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## **AC 2012-3544: TEMPERATURE DEPENDENCE OF THE ENERGY GAP OF INP QUANTUM DOTS: A SOPHOMORE-LEVEL NANOMATERIALS EXPERIMENT**

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# Temperature dependence of the energy gap of InP quantum dots: a sophomore-level nanomaterials experiment

## Abstract

This paper presents a sophomore-level experiment that allows students to see the “particle-in-a-box” behavior of a real system (quantum dots of different sizes) and explores the temperature dependence of the quantum dots’ energy gap. Quantum dots are nanometer-sized clusters of atoms that contain anywhere from a few to a few thousand atoms. Because of their size, quantum effects become important, which makes them interesting to study and potentially useful for technological applications. For semiconductor quantum dots of a given material, the size of the quantum dot determines the energy gap (the energy difference between the HOMO – highest occupied molecular orbital, and the LUMO – lowest unoccupied molecular orbital) of that particular quantum dot. As a result of their different sizes, the indium phosphide quantum dots studied (which we obtained from CENCO Physics) emit light of different wavelength when excited by ultraviolet light. In addition to being size dependent, the energy gap also depends on temperature. In the experiment, the quantum dots are exposed to different temperatures and, by using a spectrometer, the wavelengths at which they emit light when excited by an ultraviolet source are recorded and compared. Using the model of an electron and a hole inside a spherical infinite potential well, the recorded wavelengths can be related to the size of the quantum dots at various temperatures. The experimental data is then compared to the changes that would be expected from classical volume expansion and from the Varshni equation. Both methods provide an adequate explanation of the temperature dependence of the energy gap of the quantum dots studied.

## Introduction

A now standard experiment in physics and chemistry courses, where students are first exposed to the ideas behind quantum mechanics, is to either synthesize<sup>1,2</sup> or use commercially available<sup>3,4</sup> quantum dots of different sizes in order to see the “particle-in-a-box” behavior of a real system. The wavelengths at which the different quantum dots emit light when excited by an ultraviolet source are recorded with a spectrometer and compared. Quantum dots of smaller radii emit light of shorter wavelength. Using the model of an electron and a hole inside a spherical infinite potential well, the recorded wavelengths can be related to the size of the quantum dots.

In this paper, we present an extension to the experiment described above that explores the temperature dependence of the wavelength of the emitted light, and hence the temperature dependence of the quantum dots’ energy gap. This experiment is particularly well-suited for sophomore-level *Modern Physics* courses and introductory *Condensed Matter* or *Materials Science* courses, as it naturally leads to a discussion of crystalline structure and volume expansion.

## Background

Quantum dots are nanometer-sized clusters of atoms that contain anywhere from a few to a few thousand atoms. Because of their size, quantum effects become important, which makes them interesting to study and potentially useful for technological applications. For semiconductor quantum dots of a given material, the size of the quantum dot determines the energy gap (the energy difference between the HOMO – highest occupied molecular orbital, and the LUMO – lowest unoccupied molecular orbital) of that particular quantum dot. Following the handout that accompanies the CENCO Physics quantum dots,<sup>5</sup> the simplest approach for modeling a quantum dot in an excited state is as a spherical infinite potential well for an electron, excited from the HOMO to the LUMO, plus the hole that the electron left behind.

The Schrödinger equation for a spherical infinite potential well can be solved analytically, and results in the following quantized energy levels:

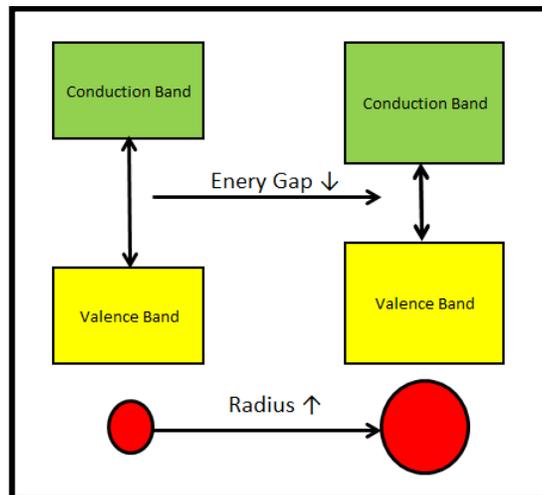
$$E = \frac{\pi^2 h^2 n^2}{2mR^2}, \quad n = 1, 2, 3, \dots \quad [1]$$

where  $h$  is Planck's constant,  $m$  is the particle's mass  $R$  is the radius of the quantum dot.

As mentioned above, for excited quantum dots there are two particles to consider, the electron and the hole, such that the energy for the first excited state becomes

$$E = \frac{\pi^2 h^2}{2m_e R^2} + \frac{\pi^2 h^2}{2m_h R^2} + E_g \quad [2]$$

where  $m_e$  is the effective mass of the electron, and  $m_h$  is the effective mass of the hole. The fact that the potential inside the quantum dot is not zero is taken into account by adding the bulk value of the semiconductor gap,  $E_g$ . From the CENCO Physics handout that accompanies the indium phosphide (InP) quantum dots, the appropriate values are  $m_e = 7.29 \times 10^{-32}$  kg,  $m_h = 5.47 \times 10^{-31}$  kg, and  $E_g = 2.15 \times 10^{-19}$  Joules. The energy gap is largest for smaller quantum dots and approaches the bulk value as the radius increases, as depicted in Fig. 1.



**Fig. 1** Conduction Band vs. Valence Band

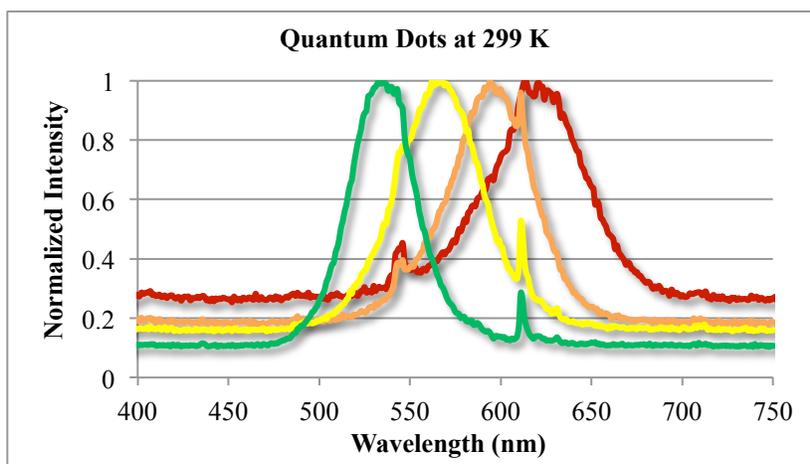
As a result of their different sizes, the quantum dots studied (which we obtain from CENCO Physics and are shown in Fig. 2) emit light of different wavelength (and hence color) when excited by ultraviolet light. The wavelength of the emitted light is inversely related to the energy gap:

$$E = hc / \lambda \quad [3]$$

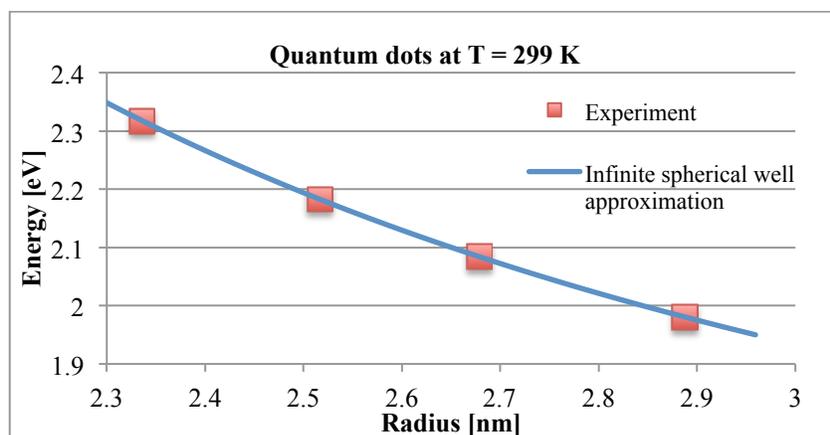
By first using a Ocean Optics USB650 Red Tide spectrometer to measure the wavelength of the emitted light, Eq. 2 can be used to estimate the radii of the different quantum dots. Fig. 3 shows the emission spectra recorded with the Ocean Optics SpectraSuite software. Intensities have been normalized to highlight the peak wavelength shift. Fig. 4 shows the relationship between the energy of the HOMO-LUMO gap and the radii of the quantum dots both from the infinite spherical well model and experimentally at a temperature of 299 K.



**Fig. 2** Cenco Physics vials containing (from left to right) quantum dots of different sizes that emit red, orange, yellow and green light. The quantum dots are excited with 405 nm near-UV light, shown above the green vial. The OceanOptics USB650 Red Tide spectrometer used in the experiment can be seen behind the quantum dot vials.



**Fig. 3** Emission spectra for (from left to right) green, yellow, orange and red quantum dots. Spectra were taken using OceanOptics spectrometers and SpectraSuite software.



**Fig. 4** Energy of emitted light vs. radius of excited quantum dot. The solid line is a plot of Eq. 2. The four data points are experimental data for (from smallest to largest) green, yellow, orange and red quantum dots.

## Temperature Dependence

The experiment as outlined in the Background section is described in the handout that accompanies CENCO Physics' quantum dots and is a standard experiment for Modern Physics lab that can be done in a short amount of time – one laboratory period or less. Temperature also impacts the size of the band gap.<sup>6, 7</sup> It was our goal to develop an undergraduate-level experiment where this parameter is explored in order to enhance our class discussion of material structure and properties.

### Experimental Procedure

#### Materials:

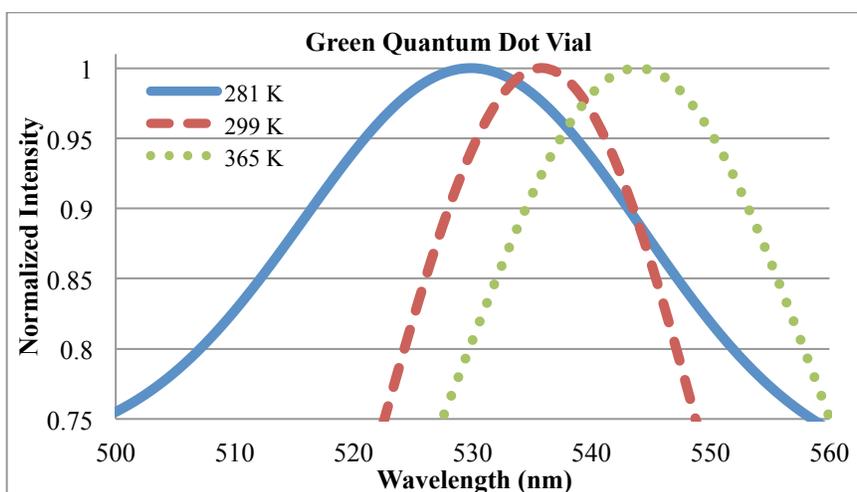
- CENCO InP Quantum Dots
- 405 nm (near-UV) light source (included with CENCO Quantum Dots kit)
- OceanOptics USB650 Red Tide Spectrometer
- SpectraSuite Software
- Large Beaker
- Infrared Thermometer
- Heating Plate
- Ice water

The quantum dot vials were first submerged in a heat bath for a few minutes as seen in Fig. 5. An infrared thermometer was used to measure the temperature of the liquid inside the quantum dot vials. The quantum dots were excited using near-UV light, and their spectra were recorded using the spectrometer within seconds after measuring their temperature. The procedure was repeated for different temperatures ranging from room temperature (299 K) to the boiling point of water (373 K). Fig. 6 shows a sample of the experimental data recorded from the green vial using the spectrometer at 281 K, 299 K, and 365 K. The intensities have been normalized and the spectra have been fit to Gaussian curves in order to highlight the shift in the peak wavelength.



**Fig. 5** Cenco Quantum Dots vial submerged in a large beaker full of hot water.

Next the quantum dot vials were submerged in ice water and then allowed to slowly warm back up to room temperature. Temperature measurements using the infrared thermometer and spectra were recorded every few minutes beginning after the vials had thawed. The full experiment was repeated three times to assure that it is easily reproducible and the measurements are consistent.



**Fig. 6** Spectra recorded for the green vial of quantum dots at different temperatures. The spectra have been normalized and fit to Gaussian curves to highlight the shift in the peak wavelength.

## Theoretical Analysis

The relationship between temperature and gap energy for some (smaller) atomic clusters has been studied using state-of-the-art theoretical and computational methods such as Density Functional Theory, Time-dependent Density Functional Theory and Molecular Dynamics.<sup>8,9,10</sup> However, because these quantum dots are large and because this is intended as a sophomore-level laboratory experiment, we have explored two different and simpler models that can explain the change in wavelength seen as the quantum dots are heated and cooled. These two models - classical thermal expansion and the Varshni equation - are described below.

Thermal expansion describes the change in volume when temperature changes:

$$\Delta V = V(1 + \beta(T_2 - T_1)) \quad [4]$$

where  $V$  is the initial volume,  $\beta$  is the volume expansion coefficient of the material, and  $T_1$  and  $T_2$  are the initial and final temperatures, respectively. The volume expansion coefficient can be related to the linear expansion coefficient,<sup>11</sup>

$$\alpha = \beta/3 \quad [5]$$

The linear expansion coefficient for InP is  $4.6 \times 10^{-6} \text{ K}^{-1}$ , which results in a volume expansion coefficient of  $1.38 \times 10^{-5} \text{ K}^{-1}$ . We took the volume at 299 K as the initial volume, and calculated the expected volume expansion. Then, using Eq. 2 and Eq. 3, the expected energy gap and emission wavelength can be found. Results are shown in Figs. 7-9.

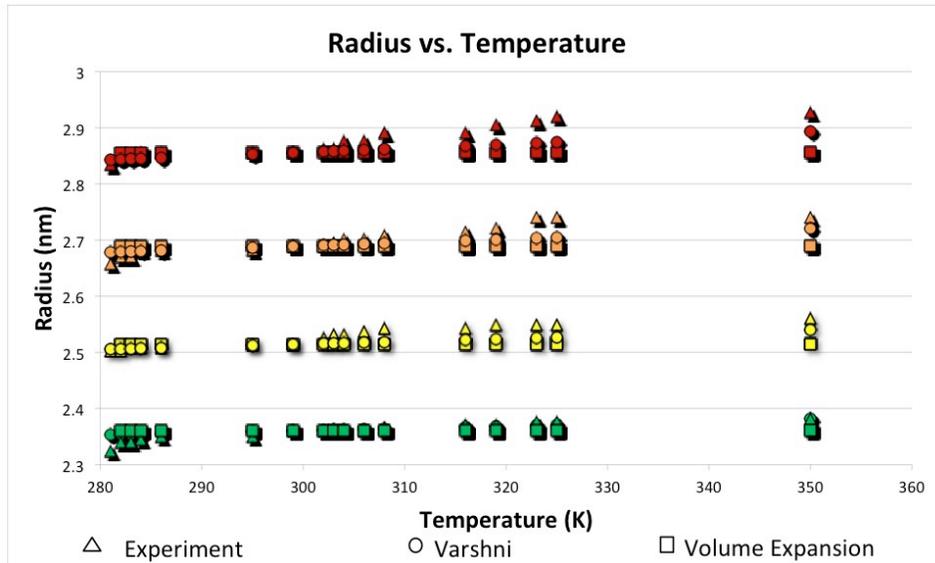
The Varshni equation,<sup>12</sup> experimentally obtained from data in various semiconductors including Si, Ge, and GaAs, is expressed as:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T+\beta} \quad [5]$$

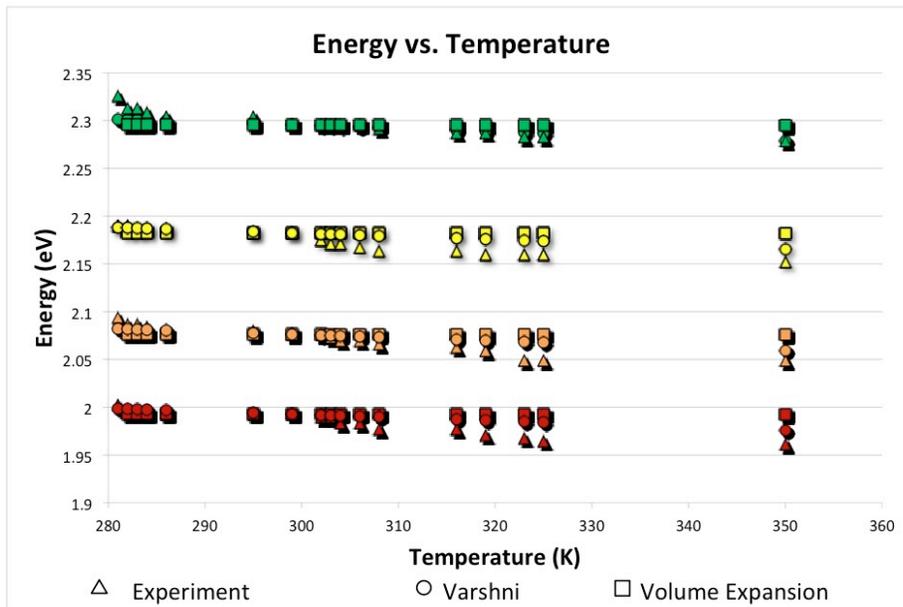
It describes the temperature dependence of the bulk energy gap and is based on two parameters. The first parameter,  $\alpha$ , is based on the expansion of the lattice due to temperature changes. The second parameter,  $\beta$ , represents the electron interaction within the lattice. For InP,  $\alpha$  is  $7.209 \times 10^{-23}$  Joules, and  $\beta$  is 335 K.<sup>12</sup>  $E_g(0)$  is the bulk energy gap at absolute zero. Using room temperature,  $T_i$ , instead of absolute zero as a reference point results in the following equation:

$$E_g(T) = E_g(T_i) + \alpha \left( \frac{T_i^2}{T_i+\beta} - \frac{T^2}{T+\beta} \right) \quad [6]$$

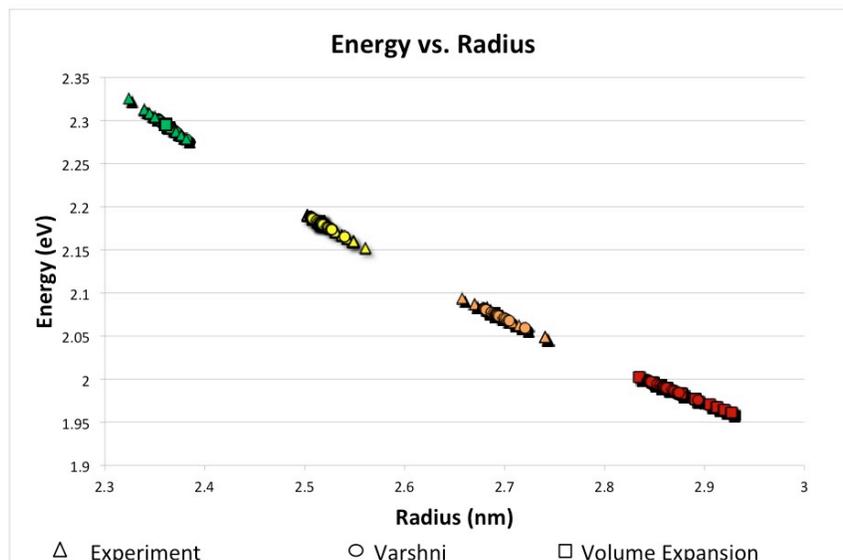
The expected energy gaps, radii, and emission wavelengths, for the vials at different temperatures were calculated using Eq. 3 and Eq. 6, and are shown in Figs. 7 and 8. Fig. 9 shows both the size and temperature dependence of the energy gap.



**Fig. 7** Experimental values (triangles), predictions from the classical volume expansion (squares) and Varshni (circles) models, of the radius versus temperature of the different quantum dots studied. From top to bottom: red, orange, yellow, and green vials.



**Fig. 8** Experimental values (triangles), predictions from the classical volume expansion (squares) and Varshni (circles) models, of the energy versus temperature of the different quantum dots studied. From top to bottom: green, yellow, orange, red vials.



**Fig. 9** Experimental values (triangles), predictions from the classical volume expansion (squares) and Varshni (circles) models, of the energy gap vs. radius of the different quantum dots studied. From left to right: green, yellow, orange, and red vials. The temperature ranges from 281 K (left-most value in each grouping) to 350 K (right-most value in each grouping).

## Results

Over a 70 K temperature range (from 281 K to 365 K) we see a continuous shift in the measured wavelength of the emitted light of 10 nm (yellow quantum dots), 11 nm (green quantum dots), and 13 nm (red and orange quantum dots). Both the volume expansion and Varshni equation models closely follow the experimental results. The former are 0.005% to 2.42% lower than experiment, whereas the latter are 0.02% to 0.56% higher than the experimental values obtained. The models' agreement with experiment was surprising, for they are both typically used for bulk materials. However, our results are in agreement with previous findings for CdSe/ZnS quantum dots. Cheng and Yan<sup>13</sup> found a peak wavelength shift of 4 to 6 nm in the temperature range 300 – 373 K, and also found that their data was in agreement with the Varshni model.

## Conclusion

We have presented a sophomore-level experiment that investigates the temperature dependence of the energy gap in quantum dots using a readily available quantum dot kit and spectrometers that are now common in Modern Physics laboratories. We have also presented two theoretical models, one classical and one experimental for bulk materials, both of which closely match the experimental results. In class, we prefer to use the volume expansion model as it works well for the quantum dots in our experiment and it provides students with an easily understandable classical approximation.

There are further experiments with the quantum dots kit that could be tried. For example, there is a distribution of sizes of quantum dots in each vial. It may be possible to extract this distribution from looking at the width of the peak in the emission spectra at a specific temperature. It would

also be interesting to automate the set up so that spectra are recorded every few minutes as the quantum dots heat or cool in order to study the dependence of the width of the peak in the emission spectra with temperature.

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