

These models are then used to calculate heat capacities, entropies and thermal expansion coefficients, and ultimately to predict the relative thermodynamic stability of minerals in a wide variety of physical environments. Although calculations of the thermodynamic properties from computer simulations is still in its early stages, the possibility of obtaining these quantities under conditions where experiments are very difficult (e.g. mantle conditions) will continue to stimulate improvements in these methods.

#### 4.5 Optical spectroscopy – visible and ultra-violet

Optical spectroscopy is concerned with transitions of electrons between outermost energy levels, which have energy differences in the range from near infra-red, through visible, to ultra-violet (Table 4.1). Such optical transitions are often responsible for the colour of minerals, produced when absorption occurs in some part of the visible spectrum. A detailed analysis of the optical spectrum provides information about electronic energy levels of the absorbing ion, and how they are affected by local structure such as the type of coordination, its symmetry and distortions, bond types, as well as interactions with neighbouring anions and cations.

The basic nomenclature of electronic structure and quantum numbers is reviewed in Appendix A.

There are various types of electronic transitions which can be observed in the UV to IR spectral range and those of most importance in minerals are:

1. Transitions in which an electron from one orbital is promoted to a higher energy orbital in the same atom. Usually this involves electrons in the unfilled *d*-orbitals of ions in the first row transition elements such as  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . These transitions involve absorption in the visible to near infra-red and are the major cause of colour in minerals. They are often called crystal field spectra for reasons which will be explained below.

2. Transitions in which an electron from an orbital on one atom is promoted to a higher energy orbital on an adjacent atom. There are two ways in which this can occur.

(i) Electron transfer from an anion to a cation e.g. transfer from a filled oxygen *p* orbital to a partially occupied  $\text{Fe}^{3+}$  *d* orbital. These transitions occur in the ultra-violet region with a high probability and produce a very intense

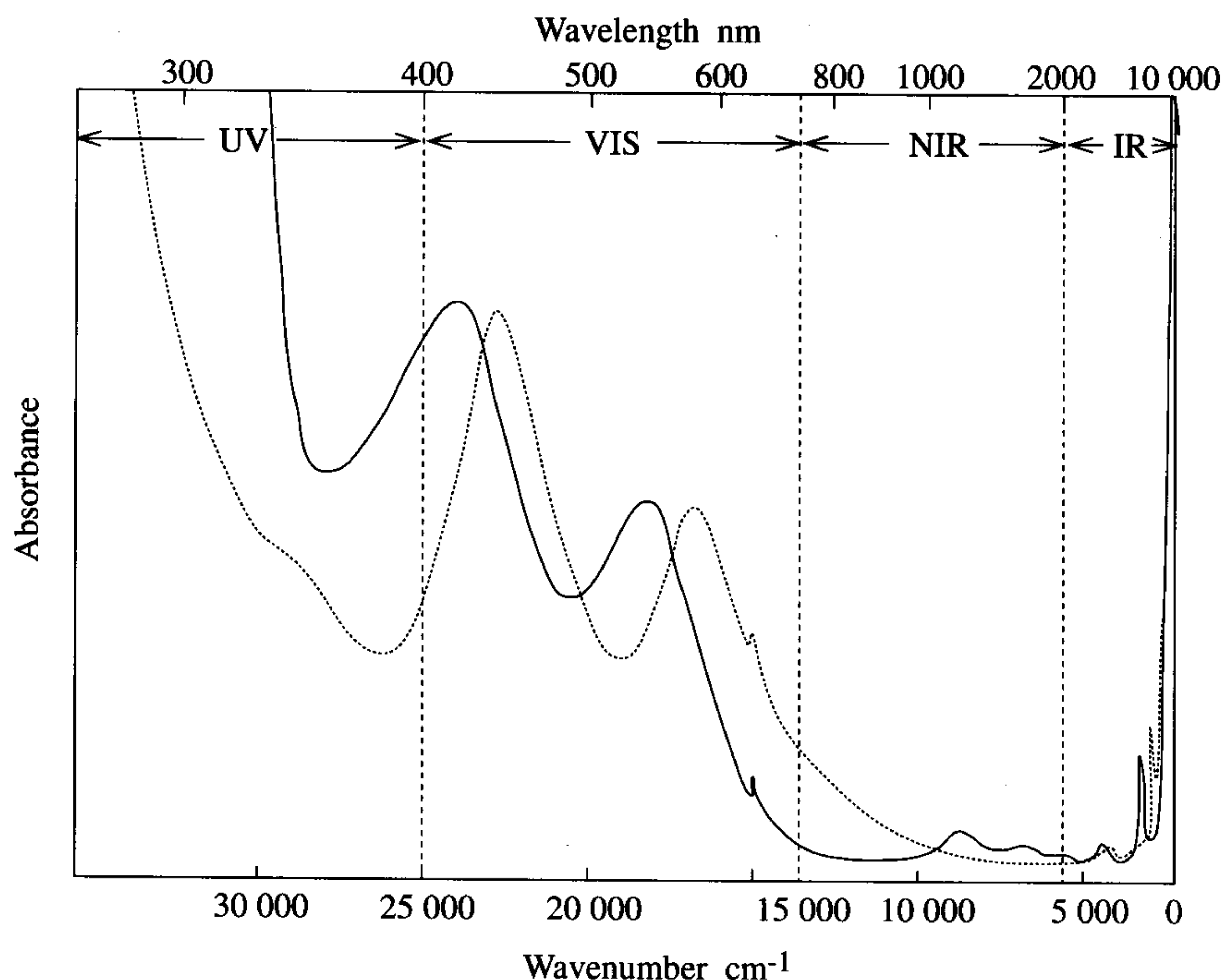
absorption, up to  $10^3$  to  $10^4$  times higher than those of crystal-field transitions.

(ii) Electron transfer from one cation to a higher energy orbital in an adjacent cation. The cations must have different oxidation states and the transfer generally occurs between cations in adjacent edge-shared coordination polyhedra, especially when metal-metal interatomic distances are small. Absorption bands for these *intervalence charge transitions* (IVCT) occur principally in the visible region with intensities between  $10^2$  and  $10^3$  times stronger than transitions between *3d* orbital energy levels.

3. Of less importance in minerals are electron transitions from a localized orbital on an atom to the conduction band which is a delocalized energy band characteristic of the whole solid. Such transitions occur in sulphide minerals with absorption in the visible/ultra-violet range e.g. the red colour of cinnabar,  $\text{HgS}$ , is due to the absorption of wavelengths shorter than 600nm. In silicates this absorption takes place at higher energies, far into the ultra-violet.

The principal features of a typical absorption spectrum in the UV to IR spectral range are shown in Figure 4.24. Energy units used in optical spectroscopy are often quoted in terms of wavelength, as well as wavenumber. At the UV end of the spectrum an absorption edge occurs beyond which the transmittance of the sample virtually drops to zero. This feature is due to oxygen  $\Rightarrow$  metal charge transfer, and in some cases due to electron transfer to the conduction band. The energy at which oxygen  $\Rightarrow$  metal transfer occurs depends on the cation and the symmetry of its coordination site. For octahedrally coordinated cations the energies decrease in order from  $\text{Cr}^{3+} > \text{Ti}^{3+} > \text{Fe}^{2+} > \text{Ti}^{4+} > \text{Fe}^{3+}$ . For  $\text{Fe}^{3+}$  in tetrahedral coordination the charge transfer occurs at lower energies, and may extend well into the visible region.

At frequencies below the absorption edge a number of broad peaks or absorption bands occur. Strong absorption bands in this region may be the result of intervalence transitions, and the weaker features are due to the intra-electronic *d-d* crystal field transitions. Most mineralogical studies have concentrated on this region, both in studies of local structural environment around transition metal cations as well as for the determination of the origin of colour and pleochroism in minerals.



**Figure 4.24.** The principal features of a typical absorption spectrum in the range from ultraviolet through to the near infra-red, shown for two different garnet samples, one with 5.5 wt%  $\text{Cr}_2\text{O}_3$  (solid line), the other with 17 wt%  $\text{Cr}_2\text{O}_3$  (dotted line). (After Langer, 1987.)

Optical spectra are obtained by passing light through a polished crystal slice which must be thin enough to transmit. Spectrometers can also be fitted to microscopes allowing work on samples a few tens of micrometres in diameter.

#### 4.5.1 Crystal field spectra

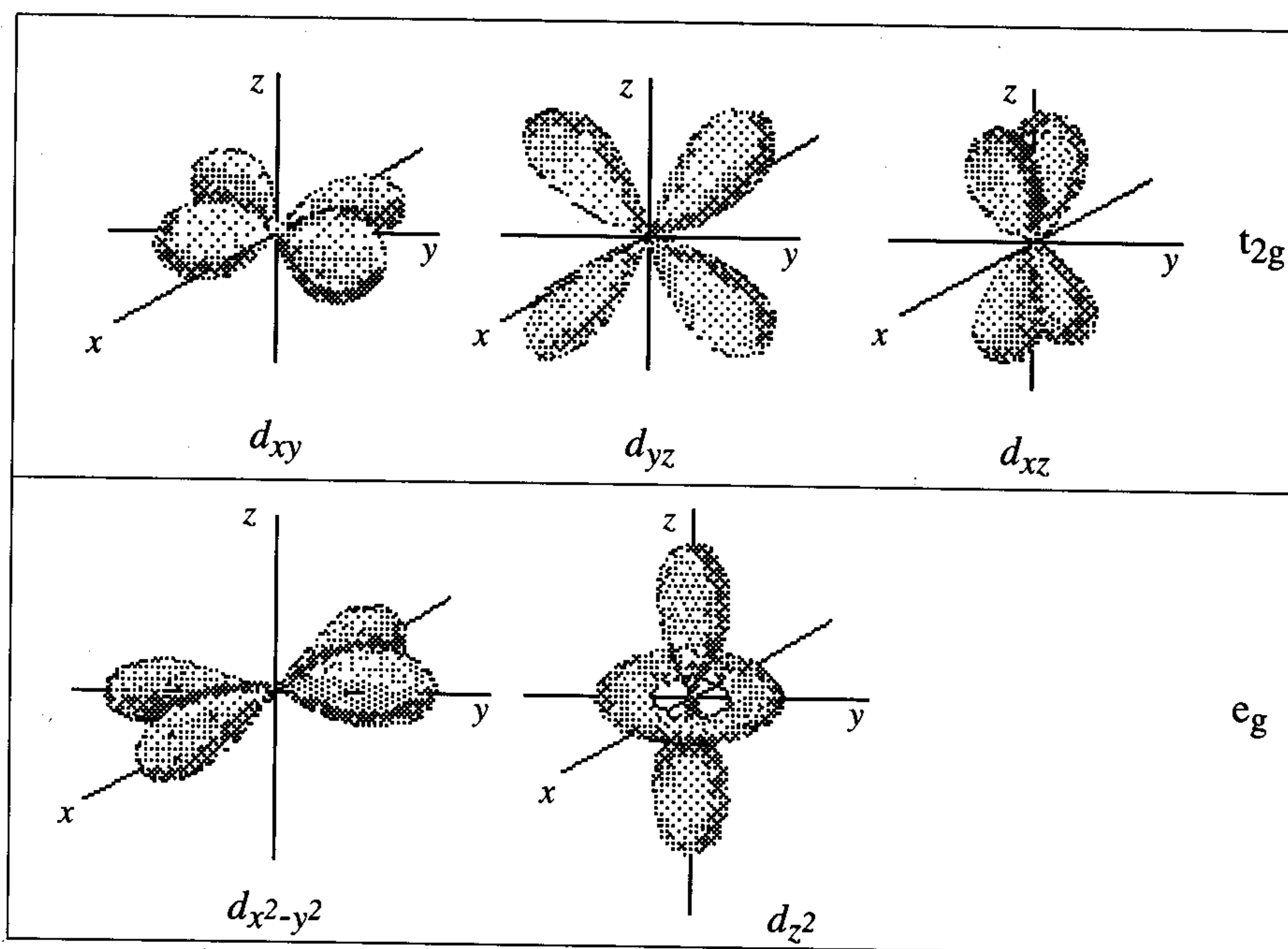
Understanding the origin of crystal field spectra involves a more detailed description of the nature of  $d$ -orbitals and their energy when the ion is in various crystallographic environments. Crystal field theory provides a simple illustration of the principles which define how electron energy levels are affected by their environment, and the description of the interaction of the symmetry of the various energy states with the symmetry of the environment are applicable in a general way to other spectroscopic methods.

The  $d$  electrons are divided into 5 orbitals, with shapes represented by the angular distribution probabilities for electrons in each orbital (Figure 4.25). On the basis of this angular distribution the 5 orbitals are divided into 2 groups, termed  $t_{2g}$  and  $e_g$  (the terminology comes from the symmetry of the wave functions of the electrons, but need not concern us here). Each orbital can accommodate 2

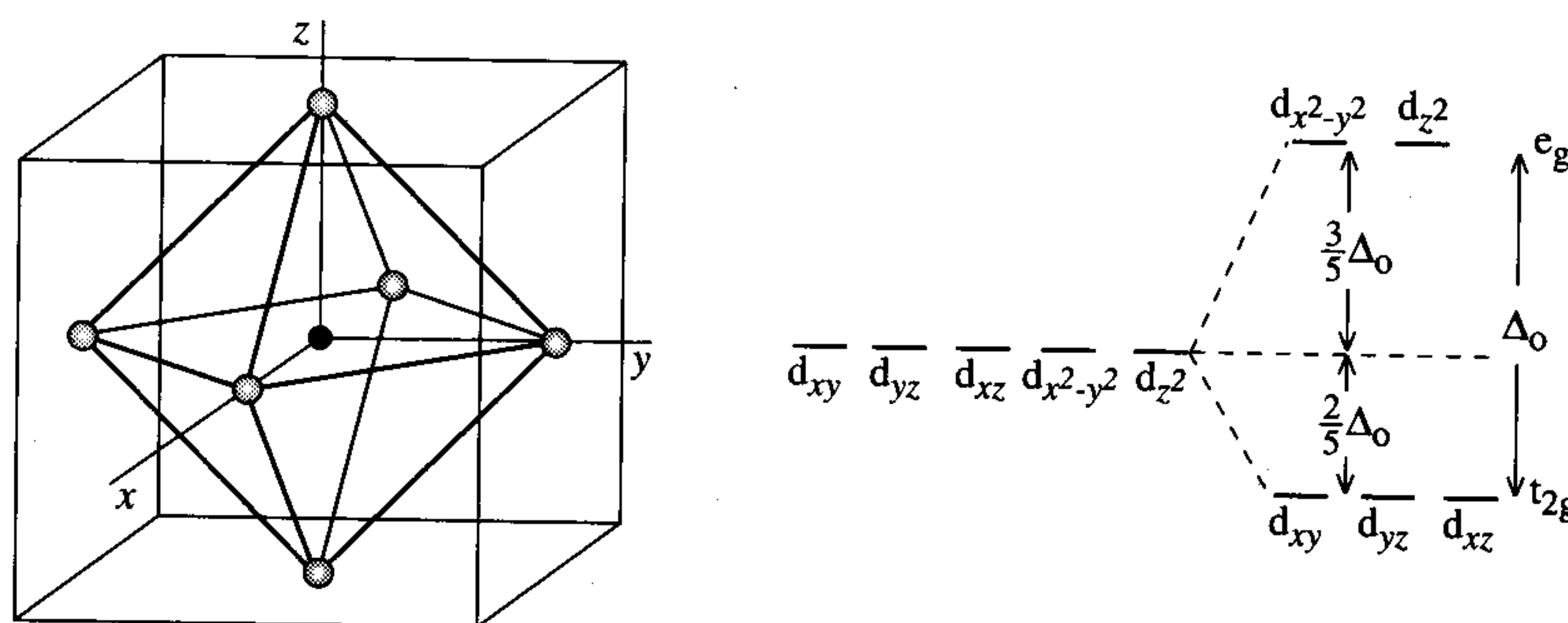
electrons spinning in opposite directions,  $m_s = \pm \frac{1}{2}$  and so 10 electrons can occupy the  $d$ -orbitals. Partly filled  $d$ -orbitals are occupied with electrons spreading out over as many orbitals as possible, one electron in each before any pairing of spins takes place. This distribution is termed the high-spin state and minimizes inter-electron repulsion (Hund's rule). The alternative arrangement where spins are paired where possible is termed the low-spin state.

In a free ion, or an ion in a spherical field, all of the  $3d$  electrons have equal probability of being in any of the  $3d$  orbitals, since they all have the same energy. When such an ion is in a crystal structure the relative energies of the  $3d$  orbitals are controlled by the different repulsive energies of the anions coordinated to it. This is where the symmetry of the orbitals is important, for if the lobes of the electron distributions of the different orbitals (Figure 4.25) point towards the anions, electrons in these orbitals are repelled to a greater extent and their energy is raised relative to orbitals which project between the anions. This can be illustrated by considering a transition metal ion in octahedral coordination.

Figure 4.26 shows an octahedron with anions at the corners, and a transition metal cation at its centre. By comparing this figure with Figure 4.25,



**Figure 4.25.** The shapes of the  $d$  atomic orbitals, representing the regions which contain most of the electron density. The orbitals are classified into two groups,  $t_{2g}$  and  $e_g$  on the basis of their orientation relative to the  $x$ ,  $y$  and  $z$  axes.



**Figure 4.26.** Crystal field splitting in octahedral coordination. When the transition metal cation (black sphere) is octahedrally coordinated by 6 anions (shaded spheres), the  $t_{2g}$   $d$  orbitals point between the anions, while the  $e_g$  orbitals point directly towards the anions (see Figure 4.25). This raises the energy of the  $e_g$  orbitals, and lowers the energy of  $t_{2g}$  orbitals relative to an ion in a spherical field. The splitting of these energy levels is designated  $\Delta_o$ .

we can see that the lobes of the two  $e_g$  orbitals point towards the anions, while the lobes of the three  $t_{2g}$  orbitals lie between the anions. This results in an energy reduction for electrons in  $t_{2g}$  relative to those in the  $e_g$  orbitals, as shown in the accompanying energy level diagram in Figure 4.26. The splitting of these energy levels, designated  $\Delta_o$ , is such that the average energy stays the same. Thus if all five orbitals were each occupied by one electron, the two electrons in  $e_g$  would each raise the energy by  $\frac{3}{5}\Delta_o$ , while the three electrons in  $t_{2g}$  would each reduce the energy by  $\frac{2}{5}\Delta_o$ , giving a net energy change of

zero. However if the ion contained only three  $d$ -electrons for example, and they were all in  $t_{2g}$ , there would be a net reduction in energy of  $\frac{3}{5}\Delta_o$ . This net reduction is termed the crystal field stabilisation energy, CFSE.

Table 4.2 lists electron configuration and CFSE for high- and low-spin states of transition metal ions in octahedral sites. This table shows that for some ions there is a significant stabilisation of the low-spin state and this tendency opposes the electrostatic interactions which favour a distribution with parallel spins over as many sites as possible (i.e. breaks

Table 4.2. Electronic configuration and crystal field stabilization energies of transition metal ions in octahedral coordination. (Burns, 1970).

Number of 3d electrons	Ion	High-spin state				Low-spin state			
		Electronic configuration		Unpaired electrons	CFSE	Electronic configuration		Unpaired electrons	CFSE
		$t_{2g}$	$e_g$			$t_{2g}$	$e_g$		
0	Ti <sup>4+</sup>			0	0			0	0
1	Ti <sup>3+</sup>	↑		1	$2/5 \Delta_o$	↑		1	$2/5 \Delta_o$
2	Ti <sup>2+</sup> , V <sup>3+</sup>	↑ ↑		2	$4/5 \Delta_o$	↑ ↑		2	$4/5 \Delta_o$
3	Cr <sup>3+</sup> , V <sup>2+</sup> , Mn <sup>4+</sup>	↑ ↑ ↑		3	$6/5 \Delta_o$	↑ ↑ ↑		3	$6/5 \Delta_o$
4	Cr <sup>2+</sup> , Mn <sup>3+</sup>	↑ ↑ ↑	↑	4	$3/5 \Delta_o$	↑ ↓ ↑ ↑		2	$8/5 \Delta_o$
5	Mn <sup>2+</sup> , Fe <sup>3+</sup>	↑ ↑ ↑	↑ ↑	5	0	↑ ↓ ↑ ↓ ↑		1	$10/5 \Delta_o$
6	Co <sup>3+</sup> , Fe <sup>2+</sup> , Ni <sup>4+</sup>	↑ ↓ ↑ ↑	↑ ↑	4	$2/5 \Delta_o$	↑ ↓ ↑ ↓ ↑ ↓		0	$12/5 \Delta_o$
7	Co <sup>2+</sup> , Ni <sup>3+</sup>	↑ ↓ ↑ ↓ ↑	↑ ↑	3	$4/5 \Delta_o$	↑ ↓ ↑ ↓ ↑ ↓	↑	1	$9/5 \Delta_o$
8	Ni <sup>2+</sup>	↑ ↓ ↑ ↓ ↑ ↓	↑ ↑	2	$6/5 \Delta_o$	↑ ↓ ↑ ↓ ↑ ↓	↑ ↑	2	$6/5 \Delta_o$
9	Cu <sup>2+</sup>	↑ ↓ ↑ ↓ ↑ ↓	↑ ↓ ↑	1	$3/5 \Delta_o$	↑ ↓ ↑ ↓ ↑ ↓	↑ ↓ ↑	1	$3/5 \Delta_o$
10	Ga <sup>3+</sup> , Zn <sup>2+</sup> , Ge <sup>4+</sup>	↑ ↓ ↑ ↓ ↑ ↓	↑ ↓ ↑ ↓	0	0	↑ ↓ ↑ ↓ ↑ ↓	↑ ↓ ↑ ↓	0	0

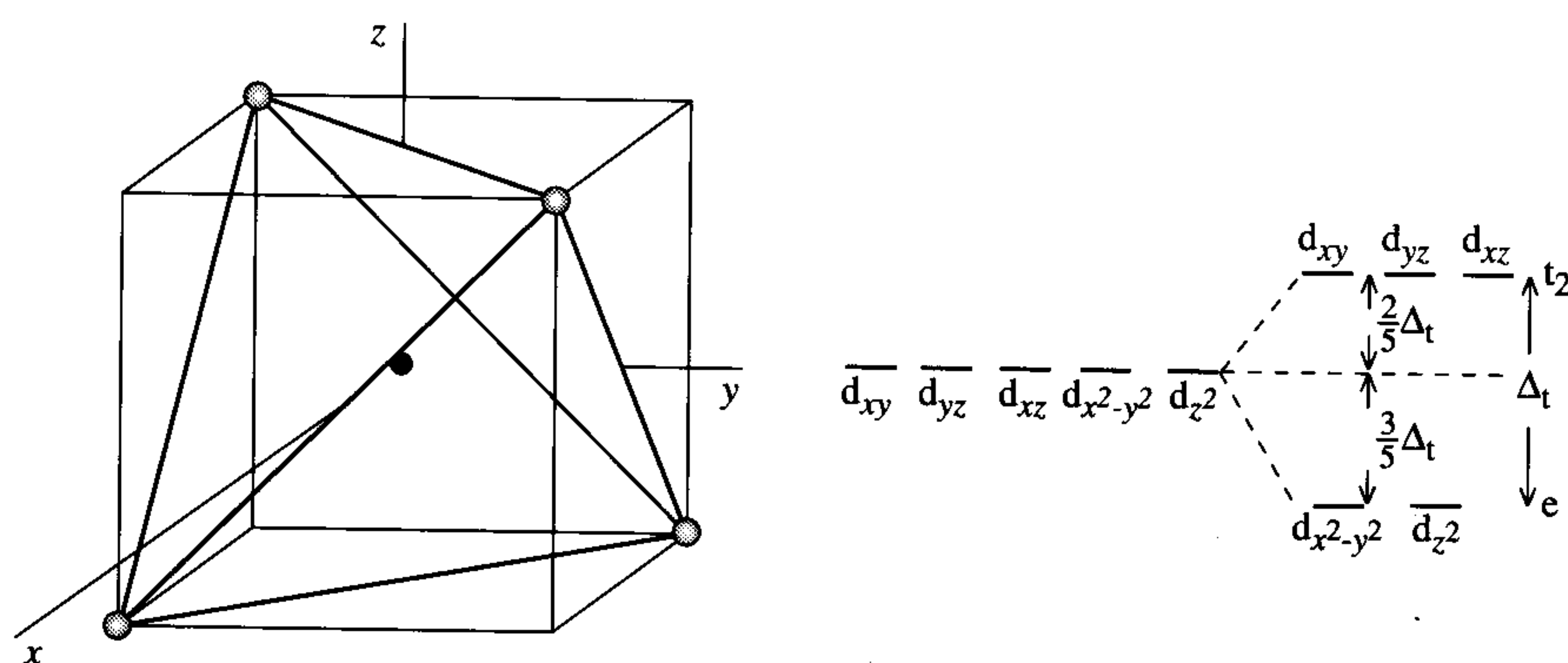


Figure 4.27. Crystal field splitting in tetrahedral coordination. When the transition metal cation (black sphere) is tetrahedrally coordinated by 4 anions (shaded spheres) the  $t_2$   $d$  orbitals point nearer to the anions than the  $e_g$  orbitals (see Figure 4.25). This raises the energy of the  $t_2$  orbitals relative to the  $e_g$  orbitals, splitting the energy levels by  $\Delta_t$ . Compare this to the situation in Figure 4.26.

Hund's rule). The result of these opposing tendencies is that while  $\text{Co}^{3+}$  and  $\text{Ni}^{3+}$  may exist as low spin states the other transition metals remain in high spin states on the Earth's surface.

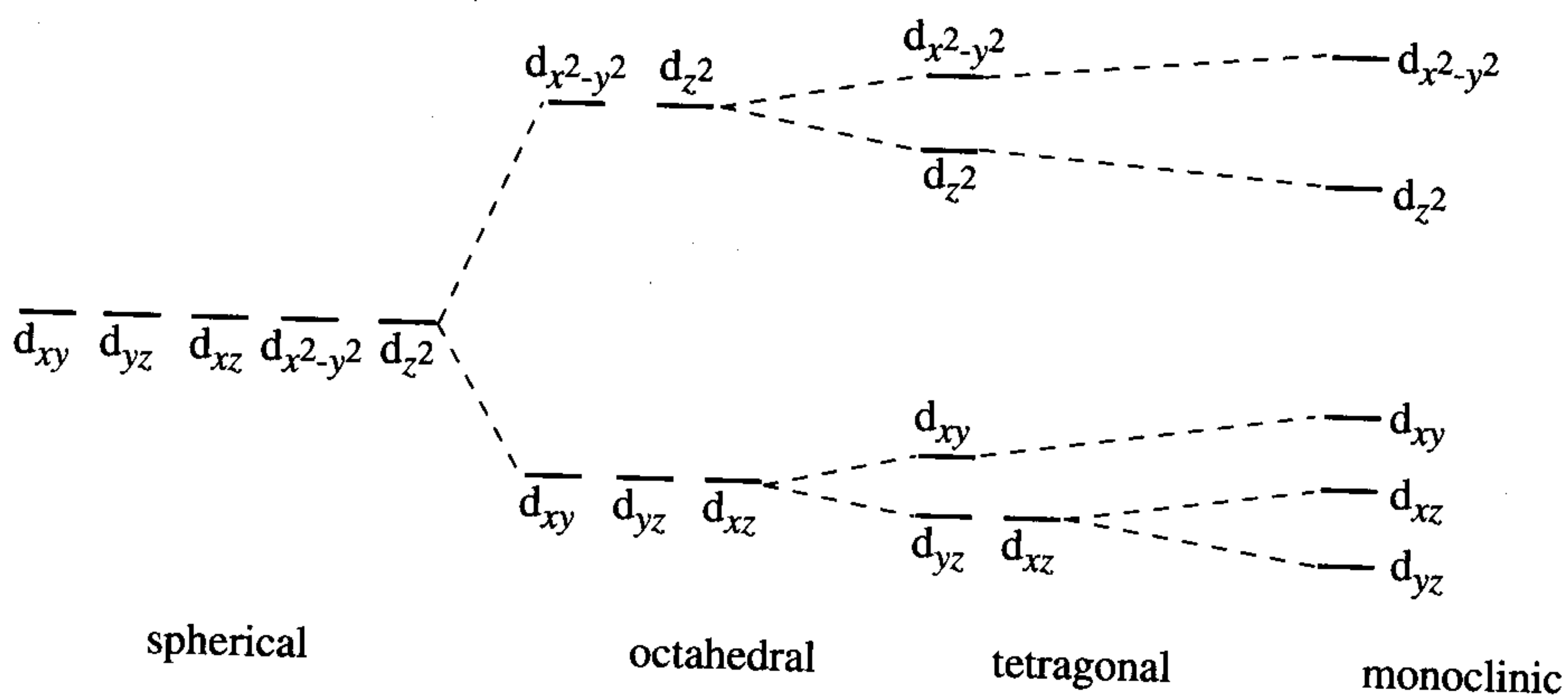
Transitions between  $t_{2g}$  and  $e_g$  orbitals are induced by light passing through the crystal, resulting in absorption at the energy defined by the octahedral crystal field splitting parameter  $\Delta_o$ . The magnitude of  $\Delta_o$  depends on the cation, its valence state, and the nature of the anions coordinated to it, as well as the cation-anion distance. The effect of this selective absorption in the visible range is that the transmitted light is coloured.

#### 4.5.2 Effect of coordination around the cation

The analysis above, for an ion in an undistorted octahedral environment can be repeated for other

symmetrical coordinations. For example, if the ion is in a tetrahedral site (Figure 4.27) the  $t_2$  orbital lobes are now repelled by the anions to a greater extent than the  $e$  orbital lobes and this reverses the energy levels relative to the octahedral case. The crystal field splitting parameter  $\Delta_t$  is not as great as in the octahedral case, as the orbital lobes are not now directly towards or between the anions. A similar energy level diagram exists for regular cubic coordination, but with a larger relative  $\Delta$  splitting.

As the symmetry of the coordination is reduced, the energy levels are split further. For example, if an octahedron is distorted to tetragonal symmetry (by extending the  $c$  axis for example), the two levels  $e_g$  and  $t_{2g}$  are split into four. Any further distortion of the octahedron to lower symmetry results in all 5 orbitals having different energies (Figure 4.28). The analysis of the degree of splitting is obviously more

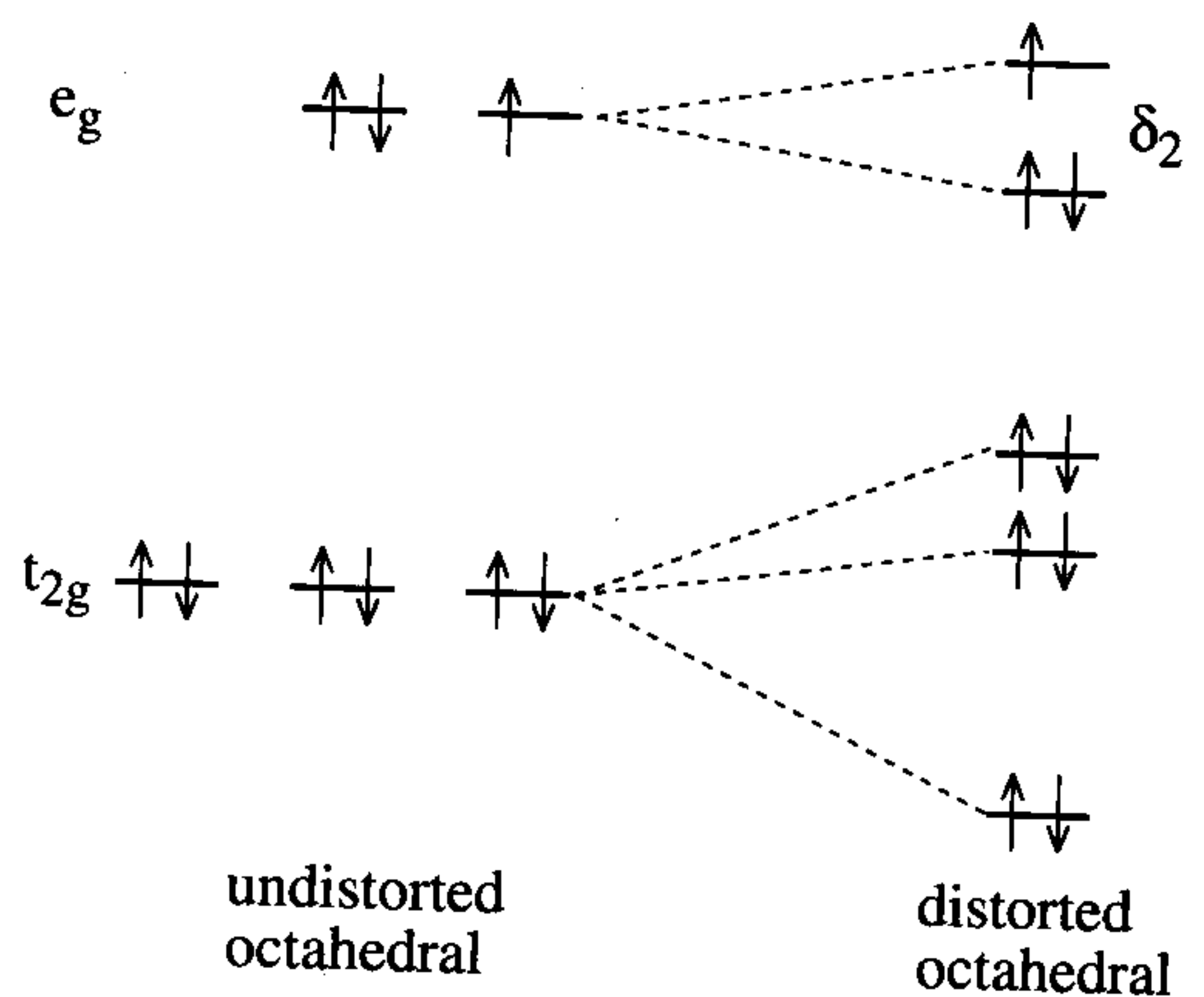


**Figure 4.28.** The effect of a progressive decrease in symmetry around the cation. In a spherically symmetric field the  $d$  orbitals are all degenerate, while in octahedral coordination they are split into two groups as described in Figure 4.26. If the octahedron is distorted to tetragonal symmetry by stretching it along the  $z$  axis the energy levels are split further. (A compression along the  $z$  axis would reverse the sense of the splitting within each group). A further distortion to monoclinic symmetry completely removes the degeneracy, resulting in five separate energy levels.

complex than in the symmetrical case, and group theoretical methods are needed to describe the symmetry of the site and the resultant energy level diagrams. The net effect of considering crystal field splitting for transition metal ions in different coordinations is to conclude that except for  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  in which there is no net CFSE for either octahedral or tetrahedral sites, transition metal ions always prefer octahedral coordination.

### 4.5.3 Jahn–Teller distortion

For some transition metal ions a distorted coordination always has a lower energy than a regular coordination as a result of the Jahn–Teller effect. The origin of this spontaneous distortion can be seen by considering the case of  $\text{Cu}^{2+}$  in an octahedral environment. As seen in Table 4.2,  $\text{Cu}^{2+}$  has electronic configuration  $(t_{2g})^6 (e_g)^3$ , and the energy level diagram for an undistorted octahedral coordination is shown in Figure 4.29. If the octahedron is distorted however, the energy levels are split into five (Figure 4.29). Although there is no net reduction in the energy associated with the  $t_{2g}$  orbitals, the fact that one of the  $e_g$  orbitals is half filled results in an overall energy reduction of  $\frac{1}{2} \delta_2$  for the distorted state. The distorted state then becomes the ground state of the ion. This will be the case whenever one  $d$  orbital is completely empty or completely full while another of equal energy is half filled. The largest Jahn–Teller distortions are found when the degeneracy is in the  $e_g$  orbitals, which occurs when they are



**Figure 4.29.** Jahn–Teller distortion for  $\text{Cu}^{2+}$  in octahedral coordination.  $\text{Cu}^{2+}$  has filled  $t_{2g}$  orbitals, but only three electrons in the  $e_g$  orbitals. In an undistorted octahedral site the  $e_g$  orbitals are all degenerate, but in a distorted coordination, they are split into two separate orbitals separated by energy  $\delta_2$ . Since two of the three  $e_g$  electrons occupy the lower of these energy levels, the net reduction in energy is  $\frac{1}{2}\delta_2$ . Thus  $\text{Cu}^{2+}$  prefers a distorted octahedral environment.

occupied by one or three electrons. Thus  $\text{Cr}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{3+}$  (low spin) are usually in distorted octahedral environments.

### 4.5.4 Anisotropy of the absorption – pleochroism

Minerals with symmetry lower than cubic are anisotropic and it is necessary to obtain separate spectra with plane polarized light vibrating along each principal axis of the optical indicatrix (see Chapter 2). For biaxial crystals three spectra, termed the  $\alpha$ ,  $\beta$  and  $\gamma$  spectra, are taken with the incident vibration