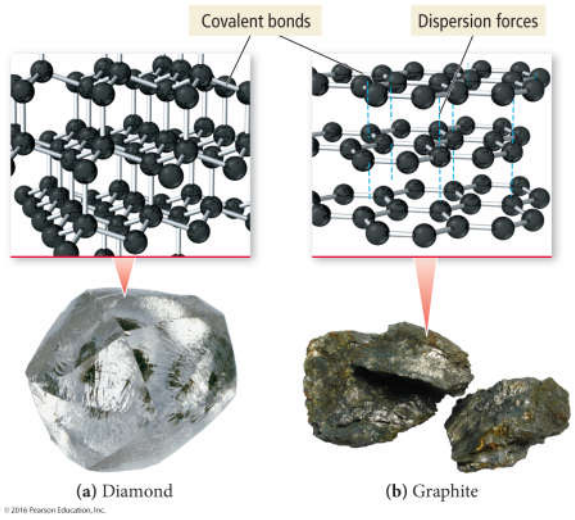
General Chemistry II
Chapter 13

Dr. Daniel T. de Lill

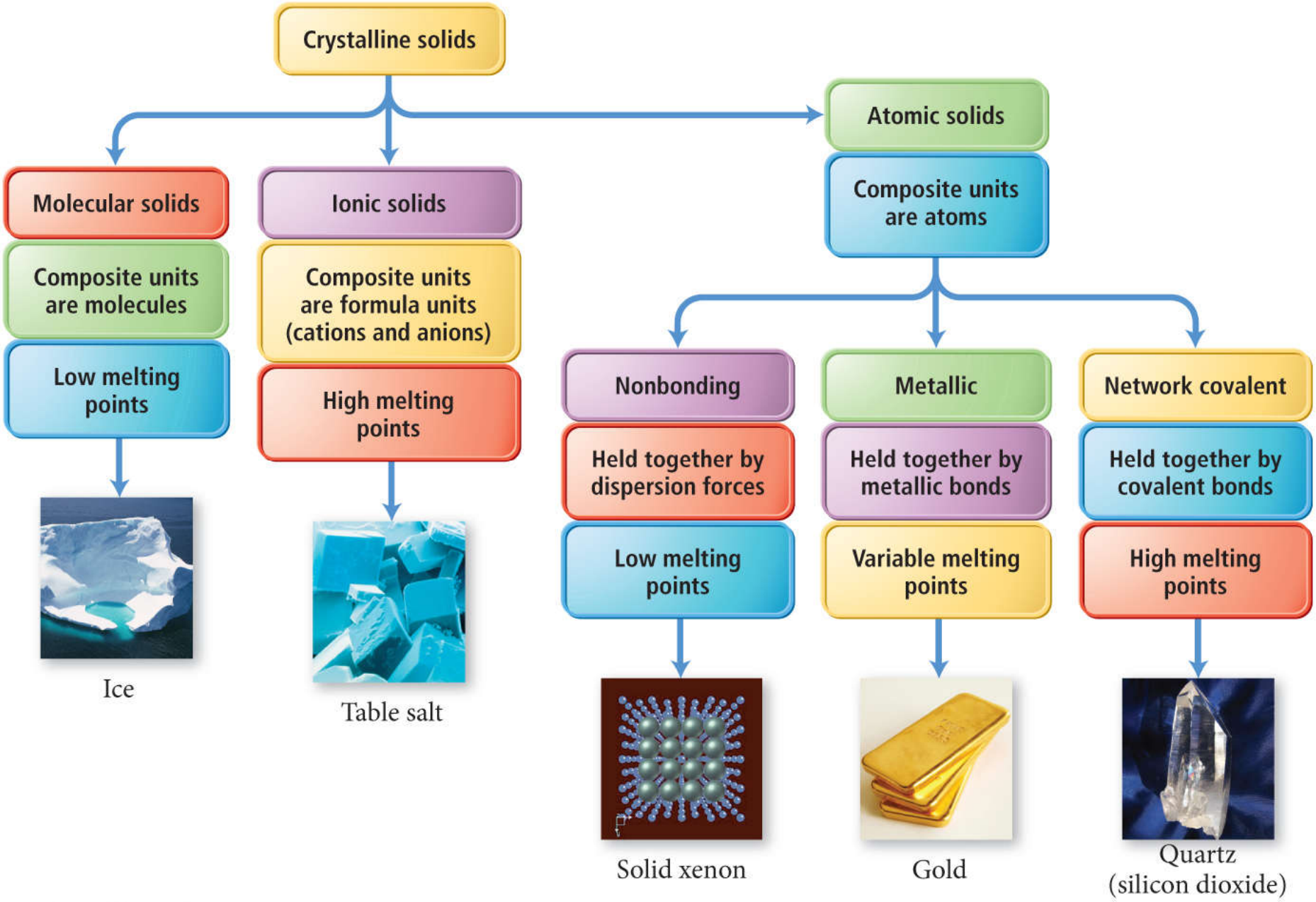
Nova Southeastern University





Solid State Chemistry & Materials Chemistry

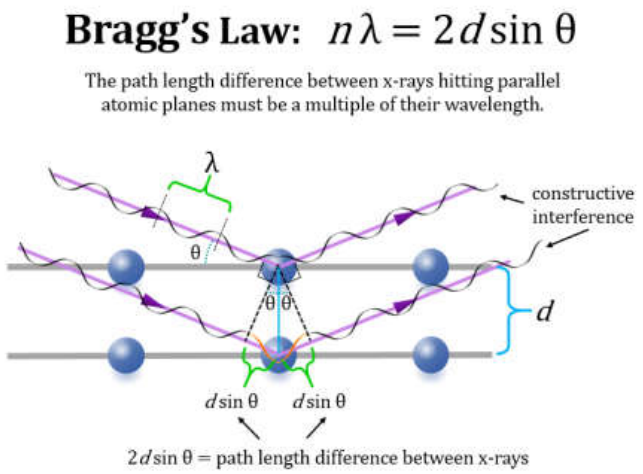
- Solid State Chemistry
  - Chemistry of materials in the solid state
- Materials Chemistry
  - The study and synthesis of compounds with unique and useful properties
  - Structure-Property Relationships

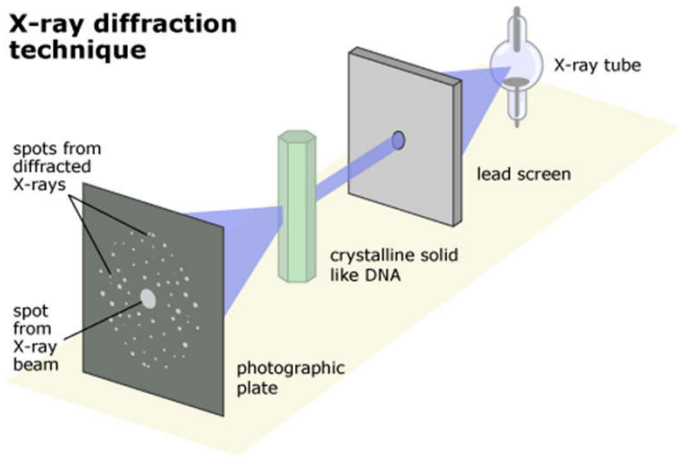


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X-Ray Crystallography

- X-Ray Diffraction
  - Technique used to determine the structure of solid, crystalline materials
  - Constructive/destructive interference
- Diffraction Patterns
  - Recall, light forms interference patterns if passed through a slit with a distance comparable to its wavelength
- Bragg's Law





https://cantorscience.org/2016/07/15/x-rays-arsenic-and-essie-top-coat/

http://undsci.berkeley.edu/article/0_0_0/dna_04

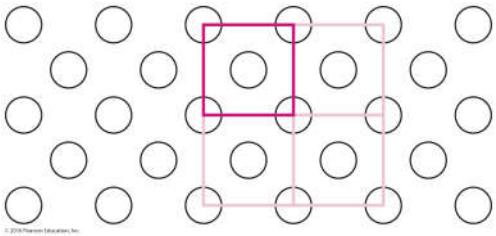
Example : Bragg's Law

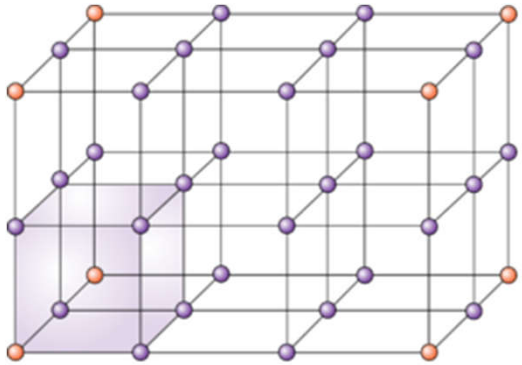
- When an X-ray beam of 154 pm is hits a crystal of Fe, maximum diffraction is seen at an angle of 32.6˚. Assuming n=1, what is the distance between layers in an Fe crystal?

DIC : Bragg's Law

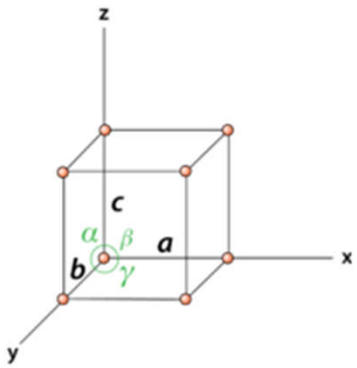
- Calculate the angle at which 154-pm X-ray will produce maximum diffraction (n=1) in Mo with d = 157 pm.

Unit Cells





Crystal Lattice



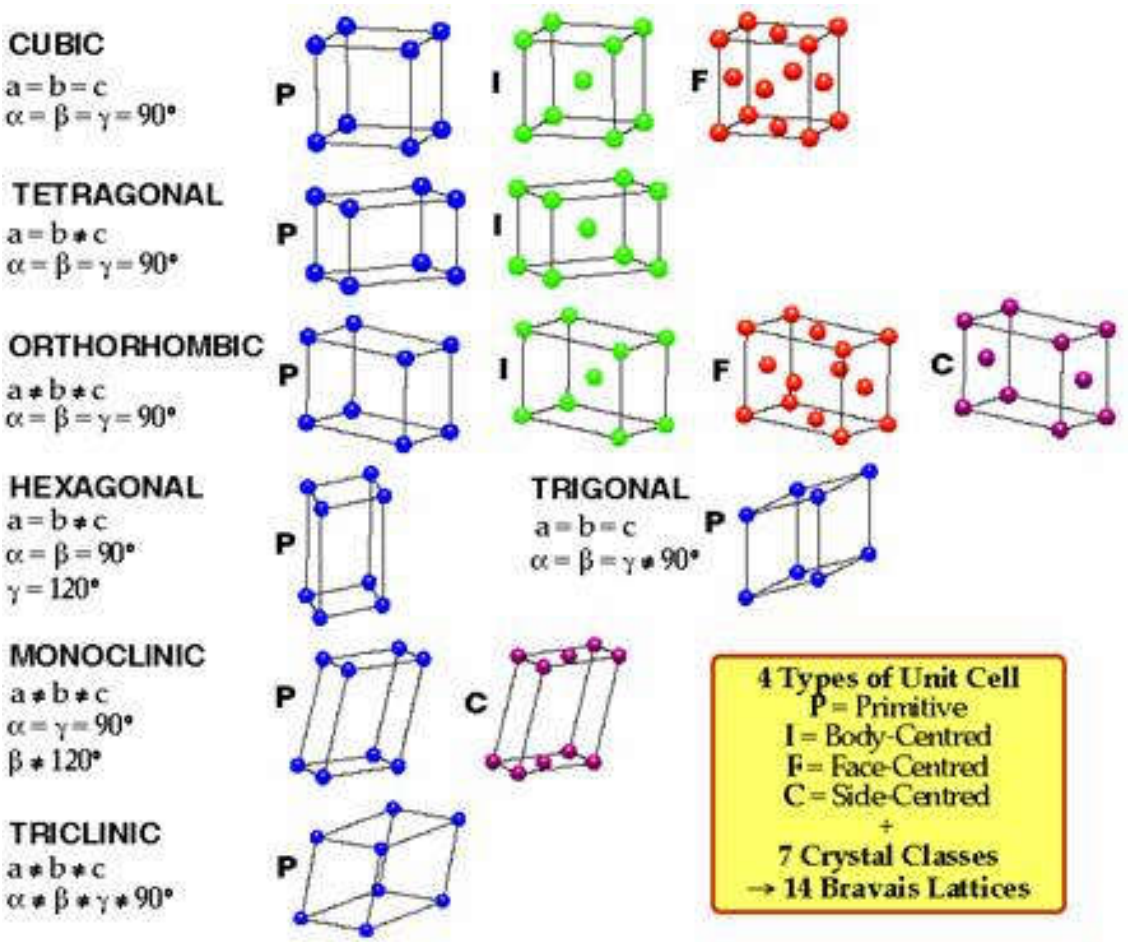
Unit Cell

- Crystalline Lattice
  - The regular arrangement of atoms within a crystalline solid
  - The smallest repeat unit of this collection of atoms that related to each other through translation only is called a unit cell
    - Translation = moving it right/left, up/down, and front/back
  - When repeated, the unit cell builds the entire crystal
  - Atoms within the unit cell are related to one another through some kind of pattern called symmetry
  - Unit cells are defined by six measurements – sides and angles (a, b, c, α, β, γ)

https://courses.lumenlearning.com/cheminter/chapter/unit-cells/

Seven Basic Crystal Classes

- All compounds will crystallize into one of seven fundamental unit cell types
  - If you incorporate possible centering, you obtain 14 Bravais lattices



http://www.asdlib.org/onlineArticles/ecourseware/Bullen_XRD/XRDModule_Theory_Crystallography_2.htm

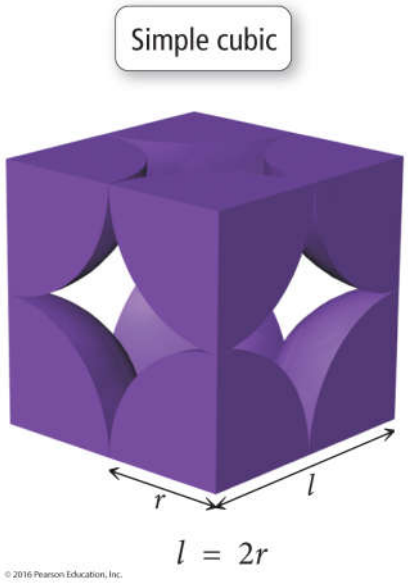
Cubic Unit Cells

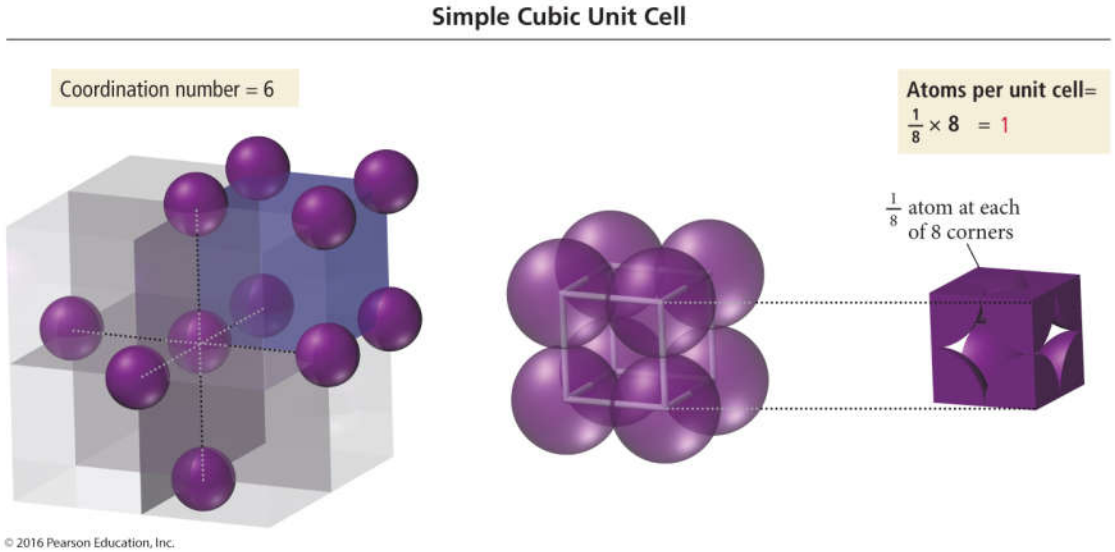
- Cubic : $a = b = c$; $\alpha = \beta = \gamma = 90^{\circ}$
- For our discussion here, all atom types are the same
  - Different colors are used only to help visualize
- Coordination Number
  - The number of atoms with which each atom is in direct contact
- Packing Efficiency
  - Percentage of the volume of the unit cell occupied by atoms

Simple (Primitive) Cubic Structure

- A cube with one atom at each corner
  - l = 2r
  - Contains 1 atom/unit cell
    - 8 x 1/8 of an atom
  - CN = 6
  - Packing efficiency is low, 52%
    - Inefficient packing

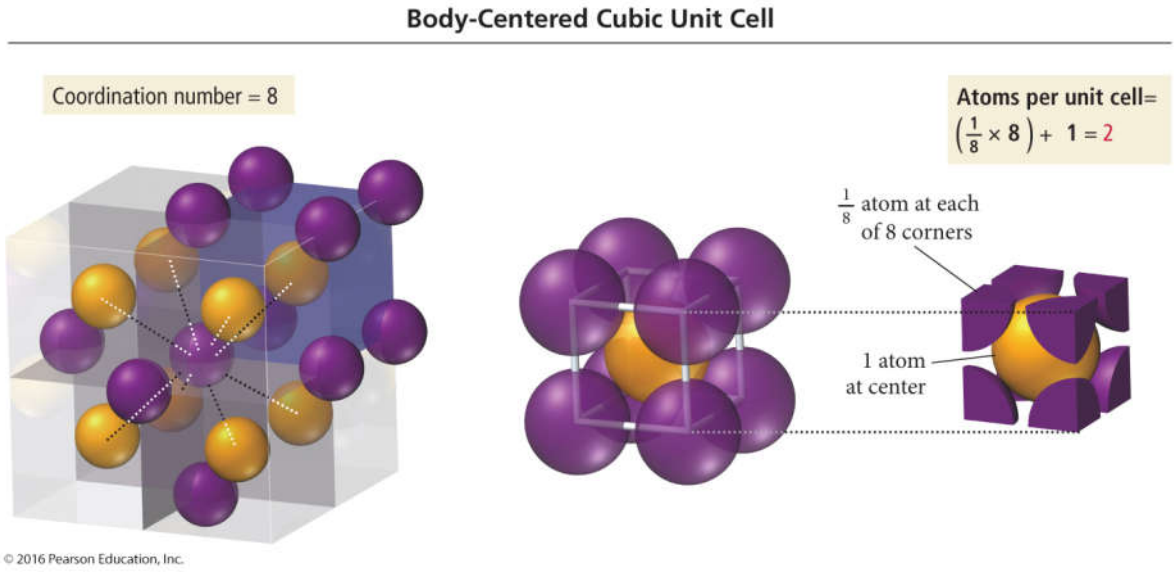
No need to memorize the formula for length, but the other details you should know for each of these structures

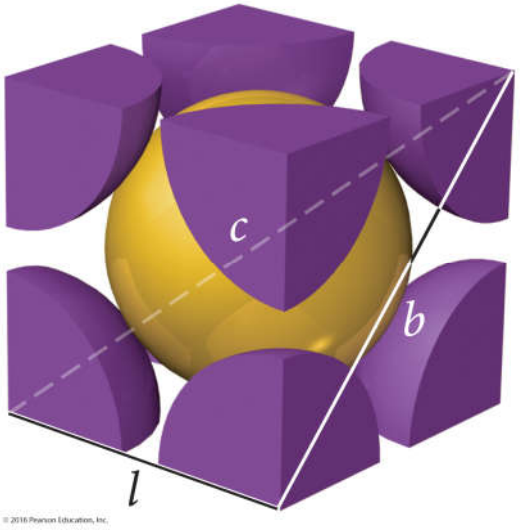




Body-Centered Cubic Structure

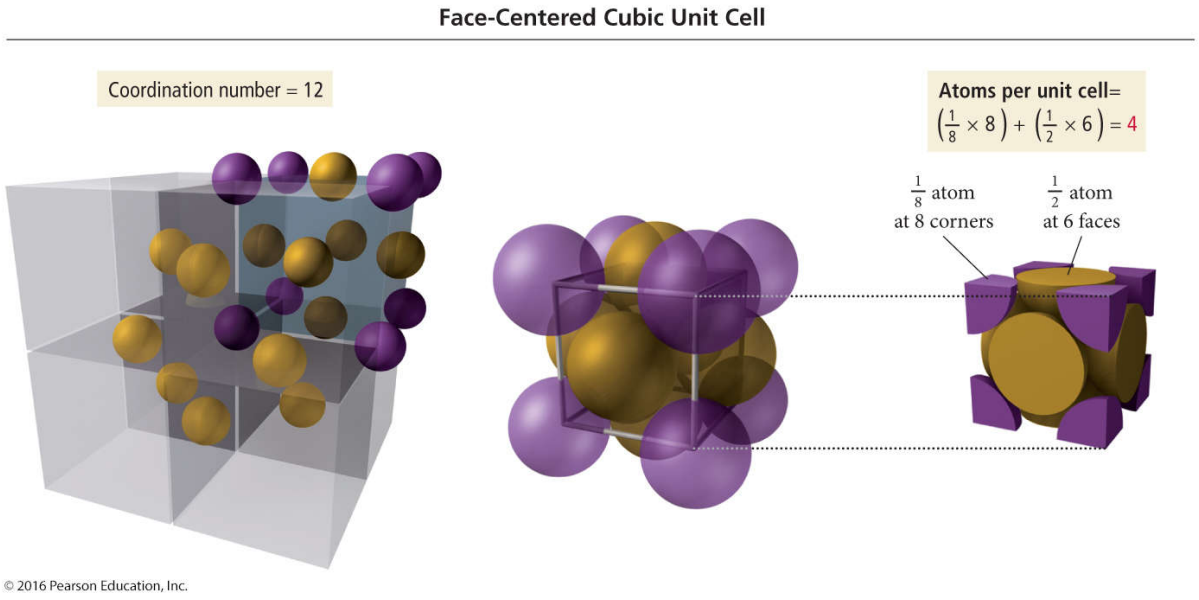
- Simple cubic structure with an extra atom directly in the cube's center
  - l = 4r/$\sqrt{3}$
  - Contains 2 atoms/unit cell
    - 8 x 1/8 of an atom in each corner + 1 atom in center
  - CN = 8
  - Packing efficiency is decent, 68%



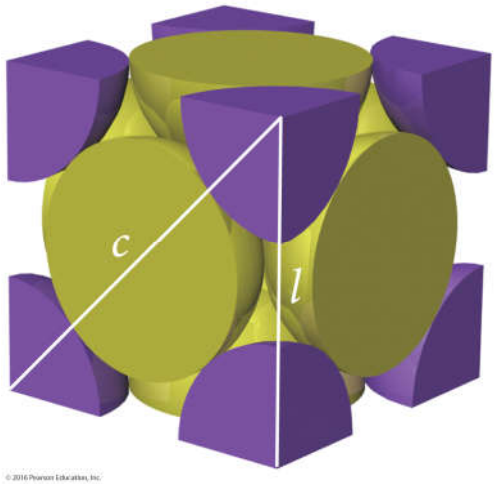


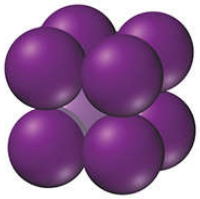
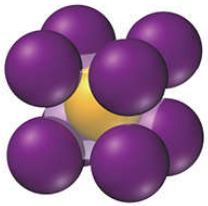
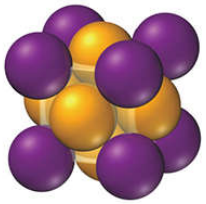
Face-Centered Cubic Structure

- Simple cubic structure with an atom in the center of each face of the cube
  - l = $2\sqrt{2}r$
  - Contains 4 atoms/unit cell
    - 8 x 1/8 of an atom in each corner + 6 x ½ of an atom in the center of each face
  - CN = 12
  - Packing efficiency is high, 74%

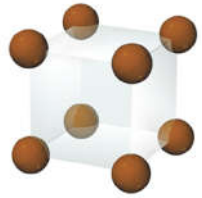


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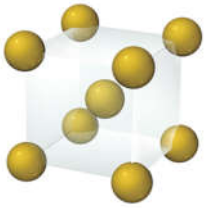


Cubic Cell Name	Atoms per Unit Cell	Structure	Coordination Number	Edge Length in terms of r	Packing Efficiency (fraction of volume occupied)
Simple Cubic	1		6	$2r$	52%
Body-centered Cubic	2		8	$\frac{4r}{\sqrt{3}}$	68%
Face-centered Cubic	4		12	$2\sqrt{2}r$	74%

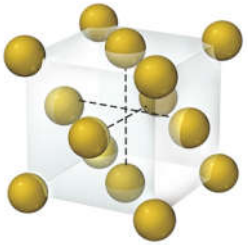
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a. Polonium



b. Tungsten



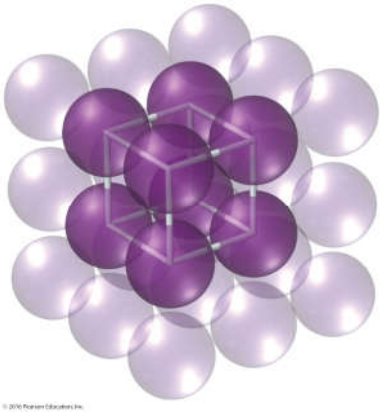
c. Nickel

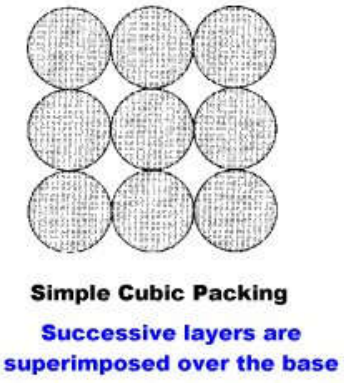
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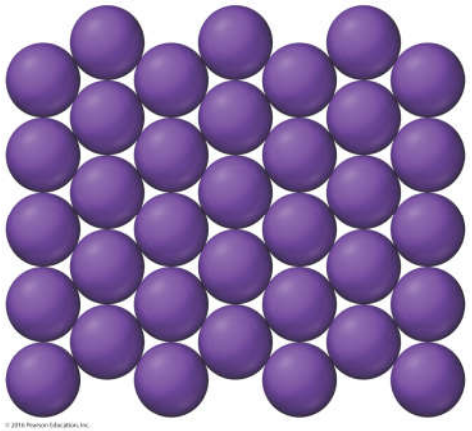
DIC – Explain the trend seen in the structures of Po, W, and Ni

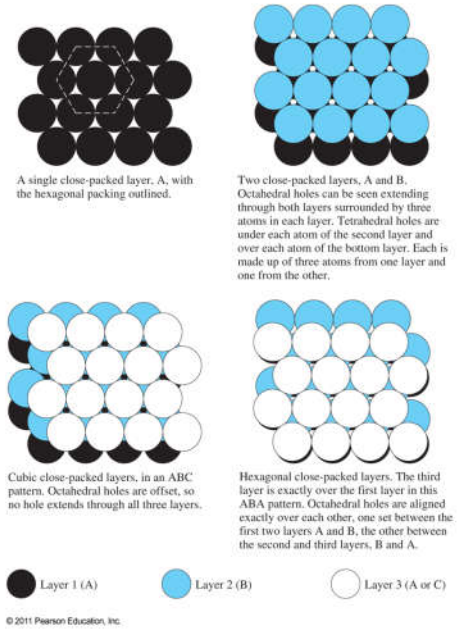
Close-Packed Structures

- Convenient to think of these atoms as lying in layers, especially for metals/ions who have nondirectional bonding
  - For primitive cubic structure, the layers are in a cubic array
    - Not an efficient way to form a monolayer from spheres
    - A hexagonal array works much better in packing
- They can stack in layers in two ways
  - ABABAB = HCP
  - ABCABC = CCP





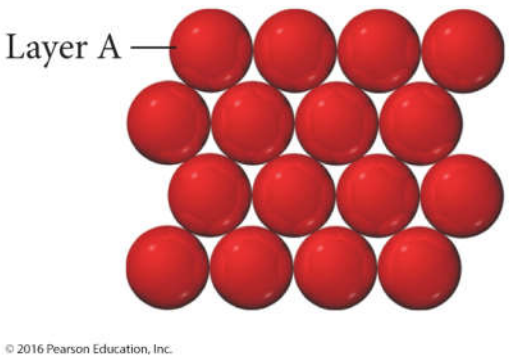




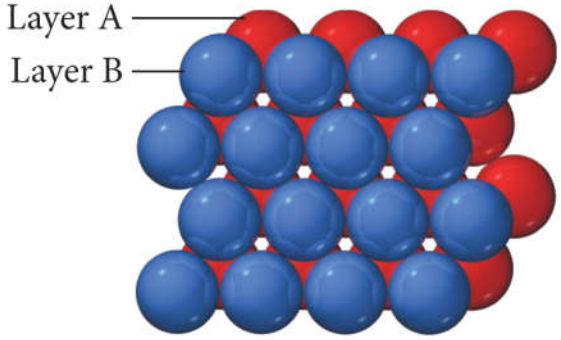
https://www.wou.edu/las/physci/ch412/lattice.html

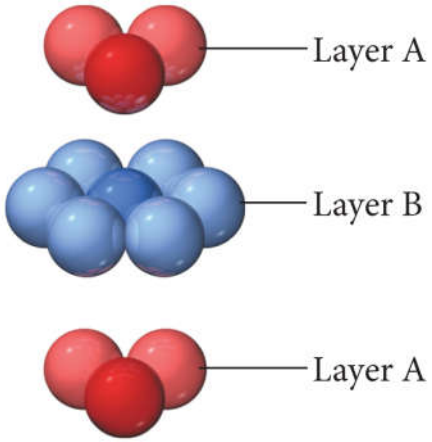
Close-Packed Structures : HCP

- ABAB stacking
- 74% packing efficiency
- CN = 12
- Hexagonal xtal class



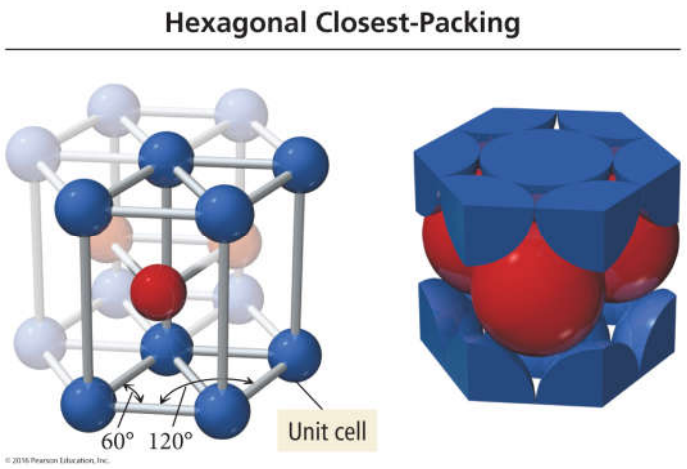
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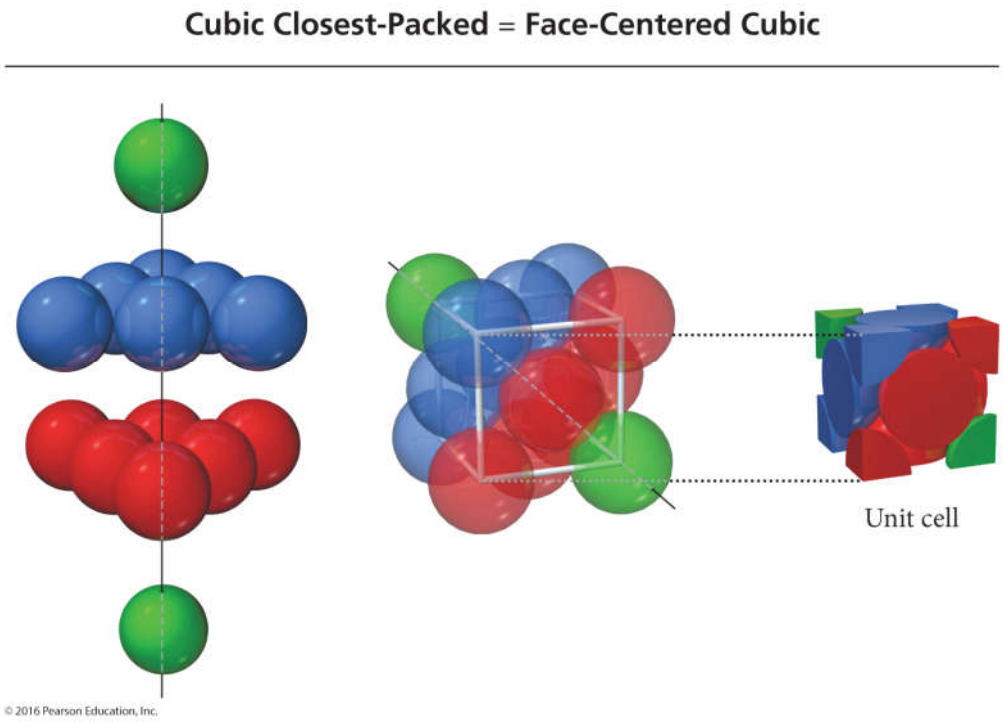
Hexagonal closest-packing

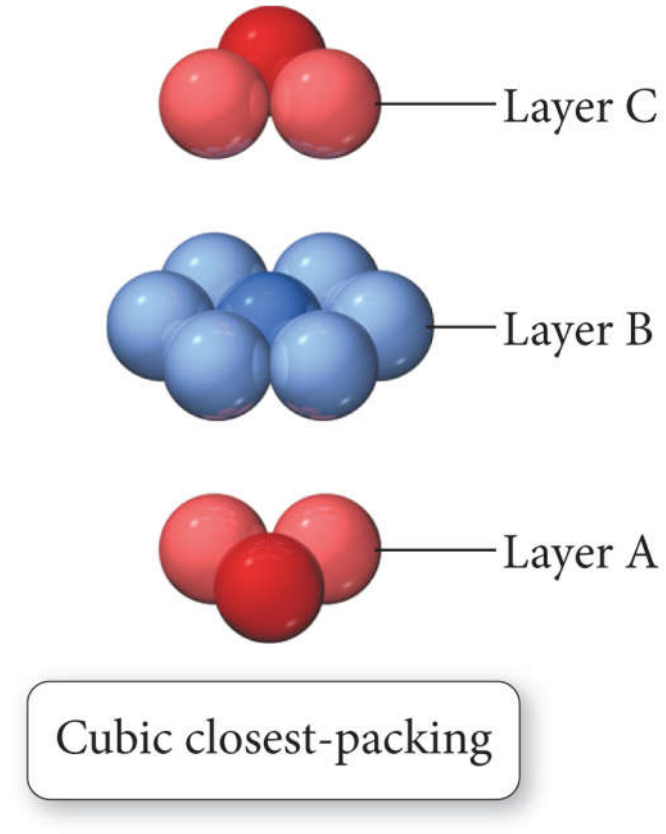
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Close-Packed Structures : CCP

- ABCABC stacking
- 74% packing efficiency
- CN = 12
- Cubic crystal class



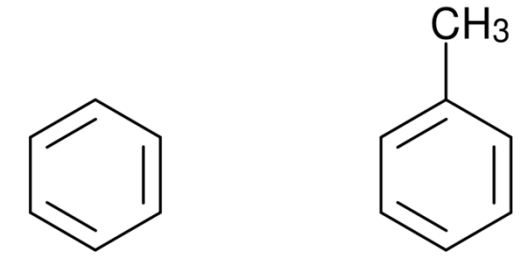


DIC – Crystal Structures

- Al crystallizes with an FCC unit cell. Al has a r = 143 pm. Calculate the density of solid crystalline Al in g/cm^3.

Molecular Solids

- Solids where the composite particles are made of molecules instead of atoms/ions
  - Ice, Dry Ice (H2O, CO2)
  - Held together by IM forces (LDF, H-bonds, Dipole-Dipole)
- Tend to have low to moderately low MPs
  - But, depends on IM forces
  - Benzene (78 g/mol, MP = 5.5 ˚C) vs. Toluene (92 g/mol, MP = -95.5 ˚C)
    - Extra methyl on toluene disrupts the packing efficiency
    - Toluene has higher mass but lower MP b/c its IM forces are weakened from the new packing



benzene toluene

https://en.wikipedia.org/wiki/BTX_(chemistry)

Molecular Solids : An Example

Journal of Molecular Structure 1104 (2016) 33–39

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journal homepage: http://www.elsevier.com/locate/molstruc

Structural, spectroscopic, and computational studies of [2,2′-bithiophene]-5-carboxylic acid

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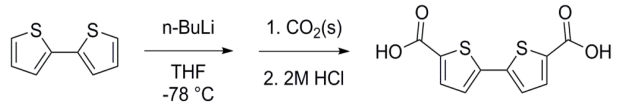
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ABSTRACT

The crystal structure of [2,2′-bithiophene]-5-carboxylic acid was obtained from *in-situ* decarboxylation of [2,2′-bithiophene]-5,5′-dicarboxylic acid during solvothermal treatment. UV–Vis absorption and fluorescence spectroscopies were conducted in solution and solid-state on these two molecules as well as the precursor, 2,2′-bithiophene. These molecules were modeled using DFT level of theory to explain the observed structural features and spectroscopy.

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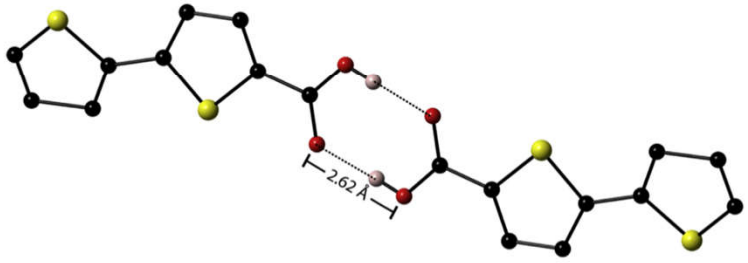


Fig. 1. Dimer unit of the title compound including interacting hydrogen atoms (white). Sulfur is yellow, carbon is black, and oxygen is red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Hydrogen bonding geometric parameters (Å, °).

Interaction	D···A	D-H	H···A	Angle
O(1)-H(1)···O(2)	2.621(3)	0.82	1.81	170

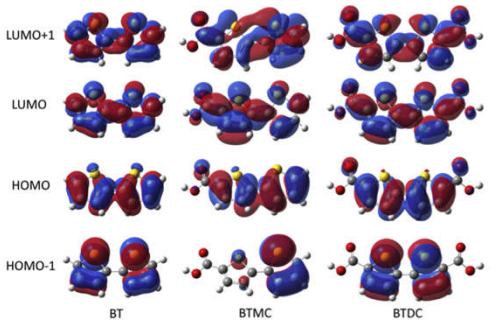
Table 4
Selected bond angles (°).

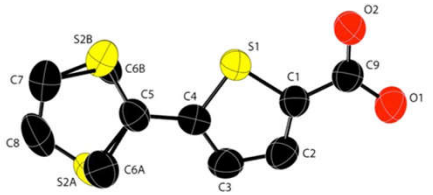
S(1)-C(1)-C(9)	119.35(18)
C(2)-C(1)-C(9)	129.5(2)
C(1)-S(1)-C(4)	91.94(11)
S(1)-C(4)-C(5)	120.14(18)
C(3)-C(4)-C(5)	129.4(2)

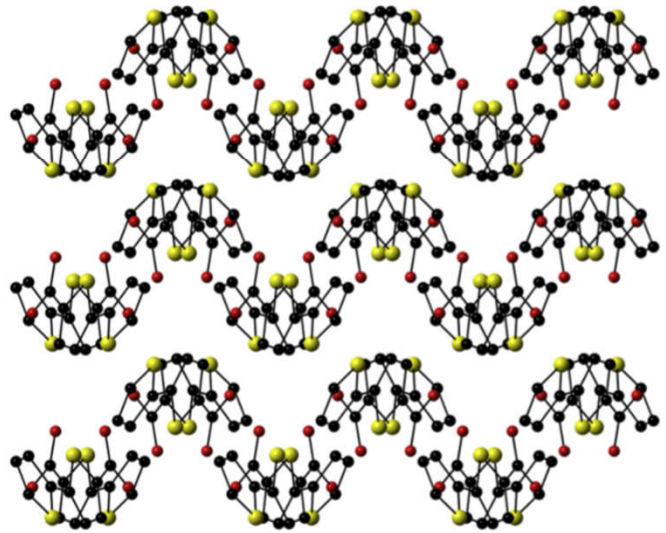
Table 1
Crystallographic information and structural refinements.

Formula	$C_9H_5O_2S_2$
Formula Weight (g/mol)	209.25
Crystal Class	Monoclinic
Space Group	*C* 2/c
a (Å)	20.4365(15)
b (Å)	12.3703(9)
c (Å)	7.2805(5)
α(°)	90
β(°)	96.508(2)
γ(°)	90
Z	8
Temperature (K)	293(2)
Cell Volume (Å^3)	1828.7(2)
Density (mg m^{-3})	1.520
μ (mm^{-1})	0.541
R_{int}	0.0305
R_1[a]	0.0428
wR_2[a]	0.1062
GOF	1.038
Total Reflections	1881

[a] $R_1 = \sum \frac{||F_o|-|F_c||}{|F_o|}$; $wR_2 = \left(\frac{\Sigma[w(F_o^2-F_c^2)^2]}{\Sigma[w(F_o^2)^2]}\right)^{\frac{1}{2}}$.

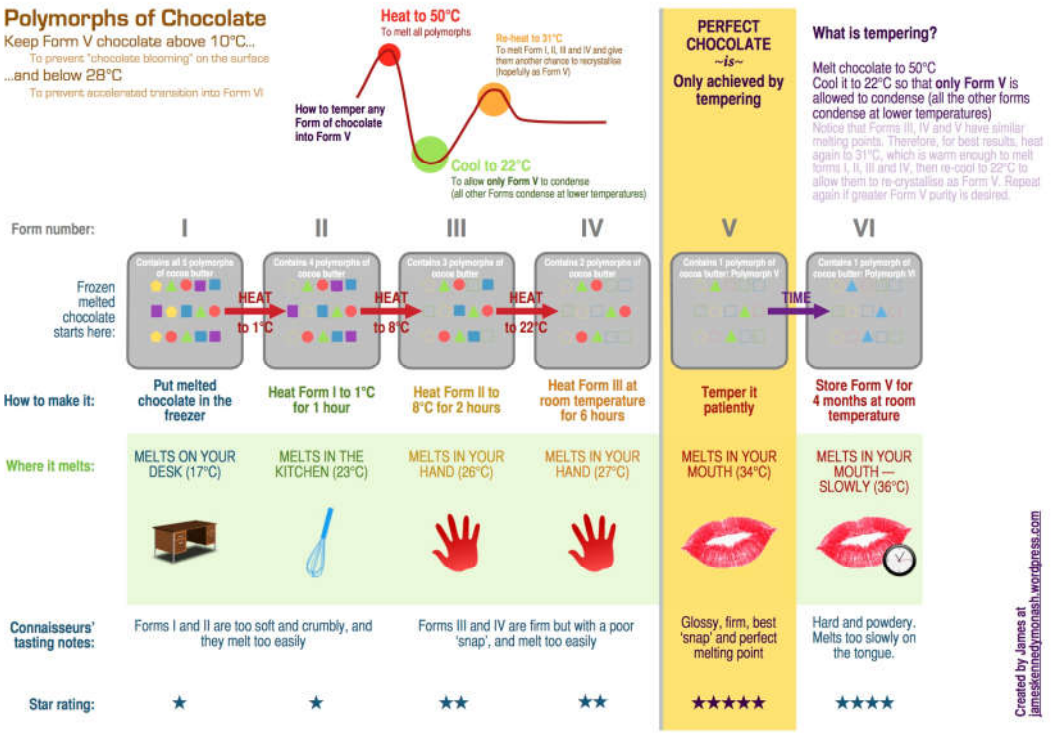


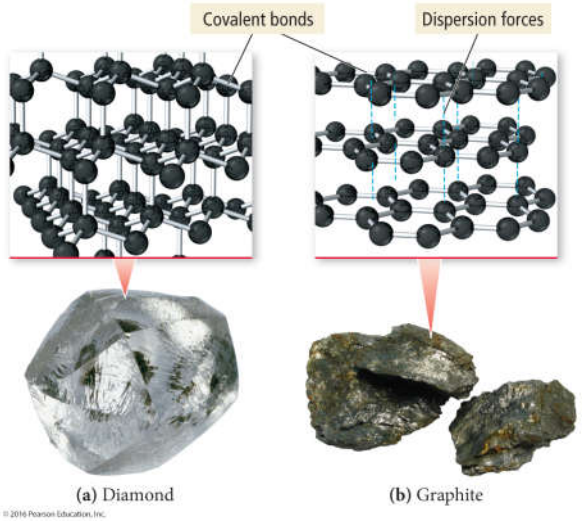




Polymorphs

- Compounds can sometimes crystallize in different structures
  - Same compound, but different solid state arrangements
  - Different packing, unit cells, and crystal classes
  - Different properties (MP, solubility, different pharmaceutical targets, etc.)





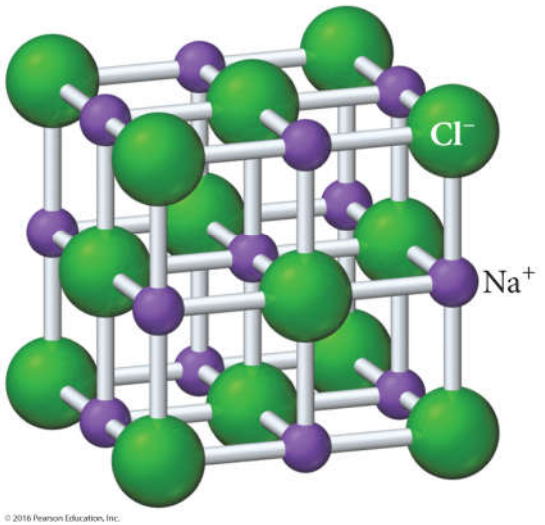
Polymorphs of elements are known as allotropes

https://jameskennedymonash.wordpress.com/polymorphs-of-chocolate/

Ionic Solids

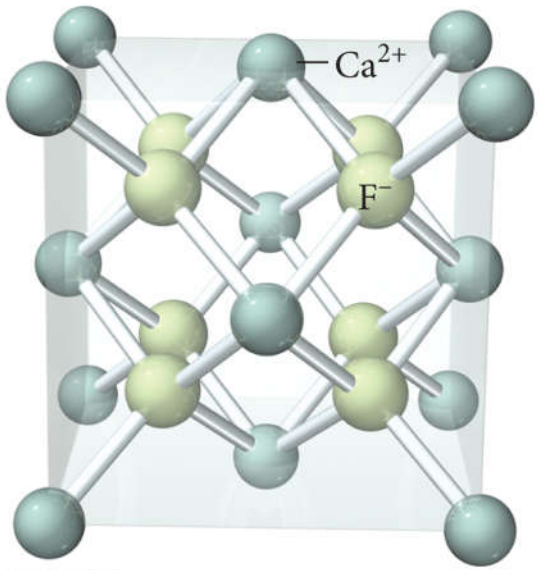
- Composite particles are ions
  - NaCl
  - CaF_2
- Held together by electrostatic (coulombic) forces
  - Much stronger than the IM forces in molecular solids
  - Usually much higher BPs than molecular solids

Sodium chloride (NaCl)



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Calcium fluoride (CaF_2)

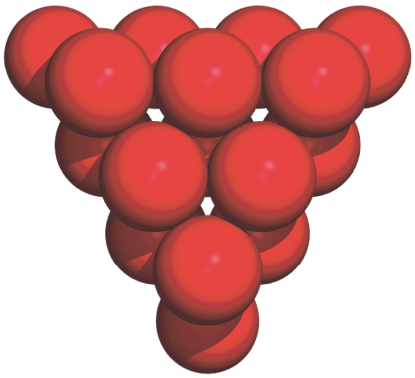


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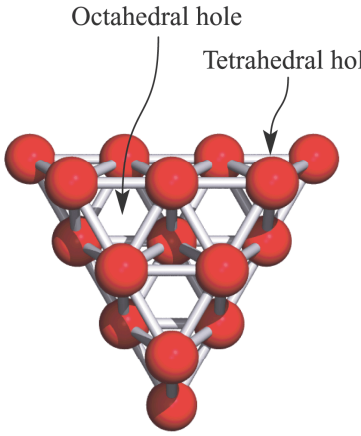
Structure of Ionic Solids

- Ionic structure is dependent on
  - Maximizing CN (more neighbors, lower the PE)
  - Maintaining charge neutrality (each unit cell much be electrically neutral)
  - Size ratio between the cation and anion
- Recall – Cations tend to be BIG and anions tend to be SMALL
- CsF, CaS – anion/cation similar in size – BCC array
- NaCl – Cl^- is almost 2x size of Na^+ – Primitive Cubic array; LiF, KCl, KBr, AgCl, MgO, CaO
- ZnS – S^{2-} is more than 2x size of Zn^{2+}, CN = 4
  - Zinc Blende structure
  - Sulfide anions in an FCC array with Zn ions in half of the tetrahedral holes
- When ratio of +/- ions are not 1:1, structure must adapt
  - Many 1:2 compounds form the fluorite structure
  - Ca ion for an FCC array with F ions in all tetrahedral holes
  - If ratio is 2:1, it is the anti-fluorite structure

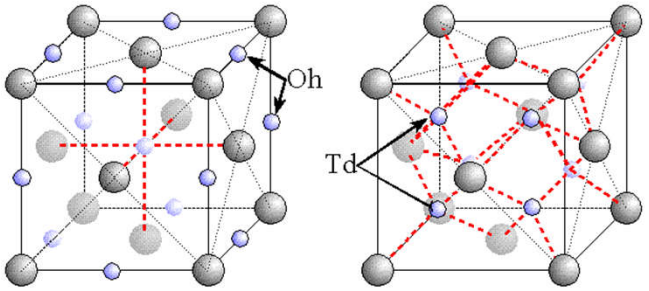
Holes



(a)

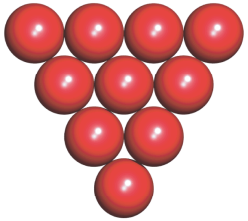


(b)



Face-Centered Cubic
Octahedral and Tetrahedral 'Holes'

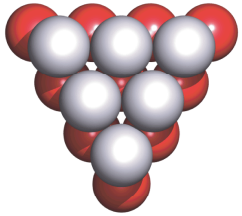
6.2



Layer A

(a)

Place one sphere over every other hollow in layer A

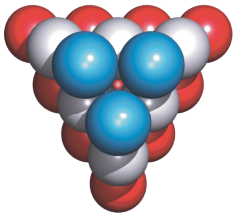


Layer A (red spheres)
Layer B (grey spheres)

Layer B contains two different types of hollow (see text)

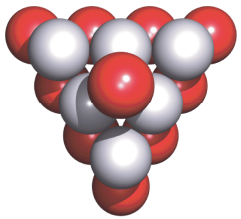
By placing spheres in one or other of these different hollows, two new layers of spheres can be produced.

(b)



Layer A (red spheres)
Layer B (grey spheres)
Layer C (blue spheres)

(c)



Layer A (red spheres)
Layer B (grey spheres)
Layer A (red sphere)

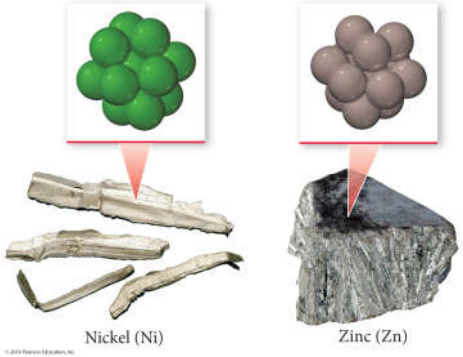
(d)

Three Types of Atomic Solids

Constituents = individual atoms; Xe, Fe, SiO_2 are some examples

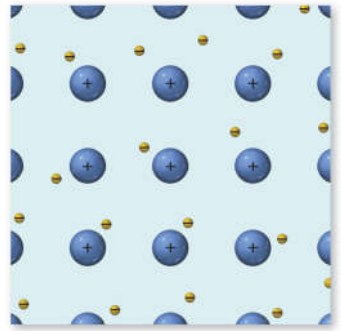
Nonbonding Atomic Solids

- Noble gases
- Weak dispersion forces
- Form close packed structures to maximize interactions
- Very low MPs that inc. uniformly with mass



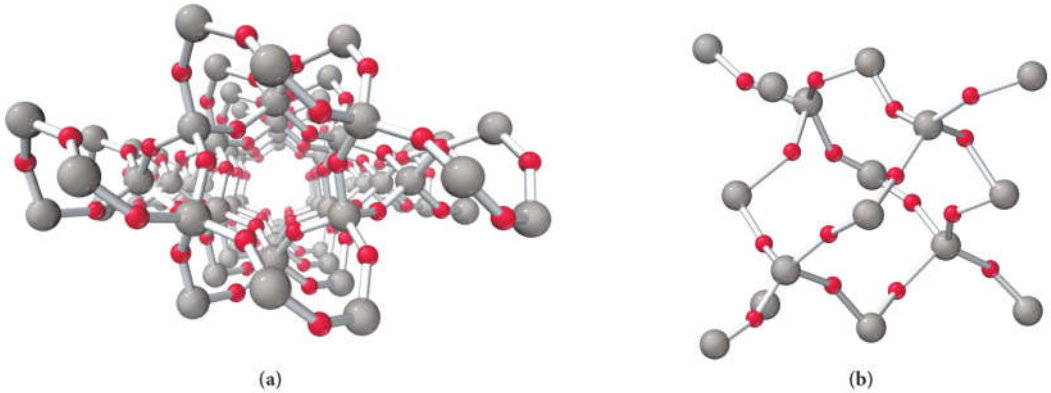
Metallic Atomic Solids

- Metals
- Metallic bonding
  - Metal cations surrounded by a "sea of e-'s"
- Nondirectional bonding – tends to form close packed structures
- Variable MPs



Atomic Solids Cont.

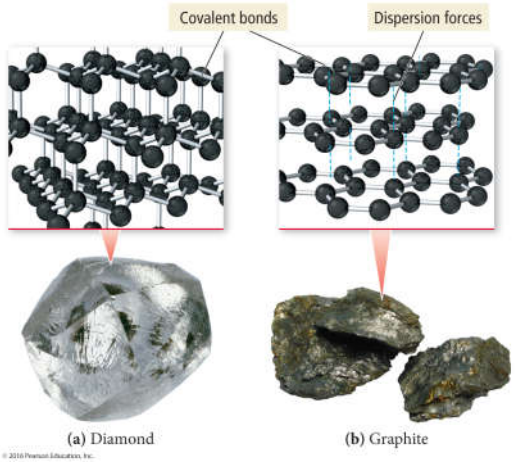
- Network Covalent Solids
  - Covalent bonds
  - Do not confuse with IONIC solid or MOLECULAR solids
    - No ions; these are atoms
    - No molecules, these are network solids
    - Like ionic structures, but with directional covalent bonds instead of nondirectional ionic bonds
      - This restriction on bonding directionality means that they tend NOT to form close packed structures
  - High MPs

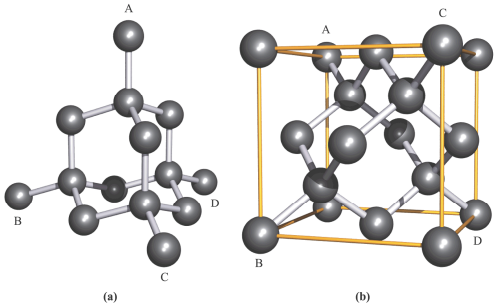


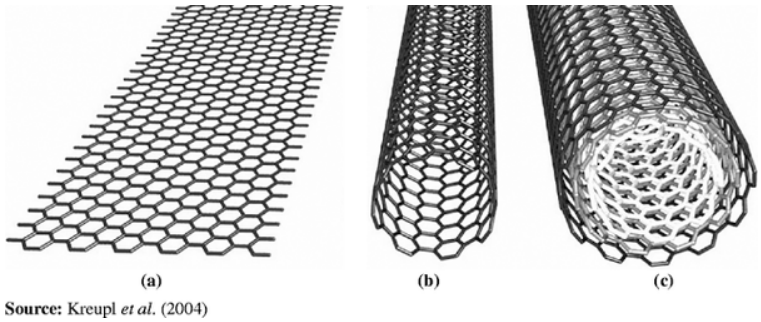
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Network Covalent Atomic Solids : Carbon

- Graphene, graphite
  - Hexagonally arranged C atoms, 142 pm bond distance, 2D sheets
  - No bonds between sheets
    - Weak LDFs, 341 pm apart
    - Sheets slide easily past each other – pencils
  - Good electrical conductor
    - Unbound pi e-
  - One Single layer = graphene
- Diamond
  - 3D network structure, C atoms in a tetrahedral arrangement
  - Nonconductor of electricity
    - All electrons are now used up for bonding
- Buckminsterfullerene
  - C atoms in pentagons and hexagons to produce a 20-sided icosahedral structure
  - Other fullerenes exist
- Carbon Nanotubes
  - Roll up a layer of graphene and cap the ends with buckyballs
  - 100xs stronger than steel, but much less dense
  - Good electrical conductor
  - https://www.youtube.com/watch?v=19nzPt62UPg

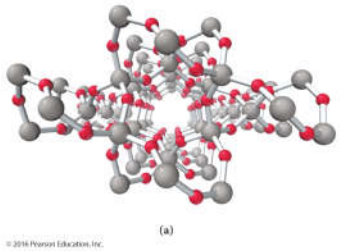


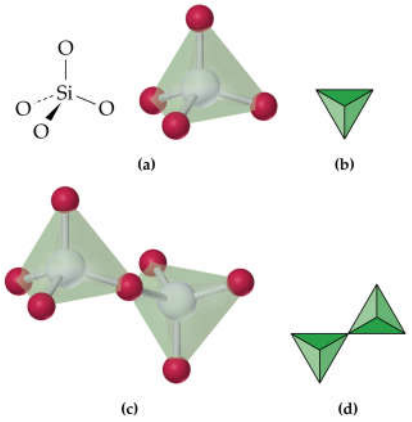




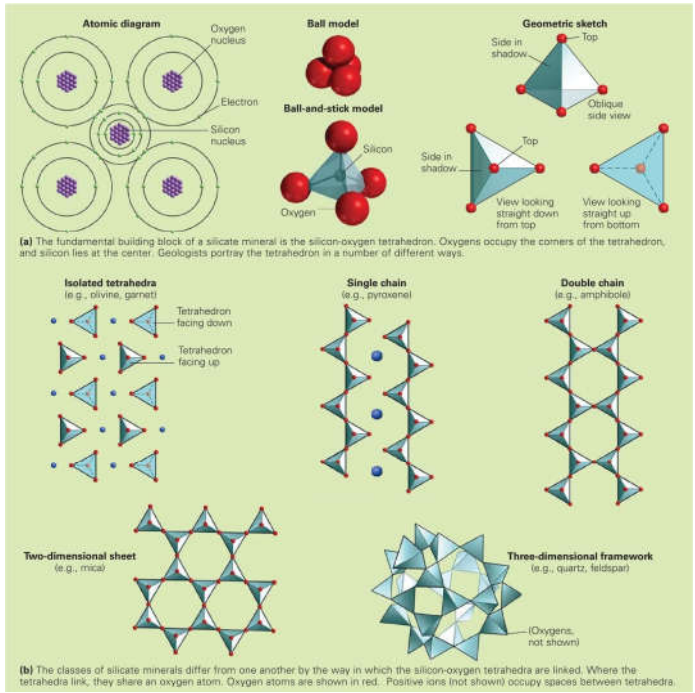
Source: Kreupl *et al.* (2004)

Network Covalent Atomic Solids : Silicates





- Si and O
- Most common network covalent atomic solids
  - Constitute ~90% of the Earth's crust
- Si bonds to 4 O to form a tetrahedron
  - Si is happy, but O does not have an octet
    - O will usually bind to a neighboring Si
- 3D = quartz (aka, silica)



http://wps.prenhall.com/wps/media/objects/602/616516/Chapter_19.html

http://geologylearn.blogspot.com/2016/02/mineral-classication.html

Ceramics

- Inorganic nonmetallic solids that are mixed with water, formed, and heated
  - Brittle, subject to thermal shock, break instead of bend
- Silicate Ceramics
  - Produced from aluminosilicate (some Si is replaced by Al) clays
  - Dishes; electrical insulators
- Oxide Ceramics
  - Al_2O_3; MgO
  - Good refractory materials – use in high Temp applications
- Nonoxide Ceramics
  - Si_3N_4, BN, SiC
  - Engine parts, nonmetallic ball bearings
  - BN = isoelectronic to C_2, so its structure mimics those of C
    - 2D = high T lubricant; 3D = abrasive; used for cutting tools

Cement

- Portland Cement is most common
  - Limestone ($CaCO_3$) and Silica (SiO_2), with some Al_2O_3, Fe_2O_3, and $CaSO_4 \cdot H_2O$
- Mix cement with sand and pebbles = concrete
  - About ½ of buildings in the world are made from concrete

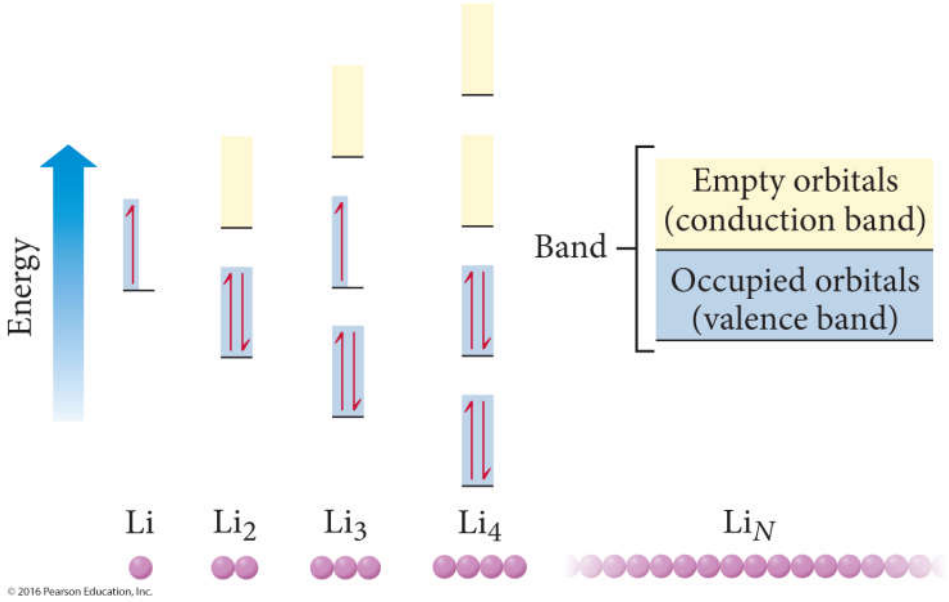
Glass

- When silica melts (T>1500 ˚C), it cools rapidly but does not recrystallize
  - The SiO change from ordered to random, going from crystalline to amorphous
  - Adding $Na(CO_3)^2$ greatly reduces the MP of the silica
- Vitreous (or fused) silica
  - Made from pure SiO_2; hard, resists high T, low thermal expansion, and transparent to visible and UV light
  - Expensive b/c of high T required
- Soda-lime glass
  - ~70% silica with Na_2O and CaO
  - Not transparent to UV light; cheaper to make; window glass
- Borosilicate glass (Pyrex)
  - Add boric oxide (B_2O_3) to soda-lime glass reduces the thermal shock that soda-lime glass is susceptible to
  - Better to withstand heating/cooling cycles without fracture; lab glassware
- Leaded glass (“crystal”)
  - Add PbO to the SiO_2
  - Increase index of refraction – more brilliant appearance; ringing sound when tapped
  - Potential toxicity from the Pb

Semiconductors

- Network solids that have variable and controlled conductivity
- Extend the concept of “sea of electrons” → Band Theory
  - Explains both metallic AND semiconducting behavior, whereas the “sea” only explains metallic conductivity
  - Treat the crystal like a giant molecule
    - “free” electrons are delocalized in orbitals that span the entire crystal structure

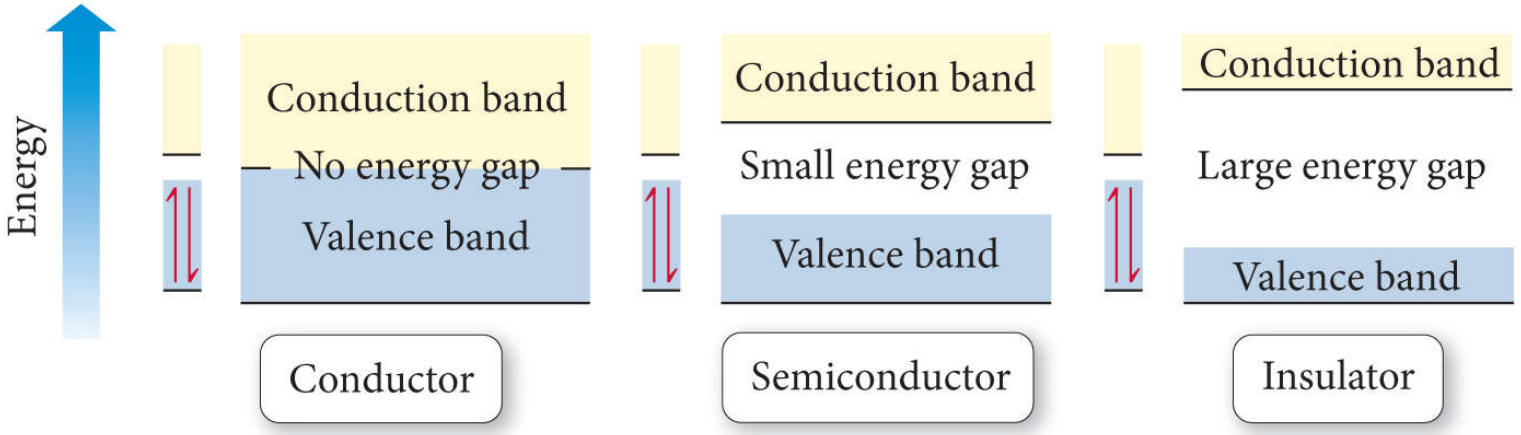
Band Theory



- Eventually, enough AOs are added that they merge into a continuous band
- Valence Band
  - Highest occupied band (~HOMO)
- Conduction Band
  - Lowest unoccupied band (~LUMO)
- Band Width
  - The energy range through which the band exists
- Band Gap
  - A gap between bands where no electron density is found

Types of Conductivity

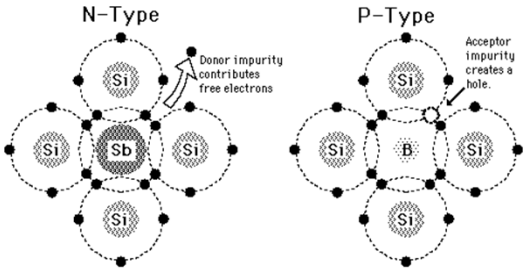
- In metals, the VB and CB overlap
  - No E gap, e- free to roam about in the CB
- Semiconductors have a small band gap
  - Inc. in T inc. population of the CB, inc. conductivity
- Insulators have large band gaps
  - Not enough E at typical temperatures to promote e- to CB

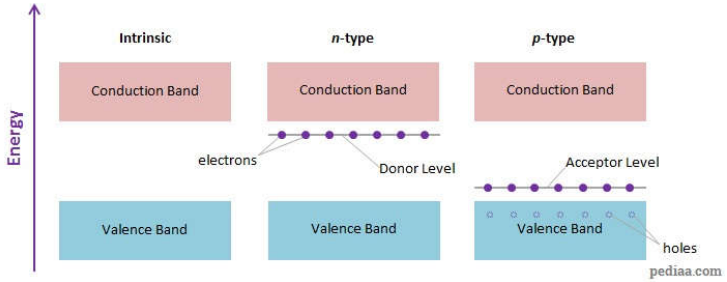


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Doping Effects on Conductivity

- Dopant – a tiny, non-stoichiometric “impurity” added to influence the properties of the bulk material
- n-type
  - n = negative; dopant donates excess e- in the CB
  - e.g., Si with tiny amounts (maybe 0.1%) of P
- p-type
  - p = positive; dopant is electron deficient, taking electrons out of the VB and leaving “holes” (absence of e-) in the VB
  - e- “hopping”
- p-n junction
  - Put a p and n semiconductor next to each other and you create an essential component of modern electrons
  - Diodes (control direction of e- flow); amplifiers (amplify small e- current into a larger one); etc.

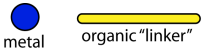


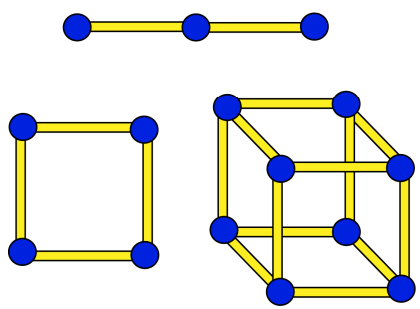


DIC – Doping Semiconductors

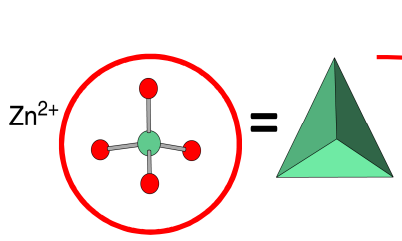
- You are a researcher attempting to influence the conductivity of Sn. What elements would be the most logical choices to attempt to p-dope Sn? How about n-doping?

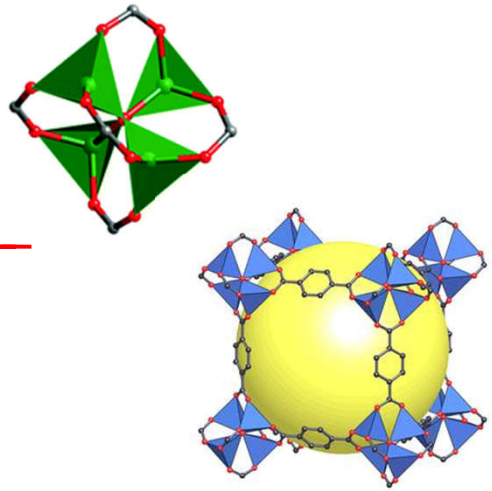
Coordination Polymers and Metal-Organic Frameworks

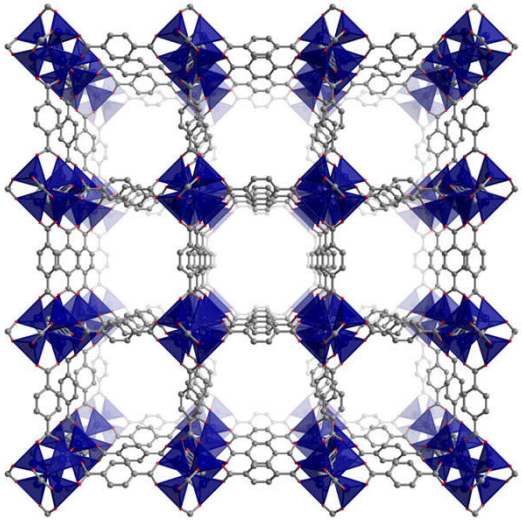




- Where the molecule meets the network solid
  - Unique properties that combine features from both molecules and solids
  - Metal centers/clusters are linked together to form 1-D chains, 2-D sheets, or 3-D networks through organic linker compounds







BPDC : An example

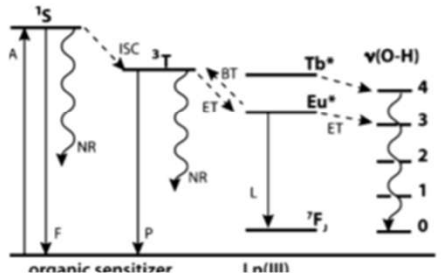
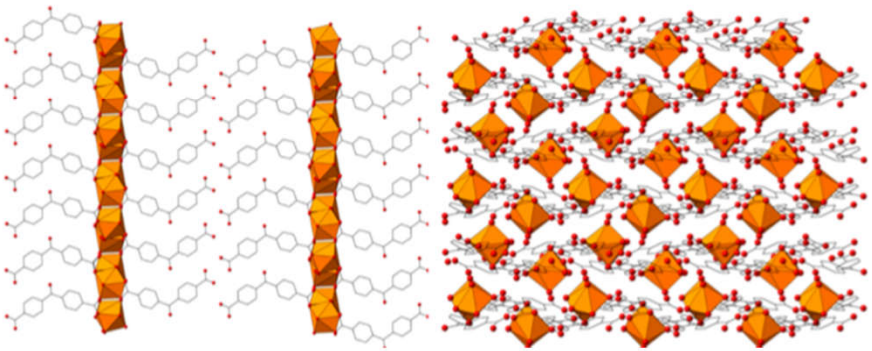
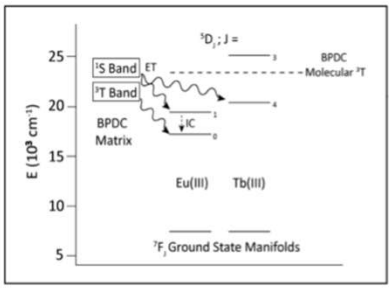


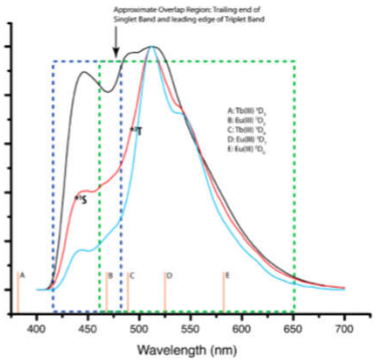
Table 1. Crystallographic Information for 1-Eu

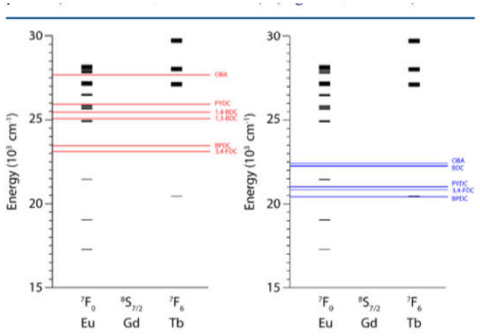
	$[Eu(C_{15}H_9O_5)_3(H_2O)_3]_n$
fw	2009.20
cryst class	monoclinic
space group	$P2_1/c$
a (Å)	27.981(2)
b (Å)	11.2983(8)
c (Å)	11.8755(9)
α (deg)	90
β (deg)	98.9390(10)
γ (deg)	90
Z	4
cell volume (Å^3)	3708.7(5)
density (mg m^{-3})	1.799
μ (mm^{-1})	1.781
temp (K)	100(2)
R_{int}	0.0916
R1[a]	0.0484
wR2[a]	0.1232
GOF	1.000
total reflns	8893

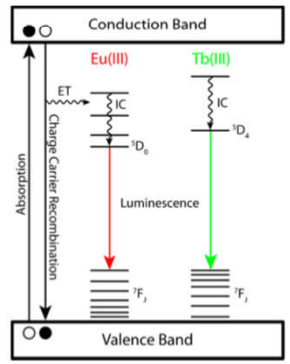
[a] $R1 = \sum \frac{||F_o| - |F_c||}{|F_o|}$; $wR2 = \left(\frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_o^2)^2]}\right)^{1/2}$.











Inorganic Chemistry — Article — pubs.acs.org/IC

Rethinking Sensitized Luminescence in Lanthanide Coordination Polymers and MOFs: Band Sensitization and Water Enhanced Eu Luminescence in $[Ln(C_{15}H_9O_5)_3(H_2O)_3]_n$ (Ln = Eu, Tb)

Jeffrey D. Einkauf,[†] Tanya T. Kelley,[†] Benny C. Chan,[‡] and Daniel T. de Lill*[,†]

[†]Department of Chemistry & Biochemistry, Florida Atlantic University, 777 Glades Road, Boca Raton, Florida 33431 United States
[‡]Department of Chemistry, The College of New Jersey, 2000 Pennington Road, Ewing, New Jersey 08628, United States

Supporting Information

ABSTRACT: A coordination polymer $[Ln(C_{15}H_9O_9)_3(H_2O)_3]_n$ (**1**-Ln = Eu(III), Tb(III)) assembled from benzophenonedicarboxylate was synthesized and characterized. The organic component is shown to sensitize lanthanide-based emission in both compounds, with quantum yields of 36% (Eu) and 6% (Tb). Luminescence of lanthanide coordination polymers is currently described from a molecular approach. This methodology fails to explain the luminescence of this system. It was found that the band structure of the organic component rather than the molecular triplet state was able to explain the observed luminescence. Deuterated $(Ln(C_{15}H_9O_9)_3(D_2O)_3)$ and dehydrated $(Ln(C_{15}H_9O_9)_3)$ analogues were also studied. When bound H_2O was replaced by D_2O, lifetime and emission increased as expected. Upon dehydration, lifetimes increased again, but emission of **1**-Eu unexpectedly decreased. This reduction is reasoned through an unprecedented enhancement effect of the compound's luminescence by the OH/OD oscillators in the organic-to-Eu(III) energy transfer process.



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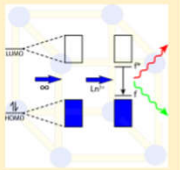
A General Model of Sensitized Luminescence in Lanthanide-Based Coordination Polymers and Metal−Organic Framework Materials

Jeffrey D. Einkauf, Jessica M. Clark, Alec Paulive, Garrett P. Tanner, and Daniel T. de Lill*

Department of Chemistry & Biochemistry, Florida Atlantic University, 777 Glades Road, Boca Raton, Florida 33431, United States

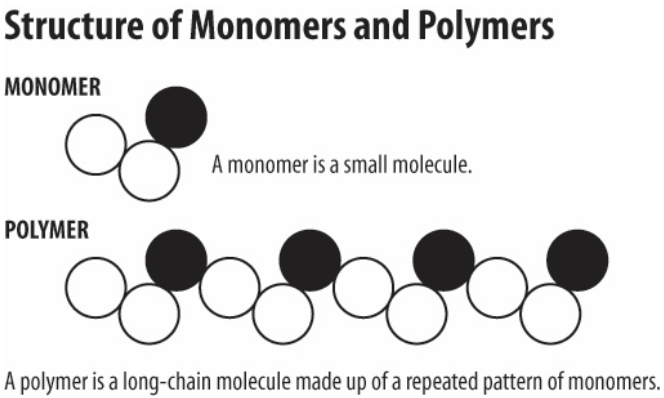
Supporting Information

ABSTRACT: Luminescent lanthanides containing coordination polymers and metal−organic frameworks hold great potential in many applications due to their distinctive spectroscopic properties. While the ability to design coordination polymers for specific functions is often mentioned as a major benefit bestowed on these compounds, the lack of a meaningful understanding of the luminescence in lanthanide coordination polymers remains a significant challenge toward functional design. Currently, the study of these compounds is based on the antenna effect as derived from molecular systems, where organic antennae are used to facilitate lanthanide-centered luminescence. This molecular-based approach does not take into account the unique features of extended network solids, particularly the formation of band structure. While guidelines for the antenna effect are well established, they require modification before being applied to coordination polymers. A series of nine coordination polymers with varying topologies and organic linkers were studied to investigate the accuracy of the antenna effect in coordination polymer systems. By comparing a molecular-based approach to a band-based one, it was determined that the band structure that occurs in aggregated organic solids needs to be considered when evaluating the luminescence of lanthanide coordination polymers.



Polymers and Plastics

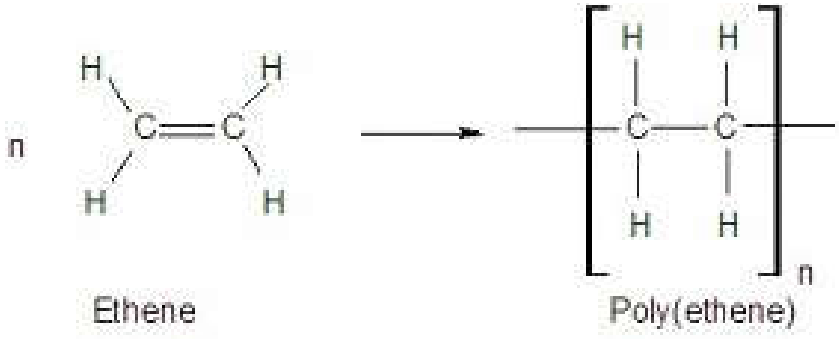
- Polymers – long, chainlike molecules created by repeating units
  - Monomer – the composition of the [repeating unit]$_n$
  - Natural (DNA, starch, proteins) and synthetic (plastics)
  - Very durable (chain length)
  - Polymers can “crystallize” to a certain extent

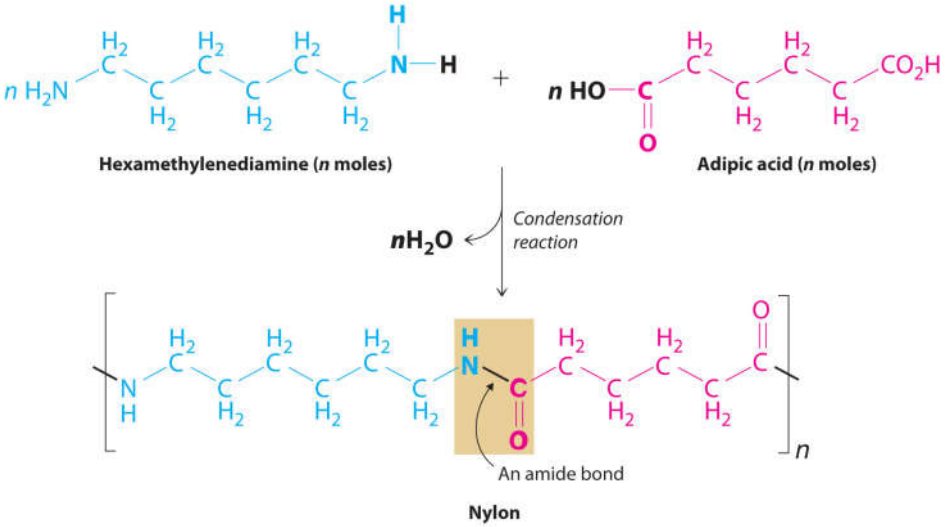


http://knowledgeclass.blogspot.com/2013/08/relationship-between-structure-and.html

Polymer Types

- Addition Polymers
  - Monomers link together without losing any atoms
  - Ethene to polyethylene; chloroethene to polyvinyl chloride (PVC)
- Condensation Polymers
  - Monomers that lose one or more atoms when linking together
  - Copolymers (consisting of two different monomers) usually form dimers through this process (nylon) that then polymerize

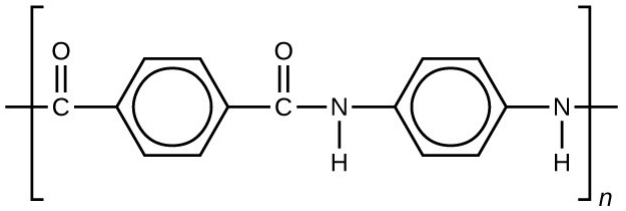




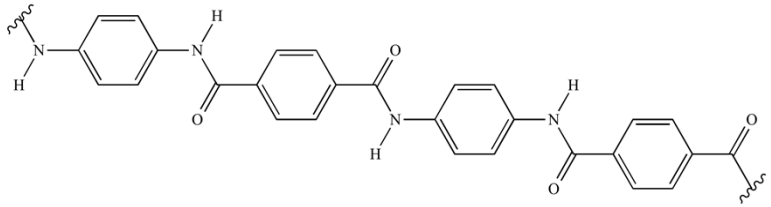
https://study.com/academy/lesson/polymerization-of-alkenes.html

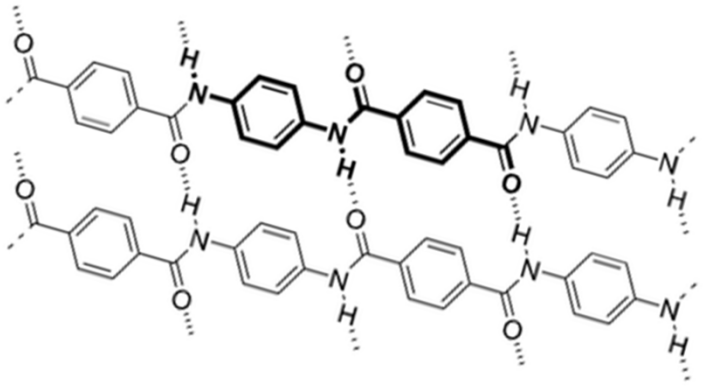
https://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/s16-08-polymeric-solids.html

DIC - Kevlar



- What makes Kevlar so strong? Do a Structural Analysis.





https://courses.lumenlearning.com/chemistryformajors/chapter/amines-and-amides/

http://www.chem.ucla.edu/harding/IGOC/K/kevlar.html

https://en.wikipedia.org/wiki/Kevlar