

# COLOR IN MINERALS

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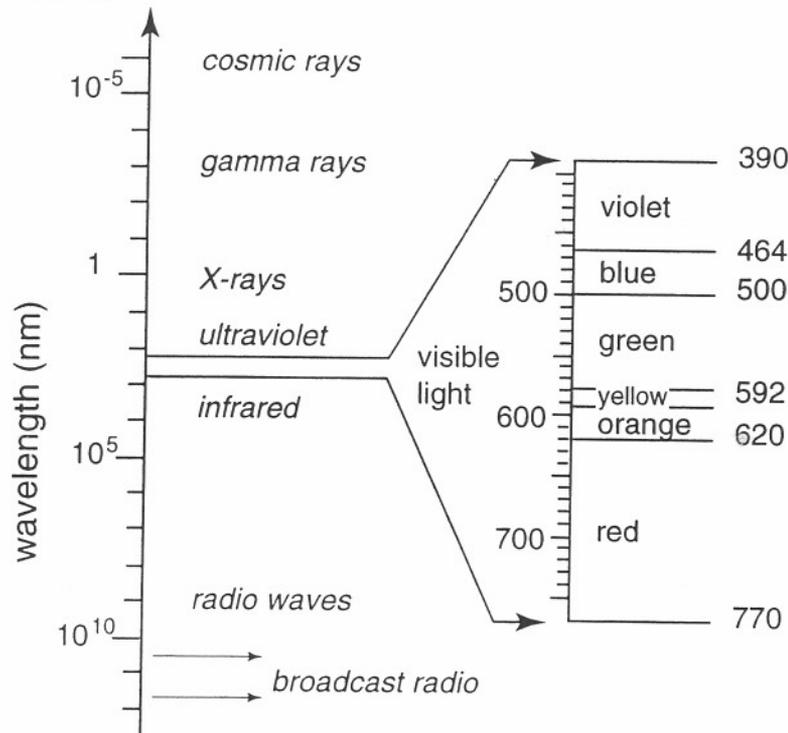
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Why do minerals have color? When is that color diagnostic, and when it is likely to fool you? Why is color important, and what can it tell us about the chemistry of minerals? Today's exercise will try to answer some of these questions, and to introduce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



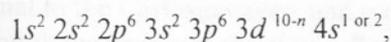
Studies of color can often be confusing because spectroscopists use a variety of units to explain their work! These units fall into two categories: those expressed in terms of the **energy** of light ( $\text{cm}^{-1}$ , eV, and kJ) or in terms of its **wavelength** ( $\mu\text{m}$ , nm, or  $\text{\AA}$ ). In the study of color in minerals, the two types of units most often used are wavenumbers ( $\text{cm}^{-1}$ ) and wavelengths (usually expressed as nm). To convert from nm to  $\text{cm}^{-1}$ , 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 Color
Nanometers (nm)	Ångstroms (Å)	Wavenumbers ( $\text{cm}^{-1}$ )	
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  $3d$ , and incompletely full  $3d$  orbitals. Another way of saying this is that they have a configuration of

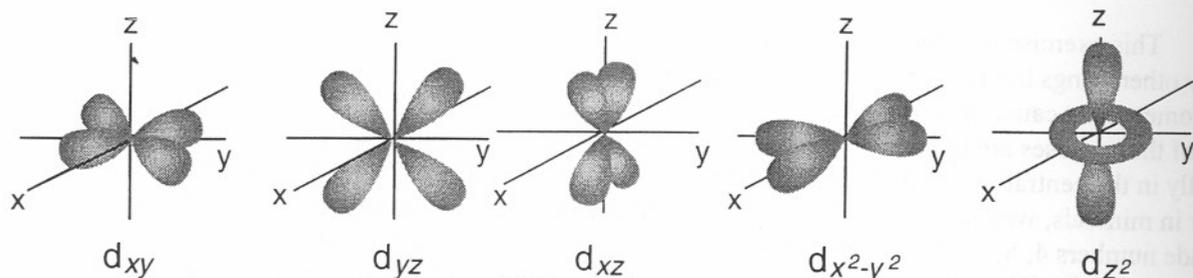


where *n* is an integer from 0 to 10. How many electrons would an atom have in order for one or more to occupy a  $3d$  orbital?

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

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

The 3d 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 3d 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:

3d

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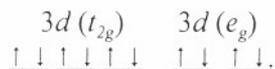
Each individual line symbolizes one of the five 3d orbitals, and all the orbital levels lie along the

<sup>1</sup>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.<sup>2</sup>

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



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  $3d$  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  $3d$  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

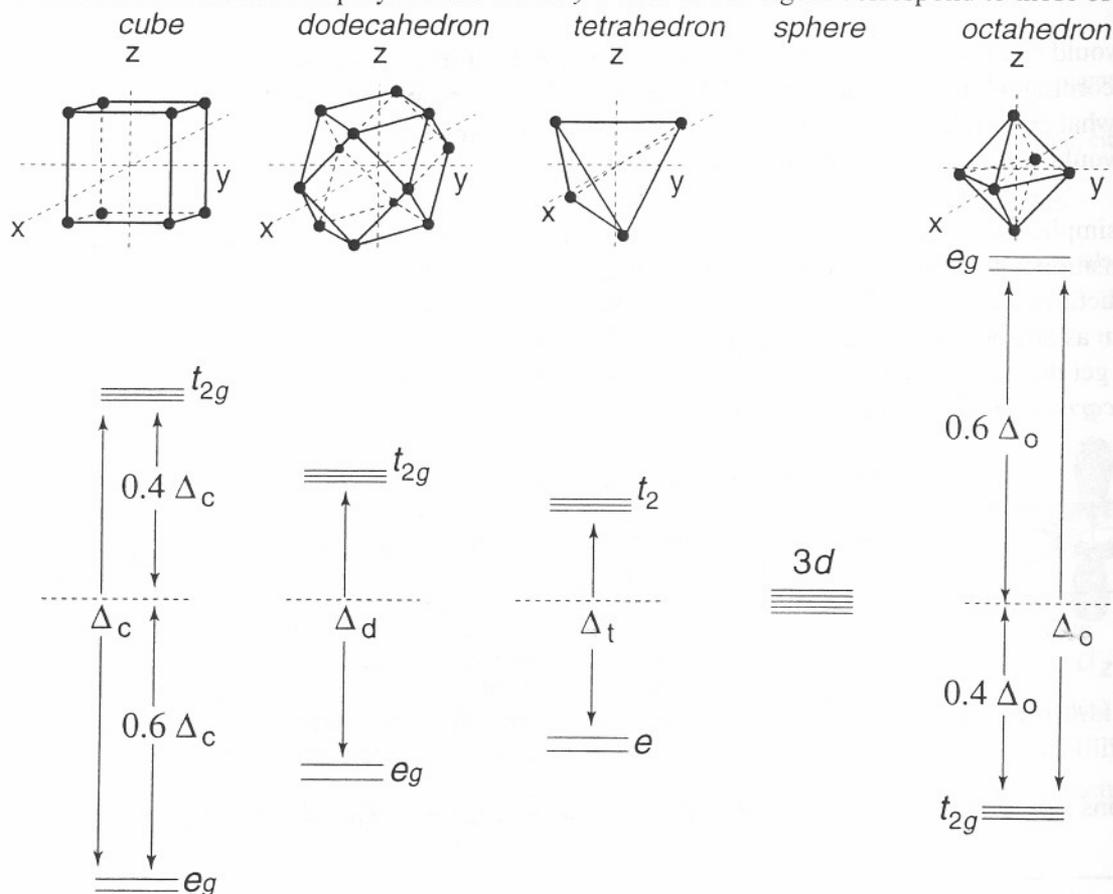
Coordination Polyhedron	Number of corners	Number of faces	Term Used	Size of Cations
tetrahedron	4	4	4-fold	smallest
octahedron	6	8	6-fold	↓
cube	8	6	8-fold	↓
dodecahedron (cuboctohedron)	12	14	12-fold	largest

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

<sup>2</sup>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 3d 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.

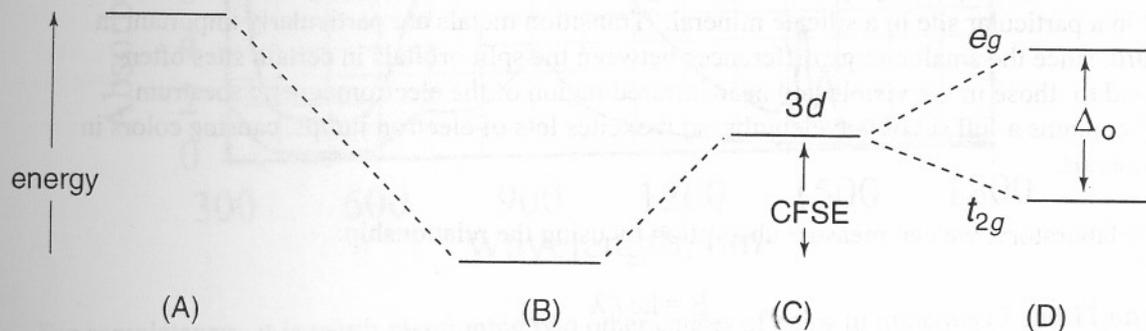
The difference in energy between the lowest orbitals and the highest orbitals is called **crystal**

**field splitting** and is represented by the symbol  $\Delta$  (or sometimes,  $10Dq$ ). 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  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$ . 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  $\Delta$  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  $\Delta$  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  $3d$  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  $3d$  electrons in a case where the anions are distributed in a sphere. (D) shows the splitting of the  $3d$  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  $0.4 \Delta_o$ . It follows that every electron in an  $e_g$  orbital would destabilize the structure by an amount equal to  $0.6 \Delta_o$ .<sup>3</sup> 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  $\Delta$ . 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  $\lambda$  = wavelength. A spectrometer passes monochromatic (single  $\lambda$ ) light through a sample of known thickness, and

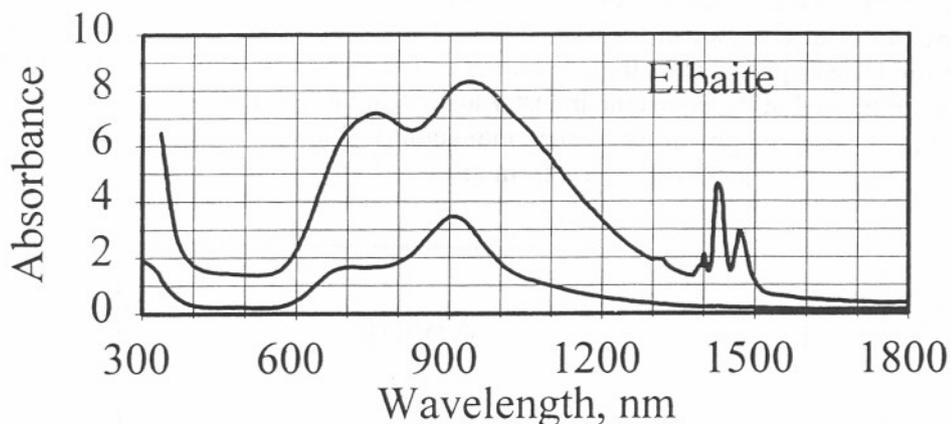
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<sup>3</sup>The multiples 0.6 and 0.4 come from simple algebra: the energy of the six possible electrons in the  $t_{2g}$  orbitals ( $6 \times 0.4 = 2.4$ ) is compensated by the energy of the four electrons in the  $e_g$  orbitals ( $4 \times 0.6 = 2.4$ ); 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  $\Delta$  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  $\Delta$  is also therefore related qualitatively to the color of the mineral.

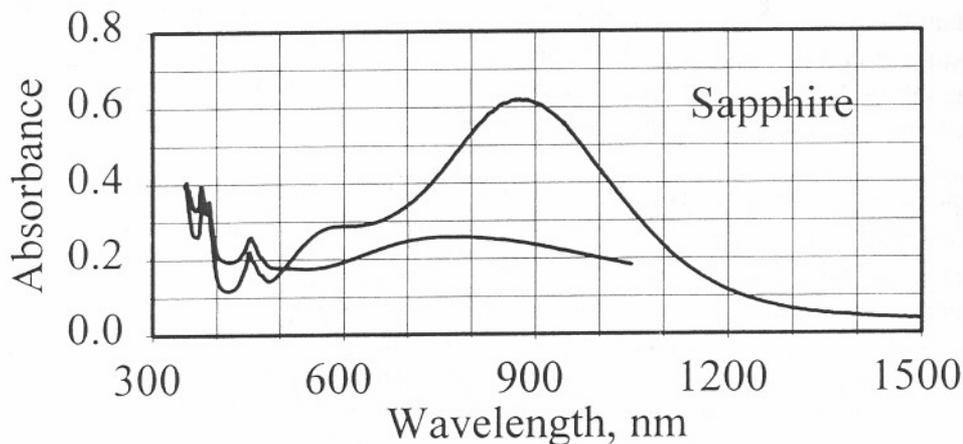
For example, here are the spectra of octahedral  $\text{Cu}^{2+}$  in elbaite, which is a kind of tourmaline. Wavelength is shown on the  $x$  axis, and the  $y$  axis shows the amount of absorbance that occurs at each wavelength. The magnitude of the absorbance is a function of the thickness of the crystal.<sup>4</sup> 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  $10,870 \text{ cm}^{-1}$  and  $14,286 \text{ cm}^{-1}$ , 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  $\text{Cu}^{2+}$  atoms. Light that passes through the elbaite is in the range from 400-600 nm, corresponding to blue light. Thus, this elbaite appears blue.



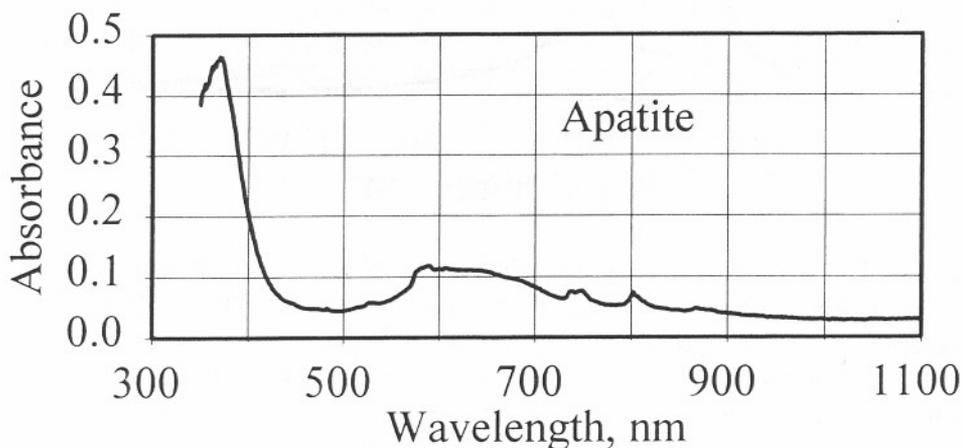
For completeness, it is worth mentioning two other causes of color in minerals (7 and 11 on Nassau's list above). Color produced by charge transfer processes is similar to crystal field-induced color, except instead of electrons jumping *between orbitals* within the same atom, electrons can jump *between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

<sup>4</sup>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  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$ , and the next instant it is  $\text{Fe}^{3+}$  and  $\text{Ti}^{3+}$ . Very small amounts of  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$  in an otherwise pure corundum crystal ( $\text{Al}_2\text{O}_3$ ), even down at ppm and maybe ppb levels, can still make a sapphire blue. In the spectrum shown here, peaks at  $25,680\text{ cm}^{-1}$  and  $22,220\text{ cm}^{-1}$  represent  $\text{Fe}^{3+}$  and the broad bands spanning  $17,800\text{ cm}^{-1}$  to  $14,200\text{ cm}^{-1}$  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  $\text{Fe}^{3+}$  substituting for  $\text{Si}^{4+}$  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  $\Delta_o$  values:

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

Cation	Number of 3d electrons	Electronic configuration					Unpaired electrons	CFSE
		$t_{2g}$			$e_g$			
Ca <sup>2+</sup> , Sc <sup>3+</sup> , Ti <sup>4+</sup>	—	—	—	—	—	—	—	0
Ti <sup>3+</sup>	—	—	—	—	—	—	—	0.4 $\Delta_o$
Ti <sup>2+</sup> , V <sup>3+</sup>	—	—	—	—	—	—	—	— $\Delta_o$
V <sup>2+</sup> , Cr <sup>3+</sup> , Mn <sup>4+</sup>	—	—	—	—	—	—	—	— $\Delta_o$
Cr <sup>2+</sup> , Mn <sup>3+</sup>	—	—	—	—	—	—	—	— $\Delta_o$
Mn <sup>2+</sup> , Fe <sup>3+</sup>	—	—	—	—	—	—	—	— $\Delta_o$
Fe <sup>2+</sup> , Co <sup>3+</sup> , Ni <sup>4+</sup>	—	—	—	—	—	—	—	— $\Delta_o$
Co <sup>2+</sup> , Ni <sup>3+</sup>	7	<u>1</u>	<u>1</u>	<u>1</u>	<u>1</u>	<u>1</u>	3	$\Delta_o$
Ni <sup>2+</sup>	—	—	—	—	—	—	—	1.2 $\Delta_o$
Cu <sup>2+</sup>	—	—	—	—	—	—	—	— $\Delta_o$
Cu <sup>+</sup> , Zn <sup>2+</sup> , Ga <sup>3+</sup> , Ge <sup>4+</sup>	—	—	—	—	—	—	—	— $\Delta_o$

Reminder: to calculate CFSE, assign a weight of 0.4  $\Delta$  for each electron that occupies a  $t_{2g}$  or  $t_2$  orbital, and 0.6  $\Delta$  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  $\Delta_o$ . Experimental data on  $\Delta_o$  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	$\Delta_o$ (cm <sup>-1</sup> )	CFSE (right column, above)	CFSE (cm <sup>-1</sup> ) in hexahydrate
Ti <sup>3+</sup>	_____	— $\Delta_o$	7,580
V <sup>3+</sup>	_____	— $\Delta_o$	15,280
V <sup>2+</sup>	12,600	— $\Delta_o$	15,120

Cr <sup>3+</sup>	_____	_____ $\Delta_o$	20,880
Cr <sup>2+</sup>	_____	_____ $\Delta_o$	8,340
Mn <sup>3+</sup>	_____	_____ $\Delta_o$	12,600
Mn <sup>2+</sup>	7,800	_____ $\Delta_o$	0
Fe <sup>3+</sup>	13,700	_____ $\Delta_o$	0
Fe <sup>2+</sup>	_____	_____ $\Delta_o$	3,760
Co <sup>2+</sup>	_____	_____ $\Delta_o$	7,440
Ni <sup>2+</sup>	_____	_____ $\Delta_o$	10,200
Cu <sup>2+</sup>	_____	_____ $\Delta_o$	7,800

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



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

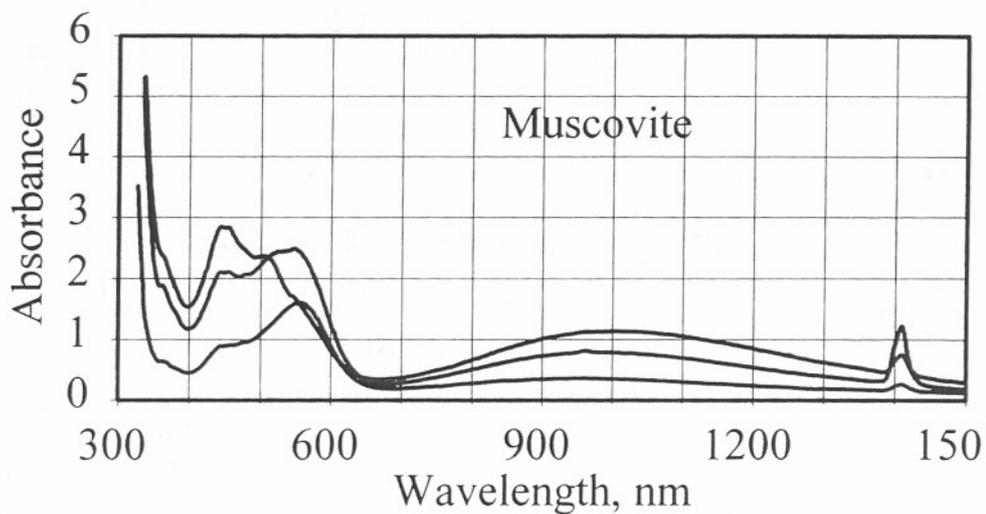
$$\Delta^{3+} > \Delta^{2+}$$

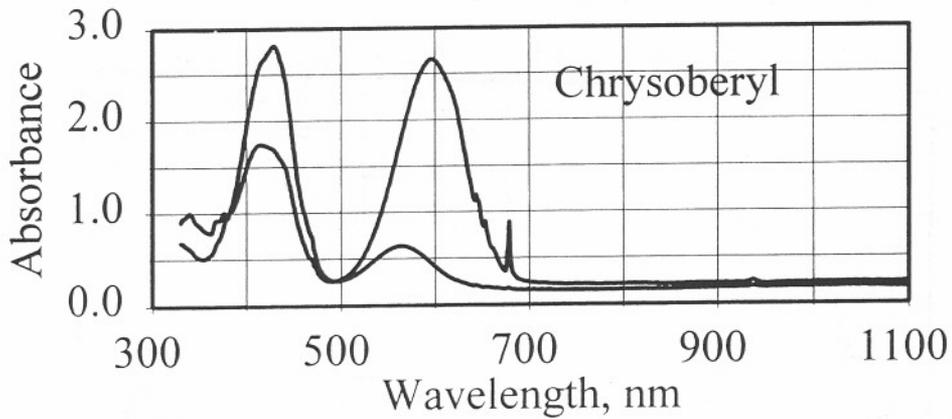
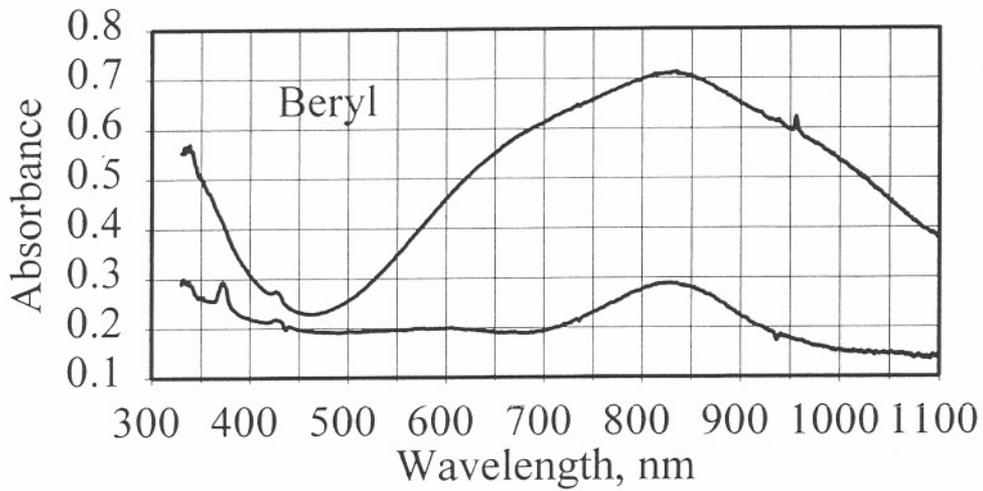
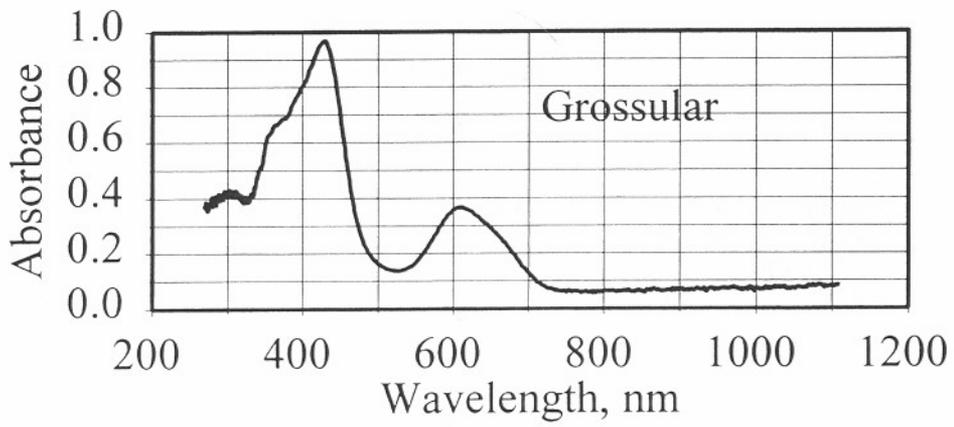
OR

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

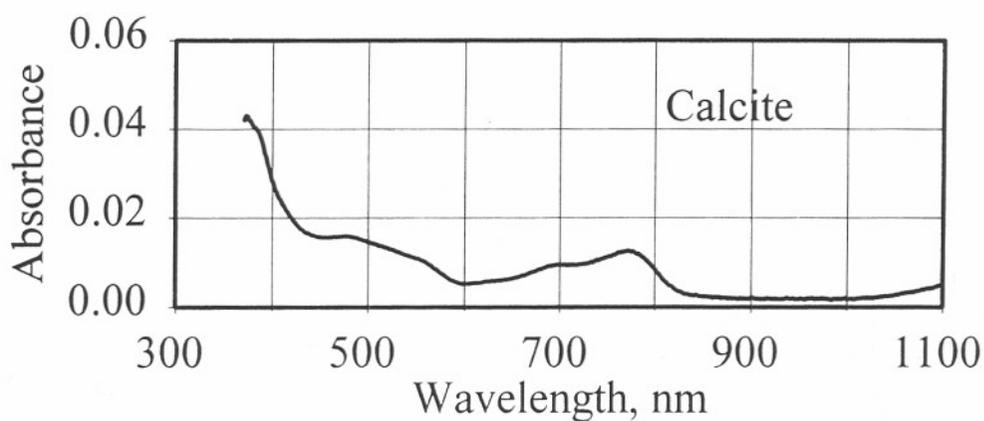
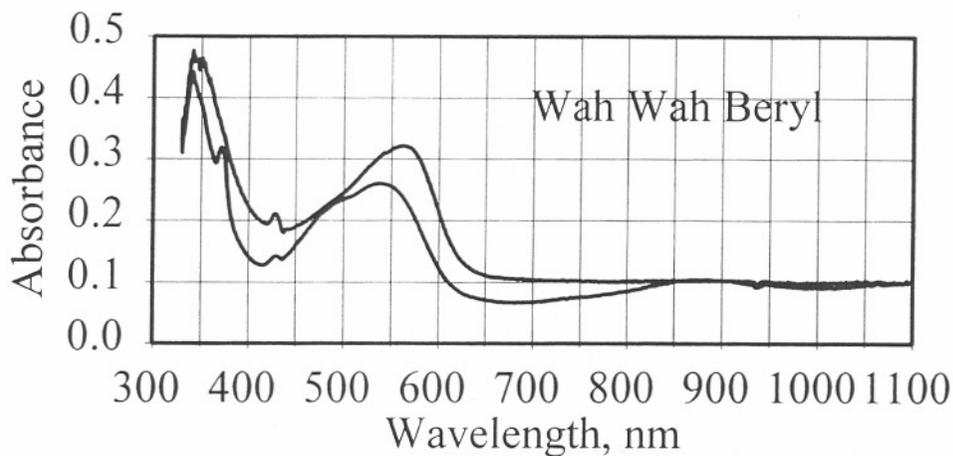
HINT: you will use this relationship to help you interpret the spectra in question #3!

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!

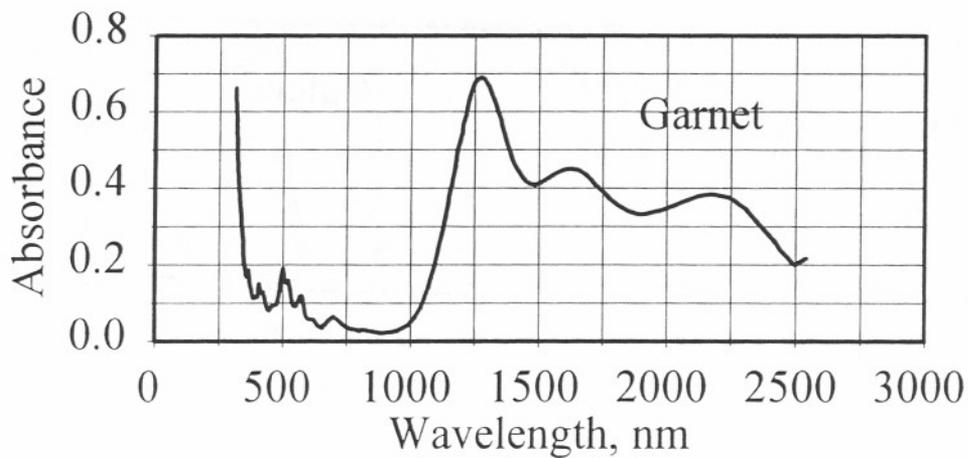
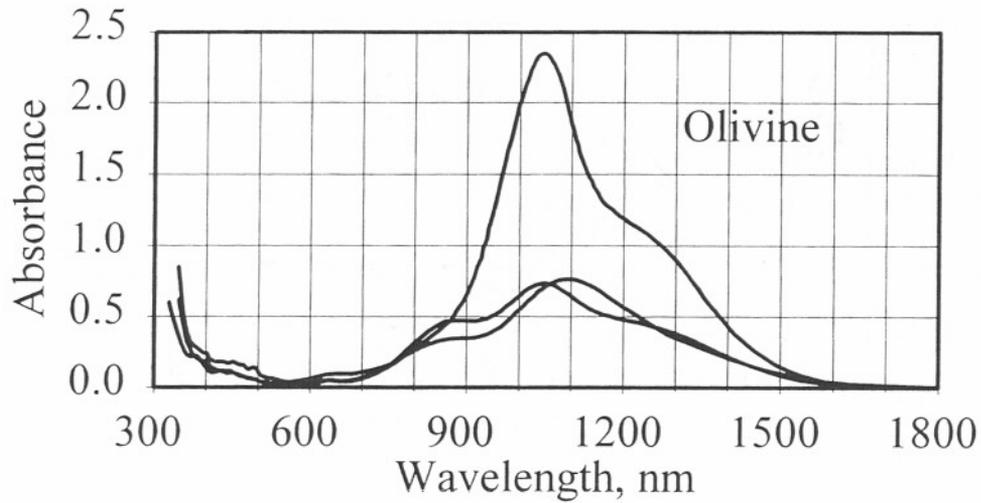




3. Earlier in this exercise, we pointed out that one of the best uses for crystal field theory is to help distinguish between multiple valence states of the same element. Two spectra containing the element Mn are shown below. One contains  $Mn^{3+}$  and the other  $Mn^{2+}$ . First, determine the maximum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



4. Below you will find spectra of  $\text{Fe}^{2+}$  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  $\text{Fe}^{2+}$  in octahedral coordination, and which in eight-fold coordination. Compare this to the minerals staurolite and spinel, in which  $\text{Fe}^{2+}$  has maximum absorbance at around 1400-2200 nm and 2070 nm, respectively. What type of coordination environment do you think the  $\text{Fe}^{2+}$  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 3d Orbitals in Tetrahedral Coordination**

Cation	Number of 3d electrons	Electronic configuration					Unpaired electrons	CFSE
		<i>e</i>		<i>t<sub>2</sub></i>				
Ca <sup>2+</sup> , Sc <sup>3+</sup> , Ti <sup>4+</sup>	—	—	—	—	—	—	0	
Ti <sup>3+</sup>	—	—	—	—	—	—	0.6 Δ <sub>t</sub>	
Ti <sup>2+</sup> , V <sup>3+</sup>	—	—	—	—	—	—	—Δ <sub>t</sub>	
V <sup>2+</sup> , Cr <sup>3+</sup> , Mn <sup>4+</sup>	—	—	—	—	—	—	—Δ <sub>t</sub>	
Cr <sup>2+</sup> , Mn <sup>3+</sup>	—	—	—	—	—	—	—Δ <sub>t</sub>	
Mn <sup>2+</sup> , Fe <sup>3+</sup>	—	—	—	—	—	—	0 Δ <sub>t</sub>	
Fe <sup>2+</sup> , Co <sup>3+</sup> , Ni <sup>4+</sup>	—	<u>1</u>	<u>1</u>	<u>1</u>	<u>1</u>	<u>1</u>	—Δ <sub>t</sub>	
Co <sup>2+</sup> , Ni <sup>3+</sup>	—	—	—	—	—	—	—Δ <sub>t</sub>	
Ni <sup>2+</sup>	—	—	—	—	—	—	0.8 Δ <sub>t</sub>	
Cu <sup>2+</sup>	—	—	—	—	—	—	—Δ <sub>t</sub>	
Cu <sup>+</sup> , Zn <sup>2+</sup> , Ga <sup>3+</sup> , Ge <sup>4+</sup>	—	—	—	—	—	—	—Δ <sub>t</sub>	

Now, use the difference between CFSE<sub>o</sub> and CFSE<sub>t</sub> 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. dodecahedral 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 <sub>o</sub> (Kj/mole)	CFSE <sub>t</sub> (Kj/mole)	OSPE (Kj/mole)
Ca <sup>2+</sup> , Sc <sup>3+</sup> , Ti <sup>4+</sup>	0	0	0
Ti <sup>3+</sup>	-87.4	-58.6	-28.8
V <sup>3+</sup>	-160.2	-106.7	—
Cr <sup>3+</sup>	-224.7	-66.9	—
Cr <sup>2+</sup>	-100.4	-29.3	—
Mn <sup>3+</sup>	-135.6	-40.2	—

Mn <sup>2+</sup> , Fe <sup>3+</sup>	0	0	0
Fe <sup>2+</sup>	-49.8	-33.1	_____
Co <sup>3+</sup>	-188.3	-108.8	_____
Co <sup>2+</sup>	-92.9	-61.9	_____
Ni <sup>2+</sup>	-122.2	-36.0	-86.2
Cu <sup>2+</sup>	-90.4	-26.8	_____
Zn <sup>2+</sup> , Ga <sup>3+</sup> , Ge <sup>4+</sup>	0	0	0

For divalent cations, the order of OSPE is:



For trivalent cations, the order of OSPE is:



Therefore, if you are crystallizing a mineral (say, a spinel) with both octahedral and tetrahedral sites in it, and you have Cu<sup>2+</sup>, Cr<sup>3+</sup>, and Ti<sup>3+</sup>, your might predict that the Cu<sup>2+</sup> and Cr<sup>3+</sup> would prefer octahedral sites, and the Ti<sup>3+</sup> 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).