Jahn–Teller effect for T terms

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The problem of the five-dimensional nuclear adiabatic potential surface shape is solved for a polyatomic system with an orbital degenerate electronic T term by taking into account both the linear and the main second-order terms of vibronic coupling to all the active (e and t_2) vibrations. It is shown that the second-order terms have an appreciable effect on the surface shape obtained earlier in the linear approximation. In particular, a new orthorhombic type of absolute minima occurs, in which the nuclear motion is localized. In addition, twelvefold extrema occur. Some physical effects are considered: 1) tunnel splitting due to transitions between the six equivalent orthorhombic minima states, 2) vibronic suppression of electron operator matrix elements, which is illustrated in the examples of spin-orbit and Zeeman splittings, and 3) structural phase transitions in crystals containing the Jahn–Teller centers under consideration. Approximate expressions are obtained for the tunnel splitting, the suppression factors, and the Curie temperatures. It is shown that, depending on the crystal parameters, a transition from the orthorhombic phase to a completely disordered one proceeds either directly or through an intermediate tetragonal phase.

1. INTRODUCTION

The problem of taking into account the electron-vibrational (vibronic) interactions in polyatomic systems with an electron-degenerate (or quasidegenerate) term, the manifestations of which are well known in the literature under the name of the Jahn-Teller effect,[1)] is most complicated in the case of the T term. In this case, in contrast with the E term, both the twofold degenerate e- and the triply degenerate t_2-vibrations are important in the effect, as a consequence of which the topological complications of the three-sheeted surface of the adiabatic potential of the nuclear motions (the essential anharmonism and the multi-valleyed character) span the five-dimensional space of e- and t_2-displacements. Limiting themselves to consideration of only the linear terms of the vibronic interaction, Opik and Pryce[2] have shown that this surface has extremal points of three types: tetragonal, trigonal and orthorhombic, and that, depending on the relation of the constants of vibronic coupling and the elastic constants, only tetragonal or trigonal points can be minima, while the intermediate orthorhombic extrema are in all cases saddle points. These representations are very important for analysis of the observed properties of many polyatomic systems, including impurity centers in crystals, complexes of transition metals, various other molecular formations (including biological ones), and also the collective properties of crystals (the cooperative Jahn-Teller effect, which leads principally to structural phase transitions).

Meanwhile, it is known from analysis of the simpler case of the E term that, with account of the quadratic terms of the vibronic coupling, the shape of the adiabatic potential surface becomes appreciably more complicated,[3,4] and in most cases, only such a complicated surface can explain the experimental data (see[1,5]). We can therefore assume that account of the quadratic terms in the case of the T term will also change the results of Opik and Pryce significantly. However, this problem has not yet been solved, so far as we know, because of its complexity (an attempt was made in[6] to take into account the quadratic terms of the vibronic coupling in the particular case of consideration of trigonal distortions only).

In the present communication, we give the results of solution of the fundamental problem of the theory of the Jahn-Teller effect for a system with an electron-degenerate T term—the features and the shape of the adiabatic potential surface are determined with account of both the linear and the most important quadratic terms of the vibronic coupling, equivalent orthorhombic minima of a new type are reported, and it is shown that localization of the nuclear motion in them leads to a series of new effects.[2)] The most essential of the latter are considered: tunnel splitting of the ground state, suppression (decrease) of the electronic characteristics of the system due to vibronic coupling, and structural phase transitions in crystals.

2. EXTREMA OF THE ADIABATIC POTENTIAL SURFACE

The Hamiltonian of a polyatomic system that allows electron-degenerate T terms in a configuration of maximum symmetry of the cubic type, with account of the quadratic terms of the vibronic coupling, can be written in the form

$$H=-\frac{\hbar^2}{2m}\sum_{\Gamma\gamma}\frac{\partial^2}{\partial Q_{\Gamma\gamma}^2}C_\alpha+U(Q),\quad \gamma\in\Gamma,\quad \Gamma=E_g,\ T_{2g}, \tag{1}$$

where

$$U(Q)=\sum_{\Gamma\gamma}\left(\frac{1}{2}K_\Gamma Q_{\Gamma\gamma}^2C_\alpha+V_\Gamma Q_{\Gamma\gamma}C_{\Gamma\gamma}\right)+W\left[Q_\xi\left(-\frac{1}{2}Q_\theta+\frac{\sqrt{3}}{2}Q_\varepsilon\right)C_\xi+Q_\eta\left(-\frac{1}{2}Q_\theta-\frac{\sqrt{3}}{2}Q_\varepsilon\right)C_\eta+Q_\theta Q_\zeta C_\zeta\right]. \tag{2}$$

Here θ, ϵ and ξ, η, ζ denote the lines of irreducible representations of E_g and T_{2g}, respectively, with the transformation properties $\theta\sim 2z^2-x^2-y^2$, $\epsilon\sim\sqrt{3}(x^2-y^2)$, $\xi\sim yz$, $\eta\sim xz$, $\zeta\sim xy$, where x, y, z are the Cartesian coordinates. The quantities V_Γ and W represent the corresponding reduced matrix elements—the constants of vibronic binding and $C_{\Gamma\gamma}$ the matrices of the Clebsch-Gordan coefficients, defined in the space of functions of the initial electron triplet:

$$C_\alpha=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix},\quad C_\theta=\begin{pmatrix}1/2&0&0\\0&1/2&0\\0&0&-1\end{pmatrix},\quad C_\varepsilon=\begin{pmatrix}-\sqrt{3}/2&0&0\\0&\sqrt{3}/2&0\\0&0&0\end{pmatrix} \tag{3}$$

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

Only the most important quadratic terms of the vibronic coupling are considered in the Hamiltonian (1). These are of symmetry $E \times T_2$ and contribute the most fundamental changes to the shape of the adiabatic potential surface. Terms of the type $E \times E$ and $T_2 \times T_2$ contribute only corrections to the quantitative relations among the parameters of the surface and were therefore omitted for simplification of calculations and analysis of the results. The results obtained below apply with equal success to both the T_1 and the T_2 terms, even and odd (in the presence of an inversion center). The spin-orbital interaction is assumed to be less than the energy of the Jahn-Teller stabilization (see below).

To find the extremal points of the adiabatic potential surface, we can use the procedure of Opik and Pryce.[2] We denote the column electron function, which is characteristic for the matrix of the potential energy $\mathbf{U}(\mathbf{Q})$, by $|\mathbf{a}\rangle$:

$$|\mathbf{a}\rangle = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}, \quad \langle \mathbf{a}|\mathbf{a}\rangle = 1. \tag{4}$$

Making use of the fact that the adiabatic potential is determined by the equation

$$\mathbf{U}(Q)\,|\mathbf{a}(Q)\rangle = \varepsilon(Q)\,|\mathbf{a}(Q)\rangle, \tag{5}$$

we can find the coordinates of its extremal points from the set of five equations:[2]

$$\langle \mathbf{a}| \frac{\partial \mathbf{U}(Q)}{\partial Q_{\Gamma\gamma}} |\mathbf{a}\rangle = 0, \quad \Gamma = E_g, T_{2g}, \quad \gamma \in \Gamma. \tag{6}$$

Solving Eqs. (5) and (6) simultaneously, with account of (2)–(4), we obtain a set of four nonlinear algebraic equations for the three components of the column $|\mathbf{a}\rangle$ and the value of ϵ at the extremum and five expressions for $Q^{(0)}_{\Gamma\gamma}$ in terms of a_i. Without writing down these equations (in view of their cumbersome nature), we give the results of their solution—the extremal points of the adiabatic potential surface $\epsilon(\mathbf{Q})$.

a) Solutions of the linear approximation always exist, independently of the values of the quadratic binding constant W—three equivalent tetragonal extrema at $a_p = 1$, $a_q = a_r = 0$, p, q, r = 1, 2, 3 and $p \neq q$, $q \neq r$, $p \neq r$ with the coordinates of one of them: $Q^{(0)}_\theta = -V_E/2K_E$, $Q^{(0)}_\epsilon = \sqrt{3}V_E/2K_E$, $Q^{(0)}_\xi = Q^{(0)}_\eta = Q^{(0)}_\zeta = 0$ (the remaining coordinates are found from symmetry), and with energy, measured from the position of the initial electron triplet,

$$E^{(E)}_{JT} = \varepsilon(Q^{(0)}) = -V_E^2/2K_E, \tag{7}$$

and four trigonal points at $a_1 = \pm a_2 = \pm a_3 = 1/\sqrt{3}$ with coordinates $Q^{(0)}_\theta = Q^{(0)}_\epsilon = 0$, $Q^{(0)}_\xi = \pm Q^{(0)}_\eta = \pm Q^{(0)}_\zeta = 2V_T/3K_T$ and energy

$$E^{(T)}_{JT} = \varepsilon(Q^{(0)}) = -2V_T^2/3K_T. \tag{8}$$

b) The position and depth of the six equivalent orthorhombic extrema are strongly influenced by the quadratic terms. We introduce the dimensionless constants

$$A = W/\sqrt{K_E K_T}, \quad B = WV_E/K_E V_T \tag{9}$$

(it follows from the stability requirement of the system that $|A| < 1$). Then we can obtain for the position of one of them (at $a_1 = a_2 = 1/\sqrt{2}$, $a_3 = 0$)

$$\begin{aligned} Q^{(0)}_\theta &= -V_E(B-2A^2)/2K_E B(1-A^2), \quad Q^{(0)}_\epsilon = Q^{(0)}_\xi = Q^{(0)}_\eta = 0, \\ Q^{(0)}_\zeta &= V_T(2-B)/2K_T(1-A^2), \end{aligned} \tag{10}$$

and for their energy

$$E^{(OR)}_{JT} = \varepsilon(Q^{(0)}) = -V_E^2(B^2+4A^2-4A^2B)/8K_E B^2(1-A^2). \tag{11}$$

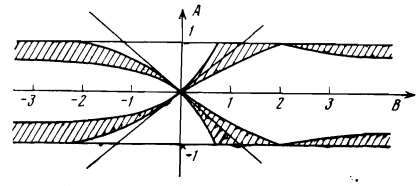

FIG. 1. Region of existence of twelve equivalent extrema of the first type (shaded region).

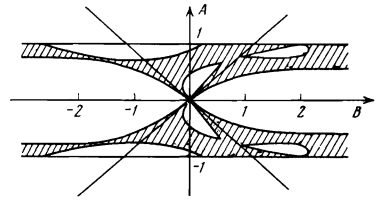

FIG. 2. Region of existence of twelvefold extrema of the second type (shaded region).

c) The "twelve-fold" (in the sense of twelve equivalent) extrema of two types are new, being absent in the linear approximation. The first type is obtained at $a_p \neq 0$, $a_q \neq 0$, $a_p \neq a_q$, $a_r = 0$. They exist only upon satisfaction of the inequalities

$$0 \leqslant 1 \pm A(2-B)/B\sqrt{3} \leqslant A^2, \tag{12}$$

which can be compared with the existence region of the twelve fold extrema of the first type on the (A, B) plane[3] (Fig. 1). We get for the components a_i of the wave functions

$$a_{1,2} = \frac{1}{\sqrt{2}}\left[1 \pm \left(1 - \frac{1}{A^2} \pm \frac{2-B}{AB\sqrt{3}}\right)^{1/2}\right]^{1/2} \tag{13}$$

(the second pair of signs in (13) correspond to the two signs in (12)), and we have for the coordinates of one extremum and the energy

$$\begin{aligned} Q^{(0)}_\theta &= -\frac{1}{2}\frac{V_E}{K_E}\frac{2A-B\sqrt{3}}{AB}, \quad Q^{(0)}_\epsilon = \frac{\sqrt{3}}{2}\frac{V_E}{K_E}\left(1 - \frac{1}{A^2} \pm \frac{2-B}{AB\sqrt{3}}\right)^{1/2}, \\ Q^{(0)}_\xi &= Q^{(0)}_\eta = 0, \quad Q^{(0)}_\zeta = \frac{1}{AK_T}(V_T + WQ^{(0)}_\theta)\left[1 \mp \frac{A(2-B)}{B\sqrt{3}}\right]^{1/2}, \end{aligned} \tag{14}$$

$$E^{(12)}_{JT} = \varepsilon(Q^{(0)}) = -\frac{1}{2}\frac{V_E^2}{K_E} + \frac{1}{8}\frac{V_E^2}{K_E}\left(\frac{2}{B} \mp \frac{\sqrt{3}}{A} - 1\right)^2. \tag{15}$$

We can easily see from comparison of Eqs. (15) and (7) that the inequality $E^{(E)}_{JT} < E^{(12)}_{JT}$ holds for any A and B, i.e., the twelvefold extrema of the first type that have been considered cannot be absolute minima.

The twelve-fold extrema of the second type are obtained at $a_p = a_q \neq a_r$, $a_i \neq 0$ (i = 1, 2, 3). In this case, at the first extremum ($a_1 = a_2$) we have $Q^{(0)}_\theta \neq 0$, $Q^{(0)}_\epsilon = 0$, and two of the three displaced trigonal coordinates are equal to one another. The characteristics of these extrema, including the region of their existence (Fig. 2) can be found only numerically in the general case, and analytically only for certain limiting values of the parameters.

A more complete investigation of the adiabatic potential surface was carried out on an electronic computer according to a specially constructed program incorporating: 1) finding the component a of the electron wave function at the extremum; 2) calculation of the normal coordinates $Q^{(0)}_{\Gamma\gamma}$ of the extremum; 3) determination of the values of the adiabatic potential at the extremum

Characteristics of the extremal points (for one of the several equivalent points of each type) at $V_E = 10^4\ cm^{-1}/Å$, $V_T = 0.866 \times 10^4\ cm^{-1}/Å$, $W = -0.5 \times 10^4\ cm^{-1}/Å^2$, $K_E = K_T = 10^4\ cm^{-1}/Å^2$

Type of point	Eigenvectors of the matrix $U(Q^{(0)})$			$\epsilon(Q^{(0)})$, $10^3\ cm^{-1}$	$Q^{(0)}_{\Gamma\gamma}$, Å	$C_{j,\Gamma\gamma}$					K_j, $10^3\ cm^{-1}/Å$
1	1	0	0	−2.50	−0.25	1	0	0	0	0	10.0
	0	1	0	5.00	0.43	0	1	0	0	0	10.0
	0	0	1	5.00	0	0	0	1	0	0	10.0
					0	0	0	0	1	0	−6.61
					0	0	0	0	0	1	−6.61
2	0.577	0.577	0.577	−2.50	0	0.823	0.009	0.227	0.236	−0.463	−8.07
	0.816	−0.408	−0.408	5.00	0	−0.010	0.823	−0.404	0.398	0.005	−8.07
	0	−0.707	−0.707	5.00	0.28	0.002	0.567	0.581	−0.584	0.003	13.7
					0.28	0	0	0.577	0.577	0.577	10.0
					0.28	0.567	−0.002	−0.338	−0.334	0.672	13.7
3	0.707	0.707	0	−4.78	0.62	0.707	0	0	0	−0.707	5.00
	−0.707	0.707	0	17.4	0	0	1	0	0	0	6.61
	0	0	1	15.6	0	0	0	0.707	0.707	0	8.49
					0	0	0	−0.707	0.707	0	10.0
					0.74	0.707	0	0	0	0.707	15.0
4	0.358	0.358	0.862	−3.06	0.39	0.779	0	−0.253	−0.253	−0.515	5.50
	0.707	−0.707	0	6.08	0	0	0.671	−0.524	−0.524	0	−9.77
	0.610	0.610	−0.506	8.42	0.33	0	0.742	0.474	−0.474	0	13.7
					0.33	0.398	0	0.648	0.648	−0.035	7.86
					0.06	0.485	0	−0.125	−0.125	0.857	11.1

1—Tetragonal extrema; 2—trigonal extrema; 3—orthorhombic extrema; 4—twelvefold extrema of the second type.

$E^{(\Gamma)}_{JT} = \epsilon(Q^{(0)})$; 4) calculation of the curvature of the adiabatic potential surface near the extremum K_j—the new force constants; 5) determination of new normal coordinates at the extremum

$$q_j = \sum_{\Gamma\gamma} C_{j,\Gamma\gamma}(Q_{\Gamma\gamma} - Q^{(0)}_{\Gamma\gamma}), \qquad (16)$$

corresponding to these new force constants.

In different regions of the (A, B) plane, some 260 variants with different combinations of the parameters of the problem (V_E, K_E, V_T, K_T, W) were computed. The results of one of them, with A = −0.5, B = −0.577 are given in the Table; the twelvefold extrema of the first kind are absent in this case. In none of the variants considered did the twelvefold extrema of either type become the lowest, although for some values of the parameters they were converted from saddle points to minima. We note the possibility of a situation in which several groups of twelvefold extrema of the second type exist simultaneously on the adiabatic potential surface; these develop from several different combinations

$$a_1^{(1)} = a_2^{(1)} \neq a_3^{(1)},\ a_1^{(2)} = a_2^{(2)} \neq a_3^{(2)},\ \text{etc.}$$

A solution is also possible in principle with all different, nonvanishing values of a_i, leading to 24 equivalent extrema, which transform into one another through symmetry operations. However, as a calculation on the computer showed, the region of existence of these roots lies beyond the limits of the region of stability of the system.

3. ORTHORHOMBIC MINIMA

In contrast to the twelvefold extrema, the orthorhombic extrema can be absolute minima which follows directly from the example given in the Table—the orthorhombic extrema have a positive curvature in all directions and are the lowest. In view of the fundamental importance of this result (we recall that in the linear approximation, orthorhombic extrema can only be saddle points[2]), let us analyze its origin and establish the region of existence of the absolute minima of the orthorhombic type.

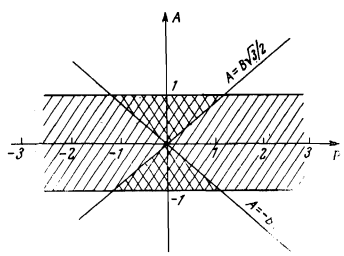

FIG. 3. Region of existence of tetragonal, trigonal and orthorhombic extrema. The depths of the first two types of extrema are the same on the straight lines $A = \pm B\sqrt{3/2}$. In the crosshatched region, the trigonal extrema are deeper than the tetragonal ones, and in the rest of the region, the tetragonal are the deeper.

We easily find from the condition $E^{(E)}_{JT} = E^{(T)}_{JT}$ that equality of the depths of the trigonal and tetragonal extrema is realized on the lines $A = \pm B\sqrt{3}/2$. In Fig. 3, the region of allowable values of the parameters A and B is divided by these lines into two parts, in one of which $|A| > B\sqrt{3}/2$ and, consequently, the trigonal extrema are deeper than the tetragonal ones, while in the other the reverse inequality holds and the tetragonal extrema are deeper than the trigonal ones. At the intersection of the lines, i.e., at W = 0 (see (9)), the depths of all three types of extrema—trigonal, tetragonal and orthorhombic—are identical and a two-dimensional trough of minima is realized on the five-dimensional adiabatic potential surface.[8,9] At $W \neq 0$, the parameters A and B are also different from zero and the depth of the orthorhombic extrema is not identical to the depth of the trigonal and tetragonal ones, as follows from (11), even for $A = \pm B\sqrt{3}/2$. In other words, with account of the quadratic terms of the vibronic coupling, the two-dimensional trough of minima is "corrugated," and hills and depressions appear along the trough (much as in the case of the E term[4,5]). Here, depending on the values of the parameters, the orthorhombic points can turn out to be both higher and lower than the tetragonal (or trigonal) points.

In the general case, the existence of a region of the parameters A and B where the orthorhombic extrema become absolute minima is quite evident. In this region, the inequalities $E^{(OR)}_{JT} < E^{(E)}_{JT}$ and $E^{(OR)}_{JT} < E^{(T)}_{JT}$ should be satisfied, and with their help we find the boundaries of the region of interest to us by using the explicit ex-

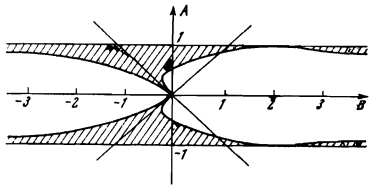

FIG. 4. Region of existence of absolute minima of the orthorhombic type (shaded region).

pressions for $E_{JT}^{(\Gamma)}$, (7), (8) and (11):

$$B=[-2A^2\pm 2A\sqrt{3(1-A^2)}]/(3-4A^2) \text{ at } B<0 \text{ or } B>1, \quad (17a)$$

$$B=2A^2\pm{}^2/_3 A\sqrt{3(1-A^2)} \text{ at } (\sqrt{3}-3)/3<B<1. \quad (17b)$$

The region of values of A and B bounded by the curves (17a) and (17b), inside which $E_{JT}^{(OR)} < E_{JT}^{(E)}$ and $E_{JT}^{(OR)} < E_{JT}^{(T)}$, is shown in Fig. 4.

4. TUNNEL SPLITTING OF THE ORTHORHOMBIC STATES

One of the most interesting consequences of the Jahn-Teller effect in polyatomic systems with strong vibronic coupling is the so-called inversion, or tunnel, splitting of the levels, due to tunneling of the system through the barriers between equivalent minima of the adiabatic potential.[4,5,10]

We shall assume that the depth of the orthorhombic minima obtained above is sufficiently great and that the nuclear motion is localized in a small neighborhood of the bottom of the minimum. Then the initial wave function of the ground state can be written in the "simple" adiabatic approximation:[11]

$$\Psi_\alpha(r, q^{(\alpha)})=\psi_\alpha(r, Q^{(\alpha)})\prod_{j=1}^{5}\Phi_0(q_j^{(\alpha)}), \quad \alpha=1,2,\ldots,6, \quad (18)$$

where $\Phi_0(q_j^{(\alpha)})$ is the wave function of the ground state of the harmonic oscillator

$$\Phi_0(q_j^{(\alpha)})=\left(\frac{m\omega_j}{\pi\hbar}\right)^{1/4}\exp\left(-\frac{m\omega_j}{2\hbar}q_j^{(\alpha)2}\right), \quad \omega_j=(k_j/m)^{1/2}, \quad (19)$$

$$q_j^{(\alpha)}=\sum_{\Gamma\gamma}C_{j,\Gamma\gamma}(Q_{\Gamma\gamma}-Q_{\Gamma\gamma}^{(\alpha)}),$$

and $\psi_\alpha(r, Q^{(\alpha)})$ is the electron wave function at the α-th minimum. In particular, for the initial electron term T_1 (the electron basis $|x\rangle$, $|y\rangle$, $|z\rangle$) we have $\varphi_1 = (|x\rangle + |y\rangle)/\sqrt{2}$ for the minimum point (10), with the components of the electron function $a_1 = a_2 = 1/\sqrt{2}$, $a_3 = 0$. The energy of the state (18) is equal to

$$E_0=E_{JT}^{(OR)}+\sum_{j=1}^{5}\hbar\omega_j/2. \quad (20)$$

It does not depend on the index α of the minimum, and consequently the state of the system is sixfold degenerate. The six functions (18) form a reducible representation of the group O_h, which splits into the irreducible $T_1 + T_2$.[12] In order to take the tunneling into account—it lifts the random degeneracy of the terms T_1 and T_2—we make use of the functions (18) as a basis for diagonalization of the complete Hamiltonian (1). Using the symmetry properties of the matrix elements, we obtain the secular equation in the form

$$\begin{vmatrix} H_{11}-E & H_{12}-SE & 0 & H_{12}-SE & H_{12}-SE & H_{12}-SE \\ H_{12}-SE & H_{11}-E & H_{12}-SE & 0 & -H_{12}+SE & H_{12}-SE \\ 0 & H_{12}-SE & H_{11}-E & H_{12}-SE & -H_{12}+SE & -H_{12}+SE \\ H_{12}-SE & 0 & H_{12}-SE & H_{11}-E & H_{12}-SE & -H_{12}+SE \\ H_{12}-SE & -H_{12}+SE & -H_{12}+SE & H_{12}-SE & H_{11}-E & 0 \\ H_{12}-SE & H_{12}-SE & -H_{12}+SE & -H_{12}+SE & 0 & H_{11}-E \end{vmatrix}=0, \quad (21)$$

where

$$H_{\alpha\beta}=\langle\Psi_\alpha|H|\Psi_\beta\rangle, \; S=\langle\Psi_1|\Psi_2\rangle. \quad (22)$$

Inasmuch as there are no repeating representations in the $T_1 + T_2$ expansion, the complete diagonalization is accomplished by construction of the correct functions with the help of projection operators.[13] As a result, we get

$$\Psi_{T_1x}={}^1/_2(\Psi_1+\Psi_2+\Psi_3+\Psi_4), \quad (23a)$$

$$\Psi_{T_1\xi}={}^1/_2(\Psi_1-\Psi_2+\Psi_3-\Psi_4). \quad (23b)$$

The energies of the triplets T_1 and T_2 are determined by the expressions

$$E(T_1)=\frac{\langle\Psi_{T_1x}|H|\Psi_{T_1x}\rangle}{\langle\Psi_{T_1x}|\Psi_{T_1x}\rangle}=\frac{H_{11}+2H_{12}}{1+2S}, \quad (24a)$$

$$E(T_2)=\frac{\langle\Psi_{T_1\xi}|H|\Psi_{T_1\xi}\rangle}{\langle\Psi_{T_1\xi}|\Psi_{T_1\xi}\rangle}=\frac{H_{11}-2H_{12}}{1-2S}, \quad (24b)$$

and, consequently, the value of the tunnel splitting is equal to

$$\delta=E(T_2)-E(T_1)=4\frac{H_{11}S-H_{12}}{1-4S^2}. \quad (25)$$

To estimate this quantity, we calculate H_{11}, H_{12} and S, neglecting the splitting of the frequencies at the minima and limiting ourselves to the case $K_E = K_T$. Then $H_{11} = E_{JT}^{(OR)} + 5\hbar\omega/2$ and

$$H_{12}=({}^5/_2\hbar\omega-{}^1/_4KQ_\theta^{(0)2}+{}^1/_2V_EQ_\theta^{(0)}-V_TQ_\zeta^{(0)}-{}^1/_4WQ_\theta^{(0)}\theta_\zeta^{(0)})S, \quad (26)$$

$$S=\frac{1}{2}\exp\left[-\frac{K}{4\hbar\omega}(3Q_\theta^{(0)2}+2Q_\zeta^{(0)2})\right], \quad (27)$$

where the quantities $Q_{\Gamma\gamma}^{(0)}$ are defined in (10). Then

$$\delta=[K(3Q_\theta^{(0)2}+2Q_\zeta^{(0)2})-3WQ_\theta^{(0)}Q_\zeta^{(0)}]\frac{S}{1-4S^2}. \quad (28)$$

We note that the quantity $(3Q_\theta^{(0)2}+2Q_\zeta^{(0)2})^{1/2}$, the square of which appears in the argument of the exponential in (27), is none other than the distance between two neighboring orthorhombic minima.

Tunnel splitting has been observed directly in experiment, in the form of splitting of the background-free line of transition to the degenerate electron term, both in the case of the E term (the transitions $A \rightarrow E$ in Eu^{2+} and Sm^{2+} and in CaF_2 and SrF_2[14]) and in the case of the T term for the transition $^4A_2 \rightarrow {}^4T_2$ in V^{2+}:MgO.[15] For the latter case, complete agreement of experiment with the earlier theory of the Jahn-Teller effect with account of only the linear terms has not been achieved to date.[1] It can be hoped that the remaining disagreements will be removed with account of the results of the present paper, which requires additional measurements to confirm the orthorhombicity of the adiabatic-potential minima in this specific case.

5. SUPPRESSION OF THE MATRIX ELEMENTS OF THE ELECTRON OPERATORS

In the calculation given above of the basic vibronic levels of a system with orthorhombic minima, the ground vibronic state that was obtained was of type T_1, i.e., the same as the initial electron term. This result confirms the general conclusion that, inasmuch as the vibronic terms in the Hamiltonian (1) do not change their symmetry, then, with account of the vibronic coupling, the degeneracy of the ground state is not lifted, but only undergoes a transition from electronic to vibronic.

The coincidence of the symmetry of the ground elec-

tronic and vibronic states materially simplifies calculation of the matrix elements of the operators of the electron physical quantities $F_{\overline{\Gamma}\overline{\gamma}}(r)$ on functions of the degenerate term and leads to a qualitatively new effect for the observable quantities. It turns out that

$$\langle\Psi_{\Gamma\gamma_1}(r,Q)|F_{\overline{\Gamma}\overline{\gamma}}(r)|\Psi_{\Gamma\gamma_2}(r,Q)\rangle=K_{\Gamma}(\overline{\Gamma})\langle\psi_{\Gamma\gamma_1}(r)|F_{\overline{\Gamma}\overline{\gamma}}(r)|\psi_{\Gamma\gamma_2}(r)\rangle, \quad (29)$$

where $K_\Gamma(\overline{\Gamma})$ is a number smaller than unity and dependent (for a given term Γ) only on the representation $\overline{\Gamma}$ according to which the operator $F_{\overline{\Gamma}\overline{\gamma}}$ is transformed. In other words, the vibronic couplings reduce (suppress) the physical observables that are described by electron operators. This result was first obtained in calculation of the spin-orbital splitting of the T term[4,16] and was then generalized to the case of an arbitrary electron operator[17] (a general proof of the suppression theorem is given, for example, in[18]).

For the considered case of orthorhombic distortions it is easy to obtain expressions for the reduction (suppression) factors $K(\Gamma)$, which are the same for the electron T_1 and T_2 terms, by division of the corresponding matrix elements from (29) as calculated on the functions (18) and on the electron functions $|x\rangle$, $|y\rangle$ and $|z\rangle$. We have

$$K(E)=(1+8S+6\tilde{S})/(4+8S),\ K(T_1)=(3S+\tilde{S})/(1+2S),\qquad K(T_2)=(1+6S)/(2+4S), \quad (30)$$

where S is given by (26) and

$$\tilde{S}=\tfrac{1}{2}\exp(-KQ_\xi^{(0)2}/\hbar\omega). \quad (31)$$

The limiting values of $K(\overline{\Gamma})$ for strong vibronic binding (small S and $\tilde{S}$) are equal to $K(E)\approx\frac{1}{4}$; $K(T_1)\approx 0$; $K(T_2)\approx\frac{1}{2}$.

It is seen from (29) that the matrix elements of the operators which are transformed according to T_1 are especially strongly reduced. In particular, the orbital momentum of the electrons and consequently the spin-orbital interaction are reduced. For example, the $^2T_2$ term, with account of vibronic coupling, is split by the spin-orbital interaction into the levels Γ_7 and Γ_8 with energies $\Delta E(\Gamma_7)=K(T_1)\lambda$; $\Delta E(\Gamma_8)=-K(T_1)\lambda/2$ (λ is the constant of the spin-orbital interaction). The splitting is obtained in qualitatively the same way as for the purely electron $^2T_2$ term, but is less by a factor of $K(T_1)$.

In the case considered, it is also necessary to take into account that in the case $K(T_1)\lambda\sim\delta$ the spin-orbit interaction mixes the adjacent $^2T_1$ level—the T_1 component of the tunnel splitting of the ground state—with the fundamental $^2T_2$ level. With account of this admixture ($^2T_1$ is split into $\Gamma_6+\Gamma_8$), we get

$$E=(\Gamma_8^{(-)})=\frac{1}{2}\{\delta-[(\delta+K(T_1)\lambda)^2+3\overline{K}^2\lambda^2]^{1/2}\}, \quad (32a)$$

$$E=(\Gamma_8^{(+)})=\frac{1}{2}\{\delta+[(\delta+K(T_1)\lambda)^2+3\overline{K}^2\lambda^2]^{1/2}\}, \quad (32b)$$

$$E(\Gamma_6)=\delta-K(T_1)\lambda, \quad (32c)$$

$$E(\Gamma_7)=K(T_1)\lambda, \quad (32d)$$

where $\overline{K}=(\tilde{S}-S)/(1-4S^2)^{1/2}$ is the "off-diagonal" reduction factor, which arises in the calculation of the off-diagonal matrix elements of the operator of the orbital angular momentum of the electron on the states of the T_1 and T_2 terms. Thus the reduction effect and tunnel splitting significantly change the fine structure of the ground multiplet.

Another example. The quadruplet Γ_8 obtained above, which arises on spin-orbital splitting of the $^2T_2$ term, belongs in the absence of the Jahn-Teller effect to the class of so-called nonmagnetic quadruplets, i.e., it is not split by the magnetic field in the linear approximation in the field, because of the mutual cancellation of the orbital and spin contributions to the Zeeman energy. The suppression of the orbital momentum by the factor $K(T_1)$, which is connected with the vibronic coupling, leads to the appearance of a linear Zeeman effect on the quadruplet Γ_8, and the splitting is isotropic and equally spaced, with the g factor

$$g=2[1-K(T_1)]/3. \quad (33)$$

It is seen from (33) that the linear Zeeman effect on the term Γ_8 disappears in the absence of the reduction effect, i.e., for $K(T_1)=1$.

6. STRUCTURAL PHASE TRANSITIONS

The phonon interaction of electron-degenerate centers of a crystal leads to structural phase transitions due to the so-called cooperative Jahn-Teller effect[1,20,21] (for pseudodegenerate centers, and also for systems without a center of inversion, dipole ferroelectric and antiferroelectric ordering is possible[1,22]). We consider here new types of structural phase transitions that may result from interaction of the orthorhombically distorted centers with electron-degenerate T terms that were discussed above.

We shall assume that the orthorhombic minima of the adiabatic potential are so deep that tunneling between them can be neglected in the study of phase transitions, and we shall choose as a basis for second quantization the vibronic functions of the ground state (18) of the Jahn-Teller centers.[23] Then the Hamiltonian of the crystal can be written

$$H=\varepsilon_0\sum_{\alpha m}a_{\alpha m}^{+}a_{\alpha m}+\sum_{\alpha m}\sum_{\Gamma\gamma}\sum_{\kappa}\gamma_{\Gamma\gamma}^{(\kappa m)}s_{\Gamma\gamma}^{(\alpha)}a_{\alpha m}^{+}a_{\alpha m}(b_\kappa+b_\kappa^{+})+\sum_{\kappa}\hbar\omega_\kappa\left(b_\kappa^{+}b_\kappa+\frac{1}{2}\right)+\frac{1}{2}\Omega\sum_{\Gamma\gamma}c_\Gamma u_{\Gamma\gamma}^2-\sqrt{\frac{\Omega}{N}}\sum_{\Gamma\gamma}g_\Gamma\sqrt{c_\Gamma}u_{\Gamma\gamma}\sum_{\alpha m}s_{\Gamma\gamma}^{(\alpha)}a_{\alpha m}^{+}a_{\alpha m}. \quad (34)$$

Here m numbers the Jahn-Teller centers and κ the vibrational modes of the crystal, and $V_{\Gamma\gamma}^{(\kappa m)}$ are the constants of vibronic binding of the electrons with symmetrized (relative to the mth center) Γ_γ combinations of normal vibrations. Inasmuch as $\langle a_{\alpha m}^{+}a_{\alpha m}\rangle=\overline{n}_{\alpha m}\leq 1$, the operators $a_{\alpha m}^{+}$ and $a_{\alpha m}$ possess Fermi commutation relations; the numbers $s_{\Gamma\gamma}^{(\alpha)}$ are determined from the equations

$$s_{\Gamma\gamma}^{(\alpha)}=\langle\Psi_\alpha|E_{\Gamma\gamma}|\Psi_\alpha\rangle. \quad (35)$$

The last two terms of the Hamiltonian (34) correspond to the elastic deformation energy and its interaction with the Jahn-Teller centers, respectively,[21] while c_Γ are the elastic constants, referred to a unit volume Ω of the crystal; g_Γ are the corresponding constants of vibronic deformation interaction. If we carry out the unitary transformation of the displacement S in the Hamiltonian (34)[21,24], where[24]

$$S=\exp\left\{\sum_m\sum_{\Gamma\gamma}\left[\sum_\kappa\gamma_{\Gamma\gamma}^{(\kappa m)}(\hbar\omega_\kappa)^{-1}(b_\kappa^{+}-b_\kappa)+\frac{g_\Gamma}{\sqrt{\Omega N c_\Gamma}}\frac{\partial}{\partial u_{\Gamma\gamma}}\right]\sum_\alpha s_{\Gamma\gamma}^{(\alpha)}a_{\alpha m}^{+}a_{\alpha m}\right., \quad (36)$$

we can then easily obtain

$$\tilde{H}=SHS^{+}=(\varepsilon_0+E_{JT}^{(0R)}+\Delta E_{str})\sum_{\alpha m}a_{\alpha m}^{+}a_{\alpha m}+\sum_\kappa\hbar\omega_\kappa\left(b_\kappa^{+}b_\kappa+\frac{1}{2}\right)$$

$$+\frac{1}{2}\Omega\sum_{\Gamma\gamma}c_\Gamma u_{\Gamma\gamma}^2-\sum_{\Gamma\gamma}\sum_{\Gamma'\gamma'}\sum_{\substack{m,n\\(m\neq n)}}\Big[\mathcal{V}_{\Gamma\gamma}^{(\varkappa m)}\mathcal{V}_{\Gamma'\gamma'}^{(\varkappa n)}+\frac{1}{2N}g_\Gamma^2\delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'}\Big]\sum_{\alpha\beta}s_{\Gamma\gamma}^{(\alpha)}s_{\Gamma'\gamma'}^{(\beta)}a_{\alpha m}^+a_{\alpha m}a_{\beta n}^+a_{\beta n},\tag{37}$$

where

$$\Delta E_{str}=-(g_E^2+g_T^2)/N.$$

It is then seen that as a result of the transformation that has been carried out, the phonon and deformation degrees of freedom have been separated, while pair interaction has appeared in the vibronic subsystem, leading to a phase transition.[25] If, as usual, we introduce the equal-time Green's functions $G_{\beta n}^{\alpha m}(t, t')$ $=\langle\langle a_{\alpha m}(t)|\alpha_{\beta n}^+(t')\rangle\rangle$, write the equations of motion for them[26] and carry out the uncoupling

$$\langle\langle a_{\gamma l}^+a_{\gamma l}a_{\alpha m}|a_{\beta n}^+\rangle\rangle=\langle a_{\gamma l}^+a_{\gamma l}\rangle G_{\beta n}^{\alpha m},\tag{38}$$

corresponding to the molecular-field approximation, we immediately obtain a set of transcendental equations for the occupation numbers $\bar{n}_{\alpha m}$. For simplicity, we shall consider ordering of a "ferromagnetic" type with localization of the nuclear motion of each of the centers at the minimum $\alpha = 1$ with coordinates (10). Then $\bar{n}_{\alpha m} = \bar{n}_\alpha$ and with account of distortions at the minimum $\bar{n}_3 = \bar{n}_4 = \bar{n}_5 = \bar{n}_6$. Introducing the order parameters

$$\bar{s}_{\Gamma\gamma}=\sum_\alpha s_{\Gamma\gamma}^{(\alpha)}\bar{n}_\alpha\quad(\Gamma=E,T_2;\ \gamma\in\Gamma),\tag{39}$$

we obtain $\bar{s}_\epsilon = \bar{s}_\xi = \bar{s}_\eta = 0$, and for $\bar{s}_\theta$ and $\bar{s}_\zeta$ (corresponding to two independent distortion directions)—the set of two equations

$$\operatorname{ch}\left(\frac{J_\zeta\bar{s}_\zeta}{kT}\right)=\frac{1-2\bar{s}_\theta}{1+\bar{s}_\theta}\exp\left(\frac{3J_\theta\bar{s}_\theta}{2kT}\right),$$
$$2\bar{s}_\zeta\exp\left(\frac{3J_\theta\bar{s}_\theta}{2kT}\right)+\bar{s}_\zeta\operatorname{ch}\left(\frac{J_\zeta\bar{s}_\zeta}{kT}\right)-\operatorname{sh}\left(\frac{J_\zeta\bar{s}_\zeta}{kT}\right)=0,\tag{40}$$

where

$$J_{\Gamma\gamma}=g_\Gamma^2+2\sum_{\substack{m\\(m\neq n)}}\sum_\varkappa\mathcal{V}_{\Gamma\gamma}^{(\varkappa m)}\mathcal{V}_{\Gamma\gamma}^{(\varkappa n)}.\tag{41}$$

It is not difficult to obtain the result from (40) that, depending on the relation between the parameters J_θ and J_ζ, two types of phase transitions are possible in the crystal. At $2J_\zeta > 3J_\theta$, there is only one phase-transition point $kT_\theta = kT_\zeta = J_\zeta/3$ with simultaneous vanishing of both order parameters, $\bar{s}_\theta = \bar{s}_\zeta = 0$. At $2J_\zeta < 3J_\theta$, an increase in the temperature leads, at $kT_\zeta = J_\zeta/3$ to vanishing of $\bar{s}_\zeta$ and then at $kT_\theta = J_\theta/2$ to vanishing of $\bar{s}_\theta$ also. In other words, the transition from the low-symmetry orthorhombic phase to a completely disordered phase can take place either directly (at $2J_\zeta > 3J_\theta$) or via an intermediate tetragonal phase (at $2J_\zeta < 3J_\theta$). Such nonequivalence of the tetragonal and trigonal distortions of the crystal is connected with the impossibility of fitting the orthorhombically distorted Jahn-Teller centers into a trigonally distorted crystal, while tetragonal stacking is possible.

From (34) we can find the equilibrium deformation of the crystal: $u_{\Gamma\gamma}^{(0)} = \bar{s}_{\Gamma\gamma}(N/c_\Gamma\Omega)^{1/2}$ which, in the low-symmetry phase, is different from zero. At $\bar{s}_\zeta \neq 0$, the crystal is distorted along [110] and at $\bar{s}_\theta \neq 0$, along the [001] axis. The corresponding elastic moduli vanish at the phase transition points.[21,24]

In systems without an inversion center, the transition to the low-symmetry orthorhombic phase can be accompanied by the appearance of spontaneous polarization of the crystal.

7. CONCLUSION

The above analysis has shown that in the Jahn-Teller effect for the T term the quadratic terms of the vibronic coupling are highly important and lead under certain conditions to the formation of six equivalent orthorhombic minima on the five-dimensional adiabatic potential hypersurface, as well as twelve each of two new types of equivalent saddle points. The regions of existence of these extrema are determined by two dimensionless combinations of the five parameters of the problem.

Special interest attaches to the possibility of localization of the nuclear motion at the new orthorhombic minima, which leads to a series of physical effects even in the ground state of the system. Thus, tunnel splitting, along with the already noted splitting of the background-free lines, leads to resonance electromagnetic absorption in the microwave region,[27] to ultrasonic absorption,[28] and to a characteristic EPR spectrum,[19] which in the limiting case of deep minima should correspond to an orthorhombically distorted system. We note that such spectra, which indicate orthorhombic distortion, have actually been observed in a number of systems with a T term: Ni^-:Ge, Pd^-:Si, Pt^-:Si.[29]

As has been noted, the effect of suppression by vibronic coupling concerns all physical quantities described by incompletely symmetric electron operators. Along with the election orbital momentum, which we have discussed, the interaction of the electron shell with the nucleus (dipole-dipole, quadrupole etc., which materially affect the EPR, nuclear quadrupole resonance and nuclear resonance) is reduced, as is the Coulomb exchange interaction[30] and so on.

The above general consideration of structural phase transitions due to the interaction of orthorhombically distorted centers in crystals also opens up new possibilities.

We add that the expressions for the observables, obtained above as functions of $Q_{\Gamma\gamma}^{(0)}$, do not depend on the approximation in which these $Q_{\Gamma\gamma}^{(0)}$ were obtained.

[1)] In a "Historical Note" prefacing the book [1], E. Teller pointed out that the effect was predicted by L. D. Landau and should by right bear his name.

[2)] Some results were published earlier for a particular case [7].

[3)] Actually, there are two regions, corresponding to the two signs in (12), but, inasmuch as they do not intersect, we can consider them as a single doubly-connected region.

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