

## Chapter 2

# Theoretical Background

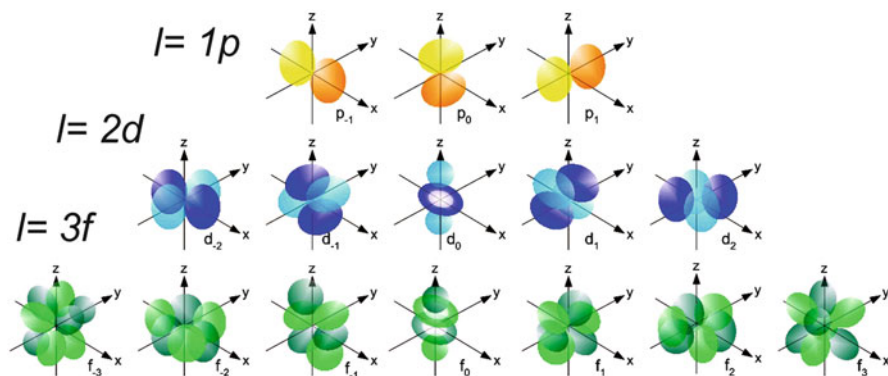
Theoretical data essential for understanding of luminescence phenomenon may be found in many books, but we believe that for specific field of minerals luminescence the fundamental books of Marfunin (1979a, b) are the best. Below we tried to present very shortly only the mostly essential data especially connected with kinetic considerations, which are the basis of time-resolved technique.

### 2.1 The s, p, d, f Atomic Orbitals

According to quantum mechanics laws, electrons in free atoms occupy so-called atomic orbitals. Each orbital is characterized by its energy and is determined by quantum numbers  $n$ ,  $l$ ,  $m_l$ , where  $n$  is the main quantum number, designated by numbers 1, 2, 3, ...,  $l$  is the orbital quantum number with 0, 1, 2 ... ( $n - 1$ ) values and  $m_l$  is the magnetic quantum number with  $-l$ ,  $-l + 1$ , ..., 0, ...,  $l - 1$ ,  $l$  values.

For explanation of luminescence properties of the atomic orbitals, their symmetry and directional properties are most important. The shape of atomic orbitals in space is determined by the  $l$  quantum number, designated as s, p, d, f for  $l = 0, 1, 2, 3$ . The number of possible orientations of the orbitals is given by the number of possible values of the  $m_l$  magnetic quantum number and is equal for the s-orbitals to 1, for the p-orbitals to 3, for the d-orbitals to 5 and for the f-orbitals to 7, according to  $(2l + 1)$  rule. In a totally symmetric surrounding all orientations of the orbitals are equivalent and correspond to the same energy value. These orbitals are called degenerate, which means they are characterized by equal energy. Figure 2.1 represents real forms of the p, d and f orbitals.

Each element is characterized by specific scheme of energy levels. When individual elements are combined forming minerals the energy levels are changed. They have now different energies and form different system of energy levels typical



**Fig. 2.1** The forms of the angular dependence functions for p, d, and f orbitals (Figgis 1966)

for mineral. The process of new energy levels system in minerals may be described using different theories of solid state physics, such as ligand field theory, molecular orbitals theory and zone theory, which are especially useful for absorption and luminescence properties explanation.

## 2.2 Point Group Symmetry

As we will demonstrate, luminescent properties, radiative transition characteristics as well as emission under site selective excitation depend of the local environment symmetry of the luminescent center. Therefore it is necessary to take into account and to describe the different local symmetry. There are two systems commonly used in describing symmetry elements of punctual groups:

1. The Schoenflies notation (1891) used extensively by spectroscopists, and
2. The Hermann-Mauguin (1935) or international notation preferred by crystallographers.

Schönflies notation is widely used to describe molecule or assemblages of atoms (polyhedron) such as local environment of an atom. Thus, it is widely used to describe the symmetry of structural sites. It is a more compact notation but less complete than Hermann-Mauguin one. It consists generally of one cap letter, followed by one subscript number and one final letter:

- Symmetry  $C_n$  for one rotational axis (cyclic);  $C_1$ : identity;  $C_n$ : the polyhedron has an n-fold axis of symmetry.
- Symmetry  $D_n$  for orthogonal axes (dihedral), n-fold axis of symmetry perpendicular to n twofold axes;
- Cubic symmetry: T for 4 axes (tetrahedral), O for 8 axes (octahedral) et I pour 20 axes (icosahedra, exists to describe molecules but not for crystals);

- Planar symmetry:
  - one subscript letter follows the rotation symmetry (by example  $C_{3h}$ ); h indicates a planar symmetry (mirror) parallel to the rotation axis (horizontal), v a mirror perpendicular to the rotation axis (vertical) and d a diagonal mirror;
  - $S_n$ , S indicates a mirror symmetry (Spiegel in German) and  $n$  invariance by a  $n$ -fold rotation around the perpendicular axis to the plan. An added superscript  $m$  number indicates sometimes that the symmetry operation is applied  $m$  times.

Table 2.1 presents the non-cubic crystallographic point groups with compared notation.

## 2.3 Absorption of the Excitation Energy

### 2.3.1 Optical Absorption Spectroscopy

It is a remarkable fact that the contemporary history of absorption and emission spectroscopy began simultaneously, from the simultaneous discoveries by Bunsen and Kirchhoff made in the middle of the nineteenth century. They observed atomic emission and absorption lines whose wavelengths exactly coincided. Stokes and Kirchhoff applied this discovery for the explanation of the Fraunhofer spectra. Nearly at the same time approximately 150 years ago, Stokes explained the conversion of absorbed ultraviolet light into the emitted blue light and introduced the term fluorescence. Apparently, the discovery of the Stokes shift marked the birth of luminescence as a science.

A rule due to Beer and Lambert is that the light absorbed per unit length in a sample depends at any wavelength only on the incident light intensity, i.e.,

$$\frac{dI(\lambda)}{dx} = -\alpha I(\lambda) \quad (2.1)$$

where  $\alpha$  is a proportionality constant called the absorption coefficient, which also depends on wavelength.

Integrating Eq. 2.1, we find for a non-reflecting sample of thickness  $t$ :

$$I_T(\lambda) = I_o(\lambda)\exp(-\alpha t) \quad (2.2)$$

where  $I_T$  is the transmitted light intensity and  $I_o$  the incident light intensity. In these terms, the transmittance spectrum is

$$T(\lambda) = I_T(\lambda)/I_o(\lambda) \quad (2.3)$$

so that

**Table 2.1** The non-cubic crystallographic point groups

	Hexagonal	Tetragonal	Trigonal	Orthorhombic	Monoclinic	Triclinic
Cyclic	$C_6$	$C_4$	$C_3$		$C_2$	$C_1$
Cyclic + vertical planes	$C_{6v}$	$C_{4v}$	$C_{3v}$	$C_{2v}$		
Cyclic + horizontal planes	$C_{6h}$	$C_{4h}$			$C_{2h}$	
	$C_{3h}$				$\frac{C_{1h}}{(C_2)}$	$m (-2)$
Improper Rotation		$S_4$	$S_6(C_{3i})$			$S_2 (C_i)$
Dihedral	$D_6$	$D_4$	$D_3$	$D_2 (V)$		
Dihedral + horizontal planes	$D_{6h}$	$D_{4h}$		$D_{2h}(V_h)$		
Dihedral + planes between axes	$D_{3h}$	$D_{2d} (V_d)$				

For cubic symmetry, T correspond to 23,  $T_h$  to  $m\bar{3}$ , O to 432,  $T_d$  to 4-3 m,  $O_h$  to  $m\bar{3}m$  and I to 532 (thus impossible for crystals, but possible for molecule) Column pairs give the Schönflies and equivalent Hermann-Mauguin international notation. *C* indicates cyclic, *D* for dihedral, *S* for spiegel (or “mirror”), with h, v and d meaning respectively horizontal, vertical and diagonal (referring to mirror plane locations). A minus before a number indicates a horizontal bar above that number. Brackets indicate equivalent alternative. The centrosymmetric point groups are shown in bold. The enantiomorphic point groups are shown in italic. The polar point groups are underlined

$$T(\lambda) = \exp(-\alpha t) \quad (2.4)$$

The absorption spectrum is given by an inversion of Eq. 2.4 i.e.,

$$\alpha(\lambda) = \frac{1}{t} \ln \left( \frac{I_o}{I_T} \right) = \frac{1}{t} \ln(T^{-1}) \quad (2.5)$$

The absorbance is defined as:

$$\log_{10} \left( \frac{I_o}{I_T} \right) \quad (2.6)$$

In optical spectroscopy a sample is illuminated by monochromatic light with a varying wavelength. The optically active centers rise from the ground to the excited states with resulting appearance of the absorption band in the optical spectrum. Useful information may be obtained from the absorption spectroscopy, which reveals the excited energy levels. Nevertheless, it has to be noted that absorption technique is much less sensitive compared to luminescence. The reason is that absorption is a subtractive process. One measures small differences in large numbers (intensity of incident light-intensity of transmitted light). This difference will be very small for very low absorbance from low concentrations. Best sensitivity is  $\sim 0.0005$  OD (optical density), but most spectrophotometers are not nearly this good. On the other hand luminescence measures any detectable light against an essentially zero background. Modern detectors are capable of measuring single photons and thus luminescence can be extremely sensitive. There are a number of different processes, which may generate optical absorption in the visible and ultraviolet wavelength range. The following transitions are of primary importance for minerals (Platonov 1979; Rossman 1988; Matsyuk and Zintchouk 2001):

- d-d or f-f electronic transitions between ligand field split spectroscopic states of the free electronic levels of transition metals or rare earth ions. This process involves an ion with a partially filled d- or f-electron shell being incorporated into a crystalline environment whose symmetry produces a difference in energy between the different orbitals (see Sect. 2.4.1). Such effects are observed within compounds containing transition metal ions as  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ti}^{3+}$ ,  $\text{Cr}^{3+}$  and associated colors characterize a range of minerals. The intensities of d-d and f-f absorption bands can vary over four orders of magnitude: these are governed both by abundance of the absorbing cation, and by a combination of the symmetry of the cation environment and quantum mechanics selection rules (see Sect. 2.4.5).
- metal to metal charge-transfer between transition metal ions differing in valence state and accommodated in interconnected polyhedra of the mineral structure. This term used to describe absorption mechanism by transfer of electrons between transition metal ions in non-metals via an input of energy in the form of photon, especially those ions, which are able to adopt multiple valence states

in minerals, such as  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ,  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  and so on. Characteristically, these bands occur in the visible part of the spectrum, and are most intensive in those minerals, which have large quantities of transition metals, and relatively short metal-metal distances.

- ligand to metal charge transfer or an interband transitions, which involve transfer of electron density from ligand to the metal cation. Charge transfer transitions not only occur between transition metal ions, but also occur in excitation of electrons between cations and anions. Within oxides, such oxygen-to-metal charge transfer absorption bands typically occur at high energies in the ultraviolet, and are extremely intense: often three to four orders of magnitude more intense than d-d transitions. Effectively, such charge transfer between anions and cations is often associated with delocalization of an electron, or photoexcitation of an electron into the conduction band of a mineral. Within many minerals, such charge transfer bands appear as an absorption edge, rather than a discrete band: this edge is simply generated because all photons with energy above that of the edge will produce electron delocalization. Absorption generated by such cation-anion charge delocalization processes is common in ore minerals such as sulfides and arsenides.
- radiation induced centers from natural sources in rocks. Such electron-hole centers produced by ionizing radiation are mostly typical for smoky quartz, blue feldspar, green diamonds, and fluorite and calcite samples.

### 2.3.2 *Luminescence Excitation Spectroscopy*

A luminescent mineral will only emit radiation when the excitation energy is absorbed. It is possible to categorize luminescence mechanisms into two general classes. In the first the process of excitation is localized near an isolated center and occurs without ionization of any species in the mineral. This type of luminescence is called intra-centric. Excitation and emission occurs due to electronic transitions at the center. In certain luminescent minerals the situation is more complicated, because the activator does not absorb the exciting radiation, but it is absorbed by the other center, which subsequently transfers it to the activator. In this case the absorbing ion is called a sensitizer. The second mechanism occurs when the excitation is light of higher energy than the band gap, or consists of very high-energy radiation or particles. Ionization effects then occur, and the emission is produced by recombination of electrons or holes at ionized centers. Laser-induced luminescence mainly belongs to the first type direct excitation of centers of emission without their ionization. But during excitation with high-energy photons in semiconductors with a small inter-band spacing, an electron transfer of impurity ions of the ground substance to the conduction band takes place. In these crystals the energy levels of defects are divided according to their position in the forbidden band into donors (near the conduction band) and acceptors (in the vicinity of the valence band).

Absorption of the excitation energy resulting in luminescence is revealed by excitation spectra. Here the emission results of the transition from the specific electronic level. The excitation spectrum is registered as the intensity of luminescence as a function of the excitation wavelength. The excitation spectrum is measured using two monochromators. One is used to separate the exciting frequency and the other is used for separating a specific region in the luminescence spectrum. The second monochromator is set to a specific frequency, whereas the first one scans the excitation frequency. The appearance of tunable lasers has made it possible to avoid using the first monochromator.

The excitation spectrum demonstrates that for an effective luminescence not only the presence of emitting level is important, but also of the upper levels with a sufficiently intensive absorption. The excitation spectra enable to choose the mostly effective wavelength for luminescence observation. The combination of excitation and optical spectroscopies enable to determine the full pattern of the center's excited levels, which may be crucial for luminescence center interpretation, energy migration investigation and so on. The main excitation bands and lines of luminescence in minerals are presented in the Table [2.2](#).

### 2.3.2.1 Selective Spectroscopy

There are a large number of cases when the spectra of luminescence center remain broad up to helium temperatures. In certain cases, this is explained by a strong electron-phonon interaction, but more often the inhomogeneous broadening, connected with several types of the same center presence, causes this. In such cases it is possible to simplify the spectrum by selective excitation of a specific center.

### 2.3.2.2 Two-Photon Absorption Spectroscopy

In most of luminescence experiments, at least in the minerals luminescence field, excitation is due to absorption of a single photon. However, it is also possible for a luminescence center to absorb two or more long-wavelength photons to reach the excited state. Two-photon excitation occurs by the simultaneous absorption of two lower-energy photons. Such excitation requires special conditions including high local intensities, which can only be obtained from laser sources.

Thus it was not observed until lasers were invented. In principal, one-photon and two-photon excitation follow different selection rules. For example, the inner shell one-photon transitions in transition metal, rare earth, and actinide ions are formally forbidden by parity selection rule. These ions have d- or f-shells and transitions within them are either even to even ( $d \rightarrow d$ ) or odd to odd ( $f \rightarrow f$ ). The electric dipole transition operator is equal to zero. The two-photon transition operator is a tensor whose components may be nonzero. Thus an important reason for doing two-photon spectroscopy is that it allows to observe the transitions directly as

allowed transitions instead of indirectly as forbidden transitions as are all one-photon spectra of transition metal ions.

In single beam two-photon spectroscopy, an intense laser beam having a frequency  $h\nu = 1/2(E_2 - E_1)$  is passed through the crystal, and the attenuation of the

**Table 2.2** Main luminescence excitation bands and lines in minerals

Center	Electronic transition	$\lambda_{\text{excitation}}$ (nm)	$\lambda_{\text{luminescence}}$ (nm)
$\text{Pr}^{3+}$	$^3\text{H}_4 - ^1\text{S}_0$	280	480, 610, 650, IR
	$^3\text{H}_4 - ^1\text{I}_1$	460	
	$^3\text{H}_4 - ^1\text{I}_0$	490	
$\text{Nd}^{3+}$	$^4\text{I}_{9/2} - ^4\text{G}_{7/2-5/2}$	580	880, 1060, 1340 380, 417 535, 600, 670
	$^4\text{I}_{9/2} - ^2\text{D}_{7/2}$	320	
	$^4\text{I}_{9/2} - ^2\text{P}_{1/2}$	380	
$\text{Sm}^{3+}$	Charge transfer	230	540, 600, 675
	$^6\text{H}_{5/2} - ^6\text{P}_{5/2}$	407	
$\text{Sm}^{2+}$	4f-5d	450, 580	650, 690, 700, 730, 780, 810
$\text{Eu}^{3+}$	Charge transfer	220	590, 610, 650, 700
	$^7\text{F}_0 - ^5\text{H}_3$	325	
	$^7\text{F}_0 - ^5\text{D}_2$	532	
$\text{Eu}^{2+}$	4f <sup>7</sup> -4f <sup>6</sup> 5d	250, 310	380–450
$\text{Tb}^{3+}$	$^7\text{F}_6 - ^5\text{D}_3$	280	380, 417, 440, 550
$\text{Dy}^{3+}$	$^6\text{H}_{15/2} - ^6\text{P}_{5/2}$	351	480, 575, 670, 760
$\text{Er}^{3+}$	$^4\text{I}_{15/2} - ^4\text{G}_{11/2}$	370	550
$\text{Ho}^{3+}$	$^5\text{I}_7 - ^5\text{G}_2$	360	550, 640, 760
$\text{Tm}^{3+}$	$^3\text{H}_6 - ^3\text{P}_0$	360	360, 480, 780, 800
$\text{Ce}^{3+}$	4f-5d	280, 320–340	350–390
$\text{Yb}^{2+}$	4f <sup>14</sup> -4f <sup>13</sup> d <sup>1</sup> ( $k_1$ - $k_4$ )	250, 280, 320	520–560
$\text{Yb}^{3+}$	$^2\text{F}_{7/2} - ^2\text{F}_{5/2}$	920, 960	975, 1014
$\text{Gd}^{3+}$	$^8\text{S}_{7/2} - ^6\text{I}_{7/2}$	270	300, 312
$\text{Mn}^{2+}$	$^6\text{A}_1(\text{S}) - ^4\text{E}, ^4\text{A}_1(\text{G})$	380–400	480–700
	$^6\text{A}_1(\text{S}) - ^4\text{T}_1(\text{G})$	560–575	
$\text{Mn}^{4+}$	$^4\text{A}_2 - ^4\text{T}_1$	420	650–700
	$^4\text{A}_2 - ^4\text{T}_2$	530	
$\text{Mn}^{5+}$	$^3\text{A}_2 - ^3\text{T}_2$	400	1100–1500
	$^3\text{A}_2 - ^1\text{E}$	590	
$\text{Fe}^{3+}$	Charge transfer	300	700–750
	$^6\text{A}_1(\text{S}) - ^4\text{E}(\text{D})$	380	
	$^6\text{A}_1(\text{S}) - ^4\text{T}_2(\text{G})$	500	
$\text{Cr}^{3+}$	$^4\text{A}_2 - ^4\text{T}_1$	410	690–1000
	$^4\text{A}_2 - ^4\text{T}_2$	550	
$\text{V}^{2+}$	$^4\text{A}_2 - ^4\text{T}_1$	410	750–850
	$^4\text{A}_2 - ^4\text{T}_2$	560	
$\text{Pb}^{2+}$	$^1\text{S}_0 - ^3\text{P}_1$	220–260	300–400
$\text{Bi}^{3+}$	$^1\text{S}_0 - ^3\text{P}_1$	280	400–650
$\text{Bi}^{2+}$	$^2\text{P}_{1/2} - ^2\text{S}_{1/2}$	270	600–650

(continued)



**Table 2.2** (continued)

Center	Electronic transition	$\lambda_{\text{excitation}}$ (nm)	$\lambda_{\text{luminescence}}$ (nm)
$\text{Ti}^{3+}$	${}^2\text{T}_{2g}$ - ${}^2\text{E}_g$	500	650–950
$(\text{UO}_2)^{2+}$	400	$\text{A}_{1g}$ - $\text{E}_{2u}$	480–580
$\text{S}_2^-$	$3\Sigma_g^-$ - ${}^2\Pi_{3/2}$	400	500–700
$\text{O}_2^-$	$3\Sigma_g^-$ - ${}^2\Pi_{3/2}$	280	400–550
$(\text{MeO}_m)^{n-}$	${}^1\text{A}_1$ - ${}^1\text{T}_1$	250–340	480–520

beam is measured. To measure attenuation directly is extremely difficult and is better to measure the proportional quantity, while the fluorescence maybe the most useful. Two-photon spectroscopy was not used yet in luminescence of minerals field, but many relevant centers have been studied in artificial compounds, such as  $\text{Cr}^{3+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Cu}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Eu}^{2+}$  (McClure 1990).

## 2.4 Radiative Return to the Ground State: Luminescence

The energy of an electronically excited state may be lost in a variety of ways. A radiative decay is a process in which a molecule discards its excitation energy as a photon. A more common fate is non-radiative decay, in which the excess energy is transferred into the vibration, rotation, and translation of the surrounding molecules. This thermal degradation converts the excitation energy into thermal motion of the environment (i.e., to heat). Two radiative processes are possible: spontaneous emission, just like radioactivity, which is a completely random process where the excited state decays:



Rate of spontaneous emission in populating state

$$f = -N_f A_{fi}, \quad (2.8)$$

where  $A_{fi}$  is the Einstein coefficient for spontaneous emission (unit  $\text{s}^{-1}$ ). It obeys 1st order kinetics:

$$\begin{aligned} \text{Rate} &= -d[\text{M}^*]/dt; \\ N_f[t] &= N_f[t=0] \exp(-kt), \end{aligned} \quad (2.9)$$

where  $k$  = rate constant for spontaneous emission =  $A_{fi} = 1/\tau$  ( $\tau$  = natural lifetime of state  $f$ , in seconds). Stimulated (or induced) emission can occur in the presence of light of the correct transition energy, incident upon the sample, acting as a stimulant for it to emit a photon of the same energy:

$$M^* + h \bar{\nu} c \rightarrow M + 2 \bar{\nu} c. \quad (2.10)$$

Rate of induced emission in populating the state:

$$f = -N_f B_{fi} \rho(\bar{\nu}), \quad (2.11)$$

where  $B_{fi}$  is the Einstein coefficient of induced emission.

## 2.4.1 Ligand Field Theory

### 2.4.1.1 The Concept of the Ligand Field

Most of the electronic spectroscopy in minerals can be interpreted by the well-known ligand field theory. The main luminescence centers in minerals are transition and rare-earth elements. The ground and excited levels in these cases are d and f orbitals, while d-d and d-f emission transitions are subjected to strong influence from nearest neighbors, so called ligands. The basic notion of a ligand field was first developed many years ago (Bethe 1929). It was supposed that the ions are undeformable spheres and the interactions, which take place between them, are due solely to the electrostatic potentials set by their charges. The charges are taken to be located at the center of the ions coincident with their nuclei. Summing potentials from the individual surrounding ions to give the total potential at any point near central ion, and then finding the effect of such a potential on the electrons of the central ion solve the problem. The fact that the original considerations were made on the potential developed near an ion, which was part of lattice, and that such a lattice could occur only in crystal, led to the term *crystal field* theory. However, later was found that few of the results of crystal field theory depend on the existence of a lattice, and it is possible to carry most of them over to the model, which is at the basis of coordination chemistry – that of the coordination cluster. By coordination cluster is meant a central metal ion associated with a number of attached ligands, the whole forming a distinguishable entity and possibly bearing a net electric charge. In the more general model of a coordination compound, the electrons of the central ion are subject to a potential, not necessarily of simple electronic origin, from the ligand atoms. The term *ligand field* theory has been employed to cover all aspects of the manner in which an ion or atom is influenced by its nearest neighbors. Ligand field theory, then, contains crystal field theory as a special case. A great many of the results of ligand field theory depend only on the approximate symmetry of the ligands distribution around the central metal ion rather than on the particular ligands or the details of their locations. Consequently, the results may be obtained in the first place from crystal field theory and then generalized to other models of the bonding. Once the mathematical formalism of the crystal field approach has been developed, calculations within this model are quite straightforward (Figgis 1966, Di Bartolo and Collins 2006).

The splitting of d orbital energies and its consequences are at the heart of crystal field theory. It is possible to examine qualitatively the effect of various distributions of ligand atoms around the central ion upon its d orbitals. The d orbitals in an isolated gaseous metal are degenerate. If spherically symmetric field of negative charges is placed around the metal, these orbitals remain degenerate, but all of them are raised in energy as a result of the repulsion between the negative charges on the ligands and in the d orbitals. On going from a spherical to an octahedral symmetry, all orbitals are raised in energy, relative to the free ion. However, not all d orbitals will interact to the same extent with the six point charges located on the  $+x$ ,  $-x$ ,  $+y$ ,  $-y$ ,  $+z$  and  $-z$  axes respectively. The orbitals which lie along these axes (i.e.  $x^2 - y^2$ ,  $z^2$ ) will be destabilized more than the orbitals which lie in-between the axes (i.e.  $xy$ ,  $xz$ ,  $yz$ ).  $\Delta_0$  or alternatively  $10Dq$  denote the extent to which these two sets of orbitals are split. The tetrahedral symmetry can be derived from a cubic symmetry where only four of the eight corners are occupied by point charges. In such a situation, it is the  $xy$ ,  $yz$ ,  $xz$  orbitals are destabilized as they point towards the incoming point charges, while the  $x^2 - y^2$  and  $z^2$  are stabilized. The crystal field splitting in a tetrahedral symmetry is intrinsically smaller than in the octahedral symmetry as there are only four ligands (instead of six ligands in the octahedral symmetry) interacting with the transition metal ion (Fig. 2.2).

The point charge model predicts that

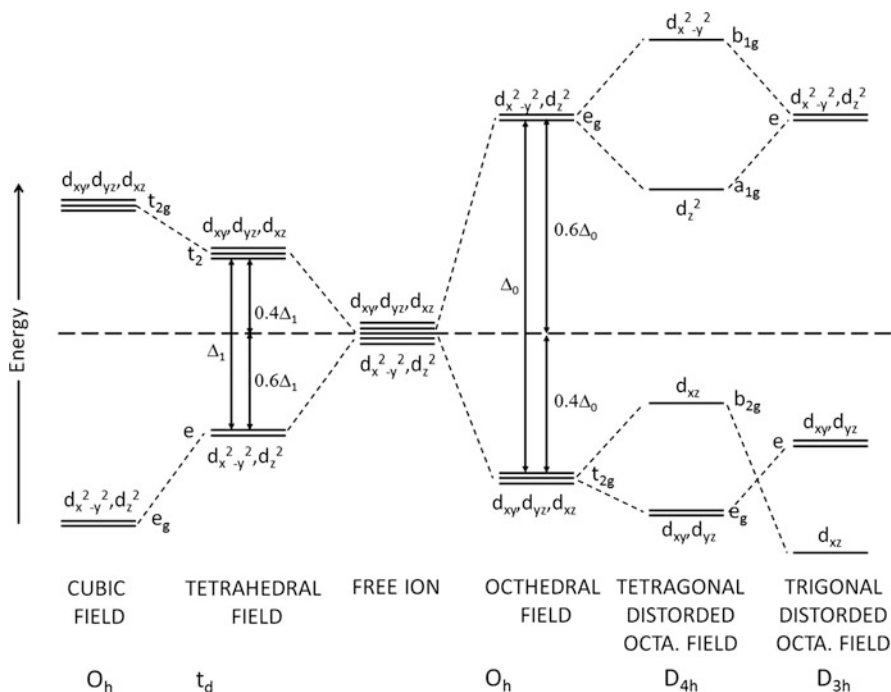
$$\Delta_t = \frac{4}{9} \Delta_o. \quad (2.12)$$

After determination of the qualitative schemes for the term splitting in the crystal fields, it is possible to go to a quantitative estimation of separation between the crystal field levels. All the electronic interactions stages can be represented quantitatively by means of the few parameters:

$$H = H_0 + H_{ee}(B, C) + H_{CF}(D_q) + H_{LS}(\xi) \quad (2.13)$$

where  $B$ ,  $C$  are inter-electronic repulsion ( $H_{ee}$ ) parameters governing term separation due to Coulomb repulsion of electrons;  $D_q$  is the cubic crystalline field parameter determining term splitting by cubic crystalline field ( $H_{CF}$ );  $\xi$  is spin-orbit coupling parameter, taking into account further splitting of ion levels in crystals due to an interaction between orbital and spin moments of an ion ( $H_{LS}$ ).

Interelectron interactions depend on the size, namely the greater the ion size, the more distant the electrons from each other, the less repulsion between them. Hence  $B$  and  $C$  decrease with decreasing of oxidation state, from the first transition series to the second and third series and from the first to the last ions within each of the series. For an ion in crystal the overlapping of transition metal and ligand orbitals leads to decrease of  $B$  and  $C$ , namely the more covalent the bonding, the less  $B$  and  $C$ . For a given transition metal ion the bond covalency depends on the ligand ions, which are arranged in the order of  $B$  decreasing in so-called nephelauxetic series:



**Fig. 2.2** Splitting of the five d-orbitals in various types of ligand fields (Bakhtin and Gorobets 1992)

$$F^- > O^{2-} > Cl^- > Br^- > S^{2-} > I^- > Se^{2-}.$$

The crystal field strength  $D_q$  is determined by the effective change of the ligands  $Q$ , by the average radius  $r$  of the d-orbital and by the ligand-metal distance  $R$ :

$$\Delta \sim \frac{(r^4)}{R^5} \quad (2.14)$$

This includes the dependence for  $D_q$  on the kind of transition metal ion, on the ligands arranged in the spectrochemical series in the order of increasing  $D_q$  ( $I^- < Br^- < Cl^- < F^- < O^{2-} < H_2O$ ), on the metal-ligand distances and on the coordination ( $D_{qoct}: D_{qcub}: D_{qtetr} = 1:8/9:4/9$ ).

It appears that the  $d^1$  and  $d^6$ , the  $d^2$  and  $d^7$ , the  $d^3$  and  $d^8$ , and the  $d^4$  and  $d^9$  configurations have great similarity in the splitting of their levels with the crystal field.

After determination of the relative energies of the d orbitals in a transition-metal complex, the distribution of the electrons has to be considered. Degenerate orbitals are filled according to Hund's rules: one electron is added to each of the degenerate

orbitals in a subshell before a second electron is added to any orbital in the subshell; electrons are added to a subshell with the same value of the spin quantum number until each orbital in the subshell has at least one electron. But such filling scheme is valid only for the high spin (or low field) configurations. If there is a large enough energy difference between the five d orbitals, as in the case if the ligand field is very large, the Hund's rule of maximum multiplicity no longer applies. As a result, the lower orbitals, for example the three  $t_{2g}$  orbitals in an octahedral system, will fill completely before any electrons enter the upper two  $e_g$  orbitals. This is low spin (or high field) configuration. Significant changes could occur in the octahedral  $3d^4$  to  $3d^7$  cases, and in the tetrahedral  $3d^3$  to  $3d^6$  cases.

### 2.4.1.2 Tanabe-Sugano Diagrams

Tanabe and Sugano taking the mutual interactions between the d-electrons as well as the crystal field into account have calculated the energy levels originating from such a configuration (Fig. 2.3). On the utmost left-hand side where crystal field  $\Delta = 0$  we find the energy levels of the free ion. Many of these levels split into two or more levels for  $\Delta = 0$ . The lowest level, i.e. the ground state, coincides with the x-axis. For the free ion the levels are marked  $^{2S+1}L$ , where S presents the total spin quantum number, and L the total orbital angular momentum. Values of L may be 0 (S), 1 (P), 2 (D), 3 (F), 4 (G), etc. The degeneracy of these levels is  $2L + 1$  and may be lifted by the crystal field. Crystal-field levels are marked  $^{2S+1}X$ , where X may be A (no degeneracy), E (two fold degeneracy) and T (three fold degeneracy). Subscripts indicate certain symmetry properties. The restrictions of these diagrams are connected with restrictions of the very model of crystalline field, the fact that the diagrams are calculated only for one B and C values, not speaking that the free ion values are taken, which differ considerably from corresponding values in crystals and the fact that splitting by cubic crystalline field only is shown without spin-orbital splitting.

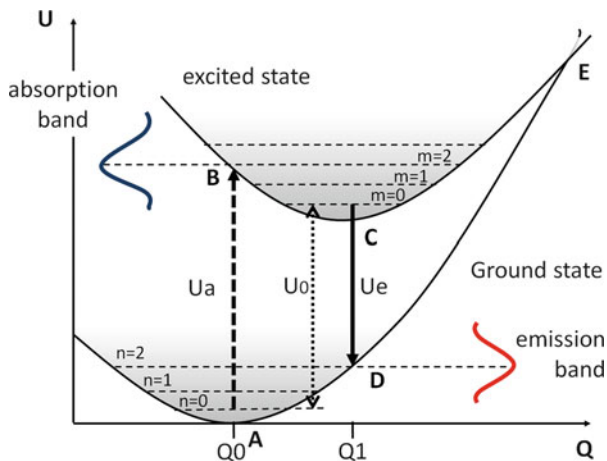
In order to use Tanabe-Sugano diagram properly, the transition probabilities have to be taken into consideration. We have a ground state and we have many excited states, but not all transitions from ground to excited state and in the opposite direction are allowed. It is all a question of probability, while some have a high probability of occurrence, namely, allowed and intense transitions and some have a low probability, namely, forbidden and weak or very weak transitions.

The following selection rules are mostly important:

- (i) There must be a change in parity (Laporte Rule) – transitions between states with the same parity are forbidden, thus all d-d transitions are forbidden
- (ii) Transitions are allowed between states with the same spin and such transitions are seen only weakly in the 3d transition metal compounds, though more strongly in the 4d and 5d series.

The Laporte selection rule formally forbids all transitions within the d shell among all the energy levels. Nevertheless, the Laporte rule can be relaxed by two





**Fig. 2.4** General scheme for explanation of luminescence transition according to the Franck-Condon principle in a configurational coordinate diagram, showing the parameters energy ( $U$ ) and configurational coordinate ( $Q$ ). The excitation from the vibrational level  $n = 0$  of the ground state to the excited state result in absorption band with the energy  $U_a$ . the relaxation of the system, i.e. from vibrational level  $m = 0$  of the excited state to the ground state, causes an emission band with the energy  $U_e$ . The energy difference between the lowest possible vibrational levels of ground and excited state ( $n = 0$  and  $m = 0$ ) is  $U_0$ , with  $U_a > U_0 > U_e$  (After Yacobi and Holt 1990 and Nasdala et al. 2004b)

configurational coordinate in the one-dimensional configurational coordinate model. In this model, the totally symmetric vibrational mode or the “breathing mode” is usually employed. Such a simple model can explain a number of facts qualitatively, such as:

- Stokes’ law; i.e., the fact that the energy of absorption is higher than that of emission in most cases. The energy difference between the two is called the Stokes’ shift;
- Widths of absorption or emission bands and their temperature dependence;
- Thermal quenching of luminescence.

It must be mentioned, however, that the one-dimensional model gives only a qualitative explanation of thermal quenching. A quantitatively valid explanation can be obtained only by a multidimensional model.

Following the path of the optical absorption transition, presume that Hooke’s law expresses the bonding force between the luminescent ion and a nearest-neighbor ion. The deviation from the equilibrium position of the ions is taken as the configurational coordinate denoted as  $Q$ . The total energies of the ground state,  $U_g$ , and that of the excited state,  $U_e$ , are given by the following relations:

$$U_g = \frac{K_g Q^2}{2} \quad (2.15)$$

$$U_e = K_e(Q - Q_0)/2 + U_0 \quad (2.16)$$

where  $K_g$  and  $K_e$  are the force constants of the chemical bond,  $Q^0$  is the inter-atomic distance at the equilibrium of the ground state, and  $U_0$  is the total energy at  $Q = Q_0$ . The spatial distribution of an electron orbital is different between the ground and excited states, giving rise to a difference in the electron wavefunction overlap with neighboring ions. This difference further induces a change in the equilibrium position and the force constant of the ground and excited states, and is the origin of the Stokes' shift. In the excited state, the orbital is more spread out, so that the energy of such an electron orbital depends less on the configuration coordinate; in other words, the potential curve has less curvature. As Fig. 2.4 shows, the nucleus of an emitting ion stays approximately at the same position throughout the optical processes. This is called the Franck-Condon principle. This approximation is quite reasonable since an atomic nucleus is heavier than an electron by  $10^3$ – $10^5$  times. The optical absorption proceeds from the equilibrium position of the ground state. The probability for an excited electron to lose energy by generating lattice vibration is  $10^{12}$ – $10^{13} \text{ s}^{-1}$ , while the probability for light emission is at most  $10^9 \text{ s}^{-1}$ . Consequently, state B relaxes to the equilibrium position C before it emits luminescence. This is followed by the emission process C-D and the relaxation process D-A, completing the cycle. At finite temperature, the electron state oscillates around the equilibrium position along the configurational coordinate curve up to the thermal energy of  $kT$ . The amplitude of this oscillation causes the spectral width of the absorption transition. When two configurational coordinate curves intersect with each other, an electron in the excited state can cross the intersection E assisted by thermal energy and can reach the ground state nonradiatively. In other words, one can assume a nonradiative relaxation process with the activation energy  $\Delta U$ , and with the transition probability per unit time  $N$  given by:

$$N = s \exp(-\Delta U/kT) \quad (2.17)$$

where  $s$  is a product of the transition probability between the ground and excited states and a frequency, with which the excited state reaches the intersection E. This quantity  $s$  can be treated as a constant, since it is only weakly dependent on temperature. It is called the frequency factor and is typically of the order of  $10^{13} \text{ s}^{-1}$ . The luminescence efficiency  $\eta$  can be expressed as:

$$\eta = \frac{W}{W + N} = \left[ 1 + \frac{s}{W} \exp \frac{-\Delta U}{kT} \right]^{-1} \quad (2.18)$$

If the equilibrium position of the excited state C is located outside the configurational coordinate curve of the ground state, the excited state intersects the ground state in relaxing from B to C, leading to a nonradiative process. As described above, the shape of an optical absorption or emission spectrum is decided by the Franck-Condon factor and also by the electronic population in the vibrational levels at thermal equilibrium. For the special case where both ground and excited states have



the same angular frequency, the absorption probability can be calculated with harmonic oscillator wavefunctions in a relatively simple form:

$$W_{nm} = e^{-S} \left[ \frac{m!}{n!} \right] S^{n-m} [L_m^{n-m}(S)]^2 \quad (2.19)$$

Here Laguerre's polynomial functions are used. The quantity  $S$  can be expressed as shown below, with  $K$  being the force constant of a harmonic oscillator and  $Q_0$  the coordinate of the equilibrium position of the excited state.

$$S = \frac{1}{2} \frac{k}{\hbar\omega} (Q - Q_0)^2 \quad (2.20)$$

Physically,  $S$  is the number of emitted phonons accompanying the optical transition. It is commonly used as a measure of electron-phonon interaction and is called the Huang-Rhys factor. At  $m=0$ , the transition probability is given by the simple relation:

$$W_{n0} = S^n \frac{e^{-S}}{n!} \quad (2.21)$$

If  $S < 1$  we are in the weak coupling mode, if  $1 < S < 5$ , in the intermediate coupling mode, if  $S > 5$ , in the strong coupling regime.

### 2.4.3 Molecular Orbital Theory

The further development of the ligand field concept takes place in Molecular Orbitals (MO) Theory. As an atomic orbital is a wave function describing the spatial probability density for a single electron bound to the nucleus of an atom, a molecular orbital is a wave function, which describes the spatial probability density for a single electron bound to the set of nuclei, which constitute the framework of a molecule.

The MO theory treats molecular bonds as a sharing of electrons between nuclei. Unlike the valence bond theory, which treats the electrons as localized balloons of electron density, the MO theory says that the electrons are delocalized. That means that they are spread out over the entire molecule. Now, when two atoms come together, their two atomic orbitals react to form two possible molecular orbitals. It emerges that the two types restrict all possible types of pair combination for s, p and d orbitals:  $\sigma$  and  $\pi$  molecular orbitals, each of them can be bonding and antibonding. Every pair of atomic orbitals forming the molecular orbital gives not one but always two molecular orbitals: bonding and antibonding. This is reflected in the formation of the two energy levels: a lower level corresponding to bonding and a higher one corresponding to antibonding. In the ground state, the bonding orbitals are usually completely occupied, while the antibonding orbitals are empty or partially occupied

by d electrons. The  $\sigma$ - bonding orbitals made from identical atomic orbitals have a center of symmetry and are referred as even. The  $\sigma$ -antibonding orbitals without a center of symmetry are uneven. On the contrary,  $\pi$ -bonding orbitals are uneven, while  $\pi$ -antibonding orbitals are even. The parity in the MO theory determines some of the selection rules for optical transitions.

The molecule energy level diagrams show the energies of the molecular orbitals made from every possible combination of the atomic orbitals. To achieve this, one constructs the energy levels for each atoms and then forms from them the molecular orbitals under following conditions: (1) the atomic orbitals should have a comparable energy, (2) they must overlap appreciably, (3) they must have a same symmetry type, (4) each pair of atomic orbitals forming a bonding molecular orbital must give at the same time an antibonding molecular orbital, (5) each of the atomic orbitals contributes in greater or lesser degree to all the molecular orbitals of the same symmetry type. The electronic state of a molecule is represented by a set of all possible molecular orbitals and term symbols are designated: for linear molecules:  $^{2S+1}\Lambda$  with  $\Lambda = 0, 1, 2$ , as  $\Sigma, \Pi, \Delta$ ; for nonlinear molecules and complexes:  $^{2S+1}\Gamma$  where  $\Gamma$  is the symmetry type (A, B: one-dimensional, non-degenerate type; E: two-dimensional, doubly degenerate; T: three-dimensional, triply degenerate).

#### 2.4.4 Discrete Variational Multi Electron Technique

The main deficiency of the ligand field theory is that its theoretical basis is mainly based on semi-empirical methods. For this reason it is not possible to discuss quantitatively the chemical difference between different ions, since the magnitude of the adjustable parameters may be determined only from experimental data. Recently the general method for the calculation of electronic structures including many-electron interactions from first principles (DV-ME–Discrete Variational Multi Electron) has been developed. By this technique, the multiplet energies are calculated in two steps: in the first step, one electron molecular orbitals (MO) and MO energies are calculated by the DV- $X_\alpha$  molecular orbital method; in the second step, the many-electron Hamiltonian, in which the interactions between two electrons are exactly described, is diagonalized within a subspace spanned by the Slater determinants made up of the obtained one electron data. This method enables to calculate multiplet structures without any restrictions on the symmetry of the crystal. It was revealed that the DV-ME method not only well reproduced the peak positions in optical spectra from first principles, but also was useful to discuss the effect of covalency and trigonal distortion of impurity-state wave functions on the multiplet structure. It was successfully applied to analyze the multiplet structures of  $3d^2$  and  $3d^3$  transition metals, f-d transitions of heavy metal ions and rare-earth ions in solids (Ishii et al. 1999, 2002).

### 2.4.5 Luminescence Decay

The mechanisms of luminescence decay from an optical center are of critical importance. In particular we have to know if there are any processes internal to the center or external to it, which reduce the luminescence efficiency. It is possible to define two decay times,  $\tau_r$ , the true radiative decay time which a transition would have in absence of all non-radiative processes, and  $\tau$ , the actual observed decay time, which may be temperature dependent, as will usually occur when there are internal non-radiative channels, and which may also be specimen dependent, as when there is energy transfer to other impurities in mineral. The quantum yield may be close to unity if the radiationless decay rate is much smaller than the radiative decay.

#### 2.4.5.1 Radiative Decay

For allowed emission transitions the true lifetime is short, namely  $10^{-7}$ – $10^{-8}$  s, for strongly forbidden transitions in solids it is much longer, a few  $10^{-3}$  s. For the two-level system (excited state and ground state) the population of the excited state decreases according to

$$dN/dt = -N_e P_{eg}. \quad (2.22)$$

The value of  $N_e$  gives the number of luminescent ions in the excited state after an excitation pulse,  $t$  the time, and  $P_{eg}$  the probability for spontaneous emission from the excited to the ground state. Integration yields

$$N_e(t) = N_e(0)e^{-t/\tau}, \quad (2.23)$$

where  $\tau$  is the radiative decay time.

In the absence of non-radiative decay processes the experimentally observed decay time equals the radiative decay time. When non-radiative processes are present, the experimental value is reduced by a factor equal to the quantum efficiency of the luminescence. There are many factors, which affect the decay time. One is due competing non-radiative processes, which shorten the measured decay time. We will consider the latter first. The experimentally observed decay time of the luminescence is given by

$$\tau = 1/(K_r + k_i) \quad (2.24)$$

where  $k_r$  is the probability of radiative decay and  $k_i$  the probability of non-radiative decay processes from the same state. If  $k_i$  is much large than  $k_r$  not only will decay time be shortened appreciably, but the luminescence intensity will be very weak. Non-radiative deactivation within a center occurs by interaction with the vibrating lattice, which depends on temperature. Thus  $k_i$  is temperature dependent.

### 2.4.5.2 Non-radiative Decay

Radiative return from the excited state to the ground state is not the only possibility of completing the cycle. The alternative is nonradiative return, i.e. a return without emission of radiation. All the energy absorbed by the mineral, which is not emitted as radiation is dissipated to the lattice (radiationless process). Actually there are many centers, which do not emit at all. Absorption and emission transitions are possible with Stokes shift. The relaxed excited state may, however, reach the crossing point of the two parabolas if the temperature is high enough and to return to the ground state in a nonradiative manner. The excitation energy is then completely given up as heat to the lattice. This model accounts for the thermal quenching of luminescence.

Another possibility to return to the ground state is by transfer of the excitation energy from the excited center ( $S^*$ ) to another center (A). The energy transfer may be followed by emission from A and species S is then said to sensitize species A. However,  $A^*$  may also decay nonradiatively and in this case species A is said to be a quencher of the S emission. The mostly important quenchers in minerals are  $Fe^{2+}$ ,  $Co^{2+}$  and  $Ni^{2+}$ , which have intense charge-transfer bands.

Let consider two centers, S and A, separated in mineral by distance R, which is so short that the centers S and A have a non-vanishing interaction with each other. If S is in the excited state and A in the ground state, the relaxed excited state of S may transfer its energy to A. Energy transfer can occur only if the energy differences between the ground and excited states of S and A are equal (resonance condition) and if a suitable interaction between both systems exists. The interaction may be either an exchange interaction (if we have wave functions overlap) or an electric or magnetic multipolar interaction. In such case, if the excitation spectrum of the A emission is measured, the excitation bands of S will be found as well, since excitation of S yields emission from A via energy transfer. If S is excited selectively, the luminescence of A also presents. Finally, the decay time of the S emission should be shortened by the presence of nonradiative energy transfer, since it shortens the life time of the excited state  $S^*$ .

If the spectral overlap consists of a considerable amount of overlap of an emission band and an allowed absorption band, there can be a considerable amount of radiative energy transfer:  $S^*$  decays radiatively and the emission band vanishes at the wavelengths where A absorbs strongly.

If we consider now transfer between two identical ions the same considerations can be used. If transfer between S ions occurs with a high rate, in a lattice of s ions there is no reason why the transfer should be restricted to one step. This can bring the excitation energy far from the site where the absorption took place. If in this way, the excitation energy reaches a site where it is lost nonradiatively (quenching site), the luminescence will be quenched. This phenomenon is called concentration quenching.

An additional delay between excitation and emission is often introduced by metastable electron states known as electron traps, which are filled during

excitation. Once an electron has become trapped in such a state it requires certain energy to release it but this can be provided thermally. Emission, which follows the emptying of such traps at a fixed temperature, is known as phosphorescence.

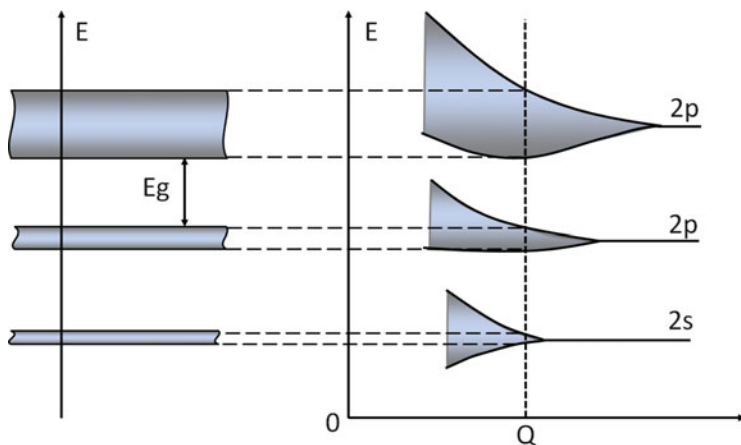
### 2.4.5.3 Special Cases of Decay

The processes involved are stepwise energy transfer, cooperative sensitization of luminescence and cooperative luminescence. As an example of stepwise energy transfer a system containing  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  may be considered. The latter ion absorbs at 970 nm ( $10,300\text{ cm}^{-1}$ ) and in phonon assisted an Er ion is excited to its  $^4\text{I}_{11/2}$  state. Then a second photon is absorbed by another Yb ion and produces  $^4\text{I}_{11/2}$ - $^4\text{F}_{7/2}$  in the excited Er by resonance energy transfer. This successive double energy transfer accounts for the fact that the excitation spectrum of such a system agrees with the reflection spectrum of  $\text{Yb}^{3+}$  and that the intensity of the resulting green emission  $^4\text{S}_{3/2}$ - $^4\text{I}_{15/2}$  (after radiationless  $^4\text{F}_{7/2}$ - $^4\text{S}_{3/2}$ ) of erbium is proportional to the square of the flux of infra-red photons. Two excited ( $^2\text{F}_{5/2}$ ) Yb ions can cooperatively excite a third ion of another rare-earth element, such as terbium, if the sum of the energies of the donor system corresponds to the excited level of the acceptor system. Cooperative luminescence is the opposite process of cooperative absorption and can be described as two excited ions that simultaneously make transitions downwards, emitting one photon having the sum of the two energy differences. A similar case where an ion emits one photon and simultaneously exciting another ion is also known.

A related phenomenon is the conversion of single visible photons with the result the quantum efficiency can be higher than 100 %. If, for example, 0.1 % of  $\text{Pr}^{3+}$  is incorporated in  $\text{YF}_3$  and excited with the mercury spectral line at 185 nm, the electron from 4f5d states decay non-radiatively to the  $^1\text{S}_0$  ( $4f^2$ ) state. This system is able to generate two visible photons by  $^1\text{S}_0$ - $^1\text{I}_6$  followed by non-radiative decay to the closely adjacent  $^3\text{P}_0$  and by transition another photon is emitted by transitions to one of the six J-levels of  $^3\text{H}$  or  $^3\text{F}$ . A condition for this cascade process is that the nephelauxetic effect for inter-shell transitions is sufficiently weakly pronounced for the lowest 4f5d state to be above  $^1\text{S}_0$  (Reisfeld and Jörgensen 1977).

### 2.4.6 Luminescence in the Band Scheme

Atoms in minerals are very close and influence strongly on each other. As a result in certain minerals the energy levels of individual atoms are combined and form the energy zones filled by electrons (Fig. 2.5). The inner atom orbitals of the individual atoms form inner energy zones totally filled by electrons. The outer atom orbitals filled by electrons form the outer energy zones filled by electrons. The last filled zone is called valence band (VB) because valence electrons take part in its occupation. The higher energy zones, following the valence zone, are empty because

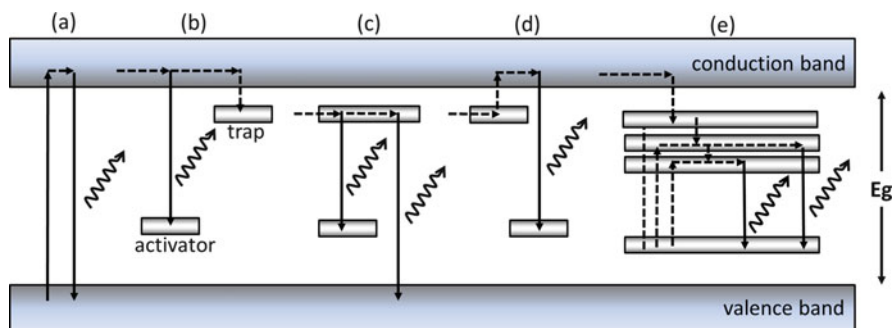


**Fig. 2.5** Energy zones formation scheme (Bakhtin and Gorobets 1992)

they are formed by empty electron orbitals. The lowest of these zones is called conductivity band (CB). The energy interval between the valence zone and conductivity zone is called forbidden zone and designated as  $E_g$ .

With small dimensions of the forbidden band the electron transfer of the impurity or of the main substance to the conduction band may take place. Most important luminescent minerals of such kind are ZnS and silver bromides. With the interband spacing of 3–4 eV a UV irradiation with a wavelength of less than 300 nm has enough energy to detach electrons and transfer them from filled valence band into an empty conduction band. Thus we have a free electron in the conduction band and a free hole in the valence band. The certain defects may catch a free electron, forming an electron center, or a free hole forming a hole center. Upon disappearance of such centers, as result of recombination with the opposite charge carrier, recombination energy serves as excitation source for luminescence center and emission appears (Fig. 2.6). The following processes are possible:

- “Intrinsic” luminescence where an electron is excited from the valence band to the conduction band, so-called interband transition. Recombination of this electron with a hole in the valence band generates a photon, the energy of which corresponds to the energy difference of the band gap (Fig. 2.6a);
- The excited electron may also recombine with an activator, with the following luminescence, or a trap, with the following electron capturing, within the forbidden gap. Traps and activator energy levels are caused by defects in the crystal lattice (Fig. 2.6b);
- Luminescence generation through direct recombination of electrons from a trap with an activator (tunneling) or with a hole in the valence band (Fig. 2.6c);
- Stimulated release from an electron from the trap to the collection band, followed by emissive recombination with an activator. This process is called



**Fig. 2.6** (a–e) Simplified sketch of electron band structure of a semiconductor mineral, showing the processes of excitation (energy absorption), non-radiative energy transfer and generation of luminescence (After Nasdala et al. 2004b)

thermoluminescence (electron release stimulated by heating) and optically stimulated luminescence (electron release stimulated by light) (Fig. 2.6d);

- “Extrinsic” luminescence, where after being excited, electrons of defect ions recombine with the ground state with luminescence emission (Fig. 2.6e).

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