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Internal hindered rotations in polyatomic systems with the Jahn–Teller effect for a ${}^2T \otimes (\epsilon + \tau_2)$ term in the limiting case of strong vibronic coupling

V Z Polinger[†] and S I Boldyrev[‡]

[†] Institute of Chemistry, Academy of Sciences of the Moldavian SSR, Grosul Str. 3, 277028 Kishinev, USSR

[‡] Kishinev State University, Sadovaja Str. 60, 277014 Kishinev, USSR

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Abstract. Point defects in crystals with cubic local symmetry in a Jahn–Teller electronic ${}^{2S+1}T$ term with significant spin–orbit coupling are shown to have additional intrinsic spherical symmetry and additional integrals of motion if the conditions of the d-mode model (equal frequencies and equal vibronic coupling to E and T_2 vibrations) are satisfied. As in the case without spin–orbit interaction considered by O'Brien for strong vibronic coupling, taking into consideration the isotropic spin–orbit coupling in the Jahn–Teller multimode ${}^{2S+1}T \otimes (\epsilon + \tau_2)$ problem, the lowest sheet of the adiabatic potential energy surface is shown to possess a two-dimensional trough. This determines the characteristic rotational energy spectrum of the system. If the conditions of the d-mode model are violated the trough becomes warped and rotations become hindered, and this is represented by appropriate changes in the rotational energy spectrum.

1. Introduction

The diverse properties of polyatomic systems in degenerate or pseudo-degenerate electronic states are determined by the Jahn–Teller effect (e.g., Bersuker 1984a). Point defects in high-symmetry crystals are the most characteristic examples of such systems. This stimulates increasing interest in the basic theory of the Jahn–Teller effect and for the interpretation of numerous experimental data accumulated in the physics of point defects in crystals. The current situation in the theory of the Jahn–Teller effect is discussed in several monographs and review articles (see, e.g., Perlin and Wagner 1984, Bersuker and Polinger 1989). An exhaustive bibliography of the papers published up to 1979 has been compiled by Bersuker (1984b).

The Schrödinger equation containing the vibronic matrix Hamiltonian describing a Jahn–Teller system can be reduced to a complicated set of differential equations whose analytical solution is possible in the limiting cases of weak and strong vibronic coupling. The analysis of these solutions shows that they describe hindered rotations of the coupled electron–phonon formation of the polaron type around the point defect. In the case of strong vibronic coupling, if the lowest sheet of the adiabatic potential energy surface (APES) possesses several sufficiently deep minima, the motion of the system is reduced to the tunnelling of the Jahn–Teller polaron between several equivalent positions

through the potential barriers separating the minima from one another. However, the theory considers mainly the simplest cases of the so called ideal vibronic systems with the orbital doublet (E term) or triplet (T term) electronic states coupled to one set of two-fold or three-fold degenerate vibrations without taking into account the effects of phonon dispersion and the spin-orbit interaction. If the latter is sufficiently weak, it can be considered as a perturbation in terms of the vibronic reduction factors (Ham 1965; see also Bersuker 1984a, Bersuker and Polinger 1989). This is the case, for instance, in cubic systems with the two-fold degenerate E term because the first-order effects of the spin-orbit interaction are absent due to the appropriate selection rules for the matrix elements. Unlike the case of systems with the T term, the effects of the first-order spin-orbit interaction are non-zero and may be significant compared with the effects of the vibronic interaction. This causes additional difficulties when considering the Jahn-Teller effect for the T-term systems because both the spin-orbit interaction and the vibronic coupling to the E and T_2 vibrational modes should be considered together, and there is no hierarchy of perturbations.

Basic ideas about the vibronic properties of the ideal $T \otimes (\epsilon + \tau_2)$ system without any spin-orbit interaction have been formulated by O'Brien (1969, 1971). It was shown that if the Jahn-Teller stabilisation energies $E_{JT}(E)$ and $E_{JT}(T)$ are equal and if the frequencies of the E and T_2 vibrations are also equal, $\omega_E = \omega_T$ (the so called d-mode model), then the lowest sheet of the APES possesses a two-dimensional continuum of minima (trough) and the energy spectrum corresponds to free rotations of the representative point at the bottom of the trough. If $E_{JT}(E) \neq E_{JT}(T)$ and/or $\omega_E \neq \omega_T$, then the rotation becomes hindered. These conclusions were confirmed by numerical calculations (O'Brien 1971, 1985), but they are not adequate for a number of experimental data because the spin-orbit interaction has been neglected in some cases where it is significant.

The aim of this paper is to solve the $^{2S+1}T \otimes (\epsilon + \tau_2)$ problem by taking into consideration a significant isotropic spin-orbit interaction $\lambda \mathbf{L} \cdot \mathbf{S}$. In this sense the present paper considers a wider class of problems, including the spin-orbit coupling for a T-term Jahn-Teller effect. The problems seem to be more realistic than the case considered by O'Brien (1969, 1971). Although initially the problem under consideration looks much more complicated than that in O'Brien's case, we have succeeded in showing that it can be understood in the same terms as those developed by O'Brien (1969).

The effects of the multimode vibronic coupling will also be considered and will be shown to produce qualitatively the same energy spectrum of the hindered rotations as in the case of an ideal vibronic system.

2. Dynamic symmetry of the multimode $^{2S+1}T \otimes (\epsilon + \tau_2)$ system in the d-mode model

Consider a point defect in a cubic crystal in a triplet electronic state ^{2S+1}T . The Hamiltonian of the electronic triplet can be written

$$\hat{H} = \hat{H}_L + \hat{H}_S + \hat{H}_{SO} + \hat{H}_{\text{vibr}} + \hat{H}_{JT}. \quad (1)$$

Here $\hat{H}_L = E_T^{(0)} \hat{C}_A$ is the electronic Hamiltonian of the degenerate T term with energy $E_T^{(0)}$, \hat{C}_A being a unit 3×3 matrix acting in the manifold of degenerate electronic states; $\hat{H}_S = \text{constant} \times \hat{S}^2$ is the Hamiltonian of the free spin; $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$, where \hat{S}_x , \hat{S}_y and \hat{S}_z are the $(2S + 1) \times (2S + 1)$ spin matrices. Both \hat{H}_L and \hat{H}_S are usually excluded

from consideration by an appropriate change of the energy reference. The third term in equation (1), $\hat{H}_{\text{SO}} = \lambda \hat{L} \cdot \hat{S}$, is the Hamiltonian of the isotropic spin-orbit interaction, where \hat{L}_x , \hat{L}_y and \hat{L}_z are the 3×3 matrices of the orbital moment acting in the electronic part of the system:

$$\hat{L}_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix} \quad \hat{L}_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix} \quad \hat{L}_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (2)$$

and λ is the spin-orbit coupling constant. The fourth term in equation (1), \hat{H}_{vibr} , is the Hamiltonian of the lattice vibrations which can be expressed in terms of the real normal coordinates:

$$\hat{H}_{\text{vibr}} = \frac{1}{2} \sum_{\kappa} (p_{\kappa}^2 + \omega_{\kappa}^2 q_{\kappa}^2). \quad (3)$$

Here the sum over κ includes all the phonon wavenumbers and phonon branches. The last term in equation (1) is the Hamiltonian of the linear Jahn-Teller coupling of the localised $2S+1T$ electronic states to the symmetrised nuclear displacements $Q_{\Gamma\gamma}$ of the nearest-neighbour atoms (Ham 1965)

$$\hat{H}_{\text{JT}} = V_{\text{E}}(Q_{\theta} \hat{C}_{\theta} + Q_{\epsilon} \hat{C}_{\epsilon}) + V_{\text{T}}(Q_{\xi} \hat{C}_{\xi} + Q_{\eta} \hat{C}_{\eta} + Q_{\zeta} \hat{C}_{\zeta}) \quad (4)$$

where V_{E} and V_{T} are the constants of the linear vibronic coupling to the E and T_2 displacements respectively and $\hat{C}_{\Gamma\gamma}$ are orbital operators, which can be expressed in terms of the orbital moment $L = 1$ matrices (Stevens 1969):

$$\begin{aligned} \hat{C}_{\theta} &= \frac{1}{2}(3\hat{L}_z^2 - 2) & \hat{C}_{\epsilon} &= (\sqrt{3}/2)(\hat{L}_x^2 - \hat{L}_y^2) \\ \hat{C}_{\xi} &= \{\hat{L}_y, \hat{L}_z\} & \hat{C}_{\eta} &= \{\hat{L}_x, \hat{L}_z\} & \hat{C}_{\zeta} &= \{\hat{L}_x, \hat{L}_y\}. \end{aligned} \quad (5)$$

Here $\{\hat{L}_i, \hat{L}_j\} = \hat{L}_i \hat{L}_j + \hat{L}_j \hat{L}_i$, $i \neq j$. The symmetrised displacements $Q_{\Gamma\gamma}$ are related to the normal coordinates q_{κ} by the orthogonal transformation

$$Q_{\Gamma\gamma} = \sum_{\kappa} a_{\kappa}(\Gamma\gamma) q_{\kappa} \quad (6)$$

where $a_{\kappa}(\Gamma\gamma)$ are the so called Van Vleck coefficients (Halperin and Englman 1975, Stegles 1977, Stevens 1969).

The Hamiltonian (1) can be transformed into another form (Toyozaawa and Inoue 1965, Bersuker and Polinger 1989):

$$\hat{H} = \hat{H}_{\text{L}} + \hat{H}_{\text{S}} + \hat{H}_{\text{SO}} + \frac{1}{2} \sum_n \sum_{\Gamma\gamma} (P_{n\Gamma\gamma}^2 + \omega_n^2 Q_{n\Gamma\gamma}^2) + \sum_n \sum_{\Gamma\gamma} V_{n\Gamma} Q_{n\Gamma\gamma} \hat{C}_{\Gamma\gamma} \quad (7)$$

where $\Gamma = \text{E}, T_2$, $\gamma \in \Gamma$ and

$$V_{n\Gamma} = V_{\Gamma} \left(\sum_{\kappa} a_{\kappa}^2(\Gamma\gamma) \delta(\omega_{\kappa} - \omega_n) \right)^{1/2}.$$

Note that $\omega_{n\text{E}} = \omega_{nT} = \omega_n$ and the E and T_2 modes can be considered together as a five-dimensional oscillator of frequency ω_n . The vibronic coupling to the E and T_2 modes can be treated as a low-symmetry (cubic) case of an isotropic interaction of electronic triplets of an atomic-type P term with five-fold degenerate vibrations possessing the transformation properties of hydrogen d functions. It follows that this $\text{P} \otimes \text{d}$ problem is a

particular high-symmetry case of the cubic symmetry $T \otimes (\varepsilon + \tau_2)$ problem in which the cubic splitting of the d mode is negligible. This is the so called d-mode model (O'Brien 1969).

It will be shown that by taking into consideration the isotropic spin-orbit interaction, the spin-orbit-vibrational moment $\mathcal{F} = S + L + \mathcal{L}$ is preserved and the Hamiltonian of the coupled $2S+1P \otimes d$ system possesses spherical symmetry.

The problem can be investigated by the method of infinitesimal operators (Bersuker and Polinger 1982). In the absence of spin-orbit and vibronic coupling, the symmetry of the Hamiltonian (7) is described by a continuous group of unitary transformations in the combined spin-orbit-vibrational space. It can be expressed as a direct product

$$G = U(3) \times U(2S + 1) \times \prod_n U([\Gamma_n])$$

where $[\Gamma_n]$ is the dimension of the representation Γ_n , where n labels the irreducible representations of the same type Γ . The unitary group $U(3)$ corresponds to the symmetry of the system with respect to the unitary transformations in the space of the three degenerate states of the electronic T term. The unitary group $U(2S + 1)$ describes the symmetry of the free spin S , and contains unitary transformation in the space of the $2S + 1$ spin states. The unitary groups $U([\Gamma_n])$ correspond to the unitary symmetry of the five-fold degenerate oscillators (all the $[\Gamma_n] = 5$). Generators of the group $U(3)$ are nine 3×3 matrices of the following form:

$$I_{pq} = |p\rangle\langle q| \quad p, q = x, y, z$$

where

$$|x\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad |y\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad |z\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

are the basis states of the electronic P term.

Analogously, the unitary group $U(2S + 1)$ has $(2S + 1)^2$ generators of the form $|\sigma\rangle\langle\mu|$, where $|\sigma\rangle$ and $|\mu\rangle$ are spinors.

The unitary symmetry of the vibrational system is more conveniently described in terms of the second quantisation creation and annihilation operators, $b_{n\Gamma\gamma}^+$ and $b_{n\Gamma\gamma}$. The vibrational Hamiltonian H_{vibr} commutes with the operators $b_{n\Gamma\gamma}^+ b_{n\Gamma\gamma}$, and therefore the latter can be used as generators of the symmetry group of H_{vibr} . Groups $U(2S + 1)$, $U(3)$ and $U(5)$ contain as a subgroup the group of rotations in three-dimensional space, $R(3)$. With respect to these rotations the above-mentioned generators of the unitary groups are tensors of the second rank which can be combined into some linear combinations that transform as irreducible representations of the group $R(3)$. The appropriate components of the irreducible tensors are determined by the following expressions:

$$\{\psi^{(l)} \times \psi^{(l)}\}_M^L = \sum_{p,q} I_{pq}(lp|q|LM), \quad (8)$$

where $p, q = -l, -l + 1, \dots, l$; $L = 0, 1, \dots, 2l$; and $(lp|q|LM)$ are the Clebsch-Gordan coefficients of the $R(3)$ group. An operator of the group

$$G = U(3) \times U(2S + 1) \times \prod_n U([\Gamma_n]),$$

depending on $9 + (2S + 1)^2 + 25N$ free parameters $\alpha_j, \beta_j^{(n)}, \gamma_j$, can be written

$$G(\alpha, \beta, \gamma) = \exp \left(i \sum_{j=0}^8 \alpha_j \hat{C}_j + i \sum_n \sum_{j=0}^4 \beta_j^{(n)} \hat{L}_j^{(n)} + i \sum_{j=0}^{(2S+1)^2-1} \gamma_j \hat{S}_j \right) \quad (9)$$

where $\hat{C}_j, \hat{L}_j^{(n)}$ and \hat{S}_j are the generators of the groups $U(3)$, $U(5)$ and $U(2S + 1)$

respectively obtained by (8). Among the parameters α_j , $\beta_j^{(n)}$ and γ_j there are three, namely α_0 , $\beta_0^{(n)}$ and γ_0 , that correspond to trivial operations of multiplication of the wavefunction by a phase factor and therefore the appropriate generators can be excluded from consideration by taking $\alpha_0 = \beta_0^{(n)} = \gamma_0 = 0$, thus reducing the symmetry to $SU(3) \times SU(2S+1) \times \Pi_n SU([\Gamma_n])$. The vibronic interaction lowers the symmetry of the system, and some of the parameters α_j , $\beta_j^{(n)}$ and γ_j ($j \neq 0$) become interrelated. These interrelations can be obtained from the condition of commutativity of the group operators (9) with the Hamiltonian (1). For small values of α_j , $\beta_j^{(n)}$ and γ_j , the operator G from (9) can be expanded with respect to α_j , $\beta_j^{(n)}$ and γ_j . Retaining the linear terms and taking into consideration the commutativity of G with the Hamiltonian (7) at $\lambda = 0$, $V_E = 0$ and $V_T = 0$, we obtain the following equation:

$$\left[\left(\sum_{j=1}^8 \alpha_j \hat{C}_j + \sum_n \sum_{j=1}^{24} \beta_j^{(n)} \hat{L}_j^{(n)} + \sum_{j=1}^{(2S+1)^2-1} \gamma_j \hat{S}_j \right) \left(\lambda \mathbf{L} \cdot \mathbf{S} + \sum_n \sum_{\Gamma_Y} V_{n\Gamma} Q_{\Gamma_Y} \hat{C}_{\Gamma_Y} \right) \right] = 0.$$

Taking into account the independence of the different generators \hat{C}_j , $\hat{L}_j^{(n)}$ and \hat{S}_j , a system of equations with respect to α_j , $\beta_j^{(n)}$ and γ_j can be obtained which has a non-trivial solution if $4V_{nT}^2 = 3V_{nE}^2$ for every n . All the parameters α_j , $\beta_j^{(n)}$ and γ_j can be expressed in terms of α_x , α_y and α_z , and the group operator of (9) takes the form

$$G = \exp(i\alpha \mathcal{F}) \quad (10)$$

where

$$\mathcal{F} = \mathbf{S} + \mathbf{L} + \mathcal{L}$$

$$\mathcal{L}_x = \sum_n [b_{n\xi}^+ (\sqrt{3}b_{n\theta} + b_{n\epsilon}) - b_{n\xi} (\sqrt{3}b_{n\theta}^+ + b_{n\epsilon}^+) + b_{n\xi}^+ b_{n\eta} - b_{n\eta}^+ b_{n\xi}]$$

$$\mathcal{L}_y = \sum_n [b_{n\eta}^+ (-\sqrt{3}b_{n\theta} + b_{n\epsilon}) - b_{n\eta} (-\sqrt{3}b_{n\theta}^+ + b_{n\epsilon}^+) + b_{n\xi}^+ b_{n\zeta} - b_{n\zeta}^+ b_{n\xi}] \quad (11)$$

$$\mathcal{L}_z = \sum_n [2(b_{n\epsilon}^+ b_{n\zeta} - b_{n\zeta}^+ b_{n\epsilon}) + b_{n\eta}^+ b_{n\xi} - b_{n\xi}^+ b_{n\eta}].$$

It follows that by taking into consideration the linear vibronic interaction and isotropic spin-orbit coupling, the symmetry of the system is reduced from the group $SU(3) \times SU(2S+1) \times \Pi_n SU([\Gamma_n])$ to the three-parameters group $R(3)$. The operators \mathcal{F}_x , \mathcal{F}_y and \mathcal{F}_z from (11) are constants of motion and represent the components of the resulting moment of rotations in the united spin-orbit-vibrational space.

In the limit of strong vibronic coupling, the lowest sheet of the APES at the minimum points may in several cases be separated from the higher sheets by a large energy gap. In this case the applicability criteria of the adiabatic approximation are fulfilled and the lowest sheet acquires the physical meaning of the potential energy of the nuclei. Calculating the diagonal matrix element of \mathcal{F} with the adiabatic electronic wavefunction of the lowest sheet, and taking into account that for the ground sheet the averages of \mathbf{L} and \mathbf{S} are equal to zero, one obtains a constant of motion which takes the form of \mathcal{L} . From the three constants of motion, \mathcal{L}_x , \mathcal{L}_y and \mathcal{L}_z , only two combinations \mathcal{L}^2 and \mathcal{L}_z commute. This means that in the limiting case of strong vibronic coupling, when the adiabatic separation of the nuclear motion from the electronic motion is valid, the generalised coordinates conjugated to the vibrational momenta \mathcal{L}^2 and \mathcal{L}_z are cyclic variables. Hence the lowest sheet of the APES possesses a two-dimensional continuum of equipotential points and, in particular, in the limiting case of strong vibronic coupling

when the Jahn–Teller destabilising forces are stronger than the stabilising effect of the spin–orbit coupling, the lowest sheet of the APES possesses a two-dimensional trough. Nuclear motion at the bottom of the trough is thus reduced to free rotations. This result is understandable because the isotropic spin–orbit coupling does not reduce the symmetry of the system as a whole and hence the lowest sheet of the APES consists of a trough whether or not the spin–orbit coupling is taken into consideration. Thus, including the isotropic spin–orbit interaction gives for the $^{2S+1}P \otimes d$ problem results similar to those of O’Brien (1969) obtained without the spin–orbit coupling. The spin–orbit coupling changes the sequence of the excited electronic states and the sheets of the APES as well as the appropriate energy gaps. It also changes the parameters of the trough, for example, its radius. Another problem is how the spin–orbit coupling changes the quantisation rules for the rotational motion at the bottom of the trough.

The above group-theoretical consideration is a general one in the sense that it relates equally to every spin multiplicity, 2T , 3T , 4T , etc. In the next section we shall show in an explicit form using the approach of O’Brien (1969) that the lowest eigenvalue of the potential energy matrix of a 2T term (the lowest sheet of the APES) in the d -mode model does not in fact depend on the angular variables, the latter being the cyclic coordinates. Within the same approach the quantisation rules will be determined for the rotations along the two-dimensional trough. As a result a conclusion will be drawn about a characteristic energy spectrum of free internal rotations in Jahn–Teller $^2P \otimes d$ systems with isotropic spin–orbit interactions.

3. Vibronic energy spectrum of the free rotations in the case of $^2P \otimes d$

The character of the nuclear motion is determined by the shape of the lowest sheet of the APES if the adiabatic separation of the nuclear motion from the electronic motion is justified. As is known, the necessary condition of such an adiabatic approximation is the smallness of the energy gaps in the nuclear energy spectrum compared with the energy separation of the ground sheet of the APES from the upper sheets. This condition can undoubtedly be satisfied in the limiting case of strong vibronic coupling for the spin multiplicity $2S + 1 = 1$, i.e. $S = 0$ (the case considered by O’Brien (1969)), and $2S + 1 = 2$, i.e. $S = \frac{1}{2}$, that is for the case of $^2T \otimes (\epsilon + \tau_2)$. Unfortunately, for larger values of S we have to deal with a small energy separation of the ground sheet of the APES at the minimum points from the upper sheets and the usual adiabatic approach becomes doubtful. Therefore, as distinct from the cases $S = 1, \frac{3}{2}, 2$, etc, the adiabatic separation of the motions for $S = \frac{1}{2}$ does not need special consideration and can be treated in the same way as O’Brien (1969) treated $S = 0$.

In this connection it is necessary to stress that the Jahn–Teller cases $^3T \otimes (\epsilon + \tau_2)$, $^4T \otimes (\epsilon + \tau_2)$, $^5T \otimes (\epsilon + \tau_2)$, etc, do not provide any understanding of the physical picture because the adiabatic separation of the nuclear motion, the only reference point in the limiting case of strong vibronic coupling, remains unknown.

A quantitative description of a $^2T \otimes (\epsilon + \tau_2)$ system can be performed under the same assumptions of the d -mode model as in O’Brien’s (1969) $^1T \otimes (\epsilon + \tau_2)$ case. As was shown above, the Hamiltonian of such a $^2P \otimes d$ system with an isotropic spin–orbit interaction is invariant under three-dimensional rotations. Let x, y, z be the direction cosines determining the orientation of a radius vector under such a rotation. They transform as the rows of the vector’s irreducible representation, D_1 , and satisfy the

equation $x^2 + y^2 + z^2 = 1$. In other words, they map onto the surface of a unit sphere in three-dimensional space (see figure 1 of O'Brien (1969)).

The spin-orbit interaction splits the 2P term into two terms, ${}^2P_{1/2}$ and ${}^2P_{3/2}$. Both are mixed by the vibronic interaction. As the Hamiltonian of the vibronic interaction, \hat{H}_{JT} from (4), is a scalar of the reference symmetry group, the group of three-dimensional rotations, the adiabatic electronic wavefunctions belong to one of the representations of this group. Let it be the Kramers doublet representation, $D_{1/2}$. This results from multiplication of ${}^2P_{1/2} = D_{1/2}$ and ${}^2P_{3/2} = D_{3/2}$ with the $D_1 = \{x, y, z\}$ representation: $D_{1/2} \times D_1 = D_{1/2} + D_{3/2}$; $D_{3/2} \times D_1 = D_{1/2} + D_{3/2} + D_{5/2}$. In the general case it should be a linear combination of the appropriate irreducible convolutions. Using the Clebsch-Gordan coefficients one obtains the following adiabatic electronic wavefunctions of the lowest sheet of the APES:

$$|\frac{1}{2}\rangle = A[-(i/\sqrt{3})(x + iy)|\frac{1}{2}, -\frac{1}{2}\rangle - (i/\sqrt{3})z|\frac{1}{2}, \frac{1}{2}\rangle] + B[-(i/\sqrt{12})(x + iy)|\frac{3}{2}, -\frac{1}{2}\rangle + (i/2)(x - iy)|\frac{3}{2}, \frac{3}{2}\rangle - (i/\sqrt{3})z|\frac{3}{2}, \frac{1}{2}\rangle] \quad (12)$$

$$|-\frac{1}{2}\rangle = A[-(i/\sqrt{3})(x - iy)|\frac{1}{2}, \frac{1}{2}\rangle + (i/\sqrt{3})z|\frac{1}{2}, -\frac{1}{2}\rangle] + B[-(i/2)(x + iy)|\frac{3}{2}, -\frac{3}{2}\rangle + (i/\sqrt{12})(x - iy)|\frac{3}{2}, \frac{1}{2}\rangle - (i/\sqrt{3})z|\frac{3}{2}, -\frac{1}{2}\rangle]. \quad (13)$$

Here $|j, m\rangle$ are the spin-orbit electronic wavefunctions of the 2P term diagonalising the spin-orbit Hamiltonian $\hat{H}_{SO} = \lambda \mathbf{L} \cdot \mathbf{S}$. A and B are free coefficients.

To find the extremum points of the lowest sheet of the APES one can use the procedure developed by Öpik and Pryce (1957). According to this procedure the following system of coupled equations has to be solved:

$$\begin{aligned} \hat{U}|a\rangle &= \varepsilon|a\rangle \\ \langle a|\partial\hat{U}/\partial Q_{n\Gamma\gamma}|a\rangle &= 0 \\ \langle a|a\rangle &= 1 \end{aligned} \quad (14)$$

where $|a\rangle$ is an eigenvector of the potential energy matrix (cf equation (7))

$$\hat{U} = \lambda \mathbf{L} \cdot \mathbf{S} + \frac{1}{2} \sum_n \omega_n^2 \sum_\gamma Q_{n\gamma}^2 + \sum_n V_n \sum_\gamma Q_{n\gamma} \hat{C}_\gamma. \quad (15)$$

In the d-mode model $\omega_{nE} = \omega_{nT} = \omega_{n2}$, $V_{nE} = 2V_{nT}/\sqrt{3} = V_n$, and \hat{C}_ξ , \hat{C}_η and \hat{C}_ζ differ from the matrices (5) by the factor $\sqrt{3}/2$. The angular dependence of the elements of the column matrix $|a\rangle$ via the direction cosines x , y and z is given by (12) and (13). In other words, one looks for the solution of equations (14) in the form of (12) or (13). Substituting this column vector $|a\rangle$ into the second equation in (14), one obtains the equilibrium coordinates of the trough:

$$\begin{aligned} Q_{n\theta}^{(0)} &= Q_n^{(0)}(-x^2 - y^2 + 2z^2) \\ Q_{n\varepsilon}^{(0)} &= Q_n^{(0)}\sqrt{3}(x^2 - y^2) \\ Q_{n\xi}^{(0)} &= Q_n^{(0)}2\sqrt{3}yz \\ Q_{n\eta}^{(0)} &= Q_n^{(0)}2\sqrt{3}xz \\ Q_{n\zeta}^{(0)} &= Q_n^{(0)}2\sqrt{3}xy \end{aligned} \quad (16)$$

where

$$Q_n^{(0)} = (V_n/12\omega_n^2)B(B - 2\sqrt{2}A). \quad (17)$$

Note that these coordinates possess the same transformation properties as in the simpler case of O'Brien (1969). From the last equation in (14) one obtains the normalisation condition $A^2 + B^2 = 3$.

Substituting the coordinates $Q_{n\gamma}$ from (16) into the potential energy matrix (15), one can easily verify that the electronic wavefunctions (12) and (13) are the eigen-functions of \hat{U} and its eigenvalue does not depend on the direction cosines x , y and z . This circumstance alone confirms the above statement that the lowest sheet of the APES possesses a two-dimensional trough and the angular variables θ and φ ($x = \sin \theta \cos \varphi$, $y = \sin \theta \sin \varphi$, $z = \cos \theta$) are cyclic coordinates. The angular coordinates cancel from the system of coupled equations originating from the matrix equation $\hat{U}|a\rangle = \varepsilon|a\rangle$. The only unknown parameters to be found remaining in the system of equations are A and B . This can be done by taking into account the normalisation condition $A^2 + B^2 = 3$; the final expressions are very large and it is not necessary to give them here.

The cyclic variables describing free rotation of the representative point along the trough can be separated from all the other variables, and it follows that every vibrational energy level is accompanied by a rotational structure of energy levels described by the Hamiltonian

$$H_{\text{rot}} = \hbar^2 \mathcal{J}^2 / 2I_0 \quad (18)$$

where \mathcal{J} is the resulting spin-orbit-vibrational moment defined in (11) and $I_0 = \sum_{n\gamma} Q_{n\gamma}^{(0)2}$ is the appropriate moment of inertia at the bottom of the trough:

$$I_0 = \frac{B^2}{36} (B - 2\sqrt{2}A)^2 \sum_n \frac{V_n^2}{\omega_n^4}. \quad (19)$$

By averaging the Hamiltonian (18) with rotational states one obtains $E_{\text{rot}} = \hbar^2 j(j+1) / 2I_0$, where j is the quantum number of operator \mathcal{J} . Hence it follows that the rotational energy levels are arranged in the sequence of energy increasing with j .

The quantisation rules can be obtained from the unambiguity condition of the vibronic wavefunction. In the adiabatic approximation this has a multiplicative form, $\Psi(r, Q) = \varphi(r, Q)\Phi(Q)$, where $\varphi(r, Q)$ is the electronic wavefunction of the lowest sheet of the APES determined in (12) and (13) and $\Phi(Q)$ is the eigen-function of the rotational Hamiltonian (18).

As can be seen from (12) and (13), the inversion in the space of the angular variables, $x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$, changes the sign of the adiabatic wavefunctions $\varphi_0(r, Q, \pm\frac{1}{2})$ and multiplies the rotational wavefunctions Y_{jm} by the factor $(-1)^j$, similarly to O'Brien's simple case without spin-orbit coupling. Therefore in order to keep the total function $\varphi_0 Y_{jm}$ unchanged, only odd values of j have to be retained. From this it follows that the ground rotational state corresponding to the lowest j , $j = 1$, is three-fold degenerate, $2j + 1 = 3$. The two-fold Kramers degeneracy of the lowest sheet of the APES should also be taken into account and therefore the ground vibronic term of the ${}^2\text{P} \otimes \text{d}$ system under consideration with the spin-orbit coupling $\lambda \mathbf{L} \cdot \mathbf{S}$ is a six-fold degenerate vibronic ${}^2\text{P}$ term with the same transformational properties as the initial electronic ${}^2\text{P}$ term. The spin-orbit splitting of the ground vibronic term, as well as of the excited rotational energy levels, is completely quenched in this approximation.

Note that the case of weak spin-orbit coupling is also covered by the present investigation. This aids understanding of the origin of the absence of the spin-orbit splitting of the ground 2P term in the limiting case of strong vibronic coupling. The perturbation analysis shows that the second-order matrix of the spin-orbit Hamiltonian calculated with the adiabatic wavefunctions (12) and (13) of the strong vibronic coupling equals zero. The spin-orbit interaction splits the ground vibronic 2P term beginning from the third-order perturbation theory.

4. Hindered rotations and tunnelling motions in the multimode ${}^2T \otimes (\varepsilon + \tau_2)$ problem

The dynamic symmetry of the Jahn-Teller ${}^{2S+1}T$ term and the possibility of internal free rotations provided by this symmetry occur in the high-symmetry case of the isotropic spin-orbit coupling, $\lambda L \cdot S$, with equal frequencies and equal Jahn-Teller stabilisation energies of the E and T_2 modes, $\omega_{nE} = \omega_{nT}$, $E_{JT}(E) = E_{JT}(T)$. In real systems these conditions are usually violated. This lowers the symmetry of the system, providing warping of the APES. Alternating minima and saddle points occur along the bottom of the trough at the lowest sheet of the APES and the above rotations become hindered.

A quantitative description of these features of the ${}^2T \otimes (\varepsilon + \tau_2)$ system can be performed in the same way as described by O'Brien (1969) and Bersuker and Polinger (1981). Violation of the high-symmetry conditions described does not cause separation of the rotational motion along the bottom of the trough from the other modes. Nevertheless, such a separation of variables can be performed in the adiabatic approximation under the assumption that the energy intervals in the energy spectrum of the hindered rotations are much less than an average vibrational quantum of the radial (orthogonal to the trough) motions. Strictly speaking, for every impurity-phonon system one can find lattice vibrations, for example, in the long-wavelength region of the acoustic branch, with a very small vibrational quantum which is much less than the energy level spacing in the rotational spectrum. By taking into account the decreasing spacing of the energy levels of the rotational spectrum with the vibronic coupling, $\Delta E_{\text{rot}} \sim V^{-2}$, $V = V_E \approx V_T$, and the smallness of the density of states of the acoustic long-wavelength phonons, the effects of non-adiabatic mixing of the rotational states by the acoustic phonons for sufficiently strong vibronic interactions can be considered, however, to be negligibly small (Bersuker and Polinger 1981). By averaging the Hamiltonian of the lowest sheet of the APES with the ground state of the radial vibrations (the fast system), one obtains the Hamiltonian for the angular motion along the bottom of the trough (the slow system):

$$H_{\text{rot}}(\theta, \varphi) = \hbar^2 \mathcal{J}^2 / 2I_0 + V(\theta, \varphi) \quad (20)$$

where $V(\theta, \varphi)$ is an angular-dependent potential energy resulting from averaging of the lowest sheet of the APES with respect to the radial coordinates. Note that, as distinct from O'Brien's case, $V(\theta, \varphi)$ in the present paper results from the ground eigenvalue of the 6×6 potential energy matrix of the Hamiltonian (7) including the spin-orbit coupling. The function $V(\theta, \varphi)$ corresponds to the cubic symmetry of the system and is an invariant of the cubic group. As in O'Brien's (1969) work, this function can be expanded in a series with respect to cubic harmonics and, if the effect of warping is not very strong, one can limit the expansion to the first non-trivial terms (in the same manner as that of O'Brien (1969)):

$$V(\theta, \varphi) \approx -E_{JT} + \Delta \{ Y_{4,0}(\theta, \varphi) + \sqrt{5/14} [Y_{4,4}(\theta, \varphi) + Y_{4,-4}(\theta, \varphi)] \} \quad (21)$$

where E_{JT} is the energy gain at the bottom of the trough. O'Brien (1969) showed that

the approximate potential energy function represented by the right-hand side of (21) has the same extremum points as the exact one, $V(\theta, \varphi)$. Taking into account the higher terms of the expansion (21) provides the possibility to consider the case when the orthorhombic points are absolute minima (Lister and O'Brien 1984).

Note that the Hamiltonian (20) with the potential energy (21) was obtained under the assumption that the symmetry of the system under consideration is cubic. It results from the rotational symmetry. If any one of the three conditions ($\omega_E = \omega_T$, $4V_T^2 = 3V_E^2$ or $H_{SO} = \lambda \mathbf{L} \cdot \mathbf{S}$) is violated, the rotational symmetry reduces to the cubic symmetry. Hence, the Hamiltonian (20) with the potential energy (21) is appropriate to the general case of a 2T term coupled to E and T_2 vibrations including the spin-orbit interaction.

Taking into account the above quantisation rules for the angular momentum (§ 3), the energy spectrum of hindered rotations in the ${}^2T \otimes (\varepsilon + \tau_2)$ case should be qualitatively the same as in figure 2 of the paper by O'Brien (1969). The only difference is the degeneracy of each level of the ${}^2T \otimes (\varepsilon + \tau_2)$ system caused by the Kramers' degeneracy of the sheets of the APES. The spin-orbit splitting of the vibronic energy levels is completely quenched under the approximations used in the present work. However, this effect cannot be considered to be a result of the vibronic reduction of the orbital angular momentum because the spin-orbit interaction is supposed to be sufficiently strong and cannot be taken into account by the usual perturbation theory within the limits of which the vibronic reduction factors are usually introduced (Ham 1965). As found by O'Brien (1969), at large positive values of Δ the nuclear motion is localised at the bottom of the four trigonal minima of the APES and the tunnelling splitting of the ground term results in the vibronic energy levels 2T_1 and 2A_2 being separated by a small energy gap. The latter is supposed to be larger than the spin-orbit splitting of the ground 2T_1 term.

At large negative values of Δ the nuclear motion is localised at tetragonal minima and the tunnelling transitions in this case are forbidden by some symmetry restrictions (Martinenas and Dagis 1969). Therefore for large negative Δ the orbital degeneracy of each vibronic energy level is a multiple of three.

5. Discussion

The considered internal rotations in the point-defect system with a 2T term coupled to E and T_2 vibrations can be interpreted as a hindered motion of a multiphonon formation of the polaron type around the point defect in the crystal.

The results of the present work allow some conclusions to be made about the characteristic energy level scheme of the ${}^2T \otimes (\varepsilon + \tau_2)$ system in the limiting case of strong vibronic coupling. Due to the Jahn-Teller effect and spin-orbit interaction, the 2T term is split into three Kramers doublets at an arbitrary point in the space of the nuclear distortions representing the three sheets of the APES. At the bottom of the trough the ground electronic term is adjoined by a phonon continuous spectrum corresponding to internal vibrations of the polaron formation. The phonon density of these vibrations in the trigonal points of the trough of the multimode ${}^2T \otimes (\varepsilon + \tau_2)$ system was investigated by Polinger and Boldyrev (1986). There were shown to be some new local and pseudo-local resonances caused by an additional defect of the force constants produced by the Jahn-Teller effect. Qualitatively we have here the same picture as in the multimode $E \otimes \varepsilon$ case (Bersuker and Polinger 1981).

The harmonic expansion of the adiabatic potential energy of the nuclei with respect to small nuclear displacements from the point of the trigonal minimum used by Polinger and Boldyrev (1986) is justified when a large number of radial vibrations (orthogonal to the angular variables of the trough, θ and φ) determine the continuous energy spectrum. At the same time the internal hindered rotations along the trough are reduced to small vibrations at the minimum. This is a very ideal approximation. In the present work the angular motion is separated and considered in a more consistent way. It was shown in § 4 that the angular motion may be reduced to a small vibration at the bottom of the minimum only in the limiting case of very large potential barriers when tunnelling can be neglected. Otherwise the character of the angular motion is much more complicated. In this sense the present paper fills a gap which was left in our previous work (Polinger and Boldyrev 1986). For an adequate interpretation of the experimental data the present work should be used together with our previous paper because they complement one another.

In the earlier paper (Polinger and Boldyrev 1986) it was also shown that the lower the phonon energy, the lower the vibrational density in the low-frequency region (tending to zero as $\omega \rightarrow 0$). This feature is well known for the usual cases of the acoustic phonon branches. The same was proved to be the case when considering the strong Jahn–Teller effect. This justifies the adiabatic separation of the angular motion along the trough from all the other nuclear motions, the latter being reduced to vibrations. The ground vibrational energy level is accompanied by a fine structure of the energy spectrum appropriate to the hindered rotations of the polaron around the point defect of the crystal. If the vibronic coupling is large enough, the energy gaps in this rotational spectrum are very small and the fine structure occurs in the weak background, low-frequency region of the vibrational density. It follows that the stronger the vibronic coupling, the less is the rotational quantum and the less is the probability of radiationless dissipation of the rotational energy into the phonon continuum, because this probability is proportional to the phonon density at the appropriate resonant frequency (cf the multimode $E \otimes \epsilon$ case investigated by Bersuker and Polinger (1981)). In other words, the stronger the vibronic coupling, the narrower the rotational spectral lines are, the latter corresponding to O'Brien's energy spectrum determined by the Hamiltonian (20) with the potential energy (21).

Hence, for a strongly coupled 2T term an experimental spectrum can be obtained that is consistent with a value of Δ of (21) with some omissions caused by the selection rules. The experimental spectral lines can be attributed therefore to the energy levels of O'Brien's (1969) figure 2 by an appropriate fit of Δ .

The rotational spectral lines are broadened by the non-adiabatic coupling of the slow angular motion to the fast radial vibrations. This coupling is stronger for a greater background of the phonon density of states. Hence, if the rotational spectral lines occur in the low-energy range of the spectrum they are narrow and clearly resolved from the background. The larger the rotational energy, the higher the energy range of the spectrum, so the corresponding rotational spectral lines are broader. In real cases the rotational structure can be observed at energies less than half of the energy of the Debye phonon.

To explain the experimental data on the spectral manifestations of the Jahn–Teller effect in impurities, the so called cluster (quasi-molecular) model is usually used. The Jahn–Teller Hamiltonian of such a model system is diagonalised numerically and an attempt is made to assign the vibronic energy levels of the discrete energy spectrum of this model system to the experimental resonances in absorption, luminescence or Raman

scattering of light in the continuous spectrum of the real impurity system. The present work allows us to conclude that such an assignment is not possible for every energy level of the discrete energy spectrum and not for every case. If the APES of the system allows separation of the internal hindered rotations, then the appropriate rotational spectrum can be assigned to some of the experimental spectral lines as mentioned above. At the same time, the discrete energy levels of the model system related to radial vibrations have nothing in common with the continuous spectrum of the real impurity system. Note that such a possibility, to separate vibronic states obtained numerically into rotational and vibrational manifolds, is dubious. Therefore, to compare the theory with experimental data for the 2T -term systems (as well as for the 1T -term case), it is more correct to use O'Brien's (1969) energy level scheme of hindered rotations which does not contain the vibration energy levels.

These results can be used for a detailed interpretation of a number of point defects in cubic crystals in their 2T electronic states when the vibronic coupling is strong enough. Thus, for example, in addition to the results of Polinger and Boldyrev (1986) the splitting of the zero-phonon line of the ${}^2E \rightarrow {}^2T_2$ luminescence in the $\text{Cu}^{2+}:\text{ZnS}$ impurity system observed by Maier and Scherz (1974) can be explained as a manifestation of the tunnelling splitting of the ground vibronic energy level with an energy gap of 14 cm^{-1} between the ground 2T_2 and nearest excited 2A_1 vibronic terms.

The Jahn–Teller effect for the cases of 3T , 4T and 5T electronic terms within the approximations used above needs a special consideration of the pseudodegenerate sheets of the APES at the minimum points and a special investigation of the quantisation rules for angular momenta different from that of the 2T term.

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