

Light-Emitting Diodes (LEDs)

Teacher Materials (includes Student Materials)

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CURRICULUM SUGGESTIONS

TOPICS

SOLIDS	QUANTUM MECHANICS	SEMICONDUCTORS
Bonding	Electron Configurations	p-n Junctions
Metals	Periodic Table	LEDs
Metallic Bonding (Valence-Bond Model)	Periodic Relationships (Trends)	
Solid Solutions	Band Theory	

OVERVIEW

This module would complement a unit on atomic structure and periodicity. Typically, is introduced in two chapters: one dealing with the nature of light and its use to determine the electronic structure of atoms; and another that relates this electronic structure to the periodic table and trends in properties. Since students would have to have a basic understanding of electron configurations, this module would be more appropriate if used later in the atomic structure and periodicity unit of the standard chemistry curriculum.

SUGGESTIONS

Demonstrations 1 and 2, and Investigation 1 could be used to introduce students to the band theory model of bonding in solids. Metallic bonding and properties especially thermal and electrical conductivity provide examples of the use of this model.

Investigation 2 could be used to introduce students to families of solid solutions having tunable structure and composition. This is important in the development of later demonstrations and experiments that deal with light emitting diodes of specific colors.

Demonstration 3 could be used to discuss semiconductors, p-n junctions, and LEDs.

Demonstration 4 and Experiment 1 could be used to further understanding of solid solutions and how their properties vary with composition. Periodic relationships such as sizes of atoms and valence configurations could also be emphasized.

SAMPLE LESSON PLAN

PREFACE

This unit should be used after students have completed units covering the quantum mechanical model of the atom, including electron configurations. It is also intended that the unit be used in conjunction with one covering the periodic table and periodic trends. The lesson plan below should therefore be considered as a framework from which an overall lesson plan may be constructed. Other demonstrations, experiments, and class activities can be inserted where appropriate. The material in this unit should complement as well as extend the typical coverage of these topics.

DAY 1 Discuss the effect of having many atoms in the solid phase in close proximity on the energy levels of the atoms in the structure (band theory).

50 minutes

Use Demonstration 1 to illustrate electrical conductivity within the framework of band theory.

DAY 2 Have the students do Investigation 1.

50 minutes

DAY 3 Discuss Investigation 1.

10 minutes

Do Demonstration 2.

40 minutes

DAY 4 Have students do Investigation 2.

DAY 5 Discuss Investigation 2.

10 minutes

40 minutes Discuss diamond and zinc blende structures (See background information for this unit) and solid solutions in conjunction with an introduction to periodicity. Topics should include trends in atomic size, electronegativity, ionization energy and metallic behavior. The relationship of each trend to electron configuration should also be established.

DAY 6 Continue the discussion from Day 5.

50 minutes

- DAY 7** Extend the discussion by emphasizing semiconducting properties. Remind students that they did an activity from the “Exploring the Nanoworld” Kit some time ago in which they learned that semiconductors are used in the construction of LEDs. Discuss the differences between n-type and p-type semiconductors and the construction of a p-n junction. Also discuss what it means to bias a junction in either a forward or reverse manner.
- 50 minutes
- DAY 8** Do Demonstration 3 as a reinforcement of the previous day’s lesson. The follow-up questions should be presented as in-class discussion questions.
- 25-30 minutes
- 20-25 minutes Begin a discussion of LEDs.
- DAY 9** Continue the discussion of LEDs and how they operate. Include the relationship between band gap energies and atomic size and electronegativity. Discuss, in turn, how the light produced depends on the size of the band-gap.
- 20-25 minutes
- 25-30 minutes Use demonstration 4 to relate the compositions of solid solutions to band gap energies. Assign the follow-up questions as homework.
- DAY 10** Have students do Experiment 1.
- DAY 11** Discuss the follow-up questions from Demonstration 4 and the results of Experiment 1. Emphasize that the solid solution series used for the LEDs is isovalent and essentially isostructural with the Group IV elements in the periodic table.
- 30 minutes
- 20 minutes Discuss the capabilities and uses of LEDs, showing examples. Examples are available at <http://mrsec.wisc.edu/edetc/LED/index.html>.
- DAY 12** Use the questions provided at the end of the unit to review.
- DAY 13** Unit exam.

Light Emitting Diodes (LEDs)

Overview

This module is intended to introduce students to the use of the periodic table to customize the properties of materials. The properties of light emitting diodes (LEDs) are controlled by chemistry. LEDs are increasingly used in a variety of lighting venues, including traffic lights, animated billboard displays, vehicle tail lights and dashboard lights. They are comprised of semiconductors whose chemical composition can be tuned using periodic properties, such as isoelectronic principles, electronegativity, and atomic radius. Variations in these properties can be used to control the color of light the semiconductors emit. Solid solutions, in which chemically similar elements like phosphorus and arsenic are substituted for one another in a crystal structure, enable the to light emitted by the semiconductor to be tuned over various regions of the electromagnetic spectrum.

Investigations and demonstrations in this module explore the structures of semiconductors that are key to LED technology, using the ICE Solid State Model Kit. These structures are correlated with chemical composition, the diffraction of light emitted by LEDs of different colors, and the voltage needed to activate them, all of which reflect the bonding trends in these solids. A simple model for understanding these trends based on bonds can be presented, as well as a more sophisticated model based on bands, which comprise combinations of atomic orbitals. A demonstration of these structural and bonding concepts can be shown by “eyeball spectroscopy,” in which the colors of some LEDs can be reversibly altered by exposing them to a cold environment like dry ice/acetone or liquid nitrogen.

The rapid movement of this technology is underscored by presenting the recent development of the long-sought-after blue LED, which was obtained by combining gallium with nitrogen. This development makes it possible to use color mixing to obtain all colors of the visible spectrum, along with white light. Technological implications of the availability of this shorter wavelength light include new kinds of display devices. Semiconductor diodes can also be used as lasers and are often employed as presentation pointers. Blue diode lasers, when they become available, offer the opportunity to create CDs with greatly enhanced storage capacity.

Light Emitting Diodes (LEDs)

Energy Characteristics of Electrons

The properties of metals are often explained using a model that these materials comprise a “negative sea of electrons surrounding positive islands of charge.” While this is a very useful metaphor to describe electrical and thermal conductivity, it falls short in describing other properties of these and related solids. To develop a more versatile model, the energy characteristics of electrons need to be considered. Individual atoms are described as having nuclei that are surrounded by electrons that occupy regions in space, called orbitals, with characteristic probabilities and associated discrete energy levels. (Figure 1) Electrons fill the lowest energy levels first. A specific “quantum” of energy must be supplied to the electron in order for it to move to a higher energy level. Any one energy level (orbital) can have a maximum of two electrons in it whose spins must be paired. If two electrons are in the same orbital, they must “spin” in opposite directions so that each has a unique set of quantum numbers.

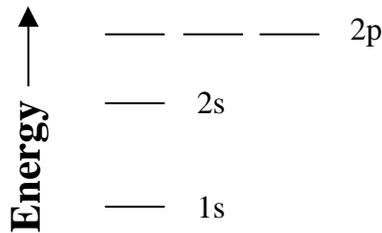


Figure 1. Energy diagram showing orbital energies.

Energy Bands

In the solid phase atoms are close together so their valence electrons have the ability to interact with one another. The core electrons have negligible interactions between atoms because they are closely associated with their nuclei. Discrete energy levels that are delocalized over the entire solid arise from the overlapping atomic orbitals. This collection of orbitals is tightly spaced in energy and comprises what is referred to as an *energy band*. Each band contains as many discrete levels as there are atoms in the crystal. Each orbital within the band can hold two spin paired electrons, just as was the case for isolated atoms. The figure below shows the energy bands of sodium. It illustrates that the highest occupied band of the alkali metals (the $3s$ band in this case) is half-filled. Although magnesium, an alkaline earth element, has its valence $3s$ bands filled and its valence $3p$ band empty, there is an overlapping of the two bands, because the lowest levels of the $3p$ band are lower in energy than the upper levels of the $3s$ band. Therefore, some electrons overflow into the upper band.

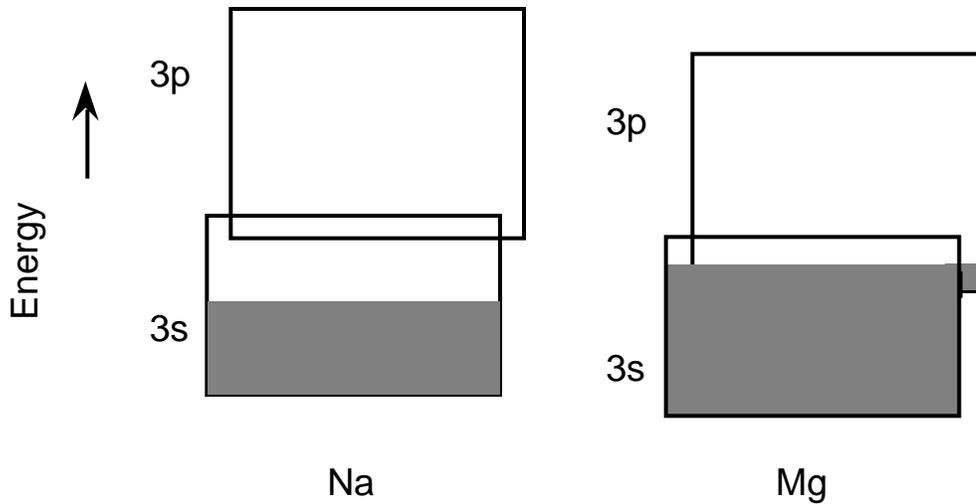


Figure 2. Energy bands of two elements.

In a band picture, band gap energy can be thought of as the energy needed to ionize (free) electrons from bands, enabling them to be mobile charge carriers. In descending the periodic table from carbon (diamond structure) to tin, the bonds become weaker, leading to a larger concentration of mobile carriers.

Conductivity and Energy Gaps

Band theory provides a framework for understanding electrical conductivity. The presence of charged particles and the ability for them to undergo net motion in a particular direction are the two conditions necessary for electrical conductivity. Valence electrons in solids are charged particles, and they move through the partially filled energy bands. Only electrons near the top of filled orbitals of partially filled bands contribute to conductivity. Metals are characterized by the presence of a partially filled band. In many other materials there are two bands to consider: a lower energy band that is filled with electrons, the valence band, and the next higher energy band that is unfilled, the conduction band. The energetic separation between these two bands is called the band gap energy. When the band gap energy is greater than about 3 eV, very few electrons can be thermally excited from the valence band into the conduction band at room temperature, and the material is an insulator. For band gap energies less than about 3 eV, some electrons can be thermally excited across the band gap, and the material is a semiconductor. A metal can be thought of as having a band gap of essentially zero.

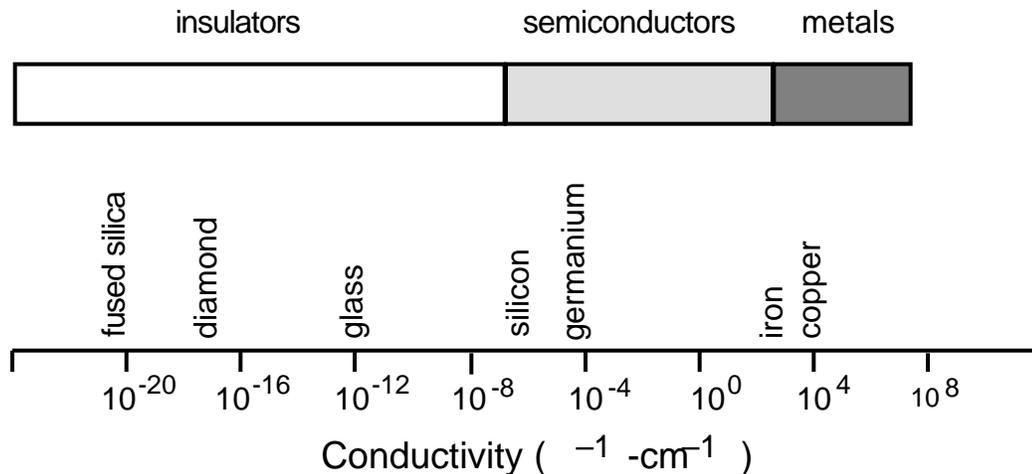


Figure 3. The entire range of conductivities of solids spans roughly 30 orders of magnitude. (From *A Materials Science Companion*, figure 7.7)

Most of the Group 14 elements have the diamond structure. In descending this group, carbon (diamond form) is an electrical insulator with a large band gap energy, silicon and germanium have smaller band gaps and are semiconductors, and tin, which has almost no band gap, is metallic. The difference can be explained by noting that as the atoms become larger and bond distances increase, orbital overlaps are reduced and the resulting energy gaps are smaller.

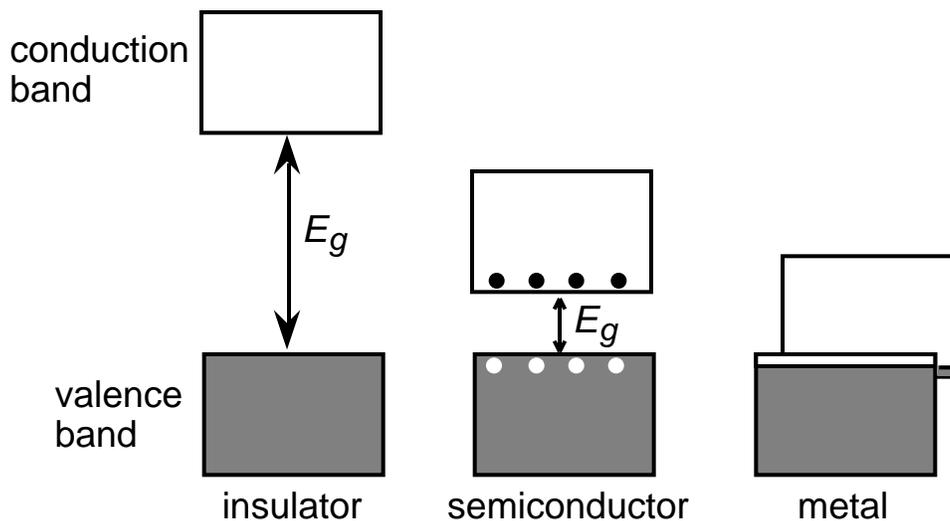


Figure 4. A general representation comparing the energy bands and gaps for insulators, semiconductors and metals. The conduction band and valence band of a metal actually overlap in energy resulting in a band gap energy of essentially zero. (From *A Material Science Companion*, figure 7.14)

The Zinc Blende Structure and Solid Solutions

Elements having the zinc blende structure contain the same number of valence electrons and have AZ stoichiometry (1:1 ratio of elements). When all of the atoms are the same element, this is the diamond crystal structure. Solids such as Ge, GaAs, ZnSe, and CuBr are isoelectronic, which means they have the same number of valence electrons. Solids that contain atoms of comparable sizes and form the zinc blende structure can be combined in various ways to form solid solutions. Solid solutions are homogeneous solids in which one type of atom (or ion) has substituted for a similar atom (or ion) in a structure. These solid solutions are similar to some alloys in that different elements occupy specific sites in each others' crystalline structures. Having almost countless numbers of stoichiometries, it is possible to adjust or "tune" the band gap energies which depend on chemical composition. For example GaAs and GaP are only one of many pairs of semiconductors that may be combined to yield solid solutions, symbolized by the formula, $\text{GaP}_x\text{As}_{1-x}$ ($0 < x < 1$). The graph below clearly shows the increase in band gap energy from GaAs to GaP. This increase is primarily the result of the periodic trend in atomic sizes, since electronegativities of both As and P are about 2.0 and the electronegativity difference is constant. The smaller size of the P atoms allows the length of the unit cell edge to decrease, which enhances orbital overlap and increases the band gap energy.

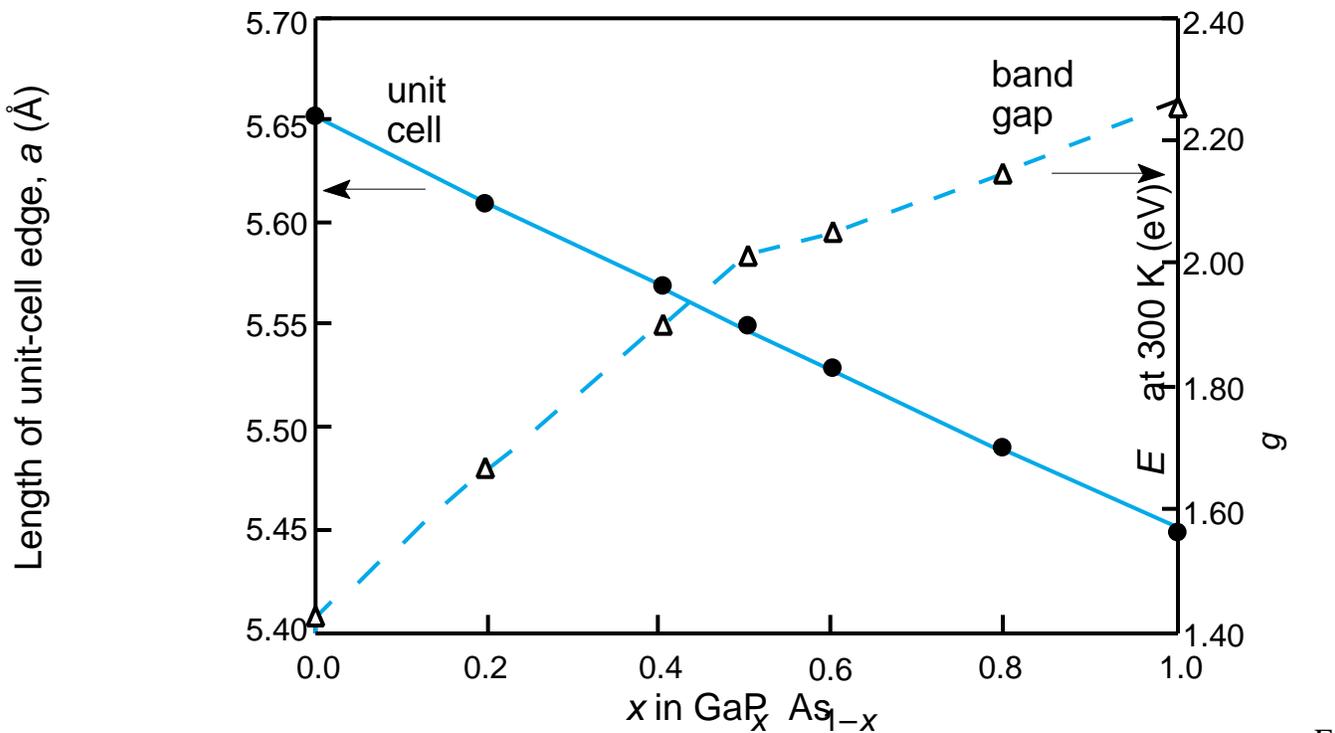


Figure 5. Trends in the cubic unit-cell parameter, a (Å), (filled circles), and the band gap at 300 K (open triangles) as a function of composition, x , for the solid solution series $\text{GaP}_x\text{As}_{1-x}$. The kink in the band gap plot at $x = 0.45$ corresponds to a

change from a direct band gap to an indirect band gap. (From *A Materials Science Companion*, figure 7.19)

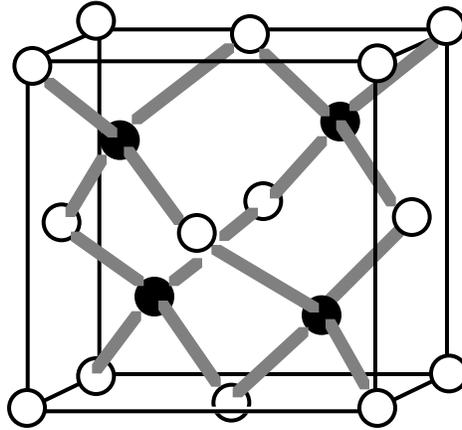


Figure 6. Drawing of a unit cell where all of the atoms are bonded to four other atoms. When all of the atoms are the same element, this is the diamond crystal structure. When the lighter colored spheres are different elements than the darker colored spheres, this structure has AZ stoichiometry and is called zinc blende. (From *A Materials Science Companion*, p. 407, figure 1)

			13	14	15	16	17
			B	C	N	O	F
			Al	Si	P	S	Cl
11	12		Ga	Ge	As	Se	Br
			In	Sn	Sb	Te	I
			Tl	Pb	Bi	Po	At

Figure 7: A portion of the periodic table emphasizing the formation of AZ solids that are isoelectric with Group 14 solids. Isoelectric pairs are indicated with similar shading; for example Ge, GaAs, ZnSe, and CuBr. (From *A Materials Science Companion*, p. 407, figure 2)

Electrons and Holes

Conductivity in a semiconductor such as silicon can be described using the localized bonding picture. Each silicon atom is bonded to four other silicon atoms in a tetrahedral geometry. Since these bonds are relatively strong, the electrons are held tightly and are not mobile. However, a few electrons can be excited out of the bonds by either absorption of thermal energy or light of at least the band gap energy. As a result, electrical conductivities near room temperature can be appreciable.

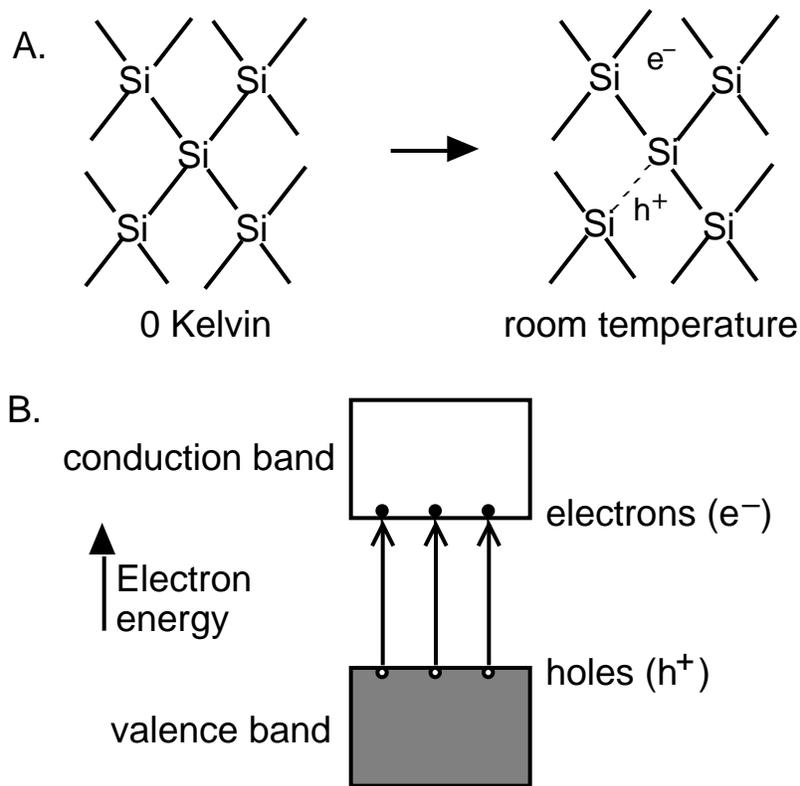


Figure 8. **A:** A localized bonding picture of a semiconductor. In the absence of heat or light, the valence electrons are localized in two-electron Si–Si bonds. However, absorption of heat or light energy produces some mobile electrons (e^-) and an equivalent number of mobile holes (h^+). The one-electron bond resulting from creation of the electron–hole pair is indicated with a dashed line. **B:** The band structure of a semiconductor using a delocalized bonding picture. Electrons (filled circles) may be excited from the valence band by absorption of light or thermal energy. Holes (open circles) are left behind in the valence band. (From *A Materials Science Companion*, figure 8.1)

One-electron bonds are created from these mobile electrons, and the missing electrons are often referred to as “holes.” These missing electrons are treated as mobile individual particles and can be represented by h^+ . The holes in the localized bonding picture roam throughout the solid, as electrons from adjacent two-electron bonds move to fill the holes. Consequently, the one-electron bonds become two-electron bonds but create new one-electron bonds. This process conserves the number of holes and effectively moves the holes throughout the crystal.

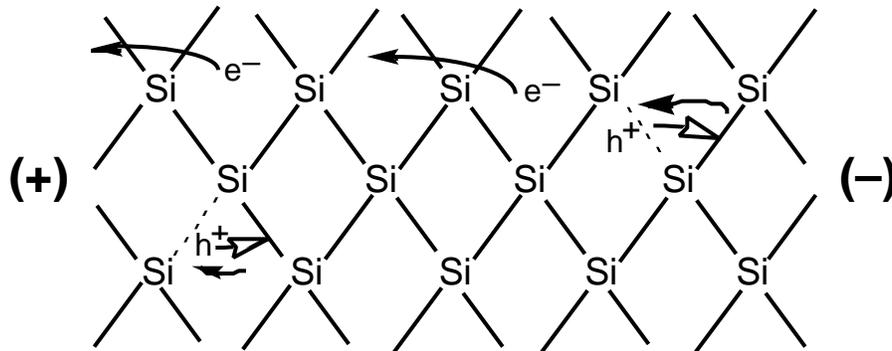


Figure 9. If a voltage is applied to a crystal of semiconducting material, the electrons migrate toward the positive terminal and the holes migrate toward the negative terminal. Two kinds of electron motion are illustrated. Excited electrons (e^-) move through the crystal toward the positive terminal. In addition, an electron in a bonding pair can jump into a one-electron bond (hole). This results in net motion of the electrons (dark arrows) and holes (open arrows) in opposite directions. This process of holes and electrons moving throughout a solid can be illustrated through a student demonstration. The picture below presents such a demonstration. (From *A Materials Science Companion*, figure 8.2)

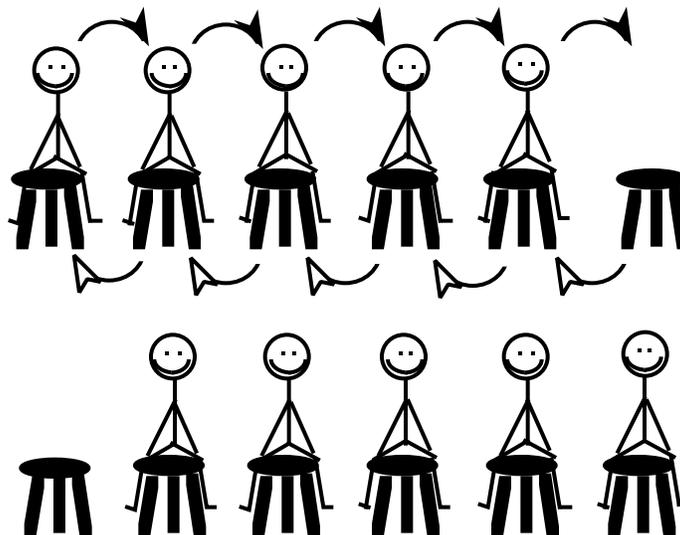


Figure 10. Hole mobility can be modeled by students. Five students are electrons and one empty chair is a hole. Having each student move one chair to the right (dark arrows) produces a result that is equivalent to the empty chair moving to the left (open-tipped arrows). (From *A Materials Science Companion*, figure 8.3)

Doping

It is possible to replace the atoms in a semiconductor with other atoms having more or fewer valence electrons, which will lead to an excess of mobile electrons or holes, respectively. This process is called doping. For example, replacement of silicon atoms with phosphorus atoms increases the mobile electron concentration and creates what is known as an n-type semiconductor (more mobile electrons than holes). Conversely, substitution of silicon atoms with aluminum atoms increases the mobile hole concentration and creates a p-type semiconductor (more mobile holes than electrons). Even substitution at parts per million level can cause million-fold enhancements in conductivity. This sensitivity is the reason for the use of clean rooms in the semiconductor industry and the kinds of clean room attire worn by industry personnel, as parts per million of contaminants can adversely affect electrical properties.



Figure 11. This enlarged image of a grain of salt on a piece of a microprocessor illustrates the small size and complexities of a microprocessor and the importance of clean rooms in manufacturing them.

A.

B.



Figure 12. A: If you've never done it before, putting on a bunny suit can take 30 to 40 minutes. The Intel pros can do it in five minutes. **B:** At the Intel Museum you can see what the Bunnypeople™ look like.

Light Emitting Diodes

There are two forms of semiconductors, n-type and p-type. An n-type semiconductor is one in which atoms with more valence electrons have been substituted into the structure of the original semiconductor. For example, a Group 15 atom could be substituted into the silicon structure. A p-type semiconductor is one in which atoms with fewer valence electrons (more holes) have been substituted into the structure of the original semiconductor. For example, a Group 13 atom could be substituted into the germanium structure. Now, if a low resistance metallic contact is made between an n-type and p-type material, the interface zone between them is referred to as a p-n junction. If a voltage is applied across this junction such that the n-type side is negative relative to that applied to the p-type side, the voltage is referred to as forward bias. Under forward bias the energy barrier for electrons and holes to flow through the junction is decreased, and negative electrons move from the n-type side to the p-type side, while positive holes are forced to move in the opposite direction.

A light emitting diode (LED) is a semiconductor p-n junction that is optimized to release light of approximately the band gap energy under forward bias, when electrons fall from the conduction band to the valence band. The electrons and holes migrate toward the junction where they recombine and release light whose energy corresponds to the band gap energy.

Uses and Capabilities of LEDs

LEDs are currently being used in various ways. One reason to use LEDs is that they last longer, and they are brighter, and are more efficient than incandescent lights. New flashlights made with LEDs are making their way into the marketplace. LEDs are

also extremely tough. This characteristic is a result of having no glass to shatter and no filament to break. Therefore, the new LED lights are shockproof and more robust than incandescent lights. Extremely efficient, the LED lamps use as little as ten percent of the electricity that an incandescent light uses. Consequently, if a light is battery-operated, an LED design requires far less battery power. Incandescent light bulbs burn out after about 25-100 hours of use, while LEDs have life spans of 100,000 hours, which is over 11 years of continuous use.

The trait of efficiency goes hand in hand with being environmentally friendly. As a result of the LED's efficiency, LEDs do not waste as much electricity nor require large supplies of batteries. They can also be solar-powered.

In addition to these reasons, LEDs are safer and more reliable. LEDs are excellent for use near explosive gases and liquids, since they can withstand large shocks and vibrations and operate at a low temperature. Due to their low failure rate, they reduce liability, especially in areas where a failed light could cause an accident. Many lights are used to warn people or to permit people to work at night under safe conditions. Light failure can result in substantial cost if it leads to an accident or lost labor.

In the automotive industry LEDs are becoming prevalent. The new lights improve automobile safety and reliability while cutting design and assembly costs. The LEDs eliminate the need for deep cavities in the car body that were required for incandescent lights. This in turn eliminates the expensive sheet-metal tooling and assembly costs associated with body cutouts required for other types of lighting. As a result, more trunk space is available and designers have flexibility in altering the car's appearance. LEDs consume less power than incandescent bulbs, which in turn frees up more electrical energy for other parts of the vehicle. This also helps with fuel economy. LEDs in vehicles are safer. Because LEDs do not require the heating of a filament to produce light, they illuminate faster than incandescent lighting, which gives drivers more time to react to other cars in front of them on the road. This cuts down on the number of accidents that occur. Therefore, LEDs with characteristics such as low power consumption, long lifetimes, brightness, and safety are increasingly being used everywhere. Here are some other examples of where they are being utilized.

- Bi-color LEDs used in programmable message boards
- Roadside vehicle speed display
- Brake lights on automobiles
- City buses, which have brake and tail lights as well as turn signals
- Some traffic signals
- Elektrik Art-prints (<http://www.cybershop2020.com/electrik.htm>)
- New railroad crossing flashers
- Exit signs
- Parking information signs
- Construction sign traffic arrows

DEMONSTRATION 1

Notes for the Instructor

PURPOSE

To demonstrate electron flow within an energy band.

METHOD

The introductory material that accompanies this unit discusses the band theory of metals and electrical conduction at some length. This demonstration will reinforce the concept that only those electrons in partially filled energy bands are capable of contributing to electrical conductivity. Furthermore, only those electrons that are near the top of the filled energy levels in the unfilled band can actually contribute in a net sense. Three clear bottles with caps; one filled completely with sand, one half-filled with sand, and one empty are needed. Tip each bottle at a 45° angle from vertical, a mechanical analog of applying a voltage, and look for the flow of sand, a mechanical analogy to the electrical current flow.

EXPECTED RESULTS

Obviously, the net movement of sand can only occur in the partially filled bottle, which makes this a good analogy for electrical conduction. A class discussion involving the following questions should clarify and extend the analogy.

FOLLOW-UP QUESTIONS

1. What does the sand represent in this demonstration? **Valence Electrons.**
2. What does the empty bottle represent? **An energy band that has no electrons in it.**
3. What does the completely full bottle represent? **A band that is completely filled with electrons.**
4. What does the half-full bottle represent? **A partially filled band.**
5. What does tilting the bottles represent? **Supplying energy to the electrons (applied voltage).**
6. What is significant about the fact that only the sand at the top of the partially filled bottle moves? **It is the movement of electrons occupying energy levels near the top of the partially filled band into the unfilled energy levels of the band that provide a net flow of carriers, representing electrical conductivity. The electrons below this level simply move into levels that were previously occupied and do not lead to a net flow of electrons.**

INVESTIGATION 1 Notes for the Instructor

PURPOSE

To have the students become familiar with the structure of graphite prior to the demonstration of the oxidative intercalation of this structure to illustrate the enhancement of electrical conductivity by removing electrons from a filled energy band.

METHOD

The students are provided with a model or preferably they are asked to construct a model of graphite using the Solid State Model Kit available from ICE. It is suggested that the students only construct that portion of the model identified by dotted lines that define the unit cell.

ANSWERS TO FOLLOW-UP QUESTIONS

1. Each carbon atom has three nearest neighbors.
2. The nearest neighbors are arranged in a trigonal planar arrangement.
3. For the graphite unit cell:

$$8 \text{ corner atoms} \times 1/8 = 1$$

$$2 \text{ face atoms} \times 1/2 = 1$$

$$4 \text{ edge atoms} \times 1/4 = 1$$

$$1 \text{ interior atoms} \times 1 = 1$$

$$= 4 \text{ atoms total}$$

4. See diagrams on page 67 of the manual that accompanies the Solid State Model Kit.
5. The fact that carbon forms only three bonds and not four means that there is a single delocalized valence electron that acts as a charge carrier when excited. The extra electron can move energetically to a nearby empty band above it. This question will probably require some class discussion and should be used nevertheless in conjunction with the intercalation demonstration that follows.

INVESTIGATION 1

PURPOSE

To become familiar with the structure of graphite. To understand on the basis of this structure why graphite is an electrical conductor.

PROCEDURE

If a model of the graphite structure has been made available to you, look at it carefully as you answer the following questions. If you are to build the model yourself, follow the instructions on page 67 of the manual that accompanies the Solid State Model Kit.

FOLLOW-UP QUESTIONS

1. How many nearest neighbors does each carbon atom have in this structure?
2. How are the nearest neighbors arranged about a given central atom? What is the name of the shape these neighbors assume?
3. How many atoms are in the unit cell ? (**HINT: Recall from your earlier investigations that a unit cell is defined as a three dimensional, six sided figure having parallel faces. When a face is reproduced and moved along its edges a distance equal to the length of the edge, generates the entire structure.**)
4. Draw the z layer sequence showing the position of the atoms at $z = 0$, $\frac{1}{2}$, and 1.
5. Consider your answer to (2) above and the following information. Carbon typically forms four bonds by sharing the four electrons in its outermost energy level (valence level). This bond formation “localizes” these valence electrons about the atom and restricts their movement throughout the remainder of the structure. In addition the formation of four bonds with other carbon atoms (such as the diamond structure) results in a completely filled band. Why then is graphite a conductor?

DEMONSTRATION 2

Notes for the Instructor

PURPOSE

To illustrate that conductivity of material can be increased by adding electrons to an empty band or, in this case, removing electrons from a filled one.

METHOD

Bromine will be used to oxidize a sample of graphite. This oxidative process removes electrons from the highest filled energy band of the carbon atoms, thus creating a partially filled band. In addition, the bromide ions produced fill in the spaces between the graphite sheets, forcing them further apart. This process causes individual graphite particles to swell, which increases the pressure inside the tube holding the graphite. The increased pressure improves the electrical contact between the particles, reduces resistance and thereby further increases conductivity. The process may be followed by comparing the relative brightness of a small light bulb placed in the circuit.

MATERIALS

2 graphite rods

Teflon tubing-approximately 3 inches long

evaporating dish

1-2 grams of graphite powder (Decolorizing Carbon-Nordit works)

ring stands and clamps

10% (by volume) Br₂ in methyl alcohol (elemental bromine may be used with caution)

6-V battery or power supply*

1-2 light bulb*

wires and alligator clips*

multimeter and leads*

* The physics department should have these materials.

PROCEDURE

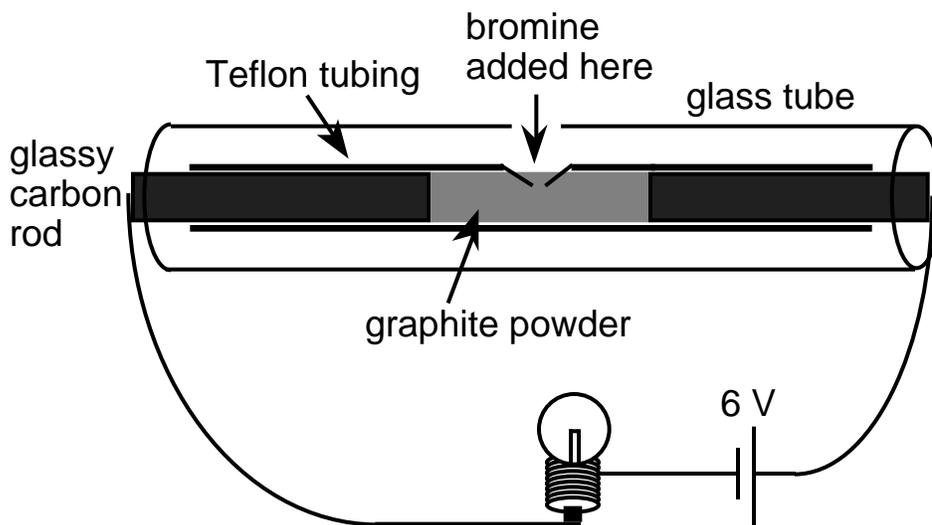


Figure 1. The conductivity apparatus for demonstrating the intercalation of bromine into graphite.

1. Place several grams of graphite powder between two graphite rods in a Teflon tube, as shown in the figure above. It helps to lubricate the rods with glycerin before inserting them. It is also recommended that the hole in the tubing be made after the powder and rods have been inserted. A small cork bore works well for making the hole.

2. Apply sufficient pressure to the rods so that the resistance between the two rods is less than 100 ohms. Clamp the apparatus in a horizontal position and place a beaker beneath it. If you wish to demonstrate the increased conductivity using a small light bulb, connect the apparatus in series with a power-supply and the bulb. The voltage should be adjusted so that the bulb just faintly glows or is dark, indicating that the carbon has a fairly high resistance. If you want to follow the resistance change with a multimeter, simply attach the meter in series with the apparatus. It will be necessary to project the image of the meter using a video camera if an entire class is to observe the changes. If you have access to a large demonstration meter it should also work well without the need to project it.

3. Place several drops of the bromine solution into the hole in the tubing. After several seconds the light will begin to glow and the meter will record a significant lowering of resistance. **CAUTION: If elemental liquid bromine is used, the demonstration should be performed in a fume hood, and the demonstrator should wear gloves, as the reagent is volatile, corrosive, and highly toxic.**

FOLLOW-UP QUESTIONS

Either prior to, during, or after the demonstration the following points should be emphasized.

1. What makes a material a good conductor of electricity? **(1) the presence of an energy band with delocalized orbitals that is (2) only partially filled with electrons.**
2. What is the band occupancy of the graphite? **It has a valance band that is filled and the next highest energy band that is relatively empty. The two bands are, however, close in energy. which accounts for the conductivity the graphite initially possesses.**
3. What is oxidation? **The loss of electrons.**
4. During the demonstration, what evidence is there that a chemical reaction took place? **The change in conductivity. Some students may wonder if the change was simply because either the bromine itself or the solvent in the solution enhanced the conductivity. Therefore some explanation or demonstration of the conductivities of these substances is probably required.**
5. Describe the nature of this chemical reaction. **Given its location in the periodic table bromine is expected to act as a reasonably strong oxidizing agent, which is exactly what occurs in this reaction. The carbon atoms are being oxidized and the bromine atoms are being reduced.**
6. How does this increase the conductivity of the carbon? **The loss of electrons results in the previously filled valence band now being only partially filled. The orbitals not used for carbon-carbon sigma bonding form a band that has been previously discussed in Investigation 1 in this unit. Therefore, carbon now fulfills the requirements for conductivity to a greater extent than it did.**

7. What happens to the bromide ions that are produced? **The bromide ions fill in the spaces (intercalate) between the layers of the two-dimensional network arrangement that constitutes the graphite structure. This causes the graphite layers to be pushed apart and individual graphite particles to exert greater pressure on each other. This increases the pressure inside the tube and further increases the conductivity. This increase in conductivity may be demonstrated by inserting another graphite rod into the hole in the tubing and pushing down. The change in resistance/conductivity is readily detected by the meter. See the figure below.**

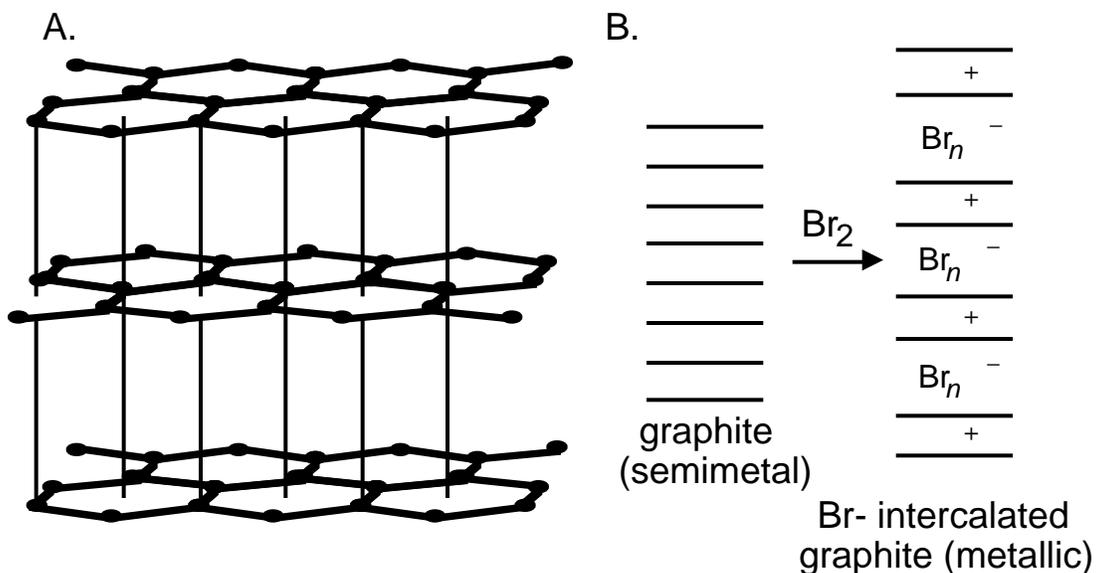


Figure 2 A: The layered structure of graphite. B: The bromine inserted between the layers of graphite and increasing the pressure thus increasing the conductivity.

DEMONSTRATION 1

Notes for the Instructor

PURPOSE

To demonstrate electron flow within an energy band.

METHOD

The introductory material that accompanies this unit discusses the band theory of metals and electrical conduction at some length. This demonstration will reinforce the concept that only those electrons in partially filled energy bands are capable of contributing to electrical conductivity. Furthermore, only those electrons that are near the top of the filled energy levels in the unfilled band can actually contribute in a net sense. Three clear bottles with caps; one filled completely with sand, one half-filled with sand, and one empty are needed. Tip each bottle at a 45° angle from vertical, a mechanical analog of applying a voltage, and look for the flow of sand, a mechanical analogy to the electrical current flow.

EXPECTED RESULTS

Obviously, the net movement of sand can only occur in the partially filled bottle, which makes this a good analogy for electrical conduction. A class discussion involving the following questions should clarify and extend the analogy.

FOLLOW-UP QUESTIONS

1. What does the sand represent in this demonstration? **Valence Electrons.**
2. What does the empty bottle represent? **An energy band that has no electrons in it.**
3. What does the completely full bottle represent? **A band that is completely filled with electrons.**
4. What does the half-full bottle represent? **A partially filled band.**
5. What does tilting the bottles represent? **Supplying energy to the electrons (applied voltage).**
6. What is significant about the fact that only the sand at the top of the partially filled bottle moves? **It is the movement of electrons occupying energy levels near the top of the partially filled band into the unfilled energy levels of the band that provide a net flow of carriers, representing electrical conductivity. The electrons below this level simply move into levels that were previously occupied and do not lead to a net flow of electrons.**

INVESTIGATION 1 Notes for the Instructor

PURPOSE

To have the students become familiar with the structure of graphite prior to the demonstration of the oxidative intercalation of this structure to illustrate the enhancement of electrical conductivity by removing electrons from a filled energy band.

METHOD

The students are provided with a model or preferably they are asked to construct a model of graphite using the Solid State Model Kit available from ICE. It is suggested that the students only construct that portion of the model identified by dotted lines that define the unit cell.

ANSWERS TO FOLLOW-UP QUESTIONS

1. Each carbon atom has three nearest neighbors.
2. The nearest neighbors are arranged in a trigonal planar arrangement.
3. For the graphite unit cell:

$$8 \text{ corner atoms} \times 1/8 = 1$$

$$2 \text{ face atoms} \times 1/2 = 1$$

$$4 \text{ edge atoms} \times 1/4 = 1$$

$$1 \text{ interior atoms} \times 1 = 1$$

$$= 4 \text{ atoms total}$$

4. See diagrams on page 67 of the manual that accompanies the Solid State Model Kit.
5. The fact that carbon forms only three bonds and not four means that there is a single delocalized valence electron that acts as a charge carrier when excited. The extra electron can move energetically to a nearby empty band above it. This question will probably require some class discussion and should be used nevertheless in conjunction with the intercalation demonstration that follows.

INVESTIGATION 1

PURPOSE

To become familiar with the structure of graphite. To understand on the basis of this structure why graphite is an electrical conductor.

PROCEDURE

If a model of the graphite structure has been made available to you, look at it carefully as you answer the following questions. If you are to build the model yourself, follow the instructions on page 67 of the manual that accompanies the Solid State Model Kit.

FOLLOW-UP QUESTIONS

1. How many nearest neighbors does each carbon atom have in this structure?
2. How are the nearest neighbors arranged about a given central atom? What is the name of the shape these neighbors assume?
3. How many atoms are in the unit cell ? (**HINT: Recall from your earlier investigations that a unit cell is defined as a three dimensional, six sided figure having parallel faces. When a face is reproduced and moved along its edges a distance equal to the length of the edge, generates the entire structure.**)
4. Draw the z layer sequence showing the position of the atoms at $z = 0$, $\frac{1}{2}$, and 1.
5. Consider your answer to (2) above and the following information. Carbon typically forms four bonds by sharing the four electrons in its outermost energy level (valence level). This bond formation “localizes” these valence electrons about the atom and restricts their movement throughout the remainder of the structure. In addition the formation of four bonds with other carbon atoms (such as the diamond structure) results in a completely filled band. Why then is graphite a conductor?

DEMONSTRATION 4

Notes for the Instructor

PURPOSE

To illustrate that LEDs of different colors may be produced by tuning the gap in energy between the top of the valence band and the bottom of the conduction band (band gap) by varying the chemical composition of semiconducting materials used to produce them.

METHOD

If LED materials are restricted to compounds having AZ stoichiometries, then the light produced by them is restricted to the band gap energies of the AZ solids. If, however, the LED is made of a solid solution comprising solids of the same structure with atoms of comparable size, then the light produced may be adjusted (tuned) by manipulating the chemical composition of the solid solution, which alters the band gaps in a predictable way. Zinc blende semiconductors such as GaAs and GaP are one pair of solids that can be combined to yield solid solutions having compositions that can be represented by $\text{GaP}_x\text{As}_{1-x}$ ($0 \leq x \leq 1$), where x and $1-x$ represent the probabilities that an atom occupying a specific site in the structure is P or As respectively. As was discussed in the background material for this unit, this change in composition results in unit-cell constants (edge lengths) that vary continuously between 5.45 Å and 5.65 Å with an accompanying change in band-gap from 1.4 eV to 2.3 eV. The light that is produced as electrons make the transition between the conduction and valence bands is roughly equivalent in energy to these gaps and correspond to wavelengths from 890 nm (GaAs) to 540 nm (GaP). This theory may be demonstrated by showing LEDs of several colors and relating those colors to both composition and band gap energies.

MATERIALS

$\text{GaP}_x\text{As}_{1-x}$ LEDs (See supplier information for Investigation 1 in the Diffraction Unit)

$\text{GaP}_{0.40}\text{As}_{0.60}$	Red	$\text{GaP}_{1.00}\text{As}_{0.00}:\text{N}$	Green
$\text{GaP}_{0.65}\text{As}_{0.35}:\text{N}$	Orange	GaN	Blue (optional)
$\text{GaP}_{0.85}\text{As}_{0.15}:\text{N}$	Yellow	GaN/phosphor	White (optional)
1-k resistor		Multimeter and leads	
9-V battery			
Battery snap			
LED socket			

PROCEDURE

1. Construct the LED circuit by wiring the resistor in series with the battery and LED socket.
2. Plug the LEDs into the socket and note the composition and color of the light emitted. The recommended order would be red, orange, yellow, and green.
3. Attach the multimeter leads across each side of the LED circuit and set the meter to read voltage. Record the voltage for each LED.

FOLLOW-UP QUESTIONS

1. Which color LED represents light with the lowest energy? **Red** Highest? **Green** Explain. $E = (hc)/\lambda$, since red has a longer λ , its energy is smaller.
2. What is a band-gap energy? **The difference in energy between the valence and conduction bands in materials.**
3. How is light produced by the LED? **The applied electric field supplies enough energy to promote electrons into the conduction band. They are not stable in this excited state and return to the ground state releasing energy as they do so. Much of this energy is in the form of light.**
4. Which color LED contains the smallest band gap? **Red.** Largest? **Green .** How can you tell? **Red light has a lower frequency and therefore lower energy. The photon energy roughly approximates the band gap. Green light has a higher frequency and higher energy.**
5. From the information provided to you during the demonstration, what factor(s) appear to be responsible for the change in band gap? **The obvious answer is composition. This would be a good time to discuss these changes in terms of periodic properties like size, valence level configurations, etc.**
6. Why can't blue light be produced from LEDs of this general composition? **The green LED has a composition that is essentially GaP. Since the band gap varies directly with the unit cell constant and since that unit cell constant has reached its minimum value when the ratio of P to As in the LED has reached its maximum, no larger band-gaps can be expected with this particular family of LEDs. Since blue light would require a larger band gap, blue LEDs can not be produced by this method.**
7. What relationship (if any) exists between the band gap energy and the measured voltage across each LED? **When voltage is applied across the the LED, nothing happens unless the energy is sufficient to excite an electron from its localized bond. Voltage is directly proportional to energy and therefore the voltage and band gap energy should be directly related.**

Student Questions after Demonstration #4

1. Which color LED represents light with the lowest energy? Highest energy? Explain.
2. What is the band-gap energy?
3. How is light produced by the LED?
4. Which color LED contains the smallest band-gap? Largest? How can you tell?
5. From the information provided to you during the demonstration, what factor(s) appear to be responsible for the change in band-gap?
6. Why can't blue light be produced from LEDs of this general composition?
7. What relationship (if any) exists between the band gap energy and the measured voltage across each LED?

5. Considering only electronegativity, rank the following in order of increasing band gap energy: $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$, $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$, $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$, $\text{Al}_{0.05}\text{Ga}_{0.95}\text{As}$
6. What usually happens to the bond distances of a material when it is cooled? Considering only bond distance, would a material's band gap be larger when warm or cold? Explain.
7. Some LED materials can be prepared by combining Ga, In, As, and P in the zinc blende structure. If the formula of the solid is $\text{Ga}_{0.45}\text{In}_x\text{As}_{0.75}\text{P}_y$, what are x and y equal to, and how would you interpret this formula based on the zinc blende structure?
8. Give a brief explanation for the following:
Why does squeezing some LED's (applying pressure to them) make their spectrum move to shorter wavelengths?

13. Two LEDs are excited with the same amount of electrical energy from a battery and emit the same number of photons. One of these LEDs is emitting green photons at around 500 nm; and the other is emitting red photons at around 700 nm. Which is doing a better job of converting the electrical energy into light energy and why (i.e., which is more energy efficient)?
14. An InP LED is connected between electrodes. Does it matter which side of the p-n junction is connected to which electrode and, if so, how do you connect it to make it glow?
15. Suggest dopants that will substitute for In to make the p-type region of the LED and for P to make the n-type region. Explain your choices.
16. 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.

INVESTIGATION 1

Notes for the Instructor

PURPOSE

To have students become familiar with the structure of graphite prior to the demonstration of the oxidative intercalation of this structure to illustrate the enhancement of electrical conductivity by removing electrons from a filled energy band.

METHOD

The students are provided with a model or preferably they are asked to construct a model of graphite using the Solid State Model Kit available from ICE. It is suggested that the students only construct that portion of the model identified by the dotted lines that define the unit cell.

ANSWERS TO THE FOLLOW-UP QUESTIONS

1. Each carbon atom has four nearest neighbors.
2. The nearest neighbors are arranged in a trigonal planar arrangement
3. For the graphite unit cell:
$$\begin{array}{r} 8 \text{ corner atoms} \times 1/8 = 1 \\ 2 \text{ face atoms} \times 1/2 = 1 \\ 4 \text{ edge atoms} \times 1/4 = 1 \\ \underline{1 \text{ interior atoms} \times 1 = 1} \\ = 4 \text{ atoms total} \end{array}$$
4. See diagrams on page 67 of the manual that accompanies the Solid State Model Kit.
5. The fact that carbon only forms three bonds and not four means that there is a single delocalized valence electron that acts as a charge carrier when excited. The extra electron can move energetically to a nearby empty band above it. This question will probably require some class discussion and should be used nevertheless in conjunction with the intercalation demonstration (Demonstration 4).

INVESTIGATION 1

PURPOSE

To become familiar with the structure of graphite. To understand on the basis of this structure why graphite is a good electrical conductor.

METHOD

If a model of the graphite structure has been made available to you, look at it carefully as you answer the following questions. If you are to build the model yourself, follow the instructions on page 67 of the manual that accompanies the Solid State Model Kit..

ANSWERS TO THE FOLLOW-UP QUESTIONS

1. How many nearest neighbors does each carbon atom have in this structure?
2. How are the nearest neighbors arranged about any given central atom? What is the name of the shape these neighbors assume?
3. How many atoms are in the unit cell? (**HINT:** Recall from your earlier investigations that a unit cell is defined as a three dimensional, six sided figure having parallel faces. When a face is reproduced and moved along its entire edges a distance equal to the length of the edge, it generates the entire structure.)
4. Draw the z layer sequence showing the position of the atoms at $z = 0$, $1/2$, and 1 .
5. Consider your answer to (2) above and the following information. Carbon typically forms four bonds by sharing the four electrons in its outermost energy level (valence level). This bond formation “localizes” these valence electrons about the atom and restricts their movement throughout the remainder of the structure. In addition the formation of four bonds with other carbon atoms (such as the diamond structure) results in a completely filled band. Why then is graphite a conductor?

INVESTIGATION 2

Notes for the Instructor

PURPOSE

To introduce students to the zinc blende structure by comparing it to the structure of diamond. To provide students with the background information necessary to make the discussion of solid solutions with AZ stoichiometry and tunable band gaps meaningful.

METHOD

The students are provided with models or are asked to construct models of diamond and zinc blende (face-centered cubic orientation) using the ICE Solid State Model Kit.

ANSWERS TO THE FOLLOW-UP QUESTIONS

1. Each carbon atom has four nearest neighbors. Each Zn atom has four nearest neighbors. Each S atom has four nearest Zn neighbors.
2. The shape defined by the nearest neighbors to each C atom is tetrahedral. The shape defined by the nearest S neighbors to each Zn atom is tetrahedral. The shape defined by the nearest Zn neighbors to each S atom is tetrahedral.
3. For the diamond unit cell:
 $8 \text{ corner atoms} \times 1/8 = 1$
 $6 \text{ face atoms} \times 1/2 = 3$
 $4 \text{ interior atoms} \times 1 = 4$
 $= 8 \text{ atoms total}$
For the ZnS unit cell:
 $8 \text{ Zn corner atoms} \times 1/8 = 1$
 $6 \text{ Zn face atoms} \times 1/2 = 3$
 $= 4 \text{ Zn atoms}$
 $4 \text{ S interior atoms} \times 1 = 4$
 $= 4 \text{ S atoms}$
4. The atoms in both structures occupy tetrahedral sites. In the diamond crystal structure all the atoms are C. In the zinc blende structure each Zn atom is tetrahedrally surrounded by 4 S atoms, and each S atom is similarly surrounded by 4 Zn atoms.
5. The zinc blende structure has AZ stoichiometry because the ratio of Zn to S atoms is 1:1.
6. See diagrams on pages 23 and 51 of the manual that accompanies the ICE Solid State Model Kit.

INVESTIGATION 2

PURPOSE

To compare the similarities and differences between the diamond and zinc blende (ZnS) structures. To understand why zinc blende is said to demonstrate AZ stoichiometry.

PROCEDURE

If models of diamond and zinc blende have been made available to you, look at them carefully as you answer the following questions. If you are assigned to build one or both of the models yourself, follow the instructions on pages 23 and 51 of the manual that accompanies the ICE Solid State Model Kit.

FOLLOW-UP QUESTIONS

1. How many nearest neighbors does each carbon atom in the diamond structure have? How many nearest S neighbors does each Zn in the ZnS structure have? How many nearest Zn neighbors does each S in the ZnS structure have?
2. What is the name of the shape defined by the nearest neighbors to each C in the diamond structure? To each Zn by S atoms in the ZnS structure? To each S by Zn atoms in the ZnS structure?
3. How many atoms of C are in the diamond unit cell? How many atoms of Zn are in the ZnS unit cell? How many atoms of S are in the ZnS unit cell?
4. How are these structures similar? How are they different?
5. How does the zinc blende structure demonstrate AZ stoichiometry? (Stoichiometry refers to the quantitative relationship between the atoms in the structure, and AZ indicates two different atoms in a 1:1 ratio.)
6. Draw the z-layer sequence showing the position of the atoms at $z = 0, 1/4, 1/2,$ and $3/4$ for both diamond and zinc blende.

PURPOSE

To measure the wavelength of the light produced by several LEDs of the $\text{GaP}_x\text{As}_{1-x}$ series of compound semiconductors and use it to approximate the band gap energy for each LED. To use the experimental results to find a relationship between x and the band gap energy using graphical analysis. To predict the composition of the LED based upon the color () of the light it produces.

METHOD

The method here is similar to that of Demonstration 4. It differs in that the focus is on experimentally determining the wavelengths rather than assessing the color qualitatively. A pre-lab discussion should address the following: (1) a definition of metals, semiconductors, and insulators in terms of band gap energies; (2) a definition of the zinc blende structure and AZ stoichiometry (see the background information for this unit); (3) the relationships between band gap energy, size, and electronegativity differences between the atoms in the structure; (4) use of solid solutions to provide many more opportunities for adjusting the band gap energy than the combinations of any two elements with AZ stoichiometry.

MATERIALS

Four LEDs (see materials for Demonstration 4)

LED plug-in circuit (see procedure for Demonstration 4)

Two meter sticks

One diffraction grating

ANSWERS TO FOLLOW-UP QUESTIONS

1. What is the relationship between the band gap energy and x in this $\text{GaP}_x\text{As}_{1-x}$ ($0 \leq x \leq 1$) series of LEDs?

The graph should indicate that as x increases, the band gap energy increases.

2. The distance between the nuclei is one factor that determines how strongly an electron is held between covalently bonded atoms. As the size of the nuclei increase, the band gap energies decrease. Considering only size, would the LED made of GaP or GaAs be redder in color?

Since P has a smaller radius than As, GaP would have the larger band gap energy and shorter associated wavelength of light produced. Therefore, the GaAs LED would be redder.

EXPERIMENT 1

PURPOSE

To find the relationship between band gap energy and composition using LEDs that utilize the $\text{GaP}_x\text{As}_{1-x}$ ($0 \leq x \leq 1$) series of solid solutions.

PROCEDURE

1. Set up the apparatus as shown in Figure 1 below.

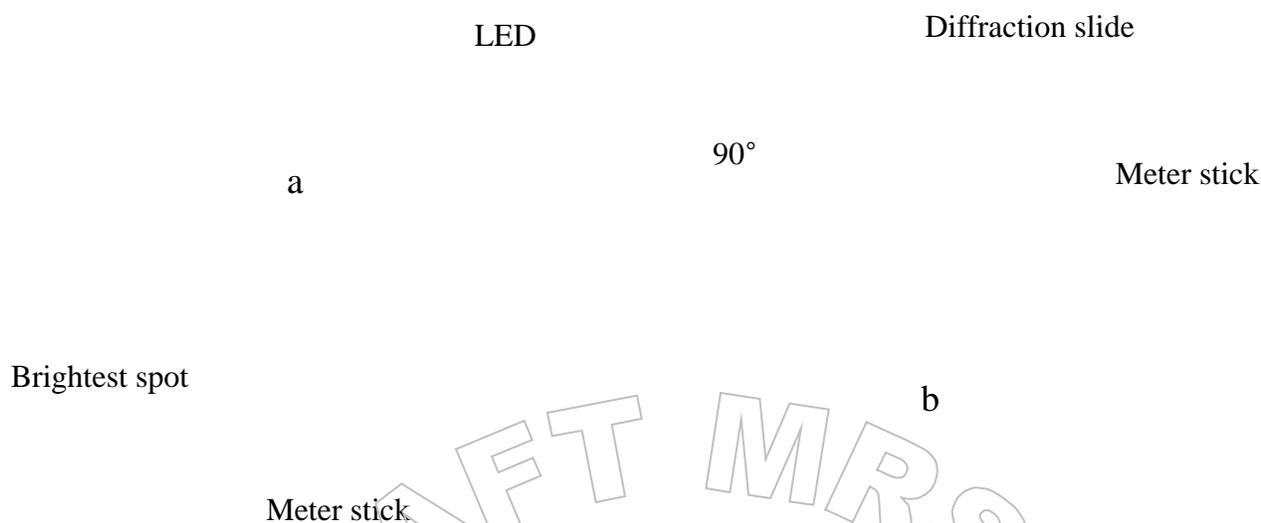


Figure 1.

2. One lab partner will position the LED directly behind the intersection of the two perpendicular meter sticks so that it is clearly visible to the other partner positioned at the end of the meter stick, directly opposite the LED. Once the team is ready, connect the LED to the battery and wait for the room lights to be turned off.
3. The partner with the diffraction grating will view the emission spectrum. The other partner will move a pencil slowly along the meter stick at the LED end of the apparatus away from the LED. The student viewing the spectrum should indicate when the pencil is at the brightest point of the spectrum on either side of the LED. At that point, measure the distance in cm from the LED to the brightest point and record as distance (X) in Data Table 1.
4. Repeat Step 3 for the other LEDs.
5. Disconnect all LEDs when you are finished.

Data Table 1

LED	COLOR	a (cm)	b (cm)	(x)
1	RED		100	0.40
2	ORANGE		100	0.65
3	YELLOW		100	0.85
4	GREEN		100	1.00

CALCULATIONS

Calculate the following and record in Data Table 2.

1. Find the distance (z) from the diffraction grating to the bright image in the spectrum for each LED. $c = \sqrt{a^2 + b^2}$
2. Find the sine of angle θ for each LED. $\sin \theta = a/c$.
3. Find the wavelength (λ) in cm: $\lambda = d \sin \theta$ where d is the distance between the lines on the diffraction grating. (Ask your instructor for this value).
4. Using the relationship between wavelength and energy, find the energy E_g that corresponds to the wavelength for each LED.

Data Table 2

COLOR	c(cm)	SIN θ	λ (cm)	E_g (eV)
RED				
ORANGE				
YELLOW				
GREEN				

ANALYSIS

From the data in Tables 1 and 2 make a graph of E_g vs. x.

FOLLOW-UP QUESTIONS

1. What is the relationship between the band-gap energy and x in this $\text{GaP}_x\text{As}_{1-x}$ ($0 \leq x \leq 1$) series of LEDs?
2. The distance between the nuclei is one factor that determines how strongly an electron is held between covalently bonded atoms. As the size of the nuclei increase, the band gap energies decrease. Considering only size, would the LED made of GaP or GaAs be redder in color?

LED Review Questions

1. Consider two samples in the form of powders: sample A is a physical mixture comprising equal moles of pure Ge and pure Si; sample B is a solid solution of composition $\text{Si}_{0.5}\text{Ge}_{0.5}$. For which of the following measurements will the two samples appear identical?

- A. X-ray diffraction
- B. elemental analysis**
- C. band gap energy measurement based on absorption of light
- D. none of the above

2. Both of the semiconductors GaAs and GaP have the zinc blende structure. From X-ray diffraction, one sample has a cubic unit cell size of 5.45 Angstroms and the other has a cubic unit cell size of 5.65 Angstroms.

- a) Which is which based on position in the periodic table?

Since As is below P in the periodic table, and both elements are being combined with the same element, Ga, in the same structure, we would expect the bigger atom (farther down in the periodic table) to result in a bigger unit cell. Thus, GaAs should be the 5.65 Å unit cell and GaP the 5.45 Å unit cell.

- b) From the relationship between atomic spacing and the resulting diffraction spots, which sample, GaAs or GaP, would have given the larger diffraction pattern and why?

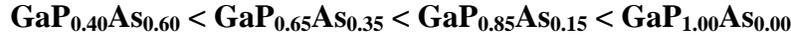
From your previous lab experiments, recall that the larger the spacing between features (dots on your optical transform slide; atoms in a crystal), the smaller the diffraction pattern. Thus, GaP with its smaller cubic unit cell should give a larger diffraction pattern than GaAs with its larger cubic unit cell.

3. Is Ga or Al more electronegative? Considering only the electronegativity difference, would GaAs or AlAs have a larger band gap energy? Explain.

Al is less electronegative than Ga. The increased electronegativity difference between Al and As relative to Ga and As suggests a greater ionic contribution to the bond and hence a larger band gap energy. Thus, AlAs would be expected to exhibit a larger band gap energy than GaAs, and it does.

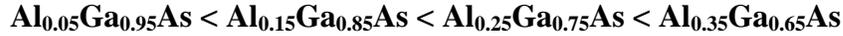
4. Considering only atomic radii, rank the following in order of increasing band gap energy: $\text{GaP}_{0.40}\text{As}_{0.60}$, $\text{GaP}_{0.65}\text{As}_{0.35}$, $\text{GaP}_{0.85}\text{As}_{0.15}$, $\text{GaP}_{1.00}\text{As}_{0.00}$

In order of increasing band gap energy:



5. Considering only electronegativity, rank the following in order of increasing band gap energy: $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$, $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$, $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$, $\text{Al}_{0.05}\text{Ga}_{0.95}\text{As}$

In order of increasing band gap energy:



6. What usually happens to the bond distances of a material when it is cooled? Considering only bond distance, would a material's band gap energy be larger when warm or cold? Explain.

Bond distances will usually contract as the material is cooled, and the band gap energy is expected to increase, since shorter bond distances usually correlate with better orbital overlap and a larger band gap energy.

7. Some LED materials can be prepared by combining Ga, In, As, and P in the zinc blende structure. If the formula of the solid is $\text{Ga}_{0.45}\text{In}_x\text{As}_{0.75}\text{P}_y$, what are x and y equal to, and how would you interpret this formula based on the zinc blende structure?

X = 0.55 and y = 0.25, Based on the zinc blende structure, Ga and In make up one part of the structure, while As and P make up the second part of the structure. Together Ga + In must be in a 1:1 ratio with As + P together.

8. Give a brief explanation for the following:

Why does squeezing some LED's (applying pressure to them) make their spectrum move to shorter wavelengths?

Applying pressure causes the LED to contract, bringing the atoms closer together. The shorter distances between atoms correspond to stronger bonds. If the energy of the emission is higher, the equation, $E = h\nu$, indicates that the frequency is higher (h is Plank's constant). From $c = \nu\lambda$, if the frequency increases, then the wavelength must decrease to maintain this relationship.

9. In a recent news clipping from *Science* magazine, a breakthrough in making blue LEDs was described. Samples of gallium nitride, GaN, can give blue emission. In our lab, the green LED was GaP. If both GaP and GaN are emitting at about their band gap energies, discuss why it is reasonable that GaN would emit in the blue part of the spectrum.

Since N is a smaller atom than P, the Ga-N bonds in GaN should be shorter and stronger than the Ga-P bonds in GaP. We thus expect a larger band gap energy for GaN (harder to remove an electron from a bond, and more energy released when the electron returns to the bond); and blue light is more energetic than green light, as would be predicted on this basis.

10. Predict what would happen to the emission spectrum of the GaN LED if it were run at low temperatures (e.g., a cold Madison day) and why.

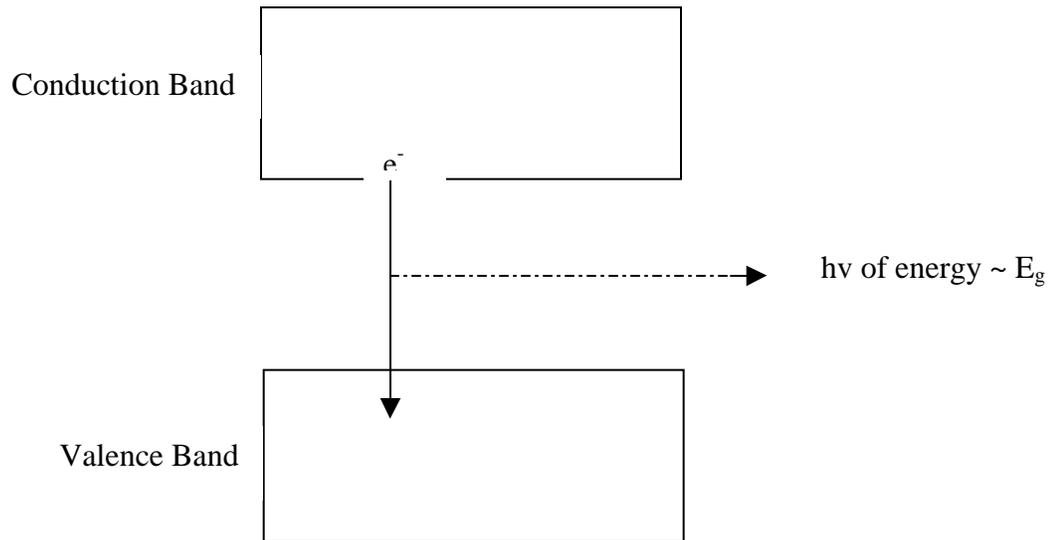
As demonstrated in class, cooling the semiconductor in a LED should cause it to contract, bringing the atoms closer together. The shorter distances between atoms corresponds to stronger bonds and a larger band gap energy. Thus, we would expect the energy of the emission to shift to higher energy (toward the violet end of the spectrum - a so-called "blue shift") if the LED were run under chilled conditions. If the LED were warmed, we would expect a shift toward the red part of the spectrum (a so-called "red-shift") for the same reason.

11. GaN is described as being harder (more resistant to mechanical damage) than ZnSe, which is also being used to construct blue LEDs. Suggest a reason why GaN is harder.

From their positions in the periodic table, we would expect shorter bonds with Ga-N relative to Zn-Se, since N is a second row element and the others are all fourth row elements. The shorter bond would be predicted to be stronger, making the material harder. Electronegativities also support a stronger bond, since there is more polarity to the Ga-N bond: Looking at the table of electronegativities, the Ga-N bonds are relatively ionic, as they have a difference in electronegativities of 1.3 (Ga is 1.7; N is 3.0); whereas the Zn-Se bonds are more covalent with a difference in electronegativities of only 0.8 (Zn is 1.6; Se is 2.4).

12. Explain with a sketch why the emission of an LED can give an estimate of the band gap energy of the solid.

In a band picture, electrons at the bottom of the conduction band drop to the top of the valence band, releasing a photon of roughly band gap energy.



13. Two LEDs are excited with the same amount of electrical energy from a battery and emit the same number of photons. One of these LEDs is emitting green photons at around 500 nm; and the other is emitting red photons at around 700 nm. Which is doing a better job of converting the electrical energy into light energy and why (i.e., which is more energy efficient)?

Green photons are more energetic than red photons (recall that the energy of photons is inversely related to the wavelength: $E = hc / \lambda$), so if the same amount of electrical energy creates as many green as red photons, more energy is recovered when green photons are produced, and the overall efficiency of the green LED is higher.

14. An InP LED is connected between electrodes. Does it matter which side of the p-n junction is connected to which electrode and, if so, how do you connect it to make it glow?

Yes, It matters which side of the p-n junction is connected to which electrode. The LED should be attached with the n-type portion connected to the negative lead and the p-type portion connected to the positive lead. The only way the LED will work is if it is set up in this manner.

15. Suggest dopants that will substitute for In to make the p-type region of the LED and for P to make the n-type region. Explain your choices.

To make a p-type region the atom that you substitute must have fewer valence electrons so that more mobile valence band holes than mobile conduction band electrons result. Therefore, a Group 12 element like Zn could be used in place of In. To make an n-type region the substituting atom must have more valence electrons so that more mobile conduction band electrons than mobile valence band holes result. Therefore, in place of P a Group 16 element like Se might be used.

16. If a material has a band gap energy in the infrared portion of the spectrum, it will appear
- black.**
 - red.
 - green.
 - colorless.

A substance with a band gap in the infrared region of the electromagnetic spectrum will absorb light throughout the visible portion of the electromagnetic spectrum and appear black.

Figure 7.18 from the Companion

5. Considering only electronegativity, rank the following in order of increasing band gap energy: $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$, $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$, $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$, $\text{Al}_{0.05}\text{Ga}_{0.95}\text{As}$
6. What usually happens to the bond distances of a material when it is cooled? Considering only bond distance, would a material's band gap be larger when warm or cold? Explain.
7. Some LED materials can be prepared by combining Ga, In, As, and P in the zinc blende structure. If the formula of the solid is $\text{Ga}_{0.45}\text{In}_x\text{As}_{0.75}\text{P}_y$, what are x and y equal to, and how would you interpret this formula based on the zinc blende structure?
8. Give a brief explanation for the following:
Why does squeezing some LED's (applying pressure to them) make their spectrum move to shorter wavelengths?

9. In a recent news clipping from *Science* magazine, a breakthrough in making blue LEDs was described. Samples of gallium nitride, GaN, can give blue emission. In our lab, the green LED was GaP. If both GaP and GaN are emitting at about their band gap energies, discuss why it is reasonable that GaN would emit in the blue part of the spectrum.
10. Predict what would happen to the emission spectrum of the GaN LED if it were run at low temperatures (e.g., a cold Madison day) and why.
11. GaN is described as being harder (more resistant to mechanical damage) than ZnSe, which is also being used to construct blue LEDs. Suggest a reason why GaN is harder.
12. Explain with a sketch why the emission of an LED can give an estimate of the band gap energy of the solid.

13. Two LEDs are excited with the same amount of electrical energy from a battery and emit the same number of photons. One of these LEDs is emitting green photons at around 500 nm; and the other is emitting red photons at around 700 nm. Which is doing a better job of converting the electrical energy into light energy and why (i.e., which is more energy efficient)?
14. An InP LED is connected between electrodes. Does it matter which side of the p-n junction is connected to which electrode and, if so, how do you connect it to make it glow?
15. Suggest dopants that will substitute for In to make the p-type region of the LED and for P to make the n-type region. Explain your choices.
16. 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.

LED Assessment

Teacher Guide

Name _____

Date _____ Hour _____

Matching

Match the word with the best definition.

- | | |
|--------------------------------|---|
| <u>F</u> 1. LED | a. the attraction of an atom for electrons |
| <u>M</u> 2. doping | b. the highest energy filled band that lies at the bottom of the band gap |
| <u>H</u> 3. solid solution | c. a type of material that is a poor conductor of electricity |
| <u>N</u> 4. semiconductor | d. applying a voltage, often done to alter electrical and optical output of a device |
| <u>I</u> 5. band gap | e. a material with a partially filled energy band |
| <u>L</u> 6. conduction band | f. a semiconductor p-n junction that is optimized to release light of about the band gap energy when electrons fall from the conduction band to the valence band under forward bias |
| <u>C</u> 7. insulator | g. containing the same number of electrons |
| <u>E</u> 8. metal | h. a homogeneous solid in which one type of atom (or ion) has been substituted for a similar atom (or ion) in a structure |
| <u>B</u> 9. valence band | i. the energy separation between the top of the valence band and the bottom of the conduction band |
| <u>K</u> 10. energy band | j. a region of the atom where electrons are most likely to be found when they have a particular energy |
| <u>J</u> 11. orbital | k. a collection of orbitals closely spaced in energy |
| <u>G</u> 12. isoelectronic | l. a band that when partially occupied by mobile electrons, permits their net movement in a particular direction |
| <u>A</u> 13. electronegativity | m. process by which atoms in a semiconductor are replaced with other atoms having more or less valence electrons, which leads to an excess of mobile electrons or holes, respectively |
| <u>D</u> 14. biasing | n. a substance conducting only a slight electrical current at room temperature |

Multiple Choice

Choose the best answer.

- C 15. An example of a solid that possesses the zinc blende structure is
- NaCl
 - CsCl
 - GaAs
 - Zn
- D 16. Energies of the electrons *within any one isolated atom* exhibit all these characteristics **EXCEPT**
- At most, only two electrons may occupy any one orbital.
 - Electrons within the same orbital must “spin” in opposite directions.
 - Electrons fill the lowest energy levels first.
 - Electrons occupy spaces in between energy levels.
- B 17. Although the alkaline earth metals have their s orbitals filled and the p orbitals empty, overlapping occurs because
- a “bridge” exists between the two types of orbitals.
 - the lowest levels of the p band are lower in energy than the upper levels of the s band.
 - the highest levels of the p band are lower in energy than the upper levels of the s band.
 - the lowest levels of the p band are higher in energy than the upper levels of the s band.
- D 18. If a material has a band gap in the ultraviolet portion of the spectrum, it will appear
- black
 - red
 - violet
 - colorless
- B 19. A semiconducting solid solution used in manufacturing an LED has the zinc blende structure and the chemical formula $\text{Al}_x\text{Ga}_{0.35}\text{As}_y\text{P}_{0.80}$, where
- $x = 0.80$ $y = 0.35$
 - $x = 0.65$ $y = 0.20$
 - $x = 1.00$ $y = 0.00$
 - $x = 0.20$ $y = 0.65$
- A 20. For electrical conductivity two conditions are necessary, namely
- the presence of charged particles and their ability to move.
 - the presence of charged particles and their stability.
 - the presence of neutral atoms and their ability to move.
 - the presence of neutral atoms and their stability.
- D 21. As the size of atoms increase in a solid, the accompanying orbital overlaps
- are increased, and the resulting energy gaps get larger.
 - are increased, and the resulting energy gaps get smaller.
 - are reduced, and the resulting energy gaps get larger.
 - are reduced, and the resulting energy gaps get smaller.

True/False

If the statement is true, write true on the line. If the statement is false, correct the underlined word and place that on the line.

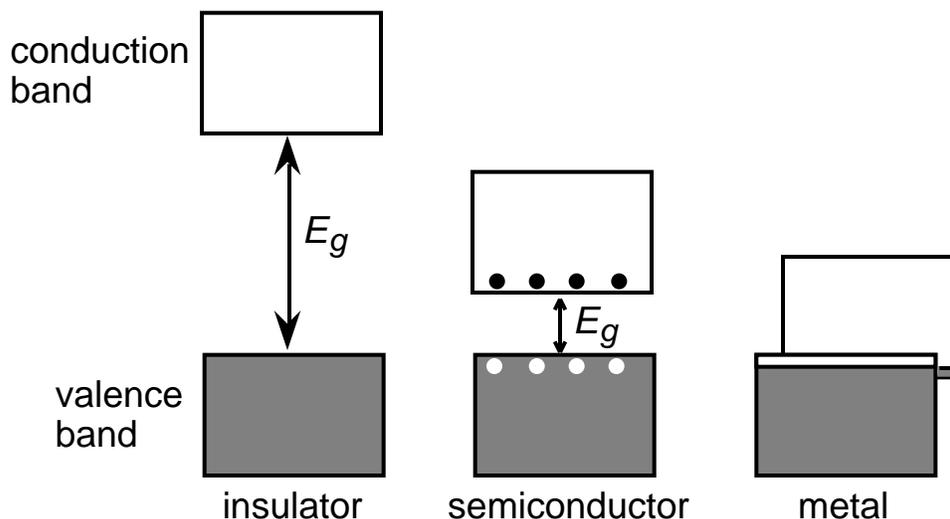
- Top 22. Only electrons near the bottom of the filled orbitals of a band contribute to electrical conductivity
- True 23. LEDs last longer, are brighter, and are more efficient than incandescent lights.
- True 24. Solids having atoms of comparable sizes and forming the zinc blende structure can be combined to form solid solutions.
- countless # of 25. Solid solutions can be formed in a few stoichiometries, which allows the “tuning” of band gap energies.
- the same # 26. Elements having the zinc blende structure contain different numbers of valence electrons.

Problems

27. Suppose you want to create a red cutoff filter (of all 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?

If red light is to be transmitted (not absorbed), then the material should have a band gap that allows it to absorb in the orange region. (This corresponds to a band gap energy of ~2.0 eV.)

28. Sketch the band-structure diagrams for an insulator, a semiconductor, and a metal.



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 energy 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.

29. 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.

InSb and CdTe are isoelectronic with α -Sn. α -Sn is metallic with a small band gap. Ionic character increases with the difference in electronegativity between atoms A and Z. As ionic character increases, so does E_g . The expected trend in band-gap energies is $\text{Sn} < \text{InSb} < \text{CdTe}$

30. Suggest a two-element (binary) compound that is isoelectronic with diamond; such a material might be expected to rival diamond in hardness.

BN is isoelectronic with diamond and is also extremely hard.

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

Phosphorus has the same number of valence electrons as arsenic, so substitution of As with P does not change the valence count. Cadmium has one less valence electron than gallium, but tin has one more electron than gallium. Substituting one half of the Ga atoms with Cd and the other half with Sn leads to the same valence count $\text{Cd}_{0.5}\text{Sn}_{0.5}\text{P} = \text{CdSnP}_2$.

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

Mg: Mg is an example of a metal. The Mg 3s band is filled but overlaps the Mg 3p band to create a partially filled band.

Si: Si is an example of a semiconductor. At relatively low temperatures few electrons would be in the conduction band, whereas at higher temperatures a greater fraction of the electrons are promoted from the valence band to the conduction band; thus, partially filled bands are created.

NaCl: NaCl is an example of an ionic insulator. Due to the large band gap energy in NaCl, this insulator contains bands that are either full or empty of electrons.

33. 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 $\text{Ga}_{0.4}\text{In}_x\text{As}_y\text{P}_{0.7}$, what are x and y equal to, and how would you interpret this formula based on the zinc blende structure?

$x = 0.6$; $y = 0.3$ the gallium and indium atoms occupy positions equivalent to zinc in the zinc blende; the arsenic and phosphorus atoms occupy positions equivalent to sulfur in zinc blende. The 1:1 stoichiometry of Zn:S dictates that the sum of the Ga and In must be equal to the sum of As and P atoms present in the solid.

LED Assessment

Name _____

Date _____ Hour _____

Matching

Match the word with the best definition.

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| _____ 3. solid solution | c. a type of material that is a poor conductor of electricity |
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