The Band Gap

Topics

(i) Planck's Equation (eV vs. wavelength) $E = h\frac{c}{\lambda}$

(ii) Interaction of light with different states of matter:

- Molecules (H_2O)
- Large molecules (macromolecules, e.g. proteins)
- Liquids (clusters of molecules - like water)
- Amorphous Solids (silica glass)

We have considered interaction of electromagnetic waves with vibration of bonds in small and large molecules and in clusters of molecules. "Light" is absorbed when its wavelength resonates with different vibration frequencies in single and aggregates of molecules. Even large molecules retain specificity by presenting a spectrum of absorption lines.

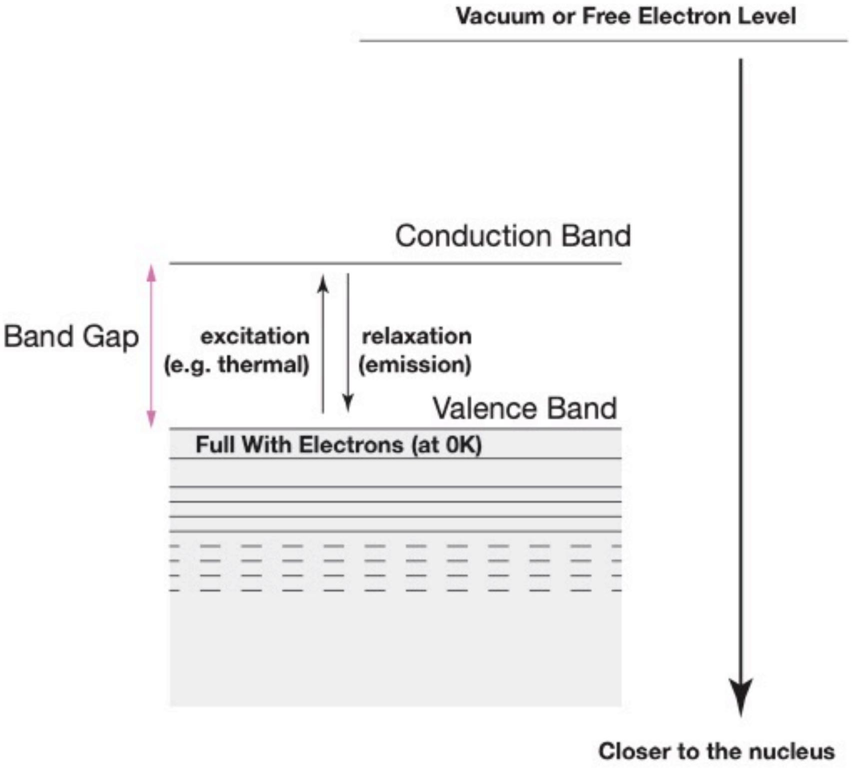
- . Crystals (a periodic structure of atoms that can be studied with a unit cell which repeats into large crystals that can be held in the hand - diamond, graphite, semiconductors, copper)

Crystals

Crystals have quantum states. These states consist of negative (electrons) and positive (holes) charges which interact with each other at different "energy level". The question is how do these energy levels give insights into the interaction of the crystal with light of different wavelengths.

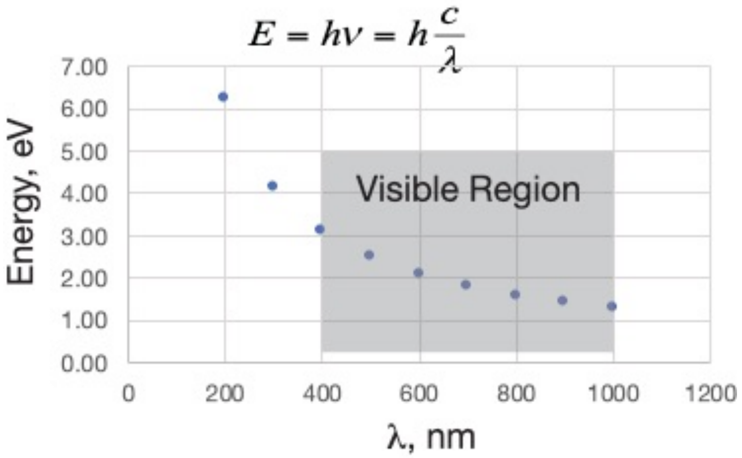
The binding energy of the electrons becomes stronger (higher eV), that is, more difficult to separate that electron away from the nucleus.

The process is to calculate the energy level diagram for a given unit cell with nuclei places periodically.



The electrons are added to occupy these energy levels. And what emerges is a band gap which separates the highest occupied energy level from across the band. The occupied part of the band structure is called the valence band, while the unoccupied levels are called the conduction band. Normally, at O degrees K the valence band is full and the conduction bad in empty.

Band gaps for various crystals are given below. As you can see some them have band gaps that correspond to the visible spectrum of electromagnetic radiation.



Crystal	E_g, ev	Crystal	E_g, ev
Diamond	5.33	PbS	0.34-0.37
Si	1.14	PbSe	0.27
Ge	0.67	PbTe	0.30
InSb	0.23	CdS	2.42
InAs	0.33	CdSe	1.74
InP	1.25	CdTe	1.45
GaAs	1.4	ZnO	3.2
AlSb	1.6-1.7	ZnS	3.6
GaP	2.25	ZnSe	2.60
SiC	3	AgCl	3.2
Te	0.33	AgI	2.8
ZnSb	0.56	Cu_2O	2.1
GaSb	0.78	TiO_2	3

The "color" of crystals of semiconductors and oxides are characterized by a "band gap". Normally the valence band is full with electrons while the conduction band is empty at 0 K. The electrons can be excited from the "top" of the valence band into the "bottom" of the conduction band, for example by thermal or optical excitation. When they relax back to the valence band they emit color.

The band gap enables a simple understanding of interaction between light and matter. For example under white light small crystals of these semiconductors emit a glow of specific color. The mechanism of emission is that the incident light excites electrons from the valence band into the conduction band. When these electrons relapse back to their home energy level, they emit light corresponding to the band gap.

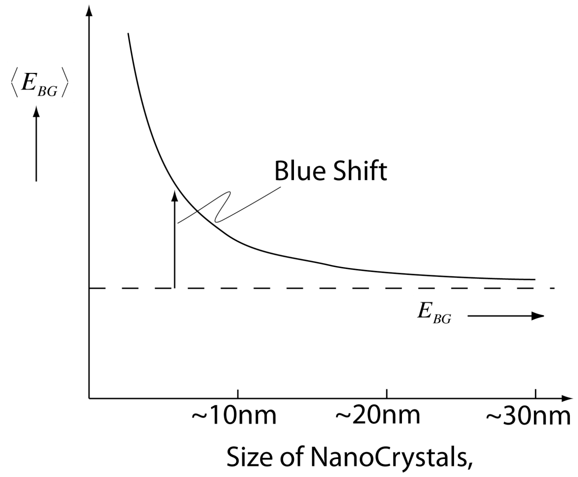
Note that CdSe has a band gap of 1.74 eV which falls in the visible region at approximately 700 nm, which borders between yellow and green. Small crystals of these semiconductors emit light of different colors, with the smaller band gaps showing red, intermediate band gaps green and larger band gaps yellow, as seen in the colors from suspensions of different semiconductor nanocrystals.

What is the "Blue shift?

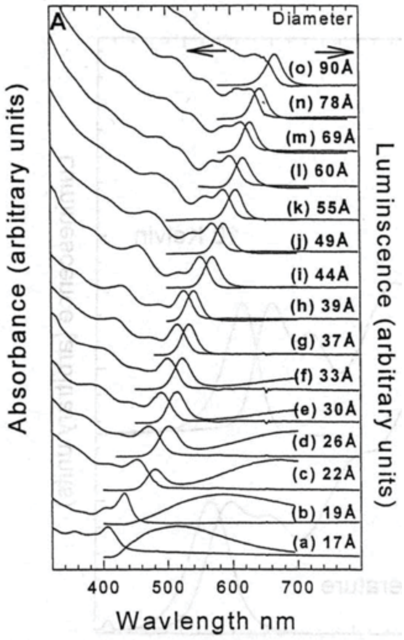
The blue shift is the emission moving to shorter wavelengths in nanoscale crystals. The band gap widens as the crystals become smaller and smaller.

$$\left\langle E_{BG} \right\rangle_{nanocrystals} - E_{BG}(\text{nominal}) = \left\langle \Delta E_{BG} \right\rangle$$

We wish to calculate the blue as the widening of the bandgap. For example the bandgap of CdSe is 1.74 eV, it may change by a fraction of an eV when the crystals become small. In CdSe as the crystal are smaller the emission can change from 1.74 eV up to 2.5 eV when the crystal size decreases down to 1.7 nm as shown below:



CdSe



The Method of Analysis

The overall problem is highly complex since the propensity of the atoms at the surface of the nanocrystals changes the bonding and the band structure, which is difficult to compute in a simple model.

We make an approximation. We consider the model for a hydrogen atom which was first developed by Niels Bohr, where he considered a nucleus of one proton with one electron precessing around the nucleus. Bohr's greater contribution was to develop a hypothesis for the orbitals of the electrons to be quantized, that each orbit has a specific radius and the electron in the orbit has a specific energy. The orbits closer to the nucleus had a higher energy, that is, it would require more eV to tear that electron away from the nucleus.

The steps in the analysis of the Bohr atom.

(i) assume the nucleus to have Z protons instead of one proton like in the hydrogen atom.

(ii) calculate the mechanics of the orbit of an electron around the nucleus such that the electrostatic attractive force is balance by centrifugal kinetic force which then prescribes the relationship between Z, the velocity, the mass of the electron and the radius of the orbit.

(iii) calculate the energy of the electron in a specific orbit, which is the sum of the electrostatic potential energy (i.e. the work required to overcome the electrostatic attraction) and the kinetic energy.

(iv) THE QUANTIZATION CONDITION: $2\pi R = n\frac{\lambda}{2}$. This equation then related the energy of the orbit to the wavelength.

(v) Can calculate the emission wavelength if the electron is excited from a lower energy level (the ground state) to next up energy level.

The Great Assumption:

We model the "electronic structure" of the nanocrystal as an electron-hole pair with the electron prescessing around the hole, which we model using Bohr atom analysis.

That we assume the size of large nanocrystal to be the ground state. As the nanocrystal becomes small the orbit radius become smaller as well, and therefore its every level is greater, that is, the band gap is wider.

The subtle trick is to use an effective mass for the hole-electron pair in the analysis.

The Bohr Atom

This is the next topic for our class.