EXPERIMENT #7
Thermal Band-Gap

GOALS

Physics
• Measure the resistance of a semiconductor as a function of temperature and determine the band-gap energy.

Technique
• Use a four-terminal connection for sensitive resistance measurements.

Error
• Repeat the heating/cooling cycle to determine if thermal equilibrium conditions are being met.

Important Constants

\[
K = 8.6 \times 10^{-5} \text{ eV/K} = 1.38 \times 10^{-23} \text{ J/K}
\]

References
• Serway, Moses, Moyer, Modern Physics, 2nd Edition
  ISBN # 0-03-004844-3, pages 283-284, 339-341
• Giancoli, Physics for Scientists and Engineers, 2nd Edition
  ISBN # 0-13-666322-2, pages 958-960

BACKGROUND AND THEORY

Surprisingly, both positive and negative charges can move and carry current in a solid. The model described below constitutes our present understanding of this field. When it is analyzed in detail, it predicts with remarkable accuracy the physical properties which are observed experimentally.

First, we must consider the basic structure of a solid, i.e., the regular spatial arrangement of its constituent atoms. That the atoms do indeed form a periodic array is well verified by the observation of diffraction patterns (similar to those of Experiment 6) which are produced when radiation or particles with wavelength comparable to the distance between the atoms is passed through the solid.

We suppose in our model that the outermost atomic electrons are free to move, even though we know that in the isolated atoms these electrons are tightly bound to the atom. We can imagine these outermost valence electrons as forming a "sea" of negative charges within the
material The neutral atoms are ionized when they lose their valence electrons to this sea, and it is these positively charged ions which make up the regular array or "lattice" observed by the X-ray diffraction experiments.

In order to solve for the motion of the electrons of this sea, the problem can be divided into two parts. The first considers the interaction forces between the electrons and the lattice of ions; the second considers the interactions of the electrons with each other. Only the first part will be discussed below, and it will be found that many accurate predictions concerning the behavior of electrons in solids can be made without ever considering the much more difficult second part.

The interaction between electrons and ions is described by a potential energy which is a minimum at each ion, where the attractive force is greatest, and is therefore periodic in space. In the microscopic domain of electrons and atoms we know that the principles of quantum mechanics must be applied in order to correctly describe the behavior of particles.

Two features of quantum physics are of particular importance in this problem. One is that the electrons can not assume arbitrary values of energy and momentum. Depending on the boundaries of and forces inside the solid, a set of discrete energy or momentum values is found, and these are the only values of energy or momentum which the electron can assume. The other feature is the startling condition that only one electron can be in a given state at a given time, i.e., only one electron in the solid can have a given momentum. (Actually, to specify the "state" of an electron more than just the momentum must be known, and it turns out that two electrons - but no more than two - can have the same momentum.)

With these two features in mind, the solution for the electron in a periodic potential can be discussed. In particular, we would like to know what are the allowed values of energy and momentum in a specimen of material. The result of a quantum mechanics calculation is shown in Fig. 1a. The energy of a state increases with increasing momentum of the state, but there are surprising “gaps” where no state has a particular energy.
In contrast, Fig. 1b shows the allowed energy levels for the same specimen which would be obtained if the ions were smeared out into a uniform background of positive charge rather than a periodic array of charges. The energy $E$ of a state is related to the allowed momentum $p$ of the state by the equation

$$E = \text{constant} + \frac{p^2}{2m}.$$ 

This happens to be the same as the familiar classical relation between energy and momentum for particles in a uniform potential. Note that the plot in Fig. 1a for electrons subject to a periodic potential is similar to Fig. 1b when not too close to the energy gaps. The appearance of wide gaps in the spectrum of allowed energy states is due solely to interaction of the electrons with the periodic potential of the ions.

In reality allowed energy states are discrete, due to the finite size of the material; however, the states are so close together that they appear to form a continuous curve - except for the gaps. The allowed states are seen to cluster into "bands", separated from each other by gaps in which there are no allowed energy levels. The fact that there are such gaps in the energy spectrum is a surprising but very important result.

If there is no energy source present to excite the electrons out of their lowest possible energy states, then each state starting from zero energy will be occupied by one electron until all of the electrons are accounted for. If, at this point, a band of states is fully occupied with no
electrons left over, then no current can flow. To understand this, consider the following. Any attempt to accelerate electrons to new states by applying a voltage across the sample can only interchange electrons between states of the filled band, unless enough energy can be provided to excite the electrons across the gap into the next higher (empty) band. However, the energy gap is usually so large compared to the energy acquired by the electrons for ordinary applied voltages that virtually no electrons can overcome the energy gap, and thus no electrons are available to participate in a flow of current. The total electron momentum of the filled band is zero to begin with and, since no net change of momentum can result from a mere interchange of electrons, it must remain zero.

The above is a description of the behavior of an insulator. Thus unexpectedly the model for "free" electrons offers an explanation of an electrical property of insulators. If, on the other hand, the number of electrons is such that one of the bands is only partly filled, then small voltages can easily accelerate electrons to adjacent energy states within the same band, and metallic conductivity will follow.

We now consider the intermediate case between an insulator and a metallic conductor, namely a semiconductor. Normally we deal with materials at finite temperatures in which case the electrons will not remain in their lowest energy states. This is analogous to the more familiar case of the molecules of a gas in which the average velocity of the molecules, and thus also their energy, increases as the temperature increases.

For the electrons in a metal at finite temperatures, it is not true that all states are filled up to a maximum energy beyond which all states are empty. Instead there is a region around this "maximum" energy (referred to as the Fermi energy) in which some levels are occupied and others unoccupied. The size of this region increases and therefore the average energy gets larger as the temperature is raised.

In the case of the completely filled band (insulators) considered earlier, the possibility exists that the gap is small enough so that at finite temperature some electrons will have energy above the gap and a corresponding number of unoccupied states will be left in the otherwise filled band. Thus a small number of charges can be moved with the application of a potential and we have described a semiconductor. We see that a semiconductor is an insulator at absolute zero, but the gap between the last filled band and the first empty one is small enough that an appreciable number of electrons are thermally excited over the gap at room temperature.

Further, the model shows how positive charge carriers can appear. As described above, a band with every state occupied can carry no current. However, if only one state with finite momentum is unoccupied, then there will be one less electron moving in the direction of that momentum state than in the opposite direction, and a net current will flow. The application of a potential will result in the acceleration of all electrons and of the unoccupied state or "hole" as well. The motion of all of the electrons is most simply described in terms of the motion of the hole. The hole, being an absence of negative charge, appears to be a positive charge. A more detailed analysis confirms this model in every way, and so even though only
the negative electrons are free to move, it appears that the charge carriers have a positive sign.

Rather than attempt an understanding of these details it is more valuable for the purposes of this course to verify experimentally the basic idea of the energy gap. It is known from both theory and experiment that the number of electrons which will have an energy greater than $E$ above their lowest possible energy state will be, on the average, proportional to $e^{-E/kT}$, where $k$ is Boltzmann's constant and $T$ the absolute temperature. In the case of a pure semiconductor, a detailed calculation based on the hypothesis of an energy gap of width $E_g$ gives the result that the number of electrons per unit volume $n$ excited above the gap is

$$n \propto e^{-E_g/2kT}.$$  

The extra factor $1/2$ in the exponent is a purely quantum effect which has been included for completeness; the essence of the result lies in the exponential dependence of the excited electron density $n$ on $1/T$ which characterizes a system with an energy barrier or gap. The proportionality factor also depends on $T$, but its variation is very much slower than the exponential function.

Thus, any property of the semiconductor which depends on the number of electrons on top of the gap should exhibit an exponential dependence on temperature. Observations of such a temperature dependence would not only confirm the existence of the gap but would determine its value as well.

The electrical conductivity is just such a property. Intuitively one would expect that the number of electrons (and holes) which are involved in the conduction process will be an important factor in determining the current which will flow when a voltage is applied. Quantitatively, the number of charge carriers (electrons or holes) per unit time which cross unit area perpendicular to their average velocity $\bar{v}$ is $n\bar{v}$. The current $I$ is just the charge times this flow, so the current which flows for a given voltage is proportional to $n$. Since $I = V/R$, the resistance $R$ is inversely proportional to the density of electrons.

$$R \propto e^{E_g/2kT}.$$  

You will be measuring the resistance of your sample (at various temperatures) by pushing a calibrated current $I$ through the sample, and measuring the voltage $V$ which results. By Ohm's law, $V = IR$, giving a resistance $R = V/I$. 

Obviously, the larger the current I, the larger your signal V. However, there is a limitation on I due to the I²R heating within the sample itself. This heating can lead to erroneous results, and if excessive, may even destroy the sample. We expect the resistance to decrease when the sample is heated, and thus by measuring the resistance at some fixed ambient temperature for several sample currents, you can find the maximum current which causes no noticeable heating.

THIS EXPERIMENT

PURPOSE
Demonstrate the existence and determine the size of the energy gap in a semiconductor by measuring its resistance as a function of temperature.

EQUIPMENT
• Digital millivoltmeter;
• Power supply with meter (0-200ma, 0-30V);
• Resistance decade box;
• Sample of InSb (indium antimonide, a semi-conductor) mounted in a protective holder;
• Thermistor;
• Thermoelectric cooler/heater, with power supply;
• Semilog graph paper.

EXPERIMENTAL SETUP
Instead of ice and a hairdryer to cool and heat the sample, we use a neat semiconductor device called a Peltier Effect cooler/heater. If you are intrigued by how this works, read the following paragraphs.

THE PELTIER EFFECT
The Peltier Effect refers to the reversible heating or cooling of the junction between two dissimilar materials when a current is passed through the junction. The direction
of the current determines whether heating or cooling takes place. Thus, if we have a circuit composed of materials A and B

![Figure 3](image)

junction 1 may be cooled and junction 2 heated, depending on the materials A and B and the current direction. The thermoelectric cooler/heater is simply a series of junctions of one type connected to a metal plate, i.e.

![Figure 4](image)

Thus, with the current in one direction, the plate is cooled, and the plate is heated with the current in the other direction. Since heat is generated in the set of junctions that are not cooled, this heat must be carried away when the current direction is such as to cool the plate. The fan at the finned heat radiator at the bottom of the thermoelectric cooler helps to accomplish this. The materials A and B in the thermoelectric cooler are impurity semiconductors of different types. One is the so-called n-type in which the current is carried by electrons in the conduction band; the other is the p-type, in which the current is carried by the positive "holes" in the filled band.

The thermistor, which is used to measure temperature, is also a semiconductor. It turns out that by choosing the proper semiconductor material, one can use the temperature
dependence of the resistivity as a calibrated thermometer. Thus one simply measures the resistance of the thermistor element and finds the equivalent temperature from the calibration chart supplied with the element.

The resistance measurements are greatly simplified if they can all be made at a constant value of the sample current, for then the resistance is obtained by dividing all measured voltage values by the same current value. In fact, since at constant current the voltage is proportional to the resistance, which in turn is proportional to $\frac{E_g}{e^{\frac{E_g}{kT}}}$, it is not even necessary to calculate the resistance: the magnitude of the energy gap can be found by studying only the voltage produced across the sample at constant current.

The power supply provided in the lab is designed to give either a constant voltage or constant current output: you would do well to use the constant current mode.

The semiconductor sample whose resistance you will measure is mounted on a copper plate imbedded in a plastic disk. The current and voltage leads to the semiconductor are arranged as shown in Fig. 2 and are connected to banana plug sockets in the plastic disk. The plastic disk also has connecting sockets for the thermistor leads. Temperature is determined by measuring the resistance of the thermistor and using the resistance versus temperature chart supplied. The copper plate on which the semiconductor is mounted is thermally connected to the cooling surface of the thermoelectric cooler with a thermally conducting paste. There is a regulated power supply to apply current to the thermoelectric cooler.
CAUTION
• To prevent excessive currents, put 100Ω in series with the power-supply lead to pin 1.
• Do not heat the thermistor more than 50°C
• And...

! VERY IMPORTANT !

Do not apply more than 1.8 amperes to the thermoelectric cooler.
Higher currents will burn out the elements.

PROCEDURE
1. Taking data points from the provided table of Resistance vs. Temperature for the Sensor Thermistor, calculate its bandgap energy.

2. Now, to calculate the bandgap energy of the sample, you will first want to determine which current directions cause cooling and heating, respectively. Apply a small current (~0.1 amperes) to find out. The temperature range that you can safely cover with the thermoelectric cooler/heater is about -15°C to +50°C. Remember not to exceed 1.8 amperes in any case.
3. The sample will heat much more rapidly than it cools. You will be measuring the temperature (by measuring the resistance of the thermistor) as the temperature changes. Simultaneously, you will be measuring the resistance of the sample. Therefore, you don't want the temperature to change too rapidly to take down the data. There is another reason for not changing temperature too rapidly. It is important that the temperature at the thermistor is the same as the sample temperature. They should be in thermal equilibrium. Too rapid temperature changes will prevent the necessary thermal equilibrium.

4. A good way to tell if you have thermal equilibrium is to compare data obtained while heating and cooling. Since cooling is fairly slow, you can start the cooling run with a current of \( \sim 0.7 \) amperes. To warm the sample, you can reduce the current until you each zero current. At that point reverse the current leads so that the thermoelectric element heats the sample.

5. Take at least 5 good data points. They must be well spaced, and taken when in thermal equilibrium.

6. Be very careful while heating not to step up the current too rapidly and be sure not to exceed \( +50^\circ \)C. Look up the resistance of the thermistor before you start heating so that you don't exceed that temperature. Your heating current steps should only be a few tenths of an ampere. You won't need 1.8 amperes to get to 50°C.

7. By reducing the current, you can now cool back to room temperature. Repeat the heating/cooling cycle several times to determine reproducibility and whether you have achieved thermal equilibrium.

8. The simplest way to analyze your data is by means of a graph. If the energy gap model is correct, we expect the resistance (or the voltage, if data are taken at constant current) to depend on the absolute temperature \( T \) according to \( R = R_\infty e^{\frac{E_g}{kT}} \).

9. Graph the data on semilog paper, or on the computer software as \( \ln R \) vs \( T^{-1} \). It is usual to express \( E_g \) in units of electron volts, so be sure you know how to do this with your result. Remember in analyzing your data that \( 0^\circ \)C = 273.2°C, and that all temperatures must be expressed on the absolute scale.

10. Measure the resistance of the indium antimonide sample as a function of temperature from about \(-15^\circ \)C to \(+50^\circ \)C. Check and comment in your report on the thermal equilibrium between the sample and the thermometer. From your data find the energy gap of the InSb sample and give your answer in electron volts. Include some measure of the experimental uncertainty. How well do your data fit the theory?

11. Use the calibration chart data for the thermistor to determine whether the thermistor behaves like a semiconductor. (Hint: Try graphing the data). Does it have an energy
TROUBLESHOOTING

- Take temperatures in Kelvin.
- Use the natural log, not base10, in your graphs.
- Take data while both cooling and heating the sample, to illuminate possible systematic error.

Properties of Semiconductor Materials

Bandgap Energy
<table>
<thead>
<tr>
<th>Material</th>
<th>Eg (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.11</td>
</tr>
<tr>
<td>Ge</td>
<td>0.67</td>
</tr>
<tr>
<td>SiC(a)</td>
<td>2.86</td>
</tr>
<tr>
<td>AlP</td>
<td>2.45</td>
</tr>
<tr>
<td>AlAs</td>
<td>2.16</td>
</tr>
<tr>
<td>AlSb</td>
<td>1.6</td>
</tr>
<tr>
<td>GaP</td>
<td>2.26</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.43</td>
</tr>
<tr>
<td>GaSb</td>
<td>0.7</td>
</tr>
<tr>
<td>InP</td>
<td>1.28</td>
</tr>
<tr>
<td>InSb</td>
<td>0.18</td>
</tr>
<tr>
<td>InAs</td>
<td>0.36</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.6</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.7</td>
</tr>
<tr>
<td>ZnTe</td>
<td>2.25</td>
</tr>
<tr>
<td>CdS</td>
<td>2.42</td>
</tr>
<tr>
<td>CdSe</td>
<td>1.73</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.58</td>
</tr>
<tr>
<td>PbS</td>
<td>0.37</td>
</tr>
<tr>
<td>PbSe</td>
<td>0.27</td>
</tr>
<tr>
<td>PbTe</td>
<td>0.29</td>
</tr>
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</table>