Zero-phonon line of Jahn-Teller systems in the case of weak electron-phonon coupling

V. S. Tsukerblat, Yu. B. Rozenfel'd, V. Z. Polinger, and V. G. Vekhter

Chemistry Institute, Moldaviar Academy of Sciences
(Submitted August 16, 1974)
Zh. Eksp. Teor. Fiz. **68**, 1117–1126 (March 1975)

The structure of the zero-phonon lines (ZPL) is considered for $A \to E(e)$ and $A \to T(t_2)$ impurity-absorption transitions in Jahn-Teller centers that interact weakly with the local oscillations. It is shown that in the absence of a frequency effect the ZPL comprise an equidistant set of lines spaced $\sim B^2/\hbar\omega$ apart, where B is the linear vibronic coupling constant. A weak frequency effect makes the ZPL structure less sharp but affects its envelope only slightly. The ZPL structure appears again in the presence of a strong frequency effect, the line intensity decreasing exponentially with frequency within each series. Effects due to interaction between Jahn-Teller centers and the continuous spectrum of the crystal oscillations are considered. It is shown that there is no temperature shift or broadening of the ZPL in second order in the linear vibronic-coupling with the crystal phonons.

The theory of zero-phonon lines (ZPL) in crystals was developed for impurity centers with nondegenerate electronic states[1,2]. The generalization of the theory to the case of orbital degeneracy is not trivial, since the electron-vibrational interaction leads to the complicated problem of the Jahn-Teller effect (JTE)[3-5], and the energy spectrum of the system cannot be obtained analytically at arbitrary coupling. Yet it is well known that the change of the spectrum by the vibronic interaction leads to a peculiar type of broadening or to the appearance of a fine structure in the ZPL. Thus, in systems with local oscillations a small change in the lattice-vibration frequencies in an optical transition (the "frequency effect"[2]) makes the ZPL structure more complicated[1]. If we disregard the ZPL broadening mechanisms due to virtual processes in which a dissipative subsystem takes part (crystal vibrations), we can propose that specific mechanisms for the structural broadening of ZPL should exist in Jahn-Teller systems. In the case of weak vibronic interactions, the indicated peculiarities are due to the fact that the levels of the vibrations active in the JTE are multiply degenerate and are not merely shifted (as in the absence of the JTE), but also split by the vibronic interaction.

The shape of the ZPL of the multiplet-multiplet transition was considered in[6-8], but the approximations assumed in those papers did not make it possible to investigate the ZPL structure due to the interaction with the local oscillations. We consider below the ZPL structure in Jahn-Teller systems with local oscillations in the case of a weak linear vibronic coupling. The results of the first two sections pertain also to the case of an interaction between a Jahn-Teller impurity center and optical vibrations of the crystal at negligibly small dispersion. The method of separating the effective mode that plays in this case the role of the local oscillation is described in[9].

The ZPL are investigated for impurity ions with cubic local symmetry for $A \to E$ and $A \to T$ transitions from the nondegenerate state A to the orbital doublet E or the triplet T (T_1, T_2). It is also assumed that the considered states are singlet in the spin, so that the problem is thus not made complicated by spin-orbit interaction effects.

In the Conclusion we consider certain consequences of the interaction with disperse crystal oscillations.

1. TRANSITION TO AN ORBITAL DOUBLET

The Hamiltonian of the electron-vibrational system will be written in the linear-harmonic approximation:

$$H(r, q) = H_e(r) + \sum_{\Gamma\gamma} V_{\Gamma\gamma}(r) q_{\Gamma\gamma} + H_{ph}(q), \tag{1}$$

where r and q are the configuration coordinates of the electrons and nuclei, $q_{\Gamma\gamma}$ are the normal coordinates and transform in accord with row γ of the irreducible representation Γ. The summation in (1) is over all the vibrational representations Γ and their rows γ, which are active in the JTE. Going over to the matrix representation in the basis of the electronic functions of the orbital doublet, and using the Wigner-Eckart theorem, we obtain the Hamiltonian of the Jahn-Teller system for the case of an orbital doublet in the form

$$H = H_0 + V,$$

where[3-5]

$$H_0 = \varepsilon_E \cdot 1 + \tfrac{1}{2}\hbar\omega(p_u^2 + p_v^2 + q_u^2 + q_v^2) \cdot 1, \tag{2}$$

$$V = B(q_u \sigma_x + q_v \sigma_y). \tag{3}$$

Here ε_E is the energy of the E level, p_γ and q_γ are the momenta and the normal coordinates of the degenerate E mode active in the JTE (the basis is chosen in standard fashion[10]; $u \sim 3z^2 - r^2$, $v \sim \sqrt{3}(x^2 - y^2)$ are the row indices of the E representation), ω is the oscillation frequency, B is the electron-vibrational interaction constant, 1 is a unit matrix, and σ_x and σ_y are the Pauli matrices in the basis $\psi_\pm = \mp(|u\rangle \pm i |v\rangle)/\sqrt{2}$ of the orbital doublet.

The Schrödinger equation with Hamiltonian (1), (2), does not admit of an analytic solution at an arbitrary coupling constant B, and reduces to a system of two coupled dynamic equations[3-5]. Subjecting the Hamiltonian (1) to a unitary transformation

$$\tilde{H} = e^{iS} H e^{-iS}, \quad S = -\frac{i}{\hbar^2\omega^2}[H_0, V], \tag{4}$$

we obtain, accurate to second order in the coupling constant,

$$\tilde{H} = H_0 + V^{(2)}, \quad V^{(2)} = \frac{1}{2\hbar^2\omega^2}[[H_0, V], V]. \tag{5}$$

Calculation of the commutators that enter in (5) yields

$$V^{(2)} = -\frac{B^2}{\hbar\omega}\left[1 + \frac{1}{2}\sigma_z(q_v p_u - q_u p_v)\right]. \tag{6}$$

Formula (6) was obtained by another method by Moffit and Thorson[11]. It makes it possible to find the energy levels which, as seen from (6), are characterized by the absolute value of the projection of the electron-vibrational angular momentum. The canonical transformation

$$Q_1 = \frac{1}{\sqrt{2}}(p_u + q_v), \quad Q_2 = \frac{1}{\sqrt{2}}(p_v + q_u),$$

$$P_1 = \frac{1}{\sqrt{2}}(p_u - q_v), \quad P_2 = \frac{1}{\sqrt{2}}(p_v - q_u) \tag{7}$$

reduces the Hamiltonian (5), (6) to the form

$$H = \varepsilon_E - \frac{B^2}{\hbar\omega} + \frac{1}{2}\left(\hbar\omega \cdot 1 - \frac{B^2}{\hbar\omega}\sigma_z\right)(P_1^2 + Q_1^2)$$
$$+ \frac{1}{2}\left(\hbar\omega \cdot 1 + \frac{B^2}{\hbar\omega}\sigma_z\right)(P_2^2 + Q_2^2), \tag{8}$$

which is more illustrative and is convenient for the investigation of ZPL. As seen from (8), the system of coupled dynamic equations corresponding to the Hamiltonian (1)—(3) split into two independent equations, owing the unitary and canonical transformations carried out in second order in the coupling constant. The corresponding potential surfaces are two identical elliptic paraboloids, turned through an angle $\pi/2$ relative to each other in the (Q_1, Q_2) plane. The states ψ_+ and ψ_- correspond now to new frequencies of the lattice vibrations, viz., the state ψ_- corresponds to the frequencies $\omega_{1,2}^{(-)} = \omega(1 \pm B^2/\hbar^2\omega^2)$, and the state ψ_+ to the frequencies $\omega_{1,2}^{(+)} = \omega(1 \mp B^2/\hbar^2\omega^2)$.

We write down the formfunction of the zero-phonon transition A → E in the form

$$K_{ZPL}(\Omega) = 2\,\mathrm{sh}^2\frac{\beta_0}{2}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\sum_{+,-}\exp[-\beta_0(n_1+n_2+1)]$$

$$\times |\langle\psi_A|d|\psi_{\pm}\rangle|^2\,\delta\Big[\hbar\Omega + \varepsilon_A + \hbar\omega_0(n_1+n_2+1) - \varepsilon_E \tag{9}$$
$$-\hbar\omega_1^{(\pm)}\Big(n_1+\frac{1}{2}\Big) - \hbar\omega_2^{(\pm)}\Big(n_2+\frac{1}{2}\Big) + \frac{B^2}{\hbar\omega}\Big],$$

where Ω is the frequency of the absorbed light, $\beta_0 = \hbar\omega_0/kT$, and ω_0 is the frequency of the E oscillations in the electronic ground state. In (9) we have neglected, for the sake of simplicity, the small deviation of the vibrational overlap integrals from unity. The integral intensity of the ZPL was normalized to unity. Introducing the notation

$$x = \Big(\hbar\Omega + \varepsilon_A - \varepsilon_E + \hbar\omega_0 - \hbar\omega + \frac{B^2}{\hbar\omega}\Big)\Big/\hbar\omega_0, \quad b = \frac{B^2}{\hbar^2\omega\omega_0},$$

$$\mu = 1 - \frac{\omega}{\omega_0}, \quad D = |\langle\psi_A|d|\psi_E\rangle|^2,$$

we rewrite (9) in the form

$$K_{ZPL}(x) = \frac{8D}{\hbar\omega_0}\,\mathrm{sh}^2\frac{\beta_0}{2}e^{-\beta_0}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}e^{-\beta_0(n_1+n_2)}\,\delta[x+(\mu-b)n_1+(\mu+b)n_2]. \tag{10}$$

It is seen from (10) that the ZPL is a superposition of two equidistant spectra with intervals $\Delta_{\pm} = |\mu \pm b|$ within each of them; their intensities are determined by the Boltzmann factors contained in (10). Thus, in the case of weak dynamic JTE, the ZPL acquire a fine structure.

At $\mu = 0$, when the frequencies ω and ω_0 coincide, we obtain

$$K_{ZPL}(x) = \frac{8D}{\hbar\omega|b|}\frac{\mathrm{sh}^2(\beta/2)e^{-\beta-\beta|x/b|}}{1-e^{-\beta/2}}\sum_{m=-\infty}^{\infty}\delta\Big(\frac{x}{b}-m\Big). \tag{11}$$

In real systems, the local oscillations interact anhar-

FIG. 1. ZPL structure for A → E transition and weak Jahn-Teller coupling with allowance for the frequency effect: $\mu = -0.08 \cdot 10^{-2}$, $(B/\hbar\omega)^2 = 0.49 \cdot 10^{-2}$, $\beta_0 = 0.26$.
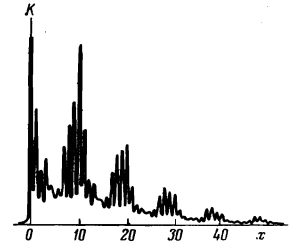
monically with the crystal modes, which have a continuous spectrum. Allowance for harmonicity of this type, as is well known[1], leads to two physical consequences: 1) a change by a finite number of times in the Debye-Waller factor (vanishing of the Bessel function I_0), 2) decay broadening $\bar{\gamma}$ of the electron-vibrational levels. The overall intensity of the ZPL for the considered problem is immaterial, and is assumed equal to unity. The decay broadening of the local-oscillation levels, as shown by Krivoglaz[1], can be taken into account phenomenologically by introducing the natural width $\bar{\gamma}$. If $\bar{\gamma} \gtrsim \Delta$, the fine structure cannot be resolved spectrally, and the effect in question is manifest by a broadening of the ZPL. In this case the line shape is described by the envelope of a "fence" of equidistant lines (11) and constitutes a symmetrical curve with exponentially decreasing wings. The ZPL half width $\delta\Omega = 2kT|b|\ln 2/\hbar\omega$ increases in this case linearly with temperature, in contrast, e.g., to Raman broadening, where $\delta\Omega \sim T^2$.[1]

At $\mu = b$ ($\Delta_- = 0$) we obtain

$$K_{ZPL}(x) = \frac{2D}{6\hbar\omega_0}\mathrm{sh}\Big(\frac{\beta_0}{2}\Big)\exp\Big(-\frac{\beta_0}{2} - \frac{\beta_0}{2}\Big|\frac{x}{\mu}\Big|\Big)\theta\Big(-\frac{x}{\mu}\Big)$$
$$\cdot\sum_{m=0}^{\infty}\delta\Big(\frac{x}{2\mu} + m\Big). \tag{12}$$

The distribution (12) is an equidistant fence whose envelope decreases exponentially to the right ($\mu < 0$) or to the left ($\mu > 0$), depending on the sign of the frequency effect.

At $\Delta_+ \gg \Delta_-$, each of the lines (12) constitutes a fence with spacing Δ_-; the line intensities within each series decrease like $\exp(-\beta x/\Delta_-)$. The cases of intermediate ratios of β and b yield more complicated ZPL pictures (see, e.g., Fig. 1). The damping constant $\bar{\gamma}$ in Figs. 1 and 2 is chosen such that the fine structure can be resolved. The scale along the ordinate axis is arbitrary, and only the relative intensity of the peaks is meaningful. The scale along the x axis is the period of the fine structure of the spectrum $(B/\hbar\omega)^2$.

2. TRANSITION TO ORBITAL TRIPLET

The modes active in the JTE for the orbital triplet (T_1, T_2) are the E and T_2 modes, the interaction with which in second order in the coupling constants yields additive contributions to the effective Hamiltonian. In this approximation, the interaction with the "adiabatic" E oscillations leads only to an equal shift of all the vibronic states (static Jahn-Teller effect). The dynamic Jahn-Teller effect takes place in the $T(t_2)$ problem (active T_2 oscillations), and the Hamiltonian of the interaction with the T_2 oscillations takes the form

$$V = C(q_{\xi}\tau_{\xi} + q_{\eta}\tau_{\eta} + q_{\zeta}\tau_{\zeta}), \tag{13}$$
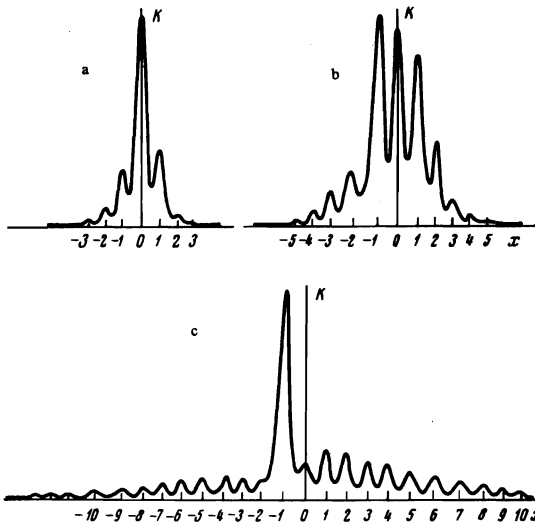
where C is the coupling constant with the trigonal

FIG. 2. ZPL structure for A → T transition and weak Jahn-Teller coupling in the absence of the frequency effect ($\mu = 0$); a) $\beta = 2.74$, b) $\beta = 1.45$, c) $\beta = 0.37$.

oscillations, and the matrices τ_γ in the basis of the electronic functions of the orbital triplet take the form

$$\tau_\xi = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}, \quad \tau_\eta = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \quad \tau_\zeta = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

(14)

With the aid of the unitary transformation (4) we obtain

$$V^{(2)} = \frac{1}{2} \frac{C^2}{\hbar\omega}(\mathbf{LS}-2),$$
(15)

where ω is the frequency of the trigonal oscillations in the excited electronic state, $\mathbf{L} = [\mathbf{qp}]$ is the angular-momentum operator of the three-dimensional oscillator, $\mathbf{q}$ and $\mathbf{p}$ are vectors with components q_ξ, q_η, q_ζ and p_ξ, p_η, p_ζ, and $\mathbf{S}$ is the vector of the effective spin $S = 1$ acting in the space of the basis functions of the orbital triplet:

$$S_\xi = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad S_\eta = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}, \quad S_\zeta = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (16)$$

so that $[\tau\tau] = -i\mathbf{S}$. The "spin-orbit interaction" (15) commutes with the total-angular-momentum operator $\mathbf{J} = \mathbf{L} + \mathbf{S}$, so that the energy levels of the system, defined by the expression[11]

$$E_{nLJ} = \hbar\omega\left(n + \frac{3}{2}\right) + \frac{1}{4}\frac{C^2}{\hbar\omega}[J(J+1) - L(L+1) - 6] + \varepsilon_T, \quad (17)$$

depend on the quantum number of the total angular momentum $J = L \pm 1$, L at $L \geq 1$ and $J = 1$ at $L = 0$, and the angular momentum of the vibrational system with specified n takes on the values $L = n$, $n - 2$, $n - 4,\ldots,1$ or 0.

The matrix element of the electron dipole moment, which enters in the expression for the transition probability, is calculated with the eigenfunctions $| nLSJM \rangle$ made up in accordance with the rule for the addition of angular momenta[12]. Since the perturbation operator acts in one (electronic) subsystem, the transition probability is calculated by the standard procedure of the theory of angular momenta[12] and leads to the appearance of a statistical weight $(2J + 1)$. The expression for the form function of the singlet-triplet transition is of the form

$$K_{\mathrm{ZPL}}(\Omega) = \frac{1}{3}\left(2\operatorname{sh}\frac{\beta_0}{2}\right)^3 \sum_{n=0}^{\infty}\sum_{J}\sum_{L}(2J+1)\exp(-\beta_0 n)\delta\Big\{\hbar\Omega + \varepsilon_A - \varepsilon_T$$

$$+ \hbar(\omega_0-\omega)\left(n + \frac{3}{2}\right) - \frac{1}{4}\frac{C^2}{\hbar\omega}[J(J+1)-L(L+1)-6]\Big\}. \quad (18)$$

Neglecting for simplicity the difference between the frequencies ω_0 and ω of the trigonal oscillations in the ground and excited states, we obtain after certain transformations

$$K_{\mathrm{ZPL}}(\Omega) = K_-(\Omega) + K_0'(\Omega) + K_0(\Omega) + K_+(\Omega); \quad (19)$$

$$K_-(\Omega) = \frac{N}{3}\sum_{n=1}^{\infty}(2n-1)e^{-n\beta}\delta\left[\hbar(\Omega-\Omega_0) + \frac{1}{2}\frac{C^2}{\hbar\omega}(n+1)\right],$$

$$K_0'(\Omega) = \frac{N}{3}[3 - e^{-\beta}]e^{-\beta}[1 - e^{-\beta}]^{-2}\delta\left[\hbar(\Omega-\Omega_0) + \frac{1}{2}\frac{C^2}{\hbar\omega}\right], \quad (20)$$

$$K_0(\Omega) = N\delta[\hbar(\Omega-\Omega_0)],$$

$$K_+(\Omega) = \frac{N}{3}\sum_{n=1}^{\infty}(2n+3)e^{-n\beta}\delta\left[\hbar(\Omega-\Omega_0) - \frac{1}{2}\frac{C^2}{\hbar\omega}n\right];$$

$$N = [1 - e^{-\beta}]^2[1 + e^{-\beta}]^{-1}, \quad \Omega_0 = \frac{\varepsilon_T - \varepsilon_A}{\hbar} - \frac{C^2}{\hbar^2\omega}.$$

Thus, the ZPL is an equidistance picket fence with spacing $C^2/2\hbar\omega$. The integral intensities of the four ZPL components (20) depend on the temperature in the following manner:

$$I_- = \frac{e^{-\beta}}{3}, \quad I_0' = \frac{e^{-\beta}(3 - e^{-\beta})}{3(1 + e^{-\beta})}, \quad I_0 = \frac{(1 - e^{-\beta})^2}{1 + e^{-\beta}},$$

$$I_+ = \frac{e^{-\beta}(5 - 3e^{-\beta})}{3(1 + e^{-\beta})}, \quad I_- + I_0' + I_0 + I_+ = 1. \quad (21)$$

At $T = 0$, as expected, the ZPL consists of only one narrow K_0 line of the $0 - 0$ transition. An increase of the temperature leads to a decrease of its intensity I_0 and to a "flareup" of the wings. From an analysis of the temperature behavior of the relative intensities I_0'/I_0 and $I_\pm^{(1)}/I_0$ of the spectral components closest to K_0' and K_0 from the left (K_-) and right (K_+) wings it follows that at $kT > \hbar\omega/\ln 2$ the intensity of the central peak K_0' prevails. In the region $kT \cong \hbar\omega/\ln 2$ the intensities I_0', I_0, and $I_+^{(1)}$ are approximately equal. Since their intensities at all temperatures greatly exceed $I_-^{(1)}$, the spectrum is asymmetrical. At $\hbar\omega/\ln(7/5)$ $< kT < \hbar\omega/\ln(9/7)$ the intensities of the lines of the left wing decrease monotonically with the number, whereas the right wing, starting with temperatures $kT \gtrsim \hbar\omega/\ln(7/5)$, has a maximum. Finally, at $kT > \hbar\omega/\ln(9/7)$, a maximum appears also in the left wing. The numbers of the corresponding lines are given by the integers closest to the expressions

$$n_{max}^{(-)} = \left|\frac{5e^{-\beta}-1}{2 - 2e^{-\beta}}\right|, \quad n_{max}^{(+)} = \left|\frac{3e^{-\beta}-1}{2 - 2e^{-\beta}}\right|. \quad (22)$$

Thus, three qualitatively different types of ZPL are possible: low-temperature (Fig. 2a), when the intensity of the $0 - 0$ transition I_0 predominates; intermediate (Fig. 2b), when the intensities I_0, I_0', and $I_+^{(1)}$ are comparable; and high-temperature, when the line K_0' is much higher than the other lines (Fig. 2c). In the case of extremely high temperatures, the intensity of the central peak I_0' behaves like $(2 - \beta^2)/6$, in which case the ZPL intensity is equally divided between K_0' and the wings K_- and K_+. The wing widths, however, increase like kT, so that their peak intensities decrease with increasing temperature. At high temperatures, it is appropriate to speak of an envelope of the ZPL wings, which in this case takes the form

$$K_{\mathrm{ZPL}}(x) = \frac{1}{3}\delta(x) + \frac{4}{3}\left(\frac{\hbar\omega\beta}{C}\right)^2|x|\exp\left\{-\frac{2\hbar\omega\beta}{C^2}|x|\right\},$$

$$x = \hbar\Omega - \left(\hbar\Omega_0 - \frac{1}{2}\frac{C^2}{\hbar\omega}\right). \tag{23}$$

Thus, in the case of high temperatures, too, the ZPL is again transformed into a narrow line, but its position is shifted by $C^2/2\hbar\omega$ towards the long-wave region relative to the frequency of the 0 – 0 transition, which comprises the entire ZPL at T = 0.

The frequency effect ($\omega_0 \neq \omega$) is taken into account in the same manner as for the A → E transition. The ZPL structure is in this case much more complicated. Without citing the corresponding results, we note only that a weak frequency effect causes broadening and asymmetry of the $K_0'(\Omega)$ line which is the most intense one at high temperatures.

3. ALLOWANCE FOR THE DISPERSION OF JAHN-TELLER OSCILLATIONS

The theory presented is based essentially on the assumed model of interaction with a single degenerate local mode. It is known, however, that allowance for the dispersion of the oscillations leads to qualitatively new consequences in the ZPL theory[1] and therefore calls for a special analysis. In the case of a strong dynamic JTE, the problem is extremely complicated[1], but in the considered case of weak coupling we can use the method of cumulative expansions. Within the framework of this approach, we lose information concerning the fine structure of the ZPL, resulting from the appearance of local and pseudolocal phonon states due to the electron-phonon interaction. This aspect of the problem is discussed by us in[9]. Without touching in this communication on the indicated subtle details, we shall discuss only the general features of ZPL in Jahn-Teller systems, neglecting the vibrational spectrum.

The transition to the crystal vibrations is effected by expanding the symmetrized displacements $q_{\Gamma\gamma}$ (Γ is the vibrational representation) in the normal lattice coordinates $Q_{\kappa\nu}$ (κ and ν are the wave vector and the polarization index):

$$q_{\Gamma\gamma} = \sum_{\kappa\nu} a_{\kappa\nu}(\Gamma\gamma)Q_{\kappa\nu}, \tag{24}$$

where the expansion coefficients $a_{\kappa\nu}(\Gamma\gamma)$ satisfy the orthogonality relation

$$\sum_{\Omega_\kappa} a_{\kappa\nu}(\Gamma\gamma)a_{\kappa\nu}(\Gamma'\gamma') = b_{\kappa\nu}(\Gamma)\delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'}. \tag{25}$$

The sign of the sum denotes here integration over the directions of κ. The operator of the Jahn-Teller interaction with the crystal modes takes the form

$$V = \sum_{\kappa\nu}\mathscr{V}_{\kappa\nu}Q_{\kappa\nu}, \quad \mathscr{V}_{\kappa\nu} = \sum_{\Gamma\gamma}V_{\Gamma\gamma}a_{\kappa\nu}(\Gamma\gamma). \tag{26}$$

The unitary transformation (4) transforms, in second order, the Hamiltonian to the form (5), where

$$V^{(2)} = -\sum_{\kappa\nu}\frac{1}{2\hbar\omega_{\kappa\nu}}\left\{\mathscr{V}_{\kappa\nu}^2 + i\sum_{\lambda\mu}P_{\kappa\nu}Q_{\lambda\mu}[\mathscr{V}_{\kappa\nu},\mathscr{V}_{\lambda\mu}]\right\}. \tag{27}$$

Thus, also in the case of a continuous oscillation spectrum, the unitary transformation (4), (5) transforms the electron-phonon interaction Hamiltonian into a form quadratic in the Bose operators, i.e., it reduces the problem of the weak dynamic JTE to the problem of the "frequency effect."

Performing now the calculations, we obtain for the E term

$$V^{(2)} = B^2\sum_{\kappa\nu}\frac{1}{\hbar\omega_{\kappa\nu}}\left\{\frac{1}{2}b_{\kappa\nu}(E)\cdot 1 - \sigma_z\sum_{\lambda\mu}P_{\kappa\nu}Q_{\lambda\mu}\right.$$
$$\left. \times [a_{\kappa\nu}(Eu)a_{\lambda\mu}(Ev) - a_{\kappa\nu}(Ev)a_{\lambda\mu}(Eu)]\right\}. \tag{28}$$

Analogously, using the commutation relation

$$[\tau_\gamma, \tau_{\gamma'}] = -i\varepsilon_{\gamma\gamma'\gamma''}S_{\gamma''}, \tag{29}$$

for the matrices (14) and (16), we obtain for the T term

$$V^{(2)} = -C^2\sum_{\kappa\nu}\frac{1}{\hbar\omega_{\kappa\nu}}\left\{b_{\kappa\nu}(T_2)\cdot 1 + \frac{1}{2}\sum_{\lambda\mu}P_{\kappa\nu}Q_{\lambda\mu}([\mathbf{a}_{\kappa\nu}\mathbf{a}_{\lambda\mu}]S)\right\}, \tag{30}$$

where $\mathbf{a}_{\kappa\nu}$ is a vector with components $a_{\kappa\nu}(T_{2\gamma})$.

The expressions for the shift and the broadening of the ZPL, with allowance for the electron-phonon interaction terms that are quadratic in the Bose operator, were obtained by Krivoglaz[1]. The temperature shift, which is the first term of the cumulative expansion of the generating function, takes the form

$$\Delta\Omega = \sum_{\kappa\nu}w_{\kappa\nu\kappa\nu}\text{cth}(\beta_{\kappa\nu}/2), \tag{31}$$

where $w_{\kappa\nu\kappa'\nu'}$ is the coefficient of the "frequency" term in the Hamiltonian of the electron-phonon interaction.

It is seen from (28), (30), and (31) that for both the A → E and the A → T transitions we have $\Delta\Omega = 0$. The absence of a ZPL temperature shift due to the interaction of the impurity electrons with degenerate modes, is an essential specific feature of the dynamic JTE in the case of weak coupling. Thus, the ZPL temperature shift observed or weak electron-phonon coupling is due only to the fully-symmetrical oscillations, and therefore the experimental data make it possible to separate their contribution in this case. Cumulants of higher order lead to a temperature broadening of the ZPL. The corresponding formulas were derived in[7,8].

4. CONCLUSION

Summarizing the results of the study of the ZPL for the weak dynamic JTE, notice must be taken of the following: In all the considered cases, the ZPL has a distinctive shape and a fine structure. In the absence of the frequency effect, the ZPL of the A → E and A → T transition constitutes an equidistant set of lines, the intervals between which do not vary with temperature and make it possible to assess the dynamic Jahn-Teller coupling. The ZPL of the A → E transition, in contrast to the A → T transition, is symmetrical, and its envelope decreases exponentially in the wings. Allowance for the frequency effect leads to a complication of the fine structure, since the n−n transition lines cease to become superimposed on one another. The line intensity is transferred in this case to the left ($\mu > 0$) or right ($\mu < 0$) wing, and this leads to an appreciable asymmetry of the ZPL. In the case of an extremely weak frequency effect $|\mu| \ll (B/\hbar\omega)^2$, each of the lines of the equidistant ZPL structure is slightly split; when account is taken of the natural line width, this leads to a broadening of the peaks of the equidistant structure. This broadening increases with the number of the peak, this being connected with the multiplicity of the splittings of the Jahn-Teller levels. At $|\mu| \gg (B/\hbar\omega)^2$ the ZPL constitutes a set of peaks due to the frequency effect, each of which is split by the dynamic JTE. Finally, at $|\mu| \sim (B/\hbar\omega)^2$ the ZPL structure is complicated and irregular, although in the particular case when the in-

tervals of the structure due to the frequency effect are multiples of the Jahn-Teller splittings, the spectrum again becomes equidistant.

All the discussed effects can be interpreted in other terms as a manifestation of the so-called electric modes[9,14], due in this case to the Jahn-Teller interaction, in the shape and structure of the ZPL.

A comparison of the theory with experiment is a separate problem, which is not discussed in this article. We note only that the condition for the appearance of a fine structure of the ZPL, namely the weak electron-phonon coupling, is practically always realized for transitions inside the 4f shell of rare-earth ions, and also for the intraconfiguration ($t_2^m e^n \rightarrow t_2^m e^n$) transitions in d shells of transition metals (e.g., the ruby R line—the transition ${}^4A_{2g}(t_2^3) \rightarrow {}^2E_g(t_2^3)$ in $Cr^{3+}:Al_2O_3$).

Attention should be called in this connection to the fact that identification of the components of the ZPL splitting to Stark components of electronic levels may not be correct. As follows from the results of the present article, this structure can have a Jahn-Teller nature and may not be due to the influence of the low-symmetry crystal fields. Lowering of the temperature leads, of course, to a vanishing of the Jahn-Teller structure, leaving in the limit at T = 0 only one line of the 0 → 0 transition, but in view of the high multiplicity of the degeneracy of the excited states, the intensities of the other lines decrease with decreasing temperature relatively slowly (see, e.g., Fig. 2a).

[1)]See in this connection the paper by Wagner [13].

[1]M. A. Krivoglaz and S. I. Pekar, Tr. instituta fiziki AN USSR, No. 4, 37 (1953); M. A. Krivoglaz, Zh. Eksp. Teor. Fiz. 48, 310 (1965) [Sov. Phys.-JETP 21, 204 (1965)].

[2]Yu. E. Perlin, Usp. Fiz. Nauk 80, 553 (1963) [Sov. Phys.-Uspekhi 6, 542 (1964)].

[3]I. B. Bersuker, Stroenie i svoĭstva koordinatsionnykh soedineniĭ (Structure and Properties of Coordination Compounds), Khimiya, 1971, Chap. IV.

[4]R. Englman, The Jahn-Teller Effect in Molecules and Crystals, Wiley-Interscience, 1972.

[5]A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Oxford, 1970.

[6]K. Nishikawa and R. Barrie, Canad. J. Phys., 41, 1135, 1823 (1963).

[7]K. V. Korsak and M. A. Krivoglaz, Fiz. Tverd. Tela 10, 2488 (1968) [Sov. Phys.-Solid State 10, 1952 (1969)].

[8]K. V. Korsak and M. A. Krivoglaz, Ukr. Fiz. Zh. 14, 373, 2019, 2030 (1969).

[9]B. G. Vekhter, V. Z. Polinger, Yu. B. Rozenfel'd, and B. S. Tsukerblat, ZhETF Pis. Red. 20, 84 (1974) [JETP Lett. 20, 36 (1974)].

[10]G. F. Koster, J. O. Dimmock, R. G. Wheller, and H. Statz, Properties of the Thirty-Two Point Groups, M.I.T. Press, Cambridge, Massachusetts, 1963.

[11]W. Moffitt and W. Thorson, Phys. Rev., 108, 1251 (1957).

[12]L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika, Nerelyativistskaya teoriya (Quantum Mechanics, Nonrelativistic Theory), Fizmatgiz (1969), Sec. 109 [Pergamon].

[13]M. Wagner, Zs. Phys., 256, 291, 1972. E. Sigmund and M. Wagner, Phys. Stat. Sol. (b), 57, 635 (1973).

[14]I. V. Levinson and É. I. Rashba, Usp. Fiz. Nauk 111, 683 (1973) [Sov. Phys.-Uspekhi 16, 892 (1974)].

Translated by J. G. Adashko

119