

Multiphonon Nonradiative Relaxation in Impurity-Phonon Systems with the Static Jahn-Teller Effect

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The theory of multiphonon nonradiative relaxation in paramagnetic impurity centers of small radius is developed within the framework of the crystal-field theory. Formulas are obtained for the probabilities of the spontaneous (at $T=0$) and quasiclassical (at high temperatures) nonradiative transitions. It is shown that the static Jahn-Teller effect causes nonradiative transitions between degenerate terms both as a result of the change of the deformation energy and as a result of its spatial reorientation. The nonradiative transition with change of spin, generated by the spin-orbit interaction, is considered. The lifetime of the ${}^4T_{2g}$ level of the Cr^{3+} ion in the ${}^4T_{2g} \rightarrow {}^2T_{1g}$ transition is calculated by way of example.

1. INTRODUCTION

NONRADIATIVE relaxation of excited states of impurity centers is defined as the transfer of localized electron excitation to the phonon subsystem. In the case of a weak coupling with the phonons, first-order perturbation theory gives perfectly satisfactory results for single-phonon relaxation. In the case of strong coupling, serious difficulties arise when it comes to calculating the probabilities of multiphonon nonradiative transitions, because the "polaron effect" (i.e., the deformation of the crystal environment, which accompanies the change of the electronic state of the local center) must be taken into account, generally speaking, in all orders in the coupling constant. The polaron effect leads to the appearance of broad optical bands (from ~ 100 to $\geq 10^3$ cm^{-1}) in the impurity-absorption and impurity-luminescence spectra, and this effect is appreciable even in the case of relatively weak electron-phonon coupling.

The polaron effect is taken into account in the theory of optical nonradiative transitions with the aid of the adiabatic approximation, the applicability of which is limited to cases where the dependence of the wave functions of the fast (electron) subsystem on the coordinates of the slow (nuclear) subsystem is weak^[1,2]. For a two-level system, such a criterion of the adiabatic approximation means smallness of the non-diagonal matrix elements of the electron-phonon interaction operator in comparison with the energy gap separating the levels. If the symmetry of a certain configuration of nuclei admits of orbital electronic degeneracy, then, according to the Jahn-Teller theorem^[3-5], the matrix of the electron-phonon interaction operator is non-zero, and in the general case there are therefore no grounds for assuming the dependence of the electronic wave functions on the coordinates of the nuclei to be weak. A more thorough investigation^[6-8] makes it possible, however, to separate three qualitatively different types of such a dependence.

1) The electronic equation of the adiabatic approximation can be diagonalized with the aid of a unitary transformation whose matrix does not depend on the vibrational coordinates. In this case, the adiabatic surface consists of intersecting parabolic sheets, the number of which is equal to the multiplicity of the degeneracy. The Jahn-Teller effect is static and the adiabatic approximation criteria are not violated. An example is

the orbital triplet of cubic groups, when the doubly degenerate vibration is active (the T-e problem).

2) The correct wave functions of the electronic equation depend strongly on the vibrational coordinates q , but at some points of q -space the adiabatic potential has minima that are deep in comparison with the zero-point oscillation energy, and the electronic wave function can be expanded in powers of $q - q_{0i}$ near these minima. The number of such minima is larger than the degeneracy multiplicity (for example, the T-t problem in the cubic group, where four minima appear). Thus, cases are possible when the adiabatic approximation is applicable (see also^[8]) only in certain regions of q -space.

3) The minimum of the adiabatic potential is reached not at isolated points but along a ring (a well known example is the E-e problem). The adiabatic-approximation criteria are violated everywhere, so that the "internal non-adiabaticity" is large—the dependence of the electronic ψ -functions on the vibrational coordinates appears already in the zeroth approximation of perturbation theory (the so-called dynamic Jahn-Teller effect)¹⁾.

We shall henceforth designate oscillations that are active in the Jahn-Teller effect as "adiabatic," and call the remaining ones "non-adiabatic." We consider in the present paper an example in which the electron-phonon interaction operator

$$\hat{H}_{int} = \sum_{\kappa\nu} v_{\kappa\nu} \hat{q}_{\kappa\nu}, \quad v_{\kappa\nu} = \sum_{i\bar{\Gamma}\gamma} v_{\kappa\nu}(\bar{\Gamma}\gamma, r_i) \quad (1)$$

($q_{\kappa\nu}$ is the dimensionless normal coordinate of the oscillation with wave vector κ belonging to the ν -th branch, $\bar{\Gamma}$ is the vibrational representation, γ is its row, and i numbers the optical electrons of the center), which is linear in the displacement of the nuclei, the adiabatic part predominates. In accordance with the definition of the adiabatic oscillations, matrices of the type $\langle \Gamma\gamma_1 | v_{\kappa\nu}(\bar{\Gamma}\gamma) | \Gamma\gamma_2 \rangle$ (Γ is the representation in accordance with which the electron function is transformed when $q_{\kappa\nu} = 0$) are diagonalized by one unitary transformation, and the adiabatic approximation leads to a system of energetically equivalent minima of the adiabatic potential, near which the electron-vibrational wave functions take the form^[12]

$$\Psi_{\Gamma\gamma}(r, q) = \psi_{\Gamma\gamma}(r, q) \prod_{\kappa\nu} \Phi_{\kappa\nu}[q_{\kappa\nu} - q_{\kappa\nu}(\Gamma\gamma)], \quad (2)$$

¹⁾For optical transitions with allowance for the dynamic Jahn-Teller effect see^[9-11].

where $q_{K\nu}(\Gamma\gamma)$ is the vibrational-subsystem configuration corresponding to the γ -th minimum of the adiabatic potential, and $\Phi_{K\nu}$ are the wave functions of the harmonic oscillators. The dependence of the electronic wave functions $\psi_{\Gamma\gamma}$ on the vibrational normal coordinates appears, in first order of perturbation theory, as the result of the inter-multiplet mixing of the electronic states by the oscillations (this effect is called non-adiabaticity). The quantities $q_{K\nu}(\Gamma\gamma)$ are calculated from the formula

$$-\hbar\omega_{K\nu}q_{K\nu}(\Gamma\gamma) = \sum_{\bar{\Gamma}\bar{\gamma}} \langle \psi^0(\Gamma\gamma) | v_{K\nu}(\bar{\Gamma}\bar{\gamma}) | \psi^0(\bar{\Gamma}\bar{\gamma}) \rangle, \quad (3)$$

where $\psi^0(\Gamma\gamma)$ are the zeroth-approximation Condon wave functions and $\omega_{K\nu}$ are the normal frequencies.

Starting with the work of Kun Huang and Rhys^[13], Krivoglaz^[1], and others (see the review^[2]), it has been customary to take the non-adiabaticity operator to be the perturbation generating the nonradiative transition $\Gamma \rightarrow \Gamma'$. We, however, are interested in the case when the non-adiabatic transition is forbidden because the matrix elements $\langle \Gamma\gamma | v(\bar{\Gamma}\bar{\gamma}) | \Gamma'\gamma' \rangle$ are equal to zero for all the adiabatic $\bar{\Gamma}$ oscillations. If the forbiddenness is not connected with the spin properties of the states Γ and Γ' , then the perturbation can be an interaction with non-adiabatic oscillations. Examples of such transitions are the nonradiative relaxation ${}^4T_2 \rightarrow {}^4A_2$ in ruby^[14] and certain relaxation transitions in rare-earth impurity ions^[15].

The general laws governing the nonradiative transition in the presence of the static Jahn-Teller effect are easiest to trace in the case when the perturbation operator is a certain interaction V in the electronic subsystem. By way of an example, we shall consider in Sec. 4 a transition generated by spin-orbit interaction^[2]. As shown earlier^[16], the transfer of excitation between discrete electron-vibrational levels $H(\Gamma \dots n_K \dots)$ and $H(\Gamma' \dots n'_K \dots)$ described by the wave functions (3) is possible because of relaxation of the final state, and proceeds at a rate

$$w(\Gamma n \rightarrow \Gamma' n') = \frac{|\langle \Gamma | V | \Gamma' \rangle|^2 \prod_x S^2(n_x, n'_x)}{(H' - H)^2 + \hbar^2 \nu^2 / 4}, \quad (4)$$

where γ^{-1} is the relaxation lifetime of the final state, and $S(n, n')$ are the vibrational overlap integrals resulting from the phonon factors of the function (2). If the vibrational frequencies ω_K belong to a discrete spectrum (local vibrations), then of the electron-vibrational states formula (4) leads at resonance to a transition probability proportional to the lifetime of the final state^[16]. If there are no local oscillations and the phonon frequencies belong to the continuous spectrum, then (4) must be integrated over the final states. In this case the result remains practically unchanged when the Lorentz factor in (4) is replaced by a δ -function. After statistical averaging over the populations of the initial vibrational sublevels and summing over the final vibrational states^[2], we thus arrive at the following expression:

²⁾The possibility of using the spin-axis interaction in diatomic molecules as the causes of nonradiative transitions was indicated by Landau and Lifshitz^[3]. Another example is nonradiative excitation transfer when the perturbation is an electrostatic or exchange interaction between impurity centers^[16].

$$w(\Gamma \rightarrow \Gamma') = \frac{1}{g(\Gamma)} \sum_{\gamma\gamma'} |\langle \Gamma\gamma | V | \Gamma'\gamma' \rangle|^2 G_{\gamma\gamma'}, \quad (5)$$

$$G_{\gamma\gamma'} = \int_{-\infty}^{\infty} \exp(-i\Omega_0 t) J_{\gamma\gamma'}(t) dt,$$

$$J_{\gamma\gamma'} = \exp \left\{ \frac{1}{2} \sum_{K\nu} \Delta_{K\nu}(\Gamma\gamma, \Gamma'\gamma') \left[\frac{\cos(\omega_{K\nu} t - i\beta_{K\nu}/2)}{\text{sh}(\beta_{K\nu}/2)} - \text{cth} \frac{\beta_{K\nu}}{2} \right] \right\},$$

$$\Delta_{K\nu}(\Gamma\gamma, \Gamma'\gamma') = [q_{K\nu}(\Gamma\gamma) - q_{K\nu}(\Gamma'\gamma')]^2, \quad (6)$$

where $g(\Gamma)$ is the degeneracy multiplicity and $\beta_{K\nu} = \hbar\omega_{K\nu}/kT$. Formula (6) contains summation and averaging over the equivalent minima of the final and initial states, respectively; Ω_0 is the frequency of the phononless line corresponding to the optical transition $\Gamma \rightleftharpoons \Gamma'$. If the adiabatic part of the interaction (1) is regarded as a perturbation when solving the electronic adiabatic-approximation equation, then^[2]

$$\hbar\Omega_0 = E_{\Gamma'} - E_{\Gamma} - \frac{1}{2} \sum_{K\nu} \hbar\omega_{K\nu} \{ \gamma_{K\nu}^2(\Gamma'\gamma') - q_{K\nu}^2(\Gamma\gamma) \}. \quad (7)$$

2. CASE OF WEAK INTERACTION WITH ACOUSTIC OSCILLATIONS. QUASICLASSICAL CASE

The methods of approximate integration with respect to t in formula (5) were discussed many times in the theory of multiphonon transitions^[2]. In an earlier paper^[14] we developed an approximation based on replacing the crystal frequencies entering in the factors $\exp(\pm i\omega_{K\nu} t)$ of formula (5) by certain values averaged over the given oscillation branch. The shortcoming of this approximation is that the phonon density contained in the final formula is replaced by a quantity $\bar{\omega}^{-1}$ which is not fully defined. Retaining the indicated approach for optical branches with small dispersions, we expand the acoustic part of the generating function (5) in a power series

$$J_{\gamma\gamma'}(t) = \exp \left(-\frac{1}{2} \sum_{K\nu} \Delta_{K\nu}(\gamma\gamma') \right) \exp \left[\sum_{\nu} z_{0\nu} \cos(\omega_{0\nu} t - i\beta_{0\nu}/2) \right]$$

$$\times \left[1 + \sum_{K\nu} z_{K\nu}(\gamma\gamma') \cos(\omega_{K\nu} t - i\beta_{K\nu}/2) + \frac{1}{2} \sum_{K\lambda\mu} z_{K\lambda\mu}(\gamma\gamma') \right.$$

$$\left. \times \cos(\omega_{K\lambda} t - i\beta_{K\lambda}/2) \cos(\omega_{K\mu} t - i\beta_{K\mu}/2) + \dots \right], \quad (8)$$

where $z_{K\nu}(\gamma\gamma') = \Delta_{K\nu}(\gamma\gamma')/2 \sinh(\beta_{K\nu}/2)$, and the quantities with the zero subscript pertain to the optical oscillations. It will be shown below that the n -th order term in the expansion (8) corresponds to a transition in which n acoustic phonons take part. In the case of an extremely weak interaction with the acoustic oscillations, the channels of nonradiative relaxation with the minimum number (1-2) of acoustic phonons have the overwhelming probability, and the series (8) can be terminated at the corresponding term. For an arbitrary interaction and at low temperatures, when the contribution of the virtual transitions with phonon absorption can be neglected, the number of terms in the series (8), which must be taken into account, is $n = E_{\geq}(\Omega_0/\omega_D)$ ($E_{\geq}(x)$ is the next higher or lower integer and ω_D is the Debye frequency. The temperature region where this approximation is valid is determined by the condition $z_{ac} < 1$, where z_{ac} is the contribution of the acoustic oscillations to the quantity $z = \sum_{K\nu} z_{K\nu}(\gamma\gamma')$. We emphasize that the expansion (8) is more accurate than the

usual perturbation theory, in which the n -phonon transition between the electronic states occurs in the n -th order, since, as is seen from formula (7), the quantity Ω_0 , which determines the order of the process, is calculated with allowance for the polaron effect.

Substituting (8) in (5) and using the well known expansion

$$e^{z \cosh \varphi} = \sum_m e^{im\varphi} I_m(z), \quad (9)$$

where $I_m(z)$ is a Bessel function of imaginary argument, we obtain after integrating with respect to t

$$\begin{aligned} G_{\gamma\gamma'} = & \exp\left(-\frac{1}{2} \sum_{\kappa\nu} \Delta_{\kappa\nu}(\gamma\gamma')\right) \left\{ \sum_p I_p(z_0) \exp(p\beta_0/2) \delta(\Omega_0 - p\omega_0) \right. \\ & + \frac{1}{2} \sum_p I_p(z_0) \exp(p\beta_0/2) \sum_{\kappa\nu} \Delta_{\kappa\nu}(\gamma\gamma') [(\bar{n}_{\kappa\nu} + 1) \delta(\Omega_0 - p\omega_0 - \omega_{\kappa\nu}) \\ & + \bar{n}_{\kappa\nu} \delta(\Omega_0 - p\omega_0 + \omega_{\kappa\nu})] + \frac{1}{4} \sum_p I_p(z_0) \exp(p\beta_0/2) \\ & \times \sum_{\kappa\lambda\mu} \Delta_{\kappa\nu}(\gamma\gamma') \Delta_{\lambda\mu}(\gamma\gamma') [(\bar{n}_{\kappa\nu} + 1)(\bar{n}_{\lambda\mu} + 1) \delta(\Omega_0 - p\omega_0 - \omega_{\kappa\nu} - \omega_{\lambda\mu}) \\ & + 2\bar{n}_{\kappa\nu}(\bar{n}_{\lambda\mu} + 1) \delta(\Omega_0 - p\omega_0 + \omega_{\kappa\nu} - \omega_{\lambda\mu}) + \bar{n}_{\kappa\nu}\bar{n}_{\lambda\mu} \delta(\Omega_0 - p\omega_0 \\ & \left. + \omega_{\kappa\nu} + \omega_{\lambda\mu})] + \dots \right\}. \quad (10) \end{aligned}$$

The first term describes a transition in which only optical phonons of one branch take part. In the concluding stage of the calculation it is possible in this case to take into account the dispersion of the optical oscillations by introducing a continuous parameter in the argument of the delta function, followed by integration (instead of summation) with respect to p . The second term is a contribution of the processes in which one acoustic phonon is produced or absorbed, and $p = E \gtrless (\Omega_0/\omega_0)$

optical phonons take part respectively. At low temperatures, when $\bar{n}_\kappa < 1$, the process with production of acoustic phonon predominates. If $E \gtrless (\Omega_0/\omega_0) < z_0 \sinh(\beta_0/2)$ (narrow gap, strong interaction with optical phonons), then $e^{p\beta_0/2} I_p(z)$ increases with increasing p , and when the temperature increases the process with absorption of the acoustical phonon can become predominant. Among the processes with two acoustic phonons, which are represented by the last term of (10), the principal role is played at low temperatures by the radiative transition, and when the temperature is increased the relative role of the Raman transition and of the transition with absorption of two acoustic phonons increases.

We emphasize that formula (10) takes into account accurately, in all orders in the coupling constant, the optical phonon creation and annihilation processes that are compatible with the energy conservation law. At low temperatures ($kT \ll \hbar\omega_0$), when the absorption of the optical phonons can be neglected, the Bessel functions in (10) are replaced by the highest-order term of the corresponding power series, and we obtain the well known temperature dependence $(\bar{n}(\omega_0) + 1)^p$ for the probability of the process with emission of p optical phonons.

We consider next the high-temperature region, when $z \gg 1$. In this case we can use the quasiclassical description of the phonon subsystem, which reduces in the zeroth approximation to an expansion of the exponential in (6) in powers of t up to terms $\sim t^2$ inclusive. Formula (5) takes the form

$$\begin{aligned} w(\Gamma \rightarrow \Gamma') = & \frac{1}{g(\Gamma)} \sum_{\gamma\gamma'} |\langle \Gamma'\gamma' | V | \Gamma\gamma \rangle|^2 \left[\frac{2\pi}{\sigma(\Gamma\gamma, \Gamma'\gamma')} \right]^{1/2} \\ & \times \exp\left[-\frac{\Omega_{me}^2(\gamma\gamma')}{2\sigma(\Gamma\gamma, \Gamma'\gamma')}\right], \quad (11) \end{aligned}$$

where

$$\Omega_{me}(\gamma\gamma') = \Omega_0 - \frac{1}{2} \sum_{\kappa\nu} \omega_{\kappa\nu} \lambda_{\kappa\nu}(\Gamma\gamma, \Gamma'\gamma') \quad (12)$$

is the frequency of the maximum of the Gaussian luminescence band resulting from the transition $\Gamma\gamma \rightarrow \Gamma'\gamma'$, and

$$\sigma(\Gamma\gamma, \Gamma'\gamma') = \frac{1}{2} \sum_{\kappa\nu} \omega_{\kappa\nu}^2 \Delta_{\kappa\nu}(\Gamma\gamma, \Gamma'\gamma') \operatorname{cth}(\beta_{\kappa\nu}/2) \quad (13)$$

is the second moment of the band.

A criterion for the approximation (11) can be established with the aid of the theory of central moments, which yields the corrections to the Gaussian shape of the band with the aid of the so called Edgeworth series (cf., e.g., [17]) in powers of $\Omega - \Omega_{me}$. The condition for the applicability of formula (11) is rapid convergence of this series at $\Omega = 0$, and reduces to the inequality

$$\frac{\Omega_{me}\sigma^{(3)}}{2\sigma^2} \left| 1 - \frac{\Omega_{me}^2}{3\sigma^2} \right| \ll 1, \quad (14)$$

where σ and Ω_{me} are the values of (12) and (13), with the symbols Γ and γ omitted for brevity, and

$$\sigma^{(3)}(\Gamma\gamma, \Gamma'\gamma') = \frac{1}{2} \sum_{\kappa\nu} \omega_{\kappa\nu}^3 \Delta_{\kappa\nu}(\Gamma\gamma, \Gamma'\gamma').$$

For large energy gaps ($\Omega_0 \gtrsim 10^4 \text{ cm}^{-1}$), the inequality (14) is a rather stringent condition and calls, as a rule, for unrealistically high temperatures. If, however, the energy gap is small and the deformation of the crystal line environment (the Stokes losses) accompanying the electronic transition $\Gamma \rightarrow \Gamma'$ is relatively large, then the criterion (14) is satisfied in the observable high-temperature region.

3. HAMILTONIAN OF ELECTRON-PHONON INTERACTION AND PARAMETERS OF MULTIPLY-MULTIPLY NONRADIATIVE TRANSITIONS

The subsequent calculation is for an impurity paramagnetic ion in an ionic-crystal matrix. The electron-phonon interaction operator is derived by a point model of the crystal field. We emphasize, however, that since the principal role is played by considerations connected with the symmetry of the crystalline environment, the main qualitative results of the theory remain valid also when account is taken of the finite dimensions of the ligands, of the covalence of the bonds, etc. The approximations of Sec. 2 are not used here. The radius of the state of the electrons of the unfilled shell is assumed to be small, and only their interaction with the displacements ΔR_α of the ions of the first coordination sphere will be taken into account. In the absence of local oscillations, the electron-phonon interaction results from modulation of these displacements by the optical and acoustic lattice vibrations

$$\Delta R_\alpha = \sum_{\kappa\nu} (\hbar/M\omega_{\kappa\nu})^{1/2} e_{\kappa\nu} q_{\kappa\nu} \cos(\kappa R_{\alpha 0} - \delta_{\kappa\nu}), \quad (15)$$

where M is the mass of the crystal, $e_{\kappa\nu}$ is a unit vector

of the polarization of the crystal mode, $\delta_{\kappa\nu}$ is its phase, and $\mathbf{R}_{\alpha 0}$ is the equilibrium position of the α -th ion of the lattice. On the other hand, the symmetrized displacements of the ions of the first coordination sphere can be calculated in accordance with the rule (see^[3])

$$Q(\bar{\Gamma}\bar{\gamma}) = \frac{g(\bar{\Gamma})}{g(\bar{G})} \sum_{\hat{G}} \Gamma_{\bar{\gamma}}(\bar{\Gamma}, \hat{G}) \hat{G} \Delta R_{ai}, \quad (16)$$

where \hat{G} is the group-symmetry operation, $\Gamma_{\bar{\gamma}}(\bar{\Gamma}, \hat{G})$ is the matrix of this transformation in the representation $\bar{\Gamma}$, $g(\bar{G})$ is the order of the group, and $i = x, y, z$.

Expressing the electron-phonon interaction operator in the form

$$H_{int} = \sum_{\bar{\Gamma}\bar{\gamma}} V(\bar{\Gamma}\bar{\gamma}, \mathbf{r}_i) Q(\bar{\Gamma}\bar{\gamma})$$

and substituting in it the expressions (16) and (15), we obtain an interaction Hamiltonian in the form (1), where

$$v_{\kappa\nu}(\bar{\Gamma}\bar{\gamma}, \mathbf{r}_i) = (\hbar/M\omega_{\kappa\nu})^{1/2} a_{\kappa\nu}(\bar{\Gamma}\bar{\gamma}) V(\bar{\Gamma}\bar{\gamma}, \mathbf{r}_i), \quad (17)$$

$$a_{\kappa\nu}(\bar{\Gamma}\bar{\gamma}) = \frac{g(\bar{\Gamma})}{g(\bar{G})} \sum_{\hat{G}} \Gamma_{\bar{\gamma}}(\bar{\Gamma}, \hat{G}) \hat{G} e_{\kappa\nu}^{\mu} \cos(\kappa \mathbf{R}_{\alpha 0} - \delta_{\kappa\nu}). \quad (18)$$

In the point model of the crystal field we have

$$V(\bar{\Gamma}\bar{\gamma}, \mathbf{r}_i) = \left. \frac{\partial v(\mathbf{r}_i, \dots, \mathbf{R}_{\alpha 0})}{\partial Q(\bar{\Gamma}\bar{\gamma})} \right|_{q=0}, \quad (19)$$

where $v(\mathbf{r}_i, \mathbf{R})$ is the potential energy of the electrostatic interaction of the i -th electron with the surrounding ions.

The structure of the matrices of the tensor operators $v(\bar{\Gamma}\bar{\gamma})$ is established with the aid of the Wigner-Eckart theorem^[18]. We consider by way of an example the T states of the group O_h , for which $[T_1^2] = [T_2^2] = A_1 + E + T_2$, and introduce the following numbering of the basis functions^[18]:

$$E (u \sim 3z^2 - r^2, v \sim \sqrt{3}(x^2 - y^2));$$

$$T_1 (a \sim yz(y^2 - z^2), \beta \sim xz(z^2 - x^2), \gamma \sim xy(x^2 - y^2));$$

$$T_2 (\xi \sim yz, \eta \sim zx, \zeta \sim xy).$$

For the matrices of the interaction with the E-vibrations we obtain

$$\langle T_{\bar{\gamma}} | V(Eu) | T_{\bar{\gamma}'} \rangle = -1/2 3^{-1/2} \langle T \| V(E) \| T \rangle (1 - 3/2 S_z^2 + 3/2 S_z),$$

$$\langle T_{\bar{\gamma}} | V(Ev) | T_{\bar{\gamma}'} \rangle = 1/2 \langle T \| V(E) \| T \rangle (-1 + 3/2 S_z^2 + 1/2 S_z), \quad (20)$$

where $\langle \dots \| \dots \| \dots \rangle$ is the reduced matrix element, and S_z and $\mathbf{1}$ are respectively the spin-1 and unit matrices. In a similar presentation, the matrices of the operator \mathbf{V} for the case $T_{2\gamma}$ are not the diagonal, and consequently, the trigonal vibrations are nonadiabatic in this case.

We consider a case in which the interaction with the T_2 -vibrations is relatively small. Estimates of the ruby absorption-band parameters show that this case is indeed realized for the T states of the Cr^{3+} ions^[12,17]. Neglecting the interaction with the non-adiabatic T_2 vibrations and solving the electronic Schrödinger equation in the adiabatic approximation, we obtain for the equilibrium configurations of the crystal with a degenerate electronic T-term

$$q_{\kappa\nu}[T, \xi(\alpha)] = -(3M\hbar\omega_{\kappa\nu}^3)^{-1/2} \{ [-1/2 a_{\kappa\nu}(Eu) + 1/2 \cdot 3^{1/2} a_{\kappa\nu}(Ev)] \times \langle T \| V(E) \| T \rangle + a_{\kappa\nu}(A_1 e) \langle T \| V(A_1) \| T \rangle \}, \quad (21)$$

$$q_{\kappa\nu}[T, \eta(\beta)] = -(3M\hbar\omega_{\kappa\nu}^3)^{-1/2} \{ [-1/2 a_{\kappa\nu}(Eu) - 1/2 \cdot 3^{1/2} a_{\kappa\nu}(Ev)] \times \langle T \| V(E) \| T \rangle + a_{\kappa\nu}(A_1 e) \langle T \| V(A_1) \| T \rangle \},$$

$$q_{\kappa\nu}[T, \zeta(\gamma)] = -(3M\hbar\omega_{\kappa\nu}^3)^{-1/2} \{ a_{\kappa\nu}(Eu) \langle T \| V(E) \| T \rangle + a_{\kappa\nu}(A_1 e) \langle T \| V(A_1) \| T \rangle \},$$

where ξ, η, ζ pertain to the T_2 -term, α, β, γ to T_1 , and e is the basis of the representation A_1 . The energy of the Jahn-Teller deformation (the "polaron" effect) is determined by the expression

$$\Delta E_{JT}(T) = -1/2 \sum_{\kappa\nu} \hbar\omega_{\kappa\nu} q_{\kappa\nu}^2(T\gamma), \quad (22)$$

which does not depend on the index γ numbering the degenerate states within the limits of the T-term. In fact, the following orthogonality relation holds for the quantities in (18):

$$\sum_{\Omega_{\kappa}} a_{\kappa\nu}(\Gamma\gamma) a_{\kappa\nu}(\Gamma'\gamma') = \sum_{\Omega_{\kappa}} a_{\kappa\nu}^2(\Gamma\gamma) \delta_{\Gamma\Gamma'} \delta_{\gamma\gamma'} \equiv b_{\kappa\nu}(\Gamma) \delta_{\Gamma\Gamma'} \delta_{\gamma\gamma'}, \quad (23)$$

where the summation is carried out over the directions of the vector κ . Performing this operation after substituting (21) in (22) and averaging over the directions of $e_{\kappa\nu}$, we obtain

$$\Delta E_{JT}(T) = -1/6 \sum_{\kappa\nu} \frac{1}{M\omega_{\kappa\nu}^3} [b_{\kappa\nu}(E) |\langle T \| V(E) \| T \rangle|^2 + b_{\kappa\nu}(A_1) |\langle T \| V(A_1) \| T \rangle|^2], \quad (24)$$

which contains only the reduced matrix elements of the electronic operators. We note that, unlike in the papers of Van Vleck^[19] and Kristofel^[20], formulas (21) and (24) describe the static Jahn-Teller effect in interactions with crystal modes.

Proceeding to the calculation of the parameters of the Stokes losses $\Delta_{\kappa\nu}(\Gamma\gamma, \Gamma'\gamma')$, which characterize the change of the equilibrium configuration of the lattice in an electronic transition, we consider first the transition $T \rightarrow A$. For the orbital singlet A, only fully-symmetrical vibrations are active ($[A^2] = A_1$), and therefore

$$q_{\kappa\nu}(A) = -(\hbar M\omega_{\kappa\nu}^3)^{-1/2} a_{\kappa\nu}(A_1 e) \langle A \| V(A_1) \| A \rangle. \quad (25)$$

We can now easily show with the aid of (21) and (25) that all three $T \rightarrow A$ transitions are characterized by a single Stokes-loss parameter

$$D_{\kappa\nu}(T\gamma, A) = \sum_{\Omega_{\kappa}} \Delta_{\kappa\nu}(\gamma) = \frac{1}{3\hbar M\omega_{\kappa\nu}^3} [b_{\kappa\nu}(E) |\langle T \| V(E) \| T \rangle|^2 + b_{\kappa\nu}(A_1) |\langle T \| V(A_1) \| T \rangle - 3^{1/2} \langle A \| V(A_1) \| A \rangle|^2] \equiv D_{\kappa\nu}. \quad (26)$$

Accordingly, the three generating functions (6) of formula (5) coincide, and the latter takes the form

$$w(T \rightarrow A) = 1/3 G \sum_{\gamma} |\langle T_{\bar{\gamma}} | V | A \rangle|^2. \quad (27)$$

This result is perfectly understandable, since the minima are energetically equivalent and differ only in the spatial orientation of the lattice polarization along the three tetragonal axes; the activation energies for the transitions from these minima to the singlet state are identical.

For transitions of the $T \rightarrow T'$ type there are nine quantities $\Delta_{\kappa\nu}(T\gamma, T'\gamma')$, but after averaging there remain only two Stokes-loss parameters:

$$D_{\kappa\nu}(T\gamma, T'\gamma') = D_{\kappa\nu}^{(1)}(T, T') \delta_{\gamma\gamma'} + D_{\kappa\nu}^{(2)}(T, T') (1 - \delta_{\gamma\gamma'}); \quad (28)$$

$\delta_{\gamma\gamma'} = 1$ if $\gamma = \gamma'$ for the transitions $T_1 \rightarrow T_1, T_2 \rightarrow T_2$ or $\gamma = \xi, \gamma' = \alpha; \gamma = \eta, \gamma' = \beta; \gamma = \zeta, \gamma' = \gamma$ for the transitions $T_1 \rightleftharpoons T_2; \delta_{\gamma\gamma'} = 0$ in all the remaining cases.

$$\text{Here } D_{\kappa\nu}^{(1)}(T, T') = \frac{1}{3\hbar M \omega_{\kappa\nu}^3} [b_{\kappa\nu}(E) |\langle T \| V(E) \| T \rangle - \langle T' \| V(E) \| T' \rangle|^2 + b_{\kappa\nu}(A_l) |\langle T \| V(A_l) \| T \rangle - \langle T' \| V(A_l) \| T' \rangle|^2], \quad (29)$$

$$D_{\kappa\nu}^{(2)}(T, T') = \frac{1}{3\hbar M \omega_{\kappa\nu}^3} \{ b_{\kappa\nu}(E) [|\langle T \| V(E) \| T \rangle|^2 + |\langle T' \| V(E) \| T' \rangle|^2 + \langle T \| V(E) \| T \rangle \langle T' \| V(E) \| T' \rangle] + b_{\kappa\nu}(A_l) [|\langle T \| V(A_l) \| T \rangle - \langle T' \| V(A_l) \| T' \rangle|^2] \}, \quad (30)$$

The parameter $D^{(1)}$ corresponds to three transitions between identically oriented Jahn-Teller minima of the adiabatic potentials. If at the same time $\Delta E_{JT}(T') = \Delta E_{JT}(T)$, then $D^{(1)} = 0$, and the activation energy of the above-barrier transition (quasiclassical, see formula (11)) becomes infinitely large. The parameter $D^{(2)}$ characterizes six transitions with change of orientation of the equivalent minima. With this, $D^{(2)}$ differs from zero and the activation energy remains finite also in the case of a constant energy of the Jahn-Teller deformation. The possibility of an activation transition as a result of spatial reorientation of the lattice deformation is an essential feature of the multiplet-multiplet nonradiative transitions. Taking the foregoing into account, formula (11) takes the form

$$w(T \rightarrow T') = \frac{1}{3} \left[G^{(1)} \sum_{\nu} |\langle T_{\nu} \| V | T'_{\nu} \rangle|^2 + G^{(2)} \sum_{\nu\nu'} |\langle T_{\nu} \| V | T'_{\nu'} \rangle|^2 (1 - \delta_{\nu\nu'}) \right]. \quad (31)$$

The presence of two Stokes-loss parameters in the $T \rightarrow T'$ transition leads to a doublet splitting of the corresponding band^[12].

4. THE TRANSITION ${}^4T_2(t_2^2e) \rightarrow {}^2T_1(t_2^3)$ IN A Cr^{3+} ION WITH OCTAHEDRAL SURROUNDING

By way of an application of a developed theory, we consider the transition indicated in the heading and playing an important role in the kinetics of the formation of the inverted population of the working 2E level of a ruby laser and in the temperature dependence of the luminescence R-line (the transition ${}^2E_g \rightarrow {}^4A_{2g}$) of ruby and similar systems^[21,22]. For a six-coordinated octahedral system, application of formula (18) yields

$$a_{\kappa\nu}(A_{1g}) = \frac{2 \sin \delta_{\kappa\nu}}{6^{1/2}} \sum_{j=x,y,z} e_j^{\nu} \sin \alpha_j R, \quad (32)$$

$$a_{\kappa\nu}(E_u) = \sin \delta_{\kappa\nu} (e_x^{\nu} \sin \alpha_x R - e_y^{\nu} \sin \alpha_y R).$$

For $b_{\kappa\nu}$ we obtain

$$b_{\kappa\nu}(A_{1g}) = \frac{1}{6} - \frac{1}{2} \frac{\sin 2\xi}{2\xi} + \frac{\sin 2\xi}{(2\xi)^2} - \frac{\cos 2\xi}{(2\xi)^2} - \frac{\sin(2^{1/2}\xi)}{2^{1/2}\xi} + 3 \frac{\sin(2^{1/2}\xi)}{(2^{1/2}\xi)^2} - 3 \frac{\cos(2^{1/2}\xi)}{(2^{1/2}\xi)^2},$$

$$b_{\kappa\nu}(A_{1g}) = \frac{1}{6} - \frac{1}{2} \frac{\sin 2\xi}{(2\xi)^2} + \frac{1}{2} \frac{\cos 2\xi}{(2\xi)^2} + \frac{1}{2} \frac{\sin(2^{1/2}\xi)}{2^{1/2}\xi} - \frac{3 \sin(2^{1/2}\xi)}{2 (2^{1/2}\xi)^2} + \frac{3 \cos(2^{1/2}\xi)}{2 (2^{1/2}\xi)^2},$$

$$b_{\kappa\nu}(E_g) = \frac{1}{6} - \frac{1}{2} \frac{\sin 2\xi}{2\xi} + \frac{\sin 2\xi}{(2\xi)^2} - \frac{\cos 2\xi}{(2\xi)^2} + \frac{1}{2} \frac{\sin(2^{1/2}\xi)}{2^{1/2}\xi} - \frac{3 \sin(2^{1/2}\xi)}{2 (2^{1/2}\xi)^2} + \frac{3 \cos(2^{1/2}\xi)}{2 (2^{1/2}\xi)^2},$$

$$b_{\kappa\nu}(E_g) = \frac{1}{6} - \frac{1}{2} \frac{\sin 2\xi}{(2\xi)^2} + \frac{1}{2} \frac{\cos 2\xi}{(2\xi)^2} - \frac{1}{4} \frac{\sin(2^{1/2}\xi)}{2^{1/2}\xi}$$

$$+ \frac{3 \sin(2^{1/2}\xi)}{4 (2^{1/2}\xi)^3} - \frac{3 \cos(2^{1/2}\xi)}{4 (2^{1/2}\xi)^2}, \quad (33)$$

where the indices l and t pertain to the longitudinal and transverse vibrations, R is the distance from the center of the octahedron to the vortex, and $\xi = \kappa R$.

The energy gap for the transition ${}^4T_2 \rightarrow {}^2T_1$ is $\hbar\Omega_0 = 1700 \text{ cm}^{-1}$ ^[23]. At low temperatures, when the stimulated emission of the phonons can be neglected, the greatest probability is possessed by nonradiative decay channels with a minimum number of phonons. Assuming for ruby the values $\omega_{\omega} = 1200 \text{ cm}^{-1}$ and $\omega_{ot} = 1000 \text{ cm}^{-1}$ for the optical-phonon frequencies and $\omega_{JD} = 1000 \text{ cm}^{-1}$ and $\omega_{tD} = 700 \text{ cm}^{-1}$ for the Debye frequencies of the acoustic phonons, we consider respectively two types of two-phonon transitions:

1. Transition with participation of one acoustic and one optical phonon, described by the second term of formula (10) with $p = 1$. Using the low-temperature asymptotic form of the Bessel functions, we obtain

$$G^{(k)} = \frac{1}{2} a_0^{(k)}(T_2, T_1) \sum_{\kappa\nu=l,t} D_{\kappa\nu}^{(k)}({}^4T_2, {}^2T_1) \delta(\Omega_0 - \omega_0 - \omega_{\kappa\nu}), \quad (34)$$

where $k = 1$ and 2 , and $a_0^{(k)}$ is the Pekar-Kun Huang function for optical phonons:

$$a_0^{(k)}(T_2, T_1) = \sum_{\kappa\nu} D_{\kappa\nu}^{(k)}({}^4T_2, {}^2T_1). \quad (35)$$

Substituting (28) in (35) and changing over to integration in κ space, we obtain

$$a_0^{(1)}({}^4T_2, {}^2T_1) = \frac{1}{24\hbar\rho\omega_0^3 R^3} \{ [B_l(E) + 2B_t(E)] |\langle {}^4T_{2g} \| V(E) \| {}^4T_{2g} \rangle - \langle {}^2T_{1g} \| V(E) \| {}^2T_{1g} \rangle|^2 + [B_l(A_1) + 2B_t(A_1)] |\langle {}^4T_{2g} \| V(A_1) \| {}^4T_{2g} \rangle - \langle {}^2T_{1g} \| V(A_1) \| {}^2T_{1g} \rangle|^2 \},$$

$$a_0^{(2)}({}^4T_2, {}^2T_1) = \frac{1}{24\hbar\rho\omega_0^3 R^3} \{ [B_l(E) + 2B_t(E)] [|\langle {}^4T_{2g} \| V(E) \| {}^4T_{2g} \rangle|^2 + |\langle {}^2T_{1g} \| V(E) \| {}^2T_{1g} \rangle|^2] + \langle {}^4T_{2g} \| V(E) \| {}^4T_{2g} \rangle \langle {}^2T_{1g} \| V(E) \| {}^2T_{1g} \rangle + [B_l(A_1) + 2B_t(A_1)] |\langle {}^4T_{2g} \| V(A_1) \| {}^4T_{2g} \rangle - \langle {}^2T_{1g} \| V(A_1) \| {}^2T_{1g} \rangle|^2 \}, \quad (36)$$

where

$$B_{\nu}(\bar{\Gamma}) = \int_0^{\xi_D} b_{\kappa\nu}(\bar{\Gamma}) \xi^2 d\xi, \quad \xi_D = \nu_D R.$$

Substituting here the expressions (33), we get

$$B_l(A_1) = \frac{1}{6} \xi_D^3 - \frac{1}{2} \sin 2\xi_D + \xi_D \cos 2\xi_D + \text{Si}(2\xi_D) + 4\xi_D \cos 2^{1/2}\xi_D - 8 \cdot 2^{1/2} \sin 2^{1/2}\xi_D + 6 \cdot 2^{1/2} \text{Si}(2^{1/2}\xi_D),$$

$$B_t(A_1) = \frac{1}{6} \xi_D^3 + \sin 2\xi_D - \text{Si}(2\xi_D) + 8 \cdot 2^{1/2} \sin 2^{1/2}\xi_D - 4\xi_D \cos 2^{1/2}\xi_D - 6 \cdot 2^{1/2} \text{Si}(2^{1/2}\xi_D),$$

$$B_l(E) = \frac{1}{6} \xi_D^3 - \frac{1}{2} \sin 2\xi_D + \xi_D \cos 2\xi_D + \text{Si}(2\xi_D) - 2\xi_D \cos 2^{1/2}\xi_D + 4 \cdot 2^{1/2} \sin 2^{1/2}\xi_D - 3 \cdot 2^{1/2} \text{Si}(2^{1/2}\xi_D),$$

$$B_t(E) = \frac{1}{6} \xi_D^3 + \sin 2\xi_D - \text{Si}(2\xi_D) - 4 \cdot 2^{1/2} \sin 2^{1/2}\xi_D + 2\xi_D \cos 2^{1/2}\xi_D + 3 \cdot 2^{1/2} \text{Si}(2^{1/2}\xi_D). \quad (37)$$

Using the Debye dispersion law $\omega_{\kappa\nu} = \nu_{\gamma} \kappa$ for the acoustic phonons and changing over in (34) to integration with respect to ω_{κ} , we reduce (34) to the final form

$$G^{(1)}({}^4T_2, {}^2T_1) = \frac{a_0^{(1)}({}^4T_2, {}^2T_1)}{12\hbar\rho\pi^2(\Omega_0 - \omega_0)} \left\{ \left[\frac{b_{\kappa\nu}(E)}{\nu^3} + \frac{2b_{\kappa\nu}(E)}{\nu^3} \right] |\langle {}^4T_2 \| V(E) \| {}^2T_1 \rangle|^2 + \left[\frac{b_{\kappa\nu}(A_1)}{\nu^3} + \frac{2b_{\kappa\nu}(A_1)}{\nu^3} \right] |\langle {}^4T_2 \| V(A_1) \| {}^4T_2 \rangle - \langle {}^2T_1 \| V(A_1) \| {}^2T_1 \rangle|^2 \right\}, \quad (38)$$

³⁾We emphasize that this quantity must be determined from the frequency of the phononless line of the U-band and not from the position of its maximum.

where $\kappa_\nu = (\Omega_0 - \omega_0)/v_\nu$, $\nu = l, t$. The analogous expression for $G^{(2)}$ is omitted to save space.

2. The transition with participation of a transverse and a longitudinal acoustic phonon, described by the third term of (10) with $p = 0$ and $\bar{n}_{\kappa\nu} = 0$, is given by

$$G^{(k)} = \frac{1}{2} \sum_{\kappa} D_{\kappa l}^{(k)} D_{\kappa t}^{(k)} \delta(\Omega_0 - \omega_{\kappa l} - \omega_{\kappa t})$$

$$= \frac{L^3}{16\pi^3 v_l} \sum_{\kappa} D_{\kappa l}^{(k)} D_{\kappa t}^{(k)} \lambda^2, \quad \lambda = (\Omega_0 - \nu_{\kappa})/v_l, \quad (39)$$

L^3 is the value of the main region of the crystal. It is necessary to substitute in (39) the Stokes-loss parameters (28) or (29) with the values of $b_{\kappa\nu}$ from (33), and to integrate with respect to κ . The resultant formula is too cumbersome to present here. It is more convenient in fact to calculate $G^{(k)}$ by a numerical method using tabulated values of $D_{\kappa\nu}$.

To calculate the reduced matrix elements of the operators $v(\Gamma\gamma)$ which enter in the foregoing formulas, we use the theory of the crystal field. For the Cr^{3+} ion, the most convenient is the approximation of a strong crystal field. We neglect here the mixing due to the Coulomb interaction of states having identical symmetry and pertaining to different configurations $t_2^3 e^3$, bearing in mind that the term ${}^4T_2(t_2^3 e)$ is encountered once, and allowance for the mixing of the term ${}^2T_1(t_2^3)$ leads only to small corrections^[18]. Accurate to terms $\sim R^4/R^4$, the electron-phonon interaction operators are^[19]

$$V(A_{1g}, r_i) = -2B6^{-1/2}(x_i^4 + y_i^4 + z_i^4 - 3/5r_i^4),$$

$$V(Ev, r_i) = A(x_i^2 - y_i^2) + B(x_i^4 - y_i^4); \quad (40)$$

$$A = 1/4ee^*(18R^{-4} - 75R^{-6}r^2), \quad B = 175ee^*/8R^6,$$

where e^* is the effective charge of the oxygen ion. The wave functions of the T-states of the indicated configurations are

$$|{}^4T_{2g}, M = 3/2, \zeta\rangle = |\xi\eta\nu\rangle; \quad |{}^2T_{1g}, M = 1/2, \gamma\rangle = 2^{-1/2}(|\xi\xi\xi\rangle - |\xi\eta\bar{\eta}\rangle),$$

where $|\dots\rangle$ is the Slater determinant and the single-electron states $\xi, \bar{\xi}, \eta, \bar{\eta}, \zeta$ and ν contain also spin functions. Now the general formulas of Sec. 3 become much simpler, since

$$\langle {}^2T_{1g}(t_2^3) | \sum_{\kappa} V(Ev, r_i) | {}^2T_{1g}(t_2^3) \rangle$$

$$= \langle \xi | V(Ev) | \xi \rangle + \langle \eta | V(Ev) | \eta \rangle + \langle \zeta | V(Ev) | \zeta \rangle = 0, \quad (42)$$

as can be verified by direct substitution of the basis functions of the T_2 and E representations chosen above. As a result it turns out (see formulas (28) and (29)) that $D^{(1)} = D^{(2)}$, and (31) goes over into the usual (single-term) adiabatic-approximation formula. Thus, the strong-crystal-field approximation leads in this case to the loss of the specific feature connected with allowance for the Jahn-Teller effect in the triplet-triplet transition. Calculation of the corrections connected with the interconfiguration mixing entails no fundamental difficulty, but these corrections are small and exert no influence on the order of magnitude of the calculated transition probability.

We note that by virtue of relations (21) and (24), and also the easily verified relation $\langle {}^2T_{1g} | V(A_1) | {}^2T_{1g} \rangle = \langle {}^4A_{2g} | V(A_1) | {}^4A_{2g} \rangle$, the optical intraconfigurational transition ${}^2T_{1g}(t_2^3) \rightarrow {}^4A_{2g}(t_2^3)$ is not accompanied by deformation of the crystalline surroundings, and consequently appears in the form of a phononless line. In the

observed spectrum of ruby^[22], the indicated transition indeed corresponds to a narrow line with a weakly pronounced vibrational structure, and this can be regarded as an experimental verification of the approximation (41).

Further, as shown by direct calculation,

$$\langle {}^4T_{2g} \| V(E) \| {}^4T_{2g} \rangle = \langle {}^4T_{2g} \| V(A_1) \| {}^4T_{2g} \rangle - \langle {}^2T_{1g} \| V(A_1) \| {}^2T_{1g} \rangle = \frac{150}{54^{1/2}} \frac{Dq}{R}, \quad (43)$$

$$Dq = ee^* \langle r \rangle / R^3. \quad (44)$$

Thus, the reduced matrix elements are expressed in terms of a single parameter Dq , which characterizes the splitting of the d-term by the static crystal field and is determined from spectroscopic data.

Since the states under consideration have different multiplicities, as already indicated in Sec. 1, the operator of the perturbation generating the nonradiative transition is the spin-orbit interaction. The transition probability (31) will contain the factor

$$F = \sum_{M\gamma, M'\gamma'} |\langle \alpha S \Gamma M \gamma | H_{so} | \alpha' S' \Gamma' M' \gamma' \rangle|^2. \quad (45)$$

We represent the operator $H_{so} = \sum_i \lambda_0 \hat{L}_i \hat{S}_i$ in the form

of a contraction of the irreducible tensor T_1 , made up of the components of l , with a spherical tensor of rank 1, made up of the components of \hat{s} ^[18],

$$H_{so} = \sum_{q\gamma} C_{q\gamma} V_{q\gamma}(T_1), \quad V_{\pm 1\mu}(T_1) = \sum_i \hat{s}_{i\pm 1} t_{i\mu},$$

$$V_{0\gamma}(T_1) = \sum_i \hat{s}_{i0} t_{i\gamma}; \quad \sum_{q\gamma} |C_{q\gamma}|^2 = 3, \quad (46)$$

$\mu = \alpha, \beta$; $\hat{s}_{\pm 1} = \hat{s}_x \pm i\hat{s}_y$, $\hat{s}_0 = \hat{s}_z$. Then, using the Wigner-Eckart theorem for double tensor operators and the orthogonality conditions for the Clebsch-Gordan coefficients, we obtain the "sum rule":

$$F = |\langle \alpha S \Gamma \| V(T_1) \| \alpha' S' \Gamma' \rangle|^2, \quad (47)$$

after which we get

$$\langle t_2^3 e^4 T_{2g} \| V(T_1) \| t_2^3 T_{1g} \rangle = -3^{-1/2} \langle t_2 \| V(t_1) \| e \rangle = i^{(2/3)^{1/2}} \lambda_0. \quad (48)$$

The numerical calculations with the aid of the foregoing formulas were performed for ruby with the following values of the parameters: $\rho = 4 \text{ g/cm}^3$, $v_l = 1.2 \times 10^6 \text{ cm/sec}$, $v_t = 6.7 \times 10^5 \text{ cm/sec}$, $R = 2 \times 10^{-8} \text{ cm}$, and $Dq = 1800 \text{ cm}^{-1}$; $w({}^4T_2 \rightarrow {}^2T_1)$ was calculated for the limiting cases of low temperatures with formulas (34) and (39) in high temperatures with formula (11). The spontaneous ($T = 0$) transition with participation of one optical and one acoustic longitudinal and transverse phonon have respective probabilities 1.59×10^9 and $1.1 \times 10^{10} \text{ sec}^{-1}$; the spontaneous transition with participation of two acoustic phonons has a probability $6.4 \times 10^9 \text{ sec}^{-1}$. Thus, at low temperatures the main channel of nonradiative relaxation of the 4T_2 term is generation of optical and acoustic phonons. This result agrees with the experimental data of Pollak^[24,25], who obtained a lifetime $\tau({}^4T_{2g} \rightarrow {}^2E_g) = 5 \times 10^{-10} \text{ sec}$. We note that the transition ${}^2T_1 \rightarrow {}^2E$ occurs much more rapidly^[26], and therefore $\tau^{-1}({}^4T_2 \rightarrow {}^2E) \approx w({}^4T_2 \rightarrow {}^2T_1)$. The inequality (14), which determines the temperature region in which the quasiclassical formula (11) is valid for the transition in question, is satisfied with $T \gg 500^\circ \text{ K}$. Calculation

yields $w(700^\circ\text{K}) = 2.1 \times 10^{10} \text{ sec}^{-1}$ and $w(800^\circ\text{K}) = 2.33 \times 10^{10} \text{ sec}^{-1}$. The probability $w(^4T_2 \rightarrow ^2T_1)$ was first calculated by Malkin^[26] and later in our earlier papers^[27,28], where the value obtained for w was smaller than almost two orders of magnitude than in the present paper. The discrepancy lies in the fact that the calculation in^[26] was performed by perturbation theory in an approximation with a weak electron-phonon coupling, and the calculation in^[27] did not take into account the polaron effect when the energy gap was determined, and the employed electronic functions^[29] in the basis of the weak crystal field were not accurate enough.

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