Anomalous thermal broadening of the optical lines of impurity centers in a glass

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The anomalies of thermal broadening of optical impurity lines in a glass can be explained in terms of the interaction of an impurity ion with low-frequency, localized modes.

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1. It has been established recently that the uniform halfwidth $\Gamma(T)$ of the optical, phonon-free lines (PFL) of rare-earth ions in glass, which can be measured as a result of selective excitation, is two orders of magnitude larger than that of PFL of the same ions in a crystal.[1] An increase of the halfwidth $\Gamma(T)$ is described by the T^2 law over a broad temperature range (8–300 K).[2] These anomalies, in the opinion of the authors of Refs. 1 and 2, cannot be accounted for by the Raman mechanism of PFL broadening. These authors have hypothesized that the two-level systems proposed by Anderson *et al.*[3] and by Phillips[4] play an important role in thermal broadening of optical PFL in a glass. This hypothesis has been used for a single-phonon mechanism of PFL broadening, which was analyzed in Ref. 5. As mentioned in Ref. 2, however, the formula of Ref. 5 is difficult to reconcile with the T^2 law in the high-temperature region. The question of the nature of the anomalies, therefore, remains open.

In this letter we show that the mentioned anomalies in $\Gamma(T)$ can nonetheless be explained in the context of the two-phonon Raman mechanism of PFL broadening. However, the interaction of an impurity center with the localized, low-frequency modes in this case must be taken into account.

2. Many experimental data, in particular, those for Raman scattering,[6] indicate that glasses have localized modes with frequencies of several cm^{-1}. Let us assume

that one of these modes corresponds to a quasilocal oscillation of an impurity ion along the coordinate R. Thus the weighted density of phonon states

$$f^g(\nu) = \frac{1}{2}\int_{-\infty}^{\infty} e^{i\nu t} < R(t)R(0) >_g dt = \frac{\pi}{2\nu}\sum_{\kappa} u^2_{g\kappa}\delta(\nu - \nu_{g\kappa}) \quad (1)$$

has a peak in the electronic ground state ($g=0$) at the frequency ν_0 and in the excited state ($g=e$) at the frequency ν_e. Let us analyze an optical 0-0 transition in an impurity center. A variation of the adiabatic potential can be written as follows:

$$H_{el-ph} = (R-a)\frac{U^e}{2}(R-a) - R\frac{U^0}{2}R = a\frac{U^e}{2}a - aU^eR + R\frac{W}{2}R. \quad (2)$$

It has been established that the PFL broadening is governed solely by the $H_{el\text{-}ph}$ part quadratic in R and that the linear part does not contribute to it.[7] The formula for $\Gamma(T)$ was derived in Ref. 7 for an arbitrary value of W. The imaginary part of the expression (27) in Ref. 7 can be represented in a simple form[1)]:

$$\Gamma(T) = \int_0^{\infty} \ln\left(1 + \frac{W^2 f^0(\nu) f^e(\nu)}{\mathrm{sh}^2(\nu/2kT)}\right)\frac{d\nu}{\pi}. \quad (3)$$

Using the Lorentz function with a halfwidth 2γ to approximate $2\nu f^g(\nu)$, we can calculate the frequency integral. Since $2\gamma \ll \nu_g$ and $W \cong (\nu_e^2 - \nu_0^2)/2$, we obtain the following expression for temperatures that satisfy the inequality $kT \gg \nu_g$:

$$\Gamma(T) = \Gamma_0^2(T)\frac{\gamma}{\Delta^2+\gamma^2}\left(1 - \frac{\Gamma_0^2(T)}{4}\frac{5\gamma^2+\Delta^2}{(\Delta^2+\gamma^2)^2} + \ldots\right), \quad (4)$$

where $\Gamma_0(T) = \Delta(kT/\nu_g)$ and $\Delta = \nu_e - \nu_0$. We denote by ν_g the frequency $\nu_e \cong \nu_0$. We cannot limit ourselves to the first term in Eq. (4) when $\Delta/\gamma \gg 1$, but we can do so when $\Delta/\gamma \ll 1$ only on condition that $\Gamma_0(T)/\gamma < 1$. Thus,

$$\Gamma(T) \cong \frac{\Gamma_0^2(T)}{\gamma} aT^2. \quad (5)$$

If, for example, $\nu_g = 6\ \mathrm{cm}^{-1}$ and $\Delta/\gamma \sim 10^{-2}$, then Eq. (5) will be valid over a broad temperature range 8-300 K. At low temperatures we can have

$$\frac{\Gamma_0^2(T)}{\gamma} >> 18\pi\nu_D\left(\frac{W}{\nu_D^2}\right)^2\left(\frac{kT}{\nu_D}\right)^7\int_0^{\nu_D/kT}\frac{x^6e^x dx}{(e^x-1)^2}, \quad (6)$$

where the right-hand side of the inequality describes the halfwidth of the PFL, which is governed by the interaction of an impurity center with the acoustic phonons.[8] By setting, for example, $\Delta/\gamma = 7\times10^{-2}$, $\gamma = 2\ \mathrm{cm}^{-1}$, and $\nu_g = 6\ \mathrm{cm}^{-1}$ for a localized oscillation, and $\nu_D = 300\ \mathrm{cm}^{-1}$ and $W/\nu_D^2 = 2\times10^{-2}$ for Debye-model phonons, we can see that the left-hand side of Eq. (6) is two orders of magnitude larger than the right-hand side, since the integral in Eq. (6) is equal to approximately 200 when $kT = 60\ \mathrm{cm}^{-1}$.

3. Let us assume that glass has a large number of impurity ions that differ in the energy of electronic excitation and in frequency ν_g, i.e., the parameter α. A selective

laser excitation of the 0-0 transition region can eliminate the energy nonuniformity of electronic excitation but not the nonuniformity of the parameter α. A "uniform," phonon-free luminescence line, which has been recorded in experiments with selective excitation,[1] can therefore be described by the equation

$$I(\omega) = \int_0^\infty \frac{\alpha T^2/2}{(\omega - \omega_l)^2 + (\alpha T^2/2)^2} N(\alpha, \omega_l) d\alpha, \tag{7}$$

where ω_l is the frequency of exciting light and $N(\alpha, \omega_l)$ is the distribution function of the centers in which the frequency of the 0-0 transition is equal to ω_l. It follows from Eq. (7) that the halfwidth of a "uniform" PFL may depend on the wavelength of exciting light, as observed in Ref. 2. In fact, the halfwidth of such a PFL is equal to $\Delta\omega(T, \omega_l) = \Omega(\omega_l)T^2$, where Ω is a root of the equation

$$\int_0^\infty \left(\frac{\alpha}{\Omega^2 + \alpha^2} - \frac{1}{2\alpha} \right) N(\alpha, \omega_l)\, d\alpha = 0. \tag{8}$$

Nonresonance phototransitions with ω_l do not contribute to a line luminescence because of ν_g straggling of the centers and because of weak electron-phonon interaction.

The standard, two-phonon Raman mechanism for interaction of impurity centers with low-frequency localized modes, therefore, cannot explain all the basic anomalies of PFL broadening, which were discussed in Refs. 1 and 2.

[1)]We have assumed that $\hbar = 1$.

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