tions, except that instead of the orthogonal functions exp $(i\omega_k t)$ it is convenient to use the functions e_k in this case (see Ref. 17).

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Neodymium electron energy deactivation and transfer in highly concentrated phosphate glasses

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The kinetic and spectral luminescence characteristics of neodymium ions in highly concentrated phosphate glasses are measured in the 4.2 to 300 K range. Dipole-dipole interaction between the neodymium and hydroxyl ions is observed and leads to static nonradiative transfer of energy from the neodymium ions to the disordered acceptor OH^- group. Migration quenching of luminescence in neodymium by OH^- particles is observed at high active-ion concentrations. The values of the microscopic parameters for static quenching interaction between neodymium and hydroxyl ions and for migration donor-donor neodymium–neodymium interaction are determined. Three neodymium–neodymium quenching mechanisms are distinguished and investigated experimentally: 1) static dipole-dipole energy transfer via the intermediate levels $^4I_{15/2}$ and $^4I_{13/2}$ with the participation of $\sim 800\ \mathrm{cm}^{-1}$ phonons; 2) hopping migration of energy along neodymium ions with subsequent quenching by mechanism (1); 3) quenching under ultrarapid migration conditions along neodymium ions. The micro- and macroparameters of the quenching and neodymium–neodymium migration interactions are determined. The causes of the anomalously weak concentration quenching of luminescence in the investigated glasses are explained.

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1. INTRODUCTION

The interaction of excited activator centers with one another, with random impurities, and with the base on which they are located determine in final analysis such an important characteristic of a luminescent medium as the quantum yield. This characteristic, in particular, is used to assess the prospects of using a particular matrix as an active laser medium and to determine the optimal concentration of the active ions at which the processes of concentration quenching of the luminescence (CQL) are still quite weak. The search for media that permit the use of high concentrations of active ions and have a weakly pronounced CQL effect, which is being pursued actively of late, is due to the need for developing miniature effective sources of coherent radiation for integrated optics and for optical-communication systems. In addition, the development of technological materials with increased concentration of active particles make it possible to increase the energy output per unit volume and to miniaturize the existing laser systems. The most considerable successes in the search of such materials were attained among condensed phosphates, both in crystalline form with weak CQL,[1] and in glassy form.[2-5]

An investigation of the effect of anomalously weak luminescence quenching of Nd^{3+} ions in $La_{1-x}Nd_xP_5O_{14}$ crystals has made it possible to determine the causes of the weak CQL in these crystals.[6] It is of interest to carry out similar investigations on glass, for the purposes of formulating the general conditions for weak luminescence quenching of Nd^{3+} in condensed solids. This was indeed the purpose of the present study.[1)]

II. OBJECTS OF INVESTIGATION AND EXPERIMENTAL PROCEDURES

The object of the investigation was chosen to be Li-Li_{1-x}–Nd_x-phosphate glass,[3,4] which has weak CQL of Nd^{3+}. The value $x=1$ corresponds to an Nd^{3+} concentration $n=2.7\times10^{21}$ cm^{-3}. The glass was synthesized in platinum crucibles heated with RF current. The degree of dehydration was regulated by the heating time and was estimated from the peak reflection coefficient K_{OH^-} at the wavelength $\lambda=3.33$ μm.

The processes of interest to us in the synthesized samples were investigated by analyzing the kinetics of the decay of the metastable state $^4F_{3/2}$ at temperatures 4.2, 77, and 300 K by the procedure of Ref. 8. The luminescence was excited with a rhodamine-6G laser generating at $\lambda=0.5673$ μm, corresponding to the transition between the lower Stark component of the ground state $^4I_{9/2}$ and the upper component of the states $^2G_{7/2}$, $^4G_{5/2}$, of Nd^{3+}. The Nd^{3+} luminescence quantum yields (LQY) cited in this paper were obtained by an indirect method using the decay curves of the excited state $^4F_{3/3}$.

III. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

We consider the experimental data obtained by us and characterizing the luminescence quenching of Nd^{3+} in the investigated glass.

Figure 1 shows a family of curves that demonstrate the kinetics of the luminescence damping of Li–La–Nd-phosphate glass with different Nd^{3+} concentrations. The curves were obtained at a temperature 4.2 K on well-dehydrated glass specimens with absorption coefficient K_{OH^-} in the range 1.7–4.0 cm^{-1}. It is seen from the figure that an increase of the Nd^{3+} concentration from 2.7×10^{19} to 2.7×10^{21} cm^{-3} leads to a gradual increase of the rate of deactivation of the excited state; the damping kinetics in the samples with $n>10^{21}$ cm^{-3} turns out to be close to exponential. An analysis of the concentration dependence of the absorption coefficient $K_{Nd^{3+}}$ in the $^4I_{9/2}\rightarrow{}^4F_{3/2}$ transition shows that the oscillator strength of this transition remains unchanged when the Nd^{3+} concentration changes. This allows us to conclude that the acceleration of the decay of the metastable level $^4F_{3/2}$ with increasing Nd^{3+} concentration is not due to a change in the rate of radiative relaxation, but is due completely to the development of concentration effects that lead to quenching of the Nd^{3+} luminescence.

Figure 2 shows the concentration dependences of the LQY from the $^4F_{3/2}$ level at temperatures 4.2, 77, and 300 K, which characterize the effectiveness of the Nd^{3+} CQL process in our glass. It can be seen that when the concentration changes by two orders of magnitude the LQY decreases only by several times, thus indicating that the Nd^{3+} CQL effect is weak in our glass. Remaining practically unchanged on going from room temperature to nitrogen temperature, the LQY increases upon cooling to helium temperature. The squares in the figure show the values of the quantum yeild at 77 K in samples with the same Nd^{3+} concentration ($x=0.40$) $n=1.1\cdot10^{21}$ cm^{-3} and different residual water contents (2.3 and 23 cm^{-1}). It is seen that an increase of the water content leads to a substantial drop of the quantum yield (to a quenching of the Nd^{3+} luminescence). The diversity and complexity of the luminescence quenching process, which were demonstrated in the foregoing examples, hinder the investigation of the mechanisms of nonradiative loss of electronic excitations and of their singularities. We have therefore chosen the experimental conditions in our investigation such that the different channels of nonradiative decay were separated, so that this decay could be studied in the absence of competing processes. In the first stage of the investigation we attempted, using a low concentration of the active ions $n=2.7\times10^{19}$ cm^{-3} and a low experimental temperature $T=4.2$ K, to exclude the possible Nd^{3+}–Nd^{3+} interactions and to investigate only the static energy transfer from the Nd^{3+} ions to the OH^- hydroxyl particles.

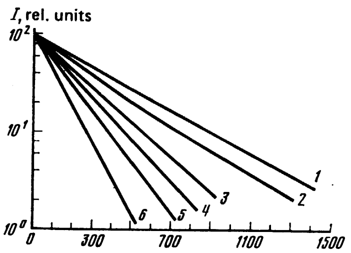

FIG. 1. Kinetics of luminescence damping from the level $^4F_{3/2}$ of the Nd^{3+} ion in Li-La-Nd-phosphate glasses with different Nd^{2+} concentrations at $T=4.2$ K: curve 1) $x=0.01$; $K_{OH^-}=2.85$ cm^{-1}; curve 2) $x=0.2$, $K_{OH^-}=1.7$ cm^{-1}, curve 3) $x=0.4$, $K_{OH^-}=2.28$ cm^{-1}, curve 4) $x=0.45$, $K_{OH^-}=1.7$ cm^{-1}, curve 5) $x=0.75$, $K_{OH^-}=3.95$ cm^{-1}, curve 6) $x=1.0$, $K_{OH^-}=2.32$ cm^{-1}.

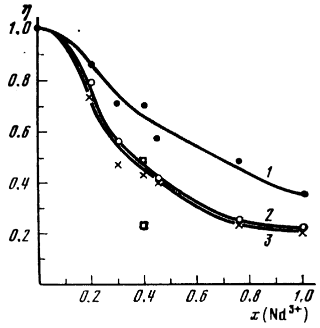

FIG. 2. Concentration dependences of LQY η from the $^4F_{3/2}$ level of the Nd^{3+} ion, obtained for the same samples as in Fig. 1 at temperatures $T=4.2$ K—curve 1, $T=77$ K—curve 2, $T=300$ K—curve 3.

III. 1 DIRECT STATIC Nd^{3+}-OH^- ENERGY TRANSFER

Figure 3 shows the decay curves of the metastable state $^4F_{3/2}$, plotted at an Nd^{3+} concentration $x=0.01$ for samples subjected to different degrees of dehydration. The form of the kinetics obtained for the sample with the smallest water content is well described by an exponential with a damping constant corresponding to the radiative lifetime, a result confirmed by the data of Refs. 4 and 9.

The onset and growth of deviations from exponential behavior of the curves during the initial stages of the decay at $T=4.2$ K as the water content in the glass increases (see Fig. 3, curves 1, 2, and 3), and the preservation of the exponential dependence with constant τ_0 during the final stages, are typical of static quenching of luminescence of the donors (the Nd^{3+} ions) as a result of energy transfer to a disordered assembly of acceptors (OH^- group). Forster and Galanin[10,11] obtained an analytic expression for the luminescence damping kinetics of the donors in the case of dipole-dipole interaction with a disordered assembly of acceptors (Forster kinetics):

$$I(t)=I(0)\exp(-\gamma t^{1/2}-t/\tau_0). \quad (1)$$

Here

$$\gamma={}^4/_3\pi^{3/2}C_{DA}^{1/2}n_A \quad (2)$$

is the macroscopic parameter of the Forster decay and characterizes the rate of decay $-\gamma/t^{1/2}$ at each instant of time, n_A is the number of energy acceptors per cm^3, C_{DA} is the microscopic parameter of the elementary donor—acceptor quenching interaction $P_{DA}=C_{DA}/R_{DA}^6$, which depends on the oscillator strengths of the interacting transitions and on the overlap integral of the donor luminescence spectrum and acceptor absorption spectrum. In accord with (1), we have analyzed the kinetic dependences of the damping of the luminescence of Nd^{3+} ions for samples with different contents of OH^- hydroxyl groups ($K_{OH^-}=2.85$, 6.33, and 15 cm^{-1}).

Figure 4 shows plots of the differences the logarithms of the intensity of the luminescence for a sample without ($K_{OH^-}=2.85$ cm^{-1}) and with quenching ($K_{OH^-}=6.33$ and 15 cm^{-1}), $\ln I^0(t)-\ln I(t)$, as functions of the time t (curves 1 and 3) and of $t^{1/2}$ (curves 2 and 4). The linearity of the plots in $t^{1/2}$ coordinates indicates good agreement between the decay curves and the theoretical law $\ln I^0(t)-\ln I(t)=\gamma t^{1/2}$. This points to a dipole-dipole mechanism of the interaction of the Nd^{3+} ions with the OH^- groups.[2)] From the slopes of the linear plots 2 and 4 we determined the numerical values of the parameters γ for the given type of quenching interaction.

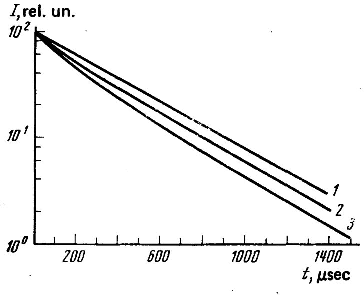

FIG. 3. Kinetics of damping of luminescence from the $^4F_{3/2}$ level of the Nd^{3+} ions under conditions of static quenching $Nd^*\rightarrow OH^*_-$ as a function of the concentration of the hydroxyl groups ($T=4.2$ K). Curve 1) $x=0.01$, $K_{OH^-}=2.85$ cm^{-1}, curve 2) $x=0.01$, $K_{OH^-}=6.33$ cm^{-1}, curve 3) $x=0.01$, $K_{OH^-}=15$ cm^{-1}.

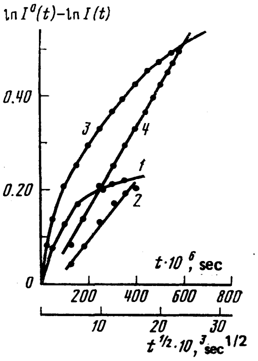

FIG. 4. Plots of the difference of the logarithms of the intensities of the luminescence $\ln I^0(t)-\ln I(t)$ as functions of the time t (curves 1 and 3) and of $t^{1/2}$ (curves 2 and 4) for samples with $x=0.01$ and respectively $K_{OH^-}=6.33$ cm^{-1} and $K_{OH^-}=15$ cm^{-1}; $T=4.2$ K.

The points in Fig. 5 are the experimental values of γ as functions of K_{OH^-}. The value $\gamma=46$ $sec^{-1/2}$, corresponding to $K_{OH^-}=23.7$ cm^{-1}, was obtained as a result of an analysis of the kinetics of the decay of the sample with high Nd^{3+} content, $x=0.40$ ($n=1.1\cdot10^{21}$ cm^{-3}) when account is taken of the presence of the Nd^{3+}-Nd^{3+} quenching interaction. It is seen from Fig. 5 that the experimental points agree fairly well with the linear relation $\gamma\sim n_A$, which follows from the theory. The slope of the linear relation $\gamma=f(n_A)$ allows us to estimate the microscopic parameter of the quenching interaction $C_{DA}(Nd^{3+}-OH^-)$ provided that the exact concentration of the quenchers (OH^- groups) in the investigated samples is known. At the present time, however, it is possible to monitor with good accuracy only the relative water content in the phosphate glasses, by using the IR absorption intensity. One can attempt to determine the absolute water content by starting with

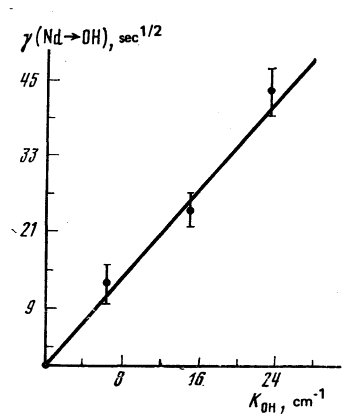

FIG. 5. Concentration dependence of the macroscopic parameter of the scattered quenching interaction $Nd^*\rightarrow OH^*_-$.

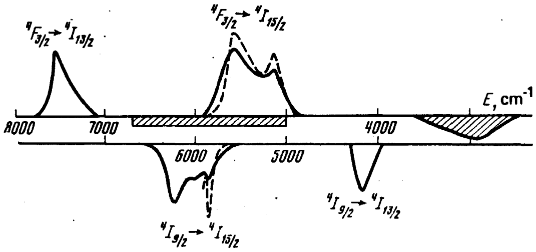

FIG. 6. Luminescence and absorption spectra of Nd^{3+}, corresponding to the transitions $^4F_{3/2}\to{}^4I_{15/2}$, $^4F_{3/2}\to{}^4I_{13/2}$, $^4I_{9/2}\to{}^4I_{13/2}$, $^4I_{9/2}\to{}^4I_{15/2}$ (solid line $T=300$ K, dashed $T=77$ K). The regions of absorption of the fundamental and first overtones of the OH$^-$-group oscillations are shaded.

a comparison with the oscillator strengths of the corresponding vibrational transitions of the OH$^-$ groups in crystals and glasses with known water content, or else by measuring the intensity of the EPR signals from the paramagnetic H centers produced in gamma-irradiated phosphate glasses and comparing it with the corresponding EPR signals in silicate glasses with known water content.[3)] In our calculations we shall use the data of Ref. 13, which yield $N(\mathrm{OH}^-)\ [\mathrm{cm}^{-3}]=10^9\ K_{\mathrm{OH}^-}$. On the basis of this estimate we obtain for the microscopic parameter of the quenching interaction the value $C_{DA}(\mathrm{Nd}^{3+}\to\mathrm{OH}^-)=6.0\cdot10^{-40}$ cm^6/sec. We note that an increase of the temperature from 4.2 to 77 and 300 K does not change the kinetics of the nonradiative decay, and points to the absence of a temperature dependence of the observed type of quenching interaction Nd^{3+} →OH$^-$, i.e., $\gamma(\mathrm{Nd}^{3+}-\mathrm{OH}^-)$ and $C_{DA}(\mathrm{Nd}^{3+}\to\mathrm{OH}^-)\neq f(T)$.

The foregoing facts show that one of the effective channels of nonradiative deactivation of excitation from the metastable level $^4F_{3/2}$ in phosphate glass is direct static energy transfer to the disordered assembly of acceptors (the OH$^-$ ions randomly distributed in the glass) on account of the Nd^{3+}–OH$^-$ dipole-dipole interaction, which takes place in accord with the present theoretical premises. Just as in the case of the quenching of Nd^{3+} luminescence by water, in the case of solutions[14] the most probable model of the degradation of the excitation energy of Nd^{3+} in Nd^{3+}–OH$^-$ interactions in glass should be taken to be the replacement of the electronic excitation of the Nd^{3+} by excitation of the resonant vibrational transition of the OH$^-$ complex at the corresponding overtone.

Figure 6 shows the positions of the Nd^{3+} luminescence bands corresponding to the transitions $^4F_{3/2}\to{}^4I_{15/2}$, and $^4F_{3/2}\to{}^4I_{13/2}$ as well as the absorption bands of the fundamental tone of the OH$^-$ groups and of its first overtone in the energy scale. As seen from the figure, the luminescence spectra of Nd^{3+} can overlap the absorption spectra of the first overtone of the OH$^-$ groups.

III. 2 QUENCHING Nd^{3+}-Nd^{3+} INTERACTIONS

As shown in Sec. III. 1, a decrease of the concentration of the residual OH$^-$ hydroxyl groups in the glass (dehydration) weakens the Nd^{3+}–OH$^-$ interaction and can lead in the final analysis to an elimination of the channel of direct static quenching of the luminescence of the Nd^{3+} ions by the water in the phosphate glass. Taking this into account, we proceed now to study the Nd^{3+} luminescence quenching due to the increase of the Nd^{3+} concentration, in dehydrated samples.

With increasing concentration of the active ions in the glass the excited Nd^{3+} turns out to be surrounded also by unexcited ions. The latter interact with the excited ion and can play a double role. First, acting as energy acceptors, they cause a cross-relaxation ($\mathrm{Nd}^*\to\mathrm{Nd}_*$) quenching interaction with the excited ion.[4)] Second, acting as donor energy carriers, they transport the energy (migration over the metastable levels of the donors) to one of the energy acceptors, in our case the OH$^-$ or Nd^{3+} particles.

We now list the actual additional Nd^{3+} luminescence-quenching channels that can appear as a result of the indicated Nd^{3+}–Nd^{3+} interaction.

1. Direct static quenching $\mathrm{Nd}^*\to\mathrm{Nd}_*$.

2. $\mathrm{Nd}^*\to\mathrm{Nd}^*$ migration followed by quenching $\mathrm{Nd}^*\to\mathrm{Nd}_*$.

3. $\mathrm{Nd}^*\to\mathrm{Nd}^*$ migration followed by quenching by the hydroxyl particles $\mathrm{Nd}^*\text{–}\mathrm{OH}^-_*$.

To determine the Nd^{3+}–Nd^{3+} quenching probability which is not connected with the presence of extraneous impurities, we used the fact that the energy migration over the metastable levels of rare-earth ions has a rule a strong temperature dependence.[8,15,16] The migration rate always decreases when the temperature decreases from 77 to 4.2 K. Thus, analyzing the quenching at helium temperature we can hope to weaken strongly the migration channels of the nonradiative losses and separate in pure form the direct static $\mathrm{Nd}^*\to\mathrm{Nd}_*$ quenching.

It is seen from Fig. 1 that the kinetics of the luminescence damping for the sample with concentration $x=0.2$ ($n=5.4\cdot10^{20}$ cm^{-3}) has a characteristic non-exponential behavior at the start of the decay and becomes exponential with $\tau_0=375$ μsec during the final stage. This non-exponential behavior cannot be due in this case to the presence of OH$^-$ groups in the sample, since their concentration is very low, $K_{\mathrm{OH}^-}=1.7$ cm^{-1} (see Sec. III. 1).

An analysis of the non-exponential behavior of the kinetics, similar to the previously described analysis (see Sec. III. 1), yields a decay of the form $\exp(-\gamma t^{1/2}-t/\tau_0)$, which is typical of the direct dipole-dipole $\mathrm{Nd}^*\to\mathrm{Nd}_*$ quenching interaction with microscopic parameter $\gamma(\mathrm{Nd}^*\to\mathrm{Nd}_*)=22$ sec$^{-1/2}$. Knowing the concentration of the active Nd^{3+} in this sample, we can determine from Eq. (2) the microscopic parameter of the direct quenching interaction: $C_{DA}(\mathrm{Nd}^*\to\mathrm{Nd}_*)=3\cdot10^{-41}$ cm^6/sec.

As seen from Fig. 1, an increase of the concentration of the active Nd^{3+} makes the entire decay kinetics exponential and increases the decay rate.

Before we analyze the dependence of the probability $W(\mathrm{Nd}^{3+}\to\mathrm{Nd}^{3+})$ of the nonradiative deactivation of the $^4F_{3/2}$ level on the concentration of the Nd^{3+} ions, let us dwell on the possible reasons why the decay becomes exponential at $T=4.2$ K.

It is known[10] that the form of the kinetics of the decay in the presence of quenching donor-acceptor interactions is a reflection of the character of the spatial distribution of the acceptors around the excited donors, i.e., in our case the Nd^{3+} ions. The exponential behavior observed by us in the damping can be treated either as the presence of an ordered arrangement of the active particles (static ordering) or as the presence of an additional "low-temperature" energy-migration process that smoothes out the fluctuations of the quenching probabilities for the different donors (dynamic ordering).

The first assumption, that of static ordering, seems at first glance to be not very probable for a glassy material, but some order in the arrangment of the activator ions can be expected at appreciable activator concentrations, when the statistical average (most probable) distance between ions, which depends on the concentration like $R_{av}=(4\pi n/3)^{-1/3}$, turns out to be close to the minimum possible ion–ion distance R_{min} in the given medium. By virtue of the singularities of the phosphate structure, the quantity R_{min} may turn out to be quite large. Thus, crystalline phosphates with close compositions are characterized by an isolated disposition of the neodymiumoxygen dodecahedra NdO_8 (Refs. 17 and 18), which leads to large Nd^{3+}–Nd^{3+} distances $R_{min}(NdP_5O_{14})=5.19$ Å (Ref. 17) and $R_{min}(LiNdP_4O_{12})=5.64$ Å (Ref. 18). If we assume a similar disposition of the neodymium-oxygen complexes for the glassy phosphates, then even at an Nd^{3+} concentration $x=0.45$ ($n=1.2\cdot10^{21}$ cm^{-3}) we obtain $R_{av}=5.6$ Å, which is close to the minimal distance R_{min}. That is to say, at this concentration a large number of Nd^{3+} ions are already atfixed distances $R\approx R_{min}$, and this can lead to ordering of the quenching process and make the decay kinetics exponential. Further increase of the concentration of the active ions will lead only to an increase in the number of nearest NdO_8 complexes located at smallest possible distance from the complex with the excited Nd^{3+} ion (Nd^*O_8), but without a decrease in the distances between them ($R_{min}=$ const). We can propose the following expression for the quenching probability in this case:

$$W(Nd^{3+}-Nd^{3+})=12\frac{C_{DA}}{R^6_{min}}\frac{n}{n_{max}}. \tag{3}$$

The coefficient 12 is here the maximum number of Nd^{3+} ions located at the distance R_{min}, i.e., the coordination number corresponding to the closest packing of the neodymium-oxygen complexes of radius $R_{min}/2$ (assuming them to be spherical), $C_{DA}/R^6_{min}=P_{DA}$ is the probability of the quenching interaction for a pair of Nd^{3+} ions at a distance R_{min}, and $n/n_{max}=c$ is the relative concentration (fraction) of the sites in the nearest surrounding of Nd^*O_8 occupied by other NdO_8 complexes at a given R_{min}.

Expression (3) is the analog of the lattice sum which is used in the calculation of quenching in highly concentrated crystals.[19] The maximum possible concentration of the active ions in glass at a fixed R_{min} can be obtained from the condition of the closest packing of the NdO_8 complexes with radius $R_{min}/2$, $n_{max}=2^{1/2}R^{-3}_{max}$. We rewrite (3) in the form

$$W^0(Nd^{3+}-Nd^{3+})=\frac{12}{2^{1/2}}\frac{C_{DA}}{R^3_{min}}n. \tag{4}$$

The quenching probability is proportional here to the Nd^{3+} concentration in the first degree and depends on the values of the microscopic parameters C_{DA} and R_{min}.

The other possibility, dynamic migration ordering of the kinetics of the nonradiative energy transfer, is quite probable in condensed neodymium-containing media.[8,19,20] We can distinguish here between two Nd^{3+}–Nd^{3+} quenching mechanisms in which migration takes part.

1. Migration-controlled quenching when the quenching probability $\overline{W}(Nd^{3+}-Nd^{3+})$ is proportional to the square of the Nd^{3+} concentration and depends on the effectiveness of both the donor-acceptor interaction, $C_{DA}(Nd^{3+}-Nd^{3+})$, and of the donor-donor interaction, $C_{DD}(Nd^{3+}-Nd^{3+})$ of the Nd^{3+} ions.[19,20] For hopping migration which is typical of Nd^{3+} ions, the expression takes the form

$$W(Nd^{3+}-Nd^{3+})=\pi(2\pi/3)^{5/2}n^2(C_{DD}(Nd^{3+}-Nd^{3+}))^{1/2}(C_{DA}(Nd^{3+}-Nd^{3+}))^{1/2}. \tag{5}$$

2. The second mechanism is supermigration, when the migration rate is so high that the final donor-acceptor energy transfer act is the limiting stage of the quenching process. In this case the quenching probability $W^0(Nd^{3+}-Nd^{3+})$ is proportional to the first degree of the concentration Nd^{3+} and depends only on the effectiveness of the donor-acceptor interactions $C_{DA}(Nd^*\rightarrow Nd_*)$ and on the minimal Nd^{3+}–Nd^{3+} distance (R_{min}) (Ref. 21):

$$W^0(Nd^{3+}-Nd^{3+})=\frac{2}{3}\pi^2\frac{C_{DA}n}{R^3_{min}}. \tag{6}$$

It is interesting to note that expression (6), apart from a numerical coefficient 1.28, agrees with expression (4) obtained by us for the quenching probability in the case of static ordering; this indicates that the quenching interactions of Nd^{3+} with the nearest neighbor Nd^{3+} plays the decisive role even under supermigration conditions. It can be shown that our reasoning concerning the dynamic migration ordering of the decay at a temperature 4.2° K does not contradict those cases in which "freezing" of the migration takes place when the samples are cooled from 77 to 4.2 K.[8,15,16] Indeed, as shown in Refs. 22 and 23, energy migration over Nd^{3+} ions in glasses can be quite effective even at helium temperature, but under the mandatory condition that the hopping not require for its activation that phonons be drawn from the lattice. That is to say, the migration proceeds effectively only downward on the energy scale with emission of phonons (red shift), and since the number of neighbors having a lower metastable-level energy decreases rapidly with each hop (it is described by a Gaussian inhomogeneous profile), the migration stops after several hops. Such a local migration averages the Nd^{3+}–Nd^{3+} quenching rate in different centers, but cannot provide excitation over large distances, as would be required for quenching by extraneous impurities (e.g., by OH$^-$ groups).

Equations (5) and (6) pertain to different sections of the concentration dependence of the quenching probability.[19] Thus, the hopping mechanism of migration [expression (5)] is characterized by lower values of the concentration. The increase of the concentration takes place, when a certain critical concentration n^* is reached,[19] from expression (5) to expression (6), i.e., from the migration region to the supermigration region. The general form of the concentration dependence of the quenching probability under migration conditions can be written as a produce of two functions:

$$W(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})=W^0(n)y(n). \tag{7}$$

Here $W^0(n)$ is the limiting value of the quenching rate under supermigration conditions and is specified by Eq. (6), while $y(n)$ is a function that is linear in n at concentrations less than critical $n<n^*$, and equal to unity at $n>n^*$:

$$y(n)=\begin{cases}(^2/_3\pi)^{3/2}C_{DD}{}^{1/2}/C_{DA}{}^{1/2} & n<n^*,\\ 1 & n>n^*.\end{cases} \tag{8}$$

Taking into account the expression

$$n^*=C_{DA}{}^{1/2}/C_{DD}{}^{1/2}(^2/_3\pi)^{3/2}R_{min}^3 \tag{9}$$

we can rewrite $y(n)$ in the simple form

$$y(n)=\begin{cases}n/n^* & n<n^*,\\ 1 & n>n^*.\end{cases} \tag{10}$$

Equation (7) describes the entire concentration dependence and coincides with (5) at $n<n^*$ and with (6) at $n>n^*$. From an examination of (7), (9), and (10) it is seen that one can attain a decrease of the quenching at fixed values of C_{DA}, $R_{\min}$, and n, i.e., at fixed $W^0(n)$, only by decreasing $y(n)$, i.e., by increasing the critical concentration n^* via a decrease of the effectiveness C_{DD} of the donor-donor interactions. Thus, from the point of view of maintaining a high luminescence quantum yield of Nd^{3+} it is preferrable to have small values of C_{DD} and a quadratic dependence of $W(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})=f(n)$. It must be remembered here that this quadratic dependence (5), which has a faster rate of change, will never lead to a stronger quenching that the slow linear dependence (6), since the latter sets the limit under the given conditions (fixed C_{DA} and $R_{\min}$).

We now stop to consider the concentration dependence of the Nd^{3+}–Nd^{3+} quenching probability observed by us in the investigated Li–La–Nd-phosphate glass (Fig. 7). The experimental values of $W(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})=1/\tau(n)-1/\tau_0$ are marked in Fig. 7 by the points. The dashed lines 1 and 2 in the same figure show the quadratic [corresponding to expression (5)] and linear [expression (6)] concentration dependences which were drawn to provide a best fit to the experimental values. The solid line in the figure shows the general concentration dependence corresponding to Eq. (7). We see that for samples with Nd^{3+} ion concentration $x<0.45$ ($n=1.2\cdot10^{21}$ cm^{-3}) the experimental points fit better the quadratic dependence, whereas at $x>0.45$ the values for $W(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$ correspond to the linear law. This experimental situation agrees with the theoretical analysis presented above, i.e., up to the critical concentration $n^*=1.2\times10^{21}$ cm^{-3} we are dealing with the migration mechanism of the Nd^{3+}–Nd^{3+} luminescence quenching, and at $n>n^*$ we are dealing with the supermigration mechanism. Substituting in (5) the parameter $C_{DA}(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$, of the quenching donor-acceptor interaction, we can estimate from the course of the quadratic dependence of the quenching probability $\overline{W}=f(n)$ under migration condition the microscopic parameter of the migration donor-donor interaction, $C_{DD}(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$, which turns out to be $C_{DD}(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})=2\cdot10^{-40}$ cm^6/sec. We recall that the obtained microscopic parameter is approximate and corresponds to local energy migration over the Nd^{3+} ions at $T=4.2$ K, when the long-range migration is completely frozen.

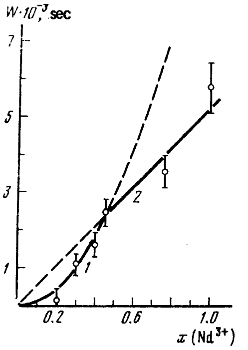

FIG. 7. The concentration dependences of the quenching probability: curve 1—under migration conditions $W\sim n^2$, curve 2—supermigration $W^0\sim n$. Solid line—general relation $W(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})=f[n(\mathrm{Nd}^{3+})]$ corresponding to Eq. (7).

Substituting the microscopic parameter $C_{DA}(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$ in (6) we obtain from the linear concentration dependence of the quenching probability under supermigration condition, $W^0=f(n)$, the last unknown microscopic parameter $R_{\min}=4.7$ Å. We see that the shortest-approach Nd^{3+}–Nd^{3+} distance in Li–La–Nd-phosphate glass turns out to be close to the corresponding value for crystalline phosphates with compositions $\mathrm{NdP_5O_{14}}$ ($R_{\min}=5.19$ Å), $\mathrm{LiNdP_4O_{12}}$ ($R_{\min}=5.64$ Å). So large a value of $R_{\min}$ is one of the main causes of the anomalously weak Nd^{3+}–Nd^{3+} concentration quenching in our glass.

From the condition that the $\mathrm{NdO_8}$ polyhedra (with radius $R_{\min}/2=2.35$ Å) have the closest packing, we can estimate the maximum Nd^{3+} concentration in the material with weak concentration quenching preserved:

$$n_{max}=2^{1/2}R_{min}^{-3}\approx1.3\cdot10^{22}\,\mathrm{cm}^{-3}.$$

This concentration $n_{\max}$ is obtained from the considered quenching model and is not dependent on the concrete chemical composition.

It is of interest to compare the investigated phosphate glass with crystalline phosphates also with respect to another most important microscopic parameter, which determines the Nd^{3+}–Nd^{3+} quenching effectiveness, namely C_{DA}. Since there are no such published data on crystalline phosphates, we have calculated the microscopic parameters $C_{DA}(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$ for neodymium pentophosphate and for double Li–Nd metaphosphate by Eq. (6), using the values of $W(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$, $R_{\min}$, and n taken from the literature[5), 17, 18] The calculated microscopic parameters turned out to be $C_{DA}(\mathrm{NdP_5O_{14}}) = 3.0\cdot10^{-41}$ cm^3/sec, $C_{DA}(\mathrm{LiNdP_5O_{12}}) = 2.7\cdot10^{-41}$ cm^3/sec, C_{DA}(Li-La-Nd-phosphate glass) $= 3.0\times10^{-41}$ cm^6/sec. The cited figures show that the effectiveness of the cross-relaxation quenching interaction Nd^{3+}–Nd^{3+} in all three media is practically the same, i.e., it does not change on going from the crystal to the glass. The results allow us to conclude that the cause of the anomalously weak Nd^{3+}–Nd^{3+} concentration quenching in Li–La–Nd-phosphate glass, just as in the crystalline phosphates, is the combination of the small value of $C_{DA}(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$ and the large value of the shortest distance $R_{\min}(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$. We note that satisfaction of only one of these conditions may not be sufficient to maintain a high quantum luminescence yield. Thus, for example the value of $C_{DA}(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$ obtained in Ref. 17 for $\mathrm{LaF_3-NdF_3}$ crystals is also small: 3×10^{-41} cm^6/sec. However, $R_{\min}$ is also small, and the result is therefore a strong concentration quenching of the luminescence and a small luminescence quantum yield.

Which are the actual electronic Nd^{3+} transitions that take part in the cross-relaxation quenching interaction of the neodymium ions? The upper half of Fig. 6 shows the spectra of the luminescence from the metastable level $^4F_{3/2}$ to the lower levels $^4I_{15/2}$ and $^4I_{13/2}$. The absorption spectra closest in energy, which corresponded to transitions from the ground level $^4I_{9/2}$ to $^4I_{13/2}$ and $^4I_{15/2}$, are shown in the lower part of Fig. 6. It is seen from the figure that exact resonance is observed only for transitions to the $^4I_{15/2}$ level:

$$\text{I Scheme } E_l(^4F_{3/2}\to{}^4I_{15/2}) = E_a(^4I_{9/2}\to{}^4I_{15/2})$$

(resonant interaction scheme).

For the two other groups of transitions, the energy-resonance condition, which is necessary to realize the quenching interaction, can be satisfied only with participation of phonons:

$$\text{II Scheme } E_l(^4F_{3/2}\to{}^4I_{13/2}) = E_a(^4I_{9/2}\to{}^4I_{15/2}) + \hbar\omega_{\mathrm{ph}}\,(800\ \mathrm{cm}^{-1}),$$
$$\text{III Scheme } E_l(^4F_{3/2}\to{}^4I_{15/2}) = E_a(^4I_{9/2}\to{}^4I_{13/2}) + \hbar\omega_{\mathrm{ph}}\,(800\ \mathrm{cm}^{-1})$$

(nonresonant interaction schemes). The excess of the electron energy $E_l - E_a$ is transformed here directly in the course of the excitation transfer into lattice vibrations.

To determine the contribution of the resonant and nonresonant schemes of the process, were measured the overlap integrals for scheme I of the process at two temperatures, 300, and 77 K. The result is shown in Fig. 8. It turned out that lowering the temperature from 300 to 77 K decreases the overlap integral by at least a factor of 7, whereas the integral intensity of the luminescence changes little. We note immediately that the obtained overlap integrals do not reflect the real picture of the interaction for a pair of Nd^{3+}ions, since the employed luminescence and absorption spectra are inhomogeneously broadened, i.e., collective. However, we see that the strong decrease of the overlap integral with decreasing temperature is due to freezing of the short-wave part of the luminescence spectrum and of the long-wave part of the absorption spectrum, i.e., freezing of transitions with excitation of stark components which are populated only at room temperature. This process leads to no less an abrupt weakening of the interaction also for the Nd^{3+}–Nd^{3+} pair. In addition, cooling the samples to nitrogen temperature should be accompanied by a narrowing of the homogeneous component of the broadening, which can lead only to an even sharper decrease of the true overlap integral for the ion pair compared with the results obtained by us from the collective spectra.

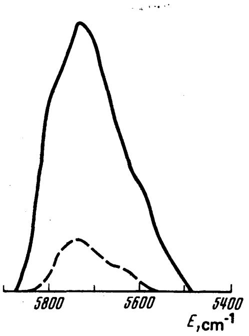

FIG. 8. Overlap integrals of luminescence and absorption spectra of Nd^{3+}, corresponding to the transitions $^4F_{3/2}\to{}^4I_{15/2}$ and $^4I_{9/2}\to{}^4I_{15/2}$. Solid line for $T = 300$ K, dashed for $T = 77$ K.

We can therefore conclude that if the investigated Nd^{3+}–Nd^{3+} quenching channel is due mainly to cross-relaxation resonant interaction (scheme I) via the $^4I_{15/2}$ level, then the quenching probability itself should have a strong temperature dependence and it should increase sharply when the temperature is raised from 77 to 300 K. In fact, as shown by the measurements, no such thing occurs, and the rate of quenching at these temperatures is approximately the same (see Fig. 2). This independence of the direct Nd^{3+}–Nd^{3+} quenching of temperature in the temperature range 77–300 K can be understood only within the framework of the nonresonant Nd^{3+}–Nd^{3+} interactions (schemes II and III), when a part is played in the energy transfer by the oscillations of the base, with a frequency much higher than the thermal energy corresponding to the maximum phonon density $\hbar\omega_{\mathrm{ph}} \gg kT$.

We can thus state that the effectiveness $C_{DA}(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$ of the cross-relaxation quenching interactions does not depend on temperature in the range 4.2–300 K, owing to the dominant role of the nonresonant interactions of the transitions $^4F_{3/2}\to{}^4I_{13/2}$, $^4I_{9/2}\to{}^4I_{15/2}$ and $^4F_{3/2}\to{}^4I_{15/2}$, $^4I_{9/2}\to{}^4I_{13/2}$, which proceed with emission of the phonons of energy $\hbar\omega_{\mathrm{ph}} \sim 800$ cm^{-1}. We note that crystalline phosphates are also characterized by the absence of a temperature dependence of the quenching probability, meaning also of $C_{DA}(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$, and this in conjunction with the agreement of the numerical values of C_{DA} allows us to conclude that the concrete schemes of the Nd^{3+}–Nd^{3+} interactions in condensed crystalline and glassy phosphates are the same. The absence of a temperature dependence of C_{DA} shows that the quenching probability $W(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$ at $n \geq n^*$ [see expression (7)] will not increase when the temperature is raised from 4.2 to 300 K. At $n<n^*$ some increase of $W(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$ with temperature, to values corresponding to the linear $W^0(n)$ dependence, can be due only to an increase of the effectiveness of the donor-donor migration interactions $C_{DD}(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$. The increase of C_{DD} leads to a decrease of n^*, i.e., to an extension of the linear $W^0(n)$ dependence (straight line 2 in Fig. 7) into the region of lower concentrations.

It is seen from Fig, 2 that in the region of high concentrations of Nd^{3+} ($n>n^*$) one observes a substantial decrease of the luminescence quantum yield of Nd^{3+} when the temperature is raised from 4.2 to 77 K. This points to the existence of one more, not yet considered by us, channel of nonradiative losses in Li–La–Nd-phosphate glass, the effectiveness of which increases with increasing Nd^{3+} concentration, and having an activation energy corresponding to the temperature range 4.2–77 K. This channel can be only the migration of the excitation energy over the Nd^{3+} ions with subsequent quenching by the hydroxyl particles: $\mathrm{Nd}^*\to\mathrm{Nd}^*\to\ldots\to\mathrm{Nd}^*\to\mathrm{OH}^-_*$.

III. 3 "LONG-RANGE" ENERGY MIGRATION OVER THE Nd^{3+} IONS TO THE QUENCHING OH^- HYDROXYL IONS

In Sec. III. 2, when discussing the energy migration and its role in the deactivation of the electronic excitation of the Nd^{3+} ions, we have considered only local energy migration over several inter-ion distances $R(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$ and its influence on the kinetics and rates of the luminescence quenching of Nd^{3+}, and disregarded the long-range migration quenching channel. This is justified if the investigated material either contains no extraneous centers that quench the luminescence of neodymium (for example, OH^- groups), or if their number is very small, and the long-range energy migration to these centers is weakened for some reason (for example, because of the low temperature and the appreciable inhomogeneous broadening). In Sec. III. 1 we have shown that the hydroxyl ions are very effective quenchers of the Nd^{3+} luminescence even at very small activator concentrations. Their negative interaction manifests itself even more strongly in glasses with high Nd^{3+} concentrations. Long-range energy migration over the metastable Nd^{3+} ion levels ensures a rapid approach of the excitation to the quenching center (OH^- group), which leads to a high probability of the vanishing of the excitation $\mathrm{Nd}^*\to\mathrm{Nd}^*\to\ldots\to\mathrm{Nd}^*\to\mathrm{OH}^-_*$ even at those OH^- group concentrations when the direct static quenching $\mathrm{Nd}^*\to\mathrm{OH}^-_*$ is negligible. As shown by us above, the cross-relaxation $\mathrm{Nd}^*\to\mathrm{Nd}^*$ energy transfer does not depend, under supermigration conditions, on the temperature in the investigated temperature range 4.2–300 K. Using the additivity of the quenching probabilities $W^0(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$ and $\overline{W}(\mathrm{Nd}^{3+}-\mathrm{OH}^-)$, we calculated the probabilities of the $\mathrm{Nd}^*\to\mathrm{OH}^-_*$ quenching as a result of long-range migration using the formula $\overline{W}(\mathrm{Nd}^{3+}-\mathrm{OH}^-)=1/\tau^{77K}-1/\tau^{4.2K}$, and investigated its dependence on the concentration of the Nd^{3+} donors and OH^- acceptors.

The theory considers two models of long-range migration over the donors with subsequent quenching by acceptors. The first is the diffusion model and is valid in the case when $C_{DA}\gg C_{DD}$. The expression for the probability of migration damping in a disordered medium, in the case of dipole-dipole donor-donor and donor-acceptor interaction, takes the form[20]

$$\overline{W}=(4/_3\,\pi)^2(1/_2)^{3/4}C_{DD}{}^{3/4}C_{DA}{}^{1/4}\,n_A n_D. \tag{11}$$

The second, hopping, model of energy migration[21] is valid is $C_{DD}>C_{DA}$, and the expression for the probability of the migration quenching takes the form

$$\overline{W}=\pi(2/_3\pi)^{3/2}C^{1/2}_{DD}C^{1/2}_{DA}n_A n_D. \tag{12}$$

We see that both models lead to a direct proportionality of the quenching probability to the concentration of either the acceptors or donors, thus explaining the strong decrease of the quantum yield as a result of this quenching mechanism precisely at high concentration of the Nd^{3+} ions (see Fig. 2).

Knowledge of both concentrations, of the donors Nd^{3+} and of the acceptors OH^-, in different samples makes it possible to plot the function $\overline{W}(\mathrm{Nd}^{3+}-\mathrm{OH}^-)=f(n_A n_D)$. Figure 9 shows the function $\overline{W}(\mathrm{Nd}^{3+}-\mathrm{OH}^-)=f(K_{\mathrm{Nd}^{3+}}K_{\mathrm{OH}^-})$, where $K_{\mathrm{Nd}^{3+}}$ is the coefficient of absorption of Nd^{3+} ions at the wavelength $\lambda=0.873$ μm, and is proportional to the Nd^{3+} concentration, while K_{OH^-} is the coefficient of absorption of the OH^- group in the vibrational transition with $\lambda=3.33$ μm, and is proportional to the concentration of the OH^- groups. It is seen from the figures that this dependence is well described by the linear relation $\overline{W}(\mathrm{Nd}^{3+}-\mathrm{OH}^-)\sim n(\mathrm{Nd}^{3+})n(\mathrm{OH}^-)$, which is typical of the long-range migration quenching process $\mathrm{Nd}^*\to\mathrm{Nd}^*\to\ldots\to\mathrm{Nd}^*\to\mathrm{OH}^-_*$. From the slope of this line we could, by substituting in (11) or (12) the known value of the microparameter of the quenching interaction $C_{DA}(\mathrm{Nd}^{3+}-\mathrm{OH}^-)$, an important microscopic parameter that characterizes the donor-donor interaction Nd^{3+}–Nd^{3+} at $T=77$ K, namely $C_{DD}(\mathrm{Nd}^{3+}-\mathrm{Nd}^{3+})$. However, in order to establish correctly the model and the conditions of its applicability, we must know C_{DD} beforehand. We shall attempt to calculate the value of C_{DD} from both models and compare it with the conditions for the applicability of these models. Substituting in (11) the value $C_{DA}=6.0\times10^{-40}$ cm^6/sec (see Sec. III. 1) and the values of W, n_D, and n_A from Fig. 9, we obtain the value $C_{DD}=1.1\cdot10^{-38}$ cm^6/sec. Comparison of C_{DD} with C_{DA} shows that $C_{DD}\gg C_{DA}$, i.e.,

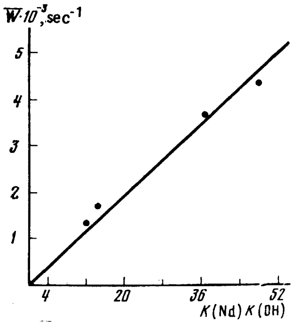

FIG. 9. Dependence of the probability of migration quenching probability on the product of the Nd^{3+} donor concentration by the OH^- acceptor concentration: $\overline{W}(\mathrm{Nd}^{3+}-\mathrm{OH}^-)=f(K_{\mathrm{Nd}^{3+}}K_{\mathrm{OH}^-})$.

the condition for applicability of the diffusion model is clearly not satisfied. It follows therefore that our experimental situation agrees better, in all probability, to the hopping model of migration. Let us verify this. A distinguishing feature of expression (12) for the probability of hopping migration over the donors to the acceptor is its proportionality to the product $n_A C_{DA}^{1/2}$. As we have seen from Sec. III.1, it is precisely this product which characterizes the direct static donor-acceptor quenching ($\mathrm{Nd}^* \to \mathrm{OH}_*$), and is directly measured from the analysis of the Forster non—exponential relation (2). Substituting (2) in (12), we get

$$\overline{W} = \tfrac{1}{3}\pi^2 (\tfrac{2}{3})^{1/2} \gamma C_{DD}^{1/2} n_D. \tag{13}$$

We see therefore that even without knowing the exact values of n_A and $C_{DA}^{1/2}$ separately, by determining from experiment their product $n_A C_{DA}^{1/2}$, i.e., the macroscopic parameter of the Forster decay γ, we can calculate the exact value of C_{DD}. This is particularly important in the analysis of quenching by residual impurities (in our case by OH^- groups), whose concentrations can be estimated but are very difficult to calculate exactly.

Substituting in (13) the necessary values of $\overline{W}$ and n_D from Fig. 9 and $\gamma(n_A)$ from Fig. 5 of Sec. III.1, we obtain the values of the microscopic parameter of the migration donor-donor interaction $C_{DD}(\mathrm{Nd}^{3+} - \mathrm{Nd}^{3+}) = 10^{-38}$ cm^6/sec. We see that the value $C_{DD} \gg C_{DA}$ satisfies the condition for the applicability of the hopping model of migration, i.e., the last value of the microscopic parameter $C_{DD}(\mathrm{Nd}^{3+} - \mathrm{Nd}^{3+})$ has been correctly calculated.

A comparison of the value $C_{DD}(\mathrm{Nd}^{3+} - \mathrm{Nd}^{3+}) = 2 \cdot 10^{-40}$ cm^6/sec for "local" migration at $T = 4.2$ K (Sec. III.2) with the value $C_{DD}(\mathrm{Nd}^{3+} - \mathrm{Nd}^{3+}) = 10^{-38}$ cm^6/sec for the "long-range" migration at $T = 77$ K shows an appreciable increase of the migration interaction with increasing temperature. This circumstance is reflected also in the character of the Nd^{3+}–Nd^{3+} quenching interactions. As follows from (9), the critical concentration drops to $n^* = 1.9 \times 10^{20}$ cm^{-3} ($x = 0.07$), i.e., at high temperature ($T > 77$ K) the concentration dependence of the quenching $W(\mathrm{Nd}^{3+} - \mathrm{Nd}^{3+}) = f(n_{\mathrm{Nd}^{3+}})$ is linear in the entire observable section. Knowledge of the microscopic parameter $C_{DD}(\mathrm{Nd}^{3+} - \mathrm{Nd}^{3+})$ and the closest-approach distance $R_{\min}(\mathrm{Nd}^{3+} - \mathrm{Nd}^{3+})$ makes it possible to calculate the rate of energy migration over the metastable levels of the Nd^{3+} ions at high Nd^{3+} concentrations:

$$P_{DD} = \frac{C_{DD}}{R^6_{min}} = \frac{10^{-38}}{1.1 \cdot 10^4 \cdot 10^{-48}} \approx 10^6 \ [\mathrm{sec}^{-1}].$$

This quantity is very important for the analysis of the suitability of a given glass as a laser medium with inhomogeneously broadened spectrum.

IV. CONCLUSION

Thus, as a result of the choice of the corresponding research procedure, objects, and experimental conditions we were able to resolve the complex process of the quenching of the luminescence of Nd^{3+} ions in a highly concentrated neodymium glass into individual components corresponding to different mechanisms of annihilation of the electronic excitation in a given material. The main results of the work can be formulated as follows.

1. A dipole-dipole interaction mechanism was established between the active Nd^{3+} ions and the hydroxyl particles OH^-; this mechanism leads to static nonradiative energy transfer from the Nd^{3+} to the disordered assembly of acceptors—to the OH^- groups. The microscopic parameter of this quenching interaction is estimated at $C_{DA}(\mathrm{Nd}^{3+} - \mathrm{OH}^-) = 6.0 \cdot 10^{-40}$ cm^6/sec.

2. It was established that the quenching of the Nd^{3+} luminescence by the OH^- groups at high concentrations of the active Nd^{3+} ions is connected with the long-range migration of the excitation over the metastable levels of the Nd^{3+} ions (at $T > 4.2$ K) towards the quenching centers-the OH^- groups present in glass even in very small concentrations. The microscopic parameter of the migration donor-donor interaction is determined to be $\mathrm{Nd}^{3+} - \mathrm{Nd}^{3+}$ $C_{DD} = 10^{-38}$ cm^6/sec.

3. Three $\mathrm{Nd}^* \to \mathrm{Nd}_*$ quenching mechanisms were experimentally distinguished and investigated.

a) Nonresonant static dipole-dipole $\mathrm{Nd}^* \to \mathrm{Nd}_*$ energy transfer via the intermediate levels $^4I_{15/2}$ and $^4I_{13/2}$ with participation of phonons of energy $\hbar\omega_{\mathrm{ph}} \sim 800$ cm^{-1}.

b) Hopping $\mathrm{Nd}^* \to \mathrm{Nd}^*$ energy migration over the metastable levels with subsequent quenching $\mathrm{Nd}^* \to \mathrm{Nd}_*$ by mechanism *a*.

c) $\mathrm{Nd}^* \to \mathrm{Nd}_*$ quenching under conditions of ultrafast energy migration over the metastable levels $^4F_{3/2}$.

The macroscopic parameters $\gamma(\mathrm{Nd}^{3+} - \mathrm{Nd}^{3+})$, $\overline{W}(\mathrm{Nd}^{3+} - \mathrm{Nd}^{3+})$, $W(\mathrm{Nd}^{3+} - \mathrm{Nd}^{3+})$ and the microscopic parameters $C_{DA}(\mathrm{Nd}^{3+} - \mathrm{Nd}^{3+})$, $C_{DD}(\mathrm{Nd}^{3+} - \mathrm{Nd}^{3+})$ of the quenching and migrational interactions Nd^{3+}–Nd^{3+} were determined. It is shown that one of the causes of the anomalously weak concentration Nd^{3+}–Nd^{3+} quenching in Li–La–Nd-phosphate glass is the low effectiveness of the Nd^*–Nd_* quenching interactions, a property possessed also by crystalline phosphates: C_{DA} (Li–La–Nd-phosphate glass) $\approx C_{DA}(\mathrm{NdP_5O_{14}}) \approx C_{DA}(\mathrm{LiNdP_4O_{12}}) \approx 3 \cdot 10^{-41}$ cm^6/sec, and the effectiveness of the resonant quenching interactions via the $^4I_{15/2}$ level turns out to be less than the effectiveness of the nonresonant ones. The second cause is the large distance between the minimum closest approach of the Nd^{3+}, namely 4.7 Å, which is only slightly lower than the similar quantity for crystals.

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[1] The paper was published earlier in the form of a preprint of the Physics Institute of the Academy of Sciences.[7]

[2] A similar conclusion was reached by Gapontsev *et al.*[12]

[3] The latter method of determining the absolute content of OH^- groups in our glass was developed by Rybaltovskii and Tikhomirov[13] of the Nuclear Physics Institute of the Moscow State University.

[4] The downward shift of the asterisk that follows the ion symbol indicates here the loss of the excitation energy as a result of the interaction.

5) To verify the validity of the employed expression (6) in the calculation of C_{DA} we have compared the results of the calculation[24] of C_{DA} for KNdP$_4$O$_{12}$, obtained by formula (6) with the results of a determination of C_{DA} with the aid of the calculation of the lattice sum with summation over the nearest 14 ions. The results turned out to be close: $C_{DA}(6) = 6.8\times10^{-41}$ and $C_{DA}(\Sigma) = 6\times10^{-41}$ cm^6/sec.

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Polarization and spectral composition of the radiation of nonrelativistic electrons interacting with a rough surface

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The polarization and spectral composition of radiation produced when nonrelativistic electrons enter into a substance having a varying degree of surface roughness are measured. It is shown that at large electron entry angles, and particularly at glancing angles of incidence on the surface, the radiation is due to the surface roughnesses. The degree of polarization of radiation reaches $\sim 40\%$. The spectral density of the radiation energy depends on the optical constants of the substance, on the degree of its surface roughness, and on the angle of entry of the electron into the substance. The radiation intensity at glancing entry is larger by about an order of magnitude than the intensity of transition radiation at normal incidence.

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1. The radiation produced when nonrelativistic electrons enter into a substance has been the subject of many studies.[1,20] Most experiments were undertaken to investigate transition radiation.[21] The earlier work is analyzed in a review by Frank.[22] The measurements were made mainly for the visible part of the spectrum; there are also data for the vacuum ultraviolet region.[23,24]

In the cited experiments there were analyzed the