Homogeneous fluorescence linewidths for amorphous hosts

S. K. Lyo
Sandia Laboratories, Albuquerque, New Mexico 87185*

R. Orbach
Department of Physics, University of California, Los Angeles, California 90024

(Received 22 June 1979)

A contribution to the homogeneous linewidth of optical transitions in amorphous hosts is calculated. The microscopic process is diagonal in the phonon interaction with two level systems (TLS) common to amorphous materials, and diagonal in the coupling between TLS and the optical center. The model predicts an optical homogeneous linewidth proportional to the square of the temperature at low temperature.

I. INTRODUCTION

Optical linewidths in amorphous hosts are known to be anomalously large compared to crystalline hosts.[1] A recent report[2] showed the homogeneous width of optical transitions to increase as the square of the temperature over a wide temperature regime. This behavior cannot be understood with any previous calculation.[3] The purpose of this paper is to present a new calculation which gives the correct temperature dependence and magnitude of the optical linewidth.

Amorphous solids are known to possess centers, known as two-level systems (TLS),[4,5] which generate anomalous properties such as a linear term in the specific heat,[6,7] and nonlinear ultrasonic propagation.[8] These centers have been interpreted in terms of a distribution of double-well sites with random relative energies, between which tunneling can take place through barriers of random heights. The process we calculate involves diagonal electrostatic coupling between the TLS and the optical center and diagonal phonon modulation of the double-well site energies. The resulting homogeneous optical linewidth is proportional to T^2 at temperatures low compared to the maximum TLS energy splittings or the Debye temperature, whichever is lower, and to T at high temperatures. Previous treatments[3] have considered only the high-temperature limit for this process, or the full temperature range for diagonal coupling between the TLS and the center and off-diagonal coupling between the TLS and the phonons.

II. CALCULATION OF THE OPTICAL LINEWIDTH

Consider an optical transition which takes place between two levels, designated by $|0\rangle$ (the ground level) and $|1\rangle$ (an excited level). Let there be an electrostatic interaction between the optical energy levels and the TLS. In general, the strength of the coupling will depend on the state in which the optical ion resides, as well as the difference in coupling to the wells from which the TLS is composed. Let $(V_j)_i$ represent the difference in the strength of the coupling Hamiltonian between the two wells for the optical ion in the state j for the ith TLS. Then an effective matrix element exists for V_j acting between the eigenstates of the TLS

$$\langle\psi_-|H_{\rm int}|\psi_+\rangle=\frac{(V_j)_i}{E}\hbar\omega_0\exp(-\lambda)\ , \tag{1}$$

where the states $|\psi_+\rangle$ and $|\psi_-\rangle$ represent the eigenstates of the TLS, $\hbar\omega_0$ is an energy of the order of the zero-point vibrational energy within one of the wells, the factor $\exp(-\lambda)$ corresponds to the overlap between the vibrational wave functions of the two wells of the TLS, and $E=[\Delta^2+[\hbar\omega_0\exp(-\lambda)]^2]^{1/2}$, where Δ is the energy asymmetry of the TLS's wells. In addition to Eq. (1), we assume that the energy levels of each well are coupled to the running wave phonon field. We require that the coupling be different at the two well sites

$$\langle L|H_{\rm ph}|L\rangle=f_L\epsilon_L\ ,\quad \langle R|H_{\rm ph}|R\rangle=f_R\epsilon_R\ , \tag{2}$$

where L,R label the "left," "right" wells, respectively, f_L,f_R the respective phonon coupling strengths, and ϵ_L, ϵ_R the respective lattice strains at the appropriate sites. For sufficiently long-wavelength phonons ($\epsilon_L\simeq\epsilon_R=\epsilon$),

$$\langle\psi_+|H_{\rm ph}|\psi_+\rangle-\langle\psi_-|H_{\rm ph}|\psi_-\rangle=(f_L-f_R)\frac{\Delta}{E}\epsilon\equiv f\frac{\Delta}{E}\epsilon\ . \tag{3}$$

The frequency modulation of the optical energy levels for phonon emission takes place via the two processes pictured in Fig. 1. Notice that the order of the interactions (1) and (2) are reversed for the two processes shown in Fig. 1. The process corresponding to phonon absorption gives the same contribution to the linewidth as phonon emission. Using the method of McCumber and Sturge,[9] the optical linewidth for the transition $|1\rangle \leftrightarrow |0\rangle$ is given by

$$\Delta\omega = \frac{4\pi}{\hbar} \sum_{i,\vec{q},s} \int d\Delta d\omega_0 d\lambda df P(\Delta, \omega_0, \lambda, f) \times \frac{[\hbar\omega_0 \exp(-\lambda)]^2 f^2 \langle (V_1 - V_0)_i^2 \rangle_{\rm av} \Delta^2 \exp(-\beta E/2)}{E^4 (\hbar\omega_{\vec{q},s})^2 \cosh(\beta E/2)} \times |\langle n_{\vec{q},s}+1|\epsilon|n_{\vec{q},s}\rangle|^2 \delta(E - \hbar\omega_{\vec{q},s}) \ . \quad (4)$$

Here, $(V_1 - V_0)_i$ represents the difference in interaction constants to the ith TLS site, $n_{\vec{q},s}$ denotes the equilibrium boson occupation function for a phonon of wave vector $\vec{q}$ and polarization vector s, and P the probability distribution function normalized to $\int P d\Delta d\omega_0 d\lambda df \equiv 1$.

Following Anderson, Halperin, and Varma,[4] we perform the statistical averaging in Eq. (4). The acceptable range of λ is given by the condition that the level separation of the TLS be larger than the tunneling integral [i.e., $\lambda_{\rm min} = \ln(2\hbar\omega_0/\Delta) < \lambda$], and that the thermal equilibrium be achieved within the time t of the experiment [i.e., $\lambda < \lambda_{\rm max} = \frac{1}{2}\ln W_t t$, where $W_t \exp(-2\lambda)$ is the phonon-assisted tunneling rate at a TLS with energy $E \simeq k_B T$]. Note that $\lambda_{\rm min}$ and $\lambda_{\rm max}$ have a very slow energy dependence. Assuming that the probability distribution function P is slowly varying in Δ and λ in their relevant regimes, we approximate $P \cong P(0, \omega_0, \lambda_{\rm min}, f)$ and transform the Δ integration into an E integration. We carry out the λ integration and the sums over $\vec{q}$ and s assuming a Debye approximation to find

$$\Delta\omega = \frac{(k_B T)^2 \eta D \langle V^2 \rangle}{12\pi^2 \hbar^2 v^5 \rho B} \int_0^{\Theta/T} \frac{x e^{-x} dx}{1 - e^{-2x}} \ , \quad (5)$$

where η is a constant of order unity, v the sound velocity, ρ the mass density, Θ the Debye temperature, B the TLS bandwidth, and $\langle V^2 \rangle = \langle \sum_i (V_1 - V_0)_i^2 \rangle_{\rm av}$. The quantity $k_B\Theta$ in Eq. (5) should be replaced by the cutoff energy of the TLS splittings should the latter be smaller than the Debye energy. The quantity D is given by

$$D = 3\pi B \int d\omega_0 df P(0, \omega_0, \lambda_{\rm min}, f) f^2 \ .$$

The factor B in the above equation is introduced for normalization purposes: $B \int P d\omega df d\lambda \simeq 1$. For temperatures below Θ, Eq. (5) reduces to

$$\Delta\omega = \frac{(k_B T)^2 \eta D \langle V^2 \rangle}{96\hbar^4 v^5 \rho B} \ . \quad (6)$$

Note that for a TLS density of states proportional to E^η, the width in Eq. (6) is given by $\Delta\omega \propto T^{2+\eta}$.

It is possible to obtain an estimate for the magnitude of Eq. (6) if one approximates[4]

$$D \simeq \frac{1}{\lambda_{\rm max}} \left(\frac{\lambda_{\rm min}}{\lambda_{\rm max}} \right)^\xi 3\pi \langle f^2 \rangle_{\rm av} \ .$$

For typical parameters,[4] $\xi = 1$, $\langle f^2 \rangle_{\rm av} \simeq 1$ eV^2, $\lambda_{\rm min} \simeq 5$, and $\lambda_{\rm max} \simeq 10$, we find $D = 0.5$ eV^2. The TLS bandwidth B is taken as 0.1 eV. The inhomogeneous linewidth of optical transitions in glasses is of the order of hundreds of wave numbers. In the absence of detailed structural data concerning the local environment of the optical center, we are forced to make a very strong assumption concerning the magnitude of the coupling between the optical ion and the TLS. We associate the inhomogeneous broadening of the optical transition with the coupling strengths to TLS which are "static" on the time scale of the optical transition. This allows us to take $\langle V^2 \rangle$ of the order of the square of the inhomogeneous width. For the case of BeF_2 we take[7] $\langle V^2 \rangle \simeq (60\ {\rm cm}^{-1})^2$, $v = 3.0 \times 10^5$ cm/sec, and $\rho = 2.0$ g/cm^3. Inserting

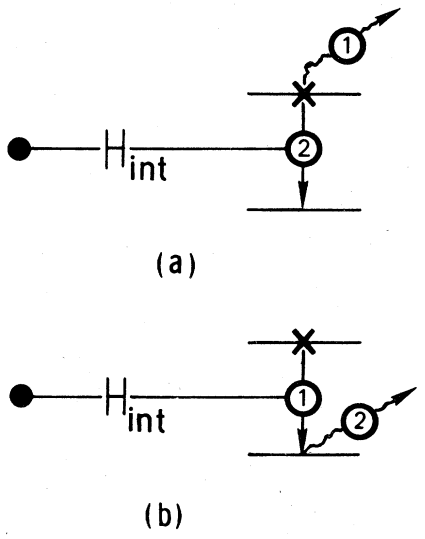

FIG. 1. Important processes for the t matrix. Black dots represent the ion or the spin interacting with TLS. In (a) a phonon is emitted (directed wiggly line) in the upper level of TLS and then tunneling takes place. In (b) the order is reversed. The circled numbers indicate the sequence in the perturbation chain.

all these estimates into Eq. (6), we obtain

$$\Delta\omega \simeq 2.1 \times 10^{-4} T^2 \text{ cm}^{-1} \quad (7)$$

for T in K. This implies a homogeneous linewidth of 0.02 cm^{-1} at 10 K, in reasonable agreement with the very recent results of Hegarty and Yen[2] for the $^3P_0 - {}^3H_4$ resonant transition in Pr-doped BeF_2 glass at low temperatures and Selzer *et al.*[1] and Avouris *et al.*[1] for the $^5D_0 - {}^7F_0$ resonant transition in Eu-doped silicate glass at higher temperatures.

III. CONCLUSIONS

In conclusion, we have exhibited a one-phonon-assisted relaxation process whose signature is a quadratic temperature dependence extending down to the lowest of temperatures. It appears to explain quantitatively the temperature-dependent homogeneous linewidth for optical transitions in glasses.

Note added in proof. It has been pointed out to us [S. Alexander (private communication)] that the tunneling between the inequivalent wells of the TLS mixes states very much as the Bogoliubov transformation in superconductivity. Fluctuations associated with the diagonal phonon coupling at one TLS site by themselves would do nothing. The tunneling matrix element mixes the two TLS wells, so that phonon-induced fluctuations give rise to an interruption of the phase of the optical center via the electrostatic interaction between the TLS wells and the optical center. For superconductors, the fluctuations of the order parameter above T_c mix electron hole pairs into hole electron pairs, giving rise to a divergence of the imaginary part of the conduction-electron susceptibility at small energy, and hence of the nuclear-spin-lattice relaxation rate. See T. Maniv and S. Alexander [Solid State Commun. 18, 1197 (1976)].

ACKNOWLEDGMENTS

The present work has been supported by the U.S. Department of Energy (S. K. Lyo) under Contract No. DE-AC04-76-DP00789, and the U.S. Office of Naval Research (R. Orbach) under Contract No. N00014-75-C-0245. The authors wish to thank Dr. J. Hegarty, Professor W. M. Yen, and Professor T. Holstein for very valuable discussions.

---

*U.S. Department of Energy facility.

[1]P. M. Selzer, D. L. Huber, D. S. Hamilton, W. M. Yen, and M. J. Weber, Phys. Rev. Lett. 36, 813 (1976); P. Avouris, A. Campion, and M. A. El-Sayed, J. Chem. Phys. 67, 3397 (1977).

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

[3]J. Szeftel and H. Alloul, J. Non-Cryst. Solids 29, 253 (1978); T. L. Reinecke, Solid State Commun. 32, 1103 (1979).

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

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

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

[7]R. B. Stephens, Phys. Rev. B 8, 2896 (1973).

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

[9]D. E. McCumber and M. D. Sturge, J. Appl. Phys. 34, 1682 (1963).