the experimental value of R is decreasing as $T-T_c \rightarrow 0-$.

[13] Y. Suezaki and H. Mori, Prog. Theor. Phys. 41, 1177 (1969); also see S. Takada, Prog. Theor. Phys. 46, 15 (1971).

[14] Throughout this Letter we neglect weakly temperature-dependent prefactors.

[15] It has been pointed out to us (by J. Torrance) that a linear $\ln\rho$-versus-T^{-1} plot does not guarantee that $\langle\Delta\rangle$ = const but merely that $\langle\Delta\rangle = \Delta_0 - AT$, where A is arbitrary. Such a temperature dependence for $\langle\Delta\rangle$ is clearly noncritical and would not affect the major conclusions of this Letter.

[16] C. S. Jacobsen, D. B. Tanner, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 33, 1559 (1974).

[17] We cannot rule out the possibility that the sharp apparent saturation of $\langle\Delta\rangle$ might be related to the unusual change in the a-axis lattice constant below 47 K (see Ref. 6).

[18] We assume a two-component order parameter.

[19] J. C. Scott, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 3131 (1974).

[20] See, for example, M. E. Fisher and R. J. Burford, Phys. Rev. 156, 583 (1967).

[21] T. Kasuya and A. Kondo, Solid State Commun. 14, 249 (1974).

[22] Experimentally we find the critical exponent for the divergence in dR/dT to be 1.09 ± 0.15. Thus R itself is weakly divergent.

[23] D. Guidotti and P. M. Horn, to be published.

Anomalous Fluorescence Linewidth Behavior in Eu^{3+}-Doped Silicate Glass*

P. M. Selzer, D. L. Huber, and D. S. Hamilton
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

and

W. M. Yen
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706, and Lawrence Livermore Laboratory, Livermore, California 94550
and

M. J. Weber
Lawrence Livermore Laboratory, Livermore, California 94550

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We compare optical-homogeneous-linewidth measurements for the resonant $^5D_0 - {}^7F_0$ transition of Eu^{3+}-doped silicate glass and $YAlO_3$, using fluorescence line narrowing. The linewidth in the amorphous host is two orders of magnitude larger than in the crystal and exhibits an unusual temperature dependence. This behavior indicates an additional ion-lattice linewidth mechanism probably arising from an interaction between the Eu ions and "disorder modes" in the glass. Possible models are discussed.

Since the discovery of the anomalous low-temperature specific heat of amorphous materials by Zeller and Pohl in 1971,[1] there has been a renewed interest in the thermal and optical properties of these systems. Recent nuclear-spin-relaxation,[2] ultrasonic-attenuation,[3] Raman-scattering,[4] and infrared-absorption[5] experiments have all confirmed the existence of low-energy "disorder modes," consistent with the theory of Anderson, Halperin, and Varma[6] and Phillips.[7] These modes are associated with groups of atoms which can sit in either of two equilibrium positions, separated by potential barriers of varying heights.

In this Letter, we report on optical-linewidth measurements, using fluorescence line narrowing[8] (FLN) of the rare-earth ion Eu^{3+} doped into silicate glass at 2.6 mol%. Our results show an unusual temperature dependence for the homogeneous linewidth, never observed previously, and significantly different from that found in crystals. It indicates an additional ion-lattice linewidth mechanism which probably arises from an interaction between the Eu ions and the ensemble of two-level systems (TLS) comprising these "disorder modes."

It is well known that for an optically active impurity ion in a solid, homogeneous linewidths generally result from nonradiative relaxation processes, either longitudinal or transverse, mediated by lattice phonons. The ion-lattice coupling strength and the phonon density of states determine the magnitude of the linewidth; its temperature dependence reflects phonon occupation numbers and the type of process involved (direct, Raman, or Orbach).[9]

In order to overcome the extreme inhomogeneous broadening of optical transitions in impurity-doped glasses,[10] we have used FLN, whereby a laser pulse much narrower spectrally than the inhomogeneous width of the transition interacts with only a small population of ions in resonance with the exciting beam. It has recently been shown, however, that the true homogeneous width can only be extracted from measurement of a resonant transition (i.e., fluorescence of the same frequency as the exciting light).[11] We have therefore obtained linewidth measurements on the very weak $^5D_0$-$^7F_0$ resonant Eu^{3+} transition, centered at 17300 cm^{-1}, whose homogeneous width at 2 K is found to be less than 10^{-5} that of the inhomogeneously broadened line. These levels are particularly attractive for this study since the $J = 0$ states have no Stark splitting, thereby leaving very few channels for ion-phonon relaxation and greatly simplifying the analysis. In order to illustrate the unique linewidth behavior in the glassy host, its temperature dependence is compared with that of the same transition for Eu in a crystal with low site symmetry: 0.25-mol% Eu-doped $YAlO_3$. Since the impurity ion in both glass and crystal have an oxygen coordination and their energy level schemes are closely matched, their ion-lattice coupling strengths should be of comparable magnitude.

The $^5D_0$ state in both systems was excited by a high-resolution nitrogen-pumped dye laser[12] using rhodamine 6G dye. Three methods were used to obtain linewidths in different temperature regimes. For the 1.7-2-K range, the sample was immersed in superfluid He. An external confocal etalon and single-stage optical amplifier cell[13] were used to generate a laser linewidth of approximately 50 MHz. For temperatures above 7 K, the samples were carefully thermally connected to the cold finger of a variable-temperature Dewar. In this range only the intracavity etalon was used, resulting in a 1-GHz laser linewidth but considerably better signal-to-noise ratio. In both cases the fluorescence was analyzed with a pressure-scanned Fabry-Perot interferometer with a typical finesse of 25, whose free spectral range varied between 4.2 and 150 GHz depending on the plate spacing. For the highest-temperature measurements on the glass, a 1-m spectrometer was employed instead of the interferometer.

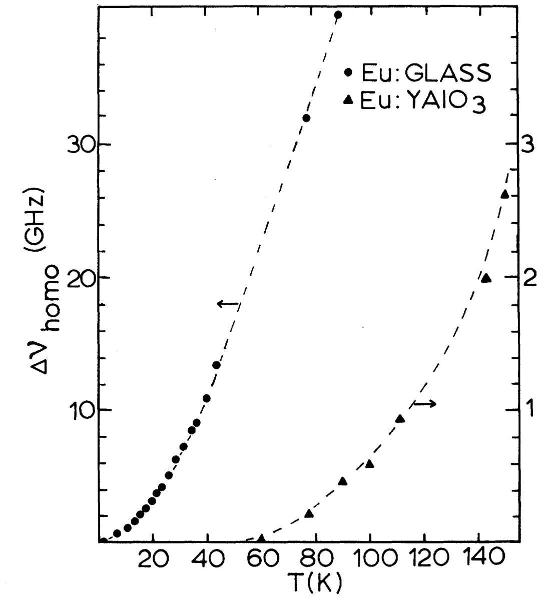

FIG. 1. Temperature dependence of the homogeneous linewidth for the $^5D_0$-$^7F_0$ resonant transition in 2.6-mol% Eu^{3+}-doped silicate glass and in 0.25-mol% Eu^{3+}-doped $YAlO_3$. The silicate glass has the following composition in mol%: 72% SiO_2, 15% Na_2O, 5% BaO, 5% ZnO, and 3% Eu_2O_3. The site symmetry for Eu^{3+} in $YAlO_3$ is C_{1h}.

Since the resonant fluorescence is quite weak, a gated photon-counting scheme was used for all linewidth measurements. By examining the fluorescence at different delays after the 10-nsec excitation pulse, we were able to assess the contributions of radiation trapping, nonradiative energy transfer, or other possible time-dependent effects (see discussion below). In the glass, no time dependence of the narrowed fluorescence profile was observed below room temperature. In the crystal, however, radiation trapping at low temperatures necessitated a small gate width, zero delay, and careful attention to geometry.

The date from our homogeneous-linewidth measurement is shown in Fig. 1. These points are derived from the expression[11] (assuming Lorentzian profiles)

$$\Delta\nu_{meas} = \Delta\nu_{instrument} + 2\Delta\nu_{homo}. \tag{1}$$

It is apparent that the lifetime broadening due to nonradiative relaxation is significantly greater in the glass than in the crystal, with glass linewidths typically two orders of magnitude larger.

To illustrate more clearly the different temperature dependence of the two systems, Fig. 2 gives a log-log plot of the same data. It is seen that between 7 and 80 K the glass linewidth can be described by a T^{α} dependence, where $\alpha = 1.8 \pm 0.2$. In contrast the crystal data are inconsistent with a power-law behavior: The homoge-

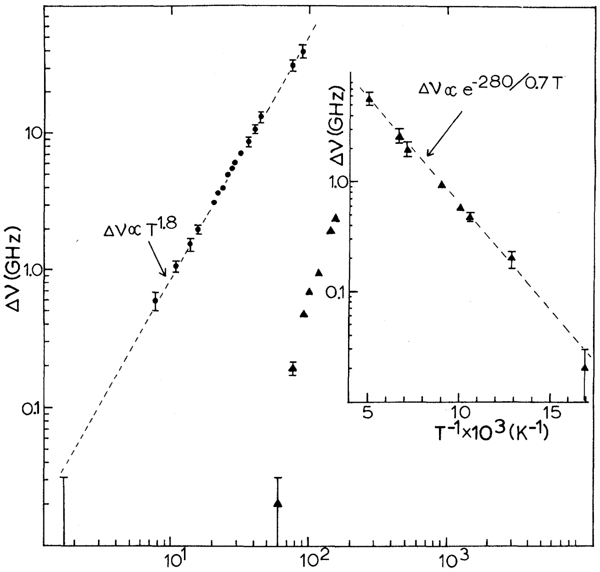

FIG. 2. Log-log plot of the data from Fig. 1, using the same symbols. Inset is a semilog plot of the Eu:$YAlO_3$ data with an exponential fit. The Boltzmann factor, k, is in units of cm^{-1} K^{-1}.

neous linewidth of ions in crystals can be fitted by a combination of direct and Raman processes, with the direct dominating at lower temperatures (typically below 100 to 200 K).[9] Because of the simplicity of the Eu^{3+} level scheme, with only the lowest $^7F_1$ level at a distance of approximately 280 cm^{-1} above the ground state likely to contribute to the direct term below room temperature, the dependence of the linewidth below 200 K might be expected to be fitted by an exponential expression with but a single adjustable parameter:

$$\Delta\nu_{\text{homo}} \simeq Ae^{-\Delta E/kT}, \tag{2}$$

where $\Delta E = 280$ cm^{-1}. The inset in Fig. 2 shows a semilog plot of the crystal data and a calculated fit from Eq. (2). Our results are clearly consistent with this type of behavior.

In the glass, the lowest $^7F_1$ level is 150 cm^{-1} above the ground state for ions excited at 17 360 cm^{-1}.[14] Thus, one would again expect a similar exponential linewidth dependence with $\Delta E = 150$ cm^{-1} and perhaps an additional T^7 component from the Raman contribution at higher temperatures. (The T^7 behavior comes from assuming the usual Debye-like density of phonon states, which is shown to be a reasonable approximation within a limited range, even for the glass.[1]) The unequivocal deviation from this type of behavior and the significantly broader linewidths indicate an additional ion-lattice relaxation mechanism not present in crystals.

Recent measurements on nuclear spin-lattice relaxation in amorphous materials[2] have revealed an additional contribution to T_1 compared with the same substance in crystalline form, which has a $T^{-\alpha}$ temperature dependence, with $1 < \alpha < 2$ over the interval $1.2 < T < 100$ K. In particular, in the case of $(Na_2O)_{0.3}(SiO_2)_{0.7}$, a system roughly comparable to ours, Szeftel and Alloul[15] find $\alpha = 1.4 \pm 0.1$ for the ^{23}Na nucleus. The similarities in the temperature dependence as well as in the magnitudes relative to the crystalline counterparts suggest that the same mechanism is responsible for both the T_1 behavior and the homogeneous linewidth. In both cases the effects are attributed to the random modulation of the crystalline field arising from incoherent transfer between different configurations of the ensemble of TLS. By exploiting the analogy between the TLS and a spin-$\frac{1}{2}$ system we can derive an expression for the optical linewidth which takes the form

$$\Delta\nu = \pi \sum_{ij} A_{oi} A_{oj} \int_{-\infty}^{+\infty} dt \, \langle [S_z^{\,i}(t) - \langle S_z^{\,i} \rangle][S_z^{\,j}(0) - \langle S_z^{\,j} \rangle] \rangle, \tag{3}$$

where A_{oi} is the shift in the optical frequency brought about by a spin flip of the ith TLS, and the angular brackets denote a thermal average. After postulating exponential decay of the correlation function, which is characterized by a time τ_i, we obtain the result

$$\Delta\nu = 2\pi \sum_i \tau_i A_{oi}^2 (\tfrac{1}{4} - \langle S_z^{\,i} \rangle^2) = \tfrac{1}{2}\pi \sum_i \tau_i A_{oi}^2 \operatorname{sech}^2(E_i/2kT) = \tfrac{1}{2}\pi \int_0^\infty dE [\tau A_0^2(E)]_{\text{ave}} n(E) \operatorname{sech}^2(E/2kT), \tag{4}$$

where $[\tau A_o^2(E)]_{\text{ave}}$ is the average of $\tau_i A_{oi}^2$ over the TLS with energy splittings E and $n(E)$ is the density of states of the TLS.

Assuming a constant density for those states contributing significantly to the integral, we obtain the result that $\Delta\nu$ is approximately proportional to T (compared to the experimental value $T^{1.8 \pm 0.2}$) only if $[\tau A_o^2]_{\text{ave}}$ is a constant or more generally a weak function of E and T. If we make the plausible assumption that A_o^2 is independent of energy, we conclude that the average correlation time τ_{ave} must be approximately constant. A constant value rules out a significant contribution to the correlation time from TLS relaxation processes involving the absorption or emission of real phonons.[2] Alternative TLS relaxation mechanisms postulate the transfer of excitation between TLS with approximately the same energy. Reinecke and Ngai[16] have discussed indirect transfers involving a nucleus (or Eu^{3+} ion in our case), which can be thought of as the Raman-like scattering of the TLS off the nucleus. With a constant density of states such a mechanism gives rise to a linewidth proportional to T.[17] In addition to Raman-like processes we believe that it is important to consider transfer mechanisms associated with the direct interaction between resonant TLS. Such interactions, which might arise, for example, from the absorption and emission of virtual phonons, can lead to a correlation time which is weakly dependent on T and E and thus (with a constant density of states) to a linewidth approximately proportional to T.[18]

Unfortunately it is not possible to obtain quantitative estimates of the linewidths associated with any of these mechanisms. We are able, however, to put an upper limit on τ_{ave} from our time-resolved measurements. If the correlation time were on the order of the radiative lifetime of the $^5D_0$ state (≈ 1 msec),[14] we would expect to observe shifts or changes in linewidths on this time scale. Using a 0.25-msec gate, we saw no detectable changes in line shape, width, or position when varying the delay between 0 and 2 msec in different temperature regions. Noting that the line shape appeared Lorentzian in all cases, we conclude that τ_{ave} must be $\ll 100$ μsec.

Further experiments are presently underway with different glass and crystalline hosts to determine the universality of this unusual linewidth behavior in amorphous materials.

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[1] R. C. Zeller and R. O. Pohl, Phys. Rev. B 4, 2029 (1971).

[2] M. Rubinstein, H. A. Resing, T. L. Reinecke, and K. L. Ngai, Phys. Rev. Lett. 34, 1444 (1975).

[3] B. Golding, J. E. Graebner, B. I. Halperin, and R. J. Schultz, Phys. Rev. Lett. 30, 223 (1973).

[4] G. Winterling, Phys. Rev. B 12, 2432 (1975).

[5] K. K. Mon, Y. J. Chabal, and A. J. Sievers, Phys. Rev. Lett. 35, 1352 (1975).

[6] P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. 25, 1 (1972).

[7] W. A. Phillips, J. Low. Temp. Phys. 7, 351 (1972).

[8] A. Szabo, Phys. Rev. Lett. 27, 351 (1971).

[9] For an excellent review, see B. DiBartolo, *Optical Interactions in Solids* (Wiley, New York, 1968), Chap. 15.

[10] L. A. Riseberg, Phys. Rev. Lett. 28, 789 (1972).

[11] T. Kushida and E. Takushi, Phys. Rev. B 12, 824 (1975).

[12] R. Flach, I. S. Shahin, and W. M. Yen, Appl. Opt. 13, 2095 (1974).

[13] R. Wallenstein and T. W. Hänsch, Opt. Commun. 14, 353 (1975).

[14] The splitting between the $^7F_0$ and $^7F_1$ levels varies between 300 and 150 cm^{-1} as a function of excitation frequency. We chose to pump the transition on the high-energy side to avoid the possibility of simultaneously exciting ions from the thermally populated $^7F_1$ level at higher temperatures. For a detailed discussion of the energy levels and lifetimes of this glass sample, see C. Brecher and L. A. Riseberg, Phys. Rev. B 13, 81 (1976).

[15] J. Szeftel and H. Alloul, Phys. Rev. Lett. 34, 657 (1975).

[16] T. L. Reinecke and K. Ngai, Phys. Rev. B 12, 3476 (1975). These authors attribute values of $\alpha > 1$ to a weak energy dependence of the density of states.

[17] Strictly speaking, the calculation of $\Delta\gamma$ with the Raman mechanism is carried out with Eq. (3) and does not involve the introduction of a correlation time.

[18] The analogy here is to a spin-$\frac{1}{2}$ system where the spins interact via a transfer term $t_{ij}(S_+^i S_-^j + S_-^i S_+^j)$. The correlation time is then on the order of $\hbar/\bar{t}_{ij}$, where $\bar{t}_{ij}$ is the average interaction between neighboring quasi-resonant (i.e., $|E_i - E_j| \lesssim t_{ij}$) TLS.