

MODERN METHODS IN THE THEORY OF MANY-PHONON PROCESSES

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1. INTRODUCTION

MANY-PHONON processes are customarily defined in solid state theory as quantum transitions in which the energy of the lattice is changed during one act by an amount which exceeds by many times (as many as several dozen) the energy of the vibrational quantum.

In optical many-phonon processes the absorption (emission) of a light quantum is accompanied by phonon production, which leads to the appearance of broad light-absorption bands (luminescence). Many-phonon processes of the optical type arise also in interactions between nuclear radiations (neutrons or gamma quanta) and crystals.

In nonradiative (thermal) many-phonon transitions, the electron excitation energy is transferred directly to the lattice (or vice versa). A study of the kinetics of luminescence and photoconductivity shows that nonradiative transitions frequently have high probability and are capable of competing with optical transitions. Nonradiative transitions include also recombination of electrons with local centers and holes, inelastic scattering of electrons by local centers, etc.

By defining a phonon as an elementary excitation corresponding to small oscillations of the nuclei near the sites of the crystal lattice, we assume by the same token that these small oscillations and the electron motion can be regarded as weakly-interacting subsystems. In some problems of solid-state physics (for example, in the theory of electric conductivity of atomic semiconductors), the above-mentioned weak interaction is regarded as a small perturbation that causes transitions between the electron states. In this case, however, many-phonon transitions can arise only in the higher-order approximations of perturbation theory and accordingly have very low probabilities, in contradiction to the experimental facts presented above.

An alternate approach to the problem is the adiabatic approximation. Let us consider a crystal whose lattice contains defects (impurity atoms or ions, vacant sites, dislocations) and let us assume that the electrons localized near the defects are more weakly bound than the crystal electrons proper. The latter can be regarded as a "fast" subsystem of the adiabatic approximation, and the role of the "slow" subsystem is assumed by the weakly bound electrons and atomic nuclei^[1].

Confining ourselves to transitions in which the state of strongly bound electrons does not change, we arrive at the Hamiltonian

$$H = H_e(r) + H_n(R) + V(r, R), \quad (1.1)$$

where $H_e(r)$ and $H_n(R)$ depend only on the dynamic variables of the weakly bound electrons (r) and nuclei (R) respectively; V includes all terms of the interaction between the weakly bound electrons and the nuclei, and also the energy of the fast subsystem (crystal's own electrons) for a fixed configuration (r, R) of the slow subsystem.

We assume further that the position vector of any nucleus is

$$R = R_0 + u, \quad (1.2)$$

where R_0 is a fixed vector corresponding to a definite lattice site and u is a small displacement. Expanding $H_n(R)$ in the displacements u and introducing suitable normal coordinates $\dots q_\kappa \dots$ ^[2], we obtain in the harmonic approximation

$$H_n(R) = H_n(R_0) + \sum_{\kappa} \frac{\hbar \omega_{\kappa}}{2} \left(q_{\kappa}^2 - \frac{\partial^2}{\partial q_{\kappa}^2} \right), \quad (1.3)$$

where the summation extends over all modes of the crystal vibrations and the local vibrations^[3] due to disturbances to the ideal structure of the lattice.

As a rule, only the linear terms are retained in the corresponding expansion of the interaction energy V , and then

$$V(r, R) = V_0(r) + \sum_{\kappa} A_{\kappa}(r) q_{\kappa}, \quad (1.4)$$

where $V(r) \equiv V(r, R_0)$ includes the periodic potential energy of interaction between the electrons and the "frozen" ideal lattice, and the potential energy of the electrons in the nonperiodic field produced by the lattice defects.*

Choosing $H_n(R_0)$ as the zero energy level, we obtain

$$H = \bar{H}_e(r) + \sum_{\kappa} A_{\kappa}(r) q_{\kappa} + \sum_{\kappa} \frac{\hbar \omega_{\kappa}}{2} \left(q_{\kappa}^2 - \frac{\partial^2}{\partial q_{\kappa}^2} \right), \quad (1.5)$$

where

$$\bar{H}_e(r) = H_e(r) + V_0(r). \quad (1.6)$$

The electron-phonon interaction term in (1.5) cannot be responsible for the many-phonon transitions in the first approximation of perturbation theory. We therefore apply again the adiabatic approximation to the

*The nonperiodic part V_0 includes also the interaction between the electrons and the lattice deformations which they produce (polaron effect).

Hamiltonian (1.5), taking this time the weakly bound electrons as the fast subsystem^[4]. It is assumed that the minimum excitation energy of the latter is large compared with the Debye phonon energy. The approximate eigenfunction of the Hamiltonian (1.5) is sought in the form

$$\Psi(r, q) = \psi(r, q) \Phi(q), \quad (1.7)$$

where the electron ψ -function satisfies the Schrödinger equation

$$[\bar{H}_e(r) + \sum_{\kappa} A_{\kappa}(r) q_{\kappa}] \psi(r, q) = E(q) \psi(r, q). \quad (1.8)$$

If we neglect in the zeroth approximation the so-called non-adiabaticity operator

$$\mathcal{L}\Psi = - \sum_{\kappa} \hbar \omega_{\kappa} \left[\frac{\partial \psi}{\partial q_{\kappa}} \frac{\partial \Phi}{\partial q_{\kappa}} + \frac{\Phi}{2} \frac{\partial^2 \psi}{\partial q_{\kappa}^2} \right], \quad (1.9)$$

then

$$\left[E(q) + \sum_{\kappa} \frac{\hbar \omega_{\kappa}}{2} \left(q_{\kappa}^2 - \frac{\partial^2}{\partial q_{\kappa}^2} \right) \right] \Phi = H \Phi, \quad (1.10)$$

where H — approximate eigenvalue of the total Hamiltonian (1.5).

The electron equation (1.8) is solved by perturbation theory, with a perturbation operator

$$W = \sum_{\kappa} A_{\kappa}(r) (q_{\kappa} - q_{\kappa s}), \quad (1.11)$$

where $q_{\kappa s}$ are the normal coordinates q_{κ} for which the adiabatic potential of (1.10) has a minimum. The index s pertains to the zeroth-approximation electron state, which is determined from the equation

$$[\bar{H}_e(r) + \sum_{\kappa} A_{\kappa}(r) q_{\kappa s}] \psi_s^0 = E_s^0 \psi_s^0. \quad (1.12)$$

The level E_s^0 is assumed nondegenerate, and consequently

$$\psi_s(r, q) = \psi_s^0 + \sum_{s' \neq s} \frac{W_{s's}}{E_s^0 - E_{s'}^0} \psi_{s'}^0 + \dots, \quad (1.13)$$

$$E_s(q) = E_s^0 + W_{ss} + \sum_{s' \neq s} \frac{|W_{s's}|^2}{E_s^0 - E_{s'}^0} + \dots, \quad (1.14)$$

where

$$\begin{aligned} W_{s's} &= \sum_{\kappa} A_{\kappa s's} (q_{\kappa} - q_{\kappa s}), \\ A_{\kappa s's} &= \int \psi_{s'}^0 A_{\kappa}(r) \psi_s^0 dr. \end{aligned} \quad (1.15)$$

In formulas (1.13)–(1.15) the index s' numbers the eigenvalues and the eigenfunctions of (1.12) for a fixed potential energy $\sum_{\kappa} A_{\kappa}(r) q_{\kappa s}$. These solutions are customarily called “non-self-consistent,” to distinguish them from the “self-consistent” state ψ_s^0 . If we assume

$$q_{\kappa s} = - \frac{A_{\kappa s's}}{\hbar \omega_{\kappa}}, \quad (1.16)$$

then the adiabatic potential of (1.10) assumes after the substitution (1.14) the form

$$\begin{aligned} U_s(q) &= J_s + \sum_{\kappa} \frac{\hbar \omega_{\kappa}}{2} (q_{\kappa} - q_{\kappa s})^2 \\ &+ \sum_{\kappa, \lambda} B_{\kappa\lambda}^{(s)} (q_{\kappa} - q_{\kappa s}) (q_{\lambda} - q_{\lambda s}). \end{aligned} \quad (1.17)$$

where

$$B_{\kappa\lambda}^{(s)} = \sum_{s' \neq s} \frac{A_{\kappa s's} A_{\lambda s's}^*}{E_s^0 - E_{s'}^0}, \quad (1.18)$$

$$J_s = E_s^0 + \sum_{\kappa} \frac{\hbar \omega_{\kappa}}{2} q_{\kappa s}^2. \quad (1.19)$$

The most significant results in the theory of many-phonon transitions were obtained neglecting the second-order correction to the energy in (1.14), and accordingly, the nondiagonal terms of the quadratic form (1.17). In this approximation, the adiabatic wave functions (1.7) assume the form

$$\Psi_{s,n}(r, q) = \psi_s(r, q) \prod_{\kappa} \Phi_{n_{\kappa}}(q_{\kappa} - q_{\kappa s}), \quad (1.20)$$

where $\Phi_{n_{\kappa}}$ is the wave function of the one-dimensional harmonic oscillator.

The eigenvalues of (1.10) are accordingly

$$H_{s,n} = J_s + \sum_{\kappa} \hbar \omega_{\kappa} \left(n_{\kappa} + \frac{1}{2} \right). \quad (1.21)$$

The wave functions (1.20) form a complete orthonormal system. It must be emphasized, however, that the orthogonality of the wave functions (1.20), which belong to different electron states, is due to the electronic components. The corresponding phonon functions are not orthogonal, owing to the dependence of the displacements $q_{\kappa s}$ on the electron states. This makes many-phonon transitions possible even in the first approximation of perturbation theory, as first noted by Frenkel^[5].

Proceeding to a discussion of the role of the non-diagonal terms of the adiabatic potential (1.17), we write the phonon Hamiltonian (1.10) in the form

$$H_s = J_s + \frac{1}{2} \sum_{\kappa, \lambda} \left[\Omega_{\kappa\lambda}^{(s)2} x_{\kappa}^{(s)} x_{\lambda}^{(s)} - \hbar^2 \delta_{\kappa\lambda} \frac{\partial^2}{\partial x_{\kappa}^{(s)2}} \right], \quad (1.22)$$

where

$$x_{\kappa}^{(s)} = \sqrt{\frac{\hbar}{\omega_{\kappa}}} (q_{\kappa} - q_{\kappa s}), \quad (1.23)$$

$$\Omega_{\kappa\lambda}^{(s)2} = \omega_{\kappa}^2 \delta_{\kappa\lambda} + \frac{B_{\kappa\lambda}^{(s)}}{\hbar} \sqrt{\omega_{\kappa} \omega_{\lambda}}. \quad (1.24)$$

The potential energy in (1.22) is a positive definite quadratic form in the variables $x_{\kappa}^{(s)}$, and consequently there exists a unitary transformation

$$x_{\kappa}^{(s)} = \sum_{\lambda} S_{\lambda\kappa}^{(s)} y_{\lambda}^{(s)}, \quad (1.25)$$

which reduces the matrix $\Omega_{\kappa\lambda}^{(s)2}$ to the diagonal form $\omega_{\kappa}^{(s)2} \delta_{\kappa\lambda}$. After making the substitution

$$Q_{\kappa}^{(s)} = \sqrt{\frac{\omega_{\kappa}^{(s)}}{\hbar}} y_{\kappa}^{(s)} \quad (1.26)$$

the Hamiltonian (1.22) is reduced to the Hamiltonian of a system of independent oscillators

$$H_s = J_s + \sum_{\kappa} \frac{\hbar \omega_{\kappa}^{(s)}}{2} \left[Q_{\kappa}^{(s)2} - \frac{\partial^2}{\partial Q_{\kappa}^{(s)2}} \right], \quad (1.26')$$

which differs from the initial phonon Hamiltonian (1.3) in a redefinition of the normal coordinates

$$Q_{\kappa}^{(s)} = \sum_{\lambda} S_{\kappa\lambda}^{(s)*} \sqrt{\frac{\omega_{\kappa}^{(s)}}{\omega_{\lambda}^{(s)}}} (q_{\lambda} - q_{\lambda s}), \quad (1.27)$$

and a renormalization of the phonon frequencies ($\omega_{\kappa} \rightarrow \omega_{\kappa}^{(s)}$), which turn out to be different in different electron states. This effect (henceforth called the "frequency effect") can, along with the displacement of the normal coordinates, serve as a cause of the many-phonon transitions.*

The general mathematical theory of diagonalization of quadratic forms of the type (1.17) was developed by Bogolyubov^[7] (see also^[8]). In the present review we consider only the simplest case, when the matrix S can be obtained in final form by perturbation-theory methods^[2]. The problem reduces to a solution of the system of equations

$$\sum_{\mu} S_{\mu\lambda}^{(s)} \Omega_{\mu}^{(s)2} = S_{\kappa\lambda}^{(s)} \omega_{\lambda}^{(s)2} \quad (1.28)$$

under the additional unitarity condition

$$\sum_{\mu} S_{\kappa\mu}^{(s)} S_{\lambda\mu}^{(s)*} = \delta_{\kappa\lambda}. \quad (1.29)$$

We assume that: a) the unperturbed spectrum of the phonon frequencies of the crystal is not degenerate; b) there exists a small parameter ϵ such that $A_{\kappa s}$'s $\sim \epsilon^0$ and $B_{\kappa\lambda}^{(s)} \sim \epsilon^2$. In this case the use of standard perturbation theory yields (accurate to terms $\sim \epsilon^3$)

$$\omega_{\kappa}^{(s)} = \omega_{\kappa} + \frac{B_{\kappa\kappa}^{(s)}}{2\hbar}, \quad (1.30)$$

$$S_{\kappa\lambda}^{(s)} = \delta_{\kappa\lambda} + \frac{B_{\kappa\lambda}^{(s)} \sqrt{\omega_{\kappa} \omega_{\lambda}}}{\hbar (\omega_{\kappa}^2 - \omega_{\lambda}^2)}. \quad (1.31)$$

An account of the frequency effect gives rise in the theory of many-quantum transitions to certain mathematical difficulties, connected with the fact that the matrices $\Omega_{\kappa\lambda}^{(u)2}$ and $\Omega_{\kappa\lambda}^{(g)2}$, which pertain to different electron states, cannot be diagonalized by a single unitary transformation. In other words, there is no system of normal lattice coordinates common to two different electron states. Methods of taking the frequency effect into account will be considered in Secs. 5-7. In Secs. 3 and 4 we consider the main results of the theory, obtained neglecting the frequency effect.

In the literature on many-phonon transitions there are encountered variants of the adiabatic approximation which differ somewhat from that given above. Some

authors take the perturbation of (1.8) to be not the expression given by (1.11), but the entire interaction term^[6]. Generally speaking, the criterion of applicability of the adiabatic approximation to the electron of the local center can be satisfied also in the case of weak electron-phonon interaction*. By virtue of the linearity of the operator (1.11), both variants of the solution of (1.8) lead to expressions of the same type, which differ only in the choice of the zeroth-approximation electron ψ -functions. However, as will be explained later on, the parameters that characterize the "many-phonon nature" of the process, depend quadratically on the electron-phonon coupling constant, and are thus small in the case of a weak interaction.

A systematic expansion in a small parameter (λ), first proposed in molecular theory by Born and Oppenheimer^[9], is sometimes used in adiabatic perturbation theory. The small parameter λ is introduced in such a way that the nuclear kinetic energy operator is proportional to λ^4 , while the displacements $q_{\kappa} - q_{\kappa s}$ of the normal oscillators are proportional to λ (a detailed development of the method is found in^[2] and a generalization to include the case of the polaron is given in^[7]). It must be borne in mind that the formal parameter λ does not coincide with the parameter ϵ introduced for the derivation of (1.30) and (1.31).[†] Therefore, in particular, in the " ϵ method" the frequency effect arises in the next higher perturbation theory approximation compared with the displacement effect, whereas in the " λ method" both effects are of equal weight.

We note, finally, that the appearance of many-phonon transitions in the interaction between neutrons or γ -photons and the crystal lattice is generally speaking not connected with the use of the adiabatic approximation. In both indicated cases, the perturbation operator contains a factor $\exp(\mathbf{k} \cdot \mathbf{u}_N)$, where \mathbf{u}_N is the vector of the displacement of the nucleus from the N-th lattice site and \mathbf{k} the wave vector of the neutron (γ -quantum). If \mathbf{k} is large the phonon matrix elements corresponding to many-phonon transitions can no longer be regarded as small. A consistent theory of this type of many-phonon transitions was developed by Lamb^[10] even before the war. The theory of the Mössbauer effect is presently developing along the same lines (see, for example,^[11]). The mathematical methods of the theory of optical and nonradiative transitions in local centers of crystals, to which the present article is devoted, are identical with the methods of the theory of many-phonon interactions between nuclear radiation and crystals.

*This remark does not pertain to the polaron. The adiabatic theory of polarons presupposes a strong interaction^[1].

[†]It is easy to note that $\epsilon^2 \sim \hbar \omega / |\Delta E|$, where ω - maximum phonon frequency and ΔE - energy gap between the level E_s^0 and the nearest level E_s^0 .

*Nonradiative transitions in the local center of the semiconductor are considered in^[6]. Many-phonon behavior is obtained as a result of the frequency effect, if the displacement effect is neglected.

2. PROBABILITIES OF MANY-PHONON TRANSITIONS

We consider optical and nonradiative transitions between moving discrete electron levels of a local center. These levels and all the quantities pertaining to them are designated by the indices g (ground state) and u (excited state). The phonon occupation numbers are denoted by $\dots n_k \dots$ or (n) and $\dots n'_k \dots (n')$ for the initial and final states, respectively.

The formulas presented below are not connected with any specific models of the local centers or with the applicability of the effective-mass method. It is merely assumed that $E_u^0 - E_g^0 \gg \hbar\omega$ and the criterion for the adiabatic approximation is consequently satisfied.

The probabilities for the absorption and emission of light in the transitions $g \leftrightarrow u$ are calculated by the method of quasiclassical radiation theory, which interprets the field of a light wave as being an external spatially homogeneous electric field \mathcal{E} , which varies in time with cyclic frequency Ω .^[12] The perturbation operator is chosen in the form $-(M(\mathbf{r}), \mathcal{E})$, where $M(\mathbf{r})$ is the effective dipole moment of the absorbing center, which takes into account the additional interaction of the localized electrons with the crystal, resulting from the inertialess polarization of the strongly bound electrons by the light-wave field^[4].

The probability (per second) of absorption of a light quantum is

$$\omega_{g,n \rightarrow u,n'} = \frac{4\pi^2 S(\Omega) |\langle u,n' | M | g,n \rangle|^2}{3\hbar^2 c n(\Omega)}, \quad (2.1)$$

where the transition frequency is

$$\Omega = \frac{H_{u,n'} - H_{g,n}}{\hbar}, \quad (2.2)$$

$S(\Omega)$ is the spectral density of the flux incident on the radiation center [in (2.1) averaging is carried out over this radiation]; $n(\Omega)$ is the refractive index and c the velocity of light in vacuum.

The absorption coefficient is

$$\tau(\Omega) = \frac{N_g \hbar \Omega \omega_{g,n \rightarrow u,n'}}{S(\Omega)} = \frac{4\pi^2 N_g \Omega}{3\hbar c n(\Omega)} |\langle u,n' | M | g,n \rangle|^2, \quad (2.3)$$

where N_g is the concentration of the absorbing centers. For comparison with experiment, the value of (2.3) must be averaged over the phonon occupation numbers in the initial state and summed over all the final states of these numbers compatible with the energy conservation law (2.2). It is thus necessary to calculate

$$\bar{\tau}(\Omega) = Av(n) \sum_{(n')} \tau(\Omega), \quad (2.4)$$

where $Av(n)$ denotes the aforementioned averaging. It is carried out under the assumption that the initial distribution of the phonon occupation number is in statistical equilibrium. The symbol $\hat{}$ in (2.4) indicates that the summation must be carried out under the additional condition (2.2).

The calculation of the matrix element contained in

(2.3) is a difficult task, since the electron wave functions of the local center, as well as the effective dipole moment M , are usually not well known. It turns out, however, that under certain simplifying assumptions, the most important information concerning the form of the absorption bands can be extracted from the "phonon" part of the matrix element. In particular, if a) we neglect the frequency effect and b) we confine ourselves to the electron wave functions of the zeroth approximation in (13) (the so-called Condon approximation), then

$$\langle u,n' | M | g,n \rangle = M_{ug} \prod_{\kappa} \langle n'_\kappa | n_\kappa \rangle, \quad (2.5)$$

where

$$M_{ug} = \int \psi_u^* M(\mathbf{r}) \psi_g^0 d\mathbf{r}, \quad (2.6)$$

$$\langle n'_\kappa | n_\kappa \rangle = \int_{-\infty}^{\infty} \Phi_{n'_\kappa}(q_\kappa - q_{\kappa u}) \Phi_{n_\kappa}(q_\kappa - q_{\kappa g}) dq_\kappa. \quad (2.7)$$

The absorption band is usually a bell-shaped curve. The factor $\Omega/n(\Omega)$ in (2.3) remains practically constant within the half-width of this curve, and it can be taken outside the $Av(n) \sum_{(n')} \dots$ sign at the value corresponding to the maximum of the band. Then the problem reduces to the calculation of

$$I_{ug}(\Omega) = |M_{ug}|^2 Av(n) \sum_{(n')} \prod_{\kappa} |\langle n'_\kappa | n_\kappa \rangle|^2. \quad (2.8)$$

Expression (2.8) was first evaluated by Pekar^[13] and almost simultaneously and independently by Huang Kun and Rhys for the particular case of an "Einstein crystal," that is, neglecting the dispersion of the phonon frequencies. In^[13,14] the transition probabilities are evaluated by a direct combinatorial method, in which a number of phonons (specified by the energy conservation law) is generated. A detailed exposition of the direct summation method can be found in Pekar's book^[1]. The main results will be derived in Sec. 3 as a particular case of more general formulas which take into account the dispersion of the normal oscillations of the crystal.

By generalizing Einstein's known concepts to include the case of the electromagnetic field in the crystal, we can easily obtain for the probability (per second) of the spontaneous optical transition $u, n \rightarrow g, n'$ a formula^[4]

$$\omega_{u, n \rightarrow g, n'} = \frac{4n(\Omega) \Omega^3}{3\hbar c^3} |\langle g, n' | M | u, n \rangle|^2, \quad (2.9)$$

where

$$\hbar\Omega = H_{u, n} - H_{g, n'}. \quad (2.10)$$

Expression (2.9) must again be averaged over the initial distribution (n) and summed over the final values (n') of the occupation numbers:

$$\omega_{ug} = Av(n) \sum_{(n')} \omega_{u, n \rightarrow g, n'}. \quad (2.11)$$

It must be borne in mind, however, that if the local center has gone over into the excited state after the absorption of the photon, then the equilibrium of the phonon system is disturbed by the heat release (phonon generation). Therefore, in applying (2.11) to the band theory of impurity photoluminescence, we must assume that the lifetime of the excited center relative to spontaneous emission of light is large compared with the phonon relaxation time. If this condition is not satisfied, then the impurity photoluminescence act represents resonance scattering of the photon, and the excited electron-vibrational state of the system is virtual^[15].

In most papers on the theory of many-phonon nonradiative transitions it is assumed, following an idea first advanced by Adirovich^[16], that the perturbation is the non-adiabaticity operator (1.9).

The electron matrix element of this operator, calculated with the aid of the zeroth-approximation wave function (1.13) for the final state and the first-approximation wave function for the initial state, is of the form

$$\mathcal{L}_{ug} = - \sum_{\kappa} \hbar \omega_{\kappa} \left(\sum_{g' \neq g} \frac{A_{\kappa g' g}}{E_g^0 - E_{g'}^0} \int \psi_u^0 \psi_{g'}^0 dr \right) \frac{\partial}{\partial q_{\kappa}}. \quad (2.12)$$

(2.12) can be regarded as a perturbation operator acting in the phonon subsystem. Further simplification of (2.12) can be obtained by assuming orthogonality of the zeroth-approximation electron wave functions ψ_u^0 and $\psi_{g'}^0$, and by taking the energy difference $E_g^0 - E_{g'}^0$, for some average value ΔE_{gu} , outside the sign of summation with respect to g' . Substituting in explicit form $A_{\kappa g' g}$ from (1.15) and using the completeness condition

$$\sum_{g'} \psi_{g'}^0(r) \psi_{g'}^0(r') = \delta(r' - r), \quad (2.13)$$

we get

$$\mathcal{L}_{ug} = \sum_{\kappa} \mathcal{L}_{\kappa}^{(ug)} \frac{\partial}{\partial q_{\kappa}}, \quad (2.14)$$

$$\mathcal{L}_{\kappa}^{(ug)} = - \frac{\hbar \omega_{\kappa}}{\Delta E_{gu}} A_{\kappa ug}. \quad (2.15)$$

If we put

$$\Delta E_{gu} = E_g^0 - E_u^0, \quad (2.16)$$

then the operators of the direct and inverse transitions are related by

$$\mathcal{L}_{ug}^* = - \mathcal{L}_{gu}. \quad (2.17)$$

The probability of nonradiative transition is calculated from the formula

$$p_{ug} = \frac{2\pi}{\hbar} Av(n) \sum_{(n')} |\langle n' | \mathcal{L}_{gu} | n \rangle|^2 \delta(H_g, n - H_u, n'). \quad (2.18)$$

The probability of nonradiative transition was calculated in the absence of dispersion of the phonon frequencies in accordance with (2.18) in^[14] by the direct summation method. A detailed description of this method (as applied to nonradiative transitions) is contained in^[17]. The corresponding results will be given in Sec. 3.

Many-phonon nonradiative transitions are not necessarily connected with the non-adiabaticity of the electron motion. In ionic crystals the localized electron usually interacts strongly with the optical vibrations of the lattice. In this case weak interaction with the acoustic vibrations can cause nonradiative transitions in which one acoustic phonon and many optical phonons participate^[18]. Methods of calculating the probabilities of such transitions do not differ essentially from the corresponding methods of phototransition theory.

3. METHOD OF GENERATING POLYNOMIALS

The first theory of impurity absorption and luminescence bands with account of the dispersion of the crystal phonon frequencies was constructed in the basic paper of Pekar and Krivoglaz^[19], who calculated the value of I_{ug} (2.8) by a method similar to the Darwin-Fowler method of calculating thermodynamic quantities in statistical physics^[20].

Introducing the frequency of the "pure electronic" transition

$$\Omega_{ug} = \frac{J_u - J_g}{\hbar} \quad (3.1)$$

and neglecting the frequency effect, we write the energy conservation condition (2.2) in the form

$$\sum_{\kappa} \omega_{\kappa} (n'_{\kappa} - n_{\kappa}) = \Omega - \Omega_{ug}. \quad (3.2)$$

Imposing on the lattice waves the condition that they be cyclic in the volume L^3 , we can choose the unit for the frequency $\bar{\omega}$ such that all the frequencies ω_{κ} are expressed by integers. In this case we retain for the frequencies ω_{κ} the previous notation and put

$$\Omega - \Omega_{ug} = p\bar{\omega}. \quad (3.3)$$

We consider, further, the product of the polynomials

$$P(z) = \prod_{\kappa} P_{\kappa}(z) \equiv \prod_{\kappa} (|\langle n'_{\kappa} | n_{\kappa} \rangle|^2 + |\langle n_{\kappa} + 1 | n_{\kappa} \rangle|^2 z^{\omega_{\kappa}} + |\langle n_{\kappa} + 2 | n_{\kappa} \rangle|^2 z^{2\omega_{\kappa}} + \dots + |\langle n_{\kappa} - 1 | n_{\kappa} \rangle|^2 z^{-\omega_{\kappa}} + |\langle n_{\kappa} - 2 | n_{\kappa} \rangle|^2 z^{-2\omega_{\kappa}} + \dots). \quad (3.4)$$

It is easy to note that if the product is expanded, the coefficient of z^p is found to equal

$$\sum_{(n')} \prod_{\kappa} |\langle n'_{\kappa} | n_{\kappa} \rangle|^2, \quad (3.5)$$

where $\hat{\ }^{\wedge}$ denotes that the summation must be carried out under the additional condition (3.2). Expression (3.5) is directly contained in (2.8). Therefore, employing the Cauchy theorem, we obtain immediately

$$I_{ug}(\Omega) = |M_{ug}|^2 Av(n) \frac{1}{2\pi i} \oint \frac{P(z) dz}{z^{p+1}}, \quad (3.6)$$

where the integration contour encircles the point $z = 0$.

The remainder of the problem consists of calculating $P(z)$, which assumes the role of a generating func-

tion for the transition probability. We note immediately that the idea of calculating the generating function (in place of directly calculating the transition probability) turned out to be quite fruitful and was used subsequently by many authors.

If we disregard local oscillations, then we can calculate the function (3.4) by using the fact that

$$\Delta_{\kappa} \equiv q_{\kappa u} - q_{\kappa g} \sim \frac{1}{L^{3/2}} \sim N^{-1/2}, \quad (3.7)$$

where N is the number of factors in (3.4), equal to the number of vibrational degrees of freedom of the crystal. Since we intend to take the limit as $N \rightarrow \infty$ in the final result, it is sufficient to retain in $P_{\kappa}(z)$ terms up to order N^{-1} inclusive. In this approximation, the "Condon" integrals (2.7) can be readily calculated by expansion in powers of Δ_{κ} , and we obtain

$$\left. \begin{aligned} \langle n_{\kappa} | n_{\kappa} \rangle &= 1 - \frac{\Delta_{\kappa}^2}{2} \left(n_{\kappa} + \frac{1}{2} \right) + \dots, \\ \langle n_{\kappa} + 1 | n_{\kappa} \rangle &= -\Delta_{\kappa} \sqrt{\frac{n_{\kappa} + 1}{2}} + \dots, \\ \langle n_{\kappa} - 1 | n_{\kappa} \rangle &= \Delta_{\kappa} \sqrt{\frac{n_{\kappa}}{2}} + \dots \end{aligned} \right\} \quad (3.8)$$

where $\langle n_{\kappa} + r | n_{\kappa} \rangle$ tends to zero more rapidly than N^{-1} for $|r| > 1$. In other words, the transitions for which one of the phonon occupation numbers changes by more than unity make no contribution to the generating function. Substitution of (3.8) in (3.4) yields

$$P(z) = \exp \left\{ -\frac{1}{2} \sum_{\kappa} \Delta_{\kappa}^2 \left(n_{\kappa} + \frac{1}{2} \right) + \frac{1}{2} \sum_{\kappa} \Delta_{\kappa}^2 \left[(n_{\kappa} + 1) z^{\omega_{\kappa}} + n_{\kappa} z^{-\omega_{\kappa}} \right] \right\}. \quad (3.9)$$

By virtue of (3.7), the generating function (3.9) can be represented by a product of statistically independent factors, which depend linearly on n_{κ} . Therefore the averaging operation reduces to replacing n by their averaged equilibrium values

$$\bar{n}_{\kappa} = \frac{1}{e^{\frac{\hbar \omega_{\kappa}}{kT}} - 1}. \quad (3.10)$$

After substituting (3.9) in (3.6) and making a change of variable $z = e^W$ we get

$$I_{ug}(\Omega) = \frac{|M_{ug}|^2}{2\pi i} \oint dwe^{\varphi_p(w)}, \quad (3.11)$$

where

$$\varphi_p(w) = -pw - \frac{1}{2} \sum_{\kappa} \Delta_{\kappa}^2 \operatorname{cth} \frac{\beta_{\kappa}}{2} + \frac{1}{2} \sum_{\kappa} \Delta_{\kappa}^2 \frac{\operatorname{ch} \left(w\omega_{\kappa} + \frac{\beta_{\kappa}}{2} \right)}{\operatorname{sh} \frac{\beta_{\kappa}}{2}}, \quad (3.12)^*$$

$$\beta_{\kappa} = \frac{\hbar \omega_{\kappa}}{kT}. \quad (3.13)$$

The integration contour in (3.11) is shown in Fig. 1. In the complex z plane it corresponds to a unit circle with center at the origin and a cut along the negative part of the real axis.

*ch = cosh; sh = sinh, cth = coth.

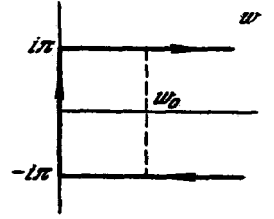


FIG. 1. Contour of integration in (3.11).

If $\Delta_{\kappa} \neq 0$, exact integration in (3.11) is possible only when the dispersion of the phonon frequencies can be neglected, by putting (in the conventional unit) $\omega_{\kappa} = \bar{\omega} = \omega$. The change of variable $w = it$ yields for non-integer p

$$\begin{aligned} & \frac{1}{2\pi i} \oint d\omega \exp[\varphi_p(\omega)] \\ &= \frac{\exp\left(-\frac{a}{2} \operatorname{cth} \frac{\beta}{2}\right)}{2\pi} \int_{-\pi}^{\pi} dt \\ & \times \exp\left[-ipt + \frac{a}{2 \operatorname{sh} \frac{\beta}{2}} \cos\left(t - \frac{i\beta}{2}\right)\right], \end{aligned} \quad (3.14)$$

where

$$a = \sum_{\kappa} \Delta_{\kappa}^2 = \sum_{\kappa} (q_{\kappa u} - q_{\kappa g})^2. \quad (3.15)$$

In the derivation of (3.14) we took account of the fact that the contributions of the horizontal lines of Fig. 1 to the integral (3.11) cancel out exactly if p is an integer. For the same reason, it is possible to make in the integral (3.14) the substitution $t - i\beta/2 \rightarrow t$, without changing the integration limits. Taking account of the well-known definition of the modified Bessel function

$$I_p(z) \equiv (-i)^p J_p(iz) = \frac{1}{2\pi} \int_{-\pi}^{\pi} dt \exp(-ipt + z \cos t), \quad (3.16)$$

we get

$$I_{ug}(\Omega) = |M_{ug}|^2 \exp\left(-\frac{a}{2} \operatorname{cth} \frac{\beta}{2} + p \frac{\beta}{2}\right) I_p\left(\frac{a}{2 \operatorname{sh} \frac{\beta}{2}}\right). \quad (3.17)$$

Formula (3.17) (first derived in [13] by direct summation, as already pointed out) determines the dependence of the coefficient of impurity absorption of light (2.4) on the frequency. For integer p , (3.17) corresponds to a set of equidistant absorption lines (Fig. 2) separated from one another by the limiting phonon frequency ω . These absorption lines have a "natural" width γ (see Sec. 4), but usually γ is small compared with ω . At the same time, experiment shows that as a rule the impurity absorption bands are not resolved into individual (phonon) lines. The reason why the lines of Fig. 2 broaden and merge into a continuous band is the dispersion of the phonon frequencies, which is not considered in the derivation of (3.17). It is assumed that when account is taken of the dispersion, the form of the absorption band must be described by (3.17) with a continuously varying pa-

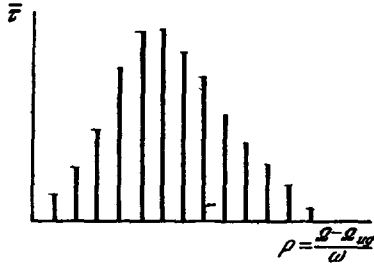


FIG. 2. Spectrum of impurity absorption of light without account of the dispersion of the phonon frequency and of the "natural" line width.

parameter p . A detailed analysis of the absorption bands has been made under this assumption in [1]. We confine ourselves only to a brief summary of the results.

According to (3.17), the absorption band is represented by a bell-shaped but not completely symmetrical curve with a maximum at $p = a/2$, that is,

$$\Omega_{\max}^{(\text{abs})} = \Omega_{ug} + \frac{a}{2} \omega. \quad (3.18)$$

At high temperatures, when the inequalities

$$\beta < 1, \quad a \gg 2 \operatorname{sh} \frac{\beta}{2} \quad (3.19)$$

are satisfied, the absorption curve has a Gaussian form

$$\bar{\tau}(\Omega) = \bar{\tau}_m \exp \left[-\frac{\beta(\Omega - \Omega_{\max})^2}{2\omega^2 a} \right] \quad (3.20)$$

with half-width

$$\delta\Omega = 2\omega \sqrt{2 \ln 2} \frac{a}{\beta} \sim \sqrt{T}. \quad (3.21)$$

At low temperatures, when

$$\beta \gg 1, \quad a \ll 2 \operatorname{sh} \frac{\beta}{2}, \quad (3.22)$$

the form of the band is determined by the relation

$$\bar{\tau}(\Omega) = \text{const} \frac{(a/2)^p}{\Gamma(p+1)}. \quad (3.23)$$

The half-width of (3.23) is

$$\delta\Omega_0 = 2\omega \sqrt{a \ln 2}. \quad (3.24)$$

Detailed experimental investigations of the form of the F absorption band in colored alkali-halide crystals at low temperatures shows that the asymmetrical curve (3.23) is in good agreement with experiment [21].

If we take account of the dispersion of the normal frequencies from the very outset, then the integration in (3.11) can be carried out only approximately. The saddle-point method was found to be quite useful here [19]. The extremal points of the function $\varphi_p(w)$ (3.12) satisfy the equation

$$\frac{1}{2} \sum_{\kappa} \Delta_{\kappa}^2 \omega_{\kappa} \frac{\operatorname{sh} \left(w\omega_{\kappa} + \frac{\beta_{\kappa}}{2} \right)}{\operatorname{sh} \frac{\beta_{\kappa}}{2}} = p, \quad (3.25)$$

which, by virtue of the monotonicity of the left half, has one real root w_0 . Neglecting the contribution of the complex roots of (3.25) (see below) we replace the integration contour of Fig. 1 by a vertical line passing through the point w_0 between the horizontal

lines $\operatorname{Im} w = \pm \pi$. The direction of this segment coincides with the direction of the "steepest descent." In fact in the vicinity of the extremal point

$$\varphi_p(w) = \varphi_p(w_0) + \frac{(w-w_0)^2}{2} \varphi_p''(w_0) + \dots, \quad (3.26)$$

where

$$\varphi_p''(w_0) = \frac{1}{2} \sum_{\kappa} \Delta_{\kappa}^2 \omega_{\kappa}^2 \frac{\operatorname{ch} \left(w_0 \omega_{\kappa} + \frac{\beta_{\kappa}}{2} \right)}{\operatorname{sh}^2 \frac{\beta_{\kappa}}{2}} > 0. \quad (3.27)$$

If the criterion of the saddle-point method is satisfied, then

$$\begin{aligned} I_{ug}(\Omega) &\simeq |M_{ug}|^2 \frac{\exp[\varphi_p(w_0)]}{2\pi} \int_{-\pi}^{\pi} e^{-\frac{\varphi_p''(w_0)v^2}{2}} dv \\ &\simeq |M_{ug}|^2 \sqrt{\frac{2\pi}{\varphi_p''(w_0)}} \exp[\varphi_p(w_0)]. \end{aligned} \quad (3.28)$$

Going over to a discussion of the frequency dependence of (3.28), we note that the function $w_0(p)$ is specified by (3.25). Therefore

$$\frac{d\varphi_p(w_0)}{dp} = \frac{\partial \varphi_p(w_0)}{\partial p} + \varphi_p'(w_0) \frac{dw_0}{dp} = -w_0, \quad (3.29)$$

and consequently $\varphi_p(w_0)$ has as a function of p a maximum at $w_0 = 0$, that is, when

$$p = p_m = \frac{1}{2} \sum_{\kappa} \Delta_{\kappa}^2 \omega_{\kappa}. \quad (3.30)$$

Expansion in the vicinity of this maximum is of the form

$$\varphi_p(w_0) = -\frac{(p-p_m)^2}{2\varphi_p''(0)} - \frac{\varphi_p'''(0)(p-p_m)^3}{6[\varphi_p''(0)]^2} + \dots \quad (3.31)$$

If we can confine ourselves in (3.31) to the quadratic term only, then the absorption curve will have a Gaussian form

$$\bar{\tau}(\Omega) = \bar{\tau}_m \exp \left[-\frac{(p-p_m)^2}{2\varphi_p''(0)} \right] \quad (3.32)$$

with half-width

$$\delta\Omega = 2 \sqrt{2 \ln 2 \varphi_p''(0) \omega^2}, \quad (3.33)$$

where

$$\varphi_p''(0) = \frac{1}{2} \sum_{\kappa} \Delta_{\kappa}^2 \omega_{\kappa}^2 \operatorname{ch} \frac{\beta_{\kappa}}{2}. \quad (3.34)$$

We note that if we neglect dispersion at this stage of the calculation, then (3.30) goes over into (3.18) while (3.21) and (3.24) are obtained from (3.32) and (3.34) at high and low temperatures, respectively.

Formula (3.28) is valid if

$$\varphi_p''(w_0) \gg 1 \quad (3.35)$$

and consequently, the integrand decreases rapidly to zero on both sides of the saddle point w_0 . In order to clarify the physical meaning of the inequality (3.35), it is simplest to replace the normal frequencies ω_{κ}

in (3.25) and (3.27) by some average value $\bar{\omega}$, choosing the latter as the unit of frequency. Then, as can be readily verified, the inequality (3.35) is satisfied for all temperatures if $p \gg 1$. p is the average number of phonons generated in the phototransition, and therefore the formulas presented above pertain to the case of a large heat release. Inasmuch as p_m (3.30) is the most probable value of p , the criterion for large heat release is the inequality

$$\frac{1}{2} \sum_{\kappa} \Delta_{\kappa}^2 \omega_{\kappa} \gg 1. \quad (3.36)$$

It is easy to verify that if inequality (3.35) is satisfied then, within the limits of the half-width of the absorption band, the cubic term in (3.31) becomes small and consequently the Gaussian curve (3.33) is a good approximation. The cubic term in (3.31), which characterizes the asymmetry of the absorption band*, remains small at high temperatures even outside the indicated limits, so that (3.32) describes well in this case practically the entire absorption band. It will be shown below (Sec. 6) that (3.32) corresponds to the quasi-classical description of the lattice vibrations. At low temperatures, the asymmetry of the absorption band becomes noticeable: $\bar{\tau}$ decreases more rapidly on the red side than on the violet side. A detailed investigation^[19] shows that when the integral of (3.11) is calculated by the saddle-point method the contribution of the complex roots of (3.25) adds to (3.28) a rapidly oscillating factor, along with the term $\exp[\varphi_p(w_0)]$. In the limiting case when there is no dispersion, this factor becomes equal to unity for integer p and zero for non-integer p . As a result, the continuous band is converted into the system of equidistant lines shown in Fig. 2. With increasing dispersion, these lines broaden and the indicated factor tends to unity. Thus, (3.28) and all the following formulas are valid for not too small a dispersion of the phonon frequencies.

In^[19] there is also considered the case of "small heat release," when the inverse of (3.35) is satisfied. The results obtained in this limiting case are given in the review^[22] and will not be discussed here.

The luminescence intensity (the energy radiated by the excited centers in a unit volume per second) is

$$R(\Omega) = N_u \hbar \Omega \omega_{ug} = \frac{4N_u n(\Omega) \Omega^4}{3c^3} I_{gu}(\Omega), \quad (3.37)$$

where N_u — concentration of the excited luminescence centers, and, as can be readily seen, I_{gu} differs from I_{ug} (3.11) only in the sign of p in the characteristic function $\varphi_p(w)$:

$$I_{ug}(\Omega_{ug} + p\bar{\omega}) = I_{gu}(\Omega_{ug} - p\bar{\omega}).$$

From the last relation and from (2.3), (2.4), and (3.37) it follows immediately that

$$\left[\frac{\bar{\tau}(\Omega) n(\Omega)}{\Omega} \right]_{\Omega=\Omega_{ug}+p\bar{\omega}} = \frac{\pi^2 c^2 N_g}{\hbar N_u} \left[\frac{R(\Omega)}{\Omega^4 n(\Omega)} \right]_{\Omega=\Omega_{ug}-p\bar{\omega}}. \quad (3.38)$$

Relation (3.38), first derived in^[4], expresses the law of mirror symmetry of the impurity absorption and luminescence bands with respect to the line of "pure electronic" transition Ω_{ug} . From (3.38) and (3.30) it follows that the Stokes shift of the maxima of the absorption and luminescence bands is

$$\Delta\Omega = \Omega_{\max}^{(abs)} - \Omega_{\max}^{(rad)} = \sum_{\kappa} \Delta_{\kappa}^2 \omega_{\kappa}. \quad (3.39)$$

A theoretical calculation of (3.39) is possible only in the rare case when the electron wave functions of the local center are known along with the law of dispersion of the phonon frequencies (for example, in the continual F-center theory^[4]). Nonetheless, it is sometimes possible to compare the theory of impurity absorption and luminescence with the experiment, by regarding the quantity $\Delta\Omega$ as a parameter of the theory. This pertains, first of all, to the case when there is no dispersion (or when it is negligibly small), and $\Delta\Omega = a\omega$. The parameter a , determined from the Stokes shift, can then be substituted in (3.21) or (3.24), and the calculated half-width of the band can be compared with the experimental value. Further, in the case of high temperatures, when $\beta\kappa < 1$, the quantity (3.34), which determines the half-width of the band (3.33), is found to be equal to

$$\varphi_p''(0) \cong \frac{kT}{\hbar} \Delta\Omega. \quad (3.40)$$

A review of the experimental facts pertaining to the law of mirror symmetry of (3.38) can be found in^[22]. We point out in addition that the position of the maxima of the infrared luminescence bands of the alkali-halide crystal F-centers was predicted on the basis of (3.39) in^[4]. This prediction of the theory was subsequently confirmed with high accuracy by experiment^[23].

Summarizing the foregoing, we can state that the method of generating polynomials^[19] turned out to be quite fruitful in the theory of optical many-phonon transitions and made it possible to establish many fundamental physical laws. At the same time, the applicability of the method is limited by a) account of only the crystal oscillations (expansion in powers of N^{-1} in the calculation of the generating function) and b) the use of multiplicative phonon functions (1.20), that is, the neglect of the frequency effect.

The first of the foregoing limitations is insignificant: by exact calculation of the Condon integrals $\langle n'_{\kappa} | n_{\kappa} \rangle$ it can be shown^[24] that (3.11) holds true also for local oscillations (of course, neglecting the frequency effect).* As to the second limitation, it must be borne in mind that although the frequency effect usually leads to small corrections to the formulas of the absorption and emission theory, nevertheless these

*The so-called third moment of the spectrum, see Sec. 5.

*These results will be obtained in Sec. 5 by a different method.

corrections correspond to observable physical effects, viz: the temperature shift of the maxima of the optical bands and violation of the mirror symmetry law (3.38). These effects were not considered within the framework of the method of generating polynomials.

Krivoglaz^[24] used the method of generating polynomials to calculate the probability of nonradiative transitions with non-adiabaticity operator (2.14) as the perturbation. Assuming that the band of vibrational levels adjacent to the "electron" level J_g of the final state forms a quasicontinuous spectrum, we can, as usual, replace the δ -function in (2.18) by the level density [in this case $(\hbar\omega)^{-1}$] and carry out the summation with account of the energy conservation law:

$$\sum_{\kappa} \omega_{\kappa} (n'_{\kappa} - n_{\kappa}) = \Omega_{ug} = p_0 \bar{\omega}. \quad (3.41)$$

The probability of the nonradiative transition $u \rightarrow g$ (per second) can now be written in the form

$$p_{ug} = \frac{2\pi}{\hbar^2 \omega} A v(n) \sum_{(n')} \left\{ \sum_{\kappa} |\mathcal{L}_{\kappa}|^2 \frac{|\langle n'_{\kappa} | \frac{\partial}{\partial q_{\kappa}} | n_{\kappa} \rangle|^2}{|\langle n'_{\kappa} | n_{\kappa} \rangle|^2} + \sum_{\kappa} \sum_{\lambda \neq \kappa} \mathcal{L}_{\kappa} \mathcal{L}_{\lambda}^* \frac{\langle n'_{\kappa} | \frac{\partial}{\partial q_{\kappa}} | n_{\kappa} \rangle \langle n'_{\lambda} | \frac{\partial}{\partial q_{\lambda}} | n_{\lambda} \rangle}{\langle n_{\kappa} | n_{\kappa} \rangle \langle n_{\lambda} | n_{\lambda} \rangle} \right\} \prod_{\mu} |\langle n'_{\mu} | n_{\mu} \rangle|^2, \quad (3.42)$$

where

$$\langle n'_{\kappa} | \frac{\partial}{\partial q_{\kappa}} | n_{\kappa} \rangle = \int_{-\infty}^{\infty} \Phi_{n'_{\kappa}}(q_{\kappa} - q_{\kappa g}) \frac{\partial \Phi_{n_{\kappa}}(q_{\kappa} - q_{\kappa u})}{\partial q_{\kappa}} dq_{\kappa}. \quad (3.43)$$

The integral (3.43) is again calculated by expansion in powers of Δ_{κ} . A contribution that does not vanish as $N \rightarrow \infty$ is made to the transition probability by the matrix elements

$$\left. \begin{aligned} \langle n_{\kappa} | \frac{\partial}{\partial q_{\kappa}} | n_{\kappa} \rangle &= -\Delta_{\kappa} \left(n_{\kappa} + \frac{1}{2} \right) + \dots, \\ \langle n_{\kappa} + 1 | \frac{\partial}{\partial q_{\kappa}} | n_{\kappa} \rangle &= \sqrt{\frac{n_{\kappa} + 1}{2}} + \dots, \\ \langle n_{\kappa} - 1 | \frac{\partial}{\partial q_{\kappa}} | n_{\kappa} \rangle &= \sqrt{\frac{n_{\kappa}}{2}} + \dots \end{aligned} \right\} \quad (3.44)$$

In place of the generating function (3.4) we now must introduce

$$Q(z) = \left[\sum_{\kappa} |\mathcal{L}_{\kappa}|^2 \frac{Q_{\kappa}(z)}{P_{\kappa}(z)} + \sum_{\kappa, \lambda \neq \kappa} \mathcal{L}_{\kappa} \mathcal{L}_{\lambda}^* \frac{R_{\kappa}(z) R_{\lambda}(z)}{P_{\kappa}(z) P_{\lambda}(z)} \right] \prod_{\mu} P_{\mu}(z), \quad (3.45)$$

where, alongside the polynomials $P_{\kappa}(z)$ from (3.4), we introduce new polynomials

$$\left. \begin{aligned} Q_{\kappa}(z) &= \left| \langle n_{\kappa} | \frac{\partial}{\partial q_{\kappa}} | n_{\kappa} \rangle \right|^2 + \left| \langle n_{\kappa} + 1 | \frac{\partial}{\partial q_{\kappa}} | n_{\kappa} \rangle \right|^2 z^{\omega_{\kappa}} + \\ &\quad + \left| \langle n_{\kappa} + 2 | \frac{\partial}{\partial q_{\kappa}} | n_{\kappa} \rangle \right|^2 z^{2\omega_{\kappa}} + \dots, \\ R_{\kappa}(z) &= \langle n_{\kappa} | \frac{\partial}{\partial q_{\kappa}} | n_{\kappa} \rangle \langle n_{\kappa} | n_{\kappa} \rangle + \\ &\quad + \langle n_{\kappa} + 1 | \frac{\partial}{\partial q_{\kappa}} | n_{\kappa} \rangle \langle n_{\kappa} + 1 | n_{\kappa} \rangle z^{\omega_{\kappa}} + \dots \end{aligned} \right\} \quad (3.46)$$

In total analogy with (3.6), we get

$$p_{ug} = \frac{1}{i\hbar^2 \omega} A v(n) \oint \frac{Q(z) dz}{z^{1-p_0}}. \quad (3.47)$$

With the aid of (3.8) and (3.44) we calculate the generating function directly, and obtain

$$p_{ug} = \frac{1}{i\hbar \omega} \oint F(\omega) e^{\varphi - p_0(\omega)} d\omega, \quad (3.48)$$

where the integration contour is shown in Fig. 1, $\varphi - p_0(\omega)$ coincides with (3.12) when $p = -p_0$, and, finally,

$$F(\omega) = \left| \sum_{\kappa} \mathcal{L}_{\kappa} \Delta_{\kappa} \frac{\text{ch} \left(\omega \omega_{\kappa} + \frac{\beta_{\kappa}}{2} \right) - \text{ch} \frac{\beta_{\kappa}}{2}}{2 \text{sh} \frac{\beta_{\kappa}}{2}} \right|^2 + \frac{1}{2} \sum_{\kappa} |\mathcal{L}_{\kappa}|^2 \frac{\text{ch} \left(\omega \omega_{\kappa} + \frac{\beta_{\kappa}}{2} \right)}{\text{sh} \frac{\beta_{\kappa}}{2}}. \quad (3.49)$$

As in the case of the optical transitions, the exact integration in (3.48) can be carried out by neglecting the dispersion of the normal frequencies (p_0 must then be regarded as an integer). We obtain

$$p_{ug} = \frac{\pi \omega}{(E_u^0 - E_g^0)^2} \times \exp \left[-\frac{a}{2} \text{cth} \frac{\beta}{2} - p_0 \frac{\beta}{2} \right] \left\{ \frac{1 + 2 \text{ch}^2 \frac{\beta}{2}}{4 \text{sh}^2 \frac{\beta}{2}} |b_{ug}|^2 I_{p_0} \left(\frac{a}{2 \text{sh} \frac{\beta}{2}} \right) + \frac{1}{2 \text{sh} \frac{\beta}{2}} \left(c_{ug} - |b_{ug}|^2 \text{cth} \frac{\beta}{2} \right) \left[I_{p_0-1} \left(\frac{a}{2 \text{sh} \frac{\beta}{2}} \right) + I_{p_0+1} \left(\frac{a}{2 \text{sh} \frac{\beta}{2}} \right) \right] + \frac{|b_{ug}|^2}{8 \text{sh}^2 \frac{\beta}{2}} \left[I_{p_0-2} \left(\frac{a}{2 \text{sh} \frac{\beta}{2}} \right) + I_{p_0+2} \left(\frac{a}{2 \text{sh} \frac{\beta}{2}} \right) \right] \right\}, \quad (3.50)$$

where we have introduced new parameters

$$\left. \begin{aligned} b_{ug} &= \sum_{\kappa} A_{\kappa u g} (q_{\kappa u} - q_{\kappa g}), \\ c_{ug} &= \sum_{\kappa} |A_{\kappa u g}|^2. \end{aligned} \right\} \quad (3.51)$$

Formula (3.50) (apart from the factor 2π) was first derived in^[14]. A detailed analysis of this formula and its application to nonradiative transitions in the discrete F-center spectrum are given in^[17] and^[25]. We confine ourselves here only to a brief discussion. We note, first, that the probability of the inverse transition ($g \rightarrow u$) is obtained by reversing the sign of p_0 in (3.48). As applied to (3.50) (bearing in mind that the Bessel functions are even in the integer index) this yields

$$p_{gu} = p_{ug} \exp \left(-\frac{\hbar \Omega_{ug}}{kT} \right). \quad (3.52)$$

p_{ug} tends to a finite limit as $T \rightarrow 0$ and (3.52) gives

the temperature dependence of the probability of thermal excitation of the local center. At high temperatures [in the sense of inequality (3.19)] (3.52) reduces to

$$p_{gu} = K \exp\left(-\frac{\Delta W}{kT}\right), \quad (3.53)$$

where the "frequency multiplier" K depends weakly on the temperature, and the activation energy is

$$\Delta W = \frac{\hbar\Omega_{ug}}{2} \left(\sqrt{\frac{p_0}{a}} + \frac{1}{2} \sqrt{\frac{a}{p_0}} \right)^2. \quad (3.54)$$

Thus, the popular formula (3.53) must be used with great caution, since the frequency multiplier and the activation energy are far from constant over a wide temperature interval. In particular, $K \gg p_{ug}|_{T=0}$.

When dispersion is taken into account for the case when condition (3.36) is satisfied, the integral in (3.48) can be estimated by the saddle-point method. Then

$$p_{ug} \simeq \frac{1}{\hbar^2 \omega \sqrt{2\pi\varphi''_{-p_0}(w'_0)}} F(w'_0) \exp[\varphi_{-p_0}(w'_0)], \quad (3.55)$$

where w'_0 is the root of (3.25) with $\Omega = 0$ (that is, $p = -p_0$). Further, if $p_0 - p_m$ is not too large, we can use (3.31) (putting $p = p_0$) and confine ourselves to the quadratic term. It is easy to verify that this approximation is valid in the case of high temperatures, when (3.40) holds. In this case the probability of nonradiative transition is again expressed by the exponential formula (3.53), where K is equal to the pre-exponential factor in (3.55). For the transition $u \rightarrow g$ the activation energy is

$$\Delta W_{ug} = \frac{\hbar\Omega_{ug}}{2} \left(\sqrt{\frac{\Omega_{ug}}{\Delta\Omega}} - \frac{1}{2} \sqrt{\frac{\Delta\Omega}{\Omega_{ug}}} \right)^2. \quad (3.56)$$

With the aid of (3.52) we obtain the activation energy for the inverse transition ($g \rightarrow u$)

$$\Delta W_{gu} = \frac{\hbar\Omega_{ug}}{2} \left(\sqrt{\frac{\Omega_{ug}}{\Delta\Omega}} + \frac{1}{2} \sqrt{\frac{\Delta\Omega}{\Omega_{ug}}} \right)^2. \quad (3.57)$$

Formula (3.54) is a particular case of this relation. Thus, even in the general case the Stokes shift $\Delta\Omega$ is an essential parameter of the theory of nonradiative transitions.

We note in conclusion that (3.55) remains in force when local oscillations are taken into account, but the pre-exponential factor $F(w)$ differs from (3.49) by an additional term, which converges to zero like N^{-1} as $N \rightarrow \infty$ for crystal frequencies (see Secs. 5 and 6).

4. ACCOUNT OF THE NATURAL LEVEL WIDTH

The excited electron-vibrational states of the crystal with local center have a nonzero width because of the spontaneous optical and nonradiative transitions to the ground state of the system. Formulas (2.3) and (2.9), obtained from the semiclassical radiation theory, do not take this circumstance into account. The cor-

responding generalization of the theory can be obtained by considering the spontaneous optical transition $u, n \rightarrow g, n'$ by the methods of quantum electrodynamics. If the radiation field is included in the zeroth-approximation Hamiltonian, then the solution of the time-dependent Schrödinger equation can be sought in the form [26]

$$\Psi = c_{un}(t) \chi_{un} \exp\left(-\frac{iH_{un}t}{\hbar}\right) + \sum_{(n')} \sum_{\Omega} c_{gn'}(t) \chi_{gn'} \exp\left[-\frac{i(H_{gn'} + \hbar\Omega)t}{\hbar}\right], \quad (4.1)$$

where χ_{un} are the electron-vibrational wave functions (1.20) multiplied by the amplitudes of the quantized electromagnetic field. The initial state of the system corresponds to the vacuum of this field, and a photon $\hbar\Omega$ is present in the final state. If we neglect non-radiative transitions, then the functions χ can be regarded as exact zeroth-approximation functions, and then the coefficients c satisfy the system of equations

$$i\hbar \frac{dc_{un}}{dt} = \sum_{(n')} \sum_{\Omega} c_{gn'} \langle un | W | gn' \rangle \exp\left[i(H_{un} - H_{gn'} - \hbar\Omega) \frac{t}{\hbar}\right], \quad (4.2)$$

$$i\hbar \frac{dc_{gn'}}{dt} = c_{un} \langle gn' | W | un \rangle \exp\left[-i(H_{un} - H_{gn'} - \hbar\Omega) \frac{t}{\hbar}\right]. \quad (4.3)$$

Neglecting the frequency effect, the matrix element of the electron-photon interaction operator is of the form

$$\langle un | W | gn' \rangle = W_{ug} \prod_{\kappa} \langle n'_{\kappa} | n_{\kappa} \rangle, \quad (4.4)$$

where, for the case of the radiation field in the crystal, the electron matrix element is

$$W_{ug} = -iM_{ug} \sqrt{\frac{2\pi\hbar\Omega}{L^3 n^2(\Omega)}}. \quad (4.5)$$

M_{ug} is the projection of the matrix element of the effective dipole moment M on the photon polarization direction.

If the local center is excited at the initial instant of time ($t = 0$), then (4.2) in (4.3) must be integrated under initial conditions

$$c_{un}(0) = 1, \quad c_{gn'}(0) = 0. \quad (4.6)$$

Putting (see [26] —the Wigner-Weisskopf method)

$$c_{un}(t) = \exp\left(-\frac{\gamma t}{2}\right), \quad (4.7)$$

we obtain after integrating (4.3)

$$c_{gn'}(t) = \frac{\langle gn' | W | un \rangle}{(H_{un} - H_{gn'} - \hbar\Omega) - \frac{i\hbar\gamma}{2}} \times \left\{ \exp\left[-\frac{\gamma t}{2} - \frac{it}{\hbar}(H_{un} - H_{gn'} - \hbar\Omega)\right] - 1 \right\}. \quad (4.8)$$

Substitution of (4.8) and (4.7) in (4.2) yields

$$\gamma = \frac{2i}{\hbar} \sum_{(n')} \sum_{\Omega} |\langle gn' | W | un \rangle|^2 \frac{1 - \exp \left[\frac{\gamma t}{2} + \frac{it}{\hbar} (H_{un} - H_{gn'} - \hbar\Omega) \right]}{(H_{un} - H_{gn'} - \hbar\Omega) - \frac{i\hbar\gamma}{2}} \quad (4.9)$$

In first approximation in the small parameter γ , we put $\gamma = 0$ in the right half of (4.9) and use the relation [26]

$$\lim_{t \rightarrow \infty} \frac{1 - e^{i\omega t}}{\omega} = \frac{\mathcal{P}}{\omega} - i\pi\delta(\omega), \quad (4.10)$$

where \mathcal{P}/ω — principal value of ω^{-1} . The imaginary part of γ yields a small shift of the electron-vibrational level, which is of no great interest to us. We therefore take γ to mean henceforth the second term of (4.10). Substituting (4.10) in (4.9) and replacing \sum_{Ω} by integration over the frequencies and the radiation direction, viz:

$$\sum_{\Omega} \dots = \frac{L^3}{4\pi^2 c^3} \int \dots n^3(\Omega) \Omega^2 d\Omega \sin\theta d\theta,$$

we get

$$\gamma = \frac{4|M_{ug}|^2}{3\hbar c^3} \sum_{(n')} \Omega^3 n(\Omega) \prod_{\kappa} |\langle n'_{\kappa} | n_{\kappa} \rangle|^2, \quad (4.11)$$

where

$$\Omega = \Omega_{ug} - \sum_{\kappa} \omega_{\kappa}(n'_{\kappa} - n_{\kappa}). \quad (4.12)$$

The value of γ depends thus on the initial phonon occupation numbers $\dots n_{\kappa} \dots$. To simplify further calculations, this quantity is best replaced by the mean statistical value

$$\bar{\gamma} = Av(n) \gamma = \frac{4|M_{ug}|^2}{3\hbar c^3} Av(n) \sum_{(n')} \Omega^3 n(\Omega) \prod_{\kappa} |\langle n'_{\kappa} | n_{\kappa} \rangle|^2, \quad (4.13)$$

where the summation over n' must be carried out without any limitations. We imagine that the summation is carried out in two stages: first under the supplementary condition

$$\sum_{\kappa} \omega_{\kappa}(n'_{\kappa} - n_{\kappa}) = p\bar{\omega}, \quad (4.14)$$

that is, with specified average heat release p , and then over all possible values of p . Then we obtain during the first stage of the calculation [see (2.9) and (2.11)] the probability W_{ug} of the spontaneous optical transition with a given heat release, and thus $\bar{\gamma}$ is the total probability (per second) of all the spontaneous optical transitions from the given initial electron state. The approximate expression for $\bar{\gamma}$ can be obtained by putting in (4.11) a slowly varying function $\Omega^3 n(\Omega)$, equal to its value at the maximum of the absorption band. Taking into consideration the fact that

$$\sum_{(n')} \prod_{\kappa} |\langle n'_{\kappa} | n_{\kappa} \rangle|^2 \equiv 1, \quad (4.15)$$

we obtain

$$\bar{\gamma} \cong \frac{4|M_{ug}|^2 \Omega_m^3 n(\Omega_m)}{3\hbar c^3}. \quad (4.16)$$

Formula (4.16) can be used for the calculation of the optical lifetime of the local centers.

The form of the radiation spectrum is determined by the quantity

$$Av(n) \sum_{(n')} |c_{gn'}(\infty)|^2 = \frac{1}{\hbar^2} Av(n) \sum_{(n')} \frac{|W_{gu}|^2 \prod_{\kappa} |\langle n'_{\kappa} | n_{\kappa} \rangle|^2}{\left[\Omega - \Omega_{ug} + \sum_{\kappa} \omega_{\kappa}(n'_{\kappa} - n_{\kappa}) \right]^2 + \frac{\gamma^2}{4}}. \quad (4.17)$$

To calculate this quantity we can, following Davydov [27], employ the method of [10]*, which starts from the identity

$$F\left(\sum_{\kappa} \omega_{\kappa}(n'_{\kappa} - n_{\kappa})\right) = \int_{-\infty}^{\infty} F(\varrho) \delta\left(\varrho - \sum_{\kappa} \omega_{\kappa}(n'_{\kappa} - n_{\kappa})\right) d\varrho = \frac{1}{\pi} \int_{-\infty}^{\infty} F(\varrho) d\varrho \operatorname{Re} \int_0^{\infty} dt \exp\left[-i\varrho t + it \sum_{\kappa} \omega_{\kappa}(n'_{\kappa} - n_{\kappa})\right]. \quad (4.18)$$

If we take the function $|W_{gu}|^2$ outside the summation sign in (4.17), then the calculation reduces to the evaluation of the function

$$J_{gu}(\Omega) = \frac{1}{\pi} \operatorname{Re} Av(n) \sum_{(n')} \int_0^{\infty} dt \left[\prod_{\kappa} e^{i\omega_{\kappa} t (n'_{\kappa} - n_{\kappa})} |\langle n'_{\kappa} | n_{\kappa} \rangle|^2 \right] \times \int_{-\infty}^{\infty} \frac{e^{-i\varrho t} d\varrho}{(\Omega - \Omega_{ug} + \varrho)^2 + \frac{\gamma^2}{4}}. \quad (4.19)$$

If, as in Sec. 3, we confine ourselves only to the crystal vibrations then, by virtue of (3.8), a nonvanishing contribution to $\sum_{(n')}$ is made only by the terms in which $n'_{\kappa} = n_{\kappa}$, $n_{\kappa} \pm 1$ and the summation in (4.19) is carried out directly. The integral over the variable ϱ is easy to calculate by the residue theory, and we obtain

$$J_{ug}(\Omega) = \frac{2}{\gamma \bar{\omega}} \operatorname{Re} \int_0^{\infty} dt e^{-\frac{\gamma t}{2\bar{\omega}} + i\varphi - p(it)}. \quad (4.20)$$

The radiation intensity is

$$R(\Omega) = \bar{\gamma} N_u \hbar \Omega^3 \frac{L^3 n^3(\Omega)}{4\pi^2 c^3} \int_0^{\pi} \sin\theta d\theta Av(n) \sum_{(n')} |c_{gn'}(\infty)|^2 = \frac{4n(\Omega) \Omega^4 N_u |M_{ug}|^2 \bar{\gamma} J_{gu}(\Omega)}{3c^3 2\pi}. \quad (4.21)$$

Comparison of this formula with (3.37) shows that (4.20) differs from the characteristic function $I_{gu}(\Omega)$ (Sec. 3) only by a constant factor. In the limiting case where the displacement is negligibly small ($\Delta_{\kappa} \rightarrow 0$) we have

*A complete exposition of the method as applied to the absorption of neutrons is given in the book [28].

$$J_{gu}(\Omega) = \frac{1}{(\Omega - \Omega_{ug})^2 + \frac{\bar{\gamma}^2}{4}} \quad (4.22)$$

and (4.21) goes over into the well-known formula for atomic emission^[26].

Exact integration in (4.20) can be carried out for negligibly small dispersion, when

$$\begin{aligned} \exp[\varphi_{-p}(it)] &= \exp\left[ipt - \frac{a}{2} \operatorname{cth} \frac{\beta}{2} + \frac{a}{2 \operatorname{sh} \frac{\beta}{2}} \cos\left(t - \frac{i\beta}{2}\right)\right] \\ &= \exp\left[ipt - \frac{a}{2} \operatorname{cth} \frac{\beta}{2}\right] \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{\left(\frac{a}{4 \operatorname{sh} \frac{\beta}{2}}\right)^{n+m}}{n!m!} e^{(it + \frac{\beta}{2})(n-m)}. \end{aligned}$$

Substituting this result in (4.20) we get, after integrating and interchanging indices,

$$J_{gu}(\Omega) = \frac{\exp\left(-\frac{a}{2} \operatorname{cth} \frac{\beta}{2}\right)}{\omega^2} \sum_{k=-\infty}^{\infty} \frac{\exp\left(\frac{k\beta}{2}\right)}{(p+k)^2 + \frac{\bar{\gamma}^2}{4\omega^2}} \sum_{m=0}^{\infty} \frac{\left(\frac{a}{4 \operatorname{sh} \frac{\beta}{2}}\right)^{k+2m}}{m!(m+k)!}.$$

The second sum coincides with the well-known power expansion of the modified Bessel function, so that finally

$$J_{gu}(\Omega) = \frac{\exp\left(-\frac{a}{2} \operatorname{cth} \frac{\beta}{2}\right)}{\omega^2} \sum_{k=-\infty}^{\infty} \frac{\exp\left(\frac{k\beta}{2}\right) I_k\left(\frac{a}{2 \operatorname{sh} \frac{\beta}{2}}\right)}{(p+k)^2 + \frac{\bar{\gamma}^2}{4\omega^2}}. \quad (4.23)$$

Formula (4.23) makes somewhat more precise the picture of the electron-vibrational spectrum given in Fig. 2. Each phonon line is now converted into a Lorentz curve which has a "natural" half-width $\bar{\gamma}$.*

With account of dispersion, the approximate integration in (4.20) has been carried out in^[27] by expanding the characteristic function φ_{-p} in powers of t . In the notation of Sec. 3, this expansion is of the form

$$\varphi_{-p}(it) = \varphi(0) + it(p - p_m) - \frac{t^2}{2} \varphi''(0) + \dots \quad (4.24)$$

Substitution in (4.20) yields

$$\begin{aligned} J_{gu}(\Omega) &= \frac{1}{\bar{\gamma} \omega} \sqrt{\frac{2\pi}{\varphi''(0)}} \operatorname{Re} \left\{ \exp \left[-\frac{(\Omega - \Omega_m + \frac{i\bar{\gamma}}{2})^2}{2\omega^2 \varphi''(0)} \right] \right. \\ &\quad \left. \times \left[1 - \Phi \left(\frac{i(\Omega - \Omega_m) - \frac{\bar{\gamma}}{2}}{\bar{\omega} \sqrt{2\varphi''(0)}} \right) \right] \right\}, \end{aligned} \quad (4.25)$$

where

*The difference between $\bar{\gamma}$ and the corresponding expression in vacuum can be seen from (4.6). It must be borne in mind, in addition, that an account of nonradiative transition $u \rightarrow g$ leads, as can be readily shown, to $\bar{\gamma} = \gamma_{\text{rad}} + \gamma_{\text{nonrad}}$. The first term coincides with (4.6) and the second is equal to the nonradiative transition probability (per second).

$$\Phi(\xi) = \frac{2}{\sqrt{\pi}} \int_0^{\xi} e^{-t^2} dt. \quad (4.26)$$

If $\bar{\gamma} \ll \bar{\omega} \sqrt{\varphi''(0)}$ and $|\Omega - \Omega_m| \lesssim \bar{\omega} \sqrt{2\varphi''(0)}$, then (4.25) goes over into the Gaussian function

$$J_{gu}(\Omega) = \frac{1}{\bar{\gamma} \omega} \sqrt{\frac{2\pi}{\varphi''(0)}} \exp \left[-\frac{(\Omega - \Omega_m)^2}{2\omega^2 \varphi''(0)} \right]. \quad (4.27)$$

After substitution in (4.21), we obtain for the intensity in the radiation spectrum

$$R(\Omega) = \frac{4N_u n(\Omega) \Omega^4 |M_{ug}|^2}{3c^3 \omega \sqrt{2\pi \varphi''(0)}} e^{-\frac{(\Omega - \Omega_m)^2}{2\omega^2 \varphi''(0)}}. \quad (4.28)$$

This result corresponds exactly to formula (3.32) for the absorption coefficient, and can be readily obtained from (3.37) and (3.28). The criterion of strong heat release (3.36) assumes in this case the role of the criterion for replacing $\varphi_{-p}(it)$ by the expansion (4.24).

Details of the foregoing method for calculating the emission bands (and absorption bands) of light can be found in^[29], where the corrections connected with the next terms of the expansion (4.24) and with the "non-Condon" terms in the electron wave function (1.13) are taken into account. In^[29] there is also obtained a small temperature correction to the expression (4.16) for $\bar{\gamma}$. The account of the frequency effect is taken in^[29] by introducing electron indices (u or g) for the frequencies ω_K , which are contained in H_{um} and $H_{gn'}$, respectively. An analysis of this type cannot be regarded as consistent, for when the frequency effect is taken into account the matrix element (4.4) can no longer be represented by a product of independent phonon factors.

The remark made in Sec. 3 concerning the limitations connected with the method of generating polynomials applies also to the Lamb method considered above^[10].

Nonradiative transitions connected with the non-adiabaticity operator have been considered in^[30] by the method of^[27]. The form of the electron wave function is not detailed in^[30], and, in particular, formula (1.13) is not used. The contribution to the probability of the transition of both terms of the non-adiabaticity operator (1.9) is taken into account, and this leads to the appearance of additional terms in the function $F(w)$ of (3.55).

5. FEYNMAN OPERATOR CALCULUS IN THE THEORY OF MANY-PHONON PROCESSES. THE METHOD OF MOMENTS

The operator calculus developed in the well-known paper by Feynman^[31] turns out to be quite fruitful not only in quantum electrodynamics, but also in the theory of many-phonon transitions. Let us consider by way of illustration formula (4.13) for the total probability (per second) of the spontaneous optical transition $u \rightarrow g$ of an excited local center to the ground state. Recogniz-

ing that in the general case M_{ug} is an operator that acts on the variables of the phonon field, we rewrite (4.13) in the form

$$\bar{\gamma} = \frac{4}{3\hbar c^3} Av(n) \sum_{(n')} \int \Omega^3 n(\Omega) d\Omega |\langle n' | M_{ug} | n \rangle|^2 \times \delta\left(\Omega - \frac{H_{un} - H_{gn'}}{\hbar}\right). \quad (5.1)$$

In (5.1) we took the relation (4.12) into account with the aid of the δ -function. The matrix element of the transition is written in general form, without assuming the possibility of representing the phonon wave functions in the form of a product of wave functions of the independent harmonic oscillators.

Going over in (5.1) to the integral representation of the δ -function, we obtain

$$\bar{\gamma} = \frac{4}{3\hbar c^3} \int n(\Omega) \Omega^3 \tilde{T}_{gu}(\Omega) d\Omega, \quad (5.2)$$

where

$$\tilde{T}_{gu}(\Omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\Omega t} I_{gu}(t) dt, \quad (5.3)$$

$$I_{gu}(t) = Av(n) \sum_{(n')} \exp\left[\frac{i(H_{gn'} - H_{un})t}{\hbar}\right] |\langle n' | M_{gu} | n \rangle|^2. \quad (5.4)$$

After simple matrix transformations, the last expression assumes the form

$$I_{gu}(t) = Av(n) \langle n | M_{gu}^+ e^{\frac{iH_g t}{\hbar}} M_{gu} e^{-\frac{iH_u t}{\hbar}} | n \rangle, \quad (5.5)$$

where H_g , H_u — phonon Hamiltonians, for which $H_{gn'}$, H_{un} , and $|n'\rangle$, $|n\rangle$ are respectively the exact eigenvalues and eigenfunctions. Formula (5.5) (first obtained by M. Lax^[32]) is quite general in character, including only the adiabatic-approximation wave function (1.7) [without details of the solution of the electron equation (1.8) and the phonon Hamiltonian (1.10)].

Let us consider first the simplest case, when we can assume that M_{gu} is a c-number and neglect the frequency effect.

We introduce the operator

$$\Delta H \equiv H_g - H_u = -\hbar\Omega_{ug} + \frac{\hbar}{2} \sum_{\kappa} \Delta_{\kappa}^2 \omega_{\kappa} + \hbar \sum_{\kappa} \omega_{\kappa} \Delta_{\kappa} (q_{\kappa} - q_{u\kappa}) \quad (5.6)$$

and make use of the Feynman formula for the "disentangling" of the exponential operator factor^[31]

$$\exp\left[\frac{i}{\hbar}(H_u + \Delta H)t\right] = \exp\left(\frac{iH_u t}{\hbar}\right) \left\{ T \exp\left[\frac{i}{\hbar} \int_0^t \Delta H(s) ds\right] \right\} \quad (5.7)$$

where

$$\Delta H(s) = e^{-\frac{iH_u s}{\hbar}} \Delta H e^{\frac{iH_u s}{\hbar}}, \quad (5.8)$$

and T is the operator of chronological ordering in the index s . By definition

$$T[A(s)B(s')] = \begin{cases} BA & \text{for } s' > s, \\ AB & \text{for } s > s'. \end{cases}$$

After substituting (5.7) in (5.5) we get

$$\begin{aligned} I_{gu}(t) &= |M_{gu}|^2 Av(n) \langle n | T \exp\left[\frac{i}{\hbar} \int_0^t \Delta H(s) ds\right] | n \rangle \\ &= |M_{gu}|^2 \exp\left[it\left(-\Omega_{ug} + \frac{1}{2} \sum_{\kappa} \omega_{\kappa} \Delta_{\kappa}^2\right)\right] \\ &\times \prod_{\kappa} \langle T \exp\left[i\omega_{\kappa} \Delta_{\kappa} \int_0^t q_{\kappa}(s) ds\right] \rangle. \end{aligned} \quad (5.9)$$

In the matrix element $\langle n_{\kappa} | \dots | n_{\kappa} \rangle$ we have made the substitution $q - q_u \rightarrow q$. We introduced the abbreviated notation

$$Av(n_{\kappa}) \langle n_{\kappa} | \dots | n_{\kappa} \rangle = \langle \dots \rangle. \quad (5.10)$$

In^[32] formula (5.9) is further transformed under the assumption that the localized electron interacts only with the crystal vibrations, so that in this case

$$\begin{aligned} T \exp\left[i\omega_{\kappa} \Delta_{\kappa} \int_0^t q_{\kappa}(s) ds\right] &= 1 + i\omega_{\kappa} \Delta_{\kappa} \int_0^t q_{\kappa}(s) ds \\ &- \omega_{\kappa}^2 \Delta_{\kappa}^2 \int_0^t ds \int_0^s q_{\kappa}(s) q_{\kappa}(s') ds' + O(N^{-3/2}). \end{aligned} \quad (5.11)$$

We introduce the phonon creation and annihilation operators Q_{κ}^+ and Q_{κ} with the aid of the relations

$$q_{\kappa} = \frac{1}{\sqrt{2}} (Q_{\kappa} + Q_{\kappa}^+), \quad (5.12)$$

with

$$Q_{\kappa} Q_{\lambda} - Q_{\lambda} Q_{\kappa} = \sigma_{\kappa\lambda}. \quad (5.13)$$

In this representation $|n_{\kappa}\rangle$ is the eigenfunction of the Hamiltonian

$$H_{u\kappa} = \frac{\hbar\omega_{\kappa}}{2} (Q_{\kappa}^+ Q_{\kappa} + Q_{\kappa} Q_{\kappa}^+) \quad (5.14)$$

and

$$Q_{\kappa}(s) = e^{-\frac{iH_{u\kappa}s}{\hbar}} Q_{\kappa} e^{\frac{iH_{u\kappa}s}{\hbar}}. \quad (5.15)$$

Differentiating (5.15) with respect to s , we readily obtain with the aid of (5.14) and (5.15)

$$Q_{\kappa}(s) = Q_{\kappa} e^{i\omega_{\kappa}s}, \quad Q_{\kappa}^+(s) = Q_{\kappa}^+ e^{-i\omega_{\kappa}s}. \quad (5.16)$$

The averaging of (5.11) is with the aid of the obvious relations

$$\left. \begin{aligned} \langle Q \rangle &= \langle Q^+ \rangle = 0, & \langle QQ \rangle &= \langle Q^+ Q^+ \rangle = 0, \\ \langle Q^+ Q \rangle &= \bar{n}, & \langle QQ^+ \rangle &= \bar{n} + 1. \end{aligned} \right\} \quad (5.17)$$

After the averaging, the integration in (5.11) [with account of (5.16)] is elementary and we obtain

$$\begin{aligned} I_{gu}(t) &= |M_{gu}|^2 \exp\left\{-i\Omega_{ug}t - \frac{1}{2} \sum_{\kappa} \Delta_{\kappa}^2 \text{cth} \frac{\beta_{\kappa}}{2}\right. \\ &\left. + \frac{1}{2} \sum_{\kappa} \Delta_{\kappa}^2 [(\bar{n}_{\kappa} + 1) e^{i\omega_{\kappa}t} + \bar{n}_{\kappa} e^{-i\omega_{\kappa}t}]\right\}, \end{aligned} \quad (5.18)$$

so that

$$\tilde{I}_{gu}(\Omega) = \frac{|M_{gu}|^2}{2\pi\omega} \int_{-\infty}^{\infty} dt \exp[\varphi_{-p}(it)], \quad (5.19)$$

where φ is again determined from (3.12). \tilde{I}_{gu} differs from the I_{gu} in (3.11) in the choice of the integration contour. This difference is connected with the fact that the meanings of the compared quantities are not quite identical. We shall return to this question later.

Formula (5.18) can be obtained^[33] without the use of (5.11). To this end, we examine the factor contained in (5.9)

$$J_{\kappa}(t) = \langle T \exp \left\{ \frac{i\omega_{\kappa}\Delta_{\kappa}}{\sqrt{2}} \int_0^t ds [Q_{\kappa}^{\dagger}(s) + Q_{\kappa}(s)] \right\} \rangle. \quad (5.20)$$

We substitute in (5.20) $Q^{\dagger}(s)$ from (5.16) and use again Feynman's formula (5.17) for "disentangling" the factor $\exp[\lambda_{\kappa}(t)Q_{\kappa}^{\dagger}]$, where

$$\lambda_{\kappa}(t) = \frac{\Delta_{\kappa}}{\sqrt{2}}(1 - e^{-i\omega_{\kappa}t}). \quad (5.21)$$

Now

$$J_{\kappa}(t) = \langle e^{\lambda_{\kappa}(t)Q_{\kappa}^{\dagger}} \exp \left\{ \frac{i\omega_{\kappa}\Delta_{\kappa}}{\sqrt{2}} \int_0^t Q_{\kappa}(s) \exp(i\omega_{\kappa}s) ds \right\} \rangle, \quad (5.22)$$

where

$$\tilde{Q}_{\kappa}(s) = e^{-\lambda_{\kappa}(s)Q_{\kappa}^{\dagger}} Q_{\kappa} e^{\lambda_{\kappa}(s)Q_{\kappa}^{\dagger}}. \quad (5.23)$$

Differentiating (5.23) with respect to s , we can readily obtain a formula which is widely used in operator calculus

$$\tilde{Q}_{\kappa} \equiv e^{-\lambda_{\kappa}Q_{\kappa}^{\dagger}} Q_{\kappa} e^{\lambda_{\kappa}Q_{\kappa}^{\dagger}} = Q_{\kappa} + \lambda_{\kappa}. \quad (5.24)$$

Analogously

$$\tilde{Q}_{\kappa}^{\dagger} \equiv e^{-\lambda_{\kappa}^*Q_{\kappa}^{\dagger}} Q_{\kappa}^{\dagger} e^{\lambda_{\kappa}^*Q_{\kappa}^{\dagger}} = Q_{\kappa}^{\dagger} - \lambda_{\kappa}^*. \quad (5.24a)$$

Substitution of (5.21) and (5.24) in (5.22) yields

$$J_{\kappa}(t) = \exp \left[\frac{-it}{2} \omega_{\kappa}\Delta_{\kappa}^2 + \frac{\Delta_{\kappa}^2}{2} (e^{i\omega_{\kappa}t} - 1) \right] \langle e^{\lambda_{\kappa}(t)Q_{\kappa}^{\dagger}} e^{-\lambda_{\kappa}^*(t)Q_{\kappa}} \rangle. \quad (5.25)$$

We use furthermore the properties of the second-quantization operators

$$|n_{\kappa}\rangle = \frac{1}{\sqrt{n_{\kappa}!}} (Q_{\kappa}^{\dagger})^{n_{\kappa}} |0\rangle, \quad \langle n_{\kappa}| = \frac{1}{\sqrt{n_{\kappa}!}} \langle 0| Q_{\kappa}^{n_{\kappa}} \quad (5.26)$$

and relations that follow from (5.24)

$$\begin{aligned} Q_{\kappa}^{n_{\kappa}} e^{\lambda_{\kappa}Q_{\kappa}^{\dagger}} &= e^{\lambda_{\kappa}Q_{\kappa}^{\dagger}} (Q_{\kappa} + \lambda_{\kappa})^{n_{\kappa}}, \\ e^{-\lambda_{\kappa}^*Q_{\kappa}} (Q_{\kappa}^{\dagger})^{n_{\kappa}} &= (Q_{\kappa}^{\dagger} - \lambda_{\kappa}^*)^{n_{\kappa}} e^{-\lambda_{\kappa}^*Q_{\kappa}}. \end{aligned} \quad (5.27)$$

Recognizing also that

$$e^{-\lambda_{\kappa}^*Q_{\kappa}} |0\rangle = |0\rangle, \quad \langle 0| e^{\lambda_{\kappa}Q_{\kappa}^{\dagger}} = \langle 0|,$$

we can rewrite the diagonal matrix element from (5.25) in the form

$$\langle n | \dots | n \rangle = \frac{1}{n!} \langle 0 | (Q + \lambda)^n (Q^* - \lambda^*)^n | 0 \rangle = n! \sum_{r=0}^n \frac{(-1)^r |\lambda|^{2r}}{(n-r)! (r!)^2}. \quad (5.28)$$

The statistical averaging of this expression is easily carried out with the aid of the Boltzmann weight factor for the harmonic oscillator

$$g_{\kappa} = 2 \operatorname{sh} \frac{\beta_{\kappa}}{2} e^{-\beta_{\kappa}(n_{\kappa} + \frac{1}{2})}, \quad \beta_{\kappa} = \frac{\hbar\omega_{\kappa}}{kT}. \quad (5.29)$$

Thus

$$\begin{aligned} J_{\kappa}(t) &= \exp \left[\frac{-it\omega_{\kappa}\Delta_{\kappa}^2}{2} + \frac{\Delta_{\kappa}^2}{2} (e^{i\omega_{\kappa}t} - 1) \right] \\ &\times (1 - e^{-\beta_{\kappa}}) \sum_{n=0}^{\infty} e^{-n\beta_{\kappa}} n! \sum_{r=0}^n \frac{(-1)^r |\lambda_{\kappa}|^{2r}}{(r!)^2 (n-r)!} = \exp \left[\frac{-it\omega_{\kappa}\Delta_{\kappa}^2}{2} \right. \\ &\left. + \frac{\Delta_{\kappa}^2}{2} (e^{i\omega_{\kappa}t} - 1) - |\lambda_{\kappa}(t)|^2 n_{\kappa} \right]. \end{aligned} \quad (5.30)$$

It is easy to verify that substitution of (5.30) in (5.9) again results in (5.18), which is consequently valid not only for crystal but also for local oscillations.

Returning to the comparison of (5.19) with (3.11), we break up the region of integration with respect to t into sections of length 2π . Then

$$\tilde{I}_{gu}(\Omega) = \frac{|M_{gu}|^2}{2\pi\omega} \int_{-\pi}^{\pi} dt \exp[\varphi_{-p}(it)] \sum_{n=-\infty}^{\infty} \exp(2\pi i p n). \quad (5.31)$$

On the other hand^[32]

$$\sum_{n=-\infty}^{\infty} \exp(2\pi i p n) = \sum_{k=-\infty}^{\infty} \delta(p - k), \quad (5.32)$$

so that p in (5.31) must be taken to be an integer. But in this case the integral in (5.31) can be readily transformed to the form (3.11): when p is integer, the contributions of the horizontal lines of the contour of Fig. 1 cancel each other exactly. Thus,

$$\tilde{I}_{gu}(\Omega) = \bar{\omega}^{-1} I_{gu}(\Omega) \sum_{k=-\infty}^{\infty} \delta(p - k). \quad (5.33)$$

Substituting (5.33) in (5.2) and changing over to integration with respect to $dp = d\Omega/\bar{\omega}$, we obtain for the integral probability of the radiation

$$\bar{\gamma} = \frac{4}{3hc^3} \sum_{p \geq -p_0}^{\infty} n(\Omega_p) \Omega_p^3 I_{gu}(\Omega_p), \quad (5.34)$$

where the summation is over integer values of p ; Ω_p is connected with p by the relation

$$p\bar{\omega} = \Omega_p - \Omega_{ug} = \Omega_p - p_0\bar{\omega}. \quad (5.35)$$

Each term in the sum of (5.34) corresponds to the transition probability with given average heat release p . The frequency interval $d\Omega$ corresponds to $d\Omega/\bar{\omega}$ terms of the sum (5.34), so that we again arrive at formula (3.37) for the spectral intensity distribution. The tran-

sition from summation in (5.34) to integration

($\sum_P \dots = \bar{\omega}^{-1} \int \dots d\Omega$) brings us back to (5.2), but now

$\bar{\omega}^{-1} I_{gu}$ appears instead of \tilde{I}_{gu} . Thus, both expressions are equivalent under the integral sign.

As already indicated, Eq. (5.5) makes it possible to take the theory of many-phonon processes outside the framework of the limitations (Condon approximation, neglect of the frequency effect), under which all the results considered in Secs. 3–4 have been obtained. We note, however, that the characteristic function (3.11) (derived under the foregoing limitations) is quite complicated and, as already seen, an analytic expression admitting of comparison with experiment can be obtained for the shape of the band only in a few limiting cases. The account of the frequency effect etc. leads to even further complication of the characteristic function, and information concerning the form of the bands, necessary for comparison between theory and experiment, is obtained with the aid of the method of moments.

We define the k -th moment of a spectrum by the relation

$$N_k = \int_{-\infty}^{\infty} \Omega^k \tilde{I}_{gu}(\Omega) d\Omega \quad (5.36)$$

and introduce the quantities

$$\bar{\Omega} = \frac{1}{N_0} \int_{-\infty}^{\infty} \Omega \tilde{I}_{gu}(\Omega) d\Omega = \frac{N_1}{N_0}, \quad (5.37)$$

$$\overline{(\Omega - \bar{\Omega})^2} = \frac{1}{N_0} \int_{-\infty}^{\infty} (\Omega - \bar{\Omega})^2 \tilde{I}_{gu}(\Omega) d\Omega = \frac{N_2}{N_0} - \left(\frac{N_1}{N_0}\right)^2, \quad (5.38)$$

$$\overline{(\Omega - \bar{\Omega})^3} = \frac{1}{N_0} \int_{-\infty}^{\infty} (\Omega - \bar{\Omega})^3 \tilde{I}_{gu}(\Omega) d\Omega = \frac{N_3}{N_0} - \frac{3N_2N_1}{N_0^2} + 2\left(\frac{N_1}{N_0}\right)^3. \quad (5.39)$$

We assume that the spectral distribution is characterized by a Gaussian curve

$$I_{gu}(\Omega) = \text{const} \cdot \exp \left[\frac{-4 \ln 2 (\Omega - \Omega_m)^2}{(\delta\Omega)^2} \right] \quad (5.40)$$

with maximum at the point Ω_m and with half-width $\delta\Omega$. Then, as can be readily verified,

$$\bar{\Omega} = \Omega_m, \quad \overline{(\Omega - \bar{\Omega})^2} = \frac{(\delta\Omega)^2}{8 \ln 2}, \quad \overline{(\Omega - \bar{\Omega})^3} = 0. \quad (5.41)$$

On the other hand, if the spectral curve is close to Gaussian, then the average frequency characterizes approximately the position of the maximum, the dispersion (5.38) characterizes the half-width, and, finally, (5.39) characterizes the asymmetry of the curve. For a quantitative comparison of theory with experiment it is necessary in this case to calculate the corresponding moment (5.36) by numerically integrating the experimental curve.

Taking the inverse Fourier transform of (5.3), we easily obtain

$$N_k = i^k \left[\frac{d^k}{dt^k} I_{gu}(t) \right]_{t=0}. \quad (5.42)$$

Thus, the generating function (the Fourier transform) for the transition probability (5.5) can be used for a direct calculation of the moments of the spectrum. In particular*

$$\left. \begin{aligned} N_0 &= \langle M_{gu}^+ M_{gu} \rangle, \\ N_1 &= \hbar^{-1} \langle M_{gu}^+ M_{gu} H_u - M_{gu}^+ H_g M_{gu} \rangle, \\ N_2 &= \hbar^{-2} \langle M_{gu}^+ H_g^2 M_{gu} - 2M_{gu}^+ H_g M_{gu} H_u + M_{gu}^+ M_{gu} H_u^2 \rangle. \end{aligned} \right\} \quad (5.43)$$

The formulas in (5.43) enable us to estimate the corrections that must be introduced into the theory of absorption and luminescence spectra to account for the frequency effect. In the Condon approximation (M_{gu} is a c -number)

$$N_0 = |M_{gu}|^2, \quad N_1 = -\frac{|M_{gu}|^2}{\hbar} \langle \Delta H \rangle, \quad N_2 = \frac{|M_{gu}|^2}{\hbar^2} \langle \Delta H^2 \rangle. \quad (5.44)$$

We assume further that the Hamiltonians H_u and H_g have been reduced by two different transformations of the type of (1.27) to the form (1.26), so that

$$-\frac{\Delta H}{\hbar} = \Omega_{ug} + \frac{1}{2} \sum_{\nu} (\omega_{\nu}^{(u)} Q_{\nu}^{(u)2} - \omega_{\nu}^{(g)} Q_{\nu}^{(g)2}). \quad (5.45)$$

It follows from (1.27) that

$$Q_{\nu}^{(g)} = \sum_{\lambda} S_{\nu\lambda}^{(g)*} \Delta_{\lambda} \sqrt{\frac{\omega_{\nu}^{(g)}}{\omega_{\lambda}}} + \sum_{\lambda, \mu} S_{\nu\lambda}^{(g)*} S_{\mu\lambda}^{(u)} \sqrt{\frac{\omega_{\nu}^{(g)}}{\omega_{\mu}^{(u)}}} Q_{\mu}^{(u)}. \quad (5.46)$$

This general relation simplifies if we use the results of diagonalization by the perturbation method from Sec. 1 [formulas (1.30) and (1.31)]:

$$Q_{\nu}^{(g)} \cong \Delta_{\nu} \sqrt{\frac{\omega_{\nu}^{(g)}}{\omega_{\nu}}} + \sqrt{\frac{\omega_{\nu}^{(g)}}{\omega_{\nu}}} Q_{\nu}^{(u)} + \sum_{\lambda} \frac{(B_{\nu\lambda}^{(g)} - B_{\nu\lambda}^{(u)}) Q_{\lambda}^{(u)}}{\hbar^2 (\omega_{\nu}^2 - \omega_{\lambda}^2)}. \quad (5.47)$$

With the same accuracy we obtain from (5.45) and (5.44)

$$\bar{\Omega} \cong \Omega_{ug} - \frac{1}{2} \sum_{\nu} \Delta_{\nu}^2 \frac{\omega_{\nu}^{(g)2}}{\omega_{\nu}} + \frac{1}{4} \sum_{\nu} \frac{[\omega_{\nu}^{(u)2} - \omega_{\nu}^{(g)2}]}{\omega_{\nu}^{(u)}} \text{cth} \frac{\beta_{\nu}}{2}, \quad (5.48)$$

$$\overline{(\Omega - \bar{\Omega})^2} \cong \frac{1}{2} \sum_{\nu} \frac{\Delta_{\nu}^2 \omega_{\nu}^{(g)4}}{\omega_{\nu} \omega_{\nu}^{(u)}} \text{cth} \frac{\beta_{\nu}}{2} + \frac{1}{8} \sum_{\nu} \frac{[\omega_{\nu}^{(u)2} - \omega_{\nu}^{(g)2}]^2}{\omega_{\nu}^{(u)2}} \text{cth}^2 \frac{\beta_{\nu}}{2}. \quad (5.49)$$

Formulas (5.48) and (5.49) have been derived for the $u \rightarrow g$ transition (emission). The corresponding formulas for the absorption can be readily written, by interchanging the indices u and g and reversing the signs in front of the sums in (5.48). We then observe that the physical consequence of the frequency effect is violation of the law of mirror symmetry of the absorption and luminescence bands, viz: the maxima of these bands are asymmetrically located relative to Ω_{ug} , and the half widths are not equal. We emphasize, however, that within the framework of our approxima-

Another derivation of (5.43) is given in [3].

tion, the corrections to the mirror-symmetry law are small ($\sim \epsilon^2$).

Another consequence of the frequency effect is the temperature shift of the maxima of the bands [third term of (5.48)]. Such a shift is actually observed for F-centers: the maximum of the F-absorption band shifts upon heating to the red side. If $\omega_K^{(g)} > \omega_K^{(u)}$ (a natural assumption), then (5.48) gives the correct sign of the temperature shift. There exist, however, other possible causes of this effect: the dependence of the crystal parameters on the temperature^[41] and corrections to the Condon approximation (see below).

Formulas (5.48) and (5.49) become exact if the non-diagonal elements $B_{\kappa\lambda}$ vanish. This case is realized in the one-oscillator model (also called the model of configuration curves)*^[35], in which account is taken of the interaction between the localized electron and a single normal oscillation. Although this model is most frequently only illustrative, it is highly popular because a small number of parameters is left in (5.48) and (5.49). By choosing these parameters it is possible, in particular, to reconcile the theory with the noticeable deviations from the mirror-symmetry law, which are observed in alkali-halide crystal phosphors^[37]. The greatest interest from this point of view is attached to work in which the parameters of the oscillator model (Ω_{ug} , ω_u , ω_g , Δ) are calculated quantum-mechanically (see, for example, the article by Kristofel'^[38], devoted to a quantum mechanical calculation of the luminescence center in KCl-Tl).

Let us consider further the corrections to the spectrum moments, arising because of the dependence of the matrix element M_{ug} on the normal coordinates of the lattice. With the aid of (1.13), carrying out transformations analogous to those used in the derivation of (2.15), we easily obtain

$$M_{ug}(q) = M_{ug}^0 \left[1 + \sum_{\kappa} \gamma_{\kappa} \Delta_{\kappa} (q_{\kappa} - q_{\kappa u}) + \dots \right], \quad (5.50)$$

$$\gamma_{\kappa} \cong \frac{\hbar \omega_{\kappa}}{\Delta E_{ug}}.$$

Substituting (5.50) in (5.43) and neglecting the frequency effect, we obtain after simple but somewhat tedious calculations,

$$\bar{\Omega} \cong \Omega_m - \sum_{\kappa} \gamma_{\kappa} \omega_{\kappa} \Delta_{\kappa}^2 \operatorname{cth} \frac{\beta_{\kappa}}{2}, \quad (5.51)$$

$$\overline{(\Omega - \bar{\Omega})^2} \cong \frac{1}{2} \sum_{\kappa} \Delta_{\kappa}^2 \omega_{\kappa}^2 \operatorname{cth} \frac{\beta_{\kappa}}{2} + \sum_{\kappa} \gamma_{\kappa} \Delta_{\kappa} \omega_{\kappa}. \quad (5.52)$$

In these formulas the terms proportional to γ^2 have been left out. Comparison of (5.51) with (5.48) shows that both corrections (frequency and "non-Condon") to the frequency of the maximum of the band have the same temperature dependence, the same sign, and finally the same order in the parameter ϵ . Formula (5.52) contains a new result: the appearance of a

*A detailed description of the configuration curve method can be found in the book by D. Curiel^[36].

temperature-independent correction to the half width of the spectral band.

Expressions (5.51)–(5.52) (neglecting the dispersion of the phonon frequency) were obtained by Meyer^[39] in the form

$$\left. \begin{aligned} \bar{\Omega} &= \Omega_m - B \omega \operatorname{cth} \frac{\beta}{2}, \\ \overline{(\Omega - \bar{\Omega})^2} &= \frac{a \omega^2}{2} \operatorname{cth} \frac{\beta}{2} + C \omega^2. \end{aligned} \right\} \quad (5.53)$$

The parameters B and C were determined from a comparison with the experimental data on the absorption F bands. This yielded $C \approx 10$, corresponding to $\gamma \approx 0.1$. It is difficult to understand this result, since it follows from (5.50) that $\gamma \approx 0.01$ for F-centers.

The mathematical techniques connected with the Feynman operator calculus were used many times in work on many-phonon nonradiative transitions^[33,40,42].

In view of the fact that the summation method, which is not connected with the expansion in N^{-1} , leads to additional terms in the formula for the probability of "non-adiabatic" nonradiative transition, we should examine the derivation of this formula. We write (2.18) in the form

$$p_{ug} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} K_{gu}(t) dt, \quad (5.54)$$

$$K_{gu}(t) = \langle \mathcal{L}_{gu}^+ e^{\frac{iH_g t}{\hbar}} \mathcal{L}_{gu} e^{-\frac{iH_u t}{\hbar}} \rangle, \quad (5.55)$$

where it is convenient to express \mathcal{L}_{gu} in terms of the creation and annihilation operators

$$\mathcal{L}_{gu} = \frac{1}{\sqrt{2}} \sum_{\kappa} \mathcal{L}_{\kappa} (Q_{\kappa} - Q_{\kappa}^{\dagger}). \quad (5.56)$$

The generating function (5.55) assumes upon substitution of (5.56) the form

$$\begin{aligned} K_{gu}(t) &= \frac{1}{2} e^{-i\Omega_{ug} t} \\ &\times \left[\sum_{\kappa} |\mathcal{L}_{\kappa}|^2 \langle (Q_{\kappa}^{\dagger} - Q_{\kappa}) e^{\frac{-iH_{g\kappa} t}{\hbar}} (Q_{\kappa} - Q_{\kappa}^{\dagger}) e^{\frac{-iH_{u\kappa} t}{\hbar}} \rangle \prod_{\mu \neq \kappa} J_{\mu}(t) \right. \\ &+ \sum_{\kappa, \lambda \neq \kappa} \mathcal{L}_{\kappa}^* \mathcal{L}_{\lambda} \langle (Q_{\kappa}^{\dagger} - Q_{\kappa}) e^{\frac{iH_{g\kappa} t}{\hbar}} e^{\frac{-iH_{u\lambda} t}{\hbar}} \rangle \\ &\left. \times \langle e^{\frac{iH_{g\lambda} t}{\hbar}} (Q_{\lambda} - Q_{\lambda}^{\dagger}) e^{-\frac{iH_{u\lambda} t}{\hbar}} \rangle \prod_{\mu \neq \kappa, \lambda} J_{\mu}(t) \right], \quad (5.57) \end{aligned}$$

where J_{μ} is given by (5.30).

We consider, for example, one of the factors in (5.57):

$$K_{2\kappa}(t) = \langle Q_{\kappa} e^{\frac{iH_{g\kappa} t}{\hbar}} Q_{\kappa}^{\dagger} e^{-\frac{iH_{u\kappa} t}{\hbar}} \rangle. \quad (5.58)$$

From (5.16) we get the commutation relations

$$\left. \begin{aligned} Q_{\kappa}^{\dagger} e^{-\frac{iH_{u\kappa} t}{\hbar}} &= e^{i\omega_{\kappa} t} e^{-\frac{iH_{g\kappa} t}{\hbar}} Q_{\kappa}^{\dagger}, \\ Q_{\kappa} e^{\frac{iH_{u\kappa} t}{\hbar}} &= e^{i\omega_{\kappa} t} e^{\frac{iH_{g\kappa} t}{\hbar}} Q_{\kappa}, \end{aligned} \right\} \quad (5.59)$$

which enable us to combine the exponential factors in (5.58) and use the previously obtained result [see the derivation of (5.25)]

$$e^{\frac{iH_{g\kappa}t}{\hbar}} e^{-\frac{iH_{u\kappa}t}{\hbar}} = e^{\frac{iH_{u\kappa}t}{\hbar}} e^{\lambda_{\kappa}(t) Q_{\kappa}^+ e^{-\lambda_{\kappa}(t) Q_{\kappa}}} e^{-\frac{iH_{u\kappa}t}{\hbar}} \exp \left[\frac{\Delta_{\kappa}^2}{2} (e^{i\omega_{\kappa}t} - 1) \right].$$

A second application of (5.59) allows us to place the factors $\exp(\pm iH_{u\kappa}t/\hbar)$ on the outer sides of the product in (5.58) and consequently leave them out. Thus

$$K_{2\kappa}(t) = \exp \left[i\omega_{\kappa}t + \frac{\Delta_{\kappa}^2}{2} (e^{i\omega_{\kappa}t} - 1) \right] \langle Q_{\kappa} e^{\lambda_{\kappa} Q_{\kappa}^+} e^{-\lambda_{\kappa}^* Q_{\kappa}^+} Q_{\kappa}^+ \rangle.$$

It remains to "disentangle" this expression (that is, to place the creation operators ahead of the annihilation operators) with the aid of the commutation relations (5.24) and (5.13). Now

$$\begin{aligned} K_{2\kappa}(t) = & \exp \left[i\omega_{\kappa}t + \frac{\Delta_{\kappa}^2}{2} (e^{i\omega_{\kappa}t} - 1) \right] \left[\langle e^{\lambda_{\kappa} Q_{\kappa}^+} Q_{\kappa}^+ Q_{\kappa} e^{-\lambda_{\kappa}^* Q_{\kappa}^+} \rangle \right. \\ & + (1 - |\lambda_{\kappa}|^2) \langle e^{\lambda_{\kappa} Q_{\kappa}^+} e^{-\lambda_{\kappa}^* Q_{\kappa}^+} \rangle \\ & \left. + \lambda_{\kappa} \langle e^{\lambda_{\kappa} Q_{\kappa}^+} Q_{\kappa}^+ e^{-\lambda_{\kappa}^* Q_{\kappa}^+} \rangle - \lambda_{\kappa}^* \langle e^{\lambda_{\kappa} Q_{\kappa}^+} Q_{\kappa} e^{-\lambda_{\kappa}^* Q_{\kappa}^+} \rangle \right]. \end{aligned} \quad (5.60)$$

All the averages contained here can be readily calculated by suitable differentiation of (5.30) with respect to the parameters λ_{κ} and λ_{κ}^* . We ultimately get

$$K_{2\kappa}(t) = [(\bar{n}_{\kappa} + 1) - |\lambda_{\kappa}(t)|^2 (\bar{n}_{\kappa} + 1)^2] J_{\kappa}(t). \quad (5.61)$$

We can calculate by the same method all the remaining elements of (5.57). These calculations yield

$$K_{gu}(t) = \bar{\omega}^{-1} F_1(it) \exp \{ \varphi_{-p_0}(it) \}, \quad (5.62)$$

where

$$F_1(w) = F(w) - \sum_{\kappa} |\mathcal{L}_{\kappa}|^2 \Delta_{\kappa}^2 \left[\frac{\text{ch} \frac{\beta_{\kappa}}{2} - \text{ch} \left(w\omega_{\kappa} + \frac{\beta_{\kappa}}{2} \right)}{2 \text{sh} \frac{\beta_{\kappa}}{2}} \right]^2, \quad (5.63)$$

with $F(w)$ coinciding with (3.49). If we neglect local oscillations, the additional term of (5.63) tends to zero like N^{-1} . Therefore the summation in this term can be carried out only over the local oscillations. After substitution of (5.62) in (5.54) we get, obviously, a singularity of the type (5.33), connected with the fact that the initial formula (2.18) contains a δ -function. Expression (5.54) must be integrated over a continuous parameter of the final state. If we choose this parameter to be p_0 and again introduce the density $\bar{\omega}^{-1}$, we obtain a formula of the type of (3.48).

In analogy with the optical transitions, the approximation in which we use (5.56) as the perturbation operator for the nonradiative transition is customarily called the "Condon approximation." However, whereas, as we have seen, in the theory of optical transitions the "non-Condon" corrections are small, in the theory of nonradiative transitions they are apparently appreciable.

The nonradiative transition occurs near the line of intersection of the surfaces $U_u(q)$ and $U_g(q)$ of the configuration space ($\dots q_{\kappa} \dots$), where $q - q_g$ is generally speaking not small and the linear approximation (1.13) for the electron wave function becomes inaccurate. Kovarskiĭ^[42] obtained, by approximate summation of the entire perturbation-theory series in (1.8), the analytical dependence of the electron wave function on the normal coordinates. The calculation of the generating function (5.55) in this approximation leads to the appearance of an additional factor in (5.62). Cases when this factor increases the transition probability by one or two orders of magnitude are indicated in^[42].

The technique for "disentangling" the operator exponentials, considered in the present section, is used also in the calculation of thermodynamic functions of crystals with allowance for the electron-phonon interaction. In this connection, mention should be made of the work of Pekar and Krivoglaz^[43] on polaron theory and of Dykman^[44] on exciton theory. A detailed exposition of these investigations is outside the scope of our paper.

6. DENSITY MATRIX

We introduce a density operator (matrix) for a system with Hamiltonian H_u :

$$\rho_u(\lambda) = e^{-\lambda H_u}, \quad \lambda = \frac{1}{kT}. \quad (6.1)$$

Then the generating function (5.5) of the many-phonon transition can be written in the form

$$I_{gu}(t) = \frac{\text{Sp} \left[M_{gu}^+ \rho_g \left(-\frac{it}{\hbar} \right) M_{gu} \rho_u \left(\lambda + \frac{it}{\hbar} \right) \right]}{\text{Sp} [\rho_u(\lambda)]}. \quad (6.2)$$

If we neglect the corrections connected with the changes in the phonon frequencies and the deviation from the Condon approximation, then (6.2) breaks up into a product of traces pertaining to the normal oscillators, and assumes the form

$$I_{gu}(t) = e^{-i\Omega_{ug}t} |M_{gu}|^2 \prod_{\kappa} \frac{\text{Sp} \left[\rho_{g\kappa} \left(-\frac{it}{\hbar} \right) \rho_{u\kappa} \left(\lambda + \frac{it}{\hbar} \right) \right]}{\text{Sp} [\rho_{u\kappa}(\lambda)]}, \quad (6.3)$$

where

$$\rho_{u\kappa}(\lambda) = \exp \{ -\lambda H_{u\kappa} \}. \quad (6.4)$$

O'Rourke^[45], in a theory of optical transitions, and Kubo^[6], in a theory of thermal ionization of a local center, called attention to the fact that the calculation by means of (6.3) is best carried out in the coordinate representation, where the density matrix of the harmonic oscillator reduces to the known expression for the Slater sum

$$\begin{aligned} \rho(q, \bar{q} | \beta) &= \sum_{n=0}^{\infty} e^{-\beta \left(n + \frac{1}{2} \right)} \Phi_n(q) \Phi_n(\bar{q}) \\ &= \frac{1}{\sqrt{2\pi \text{sh} \beta}} \exp \left\{ -\frac{1}{4} \left[(q + \bar{q})^2 \text{th} \frac{\beta}{2} + (q - \bar{q})^2 \text{cth} \frac{\beta}{2} \right] \right\}, \end{aligned} \quad (6.5)^*$$

*th = tanh

where Φ_n — wave functions of the harmonic oscillator. Here

$$\text{Sp} [\varrho (q, \bar{q} | \beta)] = \int_{-\infty}^{\infty} \varrho (q, g | \beta) dg = \frac{1}{2 \text{sh} \frac{\beta}{2}}, \quad (6.6)$$

so that (6.3) assumes the form

$$I_{gu}(t) = e^{-i\Omega_{ug}t} |M_{gu}|^2 \prod_{\kappa} 2 \text{sh} \frac{\beta_{\kappa}}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \varrho (q_{\kappa} - q_{\kappa g}, \bar{q}_{\kappa} - q_{\kappa g} | -i\omega_{\kappa}t) \times \varrho (q_{\kappa} - q_{\kappa u}, \bar{q}_{\kappa} - q_{\kappa u} | \beta_{\kappa} + i\omega_{\kappa}t) dq_{\kappa} d\bar{q}_{\kappa}. \quad (6.7)$$

After substitution of (6.5), the integration in (6.7) is readily effected by transforming the quadratic form

$$F(q, \bar{q}) \equiv -(q + \bar{q})^2 \text{th} \frac{i\omega t}{2} - (q - \bar{q})^2 \text{cth} \frac{i\omega t}{2} + (q + \bar{q} - 2\Delta)^2 \text{th} \frac{i\omega t + \beta}{2} + (q - \bar{q})^2 \text{cth} \frac{i\omega t + \beta}{2} \quad (6.8)$$

using the linear substitution

$$Q = q + \bar{q} - 2\Delta \frac{\text{sh} \frac{i\omega t + \beta}{2} \text{ch} \frac{i\omega t}{2}}{\text{sh} \frac{\beta}{2}}, \quad \bar{Q} = q - \bar{q}$$

to the diagonal form

$$F(Q, \bar{Q}) = \frac{\text{sh} \frac{\beta}{2}}{\text{ch} \frac{i\omega t}{2} \text{ch} \frac{i\omega t + \beta}{2}} Q^2 - \frac{\text{sh} \frac{\beta}{2}}{\text{sh} \frac{i\omega t}{2} \text{sh} \frac{i\omega t + \beta}{2}} \bar{Q}^2 + 2\Delta^2 \left[\text{cth} \frac{\beta}{2} - \frac{\text{ch} \left(\frac{i\omega t + \beta}{2} \right)}{\text{sh} \frac{\beta}{2}} \right]. \quad (6.8a)$$

After integrating over the variables Q and \bar{Q} , we again obtain the generating function (5.19).

In the coordinate representation, the generating function (5.57) of the nonradiative transition assumes the form

$$K_{gu}(t) = -e^{-i\Omega_{ug}t} \left[\sum_{\kappa} |\mathcal{L}_{\kappa}|^2 2 \text{sh} \frac{\beta_{\kappa}}{2} \int_{-\infty}^{\infty} \frac{\partial \varrho_{g\kappa}}{\partial q_{\kappa}} \frac{\partial \varrho_{u\kappa}}{\partial q_{\kappa}} dq_{\kappa} d\bar{q}_{\kappa} \prod_{\mu \neq \kappa} J'_{\mu}(t) + \sum_{\kappa, \lambda \neq \kappa} \mathcal{L}_{\kappa}^* \mathcal{L}_{\lambda} 4 \text{sh} \frac{\beta_{\kappa}}{2} \text{sh} \frac{\beta_{\lambda}}{2} \int_{-\infty}^{\infty} \frac{\partial \varrho_{g\kappa}}{\partial q_{\kappa}} \varrho_{u\kappa} dq_{\kappa} d\bar{q}_{\kappa} \times \int_{-\infty}^{\infty} \varrho_{g\lambda} \frac{\partial \varrho_{u\lambda}}{\partial q_{\lambda}} dq_{\lambda} d\bar{q}_{\lambda} \prod_{\mu \neq \kappa, \lambda} J'_{\mu}(t) \right], \quad (6.9)$$

where for brevity $\rho_{g\kappa}$ and $\rho_{u\kappa}$ denote respectively the integrand factors of (6.7), and

$$J'_{\mu}(t) = 2 \text{sh} \frac{\beta_{\mu}}{2} \int_{-\infty}^{\infty} \varrho_{g\mu} \varrho_{u\mu} dq_{\mu} d\bar{q}_{\mu} \quad (6.10)$$

is the already calculated factor under the product sign in (6.3) and (6.7). This quantity coincides, apart for a factor $\exp(i\omega_{\mu}t\Delta_{\mu}^2/2)$ with expression (5.20) calculated in the preceding section by the "disentangling" method.

Integration with the aid of (6.8a) again brings us to (5.62).

As was already indicated, summation in accordance with (6.5) was first applied to nonradiative transitions in [6], where, however, only local oscillations were considered (three degrees of freedom of the impurity atom), and the shift of the normal coordinates was not taken into account at all. For crystal oscillations, the foregoing method was first used in [46], which contains an error consisting in the omission of the second term of the square bracket of (6.9). This error was noted and corrected in [47].

The density matrix method was used also by the author [48], who developed a theory for thermal ionization of an F-center with production of a polaron.*

In [45] and [46] an attempt was made to account for the frequency effect by introducing electron indices (u and g) for the frequencies ω_{κ} in the Hamiltonians $H_{u\kappa}$ and $H_{g\kappa}$. That this approach is inconsistent has already been noted at the end of Sec. 4. In the basic paper by Kubo and Toyozawa [49] it is shown that the density matrix method admits of a generalization that takes consistent account of the frequency effect. To this end it is necessary to write the phonon Hamiltonian of the adiabatic approximation (1.22) in tensor form

$$H_u = J_u + \frac{1}{2} \left(\mathbf{x} \Omega_u^2 \mathbf{x} - \frac{\partial^2}{\partial \mathbf{x}^2} \right), \quad (6.11)$$

where \mathbf{x} is an N-dimensional vector with components (1.23), $\hbar = 1$, and Ω_u^2 a second-rank tensor whose elements are defined by (1.24). Let $\mathbf{x} = \mathbf{S}y$, where \mathbf{S} is a unitary operator that transforms (6.11) to the diagonal form

$$H_u = J_u + \frac{1}{2} \left(\omega_u^2 y^2 - \frac{\partial^2}{\partial y^2} \right), \quad (6.12)$$

where $\omega_u^2 = \mathbf{S}^{-1} \Omega_u^2 \mathbf{S}$ is a diagonal matrix. The density matrix for the system of oscillators (6.12) can be written with the aid of (6.5). If we take into account the change in the normalization conditions of the wave functions $\Phi_n(q)$ connected with the transition to the dimensional variables x_{κ} , then

$$\varrho (y_{\kappa}, \bar{y}_{\kappa} | \beta_{\kappa}) = \prod_{\kappa} \left(\frac{\omega_{\kappa}}{2\pi \text{sh} \beta_{\kappa}} \right)^{1/2} \exp \left\{ -\frac{1}{4} \left[(y_{\kappa} + \bar{y}_{\kappa})^2 \times \omega_{\kappa} \text{th} \frac{\beta_{\kappa}}{2} + (y_{\kappa} - \bar{y}_{\kappa})^2 \omega_{\kappa} \text{cth} \frac{\beta_{\kappa}}{2} \right] \right\}. \quad (6.13)$$

The central idea of the calculation that follows is that expression (6.13) can be readily recast in a form that is invariant with respect to the unitary transformation \mathbf{S} . This enables us to obtain directly for the density matrix the expression

$$\varrho (\mathbf{x}, \bar{\mathbf{x}} | \beta_u) = [\det (2\pi \Omega_u^{-1} \text{sh} \beta_u)]^{-1/2} \exp \left\{ -\frac{1}{4} \left[(\mathbf{x} + \bar{\mathbf{x}}) \times \Omega_u \text{th} \frac{\beta_u}{2} (\mathbf{x} + \bar{\mathbf{x}}) + (\mathbf{x} - \bar{\mathbf{x}}) \Omega_u \text{cth} \frac{\beta_u}{2} (\mathbf{x} - \bar{\mathbf{x}}) \right] \right\}, \quad (6.14)$$

*Unlike [44] and [46], where it is assumed that a band electron is produced following thermal decay of the F-center.

where $\beta_{\mathbf{u}}$ stands for the tensor $\Omega_{\mathbf{u}}/kT$, and the analytic functions of the matrices are defined in usual fashion in terms of power series.

Formula (6.7) is accordingly generalized into

$$I_{gu}(t) = |M_{gu}|^2 e^{-i\Omega_{ug}t} \det \left(2 \operatorname{sh} \frac{\beta_{\mathbf{u}}}{2} \right) \int \int d\mathbf{x} d\bar{\mathbf{x}} \varrho(\mathbf{x} - \mathbf{x}_u, \bar{\mathbf{x}} - \mathbf{x}_u | \beta_{\mathbf{u}} + i\Omega_{\mathbf{u}}t) \varrho(\mathbf{x} - \mathbf{x}_g, \bar{\mathbf{x}} - \mathbf{x}_g | -i\Omega_{\mathbf{g}}t), \quad (6.15)$$

where $d\mathbf{x}$ stands for multidimensional integration. The latter can be readily carried out with the aid of the formula

$$\int \exp \left[- \sum_{i,h} a_{ih} x_i x_h \right] d\mathbf{x} = \left[\det \left(\frac{a}{\pi} \right) \right]^{-1/2}. \quad (6.16)$$

The problem thus reduces to the elimination of linear terms from the quadratic form obtained by substituting (6.14) in (6.15):

$$F(\mathbf{x}, \bar{\mathbf{x}}) = \frac{1}{4} \left[(\mathbf{x} + \bar{\mathbf{x}} - 2\Delta) \Omega_{\mathbf{u}} \operatorname{th} \frac{\beta_{\mathbf{u}} + i\Omega_{\mathbf{u}}t}{2} (\mathbf{x} + \bar{\mathbf{x}} - 2\Delta) - (\mathbf{x} + \bar{\mathbf{x}}) \Omega_{\mathbf{g}} \operatorname{th} \frac{i\Omega_{\mathbf{g}}t}{2} (\mathbf{x} + \bar{\mathbf{x}}) + (\mathbf{x} - \bar{\mathbf{x}}) \Omega_{\mathbf{u}} \operatorname{cth} \frac{\beta_{\mathbf{u}} + i\Omega_{\mathbf{u}}t}{2} (\mathbf{x} - \bar{\mathbf{x}}) - (\mathbf{x} - \bar{\mathbf{x}}) \Omega_{\mathbf{g}} \operatorname{cth} \frac{i\Omega_{\mathbf{g}}t}{2} (\mathbf{x} - \bar{\mathbf{x}}) \right], \quad (6.17)$$

where

$$\Delta = \mathbf{x}_u - \mathbf{x}_g. \quad (6.18)$$

We introduce the notation

$$\left. \begin{aligned} \Theta_{\mathbf{u}} &= \Omega_{\mathbf{u}} \operatorname{th} \frac{\beta_{\mathbf{u}} + i\Omega_{\mathbf{u}}t}{2}, & \Theta_{\mathbf{g}} &= -\Omega_{\mathbf{g}} \operatorname{th} \frac{i\Omega_{\mathbf{g}}t}{2}, \\ \Phi_{\mathbf{u}} &= \Omega_{\mathbf{u}} \operatorname{cth} \frac{\beta_{\mathbf{u}} + i\Omega_{\mathbf{u}}t}{2}, & \Phi_{\mathbf{g}} &= -\Omega_{\mathbf{g}} \operatorname{cth} \frac{i\Omega_{\mathbf{g}}t}{2}. \end{aligned} \right\} \quad (6.19)$$

Elimination of the linear terms from (6.17) is accomplished by making the substitution

$$\mathbf{x} + \bar{\mathbf{x}} = 2\mathbf{Q} + 2(\Theta_{\mathbf{u}} + \Theta_{\mathbf{g}})^{-1} \Theta_{\mathbf{u}} \Delta, \quad \bar{\mathbf{x}} - \mathbf{x} = 2\bar{\mathbf{Q}},$$

the Jacobian of which is equal to $\det(2)$. After integration as in (6.16), the expression (6.15) for the generating function is transformed into

$$I_{gu}(t) = |M_{gu}|^2 \exp[-f(t)], \quad (6.20)$$

where

$$f(t) = i\Omega_{ug}t + \Delta \Theta_{\mathbf{u}} (\Theta_{\mathbf{u}} + \Theta_{\mathbf{g}})^{-1} \Theta_{\mathbf{g}} \Delta + \frac{1}{2} \operatorname{Sp} \ln \left[\left(2 \operatorname{sh} \frac{\beta_{\mathbf{u}}}{2} \right)^2 \Omega_{\mathbf{u}}^{-1} \operatorname{sh} (\beta_{\mathbf{u}} + i\Omega_{\mathbf{u}}t) (\Theta_{\mathbf{u}} + \Theta_{\mathbf{g}}) \times (\Phi_{\mathbf{u}} + \Phi_{\mathbf{g}}) \Omega_{\mathbf{g}}^{-1} \operatorname{sh} (-i\Omega_{\mathbf{g}}t) \right]. \quad (6.21)$$

The last term of (6.21) is the result of applying the relation

$$\det \mathbf{A} \equiv \exp[\operatorname{Sp} \ln \mathbf{A}]. \quad (6.22)$$

Formulas (6.20) and (6.21) constitute an exact expression for the generating function (of course, within the framework of the Condon approximation and the harmonic model), but a direct analysis of the form of the absorption curves and emission curves is very diffi-

cult in this case, owing to the complicated nature of $f(t)$ in (6.21). However, if we assume that these curves have a nearly Gaussian form, then theory and experiment can be compared by calculating the average frequency (5.37) and the average dispersion (5.38) of the spectral distribution. Combining (5.37) and (5.38) with (5.42) we can readily verify that these quantities coincide (apart from a factor) with the corresponding derivatives of $f(t)$ when $t = 0$. After simple but rather cumbersome transformations, we get

$$\bar{\Omega} = -i\dot{f}(0) = \Omega_{ug} - \frac{1}{2} \Delta \Omega_{\mathbf{g}}^2 \Delta \Omega_{\mathbf{u}}^{-1} + \frac{1}{4} \operatorname{Sp} \left[\Omega_{\mathbf{u}}^{-1} \operatorname{cth} \frac{\beta_{\mathbf{u}}}{2} (\Omega_{\mathbf{u}}^2 - \Omega_{\mathbf{g}}^2) \right], \quad (6.23)$$

$$\overline{(\Omega - \bar{\Omega})^2} = \dot{f}''(0) = \frac{1}{2} \Delta \Omega_{\mathbf{g}}^2 \Omega_{\mathbf{u}}^{-2} \operatorname{cth} \frac{\beta_{\mathbf{u}}}{2} \Omega_{\mathbf{g}}^2 \Delta + \frac{1}{8} \operatorname{Sp} \left\{ \left[\Omega_{\mathbf{u}}^{-1} \operatorname{cth} \frac{\beta_{\mathbf{u}}}{2} (\Omega_{\mathbf{u}}^2 - \Omega_{\mathbf{g}}^2) \right]^2 \right\}. \quad (6.24)$$

We emphasize once more that the accuracy of these formulas is limited only by the choice of the initial phonon Hamiltonian (6.11) and by the Condon approximation. The frequency effect is taken into account here in the most rigorous and general form. On the other hand, the calculation of the tensor expressions contained in (6.23) and (6.24) is hardly possible without a concrete model of the center and without suitable approximations. In the particular case when the criteria for the diagonalization of the adiabatic potential by the perturbation theory method are satisfied, (5.48) and (5.49) follow directly from (6.23) and (6.24).

A generalization of the density matrix method in the "non-Condon" case, when

$$M_{gu}(x) = M_{gu}^{(0)} + M'_{gu}x, \quad (6.25)$$

is obtained^[49] by means of the substitution

$$\mathbf{x} \equiv i \int e^{i\mathbf{k}\mathbf{x}} \frac{\partial}{\partial \mathbf{k}} \delta(\mathbf{k}) d\mathbf{k}, \quad (6.26)$$

which makes it possible to carry through to conclusion the formal integration and to obtain an expression for the generating function, differing from (6.20) by an additional factor.

In^[49] are also considered nonradiative transitions in which the role of the perturbation is played by the non-adiabaticity operator, written in tensor form

$$\mathcal{L}_{ug} = -i\mathbf{A} \frac{\partial}{\partial \mathbf{x}}. \quad (6.27)$$

We do not present the rather cumbersome resultant formula for the generating function, since it apparently does not lend itself readily to investigation. In particular, in the analysis of the nonradiative transitions in^[49], the frequency effect was not taken into account and consequently the generating function of the non-radiative transition was reduced to expression (5.9).

The density matrix method gives very lucid results in the "semiclassical" approximation, that is, in the case when the phonon wave function of the initial state

$|n\rangle$ is quasiclassical. In this case* it is possible to replace the phonon Hamiltonians H_u and H_g under the trace sign in (5.5) by the corresponding Hamiltonians of the classical system and to neglect their non-commutativity. The generating function (6.2) assumes the form

$$I_{gu}(t) = |M_{gu}|^2 \frac{\text{Sp} \left\{ Q_u(\lambda) \exp \left[\frac{it(U_g - U_u)}{\hbar} \right] \right\}}{\text{Sp} [Q_u(\lambda)]}. \quad (6.28)$$

Neglecting the frequency effect and going over in (6.28) to the coordinate representation, we get

$$I_{gu}(t) = |M_{gu}|^2 \exp \left[it \left(-\Omega_{ug} + \frac{1}{2} \sum_x \omega_x \Delta_x^2 \right) \right] \times \prod_x \int_{-\infty}^{\infty} 2 \text{sh} \frac{\beta_x}{2} \varrho(q_x, q_x | \beta_x) \exp(i\omega_x t q_x \Delta_x) dq_x. \quad (6.29)$$

After substitution of the diagonal matrix element from (6.5), the integration in (6.29) is elementary and we get

$$I_{gu}(t) = |M_{gu}|^2 \exp \left[-\frac{t^2}{4} \sum \omega_x^2 \Delta_x^2 \text{cth} \frac{\beta_x}{2} - i\Omega_{\max} t \right]. \quad (6.30)$$

It is easy to verify that substitution of (6.30) in (5.3) results in exactly a Gaussian curve for the emission (and accordingly absorption) band [see, for example, (4.27) and (4.28)].

Applying the method of [49], we can generalize (6.29) to include the case when the phonon frequencies change by electronic transition. At high temperatures, when $\tanh(\beta_u/2) \cong \beta_u/2$, we obtain with the aid of (6.11) and formula (6.14) for the density matrix

$$I_{gu}(t) = |M_{gu}|^2 \left[\det \left(\frac{\lambda \Omega_u^2}{2\pi} \right) \right]^{1/2} \exp(-i\Omega_{ug}t) \int dx \times \exp \left[-\frac{1}{2} (\lambda + it) \mathbf{x} \Omega_u^2 \mathbf{x} + \frac{it}{2} (\mathbf{x} + \Delta) \Omega_g^2 (\mathbf{x} + \Delta) \right]. \quad (6.31)$$

From this formula we can obtain the classical moments of the spectrum by the same method as used to derive (6.23)–(6.24). A somewhat different analysis of the generating function (6.31) is given by Ratner and Zil'berman[50]. The matrices Ω_u^2 and Ω_g^2 of two positive definite quadratic forms can be diagonalized by one linear (but not unitary) transformation, as a result of which the integral in (6.31) breaks up into a product of elementary integrals. Integration with respect to t in (5.3) is then carried out by expanding the logarithm of the generating function in powers of $t/\lambda \lesssim kT/\delta\Omega$. The latter quantity is as a rule small even at high temperatures. Expansion up to terms proportional to t^3 gives respectively the first three moments of the emission (absorption) band. In [51] the same method of calculating the moments is applied to a quantum generating function of the type (6.15). The case is considered when the electron of a local center interacts only with a small number of neighboring atoms

(ions) of the lattice. The elastic constants of this interaction (the frequency parameters of the adiabatic potentials) are determined by comparing the theoretical expressions and the experimental values of $\bar{\Omega}$ and $(\bar{\Omega} - \bar{\Omega})^2$ for the absorption and luminescence bands.* With the aid of these parameters it is then possible to calculate and compare with experiment the activation energy of the nonradiative transition. Good agreement was obtained in this way between theory and experiment in the case of KCl-Tl. Nonradiative transitions are also considered in [51].

7. GREEN'S FUNCTION IN THE THEORY OF MANY-PHONON TRANSITIONS

Confining ourselves to the "Condon" case in the theory of optical transitions, we write the generating function (4.14) in the form

$$I_{gu}(t) = |M_{gu}|^2 \langle T \exp \left[\frac{i}{\hbar} \int_0^t \Delta H(s) ds \right] \rangle, \quad (7.1)$$

where T is the operator of chronological ordering in the parameter s .

Expressions similar to (7.1) are encountered in quantum field theory. The difference lies in the fact that the vacuum averaging in (7.1) is replaced by averaging over a canonical ensemble, and the S matrix is replaced by the evolution operator. In this respect, our problem is perfectly analogous to problems of quantum statistics and the field methods employed in it (see, for example, [52, 53]) can be extended to the theory of many-phonon transitions.

Tyablikov and Moskalenko[54] have shown that under rather general assumptions with respect to the operator ΔH the calculation of the generating functions reduces to a solution of a system of equations for the temperature-time Green's functions.

We choose a representation in which the phonon Hamiltonian H_u is diagonal

$$H_u = J_u + \sum_x \hbar \omega_x^{(u)} \left(Q_x^+ Q_x + \frac{1}{2} \right). \quad (7.2)$$

In the same representation (with account of the frequency effect) we have

$$\frac{\Delta H}{\hbar} = -\Omega_{ug} + V, \quad (7.3)$$

$$V = \sum_x (V_x Q_x + V_x^* Q_x^+) + \sum_{x, \lambda} \left(A_{x\lambda} Q_x^+ Q_\lambda + \frac{1}{2} B_{x\lambda} Q_x Q_\lambda + \frac{1}{2} B_{x\lambda}^* Q_x^+ Q_\lambda^+ \right). \quad (7.4)$$

Assuming that the unitary transformation which reduces the Hamiltonian H_u (6.11) to the diagonal form (7.2) is known, we can assume that the coefficients of the operator (7.4) are also known.

*If the symmetry of the system makes it possible to reduce the number of parameters of the theory to four.

*We confine ourselves to the Condon approximation.

We introduce a formal parameter α and the quantities

$$U_\alpha(t) = T \exp \left[i\alpha \int_0^t V(s) ds \right] \quad (7.5)$$

and

$$J_\alpha(t) = \langle U_\alpha(t) \rangle. \quad (7.6)$$

Differentiating (7.6) with respect to the parameter α , we can show [52] that

$$\begin{aligned} \ln I_{gu}(t) - \ln |M_{gu}|^2 + i\Omega_{ug}t &= -f(t) + i\Omega_{ug}t \\ &= i \int_0^t \frac{d\alpha}{J_\alpha(t)} \int_0^t ds \langle T [V(s) U_\alpha(t)] \rangle. \end{aligned} \quad (7.7)$$

After substituting V from (7.4), we get

$$\begin{aligned} f(t) &= i\Omega_{ug}t - i \int_0^t d\alpha \int_0^t ds \left\{ \sum_{\kappa} [V_{\kappa} \varphi_{1\kappa}(s) + V_{\kappa}^* \varphi_{2\kappa}(s)] \right. \\ &\quad + \sum_{\kappa, \lambda} \left[A_{\kappa\lambda} D_{1\kappa\lambda}(s, s) + \frac{1}{2} B_{\kappa\lambda} D_{2\kappa\lambda}(s, s) \right. \\ &\quad \left. \left. + \frac{1}{2} B_{\kappa\lambda}^* D_{3\kappa\lambda}(s, s) \right] \right\}, \end{aligned} \quad (7.8)$$

where we have introduced the Green's functions

$$\varphi_{1\kappa}(s) = \frac{1}{J_\alpha(t)} \langle T [Q_\kappa(s) U_\alpha(t)] \rangle, \quad (7.9)$$

$$D_{1\kappa\lambda}(s, s') = \frac{1}{J_\alpha(t)} \langle T [Q_\kappa^+(s) Q_\lambda(s') U_\alpha(t)] \rangle. \quad (7.10)$$

The function φ_2 differs from φ_1 in the substitution $Q_\kappa \rightarrow Q_\kappa^+$, while the functions D_2 and D_3 differ in that $Q_\kappa^+ Q_\lambda$ is replaced by $Q_\kappa Q_\lambda$ and $Q_\kappa^+ Q_\lambda^+$, respectively. The functions φ and D depend on t and α as parameters. The dependence of the creation and annihilation operators on the time-dependent parameter $s(s')$ is given by (5.16).

We note that when $t = 0$

$$\begin{aligned} D_{1\kappa\lambda}|_{t=0} &\equiv D_{\kappa\lambda}^0(s, s') = \langle T [Q_\kappa^+(s) Q_\lambda(s')] \rangle \\ &= \delta_{\kappa\lambda} e^{i\omega_\kappa^{(u)}(s'-s)} [\bar{n}_\kappa \theta(s-s') + (\bar{n}_\kappa + 1) \theta(s'-s)], \end{aligned} \quad (7.11)$$

where θ is the unit step function

$$\theta(s) = \begin{cases} 1 & s > 0, \\ 0 & s < 0. \end{cases}$$

Expression (7.11) is the Green's function of the free phonon field.

Equations for the functions φ and D can be derived in the following manner. After expanding $U_\alpha(t)$ in a power series we get

$$\begin{aligned} \varphi_{1\kappa}(s) &= \frac{1}{J_\alpha(t)} \sum_{n=0}^{\infty} \frac{(i\alpha)^n}{n!} \int_0^t ds_1 \dots ds_n \langle T [Q_\kappa(s) V(s_1) \\ &\quad \dots V(s_n)] \rangle. \end{aligned} \quad (7.12)$$

According to the so-called generalized Wick's theorem [55], the average of the T-product in (7.12) is equal to the sum of n terms of the form

$$\langle T [\overline{Q_\kappa(s)} V(s_1) V(s_2) \dots V(s_n)] \rangle, \quad (7.13)$$

which differ from each other in the permutation of the indices s_1, \dots, s_n . In the statistical variant of Wick's theorem [53] the symbol $\overline{\quad}$ for chronological pairing denotes

$$\overline{Q_\kappa(s) A(s')} \equiv \langle T [Q_\kappa(s) A(s')] \rangle, \quad (7.14)$$

if A is an operator that depends linearly on the creation and annihilation operators. Pairing with a non-linear operator [for example $V(s_1)$ in (7.13)] denotes, by definition, the sum of pairings with all linear operators contained in $V(s_1)$. Using the right to rename the integration variables s_1, \dots, s_n in (7.12), we can readily show that the sum of the expressions (7.13) can be replaced by multiplication of (7.12) by n , and thus

$$\varphi_{1\kappa}(s) = \frac{i\alpha}{J_\alpha(t)} \int_0^t ds' \langle T [\overline{Q_\kappa(s)} V(s') U_\alpha(t)] \rangle, \quad (7.15)$$

where according to the foregoing definition

$$\overline{Q_\kappa(s) V(s')} = D_{\kappa\kappa}^0(s, s') \{V_\kappa^* + \sum_{\lambda} [A_{\kappa\lambda} Q_\lambda(s') + \bar{B}_{\kappa\lambda}^* Q_\lambda^+(s')]\}. \quad (7.16)$$

In the derivation of (7.16) we used (7.11) and the obvious relations

$$\overline{Q_\kappa(s) Q_\lambda(s')} = \overline{Q_\kappa^+(s) Q_\lambda^+(s')} = 0. \quad (7.17)$$

In (7.16)

$$\bar{B}_{\kappa\lambda}^* = \frac{1}{2} (B_{\kappa\lambda}^* + B_{\lambda\kappa}^*). \quad (7.18)$$

After substituting (7.16) in (7.15) we get

$$\varphi_{1\kappa}(s) = i\alpha \int_0^t ds' D_{\kappa\kappa}^0(s, s') \left\{ V_\kappa^* + \sum_{\lambda} [A_{\kappa\lambda} \varphi_{1\lambda}(s') + \bar{B}_{\kappa\lambda}^* \varphi_{2\lambda}(s')] \right\}. \quad (7.19)$$

A similar equation for φ_2 can be written readily by replacing φ_1 by φ_2 in (7.19), as well as V_κ^* and $\bar{B}_{\kappa\lambda}^*$ by V_κ , $\bar{B}_{\kappa\lambda}$. If we put $A_{\kappa\lambda} = B_{\kappa\lambda} = \bar{B}_{\kappa\lambda}^* = 0$, then (7.19) can be solved in elementary fashion. It is easy to note that in this case (that is, neglecting the frequency effect), we return to the Pekar-Krivoglaz generating function, which has already been mentioned several times.

Proceeding to a derivation of the equations for the doubletime Green's functions, we use again the generalized Wick's theorem

$$\begin{aligned} D_{1\kappa\lambda}(s, s') &= \frac{1}{J_\alpha(t)} \{ \langle T [\overline{Q_\kappa^+(s) Q_\lambda(s')} U_\alpha(t)] \rangle \\ &\quad + \langle T [\overline{Q_\kappa^+(s) Q_\lambda(s')} U_\alpha(t)] \rangle \}. \end{aligned} \quad (7.20)$$

The first of the pairings contained here gives the free

Green's function, while for the second we obtain, in complete analogy with the derivation of (7.15)

$$\overline{Q_{\kappa}^{+}(s)} U_{\alpha}(t) = i\alpha \int_0^t ds'' \langle T [\overline{Q_{\kappa}^{+}(s)} \overline{V}(s'') U_{\alpha}(t)] \rangle. \quad (7.21)$$

After substituting V from (7.4) and calculating pairings of the type (7.16), we get

$$D_{1\kappa\lambda}(s, s') = D_{\kappa\lambda}^0(s, s') + i\alpha \int_0^t ds'' D_{\kappa\kappa}^0(s, s'') \left\{ V_{\kappa\varphi_{1\lambda}}(s') + \sum_{\mu} [A_{\mu\kappa} D_{2\mu\lambda}(s'', s') + \overline{B}_{\mu\kappa} D_{2\mu\lambda}(s'', s')] \right\}. \quad (7.21a)$$

Analogously

$$D_{2\kappa\lambda}(s, s') = i\alpha \int_0^t ds'' D_{\kappa\kappa}^0(s, s'') \left\{ V_{\kappa\varphi_{1\lambda}}^{*}(s') + \sum_{\mu} [A_{\mu\kappa} D_{2\mu\lambda}(s', s'') + \overline{B}_{\mu\kappa} D_{2\mu\lambda}(s', s'')] \right\}. \quad (7.21b)$$

The equation for D_3 is obtained from (7.21b) by replacing D_2 , φ_1 , $\overline{V}_{\kappa}^{*}$, and $\overline{B}_{\kappa\mu}^{*}$ by D_3 , φ_2 , V_{κ} , and $\overline{B}_{\kappa\mu}$, respectively.

As is well known, equations for Green's functions usually form an infinite chain, which contains functions with increasing number of arguments^[52]. Equations (7.21) have the important advantage that they form [in conjunction with (7.19)] a closed system. This system can be solved by iteration. We recall (see Sec. 6) that the average frequency, the average dispersion, etc. of the emission (absorption) spectrum are determined by the corresponding derivatives of $f(t)$ with $t = 0$. To calculate the foregoing quantities (normalized moments) we can assume therefore the variable t to be a small parameter of the iteration. This method was used in^[54] to obtain the formulas

$$\overline{\Omega} = \Omega_m + \sum_{\kappa} A_{\kappa\kappa} \left(\overline{n}_{\kappa} + \frac{1}{2} \right), \quad (7.22)$$

$$\overline{(\Omega - \overline{\Omega})^2} = \sum_{\kappa} |V_{\kappa}|^2 (2\overline{n}_{\kappa} + 1) + \frac{1}{2} \sum_{\kappa, \lambda} |A_{\kappa\lambda}|^2 (\overline{n}_{\kappa} + \overline{n}_{\lambda} + 2\overline{n}_{\kappa}\overline{n}_{\lambda}) + |\overline{B}_{\kappa\lambda}|^2 (1 + \overline{n}_{\kappa} + \overline{n}_{\lambda} + 2\overline{n}_{\kappa}\overline{n}_{\lambda}), \quad (7.23)$$

which are equivalent to (6.23)–(6.24) obtained in^[49].

In^[56] there was considered a variant of the method of^[54], where it was possible, by redefinition of the complex normal coordinates, to reduce both functions φ_1 and φ_2 to a single function φ and the three functions D_1 , D_2 , and D_3 to a single function D . The number of parameters of the formula (7.23) was accordingly reduced (the parameter $\overline{B}_{\kappa\lambda}$ disappeared). A paper delivered by the authors of^[54,56] at the Fifth Conference on Semiconductor Theory (Baku, 1962) contains approximate estimates of the correction terms in (7.22) and (7.23), due to the frequency effect, for the KBr center. As expected, the corrections turned out to be small. In particular, the difference in the half-widths

of the absorption and luminescence F bands at $T = 77^{\circ}\text{K}$ was found to be ~ 0.002 eV, amounting to $\sim 1\%$ of the half-width and being one order of magnitude smaller than the observed effect^[23]. At room temperature, the frequency correction to the half-width is approximately 3%.

Along with the Condon approximation, a more general case is considered in^[54], where

$$M_{gu} = \sum_{\kappa} (M_{\kappa} Q_{\kappa} + M_{\kappa}^{*} Q_{\kappa}^{*}). \quad (7.24)$$

It turns out that in this case the transition probability [in particular, the probability of nonradiative transition with perturbation operator (5.56)] is expressed in terms of the Green's functions (7.9) and (7.11).

8. CONCLUSION

During the last 13–14 years the theory of many-phonon transitions and local centers has made great strides. Starting from the adiabatic model of the local center, the theory has made it possible to establish even during the first stage of this development the fundamental physical properties of the impurity absorption and luminescence bands, properties connected with the electron-phonon interaction, such as the shift of the maxima of the bands relative to the frequency of the "pure electronic" transition, the presence of broad spectral bands and the dependence of the half-widths of these bands on the heat-release constant and the temperature, and the law of mirror symmetry of the absorption and emission bands. At the present stage, more general methods have been developed, which account for the subtle corrections connected with the frequency effect, the inaccuracy of the Condon approximation, etc. Under these conditions, the problem coming to the foreground is that of comparing theory with experiment, which can be done only by a joint effort of theoreticians and experimenters. Without pretending to set up a program for these joint investigations, we wish to mention some problems which in our opinion are of interest.

1) Theoretical and experimental study of the phonon spectrum of impurity crystals, including local oscillations. The error in the estimate of the parameters of the many-phonon transitions, due to the neglect of dispersion, can hardly be smaller than the errors connected with the aforementioned subtle effects. In the determination of the law of dispersion of the normal frequencies, a decisive role should apparently be played by experimental methods (in particular, neutron scattering, the Mössbauer effect, etc.), for the theoretical calculations of the natural oscillations offer serious mathematical difficulties even for ideal (impurity-free) crystals^[57].

2) Further study of cases in which the law of mirror symmetry is violated. The authors of an overwhelming majority of theoretical and experimental papers on

impurity luminescence spectra unanimously attribute these violations to the frequency effect. However, it can be seen with the F centers as an example that the contribution of the crystal oscillations to the frequency effect is small and apparently lies within the limits of experimental error.* Judging from [38], local oscillations make a large contribution to the frequency effect, but it is far from obvious that even in the case of local states of "small radius" it is possible to neglect the interaction between the electron and the crystal vibrations in the calculation of the parameters. It is necessary to develop local-center models that can take into account all the essential interactions with the phonons.

At the same time it is necessary to investigate other possible causes of deviations from the mirror symmetry law, viz: the transfer of excitation also to closely located electron levels, the incomplete relaxation of the phonon distribution, etc.

3) Clarification of the role of the anharmonicities of the oscillating subsystem. We refer here not only to the determination of some new small corrections to the moments of the spectrum, but to the utterly uninvestigated problem of the relaxation time in the phonon subsystem.

4) Particular attention should be paid to the theory of nonradiative transitions, the state of which determines the reliability of the theoretical calculations of the luminescence and photoeffect quantum yields, the capture and recombination cross sections, and other important parameters. A very important role is played by nonradiative transitions in laser theory. It is necessary to study, along with the non-adiabaticity of the electron motion, also other interactions which give rise to thermal transitions. It is possible that a new approach will be found to the problem of nonradiative transition on the basis of modern theory of fluctuations (thermodynamics of irreversible processes).

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