The quadratic multimode Jahn-Teller effect for an orbital doublet

G. I. Bersuker and V. Z. Polinger

Institute of Chemistry, Academy of Science of the Moldavian SSR

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The problem of the Jahn-Teller effect for an impurity in a twofold orbitally degenerated state in the case in which allowance is made for the linear and quadratic interactions of the impurity electrons with the crystal phonons is solved. The electron–phonon interaction leads to the appearance of a many-electron formation of the polaron type localized in the vicinity of the impurity, and either executing a damped motion, or tunneling between the minima of the adiabatic potential. The energy spectrum and the properties of the vibronic states are investigated. As an example, the effect of the relaxation transitions not involving spin flip on the EPR spectrum is considered.

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1. INTRODUCTION

The impurity characteristics of crystals activated by Jahn–Teller (JT) ions include a number of specific properties that manifest themselves in a broad range of experiments.[1] To interpret these experiments, we normally use the so-called cluster approximation, which consists in the replacement of all the vibrational degrees of freedom of the crystal by one or several effective modes.[2] This approximation satisfactorily describes the integral characteristics (for example, the envelope of the impurity absorption or luminescence bands), but cannot serve as a basis for the analysis of the effects connected with the fine structure of the vibronic spectra. In particular, there is lost in the cluster treatment information about the JT-interaction-induced reconstruction of the projected density of states of the crystal.[3] This circumstance makes it necessary for us to take the interaction of the impurity electrons with the entire phonon continuum into consideration in discussing the majority of experimental situations.

The multimode JT problem is usually simplified by taking only the linear vibronic interaction into account. It is precisely within the framework of such a model that the previous attempts to investigate the multimode JT effect for an orbital doublet were made.[3-5] As a result of this approximation the symmetry turns out to be higher than the original symmetry, and this leads to additional degeneracy of certain excited vibronic states. Allowance for the quadratic electron–phonon interaction removes the "accidental" degeneracy, and additional vibronic states appear in the energy spectrum. In those cases in which the experiment under discussion does not allow the observation of, or resolution of the spectral transitions into, the indicated additional levels (because of the selection rules in the case of an optical transition, etc.), or in which the presence of such levels has no effect on the observables (some EPR situations; see below), we can restrict ourselves to the linear vibronic interaction.

It is, however, known from the results of investigations of molecules that a JT system acquires essentially new properties even when, in the presence of a strong linear vibronic coupling of the orbital E-term states to the E-vibrations, allowance is made for the weak quadratic coupling. The quadratic interaction leads to the appearance of three minima in the nuclear potential energy. In the presence of a sufficiently strong vibronic coupling, the system may become localized in one of the minima, and subsequently tunnel through the potential barriers, which leads, in particular, to the tunneling splitting of the vibronic levels. It is natural to expect that such anomalies in the behavior exist also for multimode systems, and, consequently, in the general case we should, take the quadratic vibronic coupling into account when interpreting experiments on impurity-containing crystals, for which the fine vibronic structure of the energy spectrum is of current interest.

In the present paper we solve the problem of the JT effect for an orbital doublet in the case of a strong linear and a relatively weak quadratic interaction between the impurity electrons and crystal phonons with an arbitrary dispersion law. As an example, the results obtained are used to analyze the temperature dependence of the EPR spectra of an impurity ion in a twofold orbitally degenerate state.

2. THE VIBRONIC SPECTRUM OF AN IMPURITY–PHONON SYSTEM

Let us consider an impurity center in a crystal whose symmetry admits of the existence of an electronic orbital doublet. We shall limit ourselves to the discussion of centers of small radius, and assume that the orbital doublet is separated by a substantial energy gap from all the remaining electronic states. Assuming, for simplicity, that the electrons of the impurity are localized inside the first coordination sphere, we can write the Hamiltonian of the impurity–phonon system in the form

$$H=\frac{1}{2}\sum_{\varkappa}(p_{\varkappa}^2+\omega_{\varkappa}^2q_{\varkappa}^2)+V(Q_{1\varepsilon}\sigma_x-Q_{1\theta}\sigma_z)+W[(Q_{1\varepsilon}^2-Q_{1\theta}^2)\sigma_z-2Q_{1\varepsilon}Q_{1\theta}\sigma_x]. \tag{1}$$

Here H is the sum of the Hamiltonian for the crystal vibrations and the operator for the first- and second-order electron–phonon interactions. The summation over $\varkappa$ implies the consideration of all the values of the wave vector and all the branches of the normal-mode vibrations of the lattice with the impurity; the $\omega_{\varkappa}$ are the fre-

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quencies of the normal-mode vibrations of the impurity-containing crystal, the $q_\varkappa$ and $p_\varkappa$ are the normal coordinates and the corresponding conjugate momenta, V and W are the linear- and quadratic-vibronic-coupling constants, the $Q_{1\gamma}=\sum_\varkappa a_\varkappa(1\gamma)q_\varkappa$, $(\gamma=\theta,\varepsilon)$ are the symmetrized displacements of the atoms of the first coordination sphere, the $a_\varkappa(1\gamma)$ are the Van Vleck coefficients, and σ_x and σ_z are the Pauli matrices defined in the basis of the states of the electronic doublet.

Let us go over from the normal coordinates $q_\varkappa$ to the symmetrized displacements $Q_{n\Gamma\gamma}$ of the atoms of all the coordination spheres surrounding the impurity center under consideration:

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

where n numbers the coordination spheres, the Γ are the irreducible representations according to which the displacements of the atoms of the corresponding coordination sphere transform, and the γ's denote the representation-matrix rows. For details about the transformation (2) and the explicit form of the coefficients $a_\varkappa(n\Gamma\gamma)$ in certain particular cases, see Ref. 1. With allowance for (2), we have

$$H=\frac{1}{2}\sum_{n,\gamma}P_{n\gamma}^2+\frac{1}{2}\sum_{n,m,\gamma}\omega_{nm}^2Q_{n\gamma}Q_{m\gamma}+V(Q_{1\varepsilon}\sigma_x-Q_{1\theta}\sigma_z)$$
$$+W[(Q_{1\varepsilon}^2-Q_{1\theta}^2)\sigma_z-2Q_{1\varepsilon}Q_{1\theta}\sigma_x]. \tag{3}$$

Here we have retained only the terms with $\Gamma=E$, which are the ones that are active in the JT effect. Let us note that, since ω^2 is a scalar under the operations of the symmetry group of the crystal, $(\omega^2)_{nn'}^{\gamma\gamma'}=\omega_{nn'}^2\delta_{\gamma\gamma'}$. In (3) and below the indices n and n' number both the various coordination spheres and the various E-type irreducible representations according to which the displacements of the atoms of a given coordination sphere transform.

A specific characteristic of systems with electronic degeneracy is the substantial coupling between the electronic and nuclear motions, a coupling which manifests itself in the fact that the potential-energy operator has the form of a matrix whose eigenvalues (the adiabatic potentials) are, generally speaking, devoid of the physical meaning of a potential energy. As is well known,[6] in the absence of the quadratic terms of the vibronic interaction, the multidimensional surface of the bottom sheet of the electronic doublet's adiabatic potential possesses a one-dimensional equipotential continuum of minima—a circular through whose depth (the JT energy) is proportional to the square of the linear-vibronic-coupling constant. With allowance for the quadratic vibronic interaction, there appear three minima at the bottom of the trough. Thus, in the case of a strong linear vibronic coupling, the bottom sheet of the adiabatic potential in the vicinities of the absolute minima is separated from the upper sheet by an appreciable energy gap. This indicates that, in the lowest vibronic states, the electrons are able to follow the motion of the nuclei, and that the nuclei move in the mean field of the electrons. In other words, in the case of a strong vibronic coupling for the lowest-lying states, the adiabatic potentials have the physical meaning of a nuclear potential energy, i.e., the adiabatic approximation is applicable. The criterion for the applicability of this approximation is the inequality $E_{\mathrm{JT}}\gg\hbar\omega_{\max}$ (where E_{JT} is the Jahn–Teller energy), i.e., the energy gap between the sheets of the adiabatic potential should be much greater than the highest phonon frequency of the crystal.

Let us carry out with the aid of the operator

$$S=\begin{pmatrix}\sin\frac{\Omega}{2} & \cos\frac{\Omega}{2}\\ \cos\frac{\Omega}{2} & -\sin\frac{\Omega}{2}\end{pmatrix};\quad \mathrm{tg}\,\Omega=\frac{V\sin\varphi_1-W\rho_1\sin2\varphi_1}{V\cos\varphi_1+W\rho_1\cos2\varphi_1} \tag{4}$$

a unitary transformation to the adiabatic electronic-state basis in which the electron-potential-energy matrix for an arbitrary nuclear configuration is diagonal. In (4) we use the polar coordinates: $Q_{n\gamma}=\rho_nA_{n\gamma}$ $(\gamma=\theta,\varepsilon)$, $A_{n\theta}=\cos\varphi_n$, $A_{n\varepsilon}=\sin\varphi_n$. Below we shall be interested in only the bottom sheet of the adiabatic potential, since the vibronic structure of the upper sheet's spectra is normally not observed in experiments. Omitting the terms containing nondiagonal electronic matrices, and retaining in the Hamiltonian only the terms pertaining to the bottom sheet of the adiabatic potential, we obtain

$$\tilde{H}=S^{-1}HS\approx-\frac{\hbar^2}{2}\left(\frac{\partial^2}{\partial\rho_1^2}+\frac{1}{\rho_1^2}\frac{\partial}{\partial\rho_1}+\frac{1}{\rho_1^2}\frac{\partial^2}{\partial\varphi_1^2}\right)+\frac{\omega_{11}^2\rho_1^2}{2}$$
$$+\frac{1}{2}\sum_{n\neq1,\gamma}P_{n\gamma}^2+\frac{1}{2}\sum_{n,m\neq1,\gamma}\omega_{nm}^2Q_{n\gamma}Q_{m\gamma}$$
$$+\sum_{n\neq1,\gamma}\omega_{n1}^2\rho_1Q_{n\gamma}A_{n\gamma}+\frac{\hbar^2}{4\rho_1^2}-V\rho_1-W\rho_1^2\cos3\varphi_1\left(1-\frac{3\hbar^2}{2V\rho_1^3}\right). \tag{5}$$

In deriving (5), we restricted ourselves to the case of a not too strong quadratic vibronic coupling: we took into account in the Hamiltonian only the terms linear in W. The criterion for the applicability of this approximation will be indicated below.

The coupling between the first coordination sphere, which interacts directly with the impurity center of small radius, and all the rest of the coordination spheres of the crystal is described by the following term of the Hamiltonian (5):

$$\sum_{n\neq1,\gamma}\omega_{n1}^2\rho_1Q_{n\gamma}A_{n\gamma}=\sum_{n\neq1}\omega_{n1}^2\rho_1\rho_n\cos(\varphi_n-\varphi_1).$$

Owing to the factor $\cos(\varphi_n-\varphi_1)$, the electron cloud and the deformation wave of the first coordination sphere draw the corresponding deformation of the other coordination spheres into their coupled rotary motion. As a result, a deformation wave covering the whole crystal runs around the impurity center. Furthermore, owing to the factor $\rho_1\rho_n$, the radial deformation pulsations in the first sphere can be transferred to the other coordination spheres and propagated through the crystal in the form of waves radiating from the impurity center.

In the absence of the quadratic terms of the vibronic interaction, there arises as a result of the "accidental" raising of the symmetry to the axial-symmetry level an additional integral of the $\partial/\partial\varphi_1$ motion. The motion associated with the variable φ_1 gets separated from the motion along the remaining degrees of freedom, which can be reduced to harmonic vibrations at the bottom of the trough.[3] In other words, the interaction between the first coordination sphere and all the remaining spheres occurs only on account of the ρ pulsations. This can easily be seen if we shift all the φ_n in (5) by the quantity φ_1 with the aid of a unitary transformation with the operator

$$U=\exp\left\{\varphi_1\sum_{n\neq 1}\frac{\partial}{\partial\varphi_n}\right\}=\exp\left\{-i\hbar\varphi_1\sum_{n\neq 1}(Q_{n\theta}P_{n\varepsilon}-Q_{n\varepsilon}P_{n\theta})\right\}. \tag{6}$$

With allowance for the quadratic vibronic coupling, which corrugates the bottom sheet of the adiabatic potential, the symmetry gets lowered to the point-group symmetry of the impurity center in the crystal (e.g., to cubic symmetry), and the φ_1 motion no longer separates. But in this case also it is convenient to transform the Hamiltonian with (6), as a result of which transformation the interaction of the rotation of the deformation wave of the first coordination sphere with the remaining degrees of freedom is described by only the last term in (5).

Let us seek the eigenfunction of the Hamiltonian (5) in the form $\Psi=\chi\rho_1^{-1/2}$. Performing the transformation (6), we obtain for the Hamiltonian whose eigenfunction is χ the expression

$$\begin{aligned}H={}&\frac{1}{2}\sum_n P_{n\theta}^2+\frac{1}{2}\sum_{n,m}\omega_{nm}^2 Q_{n\theta}Q_{m\theta}+\frac{1}{2}\sum_{n\neq 1}P_{n\varepsilon}^2\\&+\frac{1}{2}\sum_{n,m\neq 1}\omega_{nm}^2 Q_{n\varepsilon}Q_{m\varepsilon}+\frac{\hbar^2}{4Q_{1\theta}^2}-VQ_{1\theta}+\frac{i\hbar}{2Q_{1\theta}^2}\left[-\frac{\partial}{\partial\varphi_1}+\sum_{n\neq 1}\frac{\partial}{\partial\varphi_n}\right]^2\\&-W\cos 3\varphi_1\left(Q_{1\theta}^2+\frac{3\hbar^2}{2VQ_{1\theta}}\right).\end{aligned} \tag{7}$$

Here we have set $\rho_1\equiv Q_{1\theta}$.

Although, as has already been noted, the motion along the trough cannot in the general case be separated from the vibrations at the bottom of the minima, we can carry out an adiabatic separation of the motions if the spacing of the energy spectrum of the rotational subsystem is small compared to the spacing for the vibrational subsystem, i.e., if $\hbar\omega_{\text{rot}}\ll\hbar\omega_{\text{vib}}$. In this case the vibrations at the bottom of the minima in the trough and the rotation along the trough are respectively treated as the fast and slow subsystems. We shall assume that the condition for the applicability of the adiabatic separation of the motions in the case under consideration is fulfilled; we shall discuss this approximation at the end of the present section.

Let us consider the spectrum of the fast subsystem, whose Hamiltonian can be obtained from (7) by eliminating the terms with $\partial/\partial\varphi_1$:

$$\begin{aligned}H_{\text{vib}}={}&\frac{1}{2}\sum_n P_{n\theta}^2+\frac{1}{2}\sum_{n,m}\omega_{nm}^2 Q_{n\theta}Q_{m\theta}-VQ_{1\theta}\\&-W\cos 3\varphi_1\left(Q_{1\theta}^2+\frac{3\hbar^2}{2VQ_{1\theta}}\right)+\frac{1}{2}\sum_{n\neq 1}P_{n\varepsilon}^2+\frac{1}{2}\sum_{n,m\neq 1}\omega_{nm}^2 Q_{n\varepsilon}Q_{m\varepsilon}\\&+\frac{1}{2Q_{1\theta}^2}\left[\sum_{n\neq 1}(Q_{n\theta}P_{n\varepsilon}-Q_{n\varepsilon}P_{n\theta})\right]^2.\end{aligned} \tag{8}$$

H_{vib} contains one degree of freedom less than the original Hamiltonian (7) (φ_1 is regarded as a parameter). At not too high temperatures, when only a few of the lowest vibronic states, for which the amplitude of the nuclear displacements is small, are populated, the motion of the nuclei along these degrees of freedom can be reduced to harmonic vibrations about the equilibrium positions.

To determine the equilibrium positions $Q_{n\gamma}^{(0)}$ and $P_{n\gamma}^{(0)}$, let us write down the equations of motion for the operators $Q_{n\gamma}$ and $P_{n\gamma}$, and carry out a quantum-mechanical averaging of both sides of the equations:

$$\overline{\partial H_{\text{vib}}/\partial P_{n\gamma}}=-\bar{\dot{Q}}_{n\gamma}=0,\quad \overline{\partial H_{\text{vib}}/\partial Q_{n\gamma}}=\bar{\dot{P}}_{n\gamma}=0. \tag{9}$$

The solution, $Q_{n\gamma}^{(0)}$ and $P_{n\gamma}^{(0)}$, to this system can be sought in the form of a series in powers of V and $1/V$ (we retain only the leading terms in $1/V$):

$$\begin{aligned}&Q_{n\varepsilon}^{(0)}=P_{n\varepsilon}^{(0)}=P_{n\theta}^{(0)}=0,\\&Q_{n\theta}^{(0)}=V\omega_{n1}^{-2}/(1-2W\cos 3\varphi_1\overline{\omega^{-2}}),\end{aligned} \tag{10}$$

where

$$\omega_{nm}^{-2}=\sum_\varkappa a_\varkappa(n)a_\varkappa(m)\omega_\varkappa^{-2},\quad \overline{\omega^{-2}}=\omega_{11}^{-2}.$$

The equilibrium positions $Q_{n\gamma}^{(0)}$ and $P_{n\gamma}^{(0)}$ can, generally speaking, be determined by the above-described method, i.e., using the system of equations (9), only for the harmonic Hamiltonian. In our case we should have solved the system of equations (9) together with a chain of equations for the Green functions corresponding to the mean values of the various $Q_{n\gamma}$- and $P_{n\gamma}$-operator combinations that arise in (9) (a self-consistent solution). As can be verified, to within the leading terms in $1/V$ this more consistent method leads to the same results.

The result has a clear physical meaning. The adiabatic state of the impurity electrons at the points $Q_{n\theta}^{(0)}$ and $Q_{n\varepsilon}^{(0)}$ has a symmetry lower than the original cubic symmetry of the impurity center. Owing to the electron–phonon interaction, the atoms of the crystal lattice feel this lowering of the symmetry of the electron density, and readjust themselves to it by changing their equilibrium positions. As was to be expected, this change is proportional to the vibronic coupling constant. The static displacements (10) can be interpreted as a wave packet of the normal modes of the parent (without the JT effect) crystal. In other words, the low-symmetry electron distribution in the minima of the adiabatic potential is "dressed in a fur" of parent phonons, i.e., we are dealing with a polaron type of formation.

Making in (8) the substitution $Q_{n\gamma}\to Q_{n\gamma}^{(0)}+Q_{n\gamma}$, where the $Q_{n\gamma}^{(0)}$ are given by the expression (10), we obtain in the harmonic approximation in the $Q_{n\gamma}$ the following form of the Hamiltonian for the vibrations at the bottom of the minimum:

$$\begin{aligned}H_{\text{vib}}={}&\frac{1}{2}\sum_n P_{n\theta}^2+\frac{1}{2}\sum_{n,m}\omega_{nm}^2 Q_{n\theta}Q_{m\theta}-WQ_{1\theta}^2\cos 3\varphi_1+\frac{1}{2}\sum_{n\neq 1}P_{n\varepsilon}^2\\&+\frac{1}{2}\sum_{n,m\neq 1}\omega_{nm}^2 Q_{n\varepsilon}Q_{m\varepsilon}+\frac{1}{2Q_{1\theta}^2}\left(\sum_{n\neq 1}Q_{n\theta}^{(0)}P_{n\varepsilon}\right)^2-E_{\text{JT}},\end{aligned} \tag{11}$$

$$E_{\text{JT}}={}^1/_2V^2\overline{\omega^{-2}}/(1-2W\overline{\omega^{-2}}\cos 3\varphi_1). \tag{12}$$

Thus, in the limit of a strong linear and a relatively weak quadratic coupling, H_{vib} breaks up into a sum of two commuting parts, $H_{\text{vib}}^{(A)}$ and $H_{\text{vib}}^{(B)}$, with respect to the variables with the indices θ and ε respectively. This is explained by the fact that the symmetry of the system in the minima is lowered to D_{4h}. The E representation of the O_h group according to which the JT-active vibrations transform then becomes reducible, and breaks up into the representations A_1 and B_1. The variables with the indices θ and ε are separable because of the fact that we are considering the vibrations at a minimum lying on the θ axis, for which the coordinates $Q_{n\theta}$ and $Q_{n\varepsilon}$ transform according to the representations A_1 and B_1.

The Hamiltonian $H^{(0)}_{\mathrm{vib}}$ coincides with the Hamiltonian for the case in which only the linear vibronic interaction is taken into consideration; the density of states corresponding to it has the form[3]

$$\rho_{B_1}=\operatorname{Im} G_{B_1}(\omega+i\varepsilon)|_{\varepsilon\to 0}=\frac{1}{2}\,\frac{(\overline{\omega^{-2}})^4\omega^2\rho_0(\omega)}{[\operatorname{Re} G_0(\omega)+\overline{\omega^{-2}}]^2+\rho_0^2(\omega)}\,. \qquad (13)$$

Here $\rho_0(\omega)=\operatorname{Im} G_0(\omega)$ is a known projected E-type density of states of the parent (without allowance for the vibronic interaction) crystal, $\operatorname{Re} G_0(\omega)$ is the Hilbert transform of $\rho_0(\omega)$, and $G_0(\omega)$ is the Green function of the parent crystal. As can be seen from (13), the JT effect not only leads to the appearance of localized and pseudolocalized states, which are packets of the "old" parent (without allowance for the JT effect) crystal's phonons localized near the impurity, but radically changes the entire projected density of states of the crystal as well.

The appearance of localized and pseudolocalized JT states in the density of states corresponding to the vibrations in the A_1 subspace is also possible as a result of the quadratic vibronic interaction. Owing to the localized nature of the perturbation, the Dyson equation for the equal-time Green functions can be solved exactly, and the dispersion equation determining the positions of the localized and pseudolocalized states has the form

$$2W\cos 3\varphi_1 \operatorname{Re} G_0(\omega)+1=0. \qquad (14)$$

It is convenient to solve Eq. (14) graphically (see Ref. 3). In the case of a sufficiently weak quadratic vibronic coupling, (14) may not possess any real roots. Let us, for comparison, note that the behavior of the anomalies in the density of states of the B_1 vibrations does not depend on the vibronic-interaction constant at all, and is completely determined by the dynamical characteristics of the crystal itself.

Returning to the consideration of the slow subsystem corresponding to the rotation of the entire system as a whole along the trough, let us average the total Hamiltonian (7) over the ground state of the fast subsystem. Retaining only the leading—in order of smallness of $1/V$ and W—terms, we obtain

$$H_{\mathrm{rot}}=\alpha\partial^2/\partial\varphi_1^2+\beta\cos 3\varphi_1-E_{JT}, \qquad (15)$$

where

$$\alpha=-\hbar^2/2V^2(\overline{\omega^{-2}})^2, \quad \beta=-V^2W(\overline{\omega^{-2}})^2.$$

As was to be expected, the Hamiltonian (15), which determines the vibronic spectrum of the system, coincides in form with the corresponding Hamiltonian for the molecular E–e-type JT system considered in Ref. 7. But in contrast to the molecular case, in (15) the parameters α and β are determined by the phonon dispersion law for the crystal lattice $[\overline{\omega^{-2}}\equiv-\operatorname{Re} G_0(0)]$.

The solution to Eq. (15) can be obtained in the analytical form in the limiting case of small β by treating the term $W\rho_1\cos 3\varphi_1$ as a perturbation, and choosing as the wave functions of the zeroth approximation the solution to the linear $(E\otimes e)$ problem. The selection rules are such that the perturbation splits up those of the twofold degenerate states of the linear problem for which the quantum number that numbers them is $|m|=\frac{3}{2}(2n+1)$, where $m=\pm\frac{1}{2}, \pm\frac{3}{2}, \ldots, n=0,1,2,\ldots$. In particular, the excited level (with $m=\pm\frac{3}{2}$) closest to the ground level is split. The ground state (with $m=\pm\frac{1}{2}$) remains twofold degenerate. Corresponding to the obtained vibronic states are the slowed-down rotations of the above-discussed polaron-type formation, during which the latter undergo multiple above-the-barrier reflections. For large β, the minima of the adiabatic potential are separated from each other by barriers through which the polaron formation tunnels. In this case the polaron formation is localized for a significant fraction of the time near one of the fourfold axes of the cubic system, "occasionally" hopping from axis to axis. The solutions to (15) are investigated in detail in the quasiclassical approximation in Ref. 8, where among the expressions obtained are expressions for the magnitude of the tunneling splitting 3Γ. The vibronic energy levels for arbitrary β values are obtained numerically as functions of the parameter β/α in Ref. 7. The numerical values of the vibronic-reduction factors for the matrix elements are given in Ref. 1.

Let us discuss the criteria for the applicability of the above-obtained results. The energy spectrum for the problem under consideration is a superposition of the continuous spectrum corresponding to the fast subsystem (the vibrations at the bottom of the minima) and the discrete spectrum (in resonance with the continuous spectrum) of the slow subsystem (the damped rotation along the trough or the tunneling between the minima). Because of the strong linear vibronic coupling, the positions of the rotational levels ω_{rot} of the slow subsystem are shifted into the region of low frequencies, at which the density of states $\rho(\omega)$ of the vibrational (fast) subsystem is low [for $\omega_{\mathrm{rot}}\leq 10$–$30$ cm^{-1}, $\rho(\omega)\to 0$ as $\omega\to 0$]. Because of this, the nonadiabatic corrections due to the states of the continuous spectrum, for which the condition $(\hbar\omega_{\mathrm{rot}}\ll\hbar\omega_{\mathrm{vib}})$ for the adiabatic separation of the motions is not fulfilled, are quite small. The adiabatic motion-separation approximation also imposes a condition on the strength of the second-order vibronic interaction: $W\overline{\omega^{-2}}\ll 1$. This same condition was used in the derivation of the Hamiltonian (5).

The separation of the sheets of the adiabatic potential is possible if, with allowance for (12),

$$V^2\overline{\omega^{-2}}/(1-2W\overline{\omega^{-2}})\gg\hbar\omega_{max}.$$

In the weak-quadratic-coupling approximation $W\overline{\omega^{-2}}\ll 1$, we obtain the following limitation on the magnitude of the linear-vibronic-coupling constant: $V^2\gg\hbar\omega_{\mathrm{max}}/\overline{\omega^{-2}}$, or, in the Debye approximation for the crystal vibrations, $V^2\gg\hbar\omega^3_{\mathrm{max}}$. Large V values also ensure the applicability of the harmonic approximation.

3. THE ORIGIN OF THE ISOTROPIC EPR SPECTRUM

The effects connected with the multimode character of a JT system can manifest themselves in the infrared and optical spectra, in the EPR and Raman-scattering spectra, etc. Here we shall consider one of the questions that generally cannot be consistently considered within the framework of the molecular model: the origin of the isotropic line in the EPR spectra of paramagnetic impurity centers with a ground-state electronic doublet.

At low temperatures the EPR spectrum of an orbital doublet possesses a characteristic cubic angular dependence. As the temperature rises, there appears against the background of the cubic spectrum [e.g., at temperatures ranging from several degrees K for Ag^{2+}:MgO to several tens of degrees K for Ag^{2+}:CrO (Ref. 9)] an isotropic line that increases in intensity with the temperature. There are two possible mechanisms for the appearance of the isotropic line. One of them is connected with the increase of the Boltzman population of the singlet vibronic state closest to the ground-state vibronic doublet, and providing the EPR spectrum. The other mechanism stems from the effect of motion-induced thermal narrowing of the inhomogeneously broadened EPR line (motional narrowing).[10] In the present paper we shall consider the effectiveness of just this second mechanism.

The experiments can be discussed in the basis of the states of the ground and first-excited vibronic terms. The paramagnetic center in the sample and its immediate surroundings form a cluster that is distorted as a result of the JT effect. The random local deformations of the crystal lattice additionally distort the cluster, i.e., split the twofold degenerate vibronic ground level, and mixes its states with the excited vibronic singlet term. If the magnitude of the local strain δ ($\delta \sim 1-5$ cm^{-1}) is much smaller than the energy gap, 3Γ, between the ground and first excited vibronic states, i.e., if $\delta/3\Gamma \ll 1$, then the admixture is negligible. This means that the system is to a large extent distributed among the three minima of the adiabatic potential, and, from the point of view of the EPR spectra, the situation corresponds to the case of the multimode dynamical JT effect considered in detail in Ref. 11. For $\delta/3\Gamma \gg 1$, three new states $|i\rangle$ $(i=1,2,3)$ are formed as a result of the mixing of the excited singlet term with the split doublet. It can be shown that each of these three lowest states is localized in "its own" i-th minimum.[10] Each of the distorted configurations of the cluster, i.e., each of the minima, has its own g-factor value and, consequently, its own EPR-signal frequency. As the temperature increases, the vibrations of the surrounding crystal lattice intensify, and, under the influence of these vibrations, the cluster begins to go over from one distorted configuration into another, i.e., from a minimum to a minimum. If the probability per unit time, R, for transition between any pair of minima significantly exceeds the difference between the EPR-signal frequencies corresponding to these distorted configurations, i.e., if $R \gg |\omega_i - \omega_k|$, then instead of two signals at the frequencies ω_i and ω_k we shall observe a single isotropic signal at an intermediate frequency.

The temperature dependence of the shape of the spectrum for the three-level system actually in question here can be analyzed in much the same way as is done in Ref. 11 on the basis of the Bloch–Redfield theory. We omit this analysis here, since allowance for the phonon dispersion does not give rise to any significant features in the line shape of the low-temperature EPR signal (the shape of the spectrum is quite fully investigated in the cluster approximation in Ref. 12). On the other hand, the results for the relaxation processes of motional narrowing of interest to us can be obtained by a simpler method without a detailed analysis of the line shape.

A paramagnetic center in a crystal can be treated as a dynamical subsystem in a phonon thermostat. The dynamical subsystem is described by the Hamiltonian $H_{\rm rot}+H_{\rm def}+H_{\rm Z}$, where $H_{\rm rot}$ is the Hamiltonian, (15), for the damped rotations, $H_{\rm def}$ is the operator for the interaction of the impurity electrons with the random-lattice-deformation field,[10] and $H_{\rm Z}$ is the Zeeman spin Hamiltonian of the orbital doublet.[13] The vibrational subsystem, described by the Hamiltonian (11), acts as a dissipative subsystem. As follows from (7), the operator for the interaction between the dynamical and dissipative subsystems has, up to the leading order in the small parameter $1/V$, the form

$$V=i\hbar(\partial/\partial\varphi_1)(Q_{1\theta}^{(0)})^{-2}\sum_{n\neq 1} Q_{n\theta}^{(0)} P_{n\varepsilon}. \tag{16}$$

The random strains lock the dynamical subsystem in the i-th minimum, thereby producing the state $|i\rangle$. The single-phonon relaxation processes are accompanied by nonradiative transitions, induced by the operator (16), between pairs of states, $|i\rangle$ and $|k\rangle$, of the dynamical subsystem in the minima. The transition probability is given by the expression

$$\begin{aligned} R_{ik}&=\frac{2\pi\hbar^2M^2}{V^2\overline{(\omega^{-2})}^4}\rho_{B_1}(\omega_{ik})\,[n(\omega_{ik})+1],\\ R_{ki}&=\frac{2\pi\hbar^2M^2}{V^2\overline{(\omega^{-2})}^4}\rho_{B_1}(\omega_{ik})\,n(\omega_{ik}), \end{aligned} \tag{17}$$

where $M=\langle i|\partial/\partial\varphi_1|k\rangle$ is the vibronic-reduction factor for the angular-momentum operator,[1] $n(\omega)=[\exp(\hbar\omega/kT)-1]^{-1}$ are the phonon occupation numbers, and $\rho_{B_1}(\omega)$ is the crystal's density of states (13) renormalized by the JT interaction R_{ik} corresponds to a transition from a shallower minimum into a deeper one. As can be seen from (16), only the B_1 crystal-lattice vibrations unperturbed by the quadratic vibronic interaction are active in the transitions occurring without spin flip between the Zeeman sublevels, which are the transitions of interest to us here. This corroborates the assumption made in Ref. 11 that the weak quadratic interaction has no effect on the spectral density of that part of the dissipative subsystem which participates in the relaxation processes not involving spin flip.

The transition probability (17) coincides up to the factor[1] $M<1$ with the transition probability when allowance is made for only the linear terms of the vibronic interaction, and, thus, the estimate given in Ref. 11 for the magnitude of the quantum-mechanical transition probability $P=R/n(\omega)$ for the case of the Debye dispersion law for the lattice vibrations of the parent crystal, namely, $P \lesssim M^2 \cdot 10^{22} v^{-3}$ cm^3/sec^4, where v is the lowest of the longitudinal and transverse velocities of sound in the sample, remains valid. The characteristic values for the difference between the EPR-signal frequencies in the various distorted configurations $|\omega_i - \omega_k| \sim 0.1$ cm^{-1}. For the majority of materials $v \gtrsim 10^5$ cm/sec, which yields $P \sim 10^7$ sec^{-1}, or, in energy units, $\Delta E \sim 10^{-4}$ cm^{-1}. Thus, the inequality $R \gg |\omega_i - \omega_k|$, whose fulfillment is necessary for the motional-narrowing mechanism to be effective, is violated at temperatures characteristic of the experimental observation of the isotropic line.[9]

In (17) we have taken into account only the single-phonon processes; the probability for the n-phonon process contains the coefficient V^{-2n}, and therefore their contribution to the case, under consideration here, of a strong linear vibronic coupling is small at low temperatures.

It follows from the result obtained that the direct relaxation processes, which are present at relatively low temperatures, as a rule do not in situations with the strong JT effect lead to the narrowing of the EPR line. In other words, if the isotropic spectrum appears at low temperatures, then we can unequivocally conclude that $\delta < 3\Gamma$, and that the cause of the appearance of the isotropic line is the population of the vibronic singlet. The isotropic spectrum that arises at high temperatures allows us to conclude that $\delta \gtrsim 3\Gamma$, and that the isotropic line is due to the many-phonon relaxation.

CONCLUSION

The considered system, which comprises of impurity electrons and phonons interacting with these electrons, is, as has already been noted, a formation of the polaron type. The latter differs from the normal polaron in two respects. First, all the electrons participates in the JT effect, and, therefore, the formation in question is a many-electron one. Secondly, the vibronic coupling, which leads to the appearance of this formation, is due not only to the electrostatic but also to the exchange interaction, and is important not just in ionic crystals. In the particular case of the JT effect for a single impurity electron in an ionic crystal, the formation under discussion reduces to a normal polaron localized in the vicinity of the impurity.

The surface of the adiabatic potential is a deep trough with three minima located at its bottom. The polaron-type formation executes a damped rotary motion or tunnels (depending on the height of the potential barrier) along the trough. The B_1- and A_1-type vibrations at the bottom of the minima are internal degrees of freedom of the polaron formation. These vibrations lead to new projected density of states of the crystal, renormalized by the linear (B_1) and quadratic (A_1) vibronic interactions. The motion of the polaron formation along the trough shapes the discrete rotational vibronic spectrum.

A strong linear electron–phonon coupling changes substantially the projected density of states of the crystal: the new density is inversely proportional to the original density in the frequency regions where the latter has an appreciable value, i.e., where $\rho_0(\omega) \gg (\mathrm{Re}\, G_0 + \omega^{-2})$ [see (13)]. Pseudolocalized and localized states can, however, arise in a region where the original density of states is low or equal to zero. Thus, the considerable reconstruction of the spectrum resulting from the introduction of the JT impurity into the crystal matrix will be observed in experiments in which the projected density of states manifests itself (infrared absorption, Raman scattering, etc.). In this case the shape of the single-phonon satellite does not allow us to draw any conclusion about the form of the original density of vibrational states of the lattice. In those experimental situations in which the crystal provides a considerable background, or in which the total density of states is measured (e.g., in neutron scattering), the vibronic interaction may lead to the appearance in the vibrational spectrum of peaks whose intensity has the concentration smallness. Let us also note that, as can be shown, ρ_{B_1} is not sensitive to the defect of the lattice's force constants connected with the introduction of the impurity.[1)] These constants change the curvature of the minimum in the radial direction, while ρ_{B_1} corresponds to the vibrations orthogonal to the radius.

We have estimated the probability for the relaxation transitions occurring without spin flip under the assumption that the vibronic-interaction-redefined density of states of the crystal does not contain a pseudolocalized state in the region of low frequencies ω_{ik} ($\hbar\omega_{ik} < 10$ cm^{-1}). In the above-considered case of an extremely strong linear vibronic coupling, such a state does not arise at the low frequencies of interest to us. But the appearance of a pseudolocalized state in the region of frequencies, ω_{ik}, essential to the relaxation processes is possible in real systems with a sufficiently strong JT interaction. The appearance of such a state gives rise to the Orbach relaxation. This circumstance can radically change the temperature dependence of the shape of the spectrum and the probability for the relaxation processes.

[1)] This circumstance was pointed out to the authors by G. S. Zavt.

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