[1)]The direct transitions from A^+ to A^- centers[11] can be ignored for samples with $N_A < 5\times10^{14}$ cm^{-3}.
[2)]The formulas of the (3) and (5) type were first obtained in[13].
[3)]This value of ε_i represents the energy for the photodetachment of a hole from an isolated A^+ center; it is clear from the experiments that in the $N_A > 10^{15}$ cm^{-3} range this energy rises with N_A (for example,[19] it may reach $\varepsilon_i \gtrsim 5$ meV for Si. B).
[4)]In the ambipolar excitation case,[14] their influence is important for any value of the compensation.

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Dynamic Jahn-Teller effect for the *E*-term with allowance for phonon dispersion

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It is shown that the dynamic Jahn-Teller effect for a non-Kramers doublet leads, in the presence of phonon dispersion of active *E* vibrations, to the possibility of appearance of local and pseudolocal electron-phonon states. Criteria for appearance of such states are found. The limits of applicability of the cluster model for impurity centers are discussed. Spectral effects of local and pseudolocal states in the optical and infrared absorption and in Raman scattering of light are considered.

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1. INTRODUCTION

The problem of electron-vibrational (vibronic) interaction in systems with electron degeneracy or quasi-degeneracy is extremely complicated, owing to the impossibility of separating, in the general case, the electronic and the nuclear motions. The manifestation of the vibronic interactions in such systems is customarily called the Jahn–Teller effect (JTE). This effect has been the subject of many theoretical and experimental papers (see the books and reviews[1–6]). The greatest progress was attained in the solution of the so-called molecular vibronic problems, where the electrons, in the degenerate state, interact with a small number of vibrational degrees of freedom. This model is adequate for the description of phenomena connected with vi-

bronic interactions in molecules or complexes. It was also used to interpret the properties of impurity centers of small radius in the so-called quasi-molecular or or cluster model (see, e.g., the book[7]), where the interaction of the impurity electrons with an infinite number of lattice vibrations is replaced by an interaction with several "effective" modes. However, the use of the cluster model is justified, generally speaking, only in those cases when there are local or clearly pronounced pseudolocal oscillations in the phonon spectrum of the impurity crystal, the interaction with which prevails over the interaction with the remaining crystal oscillations. Notice should also be taken of the case of dominant interaction with extremely narrow band of optical vibrations, when the phonon dispersion can be neglected and the problem can be reduced to a molecular one.[8] Nonetheless, the cluster model is extensively used for the interpretation of experimental data even in those cases when the separation of the effective modes cannot be justified.

The present paper is devoted to an investigation of the dynamic JTE for a small-radius impurity center in an orbital doublet state (E-term), for the case of weak coupling with the crystal vibrations. The spectrum of the phonon frequencies of the impurity-containing crystal, due to the differences in the masses and in the force constants, is assumed known. The impurity concentration is assumed to be so low that the interaction between the impurity centers can be neglected.

2. HAMILTONIAN AND GREEN'S FUNCTION OF THE SYSTEM

The effective Hamiltonian of a small-radius impurity center with E-term (non-Kramers doublet), separated from all other electronic terms by a sufficiently large energy gap, has in the linear-harmonic approximation the form

$$H=\sum_{\varkappa}\frac{\hbar\omega_{\varkappa}}{2}(p_{\varkappa}^2+q_{\varkappa}^2)+k_E(Q_\theta\sigma_x+Q_\varepsilon\sigma_y). \tag{1}$$

Here $\omega_\varkappa$ are the frequencies of the normal vibrations of the impurity crystal, $\varkappa$ is an index that numbers the wave numbers and the oscillation modes, $q_\varkappa$ and $p_\varkappa$ are the normal coordinates and momenta, k_E is the coupling constant of the impurity electrons with the symmetrized displacements Q_θ and Q_ε of the atoms of the first coordination sphere, which transform in accordance with the rows θ and ε ($\theta\sim 2z^2-x^2-y^2$; $\varepsilon\sim\sqrt{3}(x^2-y^2)$) of an irreducible representation of the E type. The Pauli matrices σ_x and σ_y are defined in the basis of the electronic functions of the orbital doublet $\Psi_\pm=\mp(|\theta\rangle\pm i|\varepsilon\rangle)/\sqrt{2}$; the energy of the electronic term is assumed to be equal to zero. Expanding the symmetrized displacements $Q_\gamma(\gamma=\theta,\varepsilon)$ in the normal modes of the impurity crystal:

$$Q_\gamma=\sum_{\varkappa}a_{\varkappa}(\gamma)q_{\varkappa}, \tag{2}$$

we rewrite (1) in the form

$$H=\sum_{\varkappa}\left[\frac{\hbar\omega_{\varkappa}}{2}(p_{\varkappa}^2+q_{\varkappa}^2)+k_E\alpha_{\varkappa}q_{\varkappa}\right],$$
$$\alpha_{\varkappa}=a_{\varkappa}(\theta)\sigma_x+a_{\varkappa}(\varepsilon)\sigma_y. \tag{3}$$

The expression for the Van Vleck coefficients $a_\varkappa(\gamma)$ in the particular case of an octahedral surrounding of the impurity center, can be found, for example, in[6]. Subjecting the Hamiltonian (3) to a unitary shift transformation that eliminates the linear terms of the electron-phonon interaction, we obtain, accurate to k_E^2,

$$\tilde{H}=e^{iS}He^{-iS}\approx H+i[S,H]_--\frac{1}{2}[S^2,H]_+$$
$$=-E_{JT}+\sum_{\varkappa}\frac{\hbar\omega_{\varkappa}}{2}(p_{\varkappa}^2+q_{\varkappa}^2)-k_E^2\sigma_z\sum_{\varkappa\lambda}W_{\varkappa\lambda}\frac{p_{\varkappa}q_{\lambda}}{\hbar\omega_{\varkappa}}. \tag{4}$$

Here

$$S=k_E\sum_{\varkappa}\frac{\alpha_{\varkappa}p_{\varkappa}}{\hbar\omega_{\varkappa}},\quad E_{JT}=\frac{1}{2}k_E^2\sum_{\varkappa}\frac{a_{\varkappa}^2(\gamma)}{\hbar\omega_{\varkappa}},$$
$$W_{\varkappa\lambda}=a_{\varkappa}(\theta)a_{\lambda}(\varepsilon)-a_{\varkappa}(\varepsilon)a_{\lambda}(\theta). \tag{5}$$

It follows from (5) that the matrix $W_{\varkappa\lambda}$ transforms in accordance with the irreducible representation A_2 of the point group of the impurity center. Evidently the Hamiltonian (4) is diagonal in the space of the electronic states $\Psi_\pm$, so that in second order in k_E the electron motion is separable from the nuclear motion, and the weak dynamic Jahn–Teller effect leads to a redefinition of the phonon spectrum. We shall therefore engage henceforth in finding the redefined density of states and the corresponding spectral manifestations of the indicated effect.

We introduce the phonon Green's functions

$$D_{\varkappa\lambda}^{(1)}(t)=\langle\langle q_{\varkappa}(t)\,|\,p_{\lambda}\rangle\rangle;$$
$$D_{\varkappa\lambda}^{(2)}(t)=\langle\langle p_{\varkappa}(t)\,|\,p_{\lambda}\rangle\rangle,\quad D_{\varkappa\lambda}^{(3)}(t)=\langle\langle p_{\varkappa}(t)\,|\,q_{\lambda}\rangle\rangle,\quad D_{\varkappa\lambda}^{(4)}(t)=\langle\langle q_{\varkappa}(t)\,|\,q_{\lambda}\rangle\rangle,$$

in which, however, no averaging is carried out over the electronic variables and which thus remain electronic two times two matrices. Here, as usual, $\langle\langle A(t)\,|\,B\rangle\rangle=i\theta(t)\langle[A(t),B]_-\rangle$, and the Hamiltonian (4) enters in the formulas for the statistical averaging and the Heisenberg representation of the operators. Changing over to the matrix notation $D^{(i)}=\|D_{\varkappa\lambda}^{(i)}\|$, we write down the equations of motion for the Fourier transforms of the Green's functions $\mathbf{D}^{(1)}$ and $\mathbf{D}^{(2)}$ in the form

$$\mathbf{D}^{(1)}(\omega)=\mathbf{E}\left(i\omega-\frac{k_E^2}{\hbar^2}\sigma_z\mathbf{WE}\right)\mathbf{D}^{(2)}(\omega),$$
$$\mathbf{D}^{(2)}(\omega)=\frac{1}{2\pi}\mathbf{E}-\mathbf{E}\left(i\omega-\frac{k_E^2}{\hbar^2}\sigma_z\mathbf{EW}\right)\mathbf{D}^{(1)}(\omega), \tag{6}$$

where $E=\|\delta_{\varkappa\lambda}/\omega_{\varkappa}\|$. The system of equations (6) turned out to be closed, owing to the bilinearity of the Hamiltonian (4) with respect to the phonon variables. From (6) we obtain for $\mathbf{D}^{(2)}$ the Dyson equation

$$\mathbf{D}^{(2)}=\mathbf{D}_0^{(2)}+\mathbf{D}_0^{(2)}\mathbf{V}\mathbf{D}^{(2)}=\mathbf{D}_0^{(2)}+\mathbf{D}_0^{(2)}\mathbf{T}\mathbf{D}_0^{(2)}, \tag{7}$$

where the zeroth Green's function takes the form

$$(\mathbf{D}_0^{(2)})_{\varkappa\lambda}=\frac{1}{2\pi}\frac{\omega_{\varkappa}\delta_{\varkappa\lambda}}{\omega_{\varkappa}^2-\omega^2}, \tag{8}$$

and the role of the perturbation operator is played by

$$\mathbf{V}=2\pi\left(2i\omega\frac{k_E^2}{\hbar^2}\sigma_z\mathbf{EWE}-\frac{k_E^4}{\hbar^4}\mathbf{EWEWE}\right). \tag{9}$$

The scattering matrix $\mathbf{T}$ satisfies the equation

$$\mathbf{T}-\mathbf{T}\mathbf{D}_0^{(2)}\mathbf{V}=\mathbf{V}. \tag{10}$$

Using the orthogonality of the Van Vleck coefficients,[6] we can show that

$$\sum_{\lambda} W_{\varkappa\lambda} W_{\lambda\varkappa'} f(\omega_\lambda) = -R_{\varkappa\varkappa'} \sum_{\lambda} a_\lambda^2(\gamma) f(\omega_\lambda), \tag{11}$$

where

$$R_{\varkappa\varkappa'} = a_\varkappa(\theta) a_{\varkappa'}(\theta) + a_\varkappa(\varepsilon) a_{\varkappa'}(\varepsilon). \tag{12}$$

The matrix $\mathbf{R} = \|R_{\varkappa\lambda}\|$ is transformed in accordance with a fully-symmetrical representation A_1 of the point group of the impurity center, and by virtue of the same orthogonality relations it has the properties of a projective operator:

$$\mathbf{R}^2 = \sum_{\lambda} a_\lambda^2 \mathbf{R}.$$

From the definition of the scattering matrix T and from relation (11) we easily see that T can contain terms that transform only in accordance with representations A_1 and A_2. Starting from the indicated properties, and also from the multiplicative structure of the matrix V, we seek T in the form

$$\mathbf{T} = r\mathbf{ERE} + i\sigma_2 w\mathbf{EWE}. \tag{13}$$

The locality of the interaction of the impurity center with the crystal and the symmetry properties make it possible thus to reduce the solution of the infinite algebraic system of equations (10) relative to the matrix elements $T_{\varkappa\lambda}$ to a solution of two equations relative to the scalar coefficients r and w.[1)] As a result we obtain

$$r = \frac{1}{\Delta}[\alpha - (\alpha^2 - \omega^2\gamma^2) f(\omega)]; \quad w = \frac{\omega\gamma}{\Delta}, \tag{14}$$

$$\Delta = [1 - (\alpha + \omega\gamma) f(\omega)][1 - (\alpha - \omega\gamma) f(\omega)], \tag{15}$$

where

$$\alpha = 2\pi \frac{k_E^4}{\hbar^4} \sum_{\lambda} \frac{a_\lambda^2(\gamma)}{\omega_\lambda} = \frac{4\pi k_E^2}{\hbar^3} E_{JT}, \quad \gamma = \frac{4\pi k_E^2}{\hbar^2}, \tag{16}$$

$$f(\omega) = \frac{1}{2\pi} \sum_{\lambda} \frac{a_\lambda^2(\gamma)}{\omega_\lambda(\omega_\lambda^2 - \omega^2)}. \tag{17}$$

Equations (13)–(17) and (7) determine the sort Green's function $\mathbf{D}^{(2)}(\omega)$, and from (6) we get $\mathbf{D}^{(1)}(\omega)$. The Green's function $\mathbf{D}^{(3)}$ can be obtained with the aid of the reciprocity relation[9] $\mathbf{D}^{(3)}(\omega) = \tilde{\mathbf{D}}^{(1)}(-\omega)$, and the function $\mathbf{D}^{(4)}$ from the equation of motion that relates it with $\mathbf{D}^{(3)}$:

$$\mathbf{D}^{(4)} = \frac{1}{2\pi}\mathbf{E} + \left(i\omega\mathbf{E} - \frac{k_E^2}{\hbar^2}\sigma_2\mathbf{EWE}\right)\mathbf{D}^{(3)}.$$

3. SPECTRUM OF THE SYSTEM. LOCAL AND PSEUDOLOCAL VIBRONIC STATES

The phonon spectrum of the system, redefined by the Jahn–Teller interaction, is determined by the poles of the Green's functions, that is, by the zeroes of the function $\Delta(\omega)$. In the particular case of one extremely narrow oscillation band with frequency $\omega_\varkappa = \omega_0$, we obtain

$$\omega = \omega_0 \pm \frac{k_E^2}{\hbar^2\omega_0} \sum_{\varkappa} a_\varkappa^2(\gamma),$$

which coincides with the result of Moffit and Thorson[10] and describes the splitting of the vibronic terms in the case of a weak electron-phonon coupling. This result is understandable, inasmuch, as shown in[8], in the case of an extremely narrow vibrational band the problem reduces to the molecular one with an effective coupling constant

$$k = k_E \left(\sum_{\varkappa} a_\varkappa^2\right)^{1/2}.$$

Allowance for the phonon dispersion calls for resorting to approximate computation methods for the solution of the equation $\Delta(\omega) = 0$. An analytic solution can be obtained only in the so-called resonance approximation, when the frequency ω, which falls inside the band, is far from the frequencies of the pseudolocal oscillations and from the singularities of the state density. However, a detailed knowledge of the dispersion law as redefined by the Jahn–Teller interaction is not necessary, since most of the observed quantities are expressed in terms of integral characteristics of the spectrum. We consider therefore the most characteristic changes which occur in the density of states when the Jahn–Teller effect is taken into account. These changes are connected with the possibility of the appearance of a new type of local and pseudolocal oscillations, due to the vibronic interaction. The frequencies of these oscillations can be obtained from the equation

$$\frac{4\pi k_E^2}{\hbar^3} f_r(\omega^2) = (E_{JT} \pm \hbar\omega)^{-1}, \tag{18}$$

where

$$f_r(\omega^2) = \frac{1}{2\pi} \hat{P} \sum_{\varkappa} \frac{a_\varkappa^2}{\omega_\varkappa(\omega_\varkappa^2 - \omega^2)},$$

and the symbol $\hat{P}$ denotes the principal value in the sense of Cauchy. Using the dispersion relation

$$f_r(x) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{f_i(z)}{z - x} dz, \tag{19}$$

in which

$$f_i(x) = \frac{1}{2\sqrt{x}} \sum_{\varkappa} a_\varkappa^2 \delta(\omega_\varkappa^2 - x), \tag{20}$$

we rewrite (18) in the form

$$\frac{4k_E^2}{\hbar^3} \int_{-\infty}^{\infty} \frac{f_i(z)}{z - \omega^2} dz = (E_{JT} \pm \hbar\omega)^{-1}. \tag{21}$$

The corresponding peaks in the density of states have half-widths of the order of $f_i/(f_r^2 + f_i^2)$. The appearance of local or pseudolocal oscillations is connected thus with two circumstances. First, in order for (21) to have roots, it is necessary that the Hilbert transform[2)] (19) of the function $f_i(x)$ assume sufficiently large values. Second, in order for the resultant peaks to be narrow, it is necessary that the roots of (21) lie in the region of small values of the function $f_i(x)$. It should be noted that the Hilbert transform can assume large values only in regions where the derivative of the inverse transform $f_i(x)$ is large (the converse, generally speaking, is not true). If the $f_i(x)$ curve has a section Δx on which the derivative $f_i'(x)$ is large, say $f_i'(x) \geqslant A$, and on the adjacent sections it is small, so that $f_i'(x) \ll A$, then the Hilbert transform on these sections can be estimated from the inequality

$$|f_r(x)| > \frac{1}{\pi} A\Delta x |\ln(\Delta x)|. \quad (22)$$

The inequality (22) makes it possible to formulate the sufficient condition for the onset of local and pseudolocal oscillations due to the Jahn–Teller effect:

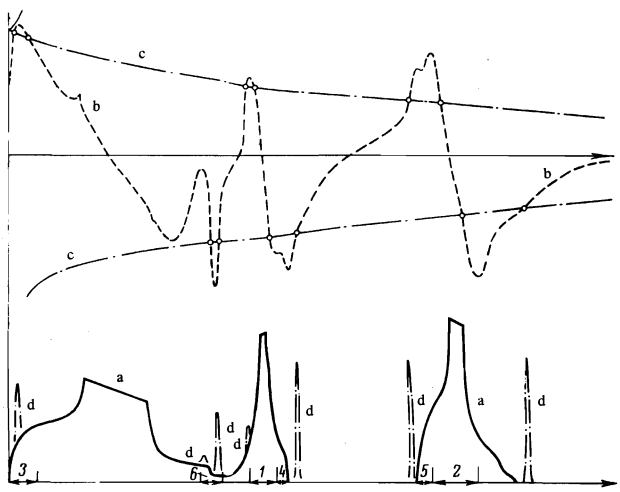
$$\frac{4k_F^2}{\hbar^3} A\Delta x |\ln(\Delta x)(E_{JT} \pm \hbar\sqrt{x})| > 1. \quad (23)$$

Since the square of the Van Vleck coefficient $a_\varkappa^2(\gamma)$ is a smooth function of the wave vector $\varkappa$ and exerts an appreciable influence on the behavior of $f_i(x)$ only in the long-wave region, where $a^2 \sim \varkappa^2$, the singularities of the function $f_i(x)$ coincide with the known singularities of Van Hove in the density of states

$$g(x) = \sum_\varkappa \delta(\omega_\varkappa^2 - x).$$

An appreciable difference between $f_i(x)$ and the ordinary density of states occurs only in the low-frequency region of the acoustic oscillation band, where $f_i(x) \sim x$, and in the high-frequency region of the optical band, where $f_i(x) \sim (\Omega_2^2 - x)^{3/2}$; here Ω_2 is the upper limit of the optical band. For the sake of brevity we shall henceforth call $f_i(x)$ the density of states. We note that the presented estimate (23) is valid also near Van Hove singularities. However (with the exception of the band boundaries, where the density of states is low), these singularities are located usually in places with large density of states and do not lead to pseudolocal oscillations.

Sections with large values of the derivative f_i' are indicated in the figure, which shows schematically the characteristic dependence of the function $4\hbar^{-3}k_E^2 f_i(x)$, its Fourier transform, and dependence of the right-hand side of (21) on $x = \omega^2$. In Secs. 1 and 2, where there is a sharp peak, the Hilbert transform has an inverted s shape. If inequality (23) is satisfied in this case, then Eq. (21) has in this region four roots, two of which fall in the region with large density of states and are therefore of no significance, while the two others lead to two additional peaks in the density of states, on opposite sides of the initial peak. The indicated splitting has a clear physical meaning. In fact, a sharp peak in the density of states can be treated as a narrow oscillation band, for which the problem reduces to the molecular one. The peculiarity of the dispersion in this situation lies in the fact that the conditions for the appearance of the splitting are limited by the inequality (23), which can be satisfied only on one of the slopes of the initial peak, and may not be satisfied at all.



Graphic solution of the dispersion equation (see formula (21) in the text): a—density of states, b—its Hilbert transform, i.e., plot of the left-hand side of (21), c—plot of the right-side of (21), d—sum of the local and pseudolocal vibronic states. The scale is arbitrary.

An interesting possibility is that of the appearance of local and pseudolocal oscillations in regions 3, 4, 5, and 6, where $f_i(x)$ experiences a jump similar to a discontinuity of the first kind. (The Hilbert transform of a function with a discontinuity of the first kind diverges logarithmically at the discontinuity point, and consequently Eq. (21) always has two roots in such places.) When the inequality (23) is satisfied, a narrow peak can occur, in particular, in the low-frequency region 3, something that cannot be explained at all within the framework of the cluster model in the case of weak electron-phonon coupling, and is a unique manifestation of the phonon dispersion.

As seen from the figure, the least stringent conditions for the onset of local and pseudolocal oscillations obtain near the limiting phonon frequency, when the right-hand side of (21) is minimal. The conditions for the appearance of gap oscillations become worse with decreasing width of the forbidden band, since the values of the Hilbert transform on the upper limit of the acoustic band and on the lower limit of optical band decrease in this case. The decrease of the width of the optical band leads to an enhancement of the inequality (22), and in the limit we obtain the result of the dispersionless case. In other words, at arbitrarily weak coupling one can always find an optical-band width for which local and gap oscillations will exist. Different oscillation modes, by virtue of the linearity of the Hilbert transformation, make additive contributions to $f_r(x)$ and can be considered independently only at a large value of the gap. With increasing gap size, the conditions for the appearance of a low-frequency pseudolocal oscillation improve, owing to the ensuing increase of the contribution made to this region by the optical branches.

The foregoing calculation is limited to the linear-harmonic approximation. However, after a new phonon spectrum is obtained from the solution of the dispersion equation $\Delta(\omega) = 0$, it is easy to take the anharmonicity into account and leads the well-known results are obtained, particularly the broadening of the spectral lines ([13], pp. 293–306). This broadening is important only for local states, which have no width at all in the linear-harmonic approximation.

4. OPTICAL AND INFRARED ABSORPTION, RAMAN SCATTERING OF LIGHT

We consider certain experimental manifestations of the Jahn–Teller effect in local and pseudolocal vibronic states.

a) *Singlet-doublet optical absorption.* Let the prin-

cipal electronic term of the impurity center be an orbital singlet, and let the excited terms include a non-Kramers doublet that interacts weakly with the E oscillations. In the linear-harmonic approximation, the form function of the one-phonon satellite for E oscillations at $T=0$ °K and at a weak electron-phonon coupling is determined by the expression

$$K(\Omega)=\frac{k_E^2}{\hbar^2}\sum_{\bar\gamma}|\langle A|d|E\bar\gamma\rangle|^2\sum_{\varkappa\lambda}(\omega_\varkappa\omega_\lambda)^{-1}\langle E\bar\gamma|\alpha_\varkappa K^{(2)}_{\varkappa\lambda}(\Omega)\alpha_\lambda|E\bar\gamma\rangle. \quad (24)$$

Here d is the operator causing the optical transition, $|A\rangle$ and $|E\bar\gamma\rangle$ are the electronic wave functions of the singlet and the doublet, while $K^{(2)}_{\varkappa\lambda}(\Omega)$ is the spectral density of the correlator connected with the Green's function $D^{(2)}_{\varkappa\lambda}(\Omega)$:

$$K^{(2)}_{\varkappa\lambda}(\Omega)=\frac{1}{i}[D^{(2)}_{\varkappa\lambda}(\Omega+i\varepsilon)-D^{(2)}_{\varkappa\lambda}(\Omega-i\varepsilon)]_{\varepsilon=+0}. \quad (25)$$

Formula (24) differs from the ordinary expression for the spectral curve of the one-phonon satellite in that it takes exact account of the restructuring of the spectrum by the electron-phonon interaction. Formula (24) is incorrect at $T\neq 0$ °K, for with increasing temperature, multiphonon processes begin to contribute to the coefficient of the one-phonon absorption, and these processes are not described by the single-particle phonon Green's function. Substituting (25) in (24) and rearranging the summation over $\varkappa$, λ, and $\bar\gamma$, we obtain:

$$K(\Omega)=4M\frac{k_E^2}{\hbar^2}\frac{f_i(\Omega)}{[1-(\alpha+\Omega\gamma)f_r(\Omega)]^2+f_i^2(\Omega)(\alpha+\Omega\gamma)^2}, \quad (26)$$

where $M=|\langle A\|d\|E\rangle|^2$ is the square of the modulus of the reduced matrix element. The equation $\Delta(\omega)=0$, which gives the redefined phonon spectrum of the system, has two systems of roots, corresponding to the two signs in (18). As seen from (26), only roots corresponding to only a positive sign of (18) appear in optical singlet-doublet absorption. This is connected with the selection rules with respect to the quantum number of the total electron-vibrational angular momentum of the vibronic system. The existence of such an integral of motion for a Jahn–Teller system with an E term, described by the Hamiltonian

$$H=\sum_n\frac{\hbar\omega_n}{2}(p_{n\theta}^2+p_{n\varepsilon}^2+q_{n\theta}^2+q_{n\varepsilon}^2)+\sum_n k_n(q_{n\theta}\sigma_x+q_{n\varepsilon}\sigma_y), \quad (27)$$

was proved by Sloncjewski.[14] The Hamiltonian (1) considered in the present paper can be reduced to the form (27), if the summation over the wave vector $\varkappa$ is carried out in two steps: first run over all the values of $\varkappa$ on the equal-frequency surface $\omega_\nu(\varkappa)=\omega_\nu$, and then integrate with respect to ω_ν. By carrying out orthogonal transformations in the subspaces of the normal vibrations pertaining to each equal-frequency surface, in a manner similar to that used in the multimode dispersionless problem,[8] we can pick out for each such surface one pair of interacting effective modes, with the remaining vibrational degrees of freedom separated. Thus, the Hamiltonian (1) can be reduced to the form (27), and therefore the Jahn–Teller system described by the Hamiltonian (1) also has a conserved total electron-vibrational angular momentum. The existence of this integral of motion offers evidence of the "accidental" increase of the symmetry of the Jahn–Teller polyatomic system with E term, from point symmetry to axial symmetry. All the states of such a system are doubly degenerate–energy each value corresponds to two states with different directions of the projection of the angular momentum on the axis. Thus, for example, one-phonon states correspond to total angular momentum values 0 and 1. Inasmuch as in the ground state of the singlet electronic term the total angular momentum is zero, and the transformation properties of the vector d correspond to the angular-momentum projection $\pm 1/2$, it is clear that this transition is allowed only to a state with total angular momentum projection ± 1. This hindrance is lifted with increasing population of the states whose total angular momentum differs from zero.

The total single-phonon absorption coefficient is obtained by adding to (26) the standard expression for the single-phonon satellite in the fully-symmetrical oscillations. In the frequency regions far from the roots of Eq. (18), expression (26) can be expanded in powers of k_E^2. The first term of the expansion has the usual form of the one-phonon E-oscillation satellite, which accounts, when allowance is made for the remarks that follow formula (23), for the initial phonon density of states of the crystal:

$$K(\Omega)=4M\frac{k_E^2}{\hbar^2}f_i(\Omega).$$

In all the regions close to the roots of Eq. (8), the indicated expansion is incorrect, and the form of the single-phonon satellite differs significantly from $f_i(\Omega)$. In particular, in those regions where, in addition to the vanishing of the expression $1-(\alpha+\Omega\gamma)f_r(\Omega)$, the initial density of states is small (see regions 3, 4, 5, and 6 in the figure), narrow Lorentz-like peaks of pseudolocal states and δ-like peaks of local and gap states appear on the optical single-phonon absorption curve. It should be noted that even in those cases when there are no pseudolocal oscillations, but Eq. (18) is "almost" satisfied, the function $K(\Omega)$ differs greatly from $f_i(\Omega)$. Of particular interest is the possible appearance of pseudolocal states in the low-frequency region, which can be erroneously interpreted as splitting of the zero-phonon line by low-symmetry fields. Analogous singularities are possessed by the single-phonon satellite of the $E\leftarrow A$ luminescence.

b) *Infrared absorption.* We consider impurity infrared (IR) absorption by centers of trigonal symmetry, where the Jahn–Teller E oscillations are dipole-active. Aligning the wave vector of the exciting radiation with the C_3 axis, we can eliminate the contribution made to the IR absorption by the fully-symmetrical oscillations. The form function of IR absorption is determined in this case, accurate to factors that depend little on the incident-light frequency Ω, by the expression

$$K_{IR}(\Omega)=(1-e^{-\hbar\Omega/kT})\sum_{\bar\gamma}\sum_{\varkappa\lambda}a_\varkappa(\bar\gamma)a_\lambda(\bar\gamma)\langle E\bar\gamma|K^{(4)}_{\varkappa\lambda}(\Omega)|E\bar\gamma\rangle, \quad (28)$$

where $K^{(4)}_{\varkappa\lambda}(\Omega)$ is the spectral density of the correlator connected with the Green's function $D^{(4)}_{\varkappa\lambda}(\Omega)$:

$$K^{(4)}_{\varkappa\lambda}(\Omega)=\frac{1}{i}[1-e^{-\hbar\Omega/kT}]^{-1}[D^{(4)}_{\varkappa\lambda}(\Omega+i\varepsilon)-D^{(4)}_{\varkappa\lambda}(\Omega-i\varepsilon)]_{\varepsilon=+0}. \quad (29)$$

Substituting (29) in (28) and rearranging the summation with respect to $\varkappa$, λ, and $\bar{\gamma}$, we ultimately obtain

$$K_{IR}(\Omega)=\Omega^2 f_i(\Omega)\left\{\frac{1+(\alpha+\Omega\gamma)\sum_{\varkappa}[a_\varkappa^2/2\pi\omega_\varkappa]}{[1-(\alpha+\Omega\gamma)f_r(\Omega)]^2+f_i^2(\Omega)(\alpha+\Omega\gamma)^2}\right.$$
$$\left.+\frac{1+(\alpha-\Omega\gamma)\sum_{\varkappa}[a_\varkappa^2/2\pi\omega_\varkappa]}{[1-(\alpha-\Omega\gamma)f_r(\Omega)]^2+f_i^2(\Omega)(\alpha-\Omega\gamma)^2}\right\}. \quad (30)$$

As seen from (30), in IR absorption, unlike optical single-phonon absorption, there is no hindrance with respect to the quantum number of the total electron-vibrational angular momentum, and both systems of the roots of (18) appear in the spectrum. In particular, local and pseudolocal oscillations that appear as a result of the Jahn–Teller effect in the frequency regions 4 and 6 (see the figure) and do not manifest themselves in the single-phonon satellite of the $E-A$ luminescence, lead to additional sharp peaks in the IR absorption. Just as in the single-phonon satellite of singlet-doublet optical absorption and luminescence, the dynamic Jahn–Teller effect leads to an appreciable difference in the shape of the IR absorption curve from the density of states of the impurity crystal in the frequency regions where $(\alpha\pm\Omega\gamma)f_r(\Omega)\approx 1$.

As noted in[15], a new type of IR absorption, connected with transitions between degenerate electronic states, is possible in impurity centers with the dynamic Jahn–Teller effect, on the principal term. Unlike in the case considered above, this transition is caused by the dipole-moment operator of the impurity electrons. The single-phonon contribution of the electrons to the IR absorption is given by

$$K_{IR}'(\Omega)=2k_E^2 M\sum_{\bar{\gamma}}\sum_{\varkappa\lambda}\frac{a_\varkappa(\bar{\gamma})a_\lambda(\bar{\gamma})}{\hbar^2\omega_\varkappa\omega_\lambda}\langle E\bar{\gamma}|K_{\varkappa\lambda}^{(2)}(\Omega)|E\bar{\gamma}\rangle, \quad (31)$$

where M' is the oscillator strength of the $E-E$ transition. Substituting (25) in (31), we obtain

$$K_{IR}'(\Omega)=8M'\frac{k_E^2}{\hbar^2}\left\{\frac{f_i(\Omega)}{[1-(\alpha+\Omega\gamma)f_r(\Omega)]^2+f_i^2(\Omega)(\alpha+\Omega\gamma)^2}\right.$$
$$\left.+\frac{f_i(\Omega)}{[1-(\alpha-\Omega\gamma)f_r(\Omega)]^2+f_i^2(\Omega)(\alpha-\Omega\gamma)^2}\right\}. \quad (32)$$

The spectral curves (30) and (32), which describe the contributions made to IR absorption by the dipole moments of the electrons and nuclei respectively, differ little in shape. The intensity of the electronic contribution is determined by the vibronic-coupling constant and by the oscillator strength of the electronic dipole transition between the states Ψ_+ and Ψ_-. This type of IR absorption can predominate in those cases when the effective charge of the nuclei is small.

c) *Raman scattering of light.* The intensity of the impurity nonresonant Raman scattering (RS) into a unit solid angle is determined by the expression[7,13]

$$K_R(\Omega)=\frac{1}{2\pi}[1-e^{-\hbar\Omega/kT}]\int_{-\infty}^{\infty}e^{-i\Omega t}\langle P^+P(t)\rangle dt, \quad (33)$$

where Ω is the difference between the frequencies of the scattered and incident light, P is the operator of the electronic polarizability, which is the scalar contraction of the polarizability tensor P_{ik} with the polarization vectors $\mathbf{e}$ and τ of the incident and scattered light:

$$P=\sum_{ik}e_i\tau_k P_{ik}.$$

To write down the operator P in matrix form, we change over to a basis that makes it possible to represent the scalar P in the form of a contraction of irreducible tensors of the considered point group. Thus, for example, for scattering by an electronic doublet of an impurity center with point symmetry O_h, the operator P can be reduced with the aid of the Wigner–Eckart theorem to the form

$$P=P_A\cdot 1+P_\theta\sigma_x+P_\epsilon\sigma_y. \quad (34)$$

The fully-symmetrical term P_A makes no contribution to the impurity Raman scattering. From (34) and (33) it follows that the spectral curve of the single-phonon impurity Raman scattering is described by the same frequency dependence (32) as the impurity IR absorption on the electronic operator, differing from it in the selection rules and in the polarization dependence.

Simultaneous use of Raman scattering and IR absorption makes it possible to distinguish the local and pseudolocal oscillations, due to the mass defect and to the change of the force constants, from the local and pseudolocal states considered in the present article and connected with the vibronic interaction. Thus, for example, for impurity centers of cubic symmetry, the T_{1u} oscillations are the active ones in IR absorption, and consequently only the usual local and pseudolocal oscillations, connected, say, with the mass defect, appear in the IR absorption spectrum. On the other hand, the Raman-scattering spectral curve duplicates the state density, restructured by the vibronic interaction, of the E_g oscillations that are active in the Jahn–Teller effect, and makes it possible to observe local and pseudolocal Jahn–Teller states. In the case of impurity centers of trigonal symmetry, the indicated separation of the Jahn–Teller local and pseudolocal states can be realized by comparing the spectral IR absorption curves of light linearly polarized in the plane of a triangle and perpendicular to the plane. Experiments on optical absorption and luminescence also make it possible to distinguish ordinary local and pseudolocal oscillations from Jahn–Teller oscillations. Indeed, Jahn–Teller local and pseudolocal states, in contrast to ordinary states, do not appear in the anti-Stokes region of the spectrum. We note, to be sure, that with increasing temperature, when multiphonon processes begin to make a contribution to the region of the anti-Stokes single-phonon absorption, the indicated states can appear there, too. The one-phonon satellite of the impurity luminescence of the $A-E$ transition at $T=0$ will reveal a phonon density of states of the singlet term, where there are no Jahn–Teller local and pseudolocal states.

5. CONCLUSION

Let us summarize the main conclusions arrived at by a study of the dynamic Jahn–Teller effect due to weak vibronic interaction of an orbital doublet with a

phonon continuum.

1. Even a weak electron-phonon coupling can lead to appreciable restructuring of the spectrum of the system, and in particular to the appearance of local and pseudolocal electron-phonon states. These singularities depend on the magnitude of the coupling constant and on the details of the structure of the phonon density of states.

2. Whereas in the cluster model the dynamic Jahn–Teller effect always leads to a splitting of the spectral peaks, in the case of phonon dispersion the appearance of new peaks cannot be of the splitting type. An example may be the appearance of a pseudolocal oscillation in that frequency region where the initial density of states takes the form of a small jump (see the figure, region 6). The new density of states can greatly differ from the initial one even in those cases when the dispersion equation (21) has no root at all and the pseudolocal oscillations do not arise.

3. The specific features of the phonon dispersion make possible the appearance of low-frequency pseudoscalar states, which cannot be explained in any way within the framework of the cluster model.

We note, finally, that the results of the present study enable us to establish the limits of applicability of the cluster model of an impurity center. In those cases when in the initial density of states there are well-defined narrow peaks, on the two slopes of which the inequality (23) is satisfied, the cluster model leads to correct results, namely the splitting of the corresponding peaks. However, even in this case the cluster model describes the aforementioned splitting only qualitatively, since its magnitude can depend in a rather complicated manner on the coupling constant, and the dependence can in particular be non-analytic.

Local and long-lived pseudolocal states due to the dynamic Jahn–Teller effect can be interpreted as bound states of a phonon with an impurity center. Similar states were investigated by Kogan and Suris[16] (local states), by Kochelaev and Aminov[17] (pseudolocal states) for the case of two close singlet electronic terms that are mixed by an electron-phonon interaction. The general theory of these bound states was developed in the papers of Levinson and Rashba,[18] where they are called dielectric modes and hybrid states. Favoring the appearance of local and pseudolocal states is the increase of the coupling constant (see the inequality (23)), whereas all the indicated calculations, including those in the present paper, were made in the weak-coupling approximation and are restricted by the corresponding criteria. There are grounds for assuming, however, that the increase of the coupling constants will not lead to a change in the qualitative conclusions concerning the spectral properties of Jahn–Teller systems. It appears thus that Sloncjewski was the first to show[14] that in the limiting case of strong interaction of an electronic non-Kramers doublet with a phonon continuum, local and pseudolocal states of the electron-phonon type appear and can be interpreted as bound states of the impurity center with the phonons. Thus, the appearance of bound electron-phonon local and pseudolocal states is a distinguishing feature of any Jahn–Teller situation.

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[1)]Allowance for the interaction with the E vibrations of nuclei of other coordination spheres would lead to an algebraic system of equations whose order is proportional to the number of different E-type irreducible representations.

[2)]For the properties of the Hilbert transformation see[11,12].

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