

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

PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

Legend:

- Metal (Blue)
- Semimetal (Orange)
- Nonmetal (Green)
- Alkali metal (1)
- Alkaline earth metal (2)
- Transition metals (3-10)
- Lanthanide (11)
- Actinide (12)
- Chalcogens element (16)
- Halogens element (17)
- Noble gas (18)

Standard State (25 °C; 101 kPa):
 Ne - gas, Fe - solid, Ga - liquid, Te - synthetic

LANTHANIDE

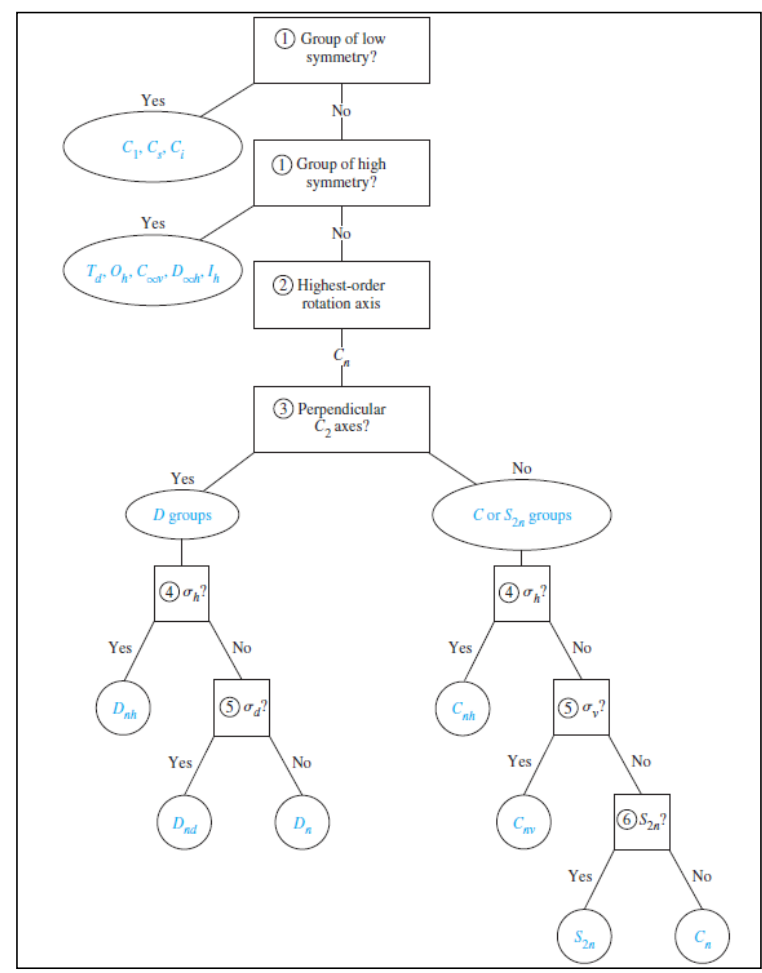
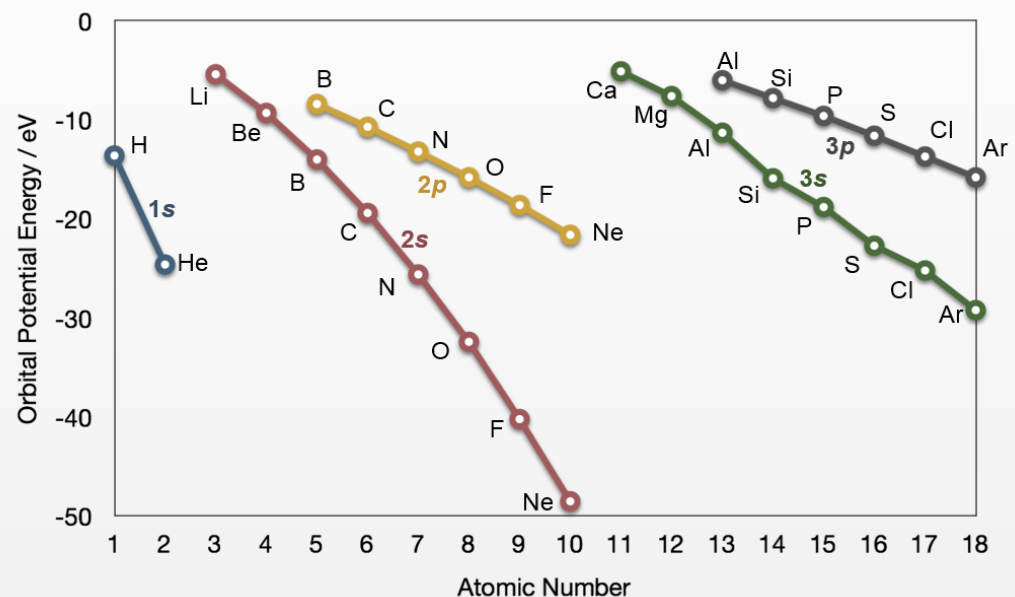
57 138.91	58 140.12	59 140.91	60 144.24	61 (145)	62 150.36	63 151.96	64 157.25	65 158.93	66 162.50	67 164.93	68 167.26	69 168.93	70 173.04	71 174.97
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LANTHANUM	CERIUM	PRASEODYMIUM	NEODYMIUM	PROMETHIUM	SAMARIUM	EUROPIUM	GADOLINIUM	TERBIUM	DYSPROSIUM	HOLMIUM	ERBIUM	THULIUM	YTTERIUM	LUTETIUM

ACTINIDE

89 (227)	90 232.04	91 231.04	92 238.03	93 (237)	94 (244)	95 (243)	96 (247)	97 (247)	98 (251)	99 (252)	100 (257)	101 (258)	102 (259)	103 (262)
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
ACTINIUM	THORIUM	PROTACTINIUM	URANIUM	NEPTUNIUM	PLUTONIUM	AMERICIUM	CURIUM	BERKELIUM	CALIFORNIUM	EINSTEINIUM	FERMIUM	MENDELEVIUM	NOBELIUM	LAWRENCIUM

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Editor: Aditya Vardhan (advir@netnet.in)



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

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

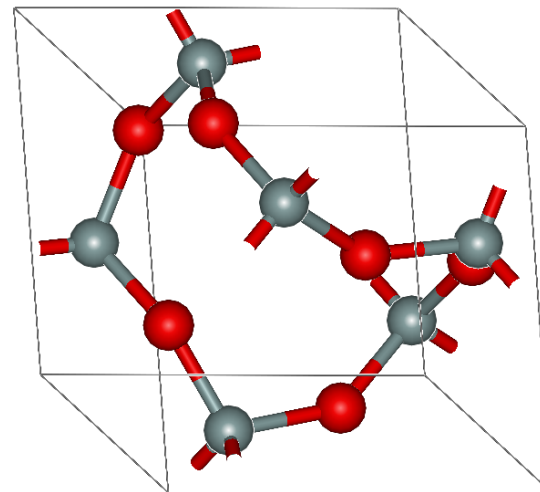
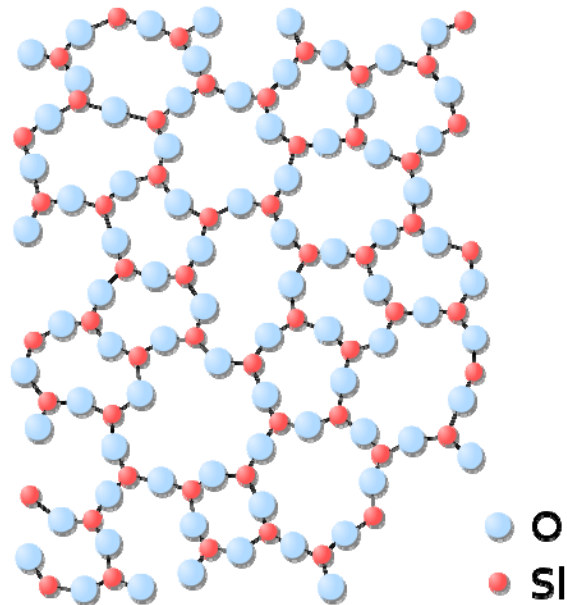
Types of Solids

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

SiO₂ glass



SiO₂ crystal (α-quartz)

Types of Solids

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

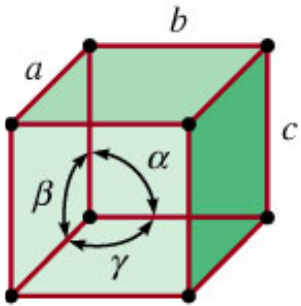
- minimizes free energy of the atoms/ions/molecules
- the *unit cell* is the smallest repeating structural unit that has the full crystal symmetry

Types of crystalline solids:

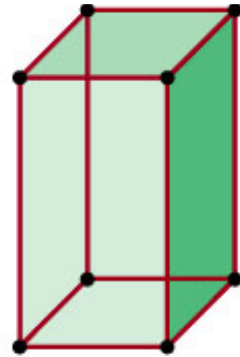
- Ionic Crystals
- Covalent or Network Crystals
- Molecular Crystals
- Metallic Crystals
- Group VIII Crystals (frozen Noble Gases)

The 7 Crystal Systems

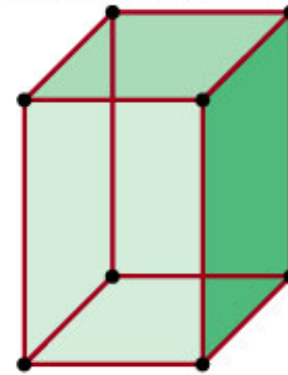
All 3D crystals belong to one of 7 *crystal systems*.



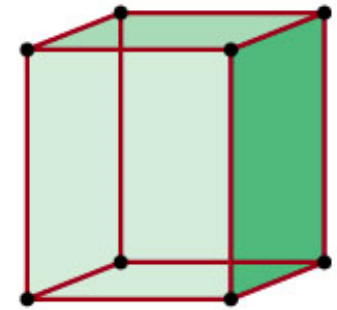
Cubic
 $a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$



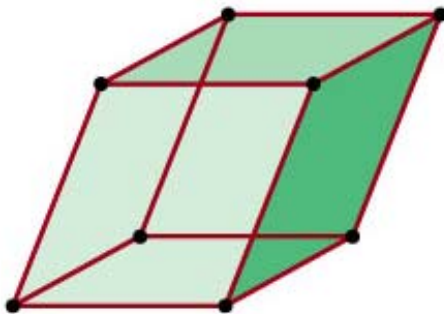
Tetragonal
 $a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



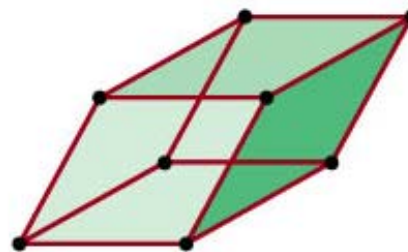
Orthorhombic
 $a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



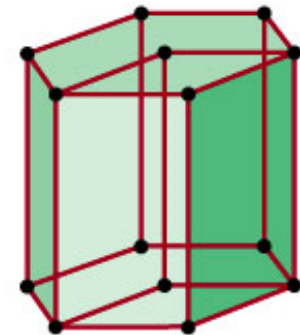
Monoclinic
 $a \neq b \neq c$
 $\gamma \neq \alpha = \beta = 90^\circ$



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



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

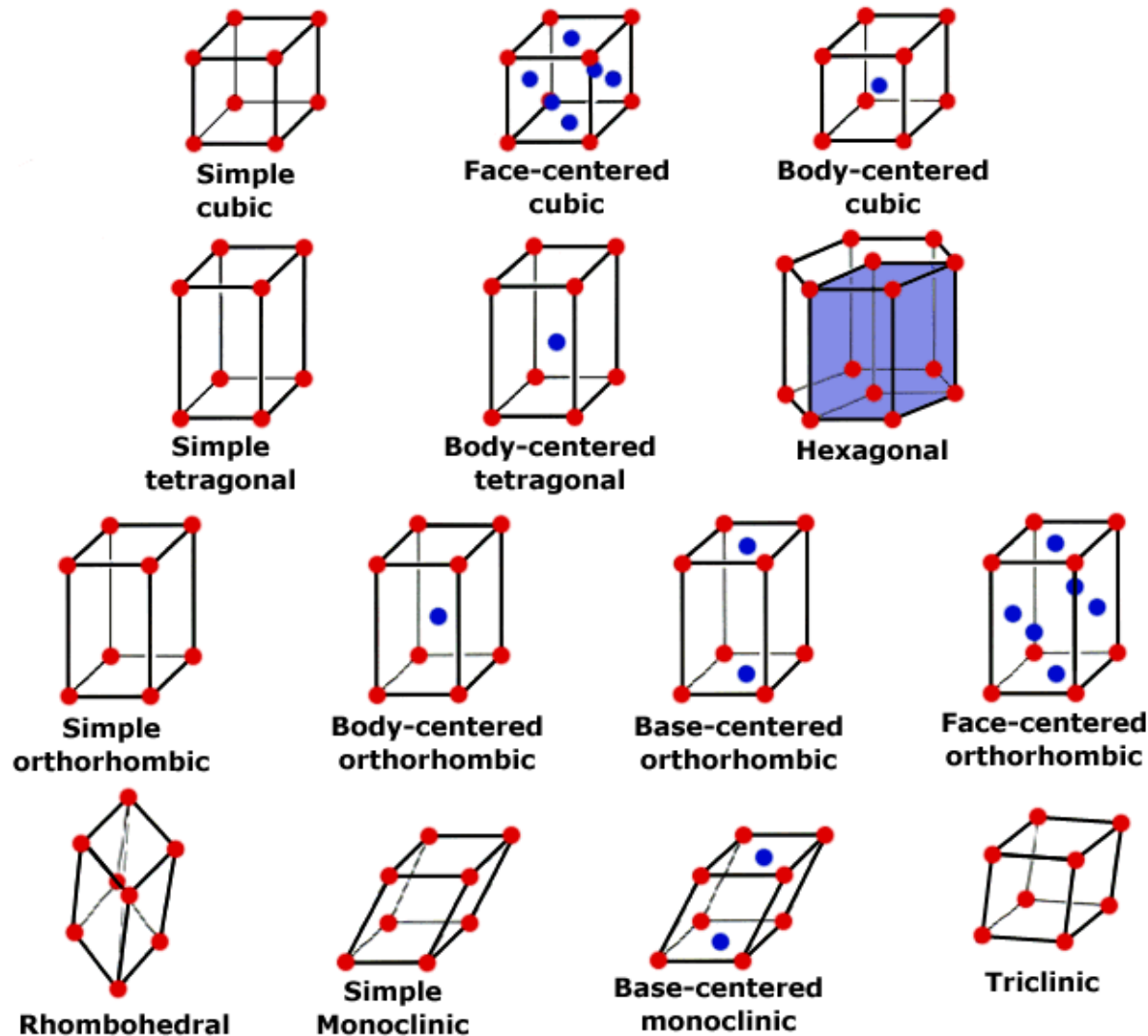


Hexagonal
 $a = b \neq c$
 $\alpha = \beta = 90^\circ, \gamma = 120^\circ$

The 14 Bravais Lattices

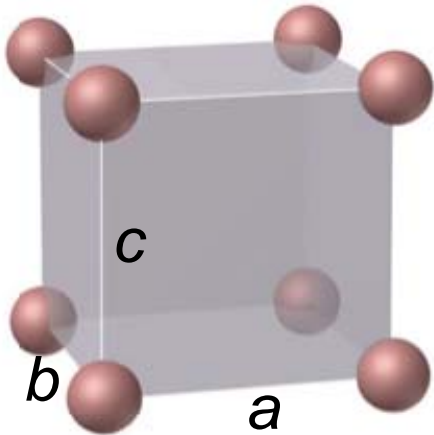
All 3D crystals belong to one of 14 Bravais lattices.

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

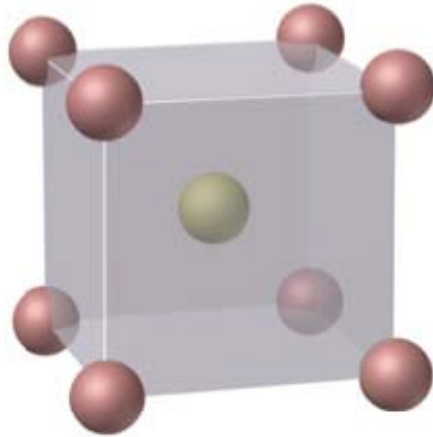


Types of Cubic Lattices

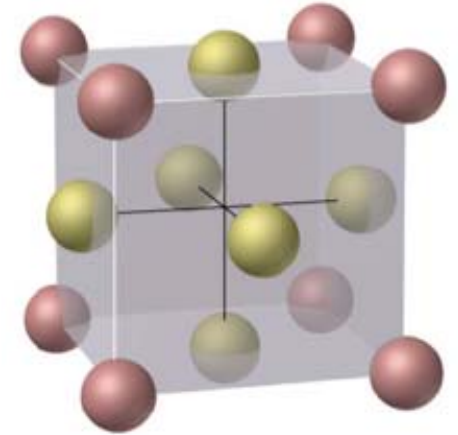
There are three cubic Bravais lattices:



Simple Cubic



Body-Centered Cubic



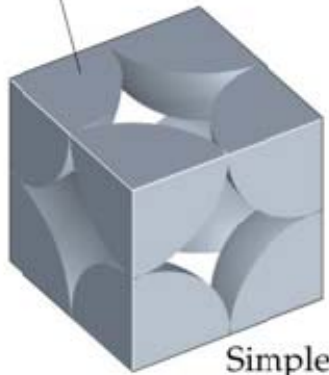
Face-Centered Cubic

- 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.

$\frac{1}{8}$ atom at
8 corners



Simple cubic

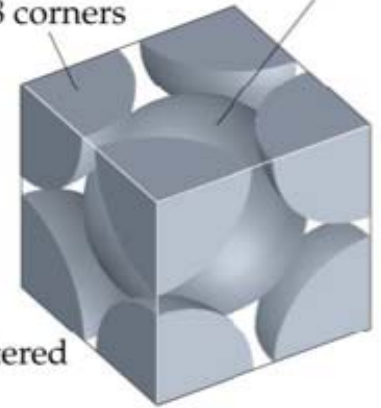
$$8 \cdot \text{atoms} \times \frac{1}{8} \cdot \text{occupancy}$$

1 atom in a
Simple Cubic cell

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

2 atoms in a
Body-Centered
Cubic cell

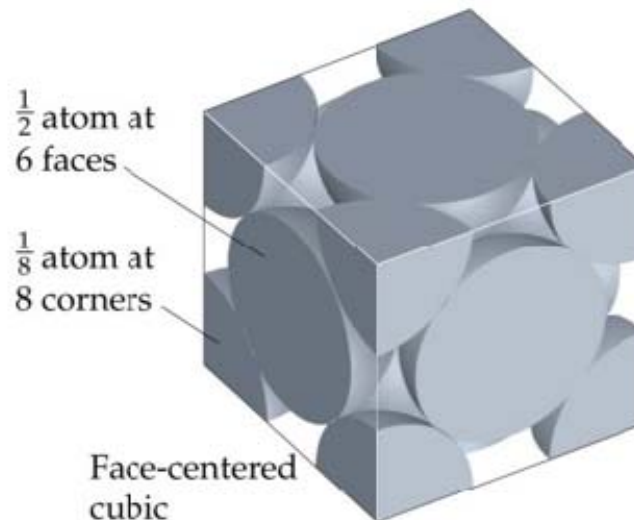
$\frac{1}{8}$ atom at
8 corners
1 atom
at center



Body-centered
cubic

$\frac{1}{2}$ atom at
6 faces

$\frac{1}{8}$ atom at
8 corners



Face-centered
cubic

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

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

corner

face center

body center

edge center

Shared Between:

8 cells

2 cells

1 cell

4 cells

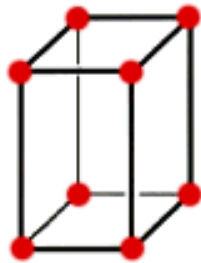
Each atom counts:

1/8

1/2

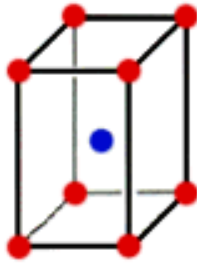
1

1/4



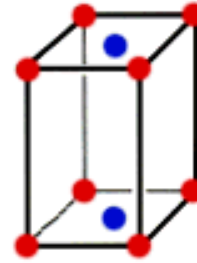
**Simple
orthorhombic**

$$8 \times 1/8 = 1$$



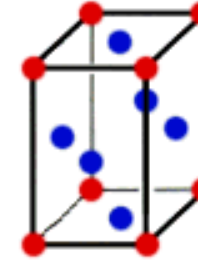
**Body-centered
orthorhombic**

$$8 \times 1/8 \\ + 1 \times 1 = 2$$



**Base-centered
orthorhombic**

$$8 \times 1/8 \\ + 2 \times 1/2 = 2$$

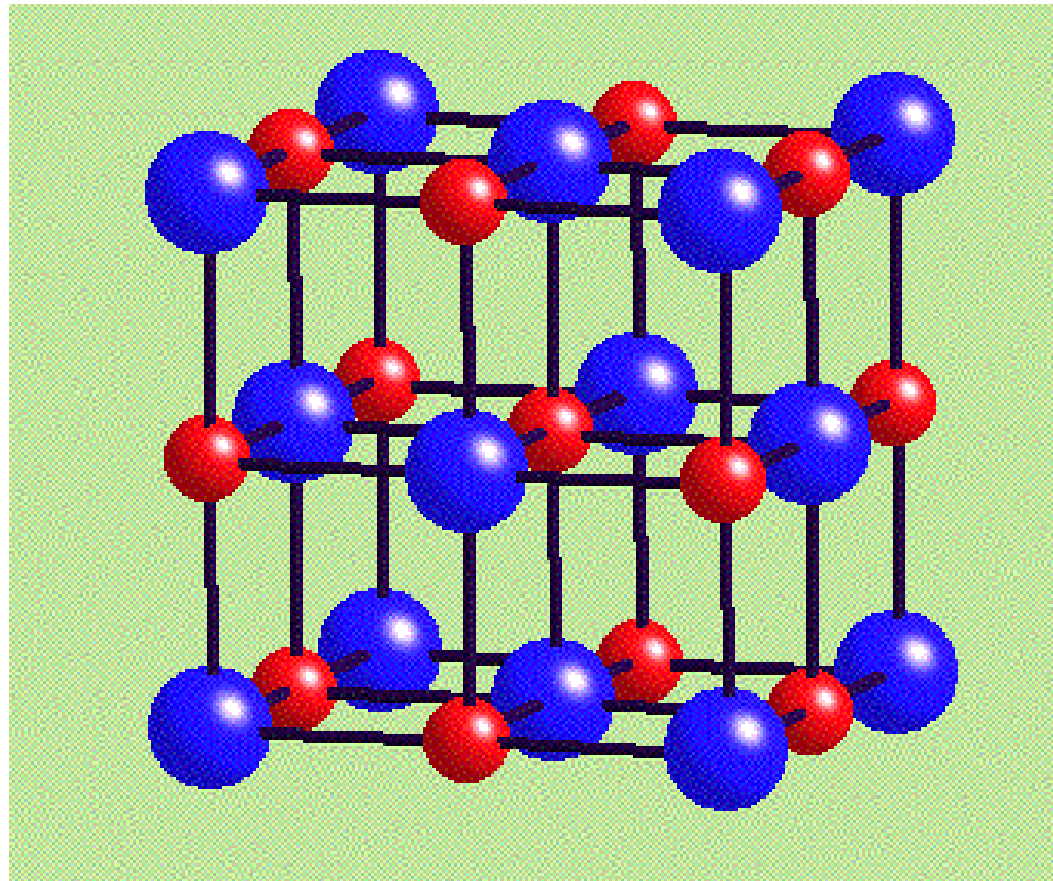


**Face-centered
orthorhombic**

$$8 \times 1/8 \\ + 4 \times 1/2 = 4$$

Contents of a Unit Cell

Consider
sodium chloride:
rock salt
(not Bravais)



Cl at corners: $(8 \times 1/8) = 1$

Na at edge centers $(12 \times 1/4) = 3$

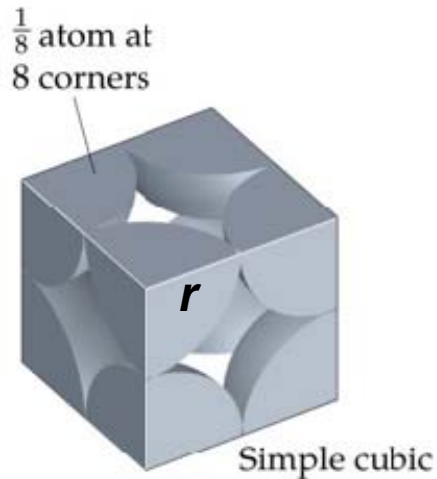
Cl at face centres $(6 \times 1/2) = 3$

Na at body centre = 1

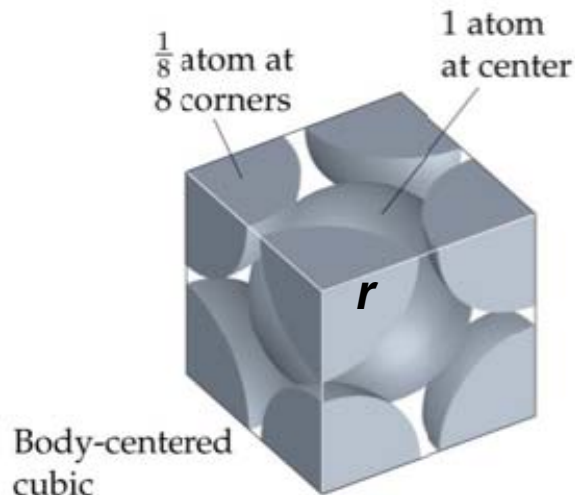
Unit cell contents: $4(\text{Na}^+\text{Cl}^-)$

Types of Cubic Cells

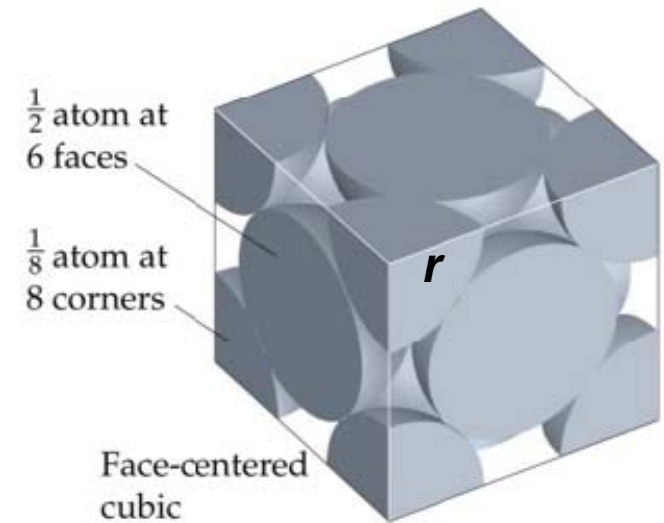
Different cubic cells result from different packing of atoms.



Simple Cubic



Body-Centered Cubic



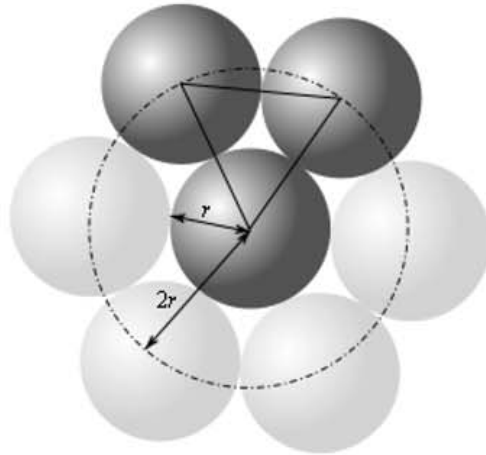
Face-Centered Cubic

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)



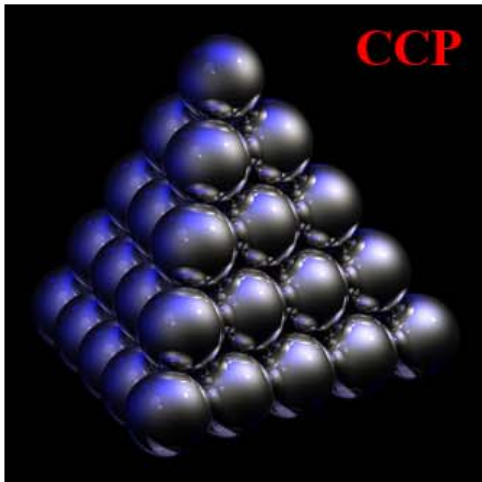
**Most efficient way
to pack spheres of single size**

- *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

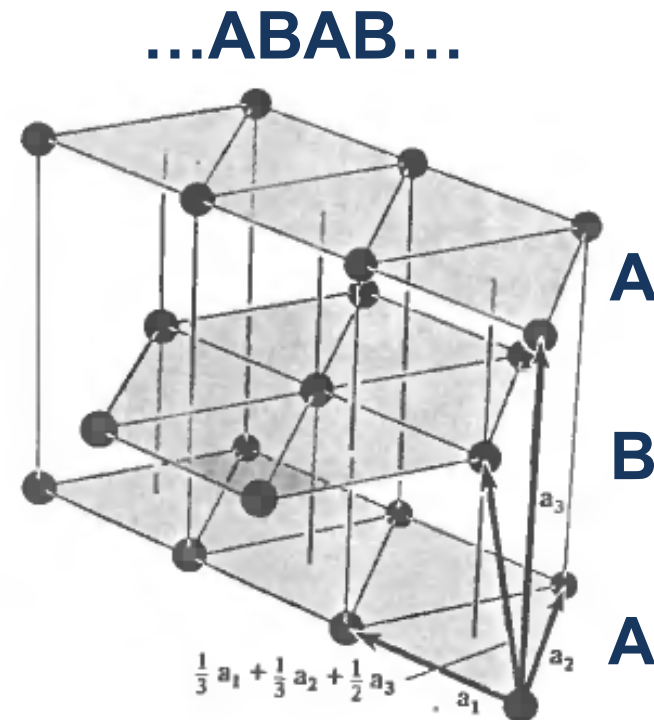
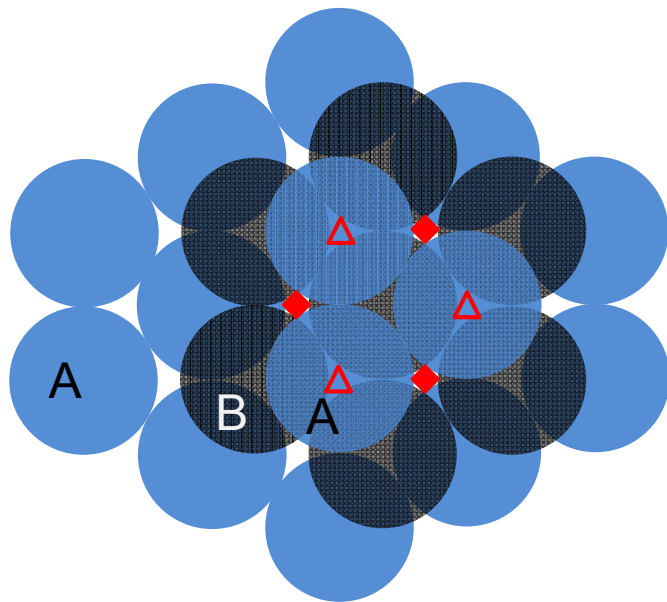
An HCP crystal is a close-packed structure with the stacking sequence ...ABABAB...

To construct:

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

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

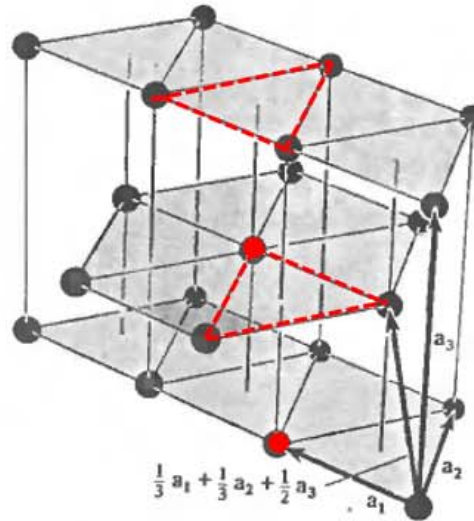
3rd layer: HCP layer positioned directly above 1st layer (repeat of layer A)



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

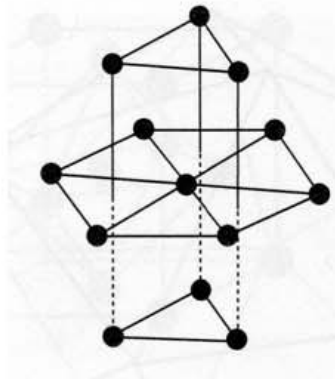
The Hexagonal Close-Packed Structure

- *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...

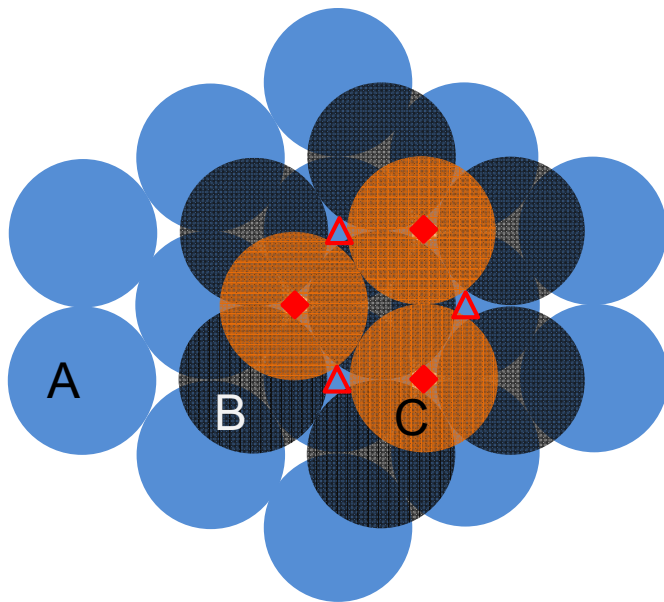
To construct:

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

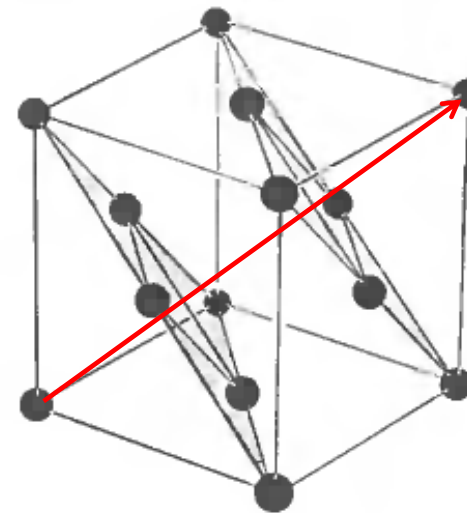
2nd layer: HCP layer with each sphere placed in alternate interstices in 1st layer (B)

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

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



...ABCABC...

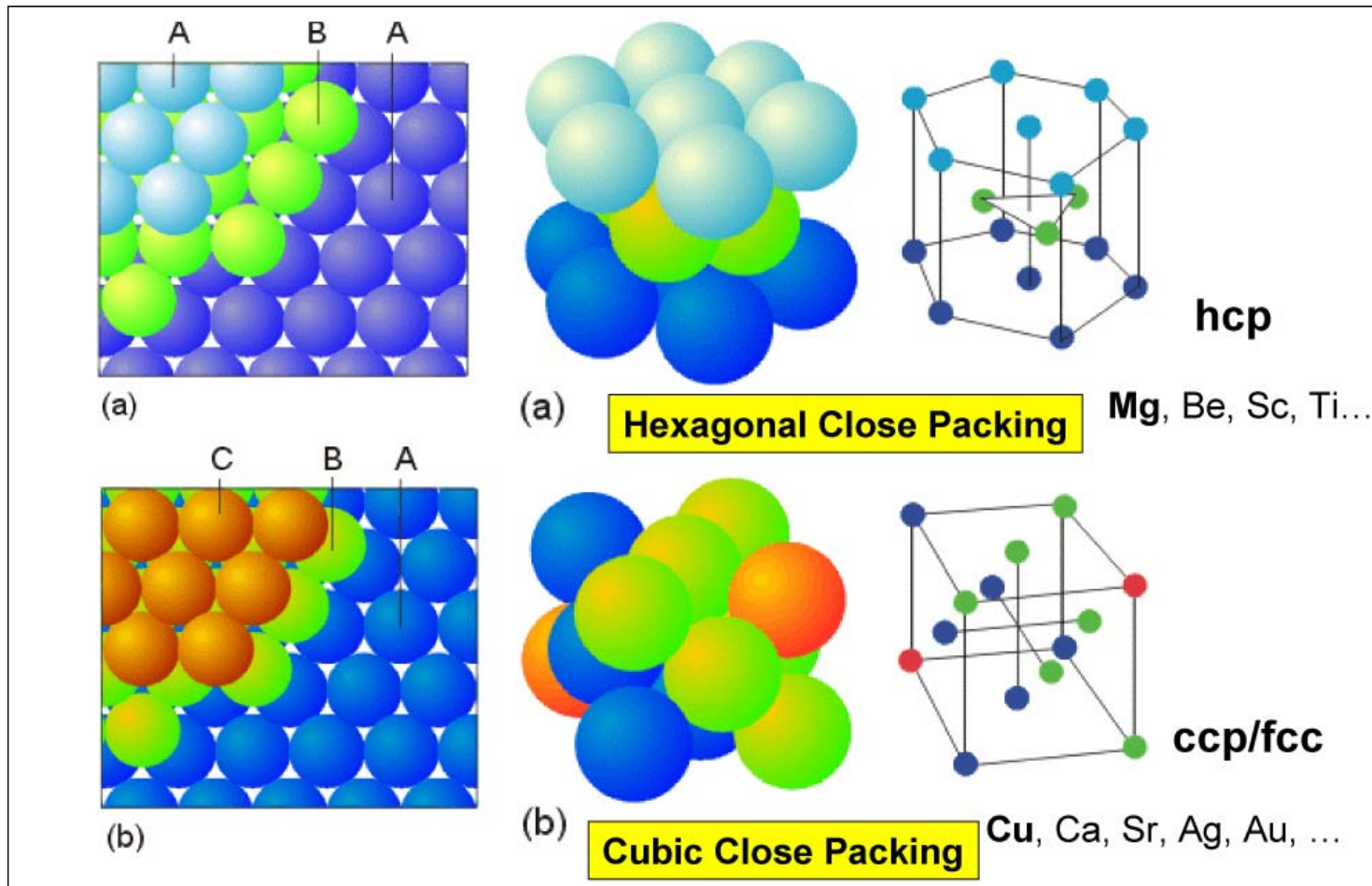


stacking
of HCP layers
along
body diagonal

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	$M / \text{g mol}^{-1}$	Melting Point / $^{\circ}\text{C}$
Kr	83.80	-157
Cu	63.55	1083
C (diamond)	12.01	3500

1 1A	2 2A	Hexagonal close-packed										Body-centered cubic		Other structures (see caption)					18 8A
		Face-centered cubic						8B				13 3A	14 4A	15 5A	16 6A	17 7A			
Li	Be	Mg										Al							
Na	Mg											Ga							
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn								
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn						
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb						

