

OPTICAL BANDS IN PARAMAGNETIC CRYSTALS WITH DEGENERATE IMPURITY TERMS

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Broad electron-vibrational impurity light absorption and luminescence bands in ionic crystals containing paramagnetic local centers are investigated within the framework of the adiabatic approximation by the moment method. The effect of configurational instability of a crystal with degenerate impurity-electron levels (adiabatic potential splitting) on the optical spectrum pattern is investigated. It is shown that Jahn-Teller distortion of the nuclear configuration in only one electron state does not lead to splitting of the optical band. The theory predicts optical band splitting only in those cases when the same vibrations which are active in the Jahn-Teller effect remove the degeneracy of both electron states involved in the photo-transition. Detailed calculations of the band parameters are performed for ions of the iron group with a d^3 shell. Y- and U-bands in pink ruby are considered as an example.

INTRODUCTION

THE optical absorption and luminescence spectra of paramagnetic ions introduced into a crystal lattice contain, besides narrow lines (like the R-lines of ruby), broad bands as well, for example Y- and U-bands.^[1,2] The narrow lines correspond to phononless optical transitions, the theory of which has been intensively developed in recent years (see, for example^[3]). A theory of the wide electron-vibrational bands has been developed by Krivoglaz and Pekar^[4] (see also the review by Perlin^[5]). Calculation of the displacement of the equilibrium configurations of the nuclei during phototransitions permitted both the positions of the maxima and the half-widths of the optical bands to be explained. In this, nondegenerate electronic states were considered, although the conclusions of the theory in full measure pertain also to those cases when the nuclear displacements do not lift the electronic degeneracy (holosymmetric vibrations).^[6] (Krisstofel' also considered non-holosymmetric vibrations.)

In crystalline fields of high symmetry, impurity ions of the transition metals form orbitally degenerate Stark states. The interaction with lattice vibrations that lift the electronic degeneracy (non-holosymmetric vibrations which transform according to non-unitary representations of the point group of the local symmetry of the impurity center) is here found to be extremely important. Apart from the effect of the distortion of the equilibrium configurations of nuclei in different electronic

states, thoroughly investigated by Krivoglaz and Pekar,^[4] the interaction of the degenerate terms with the non-holosymmetric vibrations leads to a significant change in the shape of the crystal potential surface. The minimum of the adiabatic lattice potential corresponds to several energetically equivalent equilibrium configurations that have lower energy and symmetry with respect to the perturbed lattice (Jahn-Teller effect). This paper investigates those new features in the optical spectra of impure crystals introduced by these circumstances.

1. THE GENERATING FUNCTION OF THE OPTICAL TRANSITION BETWEEN DEGENERATE ELECTRONIC STATES

Let us consider an impurity center of small radius in an ionic crystal. We choose the Hamiltonian of the impurity-phonon system in the form

$$\hat{H} = \hat{H}_0(\mathbf{r}) + \hat{V}_c + \sum_{\lambda, \rho} \hat{H}(q_{\lambda\rho}) + \hat{H}_{int}. \quad (1)$$

Here $\hat{H}_0(\mathbf{r})$ is the Hamiltonian of the free ion; \hat{V}_c is the potential energy of the optical electrons of the impurity center in the electrostatic crystal field. Since the radii of the electronic states in the impurity center are assumed small, only the interactions with ions of the first coordination sphere shall be taken into account in what follows. The term \hat{H}_{int} represents the correction to this interaction associated with the displacement of the ions of the first coordination sphere from their equilibrium positions. Limiting our treatment to

a linear approximation for these displacements and expanding them in the normal vibrational modes of the crystal, we obtain the operator for the interaction of the impurity electrons with the lattice vibrations in the form

$$\hat{H}_{int} = \sum_{\alpha} V_{\alpha}(\mathbf{r}) Q_{\alpha}, \quad Q_{\alpha} = \sum_{\lambda, \rho} a_{\alpha\lambda}^{(\rho)} q_{\lambda\rho}, \quad (2)$$

where $V_{\alpha}(\mathbf{r})$ are functions of the coordinates of the electrons of the unfilled shell which transform according to the same irreducible representations of the point group of the local symmetry of the impurity center as do the normal displacements Q_{α} . Thus, in our model the electron-phonon interaction arises as a result of the modulation of the internal crystalline field by the thermal vibrations of the lattice. We consider the case when local frequencies are absent,¹⁾ and in accordance with this the summation in the expansion (2) is carried out only over the crystal vibrations. Both the acoustic and optical branches of the normal lattice vibrations are taken into account (λ is the wave vector, ρ the polarization index). Finally,

$$\hat{H}(q_{\lambda\rho}) = 1/2 (M\omega_{\lambda\rho}^2 q_{\lambda\rho}^2 + \hat{P}_{\lambda\rho}^2/M) \quad (3)$$

is the Hamiltonian of the free vibrations of the unperturbed crystal (the normal modes are normalized to the mass M of the whole crystal).

Following the adiabatic approximation scheme, we write the electronic equation

$$[\hat{H}_0(\mathbf{r}) + \hat{V}_c(\mathbf{r}) + \hat{H}_{int}(\mathbf{r}, q)]\psi(\mathbf{r}, q) = E(q)\psi(\mathbf{r}, q). \quad (4)$$

As an example that will bring out all the main aspects of the problem under discussion, let us consider triply degenerate levels of the T-type (T_{2g} and T_{1g}) of the d-shell of a paramagnetic ion in an octahedral field O_h . The electrons in the T-states interact with all the even lattice vibrations: the holosymmetrical—representation A_{1g} (normal displacement Q_1), the tetragonal— $E_g(Q_2, Q_3)$, and the trigonal— $T_{2g}(Q_4, Q_5, Q_6)$ ^[7] (the basis for Q_{α} is specified in Van Vleck's paper^[8]). We shall consider below the case of strongest interaction with the first two types of vibration, when the terms with Q_4, Q_5, Q_6 may be left out of the Hamiltonian (2).²⁾ Investigation of the secular equation

for T-levels shows that the correct zeroth-approximation wave functions $\psi_{\alpha}^{(0)}(T)$ corresponding to the operator $\hat{H}_{int}(\mathbf{r}, q)$ are linear combinations $\sum_j c_j^{\alpha} \psi_j^{(0)}(T)$, where the coefficients c_j^{α} do not depend on the normal coordinates $q_{\lambda\rho}$.^[10] The corresponding first-order corrections to the energy depend linearly on $q_{\lambda\rho}$:

$$\begin{aligned} E_1^{(1)} &= E^{(0)} + \sum_{\lambda, \rho} (\mu a_{1\lambda}^{(\rho)} \mp \sqrt{3}\tau a_{2\lambda}^{(\rho)} + \tau a_{3\lambda}^{(\rho)}) q_{\lambda\rho}, \\ E_2^{(1)} &= E^{(0)} + \sum_{\lambda, \rho} (\mu a_{1\lambda}^{(\rho)} \pm \sqrt{3}\tau a_{2\lambda}^{(\rho)} + \tau a_{3\lambda}^{(\rho)}) q_{\lambda\rho}, \\ E_3^{(1)} &= E^{(0)} + \sum_{\lambda, \rho} (\mu a_{1\lambda}^{(\rho)} - 2\tau a_{3\lambda}^{(\rho)}) q_{\lambda\rho}. \end{aligned} \quad (5)$$

The upper sign pertains to the level T_{2g} , the lower to T_{1g} ; $E^{(0)}$ is the eigenvalue of the Hamiltonian $\hat{H}_0(\mathbf{r}) + \hat{V}_c$; μ and τ are matrix elements that depend on the choice of model and the electronic structure of the center (they are given in the Appendix for the Cr^{+3} ion in ruby).

Following Longuet-Higgins,^[11] we seek the eigenfunctions of the Hamiltonian (1) in the form of linear combinations

$$\Psi = \sum_{\alpha=1}^3 \psi_{\alpha}(\mathbf{r}, q) F_{\alpha}(q), \quad (6)$$

where $\psi_{\alpha}(\mathbf{r}, q)$ are the exact solutions of Eq. (4), and the vibrational components $F_{\alpha}(q)$ of the total wave function satisfy the system of equations

$$\begin{aligned} [E_{\alpha}^{(1)}(q) + \sum_{\lambda, \rho} \hat{H}(q_{\lambda\rho})] F_{\alpha}(q) \\ + \frac{1}{M} \sum_{\lambda, \rho} \sum_{\beta \neq \alpha} W_{\lambda\rho}^{\alpha\beta} \hat{P}_{\lambda\rho} F_{\beta}(q) = \mathcal{E} F_{\alpha}(q), \end{aligned} \quad (7)$$

$$W_{\lambda\rho}^{\alpha\beta} = \int \psi_{\alpha} \hat{P}_{\lambda\rho} \psi_{\beta} d\mathbf{r} + \frac{1}{2} \int \psi_{\alpha} \hat{P}_{\lambda\rho}^2 \psi_{\beta} d\mathbf{r} \quad (8)$$

(\mathcal{E} is the total energy of the electronic-vibrational system).

The emergence of a system of coupled equations for the vibrational functions $F_{\alpha}(q)$ is an essential feature of degenerate electronic states.^[11,12] The solution of such a system in general form is scarcely feasible. However, in the case of T-terms, the terms in the equations that interconnect the functions $F_{\alpha}(q)$ are small in the sense of the usual non-adiabaticity that arises in the solution of the electronic-vibrational problem for nondegenerate states (there is no "internal nonadiabaticity," i.e., there are correct electronic functions of the

¹⁾They could easily be taken into account in the scheme under consideration.

²⁾Detailed calculations show that this case is realized, for example, in the case of the Cr^{+3} ion in ruby^[9,10] (see also the third footnote).

zeroth approximation that are independent of the phonon coordinates $q_{\lambda\rho}$ ³⁾.

Thus, if a given degenerate T-type level is sufficiently far from all remaining levels of the appropriate symmetry ($\Delta E \gg \hbar\omega_D$, where ω_D is the Debye frequency), then the system (7) reduces to three equations, the solutions of which describe the vibrational motion of the nuclei in the harmonic approximation close to each of the three minima of the adiabatic potential of a tetragonally distorted crystal (Jahn-Teller effect).

The total wave functions of a crystal with an impurity center may in this approximation be written in the form

$$\Psi_\alpha(T) = \psi_\alpha(T) \prod_{\lambda, \rho} \Phi_{N_{\lambda\rho}}(q_{\lambda\rho} - q_{\lambda\alpha}^{(\rho)}(T)), \quad (9)$$

where $q_{\lambda\alpha}^{(\rho)}(T)$ are the equilibrium values of the normal coordinates corresponding to the α -th minimum of the adiabatic potential, $\Phi_N(q)$ are the wave functions of a harmonic oscillator. For orbitally nondegenerate states (type A) solutions of the form of (9) remain, and the equilibrium coordinates of only the holosymmetric vibrations are shifted.

The probability of an optical transition between levels Γ_1 and Γ_2 with the participation of a photon of frequency Ω is written in the form

$$W(\Gamma_1 \rightarrow \Gamma_2) = \sum_{\alpha, \beta} M_{\alpha\beta}(\Gamma_1 \rightarrow \Gamma_2) \text{Av}(\dots N_{\lambda\rho} \dots) \times \sum_{\dots N_{\lambda\rho} \dots} \left[\prod_{\lambda\rho} (S_{N_{\lambda\rho} N_{\lambda\rho}'}^{\alpha\beta})^2 \right] \cdot \delta[\hbar(\Omega_{21} - \Omega) + \sum_{\lambda\rho} \hbar\omega_{\lambda\rho} (N_{\lambda\rho}' - N_{\lambda\rho})], \quad (10)$$

$$S_{N_{\lambda\rho} N_{\lambda\rho}'}^{\alpha\beta} = \int_{-\infty}^{\infty} \Phi_{N_{\lambda\rho}}(q_{\lambda\rho} - q_{\lambda\alpha}^{(\rho)}(\Gamma_1)) \Phi_{N_{\lambda\rho}'}(q_{\lambda\rho} - q_{\lambda\beta}^{(\rho)}(\Gamma_2)) dq_{\lambda\rho}, \quad (11)$$

where Ω_{21} is the frequency of a purely electronic transition, the operation $\text{Av}(\dots N_{\lambda\rho} \dots)$ means a

³⁾Such "internal nonadiabaticity" for T-states arises on taking account of the weak interaction with the trigonal vibrations and leads to an inversion splitting δ of the electronic-vibrational levels.^[12] Henceforth, we shall assume that the criterion for the smallness^[12] of the inversion splitting is fulfilled for the electronic-vibrational states actually involved in a phototransition, which in turn guarantees the possibility of applying the adiabatic method for the description of these states. In this case, taking account of the inversion splitting (δ of the order of several inverse centimeters) in the theory of wide ($\approx 10^3 \text{ cm}^{-1}$) optical bands yields only insignificant corrections.

statistical average over the occupation numbers of the phonon field in the initial state, the primes indicate the occupation numbers of the normal oscillators in the final state, and $M_{\alpha\beta}$ is the electronic part of the probability. In the example under consideration the prohibition by parity considerations is removed from transitions within the d-shell by a static asymmetric field of symmetry T_{1u} .^[2] In contradistinction to cases in which the transition is allowed by odd lattice vibrations, the electron matrix element may be constructed within the Condon approximation, i.e., by ignoring the dependence of $M_{\alpha\beta}$ on $q_{\lambda\rho}$.

With the help of the methods set forth in Perlin's review article,^[5] it is possible to obtain the frequency distribution of the optical transition probability from Eq. (10):

$$J(\Omega) = \sum_{\alpha, \beta} M_{\alpha\beta} \int_{-\infty}^{\infty} \exp[i(\Omega_{21} - \Omega)t] J_{\alpha\beta}(t) dt, \quad (12)$$

where

$$J_{\alpha\beta}(t) = \exp \left\{ -\frac{1}{2M\hbar} \sum_{\lambda, \rho} \omega_{\lambda\rho}^{-3} \Delta_{\lambda\alpha\beta}^{(\rho)} \left[\text{cth} \frac{\beta_{\lambda\rho}}{2} - \frac{\cos(\omega_{\lambda\rho}t - i\beta_{\lambda\rho}/2)}{\text{sh}(\beta_{\lambda\rho}/2)} \right] \right\}, \quad (13)^*$$

$$\beta = \hbar\omega/kT, \quad \Delta_{\lambda\alpha\beta}^{(\rho)} = M^2 \omega_{\lambda\rho}^4 [q_{\lambda\alpha}^{(\rho)}(\Gamma_1) - q_{\lambda\beta}^{(\rho)}(\Gamma_2)]^2. \quad (14)$$

First we shall consider the simpler case of a transition with the participation of one orbital nondegenerate state. In this case

$$\begin{aligned} \Delta_{\lambda 11}^{(\rho)} &= [(\mu_1 - \mu_2) a_{1\lambda}^{(\rho)} \mp \sqrt{3} \tau a_{2\lambda}^{(\rho)} + \tau a_{3\lambda}^{(\rho)}]^2, \\ \Delta_{\lambda 21}^{(\rho)} &= [(\mu_1 - \mu_2) a_{1\lambda}^{(\rho)} \pm \sqrt{3} \tau a_{2\lambda}^{(\rho)} + \tau a_{3\lambda}^{(\rho)}]^2, \\ \Delta_{\lambda 31}^{(\rho)} &= [(\mu_1 - \mu_2) a_{1\lambda}^{(\rho)} - 2\tau a_{3\lambda}^{(\rho)}]^2. \end{aligned} \quad (15)$$

(Upper sign for transitions of the type $A \rightleftharpoons T_2$, the lower for $A \rightleftharpoons T_1$.) Assuming that the symmetry of the crystal permits one approximately to divide the optical and acoustic vibrations into longitudinal ($\rho = 1$) and transverse ($\rho = t$) types and using the symbol $\gamma_{\lambda\alpha\beta}^{(\rho)}$ to represent the result of integrating the quantities $\Delta_{\lambda\alpha\beta}^{(\rho)}$ over the directions of polarization of the optical and acoustic vibrations, we obtain

$$\gamma_{\lambda 11}^{(\rho)} = \gamma_{\lambda 21}^{(\rho)} = \gamma_{\lambda 31}^{(\rho)} \equiv \gamma_{\lambda}^{(\rho)}. \quad (16)$$

Thus, in spite of the Jahn-Teller splitting of the adiabatic potential of one of the states between which a transition takes place, the absorption (luminescence) band is found not to be split, since $J_{\alpha\beta} \equiv J$. This circumstance is illustrated in Fig. 1a

*cth \equiv coth, sh \equiv sinh.

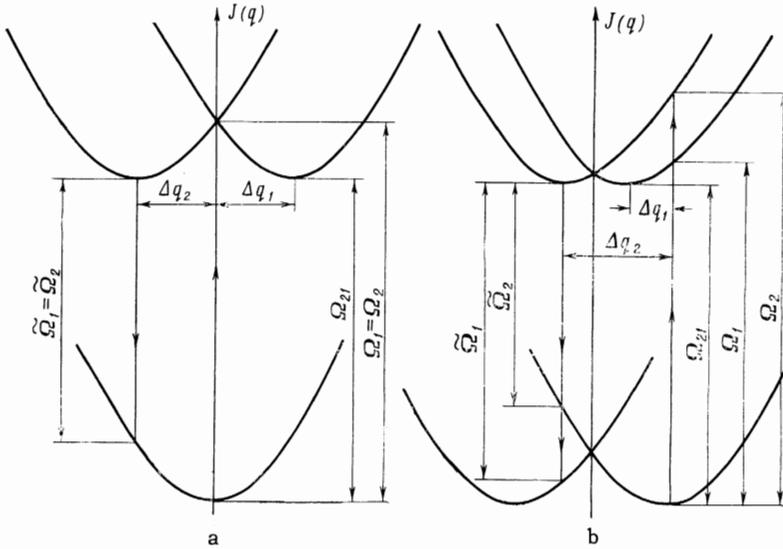


FIG. 1. One-coordinate model of configuration curves ($J(q)$ is the adiabatic potential; Ω_1 , Ω_2 , and $\tilde{\Omega}_1$, $\tilde{\Omega}_2$ are the maxima of the absorption and luminescence bands; Ω_{21} is the frequency of a purely electronic (phononless) transition): a—Jahn-Teller splitting of only one electronic term does not lead to splitting of the optical band: $\Delta q_1 = \Delta q_2$, $\Omega_1 = \Omega_2$, $\tilde{\Omega}_1 = \tilde{\Omega}_2$; b—when there is a Jahn-Teller effect in both electronic states the band of impurity light absorption and luminescence is split: $\Delta q_1 \neq \Delta q_2$, $\Omega_1 \neq \Omega_2$, $\tilde{\Omega}_1 \neq \tilde{\Omega}_2$.

and is discussed in more detail below.

Calculation of the quantities (16) gives

$$\gamma_{\lambda}^{(\rho)} = 4\pi[(\mu_1 - \mu_2)^2 a_{\rho}(\xi_{\lambda}) + 4\tau^2 b_{\rho}(\xi_{\lambda})], \quad (17)$$

where $\xi_{\lambda} = R\lambda$, R being the half-diagonal of the octahedron that forms the first coordination sphere,

$$a_l(\xi) = \frac{1}{8} \sqrt{\frac{\pi}{\xi}} \left[J_{3/2}(2\xi) + \frac{1}{2\xi} J_{5/2}(2\xi) - J_{1/2}(2\xi) + 4 \cdot 2^{1/4} J_{3/2}(\sqrt{2}\xi) + \frac{4}{3} \sqrt{\frac{\xi}{\pi}} \right],$$

$$b_l(\xi) = \frac{1}{8} \sqrt{\frac{\pi}{\xi}} \left[J_{3/2}(2\xi) + \frac{1}{2\xi} J_{5/2}(2\xi) - J_{1/2}(2\xi) - 2 \cdot 2^{1/4} J_{3/2}(\sqrt{2}\xi) + \frac{4}{3} \sqrt{\frac{\xi}{\pi}} \right],$$

$$a_t(\xi) = \frac{1}{4} \left(\frac{\pi}{2\sqrt{2}\xi} \right)^{1/2} \left[\frac{1}{2^{1/4}\xi} J_{3/2}(2\xi) - \frac{3}{\sqrt{2}\xi} J_{5/2}(\sqrt{2}\xi) + J_{1/2}(\sqrt{2}\xi) - J_{3/2}(\sqrt{2}\xi) + \frac{2}{3} \left(\frac{2\sqrt{2}\xi}{\pi} \right)^{1/2} \right],$$

$$b_t(\xi) = \frac{1}{8} \left(\frac{\pi}{2\sqrt{2}\xi} \right)^{1/2} \left[-\frac{(2\sqrt{2})^{1/2}}{\xi} J_{3/2}(2\xi) + \frac{3}{\sqrt{2}\xi} J_{5/2}(\sqrt{2}\xi) - J_{1/2}(\sqrt{2}\xi) + J_{3/2}(\sqrt{2}\xi) + \frac{4}{3} \left(\frac{2\sqrt{2}\xi}{\pi} \right)^{1/2} \right] \quad (18)$$

(J_{ν} is a Bessel function).

Thus, we obtain for the generating function of the optical transition

$$J(t) = \exp \left\{ -\frac{1}{2M\hbar} \sum_{\lambda} \sum_{\rho=l,t} \omega_{\lambda\rho} \gamma_{\lambda}^{(\rho)} \left[\operatorname{cth} \frac{\beta_{\lambda\rho}}{2} - \frac{\cos(\omega_{\lambda\rho} t - i\beta_{\lambda\rho}/2)}{\operatorname{sh}(\beta_{\lambda\rho}/2)} \right] \right\}. \quad (19)$$

We now consider the more complicated case of a transition of the type $T \rightleftharpoons T$ (both states orbitally degenerate). In this case we have nine quantities $\Delta_{\lambda\alpha\beta}^{(\rho)}$ (instead of three, as in Eq. (15)): $\alpha, \beta = 1, 2, 3$. Integration over the directions of propagation of the optical and acoustic phonons leads to two types of ‘heat-release constants’ $\gamma_{\lambda n}^{(\rho)}$:

$$\gamma_{\lambda 1}^{(\rho)} = 4\pi[(\mu_1 - \mu_2)^2 a_{\rho}(\xi_{\lambda}) + 4(\tau_1^2 + \tau_2^2 + \tau_1\tau_2) b_{\rho}(\xi_{\lambda})], \quad (20)$$

$$\gamma_{\lambda 2}^{(\rho)} = 4\pi[(\mu_1 - \mu_2)^2 a_{\rho}(\xi_{\lambda}) + 4(\tau_1^2 + \tau_2^2 - 2\tau_1\tau_2) b_{\rho}(\xi_{\lambda})], \quad (21)$$

which permits rewriting the spectral function (12) of the optical transition in the form of a sum of two terms:

$$J(\Omega) = M_1 \int_{-\infty}^{\infty} \exp[i(\Omega_{21} - \Omega)t] J_1(t) dt + M_2 \int_{-\infty}^{\infty} \exp[i(\Omega_{21} - \Omega)t] J_2(t) dt. \quad (22)$$

where the significance of the introduced quantities M_1 and M_2 becomes obvious by comparing Eqs. (22) and (12), and the subscripts on the functions $J_n(t)$ indicate the presence of two heat evolution constants (20) and (21). The latter fact is associated with the Jahn-Teller splitting of the adiabatic potentials of the crystal in both considered electron states (the presence of three equivalent minima in each) and leads, as can be seen from Eq. (22), to a doublet splitting of the impurity light absorption and luminescence bands. A schematic representation of a like splitting in the one-coordinate model of configuration curves is given in Fig. 1b.

2. OPTICAL BAND PARAMETERS

The formulas obtained above and the qualitative conclusions drawn therefrom do not depend on the choice of a model for the local center and are general in character. In order to obtain more detailed information about the band shapes it is necessary to complete the integration over t in formulas of the type of Eq. (12), which, as is known, can be done exactly only when dispersion of the phonon frequencies is neglected.^[5] Hence, for the calculation of the band parameters we shall make use of the method of moments.^[5] For each ($n = 1, 2$) component of the complex band (22) of a transition of the type $T \rightleftharpoons T$ one obtains⁴⁾

$$\bar{\Omega}_n = -\frac{1}{2M\hbar} \sum_{\lambda} \sum_{\rho=l,t} \omega_{\lambda\rho}^{-2} \gamma_{\lambda n}^{(0)}, \tag{23}$$

$$\overline{(\Omega - \bar{\Omega})^2} = \frac{1}{2M\hbar} \sum_{\lambda} \sum_{\rho=l,t} \omega_{\lambda\rho}^{-4} \gamma_{\lambda n}^{(0)} \text{cth} \frac{\beta_{\lambda\rho}}{2}, \tag{24}$$

$$\overline{(\Omega - \bar{\Omega})^3} = -\frac{1}{2M\hbar} \sum_{\lambda} \sum_{\rho=l,t} \gamma_{\lambda n}^{(0)}. \tag{25}$$

To make a quantitative comparison of theory with experiment we carried out calculations according to Eqs. (23)–(25) using the point model of the crystalline field with an effective charge e^* on the ions of the first coordination sphere. The optical vibrations were taken into account on the basis of the Einstein model ($\omega_{\lambda\rho} = \omega_{0\rho}$), the acoustic ones on the Debye model ($\omega_{\lambda\rho} = v_{\rho}\lambda$). It is possible in this approximation to calculate exactly the integrals in (23), (25), and in the limiting case of low temperatures even in (24), after which we obtain (we give only the simpler formulas for transitions of the type $A \rightleftharpoons T$):

$$\bar{\Omega} = -\frac{9(Dq)^2}{4\pi^2 d\hbar R^3 v_l^2} [(\mu_{01} - \mu_{02})^2 \Lambda_1 + 4\tau_0^2 \Lambda_2], \tag{26}$$

$$\overline{(\Omega - \bar{\Omega})^2} = \frac{9(Dq)^2}{8\pi^2 d\hbar R^4 v_l} [(\mu_{01} - \mu_{02})^2 \Lambda_3 + 4\tau_0^2 \Lambda_4], \tag{27}$$

$$\overline{(\Omega - \bar{\Omega})^3} = -\frac{9(Dq)^2(1+z)}{16\pi^2 d\hbar R^5} \Lambda_5 [(\mu_{01} - \mu_{02})^2 + 4\tau_0^2], \tag{28}$$

where $Dq = ee^*r^4/6R^5$ is the parameter of the point model of the crystalline field, d is the density of the crystal, and z is the number of branches of the longitudinal optical vibrations of the crystal; dimensionless matrix elements $\mu_0 = \mu R^6/ee^*r^4$, etc., have been introduced. The quantities Λ_i are com-

plex functions of the crystal parameters and are set forth in the Appendix.

The parameters of the components of the doublet and belonging to the transition of type $T \rightleftharpoons T$ are obtained by replacing in each of the expressions (26)–(28) the quantities τ_0^2 respectively by $\tau_{01}^2 + \tau_{02}^2 + \tau_{01}\tau_{02}$ and $\tau_{01}^2 + \tau_{02}^2 - 2\tau_{01}\tau_{02}$. The bands formed in this way are shifted differently from the frequency of the phononless peak and have different half widths (the phononless line, of course, remains unsplit because of the energetic equivalence of the minima of the adiabatic potential). Since both bands correspond to the same frequency of the phononless line, the separation between their maxima in absorption δ_{12} and luminescence $\tilde{\delta}_{12}$ is the same:

$$\delta_{12} = \tilde{\delta}_{12} = \frac{27(Dq)^2 \tau_{01} \tau_{02}}{\tau^2 d\hbar R^3 v_l^2} \Lambda_2. \tag{29}$$

This is the essential difference in the splitting of the optical bands due to the Jahn-Teller effect from the splitting arising from the presence of a static crystalline field of low symmetry. In the latter case, which is shown schematically in Fig. 2, both electronic terms are also split, and the absorption and luminescence are associated with different electronic levels; however, there would be little chance that the frequencies Δ and $\tilde{\Delta}$ would be the same (unlike Eq. (29)).

3. DISCUSSION. COMPARISON OF THEORY WITH EXPERIMENT

Thus, a rigorous calculation based on the adiabatic approximation shows that the Jahn-Teller splitting of the adiabatic potentials does not always lead to a splitting of the optical bands. This splitting can be observed in spectra only when both electronic states interact with the same crystal vibrations that are active in the Jahn-Teller ef-

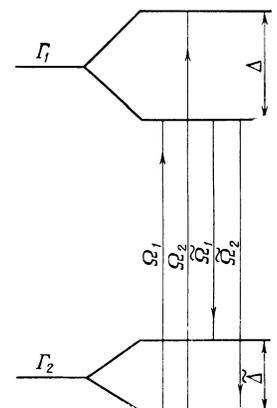


FIG. 2. Splitting of optical bands by crystalline fields of low symmetry.

⁴⁾The signs in (23), (25) correspond to a radiative transition.

fect.⁵⁾ This circumstance may be qualitatively understood on the basis of the Franck-Condon principle and the model of configuration curves. In the case of Fig. 1b, to any frozen equilibrium configuration of the initial electronic state there correspond two non-coincident final electronic states, which also leads to a doublet splitting of the optical bands.

When the Jahn-Teller effect occurs only in one of the electronic states participating in the transition (e.g., the excited one), as was shown above in the example of the $A \rightleftharpoons T$ transition, the optical band is not split, since the non-coincident excited state remains degenerate (coincidence, i.e., vibrational relaxation, leads to removal of the degeneracy); see Fig. 1a and Kristofel'.^[6]

Failure to take this circumstance into account is a source of the errors sometimes encountered in the interpretation of optical spectra. In particular, the attempt of Sorokin, Stevenson, et al.^[15] to explain the appearance of a double red band in the $4f \rightarrow 5d$ spectrum of $\text{SrF}_2 : \text{Sm}^{2+}$ by the presence of a Jahn-Teller effect in the excited $5d$ -state seems groundless to us. Another example is the observed splitting in the ${}^2T_{2g} \rightarrow {}^2E_g$ transition in $\text{Ti}(\text{H}_2\text{O})_6^{3+}$.^[16] Since both states undergo Jahn-Teller distortion,⁶⁾ the appearance of a double band agrees with the theory expounded above, whereas in^[17] it is attributed to a Jahn-Teller effect in only the excited state.

A doublet splitting of optical bands corresponding to $T \rightleftharpoons T$ transitions as predicted by this theory has apparently been observed by Low^[18] in the spectrum of $\text{MgO} : \text{Co}^{2+}$. The band in the $6000\text{--}7000 \text{ \AA}$ region, associated with the transition ${}^4T_{1g}({}^4F) \rightarrow {}^4T_{1g}({}^4P)$, can be resolved into two peaks.

A good confirmation of the qualitative conclusions of the theory is also furnished by the absence of splitting of the Y- and U-bands of ruby which arise as a result of the transition from the singlet ground state to the excited triplets ${}^4T_{1g}$ and ${}^4T_{2g}$, which undergo, as our calculations show, a strong Jahn-Teller splitting.

A comparison of the quantitative results of the theory with experiment was carried out in the example of calculating the bands of the most inves-

tigated crystal $\text{Al}_2\text{O}_3 : \text{Cr}^{3+}$ (ruby). The wave functions $\psi(A_{2g})$ and $\psi(T_{2g})$ have been given by Finkelstein and Van Vleck^[19]; the functions $\psi(T_{1g})$, according to Low,^[20] are mixtures of 4F - and 4P -states (45% 4F + 50% 4P). The matrix elements μ and τ needed for the calculation by Eq. (27) are set forth in the Appendix.

Using the same values for the crystal parameters as in^[10], we obtained 0.32 and 0.35 eV for the halfwidths of the green and blue bands of ruby, respectively. Experimentally, these quantities are 0.35 and 0.4 eV.^[1] It follows that our theory is capable of giving not only correct qualitative conclusions but also quantitative agreement with experiment.

The authors thank Yu. E. Perlin for valuable advice and a discussion of the work, and also I. B. Bersuker and B. G. Vekhter for a helpful discussion.

APPENDIX

The quantities Λ_i appearing in Eqs. (26)–(28) have the form

$$\Lambda_1 = G_1 - \sqrt{2} G_2 + 2\eta^2 \left(G_3 + \frac{1}{\sqrt{2}} G_2 \right) + \frac{zv_l^2}{4R^2\omega_{0l}^2} [L_1 - 4\sqrt{2}L_2 + 2\xi(L_3 + 2\sqrt{2}L_2)],$$

$$\Lambda_2 = G_1 + \frac{1}{\sqrt{2}} G_2 + 2\eta^2 \left(G_3 - \frac{1}{2\sqrt{2}} G_2 \right) + \frac{zv_l^2}{4R^2\omega_{0l}^2} [L_1 + 2\sqrt{2}L_2 + 2\xi^2(L_3 - \sqrt{2}L_2)],$$

$$\Lambda_3 = \Theta_1 - 4\Theta_2 + 2\eta(\Theta_3 + 2\Theta_2) + \frac{zv_l}{2\omega_{0l}R} [L_1 - 4\sqrt{2}L_2 + 2\xi(L_3 + 2\sqrt{2}L_2)],$$

$$\Lambda_4 = \Theta_1 + 2\sqrt{2}\Theta^2 + 2\eta(\Theta_3 - \Theta_2) + \frac{zv_l}{2\omega_{0l}R} [L_1 + 2\sqrt{2}L_2 + 2\xi(L_3 - \sqrt{2}L_2)],$$

$$\Lambda_5 = L_1 + 2L_3,$$

where $\eta = v_l/v_t$, $\xi = \omega_{0l}/\omega_{0t}$, and

$$G_1 = -\frac{\sin 2\xi_D}{2\xi_D^2} + \frac{\cos 2\xi_D}{2\xi_D} + \frac{2}{3}\xi_D,$$

$$G_2 = \frac{3 \sin \sqrt{2}\xi_D}{2\xi_D^2} - \frac{3 \cos \sqrt{2}\xi_D}{\sqrt{2}\xi_D} - \text{Si}(\sqrt{2}\xi_D),$$

$$G_3 = \frac{\sin 2\xi_D}{4\xi_D^2} - \frac{\cos 2\xi_D}{4\xi_D} - \frac{1}{2}\text{Si}(2\xi_D) + \frac{2}{3}\xi_D;$$

$$L_1 = -3 \sin 2\xi_D + 2\xi_D \cos 2\xi_D + 2 \text{Si}(2\xi_D) + \frac{8}{9}\xi_D^3,$$

$$L_2 = 4 \sin \sqrt{2}\xi_D - \sqrt{2}\xi_D \cos \sqrt{2}\xi_D - 3 \text{Si}(\sqrt{2}\xi_D),$$

⁵⁾The optical spectra of complexes with degenerate terms have been investigated by Vekhter.^[13] We mention also the work of Vinetskiĭ, Deĭgen, and Moroz,^[14] in which the spectrum of a color center with mirror symmetry is discussed.

⁶⁾The E_g -state leads to the appearance of three deep tetragonal minima.^[12,17]

$$L_3 = \sin 2\zeta_D - \text{Si}(2\zeta_D) + {}^8/9\zeta_D^3;$$

$$\Theta_1 = -\frac{\sin 2\zeta_D}{\zeta_D} + \cos 2\zeta_D + \frac{2}{3}\zeta_D^2 + 1,$$

$$\Theta_2 = \frac{3 \sin \sqrt{2}\zeta_D}{\sqrt{2}\zeta_D} - \cos \sqrt{2}\zeta_D - 2,$$

$$\Theta_3 = \frac{\sin 2\zeta_D}{2\zeta_D} + \frac{2}{3}\zeta_D^2 - 4;$$

the quantity $\zeta_D = R\lambda_D$, where λ is the Debye wave vector.

If we hold to Malkin's enumeration of the wave functions,^[9] then

$$\mu(A) = \langle \psi(A) | V_1(\mathbf{r}) | \psi(A) \rangle,$$

$$\mu(T) = \langle \psi_\alpha(T) | V_1(\mathbf{r}) | \psi_\alpha(T) \rangle,$$

$$\tau = \langle \psi_I(T) | V_3(\mathbf{r}) | \psi_I(T) \rangle = \langle \psi_{II}(T) | V_3(\mathbf{r}) | \psi_{II}(T) \rangle$$

$$= -\frac{1}{2} \langle \psi_{III}(T) | V_3(\mathbf{r}) | \psi_{III}(T) \rangle$$

$$= \mp 3^{-1/2} \langle \psi_I(T) | V_2(\mathbf{r}) | \psi_{III}(T) \rangle,$$

where the upper sign corresponds to $T = T_{2g}$, the lower to $T = T_{1g}$. The result of the calculation is

$$\mu_0(T_{2g}) = \frac{5}{3\sqrt{6}}, \quad \tau_0(T_{2g}) = -\frac{25}{12\sqrt{3}}, \quad \mu_0(A_{2g}) = \frac{10}{\sqrt{6}}$$

$$\mu_0(T_{1g}) = -\frac{1}{\sqrt{6}} \left(5p_1^2 + \frac{20}{3}p_1p_2 \right);$$

$$\tau_0(T_{1g}) = \frac{p_1^2}{7\sqrt{3}} \left(-\frac{18}{5} \frac{R^2 r^2}{r^4} + \frac{25}{4} \right) + \frac{9p_2^2}{5\sqrt{3}} \frac{R^2 r^2}{r^4}$$

$$+ \frac{p_1p_2}{7\sqrt{3}} \left(-\frac{108}{5} \frac{R^2 r^2}{r^4} + \frac{25}{3} \right);$$

p_1 and p_2 are the coefficients of the superposition of the 4F - and 4P -states in the crystalline field (in our case, $p_1 \approx \sqrt{0.45}$, $p_2 \approx \sqrt{0.50}$).

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