Optical echo spectroscopy and phase relaxation of Nd\textsuperscript{3+} ions in CaF\textsubscript{2} crystals

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Accumulated photon echoes have been used to investigate the mechanisms of optical dephasing in CaF\textsubscript{2} crystals activated by Nd\textsuperscript{3+} ions. Tunable picosecond laser radiation, which permits the selective excitation of various Nd\textsuperscript{3+} optical centers in the \textit{4}I\textsubscript{9/2} \textrightarrow \textit{4}G\textsubscript{5/2}, \textit{2}G\textsubscript{7/2} transition, is used. The optical phase relaxation times measured at temperatures from 9 to 50 K permit determination of the homogeneous widths of the transitions between the low-lying \textit{4}I\textsubscript{9/2} Stark level and three excited \textit{4}G\textsubscript{5/2}, \textit{2}G\textsubscript{7/2} levels, and calculation of the constants of the inter-Stark relaxation transitions in the ground and excited multiplets for the rhombic \textit{N} and \textit{M} Nd\textsuperscript{3+} centers in CaF\textsubscript{2} crystals. An analysis of the temperature dependence of the homogeneous linewidth of the transitions between low-lying Stark levels of the ground and excited states shows that the mechanism of optical dephasing in the crystals investigated is described well by direct relaxation processes with resonant inter-Stark absorption of one phonon in the ground and excited states. At \textit{T} = 9 K, the homogeneous linewidth \(\Gamma_k\) in CaF\textsubscript{2} crystals is almost an order of magnitude smaller than \(\Gamma_k\) in disordered CaF\textsubscript{2}–YF\textsubscript{3} crystals. This difference can be attributed to the significantly greater spectral phonon density of states in disordered crystals.

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1. INTRODUCTION

The investigation of fundamental optical dephasing processes in organic and inorganic glasses and crystals activated by trivalent rare-earth ions has been the subject of numerous investigations,\textsuperscript{1,2} since understanding the relaxation processes of excited states of impurity ions in a solid is not only a very important scientific problem, but also a necessary condition for creating efficient solid-state lasers. In the present work the optical phase relaxation of Nd\textsuperscript{3+} ions in CaF\textsubscript{2} crystals was investigated using accumulated photon echoes.\textsuperscript{3,4}

The structure of the optical Nd\textsuperscript{3+} centers in CaF\textsubscript{2} crystals was fully investigated in earlier studies. In Refs. 5–7 the concentration method and selective laser excitation were successfully employed to elucidate the composition of the Nd\textsuperscript{3+} centers in CaF\textsubscript{2} and to determine the positions of the Stark sublevels for each type of center. In Refs. 8 and 9 the symmetry of the principal Nd\textsuperscript{3+} centers in CaF\textsubscript{2} crystals was investigated using ESR.

Accumulated photon echoes permit direct measurement of the phase relaxation kinetics and determination of the homogeneous linewidth \(\Gamma_k\) of a transition, which is not distorted by the inhomogeneous broadening of the spectra \(\Gamma_{ih}\). In the present work we investigate the temperature dependence of the homogeneous linewidth of the \textit{4}I\textsubscript{9/2} \textrightarrow \textit{4}G\textsubscript{5/2}, \textit{2}G\textsubscript{7/2} transition in the dimeric and trimeric Nd\textsuperscript{3+} cluster centers in the temperature range 9–50 K. The experimental plot of \(\Gamma_k(T)\) can be described within terms of direct relaxation transitions between Stark sublevels of the ground and excited states, with the absorption and emission of one phonon.

2. INHOMOGENEOUS SPLITTING AND BROADENING OF THE ABSORPTION LINES OF Nd\textsuperscript{3+} IN CaF\textsubscript{2} CRYSTALS

The CaF\textsubscript{2}:Nd\textsuperscript{3+} crystals were grown by a modified Bridgeman method in a metered fluorine atmosphere in the absence of oxygen-bearing compounds.\textsuperscript{5} The concentration of NdF\textsubscript{3} was varied from 0.1 to 7 wt. %. In the cubic fluorite structure Nd\textsuperscript{3+} ions can be distributed among sites of differing structure, which have different spectral densities.\textsuperscript{5–7} According to Ref. 7, triply charged Nd\textsuperscript{3+} ions replace doubly charged Ca\textsuperscript{2+} ions during growth in a fluorinating atmosphere, and the crystal is saturated by interstitial fluorine ions to maintain electroneutrality. At very low Nd\textsuperscript{3+} concentrations, the charge compensation can be nonlocal (it can be effected by distant interstitial F\textsuperscript{−} ions) and can leave the original cubic symmetry of the ligand field around each Nd\textsuperscript{3+} ion unchanged. As the concentration of impurity Nd\textsuperscript{3+} ions and, therefore, of the F\textsuperscript{−} ions compensating them rises, they are attracted to one another to form dipoles, and the symmetry of the local environment of each Nd\textsuperscript{3+} ion changes from cubic to tetragonal (an \textit{L} center forms, in which the F\textsuperscript{−} ion occupies a nearby interstitial site).\textsuperscript{7} As the concentration is further increased, the mutual attraction of the Nd\textsuperscript{3+}–F\textsuperscript{−} dipoles leads to the formation of dimeric (Nd\textsuperscript{3+}–F\textsuperscript{−})\textsubscript{2} clusters or \textit{M} centers and tetrmeric (Nd\textsuperscript{3+}–F\textsuperscript{−})\textsubscript{4} clusters or \textit{N} centers with rhombic symmetry. In these clusters two (or four) Nd\textsuperscript{3+} ions replace two (or four) Ca\textsuperscript{2+} ions. In this case two or four fluorine ions occupy nearby free interstitial sites to achieve local charge compensation.

The relative concentration of particular optical centers in CaF\textsubscript{2}:Nd\textsuperscript{3+} crystals depends primarily on the total concen-
tration of NdF$_3$ introduced into the CaF$_2$ crystal during its synthesis. Figure 1 presents the absorption spectra of neodymium ions between the low-lying Stark sublevels of the $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$ transition in a CaF$_2$ crystal at $T=9$ K. According to Refs. 5–7, absorption at these wavelengths corresponds to a transition between the ground $^4I_{9/2}$ level and the first three Stark sublevels of the $^4G_{5/2}, ^2G_{7/2}$ multiplets of the $M$ and $N$ centers. It is clear from the figure that the absorption associated with $M$ centers dominates at an NdF$_3$ concentration equal to 0.1%. Increasing the NdF$_3$ concentration from 0.1 to 1.0 wt. % results in an increase in the concentration of the tetrameric $N$ centers in comparison with the dimeric $M$ centers. When the NdF$_3$ concentration is increased significantly (to more than 1 wt. %), the system should be treated as a crystalline solid solution. In this case NdF$_3$ is regarded not as an impurity, but as one of the components of the solid solution.

Solid solutions are characterized by statistical disorder, under which it becomes difficult to speak about order in distant coordination spheres. A significant increase in the concentration of NdF$_3$ to 7 wt. % results in an increase in the number of centers, and passage from inhomogeneous line splitting to inhomogeneous broadening of the spectra (Fig. 1, curve d), where weakly structured broad bands appear instead of sets of narrow lines. In this case, the concentrations of the various components of the solid solution are already comparable, and the $M$ and $N$ cluster centers enlarge, possibly forming tetrameric, pentameric, and more aggregated clusters. The statistics of the new clusters can be lower than that of the $M$ and $N$ cluster centers, and the statistics of the Nd$^{3+}$ states in crystal fields of different symmetry and strength lead to considerable inhomogeneous broadening of the lines (comparable to glasses), amounting $\sim 30$ cm$^{-1}$ (Fig. 1, curve d).

Figure 2 presents the absorption spectra of the CaF$_2$:Nd$^{3+}$ crystals investigated in the $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$ transition between the low-lying Stark levels as the NdF$_3$ concentration is varied from 0.1 to 1 wt. % at $T=9$ K, which were recorded with a resolution of 0.22 cm$^{-1}$. As seen from the figure, the absorption spectra consist of two groups of lines with $\lambda = 579.4$ and 579.0 nm. The minimum values of the linewidth in Fig. 2 are determined by the spectral resolution. It can be seen from the figure that varying the NdF$_3$ concentration from 0.1 to 1 wt. % results in variation of the specific concentrations of the $M$ and $N$ centers toward the more aggregated $N$ centers, while the relative splitting of the absorption coefficients within each group of lines remains constant. In the figure, each of these groups corresponds to four lines with splitting for the $M$ centers ranging from 0.9 to 4.3 cm$^{-1}$ (between the outermost lines) and splitting for the $N$ centers ranging from $\sim 1.8$ to 6 cm$^{-1}$. The lack of similar splitting in the absorption spectra in other transitions sug-

![Absorption spectra](image)

**FIG. 1.** Absorption spectra of the $M$ and $N$ Nd$^{3+}$ centers in CaF$_2$ crystals in the $^4I_{9/2} \rightarrow ^4G_{5/2}, ^2G_{7/2}$ transition at $T=9$ K for various concentrations of NdF$_3$, wt. %: a) 0.1, b) 0.3, c) 1, d) 7.