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Experiment 7

Periodic Properties and Light-Emitting Diodes

Arthur B. Ellis, Lynn Hunsberger, and George C. Lisensky

Notes for Instructors

Purpose

To relate observed properties such as the color, wavelength and energy of light, and excitation voltage for a series of compound semiconductors to composition and periodic trends.

To observe how electrical resistance of a metal changes with temperature and how electrical resistance of a semiconductor changes under illumination.

Method

A pair of circuits for light-emitting diodes (LEDs) are constructed and used to study a series of four LEDs from a family of solid-solution semiconductors that have the zinc blende structure. The light emitted by the LEDs and the voltage drop across the devices is determined; in a sense the latter is the opposite of the photoelectric effect, since here there is a threshold electrical energy needed to produce light. Both measurements are correlated with chemical composition and bonding features, including trends in internuclear distance and electronegativity differences. Liquid nitrogen is used to contract the structure, and the effect on the band gap is observed. In addition, the electrical resistance of a CdS photocell and of a copper wire are measured with a multimeter. *See* Chapters 5 and 7.

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Materials

Water-clear red LED—Mouser 592-SLH56-VT3. Label these LEDs with the formula $GaP_{0.40}As_{0.60}$

Water-clear orange LED—Mouser 592-SLH56-DT3. Label these LEDs with the formula $GaP_{0.65}As_{0.35}$

Water-clear yellow LED—Mouser 592-SLH56-YT3. Label these LEDs with the formula $GaP_{0.85}As_{0.15}$

Water-clear green LED—Mouser 592-SLH56-MT3. Label these LEDs with the formula $GaP_{1.00}As_{0.00}$

$Al_xGa_{1-x}As$ LEDs (optional, see Supplier Information)

Note: If the clear LEDs that all look identical when unlit are not marked or labeled in some manner, the LEDs are likely to become mixed up.

CdS photocells (low light resistance) —Mouser 338-76C348 or Radio Shack

150 mH RF choke (long thin copper wire in a coil)—Mouser 43LJ415

1-kΩ resistors—Mouser 29SJ250-1K

1-MΩ resistors—Mouser 29SJ250-1M

6-inch molded black battery snap—Mouser 1236005

Break-away IC sockets for LEDs—Mouser 151-5530

Soldering pencils—Mouser 381-FS030 or Radio Shack

Solder—Mouser 533-24-6040-39 or Radio Shack

Wooden spring clothespins

Diffraction gratings—Flinn holographic grating AP1714 (8 × 10-inch sheet) or Edmund card-mounted diffraction viewer C39,502

Multimeters (with alligator clips) —Mouser 585-DM-9183

LED reference strips (made in-house; see Figure 7.22)

9-V batteries

Foam cups

Liquid nitrogen

Diamond and zinc blende structural models

Answers to Warm-up Exercises

1. P has a smaller atomic radius than As. Shorter bond distances often correlate with better orbital overlap and a larger band gap. (See Chapter 7 for some qualifications to this statement.) GaP would be expected to have a larger band gap than GaAs, on this basis.

2. 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. Thus, AlAs would be expected to exhibit a larger band gap then GaAs.
3. In order of increasing band gap energy:

   $GaP_{0.40}As_{0.60} < GaP_{0.65}As_{0.35} < GaP_{0.85}As_{0.15} < GaP_{1.00}As_{0.00}$
4. In order of increasing band gap energy:

   $Al_{0.05}Ga_{0.95}As < Al_{0.15}Ga_{0.85}As; < Al_{0.25}Ga_{0.75}As < Al_{0.35}Ga_{0.65}As$
5. Bond distances will contract as the material is cooled, and the band gap energy is expected to increase, as described in answer 1.

Results

Typical results expected are shown in Figure 1 and Table 1.

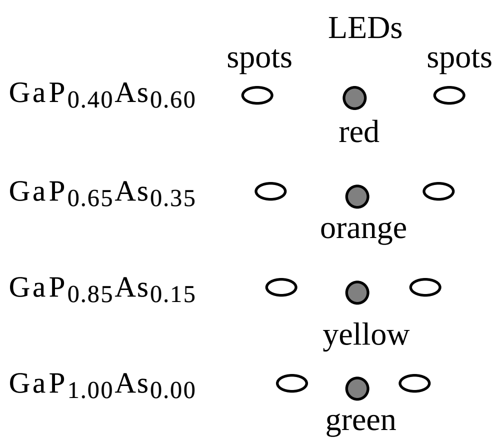


Figure 1. Color, composition, and diffraction spacing.

Table 1. LED Measurements

Composition	Color	RT λ, nm (eV)[a]	LN_2 λ, nm (eV)[b]	Volts[c]
$GaP_{0.40}As_{0.60}$	Red	637 (1.95)	621 (2.00)	1.84 (1.40)
$GaP_{0.65}As_{0.35}$	Orange	593 (2.09)	579 (2.14)	2.09 (1.51)
$GaP_{0.85}As_{0.15}$	Yellow	560 (2.21)	—	2.20 (1.58)
$GaP_{1.00}As_{0.00}$	Green	547 (2.27)	—	2.28 (1.62)
$Al_{0.35}Ga_{0.65}As$	Red	625 (1.98)	605 (2.05)	
$Al_{0.25}Ga_{0.75}As$	—	666 (1.86)	642 (1.93)	
$Al_{0.15}Ga_{0.85}As$	—	729 (1.70)	703 (1.76)	
$Al_{0.10}Ga_{0.90}As$	—	773 (1.60)	741 (1.67)	
$Al_{0.05}Ga_{0.95}As$	—	835 (1.48)	803 (1.54)	

[a]Experimental values of LED band maxima at room temperature using a spectrometer.
[b]Experimental values of LED band maxima at liquid nitrogen temperature using a spectrometer.
[c]Experimental values at liquid nitrogen temperature using a voltmeter and the 1-MΩ circuit. Values in parentheses obtained at room temperature.

Resistance

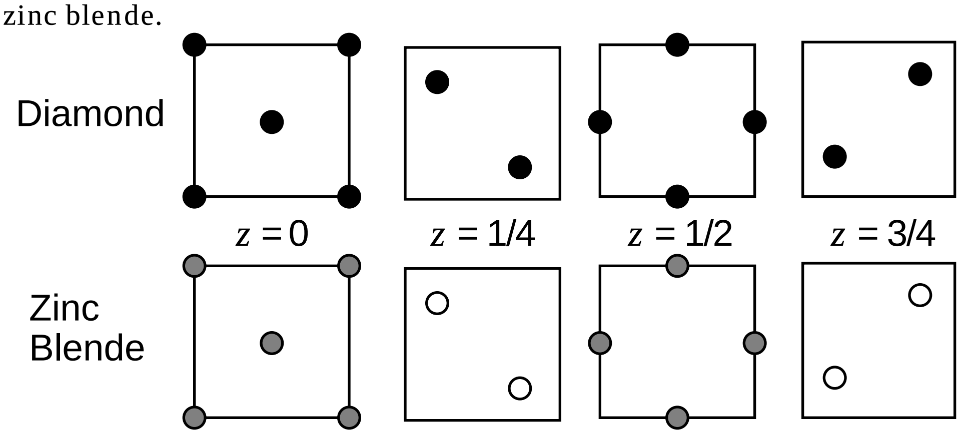
As the temperature of a metal decreases, its resistance also decreases. The small resistance to electrical current in a metal can be attributed to the vibrations of the metal atoms which scatter the mobile electrons. As the temperature is lowered, the vibrational motion of the atoms decreases, and conduction increases (i.e., resistance decreases). A resistance of 150 Ω at room temperature drops to 15 Ω at liquid nitrogen temperature.

When light of sufficient energy strikes the semiconductor, electrons are excited from their localized positions. Resistance decreases when the CdS semiconductor is exposed to visible light. Typically, a resistance of 1 kΩ in room light decreases to 15 Ω when illuminated in direct sunlight or a projector beam.

Models

How many nearest neighbors
does each carbon in the diamond structure have? 4
does the Zn in ZnS have? 4
does the S in ZnS have? 4
What is the name for the shape defined by the nearest neighbors
to each C in diamond? tetrahedral
to each Zn in ZnS? tetrahedral
to each S in ZnS? tetrahedral
How many atoms of carbon are in the diamond unit cell?
$8 \times 1/8$ = 1 corner atom
$6 \times 1/2$ = 3 face-centered atoms
4 interior atoms
8 total atoms
How many atoms of Zn are in the ZnS unit cell?
$(8 \times 1/8) + (6 \times 1/2) = 4$ atoms of zinc
How many atoms of S are in the ZnS unit cell? 4 interior atoms

Draw the *z* layer sequence showing the positions of atoms for diamond and zinc blende.



Estimate the packing efficiency for the diamond structure. Show your work. How does it compare to a closest packed structure?

$$\text{Packing Efficiency} = \frac{\text{volume occupied by atoms}}{\text{total volume of unit cell}} \times 100\%$$

Diamond built with the SSMK has eight 1-inch spheres (2.54 cm diameter) in the unit cell. The length of one side of the unit cell in the SSMK (measured with a ruler) is 5.9 cm.

$$V_{sphere} = \frac{4}{3}\pi r^3 = 1.33\pi(1.27\ \text{cm})^3 = 8.56\ \text{cm}^3\ \text{(per sphere)}$$

$$V_{sphere}(\text{total}) = 8 \times 8.56\ \text{cm}^3 = 68.5\ \text{cm}^3$$

$$V_{cell} = (\text{length of cube edge})^3 = (5.9\ \text{cm})^3 = 205.4\ \text{cm}^3$$

$$\text{Packing Efficiency} = \frac{68.5\ \text{cm}^3}{205.4\ \text{cm}^3} \times 100 = 33\%$$

A rigorous geometric calculation gives 37%. The packing efficiency for a closest packed structure is ~74%. The packing efficiency for the diamond structure is much lower than this value.

Periodic Properties and Light-Emitting Diodes

Purpose

To relate observed properties such as the color, wavelength and energy of light, and excitation voltage for a series of compound semiconductors to composition and periodic trends; to observe how electrical resistance of a metal changes with temperature and how electrical resistance of a semiconductor changes under illumination.

Introduction

The terms insulator, semiconductor, and metal are used to classify solids based on the amount of energy, called the *band gap energy*, needed to excite electrons from localized bonds to a higher energy state where the electrons are free to move about the solid. In metals the very small amount of energy required (very small band gap) leads to a large number of delocalized electrons and the high electrical and thermal conductivity of metals. Insulators require a relatively large amount of energy (large band gap) to produce mobile electrons. Semiconductors are the intermediate case corresponding to a moderate band gap.

The energy needed to remove an electron from a localized bond in the solid can be supplied by adding energy in the form of heat, electricity, or light. When an excited electron returns to the localized bond, the energy is released, sometimes in the form of light.

Periodic Trends

The distance between the nuclei (the sum of the atomic radii of the bonded atoms) is one factor that determines the strength with which an electron is held in a localized bond. In the solid elements C, Si, Ge, and α-Sn that exhibit the diamond structure, Figure 1, the atomic radii increase and the band gaps decrease rapidly going down their column of the periodic table. Diamond is an electrical insulator, Si and Ge are semiconductors, and α-Sn is a metal.

NOTE: This experiment was written by Arthur B. Ellis and Lynn Hunsberger, Department of Chemistry, University of Wisconsin—Madison, Madison, WI 53706; and George C. Lisensky, Department of Chemistry, Beloit College, Beloit, WI 53511.

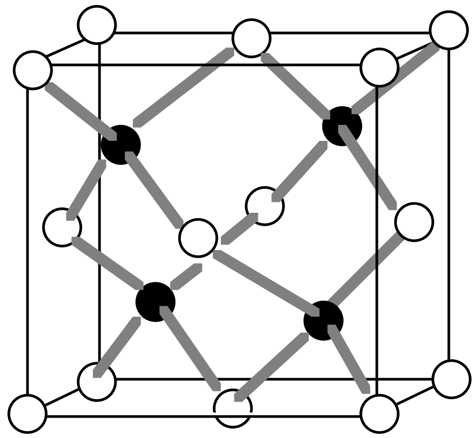


Figure 1. Drawing of a unit cell where all of the atoms are bonded to four other atoms. When all of the atoms are the same element, this is the diamond crystal structure. When the lighter colored spheres are different elements than the darker colored spheres, this structure has AZ stoichiometry and is called zinc blende.

One can imagine making a solid with the same total number of electrons as C, Si, Ge, or Sn using AZ stoichiometry. For example, if two carbon atoms are replaced with one boron atom and one nitrogen atom, the total number of valence electrons in the solid is conserved. Other combinations are indicated in Figure 2. These compounds have the zinc blende structure (Figure 1).

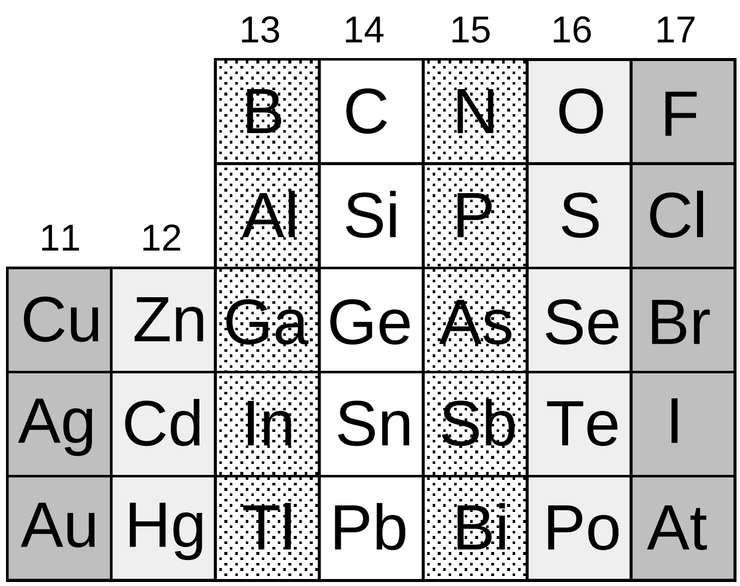


Figure 2. A portion of the periodic table emphasizing the formation of AZ solids that are isoelectronic with the Group 14 solids. Isoelectronic pairs are indicated with similar shading; for example Ge, GaAs, ZnSe, and CuBr.

The strength by which an electron is held in a localized bond also depends on the difference in electronegativity between the atoms. Ge, GaAs, ZnSe, and CuBr all have essentially the same size unit cell, but the increasing difference in electronegativity adds an ionic bonding contribution and the band gap increases for this series.

The ability to form solid solutions provides a chemical means for tuning band-gap energies that would be lacking were we restricted to the AZ stoichiometries obtainable with the elements in the periodic table. The GaP_xAs_{1-x} ($0 \le x \le 1$) solid solutions will be used in this experiment, since $GaP_{0.40}As_{0.60}$, $GaP_{0.65}As_{0.35}$, $GaP_{0.85}As_{0.15}$, and $GaP_{1.00}As_{0.00}$ are sold commercially with wires attached as LEDs (Light Emitting Diodes).

Warm-up Exercises

1. Does P or As have a larger atomic radius? Considering only atomic radii, would GaP or GaAs have a larger band gap energy? Explain.
2. Is Ga or Al more electronegative? Considering only the electronegativity difference, would GaAs or AlAs have a larger band gap energy? Explain.
3. Considering only atomic radii, rank the following in order of increasing band gap energy:

   $GaP_{0.40}As_{0.60}$, $GaP_{0.65}As_{0.35}$, $GaP_{0.85}As_{0.15}$, $GaP_{1.00}As_{0.00}$
4. Considering only the electronegativity, rank the following in order of increasing band gap energy:

   $Al_{0.35}Ga_{0.65}As$, $Al_{0.25}Ga_{0.75}As$; $Al_{0.15}Ga_{0.85}As$; $Al_{0.05}Ga_{0.95}As$
5. 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.

Procedure

Wear eye protection. Work in pairs.

One member of the team should build the single socket circuit shown in Figure 3. The second member of the team should build the identical circuit in which a 1-MΩ resistor is used instead of the 1-kΩ resistor. Solder one end of the battery snap to the resistor and the other to one lead of the socket. Complete the socket circuit by soldering the remaining end of the resistor to the remaining lead of the socket. Soldering is usually easier if you melt some solder onto each end individually before trying to join them together. A wooden spring clothespin is a convenient way to hold the socket while soldering.

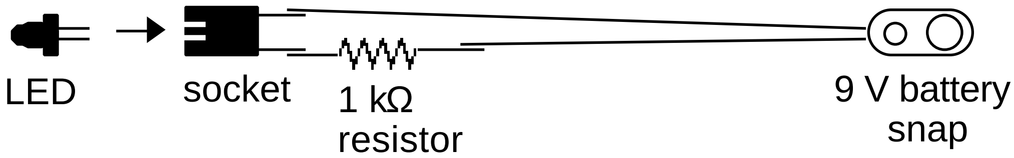


Figure 3. The circuit for the LED socket.

Color and Composition

Obtain samples of the four different GaP_xAs_{1-x} compositions. The LEDs all look identical so do not mix them up.

Using the circuit containing the 1-kΩ resistor, connect the battery snap to a 9-V battery. The circuit is "turned on" by inserting the LED into the socket. Does it matter which way the LED is inserted?

Plug each kind of LED into the socket of the circuit containing the 1-kΩ resistor. For each composition of LED, record the color of light emitted.

Wavelength and Composition

Obtain a reference strip of LEDs. View this strip through a diffraction grating oriented so that the light from the LEDs is diffracted away from the reference strip (Figure 4). For each LED, the central spot due to the undiffracted source will be the brightest. Compare the spacing length between the first diffraction spots to either side of the central spot.

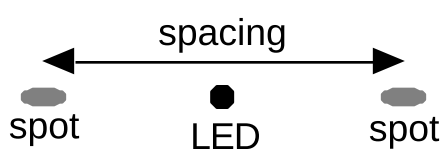


Figure 4. An LED viewed through a diffraction grating.

List the LED compositions in order of increasing diffraction spacing. The light separation by the diffraction grating is proportional to the wavelength of light, so a list of increasing spacing lengths is also a list of increasing wavelengths.

Band-Gap Energy and Composition

When a voltage is applied across the LED, nothing will happen unless the energy (voltage is proportional to energy) is sufficient to excite an electron from its localized bond. When the energy is increased beyond the band-gap energy, current can begin to flow. Measurement of the voltage for a minimum current flow thus provides another estimate of the band-gap energy.

To approximate the conditions of minimum current flow, use the circuit you built with the 1-MΩ resistor.

How much energy is required to excite an electron from its localized bond? Is the minimum voltage required for emission of light by an LED dependent on the wavelength of light emitted? To answer these questions, measure the voltage across the LED. (If the voltage is more than 3 volts, then current is not flowing through the LED and its electrical leads should be reversed.) Thermal excitation of localized bond electrons also contributes to the current; while the data obtained will not represent the actual band gap energies, the data will show the correct trend.

List the LED compositions in order of increasing voltage. Voltage is proportional to energy, so a list of increasing voltages is also a list of increasing band gap energies.

Composition, Color, Wavelength, and Energy Comparisons

You should have three lists based on the LED compositions: predicted relative band gap energies (Warm-up Exercises), observed relative diffraction spacings (wavelengths), and observed relative voltages (band gap energies). Do these lists agree?

Use the information in Table 1 to make a fourth list of composition based on the observed colors. Are your observations consistent?

Summarize your results.

Table 1. Relationship between Color, Wavelength, and Energy of Light.

Color of Light	Approximate Wavelength (nm)	Energy eV (kJ/mol)
Ultraviolet	<400	>3.1 (300)
Violet	410	3.0 (290)
Violet–blue	430	2.9 (280)
Blue	480	2.6 (250)
Blue–green	500	2.5 (240)
Green	530	2.3 (225)
Green–yellow	560	2.2 (215)
Yellow	580	2.1 (205)
Orange	610	2.0 (195)
Red	680	1.8 (175)
Purple–red	720	1.7 (165)
Infrared	>720	<1.7 (165)

Temperature and the Band Gap

For this part, you will need to work with an additional group. Both groups should insert their $GaP_{0.40}As_{0.60}$ LED into their 1-kΩ circuit. Practice holding both LEDs in a single column and viewing through the diffraction grating. LEDs of the same composition should give the same spacing. Check with your instructor if the spacing is not the same.

Dip only one lighted LED into a foam cup of liquid nitrogen for a few seconds. Does the *color* change? **CAUTION: Liquid nitrogen is extremely cold. Do not allow it to come into contact with skin or clothing, as severe frostbite may result.**

View through the diffraction grating the cold LED and, as a reference, a second room temperature LED of the same composition. Did the wavelength of the cold LED shift? Did the wavelength get longer or shorter?

Let your LED warm back to room temperature. Are any observed changes reversible?

Repeat this experiment using a pair of $GaP_{0.65}As_{0.35}$ LEDs. Do you observe the same changes?

Do your observations agree with your predictions in the Warm-up Exercises?

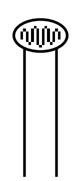
CAUTION: Do not dip the reference strip in liquid nitrogen. The circuit board used to hold the LEDs aligned in position will crack. The $GaP_{0.85}As_{0.15}$, and $GaP_{1.00}As_{0.00}$ LEDs have multiple peaks due to a very small amount of added impurity atoms used to enhance the light intensity, and these multiple peaks shift in wavelength and relative intensity with temperature; interpretation is not as simple.

Electrical Resistance in Metals and Semiconductors

Resistance measures the difficulty with which an electron moves through a material.

Use a digital voltmeter on the resistance setting (ohms or Ω) to record the resistance of a very long (about 150 m) length of thin copper wire wound in a coil, sealed in plastic and sold as an inductor or choke coil. The small resistance to electrical current (flow of electrons) in metals is due to vibrations of the atoms that interfere with the flow of electrons.

Dip the copper coil in liquid nitrogen. Does the resistance change? Why?



Use a digital voltmeter on the resistance setting (ohms or Ω) to record the resistance of a short length (about 6 cm) of CdS semiconductor. Such samples are sold commercially with wires attached as photocells. Does the resistance change with light exposure? Why?

Caution: *Do not dip the photocell in liquid nitrogen; the plastic casing will crack.*

Semiconductor Models

Obtain or build a model of the diamond and zinc blende structures.

1. How many nearest neighbors does each atom have?
2. How are the nearest neighbors arranged about the central atom? (What is the name for the shape they assume?) For ZnS, do this determination for the Zn atoms and the S atoms separately.
3. How many atoms of each type are in the unit cell? *(Hint: Remember some atoms are not entirely within the unit cell.)*
4. Draw the *z* layer sequences showing the positions of the atoms. Hint– In both structures there are atoms in the plane that forms the bottom of the unit cell cube, in planes with $z = 1/4$, $1/2$, and $3/4$ of the way up the unit cell, as well as on the top of the unit cell cube. Draw the atoms as they intersect each of these five planes.
5. For the diamond structure, estimate the packing efficiency by making the appropriate measurements on the model and recalling that the spheres have diameters of 1 inch and $V_{\text{sphere}} = \frac{4}{3}\pi r^3$.

   How does the packing efficiency compare to that of a close-packed structure?