

Chapter 12

Luminescence

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12.1 GENERAL DEFINITIONS

Luminescence is emission in the optical range of the visible, ultraviolet, or infrared light, which is an excess over the thermal radiation emitted by the substance at a given temperature, and continues after absorbing the excitation energy for a time that is significantly longer than the period of the light waves. The first part of this definition was formulated as far back as the nineteenth century, and a clarification concerning the duration of the radiation belongs to the Soviet academician S. I. Vavilov. It was this clarification that made it possible to distinguish the Cherenkov radiation (Section 5.9) from luminescence and to find out that Cherenkov radiation is a fundamentally new, previously unknown phenomenon.

Luminescence is inherent in substances in any aggregate state. Gases, liquids, solids in crystalline or amorphous state, polymers, glasses, and organic and inorganic substances can luminesce. In the vast majority of organic substances, an organic molecule has the property of luminescence. Therefore, organic substances can luminesce both in the dissolved and in the molten state. For inorganic crystals, the crystal lattice has the property of luminescence. Dissolved or melted crystals lose this property.

Luminescence is a substantially nonequilibrium type of radiation. To produce luminescence, one or another form of energy must be transferred into a luminescent substance, which then, with a greater or lesser loss, is emitted in the form of light quanta. Several different types of luminescence are distinguished, depending on the method of substance excitation:

- Photoluminescence is a luminescence of a substance, excited by light, usually ultraviolet or visible.
- Radioluminescence is a luminescence caused by ionizing radiation. In a detailed analysis, cathodoluminescence, X-ray luminescence, and some other variants of radioluminescence are isolated.
- Thermoluminescence is a luminescence that occurs when a preirradiated substance is heated. In this case, electrons and holes are released from the traps by the action of thermal fluctuations and radiatively recombined. This is the basis of the widely used method of thermoluminescent dosimetry. Thermoluminescence is used in geology, archeology, jewelry, forensics, and other industries.

- Chemiluminescence is a luminescence resulting from chemical reactions.
- Triboluminescence is a luminescence caused by mechanical influences.
- Sonoluminescence is a luminescence excited by ultrasound.

Let us mention two more phenomena, which are often present in the study of luminescence: fluorescence and phosphorescence.

Fluorescence is a radiation that rapidly decays after the excitation ceases, due to allowed transitions between levels of identical multiplicity in molecules or direct recombination of electrons and holes in crystals. The characteristic duration of fluorescence is $<10^{-6}$ s. The term “fluorescence” comes from the name of the mineral fluorite, within which it was first discovered.

Phosphorescence is a prolonged luminescence that lasts after cessation of excitation $>10^{-6}$ s, in some cases phosphorescence may last for hours. Phosphorescence occurs because of the fact that the excited molecule can appear at the level from which the radiative transition is forbidden by the quantum selection rules. Another mechanism of the appearance of phosphorescence is the capture of electrons and/or holes by deep traps. The thermal liberation of localized charge carriers gradually releases stored energy, which, in the case of charge recombination, is emitted in the form of light quanta. The name of phosphorescence comes from the name of an element of phosphorus, which has the property of glowing, when it is slowly oxidized in air.

The subdivision of luminescence into fluorescence and phosphorescence is rather arbitrary and at present has no scientific content.

According to the subject of the book, the main attention is paid to radioluminescence. Short-term light flashes caused by the excitation of a substance by ionizing radiation are called scintillations, and corresponding substances are called scintillators. The scintillation method of recording radiation is one of the most universal and widespread methods in nuclear physics and in radiation technologies.

Let us point out that luminescence is a method of removing excitation, therefore, it competes with other effects, in particular, with defect formation, dissociation of molecules, transfer of excitation energy into heat, and other processes of nonradiative energy transfer.

12.2 BASIC PARAMETERS

12.2.1 The Efficiency of Conversion of Excitation Energy Into Light

Parameters characterizing the transformation of excitation energy by ionizing radiation into light are discussed in Section 8.1.1. They are conversion efficiency and the average energy of photon formation w_{ph} . The maximum value of conversion efficiency can be $\sim 30\%$. Liquid xenon has approximately such conversion efficiency. However, in real scintillators, various reactions associated with energy loss can occur. When applied to luminescence and scintillations, processes with loss of energy are called quenching processes. Therefore, the best inorganic scintillator has a conversion efficiency of $\sim 10\%$. The light output of some scintillators, relative to NaI(Tl), is given at the end of this chapter in Table 12.2.

12.2.2 Spectrum of Luminescence

At room temperature, the emission spectrum is a broad, structureless band or several bands, possibly overlapping. At low temperatures, a structure appears in the bands, which reflects the structure of the vibrational levels of the molecule. An example of the luminescence spectrum of some scintillators is shown in Fig. 12.1. The luminescence spectrum can be represented in the dependence of the radiation intensity in the number of quanta either on the wavelength λ , or on the photon energy $h\nu$, or simply on frequency ν . The spectrum is characterized by the position of the maximum of emission band, λ_{max} or $h\nu_{max}$, as well as by the bandwidth.

For many luminophores, the emission spectrum in the wavelength scale has the form of a symmetrical bell-shaped curve and can be satisfactorily described by the Gaussian. The same spectrum of luminescence in the photon frequency scale or in proportion to the photon energy scale looks different.

By transferring the luminescence spectrum from the wavelength scale to the frequency scale, we equate the light energy L in the elementary ranges of wavelengths and photon frequencies

$$L(\lambda)d\lambda = L(\nu)d\nu. \quad (12.1)$$

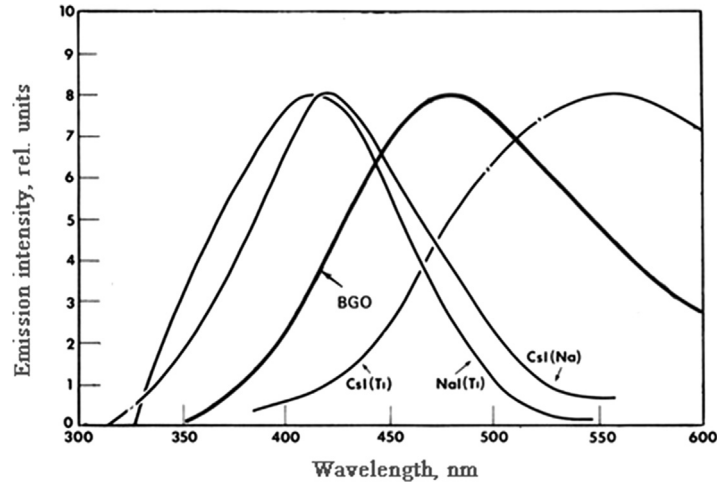


FIGURE 12.1 Luminescence spectra of some scintillators. The intensity of the luminescence of each scintillator is normalized to its maximum. The actual luminescence intensities of different scintillators are different (see Table 12.2).

Then

$$L(\nu) = L(\lambda)d\lambda/d\nu. \quad (12.2)$$

The connection of the quantities λ and ν is given by the relation

$$\lambda = c/\nu, \quad (12.3)$$

where c is the light velocity. Differentiating (12.3), we find

$$\frac{d\lambda}{d\nu} = -c/\nu^2. \quad (12.4)$$

The minus sign means that ν increases with decreasing λ . The Gaussian in the wavelength scale has the form

$$L(\lambda) = L_0 \exp \left[-\frac{(\lambda - \lambda_{max})^2}{2\sigma^2} \right], \quad (12.5)$$

where

$$\sigma = \Gamma / \sqrt{8 \ln 2}, \quad (12.6)$$

Γ is the FWHM (full width on half maximum). Substituting (12.4) and (12.5) into (12.2), one can find

$$L(\nu) = \frac{L_0 c}{\nu^2} \exp \left[-\frac{c^2}{2\sigma^2} \left(\frac{1}{\nu} - \frac{1}{\nu_{max}} \right)^2 \right]. \quad (12.7)$$

As a result, the new function has a maximum shifted relative to the value of ν_{max} , and the curve ceases to be symmetric.

In the case of photoluminescence, an important and informative parameter is the excitation spectrum, i.e., the intensity of the photoluminescence as a function of the wavelength or the energy of the photons of the exciting radiation. It shows what electronic transitions lead to the appearance of certain emission bands.

An important role in all types of luminescence is played by the absorption spectrum; it carries information on transitions from the ground state to the excited states of the molecule. As the analysis of configuration curves (Section 12.4.1) shows, in most cases the frequency of the radiation is less or equal to the frequency of the absorbed light (the Stokes' rule), and therefore the luminescence spectrum is usually located in the longer wave region than the absorption spectrum. However, the anti-Stokes ratio of the bands is also possible. One of the variants of the arrangement of the bands is shown in Fig. 12.2. When the luminescence and absorption bands overlap, the luminescent substance is just slightly transparent for its own radiation. To expand the absorption and emission bands and allow the luminescence light to freely exit the volume of the substance, activators, sensitizers, and spectrum shifters are used.

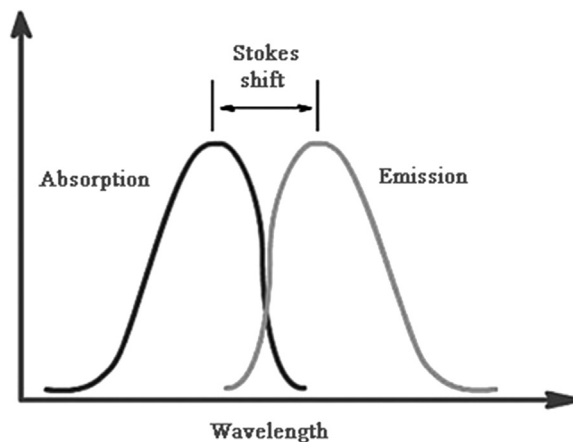


FIGURE 12.2 The typical location of the absorption and radiation spectra.

12.2.3 Kinetics of Luminescence

Another important parameter of luminescence is the temporal change in the luminescence intensity after the cessation of excitation, called the luminescence kinetics. Let us consider several variants of the luminescence kinetics.

Let charged particles, passing through matter, form n_0 excited molecules, which, passing to the ground state, emit photons. The average lifetime of molecules in the excited state is τ . It has already been pointed out that the process of excitation during the passage of charged particles through matter in the scale of the durations of molecular processes can be considered instantaneous. The kinetic equation for spontaneous transitions from the excited state to the ground state has the form

$$\frac{dn}{dt} = -n/\tau. \quad (12.8)$$

Integration of this equation with the initial condition $n = n_0$ for $t = 0$ gives

$$n = n_0 \exp(-t/\tau). \quad (12.9)$$

The formula obtained describes the change in the number of excited molecules with time. The total number of emitted photons is equal to the number of molecules that have passed to the ground state n'

$$n' = n_0[1 - \exp(-t/\tau)]. \quad (12.10)$$

The distribution of the number of emitted photons in time, i.e., the luminous intensity L , is defined as the derivative of Eq. (12.10)

$$L(t) = \frac{dn'}{dt} = \frac{n_0}{\tau} \exp\left(-\frac{t}{\tau}\right). \quad (12.11)$$

An important result of this simple conclusion is the presence of the average lifetime of molecules in the excited state τ , which is often called the time constant, in the denominator of the preexponential term. The importance of this result is to be cleared up below.

The excited state of the molecule can be removed not only by radiative transition to the ground state but also, e.g., in a collision with another molecule and the transmission of excitation energy to it. In this molecule, which can be called an extinguisher, the removal of excitation occurs nonradiatively with the excitation of vibrational levels, i.e., passes into the heat. The constant of the transfer rate of the excitation in the collision is denoted by K , the concentration of extinguishing molecules by C , and the average lifetime of the luminescing molecules in the excited state by τ_0 . Then the balance of the excited states has the form

$$\frac{dn}{dt} = -n\left(\frac{1}{\tau_0} + KC\right). \quad (12.12)$$

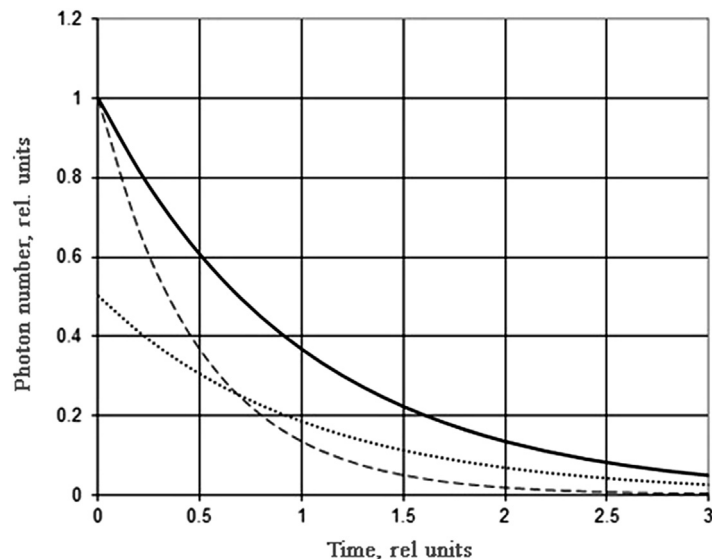


FIGURE 12.3 Forms of a scintillation pulse under different quenching conditions. The solid curve is the absence of quenching, Eq. (12.11). Dashed curve is quenching, competing with radiation, Eq. (12.15). The dotted curve is quenching before the formation of radiating excited molecules.

The solution of Eq. (12.12) is analogous to the solution of Eq. (12.8)

$$n(t) = n_0 \exp(-t/\tau), \quad (12.13)$$

where

$$\frac{1}{\tau} = \frac{1}{\tau_0} + KC \quad (12.14)$$

The intensity of the luminescence is the product of the number of excited centers by the probability of the radiative transition

$$L(t) = \frac{n(t)}{\tau_0} = \frac{n_0}{\tau_0} \exp\left(-\frac{t}{\tau}\right). \quad (12.15)$$

Eq. (12.15) in contrast to Eq. (12.11) has different τ in the preexponent and in the exponent. It is obvious that $\tau < \tau_0$. Thus, in the presence of extinction by an impurity, the initial intensity of the luminescence remains the same as in the absence of quenching, and the rate of decay of the luminescence increases.

The total number of illuminated photons is

$$N_\Phi = n_0 \frac{\tau}{\tau_0}. \quad (12.16)$$

Generally, quenching can occur at the initial stages of the transformation of the ionizing radiation energy, before the formation of the radiating center. In this case, the total number of excited molecules n_0 decreases, and the decay time τ remains unchanged. Thus, by the change in the shape of the signal, when an extinguishing impurity is introduced, it is possible to define certain details of the mechanism of energy conversion. Two variants of the pulse shape change are shown in Fig. 12.3.

In the process of luminescence, a large number of different radiation chemical reactions can occur, which leads, generally, to a wide variety of variants of the luminescence kinetics. However, real scintillation is usually described either as a simple exponent or as a sum of two exponents—the slow and the fast. It is very important that the intensity ratio of these scintillation components in some organic scintillators depends on the ionization density in the particle track. This question is considered in detail in Section 12.7. The values of τ for some scintillators are given in Table 12.2.

12.3 LUMINESCENCE OF THE RARE GASES

Noble gases are purely atomic gases. And although the formation of noble gas molecules due to the dispersion interaction is possible (Section 1.5.4), the binding energy of such molecules, however, is very small and the thermal motion easily cuts

this connection. At low temperatures diatomic molecules, i.e., dimers, can temporarily be formed, and near the boiling point, polyatomic formations, i.e., excimers, appear in gas phase. Physical processes that lead to luminescence and scintillation properties of noble elements in gaseous, liquid, and solid state can be found in Refs. [1–3].

Charged particles, passing through matter, transmit energy to atomic electrons and form electron–ion pairs and excited atoms. Ions, colliding with other atoms, form molecular ions



where X is one of the atoms of noble gases. In reaction (12.17), it is shown that two atoms of X collide with an ion. This means that a three-particle interaction process is underway. Excited atoms in the same way form molecules in the excited state



Electrons and positive ions recombine, according to the reactions



Formed in the process of recombination in the reactions (12.19) and (12.20), the excited atoms form new excited molecules as a result of the reaction (12.18).

The probability of the reaction (12.19), i.e., recombination of an electron with an atomic ion, is much less than the probability of recombination with a molecular ion (5.20). This is due to the fact that the processes (12.17) and (12.18) are very fast. In liquid xenon, the typical time for the formation of molecular states is $\sim 6 \times 10^{-12}$ s. In gaseous state, it depends on pressure, but even at atmospheric pressure molecular ions are formed much faster than recombination can occur.

In a liquid and a solid noble gas, excited atoms are called excitons, the processes of the formation of molecular states are called self-localization, and molecular ions are called self-localized holes.

The excited molecules of the noble gas X_2^* decay with the emission of luminescence quanta



Thus, the luminescence of atomic gases in all aggregate states appears to be molecular luminescence. Nevertheless, the fractions of the luminescence arising from the excitation of atoms and from ionization and subsequent recombination are distinguished.

The ground state of the noble gas molecule is the singlet $^1\Sigma_g^+$, and the excited state decays into two: singlet $^1\Sigma_u^+$ and triplet $^3\Sigma_u^+$. The difference in the energies of the excited states is insignificant, about 5 meV, which is noticeably less than the half-width of the emission bands, thus these levels do not appear in the spectra. But on the distribution of the luminescence intensity in time, the presence of two levels affects very clearly. The scintillation pulse consists of two time components, the fast and the slow (~ 2 and ~ 30 ns in liquid xenon).

The energy of the quanta emitted in the reaction (12.21) is noticeably lower than the minimum excitation energy of the atom, and the concentration of neutral molecules is negligible, so the substance is transparent for this radiation and it freely leaves very large volumes of liquid scintillators based on noble gases. The values of $h\nu_{max}$, as well as the values of the wavelength at the maximum of the emission band λ_{max} , are given in Table 12.1.

TABLE 12.1 Scintillation Properties of Liquid Rare Gases

	Liquid Ar	Liquid Kr	Liquid Xe
λ_{max} , nm	128	150	178
$h\nu_{max}$, eV	9.66	8.25	6.95
Number of photons/MeV	39 800	—	42 200
τ_{fast} , ns	5.0	2.1	2.2
τ_{slow} , ns	860	80	27

All noble gases have a very high luminescence efficiency in all aggregate states: gaseous, liquid, and solid. However, it can be seen from the table that even heavy noble gases emit in the ultraviolet region, and argon and lighter gases emit in the far ultraviolet region. Radiation of xenon passes through the windows of fused quartz. To detect the radiation of krypton and argon, it is required to use windows from LiF or MgF₂ (the absorption edge is 110 and 120 nm, respectively).

To register ultraviolet photons emitted by noble gases, the so-called spectrum shifters, i.e., substances absorbing ultraviolet photons and reemitting in the visible spectral range, are often used.

12.4 LUMINESCENCE OF ORGANIC MOLECULES, LIQUIDS, AND CRYSTALS

12.4.1 Basic Information About Organic Substances—Luminophores

Many aromatic compounds have bright luminescence. Aromatic compounds are compounds containing a conjugated ring of unsaturated bonds possessing high stability. Typical and one of the simplest aromatic compounds is benzene (C₆H₆). The structural formula of benzene is shown in Fig. 33.6A–E. For more details on aromatic compounds, see Section 33.4.5, as it describes, in particular, the features of the structure of the benzene molecule.

The best scintillation properties are possessed by organic crystals with fused benzene rings: anthracene and naphthalene. Their structural formulas are shown in Fig. 33.8.

Luminescent substances include polyphenyl hydrocarbons. The most known of them are para-terphenyl C₁₈H₁₄ and para-quaterphenyl C₂₄H₁₈. Their structural formulas are shown in Fig. 12.4. Ortho- and meta-isomers luminesce is much worse than para-form.

Substances that contain arylethylene and arylacetylene groups possess good scintillation properties. The most known scintillator with an arylethylene group is stilbene, also called as diphenylethylene, C₆H₅CH = CHC₆H₅.

Stilbene can exist in two isomeric states of cis-stilbene and trans-stilbene. Only trans-stilbene scintillates brightly. Under normal conditions, trans-stilbene is a crystalline substance, and cis-stilbene is a liquid. By light influence, isomers are able to change into each other. The structural diagrams of cis- and trans-stilbene are shown in Fig. 12.5. A good scintillator is tolane C₆H₅C≡CC₆H₅, also called as diphenylacetylene (Fig. 12.6).

The main structural property of aromatic compounds, which contribute to efficient energy transfer to light, is the presence of chains of double conjugated bonds with delocalized electrons. It has to be noted that the “hard” structure of molecules contributes to luminescence, which hinders some types of vibrations and transferring the excitation energy into heat.

Some features of the luminescence mechanism of organic molecules can be visually shown on the configuration curves (Section 1.4.9). Such curves reflect the relationship between the potential energy of a molecule and the distance between atoms. This relationship determines the configuration of the molecule. The configuration curves are almost parabolas with a

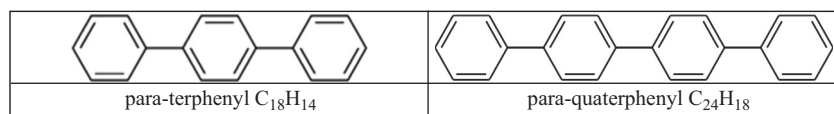


FIGURE 12.4 Polyphenyl hydrocarbons: para-terphenyl C₁₈H₁₄ and para-quaterphenyl C₂₄H₁₈.



FIGURE 12.5 Stilbenes (diphenylethylenes): cis-stilbene and trans-stilbene.

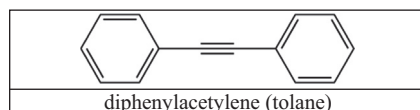


FIGURE 12.6 Structural formula of diphenylacetylene (tolane).

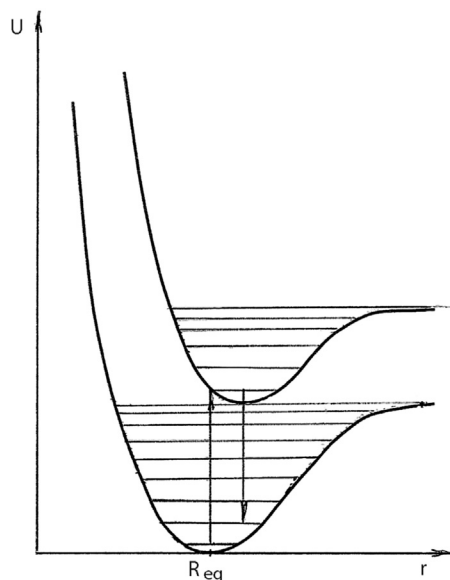


FIGURE 12.7 Configuration curves showing the origin of the emission and absorption spectra.

series of vibrational levels that are equidistant at low excitation energies. The molecule in the electronically excited state has a different geometry, compared with the main electronic state, i.e., another interatomic distance, another position of the curve minimum. Two configuration curves for the ground and excited states are shown in Fig. 12.7. Electronic excitation can be shown by an arrow pointing upward, and a radiative transition can be shown by an arrow pointing down. In accordance with the Franck–Condon principle (Section 1.4.9), the arrows are vertical, which means that during the time of electronic transitions, the configuration of the molecule remains practically unchanged. As a rule, the well of the excited level is shifted to the area of greater distances between atoms.

In most cases, the ground state of the molecules is the singlet S_0 . The excited state can be either a singlet S^* or a triplet T^* . Excitation by ionizing radiation is free of selection rules essential for optical transitions. Therefore, the molecule can be in an excited state, both singlet and triplet. The characteristic time of the singlet–singlet radiative transition is $\sim 10^{-8}$ s and of the triplet–singlet one is much larger, of the order of 10^{-2} – 10^{-4} s.

The excited molecule can return to the ground state not only by emitting a quantum of light, i.e., due to fluorescence, but also nonradiatively, e.g., by transferring the excitation energy to another molecule by one of the methods discussed in Section 12.4.2. Thus, quenching of the luminescence can occur.

From the singlet excited state S^* , the molecule can undergo the so-called intercombination conversion, i.e., transition between states with different multiplicity, and can go to the triplet level T^* . In view of the fact that the lifetime of an excited molecule in the triplet state is much greater than in the singlet state, the probability of nonradiative energy degradation from the triplet state is much higher. At radiation, transitions from the top to the bottom have a lower energy than transitions from below upward at absorption. It means that the radiation band is shifted respective of absorption band to long wave area. Such a shift is called Stokes shift.

In the optical region, the typical value of the Stokes shift usually ranges from 50 to 70 nm. If the configuration of a molecule, i.e., angles and interatomic distances, changes during excitation, the value of the Stokes shift rises up to 150–200 nm.

12.4.2 Luminescence of the Mixed Systems: Migration of Energy

If anthracene is introduced into the naphthalene crystal, then an emission band inherent in anthracene appears in the emission spectrum. At an anthracene concentration of $\sim 0.1\%$, the naphthalene emission band in the emission spectrum disappears and only the anthracene radiation is observed, although the major part of the energy of ionizing radiation is absorbed by naphthalene. At the same time, the light output of a mixed crystal is not less than the light output of pure anthracene. This means that in a mixed crystal, the excitation energy migrates from naphthalene to anthracene, toward the luminophor with longer wavelengths.

Migration of energy can lead to both sensitization and extinguishing, depending on which type of molecule intercepts the excitation energy at the final stage.

Migration of energy allows to create a variety of mixed systems, i.e., liquid and solid solutions, with what makes it possible to obtain luminophores or scintillators with a set of properties necessary for practical applications.

12.4.3 Some Information On Liquid Solutions—Scintillators

If a scintillating substance is introduced as an impurity into a nonscintillating or weakly scintillating liquid, a very efficient scintillator can be obtained. The most famous liquid scintillator is a solution of para-terphenyl in toluene. The characteristics of this scintillator are given in Table 12.2. The optimum concentration of the activator is about 3–8 g/L. At such a concentration, the energy of ionizing radiation is absorbed, practically, only by the solvent, which leads to the formation of excited states, and then the excitation energy migrates through the solution and is transferred to the molecules of the solute.

It is interesting that one of the best organic monocrystalline scintillators, i.e., anthracene, as an activating additive in liquid scintillators, is not very effective; its solutions in conventional scintillation solvents are less efficient as compared with solutions of para-terphenyl. Usually, another additive is injected into the solution, shifting the spectrum to the region of maximum sensitivity of the photodetectors. One of the most common additives is a substance called POPOP (one of the derivatives of phenyloxazole-benzene). As a result, the maximum of radiation is at 350 nm. Scintillating time is ~ 2 ns. Scintillation efficiency with respect to NaJ (Tl) is ~ 0.25 . To obtain liquid scintillators, other solvents can be used: xylene, phenyl-cyclo-oxane, vaseline, castor oil, and white spirit. Scintillating substances are diphenyloxazole (PPO) and tetraphenylbutadiene (PBD).

Liquid scintillators have two important features that determine the areas of their application.

First, it is possible to introduce into the liquid scintillator and to stir in it a substance with radioactive nuclides, the activity of which must be measured. With this mutual arrangement of the source and the detector, the maximum detection efficiency is achieved; this is how the beta activity of various organic molecules labeled with tritium is measured.

Second, the liquid scintillator can be poured into a vessel of any shape and size. The largest in size, one-piece detector, not a combination of detectors, but a single device, is a scintillation detector with liquid scintillator. Thus, the famous KamLAND (Kamioka Liquid Scintillator Antineutrino Detector) is a large neutrino detector in Honshu Island in Japan. This detector was the first to receive convincing evidence of neutrino oscillations. The main detector of the plant contains a kiloton of liquid scintillator in a transparent nylon sphere 13 m in diameter located inside the steel sphere. The scintillator consists of a solution of pseudocumene in dodecane with a small addition of diphenyloxazole, which improves the scintillation characteristics. On the inner surface of the steel sphere are 1879 photomultipliers of two types (17- and 20-inch diameter). The moment of light detection by each photomultiplier is monitored with an accuracy of approximately 3.5 ns, which allows not only to measure the energy of events but also to restore the coordinates of the scintillation flare.

TABLE 12.2 The Main Characteristics of Some Scintillators

Scintillator	Relative Light Output	λ_{\max} , nm	τ , 10^{-9} s
NaI(Tl)	1	420	250
CsI(Tl)	0.5	540	600
LiI(Eu)	0.23	470	1400
BGO ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$)	0.2	480	300
BaF ₂	0.13	310	630
	0.03	220	0.6
YAP ($\text{YAlO}_3\text{:Ce}$)	0.5	360	28
Anthracene	0.5	434	30
Naphthalene	0.24	348	96
Trans-stilbene	0.7	384	4
Para-terphenyl in toluene	0.5	440	5
NE-102	0.25	423	2

12.4.4 Some Information on Scintillating Plastics

If the scintillating material is dissolved in a liquid monomer and then the resulting solution is subjected to polymerization, a solid solution or plastic scintillator is obtained [4].

A classical plastic scintillator is a solution of para-terphenyl in polystyrene. Usually, the third component is added—the spectrum shifter. More often POPOP acts in this role. The maximum emission band of the plastic with POPOP is located at 410 nm, which corresponds to violet radiation. The decay time constant for plastic scintillators is in some units of nanoseconds.

The plastic scintillator can be of any shape; it can have considerable dimensions. Scintillators are produced in the form of cylinders, plates, granules, fibers, films, etc. Such scintillators are easy to be cut, molded, ground, and polished.

Currently, a wide range of plastic scintillators is produced serially. For example, the Nuclear Enterprises Company produces a series of scintillators, labeled as NE xxx. The properties of one of them are given in Table 12.2.

12.4.5 Mechanisms of Energy Migration

In general, the process of energy migration can be represented in the form of the reaction



where D, D*, A, and A* are ground and excited states of a donor and acceptor, respectively.

In the case of organic substances, four mechanisms of energy migration can play the major role [5,6]

1. Radiation
2. Exciton
3. Inductive resonance
4. Exchange resonance

12.4.5.1 Radiation

From the most trivial considerations, it is obvious that the simplest mechanism of energy transfer can be the emission of a photon by one molecule and its absorption by the other, i.e., radiative reabsorption. It is clear that such a process is possible only when the spectral bands of radiation and absorption are overlapped. Energy can be, actually, transmitted over considerable distances by such a mechanism, but in real systems, the efficiency of the reabsorption process is very low.

12.4.5.2 Exciton Mechanism

The quantum of the excitation energy can migrate through the crystal, and the further it goes, the more the crystal corresponds to the concept of an “ideal crystal.” The idea of such a quantum of excitation was first put forward by the Soviet physicist Ya.I. Frenkel, who called this migrating quantum an “exciton.” The translational symmetry of an ideal crystal contributes to the long-term conservation of the electron energy of a quantum, when it is transferred across a crystal. The transfer takes place very fast, in the order of 10^{-13} – 10^{-14} s. Thus, the excitation can reach the boundaries of the crystal or impurity center to which the excitation energy is transmitted. The exciton mechanism can play an appreciable role in organic single crystals.

12.4.5.3 Inductive Resonance Mechanism

The Coulomb interaction of an excited molecule with a molecule in the ground state leads to the induction of the level of excitation in the neighboring molecule where the excitation goes to. The levels are induced approximately in the same way, as in the combination of atoms into a molecule. Therefore, the inductive resonance mechanism can operate under conditions when reabsorption is impossible because of the discrepancy between the emission and absorption spectra.

The inductive resonance mechanism of energy transfer is associated with the name of the German physicist T. Förster, whose first publications on this topic date back to 1946.

The rate of inductive resonance energy transfer depends on the distance between objects and decreases with distance by r^{-m} , where $m = 6, 8,$ and 10 for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. The energy transfer efficiency varies with distance the same way as the transfer rate. Obviously, dipole–dipole

transfer is most effective. The average distance at which the transition speed is 50% of the maximum is called the Förster radius. For most systems, its value is 2–5 nm and can reach 10 nm.

Singlet–singlet and triplet–triplet interactions of excited and unexcited states can occur according to the inductive resonance mechanism.

12.4.5.4 Exchange Resonance Mechanism

As is known, the probability of a transition due to the Coulomb interaction between states of different multiplicity is essentially suppressed. There also is the exchange interaction. Exchange-resonant energy migration occurs when the electron orbitals of the donor and acceptor are overlapped. The donor and acceptor exchange electrons, i.e., the acceptor receives an excited electron. The exchange of electrons between the donor and the acceptor leads to the exchange of their spin states. The value of the total spin is preserved, when the multiplicity of the donor and acceptor changes simultaneously.

Exchange-resonance transfer occurs at distances on the order of the length of the chemical bond, i.e., 0.1–0.3 nm, when the electron wave functions of the donor and acceptor can overlap. The transfer rate for the exchange interaction decreases exponentially with distance.

12.5 LUMINESCENCE OF CRYSTAL PHOSPHORUS

Luminescence of inorganic crystals is the intrinsic property of the crystalline base, so it must be analyzed on the basis of the band scheme. Many inorganic substances luminesce on irradiation, and such substances are called crystal phosphors. If the duration of the luminescence at instantaneous excitation is shorter than $\sim 1 \mu\text{s}$, then such a crystal phosphor is considered a scintillator, and if longer, a luminophor.

The band scheme of the crystal is shown in Fig. 12.8. A charged particle transfers an electron from the valence band to the conduction band, creating an electron–hole pair. A part of the energy is spent by the particle on the creation of excitons. The formed electrons and holes recombine, as a rule, through some local center, located in the forbidden zone and is called the center of luminescence or the center of recombination. Such centers are usually the atoms of an impurity specially introduced into the substance, called the activator.

One of the most famous and most extensively studied types of crystal phosphors is alkali halide crystals. Practically, all alkali halides luminesce at a certain activation, but alkali metal iodides such as NaI, CsI, and LiI have the best scintillation properties.

The first universal inorganic scintillator is a sodium iodide crystal, activated with thallium, NaI(Tl). About 0.1% of the TlI salt is admixed with the NaI salt, the mixture is melted, and large, perfect, and transparent single crystals are grown from the melt. The NaI crystal is a typical ionic crystal built of Na^+ and I^- ions. Tl^+ ions replace Na^+ ions at the sites of the crystal lattice.

The conduction band of the crystal is formed by unfilled levels of 3s of Na (one 3s electron from the sodium atom transfers to the iodine atom). The valence band of the crystal is formed entirely by the 5p levels of iodine.

Ionization of the lattice means the detachment of the electron from I^- with the formation of a neutral iodine atom and electron transfer to the sodium ion with the formation of a neutral sodium atom. The hole in the alkali halide crystals is

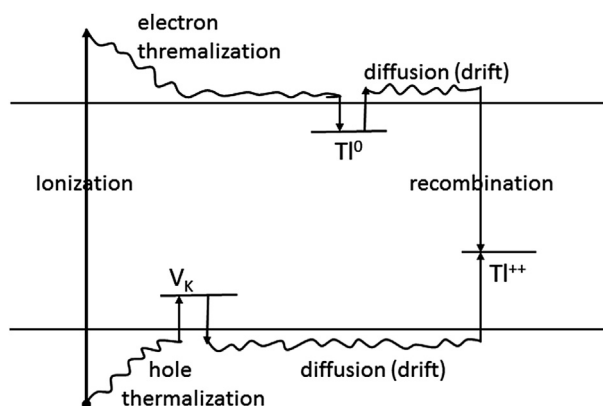
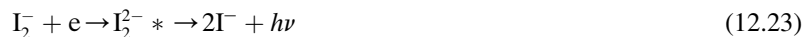


FIGURE 12.8 Zone scheme of crystal phosphor. In this scheme, the recombination of an electron with a Tl^{++} center is shown.

rapidly self-localized during several periods of lattice vibrations, and the electron appears to belong to two neighboring iodine atoms, i.e., the molecular configuration I_2^- corresponds to the self-trapped hole. This self-trapped hole is called V_K center.

At low temperatures, V_K center is stationary, and at room temperatures, it can be moved by a hopping mechanism. The recombination of an electron with V_K center corresponds to the reaction



An excited molecular iodine ion passes into the ground state with the emission of a quantum of light. The energy of these quanta lies in the ultraviolet region of the spectrum.

Radiative recombination of electrons with V_K center is very effective, but only at low (nitric) temperature. At room temperature, this radiation is almost completely quenched. To obtain an effective luminescence at room temperature, an activator is introduced into the crystal. In the case of NaI, it is thallium. Thallium is an element of the third column of the periodic table, and the electronic configuration of the outer shell is $6s^26p^1$. Thallium ions create recombination centers. From elementary energy considerations, one can determine that electrons are captured first. This corresponds to the reaction



Then a hole recombines with TI^0 center, a TI^+ ion is occurred in the excited state, and then rather complicated processes of emission are associated with the system of levels of this luminescence center.

The NaI(Tl) crystal has a significant drawback—it is very hygroscopic. Left unpacked, crystal absorbs moisture from the air and dissolves in it, while iodine colors everything in yellow. Therefore, immediately after growing, the crystals are placed in hermetic dry boxes, and in these boxes they are processed—cut, polished, and placed in a sealed package. In cases, when it is desirable to have as little ballast material on the path of radiation as possible, the packing of the scintillator is an interfering factor.

Other alkali halide crystals, e.g., CsI(Tl), CsI(Na), and Li(Eu), possess good scintillation properties.

The screen by which W. Roentgen discovered radiation was covered with a layer of luminescent platinum-cyanide barium $BaPt(CN_6)$. In the first device, which was enabled to observe individual alpha particles, the Crookes' spintaroscope, a screen coated with a layer of zinc sulfide (ZnS), was used. This substance is used up to date; however, it is very difficult to grow large transparent ZnS single crystals, and this substance could only be used in thin powder layers. Substances of the ZnS type, e.g., ZnS(Ag) or ZnCdS(Ag), are usually activated by silver. These substances have the maximum conversion efficiency for alpha particles, the alpha–beta ratio is about 2, and for the yellow-green light to which the eye is most sensitive.

The screens for radiography also use inorganic phosphors. For example, calcium tungstate ($CaWO_4$) strongly absorbs X-ray radiation, because it contains an element with a large Z and has a blue-violet light to which the X-ray film is sensitive. Such screens are called amplifying screens.

In the sixties, the bismuth germanate, $Bi_4Ge_3O_{12}$, BGO, was used in calorimeters. The density of this scintillator is 7.12 g/cm^3 ; its characteristics are given in Table 12.2. Crystals of bismuth germanate are nonhygroscopic and, therefore, they can be used without special packaging, which significantly reduces the amount of ballast material in calorimeters. A smaller conversion efficiency compared with NaI(Tl) could be an obstacle when working with nuclides of natural activity ($\sim \text{MeV}$), but this does not play a significant role in high-energy physics. A particle with a minimum ionizing ability loses in the crystal $\sim 14 \text{ MeV/cm}$.

Most of the inorganic scintillators have a time luminescence of the order of fractions or units of microseconds. However, even among the inorganic crystals, there was a scintillator with an extremely short time constant, which is a BaF_2 crystal. The main characteristics of the BaF_2 scintillator are given in Table 12.2. If the good resolution time and high timing accuracy are important parameters for this experimental task, then the BaF_2 crystal is perfectly suitable for this.

The assortment of inorganic scintillators is continuously expanding. year after year, and there appear reports on ever newer crystals with remarkable properties. For example, $YAlO_3(\text{Ce})$, i.e., yttrium perovskite, also called as yttrium orthoaluminate (YAP), is a crystal that is insoluble in inorganic acids, resistant to alkalis, and nonhygroscopic. The crystal is activated by an admixture of Ce with an optimum weight concentration of about 0.2%. The characteristics of the YAP scintillator are given in Table 12.2.

Cadmium tungstate crystals, $CdWO_4$, (CWO), are expected to be introduced into radiometry for a number of characteristics superior than BGO. Also, having high registration efficiency, CWO scintillators have better resolution, greater light output, and lower dependence on ambient temperature.

Scintillation crystals of lanthanum bromide doped with cerium $\text{LaBr}_3(\text{Ce})$ have a higher energy resolution and shorter decay time than traditional $\text{NaI}(\text{Tl})$ crystals. The energy resolution for 662 keV gamma radiation is 2.9% (19 keV), and for an $\text{NaI}(\text{Tl})$ crystal of the same size under the same conditions, the resolution is 6%, including higher recording efficiency and good temperature stability.

12.6 SCINTILLATING GLASSES

Inorganic scintillating glasses possess useful possibilities. The shape of glass-based scintillator can be arbitrary, which is difficult or impossible for single crystals. In glass, you can add various additives and change their composition due to some specific task. Glasses are usually activated by rare-earth elements, usually cerium. This results in a spectral luminescence band with a maximum of 3.2 eV (violet color).

Scintillating glasses have a conversion efficiency in their best samples reaching $\sim 10\%$ of $\text{NaI}(\text{Tl})$, but in most cases much less. The reasons why it is not possible to increase the conversion efficiency are not completely clear; at least, there are no physical limitations for this. The work on obtaining various scintillating glasses continues.

Two areas of application of scintillating glasses can be indicated: firstly, the registration of neutrons (Chapter 7), and, secondly, their ability to detect elements of an electromagnetic calorimeter, the use of which is mainly determined by economic considerations, namely, by lower costs.

12.7 DEPENDENCE OF SCINTILLATION CHARACTERISTICS ON SPECIFIC ENERGY LOSSES OF THE CHARGED PARTICLES

The basic characteristics of scintillators are that they are not constant. They can depend on certain properties of radiation and working conditions. We indicate two such dependences. The most important here is the dependence of conversion efficiency (light output) on the ionization density of the detected particles. A graph illustrating this relationship is shown in Fig. 12.9. It can be seen that as the ionization density increases, the conversion efficiency tends to fall. A simplified characteristic of this dependence is the so-called alpha–beta ratio, i.e., the ratio of conversion intensities, when the scintillator is irradiated by alpha and beta particles with energies characteristic of nuclide sources. The alpha–beta ratios for the alkali halides are ~ 0.5 , for scintillators of the ZnS ~ 2 , and for organic scintillators ~ 0.1 .

Another important dependence relates to the kinetics of the luminescence. It has already been noted that scintillation in many organic scintillators can be represented by the sum of a fast and a slow component. It is important that the ratio of intensities of the fast and slow scintillation components depends on the ionization density dE/dx of charged particles. This fact is reflected in Fig. 12.10, where scintillations in stilbene from particles of different types are shown. The scintillations are normalized to the same initial amplitude.

The dependence of the shape of the scintillation pulse on the particle type is extremely useful, as it makes it possible to separate the neutron radiation from the gamma background.

The main characteristics of some scintillators are presented in Table 12.2.

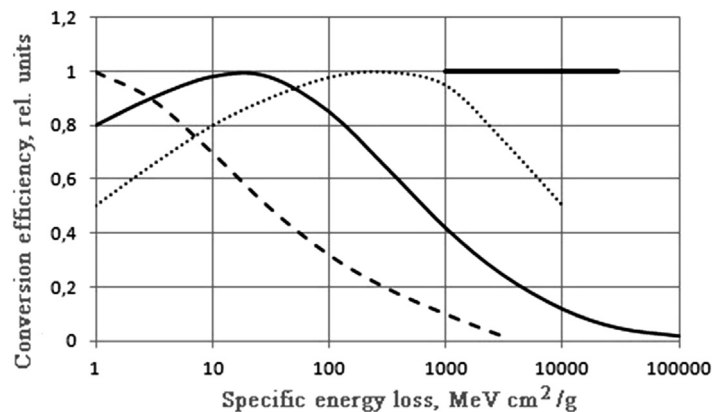


FIGURE 12.9 Dependence of the conversion efficiency of scintillators on the ionization density of the detected particles. The solid curve is for $\text{NaI}(\text{Tl})$, the dotted curve is for $\text{ZnS}(\text{Ag})$, the dashed line is for organic scintillators, and the dense straight line is for gas scintillators.

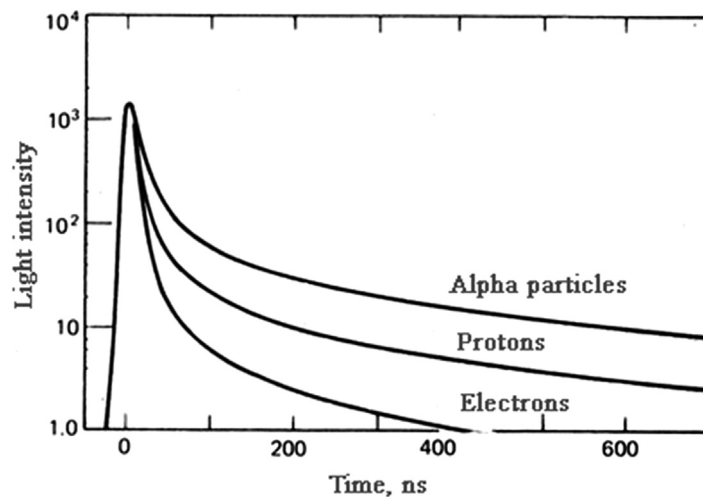


FIGURE 12.10 Time dependence of scintillation light in stilbene for different charged particles. Scintillations are normalized to the same initial amplitude.

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