# Low-temperature homogeneous linewidths of $Yb^{3+}$ in inorganic glasses

R. T. Brundage* and W. M. Yen

*Department of Physics, University of Wisconsin-Madison, Madison, Wisconsin 53706*

(Received 28 October 1985)

We have measured the homogeneous linewidth of the $^2F_{5/2}(1)$-$^2F_{7/2}(1)$ transition of $Yb^{3+}$ in silicate and phosphate glasses using fluorescence line narrowing between 6.5 and 70 K. The linewidth is observed to vary as $T^{1.9\pm0.1}$ at high temperature, changing to $T^{1.3\pm0.1}$ below 40 K. This behavior is compared to that observed in other systems and examined in light of current theories of dephasing in disordered systems.

Recent experimental studies of dephasing of optical excitations in inorganic glasses have indicated that the previously observed quadratic dependence on temperature of the homogeneous linewidth $\Delta\nu_H$ does not hold in all such systems at low temperatures.[1] Photon-echo experiments carried out on a $Nd^{3+}$-doped silica fiber revealed a $T^{4/3}$ dependence of $T_2^{-1}$ from 0.1–1.0 K,[2] and spectral hole-burning measurements in a $Pr^{3+}$-doped silicate glass display a linear temperature dependence of the width from 1.6 to 20 K.[3] Measurements of spectral hole burning in organic glasses, on the other hand, have generally shown nearly linear temperature dependences.[4] A number of theories have been proposed to explain the observed behavior, invoking coupling of the excited state to the two-level systems (TLS's) (Ref. 5) of the glass host through elastic[6] or electrostatic[7,8] interactions.

In this paper we report on fluorescence line-narrowing (FLN) experiments carried out on $Yb^{3+}$-doped inorganic glasses at 6.5–70 K. We observed for the first time in a rare-earth glass system a change in the temperature dependence of $\Delta\nu_H$ from $T^{1.9\pm0.1}$ at high temperature to $T^{1.3\pm0.1}$ below 40 K.

There have been few studies of the Yb-doped systems because of the energy of the $^2F_{5/2}$-$^2F_{7/2}$ transition of $\sim10\,000$ cm$^{-1}$, which is beyond the range of most tunable lasers and photomultipliers. The only previous reported study of homogeneous linewidths in $Yb^{3+}$-doped glasses[9] was limited to temperatures $>100$ K by the resolution of the 1.0-m Cerny-Turner spectrometer and the high excitation powers used.

We have developed a high-power pulsed narrow-band tunable laser based on the LiF:F$_2^+$ color center, which is ideally suited for FLN studies of $Yb^{3+}$ glasses.[10] It has a 3.0-GHz spectral width and is tunable throughout the inhomogeneously broadened $^2F_{5/2}$-$^2F_{7/2}$ transition, delivering peak powers of 3–5 kW in $\sim5$-ns pulse. The laser system is triggered by a mechanical chopper that blocks the fluorescence observation path while the laser is fired. This prevents saturation of the detection electronics by scattered laser light.[11] The laser wavelength was monitored by directing a fraction of the laser into a 1.0-m Ebert-Fastie spectrometer and observing the signal with a S-1 photomultiplier. The laser was tuned to wavelengths near the peak of the absorption of the $^2F_{7/2}(1)$-$^2F_{5/2}(1)$ transition. The fluorescence spectrum was measured with a pressure-scanned Fabry-Perot etalon spectrometer, with a typical finesse of 17 and a free spectral range of either 30 or 90 GHz. A Varian VPM-159A photomultiplier was used to

detect the fluorescence. The InGaAsP photocathode of this device has an unsurpassed sensitivity at these wavelengths, but is unstable at room temperature and no longer commercially available. The signal was converted to pulses by a 50-MHz amplifier discriminator and counted by a gated counter, whose output was recorded by a plotter. Typical peak signal levels were less than 30 KHz, and the signals were averaged over between 50 and 200 laser shots. Laser profiles were measured frequently during an experimental run by scattering laser light off the sample holder through the collection optics to the etalon spectrometer and then scattering the light again at the input pinhole to the spectrometer with a frosted glass plate. The laser signal was measured using a boxcar averager.

Two glass samples were used in these studies; their compositions and spectral properties are listed in Table I. The samples were cut and polished into $\sim0.2\times0.5\times1.0$-cm$^3$ pieces and attached to the sample holder with copper tape and General Electric 7031 varnish. Calibrated germanium and platinum resistance thermometers were attached to the sample holder in a similar manner. The samples were placed in a Janis Super Varitemp gas-flow cryostat and were cooled by flowing helium gas. The temperature of the samples was controlled by varying the current through a heating coil wrapped around the copper vaporizer at the bottom of the cryostat. This method minimized problems due to the poor thermal conduction of the glass samples at low temperature.

The data were entered into a computer using an interactive digital plotter. Because of the comparable resolution of the laser system and the etalon spectrometer, the laser profiles were fit to convolutions of an Airy function as mea-

TABLE I. Compositions and spectral properties of the $^2F_{5/2}(1)$-$^2F_{7/2}(1)$ transition of glasses.

|  | Silicate |  | Phosphate |  |
| --- | --- | --- | --- | --- |
| Composition (mole %) | $Yb_2O_3$ | 0.05 | $Yb_2O_3$ | 0.05 |
|  | $SiO_2$ | 74.95 | $P_2O_5$ | 67.45 |
|  | $Na_2O$ | 15.0 | $Al_2O_3$ | 22.5 |
|  | BaO | 5.0 | $Na_2O$ | 10.0 |
|  | ZnO | 5.0 |  |  |
| Inhomogeneous width | 60 cm$^{-1}$ |  | 50 cm$^{-1}$ |  |
| Peak absorption | $\sim974$ nm |  | $\sim975$ nm |  |

sured by the response of the etalon system to a He-Ne laser and a Gaussian representing the color-center laser. The resultant profile was then convolved with a Lorentzian used to model the fluorescence profile, which was varied using a grid search routine to determine the best fit to the observed spectrum. The full width at half maximum of the Lorentzian fluorescence profile is twice the homogeneous width of the transition.[12]

The results of the computer fits to the line profiles for the phosphate glass are shown in Fig. 1 in a log-log plot. The two lines are power-law fits to the data above and below 40 K, with $\Delta\nu_H \propto T^{1.8}$ and $T^{1.3}$, respectively. Similar behavior is observed in the magnitude and temperature dependence in the silicate glass, with $\Delta\nu_H \propto T^{1.3}$ below 40 K and $\propto T^{2.0}$ above. The data are inconsistent with an exponential dependence on temperature.

In comparing these data to previous results, it is observed that the magnitude of the broadening is always less in $Yb^{3+}$-doped glasses than that observed in other rare-earth metals in glasses at the same temperature[3,13-18] despite the weaker temperature dependence below 40 K. Above 40 K, the width parallels that observed in the other rare-earth transitions that have been studied. There have been few FLN studies of rare-earth ions below 40 K[13,14] due to the high spectral resolution required. These studies indicate that the $T^2$ dependence continues at least to 10 K for the $^3P_0$-$^3H_4(1)$ transition of $Pr^{3+}$ and the $^5D_0$-$^7F_0$ transition of $Eu^{3+}$ in inorganic glasses. Other techniques, such as spectral hole burning[3] or photon echoes,[2] are limited to temperatures below $\sim 20$ K by the power required to burn holes in the former case and the required temporal resolution in the latter. Confirmation of the $\sim T^2$ dependence of the width of the $^5D_0$-$^7F_0$ transition has been made by spectral hole-burning measurements at 1.6 K, while measurements of the $^1D_2(1)$-$^3H_4(1)$ transition of $Pr^{3+}$ in silicate glass reveal a $T^{1 \pm 0.2}$ behavior from 1.6-20 K.[3] The width
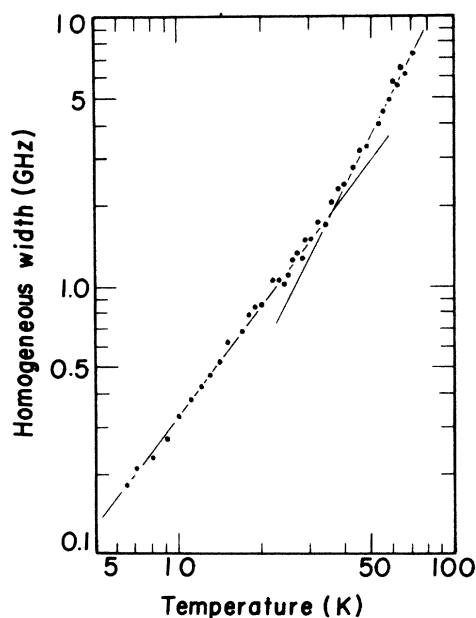


FIG. 1. Homogeneous linewidth of $^2F_{5/2}(1)$-$^2F_{7/2}(1)$ transition of $Yb^{3+}$ in phosphate glass as a function of temperature. The two lines are power-law fits to the data with $\Delta\nu_H \propto T^{1.3}$ and $T^{1.8}$.

of the latter transition is a factor of 10 greater than that observed in $Yb^{3+}$ over most of this temperature range. Accumulated photon-echo[19] experiments confirm the $^1D_2(1)$-$^3H_4(1)$ results and were also used to study the $^4G_{5/2},^2G_{7/2}$-$^4I_{9/2}$ transition of $Nd^{3+}$, which exhibited a $T^{2.2}$ behavior down to 10 K.[18]

The observation of a change in temperature dependence in the present study is unique among the reported data, although such a change is predicted to occur between 1.0 and $\sim 10$ K for the $^4F_{3/2}$-$^4I_{9/2}$ transition of $Nd^{3+}$, from comparison of the photon echo[2] and recent FLN measurements.[20] None of the current theories of line broadening in glasses predict such a break for broadening due to a single mechanism. A $T^2$ dependence at temperatures greater than one-half the Debye temperature is predicted for a Raman process in crystalline hosts, as is observed.[21] The observation of a change in the temperature exponent could be indicative of the limit of dominance of the TLS over the Raman process. It has been pointed out that the anomalous low-energy density of phonon states in glasses could extend the interval over which the Raman process varies as $T^2$ to lower temperatures,[22] though it seems unlikely that this could account for data at temperatures as low as 1.6 K.

Current theories of line broadening due to TLS's predict a variation in the observed temperature dependence of $\Delta\nu_H$ on the coupling of the rare-earth ion and the TLS and on the energy density of states of the TLS. The coupling between the rare-earth ion and the TLS is assumed to be dominated by one term in a multipolar expansion of the interaction and is characterized by the parameter $n$ for an interaction of the form $A/r^{2n}$. The energy density of states of the TLS varies as $E^\mu$, where $\mu$ is expected to be near zero. Specific-heat measurements indicate that $\mu = 0.3$ in $SiO_2$.[23]

Lyo[7] has calculated the temperature dependence of $\Delta\nu_H$, assuming an electrostatic coupling between the rare-earth ion and the TLS, with the result that $\Delta\nu_H \propto T^{4+\mu-9/n}$. With $\mu = 0.3$ the model suggests a dipole-dipole coupling of the rare-earth ion and the TLS. Recently, Lyo and Orbach[8] have extended the theory to include the effects of fractons[24] on $\Delta\nu_H$. This introduces the parameter $\bar{d}$, the spectral dimensionality of Ref. 24, into the temperature dependence. Their result is that for $\mu = 0$, $\Delta\nu_H \propto T$ for dipole-dipole, $\propto T^{1+\bar{d}/4}$ for dipole-quadrupole, and $\propto T^{1+2\bar{d}/5}$ for quadrupole-quadrupole coupling. If we use the value of $\bar{d} = \frac{4}{3}$ as found by Alexander and Orbach[24] for percolating networks, the low-temperature data are consistent with a quadrupole-dipole coupling. It was suggested by Lyo and Orbach that fractons are important at temperatures corresponding to vibrational energies with wavelengths shorter than the length where the fractal system begins to exhibit self-similarity. It is not clear at present how inorganic glasses can be described by fractals.

Huber, Broer, and Golding[6] have suggested that the electrostatic interaction is too small to account for the observed linewidth of rare earths in glasses, and have proposed a model based on an elastic interaction. Their result is that $\Delta\nu_H \propto T^{1+\mu}$ for a dipole-dipole coupling, the same as the Lyo-Orbach theory.[7,8] The decay of the coherence function of the excited state departs from an exponential for couplings of higher order than dipole-dipole. This was not observed in the photon-echo experiment carried out on the $Nd^{3+}$-doped fiber.[2] Nonexponential decay of the coherence function would result in a non-Lorentzian line shape in FLN experiments. It is doubtful that the data presented

here are of sufficient quality to allow a determination of the coupling through a line-shape analysis.

In summary, we have observed a change in the temperature dependence of the homogeneous linewidth of $Yb^{3+}$ in inorganic glasses from $T^{1.9}$ to $T^{1.3}$ below 40 K. The small homogeneous broadening of the $Yb^{3+}$ transition, relative to that observed for other rare-earth ions, may be responsible for the observation of the weaker TLS-mediated dephasing at temperatures as high as 40 K, while similar behavior is observed in $Nd^{3+}$ only below 1 K. This is probably due to the weak dipole moment of the $Yb^{3+}$ ion, as reflected by the long radiative lifetime (3 ms) of the excited state, reducing the effectiveness of the Raman process. The linear temperature dependence of the $^1D_2$-$^3H_4$ homogeneous width is inconsistent with this picture, however, as is the $T^2$ dependence observed in $Eu^{3+}$ at 1.6 K. Clearly, further studies of dephasing below 40 K are called for to understand fully the origin of low-temperature broadening in glasses.

*Present address: National Bureau of Standards, Gaithersburg, MD 20899.

[1] For a review of laser spectroscopy in glasses, see M. J. Weber, in *Laser Spectroscopy of Solids,* edited by W. M. Yen and P. M. Selzer (Springer-Verlag, Berlin, 1981).

[2] J. Hegarty, M. M. Broer, B. Golding, J. R. Simpson, and J. B. MacChesney, Phys. Rev. Lett. **51**, 2033 (1983).

[3] R. M. Macfarlane and R. M. Shelby, Opt. Commun. **45**, 46 (1983).

[4] S. Völker, R. M. Macfarlane, A. Z. Genack, H. P. Trommsdorff, and J. H. van der Waals, J. Chem. Phys. **76**, 1926 (1977).

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

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

[7] S. K. Lyo, Phys. Rev. Lett. **48**, 688 (1982).

[8] S. K. Lyo and R. Orbach, Phys. Rev. B **29**, 2300 (1984).

[9] M. J. Weber, J. A. Paisner, S. S. Sussman, W. M. Yen, L. A. Riseberg, and C. Brecher, J. Lumin. **12/13**, 729 (1976).

[10] R. T. Brundage and W. M. Yen, Appl. Opt. **24**, 3687 (1985).

[11] M. M. Broer, C. G. Levey, and W. M. Yen, Rev. Sci. Instrum. **54**, 76 (1983).

[12] John Hegarty, R. T. Brundage, and W. M. Yen, Appl. Opt. **19**, 1889 (1980).

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

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

[15] J. M. Pellegrino, W. M. Yen, and M. J. Weber, J. Appl. Phys. **51**, 6332 (1981).

[16] J. R. Morgan and M. A. El-Sayed, Chem. Phys. Lett. **84**, 215 (1981).

[17] P. Avouris, A. Campion, and M. A. El-Sayed, J. Chem. Phys. **67**, 3397 (1977).

[18] R. M. Shelby, Opt. Lett. **8**, 88 (1983).

[19] W. H. Hesselink and D. A. Wiersma, Phys. Rev. Lett. **43**, 1991 (1979).

[20] R. T. Brundage, S. I. Yun, Ronald J. Tonucci, and W. M. Yen, J. Non-Cryst. Solids (to be published).

[21] R. Flach, D. S. Hamilton, P. M. Selzer, and W. M. Yen, Phys. Rev. B **15**, 1248 (1977).

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

[23] C. Casjaunios, A. Ravex, M. Vandorpe, and S. Hunklinger, Solid State Commun. **17**, 1045 (1975).

[24] S. Alexander and R. Orbach, J. Phys. (Paris) Lett. **43**, L625 (1982).