

Temperature dependence of the homogeneous width of Eu^{3+} spectral lines in silicate glass measured by accumulated photon echoes

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The temperature-dependent homogeneous width of the ${}^5D_0-{}^7F_0$ transition of Eu^{3+} in a pure silicate glass fiber has been measured by accumulated photon echoes between 1.6 and 44 K. The temperature dependence of the homogeneous width shows a crossover from T -linear ($T < 7$ K) to T^2 ($T > 7$ K). The whole temperature dependence of the homogeneous width between 1.6 and 44 K can be explained by the configurational changes of the glass which is modeled by two-level systems (TLS's) and a Raman process involving low-frequency vibrational modes of the silicate glass (the rotations of SiO_4 tetrahedra). The T -linear temperature dependence is attributed to the TLS process. The anomalous T^2 dependence down to 10 K cannot be explained by only one process, but can be explained by the contributions of both the TLS process and the Raman process. Above 40 K, the Raman process becomes the dominant dephasing mechanism.

The optical homogeneous widths of ions or molecules in glasses exhibit an anomalous behavior in both their magnitude and temperature dependence when compared to the same species in crystals.¹ The anomalous behavior of the optical homogeneous widths of ions and molecules in glasses at low temperatures is generally considered to be caused by the local configurational changes in glasses which are often modeled by the two-level systems (TLS's),^{1,2} and elastic dipole-dipole interaction between guest ion (molecule) and TLS's is considered to be the dephasing mechanism.^{2,3}

Many studies of the homogeneous widths of molecules have advanced our knowledge of properties such as low- and high-temperature dephasing and spectral diffusion.^{1,4} However, the mechanisms of the homogeneous widths of ions in glasses are still not fully understood mainly because of the lack of reliable data on the temperature dependence of the homogeneous width of ion-doped glasses over a wide temperature range. For example, the temperature dependence of the homogeneous width of the ${}^5D_0-{}^7F_0$ transition of Eu^{3+} in silicate glass is T -linear between 0.4 and 3.3 K,⁵ and T^2 between 7 and 90 K (Ref. 6) and between 150 and 800 K.⁷ Although the temperature dependence of the homogeneous width in three temperature ranges has been measured, we do not know exactly how the homogeneous width changes between 3.3 and 7 K. Using the data of Refs. 5–7, Gladenkova and Osad'ko explained the temperature dependence of Eu^{3+} in a silicate glass in a wide temperature range ($0.4 < T < 500$ K).⁸ They assumed a quadratic Ramanlike interaction with a TLS and a quadratic interaction with a low-frequency localized vibration besides acoustic phonons in their treatment. However, the nature of the localized vibration is not clear and the simultaneous use of the data of Refs. 5–7 is not appropriate for the discussion

of temperature dependence. It is therefore necessary to measure the temperature-dependent homogeneous width of ion-doped glasses over a wide temperature range and investigate the dephasing process.

In this paper, we report the temperature dependence of the homogeneous width of Eu^{3+} in a pure silicate glass fiber between 1.6 and 44 K measured by accumulated photon echoes. The mechanism of the homogeneous width is quantitatively discussed by taking into account the TLS dephasing process and a Raman process of nonacoustic phonon modes of silicate glasses. A good agreement is obtained between the theory and the experiment. Especially noteworthy is that the anomalous low-temperature T^2 dependence down to 10 K can be explained by the contributions of the TLS and Raman processes. We believe that similar dephasing processes also dominate in other ion-doped inorganic glasses.

Accumulated photon echo experiments were performed in the ${}^5D_0-{}^7F_0$ transition (wavelength of 575 nm corresponding to the center of the inhomogeneous broadening) of Eu^{3+} in a pure silicate glass fiber using a mode-locked dye laser (Spectra Physics 3500) with pulse repetition rate of 82 MHz and a pulse width of 4 psec.

The experimental setup is shown in Fig. 1. A collinear excitation beam configuration was used.⁹ The output of the dye laser was divided by a beam splitter (B.S.) and an optical chopper modulated the pump beam E_1 and the probe beam E_2 at frequencies f_1 of 1.0 kHz and f_2 of 0.83 kHz, respectively. The summed frequency ($f_1 + f_2$) component of the output beams from the fiber sample was detected by a lock-in amplifier. In this configuration the echo signal was detected as the interference between the probe beam and the echo beam, which is known as the heterodyne detection of accumulated photon

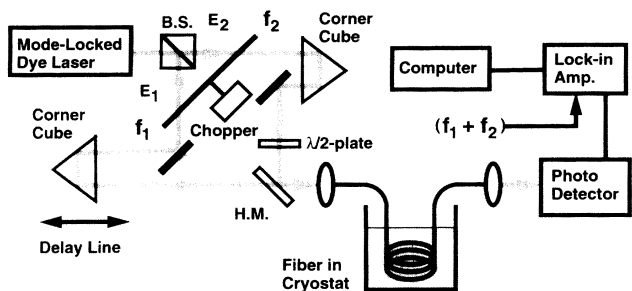


FIG. 1. Experimental setup for accumulated photon echoes using a mode-locked dye laser. The intensities of the pump beam E_1 and the probe beam E_2 were modulated by an optical chopper. The heterodyne detected echo signal was measured by changing the delay time τ_{12} between the pump and probe beams. B.S., beam splitter; H.M., half mirror.

echoes.¹⁰ Echo decay curves were measured by changing the delay time τ_{12} between the pump and probe beams. The decay constant of the echo decay curve gives $T_2/2$, where T_2 is the dephasing time. The homogeneous width Γ_h is given by the relation $\Gamma_h = 1/(\pi T_2)$.

A sample of 36.3 ppm Eu^{3+} in a pure silicate glass single-mode fiber (cutoff wavelength of 550 nm) of length 130 m was coiled to a diameter of 4 cm in a cage, and the cage was then placed in a cryostat. The transmission loss at a wavelength of 575 nm and temperature 77 K was ~ 7.5 dB. Below 4.25 K, the cage was immersed in liquid helium and sample temperature was controlled by pumping the cryostat. Above 4.25 K, the cage was suspended in cold helium atmosphere and was in some cases heated by film heaters. The accuracy of the temperature was within ± 0.1 K below 4.25 K and ± 0.6 K above 4.25 K. Using the fiber sample, we could easily measure the homogeneous width of the sample below 4.25 K. If we had used a bulk sample, the bubbles in the liquid helium would have scattered the beams and no echo signals could have been observed.

The excitation beams were combined with a half mirror (H.M.) and focused on the fiber sample with an objective lens. Both ends of the fiber sample were out of the cryostat and were kept at room temperature. The length of the ends were only 4 m, so we could ignore the echo signal contribution from them. In this configuration, we could not measure the input intensities of the excitation beams. Typical output intensities of the pump and probe beams were 0.30 and 0.15 mW, respectively. The estimated input power of the pump and probe beams were about 5.6 times that of the output beams. We checked that the echo decay times did not change when we attenuated the input beam intensities 25% of the above values.

Figure 2 shows a typical echo decay curve at 12.9 K. Since the chopping frequencies of the optical chopper f_1 and $f_2 \sim T_1^{-1}$ where T_1 ($=800 \mu\text{sec}$) is the excited state (5D_0) lifetime of Eu^{3+} , the echo decay curve shows a constant background due to the population relaxation as

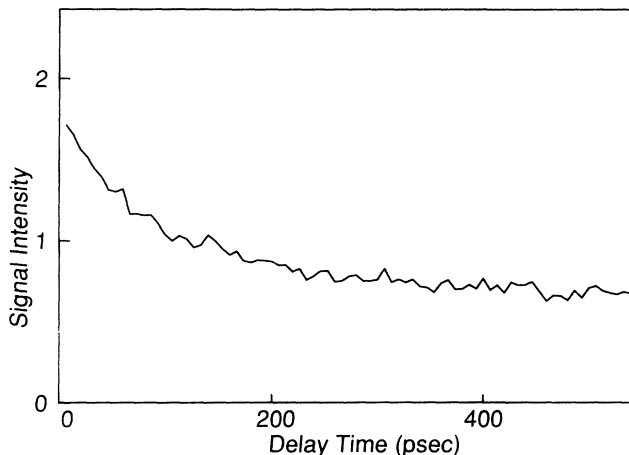


FIG. 2. Echo decay curve with arbitrary ordinate-axis units of Eu^{3+} in silicate glass at 12.9 K. Excitation wavelength was 575 nm.

well as an echo decay component. If the chopping frequencies f_1 and $f_2 \gg T_1^{-1}$, the population cannot follow the light modulation of the optical chopper and no constant background can be observed. T_2 of 213 psec was obtained from the echo curve. Since the oscillator strength of Eu^{3+} is smaller than those of Nd^{3+} and Pr^{3+} , it is usually difficult to observe an echo signal from Eu^{3+} -doped glasses, and so far no observation of the accumulated photon echoes in Eu^{3+} -doped glasses has been reported. The reason for our success probably lies in the use of a fiber sample. With the noncollinear excitation beam configuration typically used with bulk samples, the interaction length of the excitation beams are not long and scattered lights from the sample often obscure the echo signal. In our case, however, the interaction length of the sample is long and all the output beams from the fiber sample contribute to the echo signal.

The temperature dependence of the homogeneous width $\Gamma_h(T)$ is shown in Fig. 3. Since the lifetime of the 5D_0 level is 800 μsec , Γ_h does not necessarily mean a

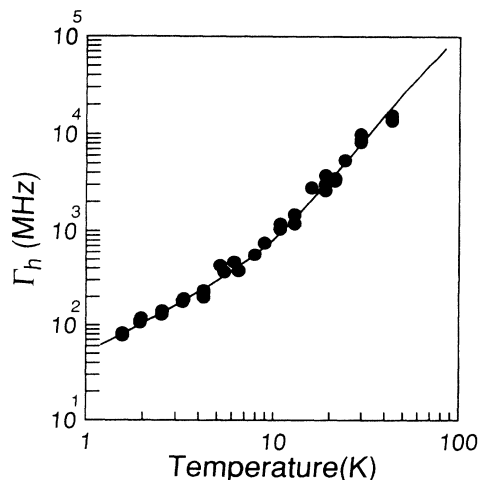


FIG. 3. Temperature-dependent homogeneous width of ${}^5D_0-{}^7F_0$ transition of Eu^{3+} in a pure silicate glass between 1.6 and 44 K. The solid curve is a theoretical fitting (see text).

pure homogeneous width and spectral diffusion probably contributes to the measured homogeneous width.⁹ The measured homogeneous width corresponds to the linewidth measured at the time separation of 800 μsec between the burn and probe pulses in time-resolved hole-burning spectroscopy. The temperature dependence of the homogeneous width Γ_h is $\Gamma_h \propto T$ -linear at $T < 7$ K and $\Gamma_h \propto T^2$ at $T > 7$ K, and changes smoothly from T linear to T^2 .¹¹

The homogeneous width of $\text{Eu}^{3+}:\text{YAlO}_3$ crystal between 60 and 150 K was measured by Selzer *et al.* and its origin was attributed to the direct one-phonon process between the 7F_1 and 7F_0 levels.⁶ In the case of Eu^{3+} in silicate glasses, the 7F_1 level is roughly 150–400 cm^{-1} above the 7F_0 level. If a one-phonon process between the 7F_1 and 7F_0 levels dominated the dephasing in the measured temperature range (1.6–44 K), a more rapid change than T^2 would be observed. However, the temperature dependence of the homogeneous width of Eu^{3+} in silicate glass differs considerably from this type of behavior and its width is much broader than that of YAlO_3 crystal at $T < 150$ K.⁶ This indicates that another dephasing mechanism dominates below 44 K. Selzer *et al.* discussed the possibility of the TLS dephasing process.⁶ A T^2 temperature dependence was also observed in the 3P_0 – 3H_4 (1) transition of Pr^{3+} in BeF_2 and GeO_2 glasses between 8 and 300 K.¹²

In the standard theory of the TLS dephasing process, if the density of states of the TLS's $\rho(E) \propto E^\mu$, the temperature dependence of the homogeneous width Γ_h becomes $\Gamma_h \propto T^{1+\mu}$.^{1,13} We must choose μ of 1 to explain the T^2 dependence, but this contradicts the usually considered constant density of the TLS states (where $\mu \approx 0$).² Assuming a constant density of the TLS states, Lyo and Orbach derived a TLS dephasing process that explains the anomalous low-temperature T^2 dependence of the homogeneous width.¹⁴ However, their model cannot explain the T -linear dependence which is pronounced at $T < 7$ K.

The T -linear dependence of the specific heat of glasses becomes prominent at $T < 1$ K and this has been successfully explained by the TLS process with a constant density of TLS states.¹⁵ This means that the TLS process becomes dominant in specific heat at $T < 1$ K. In the optical regime, the situation should be similar and the TLS process should become dominant at $T < 7$ K in silicate glasses. In Nd^{3+} -doped silicate glass fiber, nearly T -linear ($T^{1.3}$) temperature dependence was observed between 0.1 and 1 K using two-pulse photon echoes and its dephasing mechanism was attributed to the TLS process.⁹ Therefore, not the T^2 dependence but the T -linear dependence should be attributed to the TLS dephasing process. Similar magnitudes of the homogeneous widths of Pr^{3+} were observed in both glasses and a crystal at $T > 70$ K.¹² This fact supports the above idea.

The anomalous T^2 dependence at temperatures down to 10 K cannot be attributed to the TLS process, so what is the origin of the anomalous T^2 dependence? In a Raman process with acoustic phonons, T^2 temperature dependence follows with temperature down to $0.5T_D$, where T_D is the Debye temperature of the material. In

the case of a silicate glass, $T_D = 500$ K and the Raman process with acoustic phonons cannot explain the T^2 dependence down to 10 K. However, the anomalous low-temperature T^2 dependence suggests a more enhanced density of the low-frequency modes of glasses compared to that in the Debye model.

Huber suggested that the low-temperature T^2 dependence below $0.5T_D$ was caused by the low-lying vibrational modes of glasses.^{16,17} In the neutron-scattering experiments of silicate glasses, a more enhanced density of low-frequency modes than in the Debye model with frequencies < 4 THz was observed and the additional modes were attributed to the rotations of SiO_4 tetrahedra.¹⁸ The calculation of the specific heat of silicate glasses between 4 and 20 K using the density of states obtained from the neutron-scattering experiments showed that the enhancement of the specific heat of silicate glasses is caused by the low-frequency vibrational modes (the rotations of SiO_4 tetrahedra).¹⁸ Huber calculated the Raman process with these modes between 10 and 300 K, and showed T^2 temperature dependence down to 40 K.¹⁷ Below 40 K, the homogeneous width changes more rapidly than T^2 .

In the Raman process considered by Huber, no adjustable parameters were used in the calculation of the temperature dependence of the homogeneous width and the nature of the low-frequency modes is clear. Therefore, in the following, we interpret the temperature-dependent homogeneous width of Eu^{3+} in a silicate glass using the TLS process and the Raman process considered by Huber.

Between 1.6 and 7 K, the homogeneous width shows a T -linear dependence. Therefore, we assume a constant density of the TLS states, and write the contribution of the TLS's as $\Gamma_{\text{TLS}}(T) = AT$, where A is a fitting parameter. Next, we write the contribution of the Raman process as $\Gamma_{\text{Raman}}(T) = BF(T)$, where B is a fitting parameter and $F(T)$, which was calculated by Huber, is normalized to unity (no dimension) at $T = 10$ K; $F(10) = 1$ (see Fig. 2 of Ref. 17). The temperature dependence of the Raman process below 10 K was not calculated.¹⁹ However, the experimentally obtained temperature dependence of the homogeneous width shows that the contribution of the Raman process should be negligible compared to the contribution of the TLS process at $T < 7$ K. The homogeneous width $\Gamma_h(T)$ is therefore given by $\Gamma_h(T) = \Gamma_{\text{TLS}}(T) + \Gamma_{\text{Raman}}(T)$.

The solid curve in Fig. 3 is a theoretical curve obtained when $A = 49.0$ MHz/K and $B = 323$ MHz. The agreement between the experiment and the theory is quite satisfactory. The whole temperature dependence of Eu^{3+} in a pure silicate glass between 1.6 and 44 K is well explained by the TLS process and the Raman process. The T^2 temperature dependence down to 10 K cannot be explained by either the TLS process nor the Raman process, but can be explained by taking both processes into account. The anomalous low-temperature T^2 dependence of ion-doped glasses at temperatures down to 10 K has been explained by only one process and often by TLS process. This is not, however, necessarily true. We consider that it is necessary to measure the homogeneous

width of ion-doped glasses over a wide temperature range using one sample to avoid this kind of misunderstanding. Above 40 K, the Raman process with the low-frequency modes of the silicate glass should dominate the dephasing.

High-temperature ($T > 70$ K) homogeneous widths of Pr^{3+} in glasses and a crystal are comparable in magnitude,¹² and a similar dephasing process (probably a Raman process with acoustic phonons) seems to dominate in both materials. Assuming that the density of states of acoustic phonons obeys the Debye model, we expect that acoustic phonons probably contribute to the dephasing process of Eu^{3+} at $T > 250$ K.

We have measured the homogeneous width of Eu^{3+} in a pure silicate glass fiber between 1.6 and 44 K. The temperature dependence of the homogeneous width is proportional to T -linear at $T < 7$ K, and proportional to T^2 at $T > 7$ K. The whole temperature dependence of the homogeneous width between 1.6 and 44 K can be explained by two dephasing processes: the TLS process associated with the local configurational changes of glasses and the Raman process with the low-frequency vibrational modes (the rotations of SiO_4 tetrahedra). The anomalous T^2 temperature dependence down to 10 K can be explained by taking both processes into account. It cannot be explained by only one process.

¹*Persistent Spectral Hole-Burning: Science and Application*, Topics in Current Physics Vol. 44, edited by W. E. Moerner (Springer-Verlag, Berlin, 1988).

²*Amorphous Solids: Low-Temperature Properties*, Topics in Current Physics Vol. 24, edited by W. A. Phillips (Springer-Verlag, Berlin, 1981).

³D. L. Huber, M. M. Broer, and B. Golding, *Phys. Rev. Lett.* **52**, 2281 (1984).

⁴D. W. Pack, L. R. Narasimhan, and M. D. Fayer, *J. Chem. Phys.* **92**, 4125 (1990); K. A. Littau, Y. S. Bai, and M. D. Fayer, *ibid.* **92**, 4145 (1990).

⁵P. J. Van der Zaag, B. C. Schokker, Th. Schumidt, R. M. Macfarlane, and S. Völker, *J. Lumin.* **45**, 80 (1990).

⁶P. M. Selzer, D. L. Huber, D. S. Hamilton, W. M. Yen, and M. J. Weber, *Phys. Rev. Lett.* **36**, 813 (1976).

⁷J. R. Morgan and M. A. El-Sayed, *Chem. Phys. Lett.* **84**, 213 (1981).

⁸S. N. Gladenkova and I. S. Osad'ko, *Chem. Phys. Lett.* **187**, 628 (1991).

⁹M. M. Broer, B. Golding, W. H. Haemmerle, J. R. Simpson, and D. L. Huber, *Phys. Rev. B* **33**, 4160 (1986).

¹⁰W. H. Hesselink and D. A. Wiersma, *Phys. Rev. Lett.* **43**,

1991 (1979).

¹¹We also observed similar temperature dependence in the $^4I_{9/2} - ^4F_{3/2}(1)$ transition of Nd^{3+} in a pure silicate glass fiber using accumulated photon echoes.

¹²J. Hegarty and W. M. Yen, *Phys. Rev. Lett.* **43**, 1126 (1979).

¹³R. Silbey and K. Kassner, *J. Lumin.* **36**, 283 (1987).

¹⁴S. K. Lyo and R. Orbach, *Phys. Rev. B* **22**, 4223 (1980); S. K. Lyo, *Phys. Rev. Lett.* **48**, 688 (1982).

¹⁵P. W. Anderson, B. I. Halperin, and C. M. Varma, *Philos. Mag.* **25**, 1 (1972); W. A. Phillips, *J. Low Temp. Phys.* **7**, 351 (1972).

¹⁶D. L. Huber, *J. Non-Cryst. Solids* **51**, 241 (1982).

¹⁷D. L. Huber, *J. Lumin.* **36**, 327 (1987).

¹⁸U. Buchenau, N. Nücker, and A. J. Dianoux, *Phys. Rev. Lett.* **53**, 2316 (1984); U. Buchenau, N. Nücker, and A. J. Dianoux, *ibid.* **56**, 539 (1986); U. Buchenau, M. Prager, N. Nücker, A. J. Dianoux, N. Ahmad, and W. A. Phillips, *Phys. Rev. B* **34**, 5665 (1986).

¹⁹For convenience, we assume a T^3 temperature dependence at $T < 10$ K which smoothly connects with the calculated curve at 10 K.

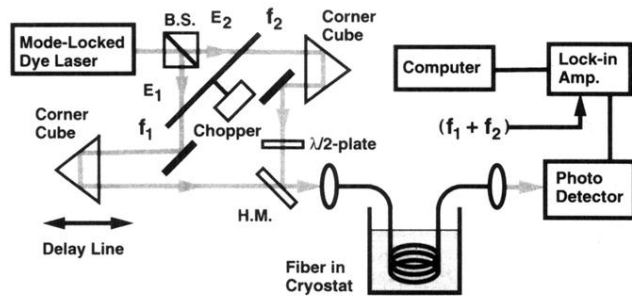


FIG. 1. Experimental setup for accumulated photon echoes using a mode-locked dye laser. The intensities of the pump beam E_1 and the probe beam E_2 were modulated by an optical chopper. The heterodyne detected echo signal was measured by changing the delay time τ_{12} between the pump and probe beams. B.S., beam splitter; H.M., half mirror.