Laser spectroscopy of inhomogeneously broadened lines of Eu^{3+} in glasses and migration of electron excitation over them

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A laser-spectroscopy procedure is used to study the inhomogeneous broadening of the spectral lines of Eu^{3+} and the migration of the electron excitation along these lines. A Stark-splitting diagram is constructed for a continuous distribution of the Eu^{3+} centers in silicate glass. The homogeneous components of the inhomogeneously broadened spectral lines are determined. Two types of resonant interaction, which lead to spectral migration of energy, have been observed and investigated. On the basis of a detailed analysis of the kinetics of the excitation-energy transfer, a quadrapole-quadruple mechanism is deduced for the interaction of the europium ions. The macroscopic and microscopic parameters of the ion-ion interaction are determined.

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The use of narrow-band laser sources of light has by now become a powerful tool of spectroscopy, particularly in investigations of active laser media with inhomogeneous broadening of the spectral lines. Inhomogeneous broadening, as a manifestation of a disorder in the structure of the activated medium, influences substantially the lasing processes that occur in the medium. To understand these processes, it is extremely important to investigate the interaction of monochromatic radiation with an assembly of spectrally inhomogeneous active centers, both those excited beforehand[1,2] and those in the ground state.[3–5] The most important and least investigated stage in this case is the migration of the electron excitation over the inhomogeneous contour (spectral migration). This process is intermediate between the act of pump-energy absorption and the act of energy emission in the form of coherent radiation with a spectral width much smaller than the inhomogeneous broadening, and it is precisely this process which determines the effectiveness of the generation (amplification) of the stimulated emission.

The most suitable model ion for the study of the structure of activator centers in glass and the processes of excitation migration in the case of strong inhomogeneous broadening is the ion Eu^{3+}. The convenient spectral region of the transition, the appreciable Stark splitting, in the absence of a cross-relaxation quenching channel make it possible to investigate with this ion as an example problems involving the conversion and transfer of the energy of the electron excitation and its relaxation under conditions of inhomogeneous broadening.[1]

Measurement of the luminescence spectra and of the excitation spectra (with time strobing), as well as of the kinetics of luminescence damping in selective monochromatic excitation of the components of an inhomogeneously broadened line, was performed with a specially developed installation.[6] It comprised a narrow-band laser source of excitation $\Delta\lambda < 1$ Å with tunable wavelength $\lambda = 550–625$ nm, a monochromator, and a sensitive photorecorder based on an oscillographic delayed coincidence method that made possible, in the time strobing regime, discrete counting of the photons in the range of hundreds and thousands of photons per second. At a medium signal level, when discrete photon registration is impossible, the luminescence was registered with the aid of a strobe integrator (PAR-162). By using this procedure we have studied the spectral properties of the Eu^{3+} ion in glass. The investigations were made on samples of sodium-boron-silicate glass with different concentrations of the Eu^{3+} ions: (Na_2O–15 wt.%, B_2O_3–35.0 wt.%, SiO_2–50 wt.%) + (Eu_2O_3–x wt.%, Y_2O_3–(15 – x) wt.%; x equal to 2 and 12 wt.%). The most information was provided by the luminescence spectra of the transitions $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$, obtained by time strobing and excitation with monochromatic laser radiation at wavelengths 550–625 (rhodamine-6G), 532, 354, and 266 nm (respectively the second, third, and fourth harmonics of garnet-neodymium laser emission). The presence of a large number of Stark sublevels for $^7F_2$ (five), $^7F_3$ (seven), etc., and also the appreciable inhomogeneous broadening, cause an appreciable blurring of the picture, and make the corresponding $^5D_0 \rightarrow {}^7F_2$; $^1F_3$ spectra structureless, so that their investigation is difficult. The $^5D_0 \rightarrow {}^7F_0$; $^7F_1$ luminescence spectra of the Eu^{3+} ions, following nonselective excitation and excitation with monochromatic light having λ_{exc} equal to 354 and 266 nm, turned out to be similar. A characteristic feature is that the forms of the luminescence spectra of $^5D_0 \rightarrow {}^7F_0$; $^7F_1$, for each of these three types of excitation, remain practically unchanged when the temperature was changed from 300 to 77 °K, thus attesting to the predominant fraction of inhomogeneous broadening.

The use of a tunable laser of wavelength 550–625 nm ($^7F_j \rightarrow {}^5D_0$ transitions) to excite the luminescence has led to sharp differences between the spectra as compared with nonselective excitation. Figure 1 shows some spectra obtained at 77 °K. It is seen that narrow-band excitation $^7F_0 \rightarrow {}^5D_0$; $^7F_1(\varepsilon_0) \rightarrow {}^5D_0$ causes a strong narrowing of the luminescence-line contour on the transitions $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1(\varepsilon_0)$. This points to the presence
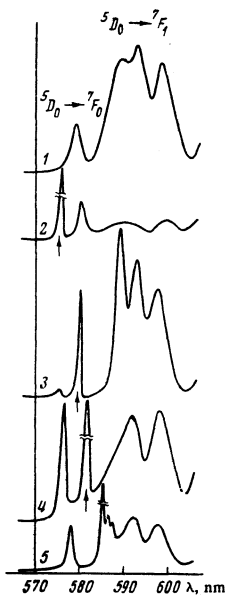
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FIG. 1. Changes in the $^5D_0 \rightarrow {}^7F_0$; $^7F_1$ luminescence spectra of Eu^{3+} ions in sodium-borosilicate glass (at $T = 77°K$) with changing character of the excitation: 1) nonselective broad-band excitation (tungsten lamp, FS-7 filter), $\lambda_{exc} = 300-420$ nm; 2-4) monochromatic excitation on the $^7F_0$; $^7F_1 \rightarrow {}^5D_0$ transitions (rhodamine-6G solution laser, the arrow indicates the wavelength of the exciting light); 5) monochromatic excitation on $^7F_1(\varepsilon_0) \rightarrow {}^5D_1$ transition (second harmonic of Nd^{3+} garnet laser), $\lambda_{exc} = 532$ nm.

FIG. 3. Arrangement of the energy levels $^7F_0$; $^7F_1(\varepsilon_0)$, $^7F_1(\varepsilon_-)$; $^7F_1(\varepsilon_+)$ (reckoned from $^5D_0$) for a continuous set of optical Eu^{3+} centers in glass (excitation $^7F_1(\varepsilon_+) \rightarrow {}^5D_0$).

of a correlation between their energies for different optical centers in the silicate-glass matrix. Indeed, if only one group of centers out of the entire assembly is selectively excited on one transition (within the limits of the laser-line width), the resultant distribution for the other transition turns out to be quite narrow. This result shows that the statement made by Denisov et al., [9,10] that there is no correlation between the energies of the transitions of the Eu^{3+} ions in silicate glass, is in error.

It is seen from Fig. 1 (Figs. 2-5) that a change of λ_{exc} leads to a strong change in the positions of the luminescence lines of the transitions $^5D_0 \rightarrow {}^7F_1(\varepsilon_0)$; $^7F_0$, but has little effect on the transitions $^5D_0 \rightarrow {}^7F_1(\varepsilon_-)$; $^7F_1(\varepsilon_+)$. We deemed it of interest to investigate the possibly most complete set of optical centers produced in the glass, including those Eu^{3+} centers whose lines in the $^7F_0 \rightarrow {}^5D_0$ absorption spectrum are located on the far wings of the inhomogeneously broadened contour (optical density $d < 10^{-3}$), and whose concentration is very small. The installation mentioned above made it possible to
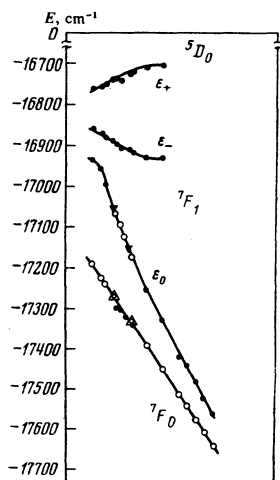
carry out such an investigation. By using monochromatic laser radiation we separated from the total number of Eu^{3+} ions the required group of centers whose luminescence spectrum was registered.

As a result of the reduction of a large number of spectra (similar to those shown by curves 2-4 of Fig. 1), with λ_{exc} varied between 567 and 590 nm, we have constructed a diagram that reflects the position of the energy levels of the Eu^{3+} ions in different environments in the glass matrix. It is shown in Fig. 2. To construct the diagram, the position of the level $^5D_0$ was assumed to be fixed, because of the large distance between it, and the remaining levels. Similar diagrams (but for a smaller range of variation of the energy) were obtained earlier for calcium-europium-phosphate[3] and europium-phosphate[5] glasses. The abscissas in our diagrams represent the position of the level $^7F_0$ relative to $^5D_0$, which characterizes the strength of the perturbation (the strength of the ligand field) acting on the europium ion in the given center (causing the shift and splitting of the energy levels). The ordinates represent the energy of the transitions $^5D_0 \rightarrow {}^7F_0$; $^7F_1$ reckoned from $^5D_0$. The light circles in the figure denote transitions that coincide in energy with the exciting photons of the laser, while the dark circles at the same abscissas represent the maxima of the remaining luminescence lines.

It is seen from the diagram that the silicate-glass ma-

FIG. 2. Arrangement of the energy levels $^7F_0$; $^7F_1(\varepsilon_0)$; $^7F_1(\varepsilon_-)$; $^7F_1(\varepsilon_+)$ (reckoned from $^5D_0$) for a continuous set of optical Eu^{3+} centers in glass (excitation $^7F_0 \rightarrow {}^5D_0$; $^7F_1(\varepsilon_0) \rightarrow {}^5D_0$). The values of the points are given in the text.
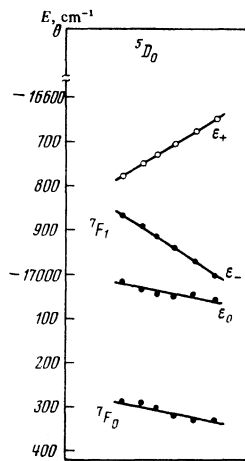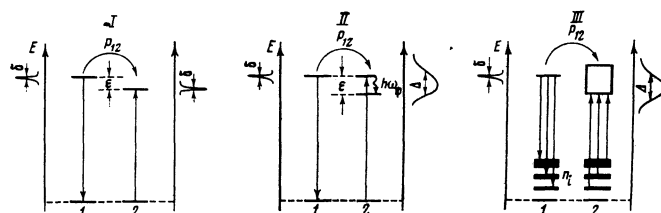

FIG. 4. Possible schemes of interaction between Eu^{3+} ions in glass, leading to spectral energy migration: I—resonant interaction (1a) on $^5D_0 \rightleftarrows {}^7F_0$ transitions; II—non-resonant interaction (1b) on $^5D_0 \rightleftarrows {}^7F_0$ transition with participation of phonons; III—resonant interaction (1c) on $^5D_0 \rightleftarrows {}^7F_1$ transition with participation of excited levels of the ^7F multiplet.
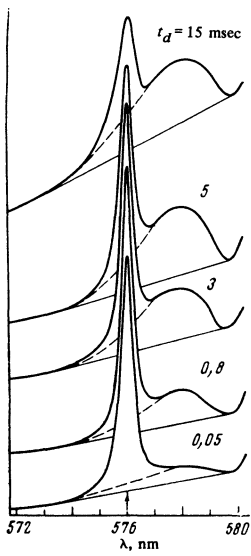
FIG. 5. Spectral manifestations of the migration. Temporal evolution of the luminescence spectrum of inhomogeneously broadened $^5D_0 \rightarrow {}^7F_0$ line on the monochromatic excitation $\lambda_{exc} = 576$ nm (t_d is the time elapsed after the instant of excitation).

trix contains a continuous set of centers, and the perturbation acting on different centers varies greatly. Thus, Stark splitting of the $^7F_1$ level in centers with minimum energy of $^5D_0 \rightarrow {}^7F_0$ amounts to approximately $\Delta E \approx 170$ cm^{-1}, whereas for centers with maximum $^5D_0 \rightarrow {}^7F_0$ energy we have $\Delta E = 600-800$ cm^{-1}. The slope of the plot of $E[{}^7F_1(\varepsilon_0)]$ x (in the central part) is approximately twice as large as for $^7F_0$ and the center of gravity of the $^7F_1$ level shifts in parallel to the shift of $^7F_0$. This corresponds to the fact that the inhomogeneous broadening of the lines of the $^5D_0 \rightarrow {}^7F_1$ transition $\Delta = 200$ cm^{-1} is approximately twice as large as the inhomogeneous broadening of $^5D_0 \rightarrow {}^7F_0$ ($\Delta = 100$ cm^{-1}).

It should be noted that Denisov et al.[10] were the first to observe the appearance of two lines for the $^5D_0 \rightarrow {}^7F_1(\varepsilon_0)$ transition following excitation of Eu^{3+} ions ($^7F_0 \rightarrow {}^5D_0$) in silicate glass by a doublet with wavelengths 576.9 and 579.1 nm from a mercury lamp. However, while denying the presence of a correlation between the energies of the transitions $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$, they attributed the appearance of the extra line to the presence of a two-center structure in silicate glass. When their data are plotted on our diagram (the light and dark triangles) it is seen that the two lines for the transition $^5D_0 \rightarrow {}^7F_1(\varepsilon_0)$ instead of a single line correspond simply to two groups of ions from the continuous set of centers, one of which is excited by the 576.9-nm mercury line, and the other by the 579.1-nm lines.

We have observed, for the first time, narrowing of the luminescence contours of the transitions $^5D_0 \rightarrow {}^7F_0$; $^7F_1$ (see Fig. 1) following nonresonant laser excitation to a higher level ($^7F_1(\varepsilon_0) \rightarrow {}^5D_1$, $\lambda_{exc} = 532.0$ nm). This proves the existence of a correlation between the energies of these levels in different optical centers of the glass, and also, in our opinion, makes it possible to determine the positions of the Stark sublevels of the state $^5D_1$, something that cannot be done by ordinary spectroscopy methods. Indeed, the absorption spectrum of the Eu^{3+} ions on the $^7F_0 \rightarrow {}^5D_1$ transition is a smooth structureless contour with inhomogeneous broadening

$\Delta = 75$ cm^{-1} ($\Delta({}^7F_1 \rightarrow {}^5D_1)$ equals respectively 150 cm^{-1}). This indicates that the Stark splitting is small in comparison with the inhomogeneous line broadening. The Stark splitting of the $^5D_1$ level can be obtained from the luminescence spectrum of the $^5D_0 \rightarrow {}^7F_1(\varepsilon_0)$ transition following the excitation of $^7F_1(\varepsilon_0) \rightarrow {}^5D_1$.

Indeed, the three distinctly observed components in the luminescence on the transition $^5D_0 \rightarrow {}^7F_1(\varepsilon_0)$ can be attributed to selective excitation of three groups of centers from the entire aggregate of the Eu^{3+} ions, for which the position of the $^7F_1(\varepsilon_0)$ ion is such that the energies of the transitions are

$$E[{}^7F_1(\varepsilon_0) - {}^5D_1(1)] = E[{}^7F_1(\varepsilon_0) - {}^5D_1(2)]$$

$$= E[{}^7F_1(\varepsilon_0) - {}^5D_1(3)] = 18\,800 \text{ cm}^{-1} .$$

After relaxation to the state $^5D_0$, in the absence of spectral migration over the Eu^{3+} ions, only these three groups of centers can appear in the luminescence, and the energy spacing between them will correspond to the Stark splitting of the $^5D_1$ level

$$E[{}^5D_1(2)] - E[{}^5D_1(1)] = E[{}^5D_1(3)] - E[{}^5D_1(2)] = 30 \text{ cm}^{-1} .$$

The value obtained in this manner turns out to be indeed smaller than the total width of the spectrum of the resonant transition, $\Delta({}^7F_0 - {}^5D_1) = 75$ cm^{-1}. The large difference between the luminescence intensities of the groups of centers with maximum energy (see Fig. 1, curve 5) and the two others is in all probability due to the fact that their excitation was on the lower Stark sublevel $^5D_1$ (1), which has a minimal homogeneous width at $T = 77$ °K.

Let us examine the nature of the broadening of the lines produced by laser excitation of Eu^{3+} ions in silicate glass. At low temperatures $T = 77$ °K the luminescence spectrum of the resonant transition $^5D_0 \rightarrow {}^7F_0$, following excitation with a laser from the level $^7F_0$ to $^5D_0$, has a width $\Delta\lambda_{exc} = 2$ Å, which is due to the instabilities of the laser wavelength. Raising the temperature to 300 °K leads to the appearance of a homogeneous component δ of the broadening of this transition as a result of the increased probability of the relaxation transitions $^7F_0 \rightarrow {}^7F_1$ with phonon absorption. Separation of the homogeneous component from the complicated Voigt contour was carried out on the basis of Posener's tables.[11] It turns out to equal 9 cm^{-1} ($\lambda_{exc} = 577$ nm). The width of the corresponding $^5D_0 \rightarrow {}^7F_1(\varepsilon_0)$ component is independent of temperature and is much larger. Monochromatic excitation of the Eu^{3+} ions on the $^7F_1(\varepsilon_0) \rightarrow {}^5D_0$ transition makes it possible to obtain homogeneous broadening of the lower Stark sublevel $^7F_1(\varepsilon_0)$, $\delta = 19.6$ cm^{-1} ($\lambda_{exc} = 581$ nm), due to the transitions $^7F_1(\varepsilon_0) \rightarrow {}^7F_0$ with emission and transitions $^7F_1(\varepsilon_0) \rightarrow {}^7F_1(\varepsilon_-)$; $^7F_1(\varepsilon_+)$ with absorption of phonons.

We note that the narrow band luminescence component on the $^5D_0 \rightarrow {}^7F_1(\varepsilon_0)$ transition corresponds to a strong but incomplete narrowing of the spectrum of the transition $^5D_0 \rightarrow {}^7F_0$, as might be expected from our diagram in Fig. 2., i.e.,

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$$\Delta(^5D_0 \rightarrow {}^7F_0) = 30\,cm^{-1} \approx 1.5 \cdot \Delta(^5D_0 \rightarrow {}^7F_1(\varepsilon_0)),$$

and not $0.5\Delta[^5D_0 \rightarrow {}^7F_1(\varepsilon_0)]$. An analogous situation took place also in the observation of the narrowing of the $^5D_0 \rightarrow {}^7F_1(\varepsilon_0)$ luminescence line following $^7F_0 \rightarrow {}^5D_0$ excitation:

$$\Delta[^5D_0 \rightarrow {}^7F_1(\varepsilon_0)] = 68\,cm^{-1} \approx (3-4)\,\Delta(^5D_0 \rightarrow {}^7F_0),$$

and not $2\Delta(^5D_0 \rightarrow {}^7F_0)$. These two facts indicate that the expressions for the energies of the level $^7F_0$ and of the sublevel $^7F_1(\varepsilon_0)$ contain, besides large terms that depend in equal fashion on the inhomogeneous external electric field in the glass, also small terms that do not correlate with one another.

An investigation of the broadening of the upper Stark component of the $^7F_1$ level was also carried out by observing the narrowing of the luminescence line at the wavelength of the excitation of $^7F_1(\varepsilon_-)$; $^7F_1(\varepsilon_+) \rightarrow {}^5D_0$. It is difficult to obtain such spectra in experiment because of the small population of the levels $^7F_1(\varepsilon_-)$ and $^7F_1(\varepsilon_+)$ at a temperature 300 °K, and particularly 77 °K. This, in conjunction with the Eu^{3+} ion transitions, which are by themselves weak, calls for an experimental setup of extremely high sensitivity.

The narrowing of the luminescence contour was observed at a wavelength that is at resonance with the exciting light. This narrowing, however, was not as strong as for the transitions $^5D_0 \rightarrow {}^7F_0$; $^7F_1(\varepsilon_0)$. This points to a large value of the homogeneous broadening, amounting to $\delta = 54-60$ cm^{-1} at $T = 300$ °K. The homogeneous character of the broadening is confirmed by the Lorentz shape of the spectrum of the narrowed line and is determined by the relaxation transitions to the levels $^7F_0$, $^7F_1$, and $^7F_2$ with absorption and emission of phonons.

Scanning the excitation over the inhomogeneous contour of the $^7F_1(\varepsilon_+) \rightarrow {}^5D_0$ transition has revealed rather strong correlated changes in the luminescence on the transition $^5D_0 \rightarrow {}^7F_1(\varepsilon_-)$ and a weak shift of the almost not narrowed lines on the transitions $^5D_0 \rightarrow {}^7F_1(\varepsilon_0)$ and $^5D_0 \rightarrow {}^7F_0$. These results are shown in Fig. 3, which is similar to Fig. 2. A comparison of the diagrams shows them to be in fair agreement for the levels $^7F_1(\varepsilon_-)$ and $^7F_1(\varepsilon_+)$, whereas the positions of the levels $^7F_1(\varepsilon_0)$ and $^7F_0$ are substantially different. This may be due to the fact that in the wavelength region 590–605 nm the Stark sublevels $^7F_1(\varepsilon_-)$, $^7F_1(\varepsilon_+)$ and $^7F_2$ overlap strongly and have a very large homogeneous width. Even in the case of a narrow-band pump source the optical centers of practically all types turn out to be excited in this case (just as in the case of nonselective excitation).

The foregoing investigation of the spectral characteristics of the inhomogeneously broadened lines allows us to proceed to the analysis of the processes connected with the transfer and conversion of the energy of a spectrally narrow packet of electronic excitations, initially having a fixed energy.

Monochromatic laser excitation permits instantaneous excitation of only a small fraction of Eu^{3+} centers having equal energy so that it becomes possible to trace the conversion of this energy by investigating the manner in which it relaxes in the glass at various temperatures and concentrations of the active Eu^{3+} ions.

As seen from the level scheme of the Eu^{3+} ions,[10] the interaction between these ions, which sets in at high concentrations of the activators, cannot destroy the electron excitation directly, but only cause it to migrate from one ion to another. In the case of fast migration, such a process can, during the lifetime of the metastable level, ensure the excitation of an uncontrollable impurity (quencher), and this leads to luminescence quenching.[12] For the Eu^{3+} ion concentrations investigated by us in the silicate glass (2 and 12 wt.%), practically no quenching of the luminescence of the Eu^{3+} ions was observed. This is evidenced by the small ($\leqslant 15\%$) change in the kinetics of the luminescence damping with the increasing europium concentration. We are interested in this case by the migration process in pure form, i.e., the transfer of excitation between like ions without quenching.

At the present time there are several methods of directly observing energy migration. One of them involves the study of the depolarizing action of migration on the luminescence of active particles.[13,14] Others use the possibility of controlling the migration over the spectrum in the case of inhomogeneous line broadening. These include observation of the "red shift" of the luminescence lines at low temperatures,[15,16] hole "burning" in the luminescence line by induced dumping,[2] and study of its relaxation,[2,20-24] as well as the inverse problem, that of laser-induced fluorescence line narrowing and the study of the kinetics of relaxation of the line wave forms.[3-5] We consider the last method to be the most convenient, since, unlike the preceding method, it does not require that the lasing conditions be satisfied in the investigated material, and makes it possible, by choosing the excitation sources, to carry out the investigations in a wide range of wavelengths, transitions, and, most importantly, at arbitrary temperatures. The fluorescence line narrowing procedure was first used to study migration by Denisov et al.,[9,10] using narrow spectral lines from a mercury lamp as the monochromatic source of excitation.

Before we turn to the experiments, we consider the possible models of the interaction of Eu^{3+} with one another (migration). Figure 4 shows three possible schemes of energy-transfer processes. Scheme I shows resonant transfer of excitation with participation of the levels $^5D_0$ and $^7F_0$. As we have seen earlier, inhomogeneous broadening creates a difference equal to ε_i between the energies of the $^5D_0 \rightarrow {}^7F_0$ transitions for different pairs of Eu^{3+} ions, (see the diagram of Fig. 2). The resonant interaction can in this case occur only as a result of overlap of the Lorentz contours of the homogeneously broadened special lines of each of the ions, and is described by the expression

$$P_{12} = P_{21} = 2\delta k / [\,(2\delta)^2 + \varepsilon_i^2\,]. \tag{1a}$$

Here k is a coefficient that includes the oscillator strengths and the dependence on the distance, δ is the

homogeneous line width of the $^5D_0 \to {}^7F_0$ transition, and depends strongly on the temperature: $\delta = 9$ cm^{-1} at $T = 300$ °K and $\delta < 1.5$ cm^{-1} at $T = 77$ °K. [25]

The homogeneous width δ being so small in comparison with the inhomogeneous $\Delta \approx 100$ cm^{-1}, the transfer will take place only to centers that are spectrally close to the excited Eu^{3+} ions, since the transfer probability decreases sharply with increasing $\varepsilon_i > 2\delta$ $(P_i \sim \varepsilon_i^{-2})$.

Scheme II pertains to the nonresonant mechanism of the interaction of the Eu^{3+} ions with participation of phonons. The temperature dependence of the energy transfer is determined in this case by the average occupation number of the phonon states:

$$P_{12} \sim (n_p+1), \quad P_{21} \sim n_p, \text{ where } n_p = \{\exp(\hbar\omega_{ph}/kT) - 1\}^{-1}.$$

Hence

$$P_{12} = P_{21} e^{-\varepsilon_{12}/kT} \tag{1b}$$

$(\hbar\omega_{ph} = \varepsilon_{12})$. The magnitude of this interaction is determined also by the oscillator strengths of the electronic transitions, by the character of the electron-phonon interaction, and by the density of the phonon states at the frequency of resonance detuning ε_{12}. In the Debye approximation, the state density is $\rho \sim \varepsilon^2$, i.e., $P_{12} \sim \varepsilon^2$.

A characteristic feature of the presence of nonresonant migration at $kT < \Delta$ is the successive motion of the energy of the electronic excitation, some of which is given up in each transfer act to the thermostat via the phonons (red shift).

Scheme III shows the resonant mechanism of the Eu^{3+} $\to$ Eu^{3+} interaction, but with participation of the Stark sublevels of the state $^7F_1$. This mechanism calls for population of these levels, so that thermal activation becomes necessary. A distinguishing feature of this interaction scheme is the large homogeneous broadening of the $^7F_1$ levels, which is comparable with the inhomogeneous width, and makes it possible for the transfer to extend even to centers that are spectrally quite remote from the excited group. The probability of the transfer is written in the form

$$P_{12} = P_{21} = \sum_i k_i n_i \frac{2\delta_i}{(2\delta_i)^2 + \varepsilon_i^2}, \tag{1c}$$

where n_i are the populations of the corresponding Stark levels of the state $^7F_1$ and $^7F_2$ $(\sum_i n_i = 1)$.

We have investigated the spectral manifestations of the migration of the excitation—spectral migration over the contour of the inhomogeneously broadened line of the $^5D_0 \to {}^7F_0$ transition. To this end, a laser with $\lambda_{exc} = 576$ nm was used to excite a group of centers on the short-wave edge of the inhomogeneously broadened contour, and the change of the line shape of the $^5D_0 \to {}^7F_0$ transition was investigated with time strobing of the luminescence signal. The measurements were performed on glass with the composition indicated above and with high concentration of Eu^{3+} ions at two fixed temperatures, 77 and 300 °K. The spectra were plotted at a strobing-

pulse duration $\Delta t = 1$–50 μsec (the registration time) and at fixed time delays t_d of the registration relative to the exciting pulse, in the range from 10 to 2×10^4 μsec ($\Delta t \leq t_d/10$). We note that the investigations were carried out in a very wide dynamic range of times and intensities. The value of t_d reached $10\tau_D^0$ (Eu^{3+}) according to the decay kinetics, corresponding to a decrease of the intensity by a factor 2×10^4 from the maximum value. This has enabled us to analyze the kinetics of energy transfer with high accuracy.

The spectra of the $^5D_0 \to {}^7F_0$ transition, obtained at room temperature, are shown in Fig. 5. The narrow spectral line $\lambda = 576$ nm corresponds to Eu^{3+} centers directly excited by monochromatic laser radiation. It is seen that the narrow component decreases in the course of time, with a corresponding increase of the broad inhomogeneously broadened spectrum with $\lambda_{max} = 578$ nm. Analysis shows that the broad band resulting from the migration corresponds exactly to the luminescence spectrum of the $^5D_0 \to {}^7F_0$ transition of the Eu^{3+} ions when all the optical centers are nonselectively excited (see Fig. 1). Changes of this type can be treated as a manifestation of the spectral (meaning also spatial) energy migration from centers with fixed energy to all the remaining centers.

For a theoretical analysis of the effect of spectral migration, we have used the model of static donor-acceptor transport. We regard the centers that are directly excited by the laser as donors (they emit a narrow spectrum, Fig. 5), and all the remaining, unexcited centers as acceptors (they emit a broad spectrum, Fig. 5).

The obtained luminescence spectra with time strobing enable us to study the kinetics of the energy transfer process from the excited Eu^{3+} centers (donors) to the unexcited ones (acceptors). Two types of processes can be separated in the transfer of electronic excitation: 1) energy transfer in an ordered assembly of ions, 2) transfer with the interacting particles having a disordered statistical distribution. In the former case the kinetics of the damping of the excited donors is given by

$$n_D(t) = n_D(0) e^{-t/\tau_D^0} e^{-Wt}, \quad W = \sum_i P_{DA_i}',$$

where the transfer probability (the summation is carried out over the ordered assembly of ions) is the same for all the donor ions. In the second case (disordered arrangement of the ions) the quenching probability of each donor depends on its acceptor surrounding and fluctuates strongly from ion to ion:

$$W_j = \sum_i P_{D_j A_i}.$$

The kinetics for the damping of the assembly of donor ions differs in this case substantially from exponential, since it is a sum of exponentials with different decay rates W_j.

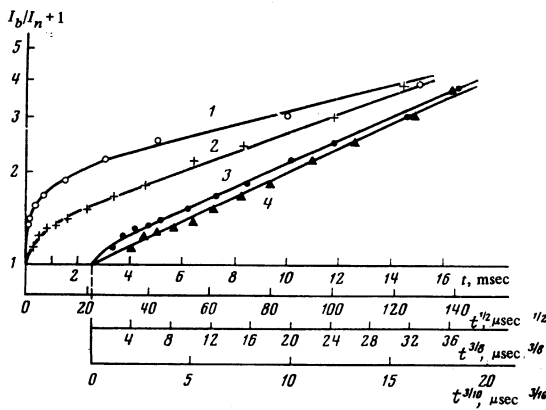For a dipole-dipole interaction, kinetics of this type were first obtained in[26,27]:

FIG. 6. Analysis of the kinetics of the spectral migration with the aid of different models of static $Eu^{3+} - Eu^{3+}$ donor-acceptor energy transfer. Curve 1—energy transfer in an ordered assembly of ions, $\ln(I_b/I_n +1) = Wt$; curves 2–4—transfer for a disordered statistical arrangement of the interaction particles $\ln(I_b/I_n +1) = (t/\tau_R)^{3/s}$ for different degrees s of the multipolarity $s=6$ (curve 2), $s=8$ (curve 3), $s=10$ (curve 4).

$$n_D(t) = n_D(0) \exp\{-\gamma t^{1/2} - t/\tau_D^0\}. \tag{2}$$

The extension of this result to include multiple interactions of higher order leads to the expression[28,29]

$$n_D(t) = n_D(0) \exp\left[-\frac{t}{\tau_D^0} - \Gamma\left(1 - \frac{3}{s}\right)\frac{n_A}{c_0}\left(\frac{t}{\tau_D^0}\right)^{3/s} \right], \tag{3}$$

where s is the degree of multipolarity of the interaction ($s = 6$, 8, 10). Analyzing the experimentally observed kinetics of the transfer process, we can ascertain whether quenching is ordered or disordered, and also, more importantly, determine the degree of multipolarity s and the microscopic parameters of the interaction between the Eu^{3+} ions. Expression (3) can be rewritten in the form

$$n_D(t) = n_D(0) \exp\{-t/\tau_D^0\} \exp\{-(t/\tau_R)^{3/s}\}, \tag{4}$$

where

$$\tau_R = \tau_D^0 \Big/ \left[\Gamma\left(1 - \frac{3}{s}\right)\frac{n_A}{c_0}\right]^{s/3} \tag{5}$$

is the characteristic transfer time and Γ is the Gamma function.

Recognizing that the lifetime of Eu^{3+} remains practically unchanged when the excitation is scanned over the spectrum ($\tau_D^0 = \tau_A^0 = 2$ msec), i.e.,

$$n_D(t) + n_A(t) = [n_D(0) + n_A(0)] \exp(-t/\tau_D^0),$$

we obtain for disordered decay

$$\ln(n_A(t)/n_D(t) + 1) = (t/\tau_R)^{3/s} \tag{6}$$

and for ordered decay

$$\ln(n_A(t)/n_D(t) + 1) = Wt. \tag{7}$$

The narrow spectral range in which all the migration

processes develop (see Fig. 5) enable us to neglect small changes in the sensitivity of the apparatus and in the photon energies (they amount to less than 10%) and assume that $n_A(t)/n_D(t)$ is equal to I_b/I_n (the ratio of the areas of the broad and narrow peaks of the luminescence (see Fig. 5)). Data reduced in this manner are shown in Fig. 6 in the form of plots of $\ln(I_b/I_n +1) = Wt_d$ (curve 1), and $\ln(I_b/I_n +1) = (t_d/\tau_R)^{3/s}$ (curves 2, 3, and 4 for $s = 6$, 8 and 10, respectively). It is seen from the figure that the quadrupole-quadrupole ($s = 10$) ion-ion interaction for a disordered assembly of Eu^{3+} ions in glass describes in the best manner the kinetics of the spectral migrations.[3] It should be noted, however, that in our use of the donor–acceptor energy-transfer process to describe the spectral migration between like ions we have neglected the important condition that the donor–acceptor transfer be irreversible, $P_{DA} \ll \tau_A^{-1}$, a condition for which the foregoing expressions are valid.

This approximate approach, but for the inverse situation (relaxation of the gap in an inhomogeneously broadened luminescence line) was first proposed in[24], where it was also noted that the obtained solution ($e^{-\gamma\sqrt{\tau}}$) decreases with time somewhat more rapidly than the true solution. Thus, the discrepancy between the experimental curve and the theoretical ones for the dipole-dipole and dipole-quadrupole mechanisms cannot be decreased, and only increases when the reverse transfer is taken into account.

The complicated non-exponential curves obtained by us for the description of the kinetics of the relaxation of the shape of the inhomogeneously broadened line following excitation by a laser demonstrate that it is impossible to describe it by a single parameter, the migration probability, as is frequently done in the investigation of the clogging of the "hole."

From the slope of curve 4 of Fig. 6 we have determined the value of the characteristic transfer time between the Eu^{3+} ions at $T = 300$ °K, namely $\tau_R = 6.6$ msec. Assuming a uniform distribution[4] of the Eu^{3+} ions ($n_A = 10^{21}$ cm^{-3}), we can determine from formula (5) the critical concentration $c_0 = 1.72 \times 10^{21}$ cm^{-3} and the Forster interaction radius $R_0 = (3/4\pi c_0)^{1/3} = 5.2$ Å, which is connected with the microscopic parameter of the interaction of the Eu^{3+} ions:

$$C_{DA}(Eu \leftrightarrow Eu) = R_0^{10}/\tau_D^0 = 7.3 \cdot 10^{-71} \text{ cm}^{10}/\text{sec} . \tag{8}$$

The probability of the interaction of the Eu^{3+} ions over the average distance is

$$P_{av} = \frac{C_{DA}}{R_{uv}^{10}} = \frac{1}{\tau_R[\Gamma(1 - ^3/_{10})]} = \frac{1}{2.43 \cdot \tau_R} = 62 \text{ sec}^{-1} . \tag{9}$$

The probability obtained in this manner is smaller by approximately a factor of 8 than the rate $\tau_A^{-1} = 500$ sec^{-1} of the acceptor radiative decay ($P_{DA} \ll \tau_A^{-1}$); this, in all probability, explains the good agreement between the irreversible transfer model[28] and the experimental relation.

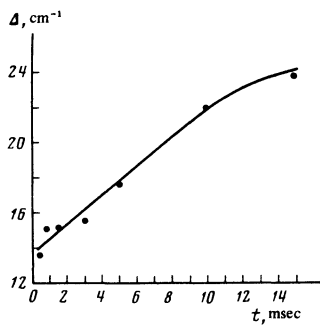We have investigated in similar manner the spectral migration at 77 °K. The kinetics of the spectral migra-

FIG. 7. Time dependence of the broadening of the narrow component of the $^5D_0 - {}^7F_0$ spectrum (spectral migration).

therefore that spectral migration with participation of phonons should have a number of distinguishing features: 1) a difference between the probabilities of transfer to different spectral components of the inhomogeneously broadened line (a change in the form of the acceptor luminescence band in comparison with their distribution in energy); 2) temperature-dependent changes in the form of the acceptor spectrum (relative weakening of the short-wave and strengthening of the long-wave line wing—red shift with decreasing temperature $kT < \Delta$); 3) the existence of a "red shift" of the broad band (the acceptor emission) with increasing delay ($kT < \Delta$). It is precisely the presence of these distinguishing features of the nonresonant migration which enables the researchers to identify it reliably.[15,16]

An analysis of the experimental data obtained by us on spectral migration (see Fig. 8) shows that in our case all the three mentioned attributes are absent, although at $T = 77$ °K we have $kT = 54$ cm^{-1}, which is much less than the inhomogeneous broadening $\Delta = 100$ cm^{-1}. Indeed, the changes of the temperature and of the delay time cause a change in the intensity, and not a change in the shape of the acceptor spectrum (the broad bands on Figs. 5 and 8).

Let us stop to discuss scheme III of the Eu^{3+} – Eu^{3+} interaction. It is necessary to show how the electron excitation is transferred in accordance with this scheme with equal probability to different centers that differ in the spectrum. An essential role is played here by the value of the homogeneous broadening of the $^5D_0 \to {}^7F_1$ transitions, and also by the deviation from the correlation in the $^5D_0 \to {}^7F_1$ and $^5D_0 \to {}^7F_0$ spectra. Thus, while the energy of the $^5D_0 - {}^7F_0$ transition is strictly fixed with a width $\Delta = 16$ cm^{-1} the luminescence of the transition $^5D_0 \to {}^7F_1(\varepsilon_0)$ turns out to be much wider: $\Delta = 68$ cm^{-1}. Even after the first transfer act, the spectral distribution of the ions excited as a result of this act is exactly the same as when the ions are directly excited by a light source having a width equal to the width of the spectrum of the luminescence on the interacting transi-
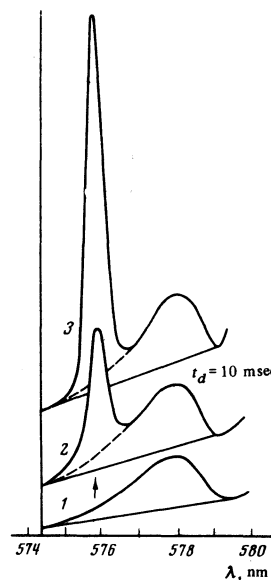
tion also turns out to be close to that obtained for the quadrupole-quadrupole interaction mechanism. However, the characteristic Eu^{3+} – Eu^{3+} transfer time at $T = 77$ °K is much larger: $\tau_R = 150$ msec, $c_0 = 4.4 \times 10^{21}$ cm^{-3}, $R_0 = 3.8$ Å, $C_{DA} = 3.2 \cdot 10^{-72}$ cm^{10}/sec, and $P_{av} = 2.73$ sec^{-1}. It is seen that when the temperature is lowered from 300 to 77 °K the probability of the Eu–Eu interaction becomes much weaker, i.e., a "freezing of the migration" is observed.

Let us examine in greater detail the causes of such a temperature dependence.

From a preliminary analysis of the first scheme of the interaction of the Eu^{3+} ions (see Fig. 4) it is seen that it cannot lead to the appearance of an additional broad band on the $^5D_0 - {}^7F_0$ transition, and is only capable of causing a certain broadening of the narrow component with changing delay time. This effect was observed by us experimentally at $T = 300$ °K and is shown in Fig. 7. Lowering the temperature to 77 °K has led to a vanishing of this effect as a result of the abrupt decrease in the homogeneous width of the resonant-transition line. At the same time, cooling left the shape of the broad band unchanged, although its intensity did decrease.

We must thus determine which of the mechanisms (II or III) predominates in the interaction of the Eu^{3+} ions in sodium-borosilicate glass.

In an investigation[3] of spectral migration in calcium-europium-phosphate glass, the second mechanism, namely nonresonant interaction with participation of phonons within the limits of the inhomogeneous contour, was proposed, whereas Yen et al.,[5] in a study of europium-phosphate glass, ascribe a pure resonant character to such an Eu^{3+} – Eu^{3+} interaction with participation of the excited ^7F levels of the multiplet (scheme III). The fact that the inhomogeneous broadening of the resonant $^5D_0 \to {}^7F_0$ transition of the Eu^{3+} ions is approximately twice as large in the sodium-borosilicate glass investigated by us as in the phosphate glass makes it possible to identify with greater reliability the mechanism of the Eu^{3+} – Eu^{3+} interaction in this matrix.

As already noted, energy transfer with participation of phonons within the limits of the inhomogeneous line width (scheme II of Fig. 4) depends substantially both on the detuning ε_{12} (the phonon-state density $\rho \sim \varepsilon^2$ increases with increasing detuning) and on the temperature-dependent occupation of these states $\{{}^{n_p+1}_{n_b}\}$. We see

FIG. 8. Temperature variations of the spectral migration over the Eu^{3+} ions ($t_d = 10$ msec; $\Delta t = 50$ μsec). Curve 3—$T = 77$ °K, $\lambda_{exc} = 576$ nm; curve 2—$T = 300$ °K, $\lambda_{exc} = 576$ nm; curve 1—$T = 300$ °K, nonselective excitation.

tion. In other words, transfer via the $^5D_0 \rightleftarrows {}^7F_1(\varepsilon_0)$ transition is equivalent to excitation of acceptors from the $^7F_1(\varepsilon_0)$ level to the $^5D_0$ level by light having a spectral width $\Delta_b = 68$ cm^{-1}. On account of the noncorrelating part, the spectrum on the $^5D_0 - {}^7F_0$ transition acquires a width

$$\Delta({}^5D_0 - {}^7F_0) = 1{,}5\Delta[{}^5D_0 - {}^7F_1(\varepsilon_0)] = 100 \text{ cm}^{-1} ,$$

which is equal to the inhomogeneous width of the luminescence in the case of nonselective excitation.

Allowance for interaction via the two upper Stark sublevels of $^7F_1$ and via the $^7F_2$ level leads to an even greater violation of the selectivity in the case of the excitation transfer, inasmuch as their homogeneous broadening is much larger and their position correlates very weakly with the $^7F_0$ level. Monochromatic excitation on the $^5D_0 - {}^7F_0$ transition has practically no effect on the widths of the inhomogeneous $^5D_0 - {}^7F_1(\varepsilon_-)$, $^5D_0 - {}^7F_1(\varepsilon_+)$, and $^5D_0 - {}^7F_2$ spectra, and transfer with participation of these transitions takes place just as under nonselective excitation. It can therefore be concluded that one act of $Eu^{3+} - Eu^{3+}$ electron excitation transfer with participation of the excited ^7F_j levels leads to a total loss of the selectivity of the excitation. It is this which explains the presence of a broad band of acceptor luminescence on the $^5D_0 - {}^7F_0$ transition (see Fig. 8).

We note that even though a direct quadrupole transition between the $^5D_0 - {}^7F_1$ levels is forbidden, $\Delta J = 1$, it can be realized on account of mixing with the allowed $^5D_0 - {}^7F_2$ transition. Estimates show that in our case the admixture of the $^5D_0 - {}^7F_2$ transition to the $^5D_0 - {}^7F_1$ transition can amount to more than 3%. Understandably, scheme III of the excitation transfer can be realized only at a nonzero population of the excited levels of the $^7F_1$; $^7F_2$ multiplet, i.e., it should have an appreciable temperature activation in the range 77–300 °K. Measurements show indeed that the transfer probability increases strongly, namely by 23 times, when the temperature is raised from 77 to 300 °K, thus confirming that the excited ^7F levels of the multiplet take part in the $Eu^{3+} - Eu^{3+}$ interaction (scheme III). We cannot dwell here on a more detailed analysis of the temperature dependence, since it requires a detailed study of the values of the $\delta({}^7F_j) = f(T)$ and $C_{DA} = f(T)$ broadening, and knowledge of the oscillator strengths of the transitions, all of which are subjects for further research.

Thus, two schemes of resonant migration are realized in our case, with participation of the lower level $^7F_0$ (I) and with participation of the higher levels ^7F_j ($j \geqslant 1$), and these schemes differ substantially in their effect on the relaxation of the narrowed lines. We note that our results attest to the correctness of the statement made by Yen et al.,[5] that migration over the Eu^{3+} ions in phosphate glass has a pure resonance character, inasmuch as these mechanisms predominate even in silicate glasses, which have very large inhomogeneous broadening.

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[1] An analysis of the influence of the inhomogeneous broadening on the rate of spatial migration of the excitation over the metastable levels of ions not subject to cross relaxation is given in[6,7].

[2] In the radio-frequency band, analogous effects of hole "burning" and relaxation in an inhomogeneously broadened line were investigated earlier in studies of ESR.[17–19]

[3] We note that merely the satisfaction of the law (6) in a wide range of times t_d (in our case, 2×10^3) makes it possible to identify reliably the multipolarity of the ion-ion interaction.

[4] The values of the parameters R_0 and C_{DA} should be regarded as upper bounds, since the segregation phenomenon can cause the local concentration of the activator (Eu^{3+}) in the glass to be somewhat larger than the average (n_A).

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Cooling and capture of atoms and molecules by a resonant light field

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A detailed classical analysis is presented of the method of cooling and capturing atoms and molecules by a resonant light field. The light-pressure forces acting on a particle in a three-dimensional standing light wave are determined. It is shown that these forces can be used for effective cooling and spatial capture of cold particles in the nodes or antinodes of a light field. The use of the method for the observation of narrow spectral lines in optical spectra or atoms or molecules, and for spectroscopic investigations for exceedingly small numbers of atoms, is considered.

1. INTRODUCTION. FORMULATION OF PROBLEM

It is known that an atom or a molecule is acted upon in a light field by light-pressure forces[1] due to the recoil produced when the atom or molecule scatters a light photon. Thus, in a nonresonant light field the particles are acted upon by a striction force[2-4] due to the Compton scattering of the light by the atom or molecule. In a resonant light field, the particles are acted upon by forces of two types: the force of the spontaneous light pressure, and the force which we shall call henceforth the induced-light-pressure force. For example, in the case of a one-dimensional standing light wave, the force of the spontaneous light pressure is due recoil following absorption of a plane light wave by the particle and emission of a spherical light wave,[5,6] while the induced light-pressure force is produced by recoil due to induced absorption and emission of a plane light wave.[6,7]

An important and highly promising region of application of the light pressure is optical spectroscopy of ultrahigh resolution without Doppler broadening, based on registration of narrow spectral lines in atoms or molecules whose motion is either completely stopped or considerably limited by the light-pressure forces.[4] Indeed, the elimination of the particle motion in a low-pressure gas leads not only to a vanishing of the Doppler broadening of the spectral lines, but simultaneously to a vanishing of all the broadening sources due to the particle motion[8] (broadening due to the finite time-of-flight of the particles through the light beam, broadening due to the quadratic Doppler effect, etc.), and makes it possible in principle to obtain spectral lines with widths

determined only by the properties of the quantum transitions of the atoms or molecules themselves. In addition, the use of light pressure to limit the spatial displacement of the particles in a low-pressure gas and for a prolonged containment of particles in fixed region of space makes it possible to carry out spectroscopic investigations of extremely small numbers of atoms or molecules, and permit in principle to realize ultrahigh-resolution spectroscopy of individual atoms or molecules (monatomic spectroscopy).

Earlier studies[4,9-11] considered new possibilities of spectroscopy without Doppler broadening of the atoms and molecules, based on the use of the light pressure to alter the velocity distribution of particles in a low-pressure gas. It was proposed[4] to use the nonresonant recoil force to capture particles in the field of a standing light wave. It turns out that in a standing light wave having a frequency outside the resonant transitions of the atom or molecule, particles having sufficiently small velocity projections on the light-wave propagation direction execute, under the influence of the nonresonant recoil force, finite vibrational motions near the nodes or antinodes of the field. As a result of these vibrational motions of the atom or molecule, a narrow resonance can exist at the center of the Doppler-broadened absorption line observed in the direction of the wave vector of the light wave; this resonance has a width determined by the natural line width and by the flight broadening.[4,11] In the case of three-dimensional standing light wave, this method makes possible the spatial capture of slow particles and permits registration, for any direction of the sounding light field, of a narrow resonance with a width

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