The theory of homogeneous impurity band shape in polymers and glasses

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We examine the influence of vibrational and tunnel excitations of polymers and glasses on the shape of the homogeneous optical band of an impurity center. An analytic expression is obtained for the optical band shape in the vicinity of a zero-phonon line (ZPL) for interactions of arbitrary strength between the optical electrons of the impurity center and the nuclear vibrations and excitations of tunnel systems. At low temperature, the formulas found for the ZPL half-width and shift go over to the corresponding formulas of the "exchange model" used to consider dephasing in spin systems. Numerical calculations of the optical band shape are carried out, and its behavior is analyzed for different values of the physical parameters.

1. INTRODUCTION

In the last few years, it has been found using selective spectroscopy methods that strong inhomogeneous broadening is the primary reason why the impurity bands in polymers and glasses are relatively structureless.

Selective spectroscopy techniques eliminate this inhomogeneous broadening, yielding highly structured fluorescence spectra as well as so-called "hole-burning spectra.[1,2] These structured spectra, which will be called selective below, are not, strictly speaking, homogeneous, by which we mean the spectra of individual impurity centers. Indeed, in addition to a spread in the resonant electron frequency, impurity centers in such disordered systems as polymers and glasses possess a spread in other parameters, for example, in dynamic interaction with the environment, which affects the shape of a homogeneous optical band. Therefore, the theoretical processing of measured selective spectra is a more complicated problem than the processing of homogeneous spectra of impurity centers in crystals. The first step to solve this problem should be the construction of a theory of a homogeneous impurity center band in polymers and glasses.

Why then cannot we restrict ourselves to the theory developed earlier for impurity centers in crystals,[3,4] when considering polymers and glasses? The point is that additional degrees of freedom, so called two-level systems (TLS), exist in polymers and glasses.[5,6] They are responsible for low-temperature anomalies of various physical properties of glasses[7] and reveal themselves in selective spectra as well.[8,9] Hence the theory of homogeneous optical bands of polymers and glasses should allow for the interaction of optical electrons of an impurity center with both phonons and TLS excitations, which will be called tunnelons in what follows. In other words, we should allow for both electron-phonon and electron tunnelon interactions.

We shall restrict ourselves to the consideration of optical bands of impurity centers, in which only two electron levels should be taken into account. The optical band of such an impurity center in a crystal consists of a zero-phonon line (ZPL) and an accompanying phonon wing (PW). The linear Franck–Condon interaction is known to determine PW and ZPL intensity but have no effect on ZPL halfwidth and shape. Conversely, the Franck–Condon interaction quadratic in the phonon operators results in ZPL temperature broadening but contributes insignificantly to PW intensity.[4] Nearly the same situation occurs as regards the linear and the quadratic electron-tunnelon interaction.[10,11] Reasoning from the foregoing and noting that ZPL is the primary object under study in selective spectra, we shall restrict ourselves to consideration of quadratic electron-phonon and electron-tunnelon interactions in the present paper.

These interactions are responsible not only for the broadening of the zero-phonon or zero-tunnelon lines (the 0–0′ transition in Fig. 1) but also for the intensity and halfwidth of the 1–1′, 2–2′, etc. transitions. These transitions do not vary the total number of phonons or tunnelons. On this basis some authors include them in the ZPL. These transitions do not affect the ZPL halfwidth noticeably. However, they cannot be ignored in the wings of this line. We have succeeded for the first time in finding a method for calculating the whole system of quantumless transitions, which does not rely upon the smallness of the quadratic electron-phonon and electron-tunnelon interactions. The presentation of this method and the results of the calculations of the whole system of quantumless transitions using this method are the subject of the present paper.

2. ELECTRON-PHONON AND ELECTRON-TUNNELON INTERACTIONS

The theoretical approach of Born and Oppenheimer[12] to a system of interacting electrons and nuclei undoubtedly remains valid even if tunnel transitions as well as vibrations exist in the system of nuclei. In this case, the system of nuclei in the adiabatic approximation is described by the adiabatic Hamiltonians $H^{g,e}$, which are obtained by averaging the complete Hamiltonian over the ground (g) and

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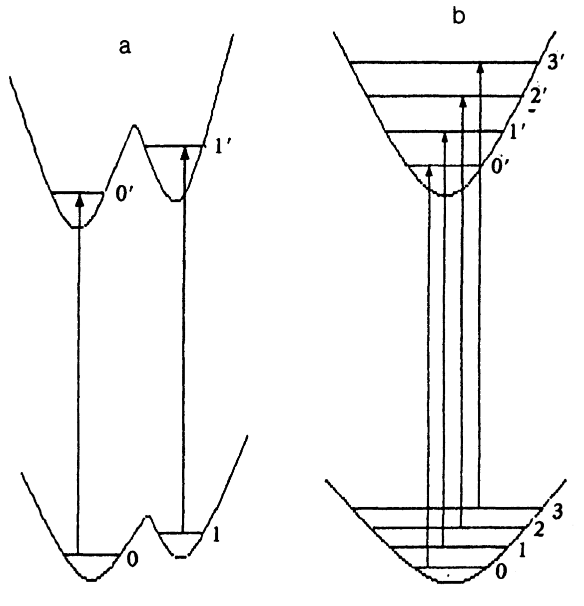

FIG. 1. Diagram of the energy levels and potential curves of an impurity center in the ground and the excited electron states in the cases of tunnel (a) and vibrational (b) nuclear motion. The arrows mark only those optical transitions in the absorption spectrum which are analyzed in the present paper.

the excited (e) electron states of an impurity center. In the absence of TLS, the Hamiltonians $H^{g,e}$ depend only on the phonon coordinates $\vec{R}$:

$$H^{g,e}=H^{g,e}_{\rm ph}=\hat{T}_R+U^{g,e}(\vec{R}), \tag{1}$$

where $\hat{T}_R$ and $U^{g,e}(\vec{R})$ are the operators of the kinetic and potential energy of the nuclei. In polymers and glasses, we should add to $H^{g,e}_{\rm ph}$ an operator depending on the Pauli matrix $\hat{\sigma}_z$ describing tunnel degrees of freedom, i.e., TLS:

$$H^{g,e}=H^{g,e}_{\rm ph}+H^{g,e}_{\rm TLS}, \tag{2}$$

where

$$H^{g,e}_{\rm TLS}=\frac{1}{2}\sum_{j=1}^{N}\varepsilon_j^{g,e}\hat{\sigma}_{zj}\,. \tag{3}$$

Here $\varepsilon_j^{g,e}$ is the energy of the jth TLS for an electronically excited (e) and unexcited (g) impurity.

The Pauli matrix $\hat{\sigma}_{zj}$ may be expressed in terms of the operators c_j and c_j^+ obeying the Fermi commutational relations:

$$\hat{\sigma}_{zj}=c_j^+c_j-c_jc_j^+\,. \tag{4}$$

Clearly, c_j^+ and c_j are the creation and annihilation operators for an excitation in the jth TLS, i.e., the jth tunnelon. The operator $H^{g,e}_{\rm TLS}$ may be expressed in terms of the tunnelon operators:

$$H^{q,e}_{\rm TLS}=\sum_{j=1}^{N}\varepsilon_j^{g,e}c_j^+c_j\,. \tag{5}$$

Here, we have omitted a constant, which may be included later in the electron interaction energy.

The difference $\hat{\Lambda}=H^e-H^g$ between the two adiabatic Hamiltonians is the Franck–Condon interaction, which determines the shape of the homogeneous optical band. In polymers and glasses, it consists of two terms: $\hat{\Lambda}=\hat{\Lambda}_{\rm ph}+\hat{\Lambda}_{\rm TLS}$, where $\hat{\Lambda}_{\rm ph}=H^e_{\rm ph}-H^g_{\rm ph}$ and $\hat{\Lambda}_{\rm TLS}=H^e_{\rm TLS}-H^g_{\rm TLS}$ describe the electron-phonon and the electron-tunnelon interactions respectively. Approximating the potential function $U^{g,e}(\vec{R})$ by a quadratic form, we get the following expressions for the interactions:

$$\hat{\Lambda}_{\rm ph}=\vec{R}-\frac{W}{2}-\vec{R},\quad \hat{\Lambda}_{\rm TLS}=\sum_{j=1}^{N}\Delta_jc_j^+c_j, \tag{6}$$

where $W=U^e-U^g$ is the difference of the force matrices and $\Delta_j=\varepsilon_j^e-\varepsilon_j^g$ is the difference of the tunnelon energies. We do not take into account the shift of equilibrium positions, which gives rise to a linear electron-phonon interaction making no contribution in ZPL broadening.

3. GENERAL FORMULAS FOR THE OPTICAL BAND SHAPE

The expression describing the shape of the optical absorption band of an impurity center has the form[13,14]

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt e^{i(\omega-\omega_0)t}\langle\hat{I}(t)\rangle_g, \tag{7}$$

where ω_0 is the resonant frequency of the impurity center, and

$$\hat{I}(t)=\exp(iH^gt)\exp(-iH^et), \tag{8}$$

$$\langle...\rangle_g={\rm Tr}[\exp(-\beta H^g)...]/{\rm Tr}[\exp(-\beta H^g)]. \tag{9}$$

The function $\langle\hat{I}(t)\rangle_g$ describes the time behavior of the dipole correlator, whose Fourier component is known to govern the shape of the absorption band.

The operator $\hat{I}(t)$ satisfies a simple equation

$$\frac{d}{dt}\hat{I}(t)=-i\hat{\Lambda}(t)I(t), \tag{10}$$

where

$$\hat{\Lambda}(t)=\exp(iH^gt)\hat{\Lambda}\exp(-iH^gt). \tag{11}$$

Solving Eq. (10) with the initial condition $\hat{I}(0)=1$, we find that

$$\begin{aligned}\hat{I}(t)&=\sum_{n=0}^{\infty}\int_0^t dt_1\int_0^{t_1}dt_2...\int_0^{t_{n-1}}dt_n\hat{\Lambda}(t_1)\hat{\Lambda}(t_2)...\hat{\Lambda}(t_n),\\&=\sum_{n=0}^{\infty}\frac{1}{n!}\int_0^t t_1\int_0^t dt_2...\int_0^t dt_n\hat{T}\hat{\Lambda}(t_1)\hat{\Lambda}(t_2)...\hat{\Lambda}(t_n).\end{aligned} \tag{12}$$

The time-ordering operator $\hat{T}$ arranges the operators $\hat{\Lambda}$ in such a way that their times increase from right to left. Since the phonon operators R commute with the tunnelon operators c_j^+ and c_j, Eq. (9) may be averaged independently over the phonon and the tunnelon subsystems:

$$\langle\hat{I}(t)\rangle_g=\langle\hat{I}_{\rm ph}(t)\rangle_{g,\rm ph}\langle\hat{I}_{\rm TLS}(t)\rangle_{g,\rm TLS}, \tag{13}$$

where the averages on the right side are described by Eq. (9), where H^g are replaced by $H^g_{\rm ph}$ and $H^g_{\rm TLS}$ respectively.

Let us first consider the calculation of the phonon average in Eq. (13). In this case, the operator (12) is averaged, where the operators $\hat{\Lambda}_{\rm ph}=\vec{R}(W/2)\vec{R}$ are substituted for the operators $\hat{\Lambda}$. If the impurity center is electrically neutral, only solvent molecules in its immediate vicinity experience the change of its electron state. In this case, the interaction is local, and we may restrict ourselves to the consideration of only one matrix element in the $\hat{W}$ matrix, taking $\hat{\Lambda}_{\rm ph}=(W/2)R^2$.

The calculation of the averages of the $\hat{\Lambda}_{\rm ph}$ products in formula (12) is performed in accordance with the rules worked out by Wick, Bloch, and Dominisis.[15] Here the averages of the products of $\hat{\Lambda}_{\rm ph}$ are decomposed into the products of causal single-frequency phonon Green's functions:

$$\begin{aligned} D(t)&=-i\langle\hat{T}R(t)R(0)\rangle\\ &=-i[\langle R(t)R(0)\rangle\theta(t)\\ &\quad+\langle R(0)R(t)\rangle\Theta(-t)], \end{aligned}\tag{14}$$

where $\theta(t)$ is the Heaviside step function. The calculation of the averages in Eq. (14) brings us to the following expression:

$$D(t)=D_+(t)\theta(t)+D_+(-t)\theta(-t),$$

where

$$\begin{aligned} D_+(t)=\int_{-\infty}^{\infty}\frac{d\nu}{2\pi i}\Gamma_{\rm ph}(\nu)[(n(\nu)+1)e^{-i\nu t}\\ +n(\nu)e^{i\nu t}]. \end{aligned}\tag{15}$$

Here, $n(\nu)=[\exp(h\nu/kT)-1]^{-1}$, the spectral function $\Gamma_{\rm ph}(\nu)$ is determined by the amplitude of vibrations of the molecular coordinate R at the frequency ν.[16]

The calculation of the averages in formula (12) yields the following result:

$$\langle\hat{I}_{\rm ph}(t)\rangle_{g,{\rm ph}}=\exp\phi_{\rm ph}(t),\tag{16}$$

where

$$\begin{aligned} \phi_{\rm ph}(t)&=\frac{W}{2}\int_0^t d\tau\Big[D(+0)+W\int_0^\tau dt_1D(\tau-t_1)\\ &\quad\times D(t_1-\tau)+W^2\int_0^\tau dt_1\int_0^\tau dt_2D(\tau-t_1)\\ &\quad\times D(t_1-t_2)D(t_2-\tau)+\ldots\Big]\\ &=\frac{W}{2}\int_0^t d\tau S(+0,\tau). \end{aligned}\tag{17}$$

Here, $S(+0,\tau)$ denotes the infinite series in the square brackets. Evidently, it is a solution of the integral equation

$$S(x,\tau)=D(x)+W\int_0^\tau dyD(x-y)S(y,\tau)\tag{18}$$

at $x=+0$.

The tunnelon average $\langle I_{\rm TLS}(t)\rangle_{g,{\rm TLS}}$ is calculated in a similar way. In this case, the casual single-frequency tunnelon Green's function appears in the calculations

$$\begin{aligned} G_j(t)&=-i\langle\hat{T}c_j(t)c_j^+(0)\rangle\\ &=-i[\langle c_j(t)c_j^+(0)\rangle\theta(t)\\ &\quad-\langle c_j^+(0)c_j(t)\rangle\theta(-t)]. \end{aligned}\tag{19}$$

The calculation of this function yields[10]

$$\begin{aligned} G_j(t)=\int_0^\infty\frac{dE}{\pi i}\Gamma_j(E)[(1-f(E))\theta(t)\\ -f(E)\theta(-t)]e^{-iEt}, \end{aligned}\tag{20}$$

where $f(E)=[\exp(E/kT)+1]^{-1}$ and $\Gamma_j(E)$ is the spectral function of the jth tunnelon.

When calculating $\langle I_{\rm TLS}(t)\rangle_{g,{\rm TLS}}$, we should take into account the Fermi nature of the operators c_j^+ and c_j. The result is

$$\langle I_{\rm TLS}(t)\rangle=\exp\sum_j\phi_j(t),\tag{21}$$

where

$$\begin{aligned} \phi_j(t)=-\Delta_j\int_0^t d\tau[G_j(-0)-G_j(+0)\\ +S_j(+0,\tau)]. \end{aligned}\tag{22}$$

Here, the function $S(+0,\tau)$ also describes an infinite series, which is a solution of the equation

$$S_j(x,\tau)=G_j(x)+\Delta_j\int_0^\tau dyG_j(x-y)S_j(y,\tau)\tag{23}$$

for $x=+0$. Equation (23) resembles Eq. (18) derived for the phonon system. They differ only in their Green's functions.

The impurity center optical band allowing for the quadratic interaction in all orders in the coupling constants W or Δ_j is thus described by

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dte^{i(\omega-\omega_0)t}+\phi_{\rm ph}(t)+\sum_j\phi_j(t),\tag{24}$$

where the cumulant functions $\phi_{\rm ph}(t)$ and $\phi_j(t)$ are determined by formulas (17) and (22). Clearly, the problem is reduced to the solution of the integral equations (18) and (23).

4. THE CALCULATION OF THE TUNNELON CUMULANT FUNCTION $\phi_j(t)$

We shall simulate the spectral function of the j-th tunnelon by a Lorentzian curve with a halfwidth 2γ. The subscript j will be omitted in this section. The tunnelon energy in the ground state is denoted by ε. Taking into account that

$$\Gamma(E)f(E)=\frac{\gamma}{(E-\varepsilon)^2+\gamma^2}f(E)$$

$$\cong\frac{\gamma}{(E-\varepsilon)^2+\gamma^2}f(\varepsilon) \tag{25}$$

we can rewrite the tunnelon Green's function in the following simplified form:

$$G(t)=-i(1-f)e^{-i(\varepsilon-i\gamma)t}\theta(t)$$

$$+ife^{-i(\varepsilon+i\gamma)t}\theta(-t). \tag{26}$$

Here we have written $f=f(\varepsilon)$, and $1/2\gamma$ is the tunnelon lifetime.

The function $S(x,\tau)$ will be sought in the following form:

$$S(x,\tau)=S_1(\tau)e^{-i\Omega_1 x}+S_2(\tau)e^{-i\Omega_2 x}, \tag{27}$$

where $S_{1,2}(x,\tau)$ and $\Omega_{1,2}$ are unknown functions and complex frequencies. Let us substitute formulas (26) and (27) into the integral equation (23), perform integration over y and collect all the terms with identical exponentials. Instead of the integral equation (23), we obtain the following algebraic equation

$$e^{-i\Omega_1 x}S_1(\tau)\left[1-\Delta\frac{1-f}{\Omega_1-\varepsilon+i\gamma}-\Delta\frac{f}{\Omega_1-\varepsilon-i\gamma}\right]$$

$$+e^{-i\Omega_2 x}S_2(\tau)\left[1-\Delta\frac{1-f}{\Omega_2-\varepsilon+i\gamma}-\Delta\frac{f}{\Omega_2-\varepsilon-i\gamma}\right]$$

$$=e^{i(\varepsilon-i\gamma)x}(1-f)\left[1+\Delta\frac{S_1(\tau)}{\varepsilon-i\gamma-\Omega_1}+\Delta\frac{S_2(\tau)}{\varepsilon-i\gamma-\Omega_2}\right]$$

$$+e^{i(\varepsilon+i\gamma)x}f\left[\frac{S_1(\tau)}{\varepsilon+i\gamma-\Omega_1}e^{i(\varepsilon+i\gamma-\Omega_1)\tau}\right.$$

$$\left.+\frac{S_2(\tau)}{\varepsilon+i\gamma-\Omega_2}e^{i(\varepsilon-i\gamma-\Omega_2)\tau}\right]. \tag{28}$$

This equation is satisfied at any x value, if all the factors multiplying the exponents are zero. This condition is met, if the unknown frequencies $\Omega_{1,2}$ are the roots of the equation

$$1-\Delta\left(\frac{1-f}{\Omega-\varepsilon+i\gamma}+\frac{f}{\Omega-\varepsilon-i\gamma}\right)=0 \tag{29}$$

and the unknown functions $S_1(\tau)$ and $S_2(\tau)$ are the solutions of the following system of equations

$$\frac{S_1}{\Delta_1}+\frac{S_2}{\Delta_2}=-\frac{1}{\Delta};\quad \frac{S_1}{\bar{\Delta}_1}e^{i\bar{\Delta}_1\tau}+\frac{S_2}{\bar{\Delta}_2}e^{i\bar{\Delta}_2\tau}=0. \tag{30}$$

Here we have introduced the notation

$$\Delta_{1,2}=\varepsilon-i\gamma-\Omega_{1,2},\quad \bar{\Delta}_{1,2}=\varepsilon+i\gamma-\Omega_{1,2}. \tag{31}$$

Equation (29) has two roots

$$\Omega_1=\varepsilon+\frac{\Delta}{2}+\Omega_0-i\gamma_0,\quad \Omega_2=\varepsilon+\frac{\Delta}{2}-\Omega_0+i\gamma_0, \tag{32}$$

where

$$\Omega_0=\pm\left\{\frac{1}{2}\left[\left[\left(\frac{\Delta^2}{4}-\gamma^2\right)^2+\gamma^2\Delta^2(1-2f)^2\right]^{1/2}\right.\right.$$

$$\left.\left.+\frac{\Delta^2}{4}-\gamma^2\right]\right\}^{1/2}, \tag{33}$$

$$\gamma_0=\left\{\frac{1}{2}\left[\left[\left(\frac{\Delta^2}{4}-\gamma^2\right)^2+\gamma^2\Delta^2(1-2f)^2\right]^{1/2}\right.\right.$$

$$\left.\left.-\frac{\Delta^2}{4}+\gamma^2\right]\right\}^{1/2}. \tag{34}$$

The sign of the frequency Ω_0 has to agree with that of the coupling constant Δ. It is easy to verify that $\gamma_0<\gamma$. Therefore, we have $\gamma_0\to 0$ for a long-lived tunnelon. Solving Eq. (30) and substituting this solution in Eqs. (27) and (22), we get the following expression for the tunnelon cumulant function:

$$\phi(t)=it\bar{\Delta}_2+\ln(1-\alpha e^{i(\bar{\Delta}_1-\bar{\Delta}_2)t})-\ln(1-\alpha), \tag{35}$$

where

$$\alpha=\Delta_1\bar{\Delta}_2/\Delta_2\bar{\Delta}_1. \tag{36}$$

In the derivation of Eq. (35), we have used the fact that $G(-0)-G(+0)=i$.

5. THE ELECTRON-TUNNELON BAND

We restrict ourselves to examining the case, in which only one tunnelon experiences the variation of the impurity electron state, i.e., the electron-tunnelon interaction is local. Then the sum over j should be omitted in Eq. (24). Neglecting temporarily the electron-phonon interaction too, i.e., assuming $\phi_{\mathrm{ph}}=0$, we find the following expression for the integrand in Eq. (24):

$$e^{-i\omega_0 t+\phi(t)}=e^{-i\omega_0 t}\left(\frac{1}{1-\alpha}e^{i\bar{\Delta}_2 t}-\frac{\alpha}{1-\alpha}e^{i\bar{\Delta}_1 t}\right). \tag{37}$$

This expression describes the time dependence of the dipole correlator, including the interaction of the electron dipole with the tunnelon. Taking into account the relation $\phi(-t)=\overset{*}{\phi}(t)$, we obtain the following expression in place of (24):

$$I(\omega)=\frac{1}{\pi}\operatorname{Re}\int_0^\infty dt e^{i(\omega-\omega_0)t+\phi(t)}$$

$$=\frac{1}{\pi}\operatorname{Im}\left[\frac{1}{1-\alpha}\frac{1}{\omega-\omega_0+\bar{\Delta}_2}-\frac{\alpha}{1-\alpha}\frac{1}{\omega-\omega_0+\bar{\Delta}_1}\right]. \tag{38}$$

To separate the real and the imaginary parts in the expression in the square brackets, we introduce the real functions A and B:

$$A+iB=\frac{1}{1-\alpha}. \tag{39}$$

Taking into account the fact that

$$\bar{\Delta}_2=-\Delta/2+\Omega_0+i(\gamma-\gamma_0),$$

$$\bar{\Delta}_1=-\Delta/2+\Omega_0+i(\gamma+\gamma_0),$$

we find, instead of formula (38), the following final expression for the electron-tunnelon optical band:

$$I(\omega)=\frac{1}{\pi}\left[A\frac{\gamma-\gamma_0}{(\Omega+\Omega_0)^2+(\gamma-\gamma_0)^2}\right.$$
$$\left.+(1-A)\frac{\gamma+\gamma_0}{(\Omega-\Omega_0)^2+(\gamma+\gamma_0)^2}\right]$$
$$-\frac{8}{\pi}\left[\frac{\Omega+\Omega_0}{(\Omega_0+\Omega)^2+(\gamma-\gamma_0)^2}\right.$$
$$\left.-\frac{\Omega-\Omega_0}{(\Omega-\Omega_0)^2+(\gamma+\gamma_0)^2}\right]. \tag{40}$$

Here $\Omega=\omega-\omega_0-\Delta/2$. The real functions A and B may be expressed in terms of the physical parameters Δ and γ and a temperature function f, if we make use of the expression

$$\alpha=\frac{\bar{\Delta}_2+f\Delta}{\bar{\Delta}_1+f\Delta}, \tag{41}$$

which is obtained from (36) with allowance for Eq. (29). Substituting (41) in Eq. (39), we find

$$A=\frac{\Omega_0(\Delta/2+\Omega_0-f\Delta)+\gamma_0(\gamma+\gamma_0)}{2(\Omega_0^2+\gamma_0^2)},$$

$$B=\frac{(\Delta/2-f\Delta)\gamma_0-\Omega_0\gamma}{2(\Omega_0^2+\gamma_0^2)}. \tag{42}$$

Relations (40) and (42) permit the optical band shape to be calculated numerically. Let us analyze these formulas.

We start our analysis with the case when the tunnelon is long-lived. Then we may set $\gamma=0$, and according to formulas (33) and (34), we therefore have $\gamma_0=0$ and $\Omega_0=\Delta/2$. In this case, Eq. (40) is drastically simplified, and we obtain the well-known result[10]

$$I(\omega)=(1-f)\delta(\omega-\omega_0)+f\delta(\omega-\omega_0-\Delta). \tag{43}$$

These two δ-function lines describe the 0–0′ and 1–1′ transitions depicted in Fig. 1a. The 1–1′ transition is accompanied by annihilation of a tunnelon in the ground electron state and creation of a tunnelon in the excited electron state. The interaction with a long-lived tunnelon does not cause line broadening.

Let us now consider the influence of the interaction with a short-lived tunnelon on the optical band. Comparison of Eqs. (40) and (43) shows that the finite tunnelon lifetime $1/2\gamma$ cannot be allowed for just by replacing the δ-functions in Eq. (43) by Lorentzian curves with the proper widths, because the intensities of phototransitions also depend on tunnelon lifetime. The first Lorentzian curve in Eq. (40) with a smaller halfwidth $2(\gamma-\gamma_0)$ describes the zero-tunnelon line, while the second Lorentzian curve with a halfwidth $2(\gamma+\gamma_0)$ corresponds to the 1–1′ transition. Moreover, the terms proportional to B make the Lorentzian curves asymmetric. The electron-tunnelon bands calculated from Eq. (40) for various values of the dimensionless coupling constant $\Delta/2\gamma$ and various temperatures are shown in Figs. 2a, 2b, and 2c. The scale in the abscissa is chosen so that all the zero-tunnelon lines have unit halfwidth. On this scale, the shapes of the 0–0′ and

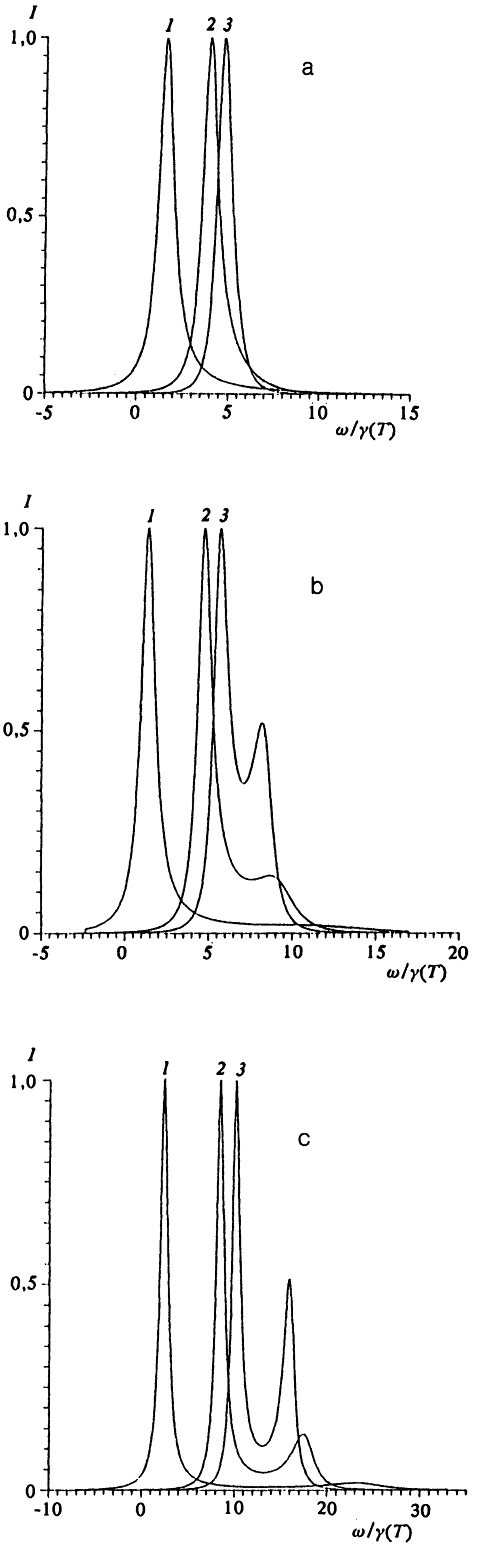

FIG. 2. a—The effect of temperature on the shape of the homogeneous electron-tunnelon band calculated from formulas (38)–(40), for various values of the dimensionless temperature $kT/\varepsilon=0.5$ (*1*); 1 (*2*); 3 (*3*) and at $\Delta/2\gamma=1$. The frequency in the x-axis is in units of ZPL halfwidth and is measured from the ZPL position at $T=0$. b—As in Fig. 2a, for $\Delta/2\gamma=2.5$. c—As in Fig. 2a, for $\Delta/2\gamma=5$.

1–1′ lines and their relative position are clearly seen.

The total intensity of the whole optical band does not depend on electron-tunnelon coupling constant and temperature. As the temperature increases, the total intensity of the zero-tunnelon line decreases, while the intensity of the 1–1′ transitions grows. Intensity is transferred from the 0–0′ to the 1–1′ line as the temperature increases, as in the case of electron-phonon spectra.

6. THE EVALUATION OF THE PHONON CUMULANT FUNCTION $\phi_{ph}(t)$

The method used in Sec. 4 for resolving the integral equation (23) can be used to calculate $\phi_{ph}(t)$ as well, if only the interaction with a quasilocal vibration is taken into account. Experiment shows that in most of the cases studied an impurity center interacts most actively with a quasilocal vibration. This vibration, as well as tunnelon, may be approximated by a Lorentzian curve with a half-width 2γ. If an approximation of the form (25) is used, the phonon Green's function (15) is transformed to

$$D(t)=-\frac{i}{2\nu}\{[(n+1)e^{-i\nu t}+ne^{i\nu t}]e^{-\gamma t}\theta(t)$$
$$+[(n+1)e^{i\nu t}+ne^{-i\nu t}]e^{\gamma t}\theta(-t)\}, \qquad (44)$$

where $n=[\exp(h\nu/kT)-1]^{-1}$, ν and $1/2\gamma$ are the frequency and the lifetime of the quasilocal phonon.

We look for the solution of the integral equation (18) in the following form:

$$S(x,\tau)=\sum_{i=1}^{4} S_i(\tau)e^{i\Omega_i x}. \qquad (45)$$

The procedure for determining the unknown functions $S_i(\tau)$ and the complex frequencies Ω_i is quite similar to that presented in Sec. 4. Substituting (44) and (45) in Eq. (18), we find the following equations for the unknown frequencies and functions:

$$\frac{\nu}{W}=\frac{(n+1)(\nu-i\gamma)}{\Omega_i^2-(\nu-i\gamma)^2}-\frac{n(\nu+i\gamma)}{\Omega_i^2-(\nu+i\gamma)^2}, \qquad (46)$$

$$\sum_{i=1}^{4}\frac{S_i(\tau)}{\Omega_i\pm\nu-i\gamma}=\frac{i}{W},$$

$$\sum_{i=1}^{4}\frac{S_i(\tau)}{\Omega_i\pm\nu+i\gamma}e^{i(\Omega_i\pm\nu+i\gamma)t}=0. \qquad (47)$$

Once the four roots Ω_i of Eq. (46) are found, we could find the four unknown functions $S_i(\tau)$ by substituting the roots in the system of four equations (47). This procedure is simple in principle, but rather cumbersome in practice. Fortunately, it can be avoided, if we consider that we do not need the whole function $S(x,\tau)$ for the cumulant function to be determined, but only its value at $x=+0$, i.e., $S(+0,\tau)$. However, the function $S(+0,\tau)$ can be expressed merely in terms of the determinant $d(\tau)$ of system (47):

$$S(+0,\tau)=-\frac{1}{W}\frac{d}{d\tau}\ln d(\tau). \qquad (48)$$

Substituting (48) in (17), we get the following expression for the phonon cumulant function $\phi_{ph}(t)$:

$$\phi_{ph}(t)=-\tfrac{1}{2}[\ln d(t)-\ln d(0)]. \qquad (49)$$

The cumulant function at $t\underset{*}{<}0$ can be found by using a simple relation $\phi_{ph}(-t)=\phi(t)$. It follows from Eq. (46) that there are only two independent complex roots $\Omega_{1,2}$, because $\Omega_3=-\Omega_1$ and $\Omega_4=-\Omega_2$. Calculating the determinant $d(t)$ of system (47), we find

$$d(t)=e^{-i(\Omega_2-\Omega_1-2i\gamma)t}[1-2ab(1-\lambda^2)e^{i(\Omega_2-\Omega_1)t}$$
$$+a^2b^2e^{2i(\Omega_2-\Omega_1)t}-\lambda^2(a^2e^{-2i\Omega_1 t}+b^2e^{2i\nu t})], \qquad (50)$$

where

$$\lambda=\frac{\Omega_1-\Omega_2}{\Omega_1+\Omega_2},$$
$$a=\frac{(\Omega_1+i\gamma)^2-\nu^2}{(\Omega_1-i\gamma)^2-\nu^2}, \qquad (51)$$
$$b=\frac{(\Omega_2-i\gamma)^2-\nu^2}{(\Omega_2+i\gamma)^2-\nu^2}.$$

Formulas (49)–(51) completely determine the phonon cumulant function $\phi_{ph}(t)$.

Let us compare expression (50), which allows for the phonon peak width γ and the temperature T, with Eq. (21) of Ref. 16 for the cumulant function h, which was calculated earlier by another method at $\gamma=0$ and $T\neq0$. If we set $\gamma=0$ in the expression for $d(t)$ and neglect the contribution of the linear electron-phonon interaction in the function h, we find that the results agree completely: $h(t)=\phi_{ph}(t)$. This proves the adequacy of two different methods for calculating the cumulant function.

The determinant may be simplified, if we note that the parameter λ in principle may not exceed unity in magnitude. In real physical systems, it is always less than unity. Indeed, in the limit $\gamma\rightarrow0$ the frequencies Ω_1 and Ω_2 transform to real frequencies of the ground and the excited states, i.e., $\Omega_2=\nu$ and $\Omega_2=\nu+\Delta$. The parameter λ satisfies $\lambda=\Delta/(2\nu+\Delta)<0.1$ even if the value $\Delta/\nu=0.2$ is taken to estimate it. To zero order in λ, we obtain the following simplified expression for the cumulant function ϕ_{ph}:

$$\phi_{ph}=i(\Omega_2-\Omega_1-2i\gamma)t-\ln(1-abe^{i(\Omega_2-\Omega_1)t})$$
$$+\ln(1-ab). \qquad (52)$$

This cumulant function resembles the tunnelon function (35) derived in Sec. 4.

7. THE ELECTRON-PHONON BAND

Substituting (49) in formula (24) and temporarily neglecting the tunnelon cumulant function ϕ_j, we find the following expression for the electron-phonon band:

$$I(\omega)=2\,\mathrm{Re}\left\{[d(0)]^{1/2}\int_0^\infty dte^{i(\omega-\omega_0)t}[d(t)]^{-1/2}\right\}. \qquad (53)$$

Let us examine this formula, substituting in it first a simplified version of the determinant, i.e.,

$$[d(0)/d(t)]^{1/2}=\exp\phi_{\mathrm{ph}}(t),$$

where ϕ_{ph} is determined from formula (52). Then, instead of (53), we find

$$I(\omega)=2\,\mathrm{Im}\left\{(1-ab)\sum_{n=0}^{\infty}\frac{(ab)^n}{\omega-n(\Omega_2-\Omega_1)-i\gamma}\right\}, \tag{54}$$

where $\Omega=\omega-\omega_0+\Omega_2-\Omega_1$. The optical band consists of an infinite sum of peaks corresponding to the 0–0′, 1–1′, 2–2′, etc. transitions depicted in Fig. 1b. All the peaks, except the 0–0′ peak, identified as the ZPL, vanish as temperature increases, because the parameter $ab=\exp(-h\nu/kT)$, when $\gamma\to 0$.

It is of interest to consider the the influence of low-frequency excitation statistics on the nature of the optical band. Recall that phonons are bosons and tunnelons are fermions. The question of the impact of statistics comes to mind in connection with the fact that the mathematical methods for calculating the electron-phonon and the electron-tunnelon bands are identical, while the optical bands obtained are fundamentally different in nature: the electron-tunnelon band consists of two peaks, while the electron-phonon band consists of a great number of peaks. This distinction in the band nature arises because the sign of ln in Eq. (35) is opposite to that in Eq. (52). Consequently, the difference in the statistics results in the opposite signs of ln and in the fundamental distinctions in the nature of the optical bands.

The shape of the electron-phonon band is most strongly affected by the parameter $W/2\nu\gamma$ describing the ratio of the phonon frequency variation and the phonon peak width. It is clear without numerical computations that the transitions 1–1′, 2–2′, etc. merge with the ZPL for $W/2\nu\gamma<1$. However, numerical calculations with formulas (50), (51), and (53) show that such merging occurs even for $W/2\nu\gamma\sim 30$ (Fig. 3). Only for $W/2\nu\gamma\sim 100$ does a structure appear near the ZPL (Figs. 4a,b). The calculation of the curves in Fig. 4a was performed with the exact formulas (49)–(51) with $W/2\nu\gamma=400$. This parameter value corresponds to $\lambda^2=0.04$. Thus, the contribution of the parameter λ in the optical band is actually small, and the transition from (50) to (52) is really justified. According to Eq. (50), the parameter λ^2 determines the intensities of transitions in which two, four, etc. phonons are created or annihilated. First, these lines are located far from the ZPL, and second, they have low intensity. Their influence is not seen in Fig. 4, although $W/2\nu\gamma=400$.

8. TEMPERATURE BROADENING AND THE SHIFT OF THE ZPL

According to (24), the actual optical band is a convolution of the electron-tunnelon and the electron-phonon bands. Hence the halfwidth of the nearly Lorentzian 0–0′ line is the sum

$$\gamma(T)=\gamma_{\mathrm{TLS}}(T)+\gamma_{\mathrm{ph}}(T), \tag{55}$$

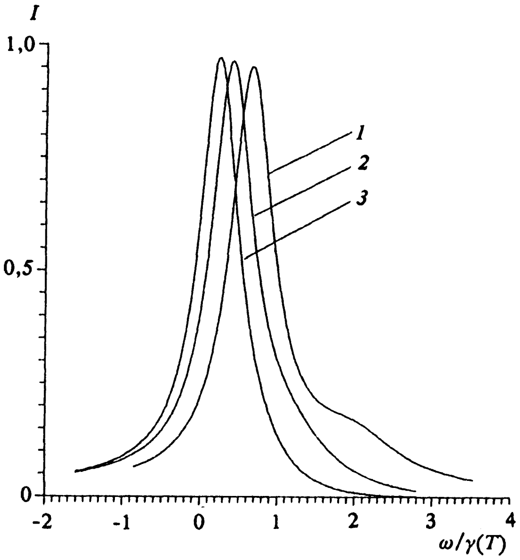

FIG. 3. The effect of coupling strength on the shape of the homogeneous electron-phonon band. Curves *1–3* are calculated from formulas (50), (53) for $W/2\nu\gamma=60$ (*1*); 30 (*2*); 15 (*3*) and for $kT/\nu=0.8$. The frequency scale is similar to that used in Fig. 2a.

where $\gamma_{\mathrm{TLS}}(T)$ and $\gamma_{\mathrm{ph}}(T)$ are the halfwidths of the zero-tunnelon and the zero-phonon lines.

Figures 2–4 indicate that the phototransitions which leave the number of phonons and tunnelons unchanged do not change the halfwidth of the 0–0′ line much, although they are located near it. It is this fact that was considered earlier in the construction of the theory of ZPL broadening and shift.[3,4,9,10,14] In this theory, formulas for ZPL halfwidth and shift were derived, which differ from that obtained in the present paper. The analysis of this problem shows that in the earlier theory the exact tunnelon and phonon Green's functions (15) and (20) were used, while in the present paper the simplified expressions (26) and (44) for these functions are used. If the exact Green's function in the final formulas of the earlier theory are replaced by the model expressions (26) and (44), then the results of the two theories are in complete agreement.[17]

Let us consider at greater length the expressions for the 0–0′ line halfwidth and shift resulting from the electron-tunnelon interaction. According to Eq. (40), we have

$$\delta_{\mathrm{TLS}}(T)=\frac{\Delta}{2}-\Omega_0(T),\quad \gamma_{\mathrm{TLS}}(T)=2[\gamma-\gamma_0(T)], \tag{56}$$

where $\Omega_0(T)$ and $\gamma_0(T)$ are defined by (33) and (34). If we introduce a dimensionless variable $x=\Delta/2\gamma$ into the last-mentioned formulas, they can be represented in the following form

$$\Omega_0(T)=\pm\frac{\gamma}{2^{1/2}}\left\{(x^2+1)\left[1-\frac{4x^2}{(x^2+1)^2}\,\mathrm{ch}^{-2}\left(\frac{\varepsilon}{2kT}\right)\right]^{1/2}+x^2-1\right\}^{1/2}, \tag{57}$$

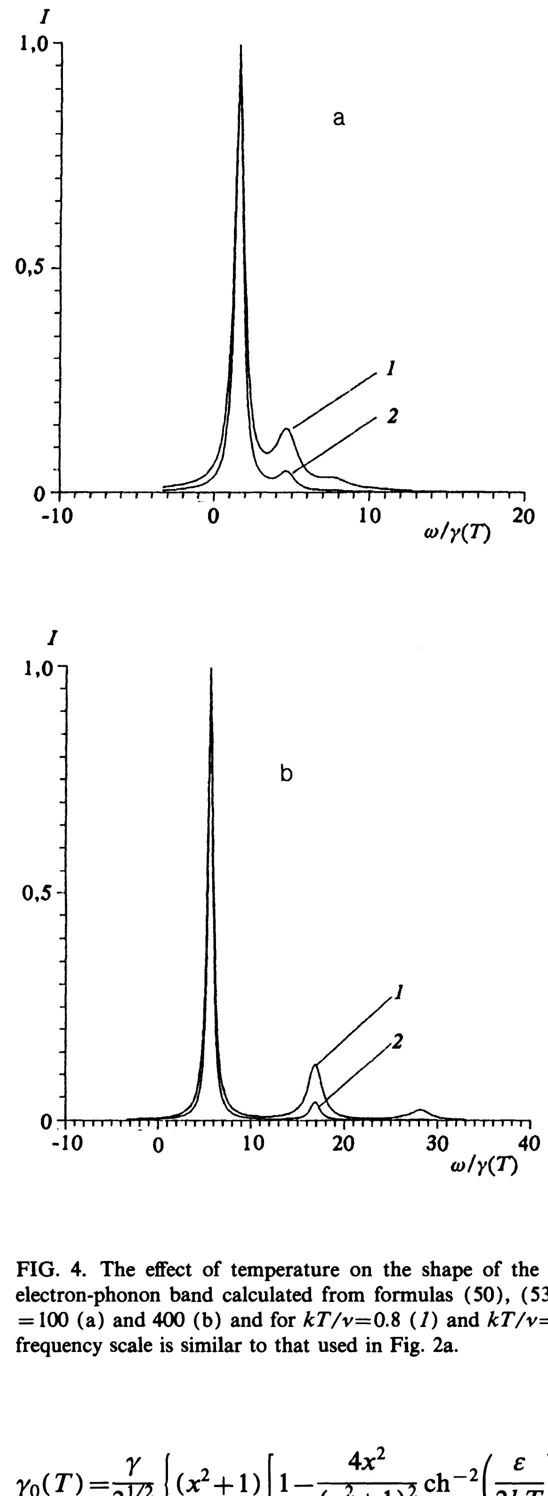

FIG. 4. The effect of temperature on the shape of the homogeneous electron-phonon band calculated from formulas (50), (53) for $W/2\nu\gamma = 100$ (a) and 400 (b) and for $kT/\nu=0.8$ (*1*) and $kT/\nu=0.4$ (*2*). The frequency scale is similar to that used in Fig. 2a.

$$\gamma_0(T)=\frac{\gamma}{2^{1/2}}\left\{(x^2+1)\left[1-\frac{4x^2}{(x^2+1)^2}\,\mathrm{ch}^{-2}\left(\frac{\varepsilon}{2kT}\right)\right]^{1/2} -x^2+1\right\}^{1/2}. \tag{58}$$

Since $\mathrm{ch}^{-2}(\varepsilon/2kT)\ll 1$ for $kT<\varepsilon$, we may expand (57) and (58) in ch^{-2}. Leaving the first nonvanishing terms, we find

$$\Omega_0(T)=\frac{\Delta}{2}-\frac{1}{4}\frac{\Delta}{1+x^2}\,\mathrm{ch}^{-2}\left(\frac{\varepsilon}{2kT}\right), \tag{59}$$

$$\gamma_0(T)=\gamma-\frac{1}{4}\frac{\Delta x}{1+x^2}\,\mathrm{ch}^{-2}\left(\frac{\varepsilon}{2kT}\right). \tag{60}$$

If we take into account the fact that at low temperature

$$\mathrm{ch}^{-2}\left(\frac{\varepsilon}{2kT}\right)\cong\exp\left(\frac{-\varepsilon}{kT}\right),$$

then after substituting (59) and (60) in (56), we find

$$\delta_{\mathrm{TLS}}(T)=\frac{\Delta}{1+(\Delta\tau)^2}\,e^{-\varepsilon/kT},$$

$$\gamma_{\mathrm{TLS}}(T)=\frac{2}{T_2}=2\,\frac{\Delta^2\tau}{1+(\Delta\tau)^2}\,e^{-\varepsilon/kT}, \tag{61}$$

where $\tau=1/2\gamma$ is the tunnelon lifetime. The results (61) coincide exactly with those of the so called "exchange model," which is used to calculate the phase relaxation time T_2 in both spin[18] and electron[19] systems. Evidently, Eqs. (56)–(58) are more general than the formulas of the exchange model.

Equations (58) and (60) for the halfwidth possess the property of temperature saturation. Indeed, if the temperature T exceeds the tunnelon energy ε, the ZPL halfwidth becomes temperature-independent. The electron-phonon mechanisms for ZPL broadening cannot result in such saturation in principle. The Korotaev group,[20] investigating temperature broadening of the 0–0′ line of perylene in *n*-octane, has recently found that under elevated pressure conditions a clearly defined plateau exists in the temperature dependence of the halfwidth at 10 K $< T <$ 20 K, and the dependence of the halfwidth in a region of 5–20 K is adequately described by Eq. (60). The authors of Ref. 20 interpret their data as a result of the manifestation of the quadratic electron-tunnelon interaction.

9. CONCLUSION

At present, theoretical processing of selective spectra of impurity centers in polymers and glasses is still in the initial stage of solution. To make significant progress, it is necessary to construct a theory of the homogeneous band, a theory of homogeneous band averaging, and finally a theory of so called "spectral diffusion."[8] In the present paper, only a theory of the homogeneous band of an impurity center in polymers and glasses has been constructed. This theory makes it possible in the near future to treat the averaging the homogeneous spectral band over the relevant parameters and include the spectral diffusion effect. The experimental data on selective spectra of impurity centers in polymers and glasses will never receive an adequate theoretical description until this program is implemented.

[1] *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*, Eds. V. Agranovich and R. Hochstrasser, North-Holland, Amsterdam, 1983.

[2] Topics in Current Physics, Vol. 44; Persistent Spectral Hole-Burning: Science and Applications. Ed. W. E. Moener, Berlin, Springer-Verlag, 1988.

[3] I. S. Osad'ko, Usp. Fiz. Nauk, **128**, 31 (1979). [Sov. Phys. Uspekhi **22**, 311 (79)]

[4] I. S. Osad'ko, in Ref. 1, p. 263.

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

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

[7] Topics in Current Physics, Vol. 24; Amorphous Solids: Low Tempera-

ture Properties, Ed. W. A. Phillips, Springer-Verlag, Heidelberg, 1981.

[8] L. R. Narasimhan, K. A. Littau, D. W. Pack *et al.*, Chem. Rev. **90**, 439 (1990).

[9] I. S. Osad'ko, Phys. Rep. **206**, 43 (1991).

[10] I. S. Osad'ko, Zh. Eksp. Teor. Fiz. **90**, 1453 (1986) [Sov. Phys. JETP **63**, 851 (1986)].

[11] I. S. Osad'ko and A. A. Shtygashev, Opt. Specktrosk. **66**, 86 (1989) [Opt. Spectrosc. (USSR) **66**, 49 (1989)].

[12] M. Born and Huang Kun, *Dynamic Theory of Crystal Lattices*, Oxford, Clarendon Press, 1954.

[13] M. Lax, J. Chem. Phys. **20**, 1752 (1952).

[14] D. Hsu and J. Skinner, J. Chem. Phys. **81**, 1604 (1984).

[15] S. V. Tyablikov, *Methods in the Quantum Theory of Magnetism*, Plenum, New York (1967).

[16] I. S. Osad'ko, Zh. Eksp. Teor. Fiz. **72**, 1575 (1977) [Sov. Phys. JETP **45**, 827 (1977)].

[17] D. V. Donskoi, N. N. Zaitsev, and I. S. Osad'ko, Chem. Phys. (to be published) (1993).

[18] C. A. van't Hof and J. Schmidt, Chem. Phys. Lett. **36**, 457 (1975).

[19] C. B. Harris, J. Chem. Phys. **67**, 5607 (1977).

[20] O. N. Korotaev, I. P. Kolmakov, M. F. Shchapov *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **55**, 417 (1992) [JETP Lett. **55**, 424 (1992)].

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