What is Solid State Chemistry?

- Chemical aspects of solids (materials)
- Chemical and physical properties of infinite, non-molecular solids
- Synthesis-structure-property-function relationships
- Materials with properties (or combinations of properties) tuned for specific applications
- Non-comprehensive, non-mathematical overview

Why Study Solid State Chemistry?

- Materials with properties (or combinations of properties) tuned for specific applications

Electronics: Diodes, transistors, photodetectors, solar cells

Ionics: Batteries, fuel cells, sensors, displays, smart windows

Optical: Fiber optics, CDs, LEDs, lasers, NLO, photon gap, displays

Magnetics: Switches, data storage, read-write heads, spectroscopy

Energy: Catalysts, chemicals, storage, conversion

Mechanical: Construction, ceramics, composites, alloys, space vehicles, tools

Environmental: Pollution prevention and removal, heavy metals, organics, NO_x

Separations: Molecular sieves, membranes, selective catalysis, purification

Biomaterials: Artificial bone, tissue, organs, biomimetics, drug delivery

Solid State Synthesis

- Direct reaction
- Vapor phase transport (VPT)
- Single crystal methods: solutions, melts, hydrothermal
- Ion-exchange
- Intercalation, injection: chemical, electrochemical
- Electrochemical: redox, anodic oxidation, oxidative polymerization
- Solid state precursors
- Dry high pressure
- Thin films:
  - Physical: sputtering, evaporation
  - Metal-Organic Chemical Vapor Deposition
  - Molecular Beam Epitaxy
  - Self-Assembly
  - Lithography
- Supramolecular chemistry
- Biomimetics
- Combinatorial materials synthesis

- Different from traditional areas of chemistry
- No precise level of synthetic control or fundamental understanding of mechanism or even properties
- Towards “rational design”

Characterization of Solids

<u>Spectroscopy:</u> <u>*Local Chemical Environment*</u>

- Vibrational
- Optical (Absorption, Luminescence)
- Solid State NMR: MAS, CP-MAS, DOR, MQ
- EPR, Mössbauer
- Ionization (UPS, XPS, AES, EELS)
- X-Ray (Absorption, Fluorescence, EXAFS)

<u>Thermal:</u> <u>*Stability, Phase Transitions, Reactions*</u>

- TGA (mass *vs*. temperature)
- DSC (thermal events, reversibility)
- MS, GC-MS
- *In-Situ* Variable-Temperature Methods

<u>Diffraction:</u> <u>*Structure, Bonding, Composition*</u>

- Powder: XRD, ND
- Single crystal: XRD, ND
- Electron Diffraction
- Optical Diffraction

<u>Microscopy:</u> <u>*Morphology, Defects, Structure*</u>

- Optical Microscopy
- Electron Microscopy (SEM-EDS, TEM-ED)
- STM, AFM, CFM

<u>Transport:</u> <u>*Conductive Behavior, Mechanism*</u>

- Electronic
- Ionic

- Always multi-analytical
- Techniques differ to conventional methods of molecular compounds
- Anisotropic, orientation-dependent data
- Separate courses on characterization methods (Chem 256B/D, 122, 151B, …)

Course Outline

- Bonding, close-packing
- Defect chemistry, smart windows, superconductors, sensors
- Crystal structures, X-ray diffraction
- Band theory, intercalation chemistry, batteries

- Solid state synthesis
- Porous materials
- Thin films, nano
- Biomaterials
- Electrical, magnetic properties
- Phase diagrams

Suggested Project Topics

- *Amorphous silicon*
- *Anitferroelectric/ferroelectric materials*
- *Biomaterials*
- *C_{60}: Endohedral, exohedral, doped, thin films*
- *Carbon and/or inorganic nanotubes*
- *Chemical vapor deposition (CVD)*
- *Colossal/giant magnetoresistance materials*
- *Combinatorial materials chemistry*
- *Crystal engineering*
- *Diamond thin films*
- *Fiber optics and inorganic photonic materials*
- *Gas storage materials*
- *High temperature superconductors*
- *Inorganic dendrimers*
- *Inorganic polymers*
- *Intrazeolite chemistry*
- *Langmuir-Blodgett films*
- *Luminescent silicon*
- *Mesoporous (20 to 500Å) inorganic materials*
- *Macroporous (> 500Å) inorganic materials*
- *Metal-organic/covalent frameworks (MOFs, COFs)*
- *Micro/nanoelectromechanical systems (MEMS, NEMS)*
- *Micro/nanofluidics*
- *Molecular beam epitaxy (MBE)*
- *Molecular electronic devices*
- *Nanofabrication*
- *Nanomaterials*
- *Organic LEDs*
- *Photoelectrochemical cells*
- *Polymer composites*
- *Quantum wells and superlattices*
- *Self-assembled thin films*
- *Smart windows*
- *Soft lithography*
- *Solar cells – inorganic*
- *Solar cells – dye-sensitized*
- *Solid state batteries*
- *Solid state fuel cells*
- *Supramolecular chemistry*
- *Thermoelectric materials*
- *Zeolites*
- *Other topics: discuss with instructor*

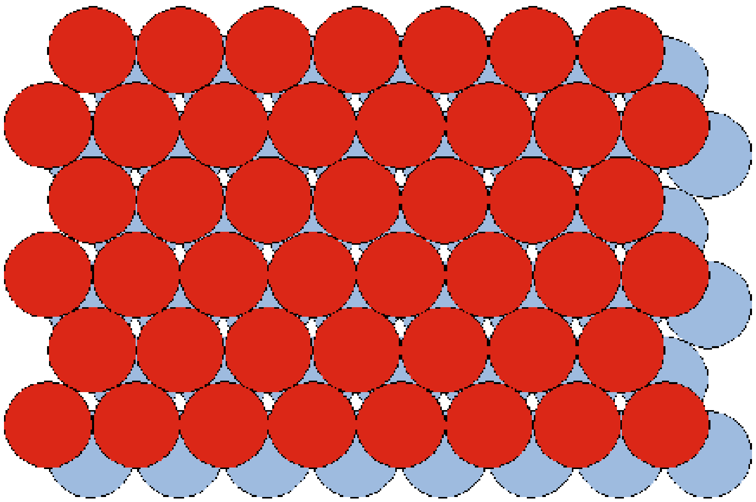
- **One student per topic**
- **Focus on the synthesis, structure, property and applications of the material**
- **Select topic (in person or by e-mail) by Monday, May 1st**
- **In-class talk (> 10 min) *or* essay (≥ 3000 word) by Monday, June 5th**
- **At least 5 real references**

Basic Concepts Necessary for Solid State Chemistry

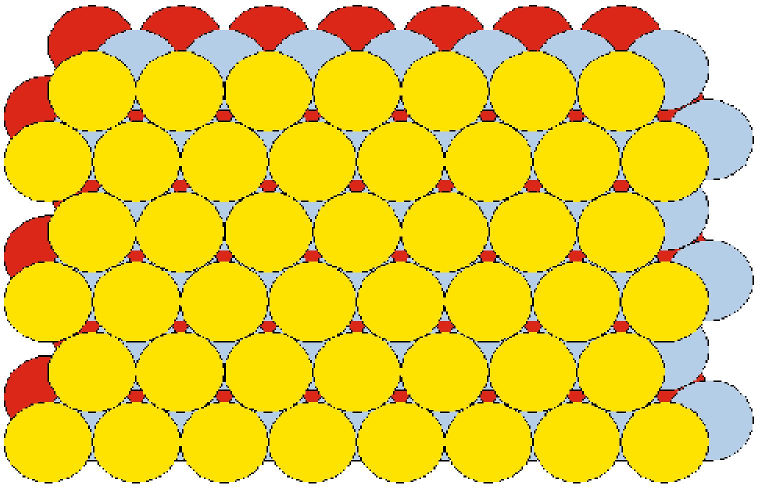
- Bonding Forces in Solids: Ionic–Covalent, Dipolar, van der Waals
- Non-Bonding Effects: Distortions, Inert Pair Effect
- Close-Packing / Hard Sphere Model
- Radius Ratio
- Crystal Lattices, Lattice Energies
- Band Theory

Cubic and Hexagonal Close Packed Lattices

For both, C.N. = 12

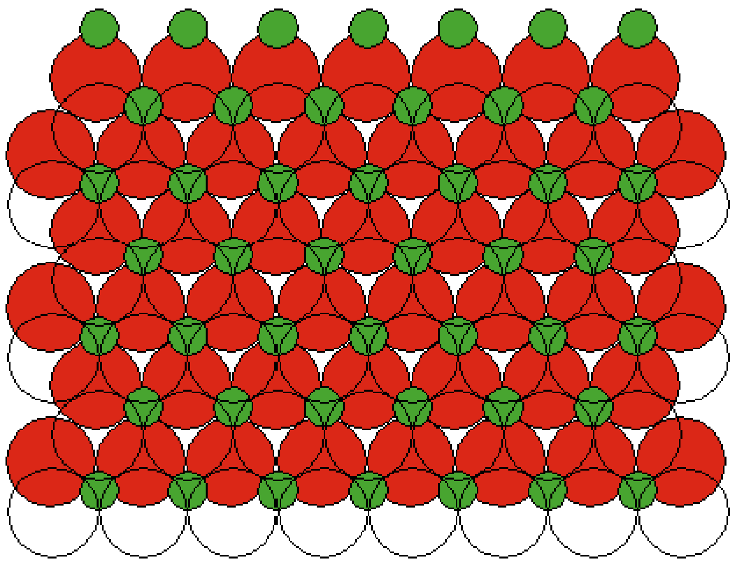


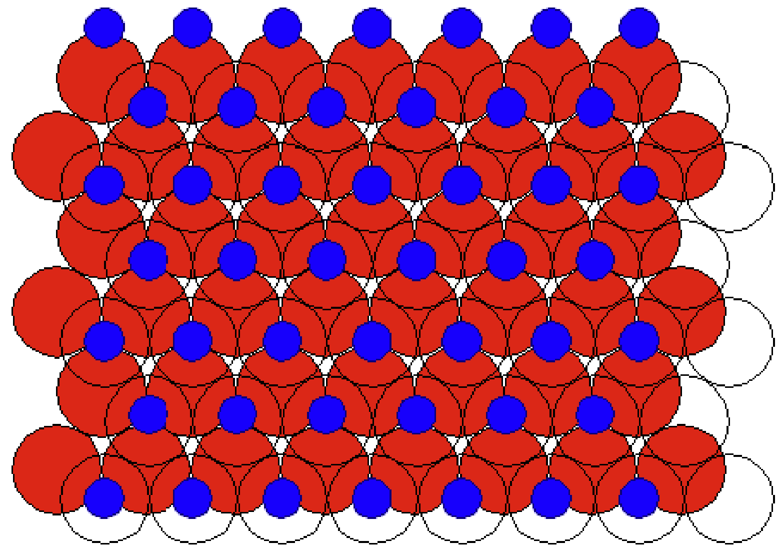
- Third (red) layer above first (red) layer
- ABABAB ≡ hcp



- Third (yellow) layer not above first **<u>or</u>** second layer
- ABCABC ≡ ccp ≡ fcc

Interstitial Sites of hcp or ccp Lattices

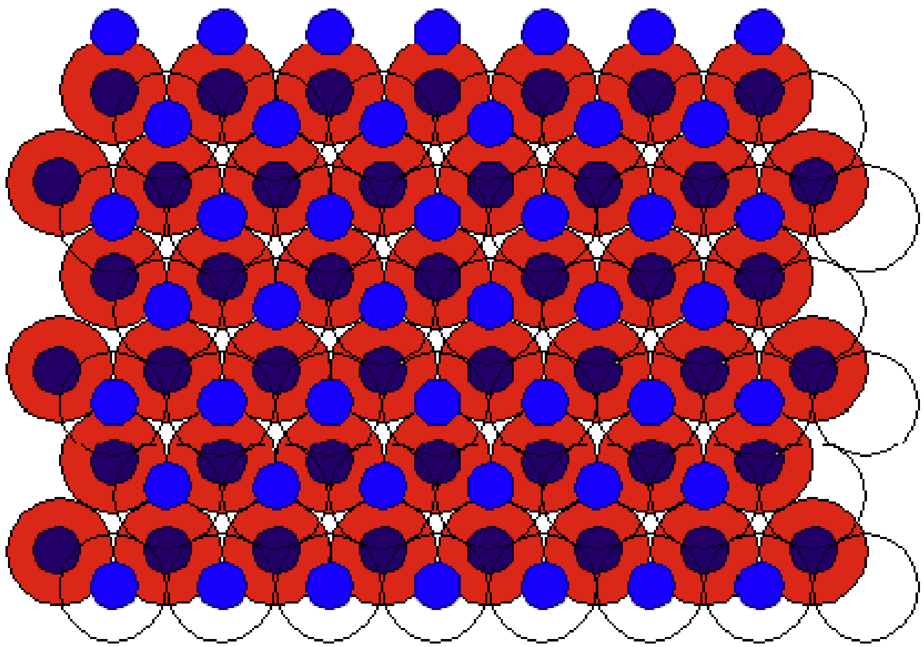




- Octahedral sites (green) between red and clear layers
- 1 O_h site per atom in lattice

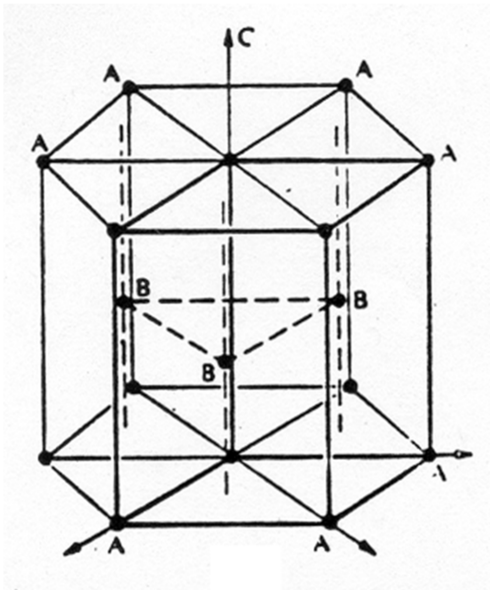
- Tetrahedral sites (blue) between red and clear layers
- 2 T_d sites per atom in lattice (see next slide)

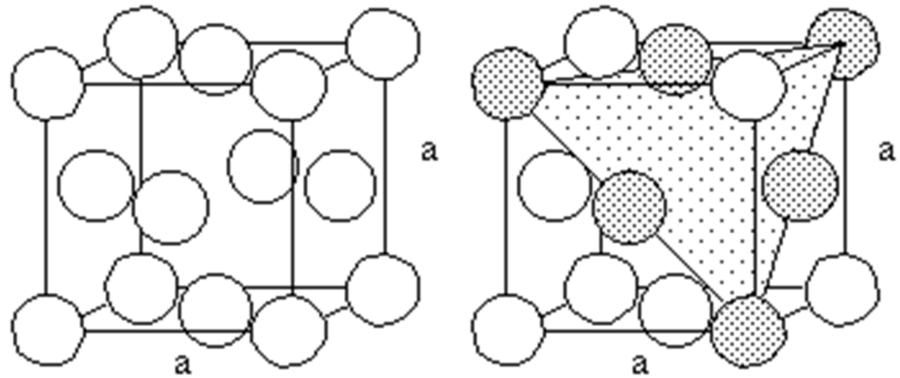
Tetrahedral Sites of hcp or ccp Lattices



- Tetrahedral sites between red and clear layers
- All occupied: dark **and** light blue
- Half occupied: dark blue **or** light blue
- Larger ion defines lattice, smaller ion resides in intersticials
- Often anion hcp or ccp, cations in sites eg: ZnS, TiS_2

Alternate View of hcp, ccp





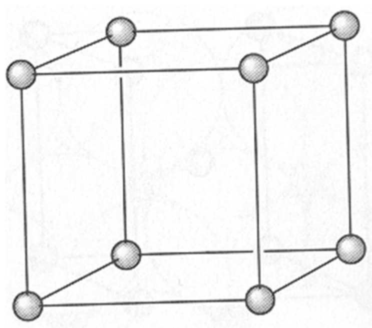
- hcp ABABAB
- 3D arrangement shows hexagonal unit cell

- fcc lattice is equivalent to ccp
- One close packed layer is body diagonal of cube

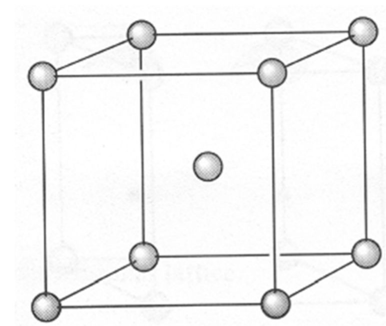
<u>For both hcp and ccp:</u>

- 74% of space occupied
- C.N. = 12 wrto neighboring atoms

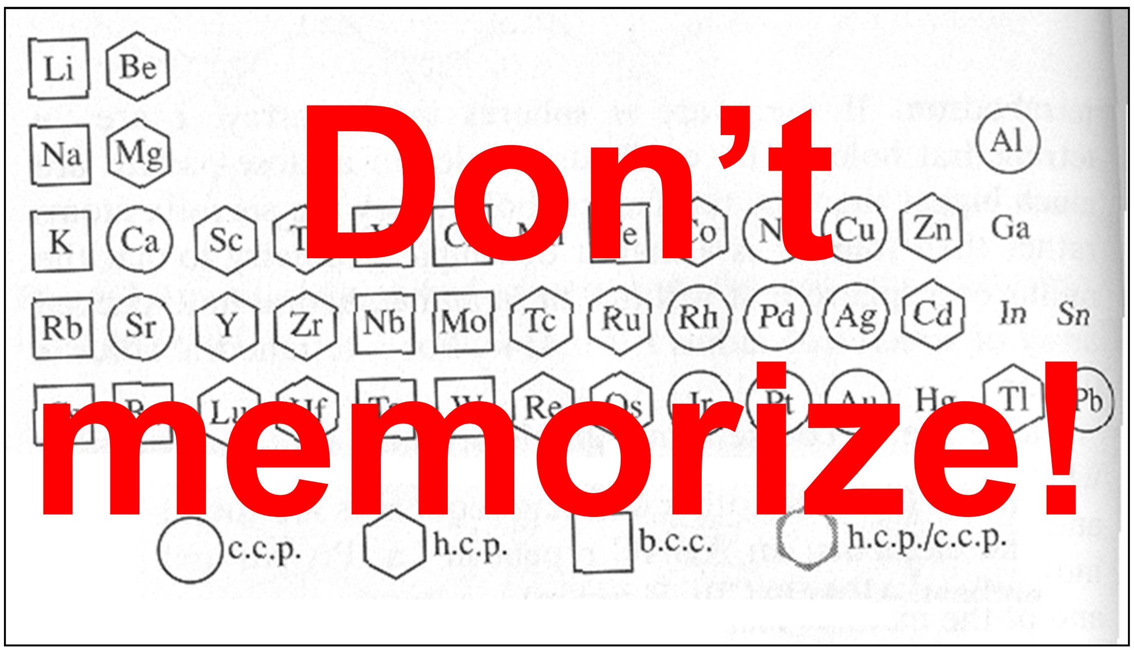
Primitive Cubic and bcc



- C.N. = 6
- Po only example for pure metal



- bcc packing efficiency: 68%
- C.N. = 8



- Occurrence of packing types for metals at ambient conditions