

CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 33: More complex structures

### References

1. Levine, *Physical Chemistry*, Chapter 23
2. Solid state handout
3. Slides distributed in class

### Key Concepts

- We developed a systematic way of talking about crystals and their associated geometry:
  1. Atom locations: points are references as fractions of lattice constants. For example the atom position  $\frac{a}{2}, \frac{a}{2}, \frac{a}{2}$  is written:  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ .
  2. Directions are treated just like vectors:
    - (a) pick an origin
    - (b) end of the vector coordinates treated like atom locations, i.e. written as fractions of cell edges.
    - (c) Specific directions are enclosed in square brackets [ ] and a family of equivalent directions in angle brackets  $\langle \rangle$ .For a hexagonal crystal we need an additional indices for the direction due to the symmetry. We want equivalent directions to have equivalent indices. (See the lecture slides of the mathematical relationship).
  3. Planes of atoms: are very important for structure determination and for understanding properties.
    - (a) Find the axial intercepts of the plane (may be negative)
    - (b) Take the reciprocal
    - (c) Clear common factorsA specific plane is enclosed in ( ) while a family of equivalent planes uses { }
- Several more interesting crystal structures involve multiple atoms types per cell and multiple cells:
  1. CsCl: A primitive cubic structure with two atoms per lattice point: one at 000, the other at  $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ . NOTE: this is NOT a BCC structure since the central atom is NOT at a lattice point.
  2. NaCl: FCC structure with one atom type at the FCC lattice points and the other at all the octahedral interstitial sites. Also, can be thought of two interpenetrating FCC “lattices”, one of Na the other of Cl.
  3. CaF<sub>2</sub>: FCC structure with Ca (the cation) at the FCC lattice sites and the F (the anion) at all the tetrahedral interstitial sites. This preserves the 2:1 stoichiometry as there are 4 FCC lattice sites per cell and 8 tetrahedral interstitials.
  4. ZnS: Also known as the zinc blend structure. Similar to the calcium fluorite structure, with one half of the tetrahedral sites occupied (i.e. Zn at the FCC lattice sites and S at one half of the tetrahedral interstitial sites).
  5. Diamond cubic: Related to ZnS with all identical atoms, for example all C or Si. Has 4-fold coordination, characteristic of sp<sup>3</sup> hybridized atoms.
  6. Graphite: Another, more stable form for elemental carbon. Hexagonal, with 3-fold coordination in the basal plane. Can be thought of as sheets of hexagonally packed C atoms packed together in layers. Highly anisotropic structure, i.e. the properties will depend heavily on crystal orientation.
- We can probe these various structure types and state of order using diffraction of x-rays, neutrons, and/or electrons.