Announcements

- Tutorials
  - Group A (Prof. Chromik)
  - Group B (Mr. Arya Fatehi)
  - Group C (Mr. Andreas Klinter)
- Office hours (Wong 2100)
  - Tuesdays 1:30 – 3:00 PM or by appt.
  - Open door policy
- WebCT quiz to appear by tomorrow AM, due Friday by 5 PM.
- Additional Ch. 3 problems to be assigned via WebCT (check tomorrow or Friday)

What will the quiz be on?

Lecture (DD/MM/YY)	Lecture Topic	Readings	Assignments
03-01-07	Course description, Atoms, Periodic Table, Electronic Structure	1.1-1.6, 2.1-2.4	
08-01-07	Bonding and Crystal Structure	2.5-2.8, 3.1-3.7	
10-01-07	Crystal Structure and Defects	3.8-3.17, 4.1-4.11	WebCT Quiz Due 12-01-07
15-01-07	Diffusion	5.1-5.6	
17-01-07	Materials Fabrication and Microstructure	11.3-11.6	Tutorial Quizzes
22-01-07	Phase Diagrams and Microstructure I	9.1-9.19	
24-01-07	Phase Diagrams and Microstructure II	9.1-9.19	WebCT Quiz Due 26-01-07

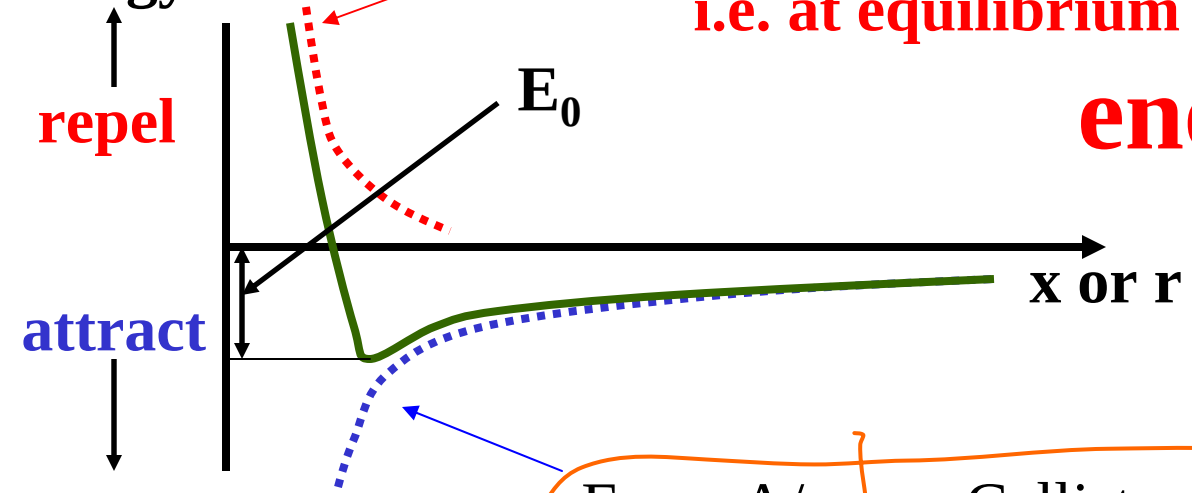
Bonding SUMMARY (from last time)

- Types of bonding
  - ‘Strong’ bonds: covalent, ionic and metallic
  - ‘Weak’ bonds: van der Waals and dipole (hydrogen)
- Which bond type depends on what is bonding (e.g. groups of atoms find most stable electron configuration)

WHY?

Minimisation of energy!

BONDING AND ENERGY



$E_R = B/r^n$ Callister 2.9

i.e. at equilibrium atomic separation

energy lowest

+1 +1

Z_1 Z_2

Na^+ Cl^-

$E_A = -A/r$ Callister 2.8

This graph can be used to conceptualize any type of bond.

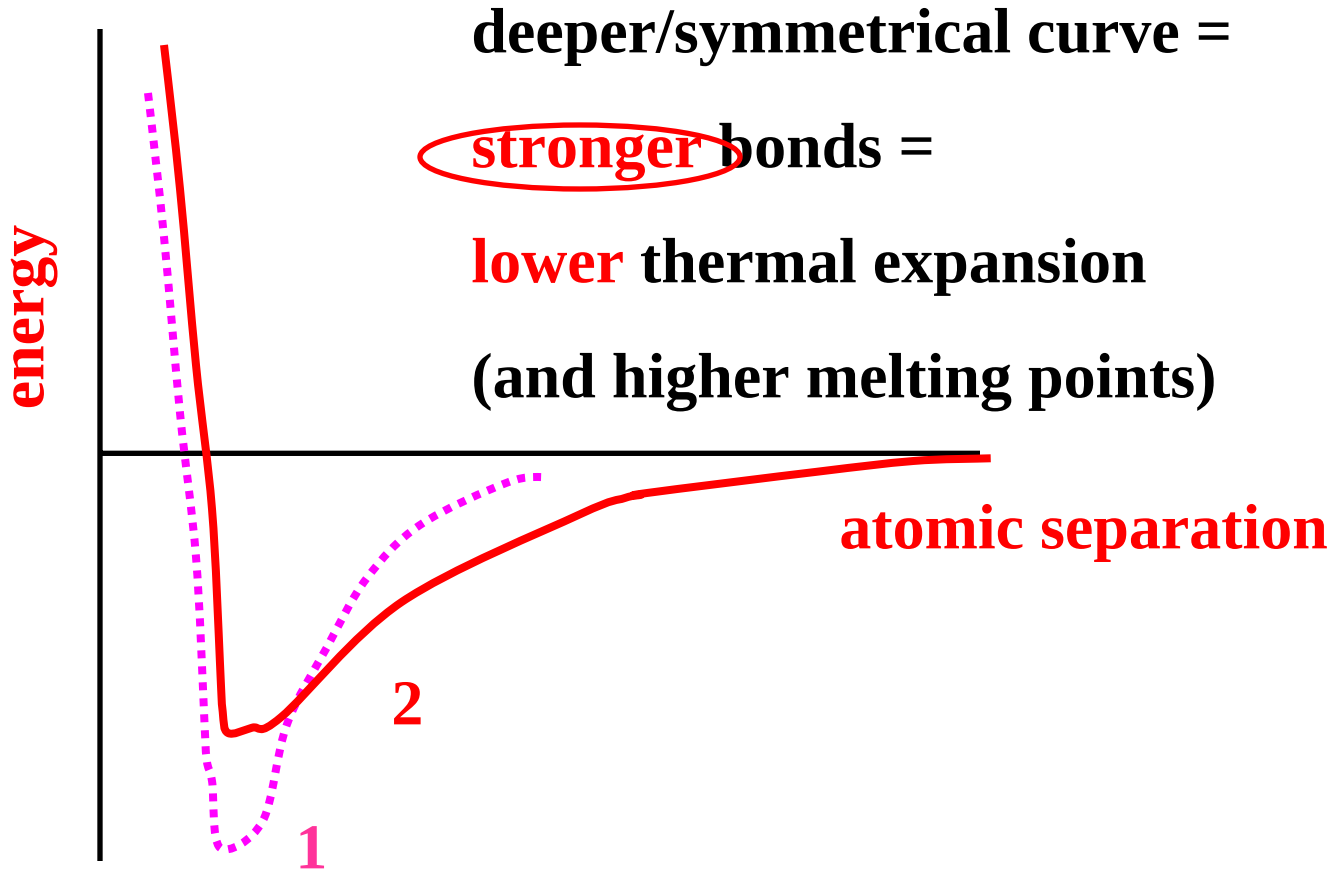
However, the functional form of E_A and E_R would differ based on bond type – changing the shape of this curve.

Homework 2.15

Note: 2.14 being worked out in tutorials

$$E_A(r) = \frac{-|Z_1 Z_2| q^2}{4\pi\varepsilon_0 r}$$

RELATION BETWEEN ATOMIC BONDING AND THERMAL EXPANSION



deeper/symmetrical curve =

stronger bonds =

lower thermal expansion

(and higher melting points)

Material 1 has stronger bonds, less thermal expansion and higher melting point than material 2.

Bond Energies

Bonding Type	Substance	Bonding Energy		Melting Temperature (°C)
		kJ/mol	eV/Atom, Ion, Molecule	
Ionic	NaCl	640	3.3	801
	MgO	1000	5.2	2800
Covalent	Si	450	4.7	1410
	C (diamond)	713	7.4	>3550
Metallic	Hg	68	0.7	−39
	Al	324	3.4	660
	Fe	406	4.2	1538
	W	849	8.8	3410
van der Waals	Ar	7.7	0.08	−189
	Cl_2	31	0.32	−101
Hydrogen	NH_3	35	0.36	−78
	H_2O	51	0.52	0

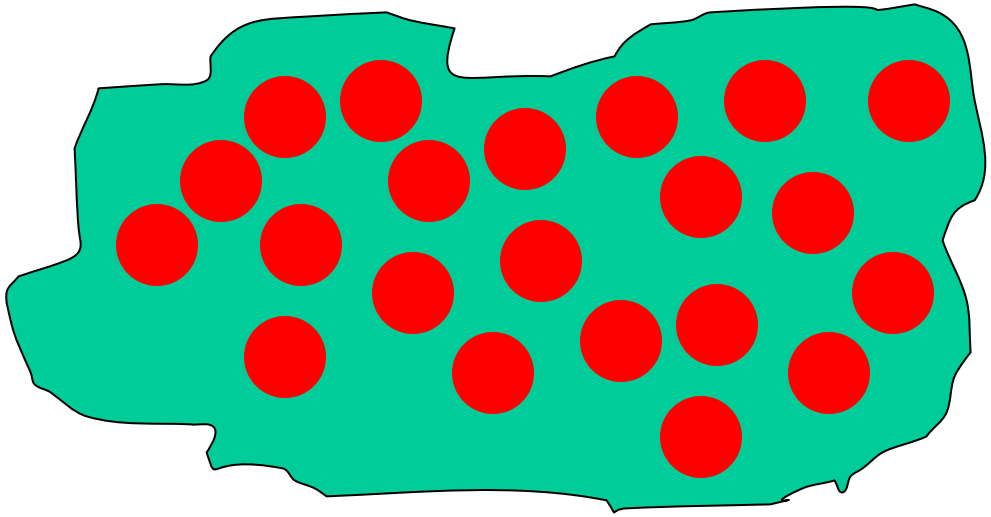
Ionic bonds are generally the strongest. But, as you can see here, the bond energy varies: (1) from type-to-type, (2) within each bond type.

Metallic bonds

All valence electrons freed up to form electron 'cloud'

All atoms share all electrons in cloud ← **Someone asked, "How can this be TRUE?"**

each atom reaches lower energy state



Cloud attracts metal ions (ion 'cores')

Non-directional forces, therefore close packed

Forces can be weak or strong
(melting points vary by 1000s of degrees)

The metallic bond

- Consider sodium, Na ($1s^2 2s^2 2p^6 3s^1$)
  - Ionic bond? $(Na^+)_7 \, Na^{7-}$
  - Covalent bond? Two Na share their $3s^1$ electrons.
  - Start adding more Na and continue sharing…
    - Eventually, the electrons 'delocalize' and are shared *(unequally)* with all of the Na ions

Insulator → metal transition

or sometimes

Insulator → metal catastrophe!

Jones, Ch. 1

One way to consider why this happens

- Polarizability
  - Many insulators may be polarized in an electric field. This creates tiny dipole moments that enhance the total field.
  - In a metal, the first step is "polarization", but the valence electrons are weakly bound. They escape into the 'electron cloud.'
- Metal vs. Insulator
  - Dependence on polarizability has been epitomized by the ratio of

$$\frac{\mathbf{R}}{\mathbf{V}}$$

Molar refractivity (optical property that is tied strongly to polarizability)

Molar volume

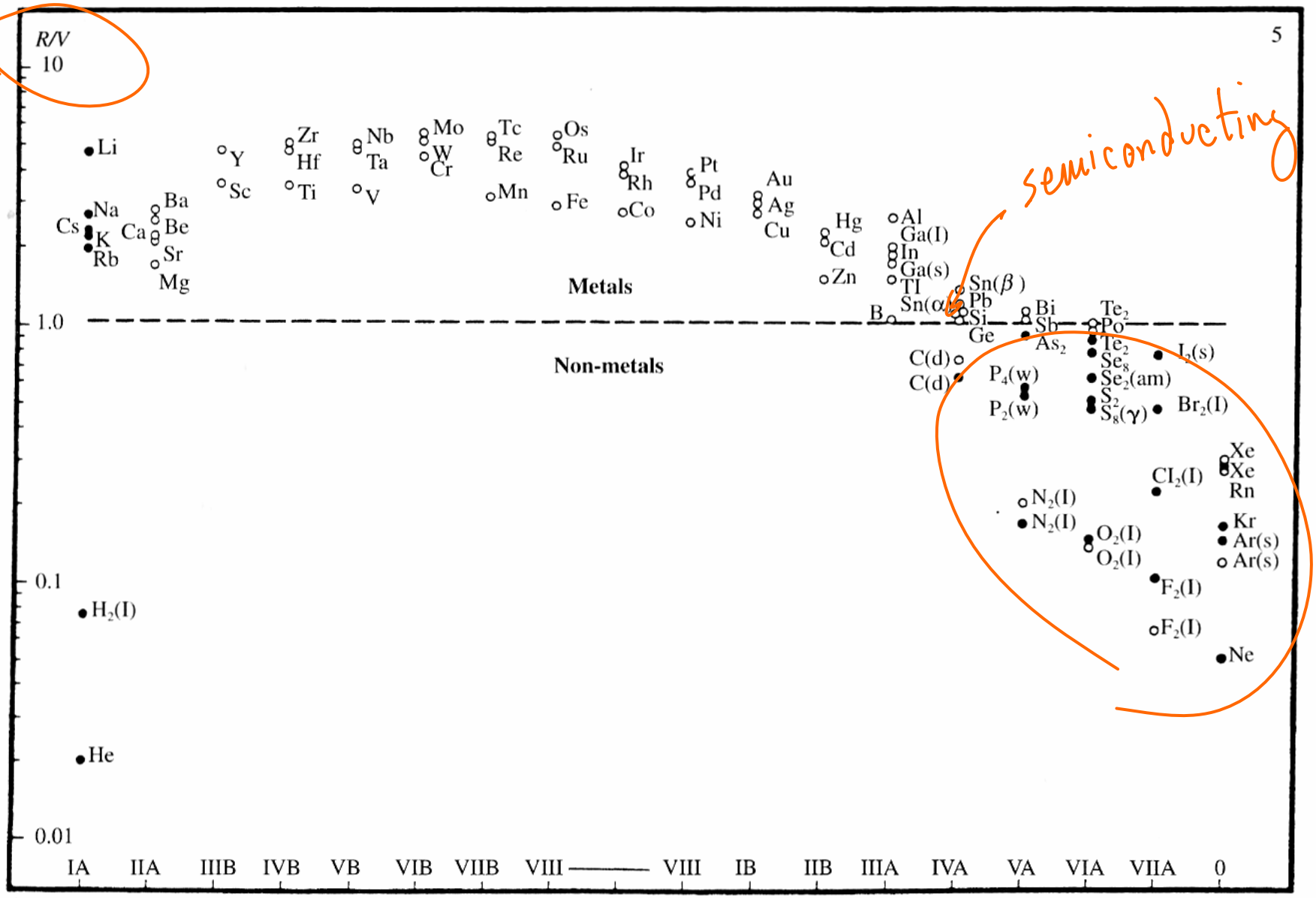


Fig. 1.13 The ratio *R*/*V* (see text) predicts very successfully which elements are metals and which are not. The filled circles are for elements which *R* and *V* are both known. The open circles are for elements for which *R* has had to be calculated. (Taken from P.P. Edwards and M.J. Sienko (1982). *Acc. Chem. Res.* **15**, 87.)

Jones, Ch. 1

This says…

- Everything would be a metal if it were dense enough (i.e. its molar volume were small.)

This predicts…

- The hydrogen at the center of Jupiter is metallic.

Summary

- Yes, there is really an electron cloud (more accurately called a conduction band).
- A metal atom ‘loses’ electrons from the unfilled shells to the conduction band
  - K $1s^2 2s^2 2p^6 3s^2 3p^6$ ($4s^1$) K loses one electron and becomes like Ar
  - Mg $1s^2 2s^2 2p^6$ ($3s^2$) Mg loses two electrons to the conduction band
  - Cu $1s^2 2s^2 2p^6 3s^2 3p^6$ ($3d^{10} 4s^1$)
    - Lose 11 electrons to become like Ar?
    - Lose the $4s^1$ electron?

ANIMATION

- Auburn website listed on WebCT

But now, moving on to crystal structure

ATOMIC PACKING

Fundamental Concepts

-Bonding can lead to very big molecules

-The atoms can be arranged either;

-randomly (amorphous (latin? without form) structure)

short range order

or,

-ordered (crystalline structure)

i.e.repeating or periodic arrangement of atoms

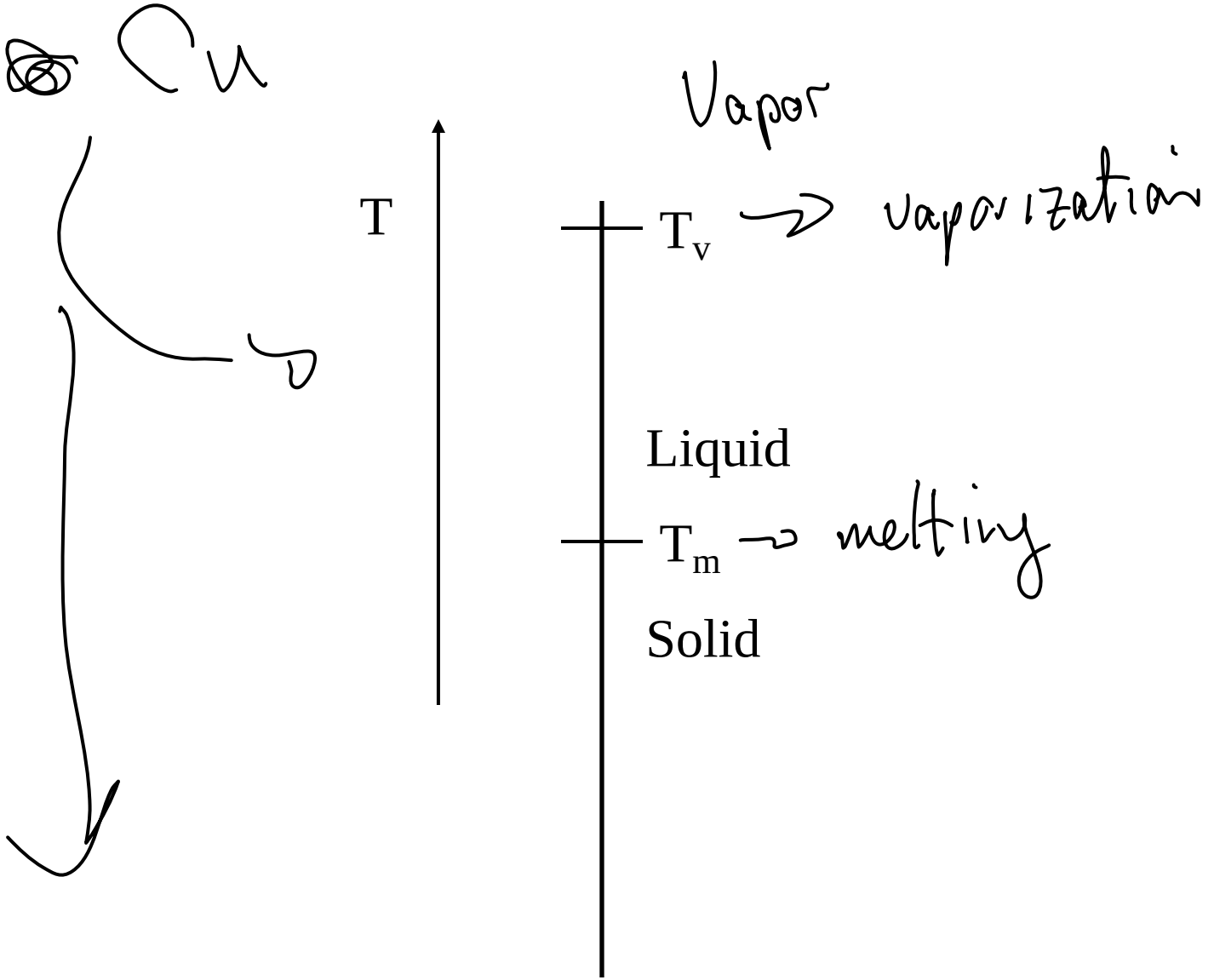
over large distances long range order

Crystal structure?

- Liquid
  - No crystal structure
  - Shape defined by a containing vessel

- Solid
  - Most solids form in organized arrays of atoms
  - Shape defined by the thermal and mechanical history (i.e. how we made it!)

Phase diagram for a pure metal?



An amorphous structure is favoured when

the 'bonding' takes place rapidly

because:

ordering takes more time*

BUT:

Under normal (i.e. industrial) circumstances

'simple' materials are crystalline,*

e.g. all metals or simple compounds (e.g. NaCl)

'Complex' materials (e.g. multi-element compounds) NiZr

are likely to be amorphous,

or a mix of amorphous and crystalline because

there is more constraint on relative positions of atoms

CRYSTAL STRUCTURES

(defines stacking of atoms)

Split the large number of atoms

(the crystal or the lattice)

into small, equal 3D groups of atoms (unit cells)

(parallelopipeds or prisms:

i.e. 3* sets of parallel faces (or planes))

- groups must all have the same 3D pattern

Joining up all the unit cells should form the crystal

-unit cells have the

"highest level of geometric symmetry"

and /or*

the smallest number of atoms

-key to using unit cells is geometry

METALLIC CRYSTAL STRUCTURES

Simplest because of

omni directional bonding;

and single component

therefore no restriction

(geometric or coulombic)

to number and positioning of nearest neighbour atoms.

High number of nearest neighbors = dense packing.

Three common unit cells: FCC HCP BCC

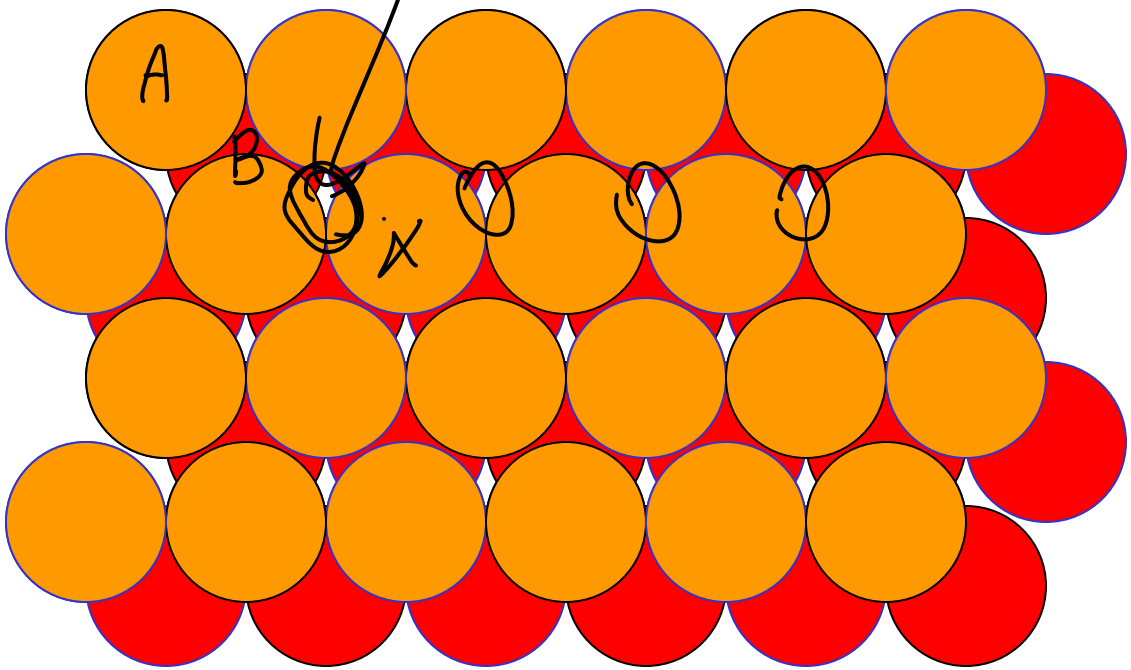
(hard sphere = ion core).

1. Hexagonal Close Packed (HCP)

(e.g. Ti, Zn, Co)

(easiest to understand in terms of close packing)

Next atom of next layer?



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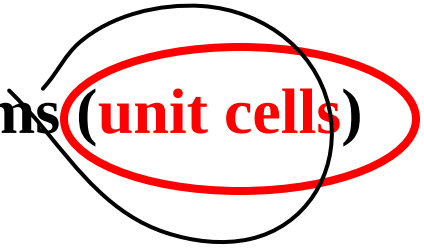

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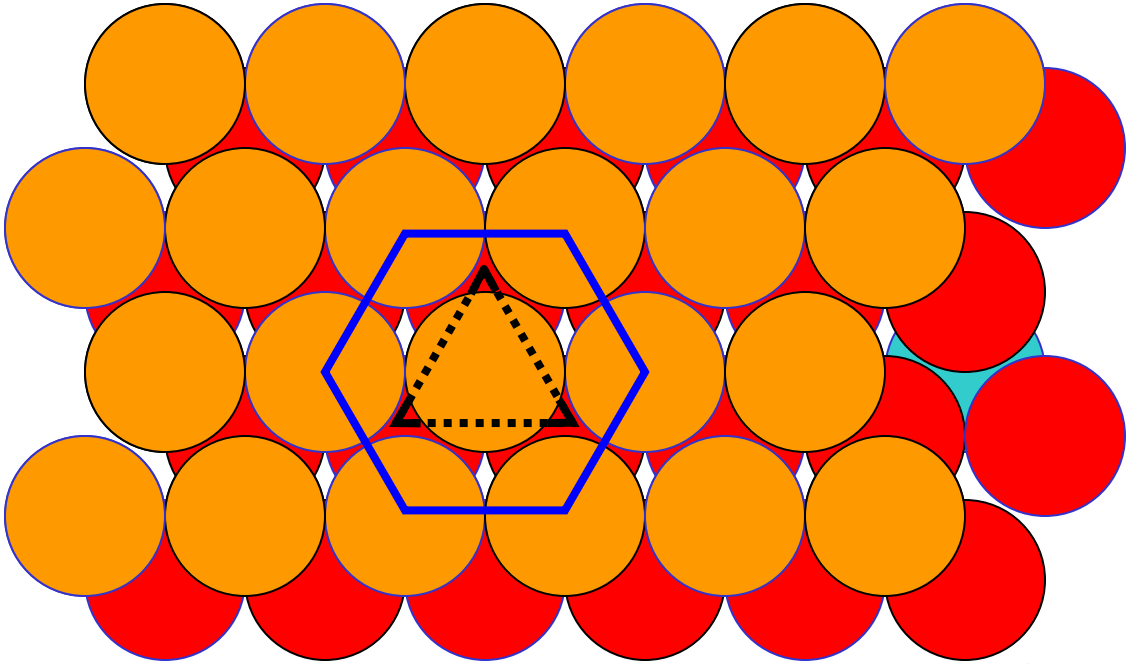
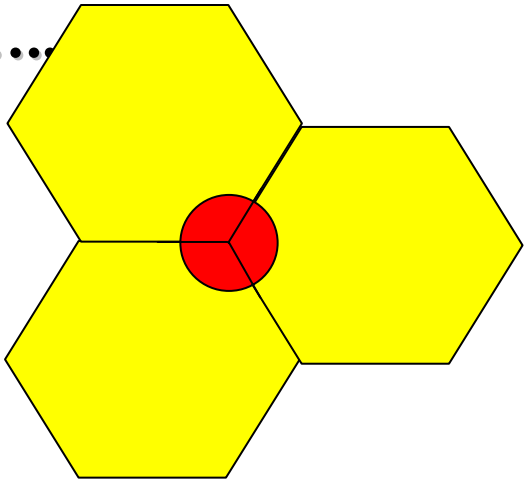


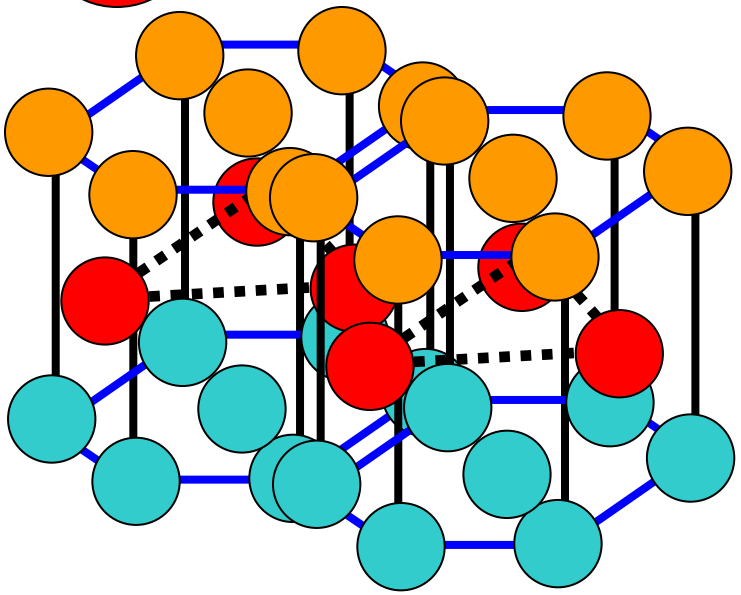
lattice

basis

y where are the atoms

THIS DOESN'T QUITE WORK……..

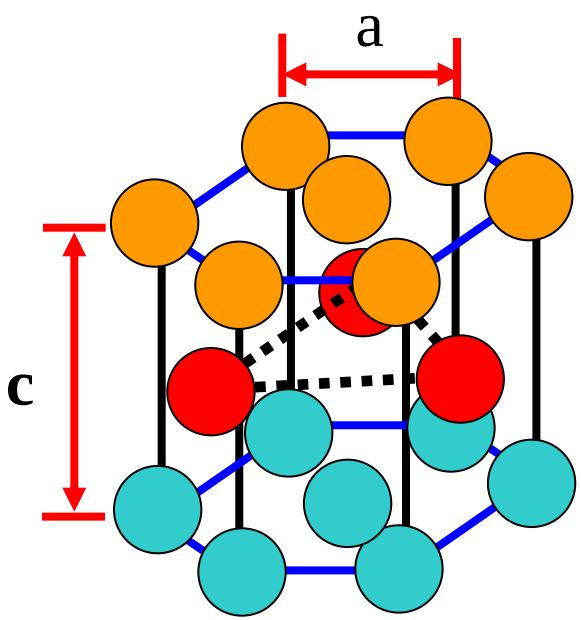




Joining up all the unit cells should form the crystal

Description of hexagonal unit cell

size of unit cell: (lattice parameters)



obtain c and a in terms of R, atom radius

ideal c/a ratio=1.633 but some deviation in real life

Geometry!

Define any shape Define any dimension in terms of R

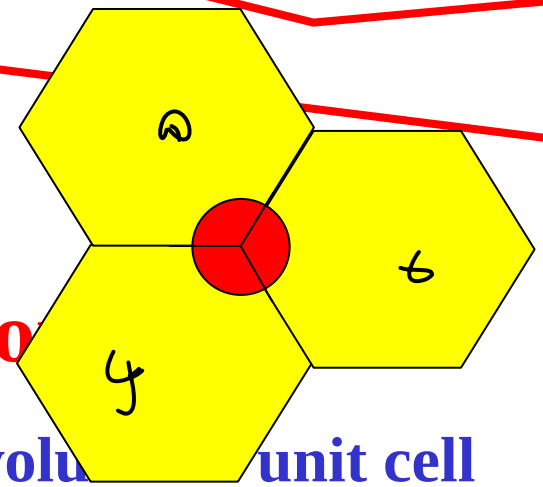
number of atoms per unit cell = 6

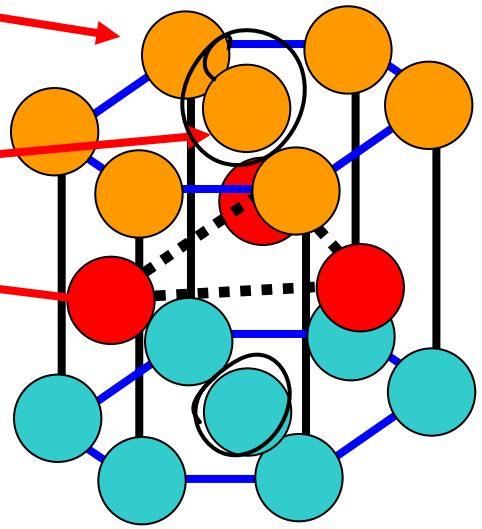
(1/ 6 of each of the 12 ‘corner’ atoms

1/2 of each of the 2 face centered atoms

3 center atoms)

(mathematically?)





atomic packing facto

volume of solid (spheres)/volu unit cell

APF =0.74* (# atoms) volume of 1 sphere

-coordination number

(number of atoms touching or nearest neighbours)

(by inspection of centre atom, above) = 12

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Closest Packing

Equal sized spheres

"Closest Packed"

Hexagonal array:

6 nearest neighbors in the plane

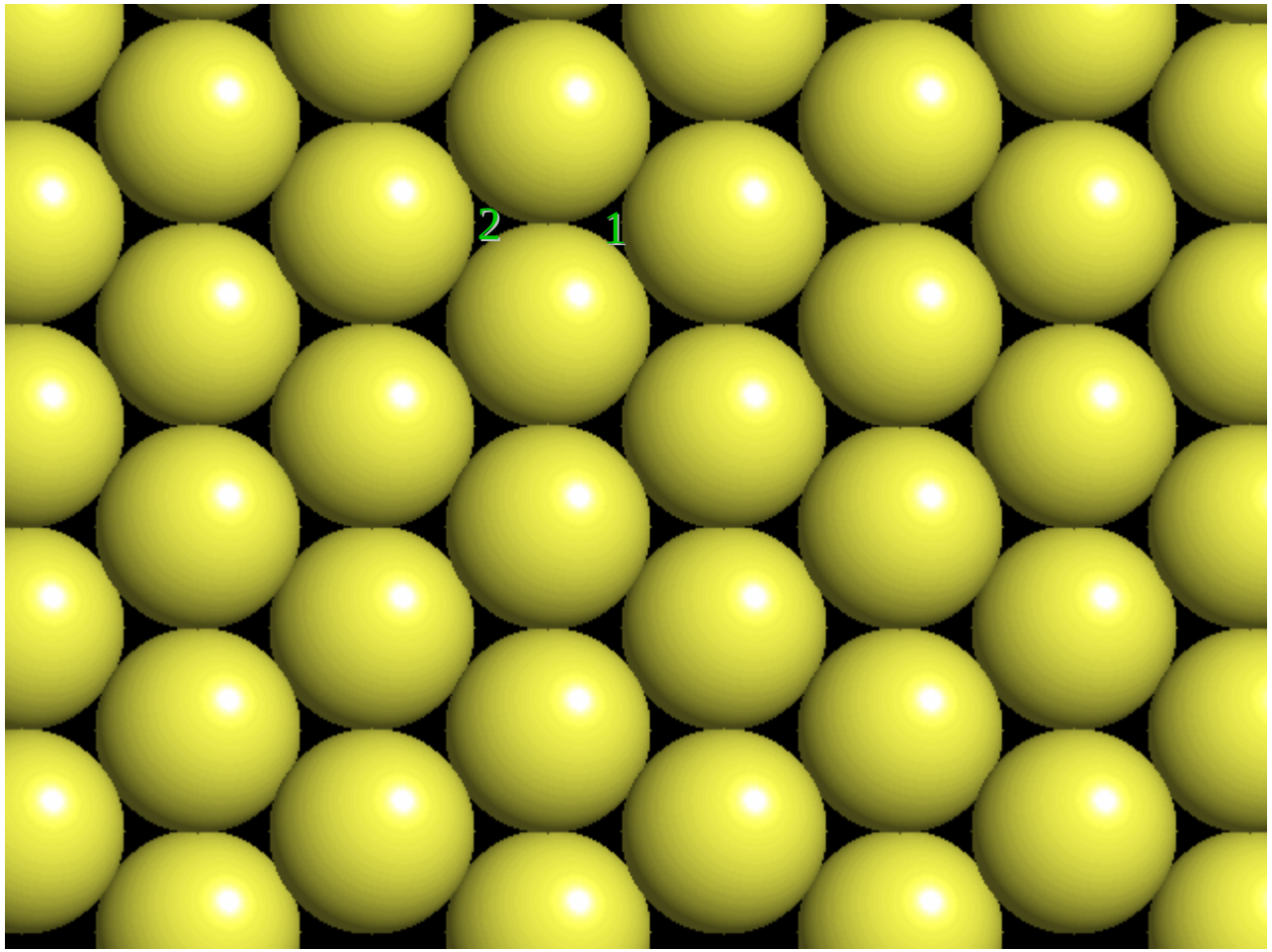
Note dimples in which next layer atoms will settle

Two dimple types:

Type 1 point NE

Type 2 point SW

They are equivalent since you could rotate the whole structure 60° and exchange them



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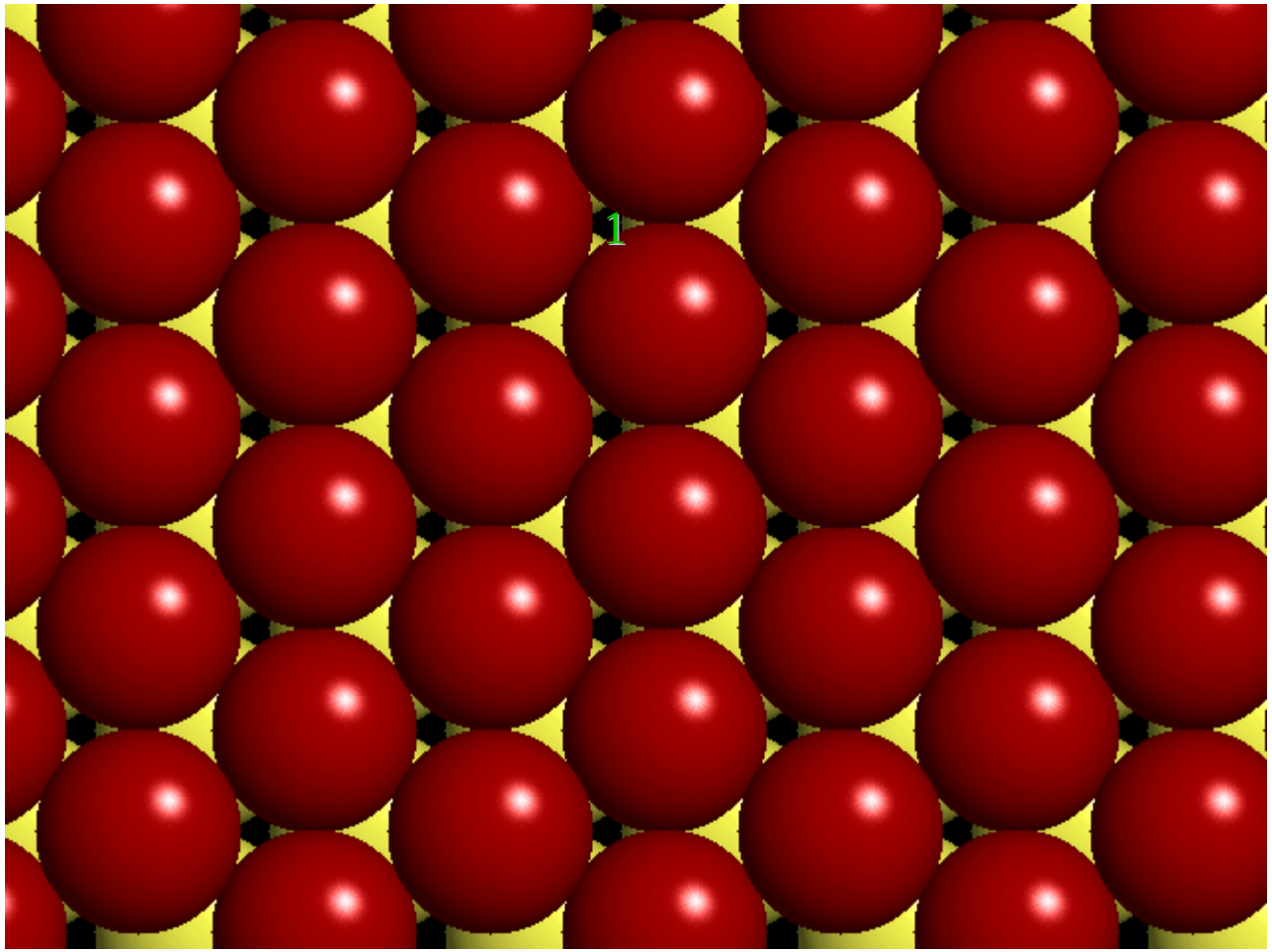
Closest Packing

Add next layer (red)

- Red atoms can only settle in one dimple type
- Both types are identical and red atoms could settle in either
- Once first red atom settles in, can only fill other dimples of that type
- In this case filled all type 2 dimples



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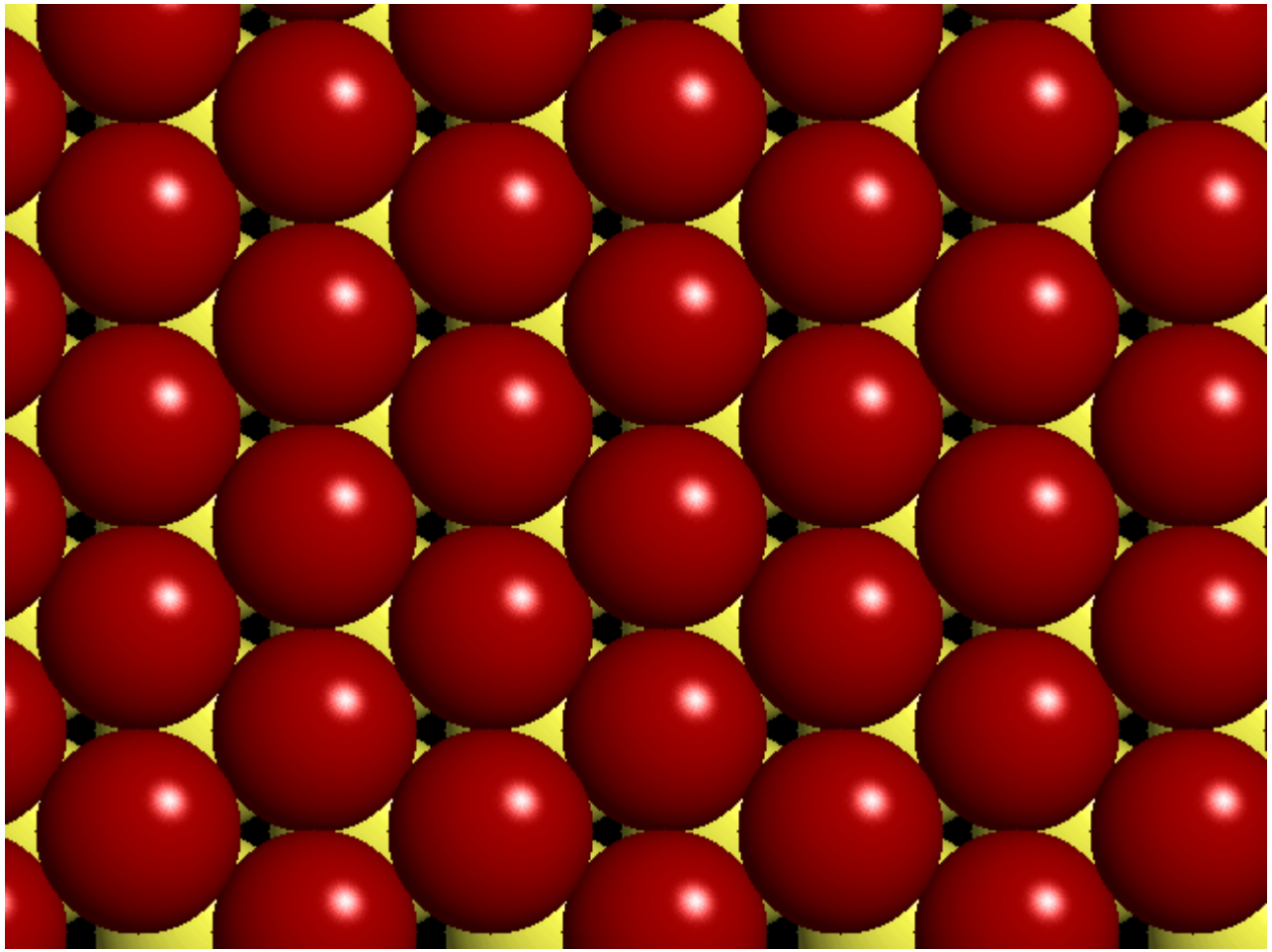
Closest Packing

Third layer ??

- Third layer dimples are now different!
- Call layer 1 A sites
- Layer 2 = B sites (*no matter which choice of dimples is occupied*)
- Layer 3 can now occupy A-type site (directly above yellow atoms) or C-type site (above voids in both A and B layers)



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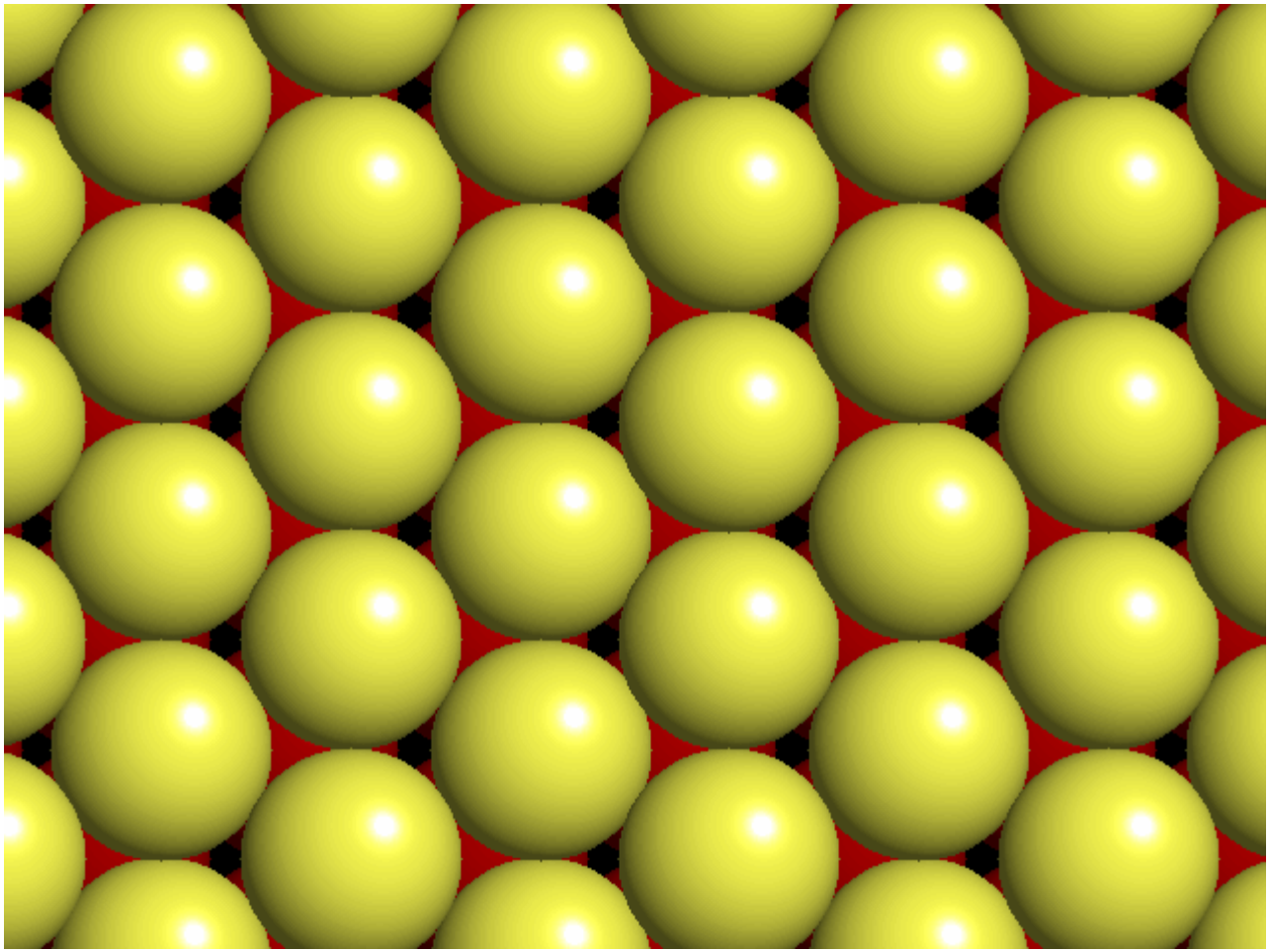
Closest Packing

Third layer:

If occupy A-type site the layer ordering becomes A-B-A-B and creates a hexagonal closest packed structure (HCP)

Coordination number (nearest or touching neighbors) = 12

- 6 coplanar
- 3 above the plane
- 3 below the plane



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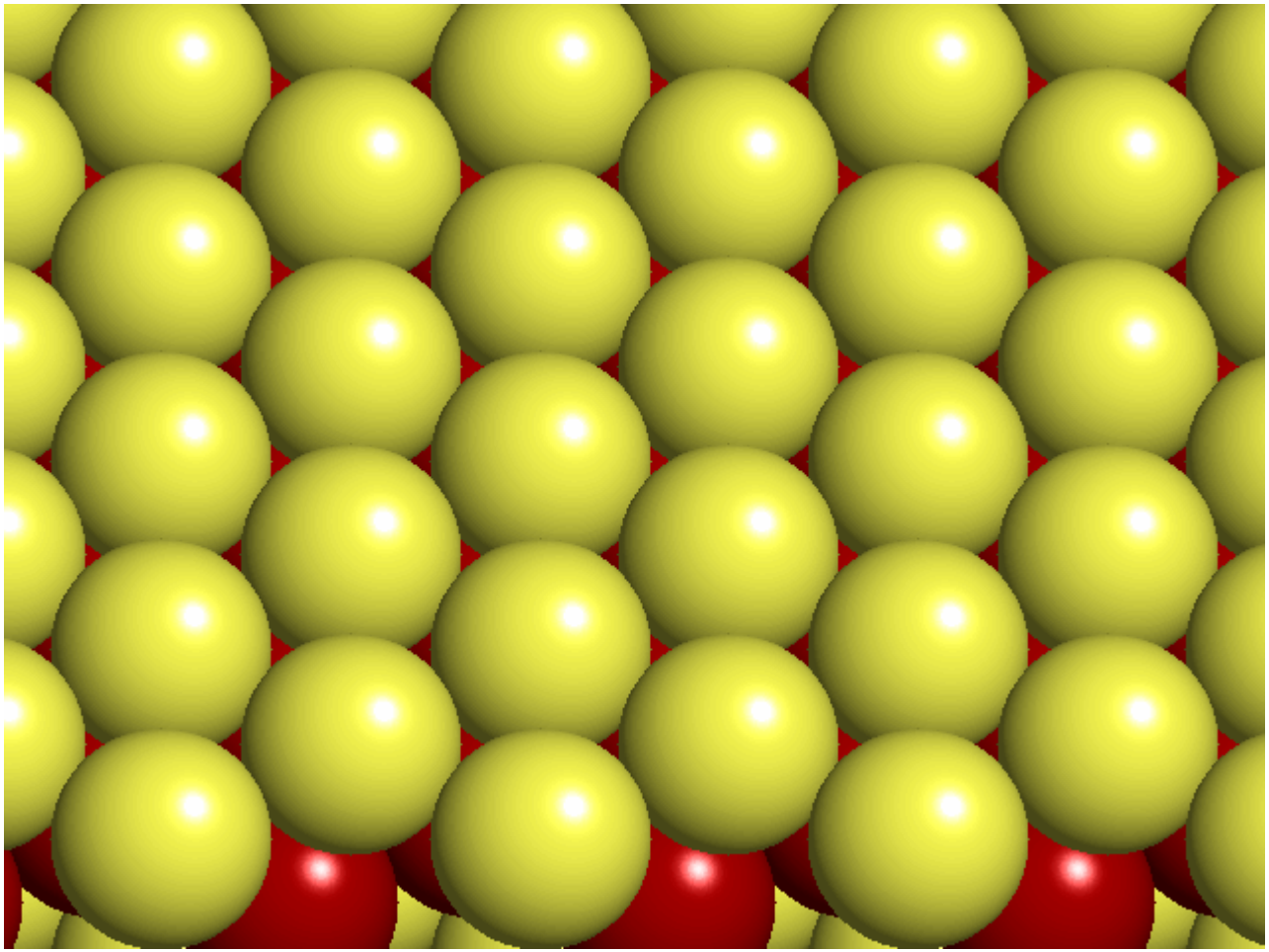

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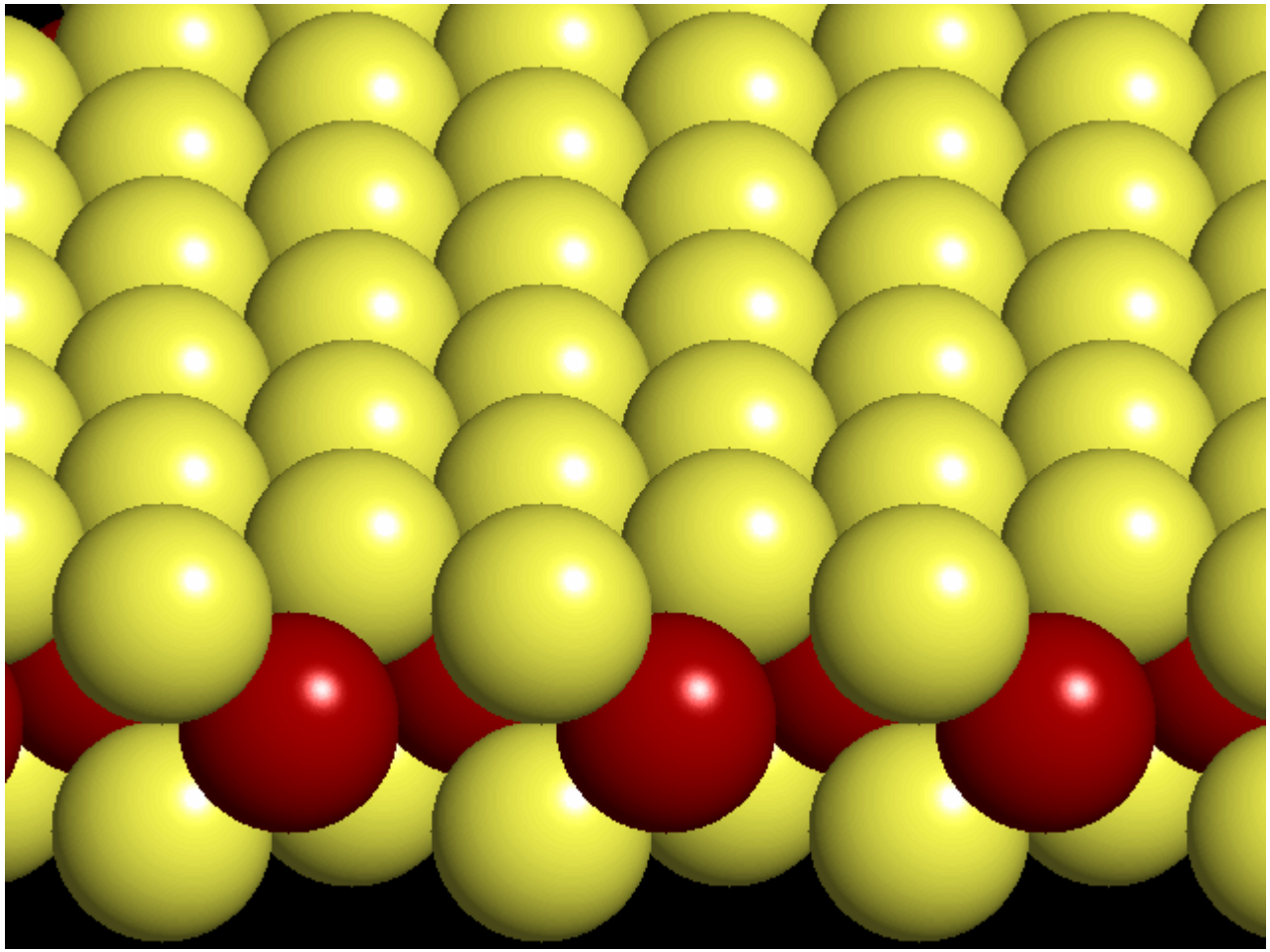

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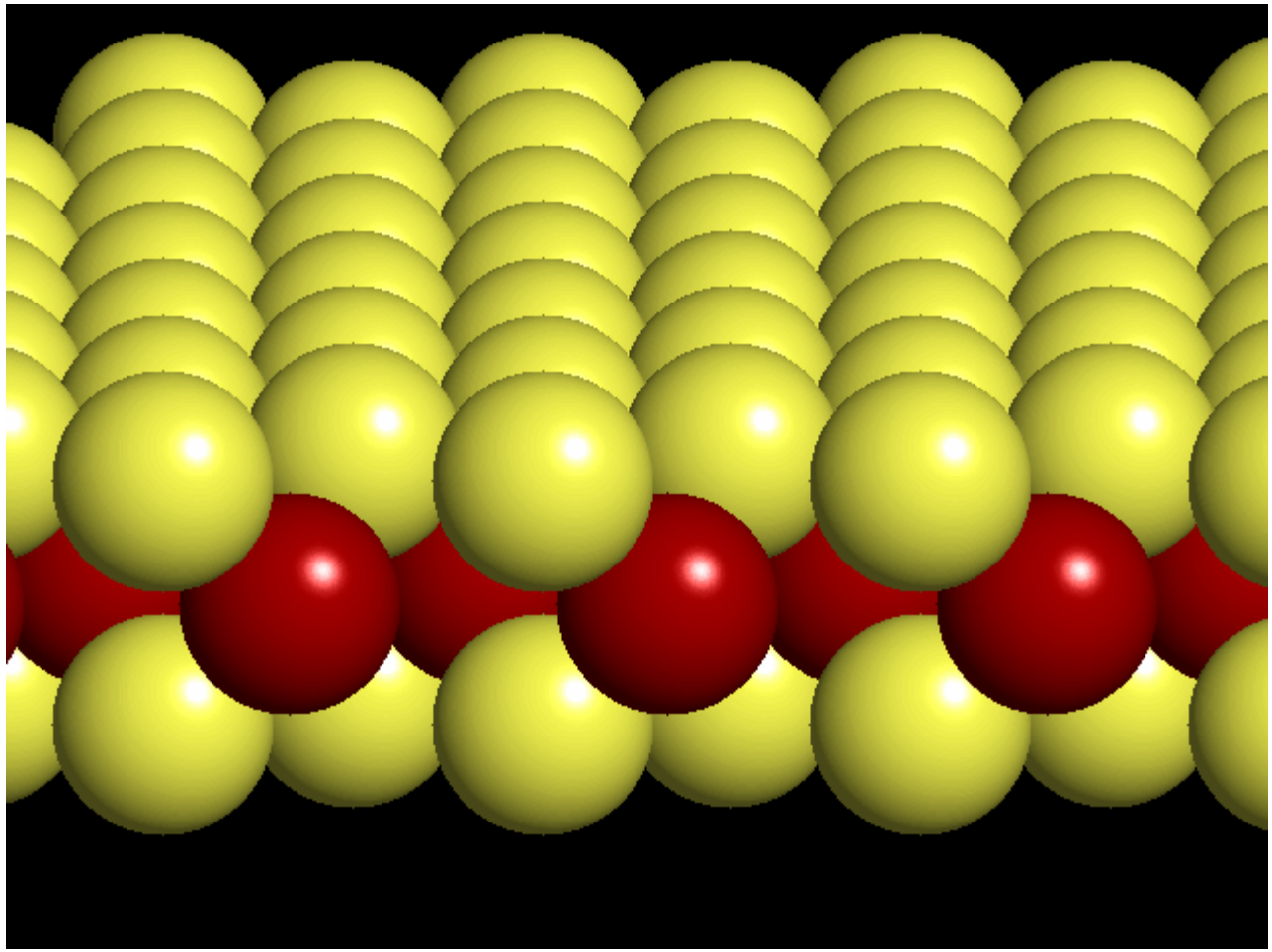

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Closest Packing

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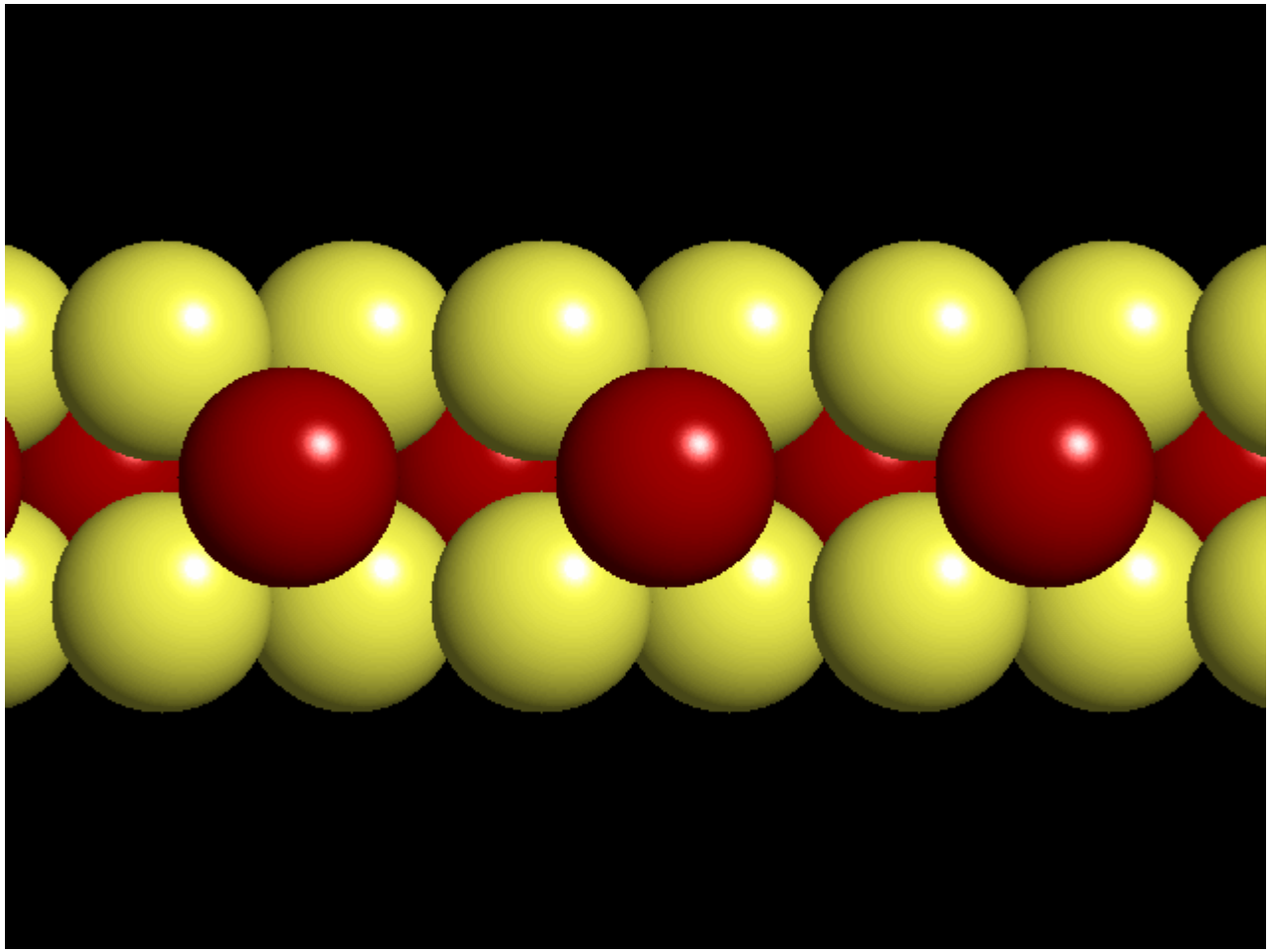
Note top layer atoms are directly above bottom layer atoms



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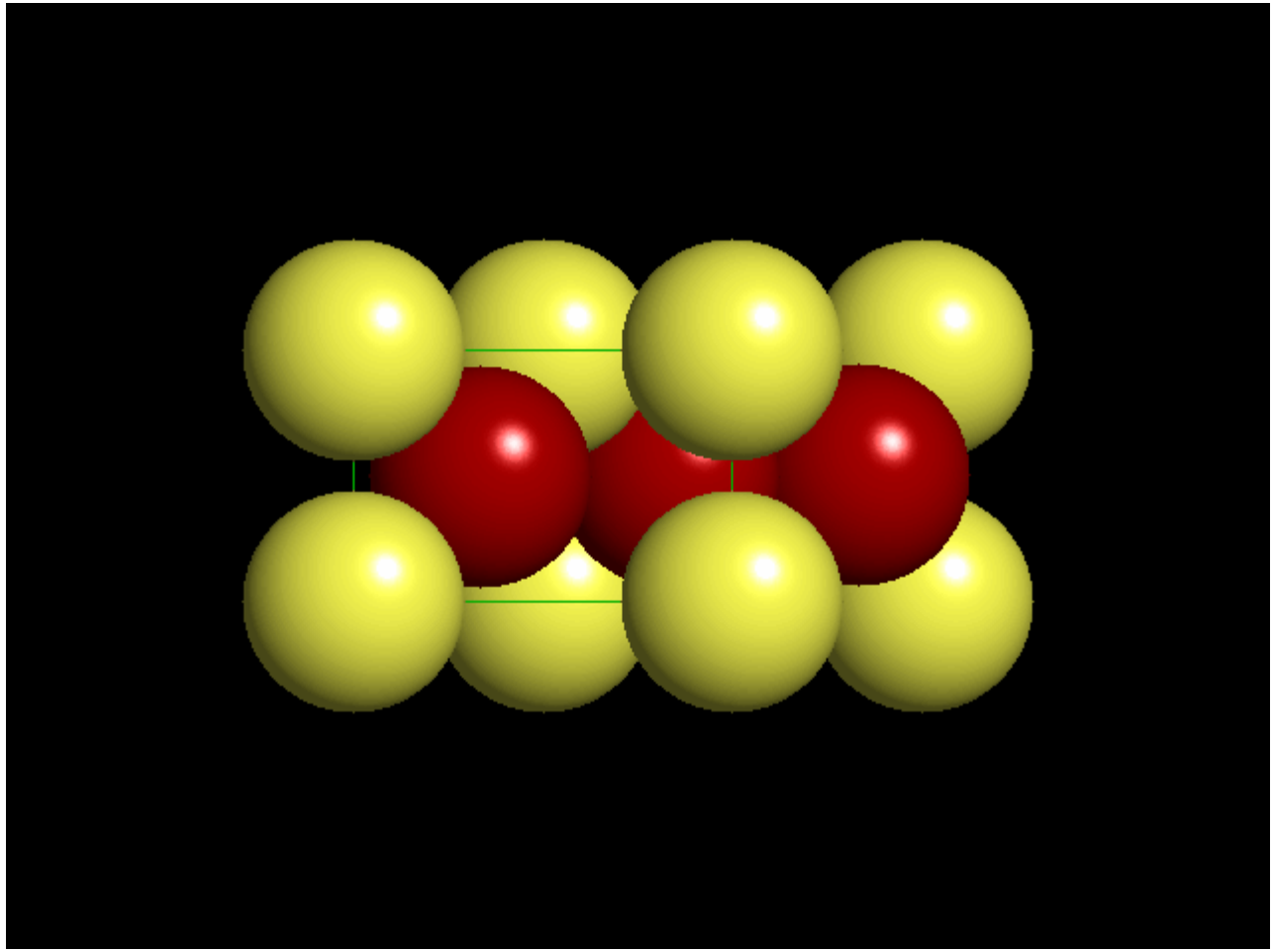
Closest Packing

Third layer:

Unit cell



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Closest Packing

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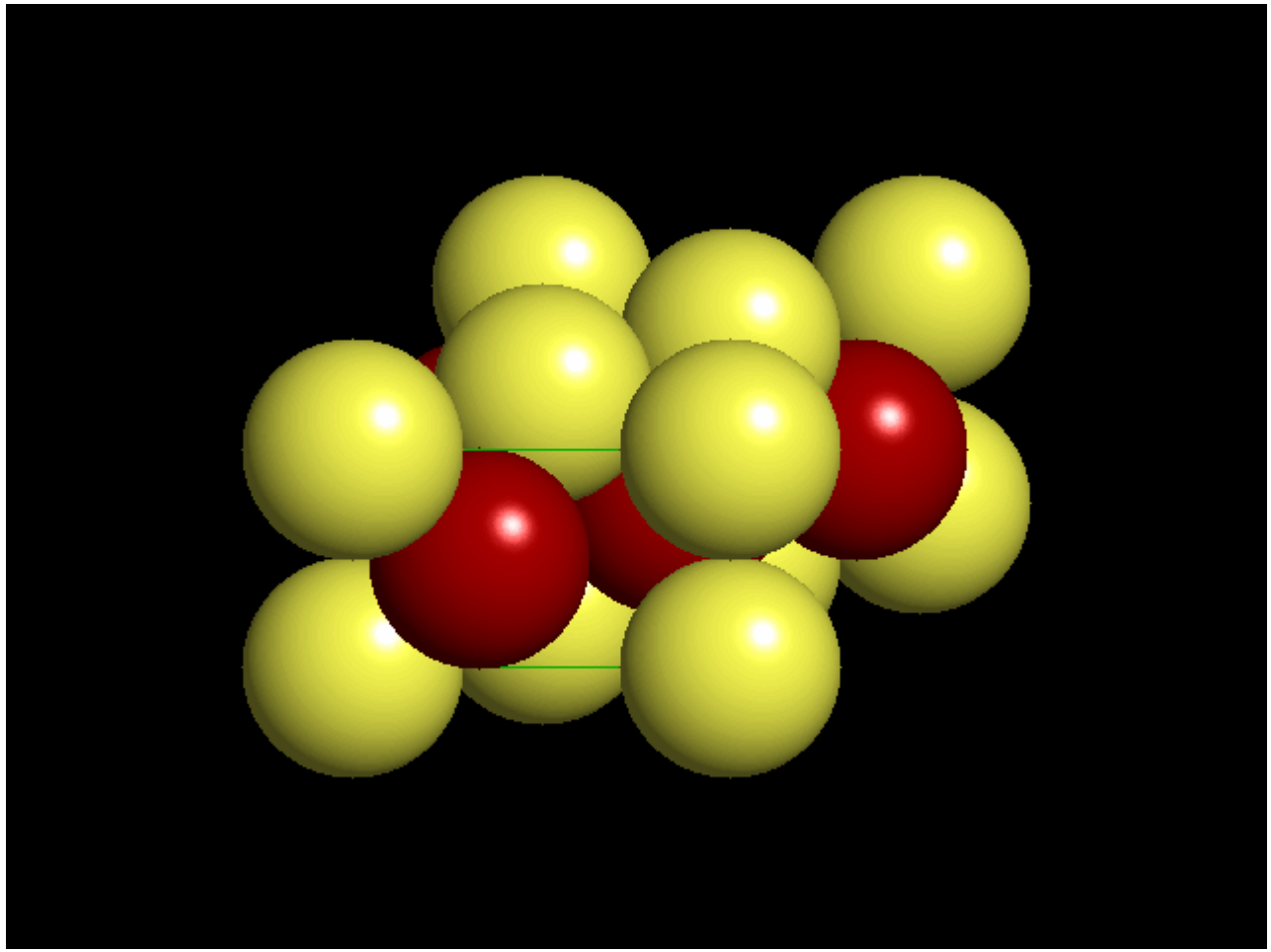
Unit cell



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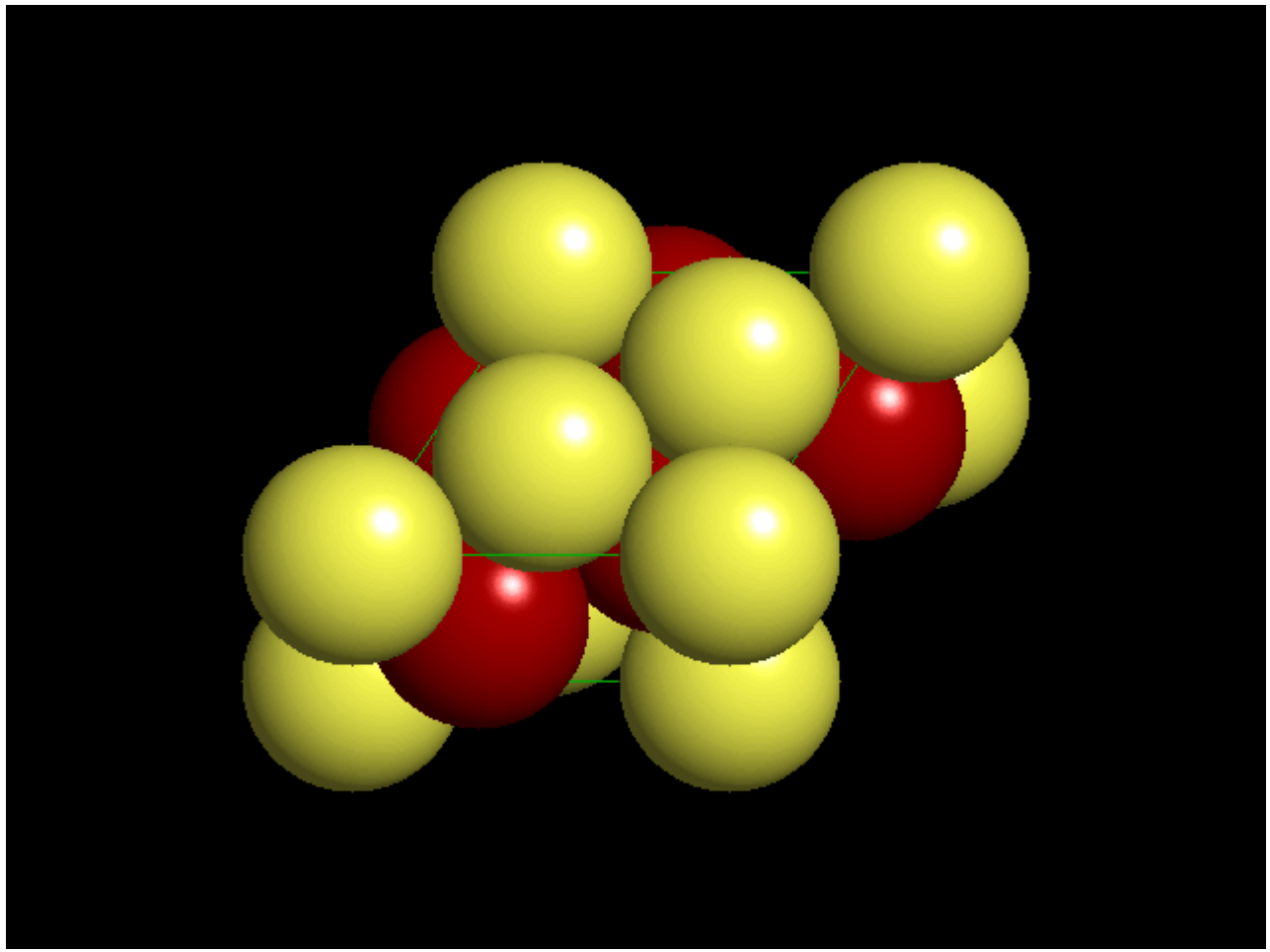
Closest Packing

Third layer:

Unit cell



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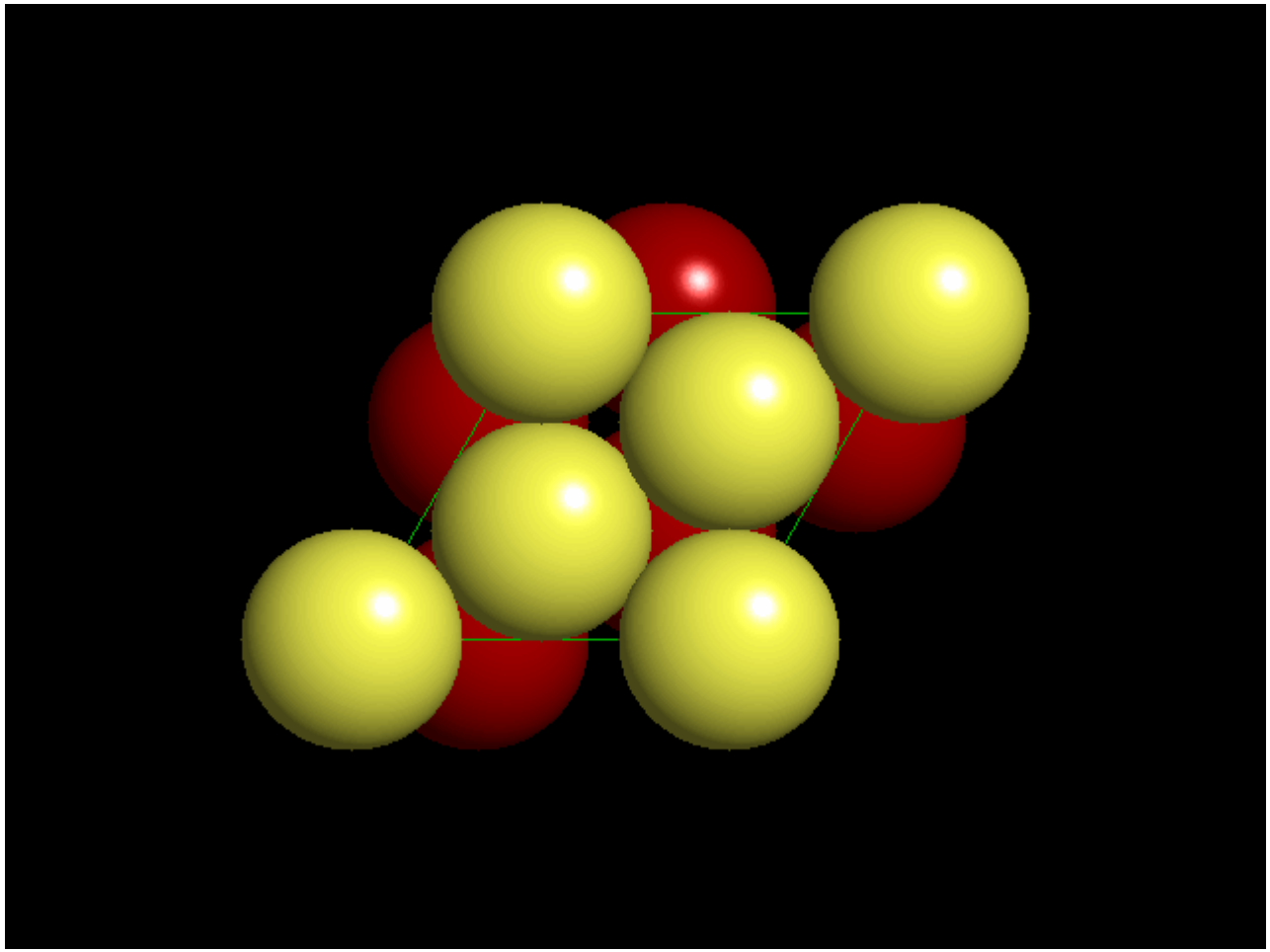
Closest Packing

Third layer:

View from top shows hexagonal unit cell



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Closest Packing

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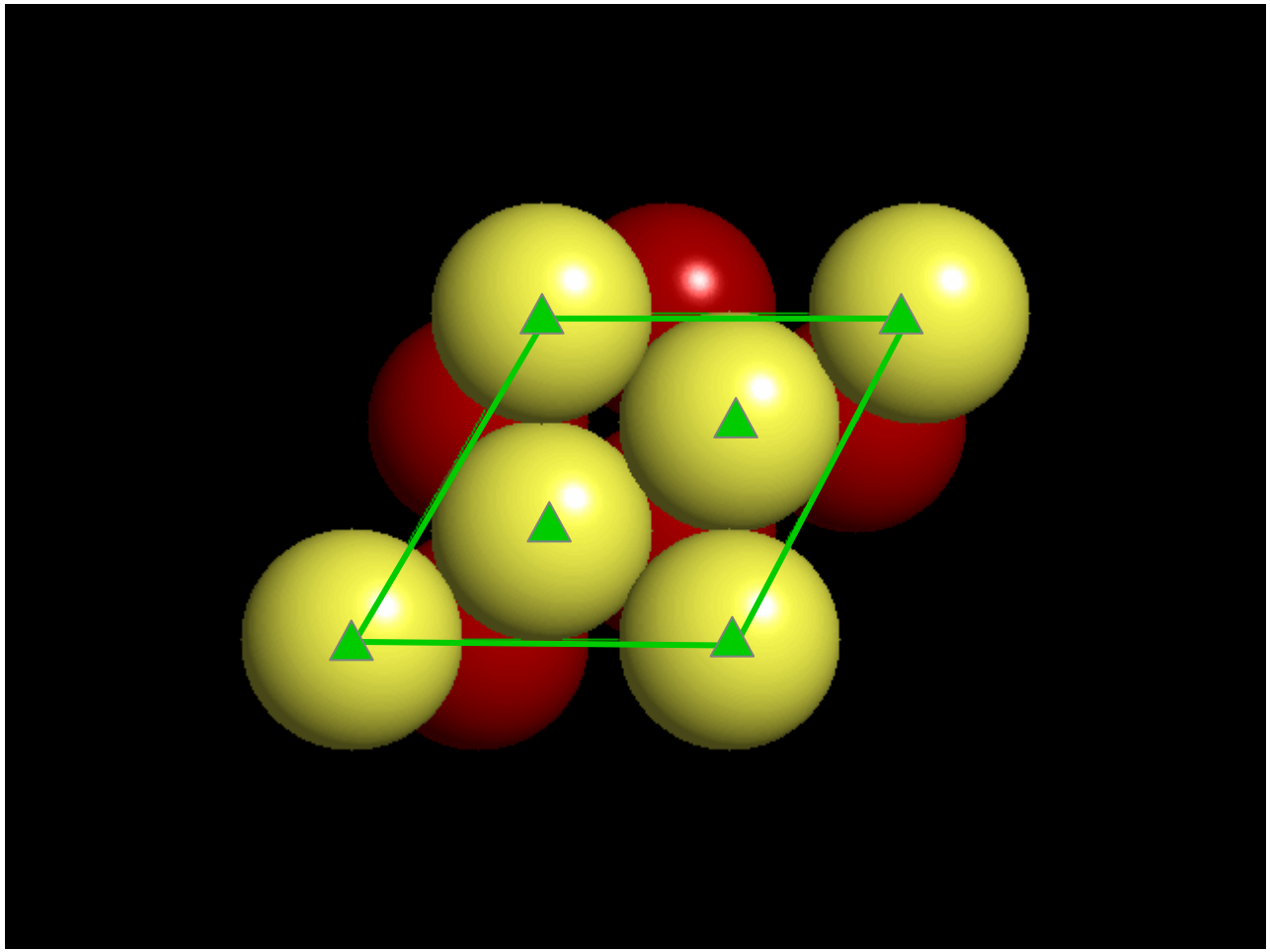
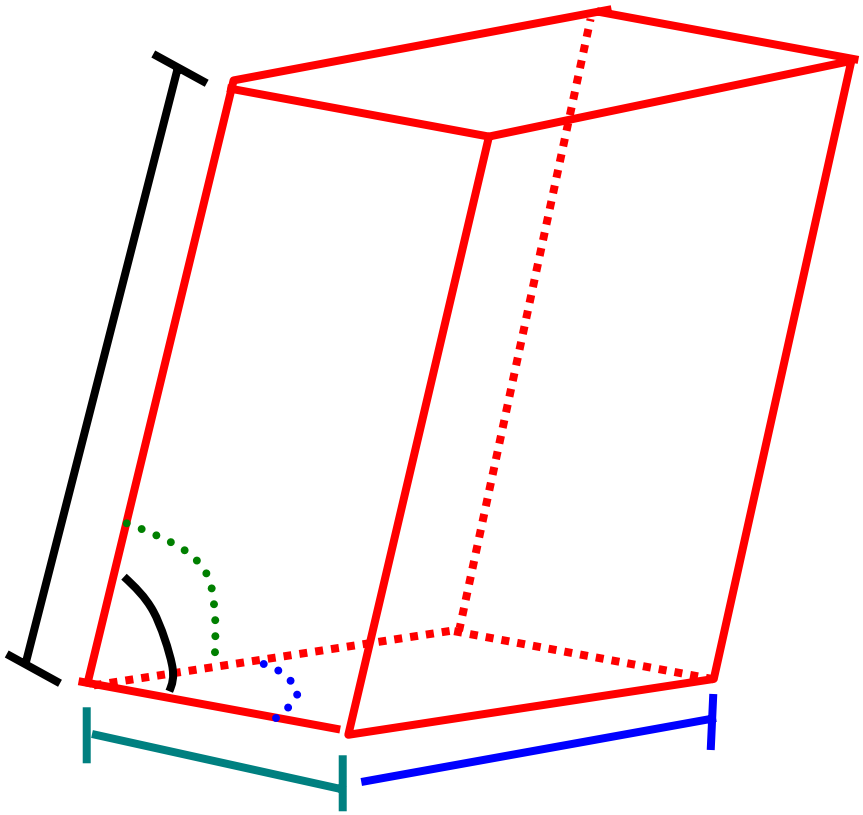
View from top shows hexagonal unit cell



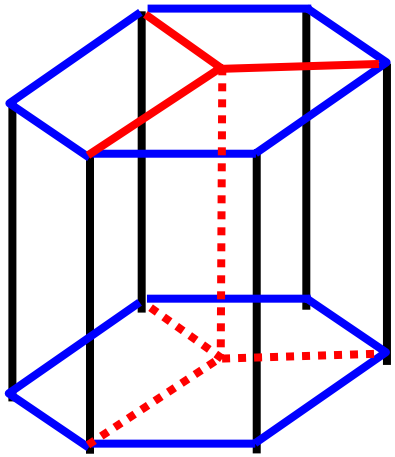
OTHER CRYSTAL SYSTEMS (UNIT CELLS)

are defined by 6 parameters, the three axial lengths

and the three interaxial angles



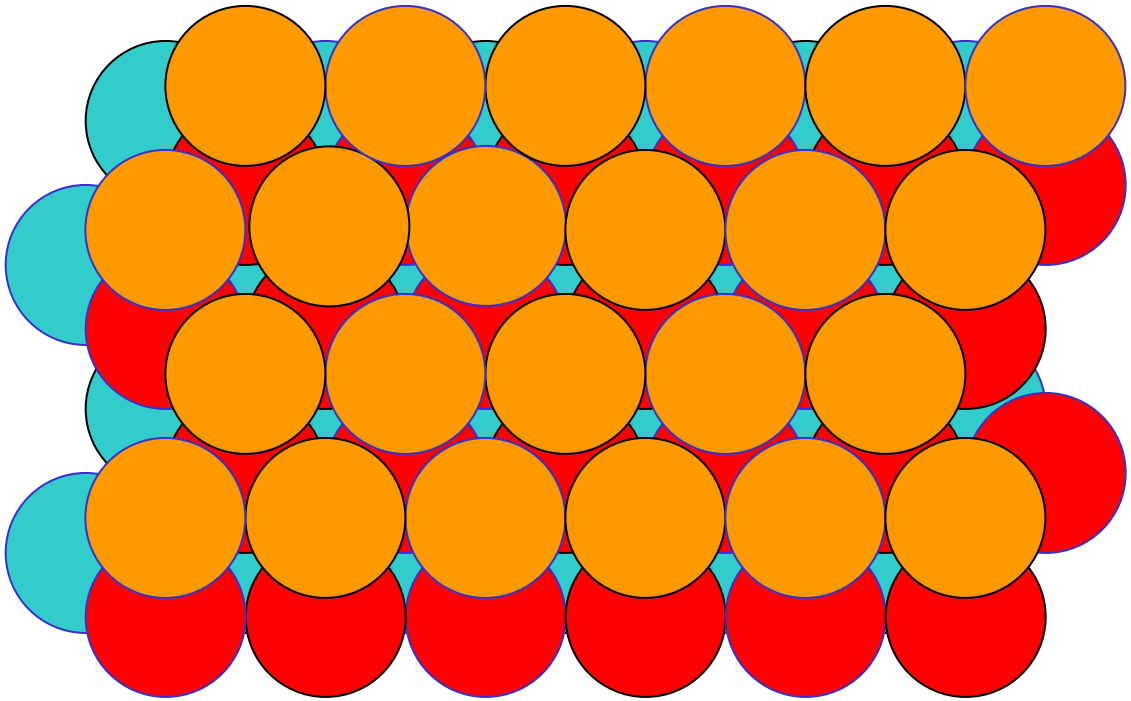
(note HCP can be broken down into 3 parallelopipeds)

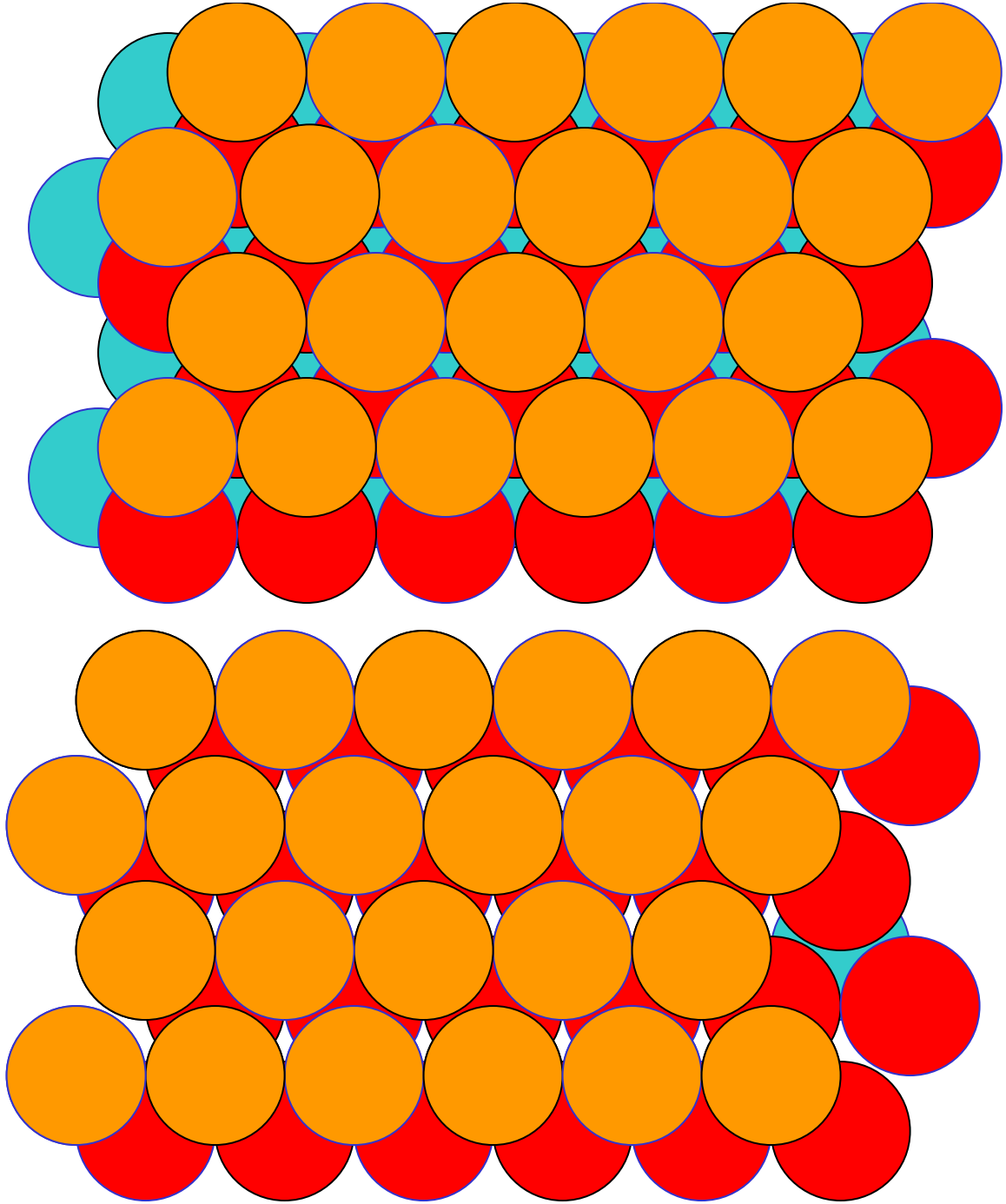


2. FACE CENTERED CUBIC (FCC)

(e.g. Cu, Al, Ag)

next easiest to understand in terms of CLOSE PACKING





packing often described in terms of ‘stacking’ of close packed layers

FCC stacking is:

abcabcabc….

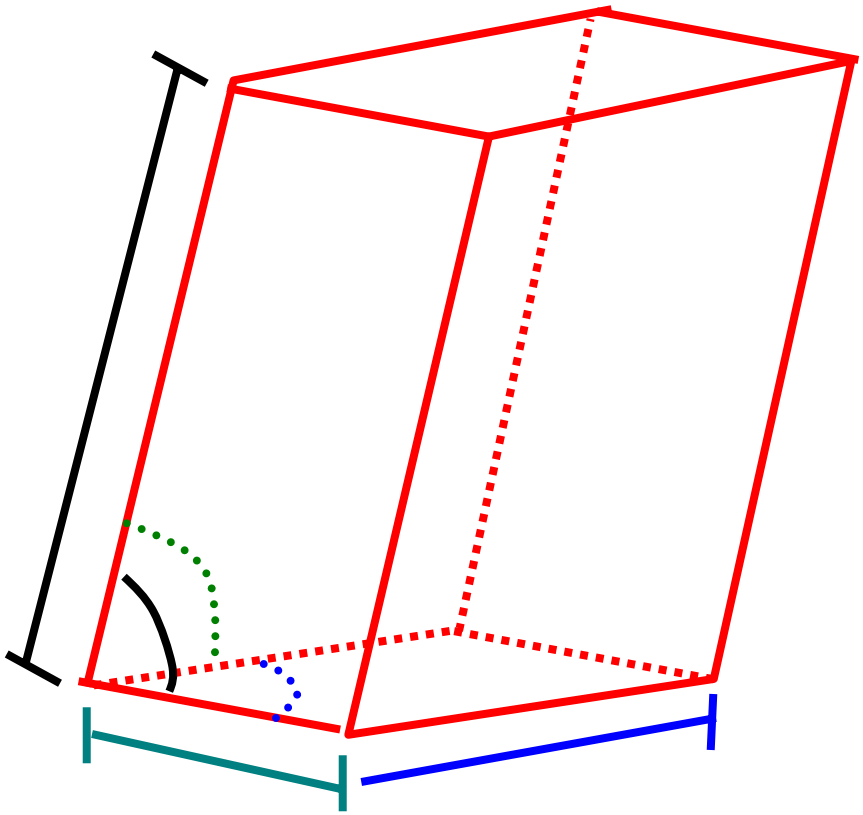
HCP is:

abababab….

OTHER CRYSTAL SYSTEMS (UNIT CELLS)

are defined by 6 parameters, the three axial lengths

and the three interaxial angles



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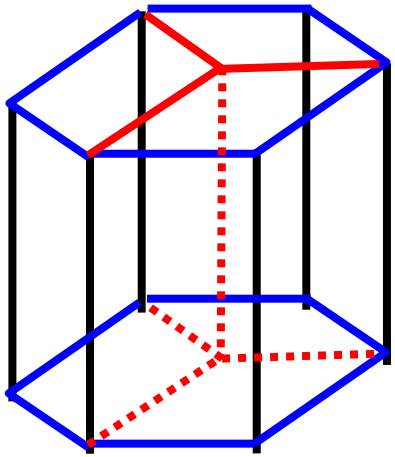

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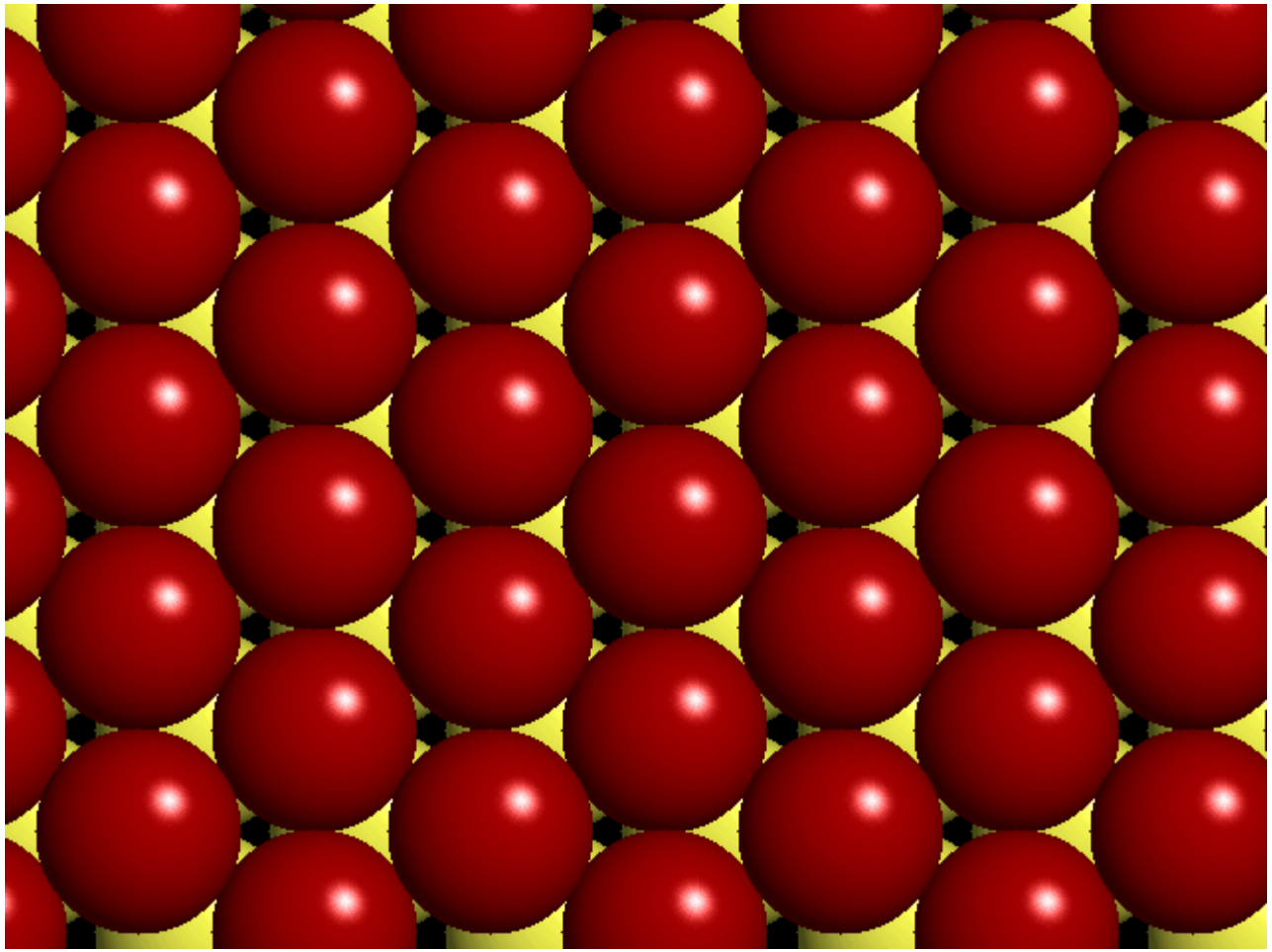
Closest Packing

Alternatively we could place the third layer in the C-type site (above voids in both A and B layers)



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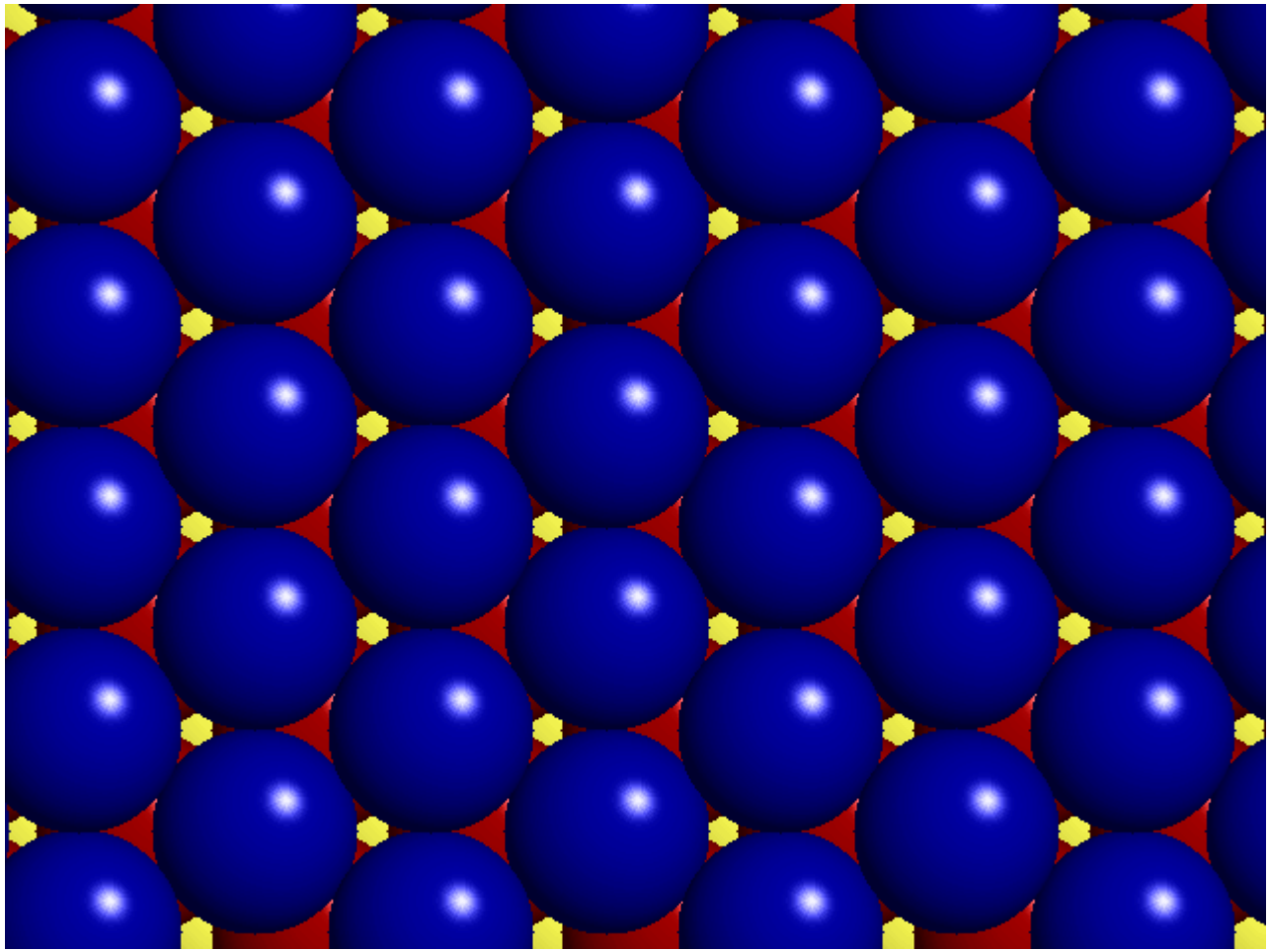
Closest Packing

Third layer:

- If occupy C-type site the layer ordering is A-B-C-A-B-C and creates a cubic closest packed structure (CCP)
- Blue layer atoms are now in a unique position above voids between atoms in layers A and B



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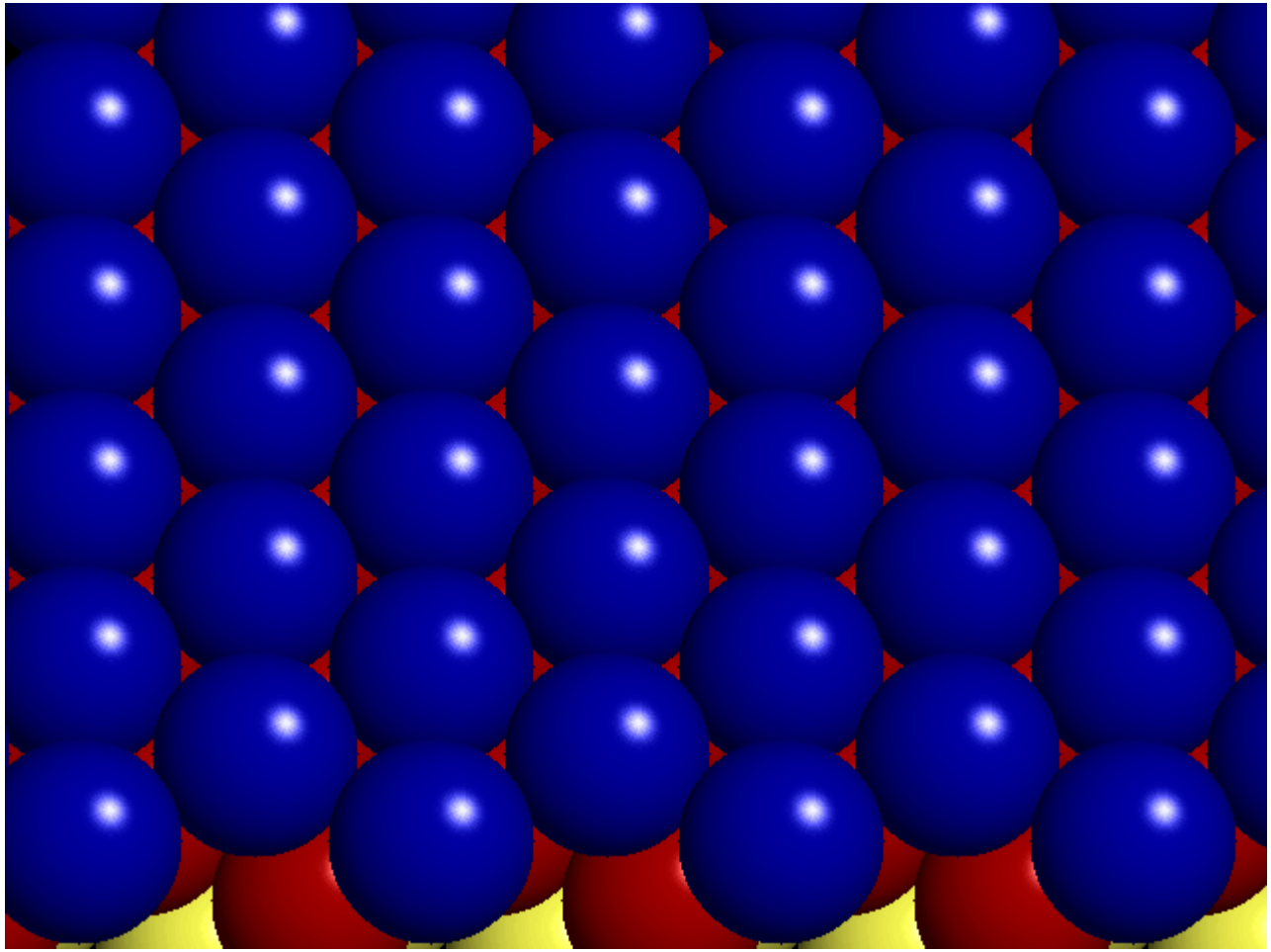


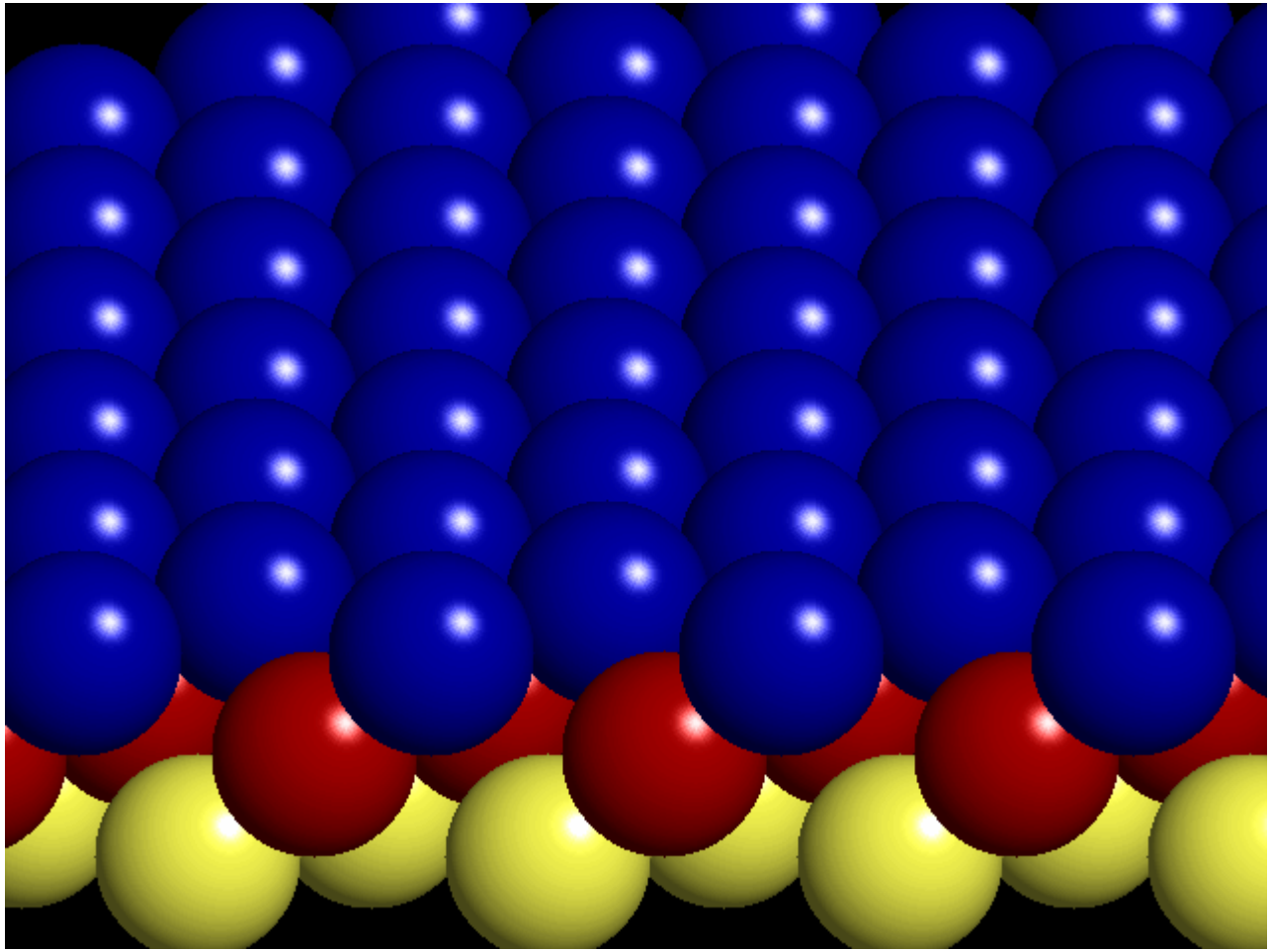
J. Winter

Whitman College

Closest Packing

Third layer:

- If occupy C-type site the layer ordering is A-B-C-A-B-C and creates a cubic closest packed structure (CCP)
- Blue layer atoms are now in a unique position above voids between atoms in layers A and B



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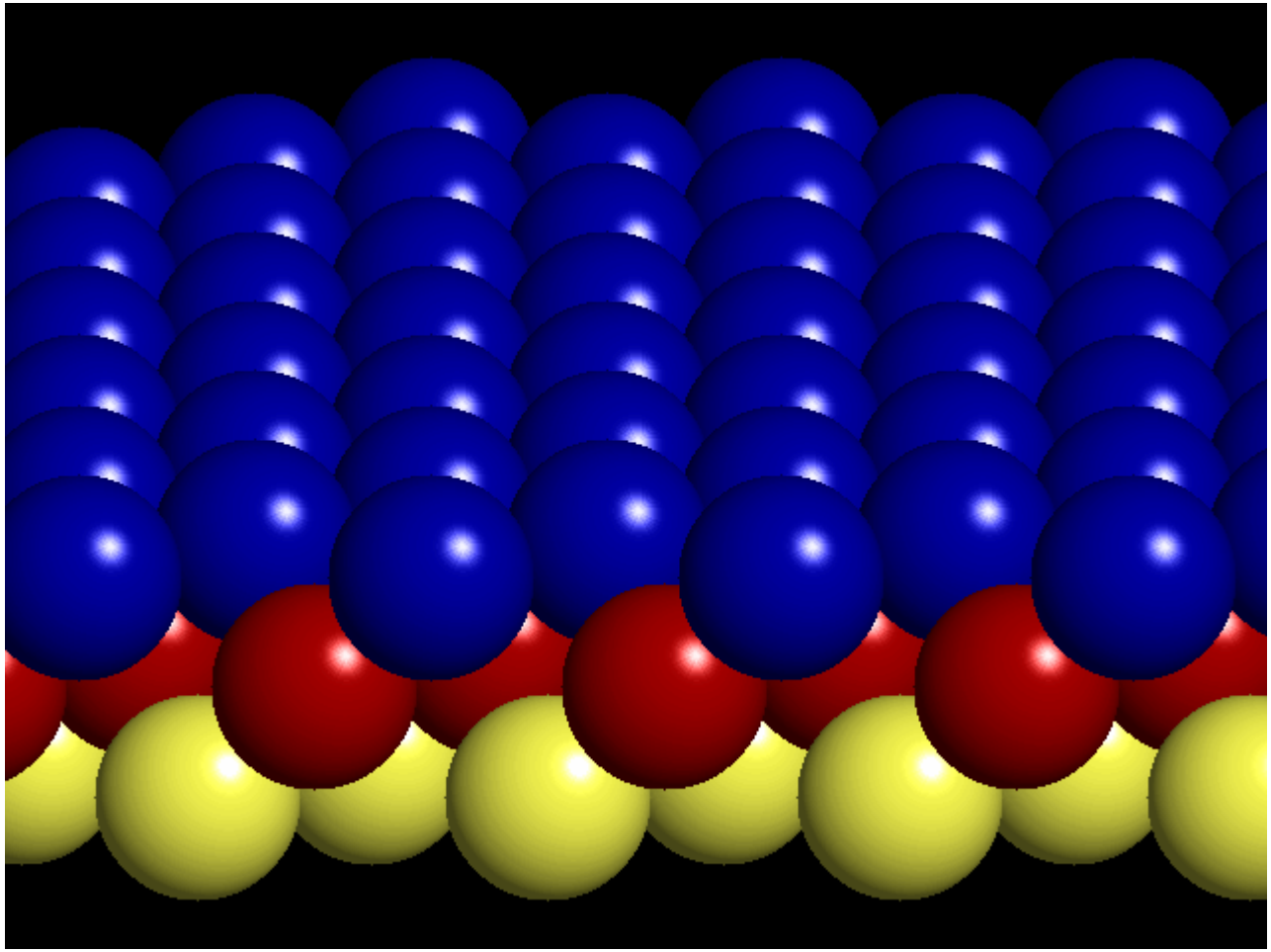

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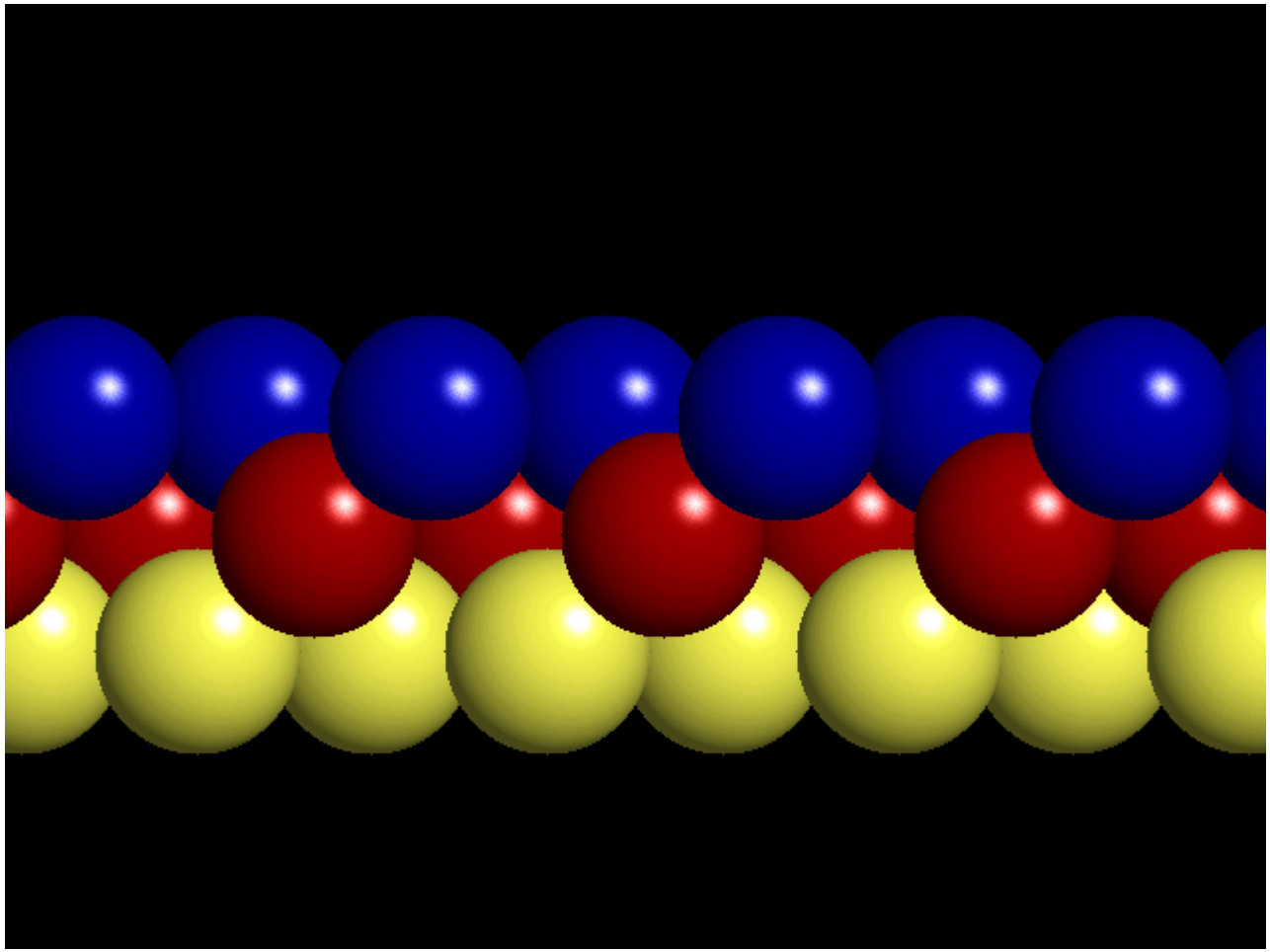

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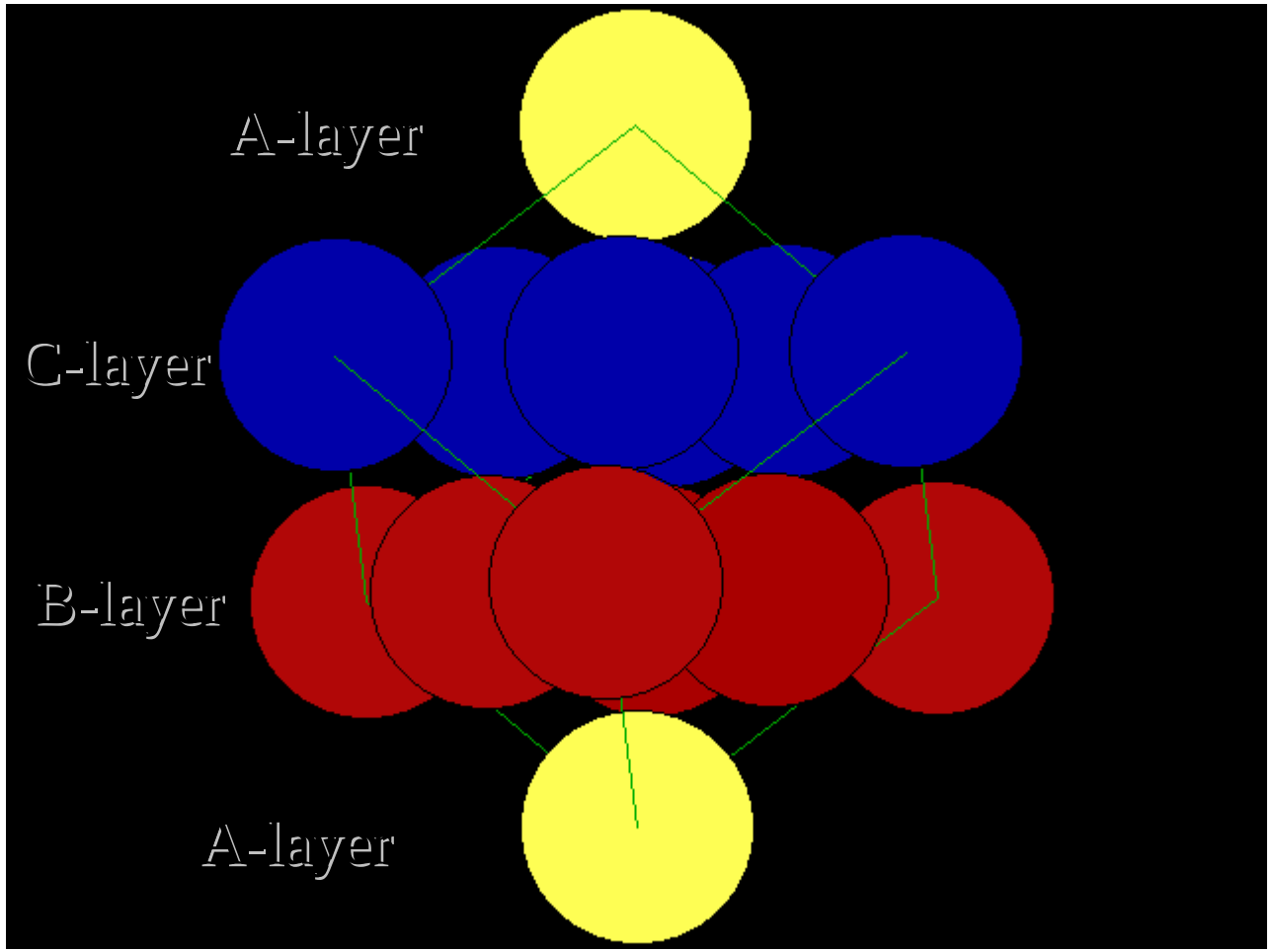
Closest Packing

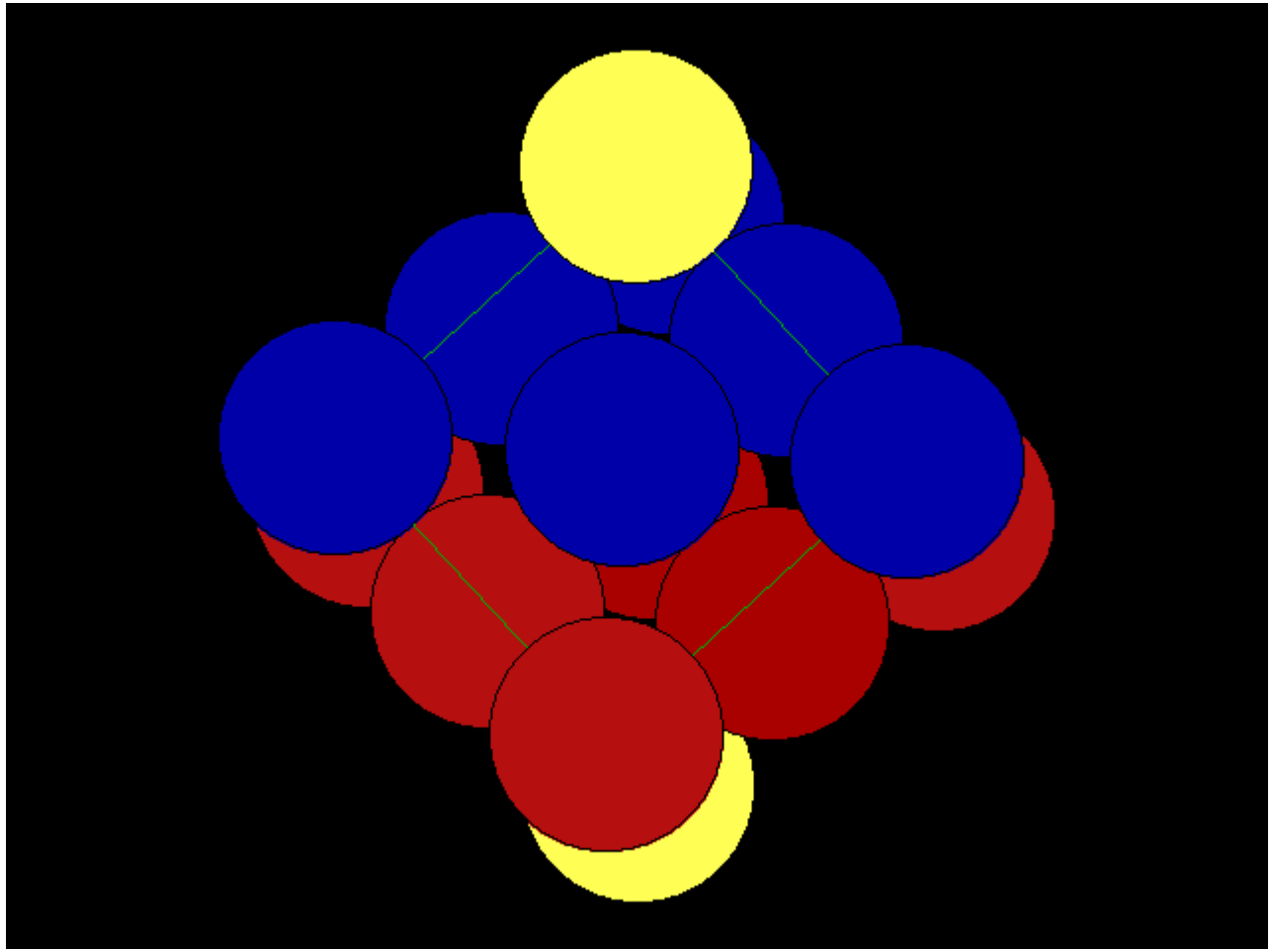
View from the same side shows the face-centered cubic unit cell that results.

The atoms are slightly shrunken to aid in visualizing the structure



Closest Packing

Rotating toward a top view



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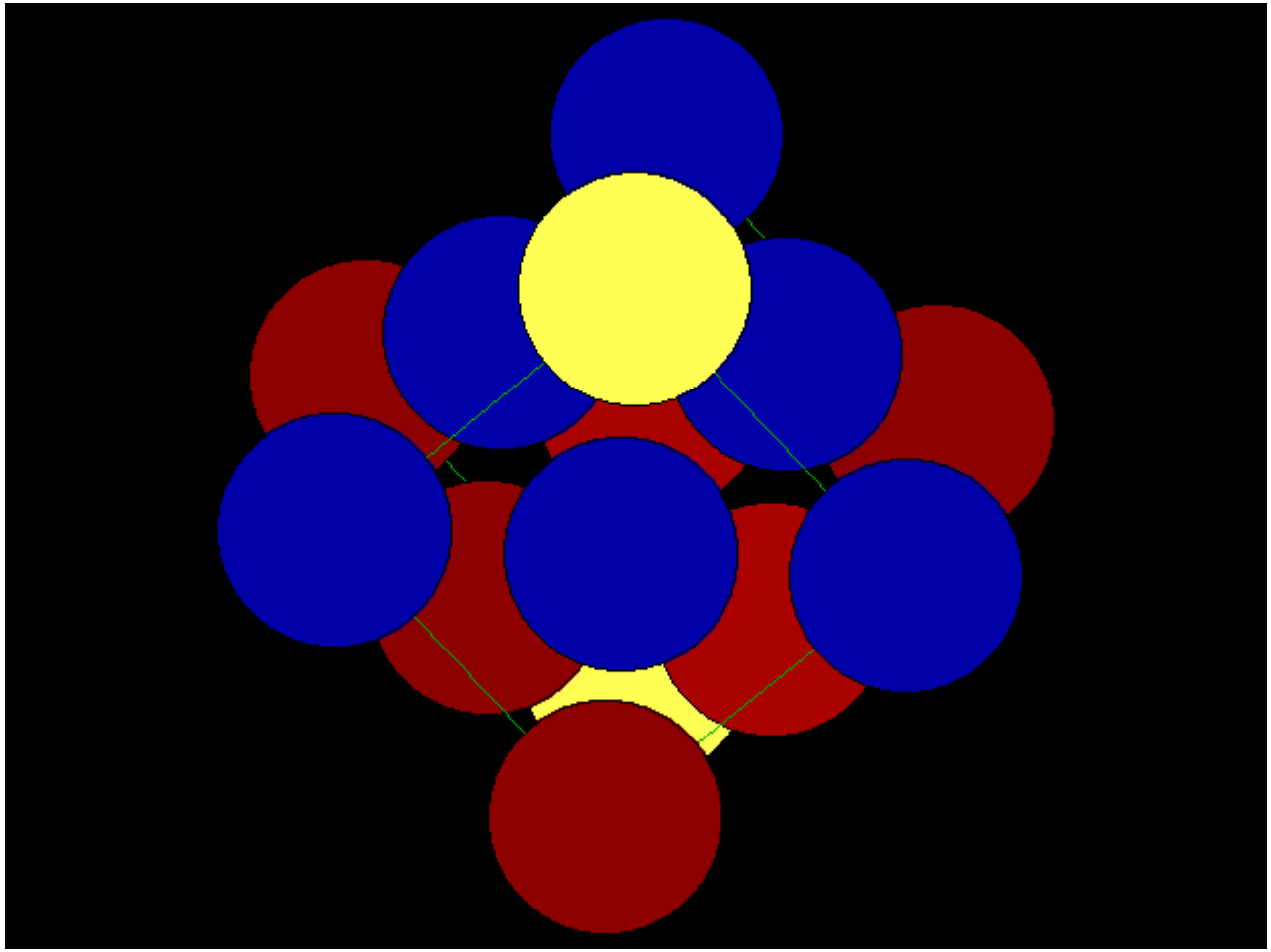
Closest Packing

Rotating toward a top view



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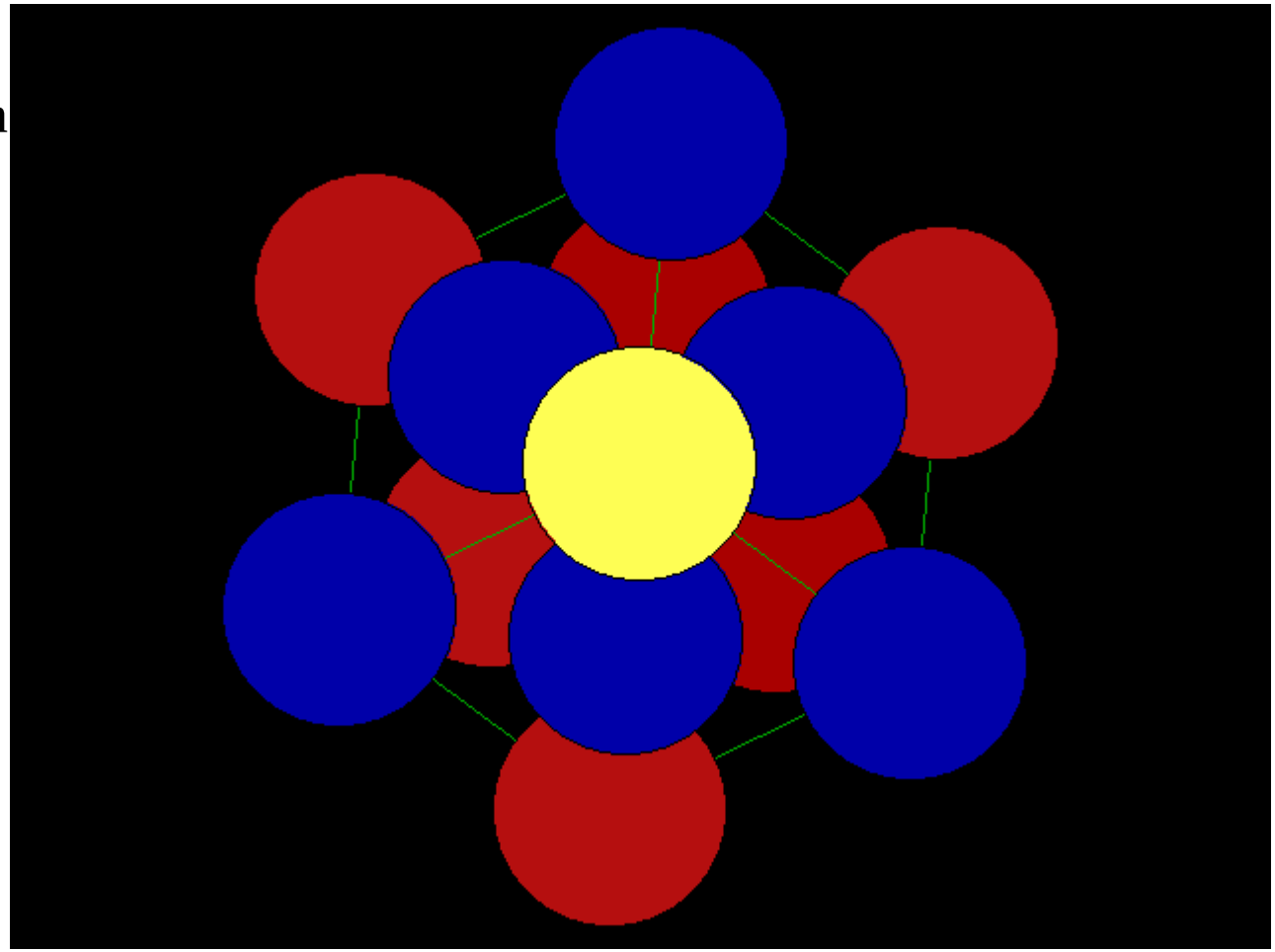
Closest Packing

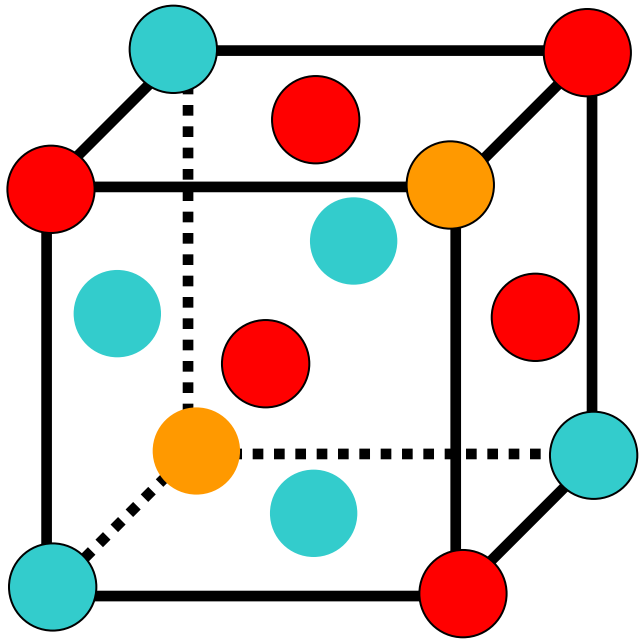
You are looking at a top yellow layer A with a blue layer C below, then a red layer B and a yellow layer A again at the bottom



UNIT CELL

Atom on each corner

Atom in center of each face of the cube



Cubic unit cell (shape)

spheres touch across face diagonals (?)

MODEL VIEW:

lattice parameter

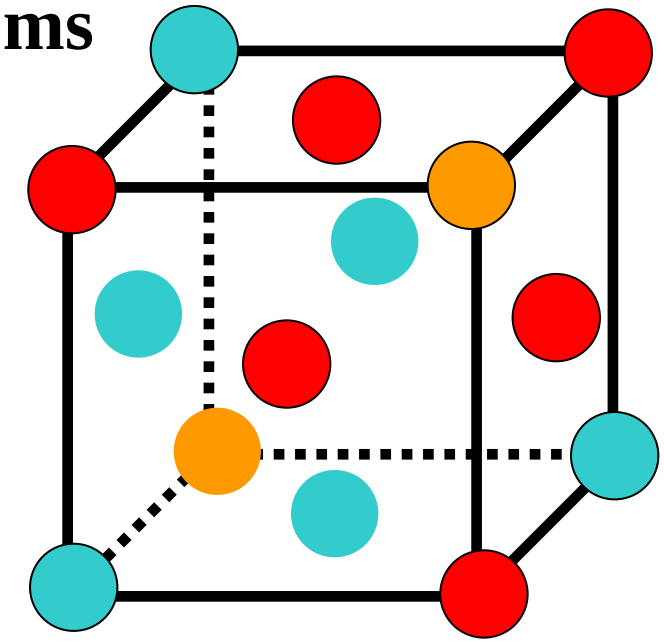
cube edge ‘a’

$$a = 2R\sqrt{2}$$

number of atoms per unit cell

1/8 of each of the 8 corner atoms

1/2 of each of the 6 face centered atoms



= 4*

atomic packing factor (APF)

APF = 0.74

-coordination number ?????

(by inspection of front face)

4 on corners and 4 on front and rear face centres

= 12*

3. BODY CENTERED CUBIC (BCC)

(e.g. Fe, Cr, W)

APF → HCP FCC

Cubic unit cell

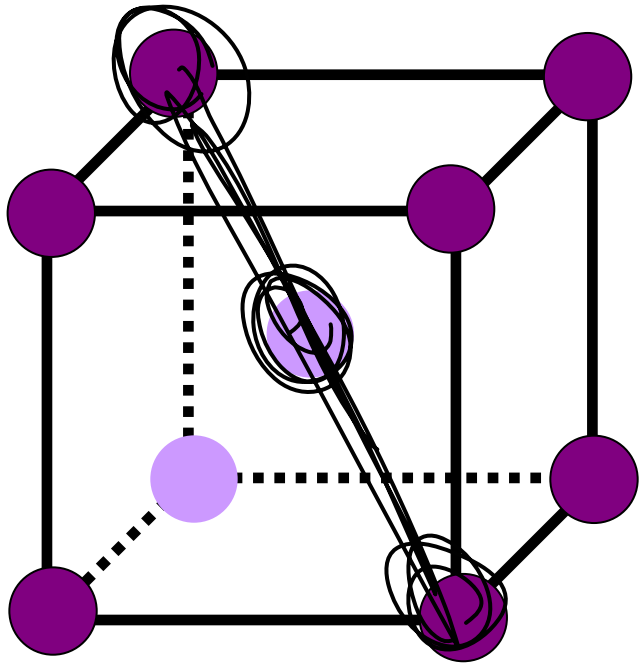
(center and corner atoms touch across cube diagonal)

(Not close packed)

lattice parameter

cube edge ‘a’

$$a = \frac{4R}{\sqrt{3}}$$



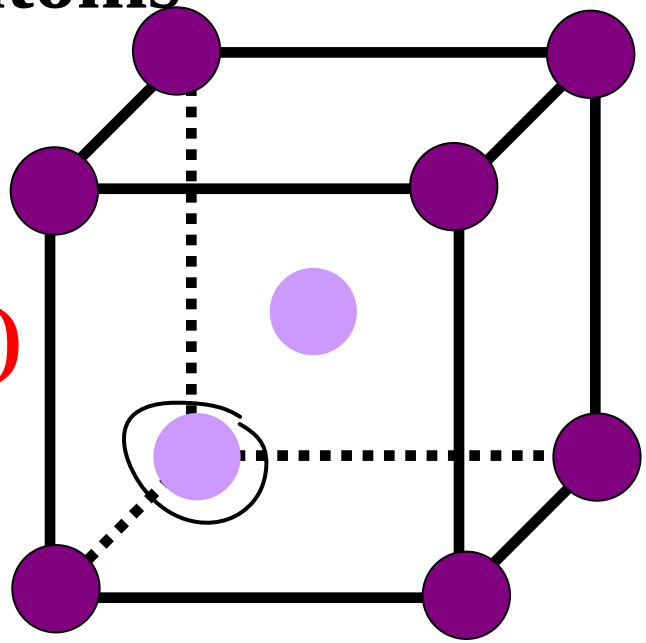
number of atoms per unit cell =

$$\frac{\text{8 corners}}{\text{8 cubes}}$$

1/8 of each of the 8 corner atoms

1 center atom

=2



atomic packing factor (APF)

APF = 0.68

-coordination number

(by inspection of center atom)

= 8

Check the Wiley website for a decent animation for BCC.

-crystallographic structure depends on external conditions (e.g. temp, pressure)…….

how it's made → thermal & mechanical and the alloying elements

-Change in crystal structure = change in some props

NOMENCLATURE

Allotropes and Phases

-an allotrope is a crystallographic variant of a pure element

-e.g. graphite and diamond are allotropes of carbon

-a polymorph (or phase) is a crystallographic variant of an alloy

-e.g. martensite is a phase of steel (Fe/C alloy)