Chapter 7 – The Solid State

Skip pp. 252 - 263.

Imperfections in Solids

Imperfections in crystal lattices are useful for explaining solid state conductivity, a topic that we will cover next. They occur when impure materials crystalize (e.g. when a some NaCl contaminates bulk $CaCl_2$ or some $FeCl_2$ is present in bulk $FeCl_3$). Defects can also arise in the crystallization process. For example, consider the face of a perfect NaCl crystal. As the next layer adds, perhaps a Na^+ ion isn't available as the layer assembles and then the hole where the missing ion should go gets sealed in as the next layer develops.

Ions missing from expected locations in the lattice represent one type of defect. This is called a Schottky defect and it can occur in several different ways. One is a stoichiometric quantity of cations and anions may be missing. (e.g. In a CaF_2 lattice, for every missing Ca^{2+} ion two F^- ions also will be absent.) A similar type of defect yields an element in more than one oxidation state. For example, if there is an Fe^{2+} ion in an $FeCl_3$ lattice (i.e. a little $FeCl_2$ gets mixed in with bulk $FeCl_3$), there will be one missing chloride ion to maintain charge balance. Correspondingly, in an $FeCl_2$ lattice, the presence of an Fe^{3+} ion will lead to an extra chloride ion.) Substitution of a different ion (both charge and element) for an expected one causes the same type of defect. (e.g. having K^+ ions in place of Ca^{2+} in CaF_2). In this case, there would be one less chloride ion as a result of the lower charge on the cations.) As the book points out, when this is done intentionally with a few percent of added agent the properties of the bulk material can change greatly.

Another defect is the replacement of an anion by one or more electrons in the crystal. This is called an F center (from the German word *farbe* (color) because these frequently cause highly colored solids). It occurs because the strength of the lattice is sufficiently large that a pure metal added to the crystal will ionize into the appropriate cation (e.g. $Na \rightarrow Na^+ + e^-$ in NaCl) and an electron to replace the missing anion. Finally, a Frenkel defect occurs when an ion is displaced from its normal site. i.e., from an octahedral lattice hole to a tetrahedral one (or vice-versa).

Conductivity in Ionic Solids

Fundamentally, conductivity is the movement of charge. Therefore, the mere existence of charge is not sufficient for a material to conduct electricity well. This explains why ionic solids are typically insulators, but when dissolved, create solutions that are excellent conductors. For solids to conduct, the ions must migrate through the lattice. As you might imagine, this is quite difficult and so only small amounts of charge can move through solid salts. In solution, ions may move reasonably freely so conduction occurs readily.

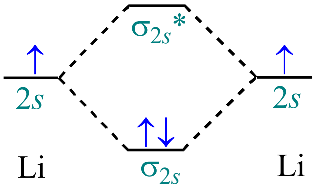
The limited conductivity in solids arises from one (or both) of two mechanisms. In the first, ions move through the solid by occupying open sites resulting from nearby defects. E.g. In a Schottky defect there is a hole where an ion should be. Conduction occurs when a nearby ion moves from its current location into that hole. In the other, ions move from interstitial site to interstitial site. Recall that not every site between anions is filled. In particular, there are two tetrahedral holes for every octahedral hole, so there are places for small ions to migrate through a solid. Generally, migration is difficult, though, and conductivities are very low.

Solids Held Together by Covalent Bonding

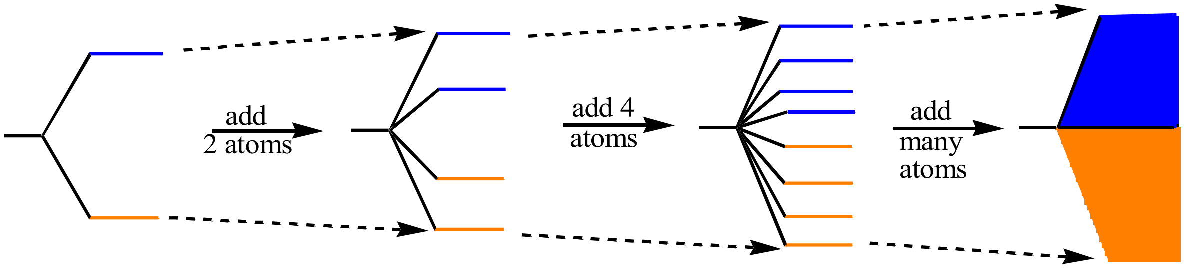
Molecules may be classified as conductors, semiconductors, or insulators. Conductors (e.g. metals) have virtually no barrier to electrical conduction with electrons moving through them easily. Insulators decompose or melt before conducting electricity. Essentially all conduction requires the input of some energy. For insulators, the added energy causes a process that breaks down the material before conduction can occur. Semiconductors are materials that require some energy input (e.g. heat or light) in order to conduct electricity. Here, a meaningful energy barrier to conduction exists, but is not so large as to prevent conduction. Most commonly semiconductors are the metalloids (semimetals), compounds of these elements, or compounds to which other substances are added to change the properties of the original substance. We will discuss each of these shortly.

Band Theory

Let's assume we are dealing with metal atoms bound only through their *s* orbitals (your book chose lithium, which is a good illustrative choice). This simplifies how the orbitals that result in conduction are formed. What is true here is generally true for all orbitals though. The first two atoms interact as we have seen in CHM 211 and, possibly, physical chemistry:



What happens if we add a third atom to create a chain? The result is just like the NO_2^- example in Chapter 5 (p. 10 of the notes). Three atoms interact to yield a bonding orbital, an antibonding orbital, and a non-bonding orbital in between. The following graphic shows the progression as additional atoms are added to the chain.



This has been done for a linear chain of atoms, but much the same thing happens for three-dimensional arrays (and requires fewer atoms because there are more connections). Each successive atom lowers the energy of the most bonding orbital slightly and raises the energy of the most anti-bonding orbital by about the same amount. As the number of atoms increases, the size of the change decreases, so that the upper and lower orbitals have an effective maximum and minimum energy, respectively. (You can think of this as approaching a limit.) Since the energy gap is relatively fixed, as the number of bound atoms increases many energy levels are compressed in a narrow energy range. (1 mol of a metal (e.g. ≈7 g_{Li}) has 6 x 10^{23} energy levels). Thus, there is a continuum of orbitals (Figure 7.21 p. 271). The highest filled orbital is called the Fermi level (ε_F). In metals, no energy gap exists between the HOMO and LUMO. Thus, electrons are not rigidly held in the bonding orbitals because of thermal energy. When a potential is applied across the metal the vacant orbitals allow the electron to flow across the metal.

Intrinsic and Photoexcited Semiconductors

In semiconductors, an energetic difference, called the band gap, exists between the "bonding" and "antibonding" collections of orbitals. The collection of low energy (bonding) orbitals is called the valence band. The high energy (antibonding) orbitals form the conduction band. In general, band gaps decrease in size down a group (e.g. the band gap in silicon is larger than that in germanium). If two or more elements form the semiconductor, the band gap decreases with decreasing difference in electronegativity.

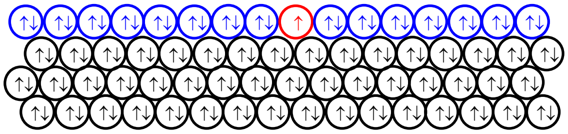
Conduction occurs in intrinsic and photoexcited semiconductors when heat or light (respectively) promotes an electron from the valence band to the conduction band. When a potential difference is applied across the material, the promoted electron will move towards the low potential electrode. Flow also occurs in the valence band because there are "holes" left behind when the electron is excited. This hole is a vacancy in an orbital on the atom. Once the promoted electron moves, the atom acquires a positive charge and an electron from a neighboring atom may move onto the originally excited atom. This occurs as a sequence of electron transfers ending at the high potential electrode (from which an electron comes). It is important to note that current flow in semiconductors is limited because only a limited number of electrons move to the higher energy conduction band.

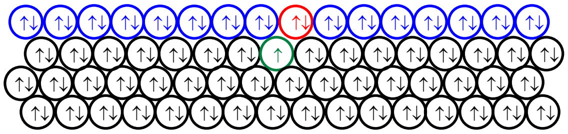
A reasonable question arises as to why band gaps exist for one group of entities (i.e. semiconductors), but not another (e.g. metals). Before addressing this question, it should be noted that a third group (i.e. insulators) also exists. The difference (to a first approximation) between a semiconductor and an insulator is the size of the energy gap between the valence (bonding) and conduction (antibonding) bands. To answer the question, let's use a real semiconductor, silicon, as an example. First, we must ask: "How is it different from a metal?" A typical metal atom binds to 12 contact neighbors (pp. 118 – 120) using all of its valence orbitals. The nature of these interactions necessitates a significant degree of delocalization in the bonding. In contrast, silicon binds to only 4 neighbors using sp^3 orbitals to do so in a localized bonding scheme. In the former case, the large number of delocalized orbitals yields a relatively small HOMO/LUMO gap. In the latter case, that gap is large enough that, even when a mole of atoms is figured in, the gap remains. Clearly, as the band gap increases, more energy is required to promote an electron from the valence band to conduction band. Insulators occur when that energy is great enough to either melt the substance or decompose it (i.e. break one of the bonds in the molecule).

Impurity and Defect Semiconductors

Another way to create or enhance the performance of a semiconductor is to add a small amount of another substance. The addition of a small, fixed amount of one substance to another to change the latter's properties is called doping with the added substance called a dopant. The second substance is frequently a semiconductor itself.

Pure germanium is a semiconductor whose performance may be enhanced by the addition of a little gallium. Begin by considering a plane of solid germanium several atoms deep with a single gallium atom along the top line of atoms (see figure below). For our purposes, we will designate the bulk germanium with black circles and all paired atoms. The top row has germanium in blue, with a red gallium atom. The gallium has one fewer electron, which we'll represent as an unpaired electron in the circle. As noted earlier, electrons have trouble flowing through pure germanium because the valence band is fully populated and electrons must be promoted into the conduction band for electrical flow. The presence of a small number of gallium atoms helps make electron flow easier as follows. Imagine that we move an electron from a neighboring germanium atom (in green) to the gallium atom. This process costs energy because the electrons are in orbitals of gallium and germanium possess slightly different energies. Still, the energy input is smaller than that required to promote an electron to the conduction band in pure germanium. Thus, depending on the dopant, these types of semiconductors may require added heat or light to function, albeit less than for the comparable





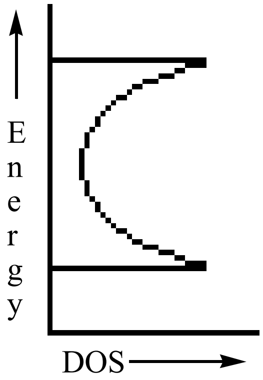
intrinsic semiconductor. In principal, moving an electron from a neighboring germanium onto this one is essentially energy neutral. Thus, electrons (and hence holes) move from germanium to germanium, bypassing the gallium dopant atoms. In reality, dopants usually appear in very low concentrations (e.g. *ca*. 1 ppm) and so are widely separated. This is because they cause anisotropy in neighboring atoms that extends further than the picture above suggests. A doped semiconductor requires wide expanses of pure material to function properly, which accounts for the low concentration of dopant employed. Gallium-in-germanium is a <u>p-type</u> semiconductor because a positive hole has been introduced into the lattice. It is called a positive because an electron is removed from the germanium lattice and this is formally an oxidation and so results in a positive charge on a germanium atom.

The reverse is an <u>n-type</u> semiconductor. Germanium doped into gallium is an example of this. Read the description on your own.

<u>Solid State Materials with Polar Bonds</u>

This section discusses a number of different topics, but the only one we will cover is density of states. On p. 3 of the notes the figures showed the progression from two interacting atoms to an (essentially) infinite number of atoms. The figures showed that as the number of atoms increased, the energy gaps between individual bonding and antibonding energy levels decreased to the point that a continuum developed for a metal. One thing that wasn't addressed was how smoothly the energy levels distributed themselves throughout that continuum. It was implied that there was a continuous vertical stacking with no degeneracies (i.e. each new atom produced a new orbital that was sandwiched between existing orbitals). In fact, when the wire gets large enough, degeneracies do occur. In the real world, substances exist in three dimensions and that generates further degeneracies as does the existence of orbital sets (e.g. the *p* orbitals).

In a semiconductor with different elements or compounds composed of more than one element, multiple gaps can exist (i.e. the valence and conductance bands may be broken up into sub-bands). Again, the possibility of degeneracies exists. A density of states (DOS) diagram displays these degeneracies. The right-hand figure at the bottom of p. 280 illustrates a very simple DOS diagram (redrawn below).



This diagram shows that energy levels tend to be compressed at both very low and very high energies for one-dimensional conducting wires. Few energy levels exist within the band at the interface between bonding and antibonding orbitals.

Figures 7.29 – 7. 32 (pp. 282 – 283) shows the DOS diagrams of two different semiconductors. As you can see, multiple band gaps exist and DOS vary widely and in a non-uniform fashion. The size of the energy gaps between bands obviously influences conductivity, but the shape and size of the bands also will, as well as the percent orbital contribution from differing elements to the band. Just as large band gaps will reduce conductivity because fewer electrons can get into the band, small DOS bands will restrict the number of electrons, thin DOS bands can also limit electron flow. Finally, bands with high levels of contributions from orbitals of widely differing electronegativities may restrict electron movement.

High Temperature Superconductors - Read on own.