

Investigation of spatial distribution of impurities in solids by the method of kinetic luminescent spectroscopy

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Nonradiative energy transfer produced in an aggregate of Sm^{3+} ions by cross relaxation interaction between the ions is investigated. The information obtainable from the kinetics of the static energy transfer for the analysis of the spatial distribution of activators in a disordered medium is analyzed. The use of the method of kinetic luminescent spectroscopy with selective laser excitation has revealed that the existence of exponential and non-exponential sections of the luminescence-quenching kinetics, corresponding to ordered and disordered distributions of the active ions. The multipolarity and the macro- and microparameters of the inter-ion interaction are determined; a dispersion of the interaction parameters from one optical center to another is observed. At an activator density higher than 10^{21} cm^{-8} the quenching macroparameter $\gamma(n)$ is observed to deviate from a linear density dependence. The shortest possible approach distance of Sm^{3+} ions in Li-La-Sm phosphate glass ($R_{\min} = 5.6 \text{ \AA}$) is found, from the form of the kinetics curve, to be close to the corresponding values for crystalline phosphates. The number of activators having spatially ordered ($R_{ii} \approx R_{\min}$) or spatially disordered ($R_{ii} > R_{\min}$) aggregates of like neighbors at various impurity densities in the glass is estimated.

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§1. INTRODUCTION

In recent years, methods were developed for spectral-luminescent and kinetic investigations of activated solids,¹⁻⁸ and a theory of collective interactions between ions was developed.⁹⁻¹⁵ This makes it possible to study the macroscopic processes of migration of the energy of electron interaction and of the nonradiative degradation of the energy, and to obtain information on the ion-ion interaction on a microlevel. What is dealt with here is a quantitative comparison of theory with experiment, verification of the coefficients, and determination of the numerical values of the microparameters that enter in the theory.^{1-3,6-8}

The attainment of quantitative results in this research field makes it possible to employ the obtained data for the solution of a new problem, namely, the analysis of the spatial distribution of an active impurity in a solid. Thus, the use of these methods in Ref. 16 has made it possible, by comparing two mechanisms of luminescence quenching of Nd^{3+} ions (static and supermigration), to estimate for the first time the distance of the shortest approach of Nd^{3+} ions in highly concentrated Li-La-Nd phosphate glass. The most convenient for analysis of the spatial distribution of the impurities are ions with strongly pronounced effect of concentration quenching of the luminescence, i.e., ion that serve both as donors and acceptors of energy.

§2. THEORETICAL QUESTIONS

The theory of static energy transport (when the electron excitations prior to the emission or quenching act do not change their positions) was proposed in Refs. 17 and 18 for the dipole-dipole ion-interaction mechanism, and was generalized in Refs. 19 and 20 to interaction with a higher de-

gree of multipolarity: dipole-quadrupole and quadrupole-quadrupole. The results of these studies and subsequent experimental investigations^{1-3,6-8,16,21} have shown that the kinetics of the luminescence damping of active ions after their instantaneous excitation has a complicated non-exponential form. It reflects the ion-ion interactions processes characterized by efficiency microparameter C_{DA} and by multipole order $S = 6, 8,$ and $10,$ and also the character of the spatial distribution $n(R)$ of the ions.

The kinetics of the luminescence damping can be divided into three time domains.

The first, during the initial stage of the kinetics, is exponential. If we neglect the rate of the radiative decay, it is given by (I is the luminescence intensity)

$$I(t) = I_0 \exp(-W_0 t) \quad (1)$$

and is characterized by the maximum possible quenching rate W_0 for the given ion aggregate. The macroparameter W_0 is determined by the sum of the probabilities of the elementary ion-ion interactions, $P_i = C_{DA}/R_i^S$ over all the possible sites of the impurity subsystem, with account taken of its filling coefficient or of the specific concentration of the active ions ($c = n/n_{\max}$)^{12,13}

$$W_0 = c C_{DA} \sum_{i=1}^N R_i^{-S} \quad (2)$$

We note that even in the simplest case, for crystals with high degree of order, calculations by means of this formula are complicated, since they call for knowledge of the complete lattice sum for each type of crystal. For disordered media (mixed crystals, glasses, and liquids) the concept of lattice sum is not defined at all, and the transition to integration is

not always possible. The most convenient turned out to be an approach proposed in Refs. 15 and 16, in which the total lattice sum was replaced by interaction with only the nearest neighbors. The calculations of concrete systems,^{1,2,16} have shown that as a result of the strong power-law dependence on the distance (R^{-6} , R^{-8} , R^{-10}), interactions with the first coordination sphere make the decisive contribution to the quenching efficiency. The expression for W_0 can then be written in the form

$$W_0 = c C_{DA} a R_{\min}^{-S}, \quad (3)$$

where a is the coordination number of the immediate surrounding and is equal to the maximum possible number of nearest neighbors, and R_{\min} is the distance between the minimum possible approach of the impurity ions (the constant of the cation sublattice for simple crystals). We note that expression (3) can be successfully used also for disordered systems (crystals, glasses, and liquids) if the spatial distribution of the active impurities in them are simulated by a distribution of hard spheres corresponding to the impurity ion or to a complex with radius $R_{\min}/2$ and with coordination number a of the packing of the complexes. The absence of exact information on the values of a and c in disordered media or in crystals which have not been sufficiently well investigated leads, at first glance, to a leeway in the calculations by Eq. (3). However, an analysis of three versions of cubic packing ($a = 4$) has shown that at a fixed impurity density and at constant R_{\min} , the product ac changes insignificantly

$$ac = 8.5nR_{\min}^3; \quad 6.15nR_{\min}^3; \quad 6nR_{\min}^3; \quad 6.15nR_{\min}^3$$

for the lattices listed above. This makes it possible to write down, with accuracy sufficient for a number of experiments, and approximate expression for W_0 :

$$W_0 = 7C_{DA} n R_{\min}^{3-S}. \quad (4)$$

It establishes a connection between the experimentally measured macroscopic quantities W_0 and n and the microparameters C_{DA} , S , and R_{\min} which characterize both the interaction and the relative ion-ion placement. The considered exponential section in the beginning of the decay kinetics is frequently called "ordered," since it involves emission of donors, the energy from which is transferred to an ordered assembly of acceptors located at a fixed distance R_{\min} from the donors. We note that despite the simplicity of the definition of the quantity W_0 on the ordered section of the decay, the expression (4) alone does not make it possible to obtain immediately the three microparameters contained in it (C_{DA} , R_{\min} , and S).

The ordered section of the luminescence damping kinetics is followed by a second non-exponential section. It reflects the kinetics of the damping of those donors for which the acceptors are at distances larger than the minimum possible. Taking into account the random character of the distribution of the acceptors at $R_i > R_{\min}$, we see that each such donor will have an individual (different from the others) deactivation rate, and all this adds up to strongly nonexponential kinetics of the damping of the luminescence of the assembly of donors. This form of decay (it is called Förster or disordered decay) can be represented by the expression

$$I(t) = I_0 \exp \left\{ - \int_0^{\infty} [1 - \exp(-C_{DA} t / R^S)] n(R) 4\pi R^2 dR \right\}. \quad (5)$$

We note that in the general case the particle density can be a function of the ion-ion distance. In this case, solving the inverse problem, we can attempt to reconstruct, from the form of the kinetics of $I(t)$, the form of this distribution function $n(R)$ for impurity ions in a medium.

At a random distribution of particles, but at a constant density $n = \text{const}$, neglecting their real dimensions ($R_{\min} \rightarrow 0$), we can obtain a simple analytic expression for the decay kinetics (see, e.g., Ref. 15)

$$I(t) = I_0 \exp(-\gamma t^{3/S}), \quad (6)$$

where

$$\gamma = \frac{4}{3} \pi \Gamma(1 - 3/S) n C_{DA}^{3/S}. \quad (7)$$

Expression (6) is valuable because its analysis makes it possible to determine immediately two independent parameters: the degree of multipolarity S and the macroparameter γ . Substituting these values together with the density in (7), we can determine the microparameter C_{DA} which characterizes the effectiveness excitations. It must be remembered, however, that expressions (6) and (7) are valid only at small acceptor densities (dilute solutions) with $c = n/n_{\max} \ll 1$ and at advanced stages of the decay, where the assumption $R_{\min} \rightarrow 0$ is not too rough.

An analysis of expression (5) along the entire time axis $0 < t < \infty$ with allowance for the shortest-approach distance R_{\min}

$$n(R) = \{n \text{ at } R \geq R_{\min}, 0 \text{ at } R < R_{\min}\}$$

was carried out in Ref. 22 for the case of dipole-dipole interaction of the particles. It demonstrates clearly the general regularities of the transition of the kinetics of the damping from the exponential to the Förster behavior, but its weak spot is the use of integration at distances $R \approx R_{\min}$, where the number of ions is discrete and limited.

In Refs. 10, 12, and 22, the Förster theory of static dipole-dipole quenching was generalized to include the case of appreciable acceptor densities $c \sim 1$; this led to the appearance of terms of second and higher degrees of the acceptor density. The experimental data on the observation of nonlinear terms in the function $\gamma = f(n)$ have still not been reported in the literature.

On the basis of Refs. 10, 12, and 23, we can find in the expression for γ the terms quadratic in the concentration at an arbitrary degree of multipolarity $S = 6, 8, \text{ and } 10$. The expression for the kinetics of the decay takes then a form similar to Eq. (6), but with the microparameter γ replaced by γ' , which is expressed as follows:

$$\gamma' = \gamma [1 + c(1 - 2^{3/S-1})]. \quad (8)$$

It can be seen that at low values of the specific density $c \ll 1$ the term that depends on c can be neglected, and we arrive at the usual expression (7) ($\gamma' = \gamma$). In the region of considerable densities, for systems with low degree of multipolarity S , the coefficient of c increases, meaning that the terms non-

liner in the concentration manifest themselves more strongly.

We note that by equating the arguments of the exponential for ordered and disordered decays [expressions (1) and (6)] it is possible to determine the limiting time of the transition from one type of decay to another:

$$t_1 = (\gamma/W_0)^{S/(S-3)} = R_{\min}^S / C_{DA}. \quad (9)$$

This expression was obtained for not too large values of the acceptor densities c and coincide in this region with the more general expression obtained in Ref. 12 for arbitrary c . It can be seen that the value of t_1 does not depend on the density and increases only when the microparameter R_{\min} increases and when the effective quenching C_{DA} decreases. This means that the ordered section of the damping kinetics, for samples with different but not too high density, should be observed in one and the same time interval. However, the degree of the change of the intensity of the luminescence in this section, meaning also the number of centers that radiate in this section, will differ strongly and depend on the total density of the particles. This makes it possible to attempt to connect the change of the intensity on the exponential section $0 < t < t_1$ with the degree of ordering of the arrangement of the active ions in the disordered medium, by writing down the fraction of the ions (donors) that have a spatially ordered assembly of nearest neighbors (acceptors), in the form¹⁾

$$p_0 = 1 - I(t_1) / I_0 \exp(-At_1). \quad (10)$$

It can be roughly estimated from the formula

$$p_0 = 1 - \exp(-W_0 t_1), \quad (11)$$

where

$$W_0 t_1 = ac = 7nR_{\min}^3 \quad (12)$$

is equal to the average number of nearest neighbors and is determined by the specific density of the impurity ions in the medium, increasing with increasing n and R_{\min} . The fraction of the ions having a disordered assembly of nearest neighbors is written in the form $p_d = 1 - p_0$.

Returning to expression (6), we note that for the Förster section of the kinetics the rates of decay of the excited state for a collective of ions is not constant and depends on the time like $\gamma/t^{(S-3)/S}$. In this case, whereas in region of small t its growth is strongly limited by the maximum velocity W_0 determined by expression (3), in the region of large t it tends to zero quite monotonically.

This, however, does not mean that the lifetime of the excitation $\tau = \infty$ as $t \rightarrow \infty$. The lower limit for the rate of decay of the excited state is usually established either by the spontaneous emission processes (A), which we did not take into account in expressions (1) and (6), or by processes of energy migration over the metastable levels \bar{W} (C_{DD}), which enhance the quenching of those active ions for which the direct quenching interaction is weak.^{1,2,11,12,16,21} It follows from this that the Förster nonstationary section of the damping kinetics, which demonstrates the disorder in the arrangement of the particles, lies in the velocity range

$$A + \bar{W} \leq \gamma/t^{(S-3)/S} < W_0. \quad (13)$$

A reliable determination of the degree of multipolarity $S = 6, 8, \text{ and } 10$ from the decay kinetics at a random disposition of the particles, let alone the subtler problem of reconstructing the function $n(R)$, requires measurement of as large as possible range of variation of $\gamma/t^{(S-3)/S}$, at any rate not less than of the same order as $W_0/(A + \bar{W}) \geq 10$.

§3. CHOICE OF OBJECT FOR INVESTIGATION AND EXPERIMENTAL PROCEDURE

The condition (13) in §2 imposes a number of requirements on the choice of the active medium. First is a high density of the direct quenching interactions C_{DA} , $W_0 \gg A$, and a low probability of the migration interactions, $\bar{W} \ll A$. These conditions are not satisfied for all the rare-earth ions. Thus, for most metastable levels of the ions Yb^{3+} , Tm^{3+} , Er^{3+} , Ho^{3+} there is no cross-relaxation quenching, and where it does exist it is accompanied by large migration velocities because of the spin-allowed optical transitions. The same situation is observed also for the Nd^{3+} ion, which is of greatest interest from the practical point of view, where the rates W_0 and \bar{W} are frequently of the same order of magnitude.¹⁶ For Eu^{3+} and Tb^{3+} ions the migration processes are strongly attenuated because the optical transitions are forbidden, but the self-quenching for them is likewise small and can be expected only for the upper metastable levels which are connected with the lower intracenter levels by nonradiative transitions.

We chose Sm^{3+} as the model ion. It is characterized by a favorable location of the metastable level for its excitation by radiation of a rhodamine-6Zh tunable laser. The forbiddenness of the optical transition ${}^4G_{5/2} - {}^6H_{5/2}$ excludes in practice the influence of the migration interaction, whereas the concentration quenching is quite strongly developed for it.⁷ The medium for activation with Sm^{3+} ions was chosen to be Li-Li-phosphate glass,²⁴ which has an anomalously weak concentration quenching when the La^{3+} ions are replaced by Nd^{3+} . As shown by our investigations,¹⁶ one of the causes of this anomaly is the large value of $R_{\min} \sim 4.7 \text{ \AA}$, which approaches the similar values for a number of crystalline phosphates, which have anomalously weak concentration quenching of the luminescence. For the reasons indicated above, however, an exact determination of R_{\min} for Nd^{3+} ions is very difficult. It is of interest in this connection to determine the minimum distance between the active ions in a given medium with the aid of the model ion Sm^{3+} , i.e., in the system $\text{Li}_2\text{O-Sm}_2\text{O}_3\text{-P}_2\text{O}_5$, which is close in its physical and chemical properties to the system $\text{Li}_2\text{O-Nd}_2\text{O}_3\text{-P}_2\text{O}_5$.

The investigations were performed on samples of Li-La-phosphate glasses with variable density of the Sm^{3+} ions ($n = [0.15; 1.52; 2.5; 9.2; 23] \times 10^{20} \text{ cm}^{-3}$), which were introduced into the glass by replacing the La^{3+} ions. The density of the Sm^{3+} ions was monitored by a microprobe analysis carried out with the Camebax instrument, and also by comparison of the absorption spectra for samples with the different densities of the Sm^{3+} ions. The luminescence damping kinetics in a large dynamic range of variation of the intensities was measured by us by a procedure based on the practically instantaneous (within 10^{-8} sec) excitation of Sm^{3+} ions

by a pulse from a tunable dye laser (rhodamine-6Zh) followed by photography of individual sections of the kinetics of the decay from the screen of an S-1-70 oscilloscope. The luminescence of the ions was registered with an FEU-70 photomultiplier. The oscilloscope had a good amplitude-frequency characteristic and a beam scan linearity better than 3%.

The use of "instantaneous" laser excitation of the luminescence is a fundamental factor, for in this case the spatial distribution of the excited ions reflects their spatial distribution in the ground state. This condition is mandatory in the derivation of expressions (1), (5), and (6) and makes the observed kinetics most informative.

§4. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

During the first stage of the investigation we studied the kinetic and density dependences of the luminescence quenching for one chosen group of optical centers that were selectively excited by laser radiation of wavelength $\lambda = 5612 \text{ \AA}$. The kinetics of the luminescence damping of the ${}^4G_{5/2}$ level of the Sm^{3+} ions was measured in a range in which the intensity varied by more than 10^4 times (Fig. 1). It can be seen from the figure that an increase of the density of the Sm^{3+} ions in the glass above $1.5 \times 10^{20} \text{ cm}^{-3}$ leads to a strong enhancement of the luminescence quenching, as is manifest by the nonexponential character of the decay kinetics. The better than 10% agreement between the damping times $\tau_1 = \tau_2 = \tau_3 = \tau_0$ measured during the final exponential stages of the decay for three densities of the Sm^{3+} ions (0.15 , 1.5 , and $2.5 \times 10^{20} \text{ cm}^{-3}$) confirms the low efficiency of the energy migration processes over the metastable level ${}^4G_{5/2}$ of the Sm^{3+} ions, namely $\overline{W} \rightarrow 0$, and allows us to consider only the static $\text{Sm}^{3+} \rightarrow \text{Sm}^{3+}$ nonradiative energy transport mechanism.

As shown in Refs. 1–3, 6, and 21 and as can be seen from expression (6), the order of the multipolarity of the cross-relaxation interactions can be determined from measurements of the quantity $3/S$ in the exponent of the parameter t . Figure 2 shows the kinetics of the nonradiative losses as a function of $\mathcal{L} = \log(I_0/I) - 0.434(t/\tau_0)$ for a sample with density $9.2 \times 10^{20} \text{ cm}^{-3}$ at different powers of the time t ,

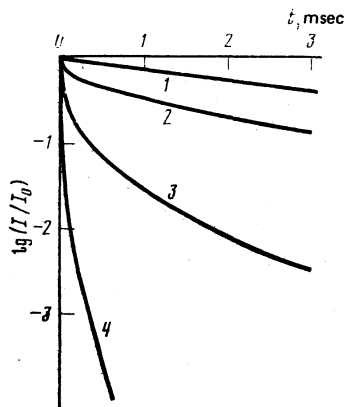


FIG. 1. Kinetics of damping of luminescence from the ${}^4G_{5/2}$ level at different densities $n \text{ [cm}^{-3}\text{]}$ of Sm^{3+} ions in glass: 1— 0.15×10^{20} , 2— 2.5×10^{20} , 3— 9.2×10^{20} , 4— 23×10^{20} .

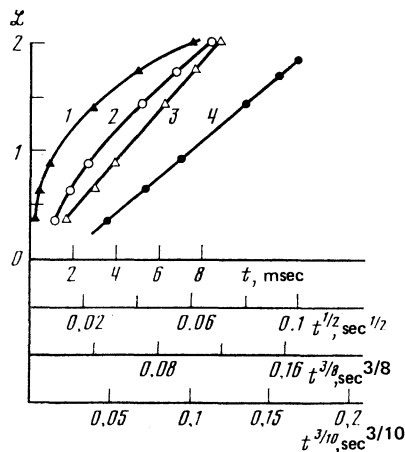


FIG. 2. Time dependences of nonradiative losses for a sample with density $n = 9.2 \times 10^{20} \text{ cm}^{-3}$: 1— $f(t)$, 2— $f(t^{1/2})$, $S = 6$; 3— $f(t^{3/8})$, $S = 8$, 4— $f(t^{3/10})$, $S = 10$.

namely $t^{1/2}$, $t^{3/8}$, and $t^{3/10}$. It can be seen that linearization of the damping kinetics corresponds to high multiplicities of the process, $S = 8$ and 10 . A similar behavior is observed also for samples with other densities of the Sm^{3+} ions. As shown in Refs. 1 and 2, by plotting the quenching (nonradiative losses) in a doubly logarithmic scale as functions of $\log t$, it is convenient to analyze the different stages of the static quenching (see Fig. 3). The slope $\tan\varphi$ of these $\log \mathcal{L} = f(\log t)$ plots yields the exponent of the parameter t , making it possible by the same token to distinguish between ordered quenching (t^1) and disordered quenching ($t^{3/S}$) and to estimate the multipolarity of the latter. It is seen from Fig. 3 that for all the densities the start of the process $t < t_1$ is characterized by $\tan\varphi = 1$, which corresponds to an ordered exponential decay, while the final stage of the process has a smaller slope and corresponds to disordered quenching. The slope $\tan\varphi$ of the plot of $\log \mathcal{L} = f(\log t)$ takes on at $t > t_1$ values 0.39 , 0.36 , and 0.41 , which are close to the value $0.375 = 3/8$, thus pointing to a dipole-quadrupole mechanism of the interaction of the Sm^{3+} ions. As can be seen from Fig. 3, the value of the time t_1 (transition from ordered to disordered decay) does not depend on the density of the Sm^{3+} ions and can be estimated at $t_1 = 40 \mu\text{sec}$.

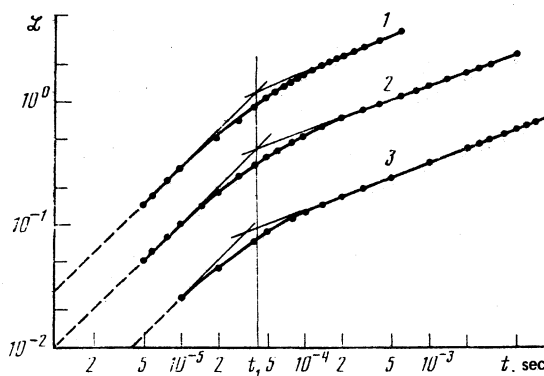


FIG. 3. Ordered and disordered sections in the kinetics of nonradiative losses: 1— $n = 23 \times 10^{20} \text{ cm}^{-3}$; 2— $n = 9.2 \times 10^{20} \text{ cm}^{-3}$; 3— $n = 2.5 \times 10^{20} \text{ cm}^{-3}$.

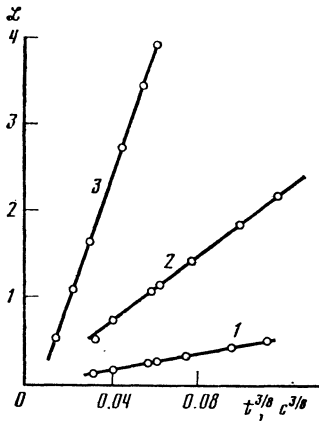


FIG. 4. Dependence of nonradiative losses \mathcal{L} on $t^{3/8}$, corresponding to dipole-quadrupole interaction at different densities n (cm^{-3}) of the impurities: 1— 2.5×10^{20} ; 2— 9.2×10^{20} ; 3— 2.3×10^{21} .

Figure 4 shows plots of the nonradiative losses \mathcal{L} for different densities vs the time raised to the power $t^{3/8}$ (dipole-quadrupole quenching mechanism). It can be seen that in these coordinates the plots are very close to straight lines, and from the slopes of these lines we can determine the quenching macroparameter γ [see expression (6)]. The density dependence of the effective quenching $\gamma'(n)$ calculated in this manner is shown in Fig. 5. It can be seen that the dependence is linear up to a density $9.2 \times 10^{20} \text{ cm}^{-3}$, and a certain enhancement of the dependence at higher densities. The theory admits of two possible causes of deviation of $\gamma(n)$ from linearity. One of the possibilities is the density dependent change of the interaction microparameter C_{DA} , due to the change of the spectral properties as a result of restructuring of the optical centers Sm^{3+} at higher densities. The probability of this effect is estimated by comparing the presented absorption spectra for the transitions ${}^6H_{5/2} \rightarrow {}^6F_{5/2}$; ${}^6H_{5/2} \rightarrow {}^6F_{7/2}$; ${}^6H_{5/2} \rightarrow {}^6F_{9/2}$; ${}^6H_{5/2} \rightarrow {}^6F_{11/2}$; ${}^6H_{5/2} \rightarrow {}^4G_{5/2}$ at different densities of the Sm^{3+} ions. The spectra turned out to be the same, thus excluding the possibility of explaining the nonlinearity of $\gamma(n)$ as being due to a change in $C_{DA}(n)$.

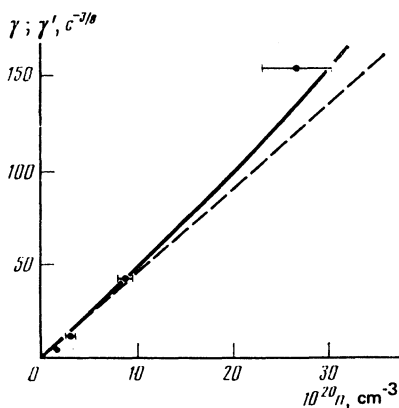


FIG. 5. Concentration dependence of the macroparameters of the quenching: theory— $\gamma = f(n)$ (dashed curve), $\gamma' = f(n)$ (solid); points—experiment. The scatter of the experimental values of the densities takes into account the different results of the microprobe analysis, of the analysis of the absorption spectra, and of the number of Sm^{3+} impurities introduced when the glass was synthesized.

The second possibility is allowance for the higher terms in the expansion of $\gamma'(n)$. We have already obtained above the form of the $\gamma = f(c)$ dependence [Eq. (8)] for the case of high powers of the multipolarity of the interaction and high acceptor densities, not restricted by the condition $c \ll 1$. A similar expression explains the observed nonlinearity of the $\gamma' = f(n)$ dependence if at a density $n \geq 2.3 \times 10^{21} \text{ cm}^{-3}$ the parameter $c = n/n_{\text{max}}$ approaches unity. This is possible at not too large a density n_{max} in the medium, when the forbidden volume per ion, meaning also the shortest approach R_{min} , is sufficiently large.

The experimentally obtained values of the macroparameter γ' , which increases linearly in the region of low densities $n(\text{Sm}^{3+}) \leq 9.2 \times 10^{20} \text{ cm}^{-3}$, enable us, using (7), to find the value of the microparameter that characterizes the effectiveness of the quenching interactions $\text{Sm}^{3+} \rightarrow \text{Sm}^{3+}$. This value turned out to be $C_{DA} = 2.3 \times 10^4 [\text{\AA}^8/\mu\text{sec}]$. Measurements of the luminescence-kinetics damping, carried out by us at 77 K, did not show substantial deviations from the experiments performed at 300 K, thus pointing to the constancy of the microparameters C_{DA} in this region of temperatures. Let us examine which transitions of the Sm^{3+} ions can be responsible for the observed concentration quenching of the luminescence.

The lower part of Fig. 6 shows the absorption spectra of three transitions that can participate in the cross-relaxation energy transfer, while the upper part shows the frequency segments that can be occupied by the luminescence spectra of three other transitions. The dashed line and the solid line shows the spectra corresponding to two temperatures, 77 and 300 K. Shortening of the frequency segments of the luminescence corresponds in this case to freezing of the upper Stark levels of the metastable state ${}^4G_{5/2}$ of the Sm^{3+} ions. The weak dependence of the quenching effectiveness on the temperature points to a decisive role in the interaction of two channels $({}^4G_{5/2} \rightarrow {}^4F_{11/2}) \rightarrow ({}^6H_{5/2} \rightarrow {}^6F_{5/2})$ and $({}^4G_{5/2} \rightarrow {}^6F_{5/2}) \rightarrow ({}^6H_{5/2} \rightarrow {}^6F_{11/2})$ (see Fig. 6). The selection rules with respect to J for both main channels $\Delta J = 2 \rightarrow \Delta J = 0$ and $\Delta J = 0 \rightarrow \Delta J = 2$ admit of the existence of dipole-quadrupole interaction between the Sm^{3+} ions. We note that in the foregoing analysis of the inter-ion interactions $\text{Sm}^{3+} \rightarrow \text{Sm}^{3+}$ we used a perturbation theory developed for particles with purely homogeneous broadening of the spectra, although there exist a number of theories

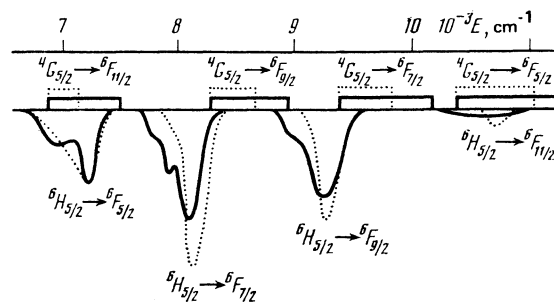


FIG. 6. Overlap of the luminescence and absorption spectra of the Sm^{3+} ions in transitions that admit of cross-relaxation interaction (dashed line $T = 77 \text{ K}$, solid $T = 300 \text{ K}$).

for solving the problem of taking into account the inhomogeneous broadening of the donor and acceptor levels in the energy transport. It is appropriate to ask the following: to what extent is ignoring the inhomogeneity of the spectrum justified in the reduction of the experimental results and wherein lies the complexity of the application of these theories? It can be seen from the results of Ref. 9 that even in the case of the simplest energy-transport schemes in two-level systems at $S = 6$ allowance for the inhomogeneous broadening in the kinetics of disordered quenching calls for knowledge of two parameters: the homogeneous (δ) and the inhomogeneous (Δ) broadening on each of the interacting transitions. Although, as shown in Refs. 7 and 25, the method of selective laser excitation makes it possible to determine these parameters for the resonant transition ${}^4G_{5/2} - {}^6H_{5/2}$, their determination for the nonresonant transitions ${}^4G_{5/2} - {}^6F_{11/2}$, ${}^4G_{5/2} - {}^4F_{5/2}$ and for the predominantly nonradiative transitions ${}^6H_{5/2} - {}^6F_{5/2}$, ${}^6H_{5/2} - {}^6F_{11/2}$ remains extremely difficult. This is due to the tremendous number of optical centers that exist in glass-like matrices and are grouped into various inhomogeneous aggregates (sets) which are individual for each transition and correlate weakly with one another in energy. However, an analysis of the formulas and diagrams of Ref. 9 shows that the situation with the investigation of the inhomogeneously broadening media is not hopeless. It turned out that a transition from a purely homogeneous problem to an inhomogeneous one with an inhomogeneity parameter Δ/δ reaching up to 10, alters the coefficient in the expression (7) for $S = 6$ by only 30%. In our case such large inhomogeneity parameters in the interacting transitions are little likely even at 77 K, let alone room temperature. The situation for the Sm^{3+} ions becomes easier, furthermore, because in the quenching interaction there participates a very large number of electronic transitions between different Stark sublevels, the homogeneous broadening of which may not freeze even at low temperatures, owing to the presence of relaxation transitions

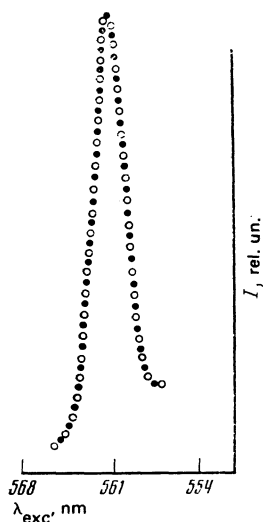


FIG. 7. Spectra of monochromatic excitation of luminescence for a sample with $n = 1.5 \times 10^{20} \text{ cm}^{-3}$ (there is no concentration quenching), plotted at $t_3 = 100 \mu\text{sec}$ (O) and at $t_3 = 5 \text{ msec}$ (●).

with phonon emission in the cooled medium. As a result one can regard the spectra of the interacting transitions of the Sm^{3+} ions as quasihomogeneous and find average values of the microparameters C_{DA} by using the formula of the homogeneous problem for the calculations.

We have carried out the foregoing analysis for only one group of the optical centers Sm^{3+} (donors), extracted from the entire aggregate by 5612-Å monochromatic laser excitation. It is of interest, however, to investigate also the relaxation characteristics of other optical centers that make up the inhomogeneously broadened contour of the resonant transition ${}^4G_{5/2} - {}^6H_{5/2}$. A method for investigating the variance of the radiative probability of the transitions and the damping times of the luminescence from center to center was proposed by us in Ref. 26 in an investigation of the Nd^{3+} in LGS-28 glass. It is based on plotting the spectra of the monochromatic excitation when recording the time-resolved luminescence at $t'_3 \ll \tau$ and $t'_3 \gg \tau$. A comparison of these spectra with each other and with the absorption spectrum of the corresponding transition demonstrates clearly the effectiveness of both the radiative and nonradiative transitions in different optical spectra.

Figure 7 shows the excitation spectra of Sm^{3+} ions on the transition between the lower Stark components of the levels ${}^4G_{5/2}$ and ${}^6H_{5/2}$. They were measured for a sample with low impurity density $n = 1.5 \times 10^{20} \text{ cm}^{-3}$ at different delay times of the instant of registration of the luminescence from the instant of its excitation: $t'_3 = 10^{-4} \text{ sec}$ and $t'_3 = 5 \times 10^{-3} \text{ sec}$. The luminescence was recorded in this case in integral fashion for all the centers on the ${}^4G_{5/2} - {}^6H_{7/2}$ transition. It can be seen that these spectra coincide and are furthermore identical with the absorption spectrum of the transition, thus indicating the absence of a variance in the probability of the radiative transitions $A(\lambda)$ and the intrinsic lifetimes $\tau_0(\lambda)$ for different centers.

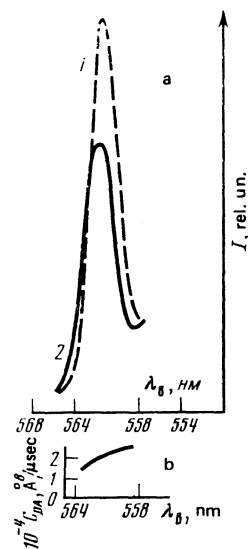


FIG. 8. a) Spectra of monochromatic excitation of the luminescence for a sample with $n = 23 \times 10^{20} \text{ cm}^{-3}$ (strong quenching), plotted at $t_3 = 5 \mu\text{sec}$ (curve 1) and at $t_3 = 350 \mu\text{sec}$ (curve 2). b) Spectral dispersion of the microparameter $C_{DA}(\lambda_{\text{exc}})$.

We measured in analogous fashion the excitation spectra of samples of glasses with strongly pronounced concentration quenching at high densities of Sm^{3+} . They are shown in Fig. 8. It can be seen from the figure that lengthening the delay time leads to a strong deformation of the excitation spectra. The relative decrease of the luminescence intensity observed upon excitation to the short-wave edge of the absorption spectrum at $t_3' = 3.5 \times 10^{-4}$ sec points to a more strongly pronounced quenching of the luminescence for these groups of centers [we recall that $A \neq f(\lambda)$ and $\tau_0 \neq f(\lambda)$]. Knowledge of the kinetics of the luminescence damping for one excitation wavelength $\lambda = 5612 \text{ \AA}$ (see Fig. 1) and comparison of the excitation spectra 1 and 2 of Fig. 8 makes it possible to calculate the change of the quenching macroparameter γ and of the microparameter C_{DA} as functions of the wavelength of the laser excitation for different optical centers. The last dependence is shown in Fig. 8b and demonstrates the increase of the effectiveness of inter-ion interactions for centers with large metastable-level energies. The proposed procedure of investigating the quenching facilitates greatly the analysis of the effectiveness of the inter-ion energy transfer in a system with continuous set of optical centers.

In the analysis of the experimental data we were interested so far only in the final disordered stage of the kinetics of the luminescence damping, whereas earlier (in §2) we noted the important role of the "ordered" section of the kinetics ($0 < t < t_1$). The ordered part of the kinetics of the damping carries direct information on the most important parameters of the spatial arrangement of the impurity ions, namely, on the shortest-approach distance of the particles and on the fraction p_o of the ions that go over into the spatially ordered (with respect to distance) states.

Figure 9 shows the ordered and transition regions of the kinetics of luminescence damping for different densities of the Sm^{3+} ions in the investigated glass. It can be seen that the ordered region of the kinetics ($0 < t < t_1 = 40 \mu\text{sec}$) corresponds to decay of a considerable number of luminescent centers, whose quenching rate and relative density increase with increasing total density of the impurities in (Sm^{3+}) in the glass.

Using the data on the degree of multipolarity of the $\text{Sm}^{3+} - \text{Sm}^{3+}$ ($S = 8$) interaction and the value of the mi-

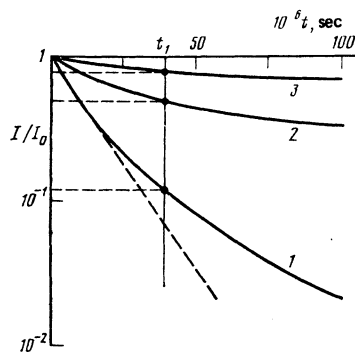


FIG. 9. Initial stage of the kinetics of damping of luminescence of Sm^{3+} ions in samples with appreciable density $n(\text{cm}^{-3})$ (ordered $t < t_1$ stage and transition region): 1— 23×10^{20} , 2— 9.2×10^{20} , 3— 2.5×10^{20} .

croparameter of the interaction $C_{DA} = 2.3 \times 10^4 \text{ \AA}^8/\mu\text{sec}$, obtained from the analysis of the disordered part of the kinetics, we can substitute in (3) the values of the velocities for the initial ordered damping of the luminescence (see Fig. 9) at different acceptor densities and find the previously unknown microparameter R_{\min} . Despite the marked difference between the effectiveness of the quenching of the luminescence, the calculated nearest-approach distance turned out to be constant over an almost tenfold range of variation of the density of the Sm^{3+} ions (replacement of La^{3+} ions by Sm^{3+}), and equal to $R_{\min} = 5.6 \text{ \AA}$, thus indicating constancy of the structure of this series of high-concentration glasses. The importance of the quantity of R_{\min} for the analysis of quenching of impurity centers follows from the same formula (3). It can be seen that the high degree of probability of quenching as a function of R_{\min} ($W_0 \sim R_{\min}^{-5}$ for Sm^{3+} ions and $W_0 \sim R_{\min}^{-3}$ for Nd^{3+} ions) leads to a strong increase of the quenching with changing distance R_{\min} . This is precisely the reason for one of the main requirements on materials with anomalously weak quenching. The large value $R_{\min} = 5.6 \text{ \AA}$ for Li-La-Sm-phosphate glass, which is close to the comparable value for several high-concentration crystal phosphates ($R_{\min} = 5.2\text{--}6.5 \text{ \AA}$, Ref. 27) and correlates fairly well with our estimate of R_{\min} for Nd^{3+} ions, is one of the most important causes of the existence of anomalously weak quenching of rare-earth ions in this glass.

We have proposed above expressions (10)–(12) with which to determine from the luminescence-damping kinetics (see, e.g., Fig. 9) the fraction of the Sm^{3+} ions that enter in the spatially ordered (p_o) and in the spatially disordered (p_d) aggregates of the particles. Calculation with these formulas yields the values of the relative densities p_o and p_d as functions of the total density of the Sm^{3+} ions in glass, as listed in the table. It can be seen from the table that in increase of the total density of the Sm^{3+} ions leads to an increase of the fraction of ions that are located at the minimum possible distance $R_{ii} = R_{\min}$ (ordered assembly) compared with ions that have arbitrarily located neighbors ($R_{ii} > R_{\min}$).

It should be noted that the absence of a strict exponential damping over the entire section of the ordered decay is not contradictory even at Sm^{3+} densities reaching $n = 2.3 \times 10^{21} \text{ cm}^{-3}$ where, as seen from the table, the greater part of the ions is in an ordered state. The "ordering" in our case characterizes only the invariance of the ion-ion distance $R_{ii} = R_{\min}$, but does not require that the number of nearest neighbors be constant; this number can vary randomly about a mean value ac if the particle density differs from the "maximum" possible ($n < n_{\max}$) set by the value of R_{\min} , and by the maximum coordination number (a), possible for this medium, of the packing of the impurity complexes.

TABLE I.

p	n, cm^{-3}		
	$2.5 \cdot 10^{20}$	$9.2 \cdot 10^{20}$	$2.3 \cdot 10^{21}$
p_o	0.15	0.53	0.88
p_d	0.85	0.47	0.12

Knowledge of R_{\min} makes it possible, given the coordination number, to determine the maximum possible density of the impurities in glass of a given composition. In our case, using the values $R_{\min} = 5.6 \text{ \AA}$ and choosing the maximum possible coordination number 12 (closest packing of the spherical complexes SmO_8), we obtain $n_{\max} = 8 \times 10^{21} \text{ cm}^{-3}$. Comparing the obtained value with the highest density of the Sm^{3+} (or La^{3+}) ions in the investigated samples, $2.3 \times 10^{21} \text{ cm}^{-3}$, we see that the investigated glass still has far from the maximum possible density of the active ions, at which all the ions are located at equal distances $R_{\min} = 5.6 \text{ \AA}$ and with equal number of neighbors, and the kinetics becomes strictly exponential over the entire time scale. At the same time, as shown by calculations of the number of aggregate centers (pairs, triads, tetrads, etc.) and by the data of the table, at $c = 0.29$ ($n = 2.3 \times 10^{21} \text{ cm}^{-3}$) the ordering manifests itself already quite strongly and the approximation of pointlike ions is no longer acceptable. As noted above, this must be taken into account also in the analysis of the concentration dependences of the quenching in the nonexponential Förster region. However, we were unable to do so before for lack of data on the values of n_{\max} and c . Substitution of the value of n_{\max} in (8) makes it possible to compare the experimentally observed relation $\gamma = f(n)$ (Fig. 5, with the one calculated from Eq. (8) (Fig. 5, solid line). It can be seen that the calculated relation agrees fairly well with the experimental one, and explains its deviation from linearity at large n .

It is of interest to compare the minimum-approach distance R_{\min} obtained by us with the statistical distribution of the inter-ion distances for nearest neighbors, when the particles are regarded as pointlike. The probability of observing a nearest neighbor at a distance R for pointlike particles is given by the expression²⁸

$$\varphi(R) = 4\pi R^2 n \exp(-4/3\pi R^3 n) \quad (14)$$

and is shown for the particle densities of interest to us in Fig. 10. Such a distribution is frequently used for dilute solutions, finding the mean statistical distance between the ions $\bar{R} = 0.9 \times (4/3\pi n)^{-1/2}$ from the position of the maximum of the probability. It can be seen that with increasing density the average distance between ions decreases. The foregoing analysis has shown that the minimum possible distance between Sm^{3+} ions in Li-La-Sm-phosphate glass is very large: $R_{\min} = 5.6 \text{ \AA}$ (it is marked on the figures by a vertical line) and in many cases exceeds the mean-statistical \bar{R} . In our model of spherical impurity complexes of radius $R_{\min}/2$, the hindrance on the distance $R < R_{\min}$ should lead to a radical change in the distribution function, decreasing its left part relative to R_{\min} (shown by dashed lines). It can be assumed that those ions that would be located in the statistical model at distances from zero to R_{\min} , are located in our case at the minimum possible distance R_{\min} , making up a spatially ordered (in distance) aggregate of ions with fixed distances between neighbors (but with arbitrary angles and numbers of neighbors). The remaining ions make up a spatially disordered group $p_d = 1 - p_o$, since their distances $R_{ii} > R_{\min}$ are allowed in our model and can be arbitrary. We see that the quantitative relation between these two assemblies will be

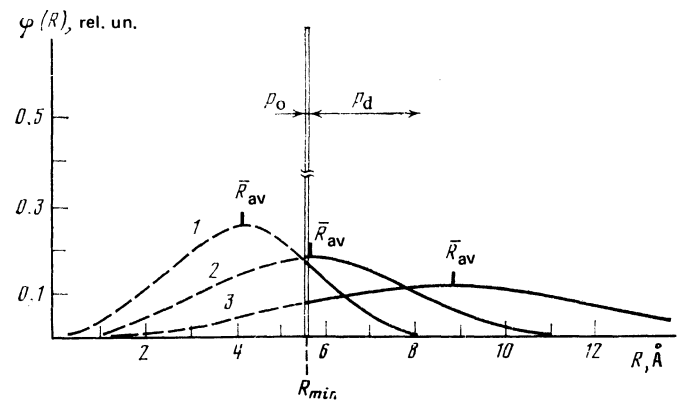


FIG. 10. Distribution function of inter-ion distances for the nearest neighbors: dashed curve—model of pointlike particles $R_{\min} = 0$, solid—allowance for the finite particle dimension $R_{\min} = 5.6 \text{ \AA}$; curve 1— $n = 2.3 \times 10^{20} \text{ cm}^{-3}$; 2— $n = 9.2 \times 10^{20} \text{ cm}^{-3}$; 3— $n = 2.5 \times 10^{20} \text{ cm}^{-3}$.

determined by the total density of the impurities and by the value of R_{\min} . Thus, it can be seen from Fig. 10 that whereas at a low density $n(\text{Sm}^{3+}) = 2.5 \times 10^{20} \text{ cm}^{-3}$ the fraction of the ions that could land in accordance with (14) in the forbidden region but are located at $R_{ii} = R_{\min}$, is relatively small,

$$p_o = \int_0^{5.6 \text{ \AA}} \varphi(R) dR = 0.18,$$

when the density is increased to $9.2 \times 10^{20} \text{ cm}^{-3}$ the value of R approaches R_{\min} and the number of the ordered ions $p_o = 0.51$ approaches the number of disordered ones $p_d = 0.49$. For $n = 2.3 \times 10^{21} \text{ cm}^{-3}$, the ordered assembly becomes dominant, since $\bar{R} < R_{\min}$, and only a small fraction of the ions is in a disordered state, $p_d = 0.17$ ($p_o = 0.83$).

A comparison of the data presented above, obtained by integration of the function $\varphi(R)$, with the data of the table shows them to be in good agreement, so that we can regard as permissible the use of similar reasoning and the use of the glass models described above. The analysis performed shows that at high densities the impurity system cannot be described by a random distribution of pointlike particles with corresponding n and \bar{R} . It turns out more similar to an ordered medium with an order parameter R_{\min} . The method proposed above for determining the microparameter R_{\min} makes it possible to carry out a purposeful search for glasslike matrices with large values of R_{\min} and to produce on their basis highly-concentrated laser media with anomalously weak quenching of the luminescence. Another aspect of the problem is uncovered by the possibility of investigating the type of spatial distribution of the impurities in various glasslike and liquid media.

The values of R_{\min} determined by optical methods and the degrees of ordering in glass are only the first step in this direction. Further progress can be accelerated by using computer reduction of the experimental data, by simulating the kinetics of the damping of the luminescence in those cases when analytic solutions are either absent or were obtained neglecting the finite dimensions of the particles. A comparison of these calculations with the observed experimental plots of the luminescence decay can yield new information

on the form of the distribution function of active impurities in disordered condensed media.

¹¹A similar treatment of the kinetics was used in Ref. 15 in an interpretation of a complicated Förster decay in the black-sphere model of the quenching with a time-varying radius.

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