**Crystal Field Theory, gemstones and color**

**The colors of transition metal compounds are highly variable. Aqueous solutions of nickel are green, of copper are blue, and of vanadium can range from yellow to blue to green to violet. What is the origin of these colors? A simple geometrical model known as crystal field theory can be used to differentiate the 5 d orbitals in energy. When an electron in a low-lying orbital interacts with visible light, the electron can be promoted to a higher-lying orbital with the absorption of a photon. Our brains perceive this as color. Rubies, dark red, and emeralds, brilliant green, are precious gemstones known since antiquity. What causes the color in these beautiful crystals? Using crystal field theory, we can explain the colors in these gemstones.**

**Learning Objectives**: Upon completion of this exercise, you should be able to:

1. Derive the crystal field splitting for d orbitals in an octahedral geometry
2. Predict the magnitude of d orbital splitting
3. Relate color, energy, wavelength, and crystal field strength

**Terms You Should Know:** orbital, octahedron, absorption spectroscopy, crystal field splitting

**Background Reading**: Atkins, Jones, & Laverman, Chapter 2, Sections 2.2, 2.6, 7.7, 7.11, 16.10, 17.3(d), 17.5, 17.8, 17.9, 17.10, 17.12

Reading from “The Science of Color,” volume 2, edited by Alex Byrne and David R. Hilbert, MIT Press, Cambridge MA, 1997, pp. 10-17.

**After Completing this Exercise, Textbook Problems You Should be Able to Answer**:

2.14, 2.16, 2.39, 2.40, 17.51, 17.53, 17.58, 17.65, 17.71

**Day 1:**

Complete the crystal field theory guided inquiry; complete student worksheet 1 in class or as homework

**Day 2:**

turn in the worksheet from day 1

complete the exercise using Crystal maker to examine the solid state structures of ruby and emerald; complete student worksheet 2 in class or as homework (due at start of next unit)

**Background Information**

Much of inorganic chemistry deals with the structure and properties of the transition metal complexes. One of the key approaches to understanding these properties is crystal field theory, which was originally developed by Bethe in the late 1920s to explain the electronic structure of metal ions in crystals using a purely electrostatic bonding model. We will use this theory to explain the color of the gemstones ruby and emerald, and will see the limitations of the theory for describing actual chemical systems.

**Day 1**

**Crystal Field Theory Guided Inquiry**

The material in this section was adapted from “A Guided Inquiry Activity for teaching Ligand Field Theory,” Johnson, B. J., and Graham, K. J., *J. Chem. Educ.*, **2015**, *92*, 1369-1372. Rather than repeat the unit here, I refer the interested instructor to the related content link. The student answer sheet for day 1 outlines the focus I chose for this unit for my students.

**Day 2**

**Solid state structures**

**Corundum**

Aluminum oxide, Al2O3 is the most common oxide of aluminum, and is commonly called alumina. The naturally occurring, thermodynamically stable, crystalline form of aluminum oxide is called corundum. This structure consists of a nearly hexagonal close-packed structure of oxygen with aluminum ions filling 2/3 of the octahedral holes. Corundum is very hard (9.0 on the Mohs scale, exceeded only by covalent structures like silicon carbide, boron nitride and diamond) and can scratch almost every other mineral. It is therefore commonly used as an abrasive. Trace transition metal contaminants in the corundum structure give rise to ruby and sapphire gems.

Let’s examine the structure of corundum in more detail. Open the CrystalMaker file entitled “Corundum.cmdf” on your laptop. You should see the unit cell, the axis system, and the unit cell contents. All of the atoms shown are positioned within the unit cell; verify that the stoichiometry of the mineral is correct.

Now let’s verify the HCP packing of the oxygen atoms in the structure. Under the “Model” menu, switch to “space filling.”

Question: since the principal quantum numbers of Al and O are 3 and 2 respectively, why are the oxygen atoms larger than the aluminum atoms?

To simplify the view, lets truncate the unit cell along the z axis. Under “Transform,” open the “set range” dialog. Reduce the range to view only from z = 0.5 – 1.0. You should see 3 rows of oxygen atoms. Now, rotate the model so you are looking down the z-axis. When looking down, you should see that some of the oxygen atoms are “missing;” they are contained in the next unit cell. Expand the range along x and y so you are viewing from 0 – 1.1 along each axis. While still looking down the z-axis, increase the z-axis range again until you can see the whole unit cell (range = 0.0 – 1.0). You may want to switch back and forth between “Space Filling” and “Ball and stick” under the “model” menu.

Questions:

a) are the oxygen atoms in an A-B-C-A-B-C arrangement or an A-B-A-B arrangement?

b) Is this CCP or HCP?

c) Is the structure a perfect lattice or is it imperfect?

Measure the bond lengths between one aluminum and its nearest neighbors. Repeat for a second aluminum atom. It may help to reduce the range along the z-axis again to simply this task. In order to more closely examine the environment around the aluminum atoms, we will construct polyhedra. Under the “edit” menu, select “bonding,” and press the “+” to add a new type of bond. Form bonds between Al and O by setting the search parameter to a value slightly larger than the Al-O bond distances you found in the previous step. Turn on the “model inspector” and edit the Al atom. It should be currently set to show “sphere” under the “polyhedron” menu. Click on that sphere and change it to one of the polyhedron options. Then, under the “model” menu, select “polyhedron.” The aluminum environments should now appear as coordination polyhedra.

Questions:

a) what is the coordination environment around the aluminum ions?

b) are the aluminum atoms centered in the polyhedra?

c) what is the average Al-O bond length?

Expand the view outwards to examine the larger 3-dimensional structure of corundum. It may help to turn off the view of the oxygen atoms and change the polyhedron options for aluminum. It is difficult to verify, but you should be able to observe that 2/3 of the possible octahedral coordination environments are filled with aluminum atoms. This is probably easiest to observe along the z axis.

In rubies, approximately 1% of the Al ions are replaced with Cr ions in the corundum lattice. Although these two metals are not the same size, the chromium ions can fit in the lattice without disrupting the overall structure.

Question:

a) In order to maintain charge neutrality, what is the charge on each Cr ion?

b) how many valence electrons are in this Cr ion?

c) draw an appropriate crystal field splitting diagram for the Cr and populate it with the electrons.

d) Given that rubies appear red, calculate the ∆o and report it in cm-1.

**Beryl**

Beryl is a mineral containing beryllium, aluminum, silicon and oxygen with the chemical formula Be3Al2Si6O18. It is a member of the family of cyclosilicate minerals along with other common minerals such as the gemstone tourmaline. These minerals contain linked “SiO4” tetrahedra in a “6-membered ring” with a stoichiometry of (SiO3)612-. Since Be always appears as a +2 cation, and Al is always a +3 cation, the charge balances, as it must. Beryl is also a hard mineral, 7.5-8 on the Mohs scale, and is found an many colors depending on the trace transition metal impurities present, giving rise to the gemstones aquamarine (blue, Fe), emerald (green, Cr), and morganite (pink, Mn).

Let’s examine the structure of beryl in more detail. Open the CrystalMaker entitled “beryl.cmdf” on your laptop. You should see the unit cell, the axis system, and the unit cell contents. All of the atoms shown are positioned within the unit cell; verify that the stoichiometry of the mineral is correct. Note, there are two water molecules (black spheres, Wa) present in this structure; deselect them to remove them from view from the toolbar.

The first structural feature we will investigate is the presence of the cyclosilicate motif. First, lets create Si-O tetrahedra for easier viewing. Under the “edit” menu, select “bonding,” and press the “+” to add a new type of bond. Form bonds between Si and O by setting the search parameter to 2.0 Å. Turn on the “model inspector” and edit the Si atom. It should be currently set to show “sphere” under the “polyhedron” menu. Click on that sphere and change it to one of the polyhedron options. Then, under the “model” menu, select “translucent+sphere+bonds.” Rotate the molecule so you are looking down the z-axis. Now, from the “transform” menu, go to “set range” and set the x- and y-axes from 0.0 – 1.5. You should see an isolated Si6O18 hexagon appear. You may want to turn off the viewing of the O atoms to simplify the view. Once you have the view, you can expand even further, from 0.5 – 2.5 along x and y. You should be able to see clearly separated cyclosilicates with Al and Be atoms in the intervening spaces.

Now lets examine the coordination environment around Be. Revert the view back to a single unit cell from the “Transform/Set range” menu. From the “bonding” menu, add a new type of bond between Be and O, and from the “model” menu, change the polyhedron type for Be from “sphere” to “translucent.” You should be able to see isolated BeO4 tetrahedra that link the cyclosilicates along the z-axis. Expand and contract the ranges to verify that the BeO4 tetrahedra are isolated from each other. A particularly good view (down the z-axis) has x- and y-axis ranges from 0 – 1.5, and z from 0 – 1.8. The Be atoms serve as “glue” that stick the large cyclosilicates together along z. From this view it should also be clear that, unlike the corundum structure, the beryl structure is a “perfect” lattice, in that all of the Al atoms line up perfectly along the z-axis.

Finally, lets examine the coordination environment around the Al atom. Revert back to a single unit cell and make sure that the O atoms are visible. Truncate so that the visible z-axis range is from 0.1 – 0.5. Measure the six Al-O bonds; are they all the same? Now create bonds between Al and O, and create a polyhedral view for the Al atom. The Al should be seen to be residing in an octahedral environment, and these AlO6 octahedra also are isolated from one another, but link with the BeO4 tetrahedra.

Questions:

a) what is the coordination environment around the aluminum ions?

b) are the aluminum atoms centered in the polyhedra?

c) what is the average Al-O bond length?

Beryl is a layered structure. There is a layer of the cyclosilicates, and then a layer of Be and Al atoms, and then another layer of cyclosilicates. The oxygen atoms link the Si, Be, and Al coordination polyhedra. For a good view of the structure, set x- and y-axes from 0.0 – 1.9, and z from 0.0 – 1.0. Then, while looking down the z-axis, expand along z. You can see that the cyclosilicates form a pore through the structure along the z-axis. Go back to the site menu and make the water molecules visible. Nature abhors a vacuum!

As in ruby, emeralds contain chromium impurities for about 1% of the aluminum atoms in the beryl lattice.

Question:

a) In order to maintain charge neutrality, what is the charge on each Cr ion?

b) how many valence electrons are in this Cr ion?

c) draw an appropriate crystal field splitting diagram for the Cr and populate it with the electrons.

d) Given that emeralds appear green, calculate the ∆o and report it in cm-1.

e) given the structures of Beryl and Corundum, explain using a physical model why the two materials have such different harndesses.

**Breakdown of CFT - covalency**

One of the useful things about crystal field theory is its predictive nature. Once we know a crystal field splitting pattern and what atoms are present, we can make predictions about ∆o, color, and other features of metals such as magnetism.

Question: Given the background of the theory, that the central metal d orbitals are split due to repulsive electronic interactions with the ligands, predict which metal complex in each pair would have a higher crystal field:

a) Cr surrounded by 6 oxygen ions at 2.0 Å. Cr surrounded by 6 water molecules at 2.0 Å

b) Cr surrounded by 6 oxygen ions at 2.0 Å. Cr surrounded by 6 oxygen ions at 1.9 Å

Go back and record here the average Cr-O distances in emerald \_\_\_\_\_\_\_ and in ruby \_\_\_\_\_\_\_. Does the color of emerald and ruby match that predicted by the distance argument you just calculated?

One of the main assumptions in crystal field theory is that the ions are point charges, and that bonding in the solid state lattice is purely ionic (that is, there are no shared electrons).

Question:

a) why is the modeling of ions in a crystal lattice as point charges reasonable?

b) why is the modeling of ions in a crystal lattice as point charges *un*reasonable?

c) looking at the structures of beryl and corundum, which seems more ionic and which seems more covalent. Why?

The ∆o of a metal ion depends on the magnitude of the charge felt by that metal ion. In purely ionic structures (which don’t really exist; even NaCl has some degree of covalency), the net charge on each anion is larger in magnitude. As structures become more and more covalent, the electronic difference between the central metal and ligand atoms becomes less. In a purely covalent lattice (diamond, which is a face centered cubic lattice of C atoms with C atoms in one half of the tetrahedral holes), there is no electronic difference between the types of atoms. Corundum is more ionic than beryl; the polysilicate chains and the beryllium atoms reduce the net negativity of each oxygen atom, so that even though the Cr-O bond lengths in emerald are shorter than the corresponding bonds in ruby, the net charge felt by the Cr atom is lower and the ∆o is lower for emerald.

The diagram[[1]](#footnote-1)‡ on the following page shows the calculated absorption bands and resulting absorption spectra for emerald and beryl.

Questions:

Indicate on the diagram how you can tell that the ∆o for beryl is lower than that for corundum.

Show (circle the transition line) the electronic transitions responsible for the green color in emerald and red color in ruby.

{{Figure 1.4 from “Readings on color; The science of color,” volume 2, by Alex Byrne and David R. Hilbert, MIT Press, 1997” is presented here.}}

1. ‡ “Readings on Color; The science of color,” volume 2, by Alex Byrne and David R. Hilbert, MIT Press, 1997 [↑](#footnote-ref-1)