

Name:

Class:

LUMINESCENCE  
It's Cool Light!

Visual Quantum Mechanics

## ACTIVITY 10

# Constructing Models to Explain Photoluminescence

### *Goal*

We have learned how impurities affect the allowed energies for a solid and have applied this knowledge to understand how a fluorescent lamp operates. We will now apply the energy diagram model to explain the properties of photoluminescent materials like the fluorescent and phosphorescent materials and devices previously explored.

Recall that photoluminescent objects glow when light is shined upon them. A photoluminescent object may emit light due to the process of phosphorescence or fluorescence. See Figure 10-1.

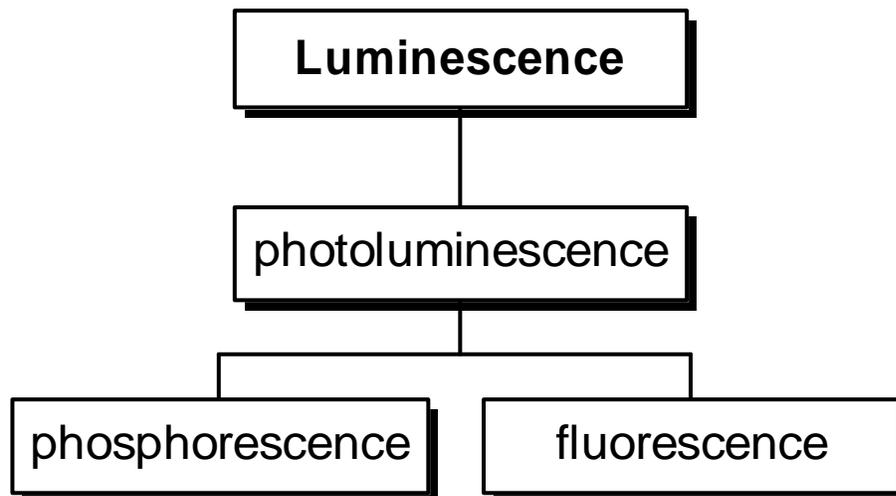


Figure 10-1: Photoluminescence

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Photoluminescent materials such as the phosphor coating found on fluorescent tubes, fluorescent minerals, and phosphorescent toothbrushes contain many solid atoms. As a result, these materials have valence and conduction energy bands that are separated by an energy gap. As we have seen, photoluminescent solids also contain many impurity atoms which result in the formation of a band of energy levels found inside the energy gap of the solid material.

As a brief review, Figure 10-2 represents an energy band diagram for the phosphor coating found in a typical "white" fluorescent lamp that emits visible light (1.6 - 3.1 eV).

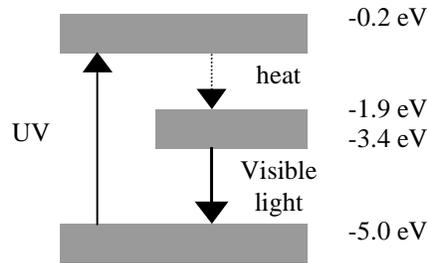


Figure 10-2: Sample Energy Band Diagram for a "White" Fluorescent Lamp

Some fluorescent minerals only emit a small part of the visible spectrum. Using Figure 10-2 as template, sketch in the space provided below an energy band diagram for a fluorescent mineral that only emits red light (1.6 - 2.0 eV) as it is exposed to UV light (3.5 eV) provided by a black light. Explain your reasoning.

In the exploration during the first activities, we found that phosphorescent materials (i.e. glow-in-the-dark paint on watches), unlike fluorescent minerals, require visible light (1.6 - 3.1 eV) to emit their characteristic faint, greenish-yellow glow (2.3 eV) after the light source is turned "off".

Based on the investigations performed on glow-in-the-dark objects and our knowledge of energy band diagrams for the fluorescent lamp and materials, create in small groups a possible energy band diagram for the phosphorescent hands of the watch. In the space provided below, sketch your prediction of the resulting energy band diagram for the glow-in-the-dark watch. Then sketch the electron transitions on your model.

You will now check your predictions by using the *Phosphorescence Spectroscopy* computer program to construct a model that will explain the properties of glow-in-the-dark objects.

Phosphorescent objects, like fluorescent materials, consists of many solid atoms with a number of impurities. As a result, energy diagrams of phosphorescent materials have an impurity state energy band located somewhere between the conduction and valence energy bands.

Open the *Spectroscopy Lab Suite* and select Phosphorescence from the *Luminescence* category of the main menu. A figure of a glow-in-the-dark toothbrush will appear on the left part of the screen and an energy scale will appear on the right part of the screen.

The energy scale contains a black set of horizontal lines located at -5 eV. These lines represent the valence (ground state) band of the phosphorescent material in the toothbrush.

Click on the Create Excited State Band button. A set of gray horizontal lines representing the excited state band (conduction band) appears next to the energy scale.

Create an impurity state band. A set of gray horizontal lines representing this energy band should appear inside the energy gap of the toothbrush. The energy band diagram is illustrated in Figure 10-3.

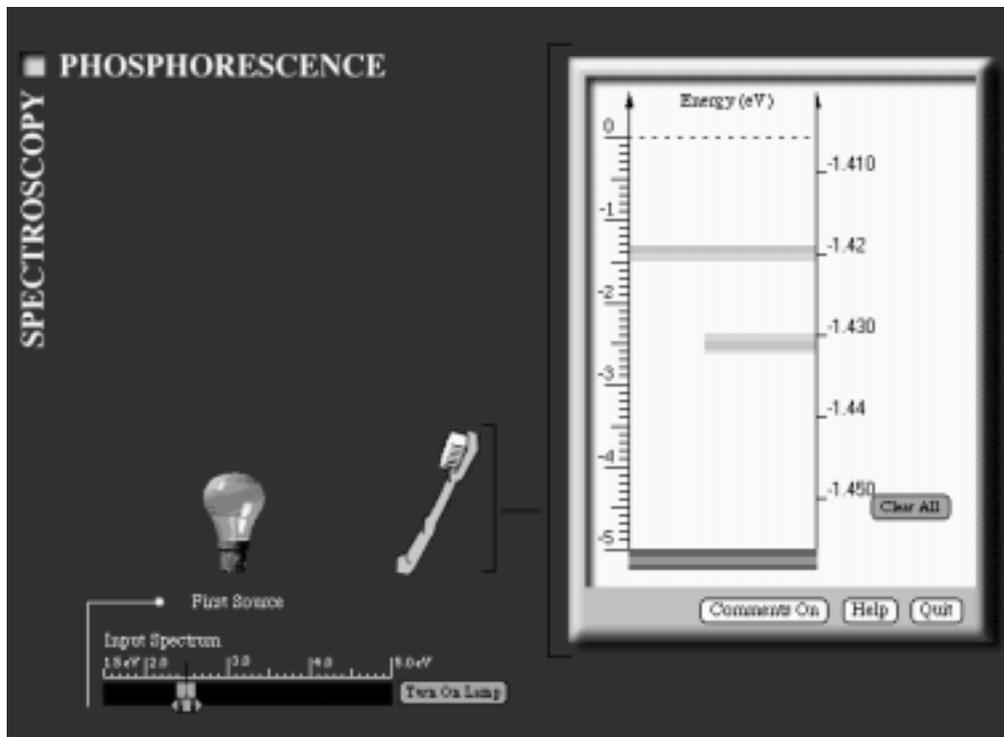


Figure 10-3: Initial Energy Band Diagram Crop of the Glow-in-the-Dark Toothbrush

The computer screen is somewhat small for representing the energies involved here. The impurity band energy is very close to the energy of the conduction band. As Figure 10-4 shows, the difference between the energies of these two bands is about 0.01 eV.

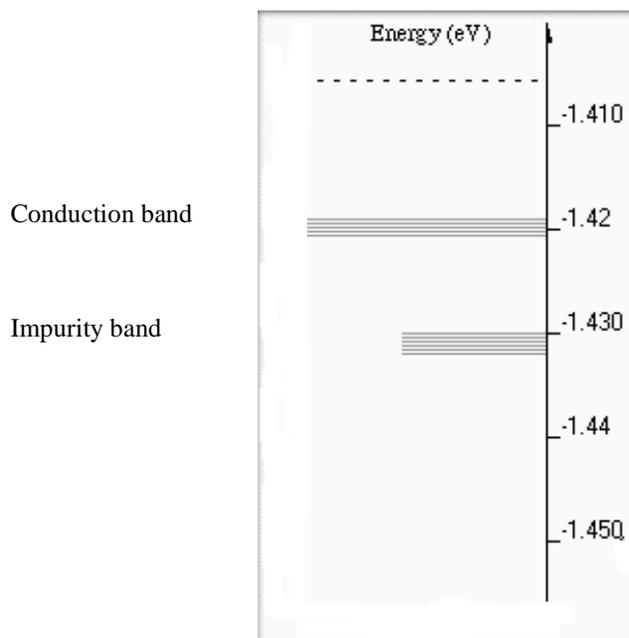


Figure 10-4: A display of the energies of the conduction band and the impurity band.

The difference between the energy of the conduction band and the valence band is much greater than that energy difference between impurity and conduction band. Figure 10-5 shows that the energy difference between the conduction and valence bands is about 3.5 eV.

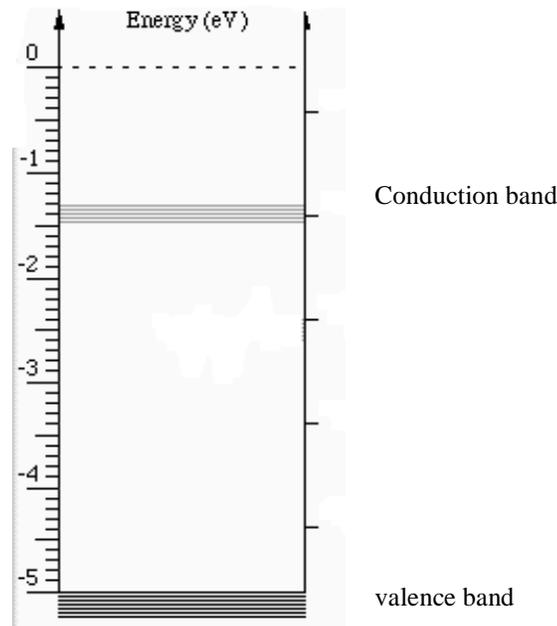


Figure 10-5: A display of the energies of the conduction and valence bands.

We run into difficulty when we attempt to display all three energies on one computer screen. If we use an energy that separates the conduction and impurity band energies, the valence band energy would be off the bottom of the screen — near your feet. On the other hand, if we display the energies of the conduction and valence band energies, the impurity band energy is so close to the conduction band energy that we cannot distinguish them.

To see all three energies conveniently we need a compromise. Our solution is to display two energy scales. The one on the right shows the correct energies for the conduction and impurity bands while the one on the left displays valence and conduction band energies. (Figure 10-6) To help you remember the bands touch only the energy scale relevant to them.

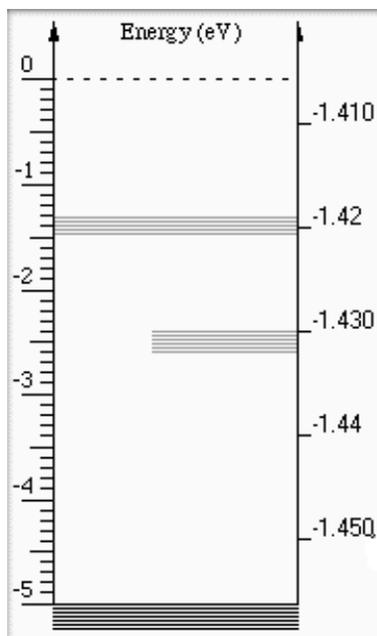


Figure 10-6: The compromise so that we can see conveniently the energies of all three energy bands.

Once the three bands are created, a lamp with variable spectrum appears on the bottom left of the screen. The input spectrum represents the energy of light absorbed by the toothbrush.

Change this energy by dragging the cursor located below the input spectrum energy scale. As you drag the cursor, a gold arrow moves up and down the energy scale of the energy diagram.

Turn on the lamp for several different energies of its spectrum.

? What energies cause transitions from the valence band to conduction band?

If you can, explain your conclusion. If you cannot, discuss your result with your instructor.

Notice that after a transition occurs, the valence band turns gray and the conduction band turns black. This change illustrates that electrons now have energies in the conduction band.

If possible, electrons will naturally lose energy. The excited electrons in the glow-in-the-dark toothbrush, however, do not necessarily lose all their energy at once. Instead these electrons lose enough energy to nearby atoms to make the transition from the conduction band to the impurity band.

A dashed downward arrow represents this transition. After this transition occurs, the conduction band turns gray and the impurity band turns black. This change indicates that electrons have lost some energy and now have energies associated with the impurity band. The change in energy is small and is generally thermal energy.

In fluorescent materials electrons have energies in the impurity state band for a very short time ( $10^{-9}$  to  $10^{-6}$  seconds). Then, they emit light as their energy changes to energy in the valence band. As a result, fluorescent materials will only glow while light of sufficient energy shine on them. In phosphorescent objects like the glow-in-the-dark toothbrush, the electrons remain in the impurity band. After this time delay the electrons emit light as their energy changes. Thus, phosphorescent materials emit light using energy that was absorbed at an earlier time. When all energy is converted to light, the object stops glowing in the dark.

Some older watch dials glow-in-the-dark indefinitely, not because of a long time delay associated with common phosphorescent objects, but because they contain radium or some other radioactive substance which continuously supplies energy to keep the process going. Fortunately, such dials are no longer used because of the potential harm of the radioactive material.

In phosphorescence, the emission of light by the glow-in-the-dark object is more complex than for fluorescence. Phosphorescent materials emit light as a result of electrons making transitions from the conduction band to the valence band. Thus, in addition to the original light, phosphorescence must involve a second external source of energy. Phosphorescence is temperature dependent. In other words, the temperature of a glow-in-the-dark toothbrush determines the degree of phosphorescence.

Because the thermal energy in a room is sufficient to cause these transitions, showing the temperature dependence is difficult. With the computer program, we can simulate much lower temperatures than you can achieve in your classroom. As demonstrated in the program, the toothbrush is dipped in liquid nitrogen that has a temperature of  $-196^{\circ}\text{C}$ . The temperature of the toothbrush is about  $-200^{\circ}\text{C}$  when it is brought near the heat lamp.

Use the cursor to change the temperature values. As before, a gold arrow will move up and down the energy scale of the energy band diagram illustrated on the right of the screen.

Turn on the heat lamp for several different temperatures. Experiment with the energies until you can give an answer and explanation for the following:

- ? How is the temperature at which an object glows in the dark related to the energy differences between the conduction and impurity energy bands? If you cannot explain why, discuss your results with your instructor.

If the heat supplied to the toothbrush provides enough energy for the toothbrush's electrons to move from the impurity band to the conduction band, a transition represented by the dashed arrow illustrated in Figure 10-7 is possible.

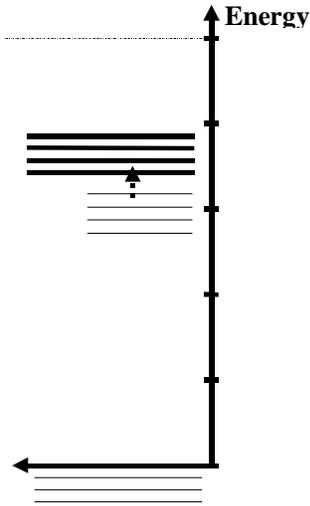


Figure 10-7: Electrons absorb thermal energy from the surrounding and make a transition back to the conduction band.

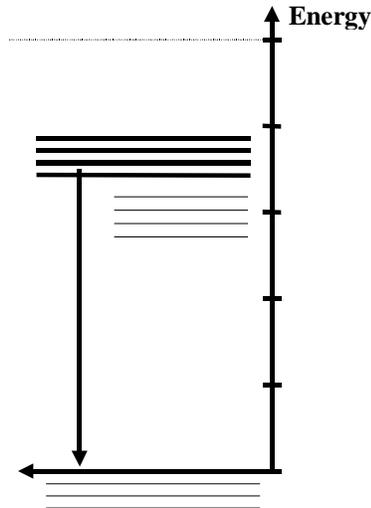


Figure 10-8: Electrons lose energy by emitting visible light and make a transition to the valence band.

The electrons in the conduction band now lose energy and return to the valence band. The output spectrum is the result of the electrons making transitions from the conduction band to the valence band (See Figure 10-8.).

Now use the computer program to create an energy band model that would produce an output spectrum characteristic of a glow-in-the-dark toothbrush at room temperature. Recall that the phosphorescent materials require visible light (1.6 – 3.1 eV) to emit their characteristic faint, greenish-yellow (2.1 – 2.6 eV) glow.

In the space provided below, sketch an energy band diagram for this situation.

When you explored the properties of glow-in-the-dark objects, you found that ultraviolet light is also effective in causing phosphorescence. You will now look at this process with the software.

In the computer program, create an energy band diagram of the glow-in-the-dark toothbrush that utilizes light (3.5 eV) from a black light UV source.

In the space provided below, sketch an energy band diagram for this situation.

? How is this energy band diagram similar to and different from the energy band diagram used to describe the glow-in-the-dark toothbrush when it exposed to visible light?

? Is the resulting energy band diagram for the phosphorescent toothbrush that is exposed to UV light consistent with the law of the conservation of energy? Explain.

In our explorations we found that phosphorescent objects do not glow after being exposed to red light. According to the model used to explain phosphorescence, red light (1.6 - 2.0 eV) does not have enough energy for the electrons to make the transition from the valence to the conduction band. When the material is exposed to green light (2.3 – 2.6 eV), however, the light provides enough energy to a relatively few electrons that make the transition. When the material is exposed to blue light (about 3.1 eV) or UV light (about 3.5 eV), more electrons attain enough energy to make the transitions to the allowed energies in the conduction band. Thus, the resulting light emission is much brighter when an UV light source, rather than a visible light source, is used.

In this unit, we have explored the physical properties of various luminescent materials and devices including glow-in-the-dark toothbrushes; fireflies; light sticks; Lifesavers®; and fluorescent lamps and objects. The quantum model of energy band diagrams explained these materials and devices. The development of this comprehensive model started with atoms of gases to explain the properties of gas lamps and ended with the atoms of solids with impurities to explain luminescent materials and the fluorescent lamp. We could say that the quantum model is very “cool” because it allows us to see everyday phenomena in a new “light” and gives us a deeper understanding and appreciation for the various processes in which matter emits light.

## Appendix: Thermoluminescence

Although phosphorescence can be classified as a form of photoluminescence, it can also be classified as a special type of luminescence called thermoluminescence. Thermoluminescence is a form of light emission that occurs when the temperature of the object is increased after exposure to some form of energy. The process of thermoluminescence has been used as a means to estimate the history and age of rocks and archaeological objects. Thermoluminescence can also be used as a tool for prospecting for uranium.

For a phosphorescent object, the energy used to stimulate light emissions is provided by the light shining on the object. For other thermoluminescent objects such as minerals found near radioactive deposits, the original addition of energy may have come from high-energy radioactive matter or cosmic radiation many years before the temperature increase resulted in thermoluminescence. These thermoluminescent objects, unlike phosphorescent objects, may require very high temperatures (400 - 500 °C) for light emission to occur.

When limestone or granite has been heated in a dark place, the emission of light can be observed during a period of rising temperature. If the rock is cooled and heated again, no light emission is observed. The rock, after having been once heated, needs to be exposed to high energy light in the form of X-rays or gamma rays in order for it to exhibit thermoluminescence. Some minerals, when taken from the ground have a color that disappears upon heating. The color will be restored after the mineral has been exposed to high energy light. Thermoluminescence can also be stimulated in solids by mechanical crushing. Crystals of sodium chloride that show no thermoluminescence can be ground up, after which they show thermoluminescence.

The emission of light may involve one or more forms of luminescence. Our chart that summarizes the different types of luminescence does not completely illustrate the relationships involved with the various forms of luminescence. We now have to expand our chart to include thermoluminescence (see Figure 10-9).

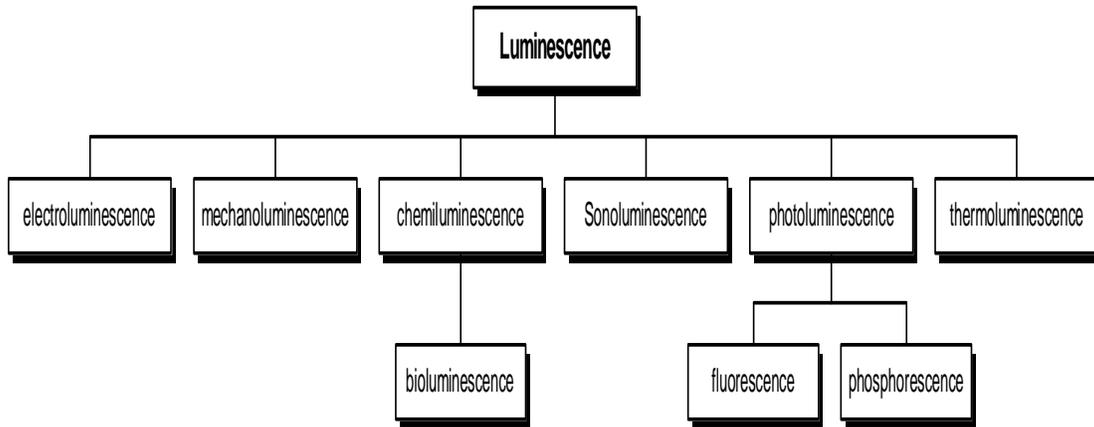


Figure 10-9: Types of Luminescence

The temperature dependency of luminescent objects does not contradict the distinction that was made between incandescence and luminescence. Recall that the key difference between these two processes of light emission is that luminescence, unlike incandescence, does not use heat as the primary mechanism for light emission.