Tunneling in glasses and anomalous low-temperature broadening of impurity optical lines

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(Submitted 16 February 1984)
Pis'ma Zh. Eksp. Teor. Fiz. **39**, No. 8, 354–357 (25 April 1984)

The low temperature broadening of an impurity center with a two-well adiabatic potential may obey a T^n law with $1 < n < 2$.

1. Hole-burning measurements of the homogeneous half-width $\gamma(T)$ of zero-phonon lines of impurity centers in organic glasses have revealed an extremely strange temperature dependence $\gamma(T)$: T^n, with $1 < n < 2$ (Refs. 1–4). Over the temperature interval $0.4 < T < 20$ K, of nearly two orders of magnitude, for example, the result $\gamma \sim T^{1.3}$ has been found.[2,3] The existing theories cannot explain this temperature dependence. It is natural to suggest that two-level systems of glasses would play an important role in the low-temperature broadening of zero-phonon lines.[5]

Two-level systems have been used in an explanation[6] of an effect observed slightly earlier[7,8]: a quadratic broadening of zero-phonon lines in the temperature interval $10 < T < 300$ K. Although it was subsequently shown[9,10] that the common expression for the half-width in fact agrees quantitatively with the experimental data,[7,8] the role played by two-level systems in the broadening of zero-phonon lines has been the sub-

 0021-3640/84/080426-04$01.00

ject of a lengthy discussion.[11-13] It has been assumed in all these studies that the reason for the broadening of the zero-phonon lines is an interaction of an impurity center with phonons through a huge set of two-level systems. The homogeneous half-width of the zero-phonon line thus depends on the distribution function of the two-level systems, and the temperature enters the expression through the average number of phonons. In this approach it is extremely difficult to explain why a localized impurity center will interact not with one or two two-level systems but with a huge number of such systems.

In this letter we examine the thermal broadening of a zero-phonon line from the conventional standpoint; i.e., we assume that the broadening is caused by a change in the vibrational states of the impurity center. If we take into account the circumstance that the adiabatic potential of an impurity center in a glass may be a two-well potential, however, we find an additional term in the homogeneous half-width of the zero-phonon line, which is dominant at low temperatures.

2. Working from the results of Ref. 14, we write the vibrational Hamiltonian of an impurity center with a two-well adiabatic potential as follows:

$$H^g = \sum_{j=1,2} (E_j - \mu)c_j^+ c_j + U(R)(c_2^+ c_1 + c_1^+ c_2) + H_{\text{ph}}(R - ac_2^+ c_2). \tag{1}$$

Here E_1 and E_2 are the lowest levels of the deep and shallow wells, μ is the chemical potential, $U(R)$ is the tunneling operator, H_{ph} is the Hamiltonian of a simple harmonic oscillator, and a is the shift of the phonon equilibrium position during the tunneling. The operators c_j and c_j^+ obey Fermi commutation relations. After electronic excitation of the impurity center, the vibrational Hamiltonian changes to $H^e = H^g + \Lambda$. We assume a change in the simple form

$$\Lambda = R\frac{W}{2}R + \Delta c_2^+ c_2 \, . \tag{2}$$

The optical absorption band of the impurity center is determined by the Fourier transform of the function

$$I(T) = \text{Sp}\left\{ e^{\frac{\Omega^g - H^g}{T}} e^{iH^g t} e^{-iH^e t} \right\} = e^{\varphi(t)}. \tag{3}$$

Evaluation the cumulant $\varphi(t)$ in the first nonvanishing approximation in Λ, we find $\varphi(t) = it\delta - |t|\gamma/2 + f(t) - f(0)$, where the function $f(t)$, which tends toward zero as time elapses, determines the shape of the phonon wing, while γ is the half-width of the zero-phonon line. This half-width is given by

$$\gamma(T) = \gamma_W(T) + \gamma_\Delta(T) = W^2 \int_0^\infty \frac{d\nu}{\pi} \frac{\Gamma_W^2(\nu)}{\text{sh}^2(\nu/2T)} + \frac{\Delta^2}{2} \int_0^\infty \frac{d\nu}{\pi} \frac{\Gamma_\Delta^2(\nu, T)}{\text{ch}^2(\nu/2T)} \, . \tag{4}$$

The first term here describes the contribution to the half-width of the ordinary quadratic interaction with phonons. The term γ_W was in fact used in Ref. 10 in a successful quantitative explanation of the experimental data of Refs. 7 and 8. The term γ_Δ describes an additional broadening of the zero-phonon line which results from the change in the parameters of the two-level system upon electronic excitation of the impurity center. The function $\Gamma_\Delta(\nu, T)$ is the imaginary part of the Fourier component of the retarded Green's function

$$G(t) = -i\,\mathrm{Sp}\left\{e^{\frac{\Omega^g - H^g}{T}}\left[c_2(t)c_2^+(0) + c_2^+(0)c_2(t)\right]\right\}\theta(t), \tag{5}$$

where $c_2(t) = \exp(iH^g t)c_2\exp(-iH^g t)$. Treating the tunneling as a perturbation, we can calculate the Matsubara function and then use it to find $G(t)$. Ignoring elastic tunneling, and treating the inelastic tunneling in the single-phonon approximation, we find[1)]

$$\Gamma_\Delta(\nu, 0) \simeq \frac{1}{2}\left[\frac{\gamma_1}{(\nu-\epsilon)^2 + \gamma_1^2} + p(\nu)\right], \tag{6}$$

where

$$p(\nu) \simeq \nu^{-2}\exp\left(-\frac{a^2}{4}\right)\sum_q\left(\frac{\partial U}{\partial R_q}\right)^2_{a/2}\delta(\nu - \nu_q). \tag{7}$$

Here $\epsilon = E_2 - E_1$ is the gap in the two-level system, ν_q is the phonon frequency, and $\gamma_1 = \epsilon^2 p(\epsilon)/2$.

The term γ_W in (4) tends toward zero as T^7, so that its contribution to the low-temperature half-width can be ignored. What is the contribution of the two-level system to be half-width of the zero-phonon line? Substituting (6) into (4), and approximating $p(\nu)$ over the interval $(0, \nu_D)$ by a step function of height p, we find

$$\gamma_\Delta(T) = \frac{\Delta^2}{8}\left\{\frac{1}{2\gamma_1}\mathrm{ch}^{-2}\left(\frac{\epsilon}{2T}\right) + 2p^2 T\,\mathrm{th}\left(\frac{\nu_D}{2T}\right)\right\}. \tag{8}$$

The first term is nearly independent of the temperature at $T > \epsilon$, and it is exponentially small at $T < \epsilon$. The second term changes almost linearly over the interval $0 < T < \nu_D$. Numerical calculations with a function $p(\nu)$ approximated as a Gaussian function with a half-width of 300 cm^{-1} and a peak at $\nu_D/2 \simeq 150\ \mathrm{cm}^{-1}$ reveal $\gamma_\Delta \sim T^{1.3}$ over the interval[2] $0.5 < T < 20$ K. The changes in the parameters of the two-level system during electronic excitation of the impurity center can thus give rise to the anomalous broadening of the zero-phonon line observed in Refs. 1–4.

[1)]When many-phonon tunneling is taken into account, expression (7) is of course changed, but the final result is not.

[2)]I wish to thank S. A. Zhdanov for carrying out the numerical calculations.

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Translated by Dave Parsons
Edited by S. J. Amoretty