

Dephasing of resonant optical transitions of Pr^{+3} in a Y_2SiO_5 crystal

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The temperature decays of the intensity of a photon echo on resonant transitions of a praseodymium atom have been studied in the crystal $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$. It is shown that the results differ substantially from those previously obtained in a number of crystal matrices and cannot be interpreted on the basis of known mechanisms of dephasing of optical transitions in impurity ions in crystals. © 1995 American Institute of Physics.

1. INTRODUCTION

The development of coherent laser spectroscopy methods and especially methods based on the excitation of echo responses by a sequence of optical pulses^{1–3} makes it possible to study in detail the mechanisms of destruction of coherence, produced on resonant optical transitions of impurity centers in solid-state matrices.⁴ The characteristic coherence-relaxation time scale T_2 , which is directly related with the homogeneous width of an optical transition,⁵ is determined by a number of physical processes arising with the interaction of an impurity center with the nearest-neighbor atomic ensemble. For impurity centers in crystal matrices it is believed^{4,5} that the relaxation of coherence on resonant optical transitions can be associated with the action of essentially three mechanisms: the Orbach mechanism, associated with the absorption and emission of phonons in levels closest to the resonant optical transition; a mechanism determined by the interaction of the acoustic phonons with the resonant optical transition levels; and, finally, a mechanism associated with the electric and magnetic multipole interaction of an impurity center with the atomic environment. However, analysis⁶ of the temperature decays of the intensity of a two-pulse photon echo in a $\text{LaF}_3:\text{Pr}^{+3}$ crystal in the resonant transition ${}^3P_0 \leftrightarrow {}^3H_4$ of the Pr^{+3} ion, performed taking into account the phonon mechanisms in accordance with the structure of the levels of the ion Pr^{+3} , did not give a satisfactory quantitative description of the experimental results. In a later work,⁷ in contrast to Ref. 6, subtle mechanisms of the temporal evolution of the echo signal in the same crystal $\text{LaF}_3:\text{Pr}^{+3}$ which were associated with the substructure of resonant transitions of a Pr^{+3} ion were discovered. The results of Refs. 8–10, where small changes (20–300 kHz) were observed in the frequency of the resonant optical transition of rare-earth ions, which depend on the intensity of the exciting laser pulses, are especially interesting. The latest experiments¹¹ on photon echoes in the crystal $\text{Y}_2\text{SiO}_5:\text{Eu}^{+3}$, performed on the resonant transitions of the Eu^{+3} ions occupying two nonequivalent positions in the Y_2SiO_5 crystal matrix showed that the frequency shifts, observed in Refs. 8–10 were induced by the optical excitation of the nearest-neighbor Eu^{+3} ions.

Therefore the dynamics of resonant optical transitions in rare-earth ions in crystal matrices is by no means completely understood and has a complicated character which is determined by the ordering of a series of relaxational processes occurring in an excited impurity center.

In the present paper we report the results of an investigation of the temperature decays of the intensity of a two-pulse photon echo observed in the resonant optical transitions ${}^3H_4 \leftrightarrow {}^3P_0$ and ${}^3H_4 \leftrightarrow {}^1D_2$ of the Pr^{+3} ion in a Y_2SiO_5 crystal. It was found that our experimental results differ substantially from those of Ref. 6. The observed discrepancies could be associated with the properties of the low-symmetry crystal matrix Y_2SiO_5 .

2. EXPERIMENT

The spectral investigations were performed with a MDR-23 monochromator combined with a detection system operating in the photon-counting mode. To obtain high spectral resolution, a narrow-band frequency-tunable laser was used to study the spectral line contours of the resonant transitions of the Pr^{+3} ion.

A two-pulse photon echo was observed in the collinear geometry, when the wave vectors of the first and second exciting laser pulses coincide with the wave vector of the photon-echo pulse.^{1,2} A coherently pumped, frequency-tunable, dye laser was used to produce two exciting optical pulses. The coherent pumping gave in the required wavelength range a peak intensity of the output laser pulses of 50 kW with a duration of 10 ns at half-height and a spectral width of 0.02 nm and time interval between laser light excitation $\Delta t \approx 35$ ns.

The photon-echo signals were recorded with a FÉU-100 photomultiplier, operating at the input of a wide-band amplifier ($\Delta f = 500$ MHz, gain equal to 20 dB). The signal from the amplifier output was fed into a S1-75 oscillograph with a visual adjustment system and in the measurement mode into a V4-24 pulsed voltmeter. The entrance window of the receiving photomultiplier was gated with a fast-response system of electro-optic shutters (three successive ML-102 shutters), strictly synchronized in time with the laser pulses.

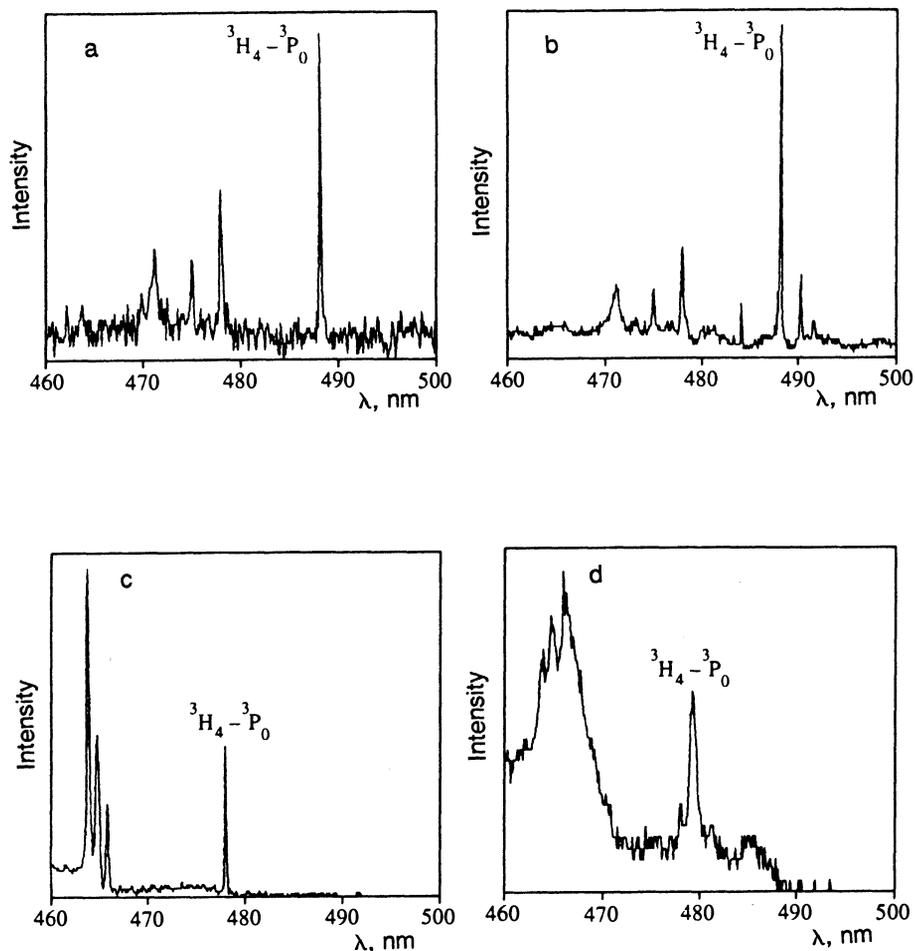


FIG. 1. Absorption spectra of a Pr^{+3} ion in the region of the resonant transition ${}^3H_4 \leftrightarrow {}^3P_0$ at temperatures of 1.5 K (a, c) and 77 K (b, d) for $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ crystals (a, b) and $\text{LaF}_3:\text{Pr}^{+3}$ crystals (c, d).

The $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ crystals with 0.3 at.% Pr^{+3} were of order 0.25 cm thick and had different optical quality. To obtain a temperature in the range 4.2–30 K, the crystals were placed in an optical helium cryostat with temperature regulation to within 0.1 K. In the cryostat the experimental crystal was placed in helium vapor.

3. EXPERIMENTAL RESULTS

In contrast to $\text{LaF}_3:\text{Pr}^{+3}$, the electronic absorption and fluorescence spectra of a Pr^{+3} ion in a Y_2SiO_5 crystal have virtually not been studied. In Ref. 12 an attempt was made to interpret the spectra of the doped crystal $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ in the temperature range 77–300 K. However, we were primarily interested in the absorption spectrum of the experimental crystal at liquid-helium temperatures.

Figure 1 displays sections of the absorption spectra of a Pr^{+3} ion in a Y_2SiO_5 crystal for the resonant transition ${}^3H_4 \leftrightarrow {}^3P_0$. In the temperature 4.2–30 K the resonant transitions ${}^3H_4 \leftrightarrow {}^3P_0$ and ${}^3H_4 \leftrightarrow {}^1D_2$ correspond to quite narrow spectral lines with half-width less than 3 cm^{-1} . A detailed investigation, performed with the aid of a tunable laser, of the contour of the spectral line corresponding to the transition ${}^3H_4 \leftrightarrow {}^3P_0$ of the Pr^{+3} ion in a Y_2SiO_5 crystal showed that at high frequencies a spectral satellite is present 8.1 cm^{-1} from the resonant transition investigated (Fig. 2). The observed spectral satellite cannot be associated with the optical transition between the multiplet components of the 3H_4 and 3P_0 terms of the Pr^{+3} ion, since the observed dou-

plet is manifested similarly for other spectral lines also. We assume that, just as in $\text{Y}_2\text{SiO}_5:\text{Eu}^{+3}$,¹¹ a Pr^{+3} ion in a Y_2SiO_5 crystal occupies two nonequivalent positions, giving two spectra which are structurally virtually identical but shifted relative to one another by the amount 8.1 cm^{-1} .

As the temperature of the $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ crystal increases up to 77 K additional peaks (Fig. 1), whose intensity depends on the temperature, appear in the long-wavelength region

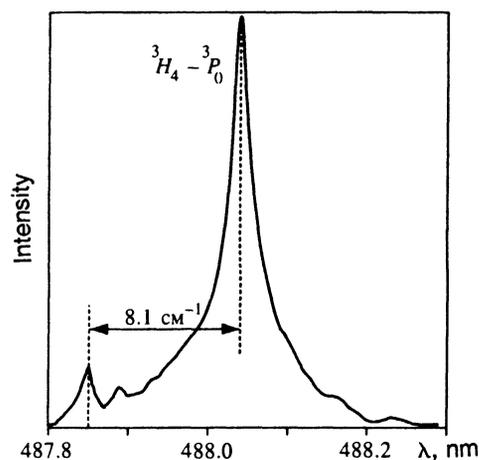


FIG. 2. Absorption spectrum of a $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ crystal at $T = 1.5 \text{ K}$. The spectrum was obtained with a high spectral resolution.

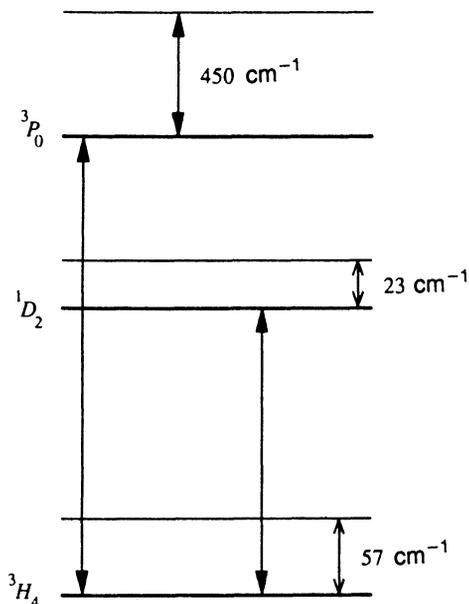


FIG. 3. Simplified energy-level scheme of a Pr^{+3} ion.

with respect to the resonant transitions ${}^3H_4 \leftrightarrow {}^3P_0$ and ${}^3H_4 \leftrightarrow {}^1D_2$. The observed frequency ranges with maxima at 56.3 cm^{-1} , 77.7 cm^{-1} , and 137.5 cm^{-1} and the characteristic temperature dependence of the intensity of the observed spectral lines show that these peaks are associated with the absorption from the thermally filled levels of the multiplet splitting of the 3H_4 term. Proceeding from the absorption spectra (Fig. 1) it follows for the excited state 3P_0 that the nearest level is split in frequency by an amount of the order of 450 cm^{-1} . However, for the 1D_2 state the 23 cm^{-1} level, which exists in the crystal $\text{LaF}_3:\text{Pr}^{+3}$, was not observed in $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ in our experiments.

Note that as the temperature increases, the widths of the spectral lines corresponding to the resonant optical transitions ${}^3H_4 \leftrightarrow {}^3P_0$ and ${}^3H_4 \leftrightarrow {}^1D_2$ of the Pr^{+3} ion increase more strongly in a LaF_3 crystal than in a Y_2SiO_5 crystal (Fig. 1). For example, the width of the spectral line associated with the transition ${}^3H_4 \leftrightarrow {}^3P_0$ of Pr^{+3} increases up to 30 cm^{-1} as the temperature of the $\text{LaF}_3:\text{Pr}^{+3}$ crystal increases from 4.2 K up to 77 K, while for a $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$

crystal the half-width of the corresponding spectral line changes very little.

Therefore it can be assumed to a first approximation that the energy-level scheme of a Pr^{+3} ion (Fig. 3) in a Y_2SiO_5 crystal is similar to that in $\text{LaF}_3:\text{Pr}^{+3}$. Figure 3 indicates only the levels which can play a key role in the dephasing of the optical resonant transitions of a Pr^{+3} ion.

Before studying the photon echo in a $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ crystal, we conducted a complete series of experiments on the photon echo on the resonant transition ${}^3H_4 \leftrightarrow {}^3P_0$ of a Pr^{+3} ion in a LaF_3 crystal. The results agreed completely with those of Ref. 6. Actually, both crystals $\text{LaF}_3:\text{Pr}^{+3}$ and $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ were located in the same optical cryostat. This made it possible to switch rapidly from one crystal to another and therefore to work in a reliably calibrated experimental system.

Figure 4a displays the experimental curve of the decay of the intensity of a two-pulse photon echo in a $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ crystal as a function of the temperature. A careful measurement of the decays of the amplitude of the photon echo on the resonant transitions ${}^3H_4 \leftrightarrow {}^3P_0$ and ${}^3H_4 \leftrightarrow {}^1D_2$ as a function of the temperature showed that in both cases the curves are identical to one another. The temperature range in which the photon-echo signal exists for a $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ crystal was almost two times wider than for $\text{LaF}_3:\text{Pr}^{+3}$. This fact is reflected in Fig. 4b, which displays in double logarithmic coordinates the temperature decays of the intensity of a two-pulse photon echo on the resonant transition ${}^3H_4 \leftrightarrow {}^3P_0$ of a Pr^{+3} ion in LaF_3 and Y_2SiO_5 crystals.

4. ANALYSIS OF EXPERIMENTAL RESULTS

It is well known⁴ that the amplitude of a two-pulse photon-echo signal is given by the expression

$$I = I_0 \exp[-\gamma(T)2\Delta t], \quad (1)$$

where I_0 is the amplitude of the photon echo which contains a temperature-independent contribution to dephasing; $\gamma(T) = 2/T_2(T)$ is the homogeneous broadening of the spectral line of an optical transition; T_2 is the irreversible transverse relaxation time; Δt is the time interval between the exciting laser pulses; and T is the temperature. The homogeneous broadening is an additive function of the corresponding relaxation processes and includes temperature-independent and

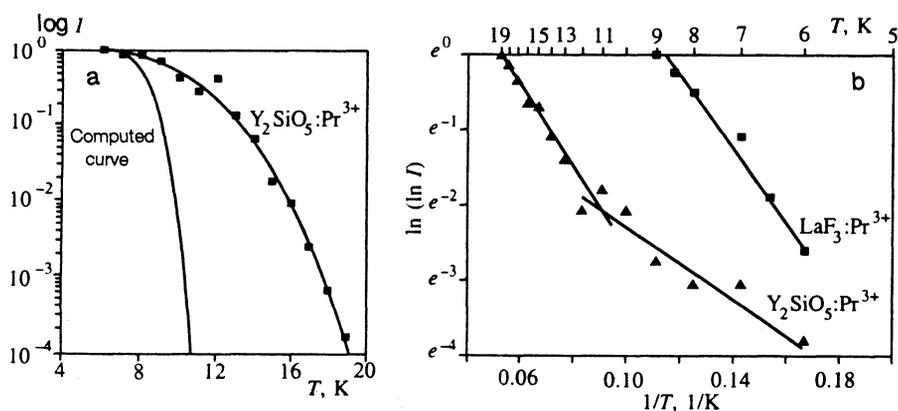


FIG. 4. Temperature decay of the amplitude of a photon echo in $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ and $\text{LaF}_3:\text{Pr}^{+3}$ crystals.

temperature-dependent contributions. In Ref. 5 the following expression, extending the previous analysis of Ref. 4, was derived to describe the temperature-dependent contributions to the homogeneous width of a spectral line:

$$\gamma(T) = \int \ln \left[1 + w^2 \Gamma^e(\nu) \Gamma^g(\nu) \sinh^{-2} \left(\frac{\nu}{T} \right) \right] d\nu, \quad (2)$$

where w characterizes the quadratic electron-phonon interaction and $\Gamma^g(\nu)$ and $\Gamma^e(\nu)$ are spectral functions associated with the probabilities of one-phonon transitions in the ground and excited states of the impurity center.

In the case of the interaction of a resonant optical transition with acoustic phonons the relation (2) gives in the low-temperature limit a corresponding contribution to the homogeneous width in the form $\gamma(T) \sim (T/\Theta)^7$, where Θ is the Debye temperature. It is obvious that in our case, since $T/\Theta < 1$ holds (for T in the range 6–20 K), this interaction can be simply neglected. Therefore the most important relaxation mechanism which makes the main contribution to the dephasing of the resonant optical transitions of a Pr^{+3} ion at temperatures in the range 6–20 K will be determined by the structure of the multiplet sublevels of the states 3P_0 , 3H_4 , and 1D_2 , i.e., for each state 3P_0 , 3H_4 , and 1D_2 we must take into account one of the close-lying levels, which are displayed in Fig. 3. Using the relation (2) and the low-temperature limit $w^2 \Gamma^e(\nu) \Gamma^g(\nu) \sinh^{-2}(\nu/T) \ll 1$ and the results of Ref. 4, we obtain the following expression for the homogeneous width of an optical transition:

$$\gamma(T) = \gamma_g \exp(-\nu_g/T) + \gamma_e \exp(-\nu_e/T), \quad (3)$$

where γ_g and γ_e are the half-widths of the corresponding multiplet levels in the ground and excited states and ν_g and ν_e are their frequencies.

In our specific case, in the temperature range 6–20 K, for the 3P_0 state the nearest sublevel split off by 450 cm^{-1} can be neglected and so for the resonant transition $^3H_4 \leftrightarrow ^3P_0$ only one term with $\nu_g = 56.3 \text{ cm}^{-1}$ need be included in the relation (3). In contrast, two terms with $\nu_g = 56.3 \text{ cm}^{-1}$ and $\nu_e = 23 \text{ cm}^{-1}$ must be included in Eq. (3) for the resonant transition $^3H_4 \leftrightarrow ^1D_2$. However, it follows from the fact that the temperature decays of the amplitude of the two-pulse photon echo are identical for the transitions $^3H_4 \leftrightarrow ^3P_0$ and $^3H_4 \leftrightarrow ^1D_2$ that $\gamma_e(23 \text{ cm}^{-1}) \ll \gamma_g(56.3 \text{ cm}^{-1})$, i.e., for both resonant transitions the main temperature contribution to dephasing is associated with the Orbach process on the 56.3 cm^{-1} sublevel of the 3H_4 ground state.

To analyze the temperature decay of the amplitude of the photon echo in a $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ crystal on the basis of the relations (1) and (3), we are missing the value of the parameter γ_g , which would be determined from independent experiments. If we use the value $\gamma_g = 2.4 \cdot 10^{-11} \text{ s}^{-1}$, found in Ref. 6 for $\text{LaF}_3:\text{Pr}^{+3}$, then the curve of the decay of the amplitude of a two-pulse photon echo will be substantially different from our curve for $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ (Fig. 4a). Therefore, at the present stage, we can solve the inverse problem and estimate the value of γ_g for $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ starting from the experimental results obtained. For this, we turn to Fig 4b and use the linear section in the temperature range

10–20 K. On the basis of the relations (1) and (3) with $\nu_g = 56.3 \text{ cm}^{-1}$, the approximation of the experimental points in the range 10–20 K by a straight line gives $\gamma_g = 6.3 \cdot 10^9 \text{ s}^{-1}$. The parameter γ_g obtained in this manner differs by almost two orders of magnitude from the value obtained in $\text{LaF}_3:\text{Pr}^{+3}$ crystal. This agrees qualitatively with the different temperature broadening of the absorption spectra of $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ and $\text{LaF}_3:\text{Pr}^{+3}$ crystals (Fig. 1), which is determined by the same relaxation mechanisms, i.e., the stronger temperature broadening of the spectrum of $\text{LaF}_3:\text{Pr}^{+3}$ also agrees with the more rapid decay of the amplitude of the two-pulse photon echo in this crystal. The difference in the values of the constant γ_g for $\text{LaF}_3:\text{Pr}^{+3}$ and $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ crystals could be associated with the peculiarities of the structure of the crystal lattice of Y_2SiO_5 .¹⁴ The point is that in the low-symmetry Y_2SiO_5 crystal with point symmetry group C_{2h} the crystal structure can be represented in the form of atomic planes and chains.¹⁴ It is possible that the phonon properties of such a crystal matrix will be strongly anisotropic. This in turn can modify the electron-phonon interaction of the impurity ions and decrease the phase relaxation rate.

To estimate the value of γ_g for $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ we deliberately chose the temperature range 10–20 K. The point is that two characteristic sections with different slopes can be separated in the curve of the decay of the amplitude of a photon echo on a double logarithmic scale (Fig. 4b). The slope on the high-temperature section is virtually identical to the slope of the experimental curve for $\text{LaF}_3:\text{Pr}^{+3}$ and agrees qualitatively with the structure of the levels of the Pr^{+3} ion (Fig. 3). The slope is related directly with ν_g and gives a value close to 56.3 cm^{-1} . This is also observed in Ref. 6. But the presence of a low-temperature section (6–10 K) on the experimental curve (Fig. 4b) with a difference slope cannot be described by a relation of the type (3). Therefore a different temperature dephasing mechanism, not associated with the Orbach process, operates in the temperature range 6–10 K. As far as we know, this is the first time that this feature has been observed in crystals. In this connection, we call attention to the results of Ref. 11, where the optical excitation of Eu^{+3} ions occupying nonequivalent crystallographic positions in the Y_2SiO_5 matrix and shifted by 5.2 cm^{-1} in energy affected the dephasing of the optical transitions of the other Eu^{+3} ions. These features are associated with the multipole magnetic interaction between the Eu^{+3} ions, but it is also possible that the Eu^{+3} ions tunnel between two nonequivalent positions. The existence of such a process engenders a new mechanism of dephasing,⁵ which can appear at low temperatures before the Orbach mechanism. This situation also occurs in the $\text{Y}_2\text{SiO}_5:\text{Pr}^{+3}$ crystal, where the praseodymium ions can tunnel between two nonequivalent positions in the crystal lattice, giving rise to a corresponding dephasing in the temperature range 6–10 K (Fig. 4b).

In summary, the value of the constant is determining the rate of the Orbach relaxation process with participation of one of the multiplet levels of the 3H_4 state was determined on the basis of an investigation of the temperature decays of the amplitude of a two-pulse photon echo in resonant transi-

tions of Pr^{+3} in a Y_2SiO_5 crystal. The existence of a low-temperature section on the experimental curve of the decay of the amplitude of a photon echo remains a mystery. We hope that experiments on a series of related crystal matrices with participation of two rare-earth ions will make it possible to determine the microscopic mechanisms responsible for this feature.

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