The Crystalline Solid State

Chapter 7

Monday, October 19, 2015

Midterm Exam I

this Friday, Oct 23, 9-9:50a

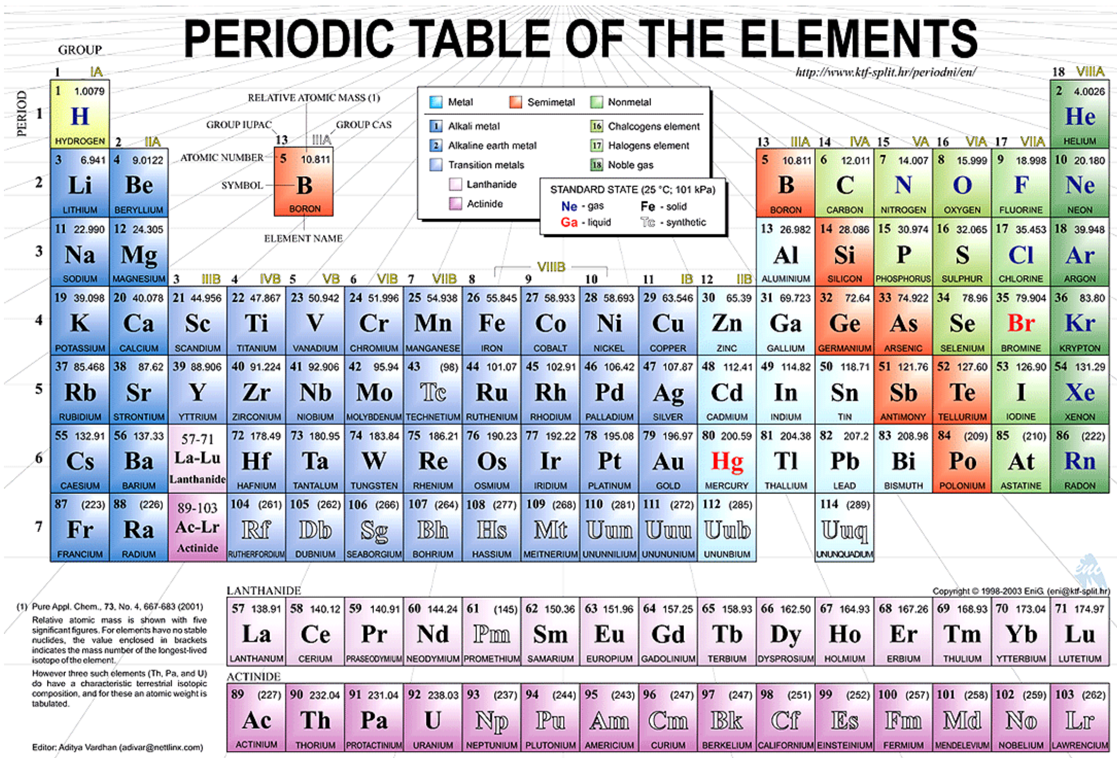
- Chapters 4, 5, and today's part of 7 (no chapter 6)
- multiple short answer problems testing basic concepts
- closed book, closed notes
- bring pen, pencil, calculator, ID
- study lectures, book, suggested and online problems
- look for seating chart on lecture room door
- don't cram!

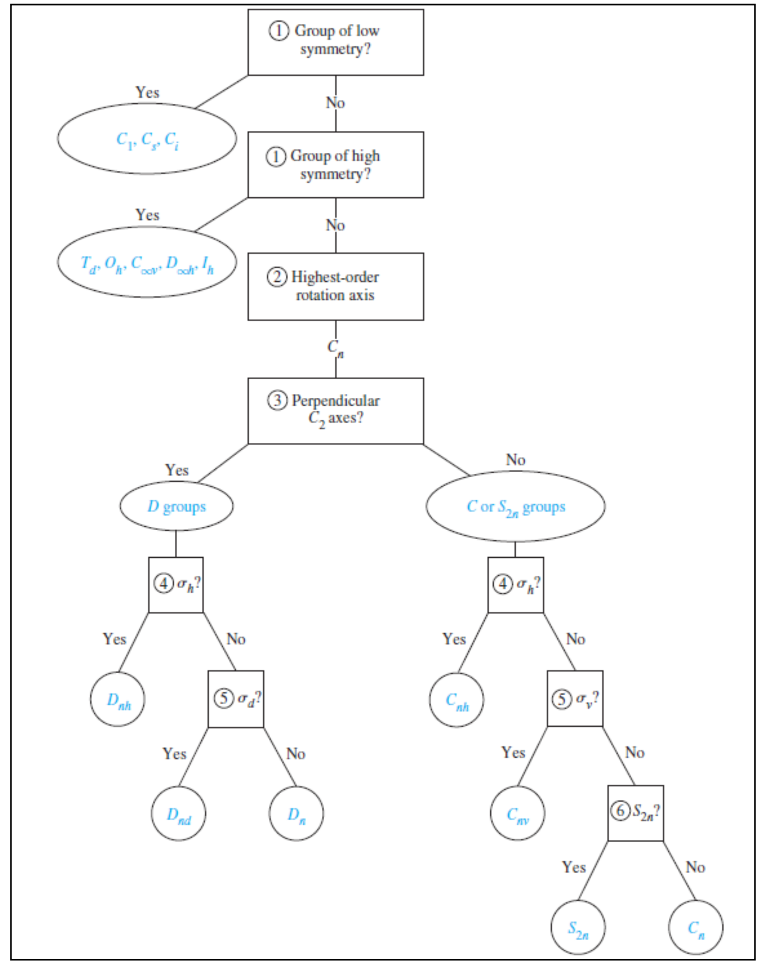
Review Sessions:

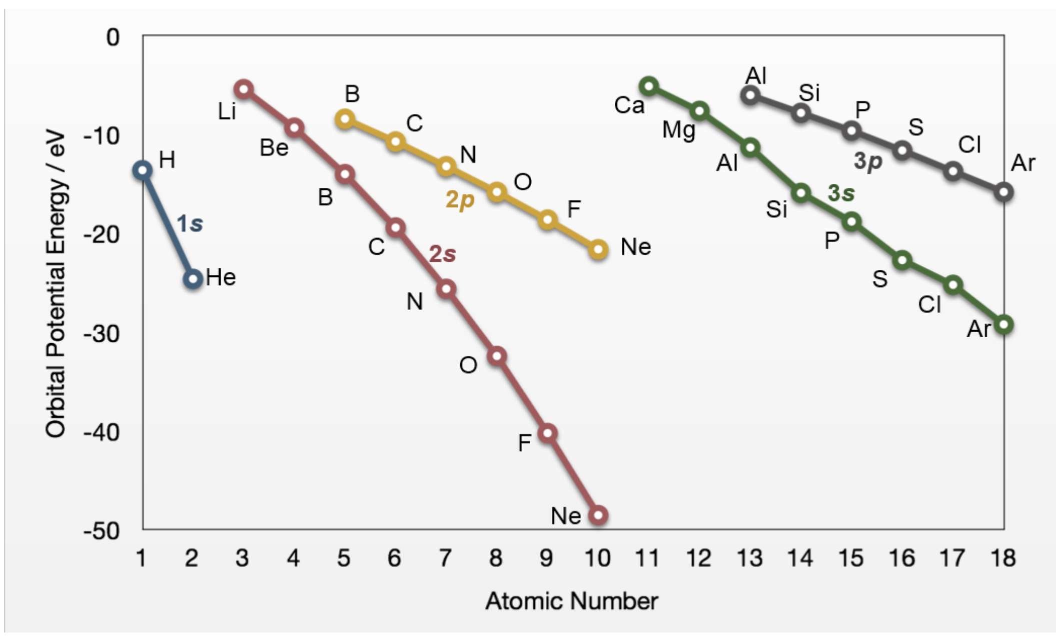
Weds, Oct 21 @ 4-6 pm, SSL 270 (Juliet)

Thurs, Oct 22 @ 5-7 pm in SSL 228 (Kyle)

Materials Provided







$$\#\text{ of irreducible representations of a given type} = \frac{1}{\text{order}} \sum_{R} \left(\#\text{ of operations in the class} \times \text{character of reducible representation} \times \text{character of irreducible representation} \right)$$

Character tables also provided (unless the point of the question is to build the table).

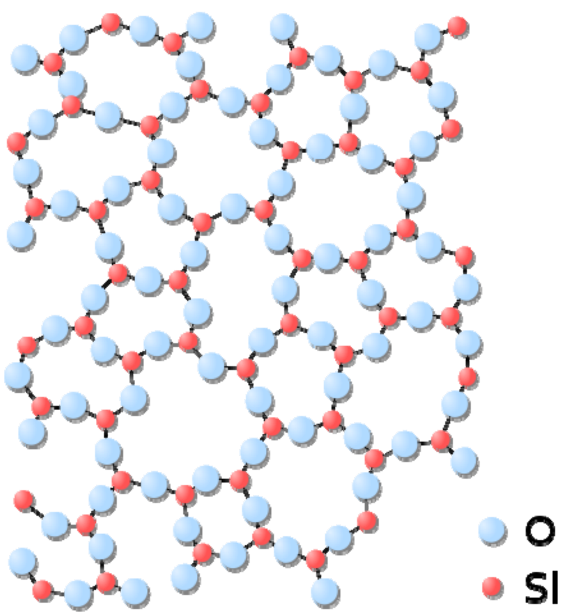
Types of Solids

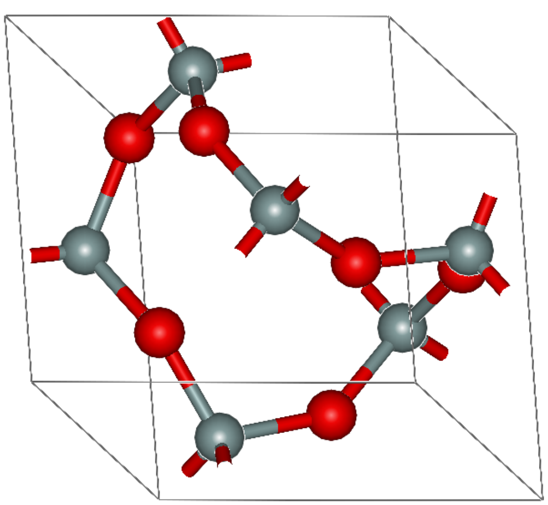
Amorphous Solids are solids that lack a regular three-dimensional arrangement of atoms. They lack long-range structural order.

Crystalline solids have atoms/ions/molecules arranged in regular, repeating patterns. They possess long-range periodicity.

- **minimizes free energy of the atoms/ions/molecules**
- **the *unit cell* is the smallest repeating structural unit that has the full crystal symmetry**

SiO_2 glass





SiO_2 crystal (α-quartz)

Types of Solids

Amorphous Solids are solids that lack a regular three-dimensional arrangement of atoms. They lack long-range structural order.

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- **minimizes free energy of the atoms/ions/molecules**
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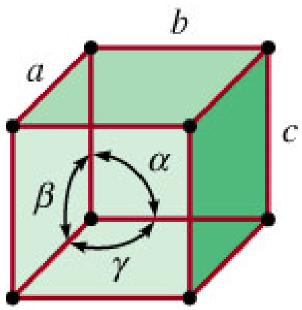
Types of crystalline solids:

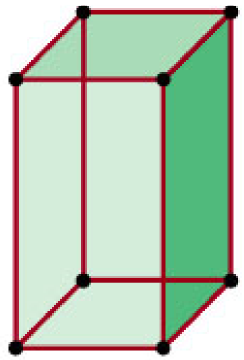
- **Ionic Crystals**
- **Covalent or Network Crystals**
- **Molecular Crystals**
- **Metallic Crystals**
- **Group VIII Crystals (frozen Noble Gases)**

The 7 Crystal Systems

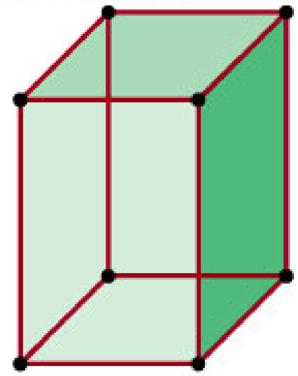
All 3D crystals belong to one of 7 *crystal systems*.



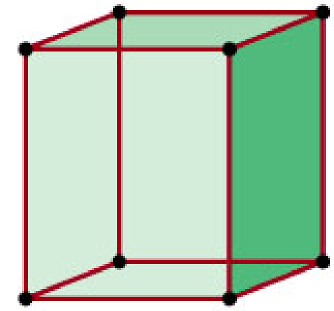
Cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$



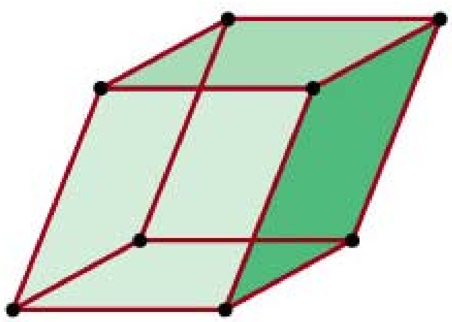
Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$



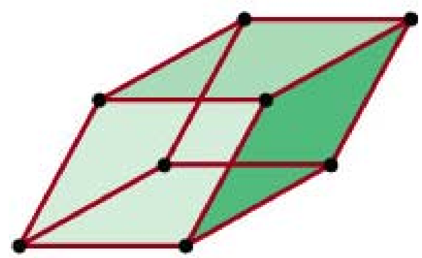
Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$



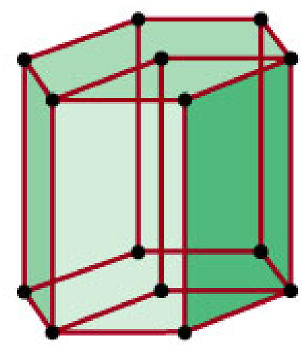
Monoclinic
$a \neq b \neq c$
$\gamma \neq \alpha = \beta = 90°$



Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$



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

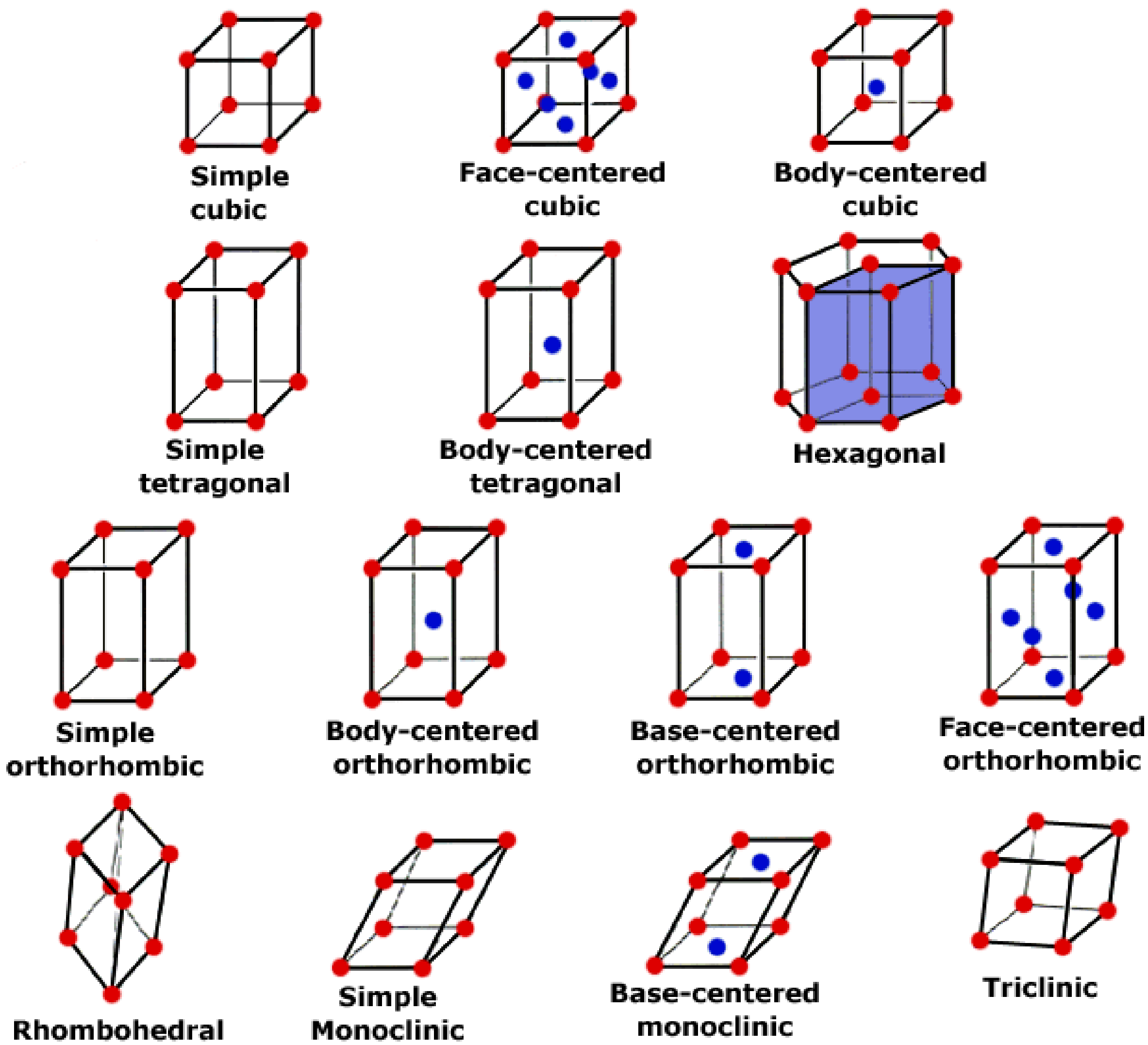


Hexagonal
$a = b \neq c$
$\alpha = \beta = 90°,\ \gamma = 120°$

The 14 Bravais Lattices

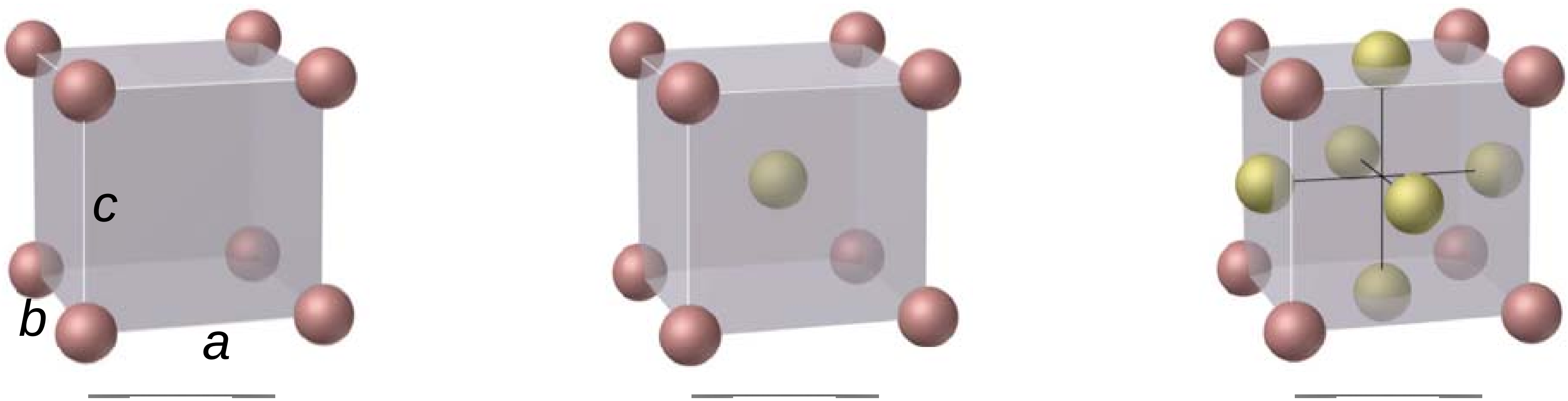
All 3D crystals belong to one of 14 Bravais lattices.

***Bravais lattice*: An infinite array of points with an arrangement and orientation that looks exactly the same from any lattice point.**



Types of Cubic Lattices

There are three cubic Bravais lattices:

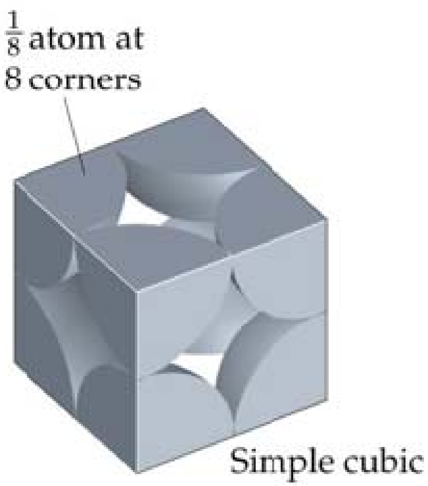


Simple Cubic | Body-Centered Cubic | Face-Centered Cubic

- **The lengths of the unit cell edges (*a*,*b*,*c*) are called *lattice constants*.**
- **For cubic crystals, *a* = *b* = *c*, so there is only one lattice constant (*a*).**

Contents of a Unit Cell

An important feature of the unit cell is the number of lattice points it contains. Atoms/ions/molecules are often located at lattice points.

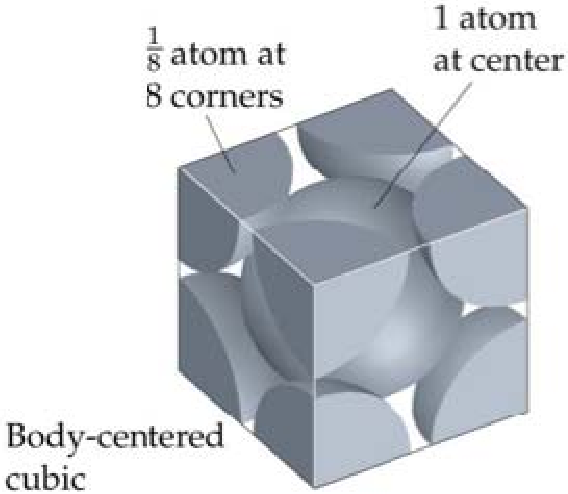


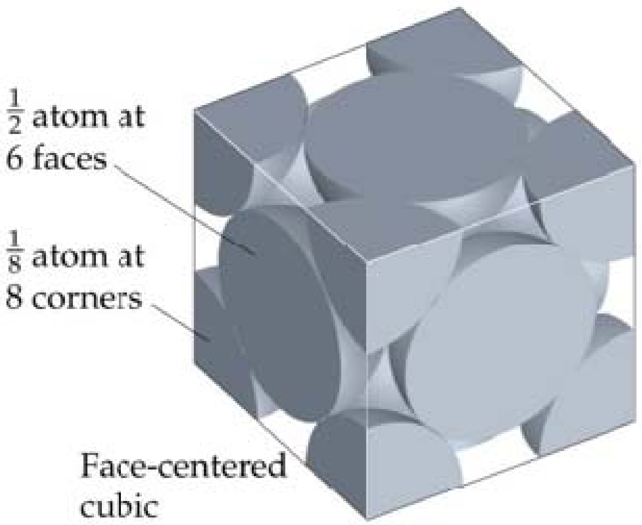
$$8 \cdot atoms \times \frac{1}{8} \cdot occupancy$$

1 atom in a Simple Cubic cell

$$8 \cdot atoms \times \frac{1}{8} \cdot occupancy + 1 \cdot atom \times 1 \cdot occupancy$$

2 atoms in a Body-Centered Cubic cell





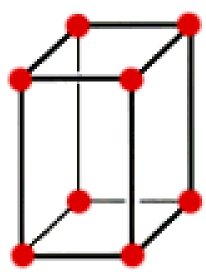
$$8 \cdot atoms \times \frac{1}{8} \cdot occupancy + 6 \cdot atoms \times \frac{1}{2} \cdot occupancy$$

4 atoms in a Face-Centered Cubic cell

Contents of a Unit Cell

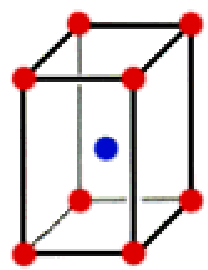
An important feature of the unit cell is the number of lattice points it contains. Atoms/ions/molecules are often located at lattice points.

Atoms	Shared Between:	Each atom counts:
corner	8 cells	1/8
face center	2 cells	1/2
body center	1 cell	1
edge center	4 cells	1/4



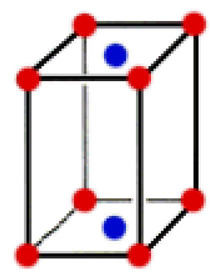
Simple orthorhombic

$8 \times 1/8 = \mathbf{1}$



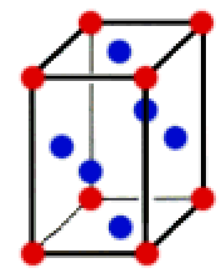
Body-centered orthorhombic

$8 \times 1/8 + 1 \times 1 = \mathbf{2}$



Base-centered orthorhombic

$8 \times 1/8 + 2 \times 1/2 = \mathbf{2}$

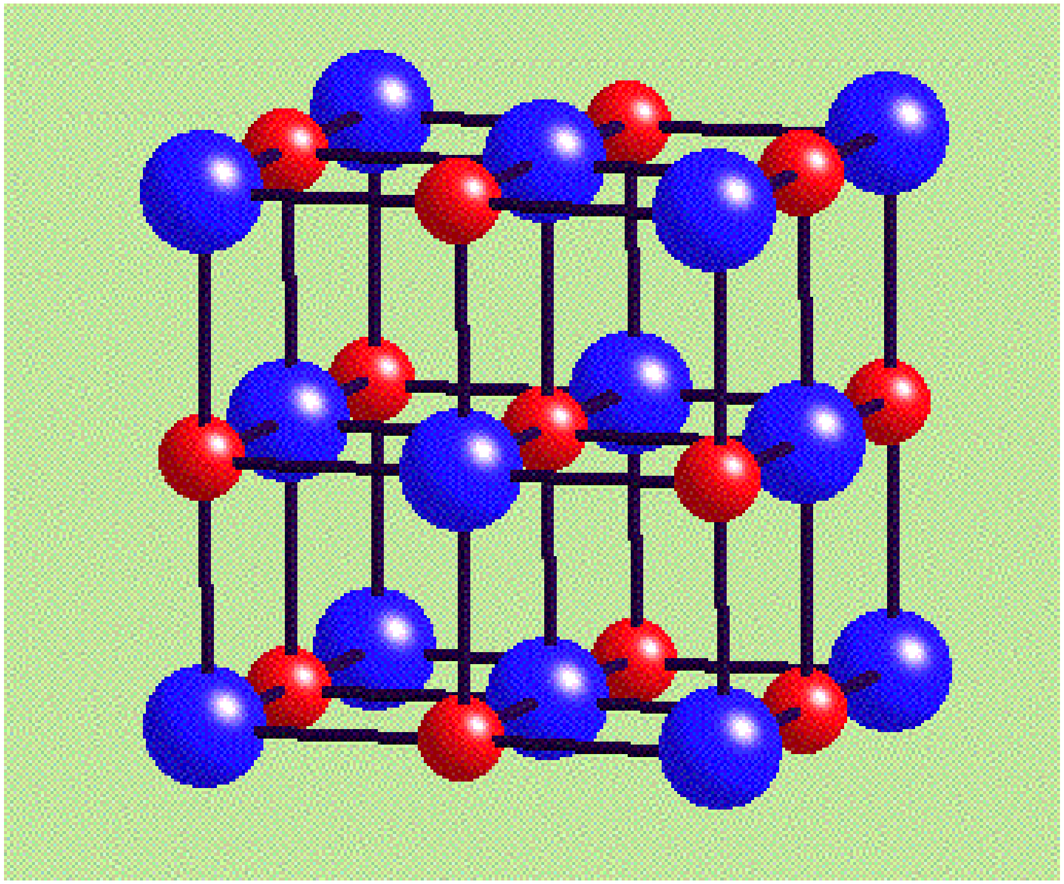


Face-centered orthorhombic

$8 \times 1/8 + 4 \times 1/2 = \mathbf{4}$

Contents of a Unit Cell

Consider sodium chloride: ***rock salt*** (not Bravais)



Cl at corners: (8 × 1/8) = 1

Cl at face centres (6 × 1/2) = 3

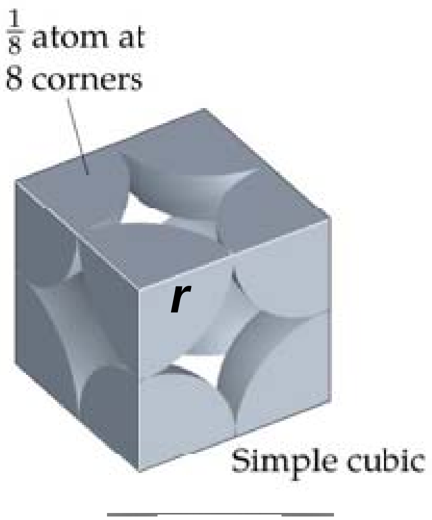
Na at edge centers (12 × 1/4) = 3

Na at body centre = 1

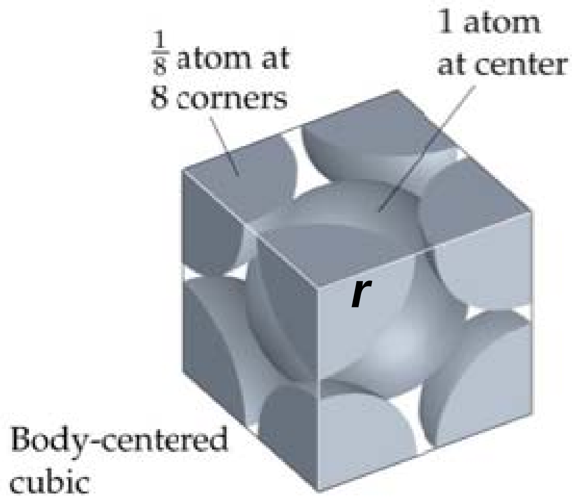
Unit cell contents: 4(Na^+Cl^-)

Types of Cubic Cells

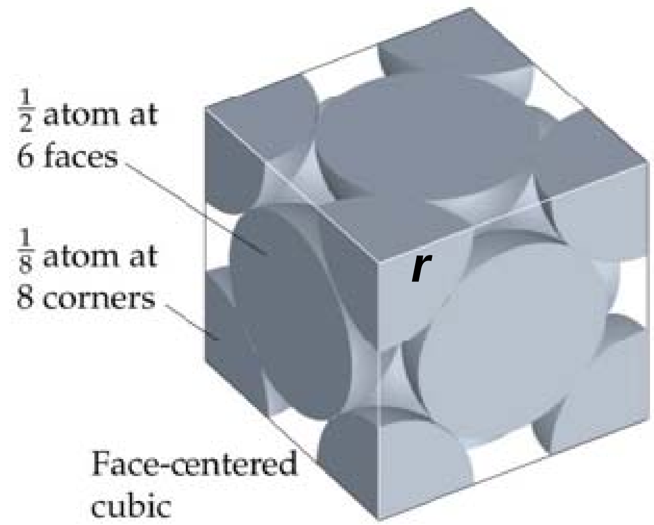
Different cubic cells result from different packing of atoms.



Simple Cubic



Body-Centered Cubic



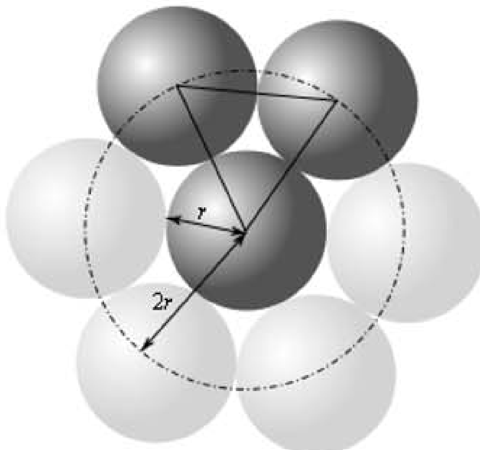
Face-Centered Cubic

Unit Cell	Atoms per cell	Coordination Number	Lattice Constant	Packing Fraction
Simple Cubic	1	6	$2r$	52%
Body-Centered Cubic	2	8	$\frac{4r}{\sqrt{3}}$	68%
Face-Centered Cubic	4	12	$2r\sqrt{2}$	74%

Close-Packed Structures

Consider the ***close-packing*** of incompressible (hard) spheres:

In 2D, regular close-packing requires an hexagonal array (HCP)



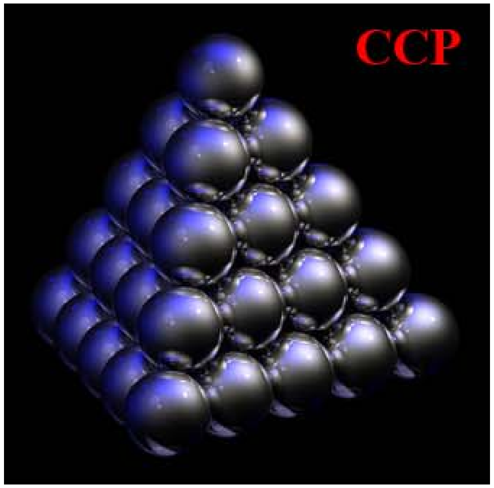
Most efficient way to pack spheres of single size

- *6 nearest neighbors*

Coordination number (CN): 6

In 3D, regular close-packing involves stacking 2D HCP arrays

Regular (crystalline) packing



Irregular packing

The Hexagonal Close-Packed Structure

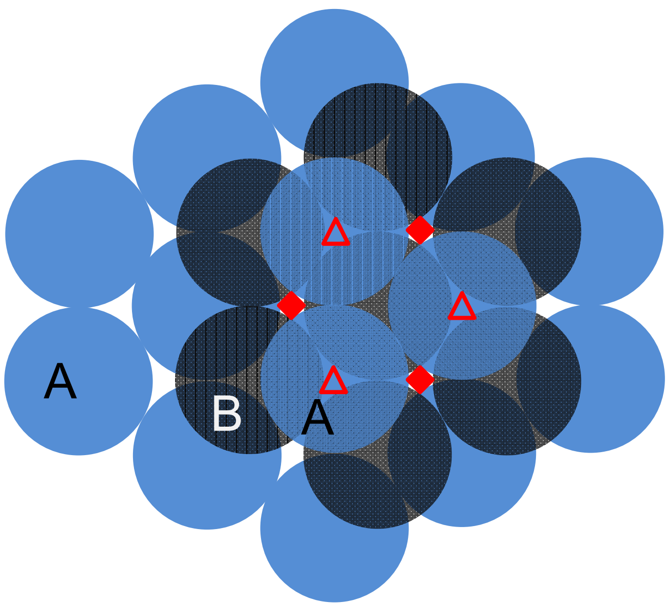
An HCP crystal is a close-packed structure with the stacking sequence …ABABAB…

To construct:

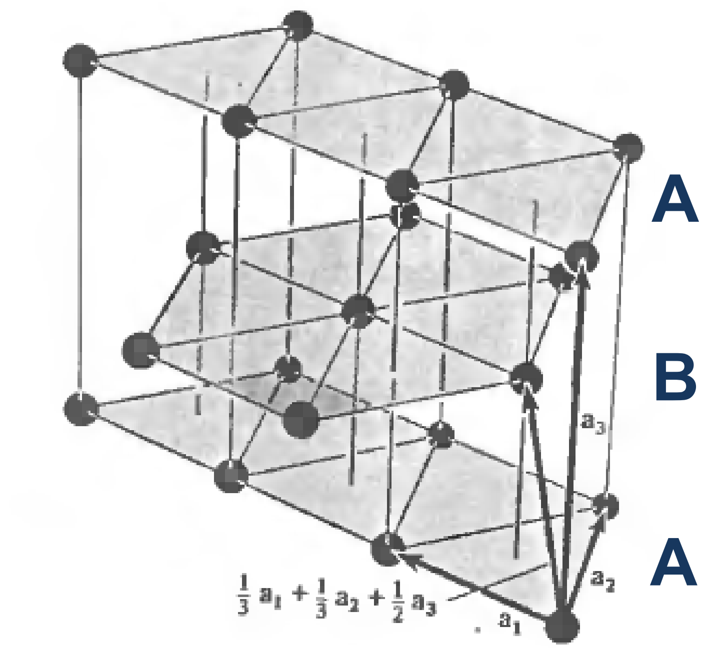
1st layer: 2D HCP array (layer A)

2nd layer: HCP layer with each sphere placed in alternate interstices in 1st layer (B)

3rd layer: HCP layer positioned directly above 1st layer (repeat of layer A)



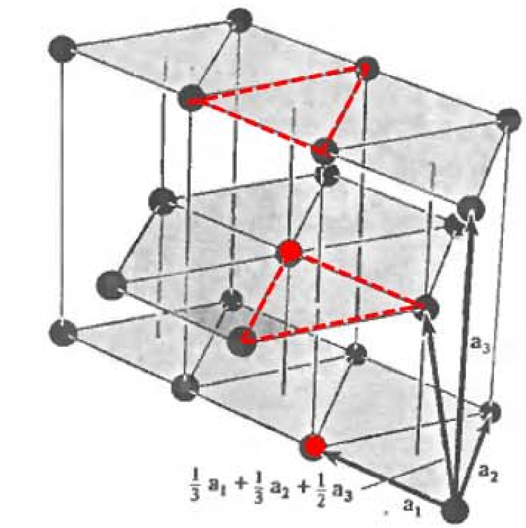
…ABAB…



HCP is two interpenetrating simple hexagonal lattices displaced by $\mathbf{a}_1/3 + \mathbf{a}_2/3 + \mathbf{a}_3/2$

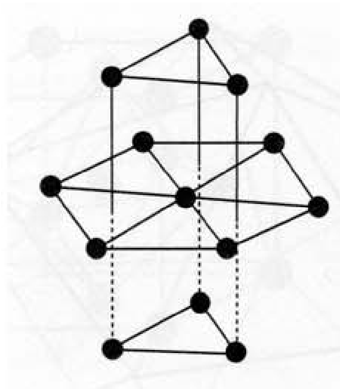
The Hexagonal Close-Packed Structure

- *not a Bravais lattice*



Orientation alternates with each layer

- *each sphere touches 12 equidistant nearest neighbors* (CN = 12)



Six in plane, six out-of-plane

- *structure has maximum packing fraction possible for single-sized spheres* (0.74)

The Hexagonal Close-Packed Structure

- *about 30 elements crystallize in the HCP form*

Table 4.4
ELEMENTS WITH THE HEXAGONAL CLOSE-PACKED CRYSTAL STRUCTURE

ELEMENT	*a* (Å)	*c*	*c*/*a*	ELEMENT	*a* (Å)	*c*	*c*/*a*
Be	2.29	3.58	1.56	Os	2.74	4.32	1.58
Cd	2.98	5.62	1.89	Pr	3.67	5.92	1.61
Ce	3.65	5.96	1.63	Re	2.76	4.46	1.62
α-Co	2.51	4.07	1.62	Ru	2.70	4.28	1.59
Dy	3.59	5.65	1.57	Sc	3.31	5.27	1.59
Er	3.56	5.59	1.57	Tb	3.60	5.69	1.58
Gd	3.64	5.78	1.59	Ti	2.95	4.69	1.59
He (2 K)	3.57	5.83	1.63	Tl	3.46	5.53	1.60
Hf	3.20	5.06	1.58	Tm	3.54	5.55	1.57
Ho	3.58	5.62	1.57	Y	3.65	5.73	1.57
La	3.75	6.07	1.62	Zn	2.66	4.95	1.86
Lu	3.50	5.55	1.59	Zr	3.23	5.15	1.59
Mg	3.21	5.21	1.62		—	—	
Nd	3.66	5.90	1.61	"Ideal"			1.63

The Cubic Close-Packed Structure

A CCP crystal is a close-packed structure with the stacking sequence …ABCABC…

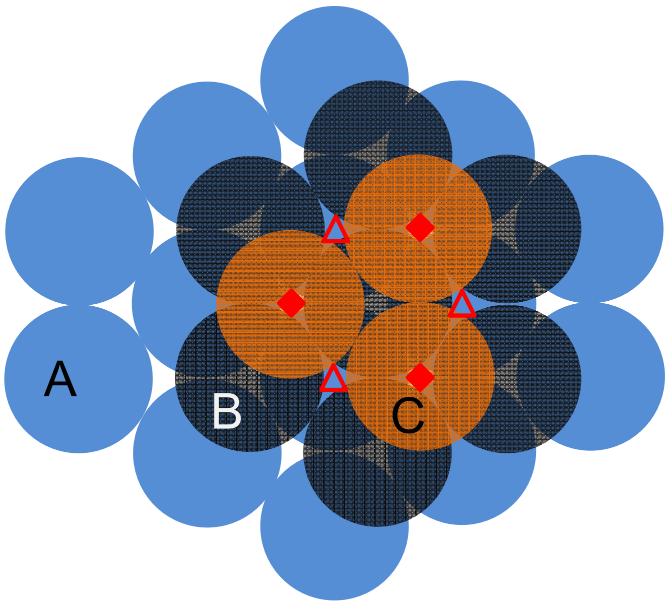
To construct:

1st layer: 2D HCP array (layer A)

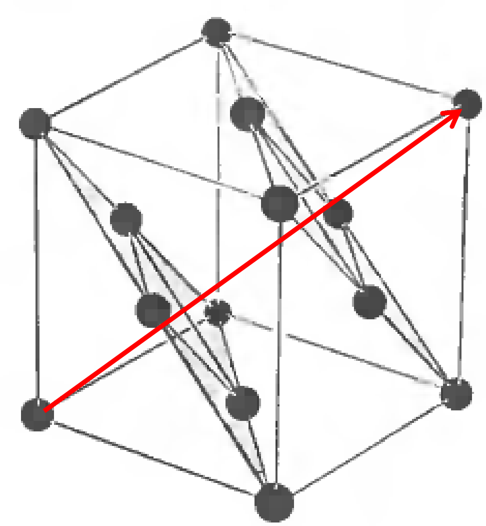
2nd layer: HCP layer with each sphere placed in alternate interstices in 1st layer (B)

3rd layer: HCP layer placed in the *other* set of interstitial depressions (squares, C)

4th layer: repeats the 1st layer (A)



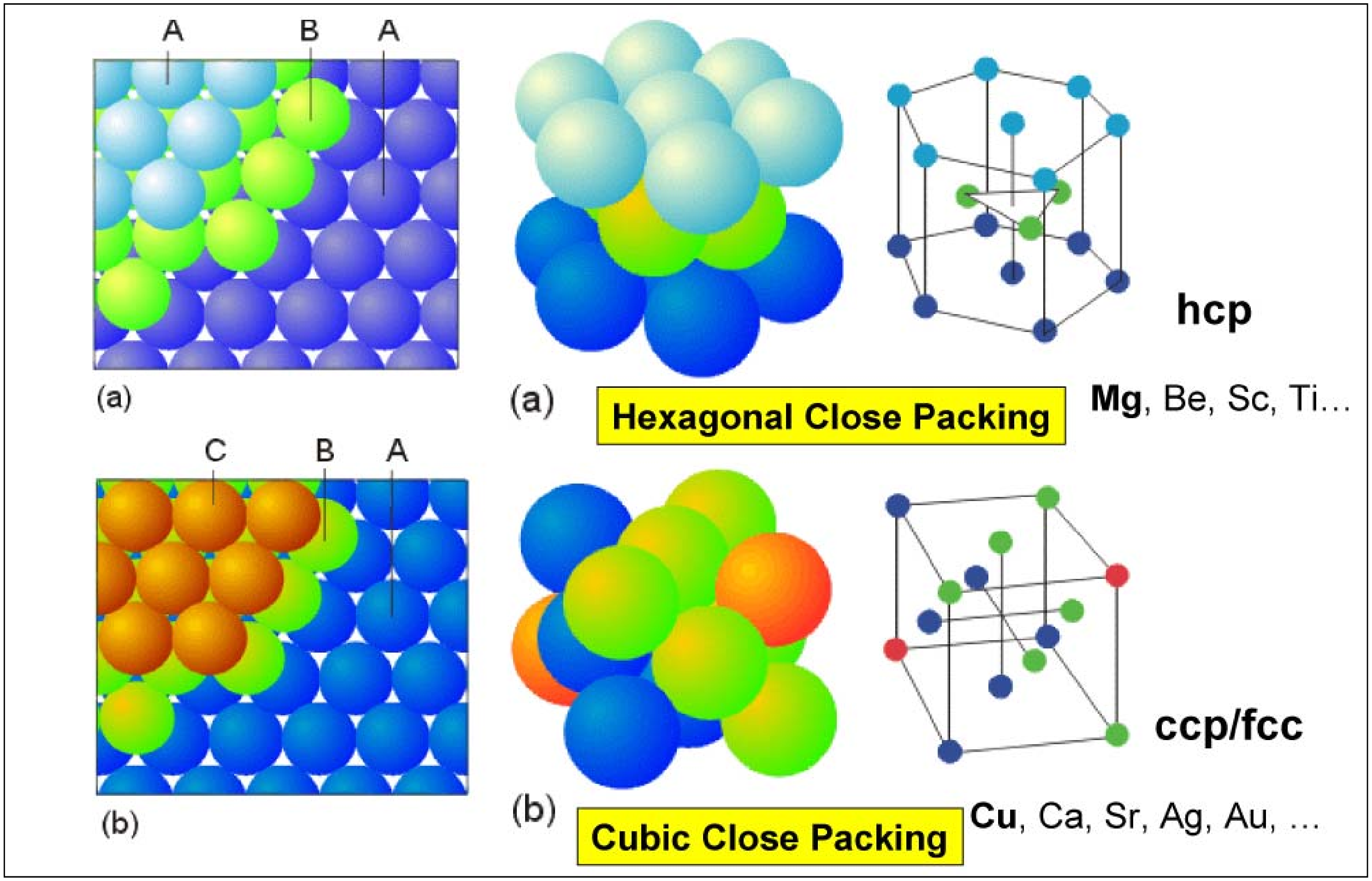
…ABCABC…



It turns out that the CCP structure is just the FCC Bravais lattice!

Close-Packed Structures

Most common are HCP and CCP, but an infinite number of stacking sequences are possible.



silicon carbide

Example: silicon carbide has over 250 *polytypes*
e.g., 6H-SiC stacking sequence …ABCACB…

Metallic Solids

- **Most metals crystallize in ccp, hcp, or bcc structures**
- **Metallic bonding is stronger than London dispersion forces, but weaker than covalent bonding**

Solid	M / g mol^{-1}	Melting Point / °C
Kr	83.80	–157
Cu	63.55	1083
C (diamond)	12.01	3500