Coexistence of tetragonal with orthorhombic or trigonal Jahn-Teller distortions in an O_h complex. II. Effect of anharmonicity

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The linear Jahn-Teller interaction of a triply degenerate T electronic term in an O_h complex with ϵ_g and τ_{2g} modes has been considered with the inclusion of anharmonic interatomic potential terms. The anharmonic terms allow the coexistence of stable distortions of different symmetry. The effect of the totally symmetric coordinate Q_1 has also been considered and its effects discussed with respect to recent experimental results.

I. INTRODUCTION

The static Jahn-Teller effect (JTE) on a triply degenerate state T of an O_h complex interacting with ϵ_g and τ_{2g} vibrational modes has been investigated both in the linear[1–4] and quadratic[5–8] approximations. As known, in the linear case tetragonal or trigonal stable distortions are possible according to the relative magnitude of the coupling constants b (ϵ_g modes) and c (τ_{2g} modes); moreover, orthorhombic stationary points exist on the lower-energy surface, but they are never minima.[2]

Recently, the analysis of Refs. 1–4 has been extended to the quadratic JTE; in this framework it was shown that orthorhombic points may become minima[5,6] and that different kinds of minima are allowed to coexist for suitable values of the quadratic coupling constants (Paper I).[7,8] On the other hand, as the second-order Jahn-Teller coupling is estimated to be of the same order of magnitude as anharmonic interatomic potential terms,[9,10] it would be better to take the two effects into account together; but such a complete treatment is not easily carried out owing to its mathematical complexity. Therefore, in Ref. 7 and in Paper I, we dealt with the quadratic JTE alone, while in the present paper the effect of cubic anharmonicity on the $T\times(\epsilon_g+\tau_{2g})$ Jahn-Teller problem is considered.

In what follows we show that the linear JTE together with anharmonicity may cause (a) the orthorhombic points of Refs. 2 and 3 to become minima (as suggested previously by Wysling and Müller[3] and Englman[11]), and (b) minima of different symmetry to coexist. Thus, the inclusion of anharmonicity leads to results analogous to those obtained with the quadratic JTE.

In Sec. II the conditions for the existence of the three kinds of minima are derived; in this section the mixing of coordinates spanning different irreducible representations is neglected and constitutes the object of Sec. III, especially as regards the totally symmetric coordinate Q_1. The results are then discussed in Sec. IV.

In order to lighten the presentation, procedural and computational details already shown in Paper I are not reported here.

II. MINIMUM CONDITIONS

The electron-lattice Hamiltonian H_{e-l}, which was obtained by the procedure described in Refs. 7 and 11, is given by

$$H_{e-l}=W+V=-(2b/\sqrt{3})(Q_2\mathcal{E}_\epsilon+Q_3\mathcal{E}_\theta)-c(Q_4\mathcal{T}_\xi+Q_5\mathcal{T}_\eta+Q_6\mathcal{T}_\zeta)+[\tfrac{1}{2}K_\epsilon(Q_2^2+Q_3^2)+\tfrac{1}{2}K_\tau(Q_4^2+Q_5^2+Q_6^2)-\tfrac{1}{6}K'_\epsilon(3Q_2^2Q_3-Q_3^3)-\tfrac{1}{6}K'_\tau Q_4Q_5Q_6]\mathcal{I}\,, \qquad (1)$$

where W is the Jahn-Teller Hamiltonian, V is the potential energy, K'_ϵ and K'_τ are the anharmonic coupling constants, and the other symbols have been defined in Paper I. In writing Eq. (1), we assume that odd vibrational modes may be neglected completely (this assumption will be retained throughout the paper); we have also omitted cubic terms involving coordinates of different symmetry and any term containing Q_1. The latter will be considered in Sec. III.

According to the Hellmann-Feynman theorem,[12,2] in order that a given nuclear configuration be stable, the expectation value of the generalized force must vanish; that is,

$$\langle a|\frac{\partial W}{\partial Q_i}|a\rangle+\frac{\partial V}{\partial Q_i}=0 \quad (i=1,\ldots,6)\ , \tag{2}$$

where $|a\rangle$ is the electronic state, $|a\rangle=a_1|x\rangle+a_2|y\rangle+a_3|z\rangle$, and obeys the eigenvalue equation

$$H_{e\text{-}t}|a\rangle=E|a\rangle\ .$$

Following the procedure of Paper I, from Eqs. (2) we find for the coordinates (Q_i^0) and energies (E_i^0) of the stationary points.

A. Tetragonal distortions, $(a_1, a_2, a_3)=(0,0,1)$

$$Q_2^0=Q_4^0=Q_5^0=Q_6^0=0,\quad Q_3^0=-(K_\epsilon/K_\epsilon')[1-(1-4B/K_\epsilon^2)^{1/2}],$$

$$E^0=(2b/\sqrt{3})Q_3^0+\tfrac{1}{2}K_\epsilon(Q_3^0)^2+\tfrac{1}{6}K_\epsilon'(Q_3^0)^3\ ,$$

where $B=bK_\epsilon'/\sqrt{3}$, plus two equivalent tetragonal distortions.[2] Note that for $K_\epsilon'\to 0$, $Q_3^0\to-(2b/\sqrt{3}K_\epsilon)$, that is, the value of the harmonic approximation; moreover, $Q_3=-(K_\epsilon/K_\epsilon')[1+(1-4B/K_\epsilon^2)^{1/2}]$ is also a solution of Eqs. (2) which corresponds to an energy maximum and diverges as $K_\epsilon'\to 0$. These points have no physical significance in the present context and we shall no longer consider them. Such an argument holds for trigonal and orthorhombic cases too.

B. Orthorhombic distortions, $(a_1, a_2, a_3)=(2)^{-1/2}(1,\mp 1,0)$

$$Q_2^0=Q_4^0=Q_5^0=0,\quad Q_3^0=-(K_\epsilon/K_\epsilon')[1-(1+2B/K_\epsilon^2)^{1/2}],$$

$$Q_6^0=\pm c/K_\tau\ ,$$

$$E^0=-(b/\sqrt{3})Q_3^0-c|Q_6^0|+\tfrac{1}{2}K_\epsilon(Q_3^0)^2+\tfrac{1}{2}K_\tau(Q_6^0)^2-\tfrac{1}{6}K_\epsilon'(Q_3^0)^3,$$

plus two equivalent couples of orthorhombic distortions.[2]

C. Trigonal distortions, $(a_1, a_2, a_3)=(3)^{-1/2}(1,1,1)$

$$Q_2^0=Q_3^0=0,$$

$$Q_4^0=Q_5^0=Q_6^0=Q^0=3(K_\tau/K_\tau')\,[1-(1+4C/K_\tau^2)^{1/2}]\ ,$$

$$E^0=2cQ^0+\tfrac{3}{2}K_\tau(Q^0)^2-\tfrac{1}{6}K_\tau'(Q^0)^3\ ,$$

where $C=cK_\tau'/9$, plus three equivalent trigonal distortions.[2] The stationary points are minima if arbitrary increments to the coordinates Q_i^0 result in a positive-definite increment of the energies E_i^0; by a procedure analogous to that of Paper I we obtain the following minimum conditions.

D. Tetragonal minima

$$-\tfrac{3}{4}\le B/K_\epsilon^2\le\tfrac{1}{4}\ , \tag{3}$$

$$\frac{b^2}{K_\epsilon}\frac{K_\tau}{c^2}>\frac{-2B/K_\epsilon^2}{-1+(1-4B/K_\epsilon^2)^{1/2}}\ . \tag{4}$$

E. Orthorhombic minima

$$-\tfrac{1}{2}\le B/K_\epsilon^2\le\tfrac{3}{2}\ , \tag{5}$$

$$\frac{b^2}{K_\epsilon}\frac{K_\tau}{c^2}<2-\theta,\quad \text{with } \theta=(1+2B/K_\epsilon^2)^{1/2}\ , \tag{6}$$

$$-\tfrac{2}{3}<C/K_\tau^2<\tfrac{2}{3}\ , \tag{7}$$

$$\frac{b^2}{K_\epsilon}\frac{K_\tau}{c^2}>\frac{1}{(K_\epsilon^2/B)(\theta-1)}\left(\frac{2}{1+\frac{3}{2}(C/K_\tau^2)}-1\right)\ . \tag{8}$$

F. Trigonal minima

$$-\tfrac{1}{4}\le C/K_\tau^2\le\tfrac{3}{4}\ , \tag{9}$$

$$\frac{b^2}{K_\epsilon}\frac{K_\tau}{c^2}<\frac{3(\phi-1)}{3-\phi}\left(\frac{1}{2C^2/K_\tau^2}-\frac{3(\phi-1)}{4C^2/K_\tau^2}-1\right)\ ,$$

$$\text{with } \phi=(1+4C/K_\tau^2)^{1/2}\ . \tag{10}$$

The boundary lines corresponding to conditions 3–10 are displayed in Fig. 1, where the encircled numbers refer to the relative conditions in the text. In Fig. 1 the horizontally shaded area corresponds to tetragonal minima (Te), vertical shading to orthorhombic minima (Or), and oblique shading to trigonal minima (Tr). In the checkered areas the coexistences Te-Or and Tr-Or are allowed. As regards tetragonal and trigonal areas, Figs. 1(a) and 1(b) are not related by any common condition and an inspection of these figures shows that the Te-Tr coexistence is also possible. An example will better visualize this point: Let us consider the set of parameters $b=c=K_\epsilon=K_\tau=1$ which, in the harmonic approximation, result in a continuum of minima.[13] It is sufficient to introduce a small positive value of B/K_ϵ^2 and a corresponding negative value of C/K_τ^2 for the coexistence Te-Tr to be possible. Figure 2 shows this coexistence for $B/K_\epsilon^2=0.1$ and $C/K_\tau^2=-0.1$. With the same parameters, by a numerical diagonalization of $H_{e\text{-}t}$ we have obtained the map of Fig. 3, where coexisting tetragonal and trigonal minima are displayed. In this figure the coordinate Q_ξ is defined as $(3)^{-1/2}Q_\xi=Q_4=Q_5=Q_6$.

III. EFFECT OF THE TOTALLY SYMMETRIC COORDINATE Q_1

As mentioned in Sec. II, the Hamiltonian (1) is not complete since the following terms should be added to the potential energy:

$$H'(Q_1,Q_j)+H'(Q_j)=\{(aQ_1+\tfrac{1}{2}K_\alpha Q_1^2)-\tfrac{1}{6}Q_1[K_\alpha' Q_1^2+K_{\alpha\epsilon}'(Q_2^2+Q_3^2)+K_{\alpha\tau}'(Q_4^2+Q_5^2+Q_6^2)]\}\mathcal{I}$$
$$-\tfrac{1}{6}K_{\epsilon\tau}'\{(Q_2+Q_3)(Q_4^2+Q_5^2)+Q_3Q_6^2\}\mathcal{I}\quad (j=2,\ldots,6)\ . \tag{11}$$

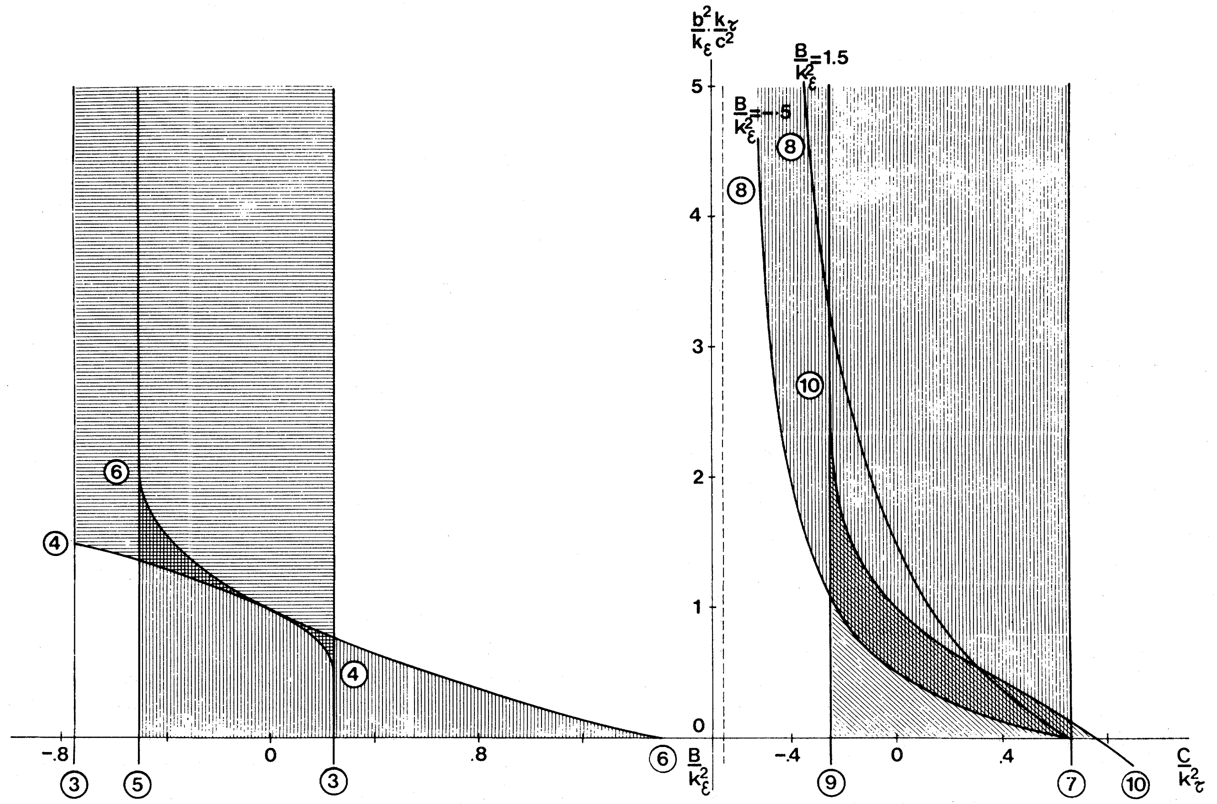

FIG. 1. (a) Domains for the existence of tetragonal (horizontal shading) and orthorhombic (vertical shading) minima, in the plane b^2K_ϵ/c^2K_τ vs B/K_ϵ^2. (b) Domains for the existence of trigonal (oblique shading) and orthorhombic (vertical shading) minima, in the plane b^2K_ϵ/c^2K_τ vs C/K_τ^2. In the checkered areas different kinds of minima coexist. The encircled numbers refer to the corresponding conditions in the text. The curve 8 depends on the value of B/K_ϵ^2, and has been drawn for the two limiting values $B/K_\epsilon^2 = -0.5$ and 1.5.

In Eq. (11) the meaning of the coupling constants a, K_α, K'_α, $K'_{\alpha\epsilon}$, $K'_{\alpha\tau}$, $K'_{\epsilon\tau}$ is self-evident. Here we shall consider in some detail only the terms containing Q_1, because of their possible relevance to some experimental results to be discussed in Sec. IV. As for the remaining terms of Eq. (11), their inclusion would not influence qualitatively the conclusions of Sec. II, although it would affect the coordinates of the orthorhombic points and the coexistence areas of Figs. 1 and 2; the Q_3Q_ξ map of Fig. 3 is practically unchanged in the neighborhood of the axes.

According to the procedure of Sec. II, the Hamiltonian $H = H_{e-l} + H'(Q_1, Q_j)$ leads to the following system for the coordinates of the tetragonal stationary point (0, 0, 1):

$$Q_2^0 = Q_4^0 = Q_5^0 = Q_6^0 = 0 \ ,$$
$$a + K_\alpha Q_1^0 - \tfrac{1}{2}K'_\alpha (Q_1^0)^2 - \tfrac{1}{6}K'_{\alpha\epsilon}(Q_3^0)^3 = 0 \ , \tag{12}$$
$$2b/\sqrt{3} + K_\epsilon Q_3^0 + \tfrac{1}{2}K'_\epsilon (Q_3^0)^2 - \tfrac{1}{3}K'_{\alpha\epsilon} Q_1^0 Q_3^0 = 0 \ ,$$

which gives

$$Q_1^0 = K_\alpha/K'_\alpha - (K_\alpha/K'_\alpha)$$
$$\times[1 - \tfrac{1}{3}(K'_{\alpha\epsilon}K'_\alpha/K_\alpha^2)(Q_3^0)^2 + (2aK'_\alpha/K_\alpha^2)]^{1/2} \ , \tag{13a}$$
$$Q_3^0 = -K_\epsilon/K'_\epsilon + \tfrac{1}{3}(K'_{\alpha\epsilon}/K'_\epsilon)Q_1^0 + (K_\epsilon/K'_\epsilon)$$
$$\times[1 + (K'_{\alpha\epsilon}/9K_\epsilon^2)(Q_1^0)^2 - (2K'_{\alpha\epsilon}/3K_\epsilon)Q_1^0 - (4bK'_\epsilon/\sqrt{3}K_\epsilon^2)]^{1/2} \ , \tag{13b}$$

where the two solutions corresponding to an energy maximum have been discarded. An exact solution of this system is cumbersome, but significant approximate results may be obtained if we assume that the cubic constants are much smaller than the elastic ones. In this case, by a power-series development of the square roots $(1 \pm x)^{1/2} \simeq 1 \pm \tfrac{1}{2}x - \tfrac{1}{8}x^2$, by substituting in (13a) for Q_3^0 its value in the harmonic approximation $[Q_3^0 = -(2b/\sqrt{3}K_\epsilon)]$, and by neglecting terms in $(Q_i^0)^3$ and $(Q_i^0)^4$, one gets

$$Q_1^0 \simeq -a/K_\alpha + a^2K'_\alpha/2K_\alpha^3 + 2b^2K'_{\alpha\epsilon}/9K_\alpha K_\epsilon^2 \ ,$$
$$Q_3^0 \simeq -2b/\sqrt{3}K_\epsilon - 2b^2K'_\epsilon/3K_\epsilon^3 \ .$$

In a similar way, one has for the orthorhombic points $(1, \pm 1, 0)$,

$$Q_2^0 = Q_4^0 = Q_5^0 = 0 \ ,$$

$$Q_1^0 \simeq -a/K_\alpha + a^2K'_\alpha/2K_\alpha^3 + b^2K'_{\alpha\epsilon}/18K_\alpha K_\epsilon^2 + c^2K'_{\alpha\tau}/6K_\alpha K_\tau^2 ,$$

$$Q_3^0 \simeq b/\sqrt{3}K_\epsilon - b^2K'_\epsilon/6K_\epsilon^3 ,$$

$$Q_6^0 \simeq \mp 3cK_\alpha/(3K_\alpha K_\tau + aK'_{\alpha\tau}) ,$$

and for the trigonal point (1, 1, 1),

$$Q_2^0 = Q_3^0 = 0 ,$$

$$Q_1^0 \simeq -a/K_\alpha + a^2K'_\alpha/2K_\alpha^3 + 2c^2K'_{\alpha\tau}/9K_\alpha K_\tau^2 ,$$

$$Q_4^0 = Q_5^0 = Q_6^0 \simeq -2c/3K_\tau + 2c^2K'_\tau/27K_\tau^3 .$$

We shall not investigate the minimum conditions, as no qualitative change is expected to occur with respect to Sec. II. We note that the $Q_2^0 \cdots Q_6^0$ coordinates of Sec. II, when $(1-4B/K_\epsilon^2)^{1/2}$, $(1+2B/K_\epsilon^2)^{1/2}$, and $(1+4C/K_\tau^2)^{1/2}$ are developed in a power series, reduce to the coordinates $Q_2^0 \cdots Q_6^0$ of this section; furthermore, the coordinates Q_1^0 of stationary points of different symmetry do not coincide because of the anharmonic terms. Thus, when minima of different symmetry coexist, they have different Q_1^0 coordinates.

IV. DISCUSSION

In the light of previous[5,6,8] and present results, it appears that Öpik and Pryce's dichotomy between tetragonal and trigonal minima depends on rather restrictive assumptions (linear Jahn-Teller effect and harmonic restoring forces) which are unlikely to be met in actual physical systems.

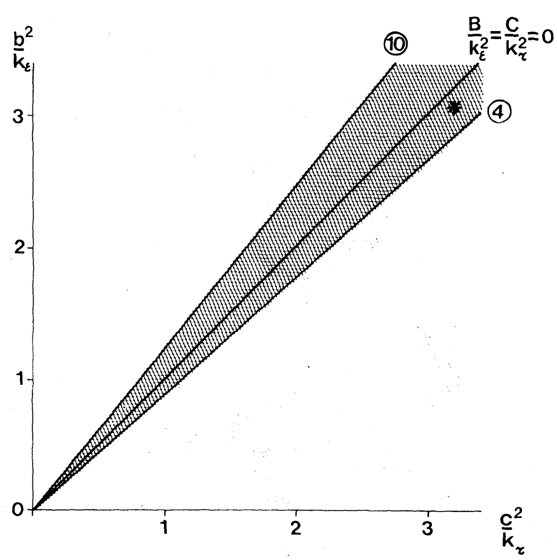

FIG. 2. Domains for the existence of tetragonal (horizontal shading) and trigonal (oblique shading) minima, in the plane b^2/K_ϵ vs c^2/K_τ. In the checkered area both kinds of minima exist. The encircled numbers refer to the corresponding conditions in the text. Curves 4 and 10 have been calculated with $B/K_\epsilon^2 = 0.1$ and $C/K_\tau^2 = -0.1$, respectively. The starred curve corresponds to the harmonic case.

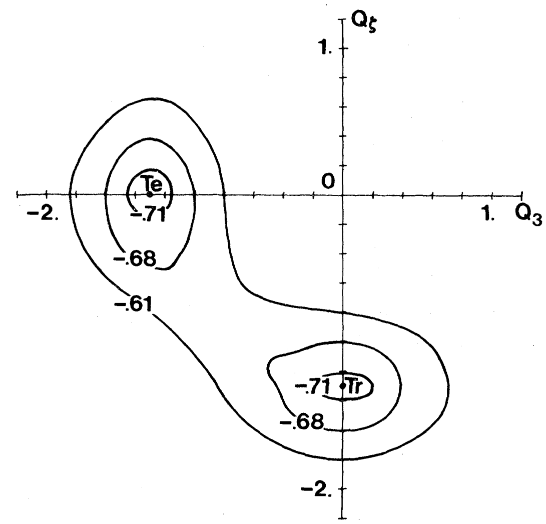

FIG. 3. Coexistence of tetragonal (Te) and trigonal (Tr) minima on the T level. The map in the Q_3Q_ζ plane is computed with $b=c=K_\epsilon=K_\tau=1$, $K'_\epsilon=0.173$, $K'_\tau=-0.9$.

The introduction of quadratic JTE or anharmonicity causes (i) the existence of orthorhombic minima, (ii) changes in the existence domains of tetragonal and trigonal minima, (iii) possible coexistence of different kinds of minima, and (iv) different kinds of minima to have different Q_1^0 coordinates.

In Paper I we have presented a model for the interpretation of the double emission excited in the A band of KI:Tl-type phosphors; the model assigns the two emissions (A_T and A_X) to coexisting minima of different symmetry; the coexistence was provided by the quadratic JTE alone. The present results reinforce our model in that both mechanisms—quadratic JTE and anharmonicity—have similar consequences when considered separately and they are reasonably expected to act in an analogous way if they were considered together.[14]

As for the totally symmetric coordinate Q_1, recent experimental results by Masunaga *et al.*[15] indicate that it plays a role in the emission process. In fact, these authors found that with increasing hydrostatic pressure, the A_T emission of KI:In becomes gradually stronger while the A_X emission tends to disappear. In this sense, increasing pressure is analogous to decreasing temperature. The pressure dependence of KI:In emissions is explained by Masunaga *et al.*[15] by the presence of two minima (stabilized by the quadratic JTE) in the Q_1 subspace, which would correspond to tetragonal and trigonal minima in the full six-dimensional space. These conclusions fit in the model we have presented in Paper I. Actually, in Paper I the coordinate Q_1 was neglected, but it is easily seen that when it is taken into account, coexisting minima of different symmetry are placed at different Q_1's. In fact, inspection of the matrix elements of the quadratic JTE, as reported in Ref. 7 shows that Q_1^0 for tetragonal and trigonal minima depend also on $b_{\alpha\epsilon}$ and $c_{\alpha\tau}$, respectively.

In the present paper we have shown that an alternative way to reach almost the same results is to include anharmonic terms which, in particular, make it possible to have minima of different symmetry with different Q_1^0's, i.e., two minima in the Q_1 subspace. This is just the scheme required in Ref. 15 in order to explain the experimental results. We also note that while the simplified mechanism suggested in Ref. 15 gives rise only to the tetragonal-trigonal coexistence, the model presented here and in Paper I also allows orthorhombic minima to coexist with other distortions.

In conclusion, apart from phosphors' luminescence, which we are mainly concerned with, it is felt that the present theoretical results would be applicable to many other physical systems because, even though the presence of a strong quadratic JTE may be questionable in some cases, anharmonic terms are, as a rule, effective. On the other hand the greater adaptability of the theory with respect to Öpik and Pryce's scheme is obtained at the expense of its incisiveness, since a larger number of parameters is introduced. As a consequence, it is difficult at the present moment to make definite previsions on particular systems, since most of the quadratic and anharmonic coupling constants are not known. One way to get an estimate of these constants seems to be the method of moments, as recently used by Nasu and Kojima.[16]

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