

Tunnel effects in polyatomic systems with electronic degeneracy and pseudodegeneracy

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We consider phenomena which are frequently designated jointly as the Jahn-Teller effect and result from dynamic electron-vibrational (vibronic) coupling in polyatomic systems with degenerate and pseudodegenerate terms. Principal attention is paid to the case of strong coupling, when the adiabatic potential in the space of the nuclear displacements that lift the degeneracy has several equivalent minima, tunneling between which leads to a number of peculiar effects. From among the latter, we consider resonant magnetic- and acoustic-wave absorption due to transitions between tunnel and tunnel-rotational levels, the temperature and frequency dependences of the EPR and hyperfine splittings in Mössbauer spectra, polarizability, etc. We discuss briefly cases of weak coupling suppression of splitting, due to perturbations that act in the electronic subsystem. For the crystalline states, the interaction of local Jahn-Teller and pseudo-Jahn-Teller distortions leads to structural transitions (the cooperative Jahn-Teller effect). In the case when the local distortions are of the dipole type, the crystal in the ordered phase turns out to be spontaneously polarized. Relations are obtained between the parameters of the vibronic coupling, the spontaneous polarization, and the Curie temperature for a number of ferroelectrics.

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1. INTRODUCTION

It is correctly assumed that the main laws governing the structure and properties of polyatomic systems became known back in the thirties immediately after the development of quantum mechanics. This does not pertain, however, to all the principally possible physical effects which, although they do follow from the principal laws, become important only when a definite stage is reached in the development of physics, particularly in the corresponding experimental capabilities. The foregoing is illustrated also by the effects of electron-vibrational (vibronic) interaction in polyatomic systems in the degenerate and pseudodegenerate states, to which this article is devoted.

In 1937, Jahn and Teller^[1] proved a theorem, according to which, the nuclear configuration of a nonlinear polyatomic system in a state with electronic degeneracy is unstable with respect to nuclear displacement that lifts this degeneracy. This statement was first formulated by L. D. Landau, a fact specially noted by Teller in "A Historical Note,"^[2] In view of the undoubted interest to Soviet scientists, we quote here Teller's statement in its entirety: "In 1934, Landau and I were at the Nils Bohr Institute in Copenhagen. We had many discussions. I told Landau of the work of my student, R. Renner, on degenerate states in the linear molecule CO₂. I explained that in this case a strong connection arises between the splitting of the electronic states and the vibrations of the nuclei, and this modifies the applicability of the Born-Oppenheimer approximation to these states.

Landau objected. He said that I must be very cau-

tious. In a degenerate electronic state, the symmetry on which this degeneracy is based (in this case, a linear arrangement of three atoms at equilibrium) is generally speaking violated. I was able to convince Landau that his doubts are unfounded (this is possibly the only time when I won an argument with Landau).

A year later, in London, I asked myself whether there exists another exception to the statement postulated by Landau. It was clear that electron degeneracy can upset the symmetry on which it is based. But how frequently must this of necessity occur? The question did not seem simple. I began to discuss this question with Jahn who, like myself, was a refugee from one of the German universities. We have reviewed all the possible symmetries and found that linear molecules are the only exception. In all other cases Landau's predictions were confirmed.

One problem remained unsolved. The proof of the so-called Jahn-Teller effect was obtained by a rather inelegant method of reviewing all the symmetries and discussing each of them in succession. Insofar as I know, there is still no general proof to this day.

This is the reason why the effect should be named after Landau. He foresaw this effect, and no one else obtained for it a proof that could satisfy a mathematician. Jahn and I performed only some spade work."

The proof of this statement by group-theory methods is quite simple. Indeed, by scanning through all the point groups it can be shown that in each of them there are such types of nuclear displacements for which the matrix elements of the linear term of the adiabatic po-

tential in the functions of the degenerate term are different from zero. It is these nonzero linear terms which are responsible for the absence of a minimum of the adiabatic potential in the direction of the corresponding nuclear displacements at the point under consideration. The absence of a minimum is clearly connected with the fact that in the presence of electronic degeneracy the symmetry of the electron distribution in the individual states is lower than the symmetry of the nuclear configuration (which leads to the degeneracy). Therefore the nuclear configuration that corresponds to the minimum of the adiabatic potential turns out to be of lower symmetry. A general proof of the Jahn-Teller theorem was obtained recently^{[3],1)}

We note^[5] that the foregoing formulation of the theorem is not specific enough and can lead to confusion unless the terminology is made more precise. Actually, in^[1] they prove only the following statement: If the adiabatic potential of a system is a formal solution of the electronic part of the Schrödinger equation (at fixed nuclei) and has several branches that cross at one point, then none of the branches of the potential has a minimum at this point. Understandably, knowledge of this singularity of the adiabatic potential is still insufficient to deduce the behavior of the nuclear subsystem. The latter can be determined only by solving the Schrödinger equation for the motion of the nuclei with the indicated potential. Therefore the Jahn-Teller theorem, strictly speaking does not lead to any definite conclusions concerning directly-observable quantities; the statement concerning the instability must be understood as an indication that the adiabatic potential has no minimum at the degeneracy point (we note that in the presence of degeneracy the potential has no clear-cut physical meaning). In the general case, such a potential does not lead to the observed distortion of the nuclear configuration^[5,6]. The most important consequence of the Jahn-Teller theorem is that the adiabatic approximation cannot be used for systems with degeneracy (or pseudodegeneracy), and the problem reduces to a solution of a complicated system of coupled equations.

In 1960–1962 one of us^[7-9] advanced the idea of tunnel splitting in Jahn-Teller-type systems. From an analysis of the form of the adiabatic potential of such systems, carried out for the simplest systems long ago by Van Vleck^[10] and more completely by Öpik and Pryce^[11] (with subsequent refinements^[9,12]), it was known that in all cases of electronic excitation the multidimensional surface of the potential has several minima that are equivalent in energy and symmetry; these minima correspond formally to an equal number of equivalent equilibrium configurations with potential barriers between them. In the case of sufficiently deep minima (and large barriers), the configuration in each of them becomes quasi-stationary and the transitions between them have the character of hindered motion (tunneling), which leads to a weak splitting of the electron-vibrational levels at each minimum (inversion or tunnel splitting).

These ideas were subsequently greatly expanded and made more meaningful. Tunnel effects and their influence on the optical, magnetic, electric, acoustic, and other properties of matter have become among the most important manifestations of vibronic interactions in systems with electronic degeneracy.

¹⁾Similar statements for linear systems were formulated by Renner^[4] and are referred to in the literature as the Renner effect.

It was thus shown that tunnel splitting greatly complicates the EPR spectrum in that, first, the orbital part of the Zeeman interaction is strongly suppressed, and second, the number of observed lines having characteristic frequency and temperature dependences is increased. Transitions between tunnel levels lead to a characteristic absorption of ultra-sound and of electromagnetic waves. The tunnel splitting is directly revealed by the splitting of the corresponding zero-phonon lines.

In highly-symmetrical molecular systems that have no dipole moment, the vibronic interaction can lead to formation of adiabatic-potential minima at which the dipole moment differs from zero. This circumstance leads to a change in a number of dielectric properties of the molecules, and in particular to a temperature-dependent polarizability and to a characteristic rotational spectrum, the appearance of which cannot be accounted for without allowance for the vibronic coupling.

It has become clear in recent years that vibronic effects play a rather important role in the investigation of interactions of molecules at short distances, which determine the mechanisms of chemical reactions.

A major part of this trend is the cooperative Jahn-Teller effect, which is being intensively developed in the last few years. Crystals containing sublattices of Jahn-Teller ions or molecules undergo structural phase transitions, namely, in the low-temperature phase the crystal becomes distorted by the correlations between the Jahn-Teller distortions of the individual lattice sites. This has led to new ideas concerning the origin of phase transitions in such crystals, and has made it possible to investigate their micromechanisms. In particular, in this approach it is possible to explain the origin of spontaneous polarization and of phase transitions in ferroelectrics.

It must be emphasized that these effects are quite general in character and pertain to almost all types of polyatomic systems. Indeed, electronic degeneracy in the ground or in the nearest excited states takes place in almost all polyatomic formations, with the exception of systems of very low symmetry. However, analogous effects appear even in these cases because of the mixing of close (pseudodegenerate) levels. One systems with pseudodegeneracy are taken into consideration, the group of objects for which the effects of vibronic interaction can turn out to be significant becomes practically all-inclusive. It includes, in particular, all types of molecular formations (in the ground or excited states), complex and organometallic compounds of transition and rare-earth elements, including those in the crystalline state, impurity centers and defects in crystals, and a number of biological systems.

From the theoretical point of view it is of interest that similar defects can arise also in other many-particle problems, for example, in exciton-phonon,^[13a] nucleon-meson,^[13b] or impurity-magnon^[14a] interactions; the problem of the cooperative Jahn-Teller effect has a direct bearing on the problem of phonon instability and phase transitions in semimetals.^[14b]

An exhaustive exposition of all the pertinent problems could be the subject of an entire monograph, and is thus beyond the scope of this article. In the present review we confine ourselves to examination of the status of the theory of the problem as a whole and of a number of its most timely applications. Greater attention

has been paid to the case of strong vibronic coupling, when the minima of the adiabatic potentials of the degenerate (or pseudodegenerate) terms are deep enough, so that the observed effects are best described in the language of tunneling. This aspect of the problem is most important for applications. At the same time, to make the exposition complete, we consider also the limiting case of weak coupling.²⁾

2. ELECTRON-VIBRATIONAL EQUATIONS FOR ELECTRON-DEGENERATE STATES³⁾

We write down the Hamiltonian of a polyatomic system in the form

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_r + \hat{\mathcal{H}}_Q + \hat{V}(r, Q), \quad (1)$$

where $\hat{\mathcal{H}}_r$ includes the operators of the kinetic energy of the electrons and of their interaction with one another, $\hat{\mathcal{H}}_Q$ is the same for nuclei, and $V(r, Q)$ is the operator of the interaction of the electrons and the nuclei (from now on, unless specially stipulated, r and Q are the symbols for all the electron coordinates r_ν and for all the nuclear coordinates Q_α). In the Born-Oppenheimer adiabatic approximation, as is well known, one solves first the electron equation

$$[\hat{\mathcal{H}}_r + \hat{V}(r, Q)] \psi_i(r, Q) = W_i(Q) \psi_i(r, Q). \quad (2)$$

Next, if the obtained i -th electronic state is not degenerate (for the considered values of Q), then the complete wave function takes the form

$$\Psi_{iK}(r, Q) = \psi_i(r, Q) \chi_{iK}(Q), \quad (3)$$

so that upon substitution in the Schrödinger equation with the Hamiltonian (1)

$$\hat{\mathcal{H}} \Psi_{iK}(r, Q) = E_{iK} \Psi_{iK}(r, Q) \quad (4)$$

we can obtain for χ_{iK} the approximate equation

$$[\hat{\mathcal{H}}_Q + W_i(Q)] \chi_{iK}(Q) = E_{iK} \chi_{iK}(Q). \quad (5)$$

It is seen from this equation, in particular, that in our case $W_i(Q)$, together with energy of the interaction of the nuclei from $\hat{\mathcal{H}}_Q$, plays the role of the potential energy of the nuclei in the field of the electrons (the adiabatic potential). In the derivation of (5), in addition to neglecting the diagonal kinetic-energy operator matrix elements in the electronic functions $\psi_i(r, Q)$, which are not very significant here (and which incidentally can be easily taken into account in the form of a correction), we neglect also the off-diagonal elements of the Hamiltonian (1):

$$\langle \Psi_{iK} | \hat{\mathcal{H}} | \Psi_{jK'} \rangle = \int dQ \chi_{iK} \left[\int dr \left(\psi_i \sum_{\alpha} \frac{\hat{p}_{\alpha}^2}{M_{\alpha}} \psi_j \hat{p}_{\alpha} + \psi_i \sum_{\alpha} \frac{p_{\alpha}^2}{M_{\alpha}} \psi_j \right) \right] \chi_{jK'} = \int dQ \chi_{iK} \hat{A}_{ij} \chi_{jK'}, \quad (6)$$

where \hat{A}_{ij} are the electronic matrix elements of the so-called non-adiabaticity operator, and \hat{P} and M are the momenta and masses of the nuclei. Therefore the criterion of the adiabatic approximation is the smallness of these off-diagonal elements in comparison with the differences $W_i(Q) - W_j(Q)$. This condition is well satisfied for sufficiently remote levels and for the values of Q that are far from the level-crossing points (or the closest-approach regions). For electron-degenerate states, when several adiabatic potentials W_i coincide at the point Q_0 (or in pseudodegeneracy, when they are close

enough to one another), the adiabatic approximation no longer holds.

Assume that in the solution of the electronic equation (2) the i -th level turns out to be f -fold degenerate at the point Q_0 : $W_i(Q_0) = W(Q_0)$, $i = 1, 2, \dots, f$. Neglecting in the equation terms of the same order as those discarded in the adiabatic approximation considered above for the nondegenerate level (the state-mixing terms of different levels of type (6)), we need retain in the expansion of the total wave function $\Psi(r, Q)$ in terms of the system of solutions $\psi_i(r, Q)$ only f terms with the electronic functions of the degenerate level

$$\Psi(r, Q) = \sum_{i=1}^f \psi_i(r, Q) \chi_i(Q); \quad (7)$$

for each of the functions $\chi_i(Q)$ we then obtain the system of equations

$$[\hat{\mathcal{H}}_Q + W_i(Q) - E] \chi_i(Q) + \sum_{j \neq i} A_{ij} \chi_j(Q) = 0 \quad (i = 1, 2, \dots, f). \quad (8)$$

Thus, the vibrational problem for an f -fold degenerate level reduces to a system of f coupled equations. However, the effects of the vibronic interaction, particularly the tunnel effects considered above, are due in the case of these equations as to the complicated character, due to the degeneracy or pseudodegeneracy, of the adiabatic potentials $W_i(Q)$, which contain several equivalent minima.

3. ADIABATIC POTENTIALS OF ELECTRON-DEGENERATE LEVELS

We consider a system having N vibrational degrees of freedom, and let the electronic level at the point $Q_{\alpha 0}$, $\alpha = 1, \dots, N$, be f -fold degenerate and transform in accordance with the representation Γ of the symmetry group of the problem. In this case we can take Q_{α} to be the normal coordinates of the system, which transform in accordance with irreducible representations of the same group.

We divide the system into atomic cores and valence electrons in such a way that all the electron-vibrational interaction in $\hat{V}(r, Q)$ can be attributed with the required accuracy to the valence electrons, and the interaction of the cores is approximated by the harmonic term $(1/2) \sum_{\alpha} k_{\alpha} Q_{\alpha}^2$, where $k_{\alpha} = M_{\alpha} \omega_{\alpha}^2$ is the force constant of the α -th normal vibration (M_{α} is the reduced mass and ω_{α} is the frequency). Expanding the operator $\hat{V}(r, Q)$ in powers of the small displacements of the nuclei from the point $Q_{\alpha 0}$, we have:

$$\hat{V}(r, Q) = \hat{V}(r, Q_0) + \sum_{\alpha} \left(\frac{\partial \hat{V}}{\partial Q_{\alpha}} \right)_{Q_0} (Q_{\alpha} - Q_{\alpha 0}) + \frac{1}{2} \sum_{\alpha, \beta} \left(\frac{\partial^2 \hat{V}}{\partial Q_{\alpha} \partial Q_{\beta}} \right)_{Q_0} (Q_{\alpha} - Q_{\alpha 0}) (Q_{\beta} - Q_{\beta 0}) + \dots \quad (9)$$

The electronic degeneracy is obtained when account is taken in (9) of only the zeroth term of this expansion. The linear terms of (9), in accordance with the Jahn-Teller theorem,^[1] have nonzero matrix elements in the functions of the electronic level, at least for several Q_{α} , so that their inclusion in (9) lifts the degeneracy of the level at $Q_{\alpha} \neq Q_{\alpha 0}$. Terms of higher order of smallness are also significant.

We put $\hat{V}'(r, Q) = \hat{V}(r, Q) - \hat{V}(r, Q_0)$. Then the corrections to the energy levels as functions of Q at small

²⁾For an explanation of a number of aspects of the problem see also [15].

³⁾For more details see, e.g., [16].

$(Q - Q_0)$ are obtained from the solution of the secular equation

$$\|V'_{ij} - \varepsilon\| = 0 \quad (i, j = 1, 2, \dots, f), \quad (10)$$

with the aid of which the adiabatic potentials are determined directly (we omit the index of the degenerate level and a constant—its energy at the degeneracy point—which is no longer significant):

$$W_i(Q) = \frac{1}{2} \sum_{\alpha} k_{\alpha} Q_{\alpha}^2 + \varepsilon_i(Q). \quad (11)$$

It is necessary to investigate (10) for each type of electronic degeneracy. Polyatomic systems of cubic symmetry (O, O_h, T, T_d) admit of doubly-degenerate E levels and triply degenerate T_1 and T_2 levels. In groups of lower symmetry, only E levels are possible. A higher degree of degeneracy is possible only in the icosahedron group, which is not considered here.

As the electronic basis of the E level we shall henceforth use the functions $|\theta\rangle$ and $|\varepsilon\rangle$, which transform respectively like $3z^2 - r^2$ and $x^2 - y^2$; for the functions of the T_2 term we choose $|\xi\rangle \sim yz, |\eta\rangle \sim xz, |\zeta\rangle \sim xy$. The case of the T_1 level will not be considered below, since the results for it are perfectly analogous to the case of the T_2 level.

The vibronic-interaction matrices constructed with these functions can be determined by using the Wigner-Eckart theorem: if $\hat{F}(\bar{\Gamma}\bar{\gamma})$ is an arbitrary operator that transforms in accordance with the row $\bar{\gamma}$ of the representation $\bar{\Gamma}$, then its matrix elements in the functions of the basis are given by the expression^[17]

$$\langle \Gamma\gamma_1 | \hat{F}(\bar{\Gamma}\bar{\gamma}) | \Gamma\gamma_2 \rangle = \langle \Gamma | \hat{F}(\bar{\Gamma}) | \Gamma \rangle \langle \Gamma\gamma_1 \bar{\Gamma}\bar{\gamma} | \Gamma\gamma_2 \rangle, \quad (12)$$

where $\langle \Gamma | \hat{F}(\bar{\Gamma}) | \Gamma \rangle = A_{\bar{\Gamma}\Gamma}$ is the reduced matrix element and $\langle \Gamma\gamma_1 \bar{\Gamma}\bar{\gamma} | \Gamma\gamma_2 \rangle$ is a Clebsch-Gordan coefficient. With allowance for the values of the latter, we have for the E level (the lower-case letters will henceforth label the representations in accordance with which the corresponding normal vibrations transform)

$$V_E(e\theta) = A \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = A\sigma_z, \quad V_E(e\varepsilon) = A \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = A\sigma_x. \quad (13)$$

For the T_2 level we obtain analogously

$$\begin{aligned} V_{T_2}(t_2\xi) &= B \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = B\tau_x, \\ V_{T_2}(t_2\eta) &= B \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} = B\tau_y, \\ V_{T_2}(t_2\zeta) &= B \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = B\tau_z, \end{aligned} \quad (14)$$

$$V_{T_2}(e\theta) = C \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = C\tau_0, \quad V_{T_2}(e\varepsilon) = C \begin{pmatrix} \frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & -\frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix} = C\tau_x, \quad (15)$$

where $A = A_{EE}^e, B = A_{T_2T_2}^{t_2}, C = A_{T_2T_2}^e$ are reduced matrix elements, the physical meaning of which will be explained below.

a) Case of E Level

In this case the nonzero matrix elements in the secular equation (10) are those of the vibrations of the type $[E^2] = A_1 + E$. The fully-symmetrical vibration of type A_1 can be excluded from consideration, since their contribution can be taken into account in the harmonic term of expression (11) by a suitable choice of the ori-

gin of the normal coordinates and frequencies. There remain the non-fully-symmetrical e-vibrations Q_{β} and Q_{ε} (the E - e problem, for short), which are the only ones that are active in the Jahn-Teller effect for the E level. The nuclear displacements corresponding to these coordinates are shown in Fig. 1 for an octahedron. With the aid of (13), the secular equation (10) with allowance for both the linear and the quadratic terms of the expansion (9) takes the form

$$[A_1 Q_{\theta} + A_2 (Q_{\xi}^2 - Q_{\eta}^2)] \sigma_x - [A_1 Q_{\varepsilon} - 2A_2 Q_{\theta} Q_{\varepsilon}] \sigma_x - \varepsilon_1 = 0, \quad (16)$$

where 1 is a unit matrix and the quantities $A_1 = (\partial V_{\beta\beta} / \partial Q_{\beta})_0$ and $A_2 = (1/2) (\partial^2 V_{\beta\beta} / \partial Q_{\beta}^2)_0$ have the meaning of the constants of the linear and quadratic vibronic coupling, respectively.

The solution of (16) can be obtained directly. Putting $Q_{\beta} = \rho \cos \varphi, Q_{\varepsilon} = \rho \sin \varphi$, we obtain

$$\varepsilon_{\pm}(\rho, \varphi) = \pm \rho \sqrt{A_1^2 + A_2^2 \rho^2 + 2A_1 A_2 \rho \cos 3\varphi} \quad (17)$$

and

$$W_{\pm}(\rho, \varphi) = \frac{1}{2} k_e \rho^2 \pm \rho \sqrt{A_1^2 + A_2^2 \rho^2 + 2A_1 A_2 \rho \cos 3\varphi}. \quad (18)$$

At small A_2 one uses frequently a linear approximation ($A_2 = 0$) for which the potential (18) is given by

$$W_{\pm}(\rho, \varphi) = \frac{1}{2} k_e \rho^2 \pm A_1 \rho \quad (19)$$

and has the form of a figure of revolution called "sombbrero" (Fig. 2).

The extremal points of the surface (18) are given by the expressions

$$\rho_0 = \pm A_1 [k_e \mp (-1)^n 2A_2]^{-1}, \quad \varphi_0 = \frac{n\pi}{3} \quad (n = 0, 1, \dots, 5), \quad (20)$$

where the upper and lower signs pertain to the cases $A_1 > 0$ and $A_1 < 0$, respectively. An analysis of the conditions for the second derivatives of the functions (18) shows that out of the six extremal points (20), three are minima and three are saddle points, and that at $A_1/A_2 > 0$ the minima correspond to the points $n = 0, 2, 4$ and the saddle points to $n = 1, 2, 5$, while at $A_1/A_2 < 0$ these two types of points exchange places (it is assumed that $k_e > 2A_2$).

Thus, when account is taken of the quadratic terms, alternating maxima and minima appear along the trough of the sombrero (Fig. 2), as is illustrated in Fig. 3. The depth E_{JT} of the minima, reckoned from the degeneracy point (the energy of stabilization in the Jahn-Teller effect), and the height Δ of the (lowest) barrier between them, as one moves along the trough, are given by the expressions

$$E_{JT} = \frac{1}{2} \frac{A_1^2}{k_e - 2A_2}, \quad \Delta = \frac{4A_2}{k_e - 2A_2} E_{JT}. \quad (21)$$

The regular functions that diagonalize (16) are written in the form

$$\begin{aligned} \psi_- &= \cos \frac{\Omega}{2} |\theta\rangle - \sin \frac{\Omega}{2} |\varepsilon\rangle, \\ \psi_+ &= \sin \frac{\Omega}{2} |\theta\rangle + \cos \frac{\Omega}{2} |\varepsilon\rangle, \end{aligned} \quad (22)$$

where

$$\text{tg } \Omega = \frac{A_1 \sin \varphi - A_2 \rho \sin 2\varphi}{A_1 \cos \varphi + A_2 \rho \cos 2\varphi}. \quad (23)$$

We note that in accordance with this relation, Ω does not coincide with φ at $A_2 \neq 0$, and the difference between them may turn out to be quite appreciable (the strong nonadiabaticity extends also over the coordinate ρ and not only φ). This circumstance, first noted in^[18], has for a long time escaped the attention of numerous work-

ers investigating this problem (In all the preceding studies it was assumed that $\Omega = \varphi$).

b) T Level in the Linear Approximation

In this case $[T_2^2] = A_1 + E + T_2$, so that in the Jahn-Teller effect, besides the tetragonal e-vibrations, there are active also trigonal t_2 vibrations $Q_\xi, Q_\eta,$ and Q_ζ (Fig. 4), and the secular equation (10), with allowance for (14) and (15) for the T_2 term takes the form

$$B(Q_\xi \tau_\xi + Q_\eta \tau_\eta + Q_\zeta \tau_\zeta) + C(Q_0 \tau_0 + Q_e \tau_e) - \epsilon^1 = 0, \quad (24)$$

where the quantities $B = (\partial V_{\eta\xi} / \partial Q_\xi)_0$ and $C = (\partial V_{\xi\xi} / \partial Q_0)_0$ have the meaning of constants of the linear vibronic coupling with the trigonal and tetragonal vibrations, respectively.

The solution of Eq. (24) in general form is quite complicated. We consider first particular cases.

1) Neglect of the vibronic coupling with the trigonal vibrations, $B = 0, C \neq 0$ (the T-e problem). In this case, since the matrices τ_η and τ_e are diagonal, the solutions of (24) are obtained directly. The surface $W(Q_\eta, Q_e)$ has in this case the form of three equivalent paraboloids, the minima of which in (Q_η, Q_e) space lie at the points $(Q_0, 0), ((-1/2)Q_0, (-\sqrt{3}/2)Q_0)$ and $((-1/2)Q_0, (\sqrt{3}/2)Q_0)$, where $Q_0 = C/k_e$. The Jahn-Teller stabilization energy is $E_{JT}^e = C^2/k_e$. We note that the character of the behavior of the sheets of the surface at the point corresponding to electronic degeneracy (Fig. 5) differs from the

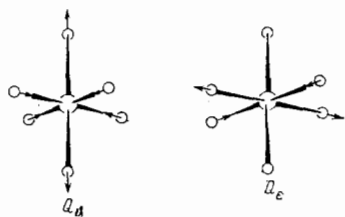


FIG. 1. Nuclear displacements corresponding to the Q_g and Q_e components of the normal e_g vibration of an octahedron.

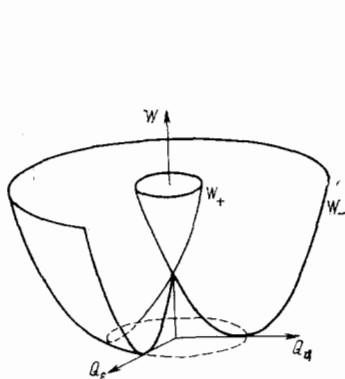


FIG. 2

FIG. 2. Shape of the potential surface in the case of the linear E-e problem.

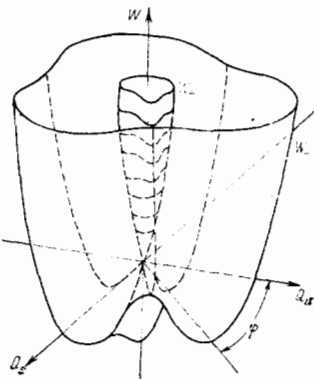


FIG. 3

FIG. 3. Shape of the potential surface of the E-e problem with allowance for the linear and quadratic terms.

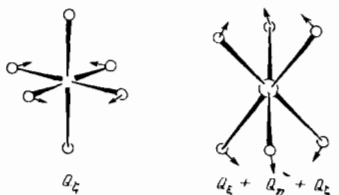


FIG. 4. Nuclear displacements corresponding to the Q_ξ and $Q_\eta + Q_\zeta$ components of the t_{1g} vibration of an octahedron.

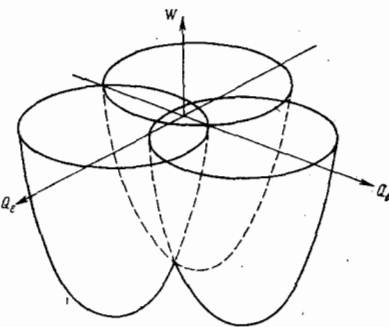


FIG. 5. Shape of the potential surface in the case of the linear T-e problem.

case of E level (see Figs. 2 and 3). Whereas for the T level the point $Q_\alpha = 0$ is a point of real intersection of surfaces, in the case of the E level it has the character of a branch point of the surfaces. The wave functions corresponding to the adiabatic potentials, unlike the E-level case considered above, are not intermixed by nuclear displacements of the E-type:

$$\psi_1 = |\xi\rangle, \quad \psi_2 = |\eta\rangle, \quad \psi_3 = |\zeta\rangle. \quad (25)$$

2) Neglect of the vibronic coupling with the tetragonal vibrations, $C = 0, B \neq 0$ (the T- t_2 problem). In this case the secular equation (24) reduces to an algebraic equation of third degree. Without solving it, we can use the method of Öpik and Pryce^[11] to determine the positions of the minima of the adiabatic potential, their depths, and the heights of the barriers between them. In three-dimensional space of the trigonal coordinates (Q_ξ, Q_η, Q_ζ) the minima lie on the four C_3 axes of the cubic system at the points $(m_\xi Q_0, m_\eta Q_0, m_\zeta Q_0)$, where $Q_0 = 2B/3k_t$ ($k_t = M\omega_t^2$ is the force constant of the trigonal displacement), and the sets (m_ξ, m_η, m_ζ) assume the values $(1, 1, 1), (-1, 1, -1), (1, -1, -1),$ and $(-1, -1, 1)$. The electronic wave functions at the minima are given by the expressions $\psi = (m_\xi|\xi\rangle + m_\eta|\eta\rangle + m_\zeta|\zeta\rangle)/\sqrt{3}$, and the depth of the minima are given by $E_{JT}^t = 2B^2/3k_t$.

3) Simultaneous allowance for both types of vibrations, $C \neq 0, B \neq 0$ (the T-(e + t_2) problem). In this case Eq. (24) becomes even more complicated, but the extremal points of the adiabatic-potential surface are quite easy to obtain in the considered linear approximation^[11]. Besides the three tetragonal points (obtained above in the T-e problem) and the four trigonal points (from the T- t_2 problem), it is possible to have here also intermediate-type extremal points of symmetry C_2 , when both the tetragonal and the trigonal coordinates are displaced. Then, if $C^2/2k_e > 2B^2/3k_t$, the tetragonal points are minima and the trigonal points are saddles. On the other hand, if the inverse inequality holds, then the trigonal points become minima and the tetragonal ones saddles. Intermediate points with energy $E = (1/4)E_{JT}^e + (3/4)E_{JT}^t$ remain saddles in this approximation in all cases. In the particular case $C^2/2k_e = 2B^2/3k_t$ there is realized a continuous sheet of minima of equal depth (two-dimensional trough in five-dimensional space), which subtends over all the three types of extremal points.^[19]

4) Quadratic approximation.^[20] The quadratic terms of the vibronic interaction can be classified by symmetry in two or three types: $e \times e, t_2 \times t_2,$ and $e \times t_2$. The most fundamental change in the form of the adiabatic-potential surface is produced by terms of the type $e \times t_2$, which mix the tetragonal and the trigonal vibrations. Allowance for these terms leads to the appearance in the left-hand side of (24) of an additional component

$$F[Q_\xi(-\frac{1}{2}Q_0 + \frac{1}{2}\sqrt{3}Q_e)\tau_\xi + Q_\eta(-\frac{1}{2}Q_0 - \frac{1}{2}\sqrt{3}Q_e)\tau_\eta + Q_\zeta Q_0 \tau_\zeta], \quad (26)$$

where $F = [(\partial^2 V_{E\eta}) / (\partial Q_e \partial Q_t)]_0$ is the corresponding reduced matrix element, having the meaning of the constant for the coupling with quadratic vibrations of the $e \times t_2$ type. The basic characteristics of the surface (11) are determined by the two dimensionless parameters $M = F(k_e k_t)^{-1/2}$, $N = FC/Bk_e$. The case $F = 0$ on the MN plane (Fig. 6) corresponds to one point $M = N = 0$. On the lines $M = \pm(\sqrt{3}/2)N$, the energies of the tetragonal and trigonal extrema, the depths and positions of which do not change when the quadratic interaction is taken into account, coincide. In the cross-hatched region, the trigonal extrema are deeper than the tetragonal ones, and in the singly-hatched region, to the contrary, the tetragonal extrema are deeper than the trigonal ones. In all cases, for the system to be stable it is necessary to have $|M| < 1$.

The most important influence is that of the allowance of the quadratic terms of the $e \times t_2$ type on the position and character of the six equivalent intermediate extrema of the orthorhombic type (which in the linear approximation can be only saddle points). Their depths and the coordinates of one of them (the coordinates of the rest can be obtained from symmetry considerations) are given by the expressions

$$\begin{aligned} E_{JT}^e &= C^2(N^2 - 4M^2N + 4M^2)[8k_e N^2(1 - M^2)]^{-1}, \\ Q_{\xi}^{(e)} &= Q_{\eta}^{(e)} = Q_{\zeta}^{(e)} = 0, \\ Q_{\xi}^{(t)} &= B(2 - N)[2k_t(1 - M^2)]^{-1}, \\ Q_{\eta}^{(t)} &= -C(N - 2M^2)[2Nk_e(1 - M^2)]^{-1}. \end{aligned}$$

As the point $F = 0$, $M = N = 0$ is approached along the lines $M = \pm(\sqrt{3}/2)N$ on the MN plane (see Fig. 6), the depth of these extrema becomes equal to the depths of the tetragonal and the trigonal extrema, $E_{JT}^e = E_{JT}^t = E_{JT}^{et}$, and the already mentioned two-dimensional trough of the minima on the five-dimensional surface of the adiabatic potential is realized. Outside this point we have $E_{JT}^e \neq E_{JT}^t$, so that when the quadratic terms of the vibronic interaction are taken into account the trough of the minima "becomes corrugated," and alternating hills and valleys appear along the trough, in full analogy, in principle, to the case of E term (see Sec. a). It is very important that the orthorhombic extrema become absolute minima (Fig. 7) for a large range of the parameters M and N.

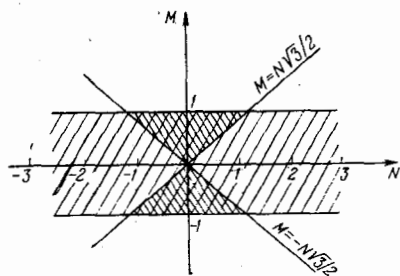


FIG. 6. Regions of existence of tetragonal (single hatching) and trigonal (cross-hatching) minima of the quadratic T - ($e + t_2$) problem.

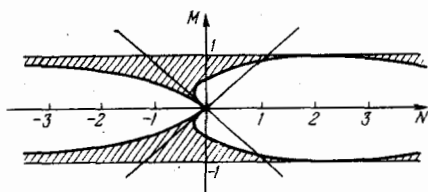


FIG. 7. Region of existence of orthorhombic minima (shaded).

In addition to these three types of extrema, when account is taken of the quadratic terms of the vibronic interaction there appear on the adiabatic-potential surface three new types of extrema, two types consisting of twelve equivalent extrema each, and the third of 24. However, the region of existence of the last type of extrema lies beyond the range of values of the parameters at which the system is stable, and the extrema of the first two types do not become absolute minima anywhere. Detailed calculations in these cases were carried out numerically.^[20]

A group-theoretical investigation of the shapes of the potential surfaces in the case of vibronic interaction is the subject of^[21].

4. INVERSION (TUNNEL) SPLITTING

After determining the adiabatic potential, the energy spectrum and the wave functions of the system can be obtained in principle by numerically integrating the system (8). The latter is a very complicated procedure and has so far been carried out completely enough for only two very simple particular cases, the linear approximations of the E - e problem^[22] and the T - t problem.^[23] A second approach to the problem was proposed by one of us.^[7-9] It makes it possible to determine relatively simply several lowest levels of the system, knowledge of which is perfectly sufficient for an approximate calculation of a number of observable physical quantities.

We consider the case of strong vibronic coupling, when the depths of the minima of the adiabatic potential are large enough, so that at the points of the minima the distance to the next sheet of the adiabatic potential (which for the E level, for example, is equal to $4E_{JT}$) becomes comparable with the usual distance between the potentials of the nondegenerate levels. Then, in the region near the minima, the system of equations (8) is decoupled and the usual adiabatic approximation becomes applicable for the nondegenerate terms.

We assume that in the zeroth approximation the states at the minima are independent, and we denote the electronic function in the i -th minimum by ψ_i , the vibrational function by χ_{iK} , and the total function by $\Phi_{iK} = \psi_i \chi_{iK}$. Since the number of equivalent minima in the system is r , in this approximation the system is r -fold degenerate. It is easy to determine which terms of the Hamiltonian must be neglected in order to obtain the solution Φ_{iK} . Regarding these terms as a small perturbation, we write down the complete wave function of zeroth approximation in the form of the linear combination

$$\Psi_{\alpha K} = \sum_{i=1}^r C_{i\alpha} \Phi_{iK} \quad (\alpha = 1, \dots, r). \quad (27)$$

Then the energy levels E and the coefficients $C_{i\alpha}$ are determined from the solution of the secular equation

$$\|\mathcal{H}_{ij}^K - E_{\alpha} S_{ij}^K\| = 0 \quad (i, j = 1, \dots, r), \quad (28)$$

where \mathcal{H} is the complete Hamiltonian and $S_{ij}^K = \int \Phi_{iK}^* \Phi_{jK} d\tau$ is the overlap integral.

It is easy to show that for $i \neq j$ we have $\mathcal{H}_{ij}^K = \mathcal{H}_{ji}^K$, $S_{ij}^K = S_{ji}^K$, and Eq. (27) can be solved directly. The obtained values of E_{α} and $C_{i\alpha}$ for $r = 3, 4$, and 6 are listed in the table. It is seen that, provided only that $\mathcal{H}_{12}^K \neq 0$, the electron-vibrational ground level at the minimum is split into two, one is nondegenerate and one is doubly degenerate (if $r = 3$) or triply degenerate (if $r = 4$),

or else we get two triply degenerate levels ($r = 6$) (see also^[24]). In the analogy with ammonia, this splitting was named "inversion"^[9]; some authors prefer "tunnel splitting" (see^[15, 25]). The criterion for the applicability of perturbation theory is smallness of the inversion splitting δ_K in comparison with the value of the vibrational quantum $\hbar\omega$ at the minimum.

a) Tunnel Splitting in the Case of the E Level

We assume that the three minima of the adiabatic potential (Fig. 3) are deep enough for the surface near each of them to have the shape of a paraboloid, in which the vibrations are described by the harmonic functions $\chi_{iK}(\mathbf{Q})$, and the electronic function can be assumed to be independent of the nuclear coordinates. Then at each minimum there is a separate proper system of normal coordinates $Q_j^{(1)}$ and $Q_j^{(2)}$ (corresponding to a tetragonally-distorted cubic system), which can be easily written down on the basis of symmetry, and the expressions for the electronic functions are determined from (22) by substituting the coordinates of the minima in Ω .

For the overlap integral we obtain

$$S_{12}^x = -\frac{1}{2} \gamma_x, \quad \gamma_x = \int dQ_\delta dQ_\epsilon \chi_x(Q_\delta^{(1)}) \chi_x(Q_\epsilon^{(1)}) \chi_x(Q_\delta^{(2)}) \chi_x(Q_\epsilon^{(2)}). \quad (29)$$

Denoting the frequencies of the two components of the e-vibrational split in the tetragonal minimum by ω_ρ and ω_φ and $p = \omega_\varphi/\omega_\rho$ we easily obtain for the vibrational ground state

$$\gamma_0 = \sqrt{\frac{16p}{3p^2 + 4(p+3)}} \exp\left(-6 \frac{p^2 + 3}{3p^2 + 4(p+3)} \frac{E_{II}}{\hbar\omega_\rho}\right), \quad (30)$$

$$\gamma_{12}^0 = \frac{3}{4} E_{II} \gamma_0 \left(1 + \frac{1}{2} \frac{A_2}{\hbar\omega_\rho - 2A_2}\right). \quad (31)$$

From this expression it seems, in particular, that $\gamma_{12}^0 > 0$ and that in the vibrational ground state there will be an inversion doublet at the bottom (see the table)⁴⁾.

The expressions for the energies and wave functions of the inversion (tunnel) levels are quite rough in this approximation, since they do not take into account the strong dependence of the electronic states at the minima on the nuclear coordinates (cf. (22)). The problem was subsequently solved also by other methods. For example, O'Brien^[26], in contrast to the analysis presented here, begins with the linear case of a sombrero with a sufficiently deep trough, for which the approximate solution (in the region near the bottom of the trough) is obtained directly:

$$\Psi(r, \rho, \varphi) = \Psi_-(r, \varphi) f_n(\rho - \rho_0) e^{im\varphi} \quad \left(m = \pm \frac{1}{2}, \pm \frac{3}{2}, \dots\right), \quad (32)$$

$$E_{n,m} = \hbar\omega_\rho \left(n + \frac{1}{2}\right) + \frac{\hbar^2\omega_\rho^2}{4E_{II}} m^2 - E_{II} \quad (n = 0, 1, \dots), \quad (33)$$

where $f_n(\rho)$ are the oscillator functions. Including now the quadratic terms of the vibronic interaction in the form of a perturbation, and assuming that they do not intermix the vibrational states with different n , we can obtain the following approximate expression for the motion along the trough:

$$\left(-\alpha \frac{d^2}{dq^2} + \beta \cos 3\varphi - E\right) \chi(\varphi) = 0, \quad (34)$$

where

$$\alpha = \frac{\hbar^2}{3M\rho_0^2} \approx \frac{(\hbar\omega_\rho)^2}{E_{II}}, \quad \beta = A_2\rho_0^2.$$

⁴⁾The sign of γ_{12}^0 in the first paper on this subject [8] is wrong.

The results of a numerical solution of this equation are shown in Fig. 8. It can be seen that already at $\beta/\alpha \geq 2$, i.e., when the quadratic barrier becomes larger than the kinetic energy of the free motion in the trough, the qualitative picture of the arrangement of the low-lying levels corresponds to that expected from the theory of inversion (tunnel) splitting.

The foregoing analysis by O'Brien^[26] cannot be regarded as sufficiently correct, since numerical estimates given in the same paper make β in the considered case of strong vibronic coupling comparable with or larger than the vibrational quantum $\hbar\omega_\rho$, and there is consequently no justification for neglecting the mixing of the vibrational states and the separation of the motions with respect to ρ and φ (furthermore, the wave functions of the inversion states are not obtained in^[26] in a form convenient for use). Recently^[18] (see also^[27]) it was proposed to use a variational principle to solve this problem. It can be shown that trial functions of the type

$$\chi_E(\rho, \varphi) = N \begin{Bmatrix} \cos(\varphi/2) \\ \sin(\varphi/2) \end{Bmatrix} \sqrt{q} \exp\left[-\frac{1}{2}u(q-1)^2 + v \cos 3\varphi\right],$$

where N is the normalization constant and $q = \rho/\rho_0$, with

The coefficients ($C_{1\alpha}, C_{2\alpha}, \dots, C_{r\alpha}$), $\alpha = 1, 2, \dots, r$, from formula (27), expressed in the form $N_\alpha(m_\alpha, n_\alpha, \dots, l_\alpha)$, where N_α is a normalization factor

Number of equivalent minima	Symmetry of inversion levels	Level energy	Coefficients ($C_{1\alpha}, C_{2\alpha}, \dots, C_{r\alpha}$)
3	E	$-\frac{H_{12}}{1-s}$	$\begin{Bmatrix} \frac{2}{\sqrt{6(1-s)}} (2, -1, -1) \\ \frac{1}{\sqrt{2(1-s)}} (0, 1, -1) \\ \frac{1}{\sqrt{3(1+2s)}} (1, 1, 1) \end{Bmatrix}$
	A	$\frac{2H_{12}}{1+2s}$	$\begin{Bmatrix} \frac{1}{2\sqrt{1-s}} (1, -1, -1, 1) \\ \frac{1}{2\sqrt{1-s}} (1, -1, 1, -1) \\ \frac{1}{2\sqrt{1-s}} (1, 1, -1, -1) \\ \frac{1}{2\sqrt{1+3s}} (1, 1, 1, 1) \end{Bmatrix}$
4	T	$-\frac{H_{12}}{1-s}$	$\begin{Bmatrix} \frac{1}{2\sqrt{1-s}} (1, -1, -1, 1) \\ \frac{1}{2\sqrt{1-s}} (1, -1, 1, -1) \\ \frac{1}{2\sqrt{1-s}} (1, 1, -1, -1) \\ \frac{1}{2\sqrt{1+3s}} (1, 1, 1, 1) \end{Bmatrix}$
	A	$\frac{3H_{12}}{1+3s}$	$\begin{Bmatrix} \frac{1}{2\sqrt{1+2s}} (1, -1, 1, 1, 0, 0) \\ \frac{1}{2\sqrt{1+2s}} (1, 0, -1, 0, 1, 1) \\ \frac{1}{2\sqrt{1+2s}} (0, -1, 0, 1, 1, -1) \\ \frac{1}{2\sqrt{1-2s}} (1, -1, 1, -1, 0, 0) \\ \frac{1}{2\sqrt{1-2s}} (-1, 0, 1, 0, 1, 1) \\ \frac{1}{2\sqrt{1-2s}} (0, -1, 0, 1, -1, 1) \end{Bmatrix}$
6	T ₁	$\frac{2H_{12}}{1+2s}$	$\begin{Bmatrix} \frac{1}{2\sqrt{1+2s}} (1, -1, 1, 1, 0, 0) \\ \frac{1}{2\sqrt{1+2s}} (1, 0, -1, 0, 1, 1) \\ \frac{1}{2\sqrt{1+2s}} (0, -1, 0, 1, 1, -1) \\ \frac{1}{2\sqrt{1-2s}} (1, -1, 1, -1, 0, 0) \\ \frac{1}{2\sqrt{1-2s}} (-1, 0, 1, 0, 1, 1) \\ \frac{1}{2\sqrt{1-2s}} (0, -1, 0, 1, -1, 1) \end{Bmatrix}$
	T ₂	$-\frac{2H_{12}}{1-2s}$	$\begin{Bmatrix} \frac{1}{2\sqrt{1+2s}} (1, -1, 1, 1, 0, 0) \\ \frac{1}{2\sqrt{1+2s}} (1, 0, -1, 0, 1, 1) \\ \frac{1}{2\sqrt{1+2s}} (0, -1, 0, 1, 1, -1) \\ \frac{1}{2\sqrt{1-2s}} (1, -1, 1, -1, 0, 0) \\ \frac{1}{2\sqrt{1-2s}} (-1, 0, 1, 0, 1, 1) \\ \frac{1}{2\sqrt{1-2s}} (0, -1, 0, 1, -1, 1) \end{Bmatrix}$

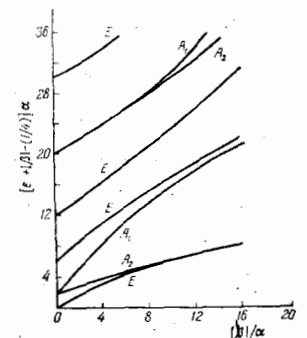


FIG. 8. Energy of the lowest levels of the E-e problem vs. the quadratic coupling parameter (in units of α).

two variational parameters u and v , satisfy all the requirements of symmetry and of the behavior of the function near the minima and under the barriers between them. Minimization of the total energy calculated with the aid of these functions makes it possible to determine the level energies and the parameters u and v as functions of the parameters of the linear and quadratic barriers $\lambda = 2E_{JT}/\hbar\omega_\rho$ and $\gamma = 2\Delta/\hbar\omega_\rho$.^[18]

b) The Case of the T Level

In particular cases of the linear T - t_2 and T - e problems, the solution is relatively easy to obtain. In the T - t_2 case with four trigonal minima of the adiabatic potential, the matrix element \mathcal{H}_{12}^K is calculated in analogy with the case of the E level, with suitable choice of the normal coordinates of the type t_2 at the minima.^[8, 9] In the linear approximation we obtain

$$\mathcal{H}_{12}^K = \frac{2}{3} E_{JT}^t \gamma_K, \quad (35)$$

and for the vibrational ground state we get

$$\gamma_0 = \exp\left(-\frac{4E_{JT}^t}{3\hbar\omega_t}\right). \quad (36)$$

More accurate calculations were carried out via numerical diagonalization of the Hamiltonian (24) with $C = 0$ ^[23] (Fig. 9).

In the case of the linear T - e problem, the electronic functions (25) are orthogonal to one another, and consequently $\mathcal{H}_{12}^K = 0$ - the ground triplet state is not split by tunneling (as follows also directly from symmetry considerations).

The solutions for the general case of the T - (e + t_2) problem encounter great difficulties due to the complicated character of the five-dimensional adiabatic potential obtained above. Calculations for certain low-lying energy levels were carried out in the linear approximation under restrictive assumptions concerning the character of the vibronic coupling with two types of vibrations. The strong coupling of the e and t_2 oscillations was considered by O'Brien,^[28] an arbitrary coupling with these oscillations under the assumption $\omega_t = \omega_e$ and $E_{JT}^t = E_{JT}^e$ was investigated in^[28, 29], while strong

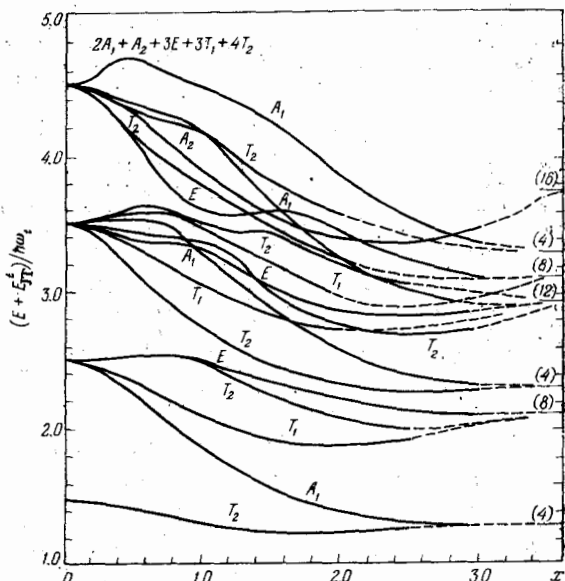


FIG. 9. Dependence of the energy of the lowest levels of the T - t_2 problem on the parameter $x = \sqrt{(3/2)E_{JT}^t}/\hbar\omega_t$.

coupling with the e vibrations and weak coupling with the t_2 vibrations were considered in^[30].

Tunnel splitting in the case of six orthorhombic minima of the adiabatic potential, which are due to the influence of quadratic terms, lead to two vibronic triplets of the type T₁ and T₂.^[20]

5. CASE OF WEAK COUPLING

In contrast to the case of deep minima considered above, it is assumed in this case that the heights of barriers between the minima are smaller than the value of the quantum of the corresponding oscillations. It is perfectly understandable that in this case the states of the systems, generally speaking, do not differ strongly from those unperturbed by the vibronic interaction and can therefore be obtained by perturbation-theory methods.^[31, 32]

We begin with consideration of the linear E - e problem. In the absence of vibronic interaction ($A_1 = 0$ in formula (16)), the Hamiltonian of the problem corresponds to a two-dimensional harmonic oscillator, the energy levels of which $E = (n + 1)\hbar\omega_e$ are $2(n + 1)$ -fold degenerate ($n + 1$ is the degeneracy multiplicity of the n-th level of the two-dimensional harmonic oscillator, and the factor 2 is due to electronic degeneracy). In second-order perturbation theory, the Hamiltonian of the problem can be reduced to the form

$$\hat{\mathcal{H}} = \frac{1}{2M} (P_x^2 + P_y^2) + \frac{1}{2} k_e (Q_x^2 + Q_y^2) - \frac{A_1^2}{2k_e} (1 + m_3\sigma_y). \quad (37)$$

where $m_3 = \hbar^{-1} (Q_\epsilon P_\epsilon - Q_\epsilon P_\epsilon)$ is the operator of the angular momentum of the nuclei in the e_g vibration. Since all the terms of this Hamiltonian commute with one another, they can be easily diagonalized simultaneously. It is easy to note that the term $m_3\sigma_y$, which describes the splitting of all levels but the ground level ($n = 0$) into doublets, is fully analogous to the spin-orbit interaction in diatomic molecules (in this case m_3 for the n-th level runs through the values $-n, -n + 2, \dots$, and $\sigma_y = \pm 1$). We note that the total splitting of the multiplet is equal to $A_1^2\hbar\omega_e n$, i.e., it becomes comparable with $\hbar\omega_e$ at sufficiently large n, even at a small coupling constant, from which it follows that the criteria of perturbation theory are violated at $n \gtrsim A_1^{-2}$.

For the T - (e + t_2) problem, in the absence of vibronic interaction, the energy levels of the three-dimensional harmonic oscillator (the t_2 vibrations) $E_n = [n + (3/2)]\hbar\omega_t$ are $3(n + 1)(n + 2)/2$ -fold degenerate, and the levels of the two-dimensional oscillator (the e-vibrations) $E_m = (m + 1)\hbar\omega_e$ are $3(m + 1)$ -fold degenerate. In second-order perturbation theory, the interaction with the e and t_2 vibrations produces additive contributions to the effect of Hamiltonian. The interaction with the e vibrations does not change the picture of the energy spectrum, and only shifts it by an amount equal to the Jahn-Teller stabilization energy. The effective Hamiltonian of the T - t problem in second-order perturbation theory takes the form^[31]

$$\hat{\mathcal{H}} = \frac{1}{2M} (P_x^2 + P_y^2 + P_z^2) + \frac{1}{2} k_t (Q_x^2 + Q_y^2 + Q_z^2) + \frac{1}{2} \frac{B^2}{k_t} (\hat{M}\hat{\lambda} - 2), \quad (38)$$

where $\hat{M} = \hbar^{-1} \mathbf{Q} \times \mathbf{P}$ is the angular momentum of the nuclei in the space of the t vibrations, and the vector matrix $\hat{\lambda}$, defined by the relations $[\hat{\lambda} \times \hat{\lambda}] = i\hat{\lambda}$, $\hat{\lambda}^2 = 2$, $[\hat{\tau} \times \hat{\tau}] = -\hat{\lambda}$, can be regarded as the matrix of the electronic angular momentum (the notation for τ is given in (14)). In this

form, the problem of the vibronic coupling in the T - t problem is perfectly analogous to the Russel-Saunders coupling of the spin and orbital angular momenta in atoms, which makes it possible to write down immediately expressions for the energy levels split by the interaction (except the level with $n = 0$):

$$E = \left(n + \frac{3}{2} \right) \hbar \omega_t + \frac{1}{8} \frac{B^2}{k_t} [L(L+1) - M(M+1) - 6].$$

Here M runs through the values $n, n-2, \dots, 1$ or 0 and given M we have $L = M \pm 1$, M at $M \geq 1$ and $L = 1$ at $M = 0$.

6. SUPPRESSION THEOREM

In all the considered cases, the vibronic ground levels have the same symmetry as the initial electronic terms in the maximally symmetrical nuclear configuration. This circumstance makes it possible to simplify greatly in a number of cases the calculations of the observed quantities. Even in the first calculation of the spin-orbit splitting of the ground vibronic state^[33] it was shown that, without allowance for the mixing with other levels, this splitting is proportional not only to the spin-orbit coupling constant, as in the case of the splitting of a pure electronic level, but to the same constant multiplied by the overlap integral of the vibrational functions in the neighboring minima γ_K as given by (29). Since $\gamma_K < 1$, this splitting as a result of allowance for the influence of the vibronic interaction turns out to be greatly decreased, sometimes by several orders of magnitude. Ham^[34, 35] generalized this idea and showed that this suppression takes place for all physical quantities if their operators depend only on the electronic coordinates. We present here a more general proof of this statement.^[30]

Assume that it is necessary to calculate the matrix element of the operator $\hat{F}_{\bar{\Gamma}\bar{\gamma}}(\mathbf{r})$, which transforms in accordance with row $\bar{\gamma}$ of the irreducible representation $\bar{\Gamma}$ of the point symmetry group, in terms of the functions of the ground vibronic multiplet $\Psi_{\Gamma\gamma}(\mathbf{r}, \mathbf{Q})$. On the basis functions of the initial electronic multiplet $\psi_{\Gamma\gamma}(\mathbf{r})$, such a matrix element can be written, in accordance with the Wigner-Eckart theorem, in the form (see^[17])

$$\langle \Psi_{\Gamma\gamma_1} | \hat{F}_{\bar{\Gamma}\bar{\gamma}}(\mathbf{r}) | \Psi_{\Gamma\gamma_2} \rangle = \langle \Psi_{\Gamma} | \hat{F}_{\bar{\Gamma}} | \Psi_{\Gamma} \rangle \langle \Gamma\gamma_1 \bar{\Gamma}\bar{\gamma} | \Gamma\gamma_2 \rangle. \quad (39)$$

On the other hand, for the wave function of the vibronic multiplet we have in the most general form

$$\Psi_{\Gamma\gamma}(\mathbf{r}, \mathbf{Q}) = \sum_{\lambda M \mu} \psi_{\Gamma\lambda}(\mathbf{r}) \chi_{M\mu}(\mathbf{Q}) \langle \Gamma\lambda M \mu | \Gamma\gamma \rangle, \quad M \in \Gamma \times \Gamma, \quad (40)$$

where the functions of only the nuclear coordinates $\chi_{M\mu}(\mathbf{Q})$ transform in accordance with row μ of the irreducible representation M and satisfy the orthogonality and normalization conditions

$$\langle \chi_{M_1\mu_1} | \chi_{M_2\mu_2} \rangle = \langle \chi_{M_1}^{\mu_1} | \delta_{M_1 M_2} \delta_{\mu_1 \mu_2} \rangle, \quad \sum_M \langle \chi_M^{\mu} | \chi_M^{\mu} \rangle = 1.$$

Taking (39) and (40) into account, we can easily write for the matrix element $\hat{F}_{\bar{\Gamma}\bar{\gamma}}(\mathbf{r})$ in the functions (40) the expression

$$\langle \Psi_{\Gamma\gamma_1}(\mathbf{r}, \mathbf{Q}) | \hat{F}_{\bar{\Gamma}\bar{\gamma}}(\mathbf{r}) | \Psi_{\Gamma\gamma_2}(\mathbf{r}, \mathbf{Q}) \rangle = \langle \Psi_{\Gamma}(\mathbf{r}) | \hat{F}_{\bar{\Gamma}}(\mathbf{r}) | \Psi_{\Gamma}(\mathbf{r}) \rangle \times \sum_M \langle \chi_M^{\mu} | \sum_{\mu_1 \mu_2} \langle \Gamma\lambda_1 M \mu_1 | \Gamma\gamma_1 \rangle \langle \Gamma\lambda_1 \bar{\Gamma}\bar{\gamma} | \Gamma\lambda_2 \rangle \langle \Gamma\lambda_2 M \mu_2 | \Gamma\gamma_2 \rangle. \quad (41)$$

The last sum can be folded with the aid of the 6Γ coefficients^[17, 36]. Omitting simple intermediate transformations, we obtain

$$\langle \Psi_{\Gamma\gamma_1}(\mathbf{r}, \mathbf{Q}) | \hat{F}_{\bar{\Gamma}\bar{\gamma}}(\mathbf{r}) | \Psi_{\Gamma\gamma_2}(\mathbf{r}, \mathbf{Q}) \rangle$$

$$= \langle \Psi_{\Gamma}(\mathbf{r}) | \hat{F}_{\bar{\Gamma}}(\mathbf{r}) | \Psi_{\Gamma}(\mathbf{r}) \rangle \langle \Gamma\gamma_1 \bar{\Gamma}\bar{\gamma} | \Gamma\gamma_2 \rangle [\Gamma] \sum_M (-1)^{j(M)} \left\{ \begin{matrix} \Gamma & \bar{\Gamma} & \Gamma \\ & M & \Gamma \end{matrix} \right\} \langle \chi_M^{\mu} \rangle,$$

where $[\Gamma]$ is the dimensionality of the representation Γ , $j(M)$ is the moment of representation M, and $\left\{ \begin{matrix} \cdot \\ \cdot \\ \cdot \end{matrix} \right\}$ is a 6Γ symbol.

Comparing this expression with (39), we see that

$$\langle \Psi_{\Gamma\gamma_1}(\mathbf{r}, \mathbf{Q}) | \hat{F}_{\bar{\Gamma}\bar{\gamma}}(\mathbf{r}) | \Psi_{\Gamma\gamma_2}(\mathbf{r}, \mathbf{Q}) \rangle = \langle \Psi_{\Gamma\gamma_1}(\mathbf{r}) | \hat{F}_{\bar{\Gamma}\bar{\gamma}}(\mathbf{r}) | \Psi_{\Gamma\gamma_2}(\mathbf{r}) \rangle K_{\Gamma}(\bar{\Gamma}), \quad (42)$$

$$K_{\Gamma}(\bar{\Gamma}) = [\Gamma] \sum_M (-1)^{j(M)} \langle \chi_M^{\mu} \rangle \left\{ \begin{matrix} \Gamma & \bar{\Gamma} & \Gamma \\ & M & \Gamma \end{matrix} \right\}.$$

We see therefore that the sought matrix element on the vibronic functions differs from the matrix element on the initial electronic functions by a coefficient $K_{\Gamma}(\bar{\Gamma})$, which depends not on the concrete form of the operator $\hat{F}_{\bar{\Gamma}\bar{\gamma}}$, but only on the representation $\bar{\Gamma}$ in accordance with which it is transformed (and on the vibronic parameters which enter in χ_M^{μ}). Since the 6Γ coefficients in form (42) are known^[17, 36], it is easy to obtain group expressions for the parameters $K_{\Gamma}(\bar{\Gamma})$ for the concrete symmetry of the operators in each point. It follows from this theorem that once the constants $K_{\Gamma}(\bar{\Gamma})$, called the suppression constants, are known, the electronic characteristics of the ground state of the system can be determined without solving the vibronic problem—it suffices to calculate the matrix elements in the initial electronic functions of the degenerate term. In particular, it is possible to determine the constants $K_{\Gamma}(\bar{\Gamma})$ from one experiment and use them to predict the results for all other experiments.

When solving the vibronic problem, it is possible to obtain also expressions for the suppression constants in terms of the vibronic-coupling constants. In particular, for the linear E - e problem the values $K_E(A_2)$ and $K_E(E)$ shown in Fig. 10 are obtained. For the linear T - e problem we can assume approximately^[34]

$$K_T(T_1) \approx K_T(T_2) \approx \exp(-3E_{JT}/2\hbar\omega_e), \quad (43)$$

$$K_T(E) = 1.$$

More exact values of these constants, with allowance for the influence of the t_2 oscillations, were obtained numerically^[28, 30]. For the case of the linear T - t_2 problem, the following approximate expressions are known^[34]:

$$K_T(T_1) \approx K_T(E) \approx \exp\left(-\frac{9E_{JT}^2}{4\hbar\omega_t}\right), \quad (44)$$

$$K_T(T_2) \approx \frac{1}{3} \left[2 + \exp\left(-\frac{9E_{JT}^2}{4\hbar\omega_t}\right) \right],$$

and agree with the results of the numerical calculation^[35] (see Fig. 10). For the orthorhombic minima at $\mathbf{k}_e = \mathbf{k}_t = \mathbf{k}$ and $\omega_e = \omega_t$ we have^[20]

$$\left. \begin{aligned} K_T(E) &= (1 + 8s + 6s^2)(4 + 8s)^{-1}, & K_T(T_1) &= (3s + s^2)(1 + 2s)^{-1}, \\ K_T(T_2) &= (1 + 6s)(2 + 4s)^{-1}, \\ s &= \frac{1}{2} \exp\left[-\frac{k}{4\hbar\omega} (3Q_0^{(2)} + 2Q_0^{(3)})\right], \\ \bar{s} &= \frac{1}{2} \exp\left(-\frac{kQ_0^{(2)}}{\hbar\omega}\right). \end{aligned} \right\} \quad (45)$$

It is seen from the presented formulas that the suppression of the electronic characteristics, due to the vibronic interaction, depends exponentially on the ratio $E_{JT}/\hbar\omega$, which determines the magnitude of the Jahn-Teller effect, and is therefore quite large in the case of a strong vibronic coupling. In particular, in all cases those suppressed most strongly are the operators of the type T_1 , to which the orbital angular momentum of the electrons belongs, and consequently also the spin-orbit interaction. An appreciable suppression of the spin-orbit splitting of the ground state (sometimes by 1 - 2 orders

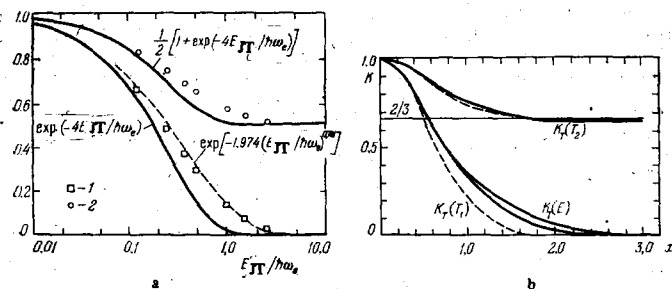


FIG. 10. a) Suppression factors $K_E(E)$ and $K_E(A_2)$ of the linear $E - e$ problem as functions of the parameter $EJT/\hbar\omega_e$ (1 and 2 indicate respectively the values of $K_E(E)$ and $K_E(A_2)$ calculated from the data of [22]; the solid lines describe the approximate expressions and the dashed line was chosen to satisfy the calculated values in the limit $0.1 \leq EJT/\hbar\omega_e \leq 3$). b) Suppression factors $K_T(E)$, $K_T(T_1)$, and $K_T(T_2)$ of the linear $T - t_2$ problem as functions of the parameter $x = \sqrt{(3/2)EJT/\hbar\omega_t}$ (the solid lines show the result of a numerical calculation [35], and the dashed lines correspond to the approximate expressions [44]).

of magnitude, see, e.g., [33]) is one of the most pronounced manifestations of the Jahn-Teller effect in systems with a T level (the E level is not split by the spin-orbit interaction in first-order approximation). Other suppressed quantities are, for example, the anisotropic (orbital) part of the Zeeman splitting, all types of interaction of the electron shell with the nucleus (dipole-dipole, quadrupole, etc.), Coulomb and exchange interactions between electron shells of Jahn-Teller's centers in crystals [37], and others. It should be noted that as soon as the physical quantities cease to be determined only by the ground state, the suppression concepts lose the simplicity described above and are no longer fundamental. In particular, in a strong vibronic interaction, the vibronic ground multiplet lies close to the next level of the tunnel splitting (Fig. 8), so that it is very frequently necessary to take into account its appreciable influence in the determination of the physical observables (see below).

In cases when $K(\Gamma) \ll 1$, it becomes important to take into account the second-order perturbation-theory corrections on the basis of the vibronic functions of the initial electronic multiplet. In the case of weak coupling, the influence of second-order terms, say, in the spin-orbit splitting of the 2T level, manifests itself only in violation of the Landé interval rules and in a splitting of the multiplets with $J \geq 2$. In the case of a strong Jahn-Teller effect, the second-order corrections are described by the usual perturbation-theory formulas, where the Jahn-Teller energy plays the role of the distance between levels, i.e., the result coincides with that expected for the static limit of the Jahn-Teller effect, when the transitions between the minima can be neglected. [34, 35]

When discussing the use of the suppression factors for the calculation of physical observables it must be emphasized once more that they remain meaningful only for operators that do not depend on the nuclear coordinates, in particular, if the electron operators calculated in second order of perturbation theory, in which account is taken of the excited electronic states (for example, in the calculation of the Zeeman splitting of the E term of octahedral systems), then when account is taken of the vibronic interaction, this operator turns out to be, generally speaking, dependent on the nuclear coordinates, and consequently the relations presented for the suppression parameters are no longer valid. [38]

7. PSEUDODEGENERACY. DIPOLE INSTABILITY

As already noted, the criterion for the applicability of the adiabatic approximation, and for the possibility of investigating the physical properties of a system in each electronic state separately, is smallness of the off-diagonal matrix elements of the Hamiltonian \mathcal{H}_{ij} of (6) in comparison with the energy differences of the adiabatic potentials $W_1(Q) - W_j(Q)$. This condition is not satisfied not only in the case of exact degeneracy, when at the point Q_0 we have $W_1(Q_0) = W_j(Q_0)$, but also if at this point the difference $W_1(Q_0) - W_j(Q_0)$ is sufficiently small (quasidegeneracy). In this case vibronic effects arise, which are formally analogous to those considered above for the case of exact degeneracy (the Jahn-Teller pseudoeffect), but containing in principle certain new qualitative features.

We consider first the simple case of two close nondegenerate electronic states ψ_1 and ψ_2 separated by an energy interval 2Δ . [11] Taking into account, as before, the linear terms of the vibronic interaction (9) in the form of a perturbation, we arrive at the secular equation (10), which assumes for the considered case the form

$$\begin{vmatrix} -\Delta - \epsilon & aQ \\ aQ & \Delta - \epsilon \end{vmatrix} = 0, \quad (46)$$

where $a = \langle \psi_1 | \partial V / \partial Q | \psi_2 \rangle$ is the linear vibronic coupling constant (the energy ϵ is reckoned from the center of the interval 2Δ).

The solutions of Eq. (46) are the vibronic corrections to the electronic energies and are obtained directly:

$$\epsilon_{\pm} = \pm \sqrt{\Delta^2 + a^2 Q^2}, \quad (47)$$

which yields, when the elastic-coupling energy in the core is taken into account in accordance with (11) (this energy is assumed to be for simplicity the same in both states)

$$W_{\pm}(Q) = \frac{1}{2} kQ^2 \pm \sqrt{\Delta^2 + a^2 Q^2}. \quad (48)$$

It is seen from this expression that when account is taken of the vibronic interaction the two adiabatic potentials vary differently: in the upper one the curvature (the oscillation frequency) increases, and in the lower one it decreases and becomes equal to zero at $a^2 = k\Delta$.

If the condition

$$\Delta \leq \frac{a^2}{k} \quad (49)$$

is satisfied, the system (in the state of the lower sheet) becomes unstable with respect to the displacements Q . The minima of the adiabatic potential lie at the points (Fig. 11)

$$\pm Q_0 = \sqrt{\frac{a^2}{k^2} - \frac{\Delta^2}{a^2}}. \quad (50)$$

It is perfectly understandable that if these minima are

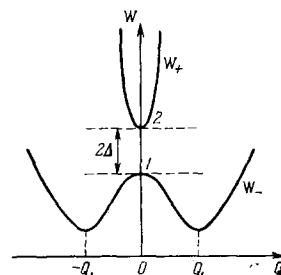


FIG. 11. Potential curves in the case of pseudodegeneracy.

sufficiently deep, so that local states are formed in them, then tunneling causes the corresponding energy levels to be split in analogy with the already considered case of several adiabatic-potential minima due to exact degeneracy.

A distinguishing feature of pseudodegeneracy is that the electronic states Γ and Γ' , which are mixed by the oscillations, can belong to different representations of the symmetry group of the problem (whereas in the case of degeneracy we have $\Gamma = \Gamma'$). This circumstance alters significantly the nuclear normal-displacement space in which the instability of the system and the complicated character of the adiabatic potential become manifest. In particular, for systems with inversion center, Γ and Γ' can have opposite parity, so that the constant Q differs from zero only for odd nuclear displacements Q , which remove the inversion center and lead to the formation of the dipole moment (dipole instability^[39, 40]). In this case the system will have a dipole moment in each of the minima of the adiabatic potential. It is perfectly obvious that this effect cannot occur in the case of interaction of the electronic states of a degenerate level, for in this case $\Gamma = \Gamma'$ and the active displacements can only be even.

Dipole instability is a rather interesting and qualitatively new aspect of the problem of polyatomic systems with electron-degeneracy and pseudodegeneracy. In particular, it leads directly to an explanation of the origin of the dipole moments of symmetrical polyatomic systems and of the spontaneous polarization of crystals (see Sec. d of Chap. 8 and Sec. b of Chap. 9 below).

8. SPECTROSCOPIC MANIFESTATIONS OF TUNNEL SPLITTINGS

We begin the discussion of the manifestations of tunnel effects with a remark concerning the influence of small perturbations due to the action of the environment, which are of interest in view of the smallness of the tunnel splitting. In the crystalline state, such perturbations can be the lattice vibrations and defects of the crystal structure (dislocations, impurities, vacancies, etc.).

The problem of the effect of oscillations of the environment of a complex or of an impurity center on the dynamics of the tunneling and the tunnel states has not yet been solved in the general case (although individual attempts at its solutions are known^[15, 41]). In the case of an isolated complex in a crystal, when its internal oscillation frequencies are much larger than the crystal frequencies, the system can be qualitatively represented in the form of a complex in a viscous continuum. In this case the transitions of the complex from one configuration to another are slowed down not only by the internal barriers, but also by the viscosity of the medium. Since the viscosity decreases with increasing temperature, in such a model the magnitude of the tunnel splitting increases with increasing temperature^[53].

A qualitatively similar conclusion is obtained when the indicated system is considered in the "triple adiabatic" approximation, in which three subsystems are separated: fast—electron motion, slow—vibrations of the complex, and slowest—vibrations of the crystal^[42]. In this approximation the tunnel splitting increases with increasing temperature in accordance with the power law c^n , where $n = [\exp(\hbar\omega/kT) - 1]^{-1}$ are the occupation numbers of the phonon states of the lattice (ω are the frequencies of the crystal vibrations). A more concrete

and sufficiently complete solution of this problem is a very complicated and still pressing problem.

The influence of the crystal-structure defects becomes particularly significant when the splittings produced by them in the complex are of the order of or larger than the tunnel splitting. It can be shown that under the influence of the strain e there occurs in the systems in question a shift of the normal coordinates $Q \sim eR$, where R is the distance between the atoms. This yields for the constant of the coupling of the electrons with the deformation V_e the relation $V_e \sim A_1 R$, which yields in turn $V_e \sim 10^4 \text{ cm}^{-1}$ for transition-metal ions. It follows therefore that even under the influence of weak strains, $e \sim 10^{-4}$ (which are practically always present in real crystals), one can expect splittings $\Delta \sim 1 \text{ cm}^{-1}$.^[35] These strains, however, have a random character (both in magnitude and in direction), so that averaging over them leaves in many cases the qualitative picture of the expected tunnel effects essentially unchanged, even if $\Delta > \delta$. However, this is not always the case, a fact that must be taken into consideration when theory is compared with experiment.

As already noted, questions connected with manifestations of vibronic interactions in electron-degenerate and pseudodegenerate states of polyatomic systems, which are grouped together in the literature under the title of the Jahn-Teller effect, constitute at present an entire trend in the physics of molecules and crystals. The exposition in this section is aimed at illustrating only some of the most interesting manifestations of these effects from the point of view of the inversion (tunneling) splitting considered above. We do not claim, naturally, complete coverage of the literature sources, especially the experimental material.

a) Optical and Acoustical Transitions

Transitions induced between close inversion levels by an electromagnetic perturbation are allowed as magnetic-dipole transitions in the presence of an inversion center in the system, and can be also electric-dipole in the absence of an inversion center (for example, in tetrahedral systems).^[43, 44] The observable dipole microwave losses when Mn^{3+} ions (E level) are introduced in yttrium iron garnets (YIG),^[45] which have a clearly pronounced frequency dependence with a maximum, can be regarded as due to such transitions. This is evidenced also by the dependence of ν_{max} on the temperature ($\nu_{\text{max}} = 15 \text{ GHz}$ at 37°K and $\nu_{\text{max}} = 56 \text{ GHz}$ at 58°K), which agrees qualitatively with the above mentioned strong dependence of the tunnel splitting on the crystal temperature.

Transitions between tunnel levels under the influence of acoustic isolations can be obtained directly^[46], since these levels, being electron-vibrational, are strongly coupled with the vibrations of the environment. If it is assumed that the natural frequencies of the oscillations of the separated complex in the crystal (local oscillations) are much higher than the acoustical frequencies, then we can regard the latter as modulating the former in the course of the interaction. A suitable transformation of the Hamiltonian of the complex makes it possible to separate the perturbation under whose influence transitions are effected between the tunnel levels with absorption of one quantum of crystal oscillations. For example, for the A \rightarrow E transition in the case of the E level (the approximation of the model of three minima in Sec. a of Chap. 4) can yield the following expression

for the coefficient of sound absorption (assuming $\hbar\omega \ll kT$ [46]):

$$\sigma = \frac{\pi}{3} \frac{NR^2 A_1^2 \omega^2}{kT v^3 d} g(\omega) L, \quad (51)$$

where N is the number of absorbing centers per unit volume, R is the shortest interatomic distance in the complex, A_1 is the vibronic constant of the linear $E - e$ problem, v is the speed of sound, d is the density of the crystal, $g(\omega)$ is absorption-line profile factor, $\int_0^\infty g(\omega) d\omega = 1$, and L is the factor of the direction of the propagation and polarization of the wave:

$$L = \sum_i m_i n_i^2 - \frac{1}{2} \sum_{i \neq j} m_i n_i m_j n_j \quad (i, j = x, y, z), \quad (52)$$

m_i and n_i are the direction cosines, respectively, of the polarization and velocity of the sound wave.

Estimates of σ by formula (51) show that it is larger by several orders of magnitude than the magnetic acoustic absorption due to transitions between spin levels (this is understandable, since the latter are coupled to the oscillations only indirectly, via the spin-orbit and orbit-lattice interactions). Thus, for example, for aqueous complexes of copper with $A_1 = 2.5 \times 10^{-4}$ dyn and for the ordinary type of crystals we can obtain [46] $\sigma \sim 10^{-11} \omega^2 L (4\pi^2 T)^{-1}$ (cgs esu). We note that under the same conditions the probability of direct pure-relaxation transitions under the influence of thermal oscillations of the lattice is given by the expression [46] $W = 4 \cdot 10^{-13} T \omega^2 / 4\pi^2$. It follows from this that, at least at low temperatures, the width of the tunnel levels is small enough in comparison with the transition frequency.

If we introduce the relaxation time τ , then we can write

$$g(\omega) = \frac{2}{\pi} \frac{\tau}{1 + (\omega - \omega_0)^2 \tau^2},$$

where $\hbar\omega_0 = \delta$ is the tunnel splitting. In view of the strong growth of τ with increasing temperature, expression (51) has a maximum as a function of T . If we neglect the dependence of δ on T (in comparison with $\tau(T)$), then this maximum is determined from the relation $(\omega - \omega_0)\tau(T) = 1$.

Absorption of ultrasound by Jahn-Teller centers in a crystal was observed by Sturge and co-workers. [25, 47] They believed however, this absorption to be more readily relaxational than resonant. They make reference to the fact that the random distortions due to the imperfection of the crystal lattice, having a larger scatter, are estimated to produce an average level splitting $\sim 1 \text{ cm}^{-1}$, much larger than the tunnel splitting, and therefore the resonant absorption could occur only at such high frequencies. We shall show that this statement is without foundation.

For simplicity we consider the case of two equivalent minima, the vibronic states of which are described by the functions $\Psi_I = (1/\sqrt{2}) \times (\Phi_1 + \Phi_2)$ and $\Psi_{II} = (1/\sqrt{2}) (\Phi_1 - \Phi_2)$ (Φ_1 and Φ_2 are the functions at the minima). The probability of the transition between them under the influence of an acoustic perturbation is proportional to the square of the matrix element

$$\langle \Psi_I | \sum_\alpha Q_\alpha | \Psi_{II} \rangle \approx Q_0,$$

where Q_0 is the absolute value of the displacement of the normal coordinate at the minimum. With allowance for the distorting perturbations, the tunnel splitting in-

creases, $\delta' = \sqrt{\delta^2 + \Delta^2}$, the wave functions take the form

$$\begin{aligned} \Psi_I &= N \left(\Psi_I - \frac{\delta' - \delta}{\Delta} \Psi_{II} \right), \\ \Psi_{II} &= N \left(\Psi_{II} + \frac{\delta' + \delta}{\Delta} \Psi_I \right) \end{aligned} \quad (53)$$

and the probability of the acoustic transition is proportional to

$$\left| \langle \Psi_I | \sum_\alpha Q_\alpha | \Psi_{II} \rangle \right|^2 \approx \left(\frac{\delta}{\delta'} \right)^2 Q_0^2,$$

where Δ is the change of the depth of the minima due to the external perturbation.

We see therefore that the probability of the transitions between the redefined states is smaller than for the unperturbed states, in a ratio $\delta^2/(\delta^2 + \Delta^2)$. In other words, large distortions $\Delta \gg \delta$ suppress the acoustic absorption, as a result of which only the centers that have been little distorted remain resonantly absorbing in the crystal (i.e., the defects in the crystals only decrease the intensity of the resonant absorption but do not eliminate it).

b) Splitting of Zero-Phonon Lines

Even very small splittings of the vibronic levels can appear in narrow lines of zero-phonon transitions in impurity centers and complexes in crystals. In a majority of cases, however, if one of the transitions to closely lying levels of the tunnel splitting is allowed in some approximation, then the second transition is forbidden in the same approximation and becomes allowed only when account is taken of the next approximation (or under the influence of additional perturbations). Therefore cases of indirect observation of inversion splitting in a split zero-phonon line are not plentiful.

Kaplyanskiĭ and Przhhevskii [48] observed flareup of a second zero-phonon line near a first one under the influence of external pressure in the transition $A \rightarrow E$ in the systems $\text{Eu}^{2+} : \text{CaF}_2$; $\text{Eu}^{2+} : \text{SrF}_2$; $\text{Sm}^{2+} : \text{CaF}_2$; $\text{Sm}^{2+} : \text{SrF}_2$ (the values of the splitting were respectively 15.3, 6.5, 27, and 26 cm^{-1}), while Chase [49] interpreted these two close zero-phonon lines as due to transitions to tunnel-split vibronic levels. The suppression of splittings of zero-phonon lines by a crystal field was considered in [50].

A more complicated case of splittings of zero-phonon lines of the $A \rightarrow T_2$ transition in $\text{V}^{2+} : \text{MgO}$ was observed by Sturge. [51] The considered system undergoes tetragonal distortions in the T_2 state, and there is no tunnel splitting at the tetragonal minima of the $T - e$ problem (Sec. b of Chap. 4). However, as shown above, (Sec. b of Chap. 3), when account is taken of the quadratic terms of the vibronic interaction, the absolute minima of the adiabatic potential, at which the nuclear motion is localized, may turn out to be orthorhombic, thus uncovering new possibilities of explaining Sturge's experiments. [51] Indeed, at these minima, on the one hand, there exist the required tetragonal displacements (together with the trigonal ones), and on the other hand, the states in them are subject to inversion splitting. [20]

c) Electron Paramagnetic Resonance

The electron-degenerate terms produced when the orbitally-degenerate states are incompletely filled with electrons have in the overwhelming majority of cases an effective spin $S \neq 0$. In conjunction with the small value of the tunnel splitting (which very frequently falls in the radio region), this is one more reason for using the EPR method to investigate tunnel effects. The Jahn-Teller ef-

fect in EPR has by now been the subject of hundreds of papers (see the reviews^[25, 35] and the corresponding chapters in the monographs^[6, 52]). From the point of view of tunnel effects, the physical picture of the phenomenon becomes understandable from the forthcoming discussion of the case of the E level.

By solving the problem of the Zeeman effect on inversion (tunnel) levels of the E_g term (for example, the Cu^{2+} ion in an octahedral surrounding) in second-order perturbation theory in the spin-orbit and Zeeman interactions, we can obtain the following expressions for the energies of these levels in a magnetic field $\mathbf{H} \parallel \text{Oz}$ (the calculations were performed using the model of three minima^[53]):

$$\left. \begin{aligned} \epsilon_{1\pm} &= \frac{1}{6} \delta_K \pm \left(1 - \frac{5}{2} \frac{\lambda}{\Delta}\right) \beta H - \frac{1}{2} \sqrt{\left(\delta_K \pm \frac{\lambda}{\Delta} \beta H\right)^2 + \frac{8\lambda^2}{\Delta^2} \beta^2 H^2}, \\ \epsilon_{2\pm} &= \frac{1}{6} \delta_K \pm \left(1 - \frac{5}{2} \frac{\lambda}{\Delta}\right) \beta H + \frac{1}{2} \sqrt{\left(\delta_K \pm \frac{\lambda}{\Delta} \beta H\right)^2 + \frac{8\lambda^2}{\Delta^2} \beta^2 H^2}, \\ \epsilon_{3\pm} &= \frac{1}{3} \delta_K \pm \left(1 - \frac{5}{2} \frac{\lambda}{\Delta}\right) \beta H; \end{aligned} \right\} (54)$$

here λ is the spin-orbit coupling constant, Δ is the energy distance to the excited term T_{2g} , and δ_K can be determined from the table and from formulas (29)–(31).

The dependence of ϵ_{iK} on H is illustrated in Fig. 12. The possible transitions between these levels are best described by dividing the region of variation H into three parts: I—low-frequency ($(\lambda/\Delta)\beta H \ll \delta_K$), II—intermediate ($(\lambda/\Delta)\beta H \sim \delta_K$) and III—high-frequency ($(\lambda/\Delta)\beta H \gg \delta_K$). In regions I and III the dependence of ϵ_{iK} on H is approximately linear, so that we can use g -factors to describe the electromagnetic absorption. Calculations show^[53] that in region I there are allowed, with the usual probability, the following three transitions shown in Fig. 12 by the arrows ($\lambda < 0$):

$$g_1 = 2 - \frac{6\lambda}{\Delta} \left(1 + \frac{1}{2} \gamma_K\right), \quad g_2 = 2 - \frac{2\lambda}{\Delta} \left(1 - \frac{3}{2} \gamma_K\right), \quad g_3 = 2 - \frac{4\lambda}{\Delta}, \quad (55)$$

whereas in region I other transitions are allowed:

$$g_{1,2} = 2 - \frac{8\lambda}{\Delta}, \quad g_{2,3} = 2 - \frac{2\lambda}{\Delta} \left(1 \pm \frac{3}{2} \gamma_K\right), \quad (56)$$

where γ_K is given by (29). In the intermediate region the probabilities of the transition of one type become constantly weaker, and those of the other become stronger on moving from one region to the other. For the angular dependence, say of the low-frequency spectrum we can obtain (the terms with γ_K have been omitted for simplicity)^[54]:

$$\left. \begin{aligned} g_{1,2} &= 2 - \frac{4\lambda}{\Delta} \pm \frac{2\lambda}{\Delta} \sqrt{1 - 3(l^2 m^2 + l^2 n^2 + m^2 n^2)}, \\ g_3 &= 2 - \frac{4\lambda}{\Delta}, \end{aligned} \right\} (57)$$

where l , m and n are the direction cosines of \mathbf{H} .

The characteristic frequency and angular dependences of the spectrum were the subject of numerous experimental tests. We note that, assuming that δ increases

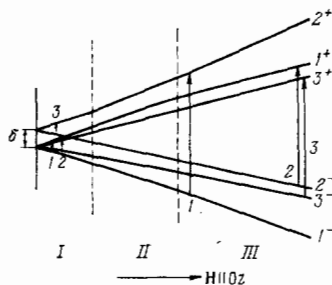


FIG. 12. Spin-inversion levels of E - e problem in a magnetic field $\mathbf{H} \parallel \text{Oz}$.

with increasing temperature, the transition from one type of spectrum to another can be observed by performing measurements at one frequency but at different temperatures. The low-frequency region I then corresponds to the high-temperature spectrum ($\delta \gg (\lambda/\Delta)\beta H$), while the high-frequency region III corresponds to the low-temperature spectrum. Of course, if region I is reached at too high temperatures, for which the rates of the relaxation transitions are high, the spectrum corresponding to this region turns out to be isotropic. Temperature transitions of this kind were observed in EPR spectrum even before tunnel effects were revealed^[55], but could be fully explained only on the basis of the tunnel effects. Tunneling exerts also a very substantial influence on the hyperfine structure of the spectra^[35, 56].

In the case of very large tunnel splittings δ , when only the lower vibronic doublet (in the case of the E level) or triplet (in the case of the T level), is populated, the EPR problem is easily solved with the aid of the suppression parameters (Chap. 6). For the EPR frequencies of the transitions in the vibronic doublet of the E level we can obtain^[35] (ν is the quantum number of the hyperfine splitting):

$$\hbar\omega_{\pm} = (g_1 \beta H + P_1 \nu) \pm K(E) (g_2 \beta H + P_2 \nu) \sqrt{1 - 3(l^2 m^2 + l^2 n^2 + m^2 n^2)} \quad (58)$$

where

$$g_1 = 2 - \frac{4\lambda}{\Delta}, \quad g_2 = -\frac{4\lambda}{\Delta},$$

P_1 and P_2 are the constants of the contact and dipole-dipole hyperfine interactions. The formulas (54)–(57) given above are obtained from (58) for the case of strong vibronic coupling, at which $K(E) \approx 1/2$ (Chap. 5). As shown by Ham^[34] and by Chase^[49], a sufficiently strong influence of the random strains due to the defects in the crystal leads in the case of EPR only to a change in the shape of the absorption line (but not to a shift of its positions). In analogy with (58), formulas were obtained for the EPR frequencies in the case of a vibronic triplet.^[34]

Tunneling affects significantly also the relaxation-transition probabilities^[42, 57-59], which manifest themselves in the EPR line widths. This effect is connected, first, with the presence of several close-lying levels (as against two in the absence of tunneling), which increases the number of relaxation channels. Second, the relaxation transitions between different orbital states are much more probable than between Kramers-conjugate states. As a result of the first of these circumstances, the relaxation probabilities, depending on the ratios of the parameters, can be proportional not only to the first (direct processes) and the seventh (Raman processes) powers of the temperature, but can also depend on the temperature like $e^{-\delta/kT}$ or T^5 . The second of the circumstances indicated above leads to an appreciable increase of the probabilities of the relaxation transitions.

It follows from qualitative considerations that tunnel effects should lead to dynamic changes of the electric-field gradient and of the hyperfine magnetic field at the nuclei, and consequently to corresponding manifestations in the hyperfine structure of the Mössbauer spectrum.^[60-62] As applied to the Mössbauer effect, the influence of tunnel effects on the line shape was determined for cases when the Mössbauer atom is of the Jahn-Teller type with degenerate electron terms 1T_2 , 2T_2 ,^[60] 5T_2 ,^[61] and 1E .^[62] In the latter case the line shape was calculated with allowance for the relaxation

transitions due to the coupling of the tunnel states with the lattice vibrations.

d) Rotational Spectrum and Average Dipole Moment of Dipole-Unstable High-Symmetry Systems

Interesting consequences of tunnel splittings are obtained in the case when a symmetrical system has a dipole moment at the minima of the adiabatic potential (dipole instability^[39, 40]). This situation, as already noted, is realized in systems with inversion centers in the presence of pseudodegeneracy between the ground state and a nearby excited state of opposite parity (Chap. 7), and also in the case of a degenerate electronic T state in high-symmetry systems without inversion centers. We shall show that because of the dipole instability such systems, which do not have a proper dipole moment, have generally speaking, in spite of the prevailing notions, a pure rotational absorption spectrum and exhibit properties that are possessed by systems having proper dipole moments^[40, 65].

Consider a polyatomic system with four sufficiently deep minima of the adiabatic potential of the dipole type (just as, e.g., in the T-t tetrahedron problem, Sec. b of Chap. 4). Owing to the tunneling, the lowest vibronic levels will be T_2 and A_1 (we put for the sake of argument $E_{A_1} > E_{T_2}$), the wave functions of which in the four-minimum model are given in (27) and in the table. With allowance for the rotation (but without allowance for the vibronic-rotational interaction), there is adjacent to each vibronic level a series of rotational levels with energies

$$E_{T_2J} = BJ(J+1), \quad E_{A_1J} = BJ(J+1) + \delta \quad (59)$$

where B is the rotational constant), and for each of these the wave function can be written in the form of a product of the function $|\Gamma_\gamma\rangle$ in accordance with (4) by the spherical-top rotational function φ_{JKM} :

$$|\Gamma_\gamma JKM\rangle = |\Gamma_\gamma\rangle \varphi_{JKM} \quad (K, M = 0, \pm 1, \dots, \pm J, \Gamma = A_1, T_2). \quad (60)$$

Knowing the wave functions, we can determine the transition probabilities and calculate the intensity of the stimulated dipole transition $\Gamma J \rightarrow \Gamma' J'$ per unit density of the radiation that causes the transition^[65]:

$$\alpha_{\Gamma J \rightarrow \Gamma' J'} = \frac{8\pi^3 p_0^2 N}{9\hbar^2 c^3 Z} (E_{\Gamma' J'} - E_{\Gamma J}) \left[\exp\left(-\frac{E_{\Gamma J}}{kT}\right) - \exp\left(-\frac{E_{\Gamma' J'}}{kT}\right) \right] C_{JJ'} g_{\Gamma J}^2 \quad (61)$$

where Z is the partition function

$$Z = \sum_J (2J+1)^2 \left[3g_{T_2J}^2 + g_{A_1J}^2 \exp\left(-\frac{\delta}{kT}\right) \right] \exp\left[-\frac{\hbar c B J(J+1)}{kT}\right],$$

$$C_{JJ'} = \begin{cases} (2J+1)(2J+3), & J' = J+1, \\ (2J+1)^2, & J' = J, \\ (2J+1)(2J-1), & J' = J-1. \end{cases} \quad (62)$$

In these formulas p_0 is the absolute value of the dipole moment of the system at the minimum, N is the number of absorbing centers per unit volume, and $g_{\Gamma J}$ is the statistical weight and depends on the spin I of the nucleus.

From (61) we see that three types of transitions with $J' = J+1$ (R transitions) are possible: $T_2 J \rightarrow T_2(J+1)$ (R), $A_1 J \rightarrow T_2(J+1)$ (R') and $T_2 J \rightarrow A_1(J+1)$ (R''), whereas the Q transitions ($J' = J$) and P transitions ($J' = J-1$) are allowed only as $T_2 J \rightarrow A_1 J$ (Q) and $T_2 J \rightarrow A_1(J-1)$ (P). An analysis of the conditions for the appearance of these series of lines, and of their frequencies and intensities, as functions of the ratio of the constants δ and B and of the temperature is given in^[65]. In particular, at $\delta > B$ and sufficiently large δ , all the series can appear (we

note that only one R series appears in the usual purely rotational spectra of systems with proper dipole moment, and in the rotational structure of the vibrational band there are three branches R, P, and Q). The intensity of this new spectrum in accordance with (61) is proportional to p_0^2 and, is consequently $(p_0/p_m)^2$ times weaker than the usual rotational spectrum (p_m is the dipole moment of the rigid-dipole molecule). Although numerical estimates are presently difficult, it can be assumed that in systems with a strong dipole instability we have $p_0 \sim 0.1$ in Debye units, which yields the estimate $(p_0/p_m)^2 \sim 10^{-2}$. Absorption of this magnitude (and even weaker by many orders) is perfectly observable (at the present time the possibility is being considered of observing the symmetrical-molecular rotational spectrum due to Coriolis interaction, which is 10^{10} times weaker than the usual spectrum^[64]).

It is quite natural to expect high-symmetry systems with dipole instability to behave in an unusual fashion in an electric field^[40, 65]. As is well known, rigid-dipole molecules differ from high-symmetry molecules (which have no proper dipole moment) in that their polarizability has a temperature dependence of the type $\alpha = p_m^2/3kT$ (symmetrical molecules have only induced polarizability with constant α). To determine the polarizability of dipole-unstable systems it is necessary to calculate their average dipole moment in an electric field E. In the case of the system of the symmetrical-top type with two minima and with tunnel splitting 2δ , the vibronic-level energies are

$$E_{\Gamma JKM} = \pm \delta + E_{JK} = \pm \delta + BJ(J+1) + (A-B)K^2,$$

where A and B are rotational constants, and the average dipole moment (under the condition $p_0^2 E \ll \delta - B$) is given by^[65]

$$\bar{p} = \frac{p_0^2 E}{3Z} \sum_{J,K} \left\{ \frac{[(J+1)^2 - K^2] [\delta \operatorname{th}(\delta/kT) - B(J+1)]}{(J+1)[\delta^2 - B^2(J+1)^2]} + \frac{(J^2 - K^2) [\delta \operatorname{th}(\delta/kT) + BJ] + (2J-1)K^2 \operatorname{th}(\delta/kT)}{J(\delta^2 - B^2J^2)} \right\} \exp\left(-\frac{E_{JK}}{kT}\right),$$

$$Z = \sum_{J,K} (2J+1) \exp\left(-\frac{E_{JK}}{kT}\right). \quad (63)$$

If, in analogy with the Langevin theory, we take into account the rotation of the molecules under the influence of the electric field classically, then we can obtain for this case a much simpler formula

$$\bar{p} = \frac{p_0^2 E}{3\delta} \operatorname{th} \frac{\delta}{kT}. \quad (64)$$

The numerical calculations by formula (63) and their comparison with (64) have shown that in this case the neglect of quantization of the rotation is perfectly legitimate. Analogous calculations for the case of four minima of the adiabatic potential lead to the expression

$$\bar{p} = \frac{p_0^2 E}{3kT} \frac{\exp(-\delta/kT) + (kT/\delta) \operatorname{sh}(\delta/kT)}{\exp(-\delta/kT) - \operatorname{ch}(\delta/kT)}. \quad (65)$$

The temperature dependences of the polarizability in accordance with formulas (63)–(65) are shown in Fig. 13. We see that the curve has two limiting regions: 1) large T, where the dependence on T^{-1} is linear and coincides with the temperature dependence of the polarizability of the rigid-dipole molecules, and 2) small T, where the polarizability ceases to depend on T, i.e., it behaves as in the case of high-symmetry molecules that have no proper dipole moment. The position of the transition region on the boundary between these limiting regions depends on the magnitude of the tunnel splitting δ : the smaller δ , the farther into the region of low temperatures (larger T^{-1}) does the region of the high-symmetry behavior shift.

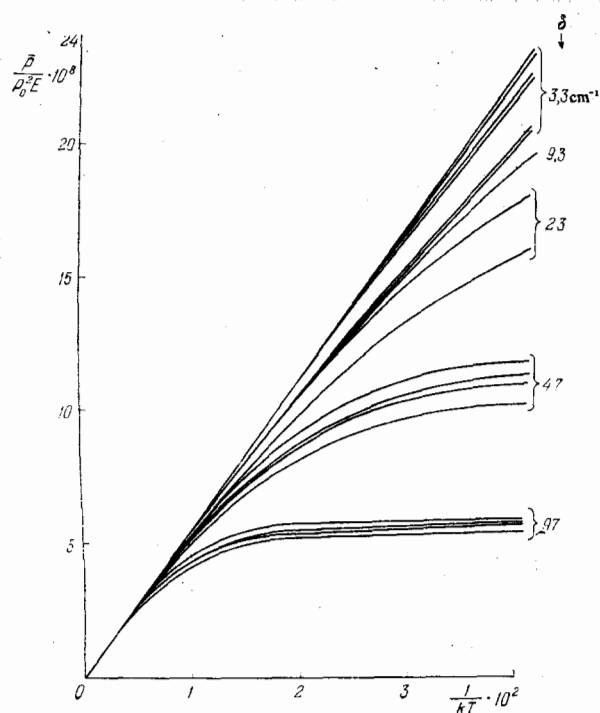


FIG. 13. Temperature dependence of the average dipole moment of a system with two minima for different values of the parameters of the inversion splitting δ (indicated on the right side in cm^{-1}) and of the rotational constant B ($0 \leq B \leq 10 \text{ cm}^{-1}$). For details see [65].

Thus, the same molecules can behave in an electric field either as rigid-dipole or as high-symmetry molecules, depending on the region of the measurement temperatures. By the same token, the fundamental difference between the two types of molecules with the respect of their polarizability is eliminated: these two types are only as limiting cases of molecules with small and large δ , respectively.

9. COLLECTIVE EFFECTS IN CRYSTALS

We consider a crystal containing a large number of Jahn-Teller centers. In the presence of strong interaction between the centers, the distortions and tunnelings on each of them are not independent, and with decreasing temperature a structural phase transition should occur, into a state in which the Jahn-Teller distortions are ordered and the tunneling on each center is suppressed (the cooperative Jahn-Teller effect).

The first studies of the cooperative Jahn-Teller effect, which date back to the late fifties, [66-68], were performed in the semiclassical approximation, in which the motion of the nuclei along the surfaces of the adiabatic potential was considered classically (without allowance for tunneling), and the interactions of the centers were considered in the molecular-field approximation. More detailed calculations, as in general the rapid development of research in this field, date back only to the last few years.

a) Spontaneous Polarization and Ferroelectric Phase Transitions

In 1965, one of us called attention to the fact that the ordering of dipole-unstable centers in a crystal leads to spontaneous polarization of the crystal, and the corresponding phase transition has a ferroelectric character [39]. This idea was subsequently further developed and sup-

plemented [69-71] (similar ideas were proposed also in [72, 73] and developed in [74]). For crystal lattices with perovskite structure (of the BaTiO_3 type) and with the structure of rock salt (of the GeTe type), the energies of the states of the electrons of the valence band were calculated with allowance for their mixing with the states of the conduction band under the influence of nuclear displacements of the dipole type (the limiting optical oscillations), which lead to spontaneous polarization [70] or antipolarization [75] (the case of pseudodegeneracy with allowance for dispersion). This has made it possible to determine the adiabatic potential of the lattice in the space of the corresponding nuclear displacements and to obtain (in analogy with (49)) a criterion for the instability of the lattice with respect to these displacements, i.e., a criterion for the possibility of a corresponding ordering in the crystal. Estimates of the temperatures of the phase transitions in such a system in semiclassical approximation [71] (assuming classical motion of the crystal over the surface of the adiabatic potential and taking into account the remaining oscillations of the crystal as the statistical reservoir) have made it possible to obtain good quantitative agreement with experimental data for BaTiO_3 .

In the course of the development of such a "microscopic theory" of the ferroelectric properties of crystals (many numerical results were obtained with computers), a number of interesting effects and regularities were revealed. Thus, for example, it turned out that in the adiabatic potential of the crystal BaTiO_3 , at the points of the minima of the surfaces, the titanium atoms are shifted in the directions of the trigonal axes, a fact corresponding to the low-temperature rhombohedral phase of the observed ferroelectricity. The remaining singularities of the surface—the saddle points and the maximum—correspond to nuclear configurations of the following orthorhombic, tetragonal, and paraelectric phases. It was concluded from this that only the low-temperature rhombohedral phase is fully ordered, and the remaining phases result from the fact that as the temperature increases the system first overcomes (by means of temperature fluctuations or tunneling) the barrier along the lowest saddle point (the observed displacements are in this case the averages of two neighboring minima), and then at higher temperatures along the next saddle point, etc. The experimental data on the diffuse scattering of x rays [76] confirm the fact that the high-temperature ferroelectric and para-phases are not completely ordered, and reveal the character of the disorder of the system on going from one phase to another (see also [77]).

Another large class of ferroelectrics can be separated in accordance with their content of tetrahedral structural units. In Sec. d of Chap. 8 it was noted that the tetrahedral system is dipole-unstable because of electron degeneracy (T level) or because of pseudodegeneracy (see also [78]), and consequently such tetrahedra may serve as a source of phase transitions in crystals. Let us illustrate this statement using as an example the well investigated crystal KH_2PO_4 . [79, 80] The origin of the spontaneous polarization in this crystal cannot be explained as being due only to ordering in the system of hydrogen bonds, since the direction of such an ordering is almost perpendicular to the observed direction of the spontaneous polarization. At the same time, from the isotopic effect it follows that the role of the hydrogen is quite appreciable in the phase transition. To reconcile

these two facts one customarily assumes a definite type of interaction between the hydrogen and the other elements of the crystal.^[81] Taking into account the instability of the PO₄ groups, at which they have four minima of the adiabatic potential, the picture of the spontaneous polarization and of the phase transitions changes appreciably. The Hamiltonian of the system can be written in the form^[82]

$$\hat{H} = -\zeta \sum_{\mu\alpha} a_{\mu\alpha}^+ a_{\mu\alpha} + \Omega \sum_m \sum_{\mu\mu'} a_{m\mu}^+ a_{m\mu'} + \omega \sum_{\alpha\alpha'} b_{\alpha\alpha'}^+ b_{\alpha\alpha'} - E \sum_{\mu\alpha} p_{\mu\alpha} a_{\mu\alpha}^+ a_{\mu\alpha} - \sum_m \sum_{\mu\alpha} V_{\mu\alpha}(m, l) a_{m\mu}^+ a_{m\alpha} b_{l\alpha}^+ b_{l\alpha} \quad (66)$$

where ζ is the chemical potential, Ω and ω are the tunneling frequencies for the PO₄ group and for the hydrogen group, respectively, E is the intensity of the external field along the polarization direction, and p_{μ} is the dipole moment of the PO₄ groups in the μ -th minimum of the adiabatic potential. Writing down the equation of motion for the Green's function and using a splitting equivalent to the molecular-field approximation, we can obtain a system of transcendental equations with respect to the occupation numbers of the minima of the PO₄ groups and hydrogen bonds, which makes it possible to determine the temperature dependence of the populations and to establish the presence of a phase transition in the system. The temperature of the phase transition depends on the tunneling frequencies of both the hydrogen bonds and the PO₄ groups. We can therefore expect the appearance of two types of isotopic effects in KDP—when the hydrogen is substituted and when substitutions are made in the PO₄ groups. The first of them is well known—deuteration increases T_c by 1.7 times.^[79, 80] The second type of isotopic effect was apparently observed recently in^[83], where it was shown that replacement of O¹⁶ in KDP by O¹⁸ changes the Curie temperature by several degrees.

b) Structural Phase Transitions

As already noted, in systems with inversion centers the Jahn-Teller distortions of the centers are not of the dipole type and do not lead to spontaneously-polarized states. Therefore in most cases the cooperative Jahn-Teller effect (or the Jahn-Teller pseudoeffect) leads to structural phase transitions of non-ferroelectric type (see, however,^[84]). An important and relatively new class of such systems are the ferroelastics^[85, 86], for which the order parameter is the deformation, and which behave with respect to external pressure like ferroelectrics in an external electric field (in particular, they can become "repolarized", i.e., their deformation can be reoriented under the influence of pressure). The following example of a model crystal with Jahn-Teller centers illustrates the origin of the structural phase transition in the general case.

We consider an ionic crystal with local symmetry D_{4h} of the cation sites, and with a doubly degenerate electronic ground state. In the Jahn-Teller effect, for the E level, the active oscillations are in this case b_{1g} of the type ($[E^2] = A_{1g} + B_{1g} + B_{2g}$). Since the valence oscillations b_{1g} correspond to a change of the length of the bond with the cation, and the deformation oscillations b_{2g} correspond to a change of the angles, the interaction with the former predominates as a rule. We write this interaction in the form $\sum_m A \sigma_z^m Q_m(b_{1g})$, where m numbers the sites, A is the vibronic coupling constant, and σ_z are Pauli matrices in an electronic basis that diagonalizes the vibronic interaction with the b_{1g} oscillations. Changing over in the usual manner^[87] to phonon operators $Q_m = \sum_k a_{mk}(b_k^+ + b_k)$, we can obtain

for the Hamiltonian of the electron-phonon system of the crystal the expression:

$$H = \epsilon_0 \sum_m n_m + \sum_{mk} A_{mk} \sigma_z^m (b_k^+ + b_k) + \sum_{\alpha} \hbar \omega_{\alpha} (b_{\alpha}^+ b_{\alpha} + \frac{1}{2}), \quad (67)$$

where n_m is the operator of the number of electrons at the site m . Next, by a unitary shift transformation, we can exclude the terms of the Hamiltonian (67) which are linear in the phonon operators. The transformed Hamiltonian $\mathcal{H} = e^{iR} H e^{-iR}$, where

$$R = \sum_m f_m \sigma_z^m, \quad f_m = i \sum_{\alpha} A_{m\alpha} (b_{\alpha}^+ - b_{\alpha}) (\hbar \omega_{\alpha})^{-1}, \quad (68)$$

takes the form^[88]

$$\mathcal{H} = \sum_{\alpha} \hbar \omega_{\alpha} (b_{\alpha}^+ b_{\alpha} + \frac{1}{2}) + (\epsilon_0 - \Delta) \sum_m n_m - \sum_{m\alpha\alpha'} A_{m\alpha} A_{m\alpha'} (\hbar \omega_{\alpha})^{-1} \sigma_z^m \sigma_z^{\alpha'}, \quad (69)$$

where $\Delta = \sum_k A_{mk}^2 (\hbar \omega_k)^{-1}$ is the Jahn-Teller stabilization energy at each site. The last term in (69) describes the distortion-induced interaction of the electronic states of different sites. In the considered case, this interaction leads, as seen from (69), to the Ising Hamiltonian.

In the investigation of the structure transitions accompanied by deformation of the crystal, it is necessary to include in the Hamiltonian (67) the strain energy and the interaction of the electrons with the strain^[88]. If the following condition is satisfied

$$A \equiv g_0^2 - \sum_{mk} \frac{A_{mk} A_{mk}}{\hbar \omega_k} > 0,$$

where g_0 is the coupling constant of the electrons with the strain, then at temperatures below the temperature of the phase transition $kT_{cr} = A$ there appears a crystal strain $u = g_0 \sqrt{\Omega} / cN \bar{\sigma}_z$, due to the cooperative Jahn-Teller effect. Here Ω is the volume of the crystal, N is the number of unit cells, c is the elastic modulus of the crystal, and $\bar{\sigma}_z$ is the average value of the operator σ_z . The spontaneous distortions of the crystal at $T < T_{cr}$ can be regarded as the result of softening of the crystal with respect to the corresponding strains. Indeed, for the elastic modulus we can obtain the expression

$$c = c_0 \frac{1 - (A/kT) \operatorname{sech}^2(A\bar{\sigma}_z/kT)}{1 - [(A - g_0^2)/kT] \operatorname{sech}^2(A\bar{\sigma}_z/kT)}, \quad (70)$$

from which it follows that $c \rightarrow 0$ as $T \rightarrow T_{cr}$.

The cooperative Jahn-Teller effect has interesting singularities in such a crystal in an external magnetic field^[88]. The point is that the components of the split ground-state doublet do not have a proper magnetic moment in the low-symmetry phase. To the contrary, states produced by a magnetic field and having a proper magnetic moment are realized only in an undistorted crystal. It follows therefore that magnetic ordering counteracts the structural ordering and vice versa, thus leading to a characteristic connection between the magnetic and structural properties. In the molecular-field approximation for $\bar{\sigma}_z$, which determines the relative Jahn-Teller strain in the crystal, we obtain the transcendental equation

$$\frac{E}{A} = \operatorname{th} \frac{E}{kT}, \quad E = \sqrt{A^2 \bar{\sigma}_z^2 + g^2 \mu^2 \gamma^2 H^2}, \quad (71)$$

where g is the spectroscopic-splitting factor of the ground-state doublet, μ is the Bohr magneton, and $\gamma = \langle \cos 2\ell \rangle$ is the average statistical factor of the vibronic reduction of the orbital angular momentum. At a given temperature, E does not depend on H if $\bar{\sigma}_z \neq 0$. With increasing H , the value of $\bar{\sigma}_z$ decreases in such a way that E remains constant. As seen from (71), the

crystal is in a low-symmetry structure-ordered phase at $T < T_{CR}$, where the temperature of the structural phase transition is given by the formula

$$kT_{CR} = \frac{1}{2} g\mu\gamma H \operatorname{arc} \operatorname{th}^{-1} \left(\frac{g\mu\gamma H}{A} \right).$$

We see that application of the magnetic field lowers T_{CR} , and no structural phase transition occurs in fields $H > H_0 = A(g\mu\gamma)^{-1}$. In other words, such magnetic fields stabilize the undistorted configuration of the lattice. The magnetic moment of the site is given by the expression $\bar{\mu} = g^2\mu^2\gamma^2HE^{-1} \tanh(E/kT)$, from which it follows that at $H < H_0$ the magnetic moment is proportional to the field: $\bar{\mu} = g^2\mu^2\gamma^2HA^{-1}$, and at $H > H_0$ in the undistorted crystal we have $\bar{\mu} = g\gamma\mu \tanh(g\gamma\mu H/kT)$. This behavior of the magnetic moment as a function of the applied field at different temperatures is shown in Fig. 14. Figure 15 shows the temperature dependence of the magnetic susceptibility.

The Jahn-Teller nature of the structural phase transitions was established undisputedly for a wide class of crystals. Much experimental and theoretical material has been gathered^[89-93] offering evidence that the structural phase transitions in rare-earth orthovanadates of the type $MeVO_4$, where Me is a rare-earth element whose ion Me^{3+} has electronic degeneracy, is of Jahn-Teller origin. These phase transitions occur at very low temperatures $T_{CR} \sim 10^0 K$ (in contrast, for example, to spinels, for which $T_{CR} \sim 10^{20} K$), and it is therefore easy to obtain for them in an external magnetic field splittings on the order of kT_{CR} , and consequently it is possible to observe the above-mentioned mutual suppression of the structure and magnetic orders. The results of the measurements of the dependence of the magnetic moment on the external field and of the susceptibility χ on the temperature agree with those in Figs. 14 and 15.

10. CONCLUSION

In this brief review we highlighted only the main aspects of the theory of tunnel effects—one of the principal manifestations of vibronic interactions in polyatomic systems with electron degeneracy and pseudodegeneracy. As noted during the course of the exposition, certain questions in the theory of vibronic interactions still await their solution. First of all, the problem of dynamic vibronic coupling with many Jahn-Teller modes has not been solved to date. Such a coupling arises in more complicated polyatomic systems, particularly for an impurity center (or any other local formation) in a crystal,

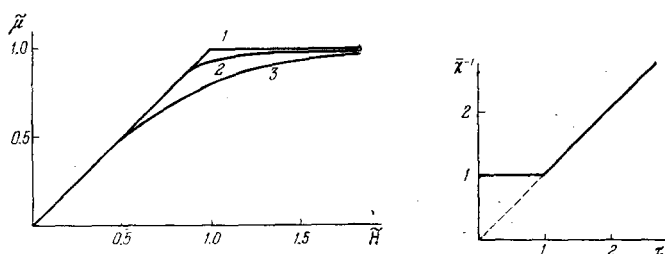


FIG. 14. Dependence of the magnetic moment $\bar{\mu} = \bar{\mu}(g\gamma\mu)^{-1}$ of a Jahn-Teller site on the magnetic field intensity ($H = H(g\gamma\mu A^{-1})$) in a crystal with cooperative Jahn-Teller effect. The relative temperature $\tau = 2kTA^{-1}$ for curves 1–3 is equal to 0.25, 0.62, and 0.94, respectively.

FIG. 15. Dependence of the reciprocal magnetic susceptibility $\bar{\chi}^{-1} = \chi^{-1}(A^{-1}g^2\gamma^2\mu^2)$ on the temperature $\tau = 2kTA^{-1}$ in a crystal with cooperative Jahn-Teller effect.

when it is impossible to separate one dominant mode or when the vibronic coupling cannot be simplified, as in the $T - e$ problem. The known attempts at solving this problem (see^[15]) actually reduce it to a single-mode problem. At the same time, a number of observed properties of degenerate systems are brought about precisely by the presence of many active Jahn-Teller modes. This circumstance influences particularly strongly the temperature dependences.

The problem of the cooperative Jahn-Teller effect in the case of intermediate dynamic vibronic coupling has not yet been fully solved. In this case it is impossible to obtain separation of the electronic and nuclear motions so as to be able to investigate the phase transitions directly. Little attention has also been paid so far to the important problem of numerically calculating the electron-vibrational coupling constants which determine the urgency with which it is necessary to take into account the vibronic interaction in concrete polyatomic molecules. This is a part of the problem of calculating multielectron polyatomic systems. When account is taken of the progress made in this field in recent years, such calculations now become urgent.

We hope that this review will help the reader to find his way more easily in this interesting problem and will stimulate further investigations in this field.

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