

Possible mechanisms for orthorhombic Jahn-Teller distortions of orbital triplets

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Many of the observations of the static Jahn-Teller effect for orbital triplets in cubic symmetry correspond to tetragonal or trigonal distortions—as predicted by linear coupling theories—but in a number of cases orthorhombic distortions or coexisting inequivalent minima of the adiabatic potential energy are observed. In the present paper we investigate systematically a number of possible theoretical explanations for these observations. Assuming that the dominant terms in the vibronic Hamiltonian are the linear vibronic couplings to e_g and t_{2g} vibrational modes, we study the influence of many other effects within a perturbative approach. The minima of the adiabatic potential energy for a triplet in cubic symmetry are first calculated to lowest order in all the coefficients for quadratic nonlinear vibronic coupling and cubic anharmonicity. This is used to determine the conditions for orthorhombic or coexisting inequivalent minima to occur. Then a perturbative approach to the problem of multilevel coupling is developed and applied to the case of a T_{2g} level vibronically coupled to another level. In lowest order, the effect of interlevel coupling is to introduce terms formally analogous to nonlinear vibronic coupling terms in the single-level problem. The conditions for having the various kinds of distortions are given and discussed in each case. The influence of induced linear vibronic coupling to another vibrational mode is then considered and it is shown that distortions other than tetragonal, trigonal, or orthorhombic may occur. Finally we calculate the exact eigenvalues of the vibronic Hamiltonian with spin-orbit coupling to a spin of $\frac{1}{2}$, including the lowest-order nonlinear vibronic couplings and anharmonicities, and discuss the role of spin-orbit coupling.

I. INTRODUCTION

The Jahn-Teller effect¹ (JTE) occurs because an orbital-degenerate state of a molecule or crystalline defect is unstable against an asymmetric distortion which lowers the energy and removes some of the degeneracy. The effect results from a linear coupling of some vibrational modes to degenerate electronic orbital states (vibronic coupling). A general theory of the JTE cannot be formulated and the standard approach consists in considering every system separately (for reviews, see Refs. 2–6). A particularly difficult case is the study of a state with threefold orbital degeneracy in cubic symmetry. In the case of a T_{2g} orbital state in O_h symmetry, the symmetric part of the direct product⁴ $T_{2g} \otimes T_{2g}$ is $A_{1g} + E_g + T_{2g}$. Thus, a T_{2g} triplet couples in first order to vibrational modes of a_{1g} , e_g , and t_{2g} symmetries. Since the linear coupling to a_{1g} modes simply redefines the zero for the amplitude of these modes, the system is usually referred to as the $T_{2g} \otimes (e_g + t_{2g})$ problem. It should be noted that the symmetric part of the direct product is the same for a T_{1g} , T_{2u} , or T_{1u} orbital state in O_h symmetry. For O and T_d symmetries, the same holds if all subscripts g and u are dropped. Finally, in the case of T_h symmetry, we obtain for the symmetric part $T_g \otimes T_g = T_u \otimes T_u = A_g + E_g + T_g$ as well as for T symmetry but without the subscripts g and u . Thus, all five cubic point groups have very similar properties. In this paper, we shall discuss the T_{2g} orbital state in O_h symmetry. A complete theoretical study of such a system is rather involved since, in addition to the

linear coupling to e_g and t_{2g} vibrational modes, one must consider the effects of nonlinear vibronic coupling and anharmonicity, of interlevel, multimode, and even spin-orbit coupling.

Experimentally, many triplet systems have been investigated using various techniques. In a number of cases, only the dynamic effects of the Jahn-Teller coupling have been observed,^{7–12} but we found reasonably persuasive data of static JTE with tetragonal ($\langle 100 \rangle$) distortions in eight cases,^{13–23} trigonal ($\langle 111 \rangle$) distortions in seven,^{24–30} and orthorhombic ($\langle 110 \rangle$) distortions in six.^{16,28,29,31–36} Furthermore, the coexistence of two stable minima of the adiabatic potential energy (APE) of different symmetry occurs in the relaxed excited states (RES) of most Tl^+ -like impurities in the alkali halides, as shown by the observation of a double A band (A_T and A_X) corresponding to the ${}^3T_{1u} \rightarrow {}^1A_{1g}$ emission. A stable tetragonal distortion in the RES is believed to be responsible for the A_T band in most cases, whereas the A_X band would be caused by a distortion of different symmetry (for a review, see Ref. 37). In general, the two coexisting minima of the APE are of tetragonal and trigonal symmetry,^{38–46} but one of the bands is believed to be caused by an orthorhombic minimum^{39,46} for $KI:Tl^+$ and $KBr:In^+$.

On the theoretical side, the first attempt to cope with a static triplet in cubic symmetry was by Van Vleck in 1939⁴⁷ who considered only the linear vibronic coupling term in the $T \otimes e_g$ and the $T \otimes t_{2g}$ problems separately. He showed that linear coupling to an e_g (or a t_{2g}) vibrational mode results in tetragonal (or trigonal) distortions. Dur-

ing the next 30 years, the problem of a static triplet in cubic symmetry remained an exclusively linear one. Öpik and Pryce⁴⁸ studied in detail the linear $T_{2g} \otimes (e_g + t_{2g})$ problem and calculated the effect of spin-orbit coupling in the cases of tetragonal and trigonal distortions for a spin of $\frac{1}{2}$. Liehr⁴⁹ discussed the topology of the APE surfaces in great detail. Vibronic eigenstates were also calculated, first for weak vibronic coupling,⁵⁰ then for only t_{2g} modes,⁵¹ only e_g modes,⁸ and finally in the $T_{2g} \otimes (e_g + t_{2g})$ case for almost equal linear vibronic coupling to both vibrational modes.⁵² If the linear vibronic coupling to e_g (or t_{2g}) vibrational modes is much stronger than the one to t_{2g} (or e_g), tetragonal (or trigonal) distortions correspond to a deep minimum of the APE. In this case, the inclusion of higher-order terms in the vibronic Hamiltonian is not likely to change the symmetry of the system. However, if tetragonal and trigonal linear Jahn-Teller stabilization energies are comparable in magnitude, although still only $\langle 100 \rangle$ and $\langle 111 \rangle$ distortions can occur,⁵³ perturbations may cause distortions other than pure tetragonal or pure trigonal.

Since the early 1970s, several explanations for the observed distortions that are inconsistent with linear coupling theory have been presented. However, since the vibronic Hamiltonian for the $T_{2g} \otimes (e_g + t_{2g})$ problem contains four quadratic nonlinear coupling terms and three cubic anharmonicity terms, in addition to the two linear vibronic coupling ones and the two harmonic potential-energy contributions, the general conditions for the APE to admit orthorhombic or coexisting inequivalent minima have never been formulated. Some authors studied the influence of one,^{54,55} two,^{56,57} three,^{58,59} or all four⁶⁰ quadratic nonlinear coupling terms in the vibronic Hamiltonian (but without the anharmonicities), or considered the effects of anharmonicity⁶¹ (but without nonlinear coupling). These authors have shown that the inclusion of almost any one of the nonlinear coupling or anharmonic terms allows orthorhombic stationary points to become absolute minima of the APE under some restricted conditions, if the two linear Jahn-Teller stabilization energies are comparable. Furthermore, $\langle 111 \rangle$ and $\langle 100 \rangle$ as well as $\langle 111 \rangle$ and $\langle 110 \rangle$, or even $\langle 100 \rangle$ and $\langle 110 \rangle$, minima can coexist in some cases.⁵⁹⁻⁶² However, the inclusion of all seven nonlinear coupling and anharmonic terms simultaneously has never been analyzed. The influence of spin-orbit coupling has been studied for tetragonal and trigonal distortions in the linear coupling case.^{48,63,64} The effects of spin-orbit coupling have also been shown to be partly responsible for the coexistence of inequivalent minima of the APE for Tl^+ -like impurities in the alkali halides, using the $a_{1g}t_{1u}$ electronic configuration.^{38,57,58,62,65,66} Finally, the distortions arising from the vibronic coupling between two levels have been calculated.⁶⁷ However, the complicated forms of these exact solutions make it difficult to see whether interlevel couplings can stabilize orthorhombic or coexisting minima.

In this paper, we attempt a more systematic and more general discussion of the problem of an orbital triplet in cubic symmetry with the restriction that linear vibronic coupling is dominant, as it is assumed to be in virtually all systems exhibiting the Jahn-Teller effect. We start with

the exact solution for the stationary points of the APE for linear vibronic coupling. In Sec. II, we determine the lowest-order influence of all quadratic nonlinear vibronic coupling terms and cubic anharmonicities. Then, we use a general perturbative approach (Appendix) to investigate the problem of interlevel vibronic coupling (Sec. III). It is shown that, in second-order perturbation theory, interlevel coupling introduces terms in the vibronic Hamiltonian which are formally analogous to the quadratic vibronic coupling terms discussed in Sec. II. Then, in Sec. IV, we go one step beyond the usual one-mode approximation by adding to the linear $T_{2g} \otimes (e_g + t_{2g})$ problem an induced linear vibronic coupling to another mode of a_{1g} , a_{2g} , e_g , t_{1g} , or t_{2g} symmetry. The various extensions to linear coupling are treated perturbatively, which is consistent with the usual approximation in dealing with the Jahn-Teller effect. This approach treats similarly all of the additions to linear coupling which are usually neglected, and thus provides a consistent perspective of the behavior of an orbital triplet in cubic symmetry. Furthermore, the individual results can be combined to represent a more general situation. In Sec. V we derive the general form of the adiabatic potential energy with spin-orbit coupling to a spin of $\frac{1}{2}$, including all nonlinear vibronic couplings and anharmonicities. The effects of spin-orbit coupling are discussed. Section VI concludes this paper with a discussion of the various mechanisms which can lead to orthorhombic or coexisting inequivalent minima of the APE.

II. $T_{2g} \otimes (e_g + t_{2g})$ PROBLEM

We consider a T_{2g} state of a defect or impurity in O_h symmetry. The orbital states are denoted by $|\xi\rangle$, $|\eta\rangle$, and $|\zeta\rangle$ and transform as yz , zx , and xy , i.e., as the T_{2g} irreducible representation of O_h . The direct product is

$$T_{2g} \otimes T_{2g} = A_{1g} + E_g + T_{1g} + T_{2g}, \quad (1)$$

where the symmetric part is $A_{1g} + E_g + T_{2g}$. Therefore, one has six time-reversal even and three time-reversal odd orbital operators.⁶⁸ Using the coupling coefficients for the group O_h , one obtains

$$\mathcal{J} = |\xi\rangle\langle\xi| + |\eta\rangle\langle\eta| + |\zeta\rangle\langle\zeta| = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (2)$$

transforming as A_{1g} ,

$$\mathcal{E}_\theta = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \quad \text{and} \quad \mathcal{E}_\epsilon = \begin{pmatrix} \sqrt{3} & 0 & 0 \\ 0 & -\sqrt{3} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (3)$$

transforming as E_g , and

$$\mathcal{T}_\xi = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \mathcal{T}_\eta = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix},$$

and

$$\mathcal{T}_\zeta = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

transforming as T_{2g} , all of which are Hermitian and time-reversal even orbital operators. The three remaining Hermitian and time-reversal odd orbital operators are

$$\mathcal{L}_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad \mathcal{L}_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix},$$

and

$$\mathcal{L}_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

which transform as T_{1g} . The vibronic Hamiltonian is given by

$$\mathcal{H}_T = g_1 \mathcal{I} + g_\theta \mathcal{E}_\theta + g_\epsilon \mathcal{E}_\epsilon + g_\xi \mathcal{T}_\xi + g_\eta \mathcal{T}_\eta + g_\zeta \mathcal{T}_\zeta, \quad (6)$$

where the functions g_i depend on the collective coordinates^{2,6} Q_θ , Q_ϵ , Q_ξ , Q_η , Q_ζ (considering only coupling to one mode of each symmetry) and transform as the orbital operators they multiply. The Q_i are linear combinations of the displacements of the ions surrounding the defect transforming as E_g and T_{2g} under the symmetry operations of O_h . They are the only symmetry modes which lead to linear vibronic coupling and hence to a Jahn-Teller effect. In this section, we will consider only one mode of each symmetry. Since the amplitudes of the normal modes are assumed to be small, we can write the functions g_i as a Taylor series in the Q_i , the first terms of which are

$$g_1 = \frac{1}{2} k_E (Q_\theta^2 + Q_\epsilon^2) + \frac{1}{2} k_T (Q_\xi^2 + Q_\eta^2 + Q_\zeta^2) + A_E Q_\theta (3Q_\epsilon^2 - Q_\theta^2) + A_T Q_\xi Q_\eta Q_\zeta + A_M [Q_\theta (2Q_\xi^2 - Q_\zeta^2 - Q_\eta^2) + \sqrt{3} Q_\epsilon (Q_\xi^2 - Q_\eta^2)] + \dots, \quad (7)$$

$$g_\theta = \frac{1}{\sqrt{3}} V_E Q_\theta + N_E (Q_\epsilon^2 - Q_\theta^2) + N_1 (2Q_\xi^2 - Q_\zeta^2 - Q_\eta^2) + \dots, \quad (8)$$

$$g_\epsilon = \frac{1}{\sqrt{3}} V_E Q_\epsilon + 2N_E Q_\theta Q_\epsilon + \sqrt{3} N_1 (Q_\xi^2 - Q_\eta^2) + \dots, \quad (9)$$

$$g_\xi = V_T Q_\xi + N_T Q_\eta Q_\zeta + N_2 Q_\xi (\sqrt{3} Q_\epsilon - Q_\theta) + \dots, \quad (10)$$

$$g_\eta = V_T Q_\eta + N_T Q_\xi Q_\zeta + N_2 Q_\eta (-\sqrt{3} Q_\epsilon - Q_\theta) + \dots, \quad (11)$$

$$g_\zeta = V_T Q_\zeta + N_T Q_\xi Q_\eta + 2N_2 Q_\zeta Q_\theta + \dots \quad (12)$$

This Taylor expansion has been implicitly assumed by all of the authors who studied the effects of some of the nonlinear coupling or anharmonic terms.⁵⁴⁻⁶⁴ Equations (7)–(12) contain all quadratic nonlinear vibronic coupling constants (N_i) and all cubic anharmonic terms (A_i). The matrix for the vibronic Hamiltonian is [see Eqs. (2)–(6)]

$$\mathcal{H}_T = \begin{pmatrix} g_1 - g_\theta + \sqrt{3} g_\epsilon & g_\zeta & g_\eta \\ g_\zeta & g_1 - g_\theta - \sqrt{3} g_\epsilon & g_\xi \\ g_\eta & g_\xi & g_1 + 2g_\theta \end{pmatrix}. \quad (13)$$

Following Öpik and Pryce,⁴⁸ it is convenient to use a variational principle to determine the stationary points of the APE. The ground-state wave function is assumed to have the general form

$$|\psi\rangle = l |\xi\rangle + m |\eta\rangle + n |\zeta\rangle \quad \text{with } l^2 + m^2 + n^2 = 1, \quad (14)$$

and the function to be minimized, $E_T = \langle \psi | \mathcal{H}_T | \psi \rangle$, is calculated to be

$$E_T = g_1 + (2n^2 - l^2 - m^2)g_\theta + \sqrt{3}(l^2 - m^2)g_\epsilon + 2mng_\xi + 2nlg_\eta + 2lmg_\zeta. \quad (15)$$

If the derivatives of E_T with respect to the five Q_i are set equal to zero, one obtains five equations which give the Q_i in terms of l , m , and n . Furthermore, minimizing with respect to l , m , and n with the restriction (14) leads to the desired stationary points. It should be emphasized that this method gives only the stationary points of the APE and not the APE itself.

A. Linear coupling case

If one neglects all nonlinear vibronic coupling and anharmonic terms in Eqs. (7)–(12), the values of the Q_i minimizing E_T are

$$Q_\theta = \frac{V_E}{\sqrt{3}k_E} (l^2 + m^2 - 2n^2), \quad Q_\epsilon = \frac{V_E}{k_E} (m^2 - l^2), \quad (16)$$

$$Q_\xi = -2 \frac{V_T}{k_T} mn, \quad Q_\eta = -2 \frac{V_T}{k_T} nl, \quad Q_\zeta = -2 \frac{V_T}{k_T} lm. \quad (17)$$

Substituting these values into Eq. (15) gives the Öpik and Pryce⁴⁸ result

$$E_T = -\frac{2V_E^2}{3k_E} + 2 \left[\frac{V_E^2}{k_E} - \frac{V_T^2}{k_T} \right] f_4, \quad (18)$$

where the function f_4 (which is invariant in cubic symmetry) is

$$f_4 = m^2 n^2 + n^2 l^2 + l^2 m^2. \quad (19)$$

If V_E^2/k_E is comparable to V_T^2/k_T , the dominant contribution to the Jahn-Teller stabilization energy is the constant term $-2V_E^2/3k_E$. However, since this term is independent of l , m , and n , it does not influence the conclusions we draw if we simply ignore it. Consequently, we will drop this constant term from all further expressions for E_T . It can easily be seen that E_T admits tetragonal

($\langle 100 \rangle$) minima if $V_T^2/k_T < V_E^2/k_E$ and trigonal ($\langle 111 \rangle$) minima if $V_T^2/k_T > V_E^2/k_E$. Orthorhombic ($\langle 110 \rangle$) stationary points are always saddle points of the APE except for $V_E^2/k_E = V_T^2/k_T$, in which case the energy is the same for any possible values of l , m , and n .

B. Nonlinear and anharmonic terms

As has been mentioned in the Introduction, if $V_E^2/k_E \gg$ (or \ll) V_T^2/k_T tetragonal (or trigonal) distortions correspond to deep minima of the APE. As long as the nonlinear coupling (N_i) and anharmonic (A_i) terms [Eqs. (7)–(12)] are small compared to V_E/k_E or V_T/k_T , they will not modify the symmetry of the system. However, if V_E^2/k_E is comparable to V_T^2/k_T , both e_g and t_{2g} vibrational modes produce comparable energy reductions and the APE may show new kinds of minima, even for small values of N_i or A_i . If one includes all quadratic vibronic coupling and cubic anharmonic terms in the functions g_i [Eqs. (7)–(12)], the energy [Eq. (15)] becomes a complicated function of the collective displacements Q_i . Assuming that the nonlinear coupling and anharmonic terms are small and that the zeroth-order solutions are given by Eqs. (16) and (17), an iterative solution can be obtained. In first order in the nonlinear coupling (N_i) and anharmonic (A_i) terms, after minimizing with respect to the Q_i , Eq. (15) is reduced to the general form

$$E_T = \alpha f_4 + \beta f_6, \quad (20)$$

where f_4 is given by Eq. (19) and f_6 (which is also invariant in cubic symmetry) by

$$f_6 = l^2 m^2 n^2. \quad (21)$$

The stationary points of the APE are now given by those of E_T [Eq. (20)]. Stauss and Krebs³² suggested that the minima of the APE could be written in the form given by Eq. (20), but considered only some of the nonlinear vibronic coupling terms and no anharmonicities. Recently, Lister and O'Brien⁶⁰ used this form for the potential energy to calculate Ham factors for the triplet problem with nonlinear coupling. The coefficients α and β are

$$\alpha = 2 \left[\frac{V_E^2}{k_E} - \frac{V_T^2}{k_T} \right] - 12 \frac{V_E^2}{k_E^2} \left[\frac{V_E A_E}{\sqrt{3} k_E} - N_E \right] + 8 \frac{V_T}{k_T} \left[\frac{V_E V_T A_M}{\sqrt{3} k_E k_T} - \frac{N_1 V_T}{k_T} - \frac{N_2 V_E}{\sqrt{3} k_E} \right], \quad (22)$$

$$\beta = 36 \frac{V_E^2}{k_E^2} \left[\frac{V_E A_E}{\sqrt{3} k_E} - N_E \right] - 72 \frac{V_T}{k_T} \left[\frac{V_E V_T A_M}{\sqrt{3} k_E k_T} - \frac{N_1 V_T}{k_T} - \frac{N_2 V_E}{\sqrt{3} k_E} \right] - 8 \frac{V_T^2}{k_T^2} \left[\frac{V_T A_T}{k_T} - 3 N_T \right]. \quad (23)$$

A detailed study⁶⁹ of the stationary point of the APE [Eq. (20)] as a function of α and β is contained in Fig. 1 and Table I. As far as absolute minima are concerned, tetragonal distortions are stable if

$$\alpha > -\frac{1}{9}\beta \quad \text{and} \quad \alpha > 0, \quad (24)$$

which is always the case if $V_E^2/k_E \gg V_T^2/k_T$ (regions 6 and 7 in Fig. 1). Trigonal distortions occur in regions 3 through 5 in Fig. 1, i.e., if

$$\alpha < -\frac{4}{9}\beta \quad \text{and} \quad \alpha < -\frac{1}{9}\beta, \quad (25)$$

and orthorhombic ($\langle 110 \rangle$) distortions are stable in regions 1 and 2 in Fig. 1, i.e., if

$$-\frac{4}{9}\beta < \alpha < 0, \quad (26)$$

which can occur only if V_E^2/k_E and V_T^2/k_T are comparable. Furthermore, in regions 2 and 3 in Fig. 1, minima of trigonal and orthorhombic symmetry coexist, one being an absolute minimum, the other a relative minimum. This occurs for

$$-\frac{1}{2}\beta < \alpha < -\frac{1}{3}\beta. \quad (27)$$

Finally $\langle 111 \rangle$ and $\langle 100 \rangle$ minima coexist in regions 5 and 6 in Fig. 1, i.e.,

$$0 < \alpha < -\frac{1}{3}\beta. \quad (28)$$

The simultaneous occurrence of tetragonal and orthorhombic minima cannot be realized in lowest order in the coefficients N_i and A_i . The coexistence of these two distortions has been investigated using some nonlinear vibronic coupling terms^{58,59} or anharmonicities⁶¹ and appears to result from higher-order contributions of these vibronic coupling constants.

In addition to the stationary points mentioned in Table I, which are all minima of the APE for some values of the parameters, there is another stationary point with lower symmetry, corresponding to monoclinic ($\langle ll'n \rangle$) distortions. However, it is a saddle point in all the regions in

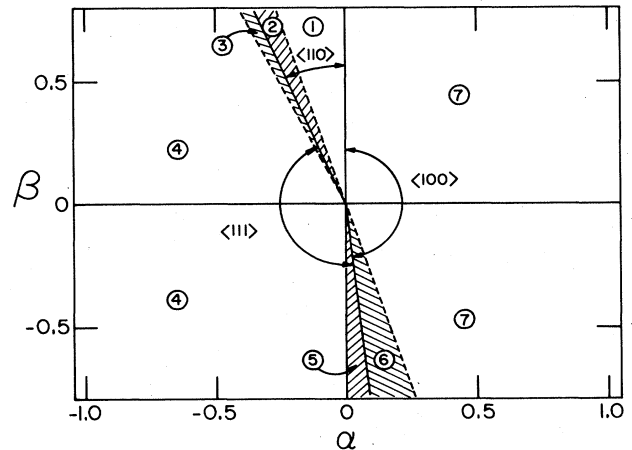


FIG. 1. Stationary point of the adiabatic potential energy [Eq. (20)] as a function of the quantities α and β which contain all the parameters in the vibronic Hamiltonian [Eqs. (22) and (23)]. Only the minima are shown. The solid lines separate the regions where tetragonal ($\langle 100 \rangle$), trigonal ($\langle 111 \rangle$), and orthorhombic ($\langle 110 \rangle$) distortions correspond to absolute minima. The shaded regions show where two inequivalent minima coexist. The boundaries of the regions and the description of the various stationary points are given in Table I.

TABLE I. Stationary points of the adiabatic potential energy (APE) for a triplet in cubic symmetry. If all linear and quadratic nonlinear vibronic coupling constants and cubic anharmonicities are included, the stationary points of the APE are those of $\alpha f_4 + \beta f_6$ [Eq. (20)], where α and β contain all the parameters in the vibronic Hamiltonian [Eqs. (22) and (23)]. Only tetragonal ($\langle 100 \rangle$), trigonal ($\langle 111 \rangle$), and orthorhombic ($\langle 110 \rangle$) distortions can be realized. Furthermore, $\langle 111 \rangle$ and $\langle 110 \rangle$ minima coexist in regions 2 and 3 in Fig. 1, as well as $\langle 111 \rangle$ and $\langle 100 \rangle$ (regions 5 and 6). ABS MAX (MIN) represent absolute maximum (minimum), MAX (MIN) represents local maximum (minimum), and SP represents saddle point.

Region (see Fig. 1)	$\langle 100 \rangle$	$\langle 110 \rangle$	$\langle 111 \rangle$
1	MAX	ABS MIN	ABS MAX
2	ABS MAX	ABS MIN	MAX
3	ABS MAX	MIN	ABS MIN
4	ABS MAX	SP	ABS MIN
5	MIN	ABS MAX	ABS MIN
6	ABS MIN	ABS MAX	MIN
7	ABS MIN	ABS MAX	MAX
	ABS MIN	MAX	ABS MAX
	ABS MIN	SP	ABS MAX

Fig. 1, where it is a stationary point.

As was mentioned in the Introduction and earlier in this section, minima of the APE other than tetragonal or trigonal can occur only if $V_E^2/k_E \approx V_T^2/k_T$. If this is the case, it can be seen from Eqs. (22) and (23) that for most values of the parameters N_i and A_i , α and β will have opposite signs and $|\beta|$ will be larger than $|\alpha|$ (since $\beta \approx -3\alpha + \dots$). In this region of the parameter space, minima of tetragonal and trigonal symmetry coexist for $\alpha > 0$ (regions 5 and 6 in Fig. 1), whereas orthorhombic distortions are realized if $\alpha < 0$ (regions 1–3 in Fig. 1). The coexistence of orthorhombic and trigonal minima is also possible (regions 2 and 3 in Fig. 1), but for a more restricted range of parameters. These limited regions of the α - β parameter space contain all of the parameter combinations which yield either orthorhombic distortions or coexisting inequivalent minima.

III. INTERLEVEL VIBRONIC COUPLING

A. Preliminary remarks

The lowest branch of the adiabatic potential-energy surface is affected by vibronic coupling to close-lying excited orbital states as well as by the vibronic coupling within the degenerate state which we analyzed in Sec. II. In some cases, the triplet level is very far away from any other level and can be considered as isolated to good approximation. However, in other cases the splittings between energy levels are sufficiently small to result in interlevel vibronic coupling but sufficiently large to allow a perturbation treatment. The effects are larger if the linear interlevel vibronic coupling results from one or both of the modes causing intralevel coupling, the e_g and t_{2g} modes.

We consider now two levels separated in energy by Δ , the lowest level being a T_{2g} orbital triplet with ground state $|0\rangle = \{|\xi\rangle, |\eta\rangle, |\zeta\rangle\}$ and Hamiltonian matrix $\mathcal{H}_0 = \mathcal{H}_T$ [Eq. (13)]. The other level—which in O_h symmetry can be an A_{1g} , A_{2g} , E_g , T_{1g} , or another T_{2g} level, since odd levels will not be linearly coupled by even

ones—is described by the Hamiltonian \mathcal{H}' . The coupling between the two levels is given by \mathcal{H}_c . The general form of the Hamiltonian matrix for the whole system is

$$\mathcal{H} = \begin{pmatrix} \mathcal{H}_T & \mathcal{H}_c \\ \mathcal{H}_c^t & \mathcal{H}' \end{pmatrix}, \quad (29)$$

where \mathcal{H}_c^t is the transpose of \mathcal{H}_c .

Stoneham and Lannoo⁶⁷ studied exact solutions to these problems and calculated the various displacements minimizing the APE. Their solutions can be applied even to very close-lying levels. Since our interest is in the case when the effects of interlevel coupling are relatively small, it is more realistic and far simpler to treat the interlevel vibronic coupling as a perturbation. This is easier to do by rederiving the results rather than taking the limiting forms of the equations of Stoneham and Lannoo. Perturbation theory applied to the present situation is developed in the Appendix. The lowest-order correction to \mathcal{H}_T [Eq. (13)], for one perturbing level, is [see Eq. (A12)]

$$-\frac{1}{\Delta} \mathcal{H}_c |n\rangle \langle n| \mathcal{H}_c^t + O\left[\frac{1}{\Delta^2}\right], \quad (30)$$

where \mathcal{H}_c (obtained from the coupling coefficients of the group O_h) describes the linear vibronic coupling between the two levels considered. The Hamiltonian \mathcal{H}' —appearing in Eq. (29) and describing the excited level—contributes first in only one of the two third-order terms [proportional to Δ^{-2} : see Eq. (A12)]. Thus, the effect of interlevel perturbation is to add d 3×3 matrices to \mathcal{H}_T , where d is the degeneracy of the excited level.

B. Coupling to an A_{1g} level

In the case of an A_{1g} level lying close to the T_{2g} ground level, the coupling matrix is

$$\mathcal{H}_c = \begin{pmatrix} g_\xi^c \\ g_\eta^c \\ g_\zeta^c \end{pmatrix} \text{ with } g_i^c = V_c Q_i, \quad (31)$$

where V_c is the linear interlevel vibronic coupling constant and the index i stands for ξ , η , or ζ . The lowest-order correction to \mathcal{H}_T is therefore

$$-\frac{1}{\Delta} \mathcal{H}_c |n\rangle \langle n| \mathcal{H}_c^\dagger = -\frac{1}{\Delta} \begin{pmatrix} (g_\xi^c)^2 & g_\xi^c g_\eta^c & g_\xi^c g_\zeta^c \\ g_\xi^c g_\eta^c & (g_\eta^c)^2 & g_\eta^c g_\zeta^c \\ g_\xi^c g_\zeta^c & g_\eta^c g_\zeta^c & (g_\zeta^c)^2 \end{pmatrix}. \quad (32)$$

In terms of the orbital operators defined in Eqs. (2)–(4), the effect of the A_{1g} - T_{2g} interlevel coupling is the effective Hamiltonian

$$\mathcal{H}_{\text{eff}} = g'_1 \mathcal{I} + g'_\theta \mathcal{E}_\theta + g'_\epsilon \mathcal{E}_\epsilon + g'_\xi \mathcal{T}_\xi + g'_\eta \mathcal{T}_\eta + g'_\zeta \mathcal{T}_\zeta \quad (33)$$

which has the same form as \mathcal{H}_T in Eq. (6). Thus, the result of a weak coupling between a T_{2g} and an A_{1g} level is to introduce new functions of the normal mode amplitudes to replace those defined in Eqs. (7)–(12). In lowest order, they are

$$g'_1 = \frac{1}{2} k_E (Q_\theta^2 + Q_\epsilon^2) + \left[\frac{1}{2} k_T - \frac{V_c^2}{3\Delta} \right] (Q_\xi^2 + Q_\eta^2 + Q_\zeta^2), \quad (34)$$

$$g'_\theta = \frac{1}{\sqrt{3}} V_E Q_\theta - \frac{V_c^2}{6\Delta} (2Q_\xi^2 - Q_\eta^2 - Q_\zeta^2), \quad (35)$$

$$g'_\epsilon = \frac{1}{\sqrt{3}} V_E Q_\epsilon - \frac{V_c^2}{2\sqrt{3}\Delta} (Q_\xi^2 - Q_\eta^2), \quad (36)$$

$$g'_\xi = V_T Q_\xi - \frac{V_c^2}{\Delta} Q_\eta Q_\zeta, \quad (37)$$

$$g'_\eta = V_T Q_\eta - \frac{V_c^2}{\Delta} Q_\xi Q_\zeta, \quad (38)$$

$$g'_\zeta = V_T Q_\zeta - \frac{V_c^2}{\Delta} Q_\xi Q_\eta. \quad (39)$$

A comparison of Eqs. (7)–(12) and (34)–(39) shows that the presence of the A_{1g} level results in the effective force constant $k'_T = k_T - 2V_c^2/3\Delta$ and in two terms equivalent to the vibronic coupling constants N_1 and N_T [Eqs. (8)–(12)]:

$$N'_1 = -\frac{V_c^2}{6\Delta} < 0, \quad N'_T = -\frac{V_c^2}{\Delta} < 0. \quad (40)$$

Using the results of Sec. II, the stationary points of the APE are those of

$$E_T = \alpha' f_4 + \beta' f_6 \quad (41)$$

[see Eq. (20)] with [see Eqs. (22) and (23)]

$$\alpha' = 2 \left[\frac{V_E^2}{k_E} - \frac{V_T^2}{k_T} \right], \quad (42)$$

$$\beta' = -\frac{36}{\Delta} \left[\frac{V_c V_T}{k_T} \right]^2 < 0. \quad (43)$$

An expansion of $1/k'_T$ has been used to obtain α' [Eq. (42)]. Since β' is always negative, it can be seen from Fig. 1 that only $\langle 100 \rangle$, $\langle 111 \rangle$, and coexisting $\langle 100 \rangle$ with $\langle 111 \rangle$ minima can be realized. In particular, trigonal and tetragonal minima coexist if the conditions given by Eq. (28) are satisfied, i.e.,

$$0 < \frac{V_E^2}{k_E} - \frac{V_T^2}{k_T} < \frac{12}{\Delta} \left[\frac{V_c V_T}{k_T} \right]^2. \quad (44)$$

Thus, V_E^2/k_E must be larger than V_T^2/k_T but the difference is limited by the effects of interlevel coupling.

C. Coupling to an A_{2g} level

Using the coupling coefficients for the group O_h , it is straightforward to see that \mathcal{H}_c contains no terms proportional to Q_θ , Q_ϵ , Q_ξ , Q_η , or Q_ζ . Therefore, in lowest order, the presence of an A_{2g} level does not modify the results described in Sec. II.

D. Coupling to an E_g level

The $T_{2g} + E_g$ vibronic coupling matrix is

$$\mathcal{H}_c = \begin{pmatrix} -g_\xi^c & \sqrt{3}g_\xi^c \\ -g_\eta^c & -\sqrt{3}g_\eta^c \\ 2g_\zeta^c & 0 \end{pmatrix}, \quad (45)$$

where the first (second) column corresponds to $|\theta\rangle$ ($|\epsilon\rangle$) and where the g_i^c are defined as in Eq. (31). Following the same steps as in Sec. III A, we obtain an effective Hamiltonian which can be written as in Eq. (33). The functions g'_i , compared to Eqs. (7)–(12), lead to the definition of the effective force constant $k'_T = k_T - 8V_c^2/3\Delta$ and of the two effective nonlinear vibronic coupling terms

$$N'_1 = -\frac{2}{3} \frac{V_c^2}{\Delta} < 0, \quad N'_T = 2 \frac{V_c^2}{\Delta} > 0. \quad (46)$$

Thus, E_T can again be written as in Eq. (41) with α' given by Eq. (42) and $\beta' = 0$. Consequently, the vibronic coupling between a T_{2g} and an E_g level does not modify in lowest order the situation described in Sec. II.

E. Coupling to a T_{1g} level

The Hamiltonian describing the interlevel coupling is

$$\mathcal{H}_c = \begin{pmatrix} \sqrt{3}g_\theta^c + g_\epsilon^c & -g_\xi^c & g_\eta^c \\ g_\xi^c & -\sqrt{3}g_\theta^c + g_\epsilon^c & -g_\zeta^c \\ -g_\eta^c & g_\xi^c & -2g_\epsilon^c \end{pmatrix}, \quad (47)$$

where the columns correspond to $|x\rangle$, $|y\rangle$, and $|z\rangle$. Two different linear interlevel vibronic coupling constants will now contribute since \mathcal{H}_c involves terms containing both e_g and t_{2g} vibrational modes. We define V_c^t and V_c^e by $g_i^c = V_c^e Q_i$ ($i = \theta, \epsilon$) and $g_j^c = V_c^t Q_j$ ($j = \xi, \eta, \zeta$). The results of the $T_{2g} + T_{1g}$ coupling are the two effective force constants $k'_E = k_E - 4(V_c^e)^2/\Delta$ and $k'_T = k_T - 4(V_c^t)^2/\Delta$, and the four effective nonlinear vibronic coupling constants

$$N'_1 = \frac{1}{6} \frac{(V'_c)^2}{\Delta} > 0, \quad N'_2 = -\sqrt{3} \frac{V'_c V'_c}{\Delta}, \quad (48)$$

$$N'_T = \frac{(V'_c)^2}{\Delta} > 0, \quad N'_E = -\frac{(V'_c)^2}{\Delta} < 0. \quad (49)$$

The function to be minimized has once more the same form [Eq. (41)], with

$$\alpha' = 2 \left[\frac{V_E^2}{k_E} - \frac{V_T^2}{k_T} \right] - \frac{4}{\Delta} \left[\frac{V'_c V_E}{k_E} - \frac{V'_c V_T}{k_T} \right]^2, \quad (50)$$

$$\beta' = \frac{36}{\Delta} \left[\frac{V'_c V_E}{k_E} - \frac{V'_c V_T}{k_T} \right]^2 > 0. \quad (51)$$

Since β' is always positive, the possible minima are $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$, and coexisting $\langle 111 \rangle$ with $\langle 110 \rangle$. In addition, α' is more negative than without interlevel coupling. The conditions for having orthorhombic distortions [Eq. (26)] are

$$-\frac{6}{\Delta} \left[\frac{V'_c V_E}{k_E} - \frac{V'_c V_T}{k_T} \right]^2 < \frac{V_E^2}{k_E} - \frac{V_T^2}{k_T} < \frac{2}{\Delta} \left[\frac{V'_c V_E}{k_E} - \frac{V'_c V_T}{k_T} \right]^2, \quad (52)$$

which are always satisfied for comparable couplings to e_g and t_{2g} vibrational modes. The conditions for coexisting trigonal and orthorhombic minima can be obtained from Eq. (27).

F. Coupling to another T_{2g} level

The last possibility of interlevel coupling in O_h symmetry is that of two T_{2g} levels. The coupling is described by

$$\mathcal{H}_c = \begin{pmatrix} -g_\theta^c + \sqrt{3}g_\epsilon^c & g_\xi^c & g_\eta^c \\ g_\xi^c & -g_\theta^c - \sqrt{3}g_\epsilon^c & g_\xi^c \\ g_\eta^c & g_\xi^c & 2g_\theta^c \end{pmatrix}, \quad (53)$$

where the columns correspond to $|\xi\rangle$, $|\eta\rangle$, and $|\zeta\rangle$. Following the same steps as before, we obtain $k'_E = k_E - 4(V'_c)^2/\Delta$, $k'_T = k_T - 4(V'_c)^2/3\Delta$, and

$$N'_1 = \frac{1}{6} \frac{(V'_c)^2}{\Delta} > 0, \quad N'_2 = \frac{V'_c V'_c}{\Delta}, \quad (54)$$

$$N'_T = -\frac{(V'_c)^2}{\Delta} < 0, \quad N'_E = \frac{(V'_c)^2}{\Delta} > 0. \quad (55)$$

Thus, E_T has the form given by Eq. (41) with

$$\alpha' = 2 \left[\frac{V_E^2}{k_E} - \frac{V_T^2}{k_T} \right] + \frac{4}{\sqrt{3}\Delta} \left[5 \frac{V'_c V_E}{k_E} + \sqrt{3} \frac{V'_c V_T}{k_T} \right] \times \left[\sqrt{3} \frac{V'_c V_E}{k_E} - \frac{V'_c V_T}{k_T} \right], \quad (56)$$

$$\beta' = -\frac{12}{\Delta} \left[\sqrt{3} \frac{V'_c V_E}{k_E} - \frac{V'_c V_T}{k_T} \right]^2 < 0. \quad (57)$$

As in the $T_{2g} + A_{1g}$ case, β' is always negative, which restricts the possible minima of the APE to tetragonal, tri-

gonal, and coexisting tetragonal with trigonal. In particular, $\langle 111 \rangle$ and $\langle 100 \rangle$ minima coexist if the conditions given by Eq. (29) are fulfilled.

G. Discussion

The effect of interlevel vibronic coupling up to a second-order perturbation theory on the linear $T_{2g} \otimes (e_g + t_{2g})$ problem is to introduce terms formally analogous to nonlinear coupling terms in the single-level problem. We have checked that, in third-order perturbation theory, the contributions of interlevel coupling are analogous to anharmonic terms and cubic nonlinearities. Therefore, as was the case in Sec. II, interlevel vibronic coupling between levels which are moderately well separated can produce orthorhombic or coexisting inequivalent minima only for comparable values of the linear Jahn-Teller stabilization energies for e_g and t_{2g} vibrational modes.

Up to second order in perturbation theory, coupling to an A_{2g} or an E_g level has no effect on the system. However, coexisting $\langle 111 \rangle$ and $\langle 100 \rangle$ minima of the APE can be realized if the perturbing level is of A_{1g} or T_{2g} symmetry, and linear vibronic coupling to a T_{1g} level may result in orthorhombic distortions (or even in coexisting $\langle 111 \rangle$ and $\langle 110 \rangle$ minima of the APE) for comparable values of V_E^2/k_E and V_T^2/k_T [see Eq. (52)]. It should be noted that in the case of an excited T_{2g} level vibronically coupled to a lower-lying level, the difference in energy Δ is negative. In this case, the discussion of the various possible couplings is a straightforward extension of that given above for a T_{2g} ground state.

IV. INDUCED LINEAR COUPLING TO OTHER VIBRATIONAL MODES

We have considered so far only the collective coordinates Q_θ , Q_ϵ , Q_ξ , Q_η , and Q_ζ which yield linear vibronic couplings. If there is a large linear coupling to these modes, then the minima of the APE occur for values of some of the coordinates which are far removed from zero. Consequently, terms in the vibronic Hamiltonian which are linear in other modes and linear or quadratic in the strongly coupled e_g and t_{2g} modes, can be quite important and result in an induced linear vibronic coupling of the otherwise uncoupled modes. Therefore, we investigated also whether this induced linear coupling can produce orthorhombic or coexisting inequivalent minima.

As in Sec. II, we consider an isolated T_{2g} orbital level, assume that the leading terms are the two linear vibronic coupling constants to e_g and t_{2g} vibrational modes, and investigate the effects of induced linear coupling to vibrational modes of a_{1g} , a_{2g} , e_g , t_{1g} , and t_{2g} symmetries (odd modes give no linear coupling). These calculations are reasonably straightforward, but the combinations of the parameters appearing in the resulting APE are complicated, concealing their physical meaning. Therefore, we shall restrict ourselves to qualitative remarks after discussing an example in some detail.

We consider first a T_{2g} orbital state coupled to a_{1g} (Q_1), e_g (Q_θ, Q_ϵ), and t_{2g} (Q_ξ, Q_η, Q_ζ) vibrational modes.

The general form for the stationary points of the APE is given by Eq. (15) with

$$g_1 = \frac{1}{2}k_E(Q_\theta^2 + Q_\epsilon^2) + \frac{1}{2}k_T(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2) + \frac{1}{2}k_1Q_1^2 + A_1Q_1(Q_\theta^2 + Q_\epsilon^2) + A_2Q_1(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2) + \dots, \quad (58)$$

$$g_i = \frac{1}{\sqrt{3}}V_EQ_i + N_1Q_1Q_i + \dots, \quad i = \theta, \epsilon \quad (59)$$

$$g_j = V_TQ_j + N_2Q_1Q_j + \dots, \quad j = \xi, \eta, \zeta \quad (60)$$

where the terms involving A_1 , A_2 , N_1 , and N_2 represent the induced linear couplings. The minima of E_T [Eq. (15)] can be calculated iteratively. In first order, we obtain

$$E_T = 2 \left[\frac{V_E^2}{k_E} - \frac{V_T^2}{k_T} \right] f_4 + \alpha f_4 + \gamma f_4^2, \quad (61)$$

where α and γ , which both contain combinations of only quadratic and cross terms in A_1 , A_2 , N_1 , N_2 , can be independently positive or negative. The function f_4 is given by Eq. (19). For large values of V_E^2/k_E (V_T^2/k_T) tetragonal (trigonal) distortions occur. For other values of the linear vibronic coupling constants, the stationary point of Eq. (61) contain complicated sets of continuous minima which extend, e.g., from $\langle ll n \rangle$ to $\langle lm 0 \rangle$ through $\langle lmn \rangle$. However, $\langle 110 \rangle$ stationary points are never absolute minima of the APE. This result is in agreement with a previous study of the $T_{2g} \otimes (a_{1g} + e_g + t_{2g})$ problem.⁷⁰ In the case of $e_g + t_{2g} + a_{2g}$ vibrational modes, the lowest-order correction is zero. In the $T_{2g} \otimes (e_g + t_{2g} + t_{1g})$ case, E_T is given by

$$E_T = 2 \left[\frac{V_E^2}{k_E} - \frac{V_T^2}{k_T} \right] f_4 - A^2(f_4 + 3f_6 - 4f_4^2), \quad (62)$$

where A depends linearly on the constants for the terms which involve the t_{1g} vibrational modes. If the first term dominates, tetragonal or trigonal distortions occur. When A^2 and $2(V_E^2/k_E - V_T^2/k_T)$ are comparable in magnitude, the minima are monoclinic corresponding to $\langle ll n \rangle$ distortions. The direction of the minima varies continuously from $\langle 001 \rangle$ to $\langle 111 \rangle$ as $2(V_E^2/k_E - V_T^2/k_T)$ varies from large and positive to large and negative. Orthorhombic ($\langle 110 \rangle$) distortions never correspond to minima of Eq. (62).

In both the $e_g + e'_g + t_{2g}$ and $e_g + t_{2g} + t'_{2g}$ cases it is more questionable to neglect the nonlinear vibronic coupling terms and anharmonicities in each mode while including cross terms with the primed mode as we did above. Clearly, if only the harmonic terms are included in g_1 [Eq. (7)] and the linear vibronic coupling terms in g_θ to g_ζ [Eqs. (8)–(12)], E_T will have the form αf_4 with α increased (decreased) if e'_g (t'_{2g}) modes are included. If bilinear terms are added (i.e., terms linear in the primed mode and linear or quadratic in the unprimed ones), they behave in a comparable way to nonlinear vibronic coupling terms and anharmonicities in the single-mode problem (Sec. II). In first order in the coefficients of the bilinear terms, E_T contains the additional term βf_6 , and in

second order the term γf_4^2 . However, the latter contribution also appears if the approach developed in Sec. II is extended to include higher-order contributions in the N_i and A_i [Eqs. (7)–(12)] or cubic nonlinear couplings and quartic anharmonicities.

Thus, the addition of an induced linear coupling to the $T_{2g} \otimes (e_g + t_{2g})$ problem complicates the analysis without enhancing the possibility of orthorhombic distortions. It should be noted that in the $e_g + t_{2g} + a_{1g}$ and $e_g + t_{2g} + t_{1g}$ cases, the corrections to the single-mode problem [Eqs. (61) and (62)] involve the squares (or cross terms) of the amplitudes for bilinear vibronic coupling. The lowest-order corrections due to a_{2g} vibrational modes are zero. Finally, the effect of two e_g or two t_{2g} modes can be simulated by effective nonlinear vibronic terms or effective anharmonicities in the one-mode problem (Sec. II). These results confirm the validity of the single-mode approximation, which is generally assumed when discussing the static Jahn-Teller effect.

V. APE WITH SPIN-ORBIT COUPLING TO A SPIN OF $\frac{1}{2}$

In Secs. II–IV, the minima of the APE have been determined using the method of Öpik and Pryce⁴⁸ which provides a simple way to investigate the various stationary points of the APE. However, when spin-orbit coupling is included in the problem, the wave function [Eq. (14)] is spin dependent and the method becomes less straightforward to use. In the case of a spin of $\frac{1}{2}$, the Hamiltonian is given by the 6×6 matrix:

$$\mathcal{H}_{s.o.} = \mathcal{H}_T \otimes \mathcal{I}_2 + 2\lambda \mathcal{L} \otimes \mathcal{S}, \quad (63)$$

where \mathcal{H}_T is the vibronic Hamiltonian [Eq. (13)], \mathcal{I}_2 is the 2×2 identity matrix, the orbital operators \mathcal{L} are given by Eq. (5), and $\mathcal{S} = \frac{1}{2}\sigma$, where σ are the Pauli matrices. The eigenvalues of $\mathcal{H}_{s.o.}$ are the solutions of a sixth-order characteristic equation where each eigenvalue is doubly degenerate (Kramers degeneracy). Since this degeneracy cannot be removed by a Jahn-Teller effect, we shall continue to talk about triplets, doublets, and singlets, although they are actually sextets, quartets, and doublets. The eigenvalues of this problem have been calculated for tetragonal ($Q_\epsilon = Q_\xi = Q_\eta = Q_\zeta = 0$) and trigonal ($Q_\theta = Q_\epsilon = 0$, $|Q_\xi| = |Q_\eta| = |Q_\zeta|$) distortions in the linear vibronic coupling case.⁴⁸ However, they can also be calculated in the general case and are given by

$$E_i = g_1 - 2(p^2 + \lambda^2)^{1/2} \sin \alpha_i, \quad (64)$$

where the three values of α_i are determined from

$$\sin(3\alpha) = \frac{q^3 + \lambda^3}{(p^2 + \lambda^2)^{3/2}}. \quad (65)$$

The functions p and q are combinations of the functions g_i [see Eqs. (7)–(12)] and contain all the linear and nonlinear vibronic coupling constants

$$p^2 = g_\theta^2 + g_\epsilon^2 + \frac{1}{3}(g_\xi^2 + g_\eta^2 + g_\zeta^2), \quad (66)$$

$$q^3 = g_\theta(g_\theta^2 - 3g_\epsilon^2) + g_\xi g_\eta g_\zeta - \frac{1}{2}[g_\theta(2g_\xi^2 - g_\xi^2 - g_\eta^2) + \sqrt{3}g_\epsilon(g_\xi^2 - g_\eta^2)]. \quad (67)$$

It should be noticed that the potential energies E_i [Eq. (64)] are obtained from a direct diagonalization of the Hamiltonian and therefore give a general form for the APE which could be used for discussions of either dynamic or static properties, with or without spin-orbit coupling.

We studied the eigenvalue E_i [Eq. (64)] for tetragonal (e.g., $Q_\theta=Q$, $Q_\epsilon=Q_\xi=Q_\eta=Q_\zeta=0$), trigonal (e.g., $|Q_\xi|=|Q_\eta|=|Q_\zeta|=Q$, $Q_\theta=Q_\epsilon=0$), and orthorhombic (e.g., $Q_\theta, Q_\xi \neq 0$, $Q_\xi=Q_\eta=Q_\epsilon=0$) distortions, and if only the linear vibronic coupling constants are included, orthorhombic distortions never correspond to minima of the APE. Furthermore, an expansion of E_i [Eq. (64)] for small nonlinear coupling and anharmonic terms shows that all nonlinear coupling terms [contained in the functions p and q , Eqs. (66) and (67)] are quenched by the spin-orbit coupling, whereas the harmonic and anharmonic terms [contained in g_1 , Eq. (7)] are independent of the spin-orbit coupling constant λ and therefore are not affected by the spin-orbit interaction. It is known that for $\lambda < 0$, a sufficiently large spin-orbit interaction can stabilize the symmetrical configuration, whereas this stabilization does not occur for $\lambda > 0$.^{5,48,71} This can be understood by realizing that a triplet is split by the spin-orbit coupling into a doublet and a singlet. If the spin-orbit coupling constant λ is negative, the singlet lies lower in energy and the position of the minimum is not significantly affected by a Jahn-Teller effect. On the other hand, for positive λ , the doublet lies lower and will therefore always be split by the Jahn-Teller coupling. We analyzed the APE [Eq. (64)] with linear vibronic coupling and harmonic terms and calculated the reduction of the Jahn-Teller stabilization energy

$$\Delta E_{JT}(\lambda) = E(Q_{\min}, \lambda) - E(Q=0, \lambda) \quad (68)$$

in the case of tetragonal (or trigonal) distortions. The (numerical) result is illustrated in Fig. 2. For positive λ , the expansions of Eq. (64) give

$$\Delta E_{JT}(\lambda) = \lambda - \frac{2V_E^2}{3k_E} + \lambda^2 \frac{k_E}{2V_E^2} \quad \text{if } \lambda \ll |VQ|, \quad (69)$$

$$\Delta E_{JT}(\lambda) = -\frac{1}{2} \frac{V_E^2}{3k_E - 4V_E^2/3\lambda} \quad \text{if } \lambda \gg |VQ|, \quad (70)$$

which shows that for λ large and positive, the Jahn-Teller stabilization energy is reduced by 75%, but the minimum of the APE corresponds to a finite distortion for any value of the spin-orbit coupling constant λ . The limit $\Delta E_{JT}(\lambda \rightarrow \infty)$ [Eq. (70)] is the dotted line in Fig. 2. On the other hand, for λ negative, the expansion for small $|\lambda|$ is

$$\Delta E_{JT}(\lambda) = -2\lambda - \frac{2V_E^2}{3k_E} + \lambda^2 \frac{k_E}{2V_E^2}, \quad (71)$$

whereas for λ large and negative, we obtain two solutions. The minimum of the APE corresponds to $\Delta E_{JT}=0$ if $|\lambda| \geq |\lambda_{\max}|$ and $\Delta E_{JT} < 0$ for $|\lambda| < |\lambda_{\max}|$, where, in lowest order, $\lambda_{\max} \approx -2V_E^2/9k_E$ [the actual value of λ_{\max} , obtained numerically, is about $-0.6V_E^2(k_E)$]. However, there is no indication that spin-orbit coupling to a spin of $\frac{1}{2}$ favors orthorhombic distortions or coexisting inequivalent minima.

VI. DISCUSSION AND CONCLUSION

An orbital triplet in cubic symmetry couples linearly only to vibrational modes of e_g and t_{2g} symmetry. If the linear coupling to e_g (t_{2g}) modes is much stronger than the linear coupling to t_{2g} (e_g) modes, tetragonal (trigonal) distortions correspond to deep minima of the APE and no small perturbation can change the symmetry of the system. Since linear vibronic coupling usually dominates in the vibronic Hamiltonian, a perturbation to linear coupling can lower the symmetry only if the trigonal and tetragonal linear Jahn-Teller stabilization energies are comparable. It could be that in an unusual system one of the higher-order terms in the vibronic Hamiltonian or perhaps even interlevel vibronic coupling turns out to be coincidentally very large. However, there should be no reason for this to be common. The rather frequent occurrences of orthorhombic distortions and of coexisting inequivalent minima of the APE for orbital triplets in cubic symmetry led us to investigate systematically the possible perturbations to linear vibronic coupling in the case where e_g and t_{2g} modes produce comparable energy reductions, with the assumption that linear vibronic coupling dominates. The mechanisms investigated are nonlinear vibronic coupling and anharmonicity (Sec. II), interlevel vibronic coupling (Sec. III), induced linear vibronic coupling (involving vibrational modes which do not otherwise have a linear coupling, Sec. IV), and spin-orbit coupling (Sec. V). Spin-orbit coupling was analyzed exactly, but only for a spin of $\frac{1}{2}$, and all the other effects were treated as perturbations to the linear coupling problem using the Opik and Pryce method.⁴⁸ Each mechanism (except spin-orbit coupling) predicts orthorhombic distortions for some values of the parameters, as well as the coexistence of trigonal and tetragonal or trigonal and orthorhombic minima. The coexistence of tetragonal and

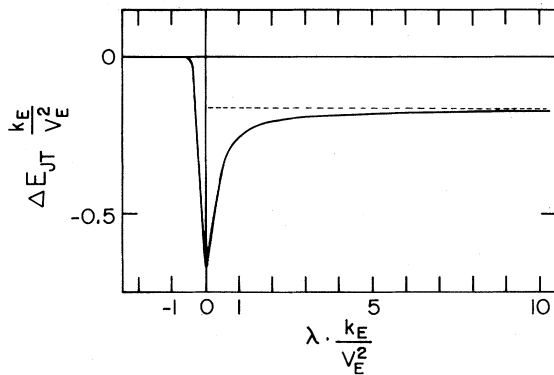


FIG. 2. Quenching of the Jahn-Teller stabilization energy [Eq. (68)] as a function of the spin-orbit coupling constant λ for tetragonal (or trigonal) distortions. As shown in Eq. (70), $\Delta E_{JT}(\lambda \rightarrow \infty) = -V_E^2/6k_E$ (dashed line), and $\Delta E_{JT}=0$ for $\lambda < 0$ and $|\lambda| \geq |\lambda_{\max}|$ (see text).

orthorhombic minima does not occur in lowest-order perturbation theory for nonlinear coupling and anharmonicity or for interlevel coupling.

The results can be summarized as follows.

The effect of nonlinear coupling and anharmonic terms in the vibronic Hamiltonian is the best candidate to explain orthorhombic and coexisting minima of $\langle 100 \rangle$ and $\langle 111 \rangle$ symmetry. For comparable values of V_E^2/k_E and V_T^2/k_T , Eqs. (22) and (23) show that the parameters α and β are very likely to have opposite signs with $|\beta| > |\alpha|$. An inspection of Fig. 1 shows then that orthorhombic distortions may occur for $\alpha < 0$, and coexisting minima of $\langle 100 \rangle$ and $\langle 111 \rangle$ symmetry for $\alpha > 0$. In lowest order in the nonlinear vibronic coupling constants N_i and anharmonic terms A_i , the coexistence of $\langle 111 \rangle$ and $\langle 110 \rangle$ minima could occur, but for a restricted range of parameters only (regions 2 and 3 in Fig. 1). The coexistence of $\langle 100 \rangle$ and $\langle 110 \rangle$ minima cannot be realized unless even higher-order effects are included.^{57-59,61}

The lowest-order effects of interlevel coupling can be expressed in terms of effective nonlinear vibronic coupling constants in the vibronic Hamiltonian. Only coupling of the T_{2g} level to an excited T_{1g} level favors $\langle 110 \rangle$ minima, whereas coupling to any other level does not. There is nothing about the cases of observed $\langle 110 \rangle$ minima which favors interlevel coupling and particularly not with a T_{1g} level. Coexisting tetragonal and trigonal minima could result from $T_{2g} + A_{1g}$ or $T_{2g} + T_{2g}$ interlevel coupling. However, this does not seem to be a reasonable explanation of the double A band observed for Tl^+ -like centers in the alkali halides since the excited states do not contain these levels. Rather, it is believed³⁷ that the double A band is due to the combined effects of nonlinear coupling and anharmonic terms in the vibronic Hamiltonian (see, e.g., Refs. 58 and 61), of spin-orbit coupling in the $a_{1g}t_{1u}$ electronic configuration^{38,57-59,62,65} and of contributions of a_{1g} vibrational modes.⁷⁰

Induced linear coupling, involving vibrational modes which do not couple linearly unless the Jahn-Teller active e_g or t_{2g} modes are significantly displaced from zero, generally gives complicated results. In both the $T_{2g} \otimes (e_g + t_{2g} + a_{1g})$ and $T_{2g} \otimes (e_g + t_{2g} + t_{1g})$ cases, the lowest-order correction due to bilinear vibronic coupling involves only the squares and cross terms of the coupling constants, and the minima of the APE include more complicated types of minima (e.g., monoclinic distortions) but not orthorhombic distortions. In the case of induced linear coupling to a_{2g} vibrational modes, the correction involves even higher-order coefficients. Finally, the inclusion of two e_g (or two t_{2g}) vibrational modes adds terms to the APE which are similar to nonlinear vibronic coupling terms and anharmonicities in the single-mode problem. Therefore, there does not appear to be any situation which would indicate that the single-mode approximation should be extended to include more vibrational modes.

We discussed the effects of spin-orbit coupling to a spin of $\frac{1}{2}$. The general form of the APE was obtained by direct diagonalization of the vibronic Hamiltonian. It has been shown that linear and nonlinear vibronic coupling is quenched by the spin-orbit interaction (although different-

ly for positive and negative λ) and that the harmonic and anharmonic terms are not affected by the spin-orbit coupling. If only the harmonic terms and the linear vibronic coupling constants are included in the Hamiltonian with spin-orbit coupling to a spin of $\frac{1}{2}$, orthorhombic distortions never correspond to minima of the APE. As to whether a spin larger than $\frac{1}{2}$ [it is 2 for Cr^{2+} (Refs. 16, 28, 29, and 31)] would permit spin-orbit coupling to increase the chances of orthorhombic distortions cannot be said with certainty, but we cannot suggest why it should.

The main approximation contained in this paper is the assumption that the harmonic elastic energy and the linear vibronic coupling terms are the largest ones in the vibronic Hamiltonian, so that any other contribution can be treated using perturbation theory (except spin-orbit coupling). It is quite evident that a perturbation approach is reasonable for the systems observed, both in the cases of interlevel coupling and induced linear coupling. It may be less obvious that nonlinear coupling and/or anharmonicity can be treated perturbatively. If these terms are not perturbations to linear coupling, is it reasonable to neglect even higher-order terms such as cubic nonlinear coupling or quartic anharmonicity? Clearly, such a problem is hopelessly complicated. However, it has always appeared that the linear coupling dominates in the Jahn-Teller effect, and we believe it to be the case here as well.

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APPENDIX: EFFECTIVE VIBRONIC HAMILTONIAN FOR MULTILEVEL COUPLING

In this analysis, we follow an approach first introduced by Pryce.⁷² We consider several levels, possibly degenerate, lying close to each other. The Schrödinger equation for the full system is

$$\mathcal{H}|\Psi\rangle = E|\Psi\rangle, \quad (A1)$$

where

$$\mathcal{H} = \mathcal{H}_{el} + \mathcal{H}_1 = \mathcal{H}_{el} + \mathcal{H}_0 + \mathcal{H}_c + \mathcal{H}', \quad (A2)$$

$$|\Psi\rangle = |0\rangle + \sum_{n \neq 0} |n\rangle. \quad (A3)$$

The eigenstates of the unperturbed system, described by \mathcal{H}_{el} , are $|0\rangle, \dots, |n\rangle, \dots$, with energies E_0, \dots, E_n, \dots , and each set $\{|n\rangle\}$ is a linear manifold of dimension equal to the degeneracy of the level considered. The perturbation Hamiltonian \mathcal{H}_1 contains \mathcal{H}_0 , which operates only within the manifold $|0\rangle$, \mathcal{H}_c which operates only between the levels $|0\rangle$ and $|n\rangle$, and \mathcal{H}' , which operates only within the manifold $|n\rangle$. Equations (A2) and (A3) can be inserted into Eq. (A1) with the result

$$(E_0 - E + \mathcal{H}_1)|0\rangle + \sum_{n \neq 0} (E_n - E + \mathcal{H}_1)|n\rangle = 0. \quad (A4)$$

If $P_n = |n\rangle\langle n|$, the projection operator of the manifold $|n\rangle$, is applied to Eq. (A4), one obtains

$$|n\rangle = -\frac{P_n \mathcal{H}_1 |0\rangle}{E_n - E} - \sum_{m \neq 0} \frac{P_n \mathcal{H}_1 |m\rangle}{E_n - E}. \quad (\text{A5})$$

Solving iteratively, one obtains

$$|n\rangle = T_n |0\rangle, \quad (\text{A6})$$

where

$$T_n = -\frac{P_n \mathcal{H}_1}{E_n - E} + \sum_{m \neq 0} \frac{P_n \mathcal{H}_1 P_m \mathcal{H}_1}{(E_n - E)(E_m - E)} - \sum_{l \neq 0} \sum_{m \neq 0} \frac{P_n \mathcal{H}_1 P_m \mathcal{H}_1 P_l \mathcal{H}_1}{(E_n - E)(E_m - E)(E_l - E)} + \dots \quad (\text{A7})$$

If we multiply now Eq. (A4) on each side by P_0 , the projection operator of $|0\rangle$, and use Eqs. (A5) and (A6), we obtain

$$T_n \approx -\frac{P_n \mathcal{H}_1}{\Delta_n} \left[1 - \frac{\epsilon}{\Delta_n} + \frac{\epsilon^2}{\Delta_n^2} + \dots \right] \left[1 - \sum_{m \neq 0} \frac{P_m \mathcal{H}_1}{\Delta_m} \left[1 - \frac{\epsilon}{\Delta_m} + \frac{\epsilon^2}{\Delta_m^2} - \dots \right] \right] + \sum_{l \neq 0} \sum_{m \neq 0} \frac{P_m \mathcal{H}_1 P_l \mathcal{H}_1}{\Delta_m \Delta_l} \left[1 - \frac{\epsilon}{\Delta_l} + \frac{\epsilon^2}{\Delta_l^2} - \dots \right] \left[1 - \frac{\epsilon}{\Delta_m} + \frac{\epsilon^2}{\Delta_m^2} - \dots \right] + \dots \quad (\text{A10})$$

If Eqs. (A8) and (A10) are combined to eliminate the remaining unknown ϵ , we obtain the effective Hamiltonian

$$\mathcal{H}_{\text{eff}} |0\rangle = E |0\rangle, \quad (\text{A11})$$

where, if the zero of the energy is chosen to be the ground-state energy of the unperturbed system,

$$\mathcal{H}_{\text{eff}} = \mathcal{H}_0 - \sum_{n \neq 0} \frac{\mathcal{H}_c |n\rangle \langle n| \mathcal{H}_c}{\Delta_n} - \sum_{n \neq 0} \frac{\mathcal{H}_0 |0\rangle \langle 0| \mathcal{H}_c |n\rangle \langle n| \mathcal{H}_c}{\Delta_n^2} + \sum_{m \neq 0} \sum_{n \neq 0} \frac{\mathcal{H}_c |n\rangle \langle n| \mathcal{H}' |m\rangle \langle m| \mathcal{H}_c}{\Delta_n \Delta_m} + \mathcal{O} \left(\frac{1}{\Delta^3} \right). \quad (\text{A12})$$

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$$\left[(E_0 - E)P_0 + P_0 \mathcal{H}_1 P_0 + \sum_{n \neq 0} P_0 \mathcal{H}_1 T_n P_0 \right] |0\rangle = 0. \quad (\text{A8})$$

We now expand

$$\frac{1}{E_n - E} = \frac{1}{(E_n - E_0) + (E_0 - E)} \approx \frac{1}{\Delta_n} - \frac{\epsilon}{\Delta_n^2} + \frac{\epsilon^2}{\Delta_n^3} - \dots, \quad (\text{A9})$$

where $\epsilon = E_0 - E$ is the difference between the ground-state energy of the unperturbed system and the exact ground-state energy, and $\Delta_n = E_n - E_0$ is the difference in energy between the lowest level and the level $|n\rangle$ without interlevel coupling. Using Eq. (A9), the operator T_n becomes

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