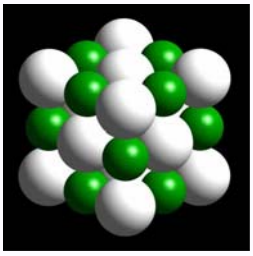
Lecture 6 - Bonding in Crystals

Binding in Crystals (Kittel Ch. 3)

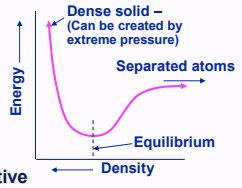


Binding of atoms to form crystals

- A crystal is a repeated array of atoms
- Why do they form?
- What are characteristic bonding mechanisms?
- How do particular mechanisms lead to particular types of crystal structures?

Binding of atoms to form crystals The Big Picture

- Binding is due to interaction of the electrons and the nuclei
  - Negative electrons and positive nuclei attract each other
  - There must also be repulsion for the solid (or liquid) to be stable at some density
- Can understand basic ideas and bonding mechanisms from quantum mechanics – Simple qualitative arguments
- Later in course - more quantitative arguments



Binding of atoms to form crystals The Big Picture

- Electronic States of atoms are crucial for understanding solids
- Core states essential - but change very little with atoms bind to form molecules, solids, ...
- Valence states change when atoms come together – they are responsible for binding

Quantum states for electrons in atoms

Valence states – highest energy occupied states

$3[s\uparrow, 2s\downarrow, p_x\uparrow, p_x\downarrow, \ldots, d, \ldots.]$
2 s, 6 p, 10 d states

$2[s\uparrow, 2s\downarrow, p_x\uparrow, p_x\downarrow, p_y\uparrow, p_y\downarrow, p_z\uparrow, p_z\downarrow]$
2 s, 6 p states

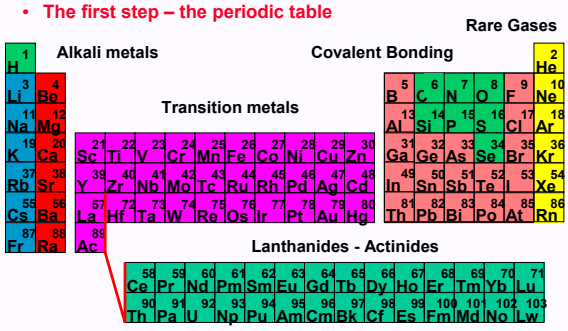
Core states lower energy completely filled states spherical

$1[s\uparrow, s\downarrow$ 2 s states

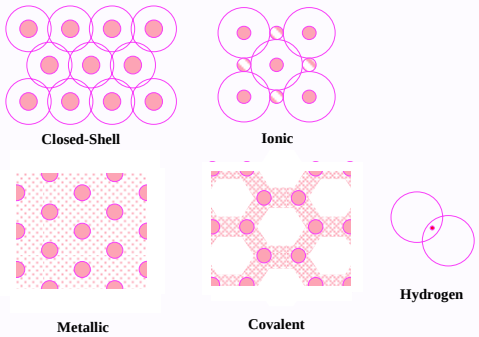
$-Ze^2/r$

Binding of atoms to form crystals The Big Picture

- The first step – the periodic table



Characteristic types of binding



Lecture 6 - Bonding in Crystals

Van der Waals Bonding

- Attraction because electrons can interact and be correlated even if they are on well-separated atoms
- Consider closed shell "inert" that do not form strong chemical bonds
- Isolated closed shell atom - electron distributed symmetrically around the atom - spherical

•What happens if two atoms come together?

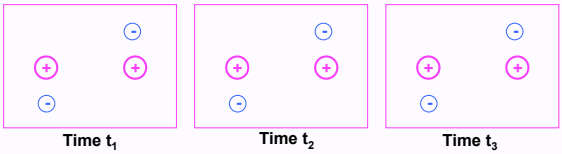
Van der Waals Bonding

- First look at only one atom (no other atom nearby)
- Consider "snapshots" of the electrons

- At any time the electron is found at different places
- On average the probablity of finding an electron is spherical around the atom
- Quantum Effect: Electron on each atom is like a fluctuating dipole - uncertainty principle
- At any time the atom has a dipole moment that averages to zero if one averages a long time

Van der Waals Bonding

- What happens if two closed shell atoms are near one another?
- Consider "snapshots" of the two atoms



- The electrons on the two atoms become correlated
- The electron interact: the energy is lower if the dipoles on the two atoms are opposite
- At any given time there is increased probability of finding the two atoms in a state with lower energy
- Energy reduced - a net attraction - because the electrons are correlated

Van der Waals Bonding

- Dipole D_1 on atom 1 creates electric field E_{12} on atom 2 proportional to $1/R^3$
- E generates dipole D_2 on atom 2:
  $D_2 = \alpha E_{12}$ where α = polarizability
- The interaction of the two dipoles is proportional to $D^2 \sim 1/R^6$
- Always attractive
- See derivation in Kittel – simplest derivation

Rare Gas Solids

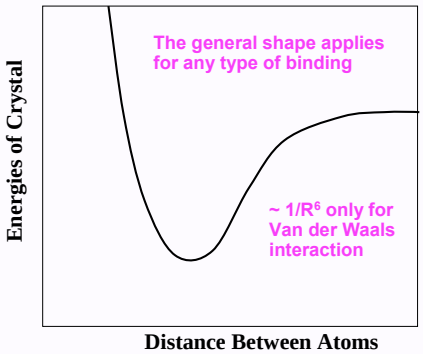
- Attractive energy ~ $1/R^6$
- The analysis breaks down at short distance where the wavefunctions overlap
  Short distance repulsion
  (Due to exclusion principle)
- Typical forms for interaction between two atoms

  $E(R) = -A/R^6 + B/R^{12}$ (Lennard-Jones)

  or

  $E(R) = -A/R^6 + B \exp(-R/\rho_0)$ (exponential)

Total Energy of Crystal

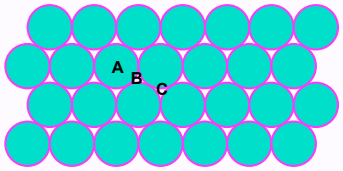


Lecture 6 - Bonding in Crystals

Rare Gas Solids

- Atoms nearly spherical
- Short-range non-directional attraction and repulsion
- $\Rightarrow$ Close packed structures HCP or FCC

Stacking hexagonal 2d layers to make close packed 3-d crystal



- Each sphere has 12 equal neighbors
- 6 in plane, 3 above, 3 below
- Close packing for spheres
- Can stack next layer as either B or C
- HCP: ABABAB… FCC: ABCABC….

Cohesive energy

- $E_{cohesion}$ per atom = E_{atom} - E_{solid} per atom
- For a pair interaction like Van der Waals this is

$E_{cohesion}$ per atom = (1/2) E_{pair} (R) x z

Interaction of any pair of atoms

Number of nearest neighbors

- $E_{cohesion}$ defined to be per unit (i.e. per primitive cell) in compounds
- Other formulas apply for other types of binding

Equilibrium Lattice Constant

- General approach:
  E(V) where V is volume

  Can use ether $E_{crystal}(V_{crystal})$ or $E_{cell}(V_{cell})$
  since $E_{crystal} = N E_{cell}$ and $V_{crystal} = N V_{cell}$
- Pressure = P = - dE/dV (units of Force/Area)
- But since $V \sim R^3$, dV/V = 3 dR/R
- Minimum energy at P = 0 $\Rightarrow$ dE/dV = dE/dR = 0
- As a function of pressure, find V(P) or P(V) by solving P = - dE/dV

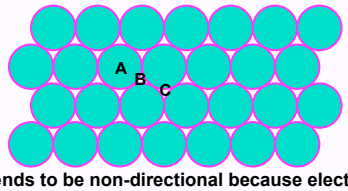
Equilibrium Lattice Constant

- Example: Rare Gas Solid
  Easiest to write energy in the form:

  $E(R) = \varepsilon [\Sigma_i (\sigma/\rho_i R)^{12} - \Sigma_i (\sigma/\rho_i R)^6]$

  where $\rho_i R$ is the distance to neighbor i, that is ρ_i is the distance in units of R
- Also $E(R) = \varepsilon [(\sigma/R)^{12} \Sigma_i (1/\rho_i)^{12} - (\sigma/R)^6 \Sigma_i (1/\rho_i)^6]$
- Values of the dimensionless sums are given in Kittel
- Minimum is for dE/dR = 0

Metallic binding



- Tends to be non-directional because electrons are spread out
- Typically leads to close packed structures
- See Kittel Table 3 - almost all metals are FCC, HCP, or BCC
- More on metals later – very important in this course since metals is a feature of solids NOT found in molecules

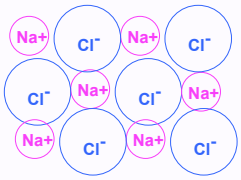
Lecture 6 - Bonding in Crystals

Ionic Solids

- Much stronger binding than Van der Waals
  Attractive energy ~ 1/R
- 1. Pay energy to form ions

- 2. Gain energy to bring ions together.

  Is there a net attraction?



Ionic Solids

- Attractive interaction ~ 1/R is very long range
- Sum over neighbors is only conditionally convergent! Must be done very carefully!
- Result: Attractive energy defined to be $-\alpha q^2/R$
  where α is the Madelung constant (depends on structure) q= charge, R = nearest neigh. dist.
- Repulsion similar to closed shell systems (exponential works best)
- Final forms

  $E(R) = -\alpha q^2/R + B \exp(-R/\rho_0)$

  or

  $E_{cell}(R) = -\alpha q^2/R + z\lambda \exp(-R/\rho_0)$

  (z = number of nearest neighbors, λ = parameter)

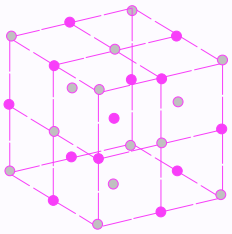
Ionic Solids

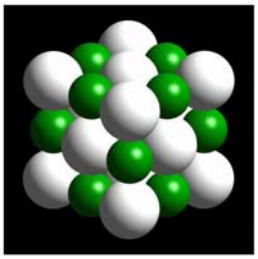
- Discussion of Madelung constant α
- General Method: Ewald sum given in Kittel appendix
- Convergent sums can be found by summing over neutral shells of neighbors

Values of α

fcc NaCl structure	1.748
bcc CsCl struc. (bcc)	1.763
fcc ZnS structure	1.638

NaCl Structure

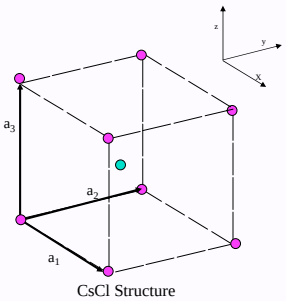




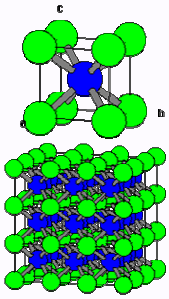
NaCl Structure with
Face Centered Cubic Bravais Lattice

Favored for ionic crystals with large size difference
Close packed negative ions with small positive ions

CsCl Structure



CsCl Structure
Simple Cubic Bravais Lattice

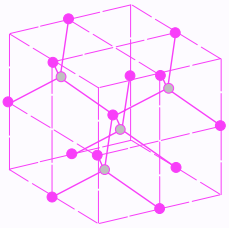


From http://www.ilpi.com/inorganic/structures/cscl/index.html

Favored for ionic crystals with small size difference

ZnS and Diamond structure

- Favored if there is strong directional covalent bonding
- Each atom has 4 neighbors in tetrahedron
- Explained by simple bonding pictures and full electronic calculations - More later



ZnS Structure with
Face Centered Cubic Bravais Lattice
C, Si, Ge form diamond structure with
only one type of atom

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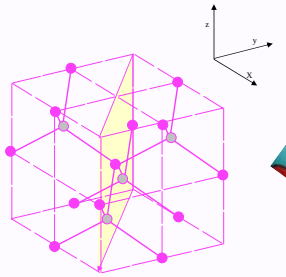
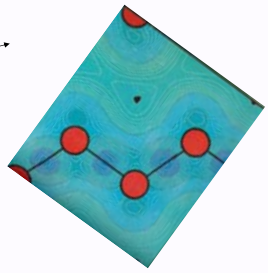
(110) plane in diamond structure crystal

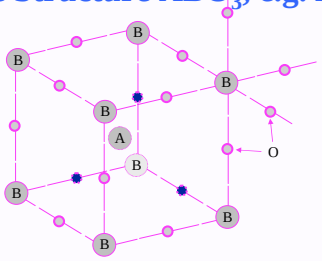


(100) plane in ZnS crystal
zig-zag Zn-S chains of atoms
(diamond if the two atoms are the same)



Calculated valence electron density
in a (110) plane in a Si crystal
(Cover of Physics Today, 1970)

Perovskite Structure ABO_3, e.g. $BaTiO_3$



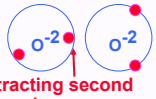
Simple Cubic Bravais Lattice

A atoms have 12 O neighbors
B atoms have 6 closer O neighbors

Hydrogen Bonds

- H is a special case
- If it is ionized it is just a single proton (unlike all other atoms in the periodic table)
- A proton can always be attracted to regions of high electron density - i.e., it can cause extra binding because it attracts electrons

Example: Water



Proton attracting second water molecule

- (Does not happen with other atoms because of the repulsion of the core electrons)

Atomic and Ionic Radii

- Atoms and Ions have typical sizes
- Governed by cores which are filled shells and do not change much in different solids
- Somewhat arbitrary, but chosen so that sum of radii is nearest neighbor distance
- Tables in Kittel

Binding of crystals

- Primary types of binding (bonding)
- Metals: Close packed structures with many neighbors – Al, Cu, Fe, …
- Van der Waals: Close packed structures for rare gases – He, Ne, … , complicated structures for low symmetry molecules,
- Ionic: Tend to form high-symmetry structures with large Madelung constants - NaCl, CsCl
- Covalent: Open structures with few neighbors, directional bonds – graphite, diamond C, Si
- Hydrogen – special ability of a proton to favor overlap of electron densities – H_2O, …

Next Time

- Elasticity, elastic waves
- Not treated in as much detail in Kittel