**Module 2b - Crystal Field Theory, gemstones and color**

**Now that we understand the basics of the solid state, we can turn our attention to more complex solids. Some solids are made of main group elements (the s and p blocks), while other also contain transition metals (the d block). 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 module, 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

**Review (material you should know or learn prior to this module):** ionic radii

**Terms you should learn:** orbital, octahedron, absorption spectroscopy, crystal field splitting

**Background Reading**: Atkins, Jones, & Laverman: Topics 3I.2, 3I.3, 1D.2-1D.4, 1E.2, 8E.1(b), 8D.1(a), 8D.2(a), 8E.2, 9B.1(d), 9C.1, 9D.1-9D.5

Reading from the textbook web supplement “Major technique 2—Ultraviolet and Visible Spectroscopy.” (available on Sakai).

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

**After completing this four-day module, textbook problems you should be able to answer**:

3I.10 (crystalmaker files for calcite and dolomite are available on Sakai), 3I.13, 3I.14, 3I.15

1D.9, 1D.10, 1D.25, 1E.7, 1E.11, 1E.13, 9C.9, 9D.1, 9D.3, 9D.5 (ligand field splitting = ∆o)

These reading assignments, and the assigned exercises, serve as a *general introduction* to concepts that you will need in order to work on the activities in the coming periods. Your conceptual understanding of these topics will be assessed during homework, concept quizzes, and exams.

**Guided Reading part 1 due by class time Wednesday Sep 28, 2016**

Read Topic 3I.2

What is the difference in the structure of CO2 and SiO2? Based on your answer, why do CO2 and SiO2 have such different properties despite being neighbors in the same group of the periodic table?

Compare Figures 3I.7 and 3I.9.

CrystalMaker files for these two structures (cristobalite and tremolite) are on Sakai.

Relate the crystal structure data and bonding in those structures with the physical properties exhibited in the Figures. You might have to explore different views of the cell.

Read Topic 3J.3

What is 125 K when converted to °C? Why are temperatures of 125-138 K considered “high temperature” in the context of superconductors?

Read Interlude: Ceramics and glasses (pp 239-240)

What is a major problem for applications of “high temperature” superconductors?

Study Figure 3J.9

What are the contents of the “123” unit cell? A filed called “Figure3J9.dae” is available on Sakai.

Read Major Technique 2—Ultraviolet and Visible Spectroscopy

Since  = c/, and E = h, what is the energy change in joules associated with 400. nm light? 700. nm light?

Energy in chemistry is usually reported on a “per mole” basis. Convert the energies you calculated above from J to J/mol. What does energy in J vs. energy in J/mol *mean* in this context? What is the mole referring to?

If an object absorbs 450 nm light, it will appear \_\_\_\_\_\_\_\_\_\_\_\_\_

If an object absorbs 570 nm light, it will appear \_\_\_\_\_\_\_\_\_\_\_\_\_\_

To learn more about superconductors, read Topic 3J.3 and the following website: <http://www.doitpoms.ac.uk/tlplib/superconductivity/index.php>. You will not need to understand the theories of conduction in these materials for Chem 23a.

What was the first material found to be a superconductor? At what temperature is this material a superconductor?

As a superconductor is cooled below its Tc, what happens to its electrical resistance?

What are two common applications of superconductors?

**In class activity Day 1**

Ultraviolet/visible spectroscopy is the process by which a material absorbs a photon of light that corresponds to an energy gap, usually between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO).

In a small group, compare and contrast this type of spectroscopy with the two others you have seen so far in Chem 23a: infrared spectroscopy and NMR spectroscopy.

In transition metal chemistry the energy gap between the HOMO and LUMO is often called the ∆o (delta-o), which we will derive during the next class period. The magnitude of ∆o is most easily measured by UV–visible spectroscopy. Given this information, what is an approximate value for ∆o?

For a d1 metal ion (a metal ion with 1 electron in the d orbital set) in an octahedral complex, draw the ground state (the lowest energy way to arrange the electron in the set of five d orbitals). The relative energies of the 5 d orbitals is given for you.



When the complex absorbs light with an energy corresponding to ∆o, an electron is promoted from the lower energy orbitals to the higher energy orbitals. Redraw the five orbital energy levels above to the right and show the new electron position.

This wavelength or energy of absorbance is related to ∆o. In a UV-vis spectrum, normally absorbance is plotted as a function of wavelength. The separation between the energy levels can be given in three different ways:

In units of wavelength. Since E=hc/the wavelength of absorbance is directly/inversely (circle one) proportional to energy.

In energy units, for example kJ/mol.

In units of cm-1. To convert to this number, convert the wavelength (normally in nm) to cm and take the reciprocal. What is the advantage of doing this, as opposed to just using wavelength? Hint: how is wavenumber related to energy?

(color wheel picture)

**Figure 2.4 from Major Technique 2 (waelengths of light in nm).**

The visible region of the spectrum runs from approximately 400 nm to 700 nm. What are these limits in cm-1?

If a solution appears yellow, what wavelength of light does it absorb?

The color that a compound *appears* is on the opposite side of the artists’ color wheel from the color of light it *absorbs*. [Ti(H2O)6]3+ absorbs light around 500 nm. What color is it?

**Guided Reading part 2 due by class time Friday Sep 30, 2016**

Read Topic 1D.2 and study Table 1D.1

Considering the radial wavefunctions, which orbitals have a non-zero probability of finding an electron at *r* = 0?

Considering the angular wavefunctions, which orbitals have a non-zero probability of finding an electron at  = 0°? At  = 0°?

Read Topic 1D.3

How many s, p, and d orbitals are there for principal quantum numbers of 1, 2, 3 and 4?

Read Topic 1D.4

Why do chemists (and physicists) *not* draw the 100% probability boundary surface for finding an electron?

Study Figures 1D.6, 1D.8, and 1D.10

Which orbitals have a non-zero probability of finding an electron at the origin?

Which orbitals have a non-zero probability of finding an electron along the z-axis? Along the x-axis?

was it easier for you to answer these two questions looking at Table 1D.1 or the Figures?

Read Topic 1E.2

Write the full ground state electronic configuration predicted by the aufbau principle for:

O:

S:

Se:

Te:

Rewrite the ground state electronic configurations for those elements using the shorthand notation for the noble gas core and only write out the valence electrons:

O:

S:

Se:

Te:

What is similar and what is different about the valence shell electrons for these elements? What does it tell you about the chemistry of these elements?

Read Topic 9C.1

What is the coordination number of the iron in the pale green complex Fe(H2O)62+? What is the oxidation state of iron?

What is the coordination number of the iron in the dark blue complex Fe(CN)64-? What is the oxidation state of iron?

What is the coordination number of the iron in the dark red complex Fe(SCN)(H2O)52+? What is the oxidation state of iron?

Based on your answers, do you see a clear or consistent trend in color, or color intensity based on either coordination number or oxidation state?

Read Topic 9D.1

What is the major assumption used in deriving crystal field theory? (Hint, the theory was developed by physicists…)

Read Topic 9D.3

Which compound would you predict has a larger ∆o, the pale green complex Fe(H2O)62+ or the dark blue complex Fe(CN)64-? Explain your answer.

**In class activity Day 2**

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 the physicist 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.

First, valence orbitals on a metal. A transition metal ion has \_\_\_\_\_\_ valence atomic orbitals:

\_\_\_\_\_\_\_ d and \_\_\_\_\_\_\_ s and \_\_\_\_\_\_\_p orbitals.

Draw each of the valence orbitals for an element in the first row of the transition series; include both angular and radial nodes. Shade the lobes of the orbitals appropriately. Include an axis system.

In octahedral[[1]](#footnote-1)‡ complexes, 6 ligands approach along the *x*-, *y*- and *z*-axes. To determine which orbitals can have significant overlap, let’s walk through all of the orbitals. Ligand orbitals are treated as either an s or a p orbital aligned with the metal-ligand bonding axis.

* Does the pz orbital of a metal overlap well with a ligand approaching on the z-axis (shown)?
* Does the py orbital of a metal overlap well with a ligand approaching on the y-axis (shown)?
* Draw the s and the px orbitals on the empty axes.
* Decide if any of these four orbitals can overlap well with a ligand approaching along the x, y, and z axes.



* Repeat the same analysis with each of the d orbitals. You may wish to refer to the pictures of the 5 d orbitals on the previous page.
* Which d orbitals have good overlap with ligands?
* Which d orbitals do not overlap with incoming ligands?

Crystal field theory (CFT) is a model based on the repulsion of metal d electrons by ligand electrons. The effect of any ligand geometry on the entire set of metal d orbitals can be modeled by a stepwise approach.

* With no ligands, the five d orbitals are equivalent in energy.
* In a uniform (spherical) field of negative charge, the orbitals remain equivalent but go to a higher energy due to electron-electron repulsion.
* When the field of negative charge is focused at the positions of the ligands, the d orbitals are no longer equivalent. *Orbitals that overlap well with ligands go up in energy, while those that do not overlap well with ligands go down in energy.*
* The barycenter in the d orbital splitting diagram is the center of the energy levels; the barycenter does not change from the original position of the 5 d orbitals. This allows us to make comparisons between different geometries.
* In octahedral geometry, the orbitals split into two groups and are separated by∆o. *This quantity is a variable* that depends on the metal and ligands. To a first approximation, shorter bonds leads to larger ∆o values.

Draw a pictoral representation of the above 5 bullet points, resulting in an energy diagram for an octahedral complex which is split by ∆o.

* On the diagram, name the two d orbitals that have gone up in energy and also the three d orbitals that have gone down in energy.
* The set that goes down in energy is called the “t2g” set, while the set that goes up in energy is called the “eg” set.
* Show, in units of ∆o, that the total energy of the orbitals that go up in energy is equal to the total energy of the orbitals that go down in energy.
* How many valence electrons would a Cr(III) metal ion have? Populate the energy splitting diagram with these electrons.

**CFT and UV-Vis Practice Problems**

1. If a solution of an octahedral metal complex appears yellow,
   * What wavelength of light is it absorbing?
   * What is the ligand field splitting ∆ for the complex in cm-1?
2. An octahedral metal complex absorbs light that is 535 nm.
   * What color is it?
   * What is the ligand field splitting ∆ for the complex in cm-1?
3. [Cu(NH3)4]+ is completely colorless while [Cu(NH3)4]2+ is intensely blue.

* Draw the splitting diagrams to explain this observation.

**CHALLENGE PROBLEM!**

**Tetrahedral geometry**

There are different splitting patterns for different geometries. Let’s look at tetrahedral, which is harder to predict because the M-L bonds don’t fall on the x, y or z axes.

* Using this picture of a tetrahedral complex, predict which orbitals overlap best with ligands.



* Predict a splitting diagram for tetrahedral.
* Predict the size of ∆t relative to ∆o assuming metal ion and ligands are the same. Hint: What causes the ∆? How are they different for tetrahedral and octahedral?

**Guided Reading part 3 due by class time Monday Oct 3, 2016**

Read Topic 9D.2

Why is a listing of ligands called a “spectrochemical series?”

Looking at the list of ligands and their relative ranking, do you see any trends in the spectrochemical series? Explain what you see.

Given the basis of crystal field theory, are there any surprising results in the spectrochemical series? Are any ligands out of place given the model?

Read Topic 9D.4

It is possible to measure the number of unpaired electrons in a metal complex by several techniques because unpaired electron spin generates a magnetic field. For an octahedral iron complex, do you expect a significant change in magnetic behavior for Fe2+ or Fe3+ if

a) ∆o is approximately constant for Fe2+ and Fe3+?

b) ∆o is significantly larger for Fe3+ than Fe2+?

c) explain your reasoning.

**In class activity Day 3 for Crystal Field and Gems**

**Revisiting octahaedral geometry**

As a class, let’s review the thought process for the octahedral crystal field splitting diagram.

1) draw negative test charges coming in around a central metal atom along ±x, ±y, and ±z

2) consider that geometry and its interaction with the 5 d-orbitals

3) which interactions lead to the most electrostatic repulsion? The least?

4) orbitals with more electrostatic repulsion move up in energy.

**Square planar geometry**

There are different splitting patterns for different geometries. Let’s look at square planar, which can be derived from octahedral. One way to think about square planar is to “pull” the ligands along the z-axis away from the metal center. This is known as an axial distortion and is seen in some “almost” octahedral complexes such as Cu(NH3)4(H2O)22+, which has 4 “close” ammonia ligands in the x-y plane, and 2 “far” water ligands along the z-axis.

* consider a square planar complex in the x-y plane. Predict which of the 5 valence d-orbitals will have *lower* interactions with the test charges as they are removed from the ±z axis. Predict which of the 5 valence d-orbitals will have *no change* in the interaction with the test charges.
* Using the information from the previous problem, predict a splitting diagram for square planar complexes. Start with the octahedral splitting diagram shown below and indicate what will change when the ligands are removed from the z axis.



Metal Ion Effects

∆o values are partially influenced by the identity of the metal ion.

Trend 1 metal oxidation state:

The ∆o valuesfor different aquacomplexes, M(H2O)6, are shown below. Complete the table with the number of unpaired electrons for each metal ion. If the ∆o values are bigger than 17,000 cm-1, then the electrons are more likely to pair up than to remain unpaired.

|  |  |  |  |
| --- | --- | --- | --- |
| # d e - | Ion | ∆o, cm-1 | spin? |
| d4 | Cr+2 | 9,250 |  |
| d3 | Cr+3 | 17,400 |  |
| d7 | Co+2 | 8,400 |  |
| d8 | Ni+2 | 8,500 |  |

The ∆o valuesfor different ammoniacomplexes, M(NH3)6, are shown below. Complete the table with the number of unpaired electrons for each metal ion. If the ∆o values are bigger than 17,000 cm-1, then the electrons are more likely to pair up than to remain unpaired.

|  |  |  |  |
| --- | --- | --- | --- |
| # d e - | Ion | ∆o, cm-1 | Spin? |
| d3 | Cr+3 | 21,500 |  |
| d6 | Co+3 | 22,900 |  |
| d7 | Co+2 | 10,200 |  |
| d8 | Ni+2 | 10,800 |  |

Explain the trend in the values of ∆ vs. the oxidation state of the metal. Explain why one complex would have a larger or smaller ∆ value than another.

Trend 2: Ligand Effects

Compare the complexes in trends 1 and 2 above. Which ligand, water or ammonia, is stronger on the spectrochemical series?

* Below are some data for octahedral Ti3+ complexes. Rate the ligands in terms of their ability to split the d orbitals (small  to large).

|  |  |  |
| --- | --- | --- |
| Ligand | Absorbance, cm-1 | Ranking (1= small  |
| H2O | 19,000 |  |
| Urea | 16,800 |  |
| F- | 17,000 |  |
| Cl- | 11,800 |  |
| Br- | 10,500 |  |

* Below are some data for octahedral Cr+3 complexes. Rate these ligands in terms of their ability to split the d orbitals (small  to large).

|  |  |  |
| --- | --- | --- |
| Ligand | d orbital splitting,  | Ranking (1= small  |
| H2O | 575 nm |  |
| Oxalate | 571 |  |
| NCS- | 562 |  |
| NH3 | 465 |  |
| en | 463 |  |
| CN- | 374 |  |

* Below are some data for octahedral Co+3 complexes. Rate these ligands in terms of their ability to split the d orbitals (small  to large).

|  |  |  |
| --- | --- | --- |
| Ligand | d orbital splitting, kJ/mol | Ranking (1= small  |
| F- | 156 |  |
| NH3 | 273 |  |
| en | 285 |  |
| H2O | 217 |  |
| Ox | 214 |  |
| CN- | 400 |  |

Using data like this for many compounds and ligands, chemists have arranged common ligands into the spectrochemical series. You do not need to memorize the order of ligands.**CHALLENGE PROBLEM**

Based on what you learned from the previous questions on relative ranking of ∆o for different ligand classes, for each cobalt complex below, draw a d-orbital splitting diagram and fill with electrons (hint: think about geometries and type of ligand).

[Co(NH3)6]2+

[Co(H2O)6]2+

Tetrahedral [CoCl4]2-

The crystal field splitting for a tetrahedral complex is smaller than that for an octahedral complex. Can you think of a reason why this is the case?

* The colors of these complexes are red, yellow and blue. Assign the correct color to each.

**Guided Reading part 4 due by class time Wednesday Oct 5, 2016**

Read Topic 9B.1(d)

Given that common oxidation states of iron are +2 and +3, what is the likely most common oxidation state of chromium when found in minerals in the Earth’s crust?

Read Topic 8E.1(b)

What is the likely most common oxidation state of aluminum in minerals from the Earth’s crust? Does this match your intuition given its placement on the periodic table?

Read Topics 8D.1(a) and 8D.2(a), and examine Figure 8D.3

What is the coordination environment of Be atoms in the beryllium hydride structure?

What color is emerald? Approximately what wavelength light would emerald absorb?

Read topic 8E.2(b)

What color is ruby? Approximately what wavelength light would emerald absorb?

Read “The Science of Color,” volume 2, edited by Alex Byrne and David R. Hilbert, MIT Press, Cambridge MA, 1997, pp. 10-17 (available on Sakai).

Assuming that the colors of rubies and emeralds are both due to an octahedral chromium environment, a) draw a picture of the electronic transition that occurs when the chromium ion absorbs light, and b) which gemstone, ruby or emerald, has a larger ∆o for chromium?

**In class activity Day 4**

**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 examine the 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.

**CHALLENGE PROBLEM**

The diagram[[2]](#footnote-2)‡ 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. ‡ the polyhedron formed when triangles join all 6 ligands has 8 faces, hence the name octahedron, which is one of the 5 Platonic solids. [↑](#footnote-ref-1)
2. ‡ “Readings on Color; The science of color,” volume 2, by Alex Byrne and David R. Hilbert, MIT Press, 1997 [↑](#footnote-ref-2)