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Chapter 7

Electronic Structure of Crystalline Solids: Bands and Periodic Properties

Isolated atoms, as well as molecules and ions that consist of small numbers of atoms, usually have characteristic, well-separated, discrete energy levels that define the electronic structure of these species. The simplest such species, the isolated hydrogen atom, is a staple of introductory presentations on electronic structure and spectroscopy. In extended crystalline solids, however, a vast number of atoms interact electronically with one another. Their overlapping atomic orbitals lead to delocalized orbitals that encompass the entire solid, and enormous numbers of delocalized orbitals are packed into a relatively small energy range.

Figure 7.1 illustrates the electronic structure of a bulk extended solid. This energetically nearly continuous set of electronic states is called a band and accounts for many of the common macroscopic properties of bulk solids. In this chapter, we will specifically discuss examples of electrical, thermal, and optical properties that result from the presence of bands in solids. Furthermore, we will show that bands arise irrespective of whether the bonding in the extended solid is principally metallic, covalent, or ionic. Although this chapter will focus on three-dimensional extended solids, bands also can arise in two-dimensional layered solids, like graphite, and in one-dimensional solids built from chains, like the conducting polymer polyaniline.

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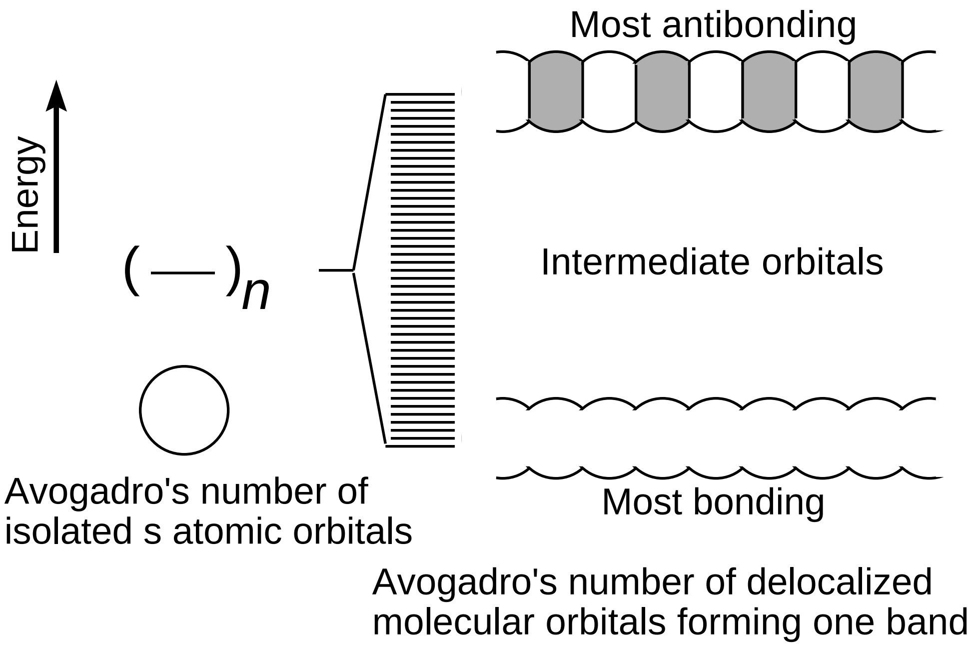

Figure 7.1. In a solid sample, s-type atomic orbitals can combine to give many delocalized orbitals that are very close in energy. The collection of these orbitals forms a nearly continuous set of energy states called a band. The top of the band is the totally antibonding combination formed, in this case, from s atomic orbitals of alternating signs, which are represented by the shaded and unshaded areas. The bottom of the band is the totally bonding combination formed by combining all of the s atomic orbitals with the same sign.

Bands in Metals

Bands result from the overlap of atomic orbitals in a solid, much as molecular orbitals form in molecular systems. In the molecular orbital theory of diatomic molecules, molecular orbitals can form when an atomic orbital from one atom overlaps with an atomic orbital from the second atom to give a lower-energy bonding molecular orbital and a higher-energy antibonding molecular orbital, each of which is delocalized over both atoms. Application of this approach to larger molecules leads to an increase in the number of molecular orbitals, because one molecular orbital is generated for each atomic orbital that is included in the model. A crystal of a metal can be regarded as an enormously large molecule for which the number of molecular orbitals, or energy levels, is on the order of the number of atoms in the solid.

The general picture of how bands arise (shown in Figure 7.1 for an s band, i.e., a band formed exclusively from combinations of s orbitals) can be fleshed out with illustrations from the alkali metals and alkaline earth metals (Figure 7.2). The relatively nondirectional bonding in the alkali metals (bcc, coordination number 8) and alkaline earth metals (hcp or bcc, coordination numbers 12 or 8) make the use of unhybridized orbitals a logical choice to describe the formation of bands in these metals. Thus, bands of interest will in general be those derived from the overlapping valence orbitals of atoms constituting the solid, for example the 3s orbitals of Na. Core orbitals like the 1s, 2s, and 2p orbitals of Na do not overlap as significantly. Much as the more stable, core energy levels that are filled with electrons are ignored in simple molecular orbital treatments of valence electronic configurations, bands derived from core orbitals typically have less significance in characterizing the chemical and physical properties of solids and will also be ignored.

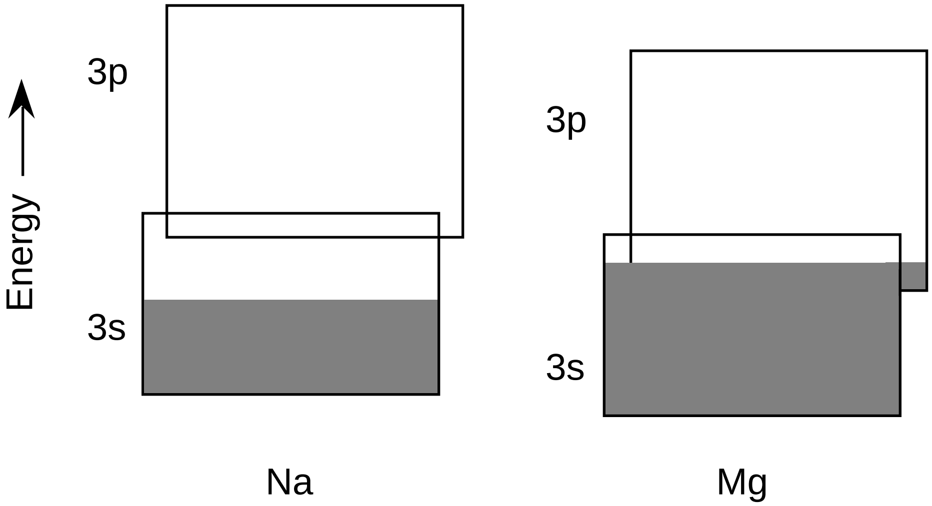

Figure 7.2. Band structure for sodium and magnesium. The 3s and 3p bands are offset for clarity. Shaded regions correspond to energy levels within the band that are occupied by electrons. (The overlap in energy between the 3s and 3p orbitals permits some of the valence electrons of magnesium to occupy energy levels in the 3p band.) Band widths and overlap are not to scale.

Figure 7.3 shows the spreading of the valence 3s orbitals of Na into a band as increasing numbers of Na atoms are combined to make the solid. The right side of the diagram presents a more molecular orbital (MO)-based view, showing the algebraic combinations of these atomic orbitals that correspond to the delocalized orbitals of the band; the most energetically stable (most bonding) combination has the fewest nodes between atoms, and the most unstable (most antibonding) combination has the most nodes between atoms, with the intermediate orbitals varying in numbers of nodes between these two extremes. For a piece of sodium with Avogadro's number, N_A, of atoms, there must be N_A energy levels within the 3s band, reflecting the conservation of 3s orbitals.

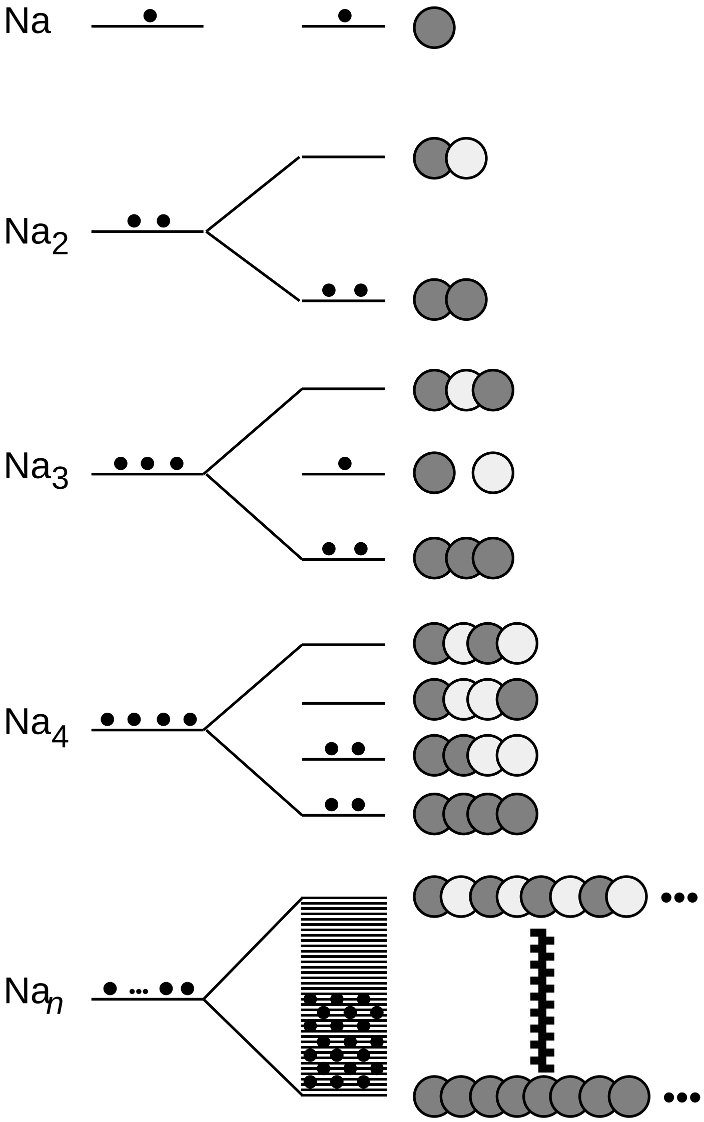

Figure 7.3. Atoms, such as Na(g), and small molecules, such as Na_2(g), Na_3(g), and Na_4(g), have well-separated energy levels. In crystalline solids, large numbers of atoms interact to produce bands of delocalized orbitals that have a relatively narrow distribution of energies. The ideas are illustrated for combinations of the 3s orbitals of sodium atoms, leading to a 3s band. The shading of orbitals (large circles) is described in Figure 7.1; the small dark circles represent electrons.

The energy spread of the band reflects the atomic overlap. As the overlap between orbitals increases, the most bonding orbital of the band is stabilized to a greater extent, the most antibonding orbital of the band is destabilized to a greater extent, and a relatively wide band (one with a large spread in energy) results. Similar considerations are applied to the MO picture of bond formation found in general chemistry texts for diatomic molecules. In contrast, if there is little orbital overlap, the energy levels of the orbitals that are combined to form the band are little affected, and a narrow band results. The net overlap of the 1s, 2s, and 2p core orbitals in Na is very small, and bands derived from these orbitals are considerably narrower than the band derived from the 3s orbitals.

The number of electrons must be preserved in the band diagram. The Pauli principle limits the population of each delocalized orbital comprising the band to two spin-paired electrons, just as would be the case for orbitals in isolated atoms, ions, or molecules. Thus, the 1s, 2s, and 2p bands are completely filled with electrons, because each such orbital of each atom contributing to these bands had its full complement of two electrons. In contrast, the 3s band is exactly half full, because each contributing Na atom has a $3s^1$ or half-full electronic configuration.

For Mg, an isolated 3s band would be filled with electrons, reflecting the individual $3s^2$ configuration of individual Mg atoms. But Mg illustrates the important property that bands can overlap in energy: Although the 3p band of magnesium would be predicted to have no electrons in it, because individual Mg atoms do not have 3p valence electrons, Figure 7.2 shows that the bottom electronic states of the 3p band are lower in energy than the upper states of the 3s band. The electronic states of the 3p band are thus energetically accessible to electrons of the 3s band, because electrons can occupy lower energy states in the 3p band. This feature is crucial to describing electrical conductivity in Mg, as will be described.

Electrical Conductivity of Metals

The conventional description of metallic bonding, as metal ions surrounded by a sea of mobile electrons, is consistent with the band picture sketched. Given the large coordination numbers of metals, the number of valence electrons is insufficient for the kind of electron sharing needed for covalent bonding. The similar electronegativities of the atoms involved precludes the electron transfer characteristic of ionic bonding. The band picture for Na suggests that the solid could be regarded as a bcc crystal of Na^+ ions surrounded by freely moving valence electrons. One plane of atoms in such a crystal is sketched in Figure 7.4.

An important property for comparing the electrical conductivities of various solids and liquids is their carrier concentration, the number of charged carriers (electrons or ions) per unit volume. Carrier concentrations are typically expressed in density units of carriers per cubic centimeter. Assuming all of the 3s band electrons are mobile, Na has the enormous carrier concentration of roughly 10^{22} electrons/cm^3.[1] For perspective, pure water, for which hydrogen ions and hydroxide ions would

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[1] In a metal, only those electrons that are near the top of the filled energy levels of an unfilled band (*see* later) are actually charge carriers. When an electric field is applied, all electrons gain energy, but most simply shift from the level that they occupied to a level that was previously occupied. As such, these electrons provide no net contribution to the conductivity. The remaining carriers near the top of the

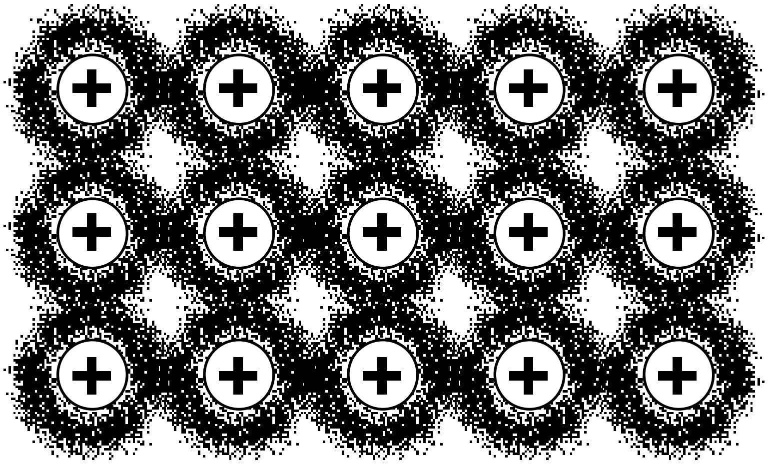

Figure 7.4. Bonding in metals can be viewed as a sea of delocalized and mobile valence electrons acting as a kind of glue to hold the metal cations together.

be the charge carriers, would have a carrier concentration of only 10^{14} ions/cm^3, while a 1 M NaOH aqueous electrolyte would have a carrier concentration of about 10^{21} ions/cm^3.[2]

For a solid to be a good electronic conductor, a property we associate with metals, a high carrier concentration of electrons is a necessary but not sufficient condition. The two requirements for good conductivity by electrons are (1) the presence of a band, whose delocalized orbitals provide a kind of electronic highway through the solid; and (2) an electronic population of the band that corresponds to its being only partially filled, typically from about 10 to 90% of its capacity.

The second requirement can be appreciated from the limiting cases of a completely empty and completely filled band. A completely empty band cannot contribute to electrical conductivity, because it has no electrons to produce the net flow of charged particles that represents an electrical current. A completely filled band is unsuitable for electrical conduction because it has no vacant orbitals for the electrons to jump into to achieve a net physical motion of charge carriers in a particular direction. But if the band is only partially filled, electrons are easily promoted into the vacant, energetically accessible orbitals of the band by absorbing thermal energy or energy from an electric field. These unpaired electrons are then free to move under the influence of an electric field such as that produced by a battery, or to be swept along by a magnetic field as in a generator.

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filled energy levels move to previously unoccupied levels and increase the conductivity *(1)*. Consequently, in sodium metal, approximately 1% of the electrons in the 3s band contribute to the conductivity.

[2] Although the number of charge carriers in sodium metal and sodium hydroxide solution is comparable, the ions, being more massive than electrons, are less mobile. Thus, the conductivity, which depends on both carrier concentration and mobility (a quantitative measure of how the charged particles respond to an electric field), is much lower in 1 M NaOH solution.

Demonstration 7.1. Electron Flow in a Band

Materials

Three clear bottles with caps, one filled with sand, one half-filled with sand, and one empty

Procedure

- Tip each bottle to about a 45° angle from vertical and watch for the flow of sand. The tilting of the bottle represents the applied potential from a battery. If the bottle is empty or completely filled, no sand moves. Only if the bottle is partly filled can sand flow toward the lower side; moreover, only the sand near the top moves, reflecting the fact that only electrons near the top of the filled energy levels contribute to conductivity.[1]

With its half-filled 3s band, Na is an excellent conductor of electricity. A half-filled s band is a general characteristic of the alkali metals because of the ns^1 electronic configurations they have in common. The alkaline earth metals owe their conductivity to the overlap of their p bands with their s bands, as noted in Figure 7.2 for Mg. Overlapping bands provide the same kind of mechanism for conductivity obtained from a single partially filled band: An enormous number of energetically proximate energy levels are accessible through absorption of energy from an electric field. As one moves through the rest of the metallic elements in the periodic table, additional atomic orbitals are found in the valence shells, and overlap of some combination of bands derived from s, p, d, and f orbitals will usually occur to provide the partial filling of bands needed for electrical conductivity.

Conductivity may be increased by adding electrons to an empty band or removing electrons from a filled band. This increase can be demonstrated by using the layered solid graphite (Chapter 5). Graphite is a poor metal (a semimetal) with only a little overlap between the highest energy filled band and neighboring higher energy empty band (contrast Mg, with substantial band overlap). The conductivity of a graphite sample can be substantially enhanced by oxidation with bromine. Oxidation removes electrons from the filled band. (The bromide ion that is generated by the reaction intercalates or moves into the spaces between the layers of the solid, as shown in Figure 7.5.)

Graphite intercalation by electron donors, such as alkali metals, or by electron acceptors, such as bromine or fluorine, is also possible. With donors, electrons are added to the higher energy band, partially filling it and also increasing the conductivity relative to pure graphite. Thus, reaction with either oxidants or reductants increases the conductivity of graphite, and enables it to reach metallic values.

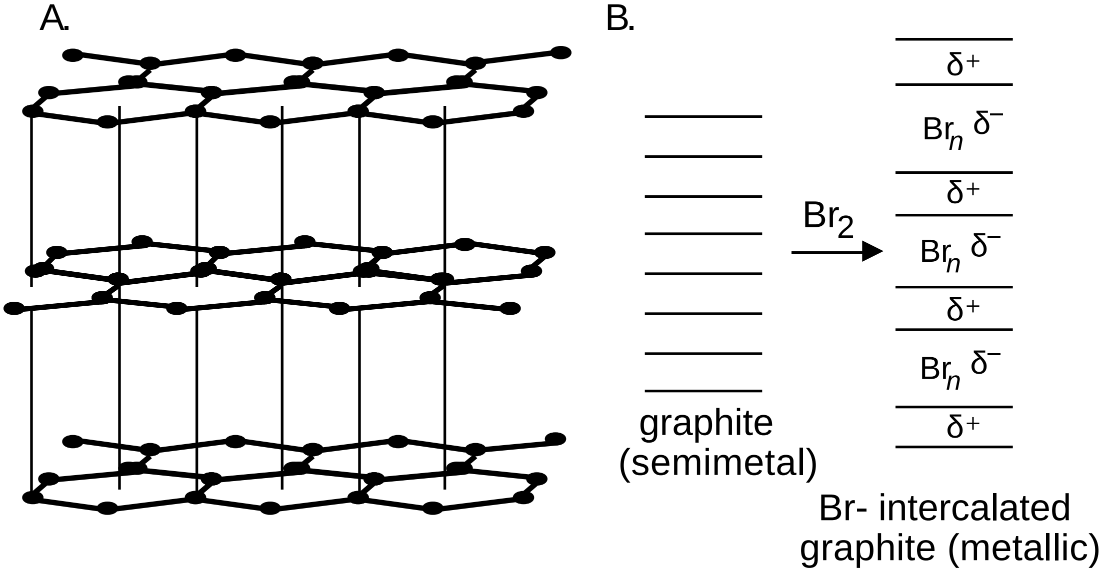

Figure 7.5. A: The layered structure of graphite. B: The oxidative intercalation of bromine into graphite removes electrons from the highest energy filled band in the graphite sheets (the sheets are represented by the parallel lines), while simultaneously forcing them further apart because of the intercalation of bromide ions between the layers.

Demonstration 7.2. Oxidative Intercalation of Graphite

Materials

Two glassy carbon electrodes or graphite rods (1/4-inch diameter)*
Teflon tubing (1/4 inch I.D.) about 3 inches long (or a Teflon cylinder with a 1/4-inch hole drilled lengthwise) with a second hole or notch cut into the center—*see* Figure 7.6
Medium-sized beaker or crystallizing dish (or a glass tube with a hole in center large enough to contain the Teflon tube)
1–2 g of crystalline graphite powder, 200 mesh (Ultra Carbon F works)*
Ring stands and clamps
10% (v/v) Br_2 in MeOH in dropper bottle
Elemental bromine (optional)
6-V battery
1–2-Ω light bulb*
Wires and alligator clips to connect the parts in series
Ohmmeter and leads

Procedure

The intercalation reaction is carried out in a section of Teflon tubing containing the graphite powder. To construct the apparatus,

- Sandwich about 5 mm of crystalline graphite powder between two glassy carbon rods in the Teflon tubing, as shown in Figure 7.6. Apply enough pressure to the graphite so that the resistance between the two rods is 10–30 Ω.
- Place this apparatus in a glass tube with a hole in the top. (The purpose of this tube is to contain excess bromine solution. Alternatively, the apparatus may be arranged so that it is held over a beaker or a crystallizing dish.) Clamp the electrode assembly in a horizontal position. Connect it in series via alligator clips to a 6-V battery and a light bulb with a resistance of 1–2 Ω. The light bulb should glow faintly or be dark, showing that the graphite powder is resistive.
- If you are using the outer glass tube, slide the glass tube off the Teflon tubing to expose the center of the tube. With a razor blade, cut a notch in the Teflon tubing to expose a small area of the graphite powder. (If a thicker Teflon cylinder is used, the notch should be precut.) Place the glass tube over the Teflon tube so that the hole in the glass is aligned with the notch in the Teflon.
- Introduce several drops of 10% v/v Br_2 in methanol solution directly into the notch, and after a few seconds the light bulb will begin to glow brightly.

CAUTION: Bromine is volatile, corrosive, and highly toxic. If a fume hood is available, elemental bromine may be used to produce a more dramatic conductivity change. In either case, the demonstrator should wear gloves. The change in conductivity is sufficient in either case to light the bulb. A solution of sodium thiosulfate can be used to decompose any unreacted bromine and to wash the apparatus upon completion of the demonstration.

The intercalation process swells the individual graphite particles, and increases the pressure inside the Teflon tubing. This improves electrical contact between particles, and thus further lowers the resistance.

Although not explicitly demonstrated here, this experiment can lead easily into a discussion of the anisotropy of layered solids. Ask students how they think the anisotropy affects the electrical and mechanical properties of graphite. What differences in conductivity might be expected using a single-crystal (*see* Chapter 6) of graphite?

*See Supplier Information

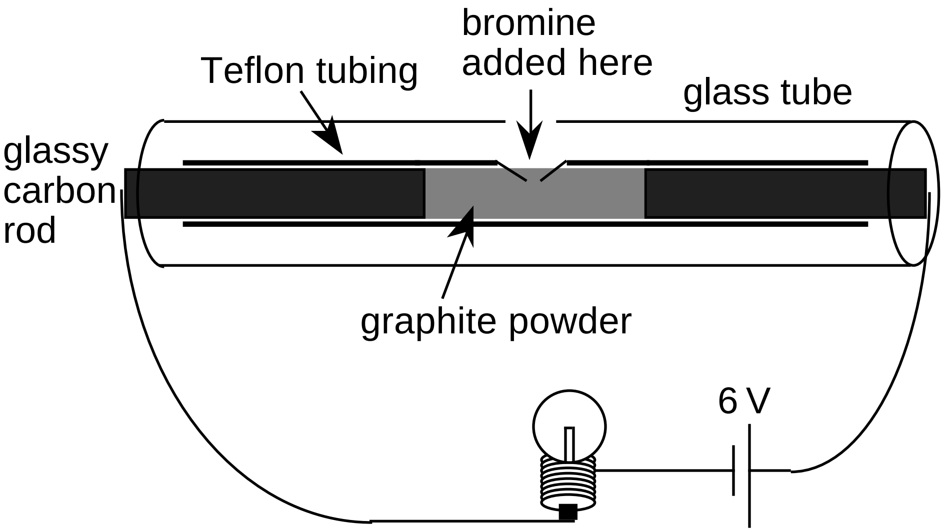

Figure 7.6. The conductivity apparatus for demonstrating the intercalation of bromine into graphite.

Laboratory. An experiment that, through chemical reduction, converts WO_3 to H_xWO_3 with an accompanying enhancement in electrical conductivity is described in Experiment 8.

Solids are generally classified as metals, semiconductors, and insulators, depending on their ability to conduct electricity. Among materials, metals have a relatively high electrical conductivity, σ (sigma). Alternatively, we can speak of the electrical resistivity, ρ (rho), which is the reciprocal of conductivity ($\sigma = 1/\rho$).[3] Conductivity is an unusual property in that it spans roughly 30 orders of magnitude—one of the largest ranges known for a physical property! An electrical conductivity scale encompassing a variety of common substances is shown in Figure 7.7.

How are new metals—be they combinations of metallic elements (alloys), ceramics, or conducting polymers—recognized as such? By the variation of how strongly they resist the motion of electrons as a function of temperature. If a substance exhibits metallic conductivity, its resistivity increases (and its conductivity decreases) as the temperature increases. In contrast, the resistivity of semiconductors and insulators (discussed later) decreases with increasing temperature. By way of illustration, the resistivity of tungsten doubles (the conductivity decreases by a factor of 2) between 750 and 1500 K. For silicon, the prototypical semiconductor, the

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[3] The experimentally measured electrical resistance of a wire, R, is related to the resistivity, ρ, by the equation $R = \rho L/A$, where L is the length of the wire and A is the cross-sectional area. Consequently, resistivity values have the units of ohm-(distance) and are usually reported in ohm-centimeters. Conductivity has the units of reciprocal ohm-centimeters, which is equivalent to mho per centimeter and siemens per centimeter.

resistivity decreases by a factor of 100 (the conductivity increases 100-fold) over the same temperature range *(3)*. The trends are illustrated in Figure 7.8.

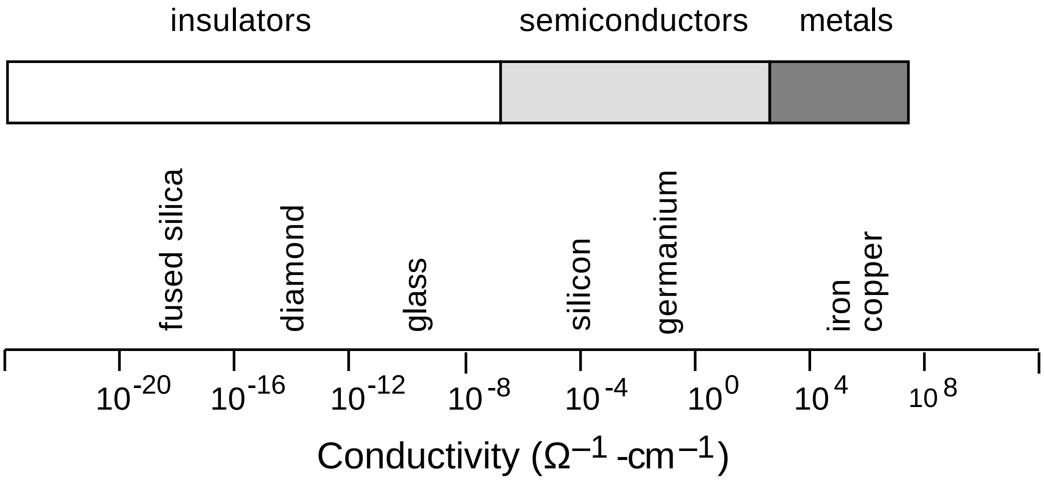

Figure 7.7. The entire range of conductivities of solids spans roughly 30 orders of magnitude. (Adapted from reference 2.)

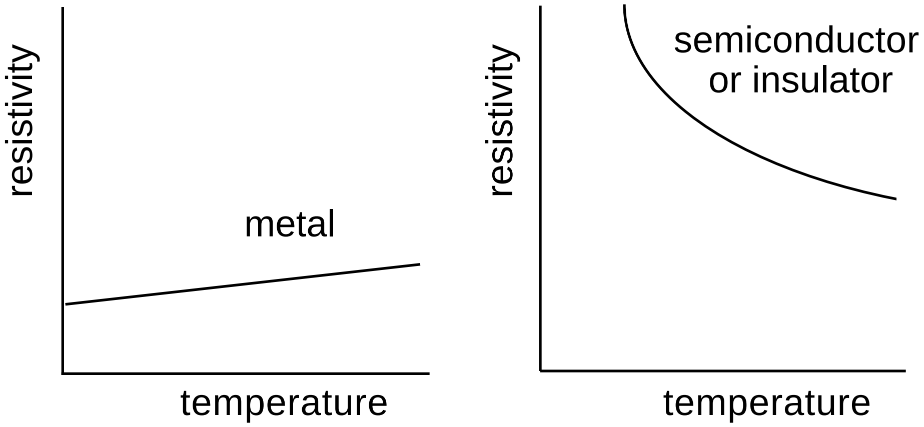

Figure 7.8. The resistivities of metals and semiconductors or insulators show different behavior when the temperature is changed. As the temperature is increased, the resistivity of a metal increases slightly, but the resistivity of a semiconductor or insulator decreases dramatically. The relative size of the effect is not shown to scale in this figure.

The electrical resistance of a solid is analogous to mechanical friction: As electrons move through a material under the influence of an electric field (away from the negative terminal and toward the positive terminal of a battery), they occasionally are scattered by the vibrating atoms of the crystal, by defects, or by impurity atoms in the solid. In this manner, part of the kinetic energy of the electrons' motion is converted into heat, just as the motion of a rolling ball is slowed as its kinetic energy is converted into heat through friction. Increasing the temperature causes the atoms in the crystal to vibrate more vigorously, enhancing the effectiveness with which electrons are scattered and leading to modest increases in electrical resistance. (The decrease in resistivity in semiconductors and insulators is discussed in a subsequent section.)

Demonstration 7.3. Electrical Resistance

Materials

Nichrome wire [22 gauge (0.025-inch diameter), 14 inches long]
Wax
9-V battery
Battery snap with two leads and alligator clips
Overhead projector with a plastic protection sheet (optional)

Procedure

- Prior to the demonstration, heat a container of wax until the wax is just above its melting point.
- Coil the middle section of the nichrome wire around a thin dowel, glass rod, or pencil such that you have about 10 turns that are about 3/8 inch in diameter. (Make sure that the coils do not cross.) This will leave a tail about 1 inch long on each end. Cool the wire in a freezer.
- Dip the coils of the wire rapidly into the heated wax and withdraw the wire immediately. (If the wire is precooled in a freezer, a satisfactory coating will result after one dip. To get even more wax on the wire, cool it in the freezer before dipping a second time.)
- Allow the wax-covered wire to cool.
- When it is time to perform the demonstration, connect the wax-coated piece of nichrome wire to the alligator clips attached to the wires from a battery snap. Press the battery snap onto the terminals of the 9-V battery. Be ready to disconnect the nichrome wire quickly. **CAUTION: Do not connect the wire for more than a few seconds, as the battery may become hot!** When electricity is passed through the wire, the wax melts and drips onto the plastic protection sheet, an effect that can be displayed on an overhead projector.

  Both the wire length and gauge are important variables that must be controlled to achieve a high enough temperature to melt the wax.

Variations

Electrical resistance can be demonstrated in a number of other ways. Toasters, electric stove burners, and light bulbs can be used to demonstrate resistive heating. Memory metal can also be employed: When a sample of memory metal is resistively heated, it will return to a shape that it has been trained to remember. (*See* Chapter 9 for a description of memory metal and the details of the demonstration.)

All of these demonstrations show that wire possesses some resistance to current flow, which results in the conversion of electrical energy to thermal energy or heat.

Demonstration 7.4. Temperature Dependence of Resistance in a Metal

Materials

Two choke coils or inductors (Mouser Electronics; *see* Supplier Information)
Hacksaw
Liquid nitrogen in a small Dewar flask
Ohmmeter

Procedure

- Use a hacksaw to remove a portion of the outer casing of one of the choke coils to show the inside. The coil contains 150 m of tightly wound Cu wire in a plastic container.
- Connect the two ends of the other choke coil to the leads of an ohmmeter and measure the resistance. A value of about 150 Ω will be found at room temperature.
- Plunge the choke coil into the liquid nitrogen. **CAUTION: Liquid nitrogen is extremely cold. Do not allow it to come into contact with skin or clothing, as severe frostbite may result. Wear gloves when transferring and using liquid nitrogen.** The resistance will be found to drop to about 15 Ω, as the metal cools. (Do not place a coil that has been cut open into liquid nitrogen, as it will crack.)

Something like a choke coil is needed for this experiment because metals are such good conductors: To obtain significant resistance values, the metal needs to be as long and thin as possible, because, for a given material, electrical resistance increases with length and decreases as the wire thickness increases.[3] The analogy can also be made that the flow of electricity is like the flow of water through pipes: Less resistance to flow obtains for pipes with larger openings and shorter lengths.

Thermal Conductivity of Metals

Partially filled bands lead not only to good electrical conductivity, but also to good thermal conductivity. If one end of a metal rod is heated, the other end will soon become warm through a process called thermal conduction, wherein heat is transferred without physically displacing atoms: At the heated end, atoms vibrate more rapidly, and the electrons in the partially filled conduction band easily absorb thermal energy (moving into the thermally accessible, unfilled energy levels of the band) and thereby increase their kinetic energy. This increased kinetic energy leads to more frequent and more energetic collisions with atoms throughout the solid, increasing their vibrational energy and effectively transferring the added thermal energy along the length of the rod. Demonstrations 7.5 and 7.6 illustrate the high thermal conductivity of metals, and Table 7.1 presents values for various materials.

Demonstration 7.5. Thermal Conductivity in the Classroom

Materials

A student desk or chair that has wooden and metal parts (or any other sources of wood and metal that are in the room)

Procedure

- Ask the students to touch the wood and the metal. Which feels cooler?
  This is a simple demonstration of the relatively high thermal conductivities of metals. A wooden lecture room chair having a metal frame can be a particularly effective example. Both the wood and metal are at thermal equilibrium and thus at room temperature. However, the metal will feel cooler to the touch than the wood because the free electrons in the partially filled band can rapidly remove thermal energy from our bodies and thereby make the metal feel cool.

Demonstration 7.6. A More Quantitative Measure of Thermal Conductivity

Materials

6-inch long, 1/4-inch-diameter rods made of various materials, including aluminum, copper, brass, wood, iron, and Plexiglas. (These rods are available from hardware or hobby stores.)
Styrofoam cup
Hot water (~150 mL)
Elbow macaroni noodles
Butter or margarine
A clock or watch capable of measuring time in seconds

Procedure

- Dip one end of each rod in butter or margarine to provide a sticky surface that will hold a piece of macaroni in place. Place a piece of macaroni on one end of each rod to be studied.
- Then place all of the rods in a Styrofoam cup with the end holding the macaroni and margarine up, as shown in Figure 7.9.
- Add hot water to the cup and begin timing. As the heat travels by conduction along each rod, the margarine melts and the macaroni falls off; relative rates of thermal conductivity are thus defined. The rate in this case is 1/time. A plot of typical data, shown in Figure 7.9, reflects the far greater thermal conductivity of metals.

Laboratory. Students can measure cooling curves for hot water in various containers. A container such as a Styrofoam cup is filled with hot water, and the temperature is monitored as a function of time. The experiment can be repeated with different container materials, amounts of water (varying surface-to-volume ratios), or initial temperatures of water. The rate of cooling should depend on the thermal conductivity of the container. If students are given thermometers, this can be done as a take-home lab. A variety of variables need to be constrained. This is a simple enough experiment that it is an opportunity to let students set up their own experimental procedure, and no further directions are included in this book.

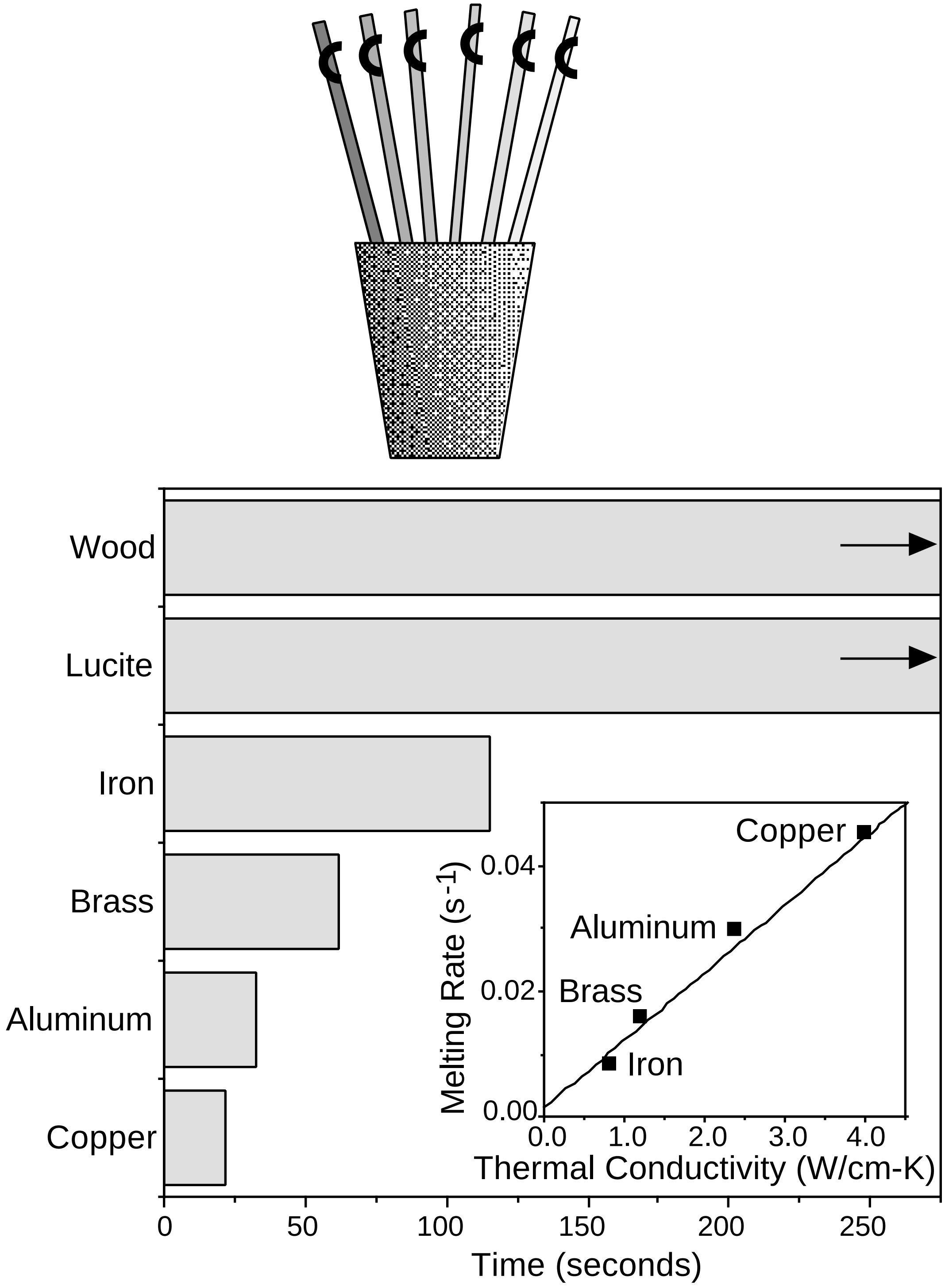

Figure 7.9. Test of thermal conductivity described in Demonstration 7.6. Typical data are shown, as is a plot of the thermal conductivity of the rod types (from Table 7.1) versus the relative melting rate (the reciprocal of the amount of time it took for the noodle to fall off the rod).

Table 7.1. Thermal Conductivities of Various Substances

Material	Thermal Conductivity (watt/cm-K)
Air	0.00026
Glass wool	0.00042
Corkboard	0.00043
Carbon tetrachloride	0.0010
White pine	0.0011
Oak	0.0015
He	0.001520
Water	0.0061
Glass	0.0072–0.0088
Hg	0.083
Concrete	0.0086–0.013
SiC	0.090 (100 °F)
NaCl	0.092 (0 °C)
ZnS (zinc blende)	0.264 (0 °C)
Al_2O_3	0.303 (100 °C)
Pb	0.353
Cs	0.359
MgO	0.360 (100 °F)
Rb	0.582
Fe	0.804
Li	0.848
K	1.025
C (graphite)[a]	1.1–2.2
Zn	1.16
Brass	1.2
Na	1.42
Mg	1.56
Be	2.01
BeO	2.20 (100 °F)
Al	2.37
Au	3.18
Cu	4.01
Ag	4.29
C (diamond)[b]	9.9–23.2

NOTE: All values are at room temperature unless otherwise noted.

[a] Value is dependent on the impurities in graphite and on the orientation of graphite, being larger in the direction parallel to the layers of carbon atoms.

[b] Value is highly dependent on impurities and defects.

SOURCE: Adapted from reference 4.

Optical Properties of Metals

Certainly one of the most characteristic features of clean metals is their shininess, or high reflectivity for visible light and other wavelengths of electromagnetic radiation. We often overlook the fact that they are also opaque. This effect is also interpretable in terms of the band structures of these solids. Figure 7.10 illustrates the kind of electronic transitions that can be expected for a metal with its partially filled band. Absorption can take place over enormous regions of the electromagnetic spectrum because of the nearly continuous nature of the electronic states within the band. The vertical arrows in Figure 7.10 represent electronic transitions ranging from very low energy (short arrows), well below the visible spectrum (infrared radiation, microwaves, radio waves, etc.), to well above the visible spectrum (long arrows), into the UV region and beyond.

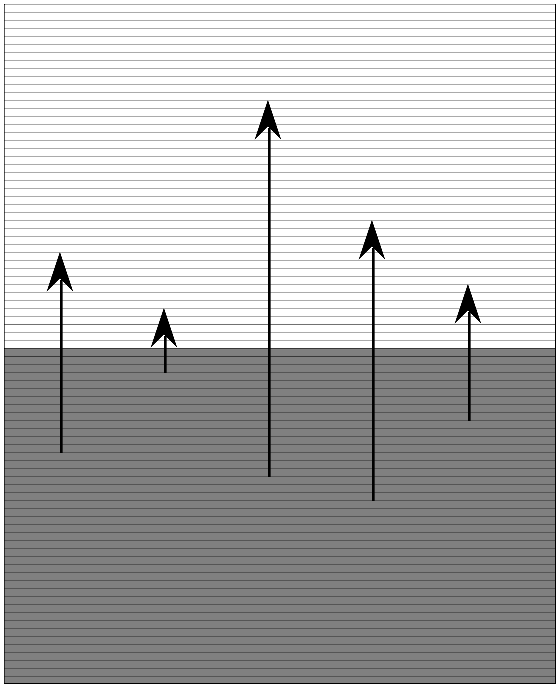

Figure 7.10. Possible electronic transitions in a half-filled band of a metal.

It may seem somewhat paradoxical, but strong absorbers of electromagnetic radiation are also strong reflectors of it. Since metals are electrical conductors, absorption of light (an electromagnetic wave) causes the many free electrons in the solid to oscillate at the frequency of the radiation and to re-radiate at the same frequency. The re-radiated light exits from the metal (as reflected light) and also cancels the incident light propagating into the metal. Figure 7.11 shows that the reflectivity of visible light from various metals typically exceeds 90%.

The colors we associate with certain metals like Cu and Au arise from nonuniform reflectivity across the visible spectrum. For Cu, in particular, the band structure leads to higher absorption and reflectivity in the red, orange, and yellow portions of the visible spectrum (Figure 7.11), and thus to the reddish color associated with the metal. The intensity of absorption and reflectivity in general is a complex function of selection rules (certain electronic transitions are favored, as they are in the spectroscopy of atomic and molecular systems) and of the density of electrons and electronic states that can be involved in the transitions.

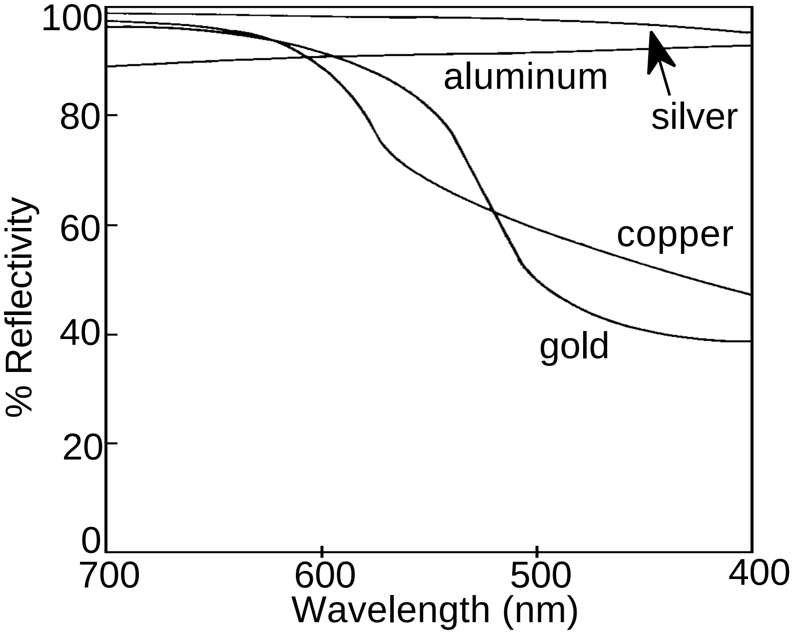

Figure 7.11. Reflectivity as a function of wavelength in the visible region of the spectrum for several metals. The color of gold and copper arises from nonuniform reflectivity across the visible region of the spectrum. (Adapted with permission from reference 2. Copyright 1983 John Wiley and Sons.)

Demonstration 7.7. Metallic Reflectivity

Mirror-quality thin films of metals like Ag and Cu can be plated onto glass surfaces by the chemical reduction of Ag^+ and Cu^{2+} ions. A silver mirror can be prepared for viewing in a large lecture hall by reduction of silver nitrate. These demonstrations have been described elsewhere *(5, 6)*. If a flat region of glass is available for the deposition, a low power laser beam can be reflected off the surface before and after deposition to highlight the metal's reflectivity. **CAUTION: Take care to ensure that the viewers will not inadvertently look directly at the beam where it emerges from the laser. Clamp or tape the laser in a fixed position so that the beam will not accidentally shift. Aiming a laser at a person or looking directly at a source of laser light can be harmful to the eye!**

Covalent Insulators and Semiconductors

Prototypical electrical insulators and semiconductors, like diamond and silicon, are found in the nonmetals portion of the periodic table. Many of these solids have the diamond or zinc blende structures discussed in Chapter 5 that feature tetrahedral bonding geometries. This more directional, covalent bonding can be described with bonds derived from the same sp^3 hybrid orbitals commonly introduced in general chemistry courses to discuss methane and related tetrahedral molecules. The families of extended solids that exhibit tetrahedral bonding provide a wealth of illustrations of periodic properties.

Localized and Delocalized Bonding Pictures

Before introducing a delocalized bonding model to describe these solids (their band structure), trends in many of the properties to be described can be discussed by using exclusively a simple localized bonding picture. In particular, periodic trends in atomic orbitals and atomic electronegativity can be used to predict trends in bond length, bond strength, and energies of electronic transitions associated with these extended solids. These correlations will be noted throughout the remainder of this chapter, in Chapter 8 and in Experiment 7 as localized descriptions. Thus many interesting properties of families of semiconductors and insulators can be described in introductory courses without recourse to bands, if desired. The delocalized model discussed in the next section will make evident some of the limitations of this localized approach.

Tetrahedral Solids

Given the technological importance of tetrahedral solids like diamond and silicon, it is not surprising that their electronic structures have been intensively investigated. A qualitative approach that will be presented here is based in part on a treatment in Cox's book *(7)*.

The methane molecule is a good starting point for describing band formation in extended tetrahedral solids. On the left of Figure 7.12 is shown a carbon atom that has been hybridized to yield four equivalent sp^3 hybrid orbitals, directed to the corners of a tetrahedron. The four hybrid orbitals conserve the original total number of valence 2s and 2p orbitals, and each holds one electron, representing the original total number of valence electrons. At the right of Figure 7.12 are the valence 1s orbitals of the four hydrogen atoms. These are combined with the four carbon sp^3 hybrid orbitals to give four bonding orbitals that are stabilized in energy relative to the atomic orbitals of carbon and hydrogen; and four antibonding orbitals that are destabilized. All eight valence electrons can be accommodated by the four bonding orbitals, representing the four sigma bonds between carbon and each of the four hydrogen atoms. (A similar picture would result for carbon tetrachloride, using, for example, one 3p orbital from each of the chlorine atoms to combine with the carbon sp^3 hybrid orbitals.)

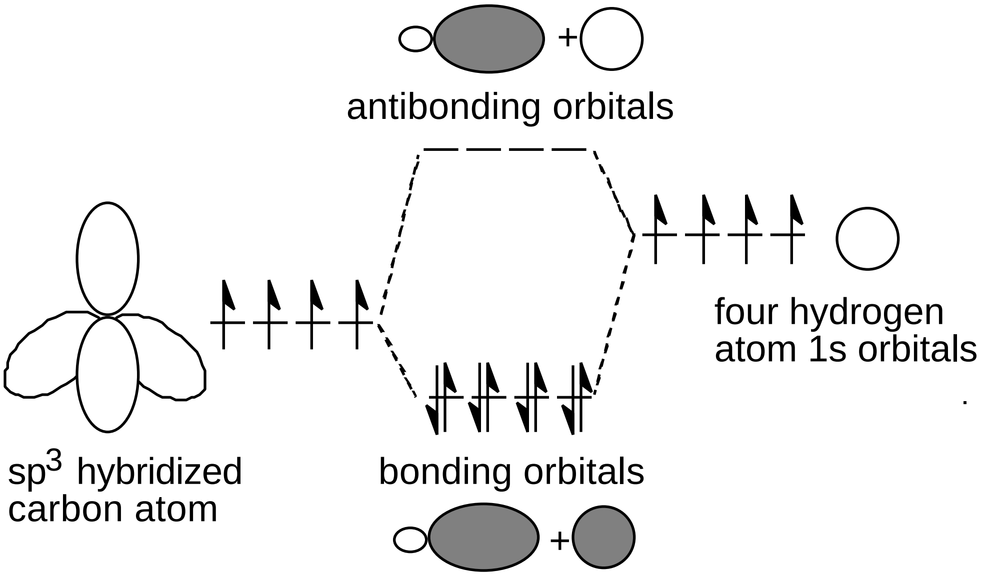

Figure 7.12. A simplified molecular orbital diagram for CH_4. The left side of the diagram shows the four sp^3 hybrid orbitals on the carbon atom (the smaller back lobes are omitted for clarity) and the 1s orbitals of the four hydrogen atoms are shown on the right. Bonding and antibonding combinations of the two sets of orbitals produce two sets of discrete energy levels. The lower set is completely filled by the eight valence electrons.

The situation in the diamond allotrope of carbon is analogous to that for methane except that the orbitals on the right side of the diagram become sp^3 hybrid orbitals of the four adjacent carbon atoms that are bonding to the central carbon atom, (Figure 7.13A.) Once again the same kind of splitting between the four bonding orbitals and four antibonding orbitals occurs. However, other, weaker orbital interactions occur, too. For example, a hybrid orbital on the central carbon atom has some overlap with the hybrid orbitals on the adjacent carbon atoms that are not pointed directly at it, as shown in Figure 7.13B. These interactions and still weaker ones with atoms yet farther away from the central atom cause the bonding orbitals to broaden into one band, the valence band, and the antibonding orbitals to broaden into a second, higher energy band, the conduction band.

Again, the total number of orbitals in the bands preserves the original number of atomic orbitals. For a large number, N, of atoms in the solid, with each atom using four valence orbitals for bonding (the 2s and three 2p orbitals), $2N$ orbitals will make up the lower energy valence band, and $2N$

orbitals will make up the higher energy conduction band. Each atom has four valence electrons. These 4*N* valence electrons of the solid can be entirely accommodated by the 2*N* orbitals of the valence band in accord with the Pauli principle's limitation of two spin-paired electrons per orbital. The result, at a temperature of absolute zero, is a filled valence band and an empty conduction band, shown in Figure 7.13.

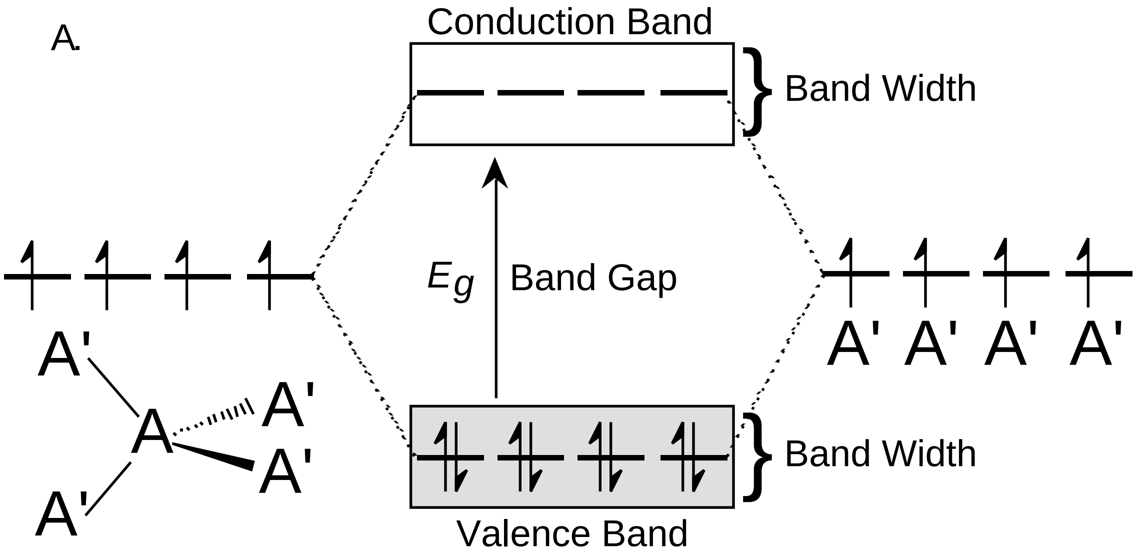

Figure 7.13A. Schematic bonding picture of the Group 14 tetrahedral solid diamond. The four equivalent hybrid orbitals on the central carbon atom are shown on the left, and one overlapping hybrid orbital from each of the adjacent carbon atoms, A', is shown on the right. These orbitals are combined to produce a set of four bonding orbitals and four antibonding orbitals (horizontal lines in the center of the picture). Secondary interactions of these orbitals (*see* part B of this figure) lead to band formation: The bonding orbitals broaden into the so-called valence band, which is completely filled with electrons (shaded) at 0 K, through the interactions of all the atoms in the solid. The antibonding orbitals broaden into the so-called conduction band, which is empty of electrons (unshaded) at 0 K.

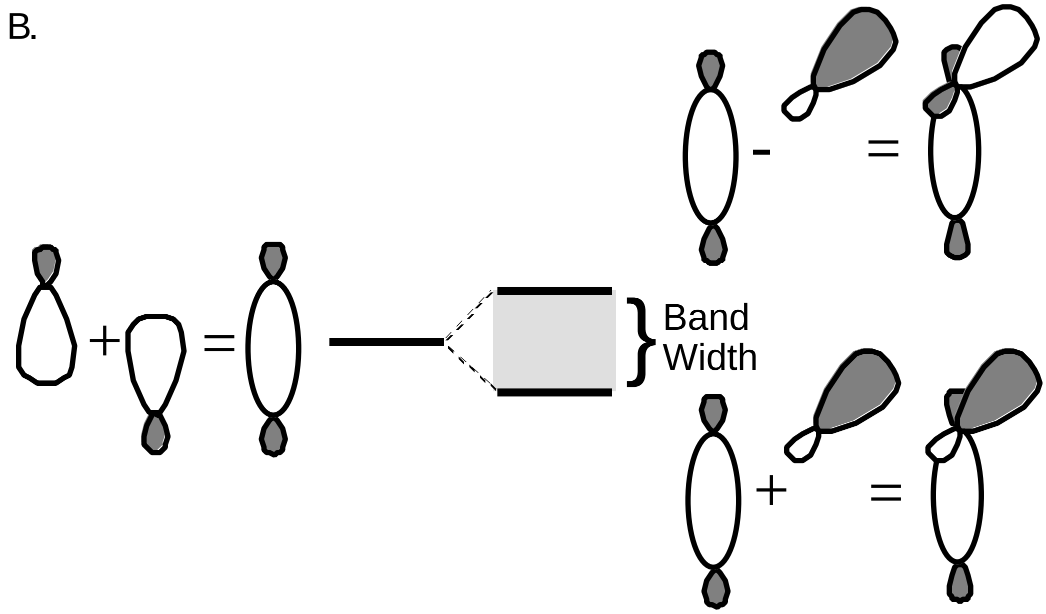

Figure 7.13B. A representation of the kind of secondary orbital interactions that cause broadening of the bonding and antibonding orbitals into bands. The bonding orbital on the left side of the diagram (shown as formed from hybrid orbitals on adjacent carbon atoms A and A' in Figure 7.13A) can have positive or negative overlap with the other hybrid orbitals of these atoms, leading to slightly stabilized (bottom combination on the right-hand side) and destabilized (top combination on the right-hand side) energy levels, respectively; shading is used to represent a change in sign. The collective effect of all of these interactions is to produce the set of tightly spaced energy levels that defines the valence band and its band width. Analogous interactions involving the antibonding orbitals cause broadening into the higher energy conduction band.

Electrical and Optical Properties of Insulators and Semiconductors Having the Diamond Structure

The energy separation between the top of the valence band and the bottom of the conduction band is a fundamental property of the solid, called its band gap, E_g, and it reflects the structure and bonding in the solid. The bands and band gap arise from the periodic, repeating arrangement of atoms in crystalline solids. The magnitude of the band gap is derived from two factors: the strength of the interaction that leads to the separation of the bonding from the antibonding orbitals (roughly, the separation in energy between the centers of the two bands shown in Figure 7.13A), and the strength of the secondary interactions that lead to the energy spread, the band width, of each band (Figure 7.13B). Both will increase as the internuclear distance decreases and the orbital overlap increases. The terms insulator, semiconductor, and metal are used to classify solids based on the size of the band gap (which is essentially zero for a metal) and the effect of the band-gap energy on electrical conductivity.

Figure 7.14 schematically illustrates how insulators and semiconductors differ from metals. In an electrical insulator, diamond being an excellent example, the valence band is essentially filled with electrons, and the conduction band is essentially empty. The band gap of an insulator is large (an arbitrary definition is that $E_g > 3$ eV ~ 300 kJ/mol; this energy corresponds to a photon of wavelength $\lambda < 400$ nm), and the relatively small amount of thermal energy available at room temperature (kT, where k is Boltzmann's constant and T is absolute temperature, is ~0.025 eV ~ 2.4 kJ/mol) ensures that few electrons will be promoted thermally across the band gap where they could then contribute to electrical conductivity. A semiconductor has a smaller band gap ($E_g < 3$ eV ~ 300 kJ/mol; $\lambda > 400$ nm), and electrons are more easily thermally promoted into the conduction band. The metal shown in Figure 7.14 corresponds to a case such as that discussed earlier for Mg, where a partially filled band arises from the energy overlap of a filled with an unfilled band.

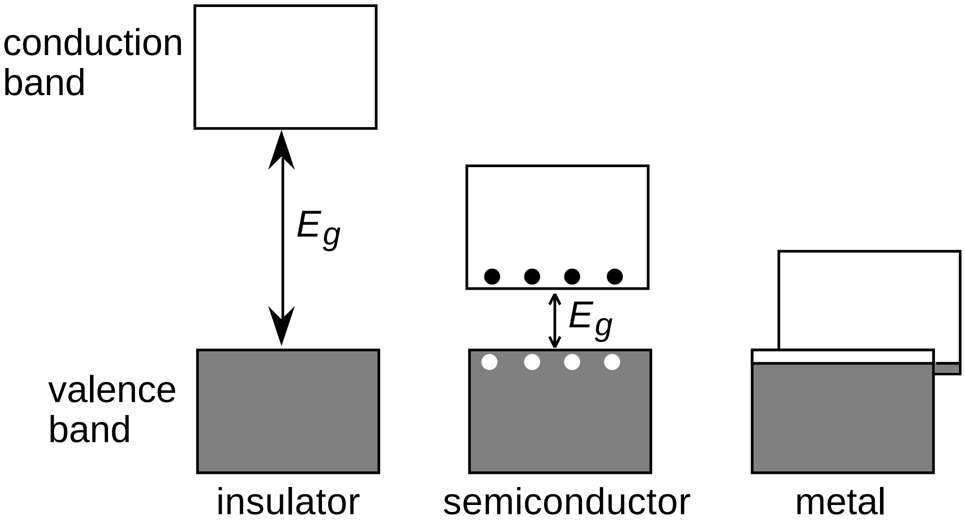

Figure 7.14. Schematic band-structure diagrams for an insulator, a semiconductor, and a metal. The band gap, E_g, shown as the double-headed arrow, is the separation between the top of the valence band and the bottom of the conduction band. The size of the band gap decreases in passing from an insulator to a semiconductor to a metal. Electron–hole pairs are shown for a semiconductor as filled circles in the conduction band (electrons) and open circles in the valence band (holes; *see* Chapter 8).

An important "litmus test" for distinguishing metals from semiconductors and insulators is the temperature dependence of electrical resistivity. As noted, metals have a resistivity that increases slowly with temperature, owing to increased scattering of the free electrons by crystal atoms with temperature. This effect occurs in semiconductors as well but is usually completely swamped by another effect: exponentially increasing numbers of charge carriers with temperature. The carrier concentrations of insulators and semiconductors at thermal equilibrium are dependent on the magnitude of the band gap *(8)*, E_g, as given by exp ($-E_g/2kT$) [or as exp ($-E_g/2RT$) on a molar basis; *see* Chapter 8]. Thus, the carrier concentrations are typically orders of magnitude below those of metals (a value of ~10^{10} carriers/cm^3 in Si at room temperature, for example, compared to ~10^{22} carriers/cm^3 in Na), but the resistivities drop rapidly with increasing temperature, as shown in Figure 7.8. (A related plot that shows the number of charge carriers as a function of reciprocal temperature for Si, Ge, and GaAs appears in Figure 8.5.)

In the Group 14 solids that crystallize with the diamond structure (C, Si, Ge, and α-Sn; *see* Chapter 5), E_g progressively decreases down the group. Table 7.2 lists the Group 14 solids, C through α-Sn, along with their cubic lattice parameters (the length of the side of the cubic unit cell), estimated bond-dissociation energies (D_0), and band-gap energies (300-K values). The size of the unit cell scales with interatomic distance in the solid and follows the expected periodic trend: the increase in atomic radius with atomic number is reflected in larger unit cells. The trend in dissociation energy reflects the greater orbital overlap obtainable as the Group 14 atoms become smaller, which leads to shorter, stronger bonds.

The trend in band gaps has to be analyzed with caution because, as noted, several factors contribute to it. The dominant effect in causing E_g to increase up the group is the increased orbital overlap with smaller internuclear separation, which causes a greater splitting between the centers of the bonding and antibonding bands derived from the sp^3 hybrid orbitals. Although the band widths do change—they increase somewhat up the group for, in part, the same reason of better overlap with smaller internuclear separation—this effect appears to be weighted less strongly in this series.[4]

Diamond has exceptionally strong covalent bonds that result from excellent orbital overlap; these bonds make diamond the standard against which the hardness of materials is measured. The large band gap of ~5.5 eV (580 kJ/mol) makes diamond a good electrical insulator. The optical properties of diamond can also be explained by the band gap, which gives the threshold energy for an electronic transition from the valence band to the conduction band. This transition would be analogous to the lowest energy electronic transition in a molecule, wherein an electron in the highest occupied molecular orbital (HOMO) is promoted to the lowest unoccupied molecular orbital (LUMO) by absorbing a photon whose energy corresponds to the energy difference in these two levels. In the extended

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[4] The interplay of factors affecting the band gap is seen by noting that the widths of the valence and conduction bands for the Group 14 solids are directly proportional to the initial energy separation between the valence s and p orbitals, ($E_s - E_p$) *(11)*. The energy difference, ($E_s - E_p$), drops from ~8.5 eV (820 kJ/mol) for carbon to ~6.6 eV (640 kJ/mol) for tin, a result suggesting that the widths of the valence and conduction bands are getting smaller as the Group 14 atoms become larger. Had there been no change in the separation between the bonding and antibonding orbitals down the group (the separation between the centers of the bands), the band gap would have increased down the group!

solid, the many filled electronic states below the valence-band edge and the many empty states above the conduction-band edge means that electronic transitions and absorption occur for a broad range of energies above the band-gap energy, as shown in Figure 7.15A. A generic absorption spectrum for insulators and semiconductors is sketched in Figure 7.15B and illustrates this onset of electronic absorption at the band-gap energy. For diamond, the E_g value of 5.5 eV (λ = 230 nm) is in the ultraviolet portion of the electromagnetic spectrum rather than in the visible portion, which ranges from violet light at ~3.1 eV (λ = 400 nm), to red light at ~1.7 eV (λ = 730 nm), making diamond transparent to visible light.

Table 7.2. Periodic Properties of the Group 14 Solids Possessing the Diamond Structure

Element	Lattice Parameter , Å[a]	D_0, kJ/mol[b]	E_g , eV (λ, nm)[c]
C	3.57	346	5.5 (230)
Si	5.43	222	1.1 (1100)
Ge	5.66	188	0.66 (1900)
α-Sn	6.49	146	< 0.1 (12,000)

[a] Repeat distance, *a*, of the cubic unit cell at 300 K, obtained from X-ray diffraction data. These values are known to greater precision, but are rounded off here for simplicity and are taken from reference 9.

[b] Bond-dissociation energy was determined from heats of atomization data from reference 10.

[c] Band-gap energy at 300 K is from reference 9.

On the basis of the explanation given for the high thermal conductivities of metals, diamond, with its paucity of free electrons, might be predicted to have poor thermal conductivity. However, diamond actually has a remarkably high thermal conductivity because of a second mechanism for transferring heat that is based on the quantized high-energy vibrations of atoms in the solid, called phonons (*see* Chapter 2, Heat Capacities). Diamond is sometimes said to have a “stiff” crystal structure because of the strong carbon–carbon bonds. The phonon mechanism also imparts high thermal conductivities to many ceramic materials like Al_2O_3 and BeO.

In descending Group 14 to silicon, the cubic unit cell's lattice constant (the length of an edge of the unit cell) expands to 5.43 Å. The reduced orbital overlap is reflected in Si–Si bonds that are longer and weaker than the C–C bonds of diamond and in a substantially smaller band gap of ~1.1 eV (110 kJ/mol). Electrons are more easily promoted across the band gap by thermal energy, and silicon is a semiconductor. Furthermore, each electron that is thermally excited across the gap helps conductivity in two ways: by helping to partially fill the conduction band and by helping to partially empty the valence band (a concept that will be elaborated upon in more detail in Chapter 8, using a formalism by which missing valence-band electrons are treated as positively charged particles called holes). The small band gap of silicon corresponds to a threshold wavelength for absorption of ~1100 nm, below the visible spectrum. Thus, crystalline silicon absorbs light from the entire visible spectrum and appears black.

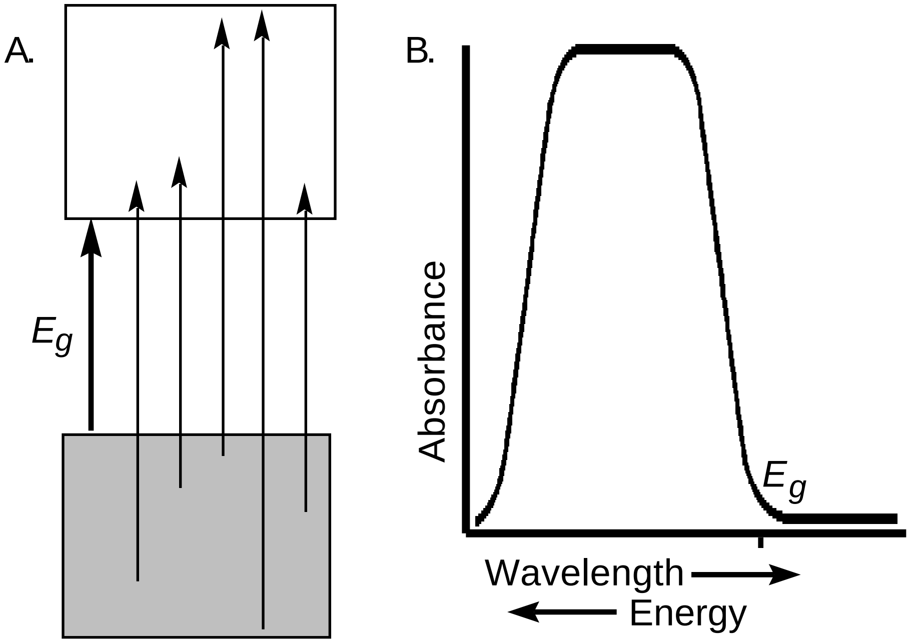

Figure 7.15. A: A band diagram showing possible transitions of electrons from the valence band to the conduction band. The bold arrow represents the minimum energy for the transition and corresponds to an electron that is promoted from the top of the valence band to the bottom of the conduction band. This energy corresponds to E_g. The longer arrows correspond to absorption of photon energies greater than E_g. B: Sketch of a generic absorption spectrum of a semiconductor. The absorbance increases sharply as the energy of light approaches the band gap of the semiconductor. Light with greater energy than the band gap is absorbed because it corresponds to a transition from an individual orbital in the valence band to another orbital in the conduction band. This feature makes some semiconductors useful as optical cutoff filters. Absorption will decline again for photons whose energies exceed the combined energies of the band widths and the band gap.

Only a modest increase in unit-cell size occurs in passing from Si to Ge (5.66 Å), presumably reflecting the interposition of the transition elements. The Ge band gap, 0.66 eV (64 kJ/mol), is slightly reduced from that of Si; absorption begins for wavelengths less than ~1900 nm, giving Ge a black color. A larger change in unit-cell size is seen in passing to α-Sn. This phase of tin, which exhibits the diamond structure, is stable only below room temperature (Chapter 9). The lattice constant of α-Sn is 6.49 Å, and the solid has a band gap of < 0.1 eV (< 9.6 kJ/mol; $\lambda > 12{,}000$ nm). In this case the valence and conduction bands are close to merging. The final member of the Group 14 elements is lead, which does not have the diamond structure. However, if Pb were to adopt this structure, it has been predicted *(12)* to be a metal having a filled s band and partially filled p band.

In a localized bonding picture, promoting an electron across the band gap can be thought of crudely as freeing one of the electrons from the directional covalent bonds in the crystal, making it a mobile charge carrier. The increasing likelihood of this happening down the Group 14 extended solids has been correlated with the trends in bond length, bond strength and atomic ionization potentials.[5] Both thermal excitation and photoexcitation can cause this ionization to occur; photoexcitation corresponds to absorption of lower photon energies as the energy requirement declines.

Demonstration 7.8. The Hardness of Diamond

Materials

Diamond scribe (available from Aldrich, Z22554-1)
Small piece of glass such as a microscope slide
Overhead projector
Penny
Piece of aluminum metal

Procedure

- Use the diamond scribe to scratch a piece of glass. This scratching can be shown on an overhead projector and contrasted with the inability of other materials like a penny or aluminum to mar the glass surface.

Demonstration 7.9. Photoconductivity of CdS

Materials

CdS photocell (obtained from Mouser or Radio Shack; *see* Supplier Information). CdS has the wurtzite structure, rather than the zinc blende structure.
Ohmmeter (ideally with an audible conductivity test function)
Light source such as an overhead projector or sunny window

Procedure

- Connect the photocell to the ohmmeter.
- Measure the resistance of the device with and without exposure to a light source to note the effect of light-induced promotion of electrons across the band gap. A multimeter with an audible conductivity test feature is an effective way to demonstrate this in a classroom.

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[5] Correlations of these parameters with band gap have all been analyzed and their limitations discussed. *See* reference 13.

Electrical and Optical Properties of Insulators and Semiconductors Having the Zinc Blende Structure

Isoelectronic–isovalent principles are compellingly illustrated with the tetrahedral extended solids.[6] The total valence-electron count of elements having the diamond structure is preserved in compounds of AZ stoichiometry having the zinc blende structure (also called “sphalerite,” after the mineral ZnS that possesses the structure), which is identical to the diamond structure except that two different kinds of atoms replace the single kind of atom in diamond (Chapter 5).

Trends in periodic properties can be used to explain the band gaps in the group of elements that symmetrically flank the Group 14 elements in the periodic table. In Figure 7.16, complementary AZ pairs are indicated with similar shading. All A atoms are tetrahedrally coordinated exclusively to Z atoms; and all Z atoms are tetrahedrally coordinated exclusively to A atoms. Solids such as Ge, GaAs, ZnSe, and CuBr are isostructural and can be considered to be isoelectronic: For example, in passing from Ge to GaAs, half of the Ge atoms are replaced by Ga atoms having one fewer valence electron, and the other half are replaced by As having one additional

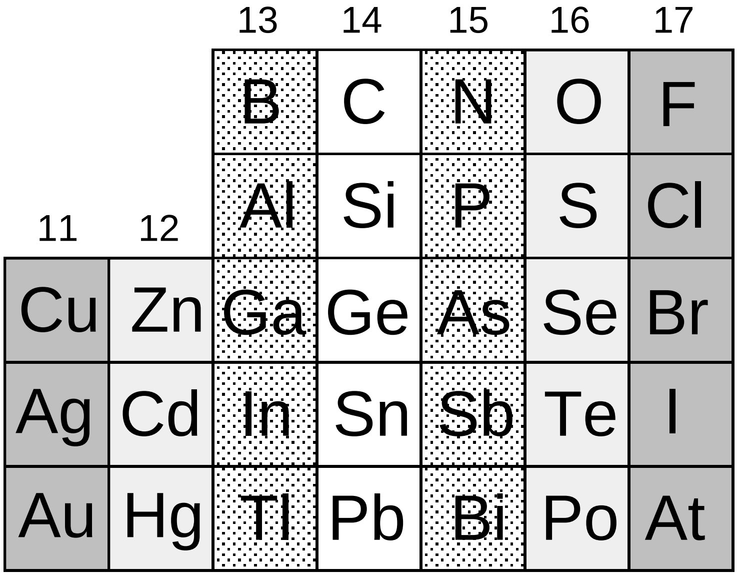

Figure 7.16. Portion of the periodic table emphasizing the formation of AZ solids that are isoelectronic with the Group 14 solids. Complementary pairs are indicated with similar shading; for example, Ge, GaAs, ZnSe, and CuBr.

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[6] As used here, isoelectronic species are those that preserve the number of valence electrons in orbitals with the same principal quantum number. The ions Na^+ and Mg^{2+} are considered to be isoelectronic with each other. The solids Ge, GaAs, and ZnSe have the same average number of valence electrons per atom and are also considered to be isoelectronic. Isovalent species are those that have the same number of valence electrons per atom, but the electrons are in orbitals with different principal quantum numbers. Thus, carbon and silicon are isovalent.

valence electron. In ZnSe, the Zn atoms that replace half of the Ge atoms have two fewer valence electrons, and the Se atoms that replace the other half have two additional electrons. Thus, the total electron count is preserved in both instances. (This trend is like playing the musical composition *Chopsticks* on the periodic table: A central "note" is struck on the table, then the two flanking columns are struck together, followed by the next two adjacent flanking columns, etc.)

In Table 7.3, the cubic unit-cell lengths (lattice parameters), the Pauling electronegativity differences, and the band-gap energies at 300 K are presented for Ge, GaAs, ZnSe, and CuBr. Structurally, in passing from Ge to CuBr, the lattice parameter is essentially constant at 5.67 ± 0.02 Å. At the same time, however, the bonding in this series acquires an increasingly ionic contribution: the electronegativity differences increase from 0.0 to 0.9 along this series. As shown in Figure 7.17 and Table 7.3, band gaps monotonically increase with the difference in electronegativity from Ge to CuBr.[7]

Table 7.3 Periodic Properties of a Family of Isoelectronic, Tetrahedral Semiconductors

Material[a]	Cubic Unit-Cell Parameter, Å[b]	$\Delta\chi$[c]	E_g, eV (λ, nm)[d]
Ge	5.66	0.0	0.66 (1900)
GaAs	5.65	0.4	1.42 (890)
ZnSe	5.67	0.8	2.70 (460)
CuBr	5.69	0.9	2.91 (430)

[a] The indicated materials have either the diamond structure (Ge) or the zinc blende structure of AZ stoichiometry in which all A atoms are bonded to four Z atoms and all Z atoms are bonded to four A atoms in a tetrahedral geometry. The solids are listed sequentially as isoelectronic semiconductors from Groups 14, 13 and 15, 12 and 16, and 11 and 17 in the periodic table (*see* Figure 7.16).

[b] Repeat distance, *a*, of the cubic unit cell at 300 K, obtained from X-ray diffraction data. These values are known to greater precision, but are rounded off here for simplicity and are taken from reference 9.

[c] Difference in Pauling electronegativities for the interatomic bonds in the crystal.

[d] Band-gap energy at 300 K from reference 9.

The trend in band gaps of this family of isoelectronic, isostructural solids is reflected in their colors, which can be predicted based on the color of transmitted light (Figure 7.18). Both Ge and GaAs have band gaps below the visible spectrum and look black. With a band gap of 2.7 eV (460 nm), ZnSe absorbs light of higher energy than indigo light and thereby acquires a yellow appearance. Pure, powdered CuBr looks white, because of its absorption onset at 2.9 eV (430 nm), which is nearly out of the visible region of the spectrum.

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[7] Because of its d-orbital bonding contributions, CuBr does not fit some of the trends in properties along the isoelectronic series as well as the other members and could be dropped from the series at the instructor's discretion. *See* reference 13 and reference 7. Reference 13 also discusses limitations on the correlation between band gap energies and electronegativity differences along this isoelectronic series (Sections 6.4.1 and 6.4.4).

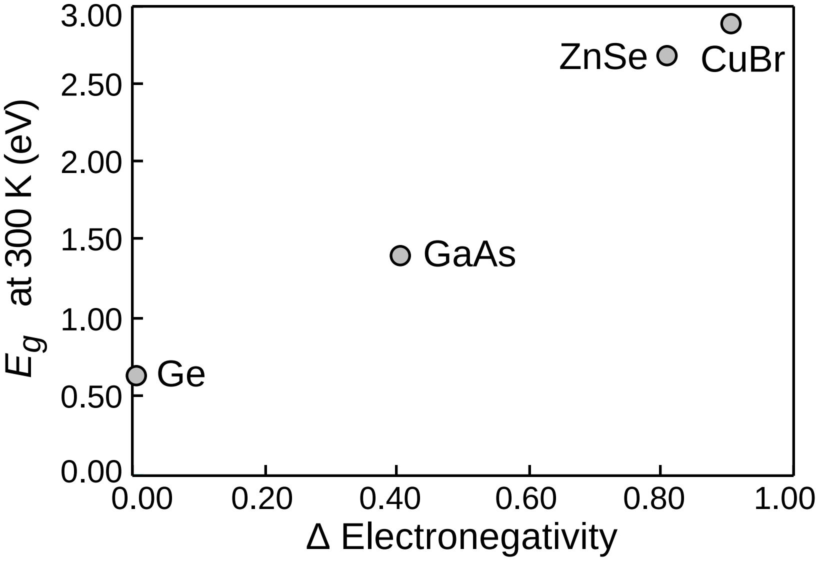

Figure 7.17. Plot of the band-gap values from Table 7.3 versus the difference in Pauling electronegativities in the same table. The unit-cell edge length is roughly constant for these materials.

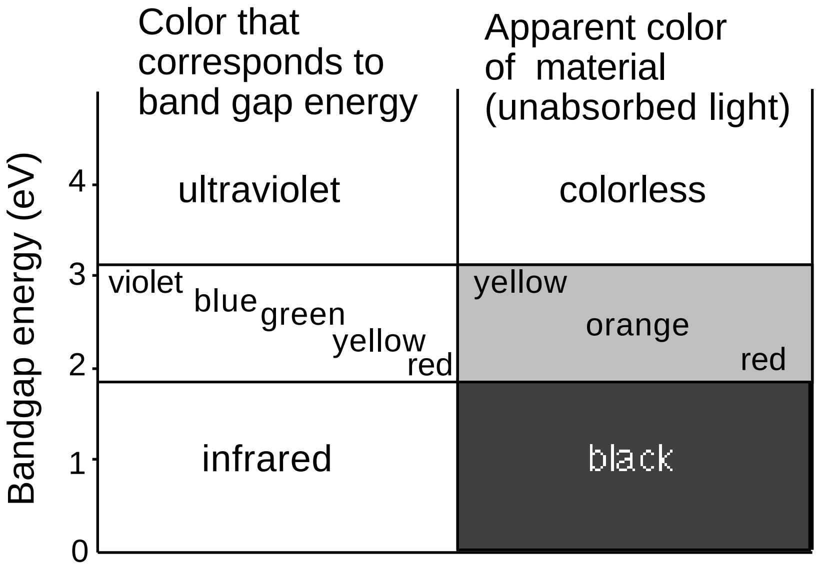

Figure 7.18. Diagram showing the relationship between band-gap energy and color. Substances with band gaps larger than the energies of visible light appear colorless, while those with band gaps below the visible region of the spectrum absorb all visible light and appear black. Materials with band gaps in the visible region of the spectrum will absorb some light above the band gap but not light below the band gap (Figure 7.15). The observed colors will be related to the colors of the unabsorbed light. (Adapted with permission from reference 2. Copyright 1983 John Wiley and Sons.)

Solid Solutions Having the Zinc Blende Structure: Tunable Band Gaps

The ability to form solid solutions between solids having the same zinc blende structure and possessing atoms of comparable size (Chapter 3) is of great technological importance. Rather than being restricted to the band gaps corresponding to the AZ stoichiometries obtainable with the elements in the periodic table, solid solutions provide a chemical means for tuning band-gap energies.

The zinc blende semiconductors GaAs and GaP constitute one of many pairs of solids that can be combined to yield solid solutions, symbolized for this family as GaP_xAs_{1-x} ($0 \leq x \leq 1$). As noted in Chapter 3, these are disordered solid solutions with the stoichiometric fractions x and $1 - x$ denoting the probabilities that an atom on a Group 15 site in the zinc blende crystal structure is P or As, respectively.

The smaller atomic radius of P relative to As leads to a smaller unit-cell constant for GaP (5.45 Å) relative to GaAs (5.65 Å). The unit-cell constants of the GaP_xAs_{1-x} solid solutions follow Vegard's law, which means that they are a weighted average of the unit cell constants of the components, that is, they vary linearly with the value of x in the formula. Thus, as shown in Figure 7.19, GaP_xAs_{1-x} solid solutions have unit-cell constants that are continuously tunable between 5.45 and 5.65 Å. There is little difference in the electronegativities of P and As (various scales rank both as having larger electronegativity), suggesting that ionic bonding contributions are similar throughout the GaP_xAs_{1-x} solid solution series. The increase in band gap from GaAs (1.4 eV; λ = 890 nm) to GaP (2.3 eV; λ = 540 nm) , Figure 7.19, appears to correlate most strongly with the reduction in internuclear distance and enhanced orbital overlap with increasing phosphorus content.

In contrast, another family of solid solutions, $Al_xGa_{1-x}As$, features an essentially constant cubic unit cell size of 5.658 ± 0.004 Å throughout the series *(14)*, but increasingly ionic bonding as Ga atoms are replaced by less electronegative Al atoms. Increasing ionic character is reflected in the increase in band gap observed in passing from GaAs (1.4 eV; λ = 890 nm) to AlAs (2.1 eV; λ = 590 nm), Figure 7.20.

The tunability of the band gap in the GaP_xAs_{1-x} and $Al_xGa_{1-x}As$ families of solids is used extensively in the design of light-emitting diodes (LEDs) and diode lasers. These devices, which will be described in more detail in Chapter 8, are becoming as common as the electric light bulb. Already, they are evident in consumer electronic products ranging from indicator lights on digital clocks and microwave ovens to compact disc players, laser printers and pointers, and fiber-optic telephone transmission lines.

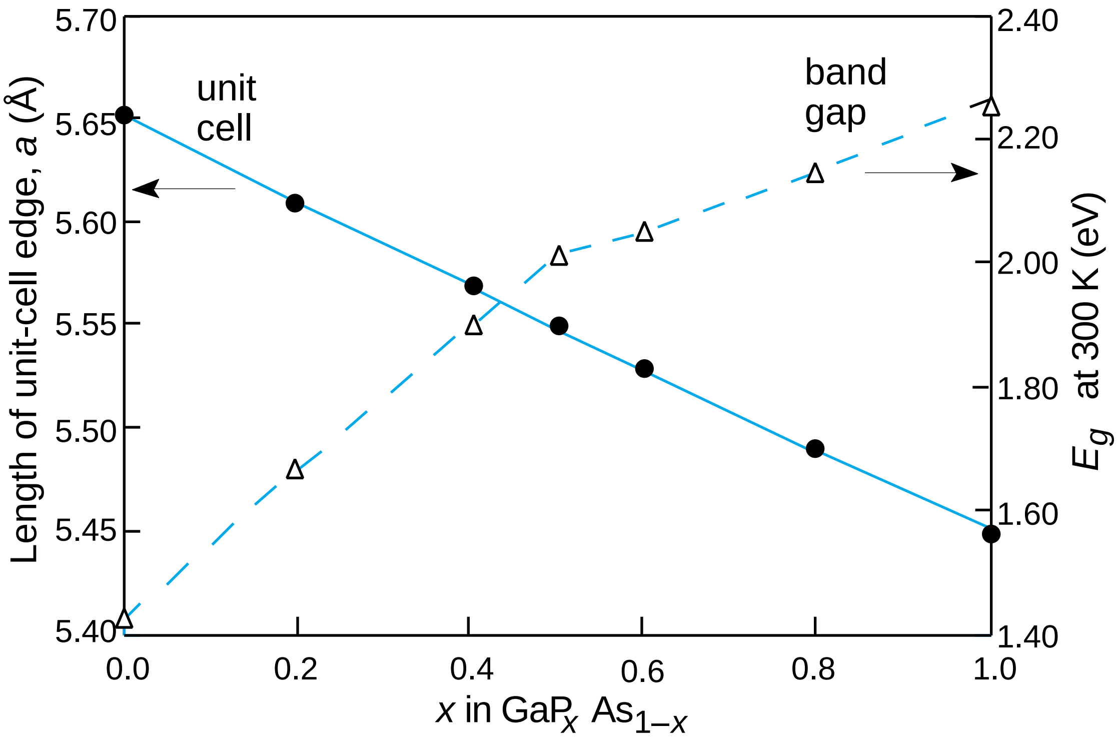

Figure 7.19. Trends in the cubic unit-cell parameter, *a* (Å), (filled circles), and the band gap at 300 K (open triangles) as a function of composition, *x*, for the solid solution series GaP_xAs_{1-x}. The kink in the band gap at $x = 0.45$ corresponds to a change from a direct band gap to an indirect band gap.[8] (Data are taken from references 14–16.)

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[8] When photons are absorbed or emitted, both energy and momentum in the solid must be conserved. For GaAs, As-rich GaP_xAs_{1-x} ($0.00 \leq x \leq 0.45$) and Ga-rich $Al_xGa_{1-x}As$ ($0.00 \leq x \leq 0.38$) samples, momentum associated with absorption or emission of a photon can be conserved exclusively by production or recombination of an electron–hole pair, respectively. Such solids, called "direct band gap" materials, absorb light strongly at the band-gap energy and emit band-gap energy light with high efficiency. In contrast, GaP, P-rich GaP_xAs_{1-x} ($0.45 \leq x \leq 1.00$), and Al-rich $Al_xGa_{1-x}As$ ($0.38 \leq x \leq 1.00$) samples, cannot conserve momentum during an electronic transition at the band-gap energy unless the absorption or emission is accompanied by a change in crystal momentum, corresponding to absorption or emission of quantized vibrations of the crystal atoms called phonons. This process is less likely, and these "indirect band gap" materials absorb light more weakly and yield less efficient radiative recombination. This feature makes them inferior LED materials, unless they are doped with an impurity atom, which permits an efficient emissive transition by relaxing these rules.

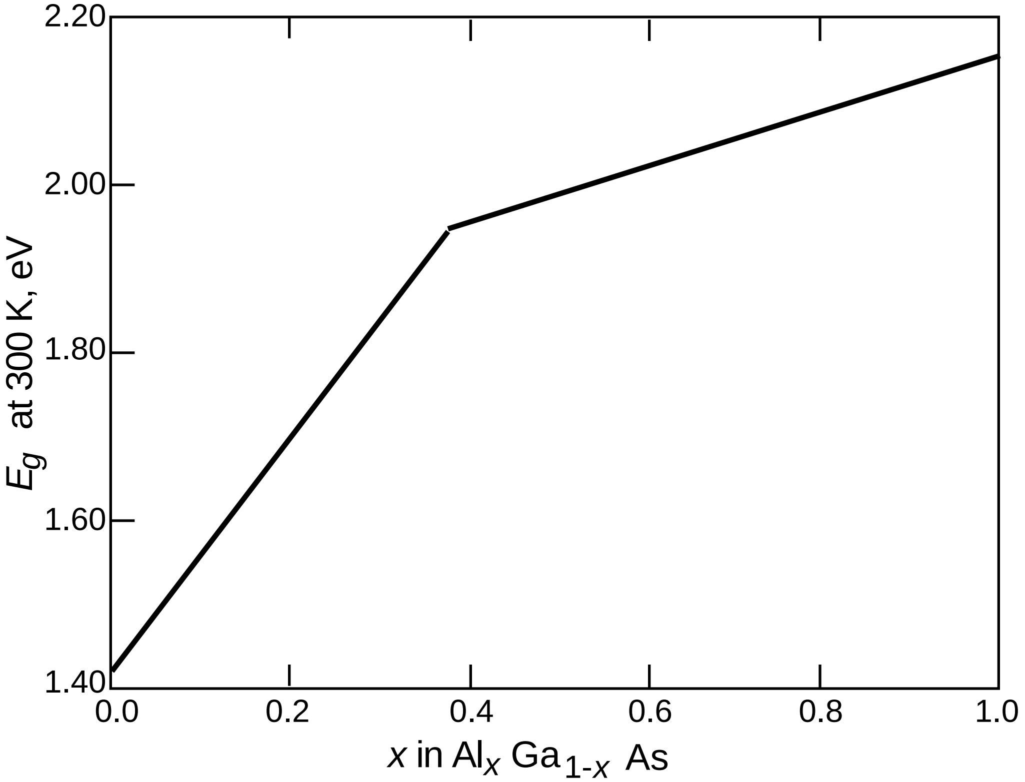

Figure 7.20. Trend in the band gap at 300 K as a function of composition, x, for the solid solution series $Al_xGa_{1-x}As$. The kink in the band gap at $x = 0.38$ corresponds to a change from a direct band gap to an indirect band gap.[8] (Data are taken from reference 17.)

The color of light emitted by these devices is often roughly the band-gap energy. This feature illustrates the basic spectroscopic principle that the energy of an electronic transition is controlled by the difference in energy of the levels between which the electron jumps: electrons can be promoted across the band gap in LEDs and diode lasers by absorbing energy from an applied electric field (a battery, e.g.). The subsequent return of the electrons from the conduction band back to the valence band releases roughly the band-gap energy (Figure 7.21A). This return is often described as a recombination of the electron in the conduction band with an absent electron in the valence band (treated as a positively charged particle called a “hole”; *see* Chapter 8) and can occur both nonradiatively (the energy is released as heat through the quantized vibrations of atoms in the crystal called “phonons”) and radiatively, producing photons of roughly band gap energy. (The simplistic localized picture corresponding to this process is that the energy needed to remove an electron from a bond in the solid can be released as a photon upon the return of the electron to the bond. As the energy associated with this process increases, so does the corresponding photon energy.) These electro-optical devices are optimized to release as much of the energy as possible as photons.

Emission spectra of LEDs are relatively narrow, as sketched in Figure 7.21B. The reason for this narrowness is that even though electrons can be created at energies well above the conduction-band edge (and holes with which the electrons will recombine at energies well below the valence-band edge), the electrons and holes will rapidly come to the band edges by losing their excess energy as heat, which is given to the crystal (holes "rise" to the valence band edge to reach lowest energy; *see* Chapter 8 and Demonstration 8.1).

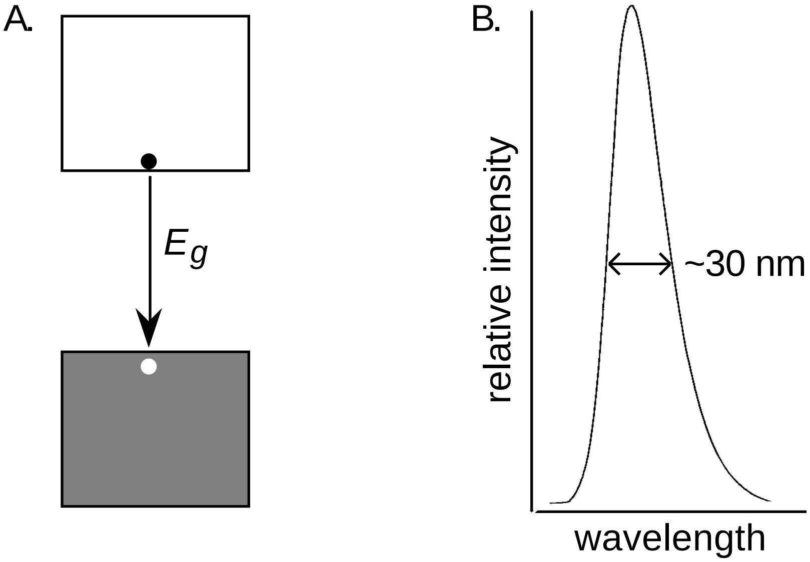

Figure 7.21. A: The return of an electron from the conduction band to the valence band can release a photon with an energy roughly equal to the band-gap energy. The electron can also return without the release of light through atomic vibrations in the crystal (phonons). B: A typical emission spectrum corresponding to the electronic transition shown in A.

Demonstration 7.10. Tunable Band Gaps Based on Solid Solutions

Materials (For electronic parts, *see* Supplier Information)

GaP_xAs_{1-x} LEDs, shown schematically in Figure 7.22A
1-kΩ resistor
9-V battery
Battery snap
LED socket
1-MΩ resistor (optional)
Liquid nitrogen
foam cup

Voltmeter
Soldering gun and solder
Magnifying lens or Micronta 30× microscope (Radio Shack)

Procedure

- Build the circuit shown in Figure 7.22B.
- Plug the available LEDs into the circuit and note the color emitted. The photon energies corresponding to the colors observed can be taken to be a rough estimate of the band gaps of the LEDs.
- To show simultaneously the range of colors that are possible in the solid solution series, you can wire together several LEDs to form a strip of red, orange, yellow, and green lights. The circuit diagram is shown in Figure 7.22C, and the assembly directions are given in Appendix 7.1.
- Use a magnifying lens or the Radio Shack Micronta hand-held microscope to see and appreciate the small size of the semiconductor chips, which is on the order of 1 mm^2.

Variation

- Another rough estimate can be made in the following way: Place a large resistor (1 MΩ) in the circuit instead of the 1–kΩ resistor so that little current passes. Plug one of the LEDs into the circuit. With the large resistor in the circuit, the LED may not appear to be lit at room temperature. Connect the voltmeter and measure the voltage drop across the LED. If the measured voltage is more than 3 volts, then the electrical leads on the LED should be reversed.
- Cool the LED in liquid nitrogen. **CAUTION: Liquid nitrogen is extremely cold. Do not allow it to come into contact with skin or clothing, as severe frostbite may result. Wear gloves when transferring and using liquid nitrogen.** Measure the voltage drop across the LED while it is cold. The measured voltage corresponds roughly to the energy (in electron-volts) of the band gap.[9] If more than 3 volts is measured, then current is not flowing through the LED, perhaps because contraction of the plastic case has broken the electrical contact; raise the LED to just above the liquid nitrogen level. Repeated dunking in liquid nitrogen seems to damage some LEDs.

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[9] Poor correlations may to some extent reflect the fact that some LEDs contain impurity atoms (called “dopants;” *see* Chapter 8) to enhance the intensity of the emitted light. Emission from the dopant-containing LEDs occurs below the band-gap energy (the dopants introduce electronic states within the band gap that are involved in the recombination mechanism that produces light) and complicates correlations of band gaps with the composition of the host semiconductor.

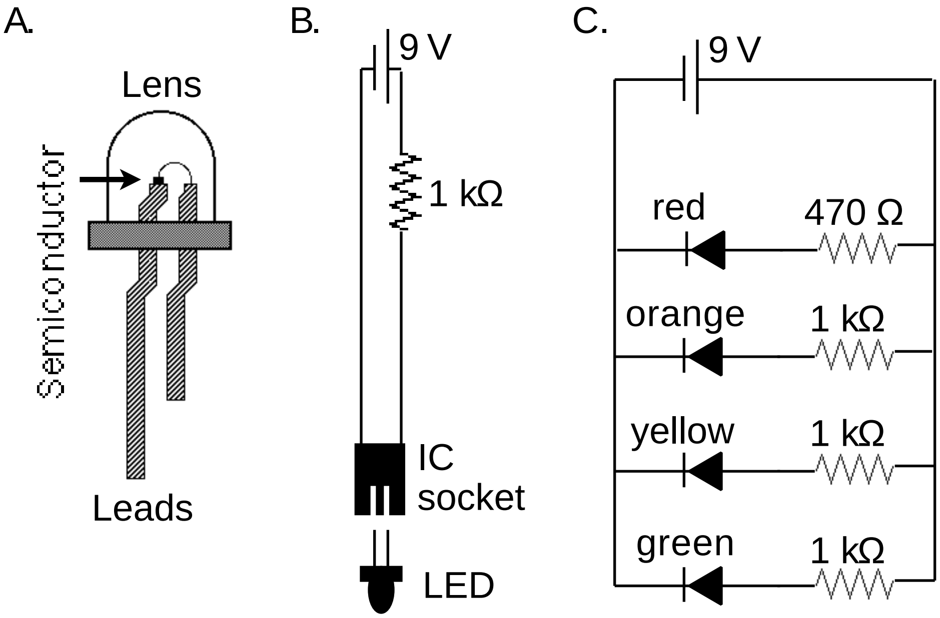

Figure 7.22. Experimental setup for the LED experiment. A: Schematic picture of a commercially available LED, showing the location of the semiconductor chip. B: Circuit diagram for a single LED. C: Circuit diagram for the reference strip of LEDs.

A visually stunning demonstration is provided by plunging an LED into liquid nitrogen. Most impressive in a darkened lecture hall is to take a commercially available $GaP_{0.40}As_{0.60}$ LED that is shown to emit weak red light at room temperature and to cause its emission to become bright orange as it is cooled in liquid nitrogen.

Demonstration 7.11. The Effect of Temperature on LED Emission

Materials

$GaP_{0.40}As_{0.60}$ (red) or $GaP_{0.65}As_{0.35}$ (orange) LED (Mouser or Radio Shack, but the flat-topped LEDs from DigiKey work especially well–*see* Supplier Information)

Circuit containing 1 kΩ resistor as described in previous demonstration

Styrofoam cup

Liquid nitrogen

Procedure

- Prepare the LED circuit as described in Figure 7.22B and insert an LED. The LED has a red or orange color at room temperature.

- After lighting the LED, darken the lecture hall.
- Immerse the LED into a Styrofoam cup filled with liquid nitrogen. **CAUTION: Liquid nitrogen is extremely cold. Do not allow it to come into contact with skin or clothing, as severe frostbite may result. Wear gloves when transferring and using liquid nitrogen.** The light intensity becomes substantially brighter and lights the cup with a red-orange or orange-yellow glow for the room temperature red and orange LEDs, respectively.

  The intensity enhancement and visible spectral shift can vary significantly; samples should be tested in advance of the demonstration. Some samples also glow more intensely when initially plunged into liquid nitrogen, but then lose intensity as they remain in the coolant. For such samples, if the LED is pulled out of the liquid nitrogen once it has reached its maximum intensity and is then held a little above the liquid nitrogen, the intensity can be maintained at what is essentially a somewhat warmer temperature than that of liquid nitrogen.

  These particular LED sample compositions were selected because their color changes illustrate a shift of the band gap to higher energy with decreasing temperature, a common feature of most semiconductors; and greatly enhanced efficiency for light emission upon cooling. Both effects are generally found with GaP_xAs_{1-x} (Figure 7.23) and $Al_xGa_{1-x}As$ (Figure 7.24) LEDs. However, not all of the GaP_xAs_{1-x} compositions of Demonstration 7.10 permit this kind of “eyeball spectroscopy.” In particular, as noted in Demonstration 7.10, LEDs that exhibit emission involving the presence of impurities (dopants) may have their spectrum dominated by those peaks, which occur at energies below the band gap and which may or may not shift in parallel with the band gap.

An increase in band gap with decreasing temperature would generally be predicted on the basis of the enhanced orbital overlap that accompanies the contraction of the crystal when it is cooled. For example, in GaP, the cubic unit-cell size shrinks from 5.451 Å at 300 K to 5.447 Å at 77 K *(18)*. (A similar effect on the unit cell size was noted in the discussion of F-centers in Chapter 6.) The increased orbital overlap is expected to contribute to an increase in the band-gap energy by increasing the separation between the centers of the valence and conduction bands, providing, as noted, that this effect is larger than the effect of the increased overlap on the widths of the two bands. For GaP, E_g increases from 2.27 eV (λ = 550 nm) at 300 K to 2.33 eV (λ = 530 nm) at 77 K.

If a spectrometer is available, the LED spectral shifts can be quantified. Clear shifts in the wavelength of emitted light to higher energy with decreasing temperature is best observed for LEDs that have a single emission peak at room temperature. LEDs with multiple emission peaks arising from the deliberate introduction of impurities into the crystal typically exhibit more complex temperature effects, Figure 7.23.[8]

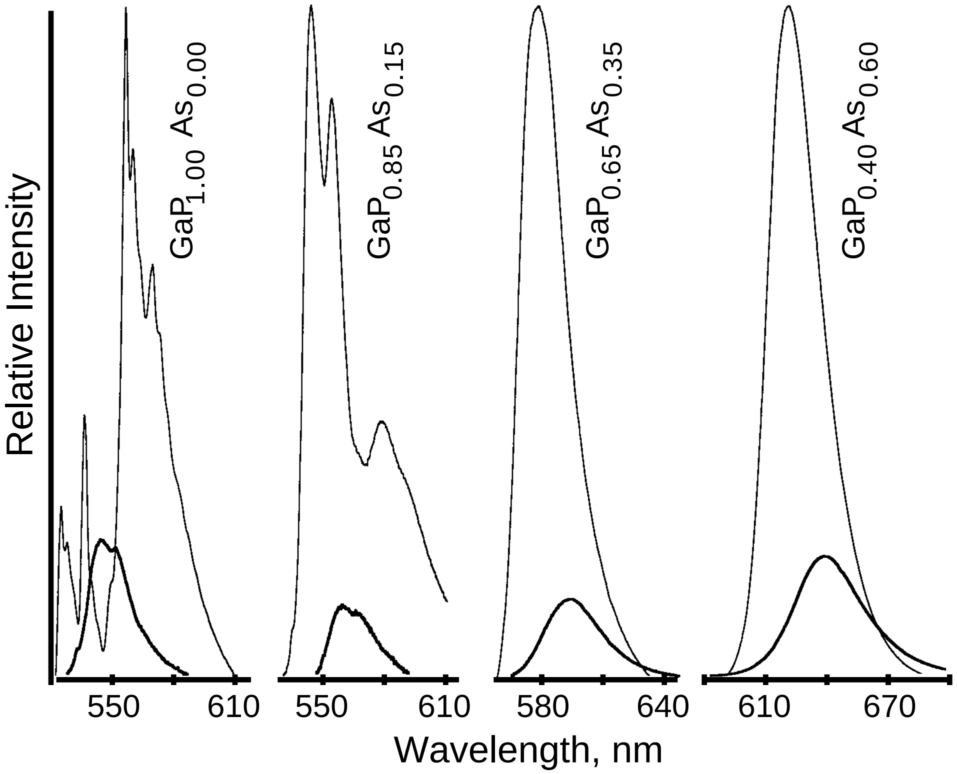

Figure 7.23. Spectra of GaP_xAs_{1-x} LEDs at room temperature (thicker lines) and at liquid nitrogen temperature. $GaP_{1.00}As_{0.00}$ and $GaP_{0.85}As_{0.15}$ are not suitable for "eyeball spectroscopy" predictions of band gap spectral shifts because of the complexity of the spectra.

The enhancement in LED intensity at low temperature reflects the competition between whether the return of the electrons from the conduction band to the valence band occurs radiatively, giving off light, or nonradiatively, giving off heat through vibrations of atoms in the crystal. At lower temperatures, the vibrations in the crystal play a less effective role (they are being "frozen out"), and lead to significant enhancements of the radiative recombination process. LED efficiency enhancements of 1–2 orders of magnitude are common in this experiment.

Laboratory. Experiment 7 has students use LEDs to study the effect of varying the chemical composition of the LED material on the wavelength of the emitted light and the effect of temperature on emitted light intensity.

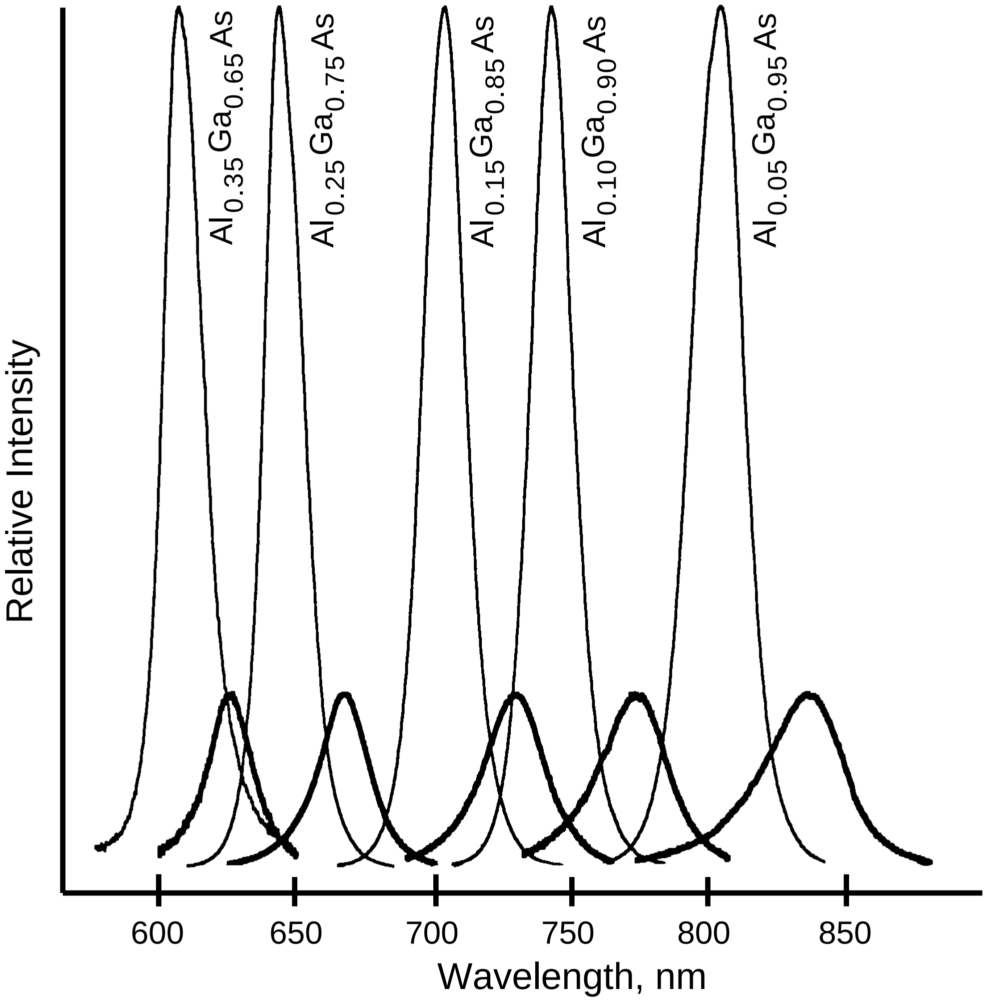

Figure 7.24. Spectra of $Al_xGa_{1-x}As$ LEDs at room temperature (thicker lines) and at liquid nitrogen temperature.

Ionic Insulators and Semiconductors

The electronic structures of extended salts may also be described with the band formalism. Sodium chloride illustrates many of the concepts used to develop the electronic structure of these solids. The large difference in Na and Cl electronegativities is reflected in the classification of this solid as ionically bonded, comprising Na^+ and Cl^- ions, as discussed in Chapter 5. Both the anion and cation are closed-shell ions; therefore, bands that are exclusively empty or full of electrons are expected, and the salts would be predicted to be insulators or semiconductors, depending on the magnitude of the band gap.

Bands in these solids reflect the importance of electrostatic interactions. A typical band diagram, that of NaCl, is shown in Figure 7.25. The valence band has primarily Cl 3p orbital character. Since Cl^- has a $3p^6$ configuration, this band is completely filled with electrons. The conduction band is derived largely from the empty 3s orbitals of Na. These 3s-derived orbitals of the conduction band are at higher energy than the 3p-derived orbitals of the valence band because of chlorine's greater nuclear charge, which stabilizes all of the atomic orbitals of the halogen relative to those of the alkali metal.

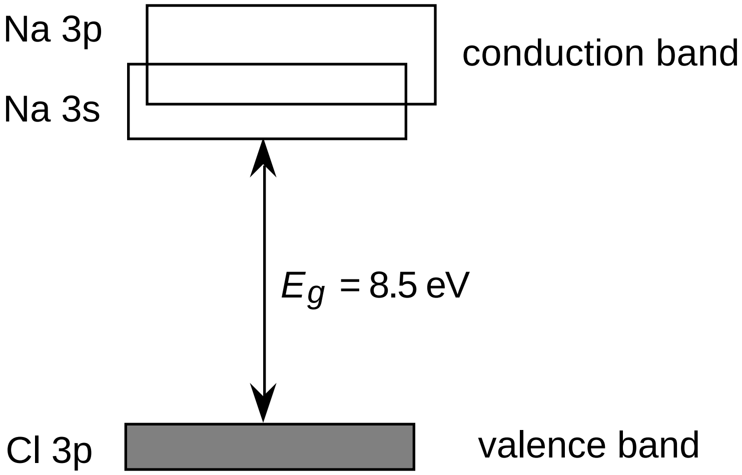

Figure 7.25. Band-structure diagram for NaCl. The valence band is primarily chlorine 3p in character. The conduction band is primarily sodium 3s in character, and there is overlap in energy with the sodium 3p band.

As shown in Figure 7.25, the two bands give rise to an enormous band gap of ~ 9 eV, nearly twice that of diamond! The large gap separating the filled valence band from the unfilled conduction band accounts for the electrically insulating nature of crystalline NaCl and for its optical transparency. In a simple localized picture, promoting an electron across the band gap is somewhat like trying to transfer an electron in the solid from Cl^- back to Na^+, an energetically costly process:

$$Cl^- + Na^+ \rightarrow Cl + Na$$

Generally ionic compounds become conductors of electricity only at high temperatures. Under these circumstances the mobile species commonly are not electrons but ions moving through lattice defects (*see* Chapter 6).[10]

Band gaps in families of salts, as in families of covalent solids, reflect the interplay of several parameters *(19)*. Some of the families of simple salts do, however, have trends in band gaps that are due principally to

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[10] In some cases, defects and impurities give rise to conductivity that is electronic in nature.

variations in electrostatic interactions, which increase with decreasing interionic distances.

Table 7.4 presents a collection of band gaps of alkali halide salts. Among the alkali halides, the largest band gap occurs for LiF, which has a value of 14 eV. These two ions are the smallest of those in the table, and their large electrostatic interaction leads to the largest splitting, in this case between a valence band that has largely 2p orbital character (from F^- ions) and a conduction band that has primarily 2s orbital character (from Li^+ ions). Band gaps are seen to either decrease or remain roughly constant as the interionic distance increases with larger cations or anions.

Salts with more covalent character, like the silver halide salts so critical to the photographic process, have smaller band gaps more typical of semiconducting materials, with absorption onsets that fall in or near the visible portion of the spectrum. Part of the reduction in band gap in these materials may be attributed to covalent interactions that widen the bands.

Table 7.4. Band Gaps for Some Ionic Compounds

Compound	Band Gap (eV)
LiF	14
LiCl	9.5
NaF	12.
NaCl	8.5
NaBr	7.5
KF	11
KCl	8.5
KBr	7.5
KI	5.8

NOTE: All of the compounds have the NaCl structure. Band gaps are approximate.
SOURCE: Adapted from reference 20.

Appendix 7.1. Assembly of LED Reference Strip

1. Slice perfboard using a band saw, cutting through lines of holes to leave strips of four holes. Use drill to slightly enlarge four holes to match diameter of battery snap wires. Spray-paint back side black. Let dry.

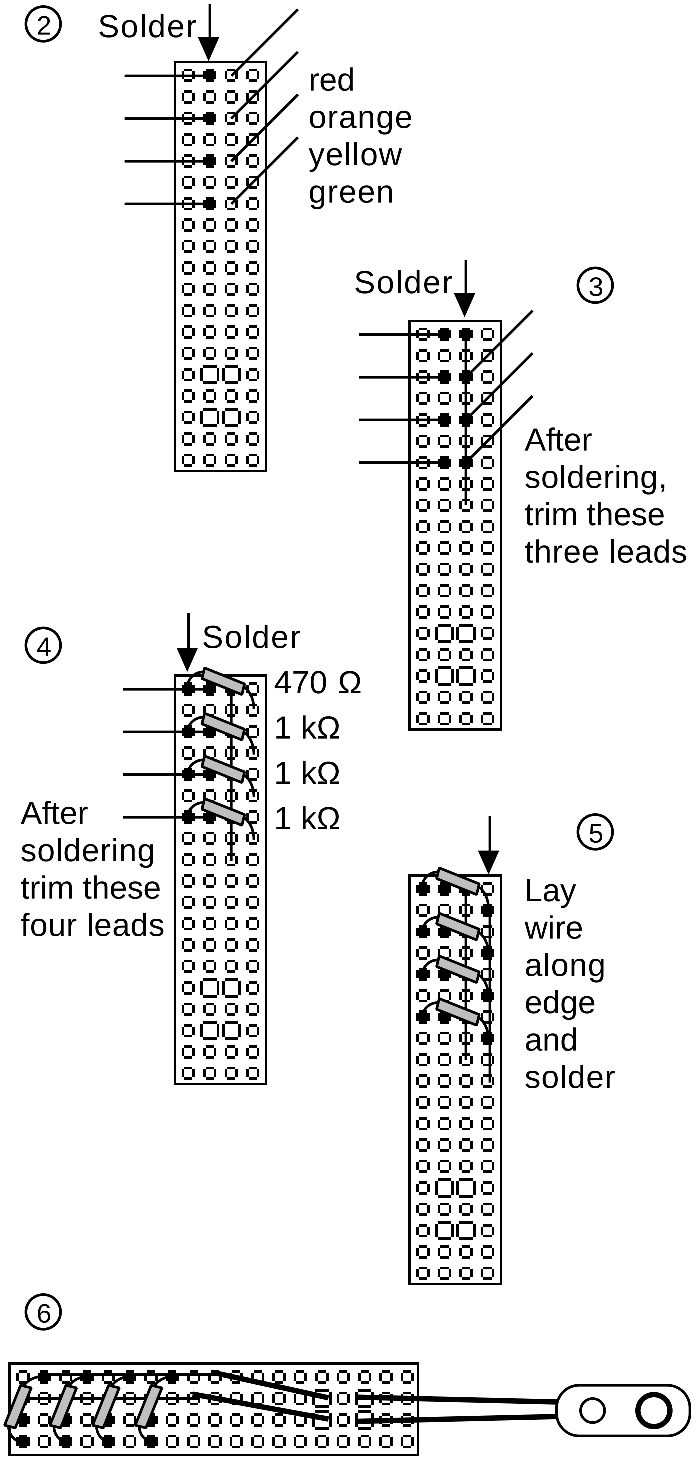
2. Attach LEDs. The plastic case goes on the black side. Leads stick through to solder side. All LEDs must be oriented the same way; for example, put the short lead on the left. Bend left leads over, flush to board and along horizontal row of holes. Solder left leads.

3. Connect one side of the LEDs by bending the lead from the top LED flush to the board and along the vertical row of holes. Solder right leads and trim indicated excess.

4. Bend resistors and position diagonally, inserting wires into outside holes. Solder left leads and trim indicated excess.

5. Take a trimmed lead and lay along the row of resistors to connect them. Solder along the outside edge. Trim excess resistor leads from the black side.

6. Attach battery snap by threading leads through the perfboard, verifying correct polarity to light LEDs. Solder.



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Additional Reading

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Acknowledgments

This chapter is based on references 21 and 22 and conversations with Thomas Kuech, University of Wisconsin—Madison, Department of Chemical Engineering; Clark Landis, University of Wisconsin—Madison, Department of Chemistry; Nathan Lewis, California Institute of Technology, Department of Chemistry; Andrew Bocarsly, Princeton University, Department of Chemistry, and Allen Adler. Demonstration 7.2 was developed by Thomas Mallouk and Steven Keller, University of Texas—Austin.

Exercises

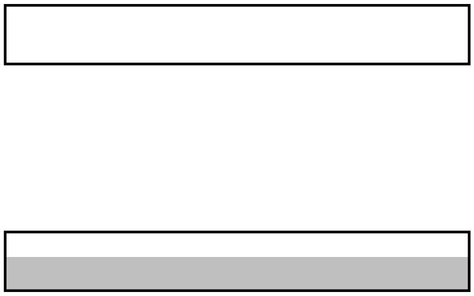
1. Choose the correct answer. A semiconducting solid solution used in manufacturing an LED has the zinc blende structure and the chemical formula $Al_xGa_{0.25}As_yP_{0.60}$, where
   a. $x = 0.75$ $y = 0.40$
   b. $x = 0.40$ $y = 0.75$
   c. $x = 1.00$ $y = 0.00$
   d. $x = 0.25$ $y = 0.60$

2. Which of the following would be expected to have the same structure and total valence electron count as α-Sn?
   a. InSn
   b. CdSb
   c. CdTe
   d. InTe

3. Choose the correct answer. If a material has a band gap in the infrared portion of the spectrum, it will appear
   a. black
   b. red
   c. green
   d. colorless

4. Which of the following is <u>not</u> a characteristic of a metal?
   a. high reflectivity of light
   b. high thermal conductivity
   c. high electrical conductivity
   d. increasing electrical conductivity with increasing temperature

5. Consider the situation shown in the diagram, in which a solid has a low energy band that is partially filled with electrons (shaded region) that is separated by a large gap from an empty higher energy band. If the solid is treated with a chemical reducing agent that completely fills the lower energy band with electrons, the solid's electrical properties will become
   a. metallic
   b. semiconducting
   c. superconducting
   d. insulating



6. Choose the correct answer. A new material will be recognized as a metal if
   a. its electrical resistivity is independent of temperature
   b. its electrical resistivity increases with increasing temperature
   c. its electrical resistivity decreases with increasing temperature
   d. its electrical resistivity is zero

7. Choose the correct answer. An example of a solid that possesses the zinc blende structure is
   a. NaCl
   b. GaAs
   c. CsCl
   d. Zn

8. Calculate the carrier concentration (in carriers per cubic centimeter) in 1 M NaOH, assuming all ions present in the solution are carriers.

9. A coil of copper wire is 150 m long and has a resistance of 150 Ω. If the resistivity of copper wire is 1.67×10^{-6} Ω-cm, find
   a. the cross-sectional area of the wire.
   b. the diameter of the wire.

10. The room-temperature band gap of CdS is about 2.4 eV. What color will a crystal of CdS appear to be?

11. Suppose that you want to create a red cutoff filter (of all of the colors in the visible region of the spectrum, the filter will transmit only red light). What should the band gap be to make such a filter out of a semiconductor?

12. The color emitted from an LED is roughly its band-gap energy. What composition, if any, of GaP_xAs_{1-x} (*see* Figures 7.18 and 7.19) would you use to make an LED that emits light that is
   a. red?
   b. orange?
   c. yellow?
   Can a blue LED be made from this family of solids? Why or why not?

13. Some LED materials can be prepared by combining Ga, In, As, and P in the zinc blende structure. If the formula of one such solid is $Ga_{0.4}In_xAs_yP_{0.7}$, what are x and y equal to, and how would you interpret this formula based on the zinc blende structure?

14. Solar cell **A** uses a semiconductor with a band gap of 1 eV. Solar cell **B** uses a semiconductor with a band gap of 2 eV. Either cell is thick enough to absorb all the light above its band gap. Both cells can work simultaneously with one on top of the other to operate more efficiently in a small space. But which cell has to be on top (first to receive the sunlight) for both to work simultaneously and why?

15. A compound has the following band diagram, with the shading representing occupancy by electrons: The solid has a completely filled lower energy band and a partially filled higher energy band.

a. Predict the electrical properties of this solid on the basis of its band diagram.
b. What would happen to the electrical properties of this compound if all of the electrons were removed from the conduction band and why? Would you use a chemical oxidizing agent or reducing agent to accomplish this and why?

16. The band gaps of $GaAs_{1-x}P_x$ solid solutions are continuously tunable from about 2.3 eV (GaP) to 1.4 eV (GaAs) at room temperature. The band gap increases linearly with x up to about $x = 0.45$ where the band gap is 2.0 eV. Assuming that the wavelength of emitted light from the solid solutions is at about the band-gap energy, calculate the value of x (i.e., what solid solution would you prepare) to obtain emission at 7000 Å from an LED.

17. Name two solids with the zinc blende structure that are isoelectronic with α-Sn, and predict how their band gaps will compare to that of α-Sn.

18. Suggest a two-element (binary) compound that is isoelectronic with diamond and that might rival it in hardness.

19. Explain why $CdSnP_2$ has the same valence electron count as GaAs.

20. Draw figures similar to those in Chapter 5, Figure 5.12A or 5.12B , for the contents of the planes in the unit cell at $z = 0$, 0.25, 0.5, and 0.75 for the semiconductors Si and GaP.

21. Explain why the partially filled band in sodium metal is exactly half filled.

22. Explain why the conductivity of a semiconductor is strongly temperature dependent.

23. Compare the electrical conductivities of semiconductors at room temperature and liquid helium temperature.

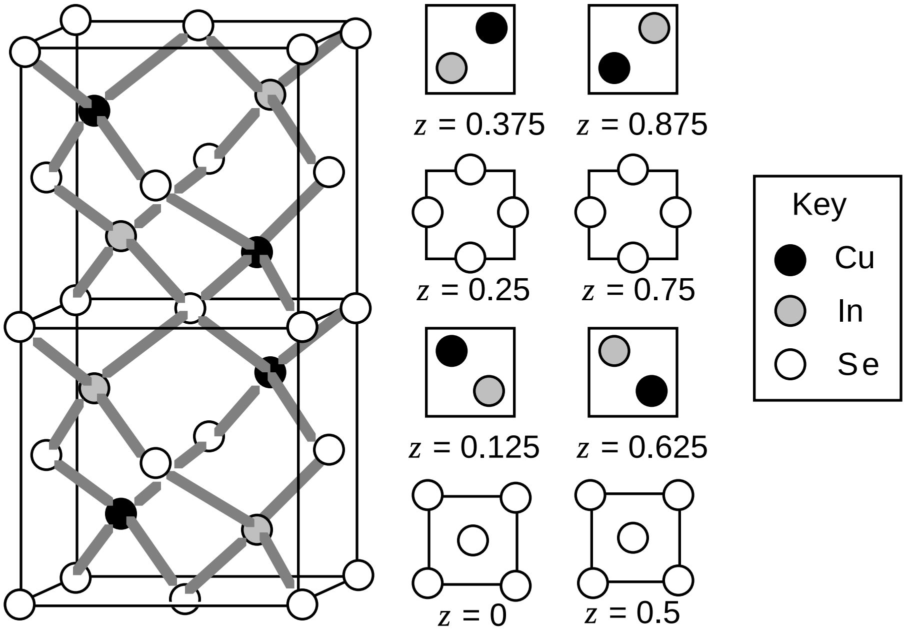
24. Which contain partially filled bands and why: Mg, Si, NaCl?

25. Why does the reaction of a small amount of bromine with graphite convert the semiconductor to a metallic conductor, but the reaction of bromine with sodium converts the metal into an insulator?

26. Consider the molecule polyacetylene, which consists of an array of the repeat unit $(–CH{=}CH–)_n$ attached end to end and extending to infinity.
   a. Draw a portion of the molecule (ignoring the ends of the molecule).
   b. What is the hybridization about each carbon? How many electrons on each carbon are used to form the sigma bond network in the molecule?
   c. What orbital is left over on each carbon? How many electrons are left over per carbon? They will form the pi bond network on the molecule. Draw a second (resonance) structure for polyacetylene. What effect will this have on the structure of the molecule?
   d. These remaining orbitals and electrons can be considered to form a one-dimensional band in polyacetylene. Use a rectangle to represent the band. Would the band be full? Empty? Half full? Explain. If polyacetylene had this structure, would it be a metal, semiconductor, or insulator? Explain.
   e. For reasons that will not discussed here (*see*, for example, reference 23), the structure of polyacetylene contains alternating short and long bond lengths and has the band structure shown below. On the basis of this information, is polyacetylene a metal, semiconductor, or insulator? Explain.

   f. On the basis of this band diagram, what would happen to the conductivity if polyacetylene were allowed to react with a small amount of an oxidizing agent such as Br_2? What would happen to the conductivity if polyacetylene were allowed to react with a small amount of a reducing agent such as Li?

27. Another compound being used for LEDs is derived from the chalcopyrite structure.

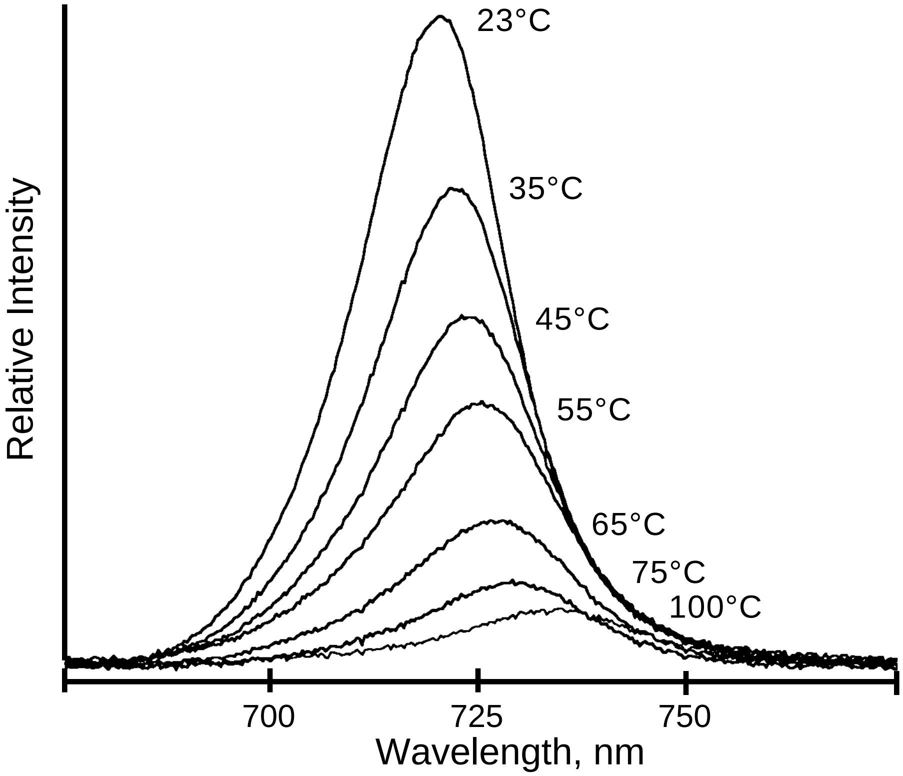


a. To what empirical formula does this compound correspond?
b. How is this structure related to the zinc blende structure?
c. Show that this structure is isovalent with the zinc blende family of semiconductors used in LEDs.

28. How would the absorption and emission spectra of a powdered 1:1 GaP and GaAs physical mixture differ from the spectra that would be seen for a $GaP_{0.5}As_{0.5}$ solid solution? (Other combinations that the instructor could use include $CdS_{0.5}Se_{0.5}$ and $Al_{0.5}Ga_{0.5}As$.)

29. Sketch the most bonding and most antibonding orbitals in a band formed by p_z orbitals in a one-dimensional solid where the atoms lie on the *z* axis.

30. The luminescence spectra of a crystal of CdSe are shown as a function of sample temperature. (Luminescence spectra are obtained by exciting the sample with light of energy greater than the band gap, and the spectrum obtained is of the light emitted by the sample as its excited electrons return from the conduction band to the valence band as in Figure 7.21.)
a) Why does the peak maximum shift as the sample is heated?
b) Why does the intensity decrease as the sample is heated?



31. Estimate the shift in band gap energy (in eV) between 300 and 77 K for $Al_{0.05}Ga_{0.95}As$ from the data in Figure 7.24. (Any of the other compositions in the figure may also be used.)