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FRACIONS AND THE HOMOGENEOUS LINEWIDTH OF THE $^5D_0 - ^7F_0$ TRANSITION IN Eu$^{3+}$-DOPED GLASSES

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Résumé - Les mesures du rétrécissement de la raie fluorescence résultant de la transition $^5D_0 - ^7F_0$ dans plusieurs verres dopés à l'Europium et ayant des structures différentes seront présentées. La largeur de raie homogène suit une loi de variation $T^2$ entre 30 et 300 K. Il a été montré que ce comportement peut être interprété à l'aide des procédés Raman avec des irrégularités dans les modes de vibration dues à la structure fractale du verre.

Abstract - Fluorescence line narrowing measurements of the $^5D_0 - ^7F_0$ transition in several structurally dissimilar Eu-doped glasses are presented. The homogeneous linewidth exhibits a $T^2$ dependence from 30 to 300 K. We show that this behavior can be accounted for by Raman processes with the anomalous vibrational modes of the fractal structure of the glass.

I - INTRODUCTION

By the use of high resolution lasers, subsets of ions within the inhomogeneously broadened spectral profile can be selectively excited in glasses so that their homogeneous linewidth can be measured. Hole-burning in absorption and fluorescence line narrowing (FLN) in emission make use of this technique. FLN experiments /1/ on Eu$^{3+}$ ions in a silicate glass have shown a homogeneous linewidth at low temperatures substantially larger than seen in crystals and a quadratic temperature dependence that is unexpected for any known linebroadening mechanism in crystals.

In this paper we report FLN measurements on Eu$^{3+}$ in three structurally dissimilar glasses at temperatures ranging from 10 to 300 K. A $T^2$ dependence for the homogeneous linewidth is observed in each of these lending support to the notion that this is a universal property of glasses. To account for these results, a simple model based on the fracton concept of Alexander and Orbach /2/ is developed for Raman and direct process broadening. Both the quadratic dependence and the approximate magnitude of the broadening are consistent with this model.

II - EXPERIMENTAL

Site selection was achieved with a nitrogen-laser-pumped tunable dye laser using coumarin dye. The 10 ns excitation pulse was narrowed to 0.15 cm$^{-1}$ by passing it through an extra-cavity etalon. The samples were mounted on the coldfinger of a closed-cycle helium cryostat permitting measurements between 10 and 300 K. The fluorescence was measured by a 1-m monochromator with slits set for 0.08 A. A shutter placed between the sample and the monochromator was opened 0.1 ms after the excitation, eliminating the possibility of contamination by scattered light. It has been shown elsewhere that energy transfer does not broaden the fluorescence on this time scale /3/.

The three europium doped glasses studied here had the following compositions in...
mole percent: lithium silicate glass (LS) 57.0 SiO₂, 27.5 Li₂O, 10.0 CaO, 2.5 Al₂O₃, 3.0 Eu₂O₃; sodium silicate glass (NS) 72.0 SiO₂, 15.0 Na₂O, 5.0 BaO, 5.0 ZrO, 3.0 Eu₂O₃; and potassium germanate glass (KG) 65.3 GeO₂, 17.0 K₂O, 17.0 BaO, 0.7 Eu₂O₃. The spectral properties of these glasses have been reported previously /3/.

For each glass excitation spectra were obtained at 577.5 nm and 580 nm on the high and low energy sides of the inhomogeneous profile of the ⁵D₀⁻⁷F₀ transition, respectively.

III - HOMOGENEOUS AND INHOMOGENEOUS BROADENING OF THE FLN LINEWIDTH

The temperature dependence of the FLN linewidth is shown in Fig. 1. These data have been reduced using the approximation of Kushida and Takushi /4/ for a resonantly excited transition,

\[ 2\Delta v = \Delta v_{\text{obs}} - \Delta v_{\text{res}} \]  

where \( \Delta v \) is the linewidth of the transition, \( \Delta v_{\text{obs}} \) is the measured fluorescence linewidth, and \( \Delta v_{\text{res}} \) is the instrumental resolution.

\[ \text{TEMPERATURE (K)} \]

\[ \text{LINEWIDTH (cm}^{-1}\text{)} \]

Fig. 1 - FLN linewidth on the high and low energy sides of the inhomogeneous profile. Δ denotes excitation at 577.5 nm; O, at 580 nm. The residual broadening at low temperatures is due to imperfect site selection as discussed in the text.

At high temperatures each linewidth has an approximately quadratic temperature dependence, but approaches a temperature-independent limit at low temperatures. This limiting value is about an order of magnitude larger than our experimental resolution. We interpret it as residual inhomogeneous broadening due to imperfect site selection. We note in this regard that such a limiting value was not observed by Selzer, et al. /1/ using a laser with an order of magnitude smaller linewidth. The reduction in the inhomogeneous linewidth by site selection makes it possible to deconvolute the homogeneous and inhomogeneous contributions by the same techniques used in crystalline hosts. The results of this procedure are displayed in Fig. 2.
Fig. 2 - Homogeneous linewidth after subtraction of the residual inhomogeneous broadening. Symbols are as in Fig. 1. All data are consistent with a $T^2$ dependence as shown by the lines.

All the homogeneous linewidths are consistent with a $T^2$ dependence over the entire temperature range. One notes, however, that the homogeneous linewidth is smaller on the high energy side of the inhomogeneous profile than on the low energy side in the LS glass. This behavior differs from that seen in the NS and KG glasses and also from the results of Morgan, et al., for a variety of glasses at room temperature /5/. This provides a clear indication that a quadratic temperature dependence may be a universal property of otherwise dissimilar glasses.

IV - FRACTONS AND THE HOMOGENEOUS LINewidth

The idea that systems with fractal structure might have an anomalous vibrational density of states was introduced by Stapleton, et al. /6/ to explain the spin-lattice relaxation time seen in iron-containing proteins. This has led to the elegant development of the "fracton" model of localized vibrations on fractal structures by Alexander and Orbach and co-workers /2,7/. They have shown that plane waves are a poor representation of the vibrational modes except at long wavelengths. They find a critical length scale $L$ for the Debye approximation, on shorter scales, the vibrations (now called fractons) are localized. The density of states for the vibrations is then

$$g_p(\omega) = d(d/L)^d\omega^{-1}/\omega_0^d \quad 1 > L$$

$$g_F(\omega) = d(d/L)^d\tilde{\omega}^{-1}/\omega_L^d \quad 1 < L$$

where $\omega_0$ and $\omega_F$ are the frequencies of the Debye phonons and fractons of characteristic length $L$; $d$, and $\tilde{d}$ are the Euclidean and Fracton dimensionalities.

The linewidth due to interaction of the electronic states with the vibrational strain field via direct processes generally has the form
\[ \Delta \nu_D = \left( \frac{2 \pi}{\hbar} \right) \sum \left| \langle \epsilon' | \epsilon \rangle \right|^2 \frac{s}{c} \langle \nu' | \nu \rangle \langle \nu' \rangle \langle \nu \rangle \delta (\hbar \omega - \Delta_j) g(\omega) d\omega, \]

and the Raman broadening is

\[ \Delta \nu_R = \left( \frac{4 \pi^2}{\hbar} \right) \left| \langle \epsilon' | \epsilon \rangle \right|^2 \sum \langle \nu' | \nu \rangle \langle \nu' \rangle \langle \nu \rangle \delta (\hbar \omega - \Delta_j) g(\omega) d\omega \]

where \( \langle \nu' | \epsilon | \nu \rangle \) is a matrix element of the average local strain, \( \langle \epsilon' | \epsilon | \rangle \) is the electrostatic matrix element for the direct or Raman process and \( \Delta_j \) is the splitting to the \( j \)th neighboring electronic state. These expressions give the conventional results for crystals when the Debye approximation is used. They may be applied to the glass problem using the dispersion relation /2/ for the fracton \( \omega = 1 - \theta / \alpha \) on a self-similar fractal of Hausdorff dimensionality \( \alpha \) and noting that the average local strain from a normal mode with amplitude \( Q \) and localization \( \ell \) should scale as \( Q/\ell \). For a direct process the temperature dependence of the linewidth will be dominated by the thermal population of vibrational quanta with energy \( \Delta_j \) as in crystals, but the magnitude will be changed in proportion to the density of states at that energy. For Raman processes one has

\[ \Delta \nu_R = a(T/\theta_0)^{\alpha} \int \frac{g(\omega)}{T} x^\alpha \exp(x-1) dx \]

\[ + A(T/\theta_L)^{p+1} \int \frac{g(\omega)}{T} x^p \exp(x-1) dx, \]

where the first integral is over the Debye-like modes and the second is over the fractons. The exponent \( p = 2\alpha (2/\alpha + 1) - 4 \). For fractal structures in a 3 dimensional glass, one has \( 3/\alpha > 2.5 \), the value for a critically percolating cluster. Alexander and Orbach /2/ conjecture that \( \alpha \) is universally \( 4/3 \); the effective medium approxima-

Fig. 3 - Contribution of the fractons to the homogeneous linewidth via Raman processes. Curve A: \( \alpha = 3, \beta = 4/3 \); curve B: \( \alpha = 2.5, \beta = 4/3 \); curve C: \( \alpha = 3, \beta = 1 \); curve D: \( \alpha = 2.5, \beta = 1 \). Note that each curve is approximately \( T^2 \) for \( T/\theta_L > 3 \). \( \theta_L \) is expected to be roughly 10 K.
tion /7/ gives \( \tilde{d} = 1 \). The specific heat of epoxy can be fit /7/ above 1 K with \( \tilde{d} = 1.3, \theta_L = 14 \) K and \( \theta_D = 29 \) K. Fig. 3 shows numerical results for the fracton contribution to the linewidth. A \( T^2 \) dependence is expected for the broadening throughout the range of our experiment if the \( \theta \)'s for our glasses are similar to those for epoxy. The contribution from the Debye-like modes is negligible at these temperatures. Similarly, the parameter \( A \) that governs the magnitude of the Raman broadening can be estimated from the McCumber and Sturge /8/ a parameter for a crystal with the same average density and sound velocity as the glass. This equivalent \( A \) is given by

\[
A = A_0 \frac{10}{(\theta_L^3 \theta_X^7)}
\]

where \( \theta_X \) is the Debye temperature of this equivalent crystal. In our glasses the homogeneous linewidth is \( \approx 10^{-4} \) \( \text{cm}^{-1} \), giving \( A = 10^2 \) cm\(^{-1} \) which is the same magnitude seen for rare earth transitions in crystals. Thus, the electron-fracton Raman process accounts for both the magnitude and temperature dependence of the homogeneous broadening in glasses. As the glass structure enters the model through \( A \), Fig. 3 suggests only a weak structural dependence if the Alexander and Orbach conjecture holds.

It is also of interest to compare the magnitude of the direct process broadening in glass to that seen in crystals. For the same equivalent crystal used to compare the Raman broadening, \( \Delta \nu_{\text{Glass}} = \Delta \nu_{\text{Xtal}} \) for \( \Delta_J / \tilde{R} < \omega_0 \); \( \Delta \nu_{\text{Glass}} = \Delta \nu_{\text{Xtal}} + \Delta \nu_{\text{Fracton}} \) for \( \omega_L < \Delta_J / \tilde{R} < \omega_0 \); and \( \Delta \nu_{\text{Glass}} = \Delta \nu_{\text{Xtal}} \) for \( \Delta_J \omega_0 \). Assuming the same coupling strength \( \langle \epsilon' \nu_0 \rangle \epsilon \rangle \) in both the glass and the crystal, the fracton contribution to the direct process broadening is \( \Delta \nu_{\text{Fracton}} = \Delta \nu_{\text{Xtal}} (1/3) \omega_0^5 \omega_L^{-q} (\Delta J / \tilde{R})^q \) where \( q = d (i + 2/3) \). Since the lowest level for a direct process is \( \approx 250 \) cm\(^{-1} \) above the ground state in Eu\(^{3+} \), no observable direct process contribution to the linewidth is expected at the temperatures of these experiments.

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