Theory of homogeneous broadening of zero-phonon lines in the impurity spectra of amorphous materials and solutions

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(Submitted 21 December 1984)
Zh. Eksp. Teor. Fiz. **88**, 2171–2184 (June 1985)

A general theory is developed for homogeneously broadened zero-phonon lines (ZPL) in the impurity spectra of disordered systems investigated by high-resolution selective spectroscopy. The homogeneous broadening of zero-phonon lines by the interaction between light-absorbing impurity centers and localized low-frequency modes is discussed. The resulting ZPL spectral distribution, averaged over the mode positions as well as characteristics, is found. The theory is applied to crystals in which impurity spectra are modulated by randomly distributed quasilocal vibrations (QV) and to amorphous media in which there are always quasilocal vibrations and low-frequency two-level modes (TLM). It is shown that, in glasses, the ZPL broadening Ω is usually due to dynamic electron-level shifts in fluctuational transitions between TLM and quasilocal vibrations during the lifetime of the excited electron state or during the existence of a hole in the spectrum in the hole-burning method. The temperature dependence of Ω is due to the reduction in the density of excited modes and an increase in their separation from the impurity centers as the temperature is reduced. The temperature dependence of Ω found in this paper can be used to explain experimental ZPL data for glasses.

1. INTRODUCTION

The interaction between electrons in impurity centers and atomic vibrations in a solid has a considerable effect on extrinsic absorption and emission spectra, and gives rise to complex electronic vibrational spectra whose widths are often greater than the spectral line widths in gases by several orders of magnitude. However, it has been shown[1] that, even for strong electron-phonon interactions, these spectra should contain exceedingly narrow zero-phonon lines (ZPL) that are much narrower than the spectral lines of gases. They are the analogs of Mössbauer lines.

In a harmonic crystal, an interaction linear in the phonon operators produces no ZPL broadening in the absence of nonradiative transitions. It simply reduces the intensity of these lines by a factor that is analogous to the Debye-Waller factor but is determined by the electron-phonon interaction.[1] The quadratic interaction and also anharmonism modulate the electron transition frequency and lead to the ZPL broadening Ω (Refs. 2–8). In the case of interaction with vibrations in the continuous spectrum (phonons), the broadening is proportional to T^2 at high temperatures and decreases rapidly like T^7 as $T \to 0$.

An important and occasionally dominant contribution to the modulation broadening of zero-phonon lines can be provided by the interaction between electrons and local or resonance quasilocal vibrations near an impurity center.[4,5] It is described by the formula

$$\begin{aligned} \Omega &= \sum_{\varkappa} \frac{V_\varkappa^2}{\Gamma_\varkappa} n_\varkappa (n_\varkappa + 1) \quad (\Omega \ll \Gamma_\varkappa), \\ \Omega^2 &\sim \sum_{\varkappa} V_\varkappa^2 n_\varkappa (n+1) \quad (\Omega \gg \Gamma_\varkappa), \end{aligned} \tag{1}$$

where $\hbar = 1$, $k_B = 1$, $n_\varkappa = [\exp(\beta\omega) - 1]^{-1}$, $\beta = 1/T$, $V_\varkappa$ is the coefficient in front of $a_\varkappa^+ a_\varkappa$ in the difference between the final and initial state Hamiltonians of the electron states, and $a_\varkappa^+$, $a_\varkappa$ are the creation and annihilation operators for the QV quanta $\varkappa$ of frequency $\omega_\varkappa$ and damping $\Gamma_\varkappa$. Since $\Gamma_\varkappa$ is usually small ($\Gamma_\varkappa \ll \omega_\varkappa$), the contribution of the quasilocal vibrations (or other localized modes) to Ω can be very large (especially in the case of low-frequency modes $\omega_\varkappa$), much greater than the contribution due to the interaction with phonons.

In addition to this type of homogeneous broadening of zero-phonon lines due to the dynamic modulation of the transition frequencies, and also nonradiative transitions, there is considerable inhomogeneous broadening in solids due to the statistical spread of the transition frequencies in a real inhomogeneously distorted specimen. This spread is quite considerable, so that it is difficult to produce an anomalously narrow zero-phonon line and to investigate the homogeneous width. However, special methods for selective laser excitation of fluorescence in a chosen group of impurity centers with an almost constant transition frequency,[9,10] and hole-burning in the absorption spectrum,[11,12] can now be used to isolate zero-phonon lines with only homogeneous broadening Ω, and to investigate this broadening. The magnitude and the temperature dependence of Ω are in agreement with the theory for impurity centers in crystals.

Considerable attention has been devoted in recent years to the homogeneous broadening of impurity ZPL in amorphous bodies. At high temperatures, it is qualitatively the same as in crystals but, at low temperatures Ω exceeds by several orders of magnitude the corresponding values for crystals, and decreases much more slowly. For Eu^{3+} doped silicate glasses, it is found[13] that $\Omega \sim T^{1.8 \pm 0.2}$ for 7 K $< T <$ 80 K, whereas, for Pr^{3+} in amorphous BeF_2 and GeO_2, it is found[14] that $\Omega \sim T^{1.85 \pm 0.2}$ in the wide temperature range between 8 and 300 K. In some organic glasses, Ω is a linear function of the temperature[15] or proportional[16] to $T^{1.2}$ or tends to a finite limit[17] as $T \to 0$.

To explain these results, it has been suggested[13,18–21] that the interaction between impurity centers and the two-level modes (TLM) introduced to explain the thermal properties of glasses[22,23] plays an important role in the homogeneous broadening of impurity ZPL. However, no account was taken in Refs. 19–21 of the normally dominant mechanism of modulation broadening, which is due to the shift of the electron levels of impurity centers in fluctuational TLM transitions during the lifetime of the excited state in selective fluorescence, or during the period between hole burning and its examination. Moreover, ZPL broadening was defined in these papers as the average $\bar{\Omega}$ of widths taken for different values of the parameters of the nearest TLM. On the other hand, a rigorous calculation must involve averaging not of the widths but of the spectral distributions of different impurity centers with different neighboring TLM, and only then can Ω be taken as the width of the resulting distribution. In our case of a large spread in the widths, the broadening Ω may be very different from $\bar{\Omega}$ and may have a different temperature dependence. In view of this, we shall calculate the broadening due to the interaction between impurity centers and the TLM, using a more rigorous averaging for the different broadening mechanisms, including the above dominant mechanism.

In addition to the TLM contribution, the ZPL broadening may also contain an important contribution due to the interaction between impurity centers and quasilocal vibrations with sufficiently small $\omega_\varkappa$ and $\Gamma_\varkappa \sim \omega^4$ [see Eq. (1)]. Such vibrations may arise, in particular, in regions of a glass in which the interatomic separation r^0 is appreciably increased and the force constants substantially reduced. For example, in a chain of atoms coupled by the Lennard-Jones forces, the force constants are found to vanish when r^0 is increased by 10%. In simple models, for example, in the case of the closely-packed incompressible spheres, or atoms bound by Lennard-Jones forces, an increase in r^0 by $\geqslant 10\%$ is observed for about 10^{-2} atoms.[24] The statistical distributions of force constants used for the simulation of two-well potentials[25] in glasses have also been found to lead to an appreciable density of quasilocal vibrations with low $\omega_\varkappa$. In contrast to the TLM, where two closely spaced levels are separated by a large gap from higher-lying levels, centers with quasilocal vibrations can have a set of almost equidistant levels. They have no effect on the linear term in the heat capacity, but may lead to a considerable increase in the coefficient of T^3 (see Section 5).

In Section 2 below, we obtain general expressions for the ZPL spectra of individual impurity centers in media containing localized modes (TLM or QV), and in Section 3 we find the resulting spectral distributions of homogeneously-broadened ZPL investigated by selective spectroscopy and average over the configurations of a disordered medium. In Section 4 we consider the simple example of ZPL broadening in crystals, due to the quasilocal vibrations of randomly distributed "extraneous" impurity centers which perturb the light-absorbing impurity centers. In Sections 5 and 6, we discuss ZPL broadening in glasses, due to the QV and TLM and, in Section 7, we compare the results with experimentally determined functions $\Omega(T)$.

2. ZERO-PHONON LINE OF A SINGLE IMPURITY CENTER IN A MEDIUM WITH LOCALIZED MODES

The Hamiltonian of an impurity center interacting with the host medium has the form

$$H=H_e+H_0+H_i, \qquad H_i=H_{iph}+\sum_{r\varkappa} c_{r\varkappa}H_{r\varkappa}, \tag{2}$$

where H_e, H_0, and H_i are the Hamiltonians for the electrons in the impurity center, the host medium, and the interaction between them. The term H_{iph} describes the interaction with phonons and $H_{r\varkappa}$ the interaction with the TLM or QV localized at **r** and characterized by internal parameters $\varkappa$, which include, for example, the QV frequency $\omega_\varkappa$ or TLM energy $E \equiv \omega_\varkappa$. It is convenient to divide the system into small portions of volume v_0 (of the order of the atomic volume) and divide the continuous parameters in $\varkappa$ (such as $\omega_\varkappa$) into small intervals, so that the localized modes can be characterized by the values of **r** and $\varkappa$ corresponding to these volume and parameter intervals ($\varkappa$ may contain discrete parameters such as, for example, the type of the mode). The component H_i should contain the sum over only those intervals of **r** on which the TLM and QV are centered. It is more convenient, however, to sum over all r and $\varkappa$ by introducing, as in (2), the random quantities $c_{r\varkappa}$, which assume the values 1 or 0, depending on whether the **r**-th volume element contains a mode with parameters falling into the particular interval of $\varkappa$.

To investigate the ZPL, let us begin by considering the light absorption cross section σ of an impurity center for fixed positions of the TLM or QV. Averaging over the positions and characteristics of the latter will be carried out later. For simplicity, we shall confine our presentation to the case of phototransitions between singlet electron levels of the impurity center, s and s', for which we can use the adiabatic approximation. We shall assume that the interaction H_i is small. Actually, our results will be valid for the more general case of systems with nondegenerate levels and small H_i if we neglect the contribution of nonradiative transitions between multiplet levels to the broadening of the ZPL. In the adiabatic approximation, the cross section σ is given by[26]

$$\sigma(\omega-\omega_{s's})=C\int_{-\infty}^{\infty} dt \exp\left[i(\omega-\omega_{s's})t-g_0(t)-\frac{\gamma_0}{2}|t|\right],$$

$$\exp[-g_0(t)]=\langle\exp(iH_s t)\exp[-i(H_s+\Delta H)t]\rangle,$$

$$H_s=H_0+H_i^s, \qquad \Delta H=H_i^{s'}-H_i^s, \tag{3}$$

where ω is the frequency of light, $\omega_{s's} = \omega_{s'} - \omega_{s'}\omega_s = (s|H_e|s)$ is the energy of the s-th electron levels of the impurity center, C is practically independent of ω within the ZPL, γ_0 is the natural width, $H_i^s = (s|J_i|s)$, and angle brackets represent averaging, with weight $\exp(-\beta H_s)$, over the initial states of the medium for fixed TLM or QV positions.

When the density of perturbing centers is low enough, we can neglect their interaction and their influence on phonons. In that case, the expression for $\exp[-g_0(t)]$ in (3) splits into the product of independent factors corresponding to the individual terms in the sum for H_i in (2) and, since $c_{r\varkappa} = 1,0$, we have

$$g_0(t)=g_{ph}(t)+\sum_{r\varkappa} c_{r\varkappa}g_{r\varkappa}(t), \tag{4}$$

where $g_{ph}(t)$ and $g_{r\varkappa}(t)$ are obtained from formula for $g_0(t)$ in (2) by replacing H_i^s with $H_{ph}^s = (s|H_{iph}|s)$ or $H_{r\varkappa}^s = (s|H_{r\varkappa}|s)$.

The spectrum of a narrow zero-phonon line is determined by the shap of the function $g_0(t)$ for large values of t, of the order of the reciprocal linewidth Ω^{-1}. The explicit expressions for $g_{ph}(t)$ and $g_r(t)$ in the region $t\sim\Omega^{-1}$ are very different, depending on the ratio of Ω^{-1} and the characteristic relaxation time t^0 of the excited medium. For phonons, we always have $t^0\sim\omega_{\mathbf{k}}^{-1}\ll\Omega^{-1}$ ($\omega_{\mathbf{k}}$ is the characteristic phonon frequency), whereas, for TLM and QV, $t^0\sim\Gamma_\varkappa^{-1}$, where $\Gamma_\varkappa$ is the damping of these modes and t^0 can be either greater or smaller than Ω^{-1}.

Let us begin with the case $\Gamma_\varkappa\ll\Omega$. The TLM or QV cannot then change their states corresponding to the Hamiltonian $H_0+H_i^s$ during the characteristic time $t\sim\Omega^{-1}$. They can be characterized by quantum numbers $n_{r\varkappa}=0,1$ for the TLM and $n_{r\varkappa}=0,1,2,\ldots$ for the QV. For a weak interaction $H_{r\varkappa}$, the change in the energy of these states during the $s\to s'$ transition can be calculated in first-order perturbation theory ($n_{r\varkappa}$ remains unaltered during transitions corresponding to the ZPL):

$$\begin{gathered}(s'n_{r\varkappa}|H_{r\varkappa}|s'n_{r\varkappa})-(sn_{r\varkappa}|H_{r\varkappa}|sn_{r\varkappa})\\ =(n_{r\varkappa}|\Delta H_{r\varkappa}|n_{r\varkappa})=V_{r\varkappa}(n_{r\varkappa}+\mathrm{const}), \quad |V_{r\varkappa}|\ll\omega_\varkappa,\ T.\end{gathered} \tag{5}$$

Calculating $g_{r\varkappa}(t)$ from (3) (with H_i^s replaced with $H_{r\varkappa}^s$) by summing over $n_{r\varkappa}$, we obtain

$$\begin{gathered}g_{r\varkappa}(t)=-\ln h_{r\varkappa}(t),\\ h_{r\varkappa}(t)=\sum_n w_\varkappa(n)\exp(-iV_{r\varkappa}nt), \quad \Gamma_\varkappa^{-1}\gg|t|,\\ w_\varkappa(n)=\exp(-\beta\omega_\varkappa n)\left[\sum_n\exp(-\beta\omega_\varkappa n)\right]^{-1},\\ n_\varkappa=\langle n_{r\varkappa}\rangle=\sum_n nw_\varkappa(n),\end{gathered} \tag{6}$$

where $n\equiv n_{r\varkappa}=0,1$ for the TLM and $n=0,1,2\ldots$ for the QV.

In the opposite limiting case of large $\Gamma_\varkappa\gg\Omega$, the important contributions in the interval (3) are those due to long times $|t|\gg t^0\sim\Gamma_\varkappa^{-1}$. In this region, the functions $g_{ph}(t)$ and $g_{r\varkappa}(t)$ are given by the following simple asymptotic expressions (see, for example, Ref. 5), in which we have neglected small (for small H_i) constant terms:

$$g_{ph}(t)={}^1/_2\gamma'|t|+i\tilde V't, \quad g_{r\varkappa}(t)={}^1/_2\gamma_{r\varkappa}|t|+i\tilde V_{r\varkappa}t, \quad |t|\gg\Gamma_\varkappa^{-1}, \tag{7}$$

where

$$\begin{gathered}\tilde V_{r\varkappa}=V_{r\varkappa}n_\varkappa+O(V^2),\\ \gamma_{r\varkappa}=2\pi\langle(\Delta H_{r\varkappa}-\langle\Delta H_{r\varkappa}\rangle),\ (\Delta H_{r\varkappa}-\langle\Delta H_{r\varkappa}\rangle)\rangle_{\omega\to0},\\ \langle A,B\rangle_\omega=\frac{1}{2\pi}\int_{-\infty}^{\infty}\langle A(t)B(0)\rangle\exp(-i\omega t)\,dt,\\ A(t)=\exp(iH_0t)A\exp(-iH_0t).\end{gathered} \tag{8}$$

Analogous formulas with $H_{r\varkappa}$ replaced with H_{iph} are valid for γ' and $\tilde V'$. Since $\omega_{\mathbf{k}}\gg\Omega$, the phonon contribution $g_{ph}(t)$ to $g_0(t)$ is always given by (7), even when (6) is valid for $g_{r\varkappa}(t)$. The damping γ' is analyzed in detail in Refs. 2–8.

In the same way, we can show that the ZPL for the $s'\to s$ transition in the emission spectrum of a single impurity center is also described to within a constant factor by the integral (3) with the same function $g_0(t)$, i.e., its intensity is proportional to $\sigma(\omega-\omega_{s's})$.

3. RESULTANT SPECTRAL DISTRIBUTION OF A HOMOGENEOUSLY BROADENED ZERO-PHONON LINE IN A DISORDERED SYSTEM

To determine the resultant spectrum produced by all the impurity centers in glass or disordered crystal, we can replace summation over the impurity centers by taking the average $\langle\ldots\rangle_c$ of their spectra over the configurations of the atoms in the medium, including averaging over the TLM or QV positions. The spread $\delta\omega_{s's}$ of the frequencies $\omega_{s's}$ of electron transitions in different impurity centers, i.e., the inhomogeneous broadening of the ZPL, is usually greater by some order of magnitude than the homogeneous broadening Ω determined by selective excitation of fluorescence by a laser of constant frequency ω_0 or by the hole-burning method. To find the ZPL spectral distribution $I(\omega-\omega_0,\omega_0)$ in the resulting fluorescence spectrum, we recall that the absorption of monochromatic radiation of frequency ω_0 for $\delta\omega_{s's}\gg\Omega$ leads to the excitation of impurity centers, whose frequencies $\omega_{s's}\simeq\omega_0$ have a distribution function proportional to $\sigma(\omega_0-\omega_{s's})$. Each of these atoms contributes during the emission of light to the ZPL in the fluorescence spectrum, the contribution being proportional to $\sigma(\omega-\omega_{s's})$, so that the resultant distribution $I(\omega-\omega_0,\omega_0)$ after averaging over the configurations is given by the following formula when (3) is taken into account:

$$\begin{gathered}I(\Delta\omega,\omega_0)=\mathrm{const}\left\langle\int\sigma(\omega_0-\omega_{s's})\sigma(\omega-\omega_{s's})\,d\omega_{s's}\right\rangle_c\\ =\frac{I_i}{2\pi}\int_{-\infty}^{\infty}dt\exp[i\Delta\omega t-g(t)],\\ \exp[-g(t)]=\langle\exp[-g_0(t)-g_0(-t)-\gamma_0|t|\rangle_c,\end{gathered} \tag{9}$$

where $\Delta\omega=\omega-\omega_0$ and I_i is the integrated ZPL intensity. The function $g(t)$ depends on ω_0 as a parameter since the $V_{r\varkappa}$ differ somewhat for groups of impurity centers with different $\omega_{s's}\simeq\omega_0$.

An analogous discussion will show that (9) will also describe the ZPL in the spectrum obtained by the hole-burning method. It was assumed in the derivation of (9) that the lifetime t_0 of the excited electron state s', or the time of existence of the hole, was much longer than the relaxation time $\Gamma_\varkappa^{-1}$ of the ZPL-broadening modes $\varkappa$, so that the thermal mode distributions in the absorption and emission of light were uncorrelated, and the corresponding averages $\langle\ldots\rangle$ of each factor of σ in (9) could be performed independently. Only these modes must be taken into account in $g(t)$. On the other hand, modes with longer relaxation times $\Gamma_\varkappa^{-1}\gg t_0$ contribute to the inhomogeneous broadening and should not be taken into account in $g(t)$ and I. The case where $\Gamma_{\varkappa}^{-1} \sim t_0$ for a particular group of modes is described by a more complicated formula that includes the four-time correlator, and will not be examined here.

When $g(t)$ is calculated from (9) and (4), the average $\langle ... \rangle_c$ must be evaluated over the TLM and QV positions, i.e., over $c_{\mathbf{r}\varkappa}$. Let us confine our attention to the case where we can neglect correlations of the TLM and QV with the impurity centers and with one another, and assume that they are randomly distributed in the medium. The $c_{\mathbf{r}\varkappa}$ are then statistically independent variables assuming the values $c_{\mathbf{r}\varkappa} = 1$ with probability $cp_{\varkappa}$ and $c_{\mathbf{r}\varkappa} = 0$ with probability $1 - cp_{\varkappa}$, where $c = v_0 N_0 \ll 1$ is the TLM or QV density (N_0 is their number per unit volume) and $p_{\varkappa}$ is the probability that their parameters will fall into the interval of $\varkappa$. Averaging $\exp[-g(t)]$ in (9) over the $c_{\mathbf{r}\varkappa}$, and taking into account (4) in the case of small $c \ll 1$, we obtain

$$g(t) = \gamma' |t| + c \sum_{\mathbf{r}\varkappa} p_{\varkappa} \{1 - \exp[-g_{\mathbf{r}\varkappa}(t) - g_{\mathbf{r}\varkappa}(-t)]\},$$

$$\times \sum_{\varkappa} p_{\varkappa} = 1, \quad c \ll 1. \tag{10}$$

Here, it is assumed that we can neglect the dependence of the damping γ' due to phonons in expression (7) for $g_{ph}(t)$ on the configurations of the medium, and that the natural width γ_0 is included in γ' (the term $\gamma' |t|$ will be usually unimportant in the ensuing discussion).

For long relaxation times of localized modes, $t^0 \sim \Gamma_k^{-1} \gg \Omega^{-1}$ (but $t^0 \ll t_0$), it follows from (10) and (6) that

$$g(t) - \gamma' |t| = c \sum_{\mathbf{r}\varkappa} p_{\varkappa} [1 - h_{\mathbf{r}\varkappa}(t) h_{\mathbf{r}\varkappa}(-t)]$$

$$= c \sum_{\varkappa} p_{\varkappa} \sum_{n,n'} w_{\varkappa}(n) w_{\varkappa}(n') \sum_{\mathbf{r}} [1 - \cos V_{\mathbf{r}\varkappa}(n - n') t],$$

$$\Omega \gg \Gamma_{\varkappa} \gg t_0^{-1}. \tag{11}$$

It is clear from (9) and (11) that, in this case, the modulation broadening of the zero-phonon line by localized modes is due to the fluctuational spread produced by them in the transition frequency shifts during the time t_0, and is unrelated to mode damping.

Usually, $\Delta H_{\mathbf{r}\varkappa}$, $V_{\mathbf{r}\varkappa}$, and $\gamma_{\mathbf{r}\varkappa}$ depend on the separation r between the impurity centers and the TLM or QV as follows:

$$\Delta H_{\mathbf{r}\varkappa} \propto \frac{1}{r^k}, \qquad V_{\mathbf{r}\varkappa} = V_{\varkappa} \frac{r_0^{\,k}}{r^k}, \qquad \gamma_{\mathbf{r}\varkappa} = \gamma_{\varkappa} \frac{r_0^{\,2k}}{r^{2k}}, \qquad r_0 = v_0^{1/3}. \tag{12}$$

The sums over $\mathbf{r}$ and n, n' in (11) can then be evaluated, and a simple expression can be obtained for $g(t)$:

$$g(t) = \gamma' |t| + \left[\frac{\Gamma(1+\alpha^{-1})}{\pi} \Omega |t| \right]^{\alpha},$$

$$\Omega^{\alpha} = \frac{2\pi^{2+\alpha} c}{3\Gamma(\alpha)\Gamma^{\alpha}(1+\alpha^{-1}) \sin(\pi\alpha/2)} \sum_{\varkappa} p_{\varkappa} V_{\varkappa}^{\alpha} W_{\varkappa}(T, \alpha),$$

$$\Omega \gg \Gamma_{\varkappa} \gg t_0^{-1}, \tag{13}$$

where

$$\alpha = \frac{3}{k} \leqslant 1, \qquad W_{\varkappa}(T, \alpha) = \sum_{n,n'} w_{\varkappa}(n) w_{\varkappa}(n') |n - n'|^{\alpha}. \tag{14}$$

For the QV and TLM, we have, respectively,

$$W_{\varkappa}(T, 1) = \operatorname{sh}^{-1} \beta\omega_{\varkappa}, \qquad W_{\varkappa}(T, \alpha) = \frac{1}{2} \operatorname{ch}^{-2} \frac{\beta\omega_{\varkappa}}{2}. \tag{14a}$$

Formulas (9) and (13) define the distribution $I(\Delta\omega, \omega_0)$. When $\pi\gamma' \ll \Omega$, this has the form

$$I(\Delta\omega, \omega_0) = \frac{I_i}{\Omega} f\left(\frac{\Delta\omega}{\Omega}, \alpha\right),$$

$$f(x, \alpha) = \Gamma^{-1}(1+\alpha^{-1}) \int_0^{\infty} \cos \frac{\pi x z}{\Gamma(1+\alpha^{-1})} \exp(-z^{\alpha})\, dz \tag{15}$$

and the integrated width Ω. When $V_{\mathbf{r}\varkappa} \sim r^{-3}$, we have $\alpha = 1$ and the distribution (15) has the Lorentz shape. For $\pi\gamma' \gtrsim \Omega$, its width is $\pi\gamma' + \Omega$ (for $\pi\gamma' \gtrsim \Omega$, the same values must be substituted in place of Ω in the above criteria). If, on the other hand, $k > 3$, the distribution (15) differs from the Lorentz distribution: it is narrower in the central region and falls off more slowly in the wings (as $|\Omega|^{-(1+\alpha)}$).

In the case of short relaxation times $\Gamma_{\varkappa}^{-1} \ll \Omega^{-1} \ll t_0$, we see from (7) that $g_{\mathbf{r}\varkappa}(t) + g_{\mathbf{r}\varkappa}(-t) = \gamma_{\mathbf{r}\varkappa} |t|$ in (10).

Summing in (10) for the power-law dependence of $\gamma_{\mathbf{r}\varkappa}$ on r (12), we find that in this case $g(t)$ is given by (13) with α replaced with $\alpha/2$, whilst $I(\Delta\omega, \omega_0)$ and its integrated width Ω (for $\Omega \gg \gamma'$) are given by

$$I(\Delta\omega, \omega_0) = \frac{I_i}{\Omega} f\left(\frac{\Delta\omega}{\Omega}, \frac{\alpha}{2}\right),$$

$$\Omega^{\alpha/2} = \frac{4\pi\pi^{\alpha/2}\Gamma(1-\alpha/2)}{3\Gamma^{\alpha/2}(1+2\alpha^{-1})} c \sum_{\varkappa} p_{\varkappa} \gamma_{\varkappa}^{\alpha/2} \quad (\gamma', t_0^{-1} \ll \Omega \ll \Gamma_{\varkappa}). \tag{16}$$

4. QUASILOCAL VIBRATIONS IN CRYSTALS

Consider, to begin with, the simple example of the broadening of impurity ZPL in crystals by QV modes in randomly distributed defects (impurity atoms) of another type (the role of the QV in optical impurity centers was investigated in Refs. 4 and 5). We shall confine our attention to defects of low symmetry, without a center of inversion, with nondegenerate QV frequencies $\omega_{\varkappa} \ll \omega_D$, and low densities $c \ll c_0 \sim (\omega_{\varkappa}/\omega_D)^3$ (ω_D is the Debye frequency), for which the interaction between the QV can be neglected.

To be specific, we shall consider the quasilocal vibrations of impurity atoms (or their groups) μ, weakly coupled to the host atoms m (the results will also be qualitatively valid in the case of mass defects). The displacements u_{μ} will be assumed to be much greater than $\mathbf{u}_m$. This means that, in the QV Hamiltonian $H_{0\varkappa}$ of a given defect, we can isolate the leading term H^0, taken for $\mathbf{u}_m = 0$, and the term H' which is linear in $\mathbf{u}_m$ and describes the interaction of the QV $\varkappa$ with phonons $\mathbf{k}$:

$$H_{0\varkappa} = H^0 + H', \quad H^0 = -\sum_{\mu} \frac{1}{2M_{\mu}} \frac{\partial^2}{\partial \mathbf{u}_{\mu}^{2}} + \frac{1}{2} V_{\mu\mu'}^{ij} u_{\mu i} u_{\mu' j}$$

$$+ \frac{1}{3} V_{\mu\mu'\mu''}^{ijl} u_{\mu i} u_{\mu' j} u_{\mu'' l}$$

$$= \sum_{\varkappa} \omega_{\varkappa} \left(a_{\varkappa}^{+} a_{\varkappa} + \frac{1}{2} \right) + \frac{1}{3} V_{\varkappa\varkappa'\varkappa''} b_{\varkappa} b_{\varkappa'} b_{\varkappa''},$$

$$H' = V_{\mu m}^{ij} u_{\mu i} u_{m j} + V_{\mu\mu' m}^{ijl} u_{\mu i} u_{\mu' j} u_{m l}, \tag{17}$$

where

$$b_\varkappa=a_\varkappa+a_\varkappa^+,\quad u_{\mu i}=\lambda_{\mu i}^\varkappa b_\varkappa,$$

$$\lambda_{\mu i}^\varkappa=\frac{1}{(2M_0\omega_\varkappa)^{1/2}}e_{\mu i}^\varkappa,\quad M_0=\sum_\mu M_\mu,$$

$$V_{\varkappa\varkappa'\varkappa''}=V_{\mu\mu'\mu''}^{ijl}\lambda_{\mu i}^\varkappa\lambda_{\mu' j}^{\varkappa'}\lambda_{\mu'' l}^{\varkappa''},\qquad \omega_\varkappa\lambda_{\mu i}^\varkappa\lambda_{\mu' j}=\frac{1}{2M_\mu}\delta_{\mu\mu'}\delta_{ij}\tag{18}$$

in which M_μ is the mass of the atom μ, $|\mathbf{e}_\mu^\varkappa|\sim 1$, and summation over repeated indices, μ, $\varkappa$, ... $i, j, l = x, y, z$ is implied.

In this example, when we consider the interaction $H_{\mathbf{r}\varkappa}$ between a QV at **r** and the impurity-center electrons at $\mathbf{r} = 0$, we shall, to be specific, take into account only the elastic interaction. It depends linearly on the tensor u_{ij} of the strain produced by the QV. For large r, we can express this tensor with the aid of the Green function $G_{ij}(t)$ (Ref. 27, Section 8) in terms of the resultant force **F** and the dipole moment tensor p_{ij} of the forces $\partial H'/\partial \mathbf{u}_m$ exerted by the QV on the crystal atoms m. It can be shown that the strains produced by the force **F** do not affect $V_{\mathbf{r}\varkappa}$ or the limit as $\omega\to 0$ of the correlator in the expression for $\gamma_{\mathbf{r}\varkappa}$ in (8) (although the contribution of **F** is important for $\omega\neq 0$). We shall therefore take into account only the strains connected with p_{ij}. We then have

$$\Delta H_{\mathbf{r}\varkappa}=(s'|H_{\mathbf{r}\varkappa}|s')-(s|H_{\mathbf{r}\varkappa}|s)=\frac{\partial\omega_{s's}}{\partial u_{i'j'}}u_{i'j'}=\frac{\chi_{ij}}{r^3}p_{ij},$$
$$\chi_{ij}=-\frac{\partial\omega_{s's}}{\partial u_{i'j'}}\frac{\partial^2 G_{ii'}(-\mathbf{r})}{\partial x_j\partial x_{j'}}r^3,\tag{19}$$

where χ_{ij} depend on the direction but not on the length of the vector **r**. Formulas (17) and (18) enable us to express p_{ij} in terms of the QV operators:

$$p_{ij}=-\sum_m\frac{\partial H'}{\partial u_{mi}}R_{mj}=L_{ij}^\varkappa b_\varkappa+L_{ij}^{\varkappa\varkappa'}b_\varkappa b_{\varkappa'},$$
$$L_{ij}^\varkappa=-V_{m\mu}^{ii'}R_{mj}\lambda_{\mu i'}^\varkappa,\quad L_{ij}^{\varkappa\varkappa'}=-V_{\mu\mu' m}^{i'j'i}R_{mj}\lambda_{\mu i'}^\varkappa\lambda_{\mu' j'}^{\varkappa'},\tag{20}$$

where the radius vector $\mathbf{R}_m$ is measured from the center of the defect at **r**.

The ZPL width can be expressed in terms of $V_{\mathbf{r}\varkappa}$ and $\gamma_{\mathbf{r}\varkappa}$. When we calculate $V_{\mathbf{r}\varkappa}$ from (5), (19), and (20), we must consider the QV states with allowance for the anharmonic term in the Hamiltonian H^0 (17). The spectral representations of the correlators in formula (8) for γ_r are also due to the anharmonism. They can be expressed in terms of the limiting values of $\langle b_\varkappa, b_\varkappa\rangle_\omega$, $\langle b_\varkappa^2-\langle b_\varkappa^2\rangle, b_{\varkappa'}\rangle_\omega$, $\langle b_\varkappa^2-\langle b_\varkappa^2\rangle, b_{\varkappa'}^2\rangle_\omega$ as $\omega\to 0$, found in Ref. 28. The final result is

$$V_{\mathbf{r}\varkappa}=V_\varkappa\frac{r_0^3}{r^3},\quad \gamma_{\mathbf{r}\varkappa}=\gamma_\varkappa\frac{r_0^6}{r^6},\quad \gamma_\varkappa=\frac{V_\varkappa^2}{\Gamma_\varkappa}n_\varkappa(n_\varkappa+1),$$
$$V_\varkappa=\frac{2\chi_{ij}}{r_0^3}\left[L_{ij}^{\varkappa\varkappa}+\sum_{\varkappa'}L_{ij}^{\varkappa'}\frac{1}{\omega_{\varkappa'}}V_{\varkappa\varkappa\varkappa'}\right]$$
$$\sim\frac{\hbar V_{00m}}{10M_0r_0^2\omega_\varkappa G_0}\frac{\partial\omega_{s's}}{\partial u_{ii}},\quad \Gamma_\varkappa\sim\frac{M_0\omega_\varkappa^4}{M\omega_D^3}.\tag{21}$$

This estimate for the QV damping $\Gamma_\varkappa$ was obtained[28] in the harmonic approximation, which is valid at $T\lesssim\omega_\varkappa$ for a weakly bound impurity atom of mass M_0 in a monatomic crystal with atoms of mass M. The above estimate for $V_\varkappa$ includes the fact that $G_{ij}(r)\sim(4\pi G_0 r)^{-1}$ in this example, where G_0 is the shear modulus.

Defects with QV's are found in crystals under identical conditions and, if c is interpreted as the concentration of defects with $\nu\sim 1$ QV modes, we must put $p_\varkappa = 1$ in formulas (13) and (16) for the ZPL width Ω. For the QV with frequencies $\omega_\varkappa$ that are not very low, we have rapid modulation, and the ZPL is described by (16) in which, according to (21), $k = 3$, $\alpha = 1$, and

$$\Omega=\frac{8\pi^4}{9}c^2\left\{\sum_{\varkappa=1}^{\nu}\left[\frac{V_\varkappa^2}{\Gamma_\varkappa}n_\varkappa(n_\varkappa+1)\right]^{1/2}\right\}^2$$
$$\sim c^2\frac{V_{00m}^2M\hbar^2\omega_D^3n_\varkappa(n_\varkappa+1)}{G_0^2M_0^3\omega_\varkappa^6r_0^4}\left(\frac{\partial\omega_{s's}}{\partial u_{ii}}\right)^2,\quad \gamma'\ll\Omega\ll\Gamma_\varkappa.\tag{22}$$

The function $f(\Delta\omega/\Omega, 1/2)$, which describes in this case the ZPL shape, is much narrower in the central part than the Lorentzian curve of the same total width Ω [the width of $f(\Delta\omega/\Omega, 1/2)$ at half height is $0.285\ \Omega$ instead of $0.636\ \Omega$ for the Lorentzian curve], whereas in the wings it falls as $\Omega^{-3/2}$. According to (22), $\Omega\propto T^2$ for $2T\rangle\ \omega_{\varkappa\max}$ and $\Omega\propto\exp(-\beta\omega_{\varkappa\min})$ for $2T\ll\omega_{\varkappa\min}$. The broadening due to phonons is $\pi\gamma'\propto T^7$ for $2T\ll\omega_D$. Hence, for low temperatures, the main effect is the broadening Ω (22) due to the QV (especially for small $\omega_\varkappa$) even when the densities are $c\ll c_0$.

In the case of slow modulation, $\Gamma_\varkappa\ll\Omega$ (low QV frequencies and relatively broad ZPL), it follows from (15) and (21) that the ZPL is a Lorentzian ($\alpha = 1$). Its width is $\Omega+\pi\gamma'$ where, according to (13), (14), and (21),

$$\Omega=\frac{2\pi^3}{3}c\sum_{\varkappa=1}^{\nu}V_\varkappa(\operatorname{sh}\beta\omega_\varkappa)^{-1},\quad \Omega\gg\Gamma_\varkappa.\tag{23}$$

It is clear from this formula that, for slow QV relaxation, $\Omega\sim T$ in the region $T>\omega_\varkappa$ and $\Omega\sim cV_\varkappa$, i.e., the ZPL width is much greater than in the case of fast relaxation for which $\Omega\sim c^2V_\varkappa^2/\Gamma_\varkappa$.

5. QUASILOCAL VIBRATIONS IN AMORPHOUS MATERIALS

As already noted in the Introduction, glasses are found to contain not only impurity but also intrinsic QV's in regions with increased interatomic separation r^0 and substantially reduced force constants. Their frequencies and other characteristics are distributed in accordance with some probability law $p_\varkappa$, and the corresponding averages must be taken in (13) and (16). The distribution $p_\varkappa$ can be related to the distributions of the force constants V_2, V_3 in the simple model[25] of a nonlinear oscillator, used to describe the TLM. The most probable is an increase in r^0 and a softening of modes in only one direction. This gives rise to the one-dimensional QV described by the effective Hamiltonian $H_{0\varkappa}\equiv H(x)$:

$$H(x)=-\frac{1}{2M}\frac{d^2}{dx^2}+V(x),$$
$$V(x)=\frac{1}{2}V_2x^2+\frac{1}{3}V_3x^3+\frac{1}{4}V_4x^4,\tag{24}$$

where M is the effective reduced mass and the expansion in powers of x is performed at the minimum point if the curve $V(x)$ has one minimum or at a maximum point if $V(x)$ has three extrema.

The potential energy $V(x)$ has one minimum for $4V_2V_4 < V_3^2$. Vibrations near this minimum are almost harmonic QV's with frequency $\omega_\varkappa = (V_2/M)^{1/2} \ll \omega_D$ if the V_2 are small in comparison with the mean force constants $\sim M\omega_D^2$ but large enough to ensure that $\omega_\varkappa > \omega_4$ [see (25)] and that anharmonic corrections to QV energy can be neglected. The probability density of the random quantities V_2, V_3 for small $|V_2|$, $|V_3|$ tends to a nonzero limit. Hence, the density $p(\omega_\varkappa)$ of the frequencies of the above QV's is proportional to the integral over $dV_3dV_2/d\omega_\varkappa$, evaluated over V_3 from zero to $(4V_2V_4)^{1/2}$, i.e. $(4V_2V_4)^{1/2}dV_2/d\omega_\varkappa \sim \omega_\varkappa^2$:

$$p_\varkappa = p(\omega_\varkappa) = D\omega_\varkappa^2, \quad \omega_D^3 \gg \omega_\varkappa^3 \gg \omega_4^3(1+n_\varkappa), \quad \omega_4^3 = V_4/M^2. \tag{25}$$

Here $D = 3\omega_m^{-3}$ if the QV frequencies lie in the interval $\omega < \omega_m$. Since, in regions with small V_2, V_3, the quantities V_4 are also smaller by an order of magnitude than their mean values, it can be shown that $\omega_4 \sim 0.1\omega_D$ for M of the order of the atomic mass.

When $4V_2V_4 < V_3^2$, the $V(x)$ curve has two minima. When the difference between their depths is such that $\sim 0.1\, V_3^4/V_4^3 \gg T, \omega_\varkappa$, we can neglect the fact that the potential has two wells and consider a QV with frequency $\omega_\varkappa \sim V_3(MV_4)^{-1/2} \ll \omega_D$ in the deeper minimum. The frequency density of such QV's is $\sim |V_2| dV_3/d\omega \sim V_3^2$ and $\sim \omega_\varkappa^2$, i.e. when the frequencies are taken into account, this affects only the value of the constant D in (25). Two-level modes appear in two-well potentials with similar depths. The total QV density may exceed the TLM density.

The QV mode with frequency density $\propto \omega_\varkappa^2$ should lead to an additional contribution to the specific heat:

$$\delta C = \frac{4\pi^4}{15v_0} DcT^3, \quad \omega_4 < 2T < \omega_m, \tag{26}$$

thus increasing the coefficient of T^3 in comparison with the value in $C_D \sim T^3$, calculated from the velocity of sound. There should also be an increase in the coefficient of ω^2 in the effective density of the vibrations, determined from inelastic neutron scattering. This increase has been seen experimentally.

To determine the effect of QV's on the ZPL width Ω in glasses, we must average over $\varkappa$ in (13) or (16) with the QV frequency distribution (25). Let us first consider the elastic interaction between an impurity center and a QV when $k = 3$, $\alpha = 1$, and $V_\varkappa$, $\gamma_\varkappa$ are given by (21). QV's with low frequencies $\omega_\varkappa \lesssim 2T$, for which damping is small in accordance with the estimate given by (21), are excited at low temperatures (but $2T > \omega_4$). Hence, at least in the region $2T < \omega_\varkappa^0$ (and $\omega_\varkappa < \omega_\varkappa^0$), where $\Gamma_\varkappa(\omega_\varkappa^0) = \Omega$, we have $\Omega \gg \Gamma_\varkappa$, and this condition is satisfied for a sufficiently broad ZPL for all QV's and $\omega_\varkappa^0 = \omega_m$. The ZPL is then described by (13)–(15) with $\alpha = 1$ and has the Lorentz shape. According to (13), (21), and (25), its broadening due to the QV is proportional to T^2 and c:

$$\Omega = \frac{\pi^5}{3} DLcT^2,$$

$$L = |{}^{\backprime}V_\varkappa|\,\omega_\varkappa \sim 0{,}1 \frac{\hbar|V_{00m}|}{G_0Mr_0^2} \left| \frac{\partial \omega_{s's}}{\partial u_{ii}} \right|, \quad \omega_4 < 2T < \omega_\varkappa^0. \tag{27}$$

Let us now substitute the following values in (27): $\delta c = C_D$ (i.e., $Dc = 9\Theta^{-3}$, where $k_B\Theta = \Theta = \omega_D$), $\hbar^2(\Theta M r_0^2)^{-1} = 10^{-3}$, $|\partial\omega_{s's}/\partial u_{ii}| = 10^3$ cm^{-1}, $|V_{00m}| = G_0$, $T = 0.1\Theta$. We then find that $\Omega \sim 1$ cm^{-1}.

QV's with $\omega_\varkappa > \omega_\varkappa^0$, for which $\Omega < \Gamma_\varkappa$, are also excited for sufficiently narrow ZPL and $2T > \omega_\varkappa^0$. The contribution of this QV group to ZPL broadening must be calculated from (16), (21), and (25). However, even when $2T > \omega_\varkappa^0$, the main contribution to Ω is due to the QV group with $\omega_\varkappa < \omega_\varkappa^0$. It is given by (13) and is proportional to T:

$$\Omega \sim \frac{2\pi^3}{3} DLc\omega_\varkappa^0 T, \quad 2T > \omega_\varkappa^0 > \omega_4, \quad \Gamma(\omega_\varkappa^0) = \Omega. \tag{28}$$

On the other hand, the QV's with $\omega_\varkappa \gg \omega_\varkappa^0$ provide a contribution to Ω which is much smaller than $\Omega^2/\Gamma(\omega_\varkappa^0) = \Omega$, and can be neglected. When $\Gamma_\varkappa \langle \Omega, \omega_\varkappa^0 \rangle \omega$, $T > \omega_4$, the contribution $\sim 10DLcM\omega_4^3(T/V_4)^{1/2}$ to Ω due to the $\sim Dcv_0^{-1}\omega_4^3$ nonharmonic QV modes with $\omega_\varkappa \sim \omega_4$ is also small in comparison with (27) and (28). It manifests itself only for $T \lesssim \omega_4$ [for $T \ll \omega_4$, the quantity $M(T/V_4)^{1/2}$ is replaced in the above estimate with $\omega_4^{-1}\exp(-\beta\omega_4)$]. It is important to note that the phonon contribution to Ω becomes important for temperatures $2T > \omega_\varkappa^0$ (or $2T > \omega_m$ for broad ZPL), for which the dependence $\Omega \sim T^2$ is replaced with $\Omega \sim T$, or $\sim T^2$ for $2T > \Theta$ (but with a different coefficient).

Similarly, we can consider ZPL broadening due to the electric dipole-quadrupole or quadrupole-quadrupole interaction between an impurity center and a QV. In these cases, we have, respectively, $k = 4$ $(\alpha - 3/4)$ and $k = 5$ $(\alpha = 0.6)$, $\hat{p}$ in (20) is the dipole or quadrupole moment operator of the QV [as before, $\sim(\lambda_\mu)^2 \sim \omega^{-1}$, as in $V_\varkappa$], and the coefficient χ_{ij} in (19) (with r^{-3} replaced with r^{-k}) determines the field shift of the transition frequency $\omega_{s's}$. In accordance with (13)–(15), (25), the ZPL shape is then described by the non-Lorentzian curves $f(\Delta\omega/\Omega,\ 3/4)$ or $f(\Delta\omega/\Omega,\ 3/5)$, and DcT^2 in the width (27) must be replaced with $(Dc)^{k/3}\, T^{k-1}$ (with the numerical factor modified somewhat), whereas in (28) we must replace $DcT\omega_\varkappa^0$ with $(DcT)^{k/3}\, (\omega_\varkappa^0)^{(2k-3)/3}$. The comparison with the width (27) is valid only if the electric interaction is very strong and exceeds the elastic interaction at $r \sim r_0$ by the factor $(\omega_m/Tc^{1/3})^{k-3}$.

6. TWO-LEVEL MODES

Low-frequency two-level modes are formed in glasses if the difference Δ between the unperturbed energies in the two neighboring potential wells and the matrix element $\frac{1}{2}W$ for tunneling through the potential barrier are sufficiently small.[22,23] When tunneling is taken into account, the resulting mixed states differ in energy by the amount $E = (\Delta^2 + W^2)^{1/2}$. Transforming to the creation and annihilation operators for the mixed states a_σ^+, a_σ ($\sigma = 0$, 1 for the lower and upper levels, respectively) and the corresponding phonon operators a_k^+, a_k (in the Debye approximation), we find that the Hamiltonian H_0+H_{ph} for the TLM $\mathbf{r}\varkappa$ interacting with phonons, and the difference $\Delta H_{\mathbf{r}\varkappa}$ between the Hamiltonians for the interaction of the impurity center in states s' and s with this mode can be written in the form (see, for example, Ref. 21)

$$H_{0\varkappa}+H_{ph}=\sum_{\sigma=0,1}E_\sigma a_\sigma{}^+a_\sigma+\sum_{\mathbf{k}}\omega_{\mathbf{k}}a_{\mathbf{k}}{}^+a_{\mathbf{k}}+\sum_{\mathbf{k}}\left(\frac{\Delta}{2E}h'+\frac{W}{2E}h''\right)(U_{\mathbf{k}}a_{\mathbf{k}}+U_{\mathbf{k}}{}^*a_{\mathbf{k}}{}^+),\tag{29}$$

where

$$h'=a_0{}^+a_0-a_1{}^+a_1,\quad h''=a_0{}^+a_1+a_1{}^+a_0,$$

$$U_{\mathbf{k}}=U\left(\frac{\omega_{\mathbf{k}}}{2\tilde{M}w^2}\right)^{1/2}\exp(i\mathbf{k}.\mathbf{r}),$$

$$\Delta H_{\mathbf{r}\varkappa}=\frac{1}{2}V\left(\frac{\Delta}{E}h'+\frac{W}{E}h''\right)\frac{r_0{}^k}{r^k}.\tag{30}$$

In these expressions, $E_0=0$, $E_1=E$, w is the velocity of sound, $\tilde{M}$ is the mass of the body, Vr_0^k/r^k is the difference between the frequency shifts of the transition $\omega_{s's}$ for unperturbed TLM states in the two potential wells, and U is the difference between the deformation potentials for these states (for brevity, the subscript $\varkappa$ on Δ, E, U, V, a_σ, a_σ^+ characterizing the TLM is not indicated explicitly). In the case of the elastic interaction, $k=3$, $V=\chi_{ij}\delta p_{ij}\,r_0^{-3}$, where χ_{ij} is given by (19) and δp_{ij} is the difference between the dipole moments of forces for the TLM states in the two wells.

There is a considerable spread in the random quantities Δ and $W=\omega_0\exp(-\lambda)$ for different TLM [$\exp(-\lambda)$ characterizes the overlap of the wave functions in the two wells and $\omega_0\sim\omega_D$ is the zero-point oscillation energy[22]]. The important region is $W_{\max}>W>W_{\min}$ or $\lambda_{\min}<\lambda<\lambda_{\max}$, where $W_{\max}=\omega_0\exp(-\lambda_{\min})\sim\Delta$ (E falls rapidly for smaller λ), and $\lambda_{\max}$ is determined by the requirement that the TLM relaxation time $\tau=\Gamma^{-1}\sim\exp(2\lambda_{\max})$ [cf. (33)] is much less than the characteristic time of observations–in this case - t_0]. Analysis of experimental data leads to $\lambda_{\max}\sim10$–20, $\delta\lambda\equiv\lambda_{\max}-\lambda_{\min}\sim5$–$10$ (Refs. 22, 29). In the adopted TLM model, for glasses,[22,23] the probability $p_\varkappa=p(\Delta,\lambda)$ of the parameters has the constant value $(\Delta_m\delta\lambda)^{-1}$ for $0<\Delta<\Delta_m\gtrsim\omega_D$ and $\lambda_{\min}<\lambda<\lambda_{\max}$, and is zero outside these intervals of Δ, λ.

As in the case of the QV, the effect of the TLM on the ZPL width is very dependent on the ratios of the parameters Ω, Γ, and t_0^{-1}. Usually, $\Gamma<10^8\ \mathrm{s}^{-1}$ for $T\sim1$ K, i.e., $\Omega\gg\Gamma$ even for small $\Omega\sim0.01\ \mathrm{cm}^{-1}$. Moreover, the condition $t_0\gg\Gamma^{-1}$ may also be satisfied (since, otherwise, the TLM would not contribute to the homogeneous broadening exceeding the natural width). Hence the main interest lies in the case $\Omega\gg\Gamma\gg t_0^{-1}$, when, for weak coupling ($\Omega\ll T$), the ZPL is described by (9) and (13)–(15). According to (12) and (13), we have $V_\varkappa=V\Delta/E$ in (13). Integrating with respect to Δ, λ with the weight $p_\varkappa=p(\Delta,\lambda)$ in the above intervals of Δ and λ, and using the function (14a) for $W_\varkappa(T,\alpha)$ (in which $\omega_\varkappa=E$), we find that the ZPL has the shape of the curve $f(\Delta\omega/\Omega,\alpha)$ (15), and its integrated width is

$$\Omega=\zeta V\left(\frac{cT}{\Delta_m}\right)^{k/3},$$

$$\zeta=\frac{3\pi}{k\Gamma(k/3)}\left[\frac{2\pi^2}{3\Gamma(3/k)\sin(3\pi/2k)}\right]^{k/3},\quad T\gg\Omega\gg\Gamma\gg t_0{}^{-1}.\tag{31}$$

For the elastic or electric dipole interaction, $k=3$, $\alpha=1$, the ZPL has the Lorentz shape and $\Omega\sim cT$ by analogy with Ref. 18. For example, when $\delta p\sim r_0^3G_0$, $c/\Delta_m\sim10^{-2}$ eV^{-1}, $T\sim1$ K, and $|\partial\omega_{s's}/\partial u_{ii}|\sim(10^3$–$10^4)\ \mathrm{cm}^{-1}$, formula (31) shows that $\Omega\sim0.001$–$0.0001\ \mathrm{cm}^{-1}$. For the dipole–quadrupole or quadrupole–quadrupole interactions, $k=4$ ($\alpha=3/4$) or $k=5$ ($\alpha=3/5$), the curve $f(\Delta\omega/\Omega,\alpha)$ (15) differs from the Lorentzian [narrower in the central region, and falls in the wings as $(\Delta\omega)^{-7/4}$ or $(\Delta\omega)^{-8/5}$], and $\Omega\propto(cT)^{4/3}$ or $\Omega\propto(cT)^{5/3}$. When $p(\Delta,\lambda)$ is not constant, but increases slowly with Δ, for example, like Δ^μ with μ small, the exponent $(1+\mu)k/3$ in the power-law expression for $\Omega(T)$ is found to be somewhat greater.

We note that, for the case we are considering, for which $\Omega\sim V(r_0/\bar{r})^k\gg\Gamma$ ($\bar{r}$ is the mean separation between the TLM with $E\sim T$), the authors of Ref. 20 obtained a result that is essentially different from (31). This difference is due to the fact that they did not take into account electron level shifts during the change in the TLM states, which provide the main contribution to Ω for $t_0^{-1}\ll\Gamma$ (this contribution is much greater than Γ).

For sufficiently narrow ZPL, the condition $\Omega\ll\Gamma$ is satisfied for the TLM group with very large Γ. Their contribution to $g(t)$ is determined by (10), (7), and (8), and is expressed in terms of the spectral representations of the $\Delta H_{\mathbf{r}\varkappa}$ correlators, i.e., h', h'' for $\omega\to0$.

The latter can be found by the Green-function method (cf. the Appendices in Refs. 5 and 28) and by taking (8), (12), (29), and (30) into account:

$$\gamma_\varkappa=\gamma_\varkappa{}'+\gamma_\varkappa{}'',\quad\gamma_\varkappa{}'=2\pi\left(\frac{V\Delta}{2E}\right)^2\langle h',(h'-\langle h'\rangle)\rangle_{\omega\to0}=\frac{V^2\Delta^2}{\Gamma E^2}e^{\beta E}(e^{\beta E}+1)^{-3}\tag{32}$$

$$\gamma_\varkappa{}''=2\pi\left(\frac{VW}{2E}\right)^2\langle h'',(h''-\langle h''\rangle)\rangle_{\omega\to0}=\frac{8\Gamma V^2\Delta^2}{E^4}(1+e^{-\beta E})^{-1},\quad T\gg\Gamma\gg\Omega\gg t_0{}^{-1},\tag{33}$$

where

$$\Gamma=\pi\sum_{\mathbf{k}}\left(\frac{WV}{2E}\right)^2n_{\mathbf{k}}\delta(E-\omega_{\mathbf{k}})=\frac{U^2W^2E}{16\pi Mv_0w^5}(e^{\beta E}-1)^{-1}.$$

ZPL broadening due to the contribution of $\gamma_\varkappa''$ was examined in detail in Refs. 19 and 21. The expression obtained there for $\gamma_\varkappa''$ is the same as that given by (32) [the expression for $\gamma_\varkappa'$ in (32) is also in agreement with Ref. 21, where it was obtained by a different method]. The ZPL width obtained in these papers was calculated simply as the average of $\gamma_\varkappa''$.

Averaging with the weight $p(\Delta,\lambda)$ between the above limits with $W_{\max} \sim \Delta$ gave[19] $\Omega \sim T^2$ (a fixed value independent of Δ was adopted for $W_{\max}$ in Ref. 21; accordingly, it was found that $\Omega \propto T$). However, it is better to average not the ZPL width of the individual impurity centers but the spectral distributions and then determine, as in Section 3 above, the width of the resulting curve. If $\gamma''_\varkappa$ were to provide the main contribution to broadening, formulas (16) and (32) would yield $\Omega \sim T^{(2+\alpha)/\alpha}$ after averaging with the weight $p(\Delta,\lambda)$ and $W_{\max} \propto \Delta$ (i.e., the result would be $\propto T^3$ for $k = 3$ instead of $\Omega \propto T^2$ as in Ref. 19).

However, it is actually found that $\gamma'_\varkappa \gg \gamma''_\varkappa$ for this group of modes with $T \gg \Gamma \gg \Omega$. The main contribution to the sum of the $p(\Delta,\lambda)\gamma'^{\alpha/2}_\varkappa$ in (16), i.e., to the function $g(t)$ (10), is provided by the region of minimum possible $W \simeq W_{\min}$ or $\Gamma \simeq \Gamma_{\min} = \Gamma(W_{\min})$. If the condition $\Gamma \gg \Omega$ were to be satisfied for all the TLM, formulas (16), (32), and (33) would lead to $\Omega' \sim (cT/\Delta_m \delta\lambda)^{2/\alpha} V^2/\Gamma_{\min}$. However, even for small Ω, there is also usually a TLM group with $\Gamma \ll \Omega$, and it is this group that provides the main contribution (31) to the ZPL width [all that is required is to interpret c in (31) as the density of TLM's with $\Omega \gg \Gamma \gg t_0^{-1}$). The quantity $\Gamma_{\min}$ for the group of modes with $\Gamma > \Omega$ is defined by $\Gamma_{\min} \sim \Omega$, and this TLM group leads to only a small correction to the ZPL width, $\delta\Omega \sim \Omega(\Omega'/\Omega)^{\alpha/2} \sim \Omega/\delta\lambda$. Like Ω, it increases with increasing T, although $\gamma'_\varkappa$ decreases at the same time.

7. DISCUSSION OF RESULTS

It follows from the above results that the homogeneous broadening Ω of impurity ZPL in disordered media at low temperatures, as studied by selective spectroscopy, is usually largely determined by dynamic frequency shifts of electronic transitions in fluctuations of occupation numbers of localized low-frequency modes during the time t_0, and is not due to mode damping. In glasses, Ω is given by (27), (28), and (31). The decrease of Ω with decreasing temperature is then due to the reduction in the density of excited TLM's and QV's in glass, and to the increase in their mean distance from the impurity center. The temperature dependence of Ω may be largely due to modes and interactions of a particular type, or the resultant effect of different modes and interactions. In the latter case, the result $\Omega \sim T^\nu$ is simply an approximation to a more complicated dependence.

The function Ω^ν with $\nu = 1.85 \pm 0.2$, observed[14] in amorphous BeF_2 ($\Theta = 380$ K) and GeO_2 ($\Theta = 308$ K) at temperatures in the range $8\ \mathrm{K} < T < 300$ K, and the analogous result with $\nu = 1.8 \pm 0.2$, obtained for silicate glasses[13] and close to $\Omega \sim T^2$, may be due to the elastic interaction between impurity centers and quasilocal vibrations. Strictly speaking, this dependence (27) is valid at "intermediate" temperatures, defined by $\omega^0_\varkappa > 2T > \omega_4 \sim 0.1\Theta$. However, this law may extend to very much lower temperatures (i.e., down to $T \sim 0.02\Theta$) if there is a slowly decreasing additional contribution to Ω, for example, the TLM contribution (31) (cf. Ref. 30). For $T > \Theta/4$, the interaction with phonons provides an important contribution ($\sim T^2$ for $T > \Theta/2$), so that the law $\Omega \sim T^\nu$ with $\nu \simeq 2$ extends to high temperatures as well.

Another possible explanation of the results $\Omega \sim T^\nu$ with $\nu \simeq 1.8$ can be based on the inclusion of the quadrupole-quadrupole interaction between the impurity center and the TLM. According to (31), we then have $\nu = 5/3$ down to the very lowest temperatures. If the principal effect is the dipole-quadrupole interaction with the TLM, we should have[16] T^ν with $\nu = 4/3$ and, in the case of elastic or dipole interaction, $\Omega \sim T$, which has been observed[15] in organic glasses. The ZPL width may tend to a nonzero limit[17] for $T \to 0$ if the levels s', s belong to multiplets and radiationless transitions to lower levels are possible.

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Translated by S. Chomet