

## CHAPTER 3

## SHEDDING LIGHT ON THE COLOUR



Colour is the most striking property of minerals; it contributes greatly to the value of gems and also provides and aids in mineral identification. What is the colour and how does it originate?

Colour is a response of the eye to the electromagnetic radiation. The human eye responds to a limited range of wavelengths, within the electromagnetic spectrum from about 3500 to 7500 Angstrom. When all wavelengths in the visible spectrum are present, the eye perceives white light; if some wavelengths are removed, or when only certain wavelengths are present, the eye detects a colour. For instance, if the blue wavelengths are removed, the eye will see the remainder as yellow light. Thus, all colours come from the differential absorption and transmission of light according to the wavelength. When white light, containing all wavelengths, shines on a mineral, some wavelengths are transmitted, giving the observed colour, while the complementary wavelengths are absorbed by the mineral. Therefore, to understand the origin of a mineral's colour is to determine what in the mineral causes absorption of certain wavelengths of light. (17,18)

The selective absorption of light depends on transition energy, which varies inversely with the wavelength and directly with the frequency:

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

Where E is energy, h is planck's constant, c is the speed of light,  $\nu$  is the frequency,  $\lambda$  is the wavelength, and  $\bar{\nu}$  is the

wavenumber. The wavenumber, the reciprocal of the wavelength or the number of wavelengths per unit length, is a useful quantity because it, as the frequency, is directly proportional to energy. All energies shall be expressed in wavenumbers ( $\text{cm}^{-1}$ ) and all wavelengths in nanometers (nm) or billionths of a meter.

Electronic processes in minerals with energies corresponding to wavelengths of visible light fall into four broad categories. By far the most important sources of colours in minerals are the transition elements, which give rise to various crystal field and charge transfer transitions.

#### Crystal field transitions

Crystal field transitions are electronic transitions between the partially **filled**, nondegenerate d orbitals (or less commonly, f-orbitals) of transition elements in a chemically coordinated environment. They explain the origin of colour in minerals which are transition metal compounds (e.g. rhodochrosite,  $\text{MnCO}_3$ , diopside,  $\text{Ca}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) and minerals which have transition metal impurities (e.g. ruby,  $\text{Cr}^{3+}$  in  $\text{Al}_2\text{O}_3$ ; citrine,  $\text{Fe}^{3+}$  in  $\text{SiO}_2$ ).<sup>(19)</sup>

Crystal field transitions are most common in minerals containing the first-row transition elements; Ti, V, Cr, Mn, Fe, Co, Ni and Cu. However, the second and third-row transition elements and particularly the lanthanide or rare earth elements also occasionally impart colour to minerals. The first-row transition elements are the first ones to have electrons in d orbitals.

The 1s, 2s, 2p, 3s and 4s orbitals are progressively filled from II through Ca, and only starting with Sc the 3d orbitals become occupied, reaching their full complement of ten electrons with Zn. The spatial distribution of electron density makes d orbital so special.<sup>(20)</sup>

As shown in figure 3.1, the five d orbitals fall into two categories, based on their orientation relative to a Cartesian coordinate system.

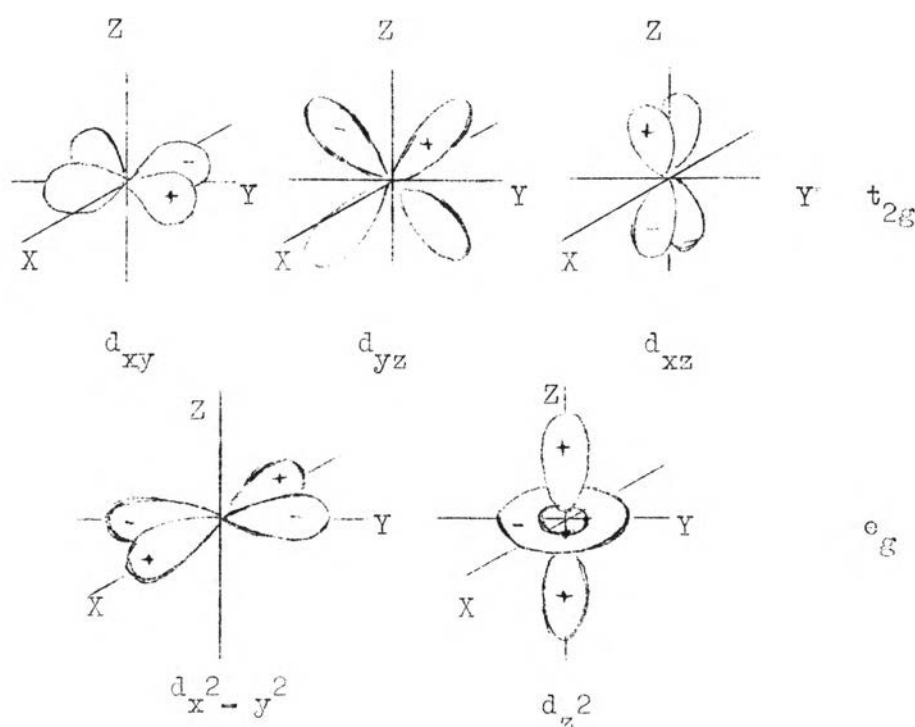


Figure 3.1. Plots of d orbitals show the regions in space where electrons in each orbital may be found with 90 % probability.<sup>(20)</sup>

Two of the  $d$  orbitals have probability lobes projecting along the Cartesian axes ( termed the  $e_g$  set), while the other three orbitals have lobes pointing between the axes ( termed the  $t_{2g}$  set).

In the isolated atom or free ion, the five  $d$  orbitals are degenerate, having the same energy. However, when a transition metal ion is placed in a coordination site in a mineral, it is no longer surrounded by a spherically symmetric charge distribution, rather it has nearest-neighbour anions which localized negative charges (e.g;  $Cr^{3+}$  in  $Al_2O_3$  which  $Cr^{3+}$  replaced  $Al^{3+}$  in normal cation sites). In a typical six-coordination octahedral site, the adjacent anions in mineral such as oxygen in  $Al_2O_3$ , may be regarded as defining the apices of an octahedron. Cartesian coordinate system, is shown in figure 3.2.

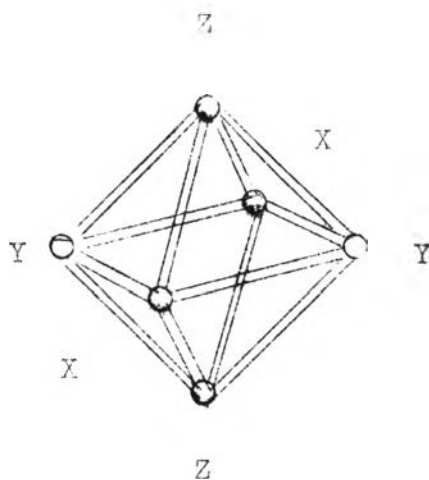


Fig.3.2 The coordinate system defined by the six oxygens of octahedral coordination site in a mineral<sup>(20)</sup>

The  $e_g$  d orbitals which have lobes pointing along the metal-anion axes are increased in energy relative to the  $t_{2g}$  d orbitals which point between the axes. In the simplest view, this results from the electrostatic or coulombic repulsion between like charges. Electrons in the  $e_g$  orbitals pointing toward negatively charged anion suffer more repulsion and hence have higher energy than electrons in  $t_{2g}$  orbitals farther away from the coordinating anions.

Thus, in an octahedral field, there is a splitting in energy of the d orbitals, as shown in figure 3.3.

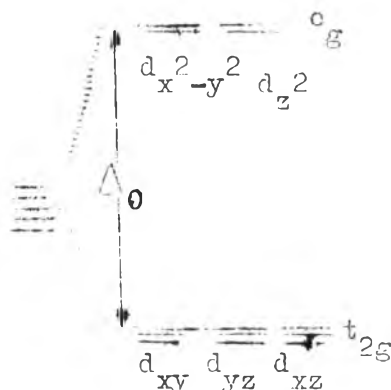


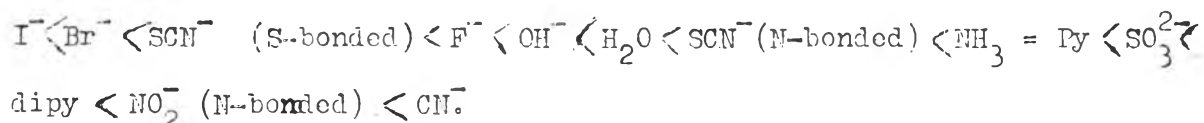
Fig. 3.3 The energy separation, or crystal field splitting ( $\Delta_0$ ) of the d orbitals of a transition metal ion located (20)

Since the d orbitals are no longer degenerate, electrons may be excited between the  $t_{2g}$  and  $e_g$  energy levels. Such transitions referred to crystal field or d-d transitions, often having energies corresponding to wavelengths of visible light and may thus cause absorption in the visible. These electronic transition can not occur if the cation has no d electrons or if the d orbitals are completely filled,

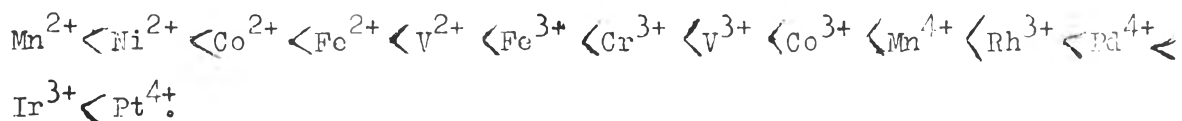
crystal field transitions do not occur in  $\text{Sc}^{3+}$  or  $\text{Ti}^{4+}$  (which have no d electrons) or in  $\text{Zn}^{2+}$  or  $\text{Cu}^{+}$  (which have ten d electrons). Crystal field transitions are observed only in those cations of Ti through Cu in the first transition series, partially filled d orbitals.

In the crystal field model, the anions are approximated by point charges or dipoles, the value of crystal field splitting energy for a particular compound depending on magnitude of both charges, it is possible to place ligands in order of increasing effective charge and increasing crystal field splitting. Furthermore, this order should be the same for all metals. Such an order of ligands called the spectrochemical series was discovered by Tschida.<sup>(21)</sup>

In abbreviated spectrochemical series, in order of increasing crystal field splitting, is



A similar series existed for the variation with metal ion is



In minerals most metal sites are highly distorted and have considerably lower symmetry than perfect octahedra or tetrahedra. The effect of such site distortion is to split further the d orbital energy levels, for the same reasons that cause the initial separations of d orbitals in an ideal octahedron. Since d orbitals have a fixed geometry, the exact arrangement of the anions determines which

orbitals will suffer the greatest degree of coulombic repulsion. Thus, the geometry of the metal coordination site determines the order and separation of d orbital energy levels. They may be split into as few as two or as many as five separation energy levels; the greater the number of energy levels, the greater the number of possible electronic transition between them.

A second complication is that many minerals have several coordination sites with different geometries, the energy levels of the transition metal's d orbitals in these minerals will be different in each site, depending on the site geometry.

To illustrate some of these points, let us consider the mineral peridot, which is a gem variety of olivine  $(\text{Fe}, \text{Mg})_2\text{SiO}_4$ . The crystal structure of olivine consists of independent  $\text{SiO}_4$  tetrahedra linked by divalent cation in six-fold coordination with oxygen. These are two sites having different geometries, designated M1 and M2, which contain  $\text{Fe}^{2+}$ . The centrosymmetric M1 site can be approximated by a tetragonally distorted octahedron (with  $D_{4h}$  symmetry); the M2 noncentrosymmetric site can be closely approximated by a trigonally distorted octahedron (with  $C_{3v}$  symmetry). The energy levels for the d orbitals of  $\text{Fe}^{2+}$  in six-fold coordination polyhedra with these symmetries (22) are shown in Figure 3.4, since  $\text{Fe}^{2+}$  has six d electrons, each of the five d orbitals is occupied by one electron, with the electron entering the lowest energy orbital.

The orbitals thus contain only one set of paired electrons and four unpaired electrons, in accordance with Hund's rule which states that electron will avoid pairing as long as there are near by, unoccupied energy levels.

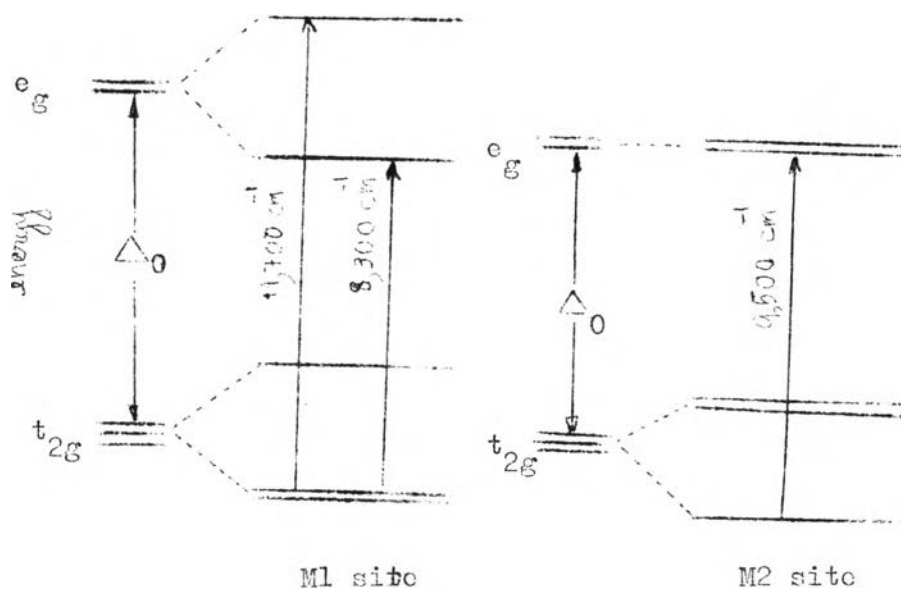


Figure 3.4 Energy levels for the d electrons of  $\text{Fe}^{2+}$  in the M1 ( $-D_{4h}$  symmetry) and the M2 ( $-C_{3v}$  symmetry) sites in peridot ( $\text{Fe}^{2+}/\text{Mg}_2\text{SiO}_4$ ) show that the initial separation of d orbitals in an octahedral field ( $\Delta_0$ ) is further resolved due to the lower symmetry of the M1 and M2 sites. (22)



If one shines monochromatized light on peridot and measures the degree of light absorption as a function of wavelength, corresponded exactly to the absorption energy differences between the nondegenerate d orbital level of  $\text{Fe}^{2+}$  in peridot. The crystal field transitions of  $\text{Fe}^{2+}$  in peridot take place mostly in the infrared region, but they do extend into the visible range. Such absorption of red light is responsible for the yellow-green(transmitted) colour, characteristic of peridot and other ferromagnesian silicates containing octahedrally coordinated  $\text{Fe}^{2+}$ .

The colour produced by a given transition element depends on its oxidation state,  $\text{Fe}^{2+}$  produces a characteristic green colour in six-fold coordination sites in minerals. What is about  $\text{Fe}^{3+}$ ? Consider the mineral chrysoberyl,  $\text{Al}_2\text{BeO}_4$ , which frequently contains some  $\text{Fe}^{3+}$  substituting for  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  in chrysoberyl absorbs weakly in the violet and blue region of the spectrum, giving the characteristic pale yellow colour of  $\text{Fe}^{3+}$  bearing chrysoberyls. Chrysoberyl has the crystal structure of olivine  $(\text{Mg,Fe})_2\text{SiO}_4$ , as one might expect from its formula, so that the Al sites occupied by  $\text{Fe}^{3+}$  in chrysoberyl have the same geometry, although some what smaller dimensions, as the Mg sites that  $\text{Fe}^{2+}$  occupies in peridot.

Therefore, differences in absorption spectra (in the same polarization) between peridot and  $\text{Fe}^{3+}$  bearing chrysoberyl, must be attributed to inherent differences in the electronic structures of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  and not to environmental factors.

Crystal field transitions in  $\text{Fe}^{3+}$  occur at higher energy and must be weaker than the d-d transitions in  $\text{Fe}^{2+}$ . In  $\text{Fe}^{3+}$  there are five unpaired d electrons, one in each of the five d orbitals. Therefore, any crystal field transition in  $\text{Fe}^{3+}$  must result in the pairing of at least two electrons in one orbital, which reduces the number of unpaired electrons from five to three.

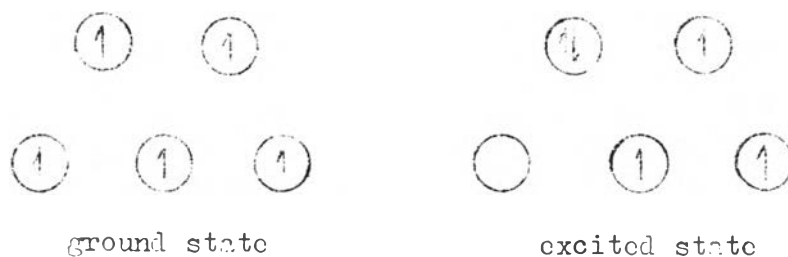


Fig. 3.5 Electrons in d orbitals of  $\text{Fe}^{3+}$  bearing chrysoberyl

Transitions which change the number of unpaired electrons, and the total spin of the cationic electron, are "spin-forbidden" and are not allowed by quantum mechanics. They are observed with a nonvanishing intensity due to spin-orbit coupling, but they are much weaker and usually occur at higher energy than normal "spin-allowed" d-d transitions. The electronic transitions in  $\text{Fe}^{3+}$  therefore, contrast with those observed in  $\text{Fe}^{2+}$  in peridot which are spin-allowed. Crystal field transition in  $\text{Fe}^{2+}$  excites the sixth d electron from a  $t_{2g}$  to an  $e_g$  orbital, they maintain the number of unpaired electrons by four and hence leave the total spin of the ion unchanged.

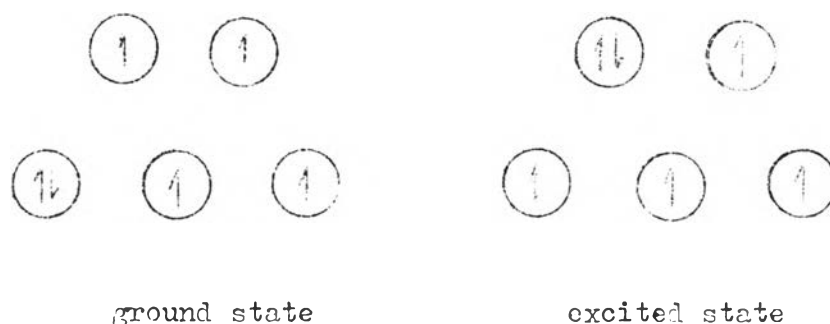


Fig 3.6 Electrons d orbitals of  $\text{Fe}^{2+}$  in peridot

The effect of changing the coordination number of the cation in the colour imparted to a mineral is also described, for example, the  $\text{Fe}^{2+}$  ion which occupies six-coordinate sites in peridot is surrounded by eight oxygen atoms, as in garnet.<sup>(23)</sup>

The crystal structure of garnet consists of an independent  $\text{SiO}_4$  tetrahedra linked by trivalent ions in octahedral coordination and divalent ions in eight-fold coordination. The general formula for garnet is  $\text{M}_3^{2+}\text{M}_2^{3+}(\text{SiO}_4)_3$ , where  $\text{M}^{3+}$  is  $\text{Al}^{3+}$  and  $\text{M}^{2+}$  are  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$ . We are now dealing with the garnet compositional endmembers, pyrope and almandine. The spin-allowed crystal field bands of  $\text{Fe}^{2+}$  in almandine occur at lower energies than those of  $\text{Fe}^{2+}$  in peridot, as one would expect from the larger mean metal oxygen distance of the eight-fold coordination site in garnet. The oxygens of the eight-fold coordination sites are farther away from the central  $\text{Fe}^{2+}$  ion, and hence its d electrons experience a "weaker" crystal field. Crystal field splitting are therefore diminished, resulting in reduction of energies of the d-d transitions. Thus, spin-allowed transitions in  $\text{Fe}^{2+}$  in almandine occur entirely outside of the visible, producing a strong red transmission; whereas these same transitions in peridot absorb in the red. This transmission

of weaker spin-forbidden transitions of  $\text{Fe}^{2+}$  in almandine (which absorbed in the blue, green, and yellow) produce the observed red colour of almandine pyrope garnets.

Other factors contributing to the colours of transition metal-bearing minerals are illustrated by those containing  $\text{Cr}^{3+}$ , such as ruby and emerald.<sup>(24)</sup> Ruby is  $\text{Cr}^{3+}$ -bearing corundum ( $\text{Al}_2\text{O}_3$ ); emerald is  $\text{Cr}^{3+}$  bearing beryl ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ). In both minerals,  $\text{Cr}^{3+}$  replaces  $\text{Al}^{3+}$  in distorted six-coordinate sites with a mean metal-oxygen distance of  $1.91 \text{ \AA}$ . The accounts for the striking difference in the colours of these two gems, containing the same transition metal ion in sites of comparable geometry, are their different bonding characters. Beryl is a ring silicate mineral and the oxygen of the  $\text{AlO}_6$  coordination sites belong also to  $\text{SiO}_4$  or  $\text{BeO}_4$  tetrahedra. Corundum is an oxide mineral, consisting of hexagonally close-packed layers of oxygen ion with  $\text{Al}^{3+}$  occupying two-thirds of the interstices between layers. In beryl, the oxygen-cation bonding has some covalent character with electron delocalization over the silicon and beryllium framework; in corundum the bonding is more ionic, with increased negatively charged electron density isolated on the oxygens. The  $\text{Cr}^{3+}$  in beryl experiences a weaker crystal field, since there is less negative charge localized on the neighboring oxygens than in corundum, so that a smaller crystal field splitting of the d orbitals occurs. This difference is the absorption spectra of the two gems. In ruby, absorption in the violet, in the green, and yellow results in a transmission in the blue. In addition, there is a strong transmission in the orange and red, giving the intense violet-red to orange-red colour of ruby. In emerald, the transitions are shifted to

the lower energy, resulting in absorption of the violet and blue and of the yellow, orange and red. This gives transmission in the green and hence the characteristic colour of emerald. The red colour of ruby is intensified by a characteristic fluorescence in the red. Thus, ruby not only absorbs all wavelengths such that red is transmitted, but it also emits red light by fluorescence.

In summary, the exact colour produced by crystal field transitions in a mineral depends on many factors. The first of these is the identity of the transition metal. The second, its oxidation state determines the number of d electrons present, a factor important in determining the intensity of crystal field transition through the spin-multiplicity selection rule. The third, the geometry of the coordination site occupied by the metal controls the splittings of the d orbitals and hence the possible crystal field transition energies. It also controls the degree to which the Laporte selection rule forbidding all d-d transitions will be relaxed and hence influenced the transition intensity. The fourth, the strength of the crystal field, which depends on the mean-metal-oxygen distance and on the degree of negative charge isolated on the coordinating oxygens (controlled by the bonding behavior of the mineral) determines the magnitude of the energy splittings of the d orbitals and hence the energies of the crystal field transitions.

### Molecular orbital transitions

Crocoite,  $\text{PbCrO}_4$ , is an orange mineral having discrete  $\text{CrO}_4^{2-}$  tetrahedra and  $\text{Pb}^{2+}$  ions. The chromate groups contain  $\text{Cr}^{6+}$  which like  $\text{Pb}^{2+}$  has no d electrons. Similarly, Vanadinite  $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ , is an orange mineral having discrete  $\text{VO}_4^{3-}$  tetrahedra, containing  $\text{V}^{5+}$  an ion which also lacks d electrons. Therefore, the colour of these minerals cannot be due to crystal field transitions. Some evidence for the covalency of mineral bonding, e.g., the difference in the energy levels of  $\text{Cr}^{3+}$  in ruby and emerald has been seen. With electron delocalization over a cluster of atoms, all the electrons of the bonding unit or cluster must be treated together using molecular orbital energy.

The most common molecular orbital transitions in minerals fall under the general heading of charge transfer, since they may be viewed as the shift of electron density from one atomic center to another. Two classes of such transition are recognized: ligand to metal and metal to metal charge transfer. In addition, there are some minerals whose colours originate from molecular orbital transitions which are not charge transfer transitions.

### Ligand-metal charge transfer (oxygen to metal)

In crocoite and vanadinite, the  $\text{CrO}_4^{2-}$  and  $\text{VO}_4^{3-}$  groups are isolated as discrete bonding units. In these clusters, valence electrons of the constituent atoms are contributed to share molecular orbitals (MO's), which are delocalized over the entire cluster. Discrete, allowed energy levels existed on these molecular orbitals, and electronic transitions can take place between them. Wavelengths of

light corresponding to allowed energy differences will be absorbed in the exciting electrons from lower to higher energy levels. Molecular orbital transitions are recognized as oxygen — metal charge transfer when the electron is excited from an orbital with oxygen p character to one of metal 3d character. In crocoite and vanadinite, oxygen — metal ( $O^{2-} \rightarrow Cr^{6+}$ ,  $O^{2-} \rightarrow V^{5+}$ ) charge transfer transitions are responsible for the strong absorption in the violet, blue and green, giving their observed orange to orange-red colours.

Holidore is an  $Fe^{3+}$ -bearing beryl in which the  $Fe^{3+}$  occupies the same  $AlO_6$  sites as does  $Cr^{3+}$  in emerald. The bonding unit of interest holidore can be approximated by the octahedral cluster  $(Fe^{3+}O_6)^{9-}$ . Crystal field transitions in  $Fe^{3+}$  are spin forbidden and occur with low intensity in the blue region of the spectrum. The major colour-producing feature is the strong absorption in the violet, giving the transmitted yellow-orange colour. This charge transfer transition, absorbs much more strongly than the spin forbidden crystal field transition in  $Fe^{3+}$ -bearing minerals, for example, citrine.

**Metal-metal charge transfer**

Metal-metal (or intervalence) charge transfer involves the transfer of an electron between transition metal ions of the variable oxidation states in adjacent metal sites. Consideration of element abundances and oxidation states reveals that  $Fe^{2+} \rightarrow Fe^{3+}$  and  $Fe^{2+} \rightarrow Ti^{4+}$  are the most common charge transfer transitions in minerals. In an  $Fe^{2+} \rightarrow Fe^{3+}$  charge transfer transition, an electron is transferred from  $Fe^{2+}$ , in site A ( $Fe_A^{2+}$ ) to  $Fe^{3+}$  in site B ( $Fe_B^{3+}$ ).



Energies of this reversible electron-hopping process correspond to wavelengths of visible light, and many minerals owe their intense blue colour.

The energy of a given charge transfer transition not only depends on the type of ions involved but it also increases with metal-metal distance. The metal-metal distance increases, the probability of the electron transfer decreases.

#### Colour centers

Some minerals have colour centers, which are imperfection in transparent solids (substitutional impurity ions, lattices vacancies, etc), that can "trap" single electron. This electron may undergo electronic transition which absorbs in visible light. If sufficient energy is supplied, the energy barrier which traps the electron in the colour center can be exceeded. In this case, the electron returns to its original location, and the colour center is destroyed. The electron may be excited back to the colour center "trap" by high energy radiation, which is why many colour centers can be destroyed by heating and recreated with gamma or X-irradiation.

Fluorite, during its growth, may develop fluorine lattice vacancies ( a deficient number of  $\text{F}^-$  ions). In order to maintain charge balance, single electron fills the fluorine vacancy, forming a type of colour center. These trapped electrons in fluorite absorb wavelengths of visible light, such that the transmitted colour of the mineral is purple.



### Band transition

Other coloured minerals, for instance realgar( $As_2S_3$ ) and sulphur, contain neither colour center nor transition metal ion. The origins of their colours may be explained by the band theory of solids, which describes the behavior of all the electrons in a mineral. In its simplest form, band theory considers the energy levels available to a single electron in a solid as it moves in the coulomb field of the fixed ion cores and all the other electrons. Because there are about  $10^{24}$  atoms in a typical mineral, the number of possible energy levels available to the electron under consideration is large. In fact, the discrete energy levels of the constituent atoms spread into nearly continuous ranges of allowable energies. Each atomic level thus becomes what is called an energy band. The electrons in the mineral fill the lowest energy levels successively, in accordance with the Pauli exclusion principle, which does not allow more than one electron to occupy each state. When all the electrons have been accounted for, the uppermost energy level occupied by any electron is referred to as the fermi level.

If the fermi level occurs in the middle of a band, the electrons in the band can easily move in an applied electric field, and the mineral is a metal; if the number of electrons present is such that the highest occupied band is exactly filled, the mineral is either a semiconductor or an insulator, depending on the magnitude of the energy gap (band gap) between the filled band and the next band of allowable energy levels. Many of the band gaps that occur in minerals correspond in energy to wavelengths of visible light, those wavelengths lower in energy than

the band gap are absorbed by the mineral. Among the relatively simple minerals whose electronic structure# have been quantitatively treated within the framework of band theory and which owe their colours to band gap transition are crocusite, realgar, cinnabar( $\text{HgS}$ ), sulphur, galena ( $\text{PbS}$ ), blue( C and B impurities) and yellow ( N impurity) diamond.