

Spectral distribution of degenerate three-dimensional local and quasilocal vibrations

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A quantum transport equation for degenerate local vibrations of cubic symmetry is derived. The transport equation takes into account the internal anharmonicity quartic in the impurity coordinates and also the decay and modulation broadening mechanisms of local vibrations. The transport equation is reduced to a system of linear algebraic equations for the calculation of the spectral distribution of local vibrations. This system is solved analytically for a highly developed fine structure of the spectrum. The possibility of a numerical analysis of the profile of a general spectrum at finite temperatures and for arbitrary ratios of the anharmonicity and relaxation parameters is discussed. Examples of numerical calculations are presented to illustrate the changes in the spectral distribution on increase in temperature and as a result of changes in the relative magnitudes of the local vibrations parameters.

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The line profile and the spectra of quasilocal and local vibrations due to transitions at the fundamental oscillator frequency were studied in Refs. 1-6. At low temperatures $T \ll \hbar\omega_0$ (ω_0 is the local vibration frequency), the line profile is Lorentzian. At higher temperatures, the line exhibits a broadening and its profile changes considerably. This is due to the fact that the spectral distribution includes a contribution from transitions between nonequidistant (because of anharmonicity) excited local vibration levels. If the deviation from equidistant distribution of the levels is greater than the broadening of each individual transition line, the spectrum of local vibrations exhibits a fine structure at temperatures $T \sim \hbar\omega_0$. Such a structure is observed, for example, in the infrared absorption spectrum of nondegenerate quasilocal vibrations in MnF_2 doped with Eu^{2+} (see Ref. 7).

The effect of internal anharmonicity on the profile of the spectral distribution of local vibrations and also on its fine structure was studied in Refs. 2, 4, and 6. The calculations of Refs. 2, 4, and 6 apply mainly to nondegenerate local vibrations since the energy spectrum of an isolated local vibration can then be easily determined. On the other hand, degenerate local vibrations had been studied experimentally, in particular, three-dimensional local vibrations transforming under the vector representation of the cubic group.⁸

Theoretical description of the spectral distribution of degenerate local vibrations is quite difficult. On the one hand, the energy levels of a large number of excited local vibration levels are required in the calculation of the temperature dependence of the spectral distribution. The energy spectrum of local vibrations in the harmonic approximation represents a set of degenerate equidistant levels. Internal anharmonicity of local vibrations leads to a shift and splitting of the levels. Since the number of states with approximately equal energies increases rapidly with the principal quantum number n [for example, for local vibrations of cubic symmetry, the number of degenerate levels is proportional to $(n+1)(n+2)/2$], the positions of the levels corresponding to high quantum numbers n are determined by a high-order secular equation.

On the other hand, the interaction of local vibrations with the vibrations of the continuous spectrum stimulates transitions between the states with different n (between the multiplets) and also within the multiplets. The latter transitions are due to mainly the scattering of continuous spectrum vibrations from local vibrations. As a result, we obtain a stochastic modulation of the phase of local vibrations which results in modulation broadening² and in hybridization of the states within each multiplet.⁹

We shall derive a quantum transport equation (see Refs. 6 and 10) and apply this quantum transport equation to study the spectral distribution of triply degenerate local vibrations of cubic symmetry. We consider arbitrary temperatures and arbitrary ratio of the relaxation width to the interval between the levels in a multiplet. Since the number of multiplets contributing to the spectral distribution of local vibrations increases with increasing temperature, we assume in our numerical calculations that the temperature is not too high compared with $\hbar\omega_0$. At temperatures $0 < T \leq 2\hbar\omega_0$, the profile of the spectral distribution of local vibrations is obtained for a number of typical parameters of the system considered. In particular, we demonstrate that a fine structure appears when the temperature is raised and is smeared at still higher temperatures.

1. HAMILTONIAN OF THE SYSTEM AND TRANSPORT EQUATION

The Hamiltonian of an isolated local vibration transforming under the representation T_{1u} of the group O_h including the quartic anharmonicity is given by

$$\begin{aligned} H_0 &= H_h + H_a; \quad H_h = \omega_0 \sum_{\chi=1}^3 n_{\chi}; \\ H_a &= \frac{1}{2} V_1 \sum_{\chi} n_{\chi}(n_{\chi}-1) + \frac{1}{2} V_2 \sum_{\chi \neq \chi'} n_{\chi} n_{\chi'} \\ &+ \frac{1}{2} V_3 \sum_{\chi \neq \chi'} a_{\chi}^+ a_{\chi'}^2; \\ n_{\chi} &= a_{\chi}^+ a_{\chi}, \quad \hbar=1, \quad |V_{1,2,3}| \ll \omega_0, \quad \chi=x, y, z. \end{aligned} \quad (1)$$

Here, a_χ^+ and a_χ are the creation and annihilation operators of local vibrations. As usual,⁸ we shall assume that the anharmonicity is described by $c \sum_\chi q_\chi^4 + c_1 \sum_{\chi \neq \chi'} q_\chi^2 q_{\chi'}^2$ (q_χ are the oscillator displacements in the direction χ). For such anharmonicity, the parameters V_2 and V_3 in Eq. (1) satisfy the relation $V_2 = 2V_3$. The renormalization of the parameters V due to the interaction with the vibrations of a continuous spectrum⁵ leads (see also the Appendix) to the parameters V_2 and V_3 that are independent.¹⁾ Formally, we can also assume that the aforementioned parameters are independent if the Hamiltonian of the internal anharmonicity of local vibrations contains nonadiabatic terms similar to $p_\chi^2 q_\chi^2$, (p_χ is the momentum component of local vibrations).

In our discussion of the relaxation of local vibrations, we shall consider both the decay effects (one-phonon for quasilocal and two-phonon effect for local vibrations) and the modulation effects. The corresponding Hamiltonian is given by

$$H = H_0 + H_0^{ph} + H_i; \quad H_0^{ph} = \sum_k \omega_k b_k b_k^\dagger; \quad H_i = \frac{1}{\sqrt{N}} \sum_{\chi k} V_{\chi k} (a_\chi + a_\chi^\dagger) (b_k + b_k^\dagger) + \frac{1}{N} \sum_{\chi k k'} V_{\chi k k'} (a_\chi + a_\chi^\dagger) (b_k + b_k^\dagger) (b_{k'} + b_{k'}^\dagger) + \frac{1}{N} \sum_{\chi k k'} V_{\chi k k'} a_\chi^\dagger a_\chi b_k^\dagger b_{k'}. \quad (2)$$

Here, b_k^+ and b_k are the creation and annihilation operators of the continuous spectrum vibrations and N is the number of atoms in a lattice. We have included in Eq. (2) only the fourth-order anharmonic terms corresponding to the scattering of continuous spectrum vibrations from local vibrations and we have assumed all the interaction parameters ($V_{\chi k}$, $V_{\chi k k'}$, $V_{\chi k k' k''}$) to be much smaller than ω_0 and the characteristic phonon frequency ω_{eff} .

The profiles of the peaks of the spectral distributions of the correlation functions are governed by the behavior of the local vibration correlation function $\langle A(t)B(0) \rangle$ for large times $t \gg \omega_0^{-1}$, ω_{eff}^{-1} . Following Ref. 6, we can assume in this region that the frequency dependence of the damping of local vibrations is smooth and write the correlation function in the second order in the interaction H_i and in the first order in the internal anharmonicity in the following form:

$$\langle A(t)B(0) \rangle = \text{Tr}_0 [\exp(iH_i t) A \exp(-iH_i t) G_B(t)], \quad (3)$$

where the operator $G_B(t)$ is the solution of a transport equation

$$\frac{\partial G_B}{\partial t} = -\hat{\Gamma} G_B - \hat{\Gamma}_m G_B - i[\hat{P}, G_B] - i[H_a, G_B]; \quad G_B(0) = [\text{Tr}_0 e^{-\lambda H_0}]^{-1} B e^{-\lambda H_0}, \quad (4)$$

The trace Tr_0 is taken over the wave functions of the Hamiltonian H_h . The operator $\hat{\Gamma}$ governs the damping of local vibrations due to decay effects

$$\begin{aligned} \hat{\Gamma} G &= \Gamma \sum_\chi ((n+1)(n_\chi G - 2a_\chi G a_\chi^\dagger + G n_\chi) \\ &+ n[(n_\chi + 1)G - 2a_\chi^\dagger G a_\chi + G(n_\chi + 1)]), \\ \Gamma &= \frac{\pi}{N} \sum_k V_{\chi k}^2 \delta(\omega_0 - \omega_k) + \frac{2\pi}{N^2} \sum_{k k'} V_{\chi k k'}^2 [(n_k + n_{k'} + 1) \delta(\omega_0 - \omega_k - \omega_{k'}) \\ &+ 2(n_k - n_{k'}) \delta(\omega_0 + \omega_k - \omega_{k'})]; \quad n = n(\omega_0), \quad n_k = n(\omega_k), \\ n(\omega) &= [\exp(\lambda \omega) - 1]^{-1}, \quad \lambda = T^{-1}. \end{aligned} \quad (5)$$

The operator $\hat{\Gamma}_m$ governs the modulation damping of local vibrations

$$\begin{aligned} \hat{\Gamma}_m G &= \Gamma_m \sum_\chi [n_\chi, [n_\chi, G]] + 2^{-1} \Gamma_m \sum_{\chi \neq \chi'} [\Lambda_{\chi \chi'}, \\ &[\Lambda_{\chi \chi'}, G]] + \Gamma_m \sum_{\chi \neq \chi'} [n_\chi, [n_{\chi'}, G]], \\ \Lambda_{\chi \chi'} &= a_\chi^\dagger a_{\chi'} + a_{\chi'}^\dagger a_\chi, \quad \Gamma_m = N^{-2} \sum_{k k'} V_{11 k k'}^2 f_{k k'}, \quad \Gamma_m = N^{-2} \sum_{k k'} V_{12 k k'}^2 f_{k k'}, \\ \Gamma_m &= N^{-2} \sum_{k k'} V_{11 k k'} V_{22 k k'} f_{k k'}, \quad f_{k k'} = \pi n_k (1 + n_{k'}) \delta(\omega_k - \omega_{k'}). \end{aligned} \quad (6)$$

Three independent parameters Γ_{mi} appear in the operator of the modulation broadening since it follows from Eq. (6) that Γ_{mi} are the components of a tensor of rank four appropriate to a cubic crystal [the operator of the decay broadening defined by Eq. (5) transforms as a tensor of rank two and has only a single independent component].

The operator $\hat{P} = P_0 \sum_\chi n_\chi$ in Eq. (4) results only in a small ($|P_0| \ll \omega_0$) renormalization of the local vibration frequency ω_0 and we shall assume that such a renormalization has been made.

2. SPECTRAL DISTRIBUTION OF THE CORRELATION FUNCTION OF THE LOCAL VIBRATION COORDINATES

It is well known that the profile of an infrared absorption line due to local vibrations is governed by the following spectral distribution:

$$Q(\omega) = \frac{1}{2\pi(n+1)} \int_{-\infty}^{\infty} \langle a_\chi(t) a_\chi^\dagger(0) \rangle e^{i\omega t} dt, \quad \omega \approx \omega_0. \quad (7)$$

We can calculate the quantity $\langle a_\chi(t) a_\chi^\dagger(0) \rangle$ from Eqs. (3)-(6) setting $A = a_\chi$ and $B = a_\chi^\dagger$. The vibrations of the continuous spectrum are already excluded from Eqs. (3)-(6) (the averaging over the thermostat) and the problem reduces to the operator equation (4) in the space of wave functions of an isolated local vibration. It is convenient to choose the wave functions $|n\alpha_r\rangle$ of a three-dimensional harmonic oscillator. Here, n is the principal quantum number defined by

$$\sum_\chi n_\chi |n\alpha_r\rangle = n |n\alpha_r\rangle$$

α is an irreducible representation of the cubic group; j is the row of the representation; the index r labels the same representations α corresponding to a given n . Because of the anharmonicity, the levels with the same n but different α_r have different energies and form a multiplet. The transport equation (4) is applicable provided the separation between multiplets ($\sim \omega_0$) is much greater than the splitting of the levels within each multiplet ($\sim V_1$).

Since $\langle n\alpha_r | H_a | n'\alpha' r' j \rangle \sim \delta_{nn'} \delta_{\alpha\alpha'} \delta_{jj'}$, it is necessary to solve a secular equation to obtain the position of the multiplet levels. The order of the secular equation depends on the number of realizations of the representation α for given n . We shall assume that the diagonalization has been performed and, therefore, $H_a | n\alpha_r j \rangle = \varepsilon \alpha_r(n) | n\alpha_r j \rangle$. In the representation of the functions $|n\alpha_r j \rangle \equiv |n\phi\rangle$, the expression $Q(\omega)$ defined by Eq. (7) as-

sumes the form

$$Q(\omega) = (n+1)^{-1} \operatorname{Re} \sum_{n\varphi\varphi'} A_{\chi}(n, \varphi, \varphi') G_n(\varphi, \varphi'; \omega),$$

$$A_{\chi}(n, \varphi, \varphi') = \langle n\varphi | a_{\chi} | n+1\varphi' \rangle, \quad (8)$$

$$G_n(\varphi, \varphi'; \omega) = \pi^{-1} \int_0^{\infty} e^{i(\omega-\omega_0)t} \langle n+1\varphi' | G_{a_{\chi}}(t) | n\varphi \rangle dt.$$

For each pair of representations α and α' , the elements $A_{\chi}(n, \alpha, j; n+1, \alpha', j')$ corresponding to different j and j' satisfy certain conditions that are independent of n but depend only on the group properties. Analogous conditions should be satisfied by the matrix elements $G_n(\varphi, \varphi'; \omega)$ since they transform under the same representation as $A_{\chi}(n, \varphi, \varphi')$.

It follows from Eqs. (4)-(6) that the function $G_n(\varphi, \varphi'; \omega)$ satisfies the following system of linear algebraic equations:

$$(-i[\Omega - \varepsilon_{\varphi'}(n+1) + \varepsilon_{\varphi}(n)] + \Gamma(n)) G_n(\varphi, \varphi'; \omega) + \sum_{k=0, \pm 1} \sum_{\varphi_1 \varphi'_1} B_k(n, \varphi, \varphi'; \varphi_1, \varphi'_1) G_{n+k}(\varphi_1, \varphi'_1; \omega) = \frac{1}{\pi(n+1)^3} A_{\chi}^*(n, \varphi, \varphi') \exp(-\lambda\omega_0 n), \quad \Omega = \omega - \omega_0, \quad (9)$$

$$\Gamma(n) = \Gamma[(2n+1)(2n+1) + 6n], \quad \varepsilon_{\varphi}(n) \equiv \varepsilon_{a_{\varphi}}(n).$$

The parameters $B_{\pm 1}$ are governed by the decay equations

$$B_{+1}(n, \varphi, \varphi'; \varphi_1, \varphi'_1) = 2\Gamma(n+1) \sum_{\chi} A_{\chi}(n+1, \varphi', \varphi'_1) A_{\chi}^*(n, \varphi, \varphi_1) \quad (10)$$

$$B_{-1}(n, \varphi, \varphi'; \varphi_1, \varphi'_1) = n(n+1)^{-1} B_{+1}^*(n-1, \varphi_1, \varphi'_1; \varphi, \varphi')$$

the quantities B_0 are governed by the modulation broadening

$$\sum_{\varphi_1 \varphi'_1} B_0(n, \varphi, \varphi'; \varphi_1, \varphi'_1) G_n(\varphi_1, \varphi'_1; \omega) = \langle n+1\varphi' | \hat{\Gamma}_m G_{a_{\chi}}(\omega) | n\varphi \rangle \quad (11)$$

since the explicit expressions for these quantities are cumbersome, we shall not quote them.

Neglecting the broadening, we find that the spectral distribution defined by Eq. (8) can be represented [see Eq. (9)] as a fine structure set of delta function lines located at frequencies $\omega_0 + \varepsilon_{\varphi}(n+1) - \varepsilon_{\varphi}(n)$. The intensity of each line is given by $(n+1)^{-4} \exp(-\lambda\omega_0 n) \sum_{\chi} |A_{\chi}(n, \varphi, \varphi')|^2$. The total intensity of the lines corresponding to a transition from the n -th to the $(n+1)$ -th level is given by $(n+1)^{-4} \exp(-\lambda\omega_0 n) (n+1)(n+2)(n+3)/6$. Since $T > \omega_0/2 \ln 2$, the latter function exhibits a maximum at $n = n_0$ ($n_0 \approx 3T/\omega_0$ provided $T \gg \omega_0$) and then decays exponentially.

Relaxation leads not only to a broadening of delta function lines but also to interference between the lines. If the anharmonicity lifts completely the random (with respect to the cubic symmetry assumed) degeneracy of local vibration levels and if the separation between the fine structure lines is much greater than their half-width

$$|[\varepsilon_{a_{\varphi}}(n+1) - \varepsilon_{a_{\varphi'}}(n)] - [\varepsilon_{a_{\varphi}}(n+1 \pm 1) - \varepsilon_{a_{\varphi'}}(n \pm 1)]| \gg \gamma(n), \quad (12)$$

we find that the interference between different lines can be neglected and their profile is Lorentzian with a half-

width

$$\gamma(n, a_{\varphi}, j; a_{\varphi'}, j') = \Gamma[(2n+1)(2n+1) + 6n] + \sum_{j_1 j'_1} B_0(n, a_{\varphi}, j, a_{\varphi'}, j'; a_{\varphi}, j_1, a_{\varphi'}, j'_1) \times A_{\chi}^*(n, a_{\varphi}, j_1, a_{\varphi'}, j'_1) A_{\chi}(n, a_{\varphi}, j, a_{\varphi'}, j'). \quad (13)$$

The contribution of the decay broadening to γ is identical for all the lines corresponding to the transitions between the n -th and $(n+1)$ -th multiplets and is proportional to the number n . The modulation broadening depends on the indices a_{φ} and $a_{\varphi'}$ but, on the whole, it also increases rapidly as a function of n . Consequently, even if the criterion of the fine structure (12) is satisfied for small n , it is violated for large n and the fine structure disappears in the wings, i.e.,

$$Q(\omega) \approx \pi^{-1} \gamma_0 / \Omega^2, \quad \gamma_0 = \Gamma + \Gamma_{m1} + 2\Gamma_{m2}, \quad |\omega - \omega_0| \gg |\varepsilon_{a_{\varphi}}(n_0)|, \quad \gamma(n_0). \quad (14)$$

It follows from Eq. (13) that the criterion (12) is violated at higher temperatures for smaller and smaller n . Since the relative intensity of the lines with small n decreases as $(n+1)^{-4}$, the fine structure is quickly smeared. On the other hand, at low temperatures satisfying $T \ll \omega_0$, the intensity of the transitions between excited levels is exponentially small. Consequently, the fine structure $Q(\omega)$ can be observed only in a narrow temperature range $T \sim \omega_0$. The corresponding number of lines is small and the lines correspond to transitions between several lowest levels.

When there is a fine structure near the maximum of the distribution $Q(\omega)$, the profile and position of the peak are governed by the transitions from the states with $n \sim n_m$. The parameter n_m is determined by the condition that the amplitude of the fine-structure lines should exhibit a maximum, i.e., the factor $(n+1)(n+2)(n+3) \exp(-\lambda\omega_0 n) / \gamma(n)$ should have a maximum. Since $\gamma(n)$ is a rapidly increasing function of n , the quantity n_m is smaller than n_0 . The smearing of the fine structure at the maximum of $Q(\omega)$ is accompanied by a decrease of $n_0 - n_m$.

For a weak internal anharmonicity ($|V_{1,2,3}| \ll \gamma_0$), the system of difference equations (11) can be solved analytically

$$G_n(\varphi, \varphi'; \omega) = \frac{1}{\pi(n+1)^3} A_{\chi}^*(n, \varphi, \varphi') \exp(-\lambda\omega_0 n) / (\gamma_0 - i\Omega), \quad Q(\omega) \approx \frac{1}{\pi} \frac{\gamma_0}{\gamma_0^2 + \Omega^2}, \quad (15)$$

where γ_0 is defined by Eq. (14). Since the interference of the transitions in the absence of an internal anharmonicity

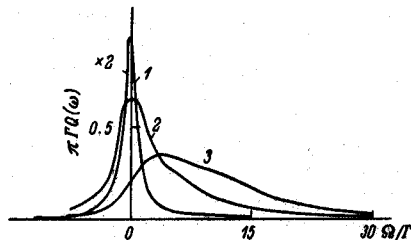


FIG. 1. Temperature dependence of the spectral distribution $Q(\omega)$ in the absence of a fine structure: $V_1/\Gamma = 2$; $V_2/\Gamma = V_3/\Gamma = 1$. Curves 1, 2, and 3 correspond to $T/\omega_0 = 0, 0.5$, and 0.9 .

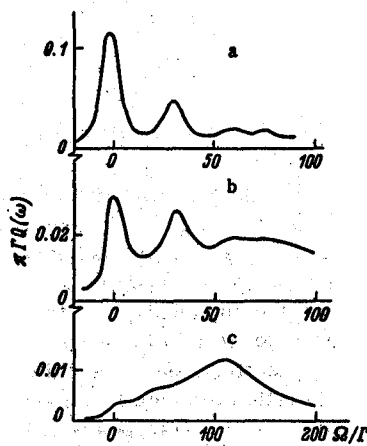


FIG. 2. Spectral distribution $Q(\omega)$ of degenerate local vibrations exhibiting a fine structure: $V_1/\Gamma = 15$; $V_2/\Gamma = V_3/\Gamma = 7.5$. The ratio T/ω_0 for the curves a, b, and c is equal to 0.67, 1, and 2.

is strong, all the individual lines in the spectrum have the same half-width γ_0 that is not determined by the Wigner-Weisskopf expression [Eq. (13)], i.e., the "paradox" of the harmonic oscillator is retained for degenerate local vibrations both for the decay and modulation types of broadening.

3. PROFILE OF THE SPECTRUM OF DEGENERATE LOCAL VIBRATIONS FOR ARBITRARY ANHARMONICITY (NUMERICAL RESULTS)

To study the spectral distribution of local vibrations for arbitrary ratios V/Γ and ω_0/T , it is necessary to solve numerically the set of linear equations (9). For simplicity, we shall assume that the modulation broadening is unimportant, i.e., $\Gamma_{m1,2,3} \ll \Gamma$. The latter inequality can be satisfied for quasilocal or low-frequency local vibrations. Equation (9) then contains five dimensionless parameters: ω_0/T , Ω/Γ , V_1/Γ , V_2/Γ , and V_3/Γ .

As already noted, the inhomogeneous term in Eq. (9) decreases exponentially with increasing principal quantum number, i.e., for $n \gg n_0$. Consequently, we can define at arbitrary temperatures $n = \tilde{n}$ for which the chain of equations (9) can be terminated so that the quantity $Q(\omega)$ can be obtained with a specified accuracy. It is quite clear that the truncated chain of equations can describe accurately the maximum of $Q(\omega)$ only for $\tilde{n} > n_m$. Hence, the quantity \tilde{n} increases with increasing temperature. At the same time, the number of equations required increases rapidly (following a power law) with \tilde{n} . As a result, only the case of low temperatures can be studied relatively easily. We shall choose $\tilde{n} = 5$ [the system (9) then reduces to a system of 310 linear equations], which makes it possible²⁾ to study the range of temperatures $T \leq 2\omega_0$ ($n_0 \leq 4$).

Since the distribution $Q(\omega)$ for a degenerate oscillator is a function of four parameters, we shall study only the most important changes of the spectrum: 1) the temperature broadening of the peak $Q(\omega)$ due to internal anharmonicity but in the absence of a fine structure; 2) temperature smearing of the fine structure; 3) dependence of the number of fine structure lines on the relative magnitudes

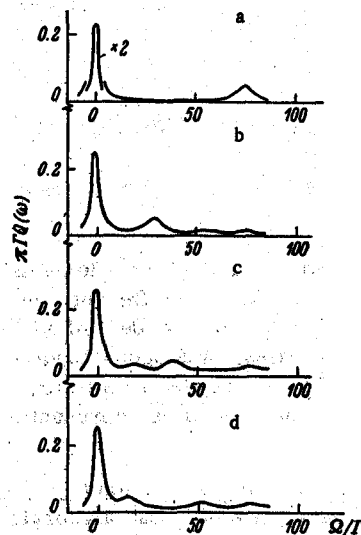


FIG. 3. Dependences of the fine structure of a degenerate local vibration on the relative magnitude of the anharmonicity parameters for $T/\omega_0 = 0.5$. a) $V_1/\Gamma = 0$, $V_2/\Gamma = 37.5$, $V_3/\Gamma = 0$; b) $V_1/\Gamma = 15$, $V_2/\Gamma = 7.5$, $V_3/\Gamma = 7.5$; c) $V_1/\Gamma = 18.75$, $V_2/\Gamma = 0$, $V_3/\Gamma = 9.375$; d) $V_1/\Gamma = 8$, $V_2/\Gamma = 21.5$, $V_3/\Gamma = 4$.

of the internal anharmonicity parameters.

It follows from Fig. 1 (our choice of the parameters V_1 , V_2 , and V_3 corresponds to a spherical oscillator with an internal anharmonicity of the type $x^2 + y^2 + z^2$) that no well-defined fine structure occurs at any temperature for $V_{1,2,3} \sim \Gamma$. When the quantity T/ω_0 is increased, the maximum of $Q(\omega)$ shifts, the peak broadens and becomes asymmetric. For $V/\Gamma \sim 1$, the interference between the transitions is quite important and $n_0 \approx n_m$. Consequently, the quantity $Q(\omega)$ for $T = 2\omega_0$ cannot be described in terms of five excited levels only (the error involved reaches 30%).

Figure 2 shows the temperature dependence of the spectral distribution of local vibrations for such a choice of the parameters that the fine structure criterion (12) is satisfied for $T \sim \omega_0$. It follows [see also Fig. 3b showing the graph of $Q(\omega)$ for the same oscillator at $T = \omega_0/2$] that the fine structure becomes well-defined when the temperature is raised and lies in the region of relatively small T/ω_0 . However, although the anharmonicity parameter is quite large ($V/\Gamma \sim 30$), the number of the fine-structure lines is small. The lines in the neighborhood of $\Omega/\Gamma \approx 30.75$ correspond to the transitions between the levels $n = 1$ and $n = 2$; in the neighborhood of $\Omega/\Gamma \approx 80$, the transitions take place between the levels $n = 2$ and $n = 3$. The half-widths of such lines are well described by Eq. (13). As the temperature is raised above the value $T \gg \omega_0$, the fine structure is gradually smeared. The smearing begins to manifest itself for large Ω/V where the contribution of the continuous spectrum is especially strong. The lines characterized by smaller n disappear earlier than the lines characterized by large n . For certain ratio of V to Γ at $T = 2\omega_0$, the fine structure practically disappears and $Q(\omega)$ represents a single highly asymmetric distribution. The maximum of this distribution lies to the left of the frequency corresponding to the transitions from the level $n = n_0 = 4$, i.e., as already noted, we obtain

$n_m < n_0$. The accuracy of the determination of the amplitude and position of the maximum on the curve 2c is of the order of 10%. To the left of the maximum, our calculated results for $Q(\omega)$ (Fig. 2c) corresponding to $\tilde{n} = 4$ and $\tilde{n} = 5$ agree with an accuracy of 1%; the agreement on the right of the maximum becomes rapidly poorer.

Figure 3 illustrates the dependence of the structure of the spectral distribution of degenerate local vibrations on the relative magnitude of the anharmonicity parameters V_1 , V_2 , and V_3 . We have chosen these parameters so that the separation between the frequency of the fundamental transition ($0 \rightarrow 1$) and the maximum transition frequency between the first and second excited levels is constant and the temperature is chosen so that the lines corresponding to the transitions between higher excited states are unimportant. Figure 3a corresponds to a quasi-one-dimensional local vibration (the vibrations in three directions are independent); there is only a single side line. Figure 3b corresponds to a spherical local vibration; two side lines corresponding to the transition $1 \rightarrow 2$ occur (a weak line at a frequency $\Omega \approx 60 \Gamma$ corresponds to one of the transitions $2 \rightarrow 3$). Figures 3c and 3d refer to a more general case of a three-dimensional local vibration of cubic symmetry and they correspond to three transitions $1 \rightarrow 2$.

The fine structure of the infrared absorption spectrum due to degenerate local vibrations has been studied only under nonequilibrium conditions.¹¹ Experiments that would measure simultaneously the relative magnitudes of the parameters V_1 , V_2 , and V_3 (for example, from the positions of higher harmonics^{12,13}) and the profile of the peak $Q(\omega)$ at the fundamental frequency in a wide interval of ω_0/T are not available. Consequently, we cannot compare quantitatively our calculated results with the experimental results for degenerate local vibrations.

Finally, we would like to point out that our calculations of $Q(\omega)$ at frequencies $\omega \sim \omega_0$ that are based on a finite \tilde{n} are valid at arbitrary temperatures (in particular, for $n_0 > \tilde{n}$). They correspond to the model of an impurity that exhibits $\tilde{n} + 2$ nearly equidistant multiplets (including the ground state) with oscillator transition probabilities and with energies of all the other levels differing considerably from $n\omega_0$. It is only necessary to replace the quantity $(\tilde{n} + 1)^3$ on the right-hand side of Eq. (9) by the corresponding partition sum of the impurity.

APPENDIX

The internal anharmonicity parameters of local vibrations $V_{1,2,3}$ in Eq. (1) are renormalized due to the interaction of each oscillator with the vibrations of the continuous spectrum. The cubic anharmonicity that is most important is described by the Hamiltonian

$$H_1^{(1)} = N^{-1/2} \sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} (a_{\mathbf{k}} + a_{\mathbf{k}}^\dagger) (a_{\mathbf{k}'} + a_{\mathbf{k}'}^\dagger) (b_{\mathbf{k}} + b_{\mathbf{k}}^\dagger). \quad (\text{A.1})$$

In the second order in $V_{\mathbf{k}\mathbf{k}'}^*$, the parameters $V_{1,2,3}$ are

given by

$$\begin{aligned} \tilde{V}_1 &= V_1 + 4P \frac{1}{N} \sum_{\mathbf{k}} V_{11\mathbf{k}} \left(\frac{\omega_{\mathbf{k}}}{4\omega_{\mathbf{k}}^2 - \omega_{\mathbf{k}}^2} - \frac{2}{\omega_{\mathbf{k}}} \right); \\ \tilde{V}_2 &= V_2 + 8P \frac{1}{N} \sum_{\mathbf{k}} \left\{ \frac{-V_{11\mathbf{k}} V_{22\mathbf{k}}}{\omega_{\mathbf{k}}} + \frac{V_{22\mathbf{k}}^2 \omega_{\mathbf{k}}}{4\omega_{\mathbf{k}}^2 - \omega_{\mathbf{k}}^2} - \frac{V_{22\mathbf{k}}^2}{\omega_{\mathbf{k}}} \right\}; \\ \tilde{V}_3 &= V_3 + 4P \frac{1}{N} \sum_{\mathbf{k}} \left(\frac{-2V_{12\mathbf{k}}}{\omega_{\mathbf{k}}} + \frac{V_{11\mathbf{k}} V_{22\mathbf{k}} \omega_{\mathbf{k}}}{4\omega_{\mathbf{k}}^2 - \omega_{\mathbf{k}}^2} \right). \end{aligned} \quad (\text{A.2})$$

It follows from Eq. (A.2) that $\tilde{V}_2 - V_2 \approx 2(\tilde{V}_3 - V_3)$. However, for low-frequency quasilocal vibrations and in the lowest approximation in the ratio of the local vibration frequency to the typical frequency of continuous spectrum vibrations, we find from Eq. (A.2) that $\tilde{V}_2 - V_2 \approx 2(\tilde{V}_3 - V_3)$. This is due to the fact that the continuous spectrum vibrations follow adiabatically the low-frequency local vibrations and the "clothing" of the local vibrations does not lead to a spatial dependence of the effective mass of local vibrations and to the appearance of terms similar to $p_y^2 q_y^2$ in the internal anharmonicity Hamiltonian. Since the phonon density of states at frequencies $\sim |V|$ is quite low, the broadening of local vibrations due to transitions between the levels within each multiplet, that is described by the Hamiltonian (A.1), can be neglected.

¹For noncentrosymmetric local vibrations, the parameters V_2 and V_3 are independent even if the renormalization of these parameters due to internal cubic anharmonicity is taken into account.^{11,12}

²At high temperatures, it is convenient to replace the system of difference equations (9) by a partial differential equation. This can be accomplished by a transition in the operator equation (4) to the representation of the wave functions of a triply degenerate harmonic oscillator in the coherent-state representation. As a result, we obtain a second-order diffusion-type equation with seven independent variables (time, three amplitudes, and three phases of an oscillator). For $T \gg \omega_0$, the latter equation transforms to the Fokker-Planck equation for the classical three-dimensional oscillator.

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