COLOR IN MINERALS

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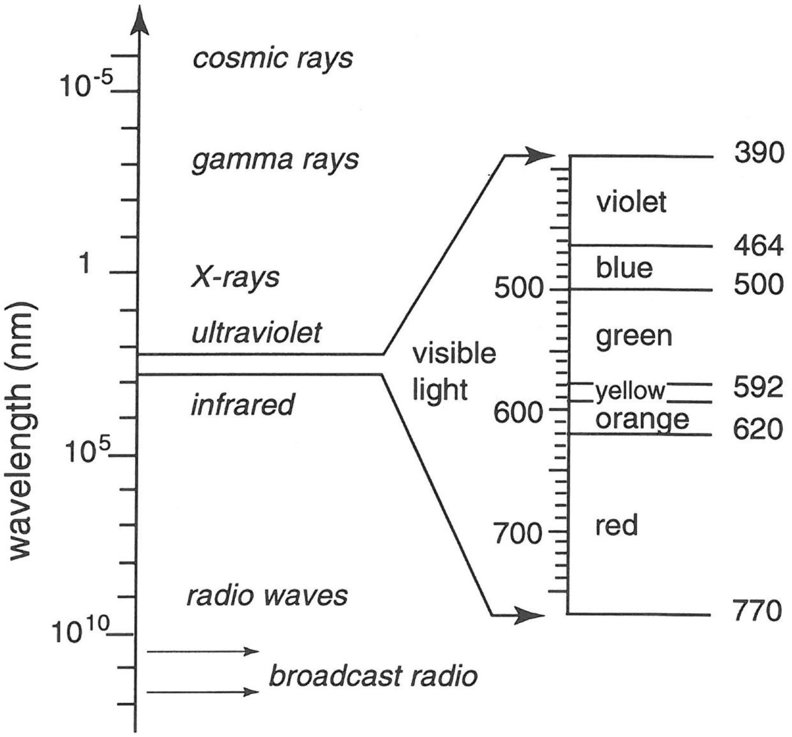
Why do minerals have color? When is that color diagnostic, and when it is likely to fool you? Why is color important, and what can it tell us about the chemistry of minerals? Today's exercise will try to answer some of these questions, and to introduce you to the fascinating world of mineral spectroscopy, where chemistry meets mineralogy!

What is color, exactly? The color perceived by the human eye can be thought of as the sum of the wavelengths that reflect or transmit off an object, with the dominant color being the dominant wavelength of light. For the most part, color comes about through the interaction of light waves with electrons (Nassau, 1980) in a range of energies that can be perceived by the human eye. Human eyes can only distinguish about 200 gradations of color (hues) in the small region of visible light from about 400-800 nm in wavelength. Your brain creates these colors by using three sets of cones in your eyes, in the same combinations used by your television set:

black white
red green
yellow blue

Notice that the wavelengths of visible light make up only a small portion of the electromagnetic spectrum shown below.



Studies of color can often be confusing because spectroscopists use a variety of units to explain their work! These units fall into two categories: those expressed in terms of the **energy** of light (cm^{-1}, eV, and kJ) or in terms of its **wavelength** (μm, nm, or Å). In the study of color in minerals, the two types of units most often used are wavenumbers (cm^{-1}) and wavelengths (usually expressed as nm). To convert from nm to cm^{-1}, simply take the reciprocal of nm and multiply times 10^7. Here's a table to help you navigate between these units:

Units Used for the Study of Color

Wavelength Units		Energy Units	Resultant
Nanometers (nm)	Ängstroms (Å)	**Wavenumbers** (cm^{-1})	Color
300	3,000	33,333	Ultraviolet
400	4,000	25,000	Violet
450	4,500	22,222	Blue
500	5,000	20,000	Green
550	5,500	18,182	Yellow
600	6,000	16,667	Orange
700	7,000	14,286	Red
800	8,000	12,500	Near-Infrared
900	9,000	11,111	Near-Infrared
1000	10,000	10,000	Near-Infrared
1500	15,000	6,667	Infrared
2000	20,000	5,000	Infrared
2500	25,000	4,000	Infrared

This exercise will focus on the chemistry that is responsible for making minerals (and many other things in our world) the colors that they are. Nassau (1987) describes the 15 phenomena that cause objects to have color; they are listed on the next page. Note that all but the first of these causes are created by interactions of electrons with electromagnetic radiation, usually in the central range of the electromagnetic spectrum. Fortunately, in order to understand color in minerals, we only need to examine a few of the items in Nassau's compilation. These include numbers 4, 5, 7, and 11 on the list. This lab will focus on colors caused by transition metals (4 and 5). We will learn to use mineral spectra to understand colors in minerals and gemstones, and in turn, learn to use color to help determine mineral crystal chemistry. In particular, we would like to use color (and the absorption spectra of minerals) to learn something about the valence states and coordination environments of transition metals in minerals.

Let's begin by concentrating on the transition elements. A transition element is a metal ion with a partly filled *d* or *f* shell. Generally this definition includes not only neutral ions with those characteristics, but also ions in their commonly-occurring oxidation states. The so-called first-series transition elements are those with full shells of electrons below 3*p*, and incompletely full 3*d* orbitals. Another way of saying this is that they have a configuration of

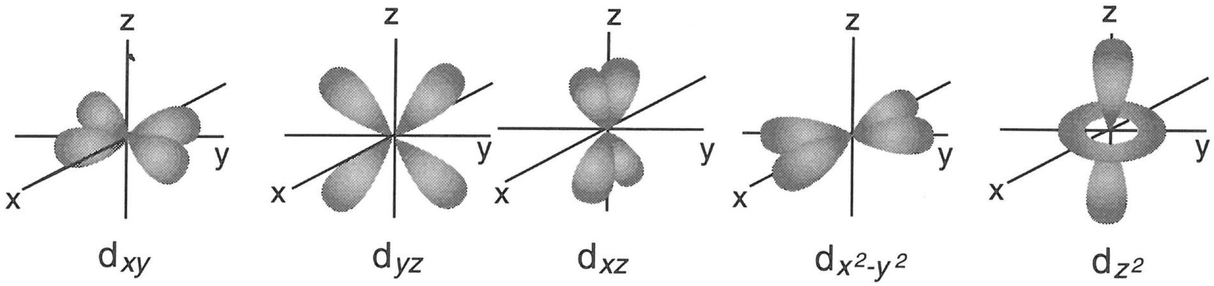
$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{\,10-n}\ 4s^{1\text{ or }2},$$

where n is an integer from 0 to 10. How many electrons would an atom have in order for one or more to occupy a 3*d* orbital?

Table 1. Examples of the fifteen causes of color (adapted from Nassau, 1987)

Number	Phenomenon	Examples
1.	**Incandescence** (release of thermal vibration energy)	flames, lamps, carbon arc, limelight; white color of the Sun results from 5700 °C emission
2.	**Gas Excitations** (excitations of specific atoms)	vapor lamps, lightning, auroras, gas lasers
3.	**Vibrations and Rotations** (rock and roll of atoms)	blue ice, water, iodine, blue gas flame
→ 4.	**Crystal Field Transitions** (where chromophore[1] is major element)	pink rhodochrosite, olivine, almandine and spessartine
→ 5.	**Crystal Field Transitions** (where chromophore is trace element)	ruby, emerald, chrysoberyl, rubellite, morganite
6.	**Molecular Orbitals in Organics** (electrons belong to several atoms)	dyes, including hair dyes and indigo blue (extracted from sea shells), bioluminescence of fireflies
→ 7.	**Intervalence Charge Transfer** (electrons shared by adjacent atoms)	blue sapphire, magnetite, kyanite, vivianite, aquamarine
8.	**Energy Bands in Metals**	copper, silver, gold, brass, iron metal
9.	**Energy bands in Semiconductors**	silicon, galena; zinc, cadmium, and vermillion paint pigments
10.	**Doped Semiconductors**	blue (B-doped) and yellow (N-doped) diamond
→ 11.	**Color Centers**	amethyst, smoky quartz, blue and yellow topaz, zircon, citrine
12.	**Dispersive Refraction**	rainbows, halos, stars in gemstones
13.	**Scattering**	blue sky, red sunset, blue moon, blue eyes, butterflies
14.	**Interference**	oil slicks, soap bubbles, coatings on camera lenses
15.	**Diffraction**	opal, moonstone, diffraction gratings, most liquid crystals

The 3*d* orbitals have the following shapes:



If an ion is *isolated* (i.e., as when floating around unbonded in outer space), all these orbitals are perfectly shaped and *have the same energy* (we call this *degenerate*). Thus, electrons filling the 3*d* orbitals of such an ion would have an equal probability of being located in any of them. Graphically, we illustrate this by a drawing like this:

3*d*

— — — — —

Each individual line symbolizes one of the five 3*d* orbitals, and all the orbital levels lie along the

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[1] A chromophore is an element that gives color to the material that contains it.

same horizontal line, meaning that they have the same energy.

If you look at the orbital shapes carefully, you will see that there are two distinct types of orbitals: d_{xy}, d_{yz}, and d_{xz}, collectively referred to as the t_2 or t_{2g} orbitals, and $d_{x^2-y^2}$ and d_{z^2}, collectively referred to as the e or e_g orbitals.[2]

In an isolated ion, a 3*d* orbital with ten electrons (all would have the same energy) would be drawn schematically like this:

$$\begin{array}{cc} 3d\,(t_{2g}) & 3d\,(e_g) \\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow} & \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}. \end{array}$$

Each electron is represented by an arrow; the up or down direction of the arrow indicates whether the electron is orbiting the nucleus in a clockwise or counterclockwise direction.

How would electrons be distributed among the 3*d* orbitals if there are fewer than ten of them? According to Hund's first rule, that electrons don't pair up until all the available orbitals, no matter what energy, already contain an electron. So for example, an element with five 3*d* electrons would have one electron in each orbital.

These simple, equal energy orbital configurations only work for isolated ions. What happens when a transition metal ion is incorporated into a mineral structure? You already know that most mineral structures contain cations in 4-fold, 6-fold, 8-fold, or 12-fold coordination polyhedra with oxygen as nearest neighbors. These polyhedra are sketched in the figure on the next page. It's easy to get these coordinations confused, unless you remember that the numbers refer to the number of *corners* on the polyhedra, as follows:

Terminology for Coordination Polyhedra

Coordination Polyhedron	Number of corners	Number of faces	Term Used	Size of Cations
tetrahedron	4	4	4-fold	smallest
octahedron	6	8	6-fold	↓
cube	8	6	8-fold	↓
dodecahedron (cuboctohedron)	12	14	12-fold	largest

The anions surrounding the transition metals in a mineral structure do not form a perfectly

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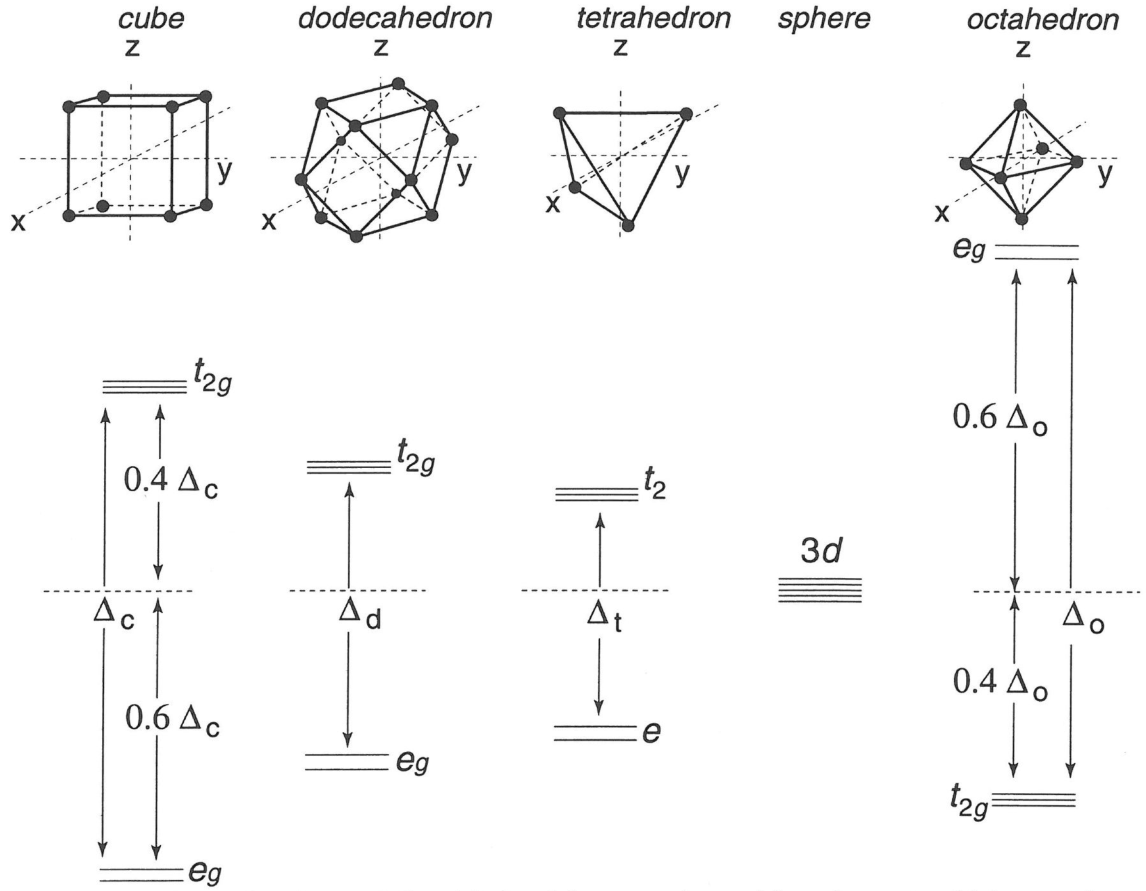
[2] The terms t_2, t_{2g}, e, and e_g come from group theory symmetry notation used by chemists to describe the shape of the orbitals: *e* means there are two orbitals per principle quantum number (so-called "two-fold degeneracy"), while *t* indicates three orbitals ("three-fold degeneracy"). The subscript 2 indicates that the sign of the wave function doesn't change with rotation around the axes diagonal to the Cartesian axes, and *g* means that the wave function does not change sign if inverted through the center of the atom. For more information, consult a chemistry text!

spherical, uniform distribution of charge around the transition metal. Instead, the charge is unevenly distributed, with negative charge being concentrated in the vicinity of the anions at the polyhedral corners. The effect of this non-spherical charge distribution is to destroy the degeneracy, which means that the energies of the orbitals are no longer all the same. Put simply, the electrons in these orbitals are repelled by the negative charge of the neighboring oxygen ions. Electrons in orbitals that are close to the oxygen neighbors are repelled more strongly than those that are further away from the oxygens. Thus the energies of the formerly equivalent 3*d* orbitals split to some with higher energies and some with lower energy levels. The total energy must stay the same.

This is shown schematically below. The degenerate energy levels for the case of an ion in a spherical field are shown in the fourth column. The small separation in the five levels is only meant to distinguish them and is not intended to imply a true energy difference. Now consider the octahedral coordination polyhedron. The *x-y-z* axes in this figure correspond to those of the previous one. Thus the $d_{x^2-y^2}$ and d_{z^2} orbitals of the central transition element, which are oriented *along* the *x*, *y*, and *z* axes, point directly toward the neighboring oxygen ions. The repulsion raises their energy compared to the three t_{2g} orbitals, which lie *between* the axes. The sum of the energies of the five orbitals is the same as for the isolated degenerate case, so the energy of the other three orbitals must be lowered to compensate for the increase in the e_g energies.



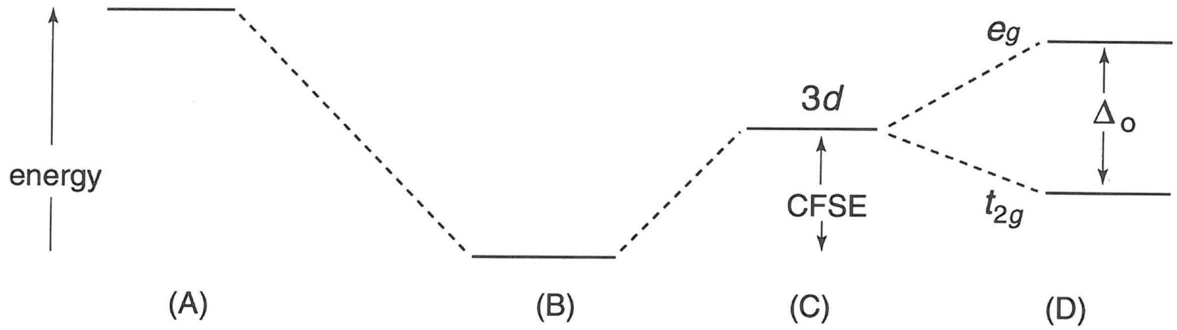
The difference in energy between the lowest orbitals and the highest orbitals is called **crystal**

field splitting and is represented by the symbol Δ (or sometimes, 10D*q*). Crystal field splitting energies are dependent on many factors, including (1) the symmetry of the coordination environment (i.e., its coordination number) as we have just learned, (2) the valence state of the cation, (3) the strength of its bond with the surrounding anions, (4) the distance between the cation and the surrounding anion, (5) pressure, and (6) temperature. Of these, (1) and (2) are extremely useful (although 3-6 also have their utilities for specific problems; see Burns' book for more information!) Many techniques for mineral analyses can tell you **what** is in your mineral, but not **where** the cations are located (i.e., what kinds of coordination polyhedra they are in) nor **which** valence states they have. For example, an electron probe analysis of a mineral might tell you that your sample contains the transition metal Fe, but it cannot tell you which sites the Fe atoms are located in, nor how much of the Fe is Fe^{3+} or Fe^{2+}. In this exercise, we will learn to use absorption spectra of minerals to tell us about the coordination number and valence state of transition metals in minerals.

You have already studied Pauling's rules and learned the usefulness of using radius ratios to predict coordination geometries of cations in minerals. Crystal field theory gives us another way to predict cation coordination, because the energies of the Δ values vary according to the coordination as seen in the figure above. This can be expressed mathematically as

$$\Delta_o : \Delta_c : \Delta_d : \Delta_t = 1 : -\frac{8}{9} : -\frac{1}{2} : -\frac{4}{9}$$

These ratios correspond to the magnitude of the splitting between t_{2g} or t_g orbitals and e_g or e orbitals. The minus sign implies that the relative stabilities of the two orbital types are reversed in the two coordinations; i.e., in octahedral coordinations, the e_g orbitals are higher energy, whereas in tetrahedral, cubic, and dodecahedral coordinations the t_{2g} orbitals are higher. **This relationship tells us that the splitting for a given transition metal will be largest when it is in octahedral coordination and smallest when it is in tetrahedral coordination**. The Δ values obtained from real absorption spectra of minerals can be therefore be used to determine which coordination environment a transition metal is occupying.



A related concept, the **crystal field stabilization energy (CFSE)**, is derived by weighting the contributions of electrons in various orbitals. It can be thought of as the total change of energy between the perfectly symmetrical state and the coordinated state. In the diagram above (after Burns, 1993), (A) represents the energies of the transition metal 3*d* orbitals in a free cation (outer space). (B) shows the energy of the orbitals once the cation is placed in a site surrounded by anions; the orbital energies decrease due to electrostatic attractions. (C) shows the change in orbital energy based on repulsion between anions and the 3*d* electrons in a case where the anions are distributed in a sphere. (D) shows the splitting of the 3*d* orbital energy levels in an octahedral crystal field.

It's actually easy to calculate CFSE, which then allows you predict which transition metals will prefer which kinds of sites in minerals. Think of CFSE as the algebraic sum of the energies of electrons in all the orbitals. Orbitals with energies that are shifted **down** as a result of crystal field splitting are considered **negative**, and orbitals that are shifted **up** are considered **positive**. For example, in octahedral coordination, each electron in a t_{2g} orbital has a lower energy than it would have in an isolated polyhedron. Therefore, every t_{2g} electron stabilizes the structure by an amount equal to 0.4 Δ_o. It follows that every electron in an e_g orbital would destabilize the structure by an amount equal to 0.6 Δ_o.[3] CFSE represents the sum of the stabilizing and destabilizing effects of cations in excited and unexcited orbitals. High values for CFSE indicate that a cation is energetically preferred in a crystal site with that coordination type.

If you have actual data for $CFSE_o$ and $CFSE_t$ (see the table in your worksheet), you can calculate a parameter called Octahedral Site Preference Energy (OSPE), which is the difference between the two values. OSPE means just what it says: it's a measure of how much that cation prefers being in octahedral coordination relative to tetrahedral coordination. This allows us to make predictions about which cations might want to go into which sites in a mineral structure.

If the energies of the orbitals are split, it becomes possible for electrons to move back and forth between orbitals when energy is added (this is usually in the form of light). These transitions, of course, must be associated with energy gain or loss to the atom. Thus an electron could jump from a lower energy level to a higher one by absorbing light with an energy equal to Δ. In other words, only a very specific wavelength would be absorbed by a particular transition element in a particular site in a silicate mineral. Transition metals are particularly important in this regard, since the small energy differences between the split orbitals in certain sites often correspond to those in the visible and near-infrared region of the electromagnetic spectrum. Sunlight contains a full set of wavelengths, so it excites lots of electron jumps, causing colors in many minerals.

In the laboratory, we can measure absorption by using the relationship:

$$E = hc / \lambda$$

where E = energy, h = Planck's constant, c = the velocity of light, and λ = wavelength. A spectrometer passes monochromatic (single λ) light through a sample of known thickness, and

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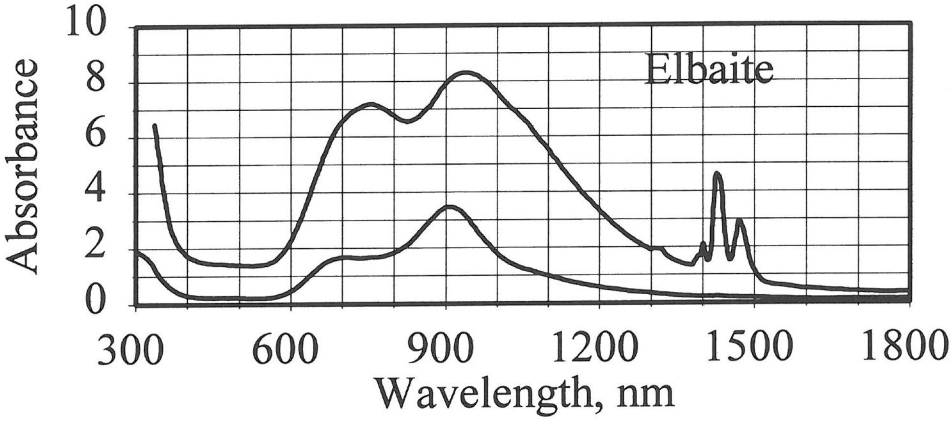
[3] The multiples 0.6 and 0.4 come from simple algebra: the energy of the six possible electrons in the t_{2g} orbitals (6 x 0.4 = 2.4) is compensated by the energy of the four electrons in the e_g orbitals (4 x 0.6 = 2.4); the total of stabilizing and destabilizing effects should be zero if all the orbitals are full!

determines the loss of intensity (absorbance) for each wavelength tested. The result is a spectrum for that mineral. The peaks in these spectra represent the wavelengths that are absorbed by the sample and the troughs correspond to the transmitted wavelengths.

The important thing for this exercise is that the value of Δ can be determined from absorption spectra of transition metal-bearing minerals because its energy generally corresponds to the visible and near-infrared region of the electromagnetic spectrum. The value of Δ is also therefore related qualitatively to the color of the mineral.

For example, here are the spectra of octahedral Cu^{2+} in elbaite, which is a kind of tourmaline. Wavelength is shown on the *x* axis, and the *y* axis shows the amount of absorbance that occurs at each wavelength. The magnitude of the absorbance is a function of the thickness of the crystal.[4] There are two lines shown corresponding to spectra taken at two different angles to the crystal, one in which light is vibrating parallel to the *c* axis, and one with light vibrating perpendicular to the *c* axis. The two spectra are different because tourmaline is a uniaxial mineral; this means that the densities of atoms in the two orientations are different. The maximum absorption in the visible region occurs in two peaks at about 10,870 cm^{-1} and 14,286 cm^{-1}, or about 920 and 700 nm. This absorption occurs in the red to infrared region of the visible light spectrum. Sunlight passing through this elbaite has its red wavelengths absorbed because they are the right energy to cause electrons to jump between split energy levels of the Cu^{2+} atoms. Light that passes through the elbaite is in the range from 400-600 nm, corresponding to blue light. Thus, this elbaite appears blue.



For completeness, it is worth mentioning two other causes of color in minerals (7 and 11 on Nassau's list above). Color produced by charge transfer processes is similar to crystal field-induced color, except instead of electrons jumping *between orbitals* within the same atom, electrons can jump *between atoms*. These intervalence transfers of charge can create very intense colors from very small numbers of shared electrons. In sapphire, for example, Fe^{2+} and Ti^{4+} ions in adjacent sites (ones that would normally be occupied by Al) pass an electron back

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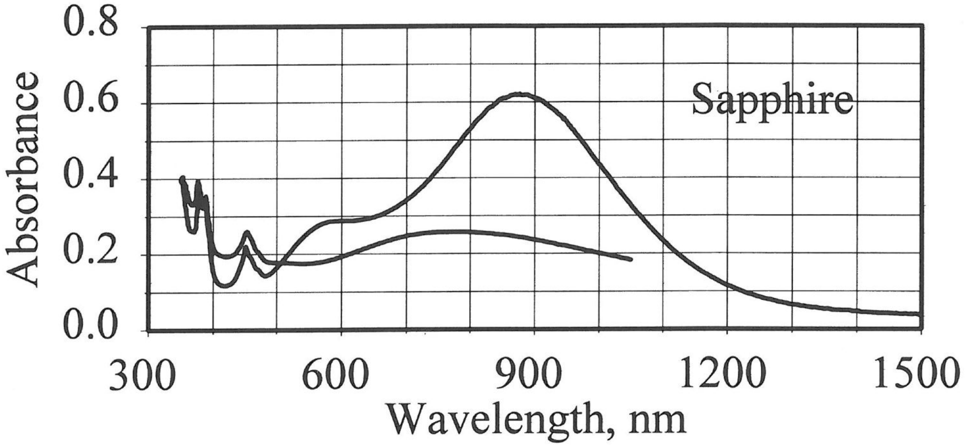
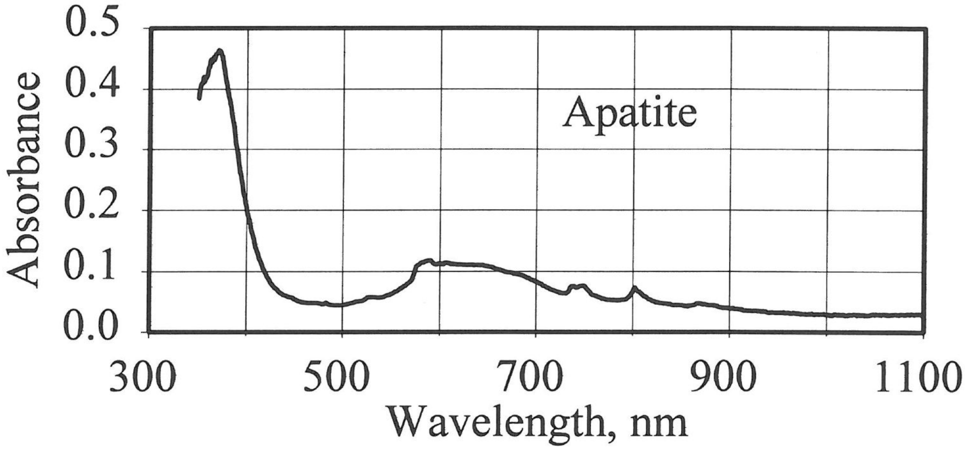
[4] In this lab exercise, absorbance is normalized so that all the spectra appear to have been measured on crystals that are 100 microns thick, in order to allow direct comparison of different spectra.

and forth. At one instant, the charge is distributed as Fe^{2+} and Ti^{4+} , and the next instant it is Fe^{3+} and Ti^{3+}. Very small amounts of Fe^{2+} and Ti^{4+} in an otherwise pure corundum crystal (Al_2O_3), even down at ppm and maybe ppb levels, can still make a sapphire blue. In the spectrum shown here, peaks at 25,680 cm^{-1} and 22,220 cm^{-1} represent Fe^{3+} and the broad bands spanning 17,800 cm^{-1} to 14,200 cm^{-1} represent intervalence charge transfer peaks.



Color can also be derived from something called a "color center" in a crystal structure. These occur when materials with otherwise perfect structures trap electrons in metastable sites. The traps can be atomic vacancies in the structure (like the electrons filling F vacancies that cause fluorite to be purple), substitutions of trace amounts of color-causing atoms for non-transition metals (as in the case of Fe^{3+} substituting for Si^{4+} in amethyst), or just locations in the crystal lattice where a minor charge deficiency provides a place for an electron to rest (as in diamond). In many cases, heat or another form of energy such as radiation can provide enough energy for an electron to "escape" from its trap, and color changes can occur. Heat and radiation treatments are frequently used in the gemstone industry to change the color of stone; for example, heat treatment can turn ugly brown zircons into gemmy blue ones. The apatite shown below has probably been heat-treated to change it from green to blue.



All of the spectra in this lab come from the Mineral Spectroscopy Home Page created by George Rossman at Caltech, which can be found at:

http://minerals.gps.caltech.edu/

Many of the spectra there can be downloaded and printed out as images or saved as ASCII text files. The Home Page contains a lot more information about color in minerals than can be given here. Check out your favorite mineral!

Name(s):____________________ ________________________ ______________________

WORKSHEETS

1. Fill in the blanks to learn more about Δ_o values:

High Spin Electronic Configurations for *3d* Orbitals in Octahedral Coordination

Cation	Number of 3*d* electrons	Electronic configuration					*Unpaired* electrons	CFSE
			t_{2g}		e_g			
Ca^{2+}, Sc^{3+}, Ti^{4+}	—	—	—	—	—	—	—	0
Ti^{3+}	—	—	—	—	—	—	—	0.4 Δ_o
Ti^{2+}, V^{3+}	—	—	—	—	—	—	—	___Δ_o
V^{2+}, Cr^{3+}, Mn^{4+}	—	—	—	—	—	—	—	___Δ_o
Cr^{2+}, Mn^{3+}	—	—	—	—	—	—	—	___Δ_o
Mn^{2+}, Fe^{3+}	—	—	—	—	—	—	—	___Δ_o
Fe^{2+}, Co^{3+}, Ni^{4+}	—	—	—	—	—	—	—	___Δ_o
Co^{2+}, Ni^{3+}	**7**	↑↓	↑↓	↑	↑	↑	**3**	Δ_o
Ni^{2+}	—	—	—	—	—	—	—	1.2 Δ_o
Cu^{2+}	—	—	—	—	—	—	—	___Δ_o
Cu^{+}, Zn^{2+}, Ga^{3+}, Ge^{4+}	—	—	—	—	—	—	—	___Δ_o

Reminder: to calculate CFSE, assign a weight of 0.4 Δ for each electron that occupies a t_{2g} or t_2 orbital, and 0.6 Δ for each electron in an e_g or e orbital; assign a positive charge to the electrons in lower (stabilizing) energy orbitals and a negative charge to those in higher(destabilizing) energy orbitals. When you sum up these contributions (write the sum in the right-hand column of each table), you get the net stabilization energy (CFSE) of each transition metal.

The table above gives the predicted CFSE for the various cations, but it is expressed in terms of a fraction multiple of Δ_o. Experimental data on Δ_o are then used to estimate an actual value for CFSE. In the following table (values from Table 2.5 in Burns, 1993), we explore the relationships between these variables.

Relationship Between Crystal Field Splittings and CFSE for Octahedral Coordination

Cation	Δ_o (cm^{-1})	CFSE (right column, above)	CFSE (cm^{-1}) in hexahydrate
Ti^{3+}	___________	_____Δ_o	7,580
V^{3+}	___________	_____Δ_o	15,280
V^{2+}	12,600	_____Δ_o	15,120

Cr^{3+}	____________	_____Δ_o	20,880
Cr^{2+}	____________	_____Δ_o	8,340
Mn^{3+}	____________	_____Δ_o	12,600
Mn^{2+}	7,800	_____Δ_o	0
Fe^{3+}	13,700	_____Δ_o	0
Fe^{2+}	____________	_____Δ_o	3,760
Co^{2+}	____________	_____Δ_o	7,440
Ni^{2+}	____________	_____Δ_o	10,200
Cu^{2+}	____________	_____Δ_o	7,800

From this table you can generate a general sequence of Δ_o values, which illustrates some of the general trends in Δ_o:

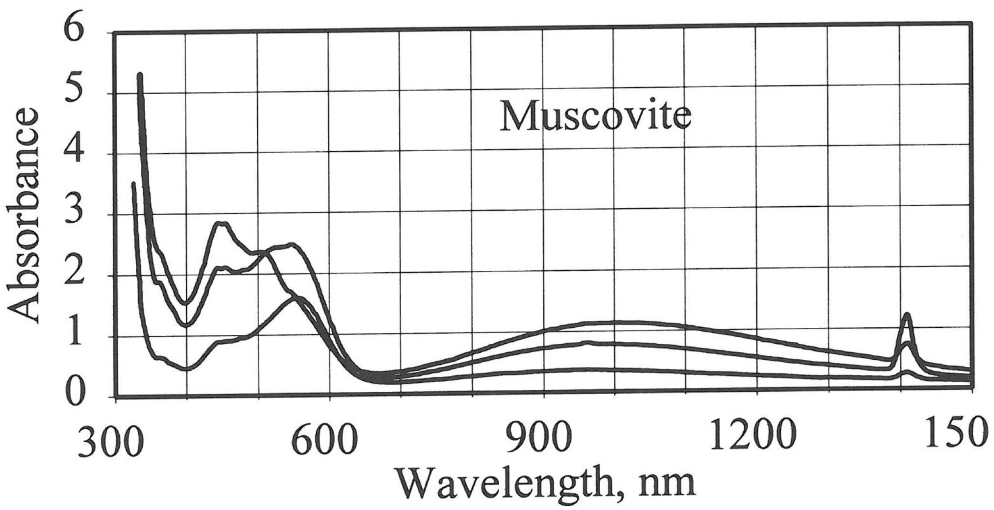
Mn^{2+} < ____< ____< ____ < ____ < ____< ____< ____< ____< ____< ____< Mn^{3+}

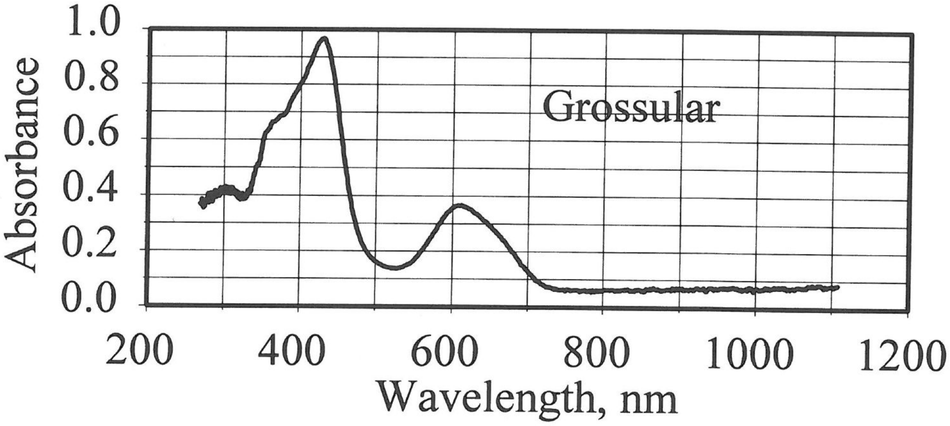
From this list, what can you conclude about the values of Δ_o for trivalent cations relative to the corresponding divalent ions? (Pick one!)

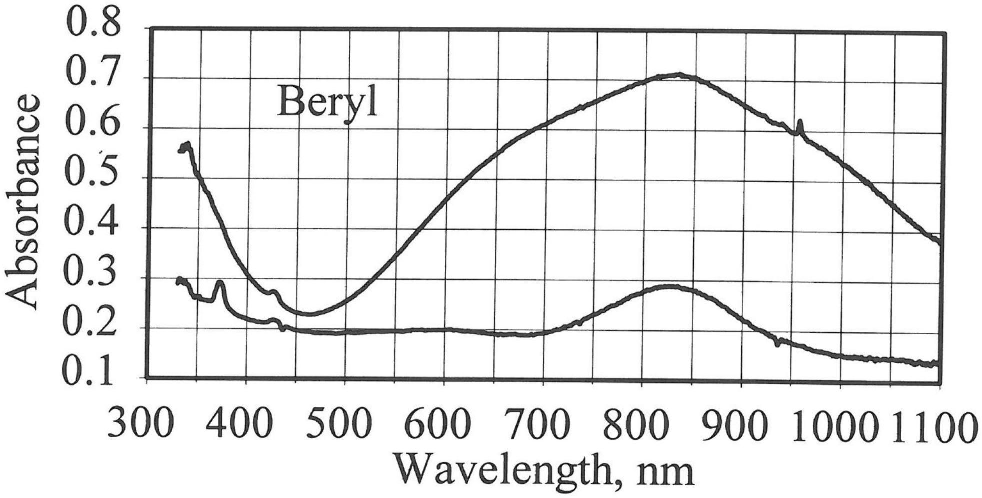
$\Delta^{3+} > \Delta^{2+}$ OR $\Delta^{3+} < \Delta^{2+}$

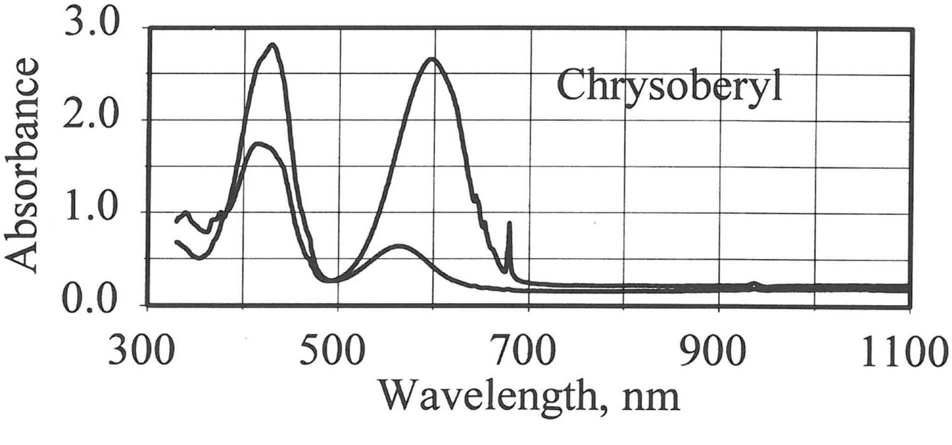
HINT: you will use this relationship to help you interpret the spectra in question #3!

2. Mystery Minerals: What color am I? For each of the spectra given below, identify the region of minimum absorption, where light is NOT being absorbed and decide what color this mineral might be! Warning: some of these minerals have unusual colors!

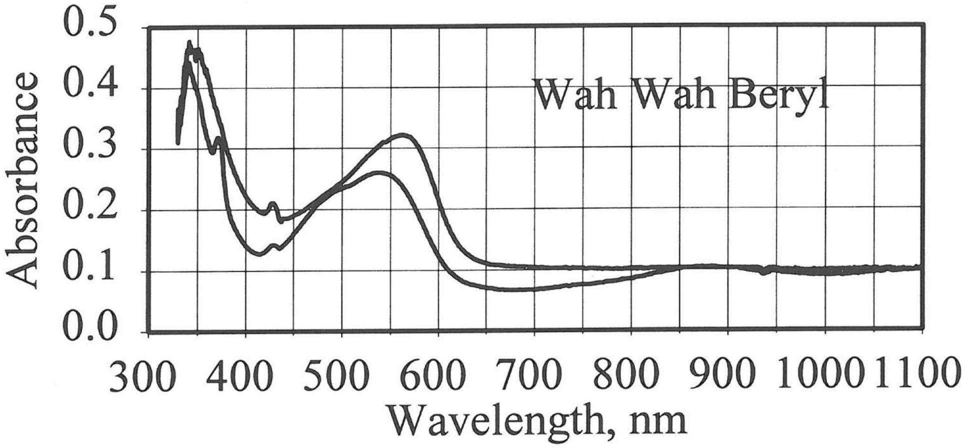


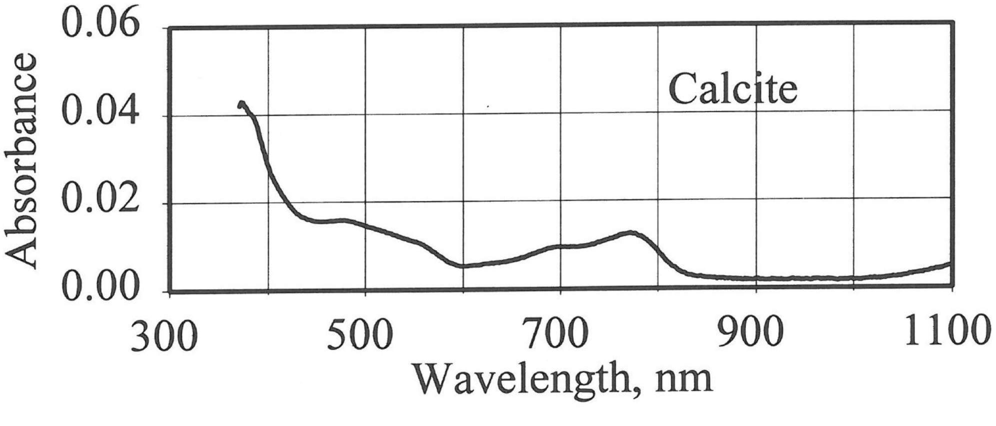

Grossular
Absorbance
1.0
0.8
0.6
0.4
0.2
0.0
200
400
600
800
1000
1200
Wavelength, nm


Beryl
Absorbance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
300
400
500
600
700
800
900
1000
1100
Wavelength, nm

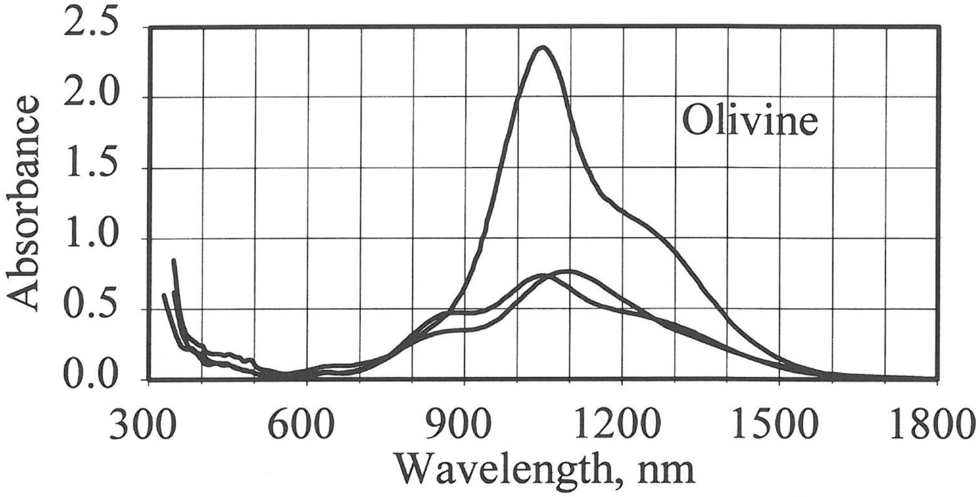

Chrysoberyl
Absorbance
3.0
2.0
1.0
0.0
300
500
700
900
1100
Wavelength, nm

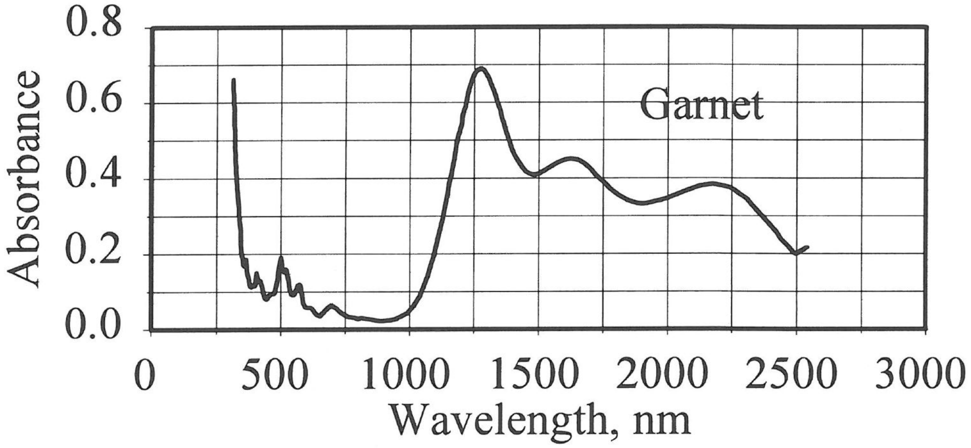
3. Earlier in this exercise, we pointed out that one of the best uses for crystal field theory is to help distinguish between multiple valence states of the same element. Two spectra containing the element Mn are shown below. One contains Mn^{3+} and the other Mn^{2+}. First, determine the maximum absorption in each and convert it to wavenumbers. Then, use the order of Δ_o values you determined in question #1 to determine which mineral contains which valence of Mn.





4. Below you will find spectra of Fe^{2+} in two minerals, fayalite (Fe-rich olivine) and pyrope (Mn- and Fe-rich garnet). Determine the energy (in wavenumbers) of the most intense absorption peak in each spectrum, and decide which one has Fe^{2+} in octahedral coordination, and which in eight-fold coordination. Compare this to the minerals staurolite and spinel, in which Fe^{2+} has maximum absorbance at around 1400-2200 nm and 2070 nm, respectively. What type of coordination environment do you think the Fe^{2+} occupies in these minerals, and why?





5. Crystal field theory is useful not just for understanding color, but for understanding why different elements occupy different sites in minerals. Calculate the CFSE values for cations in tetrahedral coordination.

High Spin Electronic Configurations for 3*d* Orbitals in Tetrahedral Coordination

	Number of	Electronic configuration					*Unpaired*	
Cation	3*d* electrons	*e*		t_2			electrons	CFSE
Ca^{2+}, Sc^{3+}, Ti^{4+}	___	___	___	___	___	___	___	0
Ti^{3+}	___	___	___	___	___	___	___	0.6 Δ_t
Ti^{2+}, V^{3+}	___	___	___	___	___	___	___	___Δ_t
V^{2+}, Cr^{3+}, Mn^{4+}	___	___	___	___	___	___	___	___Δ_t
Cr^{2+}, Mn^{3+}	___	___	___	___	___	___	___	___Δ_t
Mn^{2+}, Fe^{3+}	___	___	___	___	___	___	___	0 Δ_t
Fe^{2+}, Co^{3+}, Ni^{4+}	___	↑↓	↑	↑	↑	↑	4	___Δ_t
Co^{2+}, Ni^{3+}	___	___	___	___	___	___	___	___Δ_t
Ni^{2+}	___	___	___	___	___	___	___	0.8 Δ_t
Cu^{2+}	___	___	___	___	___	___	___	___Δ_t
Cu^{+}, Zn^{2+}, Ga^{3+}, Ge^{4+}	___	___	___	___	___	___	___	___Δ_t

Now, use the difference between CFSE$_o$ and CFSE$_t$ to calculate octahedra site preference energy, or OSPE. Note that this assumes that all the coordination polyhedra are regular and undistorted in shape. Real data from papers by McClure (1957) and Dunitz and Orgel (1957) are given below for transition metals in oxides structures (after Burns, 1993).

Note: you can also do a similar type of calculation for preferences of cations for, say, octahedral vs. dodecalhedral sites. But this is the one with the most utility, however, because most sites for transition metals in minerals are either tetrahedral or octahedral.

Octahedral Site Preference Energies of Transition Metals

Cation	CFSE$_o$ (Kj/mole)	CFSE$_t$ (Kj/mole)	OSPE (Kj/mole)
Ca^{2+}, Sc^{3+}, Ti^{4+}	0	0	0
Ti^{3+}	-87.4	-58.6	-28.8
V^{3+}	-160.2	-106.7	______
Cr^{3+}	-224.7	-66.9	______
Cr^{2+}	-100.4	-29.3	______
Mn^{3+}	-135.6	-40.2	______

Mn^{2+}, Fe^{3+}	0	0	0
Fe^{2+}	-49.8	-33.1	______
Co^{3+}	-188.3	-108.8	______
Co^{2+}	-92.9	-61.9	______
Ni^{2+}	-122.2	-36.0	-86.2
Cu^{2+}	-90.4	-26.8	______
Zn^{2+}, Ga^{3+}, Ge^{4+}	0	0	0

For divalent cations, the order of OSPE is:

Ni^{2+} > ______ > ______ > ______ > ______ > ______ = ______ = ______

For trivalent cations, the order of OSPE is:

Cr^{3+} > ______ > ______ > ______ > ______ > ______ = ______ = ______

Therefore, if you are crystallizing a mineral (say, a spinel) with both octahedral and tetrahedral sites in it, and you have Cu^{2+}, Cr^{3+}, and Ti^{3+}, your might predict that the Cu^{2+} and Cr^{3+} would prefer octahedral sites, and the Ti^{3+} wouldn't mind occupying tetrahedral sites. It turns out that this theory does accurately predict many observed mineral structures. It can also be used to predict the order by which cations will prefer to leave a melt (where metals are predominantly tetrahedrally coordinated) and enter minerals such as olivine (where they can exist in octahedral coordination).

COLOR IN MINERALS

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INTRODUCTION AND INSTRUCTOR'S NOTES

This lab exercise is adapted from one I've developed over the years to teach crystal field theory to students in my Geochemistry courses. I must confess that although my own research interests lie in this area (I had the good fortune to work with both Roger Burns and George Rossman), I have never included spectroscopy as part of my own Mineralogy courses. Why? ...because I did not think I could present it in a fashion that would make it interesting and relevant to my students without oversimplification. Now that George Rossman has a home page with easily accessible spectra and images, I've changed my mind. In preparing for this workshop, I've also reflected on the fact that the students I've had in Mineralogy are almost universally interested in gemstones, and by association, in their colors. I've tried to write this lab exercise to take advantage of that interest.

Unfortunately, most Geology departments do not have the equipment to make measurements of optical spectra in house. If you do, I encourage you to change this lab around so that the students actually take some spectra themselves. Sample preparation requires only that you have a slice of the mineral that is polished on both sides, a relatively easy undertaking with some elbow grease, a little diamond grit, and a polishing setup. If you lack the spectrometer, this "lab" becomes more of an exercise. To add a little "hands-on" work to it, you might consider pulling colored specimens from your own collections, and then ask the students to match spectra with samples. This reinforces the relationship between how the spectra look and how the colors actually appear. A visit to or from a local jeweler (look for someone with Gemological Institute of America certification) might also give you a chance to see some nice colored gems; most jewelers today also stock treated and untreated stones, which your students might want to see.

I also encourage you to take advantage of George Rossman's Mineral Spectroscopy Home Page (see information below), to which new spectra are constantly being added. Take a look at it from time to time; new updates will be added that will also stimulate good discussions of spectroscopy. Most of the entries for mineral spectra contain brief discussions of the causes of color that are applicable. You might want to ask your students to download and manipulate the spectra. The data files all contain information about the thickness of each sample when it was run; you could ask your students to download some spectra, normalize them all to the same thickness, and talk about the Beer-Lambert law and the relationship between absorption and concentration.

Finally, I encourage you to contact me (mddyar@amherst.edu) or George Rossman (see his home page for information on how to reach him) if you have questions about the subject matter presented here. I hope that some of my own enthusiasm for this subject matter and this lab will prove contagious, and inspire you to work with your students on this topic. Really, your imagination is the only limit to the interesting ways to present mineral spectra!

SHOW AND TELL

All of the spectra in this lab come from the Mineral Spectroscopy Home Page created by George Rossman at Caltech, which can be found at:

http://minerals.gps.caltech.edu/

We all owe George a huge debt of thanks for creating this facility, and I am particularly grateful that he allowed us to use the spectra in this exercise. Many of the spectra can be downloaded and printed out as images or saved as ASCII text files. This gives you an opportunity to go beyond the lab ideas presented here into territory of particular interest to you or your students.

BACKGROUND

I would insert this lab at the point in my course where I have completed the study of symmetry and want to begin basic mineral chemistry. I talk very briefly about atoms (what's a neutron, proton, electron; what are the symbols for them; charge neutrality) and then present the Schrödinger equation as a way of constructing the periodic chart. I stress that it also describes the positions of electrons in space around the nucleus, and I use some wood models to show them the shape of the orbitals. We then break into groups and run through the following exercise (it takes 30-45 minutes) to get them used to thinking about the periodic chart:

Periodic Chart Exercise

1. Use the periodic chart to decide what characterizes each of the following:

A: Transition elements (e.g., Sc through Zn; also Y through Cd)
B: Lanthanides (Ce through 72)
C: Actinides (Th through Lr)
D: Alkali Metals (e.g., Li, Na, K, Rb)
E: Alkaline Earths (e.g., Be, Mg, Ca)
F: Halogens (F, Cl, Br, I)
G: Noble Gasses (He, Ne, Ar)
H: Platinum Group Elements (e.g., Ru, Os, Rh)

2. Calculate the atomic weight of Mg_2SiO_4.

Depending on the preparation of my students, sometimes I also have the class do an exercise predicting which valences each atom likes to take on, with emphasis on rock-forming elements. At this point it is also convenient to talk about ionic radius, emphasizing the fact that atoms have different radii in different coordinations with oxygen (John Brady has an excellent lab exercise on how ionic radii can be determined!) Pauling's Rules (with corollaries) and Hund's rules are also important background for this exercise.

Once the class seems comfortable with these fundamentals of chemistry, they are ready to tackle color in minerals. The materials included here may cover one or two lab periods depending on your student population. The only materials needed would be a periodic chart of the elements and, perhaps, wood models of the shapes of the *d* orbitals to aid in understanding the crystal field theory. It's also nice to have examples of minerals of different color (only be sure you know why each one is colored the way it is -- the students are bound to ask!) If you can gather them together, it's particularly nice to have examples of something close to the six garnet end members (for obvious reasons).

I've included far more questions here than can be dealt with in a single lab period, but I am hopeful that you will choose the parts of this document that seem interesting and use them in any way you want. To help you do this, I've assembled the following table with a guide to some of the spectra that appear on the Mineral Spectroscopy Home Page, along with some references to get you started. Many other references are given in the list on the Home Page. I hope you find this useful...

Summary of Some of the Mineral Spectra Available on the Home Page

Mineral	Peak Position (nm)	Peak positions (cm^{-1})	Color	Assignment	Relevant references
ruby	556	18,000	red	Cr^{3+} (oct)	Burns, 1983
	408	24,500			
beryl (Lone P.)	820	12,200	blue	Fe^{2+} (oct)	Rossman's home page
	971	10,300			
	621	16,100			
beryl (WahWah)	556-500	18,000-20,000	red	Mn^{3+} (oct)	Rossman's home page
beryl (syn. em.)	620	16,130	green	Cr^{3+} (oct)	Rossman's home page
	425	23,530			
almandine	505	19,800	red	Fe^{2+} (8-fold)	Burns, 1993
	574	17,430			
	694	14,400			
	1309	7,640			
	1718	5,820			
andradite	854	11,700	green	Fe^{3+} in M3 (oct)	Moore and White, 1972
	588	17,000			
	441-437	22,670-22,900			
grossular	607	16,475	green	V^{3+} (oct)	Rossman, 1988
	426	23,475			
pyrope	500	20,000	red/pink	Fe^{2+} (8-fold)	Burns, 1993
	530	18,868			
	610	16,393			
	700	14,286			
spessartine	588	17,000	orange	Mn^{2+} (oct)	Frendrup and Larger, 1981
	490	20,400			
uvarovite	600	16,667	green	Cr^{3+} (oct)	Abu-Eid, 1976
	440	22,727			
sillimanite	462	21,645	yellow	Fe^{3+} (tet)	Rossman's home page
	440	22,727			
	412	24,272			
fayalite	1076	9,290	green	Fe^{2+} (oct)	Burns, 1970
	909	11,000			
	1250	8,000			
manganite	580	17,240	red	Mn^{3+} (oct)	Rossman's home page
	500	20,000			

gahnite	450	22,222	???	Zn^{2+} (tet)	Rossman's home page
	540	18,519			
	570	17,544			
	630	15,873			
	900	11,111			
spinel	400	25,000	red	Cr^{3+} (oct)	Mao and Bell, 1975
	570	17,544			
chrysoberyl	565	17,700	green	Cr^{3+} (oct)	Farrell and Newnham, 1965
(Kenya)	425	23,500			Schmetzer et al., 1980
chrysoberyl	375	26,600	yellow	Fe^{3+} (oct)	Rossman's home page
(M.G.)	440	22,727			
grunerite	1000	10,000	blue	Fe^{2+} in M4 (oct)	Mao and Seifert, 1974
	2336	4,200		“ ”	Hawthorne, 1981
	990	10,100		Fe^{2+} in M1-M3 (oct)	
	1176	8,500		“ ”	
phlogopite	840	11,900	green	Fe^{2+} (oct)	Rossman, 1984
(Ontario)	1124	8,900			
phlogopite	521	19,200	red	Fe^{3+} (tet)	Faye and Hogarth, 1969
(Kimberley)	493	20,300			Hogarth et al., 1970
	441	22,700			
	400	25,000			
muscovite	673	14,850	red	Mn^{3+} (dist. oct)	Burns, 1970
	525	19,050			
	467	21,400			
	420	23,800			
lepidolite	758	13,200	pink	Mn^{3+} (dist. oct)	Annersten and Hålenius, 1976
	548	18,250			
	458	21,850			
epidote	1056-769	9,470-12,300	green	M3 (oct) Fe^{3+}	Burns and Strens, 1967
	607-559	16,480-17,900			
	472-455	21,200-22,000			

READING LIST

The technical literature contains a wide variety of papers covering gems, color, and optical spectroscopy; projects on color in minerals make good term paper topics once students have gotten used to interpreting optical spectra of minerals. The majority of the recent work in this area has been done at Caltech, so searches of literature databases using George R. Rossman as author as a search criterion will yield a good starting point for such papers. I also recommend the *Reviews in Mineralogy* volume on *Spectroscopy* (F.W. Hawthorne, ed.), which has a good chapter in it (by Rossman) summarizing optical spectroscopy. The "bible" of this field is Roger Burns' book, Mineralogical Applications of Crystal Field Theory (1970 and 1993; Cambridge University Press). Despite the somewhat intimidating title, it contains clear explanations of all the material presented in this lab, along with data on just about every mineral group you could ever want to know about!

If you're not too familiar with this material yourself, you might want to begin with less specialized reading material. I highly recommend the following readings, which you might want to have available for eager-beaver students. Some of these papers are rather old now, but they are still (in my opinion) the best that have been written on this topic.

and to George Rossman for perennial wisdom on this subject and for helping out with a few last minute spectra. I am also grateful for all that I learned from Roger Burns and from his book.

Answers to Problems

High-Spin Electronic Configurations for 3*d* Orbitals in Octahedral Coordination

Cation	Number of 3*d* electrons	Electronic configuration t_{2g}			e_g		*Unpaired* electrons	CFSE
Ca^{2+}, Sc^{3+}, Ti^{4+}	0						0	0
Ti^{3+}	1	↑					1	$0.4\ \Delta_o$
Ti^{2+}, V^{3+}	2	↑	↑				2	$0.8\ \Delta_o$
V^{2+}, Cr^{3+}, Mn^{4+}	3	↑	↑	↑			3	$1.2\ \Delta_o$
Cr^{2+}, Mn^{3+}	4	↑	↑	↑	↑		4	$0.6\ \Delta_o$
Mn^{2+}, Fe^{3+}	5	↑	↑	↑	↑	↑	5	0
Fe^{2+}, Co^{3+}, Ni^{4+}	6	↑↓	↑	↑	↑	↑	4	$0.4\ \Delta_o$
Co^{2+}, Ni^{3+}	7	↑↓	↑↓	↑	↑	↑	3	$0.8\ \Delta_o$
Ni^{2+}	8	↑↓	↑↓	↑↓	↑	↑	2	$1.2\ \Delta_o$
Cu^{2+}	9	↑↓	↑↓	↑↓	↑↓	↑	1	$0.6\ \Delta_o$
Cu^{+}, Zn^{2+}, Ga^{3+}, Ge^{4+}	10	↑↓	↑↓	↑↓	↑↓	↑↓	0	0

Relationship Between Crystal Field Splittings and CFSE for Octahedral Coordination

Cation	Δ_o (cm^{-1})	CFSE (right column, above)	CFSE (cm^{-1}) in hexahydrate
Ti^{3+}	18,950	$0.4\ \Delta_o$	7,580
V^{3+}	19,100	$0.8\ \Delta_o$	15,280
V^{2+}	12,600	$1.2\ \Delta_o$	15,120
Cr^{3+}	17,400	$1.2\ \Delta_o$	20,880
Cr^{2+}	13,900	$0.6\ \Delta_o$	8,340
Mn^{3+}	21,000	$0.6\ \Delta_o$	12,600
Mn^{2+}	7,800	$0.0\ \Delta_o$	0
Fe^{3+}	13,700	$0.0\ \Delta_o$	0
Fe^{2+}	9,400	$0.4\ \Delta_o$	3,760
Co^{2+}	9,300	$0.8\ \Delta_o$	7,440
Ni^{2+}	8,500	$1.2\ \Delta_o$	10,200
Cu^{2+}	13,000	$0.6\ \Delta_o$	7,800

It follows that:

$$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Cu^{2+} < Fe^{3+} < Cr^{2+} < Cr^{3+} < Ti^{3+} < V^{3+} < Mn^{3+}$$

From this list it is obvious that $\Delta^{3+} > \Delta^{2+}$ is the general rule! For more information consult section 2.9 in Burns (1993).

2. Mystery minerals:

Before you do this section, remind the students of where the infrared portion of the spectrum is, and ask them if their eyes can see infrared light! This will avoid confusion over minima that occur in the IR that don’t affect color. For more information on these spectra, consult the summary table of mineral spectra for more information, or check out the Mineral Spectroscopy Home Page. There are lots of other good examples there that can be used for this type of question.

Minas Gerais **muscovite** is red-purple (Mn^{3+}).
Grossular is green (V^{3+}).
Beryl is blue (Fe^{2+}).

Chrysoberyl is green, with flashes of red (this is called the "alexandrite effect"), because it has low absorption in both the green and the red regions of the spectrum. Chrysoberyl appears green in daylight and red in incandescent light. This occurs because in daylight, red and green are transmitted equally, but the eye is more sensitive to green, so it appears green. Incandescent light happens to be enriched in low energy red wavelengths, so alexandrite transmits more red than green and it appears red!

3. The Wah Wah beryl has maximum absorbance at 550-580 nm. In wavenumbers this is 18,182 - 17,241 cm^{-1}. The calcite, on the other hand, has maximum absorption at about 780 nm, or 12,821 cm^{-1}. Because the general rule from #1 is that $\Delta^{3+} > \Delta^{2+}$, the beryl must be the Mn^{3+}, while the calcite is Mn^{2+}.

4. Olivine has maximum absorption at about 1100 nm, or 9,091 cm^{-1}, while the pyrope has a maximum at around 1260 nm (7,937 cm^{-1}). Theory predicts that $\Delta_o : \Delta_c = 1 : 8/9$, so the garnet has the Fe in eight-fold coordination, while the olivine is six-fold. In staurolite and spinel, with maximum absorbances around 1400-2200 nm (7143-4545 cm^{-1}) and 2070 nm (4831 cm^{-1}), the energies are roughly 4/9 of the value for octahedral Fe^{2+} (as in olivine), so the Fe^{2+} in those minerals is in tetrahedral coordination.

5.

High Spin Electronic Configurations for 3*d* Orbitals in Tetrahedral Coordination

Cation	Number of 3*d* electrons	Electronic configuration					*Unpaired* electrons	CFSE
		e			t_2			
Ca^{2+}, Sc^{3+}, Ti^{4+}	0						0	0
Ti^{3+}	1	↑					1	0.6 Δ_t
Ti^{2+}, V^{3+}	2	↑	↑				2	1.2 Δ_t
V^{2+}, Cr^{3+}, Mn^{4+}	3	↑	↑	↑			3	0.8 Δ_t
Cr^{2+}, Mn^{3+}	4	↑	↑	↑	↑		4	0.4 Δ_t
Mn^{2+}, Fe^{3+}	5	↑	↑	↑	↑	↑	5	0
Fe^{2+}, Co^{3+}, Ni^{4+}	6	↓↑	↑	↑	↑	↑	4	0.6 Δ_t
Co^{2+}, Ni^{3+}	7	↑↓	↑↓	↑	↑	↑	3	1.2 Δ_t
Ni^{2+}	8	↑↓	↑↓	↑↓	↑	↑	2	0.8 Δ_t
Cu^{2+}	9	↑↓	↑↓	↑↓	↑↓	↑	1	0.4 Δ_t
Cu^{+}, Zn^{2+}, Ga^{3+}, Ge^{4+}	10	↑↓	↑↓	↑↓	↑↓	↑↓	0	0

In case you're wondering, most cations in the first transition series have high spin configurations at ambient pressure and temperature. The exceptions to this are Co^{3+} and Ni^{3+}, but for simplicity, only high spin configurations are used in this lab exercise. For more information on high spin vs. low spin, see Burns (1993) or a chemistry text.

Octahedral Site Preference Energies of Transition Metals

Cation	$CFSE_o$ (Kj/mole)	$CFSE_t$ (Kj/mole)	OSPE (Kj/mole)
Ca^{2+}, Sc^{3+}, Ti^{4+}	0	0	0
Ti^{3+}	-87.4	-58.6	-28.8
V^{3+}	-160.2	-106.7	-53.5
Cr^{3+}	-224.7	-66.9	-157.8
Cr^{2+}	-100.4	-29.3	-71.1
Mn^{3+}	-135.6	-40.2	-95.4
Mn^{2+}, Fe^{3+}	0	0	0
Fe^{2+}	-49.8	-33.1	-16.7
Co^{3+}	-188.3	-108.8	-79.5
Co^{2+}	-92.9	-61.9	-31.0
Ni^{2+}	-122.2	-36.0	-86.2
Cu^{2+}	-90.4	-26.8	-63.7
Zn^{2+}, Ga^{3+}, Ge^{4+}	0	0	0

These would predict the following uptake systematics:

$$Ni^{2+} > Cr^{2+} > Cu^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}, Ca^{2+}, Zn^{2+}$$

$$Cr^{3+} > Mn^{3+} > Co^{3+} > V^{3+} > Ti^{3+} > Fe^{3+}, Sc^{3+}, Ga^{3+}$$