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The Changes in the Luminescent Properties of the Lanthanides in Consequence of Their Interaction

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Information about the changes in the luminescent properties of the lanthanide elements in consequence of their interaction and as a function of their relative amounts in the test objects is reviewed together with data on the mechanism of this process in various systems.
The bibliography includes 93 references.

CONTENTS

I. Introduction 673
II. Interaction of lanthanide activators and sensitisation of the luminescence of lanthanide ions by other substances. 673
III. Mechanism of the interaction of lanthanide activators. 678

I. INTRODUCTION

The luminescent properties of crystalline phosphors are determined by the activator. If there are several activators, then, apart from the additive properties due to each activator, there appear non-additive properties resulting from the interaction of the activators. Owing to rearrangement of the system of energy levels, the interaction may be reflected in a change in absorption and emission spectra, the duration of the excited state and the probability of energy transitions, the nature of local levels, and many other properties. Numerous examples of this phenomenon may be quoted. The sensitisation of one activator by another and also the quenching of luminescence by admixtures may be regarded as the most familiar examples of interaction between activators. The interaction between activators may be employed in some cases as a useful property, while in others one attempts to avoid it.

In practice one usually deals with crystals containing several impurities and it is of course very important to know the nature of their interactions in a particular case. Moreover, the problem of the interaction between activators is of theoretical importance, since it is associated with the problem of energy transfer in matter.

The lanthanide elements are widely used at present in engineering, particularly in laser engineering. In the manufacture of high-purity lanthanides, their luminescent properties are used for production quality control[1]. It is then often necessary to determine in one specimen several elements present simultaneously. To avoid errors in the analysis, it is necessary to know to what extent the luminescent properties of a given system may be non-additive.

II. INTERACTION OF LANTHANIDE ACTIVATORS AND SENSITISATION OF THE LUMINESCENCE OF LANTHANIDE IONS BY OTHER SUBSTANCES

The interaction between lanthanides in phosphors has been known for a long time. The sensitisation of one lanthanide by another was observed for the first time by Tomaschek[2] in the excitation of the SrS–Gd,Sm phosphor by cathode rays. The luminescence of samarium in the phosphor increased appreciably in the presence of gadolinium. It is noteworthy that in the very early studies errors might have been made owing to the lack of highly pure lanthanide preparations. Moreover, the majority of investigations dealing directly with the interaction of lanthanides have been published in the last few years. They deal with the behaviour of lanthanides mainly in crystals, both inorganic (crystalline phosphors) and organic (lanthanide complexes).

A comparatively small number of papers deal with the behaviour of lanthanides in solutions, most of them being concerned with the dependence of the luminescence of terbium and europium on other lanthanides present in solution.

Gallagher et al.[3] examined two-stage energy transfer in solutions and showed that only in the presence of terbium ions is the energy of exciting light transferred from 4,4′-di-*m*-hydroxybenzophenone (DMB) to europium. The authors concluded that terbium ions constitute an intermediate link in energy transfer from DMB to europium, sensitising europium. It has also been noted that other lanthanides (praseodymium, neodymium, samarium, holmium, erbium, and thulium) quench the luminescence of a mixture of DMB and terbium. It has been suggested that the quenching involves an exchange–resonance mechanism.

Ballard and Edwards[4] made a detailed study of energy transfer from an organic substance to a lanthanide ion as a function of the concentration of the latter and also the self-quenching by the lanthanide ion in solution. The transfer of the energy of exciting light from the organic substance to the lanthanide ion may be called sensitisation of the ion by the organic substance. This is also of interest for a wider understanding of the interaction between various components of luminescent systems.

Ballard and Edwards[4] studied the luminescence of certain lanthanide (samarium, dysprosium, terbium, and europium) nitrates in acetophenone. The intense luminescence of certain lanthanide ions is due to intermolecular energy transfer from the triplet state of acetophenone, provided that there is no self-quenching by the lanthanide ions. It has been established that the self-quenching is excluded in those cases where the difference ΔE between the energies of the resonance and lowest levels is high. When ΔE is low, self-quenching is possible.

Since the investigation was carried out at low temperature (frozen solutions), it was essentially concerned with crystalline substances containing lanthanides.

Holloway and Kestigian[5] examined a case of the quenching of terbium by neodymium, holmium, and erbium ions. The experiments were performed on aqueous solutions of the lanthanide chlorides. The degree of quenching was determined from the change in the duration of the luminescence of terbium. It was found that the probability of the quenching of the fluorescence of terbium is proportional to the square of the concentration of the lanthanide or inversely proportional to the sixth power of the distance between the ions. Such a concentration dependence ($\propto 1/R^6$) characterises a dipole–dipole interaction. The authors conclude that the quenching of the luminescence of terbium takes place by resonance energy transfer.

Heller and Wasserman[6] examined intermolecular energy transfer from an excited organic substance (aldehydes and ketones) to lanthanides (europium or terbium) in dilute solutions. The excitation spectra show that the luminescence of europium and terbium appears when ultraviolet light is absorbed by the organic molecules. The constancy of the luminescence spectrum is evidence of the absence of complex formation. It has been suggested that the energy transfer is regulated by diffusion processes, since the intensity of the fluorescence of the lanthanide diminishes with increasing viscosity. As the temperature is reduced, the intensity of the fluorescence of the lanthanide falls and the phosphorescence of the organic substance appears.

Cabezas and De Shazer[7] investigated the possibility of the sensitisation of the lanthanide ion in the europium trihexafluoroacetylacetonate complex in a liquid medium with intermolecular excitation energy transfer from the organic donor to the organic complex. Benzophenone, excited by illumination with light at $\lambda = 3800$ Å, was employed as a donor. Under these conditions, the complex is not excited. The excitation energy transfer from the triplet state of benzophenone to the triplet state of the complex with subsequent intramolecular energy transfer to the Eu^{3+} ions takes place over a period shorter than 10^{-6} s.

A similar phenomenon was described by Charles et al.,[8] who observed the transfer of the energy absorbed by the *p*-benzoylbenzoate ion in solution to the ethylenediaminetetra-acetatoeuropium ion.

Kropp[9] reported the sensitisation of europium ions by the uranyl ion in solutions: aqueous (in particular in D_2O), alcoholic, in acetonitrile, etc. The luminescence of the UO_2^{2+} ions is then quenched and the intensity of the fluorescence of europium increases. The greatest effect is observed in D_2O. It has been noted that gadolinium does not quench the luminescence of the uranyl ion, since its excited level lies relatively higher and therefore there is no energy transfer.

Briskina et al.[10] observed the transfer of the energy of exciting light from organic dyes, in particular fluorescein, to lanthanide ions (europium and terbium). The energy is transferred from metastable levels of the dye.

McCarthy and Winefordner[11] showed how great is the extent of the intermolecular energy transfer in the determination of traces of lanthanides. The sensitivity of their determination in solution may be enhanced by employing an organic energy donor.

The mechanism of energy transfer from aromatic compounds such as ketones to lanthanide ions in solutions has been examined[12] and the hypothesis that the energy transfer takes place from the triplet level of aromatic molecules to the lanthanide ions was confirmed experimentally.

In a number of investigations published in 1964–1968, a study was made of the interaction between lanthanides in glasses (solid solutions). Cabezas and De Shazer[7] reported the occurrence of energy transfer in glasses activated simultaneously by terbium and dysprosium. At high concentrations of the activator (about 3 wt. %) the enhancement of the luminescence of terbium by about 70% is observed. The authors suggest that energy transfer from dysprosium to terbium takes place via the excitation of the resonance level of Tb^{3+} ($^5D_4$) by emission from Dy^{3+} with $\lambda = 485$ nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$).

The authors also reported a sensitising effect of terbium or europium on the luminescence of neodymium in glasses (the intensity of the luminescence of neodymium increases by about 10%). They suggest that in this case the energy transfer (accompanied by emission) occurs in the region of $\lambda \simeq 580$ nm (the region of absorption by neodymium and of emission by terbium or europium).

The interaction between terbium and neodymium in a glass was studied in detail by Nakazawa and Shionoya[13]. On the basis of experimental data and theoretical calculations, they concluded that the energy transfer from terbium to neodymium takes place preferentially by a resonance mechanism and is of a dipole–quadrupole type.

In a paper by Karapetyan and Mokeeva[14] on energy transfer in glasses activated by terbium and dysprosium, the existence of two energy transfer mechanisms is indicated: with emission (from dysprosium to terbium) and without emission (resonance) (from terbium to dysprosium).

The studies by a number of investigators[15–18] dealing with the sensitisation of the luminescence of ytterbium by neodymium and praseodymium in a glass are of interest. The luminescence of ytterbium in the infrared part of the spectrum arises both on excitation with light at $\lambda = 0.93$ μm and in the ultraviolet region (the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition). The intensity and duration of the luminescence of neodymium and praseodymium then diminish. The authors conclude that the quenching takes place in the excited state and that the energy is transferred to the terbium ions by a non-radiative pathway in an inductive interaction. The probability of excited transfer per unit time depends on the degree of overlapping of the spectra, the degree of prohibition of the interacting transitions, and the donor–acceptor distance. It has been shown[16] that praseodymium can also behave as a quenching agent for the luminescence of ytterbium. It has been stated[17] that praseodymium can quench the luminescence not only of ytterbium but also of neodymium, samarium, and dysprosium.

Shionoya and Nakazawa[19] reported the sensitising effect of cerium ions on the emission by terbium or neodymium in glasses. They suggest that the energy transfer takes place via a non-radiative pathway. Gandy et al.[20] observed the sensitisation of ytterbium by cerium in a glass. Pearson and coworkers[21,22] present experimental data confirming the occurrence of non-radiative energy transfer from gadolinium to terbium in a borate glass. In another study dealing with the concentration-dependent quenching of the luminescence of gadolinium and ytterbium in glasses, Pearson and coworkers[23] concluded that the quenching occurs not only as a result of the quenching interaction in the corresponding activators, but that the process includes also quenching by an admixture of europium present in gadolinium.

Woodcock and Smitzer[24,25] investigated the sensitisation of the luminescence of erbium in a silicate glass by ytterbium ions. The mechanism of the energy transfer is represented as follows. Energy from the $^2F_{5/2}$ level of ytterbium is transferred to the $^4I_{11/2}$ level of erbium; then the erbium ion undergoes a non-radiative transition to the $^4I_{13/2}$ state, from which there is a transition accompanied

by emission at $\lambda = 1.5$ μm. Under these conditions, the duration of the fluorescence of ytterbium ($\lambda \simeq 1$ μm) and the fluorescence intensity diminish.

Artamonova et al.,[26] who reported the sensitising effect of UO_2^{2+} on the luminescence of lanthanide ions, note that in a glass the transfer of excitation energy takes place via the following chain of ions: $UO_2^{2+} \rightarrow Nd^{3+} \rightarrow Yb^{3+} \rightarrow Er^{3+} \rightarrow Tm^{3+}$. The greatest energy transfer effect is observed in the following links of the system: $UO_2^{2+} \rightarrow Nd^{3+}$ and $Nd^{3+} \rightarrow Yb^{3+}$.

The sensitisation of the luminescence of erbium in glasses by ytterbium ions was investigated in detail by Kudryashov and coworkers[27]. According to their data, in the presence of ytterbium the intensity of the luminescence of erbium ($^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition) increases by a factor greater than 3 and this occurs on excitation of the luminescence by light in the range 0.75–1.1 μm, which includes the absorption bands of both ytterbium and erbium.

It is noteworthy that in the above investigations the concentrations of the lanthanides in the liquid solutions and glasses were in most cases relatively high (several tenths per cent and above). At low lanthanide concentrations in solutions, interaction was hardly observed.

The effect of the interaction of lanthanide activators is shown most distinctly in crystals. This is probably why the number of studies on the interaction of lanthanides in crystalline specimens is much greater.

A series of studies have been made on the interaction between lanthanides in organic crystals (lanthanide complexes). Soden[28] investigated the effect of substitution of certain lanthanides on the fluorescence of hexa-antipyrine-terbium tri-iodide in crystals of the following series: $TR_{1-x}Tb_x(AP)_6I_3$ (TR = Gd, Er, Dy, Y); AP = antipyrine ($C_{11}H_{12}ON_2$), and $x = 1.0$, 0.5, 0.2, 0.1, 10^{-2}, 10^{-3}, or 10^{-6}. He noted that the presence of dysprosium does not influence the fluorescence of terbium; the intensity of the luminescence of terbium ($\lambda = 549$ nm) falls in proportion to the decrease of x. In the presence of gadolinium or yttrium the intensity diminishes more slowly than x, which is attributed to excitation energy transfer from the antipyrine complexes of these elements to the terbium complex. On introduction of erbium, a more rapid decrease of the intensity of the fluorescence of terbium is observed, which is accounted for by energy transfer from the terbium complex to the erbium complex, where non-radiative transitions take place. Thus, the sensitising effect of gadolinium and yttrium and the quenching effect of erbium on the fluorescence of terbium were demonstrated.

Van Uitert and Soden[29] present the results of a more complete investigation of the effect of substitution by other lanthanides on the fluorescence of hexa-antipyrineterbium tri-iodide and sodium–europium tungstate. A study was made of the luminescence of crystals with the composition $Tb_xM_{1-x}(AP)_3I_3$, where M = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb and $x = 1.0$, 0.5, 0.25, and 0.1 and also the series $Na_{0.5}M_{0.5-x}Eu_xWO_4$, where x varies from 3×10^{-3} to 0.5. The luminescence was excited by the emission of a mercury lamp at $\lambda = 2537$ and 3660 Å.

Van Uitert and Soden[29] believe that the distribution of excitation energy absorbed by the antipyrine molecule between terbium and M^{3+} ions in the first series of crystals is determined by the ground energy level of the M^{3+} ions. The ease of energy exchange between the antipyrine molecule and lanthanide ions increases with the total orbital angular momentum of the $4f$ electron. If the ground state of these ions is S (Ga, La, Y), a large proportion of the energy absorbed by the antipyrine molecules bound to the above ions is transferred to terbium; for the H- and F-states, the effect of M^{3+} is slight and M^{3+} ions with the ground state I (Nd, Ho, Er) cause pronounced quenching of the luminescence of terbium.

In the case of ions with the same ground state (F) the exchange of excitation energy takes place preferentially for ions with the normal positions of the multiplets (Eu and Ce—ground states $^7F_0$ and $^2F_{5/2}$) than in the case of reverse multiplets (Tb and Yb—ground states $^7F_6$ and $^2F_{7/2}$).

The quenching of the luminescence of europium in sodium tungstates obeys the same rule as in substitution by other lanthanides according to the authors' data. As an exception, cerium in a tungstate environment causes pronounced quenching of the luminescence of europium. The authors believe that this may be caused by the relatively weak attachment of its uncombined electrons to the $4f$ levels ($4d$–$5d$ transitions). It has been shown that terbium slightly sensitises europium.

Peterson and Bridenbaugh[30] observed a change in the duration of the fluorescence of terbium in the antipyrine–terbium complex on substitution by other lanthanides. They note that both the intensity and duration of the luminescence diminish when favourable conditions are created for the resonance transfer of excitation energy to another, neighbouring lanthanide. The presence of erbium, holmium, and neodymium ions greatly diminishes the duration and intensity of the luminescence of terbium.

Poluektov et al.[31] investigated the luminescence of europium in crystals of ternary phenanthroline–acetophane and phenthroline–thenoyltrifluoroacetone complexes in the presence of other lanthanides. According to the data, the intensity of the luminescence of europium depends on the composition of the deposit. They compared the logarithms of the luminescence intensity of europium and the energy difference ΔE between the triplet state of the molecule and the nearest lower energy level of an extraneous lanthanide. There is a parallelism in the form of the $\lg I_{Eu}$ and ΔE curves as a function of the element. The higher the value of ΔE, the higher is I_{Eu} (Gd, Y, La). For low values of ΔE, the luminescence of europium is quenched (Pr, Nd, Ho, Er, Tm)†.

Despite the high value of ΔE, cerium strongly quenches the luminescence of europium. The authors explain this by the characteristics of the $4f$–$5d$ transitions in cerium and also note that the quenching of the luminescence of europium by other lanthanides is observed only in crystalline complexes. In solutions, for example in benzene, the quenching of the luminescence of europium is not observed.

The same investigators[32] made a detailed study of the sensitisation of the luminescence of europium by terbium in complexes with salol, anthranilic acid, and ternary antipyrine–salicylate complexes.

The excitation of the luminescence of lanthanide ions in complexes takes place[33–36] in consequence of the transfer of the energy of the exciting light from the organic base of the complex to the lanthanide ion and energy may be transferred from both triplet and singlet levels. For this, it is necessary that the energy of the triplet or singlet level of the complex should be equal or should exceed that of the resonance level of the lanthanide ions. The redistribution of energy within the molecule takes place very rapidly, over a period less than the duration of the excited state. When the complex contains several lanthanides interacting with one another, during the excitation period there is

† It is noteworthy that the upper energy levels of praseodymium, neodymium, erbium, and thulium ions are located below the $^5D_0$ level of europium, which in fact gives rise to energy transfer.

probably a two-stage energy transfer: from the organic substance to the lanthanide ion and then from the latter to another lanthanide ion interacting with it.

The majority of the literature data on the interaction of lanthanides refer to inorganic crystals (crystalline phosphors). As early as the late 1940's, detailed investigations were made in the luminescence laboratory FIAN [Physical Institute of the USSR Academy of Sciences? (Ed. of Translation)] of the mutual effects of activator lanthanides (cerium, samarium, and europium) in crystalline alkaline earth phosphors[37,38]. A study was made of the absorption and luminescence spectra, the temperature-induced glow, the spectral sensitivity of the flash, etc. On the basis of the considerable changes in the luminescence spectra of one activator in the presence of another, the authors[37,38] suggested that the activators are located side by side and that they tend to form "complicated compounds", which constitute the luminescence centres. The probability of a random distribution of activators close to one another is insignificant when the concentrations are low (about 10^{-3}%).

During recent years a number of studies on the interaction of activator lanthanides by Soviet investigators have been published. Levshin et al.,[39] who studied the determination of small amounts of gadolinium, samarium, and europium in thorium by luminescence methods, paid some attention to this problem. They established that the luminescence of gadolinium is strongly quenched by admixtures of samarium, cerium, and neodymium when their concentrations in the specimen are about 10^{-3}% and above. The luminescence of samarium is strongly quenched by admixtures of neodymium and dysprosium. In another study by Levshin et al.,[40] energy transfer from silver to samarium ions in ZnS phosphors was considered. It was emphasised that the interaction of the activators is observed at very low concentrations (about 10^{-3}%), where the relevant species may not be close neighbours. The authors believe that the pronounced temperature dependence of the interaction is related to a change in the transfer of charge carriers through different bands. However, they do not reject the possibility of resonance energy transfer between activators as well.

Voronov and Levshin[41] investigated the interaction of the silver, samarium, thulium, and europium activators in the cathodoluminescence of ZnS-based phosphors. Samarium was chosen as the principal activator, since it is most sensitive to changes in the immediate environment. The effect of a second activator reduces to a marked redistribution of energy in the spectrum and to a change in the overall luminescence yield. At a low temperature the integral luminescence of samarium in the presence of a second activator hardly changes. Partial quenching of the luminescence of samarium is observed at room temperature. The authors believe that the quenching of the luminescence of samarium involves an electron–hole mechanism. The necessity to compensate charges, suggests a great likelihood of the formation of lanthanide ion pairs, occupying adjacent lattice sites and replacing three Zn^{2+} ions. This is indicated by the formation of deep localisation levels (about 0.5 eV) and a redistribution of energy in the spectrum.

Cherepnev and Pakhomycheva[42] and Leonov[43] investigated the sensitising effect of cerium on the luminescence of samarium in the $SrSO_4$[42] and $3MgO.B_2O_3$ phosphors[43]. Bozhevol'nov and Fakeeva[44] used the sensitising effect of cerium on the luminescence of samarium in the $PbSO_4$–Ce,Sm phosphor to increase the sensitivity of the determination of samarium by a luminescence method.

O'Connor and Hargreaves[45] reported the excitation energy transfer from cerium to neodymium in CeF_3. Blasse and Bril[46] studied the energy transfer from cerium to samarium, europium, terbium, and dysprosium.

A number of non-Soviet and Soviet investigators studied the luminescence of crystalline phosphors activated by europium in the presence of other lanthanides[47–61]. Van Uitert and coworkers published a series of papers[47–49,55] on the interaction between lanthanide activators, attention being concentrated on the luminescence of europium. In one of their papers[47] they present data on the sensitising effect of terbium on the luminescence of europium. The experiments were performed with tungstates having the composition $M_{0.5}Tb_{0.5-x}Eu_xWO_4$ and $M_{0.5}Y_{0.5-x}Eu_xWO_4$, where M = Na, K, Rb, or Cs and $x = 10^{-4}$, 10^{-3}, 10^{-2}, 10^{-1}, or 0.5. It was shown that the intensity of the luminescence of europium in alkaline earth metal tungstates increases in the presence of terbium in proportion to its concentration. Up to 90% of the energy absorbed by terbium ions is transmitted to europium ions. When terbium is replaced by yttrium, the intensity of the luminescence of europium diminishes. It was also established that the relative intensity of the luminescence of terbium and europium diminishes with increasing radius of the alkali metal ions in the crystal lattice.

In other studies[48], the authors investigated the mechanism of energy transfer from terbium to samarium in the $Na_{0.5}Y_{0.5(x+y)}Tb_ySm_xWO_4$ system, from europium to neodymium in $Na_{0.5}$(Y, Eu, Nd)$_{0.5}WO_4$ and (Y, Eu, Nd)$_2O_3$, and from dysprosium to terbium in $Na_{0.5}$(Y, Tb, Dy)$_{0.5}WO_4$.

The quenching of the luminescence of terbium by samarium is characterised by a dipole–quadrupole interaction, but the luminescence of samarium was not observed under these conditions. Energy transfer from europium to neodymium takes place mainly via a dipole–dipole interaction. Energy may be transferred from the $^4F_{9/2}$ level of dysprosium to the $^5D_4$ level of terbium in the above system at 295.77° and 4.2°K. At 295°K the reverse transfer may occur.

In the next study by Van Uitert and coworkers[49], the problem of energy transfer from the main component of the crystal to lanthanide ions and also the concentration-dependent quenching of the luminescence of lanthanide is considered. The authors conclude that the energy of the exciting light is transmitted to the activator more effectively when it is close to the absorption limit of the main component. At frequencies below the absorption limit but not in the region of absorption by the lanthanide ions, excitation via the main lattice is relatively ineffective. At frequencies in excess of the absorption limit the energy is strongly absorbed and is distributed in the lattice. Energy transfer from the main component of the crystal to the lanthanide ions may be regarded as an independent problem.

Levshin and coworkers[50] studied the energy transfer from ZnS to a lanthanide activator and concluded that in this system, following excitation via the main component, the lanthanides receive energy predominantly by an electron–hole mechanism. The process depends markedly on the nature of the activators and the relative positions of their levels.

Two studies[51,52] on the luminescence of lanthanide ions in $Cs_2(NO_2Cl_4)$ crystals also demonstrate the sensitisation of the luminescence of lanthanide ions by the main component of the crystal. It has been shown that the migration of excitation energy of uranyl ions in the crystal lattice plays a significant role in energy transfer.

Mooney and Toma [53], who studied the system YVO_4–Eu suggest a mechanism for energy transfer from VO^{3-} to Eu^{3+} in which the colinearity of the positions of the V–O–Eu ions is not obligatory, as suggested by Blasse [54]. On the basis of structural data, it is concluded that in YVO_4 the π-bonding orbitals of the VO_4^{3-} ions have a maximum electron density in the direction of Y^{3+}. Therefore, in the substitution of yttrium by europium there is maximum overlapping of these π bonding orbitals with the f orbitals of the lanthanide ions. The authors explain in this way the high effectiveness of the luminescence of europium in YVO_4. The vanadium, oxygen, and europium ions do not lie on a single straight line under these conditions.

Blasse and Bril [54] investigated the energy transfer from the main component to lanthanide ions in Ln_2WO_6, Ln_2MoO_6, and $Y_2W_{1-x}Mo_xO_6$ ($0 \leq x \leq 0.1$) activated by europium. The authors suggest that the following conditions are necessary for the effective luminescence of europium: (1) the absorbing group must be a nearest neighbour; (2) the emission and absorption spectra of these groups must overlap; (3) the centre of the absorbing group, the intermediate oxygen ion, and the europium ion must be colinear; (4) the oxygen ions surrounding europium must respond to a high-potential field.

Bril and Wanmaker [56] observed the luminescent properties of phosphors activated by europium with a base incorporating lanthanides: Gd_2O_3, Y_2O_3, La_2O_3, $GdPO_4$, $LaPO_4$, etc. The phosphors exhibited the luminescence of europium. On the basis of the excitation spectra, the authors concluded that the energy absorbed by the main lanthanide ions is transferred to the impurity europium ions.

The study by Van Uitert and Jida [55] on the interaction of lanthanide ions in crystals of different compositions is of great interest. They investigated the single crystals of sodium and potassium tungstates and aluminates containing lanthanides ranging from yttrium and cerium to ytterbium. The cases of identical (concentration–dependent quenching) and different lanthanides (their mutual influence) were examined. Identical ions in immediate proximity quench each other's luminescence. The authors believe that the interactions between the lanthanides may be direct or via oxygen (in the presence of oxygen the quenching is more pronounced). Attention was concentrated on the luminescence of europium and terbium.

When europium and terbium ions interact with those of other lanthanides, the intensity of their luminescence diminishes exponentially with decrease of the spacing between the "fluoresceing" levels of the europium and terbium ions and the nearest lower levels of other lanthanide ions.

Holloway et al. [57] obtained direct proof of energy transfer from terbium to europium. They studied compounds with the composition $(Tb_{1-x}Eu_x)_2(WO_4)_3$. The luminescence of europium ($\lambda = 6150$ Å) and terbium (5460 Å) was observed.

The luminescence of europium in the presence of terbium appears both on excitation with ultraviolet light and on excitation with light at $\lambda = 4950$ Å (λ corresponding to the excitation of the terbium ion). On the other hand, if the phosphor does not contain terbium [$(Gd, Eu)_2(WO_4)_3$], then, on excitation with light at $\lambda = 4950$ Å, the luminescence of europium is not observed. According to the authors, energy transfer from terbium to europium ions takes place by a non-radiative pathway (sensitisation of europium by terbium). The authors regard the process mechanism as obscure.

In another paper Holloway and Kestigian [58] quote data on the sensitisation of the luminescence of europium by terbium in the $Y_{3-x}Tb_xAl_5O_{12}$ system. The same study dealt with the concentration–dependent quenching of the fluorescence of terbium at 300° and 77°K. It was shown that the probability of quenching varies exponentially with the concentration of terbium.

Ropp [59] studied energy transfer from terbium to europium in Y_2O_3. Holloway and Kestigian [60] made an interesting study on energy transfer between samarium, europium, terbium, and dysprosium in sodium tungstate. They compared the experimental energy transfer data with the relative compositions of the energy levels in the interacting ions. There should be energy transfer of ions with higher excited levels to those with lower fluorescence levels (possibly via an excited state intermediate between the fluorescence levels of the acceptor ion).

Axe and Weller [61] presented experimental data on energy transfer between europium and other lanthanide ions in Y_2O_3. They reported that the addition of lanthanides such as holmium, erbium, thulium, and particularly neodymium strongly quenches the fluorescence of europium. It is suggested that the quenching is caused mainly by non-radiative resonance energy transfer from one lanthanide ion to another. The authors assert that the overlapping of adjacent zones in quadrupolar fields is of great importance in this process.

The interaction between lanthanide ions has been demonstrated also in a number of studies by other investigators. For example, Margolis et al. [62] note that the luminescence of praseodymium in $CeCl_3$ is readily excited by light at $\lambda \simeq 350$ nm (cerium absorption band). The authors wished to demonstrate experimentally that collective absorption of photons, when the energy of the exciting quantum is consumed in the simultaneous excitation of two ions‡, may be observed not only for identical ions, as shown by Varsanyi and Dieke [64], but also for different ions. Possibly in this case there is the usual transfer of energy absorbed by cerium ions to praseodymium ions.

The sensitisation of the luminescence of lanthanides by cerium has been frequently noted [42–44]. Linares [65] investigated the luminescence and excitation spectra and fluorescence lifetimes τ of europium and other lanthanide ions in CeO_2 and ThO_2. Regions corresponding to energy transfer from CeO_2 to europium, samarium, and erbium were observed in the excitation spectrum.

Scott et al. [66] considered the problem of energy transfer from praseodymium to neodymium. They made a theoretical calculation of the width of the spectral lines on the basis of a dipole interaction modulated by phonons.

Rast et al. [67] and Ewanizky et al. [68] investigated the interaction of neodymium and ytterbium in LaF_3 and CaF_2 crystals. In consequence of the transfer of excitation energy from neodymium to ytterbium, the intensity of the luminescence of ytterbium in the region of 0.97 μm increases by two powers of 10 according to Ewanizky et al. [68] In the case of divalent ytterbium, energy transfer from Yb^{2+} and Nd^{3+} is observed.

Brown [69] studied the energy transfer from thulium to holmium in Y_2O_3. The luminescence of holmium was observed on excitation with light corresponding to the absorption bands of thulium ($\lambda \simeq 590$–820 nm). A non-radiative energy transfer is suggested.

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‡ Collective or cooperative absorption may occur also in the excitation of an acceptor ion as a result of the summation of the energies of two donor ions [63]. For example, the excitation of Tm^{3+} (470 nm) by two quanta capable of exciting Yb^{3+} (960 nm).

Brown and Whiting[70] studied the interaction of lanthanides in LaF_3 and determined the quantum yield and duration of the visible fluorescence of praseodymium in an LaF_3 single crystal in the presence of other lanthanide admixtures: cerium, neodymium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, and ytterbium. The system with praseodymium and cerium was studied in detail. The concentration-dependent quenching of the luminescence of praseodymium in LaF_3 and CeF_2 was examined as a function of temperature. To interpret the experimental data, calculations were made for two simple models; (1) isolated praseodymium; (2) praseodymium adjoining another ion. It was found that the sphere of interaction extends from nearest neighbours up to about 300 atomic distances. It was shown that quadrupole interaction predominates.

In a later study by Van Uitert[71] on the concentration-dependent quenching of the fluorescence of samarium, europium, terbium, erbium, and neodymium in solid matrices, it was established that the quenching of the luminescence of samarium, terbium, and erbium ions occurs as a result of dipole-dipole interaction. The authors believe that the quenching of the fluorescence of europium is influenced by the crystal structure of the matrix.

Blasse's study[72] dealt with the concentration-dependent quenching of the luminescence of europium in $Ba_2Gd_{1-x}Eu_xM^{5+}O_6$ (M = Nd or Ta) and $Gd_{1-x}Eu_xAl_3B_4O_{12}$ with different crystal structures. The extent of the influence of the crystal structure on the concentration-dependent quenching was demonstrated.

Peterson and Bridenbaugh[73] analysed the duration of the luminescence of terbium in the presence of other lanthanide ions to investigate the interaction between pairs of lanthanides. A study was made of the duration of the excited state $(\tau)/^5D_4$ of terbium ions in a series of mixed crystals $Tb_{0.9}TR_{0.1}Cl_3.6H_2O$. It was established that the lanthanide ions which absorb light in the region corresponding to emission by terbium (europium, thulium, praseodymium, samarium, neodymium, erbium, and holmium) reduce τ, while lanthanum, gadolinium, ytterbium, yttrium, lutetium, dysprosium, and cerium, which do not absorb in the range 4875–6800 Å, hardly change τ. Erbium, holmium, and neodymium ions have the greatest effect. The intensity of luminescence varies approximately in parallel with τ. This phenomenon is explained by the resonance transfer of excitation energy from terbium to other lanthanide ions, which leads to quenching and decrease of τ.

In another study by the same investigators[73], the problem of self-quenching by neodymium in $Na_{0.5}Gd_{0.5-c}Nd_cWO_4$ was examined and it was shown that the probability of quenching is proportional to $1/r^6$, where r is the distance between the interacting ions.

Osiko and Voron'ko[74], who investigated the concentration-dependent quenching of the luminescence of neodymium in CaF_2, concluded that the resonance Nd–Nd interaction accompanied by quenching takes place only at distances of about 4 Å, corresponding to the distance between the neodymium ions in an ion pair centre (3.8 Å). On the other hand, the probability of a non-radiative energy transfer between single centres at a distance greater than 4 Å is low, as shown by the weak dependence of τ for single centres on the concentration of neodymium. Thus, according to the authors, the concentration-dependence of the quenching of the luminescence of neodymium is due to the association of neodymium ions. In consequence of the increase in the number of ion pair centres, an increase of concentration entails an increase of inactive absorption, which lowers the overall luminescence yield.

In another paper by the same investigators[75] experimental data are quoted for excitation energy transfer from erbium to holmium and thulium in CaF_2 crystals.

Porter and Moos[76] reported ion pair interaction in the $LaCl_3$–holmium system. On the basis of the relative luminescence intensities in transitions from the $^5S_2$, $^5I_4$, and $^5I_7$ levels, it was concluded that the $^5S_2 \rightarrow {}^5I_4$ transition takes place via the interaction between a pair of holmium ions. The variation of the probability of the pair interaction with concentration is linear. The effective region of interaction for the ion pair is about 7.5 Å (third nearest neighbour).

Bril and Wanmaker[77] observed energy transfer from gadolinium to terbium in $CaNaBO_3$. On excitation of the phosphor in the region 256–280 nm, both gadolinium and terbium luminesce, the fluorescence of gadolinium being weaker than in the absence of terbium. The excitation of the terbium fluorescence by emission from gadolinium (in the region of 311 nm) can be virtually excluded, since the fluorescence of terbium on excitation with light at λ = 311 nm is very weak. Consequently there is a non-radiative energy transfer from gadolinium to terbium. The quantum yield of the fluorescence of terbium sensitised by gadolinium is 60% according to the authors.

Jonson et al.[78] reported energy transfer from erbium ions to thulium and holmium ions in $CaMoO_4$ crystals. The transition takes place from the $^4I_{13/2}$ state of erbium to the $^3H_4$ state of thulium and the $^5I_7$ state of holmium. As a result of the energy transfer, it is possible to achieve an increase in the infrared emission by thulium and holmium ions. The sensitisation of the emission from thulium and holmium by erbium is used in lasers. The sensitisation of the luminescence of holmium and thulium by erbium in CaF_2 crystals was investigated by Osiko and coworkers[79].

In a study designed to elucidate the role of the effect of lanthanide admixtures in the determination of small amounts of any one lanthanide in yttrium oxide, we found[80] that, in the presence of terbium in an amount of 5×10^{-3}% and above, the luminescence of dysprosium is quenched.

Later Taylor[81] reported the observation in CaF_2 crystals at 300°K not only of the quenching of the luminescence of dysprosium by terbium at their concentrations of about 0.1 at.% but also an increase in the intensity of the fluorescence of terbium (by a factor of about 5). The study of the luminescence kinetics showed that the mechanism of energy transfer from dysprosium to terbium is non-radiative and takes place from the $^4F_{9/2}$ level of dysprosium to the $^5D_4$ level of terbium.

In connection with the development of methods for the luminescence analysis of lanthanide impurities in pure substances, Poluektov et al.[82] investigated also the effect of extraneous lanthanides on the intensity of the fluorescence of the sought lanthanide ion. The luminescence of samarium, europium, terbium, and dysprosium in different matrices was observed. The greatest luminescence yield was found in compounds of lanthanum, gadolinium, lutetium, and yttrium, which is evidence of their sensitising effect. Elements such as praseodymium, neodymium, holmium, erbium, and thulium quench fluorescence.

III. MECHANISM OF THE INTERACTION OF LANTHANIDE ACTIVATORS

There is a fairly large amount of data on the changes in the luminescence properties of lanthanides in consequence of their interaction. At comparatively low con-

centrations the interaction is reflected mainly in energy transfer from one lanthanide to another, which leads to the observation of the quenching of the luminescence of one or both interacting ions, in particular concentration-dependent quenching, the quenching of the luminescence of one ion and the sensitisation by it of that of another or only the sensitisation of the fluorescence of the other ion, and as a rule a change in the duration of luminescence.

At high concentrations or in the case of a deviation from the random distribution of lanthanide ions in the crystal lattice, it is possible to observe also other signs of the interaction: a change in the absorption and luminescence spectra—displacement of the lines and redistribution of their intensities, appearance of new lines and disappearance of old lines[74,83,84], and certain other properties.

In this review we are considering mainly processes involving the sensitisation and quenching of the luminescence of lanthanides. The experimental data on the mutual effects of lanthanides are presented in the Table below, where, together with each lanthanide, are indicated others which have a sensitising or quenching effect on its luminescence. The data are presented for liquid solutions, glasses, and organic and inorganic crystals.

Many authors have put forward hypotheses concerning the mechanism of the interaction. Most of them conclude that there is a resonance energy transfer from one ion to another (exchange-resonance or inductive-resonance)[3,5,15,19,30,34,40,48,57,66-71,73,77,87]. Only in isolated cases are other hypotheses put forward: energy transfer via emission[7,14] and energy transfer via energy bands by charge carriers[40,41,50]. Depending on the structure of the system investigated and on the specific conditions of the excitation of the luminescence, any of the mechanisms proposed is possible. When the crystalline phosphor exhibits photoconduction, energy transfer via energy bands by charge carriers is quite possible (Mott-Gurney theory[88]). When the emission spectrum of one lanthanide overlaps the absorption spectrum of another, there is a possibility of energy transfer via emission. However, it appears that most often there is an inductive resonance energy transfer process.

The theory of resonance energy transfer was described in detail by Dexter[89], who concentrated attention on the problem of the sensitised luminescence of solids. At the same time he reviewed critically other theoretical studies on the mechanism of the interaction.

In the presence of sensitised luminescence in inorganic compounds there is usually energy transfer from an allowed level of the sensitiser to a forbidden level of the activator. Some investigators (Botden[90], Kröger[91], and

Effect of lanthanide and other ionic impurities on the luminescent properties of the main lanthanide.

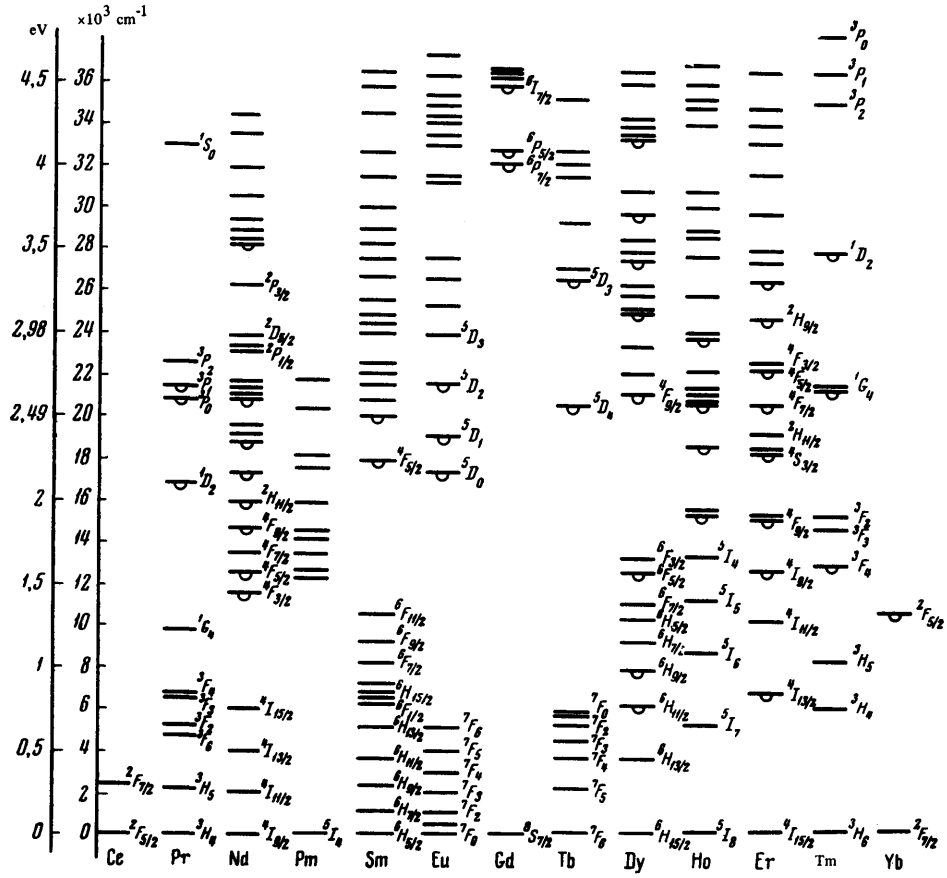
Main element	Effect of impurity	Medium			
		liquid solution	glass	organic crystal	inorganic crystal
Ce	sensitisation	4,4′-dimethoxybenzophenone[11]			
	quenching				Er[85]
Pr	sensitisation	4,4′-dimethoxybenophenone[11]			Ce[62], Cd, La[70]
	quenching		Yb[16,17]		
Nd	sensitisation	4,4′-dimethoxybenzophenone[11]	Eu[7], Tb[7,13], Ce[19], UO_2^{26}		Ce[45], Pr[66]
	quenching		Pr[17]		
Sm	sensitisation	actophenone[4], 4,4′-dimethoxybenzophenone[11]			Gd[2,82], Ce[41—44,46,65], Tb[57], La, Lu, Y[82]
	quenching		Pr[17]		Nd, Dy[39], Nd, Pr, Ho, Er, Tm[82]
Eu	sensitisation	terbium[3], acetophenone[4], aldehydes, ketones[6,12], benzophenone[7], *p*-benzoylbenzoate[8], uranyl (UO_2),[9] fluorescein[10]		Tb[29,32], Gd, La, Y[31]	Tb[47,57—59], Ce[46,62,65], La, Gd, Y[56,82], Lu[82]
	quenching			Ce[29,31], Pr, Nd, Ho, Er, Tm[31]	Ho, Er, Tm, Nd[61,82], Nd[48], Pr[82]
Gd	sensitisation				
	quenching		Eu[23]		Sm, Ce, Nd[39], Tb[77], Eu[85]
Tb	sensitisation	acetophenone[4], aldehydes, ketones[6,12], fluorescein[10], 4,4′-dimethoxybenzophenone[11]	Dy[7,14], Ce[19], Gd[21,22]	Gd, Y[28,29], La[29]	Gd[73,77,82], Dy[81], La, Lu, Y[82]
	quenching	Pr, Sm, Tm[3], Ho, Er, Nd[3,5]		Er[28—30], Nd, Ho[29,30]	Ho, Er, Nd, Tm, Pr[73,92], Eu[73], Sm[48,60,73]
Dy	sensititsation	acetophenone[7]			La, Gd, Lu, Y[82]
	quenching		Pr[17]		Tb[48,60,80], Eu, Sm[60], Pr, Nd, Ho, Er, Tm[62]
Ho	sensitisation	4,4′-dimethoxybenzophenone[11]			Er[75,78,79,86], Tm[69]
	quenching				
Er	sensitisation	4,4′-dimethoxybenzophenone[11]	Yb[24—26,27]		Ce[65]
	quenching				Tm, Ho[75,78,86]
Tu	sensitisation	4,4′-dimethoxybenophenone[11]	Er[26]		Er[75,78,86,79]
	quenching				
Yb	sensitisation	4,4′-dimethoxybenzophenone[11]	Nd[15,16,26], Pr[16], Ce[20]		Nd[67,68]
	quenching		Pr[16,17]		

others) believe that the probability of such a transition is determined by the overlapping of the wave functions of the sensitiser and the activator and that the transition is possible only when the activator and sensitiser occupy adjacent sites in the lattice[74]. Tests of this theory showed that this is not always so. Energy transfer can occur also in the case of a random distribution of sensitiser and activator ions in the crystal. When they are located close to one another (about 5 Å), there is a possibility of direct energy transfer from the sensitiser to the activator via quantum-mechanical resonance. If the excited sensitiser ion is remote from the activator ion (at a distance greater than 50 Å), the excitation energy may be transmitted by other sensitiser ions to the activator ion via resonance. Thus the formation of sensitiser–activator pairs is not obligatory. The role of the sensitiser may be fulfilled both by additional admixtures to the main component of the crystal and by the main component itself when the excitation energy is transmitted to the activator directly from the main component as the energy donor[49–54].

The hypothesis of the resonance energy transfer process is not inconsistent with the effect of various factors on energy transfer. According to the literature, these include the following:

1. The distance between lanthanide ions, which is determined mainly by their concentration[5,15,37,38,73]; the probability of dipole–dipole interaction is inversely proportional to the sixth power of the distance between the interacting ions, while the probability of dipole–quadrupole interaction is proportional to the eighth power.

2. The degree of overlapping of the bands[15,61,73] or the energy difference between interacting levels[31,55]; the energy of the excited sensitiser level should be approximately equal to, or should exceed, the energy of the resonance level of the activator, the probability of energy transfer decreasing with increase in the difference ΔE between



Comparison of schematic sets of electronic levels for triply charged lanthanide ions (the semicircles designate "fluoresceing" levels).

these levels. The transfer of excitation energy from one ion to another for large values of ΔE is accompanied by the emission of phonons with energies approximately equal to ΔE.[86]

Since the activator plays the role of a quenching agent in relation to the sensitiser, it is to be expected that the energy of the excited level of the quenching agent should be equal to or lower than that of the resonance level of the activator.

3. The degree of prohibition of the interacting transitions[15].

4. The energy of the principal level of the interacting lanthanide ions, determined by the total orbital moment[29]; the probability of energy transfer increases with increase in the total orbital angular momentum of the 4*f* electrons.

5. Temperature[6,17,40,41] and other factors; with decrease of temperature, in most cases the probability of energy transfer falls, which can be accounted for by a decrease of the overlapping of the energy levels.

Review of published data shows that the luminescence properties of lanthanides vary significantly in consequence of their interaction. The factors enumerated, which influence energy transfer, show that the interaction is intense at high concentrations. The change in luminescent properties under these conditions is greater the more complete is the overlapping of the energy levels of the interacting ions.

Only at very low lanthanide concentrations (about 1×10^{-3}% and below)[39,80,82] is there virtually no interaction and hence no changes in the optical properties. Thus in the determination of small amounts of lanthanide impurities in high-purity substances by the luminescence method the analytical errors owing to their interaction are virtually excluded in many cases. The present authors' recent studies[85,93] showed that the problem of the determination of lanthanide impurities by the luminescence method is not always simple. For example, the determination of small amounts of gadolinium (about 10^{-5}%) in europium oxide[85] by the luminescence method is impossible without preliminary enrichment and subsequent introduction of the concentrate into yttrium oxide—a donor of the excitation energy of gadolinium. The reason for this is the nature of the interaction between gadolinium and europium. The relative energy levels in the atoms of these elements (see Figure) is favourable for energy transfer from gadolinium to europium but not conversely. Thus europium behaves in this case as a quenching agent for the luminescence of gadolinium.

In relation to neodymium, holmium, erbium, and thulium, europium can behave as an energy donor and therefore the determination of these impurities in europium oxide by the luminescence method should not present difficulties, if one disregards the partial overlapping of the luminescence spectra.

In the determination of lanthanide impurities in metallic uranium[93] by the luminescence method, the overlapping of the luminescence spectra has been the chief obstacle, since uranium can also function as an effective activator of many compounds[94] and its luminescence spectrum consists of a group of broad bands in the visible region. In this case an important condition for the choice of a base for the crystalline phosphor is the absence from it of uranium luminescence, which is almost impossible, or at least the presence of luminescence with a reduced intensity only. Then it is also necessary to achieve a careful separation of the lanthanide impurity from the base element (uranium). The determination of lanthanides by the luminescence method is not interfered with by the presence of uranium only if the latter is present in an amount less than or equal to 1×10^{-3}%.

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