

Fracton contribution to the optical linewidth in glasses

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We use the previous formalism of Lyo [Phys. Rev. Lett. **48**, 688 (1982)] for optical linewidths of paramagnetic impurities in glasses to include the effects of fractal excitations (fractons). We find the optical-linewidth temperature dependence for interactions between the two-level systems and the optically active center of dipole-quadrupole and quadrupole-quadrupole character to be $T^{1+(\bar{d}/4)}$ and $T^{1+(2\bar{d}/5)}$, respectively, where \bar{d} is the spectral dimensionality of Alexander and Orbach. Use of the percolating network value for \bar{d} , $\frac{4}{3}$, predicts a temperature dependence $T^{1.33}$ for the former coupling in reasonable agreement with very recent experimental results of Völker and collaborators in organic glasses.

I. INTRODUCTION

Very recently, Lyo¹ derived a general form for optical transition linewidths in glassy hosts. His theory invoked the diagonal modulation of the optical transition energy by virtue of the electrostatic coupling of the optical species to the two-level systems (TLS) found in nearly all amorphous materials. The time dependence of the modulation originates in the phonon relaxation of the TLS energy levels. The purpose of this Brief Report is to exhibit the form for the temperature dependence of the optical linewidth if fractons² replace the phonons as the fundamental vibrational excitation mode. It is now thought (by some³) that thermal and transport properties of glasses may be dominated by fractons at excitation energies greater than a characteristic crossover energy, itself inversely proportional to the characteristic length below which the fractal structure becomes evident.

II. INTRODUCTION OF FRACTONS IN LYO'S LINEWIDTH FORMULA

Lyo¹ has found the following expression for the phonon modulated optical-center-TLS interaction contribution to the optical linewidth:

$$\Delta\omega = 2 \int dE \rho(E) \langle (4\pi/3)r_c^3 \Sigma_{\pm} P_{\pm}(E) \Gamma^{\pm}(E) \rangle_{av} , \quad (1)$$

where $\rho(E)$ is the energy density of the TLS states at splitting energy E ; r_c is a characteristic cutoff radius, such that only TLS for spatial separations from the fluorescing species $r < r_c$ contribute to the linewidth; $P_{\pm}(E)$ are the thermal populations of the (upper or lower) TLS states; and $\Gamma^{\pm}(E)$ is the lifetime broadening of the same state. Lyo shows¹

$$1/r_c^s \sim E^3 , \quad (2)$$

where s is a measure of the range dependence of the TLS-fluorescing species interaction ($s = 3, 4, 5$ for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively). He also takes

$$\Gamma^{\pm} \propto E^3 [n_E + (\frac{1}{2})(1 \pm 1)] , \quad (3)$$

where n_E is the Bose occupation number of the TLS with splitting E . Both factors, Eqs. (2) and (3), have been computed on the basis of TLS-phonon interactions. Following the rules of Ref. 2, it is easy to show that for TLS-fracton interactions, these factors become ($\hbar\omega = E$)

$$1/r_c^2 \sim \omega^{\bar{d}} \quad (2')$$

and

$$\Gamma^{\pm} \propto \omega^{\bar{d}} [n_E + (\frac{1}{2})(1 \pm 1)] , \quad (3')$$

where \bar{d} is the spectral dimension which generates the fracton density of states [$N_{fr}(\omega) \sim \omega^{\bar{d}-1}$]. Inserting Eqs. (2') and (3') into Eq. (1), and carrying out the energy integration [we take $\rho(E)$ independent of energy in the interest of simplicity], we find the following temperature dependences:

$$\Delta\omega_{fr} \sim \begin{cases} T, & \text{dipole-dipole} & (4a) \\ T^{1+(\bar{d}/4)}, & \text{dipole-quadrupole} & (4b) \\ T^{1+(2\bar{d}/5)}, & \text{quadrupole-quadrupole,} & (4c) \end{cases}$$

which should be compared with the $d=3$ result of Lyo¹ ($d = \text{Euclidean dimensionality}$) for phonons:

$$\Delta\omega_{ph} \sim \begin{cases} T, & \text{dipole-dipole} & (5a) \\ T^{7/4}, & \text{dipole-quadrupole} & (5b) \\ T^{11/5}, & \text{quadrupole-quadrupole.} & (5c) \end{cases}$$

III. APPLICATIONS AND CONCLUSIONS

The recent experiments⁴ by Völker's group on thermal broadening of optical homogeneous linewidths of free-base porphyrin in organic glasses and polymers using photochemical hole burning make interesting comparisons with Eq. (4). She and her group found $\Delta\omega \sim T^{1.30 \pm 0.1}$ from 0.4 through 20 K. It is intriguing to note that many polymers may be described topologically in terms of a percolation network.⁵ This has very significant implications because Alexander and Orbach have conjectured $\bar{d} = \frac{4}{3}$ for all percolating net-

works from $1 < d \leq 6$. Thus, for a dipole (TLS)-quadrupole (optical center) interaction Eq. (4b) would be predicted to yield an optical linewidth proportional to $T^{4/3}$, well within the error bars of the measurements of Völker and co-workers. We have made the reasonable assumption that the TLS possesses an electric dipole matrix element between its two states, while the optical center exhibits a difference in electric quadrupole moment between its ground and excited states. It is also instructive to note that if the TLS is more sensitive to quadrupolar than dipolar fields, Eq. (4c) would predict an optical linewidth proportional to $T^{1+(2\bar{d}/5)} \sim T^{1.53}$. Recently, Gorokhovskii Kikas, Pal'm, and Rebane⁶ reported an optical linewidth for a phthalocyanine derivative in isopropanol-ether glass proportional to $T^{1.5 \pm 0.3}$ between 1.8 and 4.2 K. This is a rather narrow temperature regime from which to extract a precise value for the temperature exponent. Further, we have no reason to expect the TLS to be more sensitive to quadrupolar than dipolar fields. Nevertheless, it is interesting that fracton excitations are able to provide a value for the temperature exponent which is encompassed by the experimental results.

It is also interesting to note that dipole-dipole coupling will yield an optical linewidth proportional to T , and independent of phonon or fracton densities of state. At sufficiently low temperatures, the dipole-dipole term linear in temperature [Eq. (5a)] will always dominate the higher multipole terms [Eqs. (5b) and (5c)] because of their proportionality to higher powers of temperature. The precise crossover temperature will depend on the relative strengths of the dipole-dipole versus the quadrupole-dipole interaction. Recent experiments⁷ on free-base porphyrin in polyethylene and in diglycerol exhibit a crossover to a linear temperature dependence at low temperatures from a $T^{1.3}$ dependence at higher temperatures. It is possible that this could be a manifestation of the crossover from a quadrupole-dipole coupling to a dipole-dipole coupling dominated regime.

Finally, a word should be said about the temperature range over which one would expect to observe fractons. Fractons are *short* length scale excitations, and can be expected to become important above a crossover frequency

$$\omega_{CO} \sim L^{-[1+(\theta/2)]}, \quad (6)$$

where θ gives the range dependence of the diffusion constant, and L is the length scale below which the system obeys self-similarity (inhomogeneous, or fractal geometry).

What L is appropriate to organic glasses and polymers? This is an unexplored question as yet, though recent thermal conductivity and specific-heat experiments of Kelham and Rosenberg⁸ on epoxy-resin suggest³ that ω_{CO} corresponds to approximately 8 K in that system at a length scale $L \sim 30 \text{ \AA}$. For a large polymer in the form of a random coil or a self-avoiding coil of characteristic length, say 1000 \AA , this would mean (everything else being equal) an ω_{CO} less than 0.24 K (depending, of course, on θ). Hence, for long-chain polymers, or organic glasses with long correlation lengths, fracton excitations may be relevant down to very low temperatures indeed (remembering that a slow velocity of sound would further lower ω_{CO}).

It should be remarked (as noted in Ref. 4) that nuclear magnetic resonance (NMR) longitudinal relaxation times also result from fluctuating electric quadrupolar fields. Thus, we might expect the results of NMR T_1 relaxation time measurements in glasses to follow temperature dependences not unlike Eq. (4). Comparison with the compendium of experimental results exhibited in Ref. 9 suggests that this may well be the case.

In summary, we have inserted fracton excitations for phonon excitations in fractal systems to calculate the optical homogeneous width using the formalism for phonons developed by Lyo.¹ We have found temperature dependences which may be relevant to the thermal broadening of optical homogeneous linewidths in organic glasses and polymers.

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