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CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 37: Structure factor and chemical order

References

1. Levine, *Physical Chemistry*, Chapter 23
2. Solid state handout

Key Concepts

- Primitive cells will show all reflections due to only one lattice point per unit cell. However, multiple cells (ex: BCC, FCC) will have systematic absences due to the extra lattice points in the unit cell.
- The systematic absences are quantified through the structure factor, F_{hkl} defined as follows:

$$F_{hkl} = \sum_{cell} f_n e^{2\pi i(hu_n + kv_n + lw_n)}$$

  where f_n is the atomic scattering factor of atom n and (u_n, v_n, w_n) are the coordinates of each atom in the unit cell. For example, a BCC structure might have one atom at 0,0,0 and another at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.
- The atomic scattering factor, f_n quantifies the "effectiveness" of an atoms x-ray scattering. It is a function of the chemical identity of an atom (primarily the number of electrons) and the scattering angle θ. At diffraction angles of $\theta = 0$ the number of electrons equals f_n, but the atomic scattering factor deceases as θ gets larger.
- The intensity of a diffracted beam is proportional to F^2.
- Calculation of the structure factor for specific crystal structure leads some common systematic absences:

Primitive Cubic	BCC	FCC
All reflections allowed	$h+k+l$ = even, $F \neq 0$ $h+k+l$ = odd, $F = 0$	h,k,l all even or all odd, $F \neq 0$ h,k,l mixed even and odd, $F = 0$

- When certain atom types occupy specific sites in a lattice, the material is said to be chemically ordered. The chemical order can change the symmetry of a crystal.

  For example, in CuZn, in the disordered phase the structure is BCC, with an equal chance of finding a Cu and Zn atom on each site. However, when ordered, one atom type will occupy the cube corner positions while the other will occupy the body-centered position. This structure is now a primitive cubic structure and not BCC since every lattice point must have an identical motif (set of atoms).
- High temperature favors the chemically disordered state due to entropic effects. This this state, the crystal is BCC (each lattice site has one "average" atom, which has a 50% chance of being a Cu and 50% chance of being a Zn.
- At lower temperatures, the chemical interactions win out over entropy, and the solid becomes chemically ordered. In the completely chemically ordered state, Cu atoms are always found at the cell corners and Zn at the center position (or vice-versa). This is a result of a chemical interaction which favors Cu being surrounded by 8 Zn atoms and Zn to be surrounded by 8 Cu.
- In the chemically ordered state, the structure is now primitive cubic. This is because the atom at the body centered position is not the same as the corner atom. This is why the chemically ordered structure is NOT BCC.