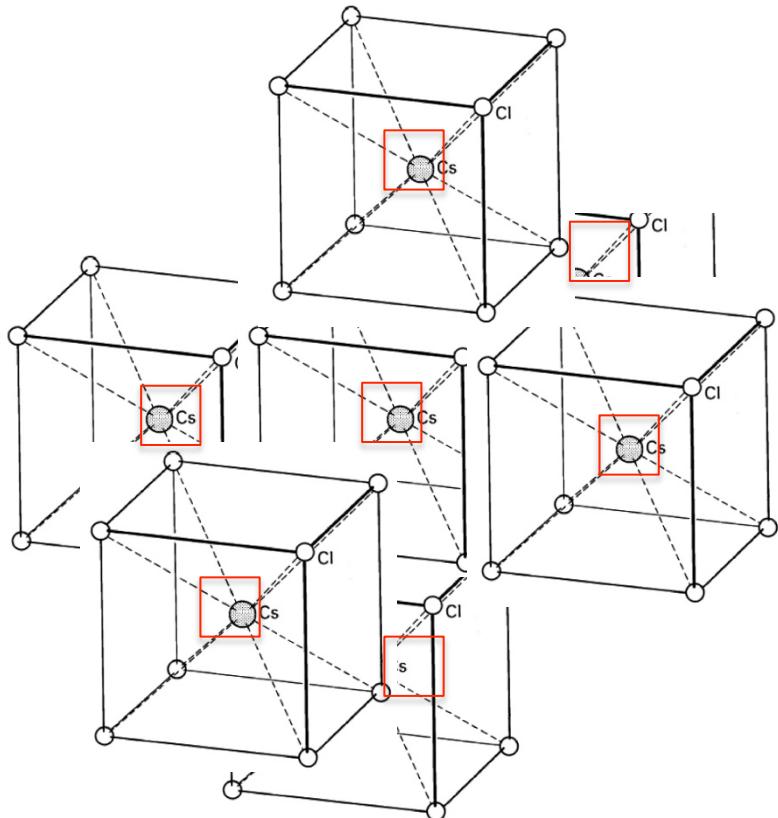


8 nearest neighbours @ $r = \sqrt{3}/2 a (+ -)$

$$E = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{8}{\sqrt{3}/2a}\right)$$

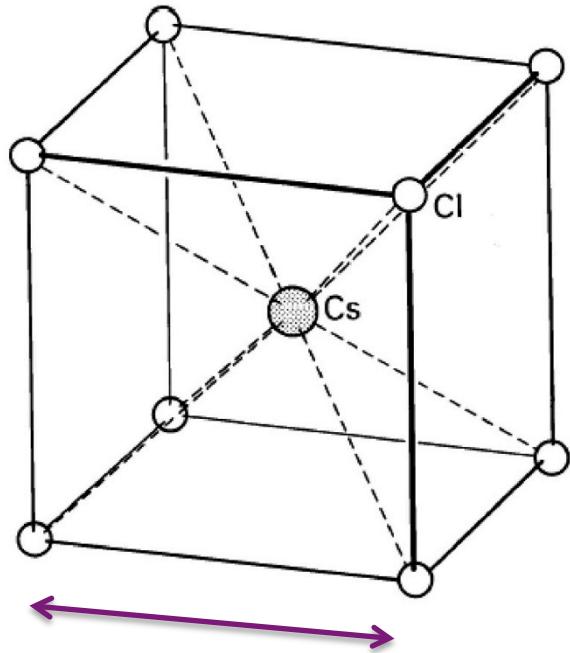
Madelung constant for CsCl

6 nearest neighbours @ $r = a$ (+ +)



$$E = + \frac{e^2}{4\pi\epsilon_0} \left(\frac{6}{a}\right)$$

Madelung constant for CsCl



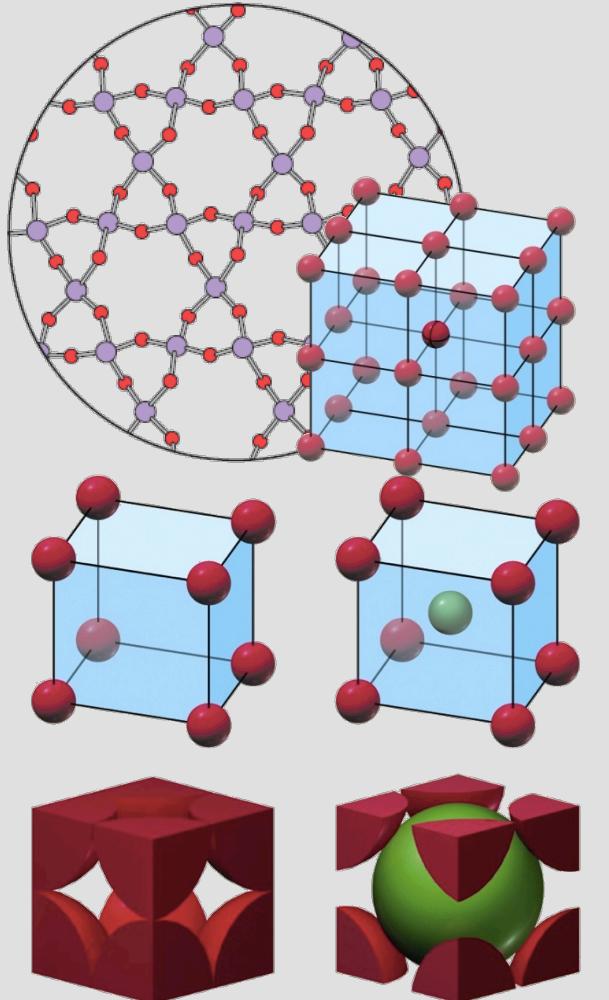
$$E = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{8}{a\sqrt{3}} - \frac{6}{2} \right)$$

$$E = -M \frac{e^2}{4\pi\epsilon_o} \frac{1}{a}$$

$$M = \left(\frac{8}{\sqrt{3}} - 6 \right)$$

the crystalline solid state

CHAPTER 3_C



topics:

unit cell

metallic crystal structures

density computations metallic/ceramic

ceramic crystal structures

directions

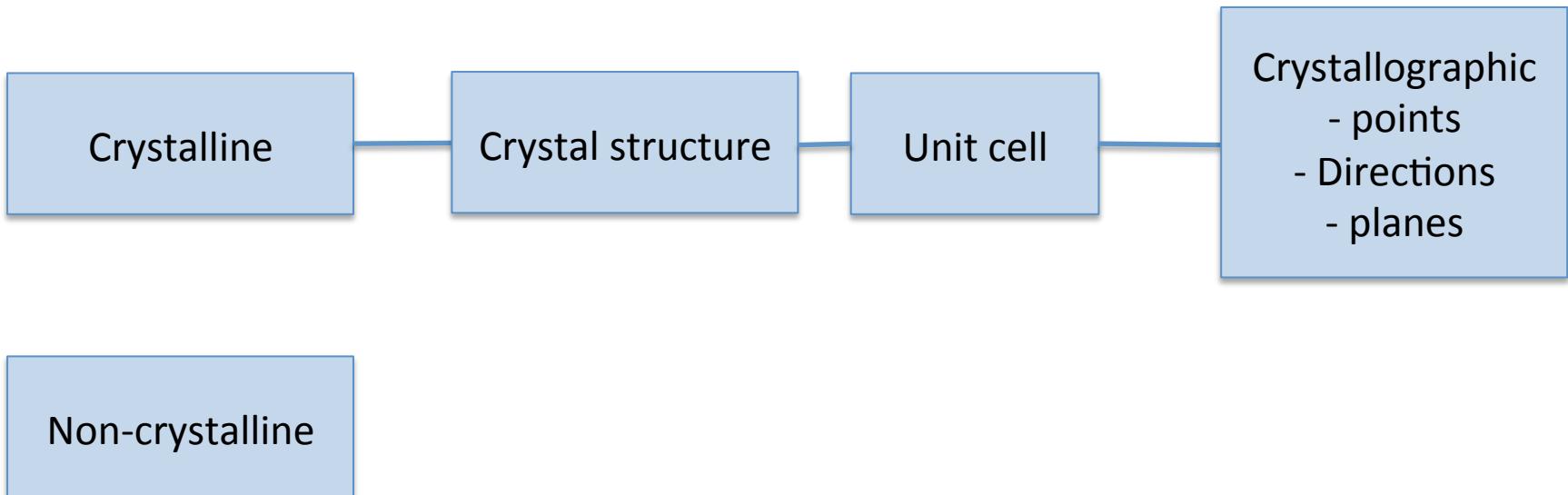
planes & densities

Subjects we will study

- What are crystals
- Crystal systems
- Crystal structure in **metals** (with a focus on cubic systems)

Why study crystal structure?

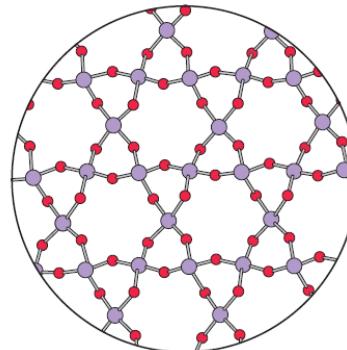
Many **properties of materials** are directly related to their crystallinity and crystal structure



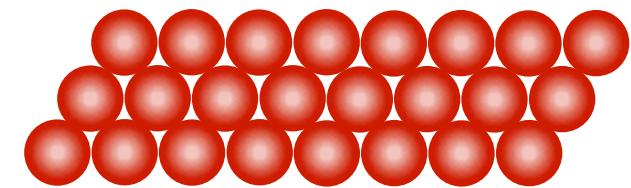
Classification of solids by atomic arrangement

Crystalline material:

- Has a well-defined ordered structure in 3D (over large range).
Atoms self-organize in a **periodic array**.
- Well defined shaped due to well-ordered particles.
- **metals** • **many ceramics** • **some polymers**



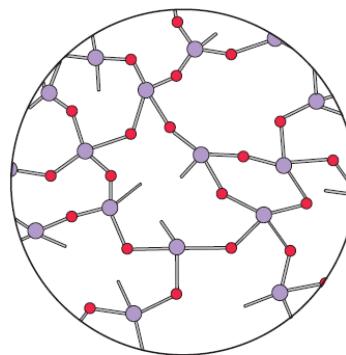
Crystalline solid



Dense,
ORDERED packing

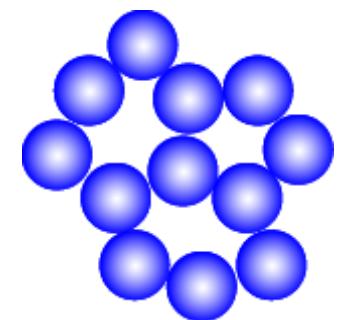
Amorphous solid (glass):

- Has a disordered structure, lacking a systematic atomic arrangement.
- Poorly defined shapes because they don't have extensive ordering of particles.
- **complex structures** • **rapid cooling**



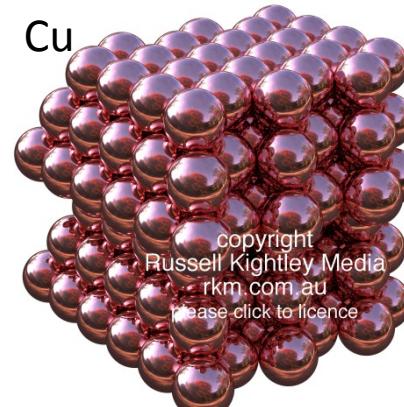
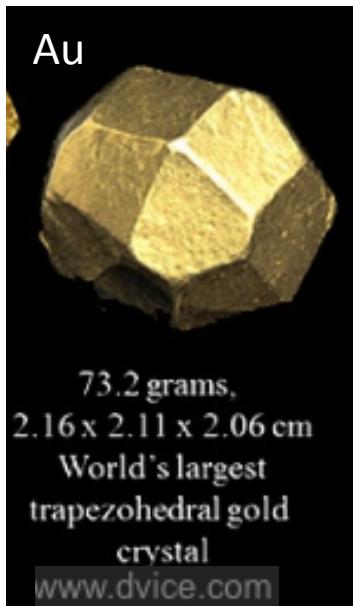
Amorphous solid

Glass



Non dense,
RANDOM packing

Some crystals (well-defined ordered structure; well-defined shape)



PbS Galena



FeS₂ Pyrite



Quartz



Попов Станислав
www.zircon81.narod.ru

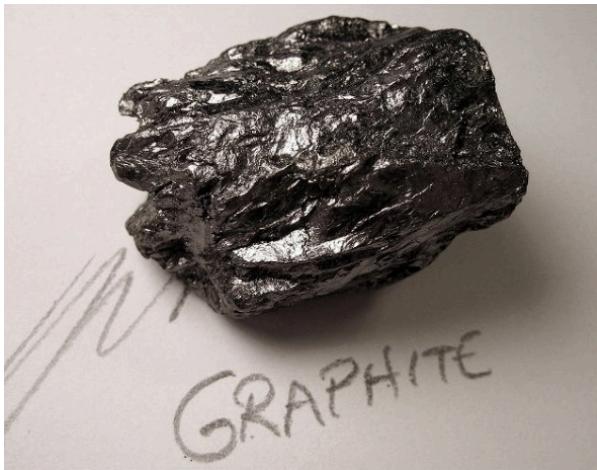


NaCl



Some amorphous solids

(disordered structure, poorly defined shapes)



powerlisting.wikia.com

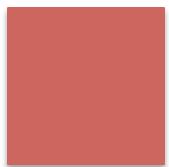
Gummite



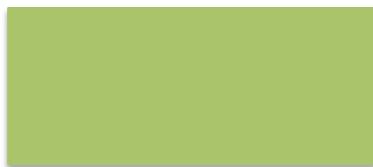
amorphous solid
*Obsidian, a volcanic
glass*

Gummite: a yellow, amorphous mineral, a mixture of oxides and silicates of uranium, formed by weathering of pitchblende (a mineral used as a source of uranium).

Stacking objects in 2-D with no voids



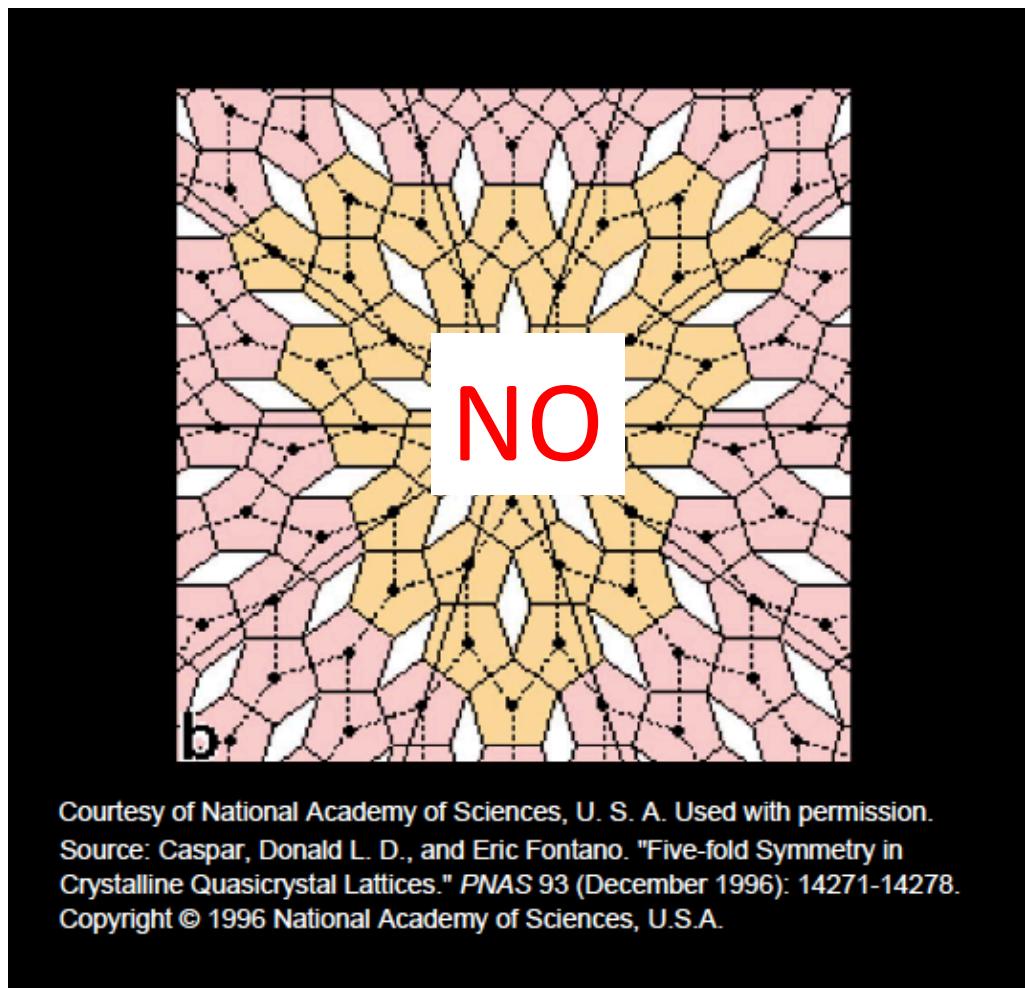
square



rectangle

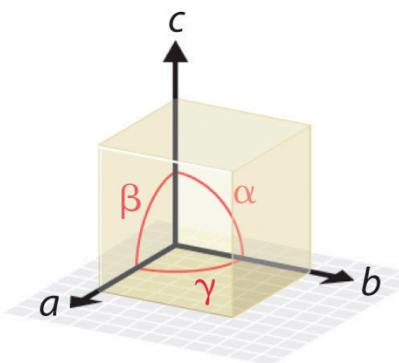


trapezoid

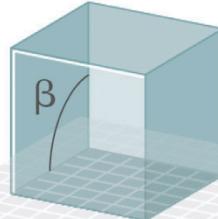


Courtesy of National Academy of Sciences, U. S. A. Used with permission.
Source: Caspar, Donald L. D., and Eric Fontano. "Five-fold Symmetry in Crystalline Quasicrystal Lattices." *PNAS* 93 (December 1996): 14271-14278.
Copyright © 1996 National Academy of Sciences, U.S.A.

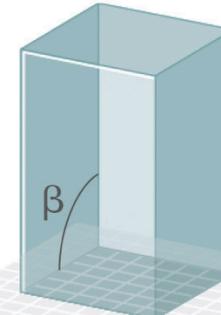
Unit cell: the repeating group – 7 ways to stack crystals in 3D with no voids



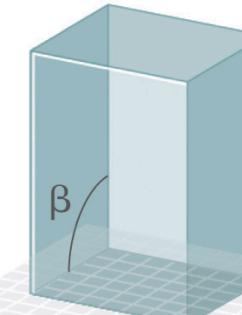
Edges and angles



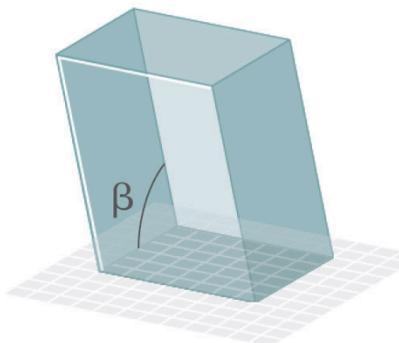
Cubic
 $a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$



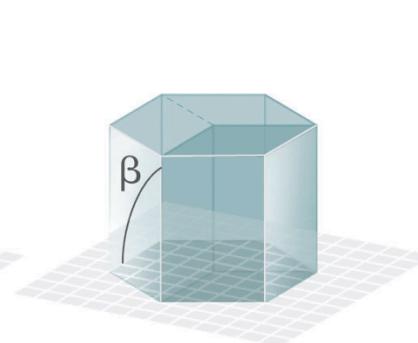
Tetragonal
 $a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



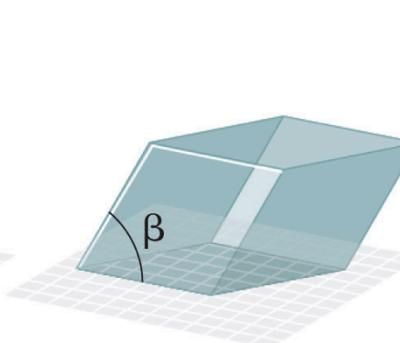
Orthorhombic
 $a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



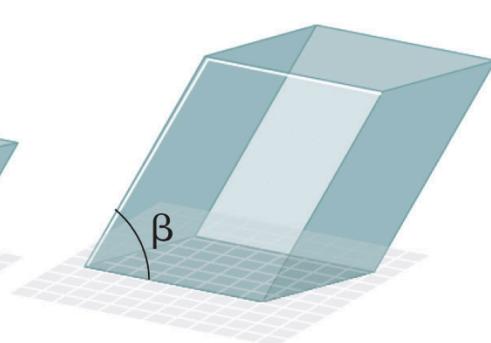
Monoclinic
 $a \neq b \neq c$
 $\alpha = \gamma = 90^\circ \neq \beta$



Hexagonal
 $a = b \neq c$
 $\alpha = \beta = 90^\circ, \gamma = 120^\circ$



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

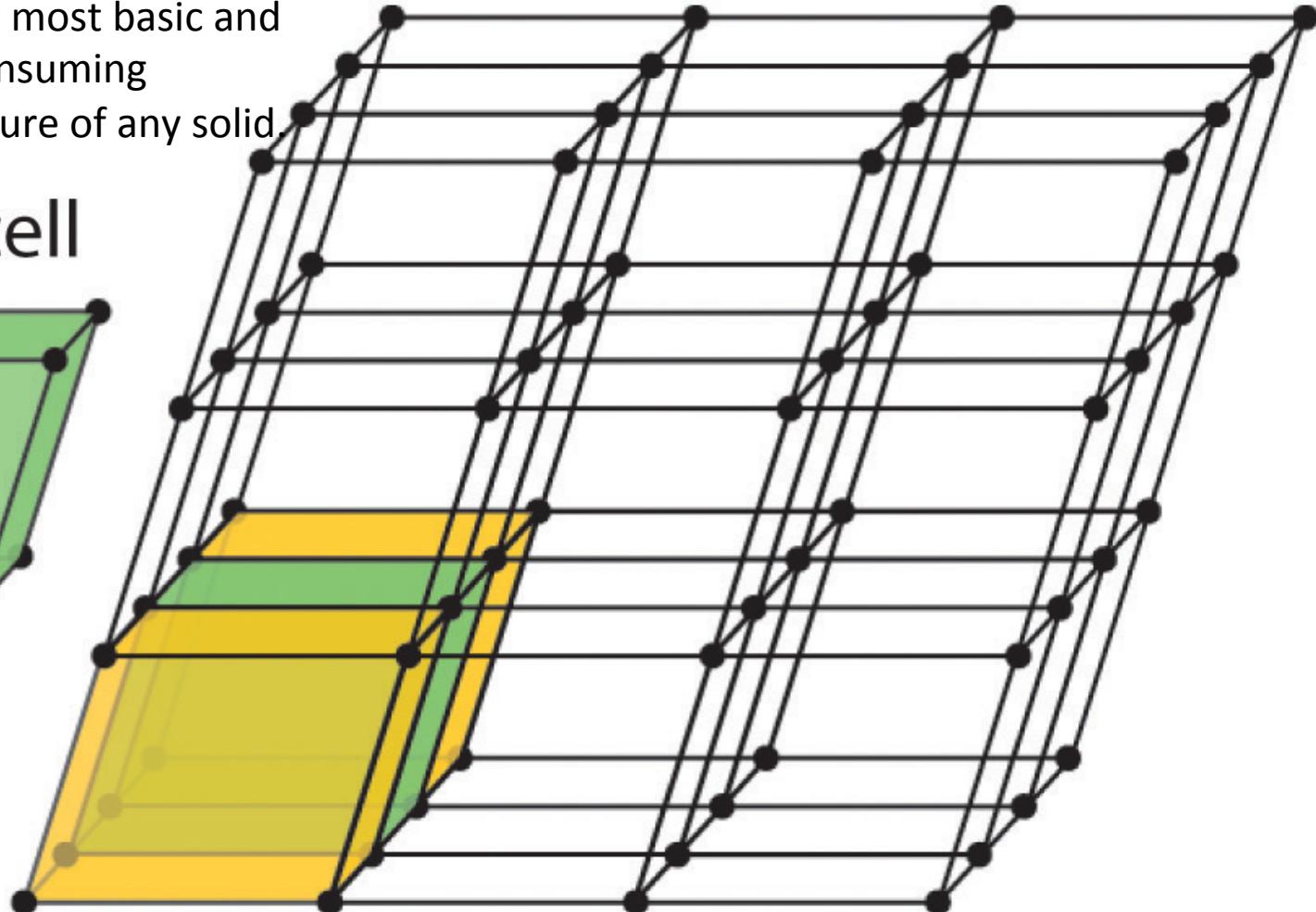
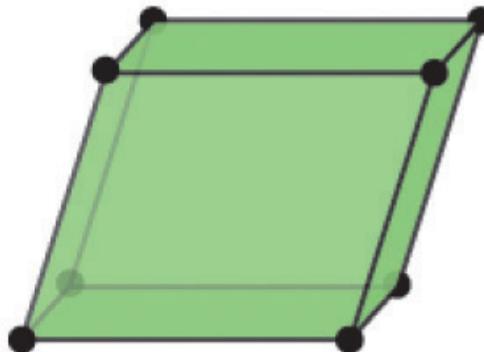


Triclinic
 $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$

Unit cell: the repeating group

A **unit cell** is the most basic and least volume consuming repeating structure of any solid.

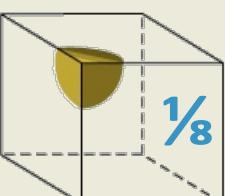
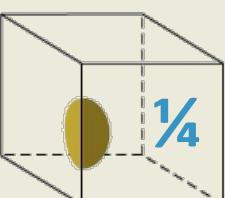
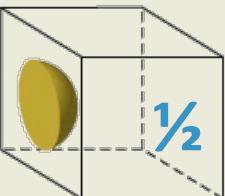
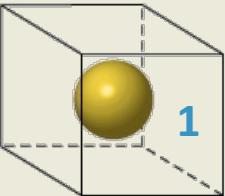
Unit cell



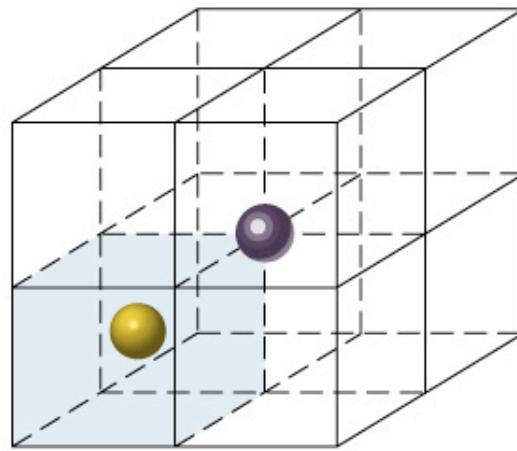
Unit cell: where atoms sit: Bravais Lattices

Bravais Lattice	Parameters	Simple (P)	Volume Centered (I)	Base Centered (C)	Face Centered (F)
		4 Lattice Types			
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^\circ$ $\alpha_{12} \neq 90^\circ$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^\circ$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^\circ$ $\alpha_{23} = \alpha_{31} = 90^\circ$				

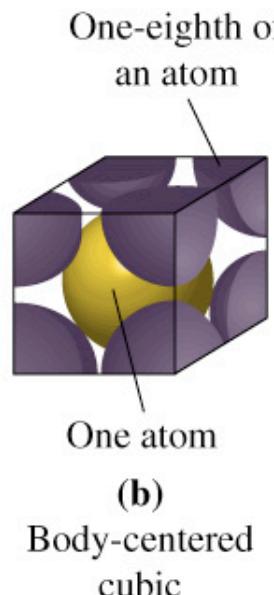
Let us look at “cubic” crystal structure



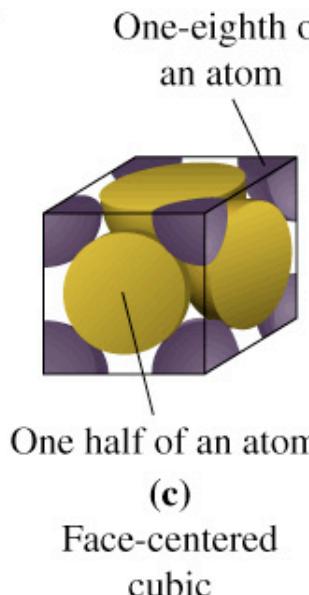
Note: for metals, all atoms are identical; the FCC and BCC atoms are shaded differently only for ease of viewing.



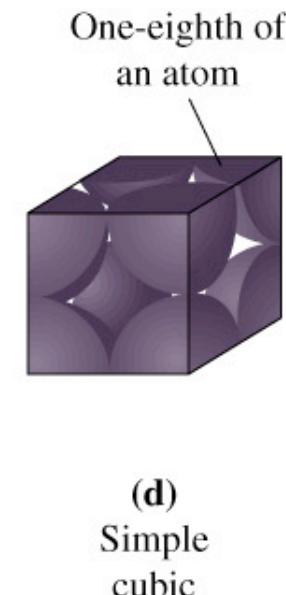
(a)



One-eighth of
an atom
One atom
Body-centered
cubic



One-eighth of
an atom
One half of an atom
Face-centered
cubic



One-eighth of
an atom
Simple
cubic

An ion in the *body* of a cell belongs entirely to that cell and counts as **1**.

An ion on a *face* is shared by two cells and contributes **$\frac{1}{2}$** .

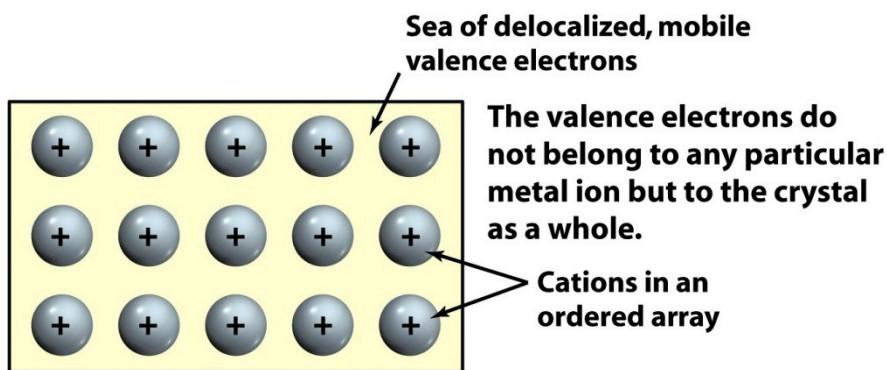
An ion on an *edge* is shared by four cells and hence contributes **$\frac{1}{4}$** .

An ion at a *vertex* is shared by eight cells, and so contributes **$\frac{1}{8}$** .

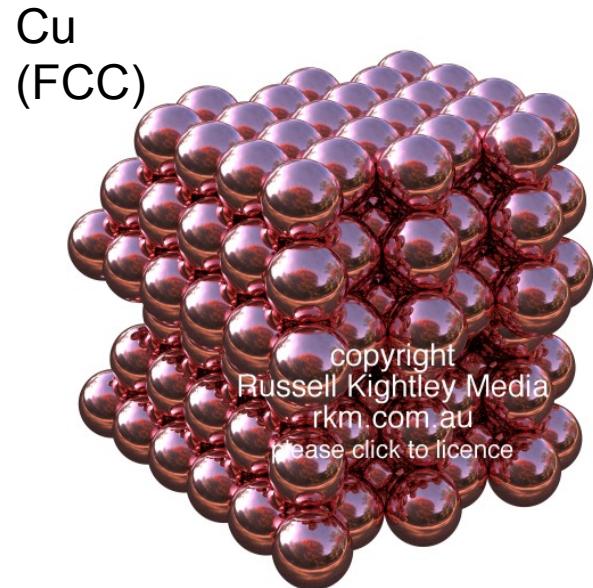
Crystal structure in **metals**

Metallic bonds (such as Au, Ag, Cu)

Can be pictured as an array of **positive ions** in a “**sea of electrons**”.



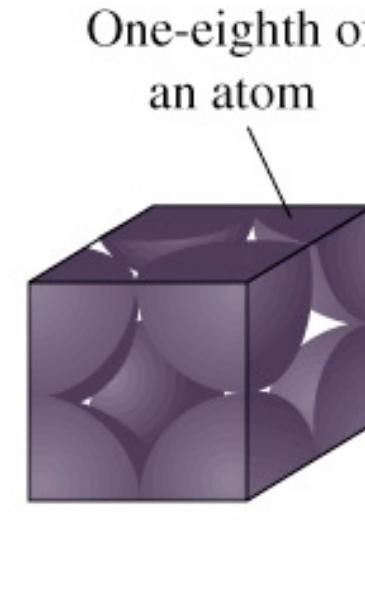
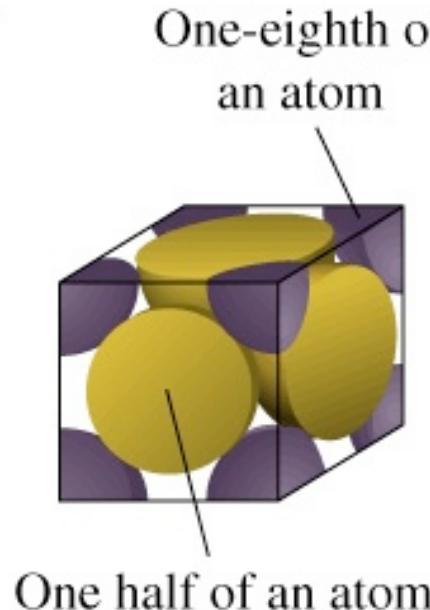
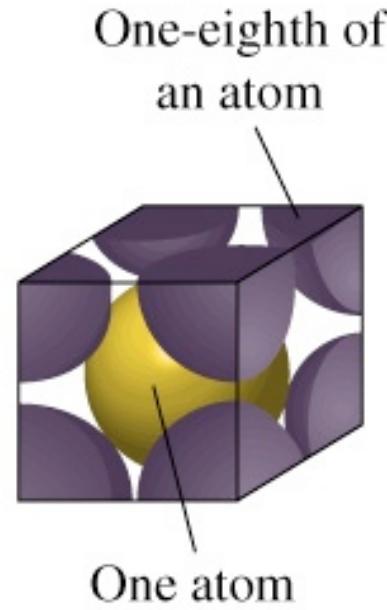
Tend to be densely packed.



REASONS FOR DENSE PACKING

- Typically, only one element is present, so all atomic radii are the same.
- Nearest neighbor distances tend to be small in order to lower bond energy.
- Electron cloud shields cores from each other.
- Metallic bonding is not directional
 - Have the simplest crystal structures.

Lattice points per cell: how many atoms we have in each unit cell



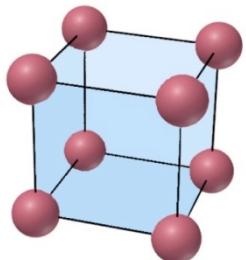
2

4

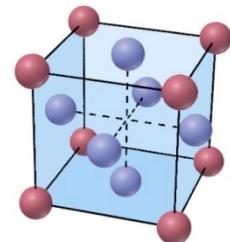
1

The relation between unit cell length (a) and radius of atom (r)

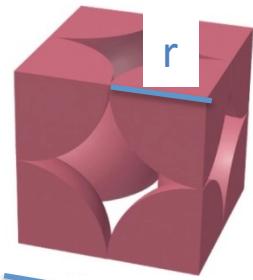
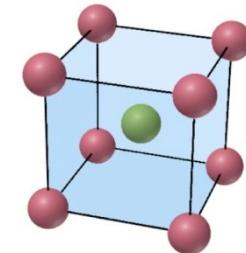
SC



FCC



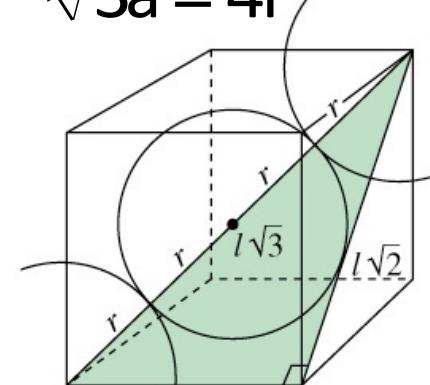
BCC



$$a = 2r$$

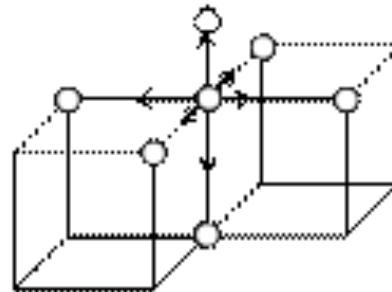
$$\sqrt{2}a = 4r$$

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



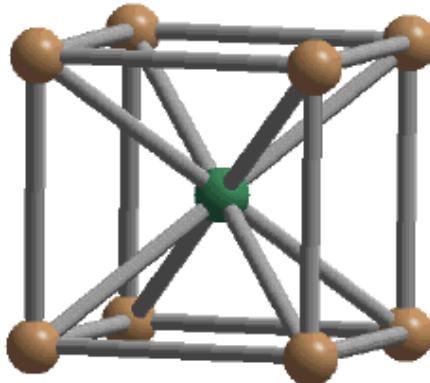
Coordination #: the number of nearest neighbors

SC



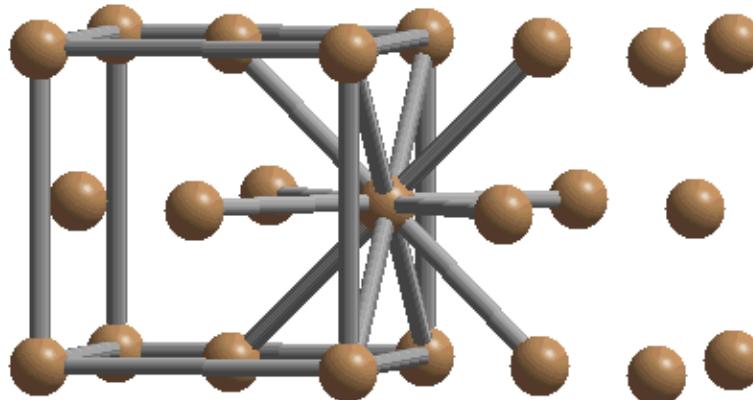
6

BCC



8

FCC

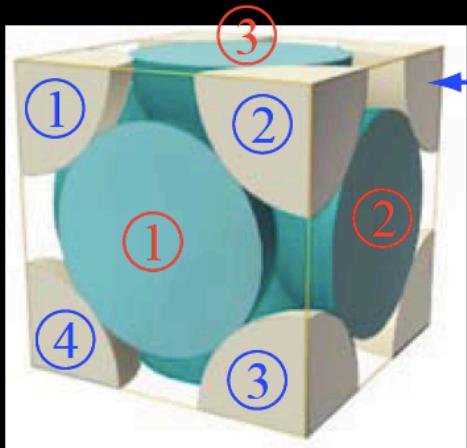


12

Atomic packing factor (APF)

$$\text{APF} = \frac{\text{volume of atoms in unit cell}}{\text{volume of unit cell}}$$

Example 1: for FCC



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

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

= 4 lattice
points/unit
cell

$$\text{APF} = (4 \times (4/3)\pi r^3)/a^3$$

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

$$\text{APF} = 0.74$$

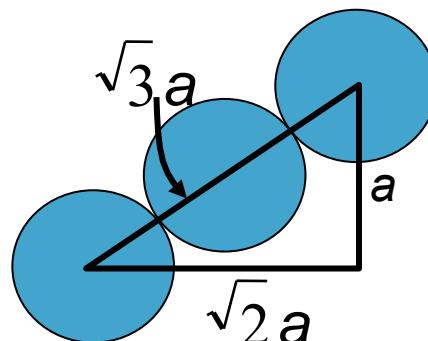
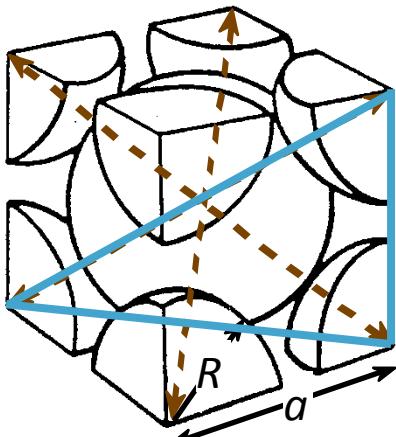
a= unit cell length

r= atoms radii

Example: Atomic packing factor (APF) for BCC

volume of atoms in unit cell

$$\text{APF} = \frac{\text{volume of atoms in unit cell}}{\text{volume of unit cell}}$$



$$4r = \sqrt{3}a \rightarrow r = \sqrt{3}a/4$$

atoms / unit cell

Volume of each atom

$$2 \quad (4/3)\pi(r)^3$$

$$\text{APF} = \frac{2 \quad (4/3)\pi(r)^3}{a^3}$$

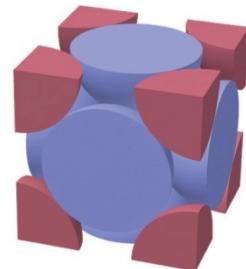
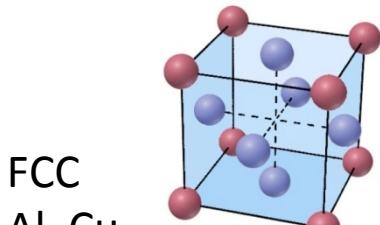
$$a^3$$

volume / unit cell

$$\text{APF} = 0.68$$

Summary

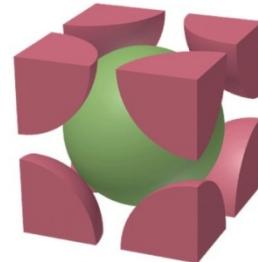
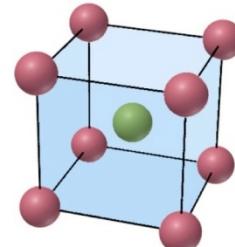
Face centered cubic (fcc)



r = radius of atom

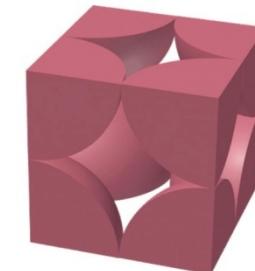
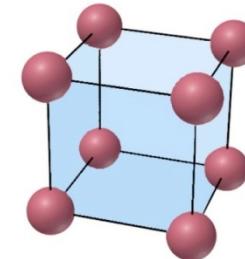
Body centered cubic (bcc)

BCC
Cr, Fe,
Mo

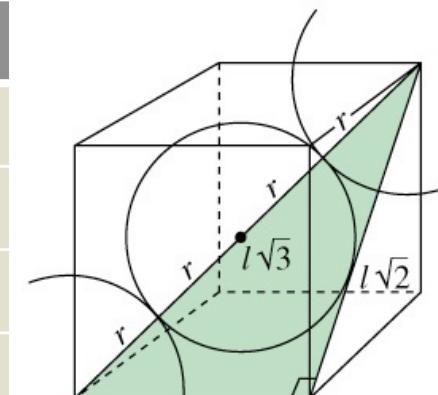


a = length of unit cell

Simple Cubic



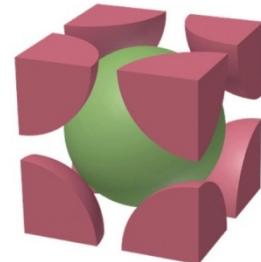
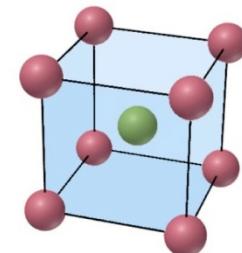
	<i>FCC</i>	<i>BCC</i>	<i>SC</i>
<i># of atoms in cell</i>	4	2	1
<i>Coordination #</i>	12	8	6
<i>Filling Fraction</i>	74 %	68%	52%
<i>Relation</i>	$\sqrt{2}a = 4r$	$\sqrt{3}a = 4r$	$a = 2r$



Calculating *theoretical density of metals*

Example: Calculate the density of iron, which has a body-centered cubic unit cell with an edge length of 286.6 pm. The molar mass of iron is 55.85 g/mol.

Measured (literature) value for iron density:
 7.874 g/cm^3



Calculating theoretical density of metals

Strategy:

A Determine the number of iron atoms per unit cell.

B Calculate the mass of iron atoms in the unit cell from the molar mass and Avogadro's number. Then divide the mass by the volume of the cell.

Solution:

A We know from Example 1 that each unit cell of metallic iron contains two Fe atoms.

B The molar mass of iron is 55.85 g/mol. Because density is mass per unit volume, we need to calculate the mass of the iron atoms in the unit cell from the molar mass and Avogadro's number and then divide the mass by the volume of the cell (making sure to use suitable units to get density in g/cm^3):

$$\text{mass of Fe} = (2 \cancel{\text{atoms Fe}}) \left(\frac{1 \text{ mol}}{6.022 \times 10^{23} \cancel{\text{atoms}}} \right) \left(\frac{55.85 \text{ g}}{1 \text{ mol}} \right) = 1.855 \times 10^{-22} \text{ g}$$

$$\text{volume} = \left[(286.6 \cancel{\text{pm}}) \left(\frac{10^{-12} \cancel{\text{m}}}{1 \cancel{\text{pm}}} \right) \left(\frac{10^2 \text{ cm}}{1 \cancel{\text{m}}} \right) \right]^3 = 2.354 \times 10^{-23} \text{ cm}^3$$

$$\text{density} = \frac{1.855 \times 10^{-22} \text{ g}}{2.354 \times 10^{-23} \text{ cm}^3} = 7.880 \text{ g/cm}^3$$

This result compares well with the tabulated experimental value of 7.874 g/cm^3 .

Theoretical density formula

$$\rho = \frac{nA}{V_C N_A}$$

Diagram illustrating the theoretical density formula:

- #atoms / unit cell (pink box) points to n .
- atomic mass (g / mol) (light green box) points to A .
- volume / unit cell (cm^3 / unit cell) (grey box) points to V_C .
- Avogadro's number 6.02×10^{23} atoms / mol (light blue box) points to N_A .

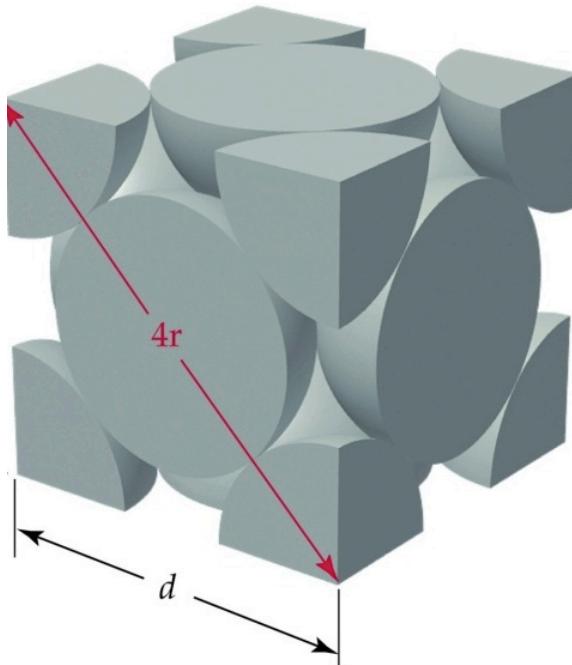
Characteristics of selected elements at 20°C

Element	Symbol	At. Weight (amu)	Density (g/cm ³)	Crystal Structure	Atomic radius (nm)
Aluminum	Al	26.98	2.71	FCC	0.143
Argon	Ar	39.95	-----	-----	-----
Barium	Ba	137.33	3.5	BCC	0.217
Beryllium	Be	9.012	1.85	HCP	0.114
Boron	B	10.81	2.34	Rhomb	-----
Bromine	Br	79.90	-----	-----	-----
Cadmium	Cd	112.41	8.65	HCP	0.149
Calcium	Ca	40.08	1.55	FCC	0.197
Carbon	C	12.011	2.25	Hex	0.071
Cesium	Cs	132.91	1.87	BCC	0.265
Chlorine	Cl	35.45	-----	-----	-----
Chromium	Cr	52.00	7.19	BCC	0.125
Cobalt	Co	58.93	8.9	HCP	0.125
Copper	Cu	63.55	8.94	FCC	0.128
Flourine	F	19.00	-----	-----	-----
Gallium	Ga	69.72	5.90	Ortho.	0.122
Germanium	Ge	72.59	5.32	Dia. cubic	0.122
Gold	Au	196.97	19.32	FCC	0.144
Helium	He	4.003	-----	-----	-----
Hydrogen	H	1.008	-----	-----	-----

Example

Nickel crystallizes in a fcc lattice. Its density is 8.90 g/cm³. What is the atomic radius of nickel in pm?

$$1 \text{ m} = 10^{12} \text{ pm}$$
$$1 \text{ cm} = 10^{10} \text{ pm}$$



Example - Solution

FCC : number of atoms per unit cell = 4

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

$$\rho = \frac{\text{mass of atoms per unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{4 \text{ atoms} \times 58.69 \text{ g/mol}}{V_{\text{cell}} \left(6.023 \times 10^{23} \right) \frac{\text{atom}}{\text{mol}}}$$

mass of atoms
per unit cell
= 8.9

$$V_c = \frac{4 \times 58.69}{6.023 \times 10^{23} \times 8.9} = 4.379 \times 10^{-23} \text{ cm}^3$$

$$V_c = a^3 \rightarrow a = 3.52 \times 10^{-8} \text{ cm}$$

$1 \text{ cm} = 10^{10} \text{ pm}$

$$\left. \begin{array}{l} \\ \end{array} \right\} \rightarrow a = 352 \text{ pm}$$

$$\sqrt{2}a = 4r \rightarrow r = \frac{\sqrt{2}(352)}{4} = 124 \text{ pm}$$