

# Multimode Jahn-Teller effect for $T$ term. Case of prevailing coupling with $E$ vibrations

V. Z. Polinger

*Chemical Institute, Moldavian Academy of Sciences*

(Submitted 18 April 1979)

Zh. Eksp. Teor. Fiz. 77, 1503–1518 (October 1979)

The  $T-(e + t_2)$  problem of the theory of the Jahn-Teller effect is solved for an orbitally degenerate electronic state localized on a point defect in a crystal. The vibronic interaction with both  $T_2$  and  $E$  vibrations is considered, with allowance for the dispersion of the lattice phonons, in the case when the coupling with the latter prevails. It is shown that the vibronic interactions leads to the onset of multiphonon electron-vibrational formations of the polaron type, which are coupled with the defect. The position and width of the local and pseudolocal vibronic states (resonances), due to the Jahn-Teller effect, are determined as well as the character and magnitude of their splittings under uniaxial deformation.

PACS numbers: 61.70.Ey, 63.20.Kr, 63.20.Dj

## 1. INTRODUCTION

Practically all the observable effects in impurity centers whose electrons are in a degenerate or quasidegenerate state are determined by the electron-vibrational (vibronic) interaction. The known mathematical difficulties of the theory of the Jahn-Teller effect, connected with the need for taking into account the nonadiabatic mixing of the degenerate electronic states by the vibrations of the nuclei,<sup>1,2</sup> are aggravated here by the infinite number of vibrational degrees of freedom. The quasi-molecular (cluster) model of the impurity center, usually employed to interpret vibronic effects,<sup>3,4</sup> describes satisfactorily also such integral characteristics as, for example, the shape of the envelope of the optical-absorption curve. At the same time, the most distinguishing feature of the Jahn-Teller effect in impurity centers are the local and pseudolocal vibronic states (resonances), the position and width of which are essentially determined by the phonon density of states of the impurity-free crystal.<sup>5,6</sup>

In the molecular (cluster) Jahn-Teller situations the energy levels and the wave functions of the vibronic state can be, at least in principle, determined with a computer. Despite the urgency of the problem, there is no general theory of vibronic resonances in the Jahn-Teller effect for impurity centers with account taken of phonon dispersion, and for the time being it is impossible to solve this problem in general form even with a computer. Nonetheless, in a number of limiting cases of strong or weak vibronic coupling it becomes possible to obtain analytic solutions. Although such limiting situations are relatively rarely realized in concrete experiments and the corresponding solutions are as rule not suitable for a quantitative comparison of the theory with experiment, they do make it possible to understand, on a qualitative level, the nature of the vibronic resonances.

The present paper is devoted to allowance for phonon dispersion in the Jahn-Teller effect for an impurity electronic  $T$ -term that interacts linearly both with  $T_2$  and  $E$  vibrations, when the coupling with the latter is strong enough and predominates. The spin-orbit interaction which is usually appreciable for the  $T$  term,

is in this case suppressed by the vibronic reduction factor  $K(T_2)=0$  can be excluded from consideration.

The Jahn-Teller instability of a cubic polyatomic system in the case of strong vibronic coupling with  $E$  vibrations lowers the local symmetry of the impurity centers to tetragonal. The frequencies of the normal vibrations of the lattice are then split, and since the vibronic interaction is localized near the impurity, specific local and pseudolocal resonances appear in the spectrum of the lattice vibrations.

We determine in this paper the position and width of these vibronic resonances, as well as the character and magnitude of their splittings in interaction of low-symmetry perturbations. In the particular case of an interaction of an electron with one extremely narrow phonon band, the cluster model becomes applicable to the dispersion and, as will be shown, all the derived expressions go over into the corresponding results of the cluster model.<sup>1)</sup>

## 2. EXTREMA OF ADIABATIC POTENTIAL AND THE ASYMPTOTIC HAMILTONIAN

We consider a defect in a cubic lattice whose crystal-field symmetry ensures the presence, in the electron energy spectrum, of an orbitally degenerate  $T$  term separated from all the remaining electronic states by an appreciable energy gap. For simplicity we confine ourselves to the case of a small-radius impurity center, whose electrons interact with the symmetrized displacements  $q_{\Gamma\gamma}$  of the nuclei only of the nearest coordination sphere. We note that this limitation does not deprive the Jahn-Teller effect of its multimode character, since the displacements of the other atoms of the crystals are elastically coupled with the displacements of the atoms of the first coordination sphere, and the impurity electrons are coupled with all the lattice vibrations because of this interaction, which gives rise to the phonon dispersion.

The harmonic Hamiltonian of the impurity-phonon Jahn-Teller system, with account taken of only terms linear in  $q_{\Gamma\gamma}$  of the vibronic interaction, is of the form

$$\hat{H} = \frac{1}{2} \sum_{\kappa} (p_{\kappa}^2 + \omega_{\kappa}^2 q_{\kappa}^2) + \sum_{\Gamma=E, T_2} \sum_{\gamma \in \Gamma} V_{\Gamma} q_{\Gamma\gamma} \hat{C}_{\Gamma\gamma} \quad (1)$$

The first term in (1) is the usual phonon Hamiltonian of the lattice, with account already taken of the redefinition of the normal coordinates and of the phonon dispersion law by the impurity mass defect and by the replacement of the force constants. The indices  $\Gamma=E, T_2$ ;  $\gamma \in \Gamma$  number the irreducible representations and their lines, in terms of which are transformed the symmetrized displacements  $q_{\Gamma\gamma}$ , which are active in the Jahn-Teller effect of the atoms of the first coordination sphere. These displacements can be expanded in terms of the complete set of normal coordinates  $q_{\kappa}$  of the crystal:

$$q_{\Gamma\gamma} = \sum_{\kappa} a_{\kappa}(\Gamma\gamma) q_{\kappa} \quad (2)$$

Here and below the summation over  $\kappa$  runs through all the normal coordinates, i.e., all the values of the wave vector in the first Brillouin zone and all the vibration modes.

For the explicit form of the coefficients  $a_{\kappa}(\Gamma\gamma)$  (the Van Vleck coefficients) and their properties in the simplest case of a single-atom cubic lattice see, e.g., Ref. 3. The matrices  $\hat{C}_{\Gamma\gamma}$  in (1) are defined in the space of three real electronic functions  $\psi_x(r)$ ,  $\psi_y(r)$ , and  $\psi_z(r)$  of the impurity  $T$  term, and are made up of the corresponding Clebsch-Gordan coefficients

$$\hat{C}_{E0} = \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \hat{C}_{E\epsilon} = \begin{pmatrix} -\sqrt{3}/2 & 0 & 0 \\ 0 & \sqrt{3}/2 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (3)$$

$$\hat{C}_{T_2\epsilon} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}, \quad \hat{C}_{T_2\eta} = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \quad \hat{C}_{T_2\kappa} = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

while  $V_E$  and  $V_T$  are the reduced matrix elements of the operator of the linear vibronic interaction—the constants of the linear vibronic coupling with the  $E$  and  $T_2$  vibrations, respectively.

The eigenvalues  $\epsilon$  of the potential-energy matrix

$$\hat{U} = \sum_{\kappa} \left\{ \frac{1}{2} \omega_{\kappa}^2 q_{\kappa}^2 + \sum_{\Gamma} V_{\Gamma} a_{\kappa}(\Gamma\gamma) q_{\kappa} \hat{C}_{\Gamma\gamma} \right\} \quad (4)$$

are called the adiabatic potentials and constitute in our case multidimensional surfaces in the space of the  $3N$  vibrational degrees of freedom of the crystal. Nonetheless, the question of the extrema of  $\epsilon(\dots q_{\kappa} \dots)$  is solved in the same manner as in molecule Jahn-Teller problems, for example with the aid of procedure of Opik and Pryce.<sup>8</sup> To this end it is necessary to solve the problem of the eigenvalues of the matrix  $\hat{U}$

$$\hat{U} |a\rangle = \epsilon |a\rangle, \quad (5)$$

$|a\rangle$  is a column of three numbers  $a_x$ ,  $a_y$ , and  $a_z$ , and represents the adiabatic electronic function in the space of three states  $\psi_x$ ,  $\psi_y$ , and  $\psi_z$  of the electronic triplet) together with the extremum conditions

$$\frac{\partial \epsilon}{\partial q_{\kappa}} = \left\langle a \left| \frac{\partial \hat{U}}{\partial q_{\kappa}} \right| a \right\rangle = 0 \quad (6)$$

and the condition for the normalization of the column

$|a\rangle$

$$\langle a | a \rangle = 1. \quad (7)$$

The system (5)–(7) will be called the system of Opik and Pryce. From (4) and (6) it is easy to obtain the equilibrium values of the normal coordinates

$$q_{\kappa}^{(0)} = -\omega_{\kappa}^{-2} \sum_{\Gamma} V_{\Gamma} a_{\kappa}(\Gamma\gamma) \langle a | \hat{C}_{\Gamma\gamma} | a \rangle. \quad (8)$$

An explicit form of the expressions of  $\langle a | \hat{C}_{\Gamma\gamma} | a \rangle$  in terms of  $a_x$ ,  $a_y$ , and  $a_z$  can be easily obtained with the aid of (3). For example,

$$\langle a | \hat{C}_{E0} | a \rangle = \frac{1}{2} a_x^2 + \frac{1}{2} a_y^2 - a_z^2.$$

Substituting (8) in (4) and using the orthogonality of the Van Vleck coefficients<sup>3</sup>

$$\sum_{\kappa} a_{\kappa}(\Gamma\gamma) a_{\kappa}(\bar{\Gamma}\bar{\gamma}) f(\omega_{\kappa}) = \delta_{\Gamma\bar{\Gamma}} \delta_{\gamma\bar{\gamma}} \sum_{\kappa} a_{\kappa}^2(\Gamma\gamma) f(\omega_{\kappa}), \quad (9)$$

where  $f(\omega_{\kappa})$  is an arbitrary function of  $\omega_{\kappa}$ , we rewrite (5) in the form

$$\sum_{\Gamma} \left( \frac{V_{\Gamma}}{\omega_{\Gamma}} \right)^2 \langle a | \hat{C}_{\Gamma\gamma} | a \rangle \hat{C}_{\Gamma\gamma} | a \rangle = \left( \frac{1}{2} \sum_{\kappa} \omega_{\kappa}^2 q_{\kappa}^{(0)2} - \epsilon \right) | a \rangle, \quad (10)$$

where

$$\omega_{\Gamma}^{-2} = \sum_{\kappa} a_{\kappa}^2(\Gamma\gamma) \omega_{\kappa}^{-2}. \quad (11)$$

Writing out the matrix equation (10) by lines, we obtain three equations that constitute (together with (7)), a system of equations for  $a_x$ ,  $a_y$ ,  $a_z$ , and  $\epsilon$ . We note that this system is of the same form as in the molecular case, when the electronic  $T$  term interacts only with two  $E$  and three  $T_2$  vibrations. We use therefore the known solutions of this system.<sup>8</sup> The three types of roots are listed in the table. With the aid of (8), (9), and (2) it is easy to verify that in the tetragonal extrema only the  $q_{E\gamma}$  are displaced, in the trigonal only the  $q_{T_2\gamma}$ , and in the orthorhombic both  $q_{E\gamma}$  and  $q_{T_2\gamma}$ . Thus, the result turns out to be the same as in the molecular case with effective frequencies  $\omega_E$  and  $\omega_T$  as defined in (11). The adiabatic potential has three tetragonal, four trigonal, and six orthorhombic extrema, and the absolute minima, depending on the relation between the Jahn-Teller stabilization energies

$$E_{JT}(E) = \frac{1}{2} V_E^2 \sum_{\kappa} a_{\kappa}^2(E\gamma) \omega_{\kappa}^{-2}, \quad E_{JT}(T) = \frac{2}{3} V_T^2 \sum_{\kappa} a_{\kappa}^2(T_2\gamma) \omega_{\kappa}^{-2}, \quad (12)$$

can become either trigonal or tetragonal extrema, whereas the orthorhombic extrema with Jahn-Teller energy

$$E_{JT}(OR) = \frac{1}{2} E_{JT}(E) + \frac{1}{2} E_{JT}(T)$$

always occupy an energy position between the trigonal and the tetragonal extrema.<sup>8</sup>

An investigation of the curvature of the adiabatic potential at the extrema can also be carried out by the method of Opik and Pryce, but additional difficulties are encountered here, due to the multimode character of the problem. In the present paper we consider the case when the vibronic interaction with the  $E$  vibrations prevails, i.e., when  $E_{JT}(E) > E_{JT}(T)$ , and the three equivalent tetragonal extrema are absolute minima of the

adiabatic potential. We investigate the curvature of one of them, corresponding for example to the solution  $a_x = a_y = 0$ ,  $a_z = 1$ , i.e., to the third column of the table. With the aid of (3) we can easily verify that for this minimum

$$\langle a | \hat{C}_{Eg} | a \rangle = -1, \langle a | \hat{C}_{Eg} | a \rangle = 0, \quad (13)$$

$$\langle a | \hat{C}_{Tz} | a \rangle = \langle a | \hat{C}_{Tz} | a \rangle = \langle a | \hat{C}_{Tz} | a \rangle = 0.$$

Substituting (13) in (8), we get

$$q_x^{(0)} = V_{Eg} a_x(E) \omega_x^{-1}. \quad (14)$$

The equilibrium normal coordinates  $q_x^{(0)}$  in (14) have a simple physical meaning. The electronic adiabatic wave function in this minimum is  $\psi_g(r)$  (since  $a_x = a_y = 0$  and  $a_z = 1$ ), i.e., it has lower symmetry relative to the initial cubic symmetry of the impurity center. Owing to the electron-vibrational interaction, the atoms of the crystal lattice "feel" this decrease of the symmetry of the electron density and adjust themselves to it by shifting their equilibrium positions. In particular, for Jahn-Teller impurity centers in ionic crystals, where the vibronic interaction is electrostatic to a considerable degree, Eq. (14) describes the polarization of the crystal lattice by the low-symmetry distribution of the electron density at the impurity center. The static displacement (14) can be interpreted as a wave packet of normal vibrations of an impurity-free crystal. In other words, the low-symmetry adiabatic state at the minimum becomes dressed by a "jacket" of initial phonons, i.e., we are dealing with multiphonon formation of the polaron type, which is localized on the impurity center.

The curvature of the surface  $\varepsilon(\dots q_x \dots)$  at the minimum can be obtained by constructing the correction of second-order perturbation theory in the small displacements  $Q_x = q_x - q_x^{(0)}$  from the minimum. We represent  $\hat{U}$  of (4) near the minimum in the form

$$\hat{U}(\dots q_x \dots) = \hat{U}(\dots q_x^{(0)} \dots) + \hat{U}_1 + \hat{U}_2,$$

where

$$\hat{U}_1 = \sum_x \frac{\partial \hat{U}(\dots q_x^{(0)} \dots)}{\partial q_x} Q_x, \quad \hat{U}_2 = \frac{1}{2} \sum_{x\lambda} \frac{\partial^2 \hat{U}(\dots q_x^{(0)} \dots)}{\partial q_x \partial q_\lambda} Q_x Q_\lambda.$$

Taking into account the contribution made to the energy  $\varepsilon(\dots q_x \dots)$  by  $\hat{U}_1$  up to second order of perturbation theory and the contribution from  $\hat{U}_2$  up to first order, we get

$$\varepsilon \approx -E_{JT}(E) + \frac{1}{2} \sum_x \omega_x^2 Q_x^2 - \alpha \omega_x^2 \sum_{x\lambda} W_{x\lambda} Q_x Q_\lambda, \quad (15)$$

where

$$\alpha = 2V_T^2/3V_E^2, \quad W_{x\lambda} = a_x(T_z \xi) a_\lambda(T_z \xi) + a_x(T_z \eta) a_\lambda(T_z \eta), \quad (16)$$

and  $\omega_E$  is defined by (11).

TABLE I. Roots of the Opik and Pryce system in the multi-mode Jahn-Teller effect for the  $T$  term that interacts linearly with the  $E$  and  $T_2$  vibrations

	Tetragonal extrema			Trigonal extrema				Orthorhombic extrema						
	$\varepsilon = -V_E^2/2\omega_E^2$			$-2V_T^2/3\omega_T^2$				$-V_E^2/8\omega_E^2 - V_T^2/2\omega_T^2$						
$a_x$	1	0	0	$3^{-1/2}$	$-3^{-1/2}$	$3^{-1/2}$	$3^{-1/2}$	$2^{-1/2}$	$2^{-1/2}$	0	$-2^{-1/2}$	$-2^{-1/2}$	0	0
$a_y$	0	1	0	$3^{-1/2}$	$3^{-1/2}$	$-3^{-1/2}$	$3^{-1/2}$	$2^{-1/2}$	0	$2^{-1/2}$	$2^{-1/2}$	0	$-2^{-1/2}$	$-2^{-1/2}$
$a_z$	0	0	1	$3^{-1/2}$	$3^{-1/2}$	$3^{-1/2}$	$-3^{-1/2}$	0	$2^{-1/2}$	$2^{-1/2}$	0	0	$2^{-1/2}$	$2^{-1/2}$

Because of the electronic degeneracy, the adiabatic potential of the Jahn-Teller system does not have, generally speaking, the meaning of the potential energy of the nuclei. However, if the motion of the nuclei is localized in such a region of  $q$ -space in which the considered adiabatic potential is separated by a considerable energy gap from all the remaining ones then, as is well known, the criteria for the adiabatic approximation are satisfied and  $\varepsilon(\dots q_x \dots)$  acquires the physical meaning of the potential energy of nuclei moving in the averaged field of all the electrons. The energy gap that separates the lower sheet of the adiabatic potential of the  $T$  term from the upper sheets is  $\sim (3/2)E_{JT}(E)$  in the vicinity of the tetragonal extrema. The characteristic energy of the nuclear motion is  $\hbar\omega_{\max}$ , where  $\omega_{\max}$  is the highest of the crystal-lattice vibration frequencies.

The condition for the applicability of the adiabatic approximation in the vicinity of the tetragonal extrema is therefore, first, satisfaction of the inequality

$$\hbar\omega_{\max} \ll \frac{1}{2}E_{JT}(E)$$

and, second, localization of the nuclear motion near these extrema. The latter condition is satisfied in the case when the tetragonal extrema are absolute minima of the adiabatic potential and we are dealing with not very highly excited states of the nuclear subsystem. Actually, the delocalization of the nuclear motion begins when the energy of excitation of the nuclei becomes comparable with the height of the orthorhombic barriers that separate the tetragonal minima.

We consider now the case of a relatively strong vibronic coupling with the  $E$  vibrations, when all the formulated conditions are satisfied and in the lowest excited states the nuclear motion has the character of small vibrations near the tetragonal minima. If the amplitude  $Q_x = q_x - q_x^{(0)}$  of these vibrations is low enough, then we can confine ourselves in the expansion of the potential energy  $\varepsilon(\dots q_x \dots)$  in powers of  $Q_x$  to the quadratic term, i.e., we can use expression (15). The Hamiltonian of the harmonic vibrations of the nuclei near one of the three tetragonal minima therefore takes the form

$$H = \frac{1}{2} \sum_x (P_x^2 + \omega_x^2 Q_x^2) - \alpha \omega_x^2 \sum_{x\lambda} W_{x\lambda} Q_x Q_\lambda. \quad (17)$$

Since tunneling between the tetragonal minima is symmetry-forbidden,<sup>9</sup> the harmonic Hamiltonian (17) is asymptotically exact. It describes correctly the lowest energy levels of the spectrum, and the smaller  $\alpha$  the larger the number of these correctly described levels. However, even at not very small values of  $\alpha$ , provided the discarded anharmonicities are small, the correctly described region of the spectrum may turn out to be substantial. The criterion for this is smallest of  $\hbar\omega_{\max}$  compared with the height of the orthorhombic barriers. Therefore the result described by the Hamiltonian (17), provided that the aforementioned criterion is satisfied, is in this sense more accurate than can be obtained by perturbation theory in  $\alpha$  (i.e., in  $V_T$ ) applied directly to the Hamiltonian (1).

We note the local character of the perturbation de-

scribed by the last term of the Hamiltonian (17). In the "κ-representation" this localization is included in the matrix  $\|W_{\kappa\lambda}\|$ , which is the sum of two terms that are multiplicative in the indices. If we change over to symmetrized displacements

$$Q_{\Gamma\gamma} = \sum_{\kappa} a_{\kappa}(\Gamma\gamma) Q_{\kappa}, \quad (18)$$

then the Hamiltonian (17) takes the form

$$H = \frac{1}{2} \sum_{\kappa} (P_{\kappa}^2 + \omega_{\kappa}^2 Q_{\kappa}^2) - \alpha \omega_E^2 (Q_i^2 + Q_n^2) \quad (19)$$

and the local character of the perturbation becomes obvious.

Thus, a weak (in the sense indicated above) interaction impurity electrons with  $T_2$  vibrations in the case of strong coupling with the  $E$  vibrations causes the adiabatic potential near the tetragonal minima to be deformed and produces an additional defect of the force constants of the  $T_2$  vibrations of the atoms of the first coordination sphere.

### 3. VIBRONIC SPECTRUM

It is easy to verify directly that the Hamiltonian (19), which describes small vibrations of the lattice at the tetragonal minimum, has tetragonal symmetry. If, for example, the atoms of the first coordination sphere form an octahedron, then the Jahn-Teller effect, in the case of strong coupling with the  $E_g$  vibrations, makes the octahedron become prolate (or oblate) along one of its fourfold symmetry axes, with the symmetry lowered from  $O_h$  to  $D_{4h}$ . The irreducible representations of the  $O_h$  group, in terms of which are transformed the normal vibrations that are of importance in the Jahn-Teller effect, become irreducible and break up into irreducible representations of the  $D_{4h}$  group:  $E_g = A_{1g} + B_{1g}$ ,  $T_{2g} = B_{2g} + E_g$ . The symmetrized displacements of the atoms of the first coordinate sphere, which transform in accord with these irreducible representations, are linear combinations of all displacements with group- $O_h$  symmetry. In the considered case of the tetragonal minimum, they are simply

$$Q_{A_{1g}} = Q_0, \quad Q_{B_{1g}} = Q_1, \quad Q_{B_{2g}} = Q_2, \quad Q_{E_g\gamma} = (Q_3, Q_n). \quad (20)$$

The vibronic interaction, and consequently the Jahn-Teller lattice distortion it produces, are localized near the impurity centers. Obviously, the associated splitting of the frequencies of the normal vibrations likewise has a local character. In other words, the state density should contain local and pseudolocal resonances that describe the frequency splitting.

The Hamiltonian (17) can be represented as a bilinear form of phonon creation and annihilation operators, and therefore its eigenvalues can be obtained by direct diagonalization of a quadratic form, for example with the aid of the Bogolyubov-Tyablikov  $u-v$  transformation, as well as by the method of Green's functions, the chain of equations for which is uncoupled in this case. Taking into account the local character of the perturbation, it is convenient to use the Schwinger variant of the Green's-function method. The integral equations of motion for phonon operators, as can be easily shown,

are in this case linear. Taking (19) and (20) into account, we have

$$\left. \begin{aligned} Q_{A_{1g}}(t) &= Q_0^{(0)}(t), \quad Q_{B_{1g}}(t) = Q_1^{(0)}(t), \quad Q_{B_{2g}}(t) = Q_2^{(0)}(t); \\ Q_{E_g\nu}(t) &= Q_3^{(0)}(t) + 2\alpha\omega_E^2 \int_0^t G_{T_2}^{(0)}(t-\tau) Q_3(\tau) d\tau \\ Q_{E_g\nu}(t) &= Q_n^{(0)}(t) + 2\alpha\omega_E^2 \int_0^t G_{T_2}^{(0)}(t-\tau) Q_n(\tau) d\tau \end{aligned} \right\}, \quad t \geq 0. \quad (21)$$

Here

$$\begin{aligned} Q_{\Gamma\gamma}(t) &= \exp(iHt/\hbar) Q_{\Gamma\gamma} \exp(-iHt/\hbar); \\ Q_{\Gamma\gamma}^{(0)}(t) &= \exp(iH_0 t/\hbar) Q_{\Gamma\gamma} \exp(-iH_0 t/\hbar), \end{aligned}$$

where  $H_0$  is the Hamiltonian of the system in the absence of a perturbation, i.e., at  $\alpha=0$ , and  $G_T^{(0)}(t)$  is the zeroth retarded Green's function:

$$G_T^{(0)}(t) = \frac{i}{\hbar} \theta(t) \langle [Q_{T\gamma}^{(0)}(t), Q_{T\gamma}] \rangle = \frac{i}{\hbar} \theta(t) \sum_{\kappa} \frac{a_{\kappa}^2(T_2\gamma)}{\omega_{\kappa}} \sin \omega_{\kappa} t.$$

Equations (21) are the phonon analog of the known Lipmann-Schwinger equations. Substituting (21) in the expressions for the retarded Green's functions

$$G_{\Gamma}(t) = i\hbar^{-1} \theta(t) \langle [Q_{\Gamma}(t), Q_{\Gamma}] \rangle,$$

we obtain

$$\begin{aligned} G_{A_{1g}}(t) &= G_{B_{1g}}(t) = G_{E_g}^{(0)}(t), \quad G_{B_{2g}}(t) = G_{T_2}^{(0)}(t), \\ G_{E_g}(t) &= G_{T_2}^{(0)}(t) + 2\alpha\omega_E^2 \int_{-\infty}^{\infty} G_{T_2}^{(0)}(t-\tau) G_{E_g}(\tau) d\tau. \end{aligned} \quad (22)$$

Changing to the Fourier representation, the integral equation (22) becomes algebraic:

$$G_{E_g}(\omega) = G_{T_2}^{(0)}(\omega) + 4\pi\alpha\omega_E^2 G_{T_2}^{(0)}(\omega) G_{E_g}(\omega),$$

from which we get

$$G_{E_g}(\omega) = G_{T_2}^{(0)}(\omega) [1 - 4\pi\alpha\omega_E^2 G_{T_2}^{(0)}(\omega)]^{-1}. \quad (23)$$

Here

$$G_T^{(0)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} G_T^{(0)}(t) dt = \frac{1}{2\pi} \sum_{\kappa} \frac{a_{\kappa}^2(T_2\gamma)}{\omega_{\kappa}^2 - \omega^2}. \quad (24)$$

As seen from (22) and (23), the  $A_{1g}$  and  $B_{1g}$  lattice vibrations, which were produced from the  $E_g$  vibrations as a result of the Jahn-Teller distortion, have remained degenerate; their corresponding frequency remains the same as without the Jahn-Teller effect, i.e., it contains no vibronic singularities. The frequency density of the  $B_{2g}$  vibrations stemming from the  $T_{2g}$  vibrations likewise remained the same. At the same time, the spectrum of the frequencies of the  $E_g$  vibrations, which were produced from the  $T_{2g}$  vibrations, changed substantially. The new dispersion law is described by the poles of the Green's function (23), i.e., by the roots of the transcendental equation

$$G_{T_2}^{(0)}(\omega) = (4\pi\alpha\omega_E^2)^{-1}. \quad (25)$$

At not too low values of  $\alpha$  there may occur in the forbidden band a discrete root of (25), corresponding to a localized gap vibration. If we introduce the projected density of the initial  $T_2$  vibrations of the lattice

$$\rho_T^{(0)}(\omega) = 2 \operatorname{Im} G_{T_2}^{(0)}(\omega + i\epsilon) \Big|_{\epsilon \rightarrow +0} = \sum_{\kappa} a_{\kappa}^2(T_2\gamma) \delta(\omega_{\kappa}^2 - \omega^2),$$

then Eq. (23) for the frequency of the local vibration can be rewritten in a more convenient integral form

$$\int_0^{\omega_{\max}} \frac{2z\rho_T^{(0)}(z)}{z^2-\omega^2} dz = \frac{1}{2\alpha\omega^2}. \quad (26)$$

In those cases when the density  $\rho_T^{(0)}(\omega)$  is known from alternate experiments or has been calculated analytically, the integral in (26) can be obtained and Eq. (26) can be solved either graphically or numerically.

It is of interest to investigate the new vibration density

$$\rho_E(\omega) = 2 \operatorname{Im} G_E(\omega + i\epsilon) |_{\epsilon \rightarrow +0}. \quad (27)$$

Introducing the function

$$r_T^{(0)}(\omega) = 2 \operatorname{Re} G_T^{(0)}(\omega + i\epsilon) |_{\epsilon \rightarrow +0},$$

which is connected with the initial density  $\rho_T^{(0)}(\omega)$  of the  $T_2$  vibrations by the dispersion relation

$$r_T^{(0)}(\omega) = \frac{1}{\pi} \int_0^{\omega_{\max}} \frac{2z\rho_T^{(0)}(z)}{z^2-\omega^2} dz, \quad (28)$$

we obtain from (23) and (27)

$$\rho_E(\omega) = \rho_T^{(0)}(\omega) \{ [1 - 2\pi\alpha\omega^2 r_T^{(0)}(\omega)]^2 + [2\pi\alpha\omega^2 \rho_T^{(0)}(\omega)]^2 \}^{-1/2}. \quad (29)$$

As follows from (29), if the projected density of the  $T_2$  vibrations  $\rho_T^{(0)}(\omega)$  is not large in the spectral region near one of the roots  $\omega_j$  of the equation

$$1 - 2\pi\alpha\omega^2 r_T^{(0)}(\omega) = 0 \quad (30)$$

then the modified vibration density in this region has a Lorentzian shape

$$\rho_E(\omega) \sim \frac{1}{\pi} \frac{\gamma_j}{(\omega - \omega_j)^2 + \gamma_j^2} \quad (31)$$

with a half-width

$$\gamma_j = \rho_T^{(0)}(\omega_j) [dr_T^{(0)}(\omega_j)/d\omega]^{-1}.$$

If any one of the roots of (30) falls in the forbidden band, where  $\rho_T^{(0)}(\omega) = 0$ , then the Lorentzian (31) degenerates into a delta function, Eq. (30) with (28) taken into account is transformed into (26), and we arrive at the local vibration discussed above. In the general case, however, it is necessary, knowing  $\rho_T^{(0)}(\omega)$ , to obtain the integral of (28) and to solve Eq. (30). A graphic solution of this equation is shown schematically in Fig. 1. It should be noted that in these spectral regions near the roots  $\omega_j$  of Eq. (30), where the initial density of the  $T_2$  vibrations is not small, the modified vibration density  $\rho_E(\omega)$  differs substantially from  $\rho_T^{(0)}(\omega)$ , although it does not have a Lorentzian shape.

A change in the curvature of the adiabatic potential, similar to that discussed above, occurs in the vicinity of each of the three tetragonal minima, leading in each of them to identically equal  $\rho_E(\omega)$ . Therefore the ground state of the system is triply degenerate, and the multiplicity of the degeneracy of each peak in  $\rho_E(\omega)$  must be multiplied by three. If it is furthermore recognized that all the poles of the Green's function  $G_E(\omega)$  are doubly degenerate, then it is obvious that all the local and pseudolocal states discussed above have sixfold degeneracy.

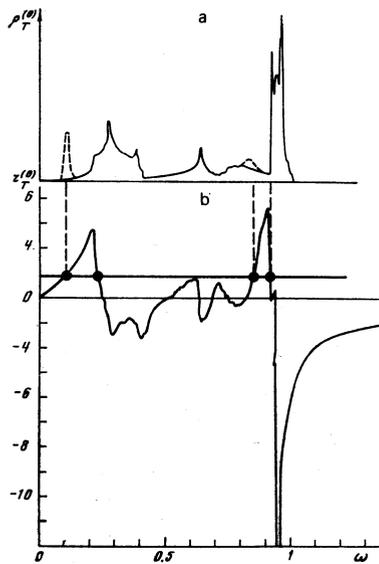


FIG. 1. Graphic solution of Eq. (30) for the frequencies of the local and pseudolocal vibrations resulting from the Jahn-Teller effect for the  $T$  term on small-radius impurity centers in a silicon crystal. a) Phonon density  $\rho_T^{(0)}(\omega)$  for the Si crystal. The dashed lines show the pseudolocal vibrations of vibronic origin. b) The Hilbert transform  $r_T^{(0)}(\omega)$  of the phonon density of the crystal Si. The frequency  $\omega$  is plotted in units of  $\omega_{\max}$ , and the function  $r_T^{(0)}$  in units of  $\omega_{\max}^2$ . The black circles mark the roots of Eq. (30).

The results are valid for any law of phonon dispersion, and particularly also in the absence of dispersion. The only requirements are that the coupling with the  $E$  vibrations be strong enough, that the tetragonal extrema be absolute minima of the adiabatic potential, and that the adiabatic approximation be valid near these minima. We can therefore compare the results obtained above with the result of the application of perturbation theory in  $V_T$  in the absence of phonon dispersion.<sup>10</sup>

Taking into account the condition for the normalization of the Van Vleck coefficients

$$\sum_{\alpha} a_{\alpha}^2(\Gamma\gamma) = 1, \quad (32)$$

we obtain from (25) in the absence of dispersion, i.e., at  $\omega_{\alpha} = \omega_i$ ,

$$\omega = \omega_i (1 - 2\alpha)^{1/2} \approx \omega_i (1 - \alpha),$$

whereas  $G_{E_{2g}}(\omega)$  has the previous pole  $\omega = \omega_i$ . The poles of the phonon Green's function yield the energy of the elementary excitations, i.e., the spacing of the equidistant vibrational spectrum. In the notation of Ref. 10 this means that

$$\hbar\omega = E_1 - E_0 = \hbar\omega_i + E_1^{(2)} - E_0^{(2)}.$$

As  $V_E \rightarrow \infty$  we obtain from Eqs. (16) and (21) of Ref. 10

$$\begin{aligned} E_1^{(2)}(A_2) - E_0^{(2)}(T_1) &= E_1^{(2)}(E) - E_0^{(2)}(T_1) = 0; \\ E_1^{(2)}(T_1) - E_0^{(2)}(T_1) &= E_1^{(2)}(T_2) - E_0^{(2)}(T_1) = -\frac{2}{3} \frac{V_T^2}{V_E^2} \hbar\omega_i = -\alpha \hbar\omega_i, \end{aligned} \quad (33)$$

which in fact corresponds to the poles given above.

The vibronic-level splitting described by Eqs. (23) is shown schematically in Fig. 2. From a comparison

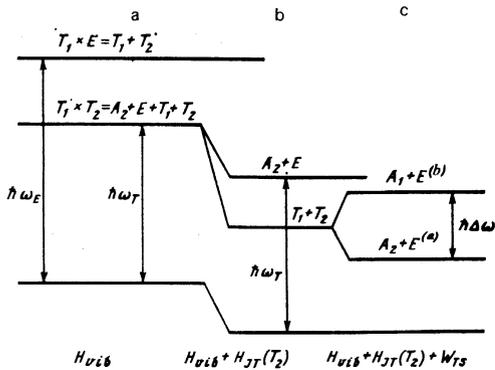


FIG. 2. Scheme showing the splitting of the lowest vibronic levels of an impurity-phonon system in the absence of phonon dispersion: a—equidistant vibrational spectrum of the system in the absence of vibronic coupling with the  $T_2$  vibrations, b—partial lifting of the random degeneracy with Jahn–Teller interaction with the  $T_2$  vibrations, c—splitting of the vibronic levels by a weak trigonal deformation.

with the vibronic levels of the Jahn–Teller cluster it becomes clear that the sixfold-degenerate local and pseudolocal states discussed above and due to the vibronic interaction with the  $T_2$  vibrations correspond to random degeneracy of the  $T_1$  and  $T_2$  terms (see Fig. 2).

#### 4. INFLUENCE OF UNIAXIAL DEFORMATIONS

Since the motion of the nuclei in the lowest vibronic states is localized near the tetragonal maxima, i.e., in those regions of configuration space of the nuclear displacements where the adiabatic approximation is valid, the influence of the deformations can be reduced to a bending of the adiabatic potential. The change of the coordinates, of the depth, and of the curvature of the tetragonal minima, due to the deformations, can be obtained by the same methods as in Sec. 1, i.e., with the aid of the procedure of Opik and Pryce.<sup>8</sup>

The tetragonal deformations oriented along the  $z$  axis (fourfold axis) are taken into account by the perturbation

$$\hat{W}_{E6} = \varepsilon \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \quad (34)$$

It is clear even from general considerations that under the influence of the perturbation (34) the three tetragonal minima cease to be equivalent. Two of them are raised in energy by  $\varepsilon/2$ , and one is lowered by  $\varepsilon$ . This leads to a lifting of the sixfold degeneracy of the local and pseudolocal vibronic states, which was discussed in Sec. 3. The two randomly merged triplets  $T_1$  and  $T_2$  are each split into a singlet and a doublet. As a result we obtain two randomly merged singlets  $A_1 + A_2$  and two merged doublets  $2E$  separated from them by  $3\varepsilon/2$ . In addition, the tetragonal deformations redetermine the curvature of each tetragonal minimum but, as shown by a calculation by the method of Opik and Pryce, the ensuing additional splitting of the vibronic levels is of next order of smallness compared with the splitting  $3\varepsilon/2$  considered above.

The trigonal deformations can be taken into account by the perturbation

$$\hat{W}_{T6} = \tau \begin{pmatrix} 0 & -1 & -1 \\ -1 & 0 & -1 \\ -1 & -1 & 0 \end{pmatrix}, \quad (35)$$

which redetermines the potential-energy matrix and accordingly its eigenvalues—the adiabatic potentials. Inasmuch as when account is taken of the perturbation (35) the total Hamiltonian remains invariant to rotations about one of the threefold axes, which transform the tetragonal minima into one another, it is clear that the three tetragonal minima, while remaining equivalent, are simultaneously shifted in energy by an equal amount under the influence of the perturbation (35). All the changes in the spectrum can be due only to the modification of the curvature of the minimum, and since this modification is the same in all three minima, it suffices to consider one of them, for example the same one that was considered in Sec. 2. Obviously, small deformations cannot alter greatly the Opik and Pryce solution (5)–(7) considered above (see Eqs. (13) and the following).

Using perturbation theory to solve this system and confining ourselves to terms linear in  $\tau$ , we get

$$|a_0\rangle = \begin{pmatrix} \tau/3\Delta \\ \tau/3\Delta \\ 1 \end{pmatrix}, \quad \Delta = E_{JT}(E) - E_{JT}(T). \quad (36)$$

Substituting (36) in (8) and in (2), we find that in the considered tetragonal minimum, with account of the trigonal deformation (35), we have

$$q_6^{(0)} = V_E/\omega_E^2, \quad q_4^{(0)} = 0, \quad (37)$$

$$q_1^{(0)} = q_3^{(0)} \cong 2\tau V_T/3\Delta\omega_T^2, \quad q_2^{(0)} = 0.$$

To determine the curvature of the potential surface near the minimum with coordinates (37), it is necessary, following Opik and Pryce,<sup>8</sup> to find the correction of second order in the small displacements  $Q_x = q_x - q_x^{(0)}$  to the energy at the minimum. For this purpose it is necessary to know not only the column  $|a_0\rangle$  corresponding to the ground state of the matrix  $\hat{U} + \hat{W}_{TS}$  at the minimum, but also the columns of the excited states  $|a_1\rangle$  and  $|a_2\rangle$  at this point. Recognizing that the contribution of the elastic energy of the normal vibrations to the potential-energy matrix is a multiple of the unity matrix and does not affect the elements of the columns  $|a_1\rangle$  and  $|a_2\rangle$ , to determine the latter it suffices to diagonalize the matrix

$$\sum_{\Gamma} V_{\Gamma} q_{\Gamma}^{(0)} \hat{C}_{\Gamma} + \hat{W}_{TS}$$

with  $q_{\Gamma}^{(0)}$  from (37). Using perturbation theory for this purpose, we obtain in the first order in

$$E_1 = E_{JT}(E) + \tau, \quad |a_1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}; \quad (38)$$

$$E_2 = E_{JT}(E) - \tau, \quad |a_2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ -2\tau/3\Delta \end{pmatrix},$$

whereas the column  $|a_1\rangle$  from (36) corresponds to the eigenvalue

$$E_0 = -2E_{JT}(E). \quad (39)$$

Taking into account the contribution made to the potential energy by the linear term of the expansion of  $\hat{U}$  in powers of  $Q_x = q_x - q_x^{(0)}$  up to second order in the small displacements  $Q_x$  from the minimum, and taking into account the contribution from the quadratic term up to first order of perturbation theory, using (36), (38), and (39), and retaining only the terms linear in  $\tau$ , we get

$$\begin{aligned} \varepsilon(\dots Q_n \dots) = & -E_{JT}(E) + \frac{1}{2} \sum_n \omega_n^2 Q_n^2 - \alpha \omega_n^2 (Q_i^2 + Q_n^2) \\ & - \frac{2\alpha\tau\omega_n^3}{E_{JT}(E)} Q_i Q_n - \frac{2\alpha\tau\omega_n^3}{3\Delta} Q_i (Q_i + Q_n) + \frac{3^{-1/2}\tau\omega_n^3 (2\alpha)^{1/2}}{\Delta} Q_n (Q_i + Q_n), \end{aligned} \quad (40)$$

where  $\alpha$ ,  $\omega_n$ ,  $E_{JT}(E)$  and  $\Delta$  are defined respectively in (15), (11), (12), and (36), and  $Q_{\Gamma\gamma}$  are given by (18).

The Hamiltonian with the potential-energy operator (40) determines the new integral equations of motion for the operators  $Q_{\Gamma\gamma}(t)$ , which take into account the trigonal perturbation

$$\begin{aligned} Q_0(t) = & Q_0^{(0)}(t) - \frac{\tau\omega_n^3 (2\alpha)^{1/2}}{\Delta\sqrt{3}} \int_0^t G_n^{(0)}(t-s) [Q_i(s) + Q_n(s)] ds; \\ Q_i(t) = & Q_i^{(0)}(t) + 2\alpha\omega_n^2 \int_0^t ds G_i^{(0)}(t-s) \left[ Q_i(s) + \frac{\tau}{E_{JT}(E)} Q_n(s) \right. \\ & \left. + \frac{\tau}{3\Delta} Q_i(s) - \frac{\tau}{\Delta(6\alpha)^{1/2}} Q_0(s) \right]; \\ Q_n(t) = & Q_n^{(0)}(t) + 2\alpha\omega_n^2 \int_0^t ds G_n^{(0)}(t-s) \left[ Q_n(s) + \frac{\tau}{E_{JT}(E)} Q_i(s) \right. \\ & \left. + \frac{\tau}{3\Delta} Q_i(s) - \frac{\tau}{\Delta(6\alpha)^{1/2}} Q_0(s) \right]; \\ Q_i(t) = & Q_i^{(0)}(t) + \frac{2\alpha\tau\omega_n^3}{3\Delta} \int_0^t G_i^{(0)}(t-s) [Q_i(s) + Q_n(s)] ds. \end{aligned} \quad (41)$$

We have throughout  $t \geq 0$ .

From (31) we find, in the approximation linear in  $\tau$ , that the retarded Green's functions

$$D_{\pm} = \langle\langle Q_i \pm Q_n | Q_i \pm Q_n \rangle\rangle$$

take in the  $\omega$  representation the form

$$D_{\pm}(\omega) = 2G_{\Gamma}^{(0)}(\omega) \{1 - 4\pi\alpha\omega_n^2 [1 \pm \tau/E_{JT}(E)] G_{\Gamma}^{(0)}(\omega)\}^{-1}. \quad (42)$$

As seen from (42), under the influence of trigonal deformation the double degeneracy of the  $E_g$  vibrations that stem from the  $T_{2g}$  vibrations, noted in Sec. 3, is lifted. It is easy to find from (42) that the splitting of the local and pseudolocal vibronic resonances at the frequency  $\omega_j$  ( $\omega_j$  is one of the roots of (30)) is given by

$$\Delta\omega_j \approx \tau r_{\Gamma}^{(0)}(\omega_j) \left[ E_{JT}(E) \frac{dr_{\Gamma}^{(0)}(\omega_j)}{d\omega} \right]^{-1},$$

where  $r_{\Gamma}^{(0)}(\omega)$  is defined in (28).

Since there are three equivalent tetragonal minima, the singlet single-phonon states corresponding to the poles of the functions  $D_{\pm}(\omega)$  and  $D_{\pm}(\omega)$  are encountered three times each, so that as a result all the single-phonon excitations are triply degenerate. In particular, in the absence of dispersion, when the problem reduces to the cluster problem, we obtain three triplets in place of the aforementioned sixfold degenerate excited state (see

Fig. 2b). These threefold degenerate terms are the result of splitting of each of two randomly merged triplets  $T_1 + T_2$  into a doublet and a singlet of the trigonal group:  $T_1 = A_1 + E^{(a)}$ ,  $T_2 = A_2 + E^{(b)}$ . These splittings are equal, and the randomly degenerate terms  $A_1 + E^{(b)}$  and  $A_2 + E^{(a)}$  make up the aforementioned triplet (see Fig. 2c).

## CONCLUSION

The Jahn-Teller effect on an impurity center rearranges substantially the vibronic states of a crystal near an impurity. As a result of the strong vibronic interaction, localized states of the polaron type are produced and represent low-symmetry inhomogeneities of the electron density, surrounded by a multiphoton jacket. At the same time, the initial cubic symmetry of the system is preserved. The ground state is a degenerate triplet, but the initial adiabatic electronically degenerate ground state becomes hybrid, vibronic. In other words, the dressed quasiparticles localized on the impurity retain the symmetry properties of the bare quasiparticles.

The vibronic impurity spectrum contains local and pseudolocal states, which correspond to vibrational excitations of the crystal lattice deformed by the Jahn-Teller effect. The position and width of the corresponding vibronic resonances in the lattice-vibration density are determined not only and not so much by the constants of the vibronic coupling, as by the form and structure of the initial density of the vibrations of the impurity-free lattice. In contrast to the local and pseudolocal vibrations due to mass defect and force constants, vibronic resonances have a higher degeneracy multiplicity, which is lifted in a rather unique manner under the influence of low-symmetry electronic perturbations.

The local and pseudolocal vibronic states due to the Jahn-Teller effect should manifest themselves in all the spectral characteristics of the impurity crystals. In optical transitions to the impurity  $T$  term, for example, vibronic resonances are present in all the multiphonon replicas of the zero-phonon line, thereby substantially complicating the corresponding curve of the coefficient of the impurity absorption of luminescence.

A comparative analysis of the infrared (IR) absorption and Raman scattering of light makes it possible to separate the considered vibronic states from the local and pseudolocal vibrations due to the impurity mass defects. Thus, in the case of an octahedral surrounding of the impurity, the latter are transformed in accordance with an irreducible representation  $T_{1u}$  of the group  $O_h$  and are dipole-active. This means that they determine the spectral density of the IR absorption. At the same time a light beam scattered, say, at a right angle to the incident beam, contains information on the  $T_{2g}$  vibrations that are active in the Jahn-Teller effect, and says nothing about the  $T_{1u}$  vibrations, which make no contribution to the Raman scattering, being parity-forbidden.

In those cases when the Jahn-Teller effect leads to the appearance of a low-frequency vibronic state, it can substantially influence the relaxation processes in EPR

spectra, the temperature dependences of various impurity susceptibilities, the specific heat, and others.

The author thanks Yu. B. Rozenfel'd for numerous helpful discussions and I. B. Bersuker for stimulating interest in the work.

<sup>1</sup>A brief review of the results of the theory of the Jahn-Teller effect for the  $T$  term, obtained within the framework of the cluster model, can be found in Ref. 7.

<sup>1</sup>I. B. Bersuker, *Elektronnoe stroenie i svoistva koordinatsionnykh soedinenii. Vvedenie v teoriyu* (Electronic Structure and Properties of Coordination Compounds. Introduction to the Theory), Khimiya, 1976.

<sup>2</sup>R. Englman, *The Jahn-Teller Effect in Molecules and Crystals*, Wiley-Interscience, 1972.

<sup>3</sup>Yu. E. Perlin and B. S. Tsukerblat, *Éffekty élektronno-kolebatel'nogo vzaimodeistviya v opticheskikh spektrakh primesnykh paramagnitnykh ionov* (Effects of Vibronic Interaction in

Optical Spectra of Impurity Paramagnetic Ions), Shtiinst, Kishinev, 1974.

<sup>4</sup>N. N. Kristofel', *Teoriya primesnykh tseftrov malykh radii-ov v ionnykh kristallakh* (Theory of Impurity Centers with Small Radii in Ionic Crystals), Nauka, 1974.

<sup>5</sup>B. G. Vekhter, V. Z. Polinger, Yu. B. Rozenfel'd, and B. S. Tsukerblat, *Pis'ma Zh. Eksp. Teor. Fiz.* **20**, 84 (1974) [*JETP Lett.* **20**, 36 (1974)].

<sup>6</sup>Yu. B. Rozenfel'd and V. Z. Polinger, *Zh. Eksp. Teor. Fiz.* **70**, 597 (1976) [*Sov. Phys. JETP* **43**, 310 (1976)].

<sup>7</sup>A. Ranfagni and G. Viliani, *Solid State Commun.* **20**, A10, 1005 (1976).

<sup>8</sup>U. Opik and M. H. L. Pryce, *Proc. R. Soc. London A* **238**, 425 (1957).

<sup>9</sup>B. P. Martinenas and R. S. Dagis, *Teor. Éksp. Khim.* **5**, 123 (1969).

<sup>10</sup>I. B. Bersuker and V. Z. Polinger, *Phys. Status Solidi B* **60**, 85 (1973).

Translated by J. G. Adashko

## Self-induced transparency is a diphenyl crystal containing pyrene and excited by its own stimulated emission

P. V. Zinov'ev, G. G. Zaitseva, Yu. V. Nabotkin, V. V. Samartsev, N. B. Silaeva, and Yu. E. Sheibut

*Physicotechnical Institute of Low Temperatures, Ukrainian Academy of Sciences, and Kazan'*

*Physicotechnical Institute of the Kazan' Branch of the USSR Academy of Sciences*

(Submitted 19 April 1979)

*Zh. Eksp. Teor. Fiz.* **77**, 1519-1527 (October 1979)

The optical self-induced transparency in a diphenyl crystal activated by pyrene is investigated theoretically and experimentally in the 1.6 to 4.1 K temperature range. For the first time in self-induced transparency studies the same crystal has been used as the generator of the stimulated radiation and as the object of the investigation. Optical pumping is carried out at 3530 Å; generation and self-induced transparency occur at 3739 Å which corresponds to the  ${}^1B_{2u} \leftrightarrow {}^1A_g$  transition in pyrene. The self-induced transparency in the crystal studied was accompanied by a delay in the pulse (by 8-9 nsec) and by a characteristic kinetics of deformation and its shape (self-broadening, self-compression, self-division, depending on the pulse intensity at the entry into the resonant medium). Both an analytic and a numerical solution of the self-consistent problem of passage under conditions of a nonequilibrium level population density difference are obtained. The electric dipole moment is found by a computer search of the solution for an experimentally determined kinetics of pulse deformation in a resonant medium.

PACS numbers: 78.45.+h, 78.20.Dj, 42.65.Gv

### 1. INTRODUCTION

The phenomenon of self-induced transparency (SIT)<sup>1</sup> consists of the bleaching a resonant medium when a laser pulse propagates through the medium (under conditions of nonlinear coherent interaction) and its power exceeds a definite threshold. The SIT is characterized by a substantial delay of the pulse in the resonant medium, by its self-broadening (or self-compression, depending on the signal power entering the sample), and by a definite deformation of the pulse waveform.<sup>2,3</sup> The SIT method makes it possible to determine the irreversible relaxation times, the electric dipole moment of resonant transitions, and other spectroscopic

information.<sup>2-6</sup>

In the present paper, the SIT procedure is used to investigate a diphenyl crystal activated with pyrene. This is a member of a new class of objects—impurity molecular crystals. Prior to this investigation, only one publication<sup>7</sup> reported observation of SIT in a similar object, namely in pentacene in *p*-terphenyl, without indication of any particular details on the conditions and singularities of the realization of the effect. The singularity of the SIT in our study lies in the fact that the crystal is excited by its own stimulated emission, i.e., it is simultaneously the radiation generator and the object of the investigation. A numerical analysis of