Theory of shape of homogeneous optical band of impurity centers in amorphous and crystalline media

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A theory is developed for the shape of homogeneous optical bands of impurity centers in amorphous and crystalline media. The theory generalizes the traditional approach to the problem of the optical-band shape to include the case when the impurity centers and the atoms can have two-well adiabatic potentials. The interaction of the optical electrons of the impurity with the tunnel degrees of freedom adds terms to the expressions for the shift and width of the no-phonon line (NPL) as well as for the phonon wing. The temperature dependence of the additional term in the expression for the NPL half-width agrees with recently observed anomalous laws of broadening of NPL of impurity centers in amorphous media. A connection is established between the NPL of the absorption spectrum and fluorescence. The theory yields new experimentally verifiable predictions.

1. INTRODUCTION

The theory of the impurity-center homogeneous band seemed well enough developed until recently,[1–4] since it could account quantitatively for the experimental facts.[3,4] Low-temperature experimental research, however, undertaken during the last two–three years, into no-phonon lines (NPL) of impurity centers in amorphous media (glasses, polymers), raised new questions that the theory of Refs. 1–4 was unable to answer. It has become obvious that the theory does not take into account important factors peculiar to amorphous media.

Amorphous media are characterized by the presence of known two-level systems (TLS).[5] The premise that the theory of the band shape must take TLS into account was apparently first stated in Refs. 6 and 7, in view of observation of a T^2-law broadening of the NPL in the wide temperature interval $8 < T < 300$ K for impurity ions in inorganic glasses.[6,7] It was shown shortly thereafter[8,9] that the "old" NPL broadening theory can explain even quantitatively the results of Refs. 6 and 7 as due to the interaction of an impurity center with low-frequency quasilocal vibrations. Nonetheless, the very idea of taking TLS into account in the theory of the optical-band form continues to attract considerable interest. This is prompted by at least two circumstances. First, many investigations have shown convincingly that TLS determine the low-temperature behavior of the heat capacity, thermal conductivity, ultrasound absorption, etc. (see the reviews[5,10]). Second, as already mentioned, unusual experimental facts were obtained a few years ago concerning the homogeneous halfwidth $\gamma(T)$ of NPL of impurity centers in amorphous media, and were at variance with the "old" theory. Some of these facts were: 1. The NPL homogeneous halfwidth $\gamma(T)$ varied like T^n, with $1 \leqslant n \leqslant 2$ (Refs. 11–19). A $T^{1.3}$ broadening was observed, for example, in the range $0.3 \leqslant T \leqslant 20$ K in organic amorphous media[15–17] and at $0.1 \leqslant T \leqslant 1$ K in inorganic ones.[18] 2. A single change,[17] and *quite recently* a double change,[19] was observed in the slope of the $\gamma(T)$ curve as the temperature was varied; a section of the curve obtained in the second of these references had an exponent $n < 1.3$. A discrepancy was observed between the residual halfwidth $\gamma(0)$ and the reciprocal fluorescence-damping time.[12,14,18]

Several theoretical models that account for the influence of TLS on the halfwidth of an optical NPL have by now been proposed.[12,20–26] The earlier ones were proposed to explain either the quadratic broadening[20,21] or the linear law.[12] These models could not explain the later observations, e.g., the $T^{1.3}$ broadening. To explain the latter, three different theories were proposed later,[23–26] but two of them disagree with experiment in certain respects. Thus, the Krigovlaz theory[23] based on averaging various homogeneous spectral distributions predicts actually a non-Lorentzian NPL contour, contrary to the experimental data.[15,19] The theory of Lyo and Orbach,[24] who modified their earlier approach[21] by replacing the phonons by the so-called "fractons," will be shown in Sec. 9 to disagree with the experimental data of Ref. 19.

The theory described below expands the theoretical approach of Refs. 25 and 26, which agrees so far with all the facts on the homogeneous halfwidth of the NPL of an impurity in an amorphous medium. This theory, which generalizes the traditional approach to the problem of the optical-band shape to include the case of two-well adiabatic potentials, pertains not only to NPL but to the entire optical band. It leads to new theoretical predictions for experiment (see Sec. 9).

2. MODEL OF IMPURITY CENTER IN AN AMORPHOUS MEDIUM

Amorphous media have degrees of freedom corresponding to tunneling of atoms or their groups from one potential well to another. This ability of the atom to be in two quantum states is accounted for by the TLS model. The model vibrational Hamiltonian of an impurity center in an

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amorphous medium is therefore best chosen in the form

$$H^g=\sum_j\sum_{s=1,2}E_{js}{}^g c_{js}{}^+c_{js}+H_{ph}{}^g\Big(R+\sum_j \xi_j{}^g c_{j2}{}^+c_{j2}\Big)$$
$$+\sum_j p_j{}^g(R)\,(c_{j2}{}^+c_{j1}+c_{j1}{}^+c_{j2}), \tag{1}$$

where

$$c_{js}\overset{+}{c}_{js'}+\overset{+}{c}_{js'}c_{js}=\delta_{ss'},\qquad c_{js}\overset{+}{c}_{j's'}-\overset{+}{c}_{j's'}c_{js}=0.$$

The subscripts $s = 1, 2$ number the lowest levels in the deep and shallow well, respectively, and j numbers the well pairs, i.e., the TLS. The phonon Hamiltonian takes into account the phonon equilibrium positions as the atom goes from one well to the other. The third term in (1) describes the tunneling. By using the canonical transformation $\exp\Sigma_j\, c^+c_{j2}\hat{\psi}_j$, where

$$\hat{\psi}_j=\sum_n \xi_{jn}{}^g\,\partial/\partial R_n,$$

we can "remove" from the phonon Hamiltonian the shift of the equilibrium positions, and reduce (1) to the form

$$H^g=\sum_{j,s}E_{js}{}^g c_{js}{}^+c_{js}+H_{ph}{}^g(\mathbf{R})+\sum_j\,[(P_j{}^g)^+c_{j2}{}^+c_{j1}+P_j{}^g c_{j1}{}^+c_{j2}], \tag{2}$$

where

$$P_j{}^g=p_j{}^g\Big(\mathbf{R}-\sum_j \xi_j{}^g c_{j2}{}^+c_{j2}\Big)\exp\hat{\psi}_j.$$

The optical-band shape of an impurity center in a crystal is known to be expressed in terms of causal phonon Green's functions

$$D_{nm}(t,\ T)=-i\langle\hat{T}R_n(t)R_m(0)\rangle_{g,\ ph}, \tag{3}$$

where the density matrix and the time dependence of the operators are determined by the Hamiltonian H^g_{ph}. In the case of amorphous media, an important role is assumed also by the causal Fermi Green's functions

$$G^j_{ss'}(t,T)=-i\langle\hat{T}c_{js}(t)\overset{+}{c}_{js'}(0)\rangle_g, \tag{4}$$

where the Hamiltonian H^g is given by (2). It is known (see, e.g., Ref. 27) that the Fourier components of the causal functions D and G are generally related to the Fourier components of the corresponding retarded functions:

$$\begin{aligned}D_{nm}{}^R&=-i\langle R_n(t)R_m(0)-R_m(0)R_n(t)\rangle_g\theta(t),\\ G^{jR}_{ss'}&=-i\langle c_{js}(t)\overset{+}{c}_{js'}(0)+\overset{+}{c}_{js'}(0)c_{js}(t)\rangle_g\theta(t).\end{aligned} \tag{5}$$

For the Fermi functions, for example, this relation takes the form

$$G^j_{ss'}(\omega,T)=\mathrm{Re}\,G^{jR}_{ss'}(\omega,T)+i\,\mathrm{th}(\omega/2T)\,\mathrm{Im}\,G^{jR}_{ss'}(\omega,T). \tag{6}$$

We can calculate the retarded functions by using the smallness of the tunneling when uncoupling the resultant equation chains. Taking into consideration the spectral representation

$$\langle P_j{}^{g+}(t)P_j{}^g(t')\rangle\cong(p_j{}^g(0))^2\int_{-\infty}^{\infty}\frac{d\nu}{\pi}I^g(\nu,T)\exp[-i\nu(t-t')] \tag{7}$$

and introducing the more convenient notation $E^g_{j1}=-\varepsilon^g_j$, $E^g_{j2}=\varepsilon^g_j$, we obtain, omitting the indices g and j, the following expression for the function $G^R_{ss'}$:

$$G_{ss'}{}^R(\omega,T)=\int_{-\infty}^{\infty}\frac{d\nu}{\pi}\frac{\Gamma_{ss'}(\nu,T)}{\omega-\nu+i0^+}, \tag{8}$$

where

$$\Gamma_{22}(\omega,T)=p^2I(\omega+\varepsilon,T)\bigg[\bigg(\omega-\varepsilon-p^2\int_{-\infty}^{\infty}\frac{d\nu}{\pi}\frac{I(\nu,T)}{\omega+\varepsilon-\nu}\bigg)^2$$
$$+p^4I^2(\omega+\varepsilon,T)\bigg]^{-1}. \tag{9}$$

An expression for $\Gamma_{11}(\omega,T)$ is obtained from (9) by reversing the sign of ε. The functions that are not diagonal in s and s' are expressed in terms of G_{22} and G_{11}:

$$\begin{aligned}G_{12}{}^R(\omega,T)&=\frac{\langle P\rangle}{\omega+\varepsilon+i0^+}G_{22}{}^R(\omega,T),\\ G_{21}{}^R(\omega,T)&=\frac{\langle P^+\rangle}{\omega-\varepsilon+i0^+}G_{11}{}^R(\omega,T).\end{aligned} \tag{10}$$

Using now the relation (6), we readily obtain an expression for the causal Fermi function:

$$G_{ss'}(\omega,T)=\int_{-\infty}^{\infty}\frac{d\nu}{\pi}\Gamma_{ss'}(\nu,T)\bigg(\frac{1-f(\nu)}{\omega-\nu+i0^+}+\frac{f(\nu)}{\omega-\nu-i0^+}\bigg). \tag{11}$$

Here $\Gamma_{ss'}=-\mathrm{Im}\,G^R_{ss'}$ and $f(\nu)=[\exp(\nu/T)+1]^{-1}$. Using a procedure similar to that described above, we can calculate also the causal phonon functions.

The interaction of the TLS with the phonons "dresses" the TLS and distorts the phonons. For brevity, we refer to the excitation quanta of the "dressed" TLS as "tunnelons," while the distorted phonons will be called phonons as before. This terminology is particularly convenient for the discussion of the shape of the broad spectral distribution that accompanies the NPL (see Sec. 6). The function $\Gamma_{ss'}(\nu,T)$ and the analogous function $\Gamma^{ph}_{nm}(\nu,T)$ obtained by allowing for the influence of the TLS on the phonons, reflect the "dressing" of the TLS and the distortion of the phonons.

3. INFLUENCE OF TLS ON THE SHAPE OF THE OPTICAL ABSORPTION BAND (GENERAL FORMULA)

Obviously, electronic excitation of the impurity center alters the vibrational Hamiltonian:

$$H^e=H^g+\Lambda, \tag{12}$$

where

$$\Lambda=\sum_j(\Delta_jc_{j2}{}^+c_{j2}+\lambda_j{}^+c_{j2}{}^+c_{j1}+\lambda_jc_{j1}{}^+c_{j2})=\sum_j\mathbf{c}_j{}^+\Lambda_j\mathbf{c}_j. \tag{13}$$

We disregard on purpose the phonon-subsystem changes, so as to investigate in pure form the influence of the TLS on the optical band. The role of the phonons will be considered below (Sec. 8).

The sought-for shape of the homogeneous optical absorption band is defined by the expression

$$J(\omega)=\frac{1}{2}\int_{-\infty}^{\infty} dt\exp[i(\omega-E)t]\langle\exp iH^g t\exp-iH^e t\rangle_g, \qquad (14)$$

where E is the energy of the electronic excitation of the impurity center. Calculation of the mean value in (14) gives rise to causal Fermi Green's functions. If the tunneling is weak, their Fourier components are described by (11). The technique of calculating (14) with the electron-tunnelon interaction (13) is quite similar to the technique used to calculate the electron-phonon band.[3,4] The result is

$$J(\omega)=\frac{1}{2}\int_{-\infty}^{\infty} dt\exp[i(\omega-E)t+\varphi(t)]. \qquad (15)$$

The cumulant function $\varphi(t)=\Sigma_j\varphi_j(t)$ satisfies the condition $\varphi(-t)=\varphi^*(t)$ and constitutes an infinite series:

$$\begin{aligned}\varphi(t)=-\mathrm{Sp}\Big\{&\int_0^t dt_1\,\Lambda G(-0)\\ &+\frac{1}{2}\int_0^t dt_1\int_0^t dt_2\,\Lambda G(t_1-t_2)\Lambda G(t_2-t_1)\\ &+\frac{1}{3}\int_0^t dt_1\int_0^t dt_2\int_0^t dt_3\,\Lambda G(t_1-t_2)\Lambda G(t_2-t_3)\Lambda G(t_3-t_1)+\dots\Big\},\\ &t>0. \end{aligned} \qquad (16)$$

Here Λ and $G(t)$ are matrices whose diagonals are the 2×2 matrices

$$\Lambda=\begin{pmatrix}0 & \lambda_j^+\\ \lambda_j & \check{\Delta}_j\end{pmatrix}\qquad G^j=\begin{pmatrix}G_{11}^j & G_{12}^j\\ G_{21}^j & G_{22}^j\end{pmatrix}. \qquad (17)$$

4. NPL BROADENING AND SHIFT IN ABSORPTION SPECTRUM

The long-time asymptotic behavior of the cumulant function is known to determine the shape and position of the NPL. Using (16) we obtain as $t\to+\infty$

$$\begin{aligned}\varphi_\infty(t)&=-t\,\mathrm{Sp}\Big\{\Lambda G(-0)+\int_0^\infty dt_2\,\Lambda G(-t_2)\Lambda G(t_2)\\ &\quad+\int_0^\infty dt_2\int_0^\infty dt_3\,\Lambda G(-t_2)\Lambda G(t_2-t_3)\Lambda G(t_3)+\dots\Big\}\\ &=-t\,\mathrm{Sp}\Big\{\Lambda G(-0)+\int_0^\infty dt_2\,\Lambda G(-t_2)S(t_2)\Big\}, \end{aligned} \qquad (18)$$

where the infinite series is expressed in terms of the solution of the integral equation

$$S(x)=\Lambda G(x)+\int_0^\infty dy\,\Lambda G(x-y)S(y),\quad x>0. \qquad (19)$$

On the basis of (19), we can represent the series (18) in the form

$$\varphi_\infty(t)=-t\,\mathrm{Sp}\{\Lambda G(-0)-\Lambda G(+0)+S(+0)\}. \qquad (20)$$

It is easy to obtain for the Fourier component of the matrix $S(x)$ the equation

$$S_+(\omega)=\Lambda G_+(\omega)+\Lambda(G(\omega)S_+(\omega))_+, \qquad (21)$$

where

$$S_+(\omega)=\int_0^\infty dx\,e^{i\omega x}S(x),\qquad G_+(\omega)=\int_0^\infty dx\,e^{i\omega x}G(x) \qquad (22)$$

are functions analytic in the upper complex ω plane. Solving (21) by iteration, we substitute the resultant infinite series in the equation

$$S(+0)=\lim_{x\to0}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega x}S_+(\omega). \qquad (23)$$

Using the analytic properties of the terms of this series, we can simplify each term, after which the series is easily summed

$$\begin{aligned}\varphi_\infty(t)=-t\{i\delta(T)+\gamma(T)/2\}=-t\,\mathrm{Sp}\Big\{&\Lambda G(-0)-\Lambda G(+0)\\ &-\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\ln(I-\Lambda G(\omega,T))\Big\}. \end{aligned} \qquad (24)$$

Obviously, $\delta(T)$ and $\gamma(T)$ describe the shift and halfwidth of a Lorentzian NPL. Using the explicit form of the function $G(\omega,T)$ we can transform (24) into

$$\begin{aligned}&i\delta(T)+\frac{\gamma(T)}{2}\\ &=\mathrm{Sp}\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\Big[i\Lambda\Gamma^g(\omega,T)-\frac{1}{2}\ln(I-\Lambda G^g(\omega,T))\Big]. \end{aligned} \qquad (25)$$

We have again labeled the Green's functions by the index g of the electronic ground state, to prevent confusion in the forthcoming comparison with NPL of the fluorescence spectrum.

5. FLUORESCENCE NPL AND ITS CONNECTION WITH ABSORPTION NPL

If the impurity center has a one-well adiabatic potential, the fluorescence band is calculated in analogy with the absorption band, by replacing ω and E with $-\omega$ and $-E$ and interchanging the Hamiltonian H^g and H^e. As a result of the last interchange we get in place of the Green's function $G^j_{ss'}$ of the electronic ground state the Green's functions of the excited state, viz.,

$$G^{je}_{ss'}(t,T)=-i\langle\hat{T}c_{js}(t)c^+_{js'}(0)\rangle_e. \qquad (26)$$

The expression for the shift δ^{fl} and halfwidth γ^{fl} of the fluorescence NPL spectrum takes then the form

$$\begin{aligned}&i\delta^{fl}(T)+\frac{\gamma^{fl}(T)}{2}\\ &=\mathrm{Sp}\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\Big[-i\Lambda\Gamma^e(\omega,T)-\frac{1}{2}\ln(I+\Lambda G^e(\omega,T))\Big], \end{aligned} \qquad (27)$$

where $G^e(\omega,T)$ is the Fourier component of the function

(26) and is defined as

$$G^{e}(\omega,T)=G^{eR}(\omega,T)+i2f(\omega)\Gamma^{e}(\omega,T)$$
$$=\int_{-\infty}^{\infty}\frac{d\nu}{\pi}\Gamma^{e}(\nu,T)\left(\frac{1-f(\nu)}{\omega-\nu+i0^{+}}+\frac{f(\nu)}{\omega-\nu-i0^{+}}\right). \qquad (28)$$

From a comparison of (25) and (27) it might seem at first glance that the NPL of the absorption and fluorescence spectra are not resonant and have different halfwidths. It can be shown, however, that to the extent that the relation

$$G^{eR}(\omega,T)=G^{gR}(\omega,T)+G^{gR}(\omega,T)\Lambda G^{eR}(\omega,T) \qquad (29)$$

between the retarded functions is valid, both NPL are resonant and are equally broadened.[1] Indeed, by using this connection we can transform the second terms in the integrands of (25) and (27) into

$$\ln\det(I-\Lambda G^{g})=\ln\det(I-\Lambda G^{gR})$$
$$+\ln\det[I-2f\Lambda\Gamma^{e}\Lambda\Gamma^{g}-i2f(I+\Lambda\Omega^{e})\Lambda\Gamma^{g}], \qquad (30)$$
$$\ln\det(I+\Lambda G^{e})=\ln\det(I+\Lambda G^{eR})$$
$$+\ln\det[I-2f\Lambda\Gamma^{e}\Lambda\Gamma^{g}+i2f\Lambda\Gamma^{e}(I-\Lambda\Omega^{g})], \qquad (31)$$

where $\Omega=\operatorname{Re}G^{R}$ and $\Gamma=-\operatorname{Im}G^{R}$. In view of (29), we obtain also

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\ln\det(I+\Lambda G^{eR})=-\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\ln\det(I-\Lambda G^{gR})$$
$$=-i\,\mathrm{Sp}\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\Lambda\Gamma^{e}(\omega,T)=-i\,\mathrm{Sp}\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\Lambda\Gamma^{g}(\omega,T), \qquad (32)$$

$$(\mathrm{I}+\Lambda\Omega^{e})\Lambda\Gamma^{g}=\Lambda\Gamma^{e}(I-\Lambda\Omega^{g}). \qquad (33)$$

According to (32), the first terms in (30) and (31) are canceled after integration by the first terms of (25) and (27). In view of (33) we obtain therefore

$$\delta(T)=-\delta^{fl}(T),\quad \gamma(T)=\gamma^{fl}(T). \qquad (34)$$

These relations are evidence that the absorption and fluorescence NPL are at resonance and are equally broadened. It was shown earlier[28,29] that these NPL properties are preserved also when interaction with phonons is taken into account.

6. OPTICAL ABSORPTION BAND SHAPE

We shall calculate the entire absorption band on the basis of (15) and (16) and by taking into account only part of the electron-tunnelon interaction, viz. the frequency shift Δ_j in the TLS. The cumulant function (16) can be represented in this particular case as

$$\varphi(t)=-\sum_{j}\Big[\Delta_j\int_{0}^{t}dt_1\,G_{22}^{j}(-0)$$
$$+\frac{\Delta_j^{2}}{2}\int_{0}^{t}dt_1\int_{0}^{t}dt_2\,G_{22}^{j}(t_1-t_2)G_{22}^{j}(t_2-t_1)+\dots\Big]$$
$$=-i\delta(T)t-\gamma(T)|t|/2+\varphi_{TK}(t). \qquad (35)$$

We shall see presently that the function φ_{TK} is responsible for phototransitions accompanied by tunnelon creation and annihilation. In the calculation of φ_{TK} we can neglect the tunneling, putting $\Gamma_{22}^{j}(\nu)=\pi\delta(\nu-\varepsilon_j)$. We obtain then for φ_{TK} the rather simple expression

$$\varphi_{TK}(t)=\sum_{j}\ln[1-f_j+f_j\exp(-i\Delta_j t)], \qquad (36)$$

where $f_j=[\exp(\varepsilon_j/T)+1]^{-1}$. Tunneling cannot be neglected in the calculation of the expression for the NPL halfwidth and shift. The result is therefore

$$i\delta(T)+\frac{\gamma(T)}{2}$$
$$=\sum_{j}\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\Big[i\Delta_j\Gamma_{22}^{j}(\omega,T)-\frac{1}{2}\ln(1-\Delta_j G_{22}^{j}(\omega,T))\Big]. \qquad (37)$$

We introduce the TLS distribution function in the splittings 2ε and in the shifts Δ:

$$N(\varepsilon,\Delta)=\sum_{j}\delta(\varepsilon-\varepsilon_j)\delta(\Delta-\Delta_j). \qquad (38)$$

Obviously, the function $N(\varepsilon,\Delta)$ is contained in all the terms of (35). We substitute (35) in (15) and expand $\exp\varphi_{TK}(t)$ in terms of $\exp(-i\Delta_j t)$. Integrating the terms of the resultant series with respect to t, we obtain the following expression for the spectral distribution that describes the absorption band:

$$J(\omega)=\exp[-M(T)]\Big(L(\omega)+\sum_{m=0}^{\infty}\Psi_{2m}(\omega)\Big), \qquad (39)$$

where

$$L(\omega)=\frac{\gamma/2}{(\omega-E-\delta)^{2}+(\gamma/2)^{2}}, \qquad (39a)$$

$$\Psi_2(\omega)=\int_{0}^{\infty}d\varepsilon\int_{-\infty}^{\infty}d\Delta\,N(\varepsilon,\Delta)\exp\Big(-\frac{\varepsilon}{T}\Big)L(\omega-\Delta), \qquad (39b)$$

$$\Psi_4(\omega)=\frac{1}{2}\int_{0}^{\infty}d\varepsilon\int_{0}^{\infty}d\varepsilon'\int_{-\infty}^{\infty}d\Delta\int_{-\infty}^{\infty}d\Delta'\,N(\varepsilon,\Delta)[N(\varepsilon',\Delta')$$
$$-\delta(\varepsilon-\varepsilon')\delta(\Delta-\Delta')]\exp[-(\varepsilon+\varepsilon')/T]L(\omega-\Delta-\Delta'), \qquad (39c)$$

. . . .

$$-M(T)=\int_{0}^{\infty}d\varepsilon\,N(\varepsilon)\ln(1-f(\varepsilon)),\quad N(\varepsilon)=\int_{\Delta\neq0}d\Delta\,N(\varepsilon,\Delta). \qquad (40)$$

According to (39), the narrow Lorentzian peak $L(\omega)$ is accompanied by a broader distribution corresponding to phototransition with creation and annihilation of one, two, etc. tunnelons. The tunnelon wing is the analog of the phonon wing produced when an impurity center interacts with phonons. If electronic excitation of the impurity center causes a shift Δ_0 in only one TLS, i.e., $N(\varepsilon,\Delta)=\delta(\varepsilon-\varepsilon_0)\delta(\Delta-\Delta_0)$, we obtain with the aid of (39)

$$J(\omega)=(1-f_0)L(\omega)+f_0L(\omega-\Delta), \qquad (41)$$

where $f_0=[\exp(\varepsilon_0/T)+1]^{-1}$. In this case the absorption spectrum consists of a doublet of lines. The temperature function $M(T)$ is the analog of the Pekar-Huang factor. This factor contains the distribution function $N(\varepsilon)$ in the 2ε splittings of all the TLS that "feel" the electronic excitation of the impurity. Obviously, $L(\omega)$ describes a "no-tunnelon" line, which we shall designate by NPL as before.

The NPL halfwidth described by the real part of (37) can be transformed into

$$\gamma(T)=-\int_0^\infty d\varepsilon \int_{-\infty}^{\infty} d\Delta\, N(\varepsilon,\Delta) \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\ln\left[1-\frac{\Delta^2\Gamma^2(\omega)\,\mathrm{ch}^{-2}(\omega/2T)}{(1-\Delta\Omega(\omega))^2+\Delta^2\Gamma^2(\omega)}\right], \tag{42}$$

where $-\Gamma$ and Ω are the imaginary and real parts of the function $G^R_{22}(\omega,T)$. In the low-temperature region of interest to us, the argument of the logarithm differs little from unity, and we can rewrite (42) in the form

$$\gamma(T)=\int_{-\infty}^{\infty} d\omega\, F(\omega)\,\mathrm{ch}^{-2}(\omega/2T). \tag{43}$$

It is shown in Refs. 25 and 26 that this equation yields readily a nearly linear broadening if the function $F(\omega)$ differs from zero in a sufficiently large spectral range. For example, if $F(\omega)$ is approximated by a Gaussian or by a polynomial, we get a $T^{1.3}$ law. Obviously, the wide-band character of the function $F(\omega)$ can be due either to the "phonon jacket" of the tunnelon, or to the distribution $N(\varepsilon,\Delta)$ over the splittings 2ε. The latest experimental data,[19] will be shown in Sec. 9 to favor the first variant.

7. NONRESONANT FLUORESCENCE

The foregoing absorption-band-shape theory is valid also if the adiabatic potential of the impurity molecule itself or of the atom has two wells (Fig. 1). Obviously, nonresonant fluorescence can set in at $\Delta<0$, since the impurity center can dump part of its energy by tunneling during its excitation time. Denoting by $n_i(\nu_1,\nu_2)$ the probability density of observing an impurity center with no-phonon transitions of frequency ν_1 and ν_2 to the ith quantum state, we can obtain the equilibrium populations from the following system of balance equations:

$$\begin{gathered}-kn_1+\Gamma n_3+p_2n_2=0,\quad kn_1-(\Gamma+p_3)n_3=0,\\ -p_2n_2+\Gamma n_4=0,\quad p_3n_3-\Gamma n_4=0.\end{gathered} \tag{44}$$

Here $k=k_0L(\nu_b-\nu_1)$ determines the pumping of the excited state. The meaning of the remaining constants is clear from Fig. 1. Obviously, the luminescence intensity is determined by the populations n_3 and n_4. At relatively weak pumping, when the probability of the stimulated transition is less than that of the spontaneous one, i.e., $k/\Gamma \ll 1$, we have

$$\begin{gathered} n_3\cong\frac{k}{p_3+\Gamma}n(\nu_1,\nu_2),\qquad n_4\cong\frac{p_3}{\Gamma}\frac{k}{p_3+\Gamma}n(\nu_1,\nu_2),\\ n(\nu_1,\nu_2)=\sum_i n_i(\nu_1,\nu_2).\end{gathered} \tag{45}$$

Denoting by $L(\nu-\nu_1)$ the fluorescence NPL corresponding to transitions from levels 3 and 4, we obtain for the fluorescence of frequency ν, produced by excitation at the frequency ν_b, the following spectral function:

$$\begin{aligned} J^{fl}(\nu,\nu_b)&=\int_0^\infty d\nu_1\, d\nu_2[L(\nu-\nu_1)n_3+L(\nu-\nu_2)n_4]\\ &=\frac{\pi k_0}{p_3+\Gamma}\Bigg[\frac{\gamma(T)}{(\nu-\nu_b)^2+\gamma^2(T)}\int_0^\infty d\nu_2\, n(\nu,\nu_2)\\ &\qquad+\pi\frac{p_3}{\Gamma}n(\nu_b,\nu)\Bigg]. \end{aligned} \tag{46}$$

The first term in the square brackets describes the resonantly excited structural fluorescence. The second represents the nonresonant fluorescence, which can also be wide-band if the impurity centers in the solution have a broad distribution in the shifts Δ, i.e., in the frequencies $\nu_2=\nu_1+\Delta$.

8. INFLUENCE OF PHONONS ON THE OPTICAL-BAND SHAPE

We have taken into account so far the influence of the phonons on the shape of the optical band only indirectly, via "dressing" the excitations in the TLS. The direct influence of the phonons on the shape of the optical band has by now been thoroughly investigated.[1-4] It can be taken into account by adding to the operator of the electron-tunnelon interaction (13) the operator of the Franck-Condon electron-phonon interaction

$$\Lambda_{ph}=(\mathbf{R}-\mathbf{a})\frac{U^e}{2}(\mathbf{R}-\mathbf{a})-\mathbf{R}\frac{U^g}{2}\mathbf{R}=\mathbf{a}\frac{U^e}{2}\mathbf{a}-\mathbf{a}U^e\mathbf{R}+\mathbf{R}\frac{W}{2}\mathbf{R}. \tag{47}$$

In this case the cumulant function is a sum $\varphi=\varphi_{\mathrm{TLS}}+\varphi_{\mathrm{ph}}$, where φ_{TLS} is defined in Eq. (16) and φ_{ph} is defined by Eq. (2) of Ref. 30. The interaction (47) leads to additional broadening and shift of the NPL and to the appearance of a phonon wing. Obviously, these effects combine with the analogous effects due to the electron-tunnelon interaction. The following formula was obtained earlier[3] for the phonon contribution to the absorption NPL half-width and shift:

$$i\delta_{ph}(T)+\frac{\gamma_{ph}(T)}{2}=\int_{-\infty}^{\infty}\frac{d\omega}{4\pi}\ln\det(I+WD^g(\omega,T)), \tag{48}$$

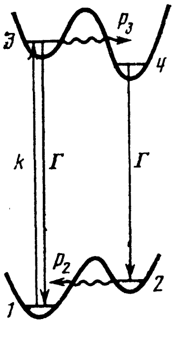

FIG. 1. Adiabatic potentials of impurity center at $\Delta<0$. The transitions 1←3 and 2←4 correspond to resonant and nonresonant fluorescence, respectively.

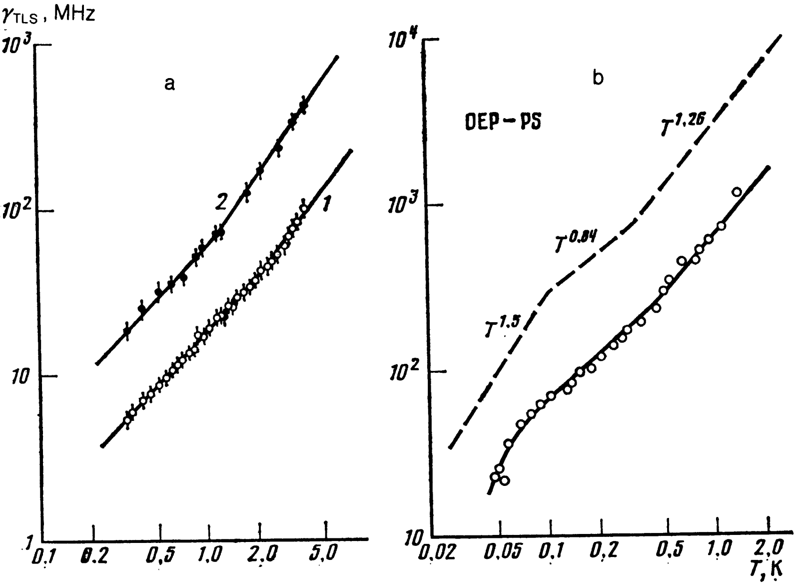

FIG. 2. Comparison of the homogeneous NPL halfwidth measured in Refs. 17 and 19 with the one calculated from Eq. (43) with the function

$$F(\omega)=A[\theta(\omega-\varepsilon_0)-\theta(\omega-\varepsilon_1)]$$
$$+a\exp\left[-\left(\frac{\omega-\varepsilon_2}{B}\right)^2\right]\theta(\omega-\varepsilon_1),$$

where $\theta(x)$ is the Heaviside step function. The values of the parameters in cm^{-1} (A and a are nondimensional) are: $A=\varepsilon_0=\varepsilon_1=0$, $B=22$, $\varepsilon_2=25$, $a=1.3\cdot10^{-3}$ (curve 1, H_2P in polyethylene); $A=\varepsilon_0=\varepsilon_1=0$, $B=22$, $\varepsilon_2=35$, $a=1.5\cdot10^{-3}$ (curve 2, H_2P in diglycerole $A=0.1$, $a=0.025$, $B=5$, $\varepsilon_0=0.065$, $\varepsilon_1=0.085$, $\varepsilon_2=10$ (H_2-octaethylporphine in an amorphous polymer—polystyrene (OEP-PS). The slopes of the dashed lines were obtained in Ref. 19 by least squares.

where the elements D^g_{nm} of the matrix are the Fourier components of the causal phonon Green's functions:

$$D_{nm}{}^g(t,T)=-i\langle \hat{T}R_n(t)R_m(0)\rangle_g. \qquad (49)$$

The phonons will be distorted by the interaction with the TLS. This distortion can be obtained by the scheme used in Sec. 2 to find the "dressing" of the TLS by phonons. After establishing the connection between D^g and the phonon function D^e of the excited electronic state, we can prove that

$$\delta_{ph}(T)=-\delta_{ph}{}^{fl}(T),\quad \gamma_{ph}(T)=\gamma_{ph}{}^{fl}(T), \qquad (50)$$

i.e., that the interaction with the phonons does not upset the resonance of the NPL and leads to equal broadening of the absorption and fluorescence NPL.

9. COMPARISON WITH EXPERIMENT

The only available experimental facts are, unfortunately, on the temperature dependences of the halfwidth and shape of the absorption-spectrum NPL.[11-19] The theory set forth above agrees with all these facts, since it yields[14,15,19] a Lorentzian NPL with homogeneous halfwidth

$$\gamma(T)=\gamma_{tun}(T)+\gamma_{TLS}(T)+\gamma_{ph}(T). \qquad (51)$$

The first term is here the sum of the tunnel widths of the levels that combine in the optical transition, the second term γ_{TLS} is described by the real part of the function (25), and the third by the real part of the function (48). It was mentioned at the end of Sec. 6 that the term γ_{TLS} yields both a linear and a near-linear $T^{1.3}$ dependence in the required temperature interval. The difference between the NPL residual halfwidth $\gamma(0)$ and the reciprocal fluorescent lifetime is apparently governed by the tunnel width $\gamma_{tun}(0)$ and attests to the two-well character of the impurity-center adiabatic potential. The quadratic broadening of homogeneous NPL in glasses, observed in Refs. 6, 7, and 14, can be quantitatively accounted for by the "old" term γ_{ph} (Refs. 8 and 9). The low-frequency quasilocal vibrations needed for such an explanation are produced in glasses as a result of distortion of the phonons by the TLS.[31] The phonon mechanism of NPL broadening causes a rapid decrease of the half-width in the low-temperature region, either like T^7 or in accordance with the $\exp(-\nu_0/T)$ law, where ν_0 is the quasilocal-vibration frequency. The tunnelon mechanism described by the term γ_{TLS} does not result in such rapid decreases of the half-width if the function $F(\omega)$ has no dip in the low-frequency region. One can therefore trace the following picture of the temperature dependence of the total NPL halfwidth.

At $T=0$ we have $\gamma(0)=\gamma_{tun}(0)$. At sufficiently low temperature, $\gamma\cong\gamma_{tun}+\gamma_{TLS}$. With further rise of temperature, the NPL half-width is determined primarily by the phonon mechanism, $\gamma\cong\gamma_{ph}$. As the temperature is raised, a transition from a near-linear broadening law to a T^2 law becomes therefore possible in accordance with the results of Ref. 18. The temperature at which the transition takes place depends on the ratio of the electron-tunnelon and electron-phonon interactions.

We examine now the extent to which the term γ_{TLS} in the "fracton" (Ref. 24) and in the "tunnelon" (Refs. 25 and 26) theories agrees with the results of studies in which the slope of the γ_{TLS} curve was observed to change once[17] or twice[19] (Figs. 2a and 2b). In the "fracton" theory the NPL broadening law depends on the rate at which the deformation potential falls off in space and varies like T, $T^{4/3}$, or $T^{23/15}$ for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions. The transition from $T^{1.3}$ to linear broadening at $T<1$ K is attributed in Ref. 24 to a change in the multipolarity of the interaction with decrease of temperature. The two changes of the slope of the γ_{TLS} curve (Fig. 2b) must apparently therefore be attributed to two changes of the multipolarity. However, even if this rather strange assumption is made, the growth of $\gamma_{TLS}(T)$ in the 0.08–0.4 K region, which is slower than linear, is not compatible with the "fracton" theory.

The "tunnelon" theory attributes the fractional powers in the NPL broadening law to presence of a "phonon jacket" of the tunnelon or to a broad distribution $N(\varepsilon,\Delta)$ of the TLS

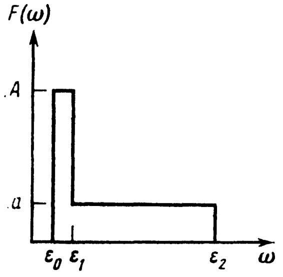

FIG. 3. The function $F(\omega)$ used to obtain Eq. (52).

in the splittings 2ε. If the impurity center interacts with only one TLS, the principal role is assumed by the "phonon jacket." In this case the function $F(\omega)$ in (43) should have a resonant part and a broad distribution. Taking the simplest variant of the function $F(\omega)$ in the form of two rectangles (Fig. 3), we can calculate analytically the integral in (43):

$$\gamma_{TLS}(T)=2T\left[A\left(\operatorname{th}\frac{\varepsilon_1}{2T}-\operatorname{th}\frac{\varepsilon_0}{2T}\right)+a\left(\operatorname{th}\frac{\varepsilon_2}{2T}-\operatorname{th}\frac{\varepsilon_1}{2T}\right)\right]. \tag{52}$$

Obviously, if $A \gg a$ there exist the following three temperature regions with different broadening laws:

$$\gamma_{TLS}(T)=\begin{cases} 4AT\exp(-\varepsilon_0/T), & T<\varepsilon_0 \\ A(\varepsilon_1-\varepsilon_0)+2aT, & \varepsilon_1<T<\varepsilon_1(A/2a) \\ 2aT, & \varepsilon_1(A/2a)<T<\varepsilon_2. \end{cases} \tag{53}$$

Even the simple equations (52) and (53) describe quantitatively the experimental results of Fig. 2b in the region $T<0.4$ K. They fail to describe the $T^{1.3}$ and $T^{1.2}$ laws only at higher temperature. If, however, the lower rectangle with amplitude a in Fig. 3 is replaced by a Gaussian, we obtain quantitative agreement between the "tunnelon" theory and the experimental data of Refs. 17 and 19 in the entire temperature range—Figs. 2a and 2b.

It must be emphasized that even though a TLS distribution function enters in it, this theory pertains to a single impurity center, i.e., actually to a homogeneous band. Since the physical parameters that govern the shape function of the optical band undoubtedly vary from center to center under the conditions of an amorphous medium, the shape function must be averaged over these parameters, as was done already in Refs. 8 and 23. Two possibilities are encountered here. If all the parameters obey a single broadening law in the range of their scatter,[8] the broadening law is likewise not altered by such an averaging. In the opposite case, this averaging alters the broadening law of the resultant spectral distribution.[23] Obviously, if the formula for the homogeneous halfwidth were not to yield the experimentally observed temperature dependences, this would be a weighty argument in favor of the fundamental importance of such an averaging. We see, however, that the equations obtained for the homogeneous halfwidth to not provide as yet such an argument. At the same time, averaging of the spectral distribution, carried out, e.g., in Ref. 23, leads in an actual case to a non-Lorentzian NPL, which does not agree with experiment.[15]

The earlier theories of NPL broadening in amorphous media did not offer, unfortunately, new predictions that would provide a check on their basic premises in independent experiments. What new predictions are made by our present theory? 1. Nonresonance fluorescence can appear. This fact should offer evidence that the adiabatic potential of the impurity center has two wells, and should therefore correlate with the presence of a residual NPL halfwidth. 2. If the impurity center in the crystal has a two-well adiabatic potential with noticeable tunneling, anomalous broadening of NPL can occur also in crystalline matrices. In this case, obviously, we come up against the situation considered above, in which only one TLS "feels" the electronic excitation of the impurity center.

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[1] Relation (29) can be regarded as the condition for resonance and equal broadening of the homogeneous fluorescence and absorption NPL. This relation is valid, for example, if $\Lambda_j=\Delta_j$.

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