

# MODEL OF ENERGY TRANSFER AND LUMINESCENCE OF EUROPIUM COMPLEXES

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## ABSTRACT

The absolute quantum yield and lifetime of  ${}^5\text{Do} \rightarrow {}^7\text{F}_j$  luminescence of the  $\text{Eu}^{3+}$  ion in europium complexes with fluorinated  $\beta$ -diketones has been measured on excitation of luminescence in the UV. So  $\rightarrow$  Si absorption band of the ligand in the temperature range 77-365 K. Based on the analysis of the experimental dependences obtained and solution of the balance equations for stationary and nonstationary cases, we have developed a new approach to the determination of the scheme and rate constants of actual transitions. The rate constants of all processes of electron excitation energy conversion have been determined. The role of the state with charge transfer in these processes has been revealed.

## INTRODUCTION

There has been increasing interest over the past decade in producing efficient photoluminescence and electroluminescence from lanthanide complexes. The narrow band  $f-f$  emissions of lanthanide ions gain a lot of interest due to a variety of optical applications. These complexes uses as luminescent labels in variety of biomedical applications, including time-resolved immunoassay and for developing of light-emitting devices (LEDs) in communication and display technologies. The emissive power of a  $\text{Ln}^{3+}$  ion strongly depends on the chemical structure and the composition of a complex. A great number of works have been devoted to investigation of the spectral and luminescence properties of complex compounds of europium. However, the answer to the question concerning the mechanisms and the efficiency of electron excitation energy conversion is still not clear [1]. The main limiting factor for improvement high technology applications of lanthanide complexes is a value of luminescent quantum yield. The basic principle for increasing the signal of luminescence is removal molecules that have high-frequency vibrational modes (e. c. O-H groups) from the central rare-earth ion. Despite of the progress in chemistry however very often the new rare-earth complexes have not a high quantum yield of the luminescence even if the ligands encloses completely the central ion from surrounding molecules of a medium. This situation is described in a lot of articles about macrocyclic ligands - criptates, podates and others [1-3]. It is obviously that there are another reasons for decreasing a quantum yield and another paths of energy losses exist. Usually for describing energy transformation in complex molecular systems the energy losses in the organic part of the molecule

(antenna-ligand) separating from one in the central ion:

$$\begin{aligned} Q &= Q_{tr}Q_{Ln} \\ Q_{Ln} &= k_{rad}/(k_{rad} + k_{nr}) = \tau k_{rad} \end{aligned} \quad (1)$$

where  $Q$  is the total quantum yield;  $Q_{tr}$  describes efficiency of energy transfer from ligand to ion;  $Q_{Ln}$  is quantum yield in central ion after exciting one;  $k_{rad}$  and  $k_{nr}$  are radiative and radiationless rate constants respectively. In one of the recent publication [4] it was reported about developing the method that allows to quantify excitation-emission process in lanthanide chelates with using eq. (1). But it is necessary to note that these equations are correct only if we ignore thermal processes (one of such processes is a back energy transfer from excited energy level of ion to triplet level of ligand). We can do it only at low temperature or, for example, in ytterbium complexes where the energy of emissive  ${}^2F_{5/2}$  level is low  $\sim 10000 \text{ cm}^{-1}$ . At room temperature in europium and terbium complexes we must take into consideration thermal processes for correct describing energy transformation processes. Experiments show that quantum yield and lifetime of the luminescence for these complexes depend from temperature very strong [5]. Many terbium complexes have not luminescence at all at room temperature. So we can't use eq. (1) in general case. For describing thermal energy processes we have to write:

$$Q_{Ln} = k_{rad}/(k_{rad} + k_{nr} + k_{nr}(T)) = \tau(T) k_{rad}$$

where  $k_{nr}(T)$  describes all thermal activated processes of quenching from luminescent level of Ln. Process of the back energy transfer to triplet level of ligand leads to decreasing luminescence lifetime, although the energy losses localizing in ligand but not in Ln (the decreasing of lifetime only reflect the fact that energy loses FROM luminescent level of Ln but not only IN ion). So, studying transformation processes with using Eq.(1) leads to methodological mistakes because we can obtain incorrect results about localizing energy losses. We can not separate contributions of energy losses in ligand and Ln:  $Q \neq Q_{tr}Q_{Ln}$ . Situation is not so simple and it is necessary to create a complex method of investigation in detail the phenomena of migration and radiationless losses of excitation energy with consideration thermal processes for further progress in this direction. . In this work, we present a method developed for determining the probabilities of radiative and radiationless processes in complex compounds of europium that determine both the efficiency of intramolecular energy transfer and the quantum yield of sensitized luminescence of  $\text{Eu}^{3+}$ . The method is based on a detailed analysis of the temperature dependences of the absolute quantum yield ( $\varphi$ ) and the lifetime ( $\tau$ ) of the luminescence of  $\text{Eu}^{3+}$  on excitation in the absorption band of an organic ligand.

## EXPERIMENT

We have studied  $\text{Eu}^{3+}$  complexes with fluorinated  $\beta$ -diketones. A general structural formula was:  $\text{Eu}(\text{L}_1)_3\text{L}_2$ , where  $\text{L}_1$  is  $\beta$ -diketone: TTA - thenoyltrifluoroacetone, BTA - benzoyltrifluoroacetone, NTA - naphthoyltrifluoroacetone;  $\text{L}_2$  is additional ligand: phen - 1,10-phenanthroline, DAPM - diantipyrylpropylmethane, DAPhM - diantipyrylphenylmethane. Chelates have been studied in polymethylmethacrylate (PMMA). Polymer samples were prepared as films of thickness about 0,1 mm deposited onto plane-parallel polished quartz plates.

Dependencies of relative values of a quantum yield with temperature were obtained with using quantum counter. The spectrum of a luminescence of europium complexes contains narrow lines in a wide spectral region and obtaining the quantum yield by standard relative method (by an integrating of a luminescence spectrum) occupies much time. It is necessary to apply express methods for determination  $\varphi$ . We used the quantum counter on the base of dispersion of light. The area of its operation includes all spectrum of an europium luminescence [6].

The correction of the obtained relative values of a quantum yield to absolute values was carried out at room temperature by an absolute method. A sample was placed inside a photometric sphere [7]. The luminescence quantum yield was measured for samples with the optical density greater than 4,0 that except an uncontrolled increasing of absorbed energy because of additional absorption of exciting light that has been dispersed by photometric sphere after passing through the sample. The large distance between the absorption and luminescence bands allows to escape reabsorption of luminescence too.

The luminescence lifetime was measured upon the Nd:YAG pulsed laser excitation (third harmonic:  $\lambda=355$  nm,  $t_{\text{imp}}=10$  ns) in a maximum of main band ( $\lambda_{\text{max}}=612$  nm). The resolution time of the registration system was 100 ns.

Comparison of the luminescence spectra of polycrystalline chelates and one in PMMA shows that the uniformity of structure of studied complexes saved in PMMA. The measuring carried out at different temperatures allow to make a conclusion that the homogeneity is saved in all temperature range.

## RESULTS and DISCUSSION

### Preliminary analysis of experimental data

The experimental dependencies  $\varphi(T)$  and  $\tau(T)$  for some of the studied complexes are shown on Fig.1 and Fig.2.. The general behavior of the temperature dependences of  $\varphi(T)$  and  $\tau(T)$  is similar to that observed earlier for solutions and crystals of fluorinated  $\beta$ -diketonates of europium [8]. In all cases, the drop in the quantum yield of luminescence with increase in temperature is more drastic and begins at lower temperatures than the decrease in the lifetime.

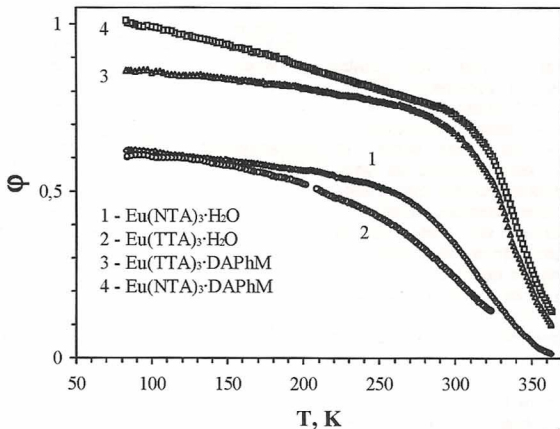


Figure 1. Absolute luminescence quantum yield with temperature for Eu(III) chelates.

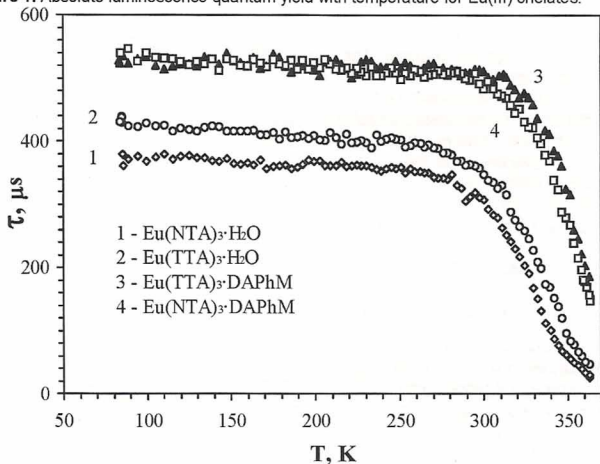


Figure 2. Luminescence lifetimes with temperature for Eu(III) chelates.

The differences in the behavior of the  $\varphi(T)$  and  $\tau(T)$  curves at low temperatures are due to the fact that  $\tau$  is influenced predominantly by radiationless transitions from the  ${}^5D_0$  level and  $\varphi$  is influenced by radiationless transitions from all the levels participating in relaxation of excitation. At low temperatures (<270 K), the low activation energy (<500  $\text{cm}^{-1}$ ) determined by the Arrhenius formula

$$\tau^{-1} - \tau_0^{-1} = A \cdot \exp(-E_a/kT),$$

where  $\tau_0$  is the lifetime in the absence of quenching processes and  $E_a$  is the activation energy, confirms that the main thermally activated radiationless process proceeds from the  ${}^5D_0$  level of the  $\text{Eu}^{3+}$  ion. The nearest  ${}^5D_1$  level is located 1780  $\text{cm}^{-1}$  higher, and its thermal population is practically absent at temperatures close to the liquid nitrogen temperature. Because of this, to take into account the slow decrease in  $i$  in luminescence with increase in temperature, it is necessary to introduce into the main diagram an additional level that lies higher than  ${}^5D_0$  but lower than  ${}^5D_1$  (level 6 in Fig. 3). The introduction of this level will also inevitably influence the behavior of the  $\varphi(T)$  curve, i.e., there will occur a slow decrease in the quantum yield of luminescence at low temperatures, as displayed by the experimental data (see Fig.2). However, the value of the quantum yield decreases more rapidly with increase in temperature than the value of  $\tau$ . This indicates the existence of other thermally activated processes with relatively small activation energies that proceed with the participation of the states  ${}^5D_1$  (additional level 7) and  $T_1$  (additional level 8).

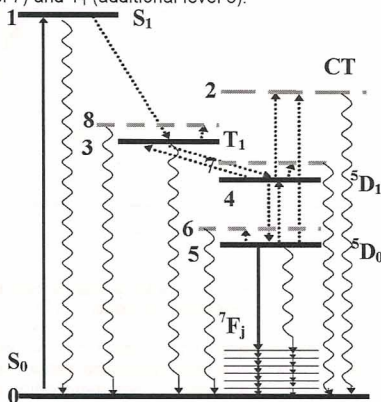
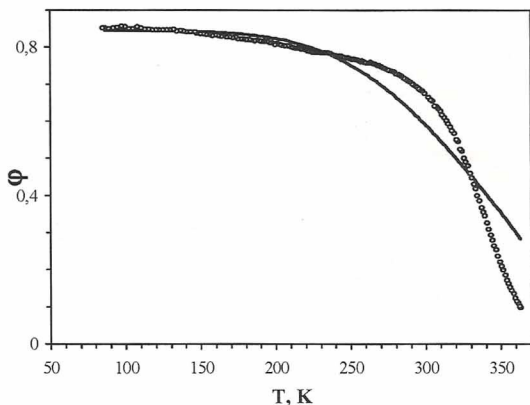


Figure 3. Scheme of energy levels for  $\text{Eu}(\text{III})$  chelates in PMMA.

Pay attention now to a temperature range 300-370K. attention on the Here,  $\phi$  and  $\tau$  decrease the most sharply. Earlier [8] it was assumed that the dependence  $\tau(T)$  can be explained by the reverse temperature population of the triplet state of the ligand and by its further deactivation. We performed preliminary calculations of the temperature dependence  $\phi(T)$  on the basis of the basic system of equations (diagram in Fig. 3 without the charge-transfer level) with account for additional states 6, 7, and 8, the necessity of introduction of which to describe the behavior of the  $\tau(T)$  and  $\phi(T)$  curves at low temperatures was demonstrated above. The results of calculation for  $\text{Eu}(\text{TТА})_3\text{-DAPhM}$  are demonstrated in the Fig.4. (for other complexes results are the same). It turned out that this calculational model was unable to explain the sharp decrease in the quantum yield in the region of high temperatures. To describe adequately the behavior of the  $\phi(T)$  curve at the temperatures 270-370 K, it is necessary to introduce a charge-transfer level located far away from  ${}^5\text{D}_0$  ( $6000\text{ cm}^{-1}$ ). Only this can ensure a large increase in the slope of  $\tau(T)$  and  $\phi(T)$  with increase in temperature.



**Figure 4.** Experimental data and calculated curve for quantum yield of  $\text{Eu}(\text{TТА})_3\text{-DAPhM}$  in approximation of quenching through triplet level of ligand.

The basic schema, being based on which one we will make further calculations, is shown in Fig.3. The positions of the states  ${}^5\text{D}_0$  and  ${}^5\text{D}_1$  were determined from the luminescence spectrum, and the position of the triplet  $\text{T}_1$  was determined from the data on the phosphorescence of the gadolinium complex. The possible physical nature of thermally activated processes we shall consider later, after clarification of the model of transitions, realization of detailed calculations of all rate constants and finding thermal barriers.

### Computation of quantum yield data

On the basis of the diagram of the levels in Fig. 3, we write the balance equations

$$dN_1/dt = A_{01} \cdot N_0 - (k_{10} + k_{13}) \cdot N_1 \quad (2)$$

$$dN_3/dt = k_{13} \cdot N_1 + k_{34} \cdot \exp(-\Delta E_{34}/kT) \cdot N_4 - k_{30} \cdot N_3 - k_{34} \cdot N_3 - k_{20} \cdot \exp(-\Delta E_{32}/kT) \cdot N_3 - k_{80} \cdot \exp(-\Delta E_{38}/kT) \cdot N_3$$

$$dN_4/dt = k_{34} \cdot N_3 + 3 \cdot k_{45} \cdot \exp(-\Delta E_{45}/kT) \cdot N_5 - k_{34} \cdot \exp(-\Delta E_{34}/kT) \cdot N_4 - k_{45} \cdot N_4 - k_{20} \cdot \exp(-\Delta E_{42}/kT) \cdot N_4 - k_{70} \cdot \exp(-\Delta E_{47}/kT) \cdot N_4$$

$$dN_5/dt = k_{45} \cdot N_4 - 3 \cdot k_{45} \cdot \exp(-\Delta E_{45}/kT) \cdot N_5 - k_{50r} \cdot N_5 - k_{50} \cdot N_5 - k_{60} \cdot N_5 \cdot \exp(-\Delta E_{56}/kT) - 3 \cdot k_{20} \cdot \exp(-\Delta E_{52}/kT) \cdot N_5$$

where  $N_i$  are populations of the levels;  $k_{ij}$  are rate constants of radiationless transitions from the  $i$  to the  $j$  level;  $k_{50r}$  are the rate constant of the radiative transition  ${}^5D_0 \rightarrow {}^7F_j$ ;  $A_{01}$  is rate constant of absorption of an excitation energy;  $\Delta E_{ij}$  is the difference between the energies of the levels  $i$  and  $j$ ;  $k$  is Boltzmann constant;  $T$  is absolute temperature.

In considering the above model, it was assumed that: 1) the nonactive absorption, including the temperature-dependent one, is absent; 2) the losses occurring prior to the intercombination conversion  $S_1 \rightarrow T_1$  are small, i.e., the quantum yield of triplet-state formation is equal to unity, in this case  $k_{13} \gg k_{10}$ ; 3)  $k_{45} \gg k_{40}$ , since the intensity of the luminescence that corresponds to the transitions  ${}^5D_1 \rightarrow {}^7F_j$  is more than two orders of magnitude weaker than the intensity of the transitions  ${}^5D_0 \rightarrow {}^7F_j$ , then  $k_{45} = 1/T({}^5D_1 \rightarrow {}^7F_j)$ ; 4)  $k_{34} \gg k_{35}$ , because the  ${}^5D_0$  level is populated via the  ${}^5D_1$  level (a fact determined experimentally).

We can equate right parts of equations (2) to 0 (stationary case). This condition is realized in measuring of quantum yields (excitation by a light from the stabilized gas-discharge xenon lamp)

Solving equations (2) we can obtain the general expression for value of the quantum yield:

$$\begin{aligned} 1/\varphi(T) = & [k_{30}/k_{34} + 1 + k_{20}/k_{34} \cdot \exp(-\Delta E_{32}/kT) + k_{80}/k_{34} \cdot \exp(-\Delta E_{38}/kT)] \times \\ & \times \{ [k_{34}/k_{45} \cdot \exp(-\Delta E_{34}/kT) + 1 + k_{20}/k_{45} \cdot \exp(-\Delta E_{42}/kT) + k_{70}/k_{45} \cdot \exp(-\Delta E_{47}/kT)] \times \\ & \times [k_{45}/k_{50r} \cdot \exp(-\Delta E_{45}/kT) + 1 + k_{50}/k_{50r} + k_{20}/k_{50r} \cdot \exp(-\Delta E_{52}/kT) + \\ & (3) \\ & + k_{60}/k_{50r} \cdot \exp(-\Delta E_{56}/kT)] - k_{45}/k_{50r} \cdot \exp(-\Delta E_{45}/kT) \} - k_{34}/k_{45} \cdot \exp(-\Delta E_{34}/kT) \times \\ & \times [k_{45}/k_{50r} \cdot \exp(-\Delta E_{45}/kT) + 1 + k_{50}/k_{50r} + k_{20}/k_{50r} \cdot \exp(-\Delta E_{52}/kT) + \\ & + k_{60}/k_{50r} \cdot \exp(-\Delta E_{56}/kT)] \end{aligned}$$

Here we do not make any supposition about possibility or impossibility of transitions from the triplet level of ligand and from the levels  ${}^5D_1$  and  ${}^5D_0$  of an ion  $\text{Eu}^{3+}$  to the level 2. Therefore we accept all formally possible paths of deactivation of electronic energy to further consideration.

For decreasing the number of unknowns arguments in Eq.(3), the luminescent lifetimes of transitions from  ${}^5D_1$  and  ${}^5D_0$  to a  ${}^7F_j$  level were

measured at the temperature 77K for all studied complexes. At  $T \rightarrow 0$  we have:

$$\begin{aligned} 1/(k_{50r}+k_{50}) &= \tau({}^5D_0 \rightarrow {}^7F_j) \\ 1/k_{45} &= \tau({}^5D_1 \rightarrow {}^7F_j) \end{aligned}$$

At low temperature the course of a curve  $\tau(T)$  is determined by thermally activated energy losses through a level 6. We can find parameters of exponent that describes a low-temperature part of dependence  $\tau^{-1}(T^{-1})$ :

$$\tau^{-1}(T^{-1}) = A + k_{56} \cdot \exp(-\Delta E_{56}/kT)$$

where  $A = k_{50} + k_{50r}$ . We can now substitute the values of an activation energy  $\Delta E_{56}$  and rate constant of transfer  $k_{56}$  into equation (3) as constants for each of studied complexes.

For obtaining the unknowns parameters  $k_{ij}$  and  $\Delta E_{ij}$  in Eq.(3) (taking into account that  $\Delta E_{42} = \Delta E_{43} + \Delta E_{32}$  and  $\Delta E_{52} = \Delta E_{45} + \Delta E_{43} + \Delta E_{32}$ ) we minimize the function of standard deviation:

$$\sigma^2 = 1/n \cdot \sum_i [\varphi_i^{-1} - \varphi^{-1}(T_i^{-1})]^2$$

Where:  $\varphi_i$  are experimentally measured values of absolute quantum yield of a luminescence at the temperature  $T_i$ ;  $\varphi^{-1}(T_i^{-1})$  are points of a theoretical curve.

### Computation of lifetime data

Executed calculations with using Eq.(3) have shown that because of presence the major number of varied parameters, it is impossible to obtain preference of some model (presence or absence of deactivation channels  $3 \rightarrow 2$ ,  $4 \rightarrow 2$ ,  $5 \rightarrow 2$  and their formally possible combinations). For different models the values of standard deviation  $\sigma^2$  are similar. It is necessary to involve into consideration independent experimental and calculation procedures, which one could raise the convergence of results of calculation and allow to select the model of transitions in the system of levels. For this purpose we will involve into consideration the luminescence lifetimes. The analysis of temperature dependence  $\tau(T)$  should give additional criterion for our calculations.

To calculate  $\tau(T)$ , we solve the system of ordinary differential equations (2) (omitting the first of these) for the population of the  $N_5$  level without equating its right-hand side to zero (a nonstationary case). This variant is realized in practice when  $\tau(T)$  of luminescence is measured. Primarily of interest to us is the time behavior of the population of the  ${}^5D_0$  ( $N_5$ ) level. Therefore, we bring system (2) to a differential equation of third order for  $N_5$  and its derivatives. We set up and solve the corresponding characteristic equation for each value of the temperature:

$$s^3 + s^2 \cdot a + s \cdot b + c = 0 \quad (4)$$

where

$$a = K_2 + K_5 + K_7$$

$$b = K_2 \cdot K_5 + K_5 \cdot K_7 + K_2 \cdot K_7 - K_1 \cdot K_3 - K_4 \cdot K_6$$



$$\begin{aligned}
c &= K_2 \cdot K_5 \cdot K_7 \cdot K_1 \cdot K_3 \cdot K_7 \cdot K_2 \cdot K_4 \cdot K_6 \\
K_1 &= k_{34} \cdot \exp(-\Delta E_{34}/kT) \\
K_2 &= -k_{30} \cdot k_{34} \cdot k_{20} \cdot \exp(-\Delta E_{32}/kT) - k_{80} \cdot \exp(-\Delta E_{38}/kT) \\
K_3 &= k_{34} \\
K_4 &= 3 \cdot k_{45} \cdot \exp(-\Delta E_{45}/kT) \\
K_5 &= -k_{34} \cdot \exp(-\Delta E_{34}/kT) - k_{45} \cdot k_{20} \cdot \exp(-\Delta E_{42}/kT) - k_{70} \cdot \exp(-\Delta E_{47}/kT) \\
K_6 &= k_{45} \\
K_7 &= -3 \cdot k_{45} \cdot \exp(-\Delta E_{45}/kT) - k_{50} \cdot k_{50} \cdot 3 \cdot k_{20} \cdot \exp(-\Delta E_{52}/kT) - \\
&\quad - k_{60} \cdot \exp(-\Delta E_{56}/kT)
\end{aligned}$$

The general solution of the third-order differential equation is written in the form

$$y = C_1 \cdot \exp(s_1 \cdot t) + C_2 \cdot \exp(s_2 \cdot t) + C_3 \cdot \exp(s_3 \cdot t)$$

where :  $s_1, s_2, s_3$  are the roots of the characteristic equation (4);  $t$  is the time.

Since we must describe the behavior of the experimental dependence  $1(7)$ , there is no need to obtain the solution in the general form. It will suffice to determine the maximum  $s_1$  that will reflect the lifetime of the  ${}^5D_0$  level. Then

$$\begin{aligned}
\tau &= Z - a/3 & (5) \\
Z &= -2 \cdot (-p/3)^{1/2} \cdot \cos(\alpha/3 - \pi/3) \\
\alpha &= \arccos\{-q \cdot [2 \cdot (-p/3)^3]^{1/2}\} \\
p &= -a^2/3 + b \\
q &= 2 \cdot (a/3)^3 - a \cdot b/3 + c
\end{aligned}$$

Having made calculations for different temperatures, we can reconstruct the theoretical curve  $\tau(T)$  using the  $k_{ij}$  and  $\Delta E_{ij}$  values determined from the calculation of the dependence  $\varphi(T)$ .

Total computation and clarification of the model of energy transitions.

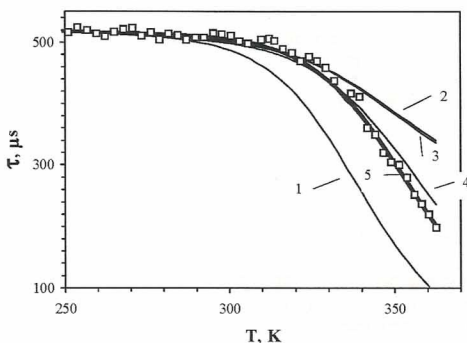
For determination the rate constants of energy transitions and location of levels, and also for clarification the model of transitions, we shall calculate functions  $\varphi(T)$  and  $\tau(T)$  by the varying parameters for the best describing both experimental dependencies by theoretical one. For this we will seek the minimum of the function:

$$Z = 1/n_1 \cdot \sum_i [\varphi_i^{-1} \cdot \varphi^{-1}(1/T_i)]^2 + R \cdot 1/n_2 \cdot \sum_j [\tau_i^{-1} - \tau^{-1}(1/T_j)]^2 \quad (6)$$

where  $R$  is the weight factor, with the aid of which the mean standard errors for the measured values of  $\varphi(T_i)$  and  $\tau(T_i)$  are equalized for the best simultaneous description of both dependences.

For clarification of the model we decrease coefficient R in the Eq.(6) so way that the minimization of the function Z makes predominantly by the first part of expression (6). Further, obtained values of parameters are used for calculating  $\tau$  and construction theoretical dependence  $\tau(T)$ . This procedure we can make for all formally possible models of transitions: only including transition  ${}^5D_0 \rightarrow 2$ ; with including transitions  ${}^5D_0 \rightarrow 2$  and  ${}^5D_1 \rightarrow 2$ ; or:  ${}^5D_0 \rightarrow 2$  and  ${}^5D_1 \rightarrow 2$  and  $T_1 \rightarrow 2$ ; including only transition  $T_1 \rightarrow 2$  etc. Levels 6,7,8 are taken into account in all variants.

The results of calculations are shown in Fig.5. As it is visible from a figure we can describe the dependence  $\tau(T)$  adequately at simultaneous description of dependence  $\varphi(T)$  only with using the model, in which the thermally activated radiationless transition to level 2 takes place from the levels  ${}^5D_0$  and  ${}^5D_1$  of the  $\text{Eu}^{3+}$  ion. The similar results were obtained from calculations of all studied complexes. Thus we have obtained channels of deactivation including level 2.



**Figure 5.** Experimental data and calculated curves for different models with participation of CT level: 1- ( ${}^5D_0 \rightarrow \text{CT}$ ); 2- ( $T_1 \rightarrow \text{CT}$ ); 3- ( ${}^5D_1 \rightarrow \text{CT}$ ); 4- ( ${}^5D_0 \rightarrow \text{CT}$ ) + ( ${}^5D_1 \rightarrow \text{CT}$ ) + ( $T_1 \rightarrow \text{CT}$ ); 5- ( ${}^5D_0 \rightarrow \text{CT}$ ) + ( ${}^5D_1 \rightarrow \text{CT}$ ) for  $\text{Eu}(\text{TTA})_3 \cdot \text{phen}$ .

The results of final calculations under the described above model are shown in the table. The value of efficiency of transition of energy from a ligand to  $\text{Eu}^{3+}$  at low temperature is :  $\varphi_{tr} = k_{34} / (k_{30} + k_{34})$ . For all complexes  $\varphi_{tr} \rightarrow 1$ , i.e., initially (after the excitation of the molecule) the energy is practically entirely transferred to the  $\text{Eu}^{3+}$  ion. Here in after we shall consider in more detail temperature effects in all channels of radiationless deactivation.

It is necessary to note that besides clarification of the model, the convergence of results to one value has increased when we using such approach. It makes the calculations quite possible for all rate constants of transitions and locations of levels despite of deviations of experimental points,

which one always present. The good correspondence of theoretical curves with experiment are shown on Fig.6.

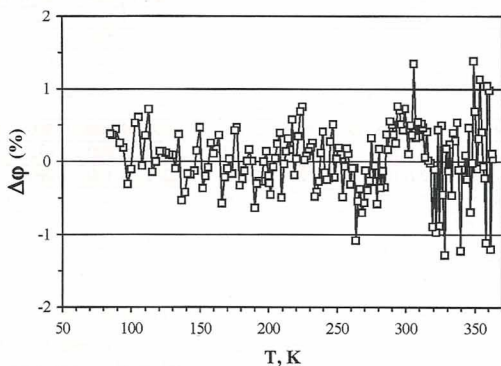


Figure 6. Deviation of calculated values of quantum yield from experimental data for  $\text{Eu}(\text{TТА})_3\text{-DAPhM}$ .

| Eu-complex                             | Rate constant $k_{ij}$ , $\text{s}^{-1}$ |                  |                  |                     |                  |      |
|--|--|------------------|------------------|---------------------|------------------|------|
|  | 30                                       | 34               | 45               | 20                  | 50               | 50   |
| $\text{Eu}(\text{TТА})_3$              | $1,1 \cdot 10^6$                         | $1,4 \cdot 10^9$ | $5,1 \cdot 10^5$ | $2,0 \cdot 10^{16}$ | $1,5 \cdot 10^3$ | 810  |
| $\text{Eu}(\text{TТА})_3\text{-phen}$  | $2,8 \cdot 10^5$                         | $8,6 \cdot 10^7$ | $5,7 \cdot 10^5$ | $1,3 \cdot 10^{13}$ | $1,3 \cdot 10^3$ | 200  |
| $\text{Eu}(\text{TТА})_3\text{-DAPhM}$ | $4,3 \cdot 10^5$                         | $3,3 \cdot 10^8$ | $5,1 \cdot 10^5$ | $6,5 \cdot 10^{13}$ | $1,6 \cdot 10^3$ | 260  |
| $\text{Eu}(\text{TТА})_3\text{-DAPM}$  | $1,1 \cdot 10^6$                         | $5,3 \cdot 10^8$ | $5,0 \cdot 10^5$ | $5,7 \cdot 10^{14}$ | $1,9 \cdot 10^3$ | 30   |
| $\text{Eu}(\text{NTA})_3$              | $4,5 \cdot 10^5$                         | $2,3 \cdot 10^8$ | $5,8 \cdot 10^5$ | $1,8 \cdot 10^{14}$ | $1,7 \cdot 10^3$ | 1020 |
| $\text{Eu}(\text{NTA})_3\text{-phen}$  | $3,5 \cdot 10^5$                         | $4,7 \cdot 10^8$ | $7,3 \cdot 10^5$ | $4,8 \cdot 10^{14}$ | $1,5 \cdot 10^3$ | 30   |
| $\text{Eu}(\text{NTA})_3\text{-DAPM}$  | $1,3 \cdot 10^5$                         | $1,6 \cdot 10^9$ | $5,5 \cdot 10^5$ | $1,5 \cdot 10^{15}$ | $1,8 \cdot 10^3$ | ~0   |
| $\text{Eu}(\text{NTA})_3\text{-DAPhM}$ | $7,4 \cdot 10^5$                         | $3,2 \cdot 10^8$ | $5,7 \cdot 10^5$ | $2,4 \cdot 10^{15}$ | $1,9 \cdot 10^3$ | ~0   |
| $\text{Eu}(\text{BТА})_3\text{-phen}$  | $3,3 \cdot 10^4$                         | $2,8 \cdot 10^8$ | $6,7 \cdot 10^5$ | $5,7 \cdot 10^{13}$ | $1,2 \cdot 10^3$ | 160  |
| $\text{Eu}(\text{BТА})_3\text{-DAPhM}$ | $7,0 \cdot 10^6$                         | $2,4 \cdot 10^8$ | $6,1 \cdot 10^5$ | $2,9 \cdot 10^{15}$ | $1,8 \cdot 10^3$ | 10   |
| $\text{Eu}(\text{BТА})_3\text{-DAPM}$  | $2,1 \cdot 10^4$                         | $4,0 \cdot 10^8$ | $5,3 \cdot 10^5$ | $6,6 \cdot 10^{14}$ | $1,9 \cdot 10^3$ | 5    |

| Eu-complex                  | Rate constant $k_{ij}$ , $s^{-1}$ |                  |                  |     |     |     |      |
|-----------------------------|-----------------------------------|------------------|------------------|-----|-----|-----|------|
|                             | 60                                | 80               | 70               | 56  | 38  | 47  | 52   |
| Eu(TTA) <sub>3</sub>        | $6,3 \cdot 10^2$                  | $5,1 \cdot 10^8$ | $3,1 \cdot 10^5$ | 190 | 210 | 360 | 7350 |
| Eu(TTA) <sub>3</sub> :phen  | $5,2 \cdot 10^2$                  | $1,5 \cdot 10^5$ | $1,6 \cdot 10^5$ | 260 | 130 | 660 | 5990 |
| Eu(TTA) <sub>3</sub> :DAPhM | $4,7 \cdot 10^2$                  | $4,2 \cdot 10^7$ | $4,7 \cdot 10^5$ | 450 | 630 | 440 | 6340 |
| Eu(TTA) <sub>3</sub> :DAPM  | $5,4 \cdot 10^2$                  | $3,5 \cdot 10^7$ | $2,2 \cdot 10^5$ | 370 | 100 | 250 | 6970 |
| Eu(NTA) <sub>3</sub>        | $5,6 \cdot 10^2$                  | $2,2 \cdot 10^8$ | $9,0 \cdot 10^6$ | 250 | 600 | 600 | 6300 |
| Eu(NTA) <sub>3</sub> :phen  | $1,7 \cdot 10^3$                  | $3,5 \cdot 10^7$ | $5,8 \cdot 10^5$ | 450 | 990 | 350 | 6820 |
| Eu(NTA) <sub>3</sub> :DAPM  | $5,0 \cdot 10^2$                  | $4,2 \cdot 10^5$ | $2,9 \cdot 10^5$ | 320 | 820 | 410 | 7190 |
| Eu(NTA) <sub>3</sub> :DAPhM | $3,8 \cdot 10^2$                  | $5,8 \cdot 10^4$ | $7,2 \cdot 10^4$ | 230 | 100 | 260 | 7260 |
| Eu(BTA) <sub>3</sub> :phen  | $3,5 \cdot 10^2$                  | $4,8 \cdot 10^8$ | $1,7 \cdot 10^6$ | 110 | 520 | 540 | 6580 |
| Eu(BTA) <sub>3</sub> :DAPhM | $3,5 \cdot 10^2$                  | $1,8 \cdot 10^7$ | $2,4 \cdot 10^6$ | 290 | 80  | 370 | 7380 |
| Eu(BTA) <sub>3</sub> :DAPM  | $1,9 \cdot 10^2$                  | $8,5 \cdot 10^8$ | $4,1 \cdot 10^6$ | 130 | 220 | 520 | 7210 |

### Determination of sensitivity indexes for parameters of model

For calculation and obtaining correct results it is necessary to study the Eq.(3) on sensitivity of the function  $\varphi^{-1}(T^{-1})$  to variation of unknown parameters. For this purpose we can calculate relative sensitivity indexes, which one are defined as:

$$S_i(T^{-1}) = (\delta f / f) / (\delta x_i / x_i)$$

where  $f = \varphi^{-1}(T^{-1})$  and  $x_i = k_{ij}, \Delta E_{32}$

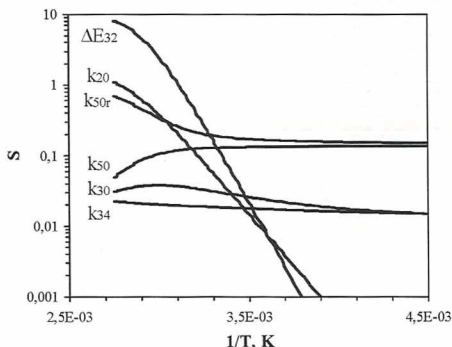


Figure 7. Sensitivity indexes for parameters of calculation with temperature.

The curves  $S_i(T^{-1})$  for some of parameters are shown on Fig.7. (numerical data are taken from outcomes of final calculations, which one was considered above). It is visible from this figure that parameters  $k_{30}$  and  $k_{34}$  have a minimum value of sensitivity indexes, i.e. in approximation of this method, these parameters have maximum sensitiveness to experimental deviations, which one always take place. Therefore the relative errors for determination of these rate constants are maximum.

### Dependence of populations of levels with temperature

We can analyze dependencies of populations of levels  ${}^5D_0$ ,  ${}^5D_1$ ,  $T_1$  with temperature. From Eq.(2) we have:

$$\begin{aligned} N_1 &= N_0 \cdot A_{01} / k_{13} \\ N_5 &= N_1 \cdot \varphi(T) \cdot k_{13} / k_{50r} \\ (7) \\ N_4 &= N_5 / k_{45} \cdot [3 \cdot k_{45} \cdot \exp(-\Delta E_{45} / kT) + k_{50r} + k_{50} + k_{20} \cdot \exp(-\Delta E_{52} / kT) + \\ &\quad + k_{60} \cdot \exp(-\Delta E_{56} / kT)] \\ N_3 &= [(k_{34} \cdot \exp(-\Delta E_{34} / kT) + k_{45} + k_{20} \cdot \exp(-\Delta E_{42} / kT) + k_{70} \cdot \exp(-\Delta E_{47} / kT)) \cdot N_4 - \\ &\quad - 3 \cdot k_{45} \cdot \exp(-\Delta E_{45} / kT) \cdot N_5] / k_{34} \end{aligned}$$

Values  $k_{13}$  and  $A_{01}$  within the described method are not determined, but it is possible to find relative populations of levels  $Q({}^5D_0)$ ,  $Q({}^5D_1)$ , and  $Q(T_1)$  with temperature. From Eq.(7) we have:

$$\begin{aligned} Q({}^5D_0) &= N_5 / (N_3 + N_4 + N_5) = 1 / K_{\Sigma} \\ Q({}^5D_1) &= N_4 / (N_3 + N_4 + N_5) = K_1 / k_{45} / K_{\Sigma} \\ Q(T_1) &= N_3 / (N_3 + N_4 + N_5) = (K_2 \cdot K_1 / k_{45} - K_3) / k_{34} / K_{\Sigma} \end{aligned}$$

where

$$\begin{aligned} K_1 &= 3 \cdot k_{45} \cdot \exp(-\Delta E_{45} / kT) + k_{50r} + k_{50} + k_{20} \cdot \exp(-\Delta E_{52} / kT) + \\ &\quad + k_{60} \cdot \exp(-\Delta E_{56} / kT) \\ K_2 &= k_{34} \cdot \exp(-\Delta E_{34} / kT) + k_{45} + k_{20} \cdot \exp(-\Delta E_{42} / kT) + k_{70} \cdot \exp(-\Delta E_{47} / kT) \\ K_3 &= 3 \cdot k_{45} \cdot \exp(-\Delta E_{45} / kT) \\ K_{\Sigma} &= 1 + K_1 / k_{45} + (K_2 \cdot K_1 / k_{45} - K_3) / k_{34} \end{aligned}$$

The calculated curves for relative populations of levels  ${}^5D_0$ ,  ${}^5D_1$ ,  $T_1$  of  $\text{Eu}(\text{TTA})_3\text{-DAFM}$  complex are shown on Fig.8. The population of triplet level of a ligand increases most fast, the population of  ${}^5D_1$  level also increases, though in less degree. The population of  ${}^5D_0$  level decreases simultaneously with quantum yield of a luminescence, though the absolute change of population is not much for this level.

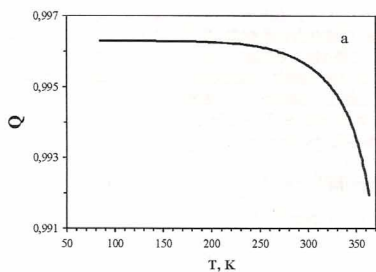


Fig.8a.

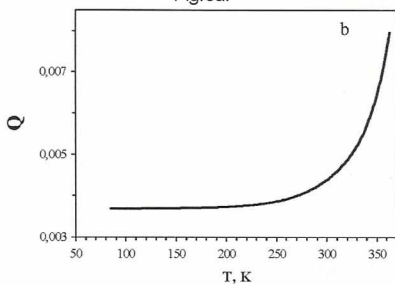


Fig.8b.

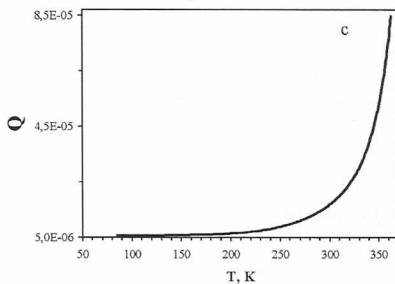


Fig.8c.

Figure 8. Relative populations of  ${}^5D_0$  (a),  ${}^5D_1$  (b) and  $T_1$  (c) levels with temperature.

Knowledge of dependencies of relative populations of levels with temperature and values of rate constants of transitions found above allows to begin consideration the problem of relative contributions of various channels of deactivation into total losses of electronic excitation energy.

### Relative contributions of various radiationless processes into total deactivation of energy

Using the schema of levels showed in a Fig.3. and system Eq.(7) we can write the equations for energy losses:

$$\begin{aligned}G_{30}(T) &= k_{30} \cdot N_3(T) \\G_{38}(T) &= k_{80} \cdot \exp(-\Delta E_{38}/kT) \cdot N_3(T) \\G_{50}(T) &= k_{50} \cdot N_5(T) \\G_{56}(T) &= k_{60} \cdot \exp(-\Delta E_{56}/kT) \cdot N_5(T) \\G_{52}(T) &= k_{20} \cdot \exp(-\Delta E_{52}/kT) \cdot N_5(T) \\G_{47}(T) &= k_{70} \cdot \exp(-\Delta E_{47}/kT) \cdot N_4(T) \\G_{42}(T) &= k_{20} \cdot \exp(-\Delta E_{42}/kT) \cdot N_4(T)\end{aligned}$$

where the losses  $G_{ij}$  correspond to the radiationless transitions  $i \rightarrow j$ .

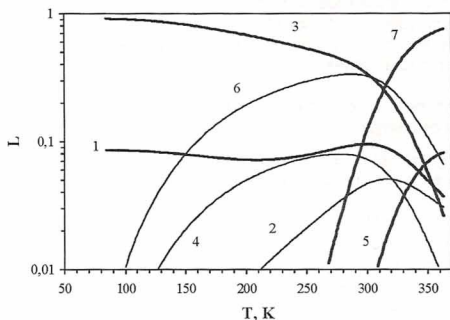
$N_3$  and  $N_4$  could be expressed through  $N_5$  in accordance with Eq.(7).  $G_{ij}(T)$  could be normalized to the total value of all losses at each value of temperature:

$$G_{\Sigma}(T) = \sum G_{ij}(T)$$

Further we can calculate dependencies of the relative contributions of each channel of radiationless losses with temperature:

$$\begin{aligned}L_{\Sigma}(T) &= k_{20} \cdot \exp(-\Delta E_{52}/kT) + k_{60} \cdot \exp(-\Delta E_{56}/kT) + k_{50} + \\&\quad + [(K_2 \cdot K_1 / K_{45} - K_3) / K_{34}] \cdot [k_{30} + k_{80} \cdot \exp(-\Delta E_{38}/kT)] + \\&\quad + K_1 / K_{45} \cdot [k_{70} \cdot \exp(-\Delta E_{47}/kT) + k_{20} \cdot \exp(-\Delta E_{42}/kT)] \\L_{30}(T) &= k_{30} \cdot (K_2 \cdot K_1 / K_{45} - K_3) / K_{34} / L_{\Sigma}(T) \\L_{80}(T) &= k_{80} \cdot \exp(-\Delta E_{38}/kT) \cdot (K_2 \cdot K_1 / K_{45} - K_3) / K_{34} / L_{\Sigma}(T) \\L_{70}(T) &= k_{70} \cdot \exp(-\Delta E_{47}/kT) \cdot K_1 / K_{45} / L_{\Sigma}(T) \\L_{42}(T) &= k_{20} \cdot \exp(-\Delta E_{42}/kT) / L_{\Sigma}(T) \\L_{50}(T) &= k_{50} / L_{\Sigma}(T) \\L_{60}(T) &= k_{60} \cdot \exp(-\Delta E_{56}/kT) / L_{\Sigma}(T) \\L_{52}(T) &= k_{20} \cdot \exp(-\Delta E_{52}/kT) / L_{\Sigma}(T)\end{aligned}$$

The calculated dependencies of the relative contributions of various channels of energy losses with temperature are shown in Fig.9.



**Figure 9.** Relative contributions of different nonradiative processes into total deactivation of energy for  $\text{Eu}(\text{TTA})_3\text{-DAPhM}$  with temperature: 1-  $L_{30}(T)$ ; 2-  $L_{80}(T)$ ; 3-  $L_{50}(T)$ ; 4-  $L_{60}(T)$ ; 5-  $L_{52}(T)$ ; 6-  $L_{70}(T)$ ; 7-  $L_{42}(T)$ .

It is visible from figures that the losses in the channel  ${}^5\text{D}_0 \rightarrow \text{S}_0$  have a main contribution to the total radiationless losses at low temperature. The increasing of thermally activated losses (including channels  ${}^5\text{D}_0 \rightarrow 6 \rightarrow \text{S}_0$ ,  ${}^5\text{D}_1 \rightarrow 7 \rightarrow \text{S}_0$  and  $\text{T}_1 \rightarrow 8 \rightarrow \text{S}_0$ ) describes a slow decreasing of quantum yield at low temperatures. At room temperature and above there is a strong increasing of losses through CT level and then these losses become primary. The relative contribution of  $\text{T}_1 \rightarrow \text{S}_0$  channel into total radiationless losses in all temperature range does not exceed 9 %. This result does not confirm the supposition about primary importance of energy losses through triplet level of ligand [8].

#### Dependence of populations of levels with time at impulsive excitation

The knowledge of location of all levels and values of rate constants of all processes allows to calculate the relative populations of energy levels with time at impulsive excitation in all temperature range. For this purpose we have calculated the system of the differential equations (2) by using Runge-Kutt method. The result of calculation is presented on Fig.10. The relative population of the  ${}^5\text{D}_0$  level reaches the maximum value  $\sim 0,3$  (at  $T=363\text{K}$ ). I.e. before the population of the  ${}^5\text{D}_0$  level reach a maximum, about 70 % of electronic excitation energy will be lost.



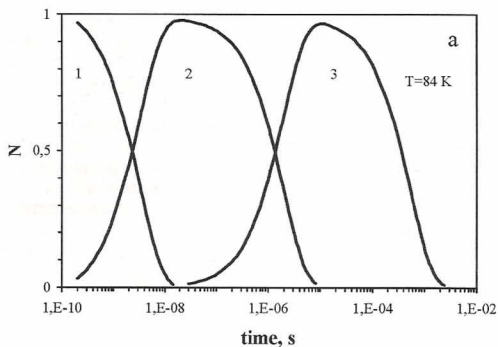


Fig.10a.

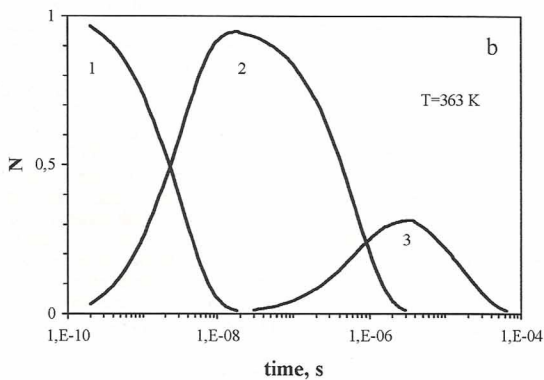


Fig.10b.

**Figure 10.** Populations of levels  $N(T_1)$  (1),  $N(^5D_1)$  (2) and  $N(^5D_0)$  (3) with time at impulsive excitation for  $\text{Eu}(\text{TTA})_3:\text{DAPhM}$  at temperature 84 K (a) and 363 K (b).

## DISCUSSION

We discuss the possible nature of the formally introduced level 2, which plays an important part in the temperature quenching of the luminescence of Eu chelates, and the associated high rate of electron excitation deactivation  $k_{20}$ . Among the tricharged lanthanide ions (the oxidation-reduction potential  $\text{Eu}^{3+}/\text{Eu}^{2+} = -0.35 \text{ V}$ ), the  $\text{Eu}^{3+}$  ion possesses the greatest electron affinity. Because of this, in many complex compounds of europium, rather low-lying states of charge transfer from the ligand to the ion are detected spectroscopically. In a number of cases, the quenching of luminescence was related to the existence of the low-lying states of charge transfer. In particular, for complexes of europium with aromatic acids, the existence of a long-wave-length charge-transfer band in the absorption spectrum leads to complete quenching of luminescence [9]. In the case of complexes of  $\text{Eu}^{3+}$  with NCS, the existence of the charge-transfer band ( $\sim 30,000 \text{ cm}^{-1}$ ) leads to a strong temperature quenching of luminescence. In this case, the preexponential factor in the Arrhenius dependence of  $k_{20}$  is also very high:  $7 \cdot 10^{14} \text{ sec}^{-1}$  for the complex  $\text{Eu}(\text{NCS})_3 \cdot \text{H}_2\text{O}$  [10].

The foregoing and the obtained fairly high rate constant of the transition ( $k_{20} = 1,3 \cdot 10^{13} \pm 2 \cdot 10^{16} \text{ s}^{-1}$ ) allow the conclusion that level 2 also corresponds to the state with charge transfer from the ligand to  $\text{Eu}^{3+}$  with reduction of the latter to  $\text{Eu}^{2+}$ . This interpretation makes it possible to explain naturally one more known experimental fact. Complexes with fluorinated  $\beta$ -diketones possess the highest quantum yield of luminescence at room temperature, which is why they have found wide application in analytical chemistry. This is explained in part by the decreased number of light hydrogen atoms in the close vicinity of the  $\text{Eu}^{3+}$  ion that take an active part in the radiationless deactivation of the  ${}^5\text{D}_0$  level of  $\text{Eu}^{3+}$ . However, another reason is apparently no less important, viz., the fluorine atom possesses acceptor properties, and substitution of hydrogen atoms for fluorinated radicals leads to an increase in the energy of the charge-transfer state and, accordingly, to a decrease in temperature quenching. It should be noted that in recent years, the low quantum yield of luminescence (at high values of the lifetime) of the complexes of  $\text{Eu}^{3+}$  with many macrocycle ligands or polydentate ones (cryptands, crown ethers, etc.) is usually explained by the existence of low-lying charge-transfer states that are located between the  $\text{S}_1$  level of the ligand and the  ${}^5\text{D}_0$  levels of the complex and that participate in relaxation processes [1, 11, 12].

The process of quenching with a small activation energy  $\Delta E_{56} \sim 250 \text{ cm}^{-1}$  can be due to the participation of the polymeric matrix itself in the radiationless deactivation of the  ${}^5\text{D}_0$  level. A radiationless transfer of energy from the  ${}^5\text{D}_0$  level to the overtones of vibrations of the fragments and side groups of polymers as a result of their "collisions" with the chelate after "defrosting" of motions can occur. The existence of levels 7 and 8 in the model of transitions can be explained in a similar way.

The investigations performed showed that the efficiency of intramolecular energy transfer from the ligand to the ion in europium complexes with fluorinated  $\beta$ -diketones is close to unity, and the radiationless degradation of the electron excitation energy is first of all due to the thermally induced transitions from the  ${}^5\text{D}_0$  and  ${}^5\text{D}_1$  levels of the ion with the participation of states with charge transfer from the ligand to  $\text{Eu}^{3+}$  with reduction of the latter to  $\text{Eu}^{2+}$ . It seems that the

donor-acceptor properties of ligands are the main factors that are responsible for the quantum yields of sensitized  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  luminescence being different from unity at room temperature. This determines the possibility of synthesizing new europium chelates (with suppression of the radiationless processes that cause quenching of luminescence) for applications in analytical chemistry and im-munofluorescent analysis.

Described above method allows to obtain rate constants in a large interval of its values. It is very important that we can investigate very short processes of energy transfer in microscale of time with using experiment in macroscale of time (luminescence lifetimes as a rule are large for lanthanides complexes). This allows to use relatively simple equipment and nevertheless to obtain information about processes inside molecule and about interaction of one with surrounding molecules. Such approach may be applied for another molecular systems which have a temperature dependent luminescence.

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