Modeling Light Emission to Explain Phosphorescence

Begin by exploring some items that glow-in-the-dark. You have some toys, tape used by theater productions and minerals. Explore what causes these items to glow. In the process address the following questions:

Does the type of light (infrared, visible, UV) affect the light emitted?
Is the time of exposure to the light important?
Is the color of visible light important?
Does the intensity of the glowing light change as a function of the time after exposure to other light?
Is temperature a factor in the glowing?
Do some materials glow only while being exposed to light?

Record your answers to these observations here.

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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 1 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).

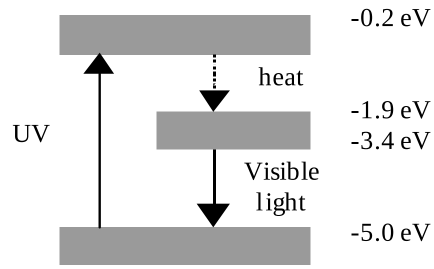

Figure 1: Sample Energy Band Diagram for a "White" Fluorescent Lamp

Some fluorescent minerals only emit a small part of the visible spectrum. Using Figure 1 as a 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 explorations at the beginning of this activity, 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 2.

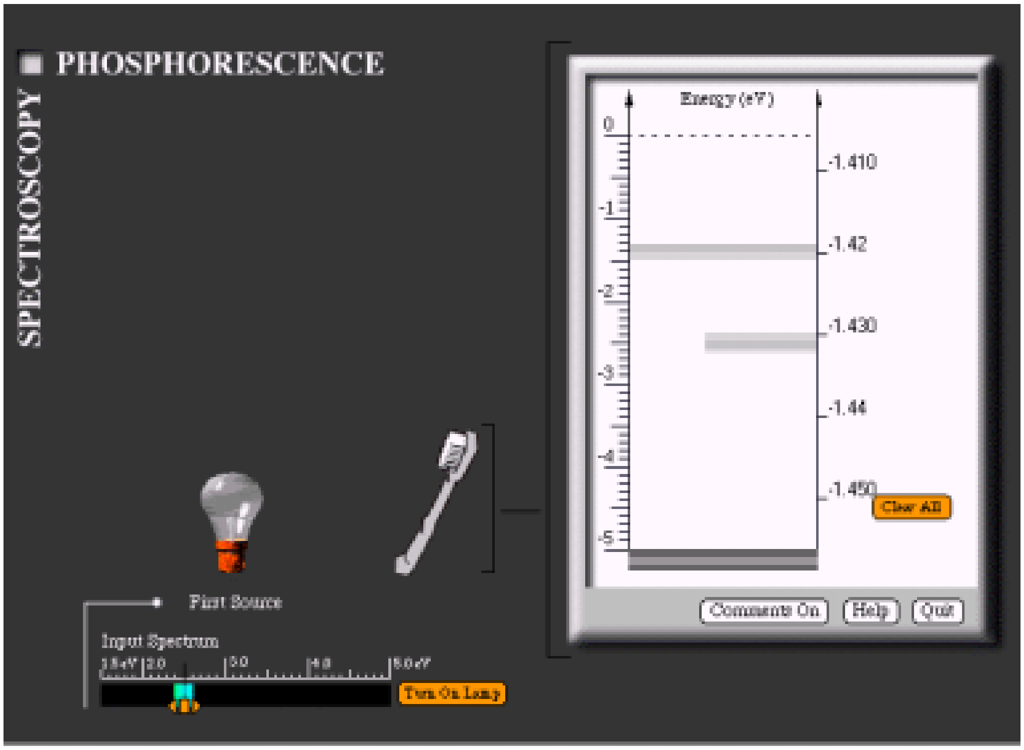

Figure 2: Initial Energy Band Diagram Crop of the Glow-in-the-Dark Toothbrush

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 3 shows, the difference between the energies of these two bands is about 0.01 eV.

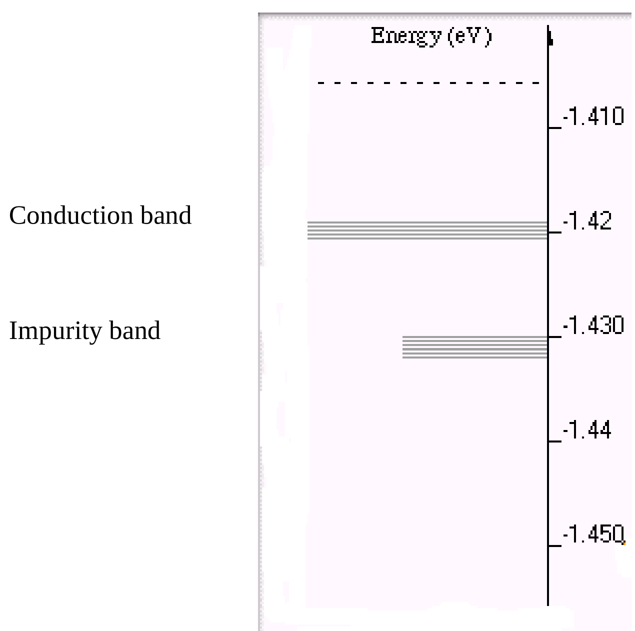

Figure 3: A display of the energies of the conduction band and the impurity band.

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 4 shows that the energy difference between the conduction and valence bands is about 3.5 eV.

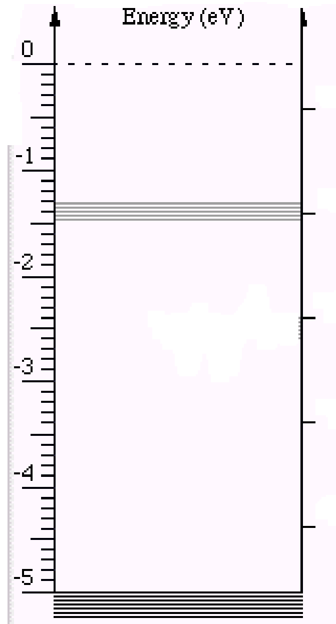

Figure 4: A display of the energies of the conduction and valence bands.

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 5) To help you remember the bands touch only the energy scale relevant to them.

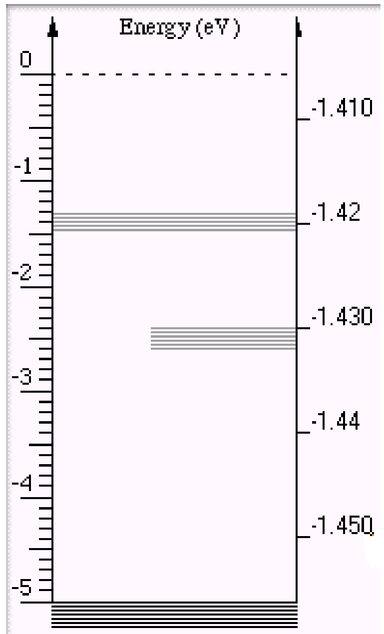

Figure 5: The compromise so that we can see conveniently the energies of all three energy bands.

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 tooth-brush.

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°C. The temperature of the toothbrush is about -200 °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 6 is possible.

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 7.).

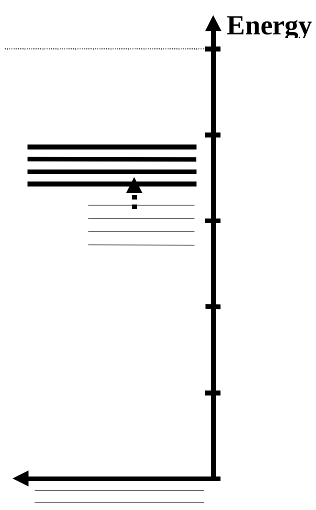

Figure 6: Electrons absorb thermal energy from the surrounding and make a transition back to the conduction band.

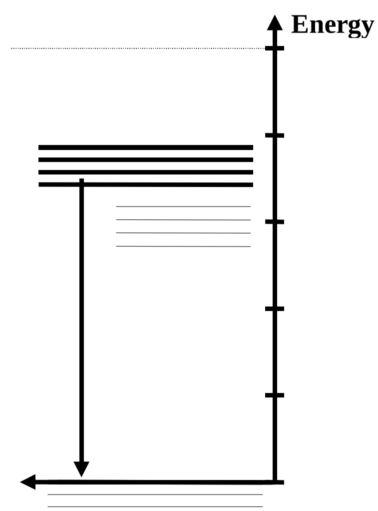

Figure 7: Electrons lose energy by emitting visible light and make a transition to the valence band.

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.

Return to the questions and observations at the beginning of this activity. Use the energy band and gap model presented here to explain all of your observations.

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.