Metals and Semiconductors

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Electrical resistance and Ohm's Law:

If an electric current I (units of A, Ampère) flows through a conductor with resistance R, then the potential difference across the ends of the conductor V (unit V, Volts) is given by Ohm's law:

$$V = IR$$
 or $R = \frac{V}{I}$

and the units of resistance are Ω , Ohms. The resistance of a material is directly proportional to its length l and inversely proportional to the cross-sectional area A. The proportionality constant is called the resistivity or the specific resistance ρ , and

$$R = \rho \frac{l}{A}$$

The unit of ρ are Ω m though Ω cm is also commonly used. ρ is an important material-dependent property that is usually a function of temperature. The value of ρ at room temperature is indicative of whether something is a metal (ρ is of the order of $10^{-6} \Omega$ -m or less) an insulator (ρ is of the order of $10^{6} \Omega$ -m or more). Materials that are somewhere in-between are called semiconductors.

The electrical conductivity σ is the inverse of the electrical resistivity $\rho.$

$$\sigma = \frac{1}{\rho}$$

The unit Ω^{-1} has a name. It is called S, Siemen.

Measuring the resistance:

Usually, the four-probe technique is employed as depicted below.



The resistance is measured using R = V/I and the resistivity is then obtained from a knowledge of A and l.

Energy bands:

We have already introduced the H_2 molecule and the notion that electrons are shared between atoms. These electrons form bonding and antibonding energy levels. In a crystal, with typically Avogadro number of atoms, the energy levels are smeared out into what are known as bands. In the simplest picture, in a covalent solid such as C (diamond) or Si, Avogadro number of bonding levels form the valence band, which is filled with electrons, and Avogadro number of antibonding levels form the conduction band which is empty.



When, in a materials such as C (diamond) or Si, an electric field is applied, if an electron goes from the left to the right in the material, this is compensated by an electron that goes from the right to the left. There is therefore almost no electrical conduction, and the electrical resistance is very high. This is a characteristic of a materials where the valence band is completely filled. The only current that is carried in the material is by electrons that are energetically promoted from the valence band to the empty conduction band. Such promotion is called thermal activation and this (in insulators) decreases the resistivity.

In insulators and semiconductors, the resistivity often varies with temperature in the following manner:

$$\rho(T) = \rho_0 \exp(\frac{E_g}{2k_{\rm B}T})$$

where ρ_0 is a constant pre-factor, and E_g is the electronic band gap — the energy separation between the top of the valence band and the bottom of the conduction band as probed by electrical transport studies.¹ A plot of log ρ vs. 1/T gives a slope which is equal to $E_g/(2k_{\rm B})$. E_g for semiconductors is Si = 1.11 eV, Ge = 0.67 eV, GaAs = 1.42 eV and CdS = 2.40 eV.

Insulators, semiconductors and metals The schematic "band structures" of these is shown the next figure. Metals have "free" electrons. This means that instead of having all bonding states filled and all antibonding states empty, they can have partially filled valence or conduction bands.



Metals are formed when there is not a simple integral relation between the number of bonds and the number of valence electrons. For example, Al has 3 valence electrons, shared, in its fcc structure, with twelve neighbors. It is difficult to make a clear separation between bonding and antibonding levels. Si on the other hand, has four valence electrons and four near-neighbors (in the diamond structure). Each Si has a bond with its neighbor with 2 electrons, and an antibond which is correspondingly empty. So Al is a very good metal and Si is a very good semiconductor. Carbon (diamond) is similar to Si in its bonding and is one of the best insulators. In

¹Other techniques, such as spectroscopy often yield different values, so it is best to specify how the band gap is measured.

general, compounds formed from atoms with half-filled or fully filled levels will be insulating or semiconducting, whereas compounds formed from atoms that have some "free" electrons will be metallic. Anything with a stable electronic configuration (noble gas, d^0 , d^{10} , etc.) usually forms an insulator.

Bonding and Energy Levels in Molecules: Consider H^{\bullet} :



 CH_4 :



Bonds in molecules to bands in solids: Consider ethene (ethylene) C₂H₄:



Consider only π bonding and antibonding levels



Silicon: Si $\uparrow \downarrow \uparrow \uparrow - 4$ sp³ bonds:



Bands and band gaps:



Electron mobility Metals have "free" electrons and these are usually knocking around in in a random fashion, much like atoms in a gas. When an electric field is applied, however, the electrons start *transporting* a current. In other words, there is a net flow of electrons, depending on the direction of the electric field. The **drift velocity** v_d describes the average velocity of the electrons in the direction of the electric field \mathcal{E} . The mobility μ_e of the electron is then obtained from

$$v_d = \mu_e \mathcal{E}$$

The conductivity σ can then be expressed

$$\sigma = n|e|\mu_e$$

where n is the number of electrons participating in the electrical transport process, and |e| is the magnitude of the electronic charge.

Examples of metals: A number of elements in the periodic table are referred to as metals. However, when discussing properties, materials with free electrons that are good conductors of electricity are also referred to as metals. Examples of metals that are also compounds are: TiO, ReO₃, BaMoO₃, TiS₂, PbO₂ etc.

Electrical resistivity of metals: Different processes in a metal can scatter electrons as they travel, increasing the electrical resistivity. The resistivity can be written as sum corresponding to the different processes:

$$\rho_{\text{total}} = \rho_t + \rho_i + \rho_d$$

where the subscripts on the RHS correspond to temperature, impurities, and deformations respectively. This is called Matthiessen's rule.

Electrons and holes, and the Hall effect Depending on whether the conduction arises from a few electrons in the conduction band or some electrons having been removed at the top of the valence band, the nature of charge carriers varies. In the former case, the carriers are negatively charged. In the latter case, the carriers effectively have positive charge — it is useful to the think of the the few electrons removed from the top of the valence band as having left behind positively charged "holes". Electrons are indicated with n and holes with p.

Hole vs. electron conduction can be distinguished by the Hall experiment where the resistance of a conductor is measured in the presence and absence of a magnetic field.



Doping of semiconductors and intrinsic and extrinsic behavior: Intrinsic semiconduction is when the electrical properties are dictated by the pure material. Extrinsic semiconduction is when small amounts of impurities or dopants (usually deliberately introduced) completely dominate the electrical transport properties.

The conductivity of an intrinsic semiconductor can be expressed

$$\sigma = n|e|\mu_e + p|e|\mu_h$$

In an intrinsic semiconductor, p = n and

$$\sigma = n|e|(\mu_e + \mu_h) = p|e|(\mu_e + \mu_h)$$