

Jahn-Teller effects in coexisting tetragonal and trigonal systems

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 7521

(<http://iopscience.iop.org/0953-8984/6/37/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 20:31

Please note that [terms and conditions apply](#).

Jahn–Teller effects in coexisting tetragonal and trigonal systems

Y M Liu, J L Dunn and C A Bates

Physics Department, The University, Nottingham NG7 2RD, UK

Received 14 June 1994

Abstract. The strongly coupled Jahn–Teller (JT) system is studied in which an ion in an orbital T_1 triplet state is coupled to both e and t_2 modes of vibrations of its neighbours. Such a system is usually considered to be either a $T \otimes (e + t_2)$ JT system, in which orthorhombic minima in the five-dimensional Q -space are lowest in energy, or a $T \otimes d$ system, which has a trough of lowest energy. However, it is possible also for the tetragonal and trigonal minima, usually associated with the $T \otimes e$ and $T \otimes t_2$ JT effects respectively, to coexist with very similar energies to each other (and be of overall lowest energy) when the bilinear term of the vibronic interaction is present. This situation is described in this paper. A set of vibronic ground states is obtained by mixing the symmetry-adapted vibronic T_1 ground states of the $T_1 \otimes e$ and $T_1 \otimes t_2$ JT systems. This is different to the set of states associated with the orthorhombic minima. Analytical expressions for the first- and second-order JT reduction factors are also derived for the coexisting system. As a consequence of this analysis, an improved version of the theory of second-order reduction factors is obtained. The reduction factors are compared to those of existing numerical calculations for the $T_1 \otimes d$ JT system and it is shown that very good agreement is obtained between the two in the strong-coupling limit.

1. Introduction

Uniaxial stress is often used as an experimental technique for the study of magnetic impurity ions in semiconductors in cases where the interaction with the surrounding lattice is strong. For orbital triplet ions in III–V semiconductors, the effect of a uniaxial stress of E-type symmetry (e.g. stress along $\langle 001 \rangle$) is usually an order of magnitude larger or smaller than that of a stress of T_2 -type symmetry (e.g. along $\langle 111 \rangle$). These two extremes are said to involve $T \otimes e$ and $T \otimes t_2$ Jahn–Teller (JT) systems respectively as in such cases the ion is strongly coupled to either e - or t_2 -type lattice vibrations. However, in a minority of cases, one finds that the two stresses have effects of a similar order of magnitude. It is usual to interpret the latter result as implying that a $T \otimes (e + t_2)$ JT effect is operating in which the lowest-energy minima in the potential energy surface are of orthorhombic symmetry (e.g. Bates 1978). In this paper, we wish to examine the alternative possibility that the orthorhombic extrema are higher in energy than both the tetragonal and trigonal wells, but that the tetragonal and trigonal wells have virtually the same energy as each other. This suggests an alternative theoretical framework for modelling the experimental results obtained on such magnetic impurity systems.

As a detailed background to this work, we note that much numerical and theoretical work exists concerning Jahn–Teller (JT) effects in which an orbital T_1 triplet level is coupled to both e and t_2 modes of vibrations of its neighbours. For example, Sakamoto (1982) calculated the energy levels and Ham reduction factors for the case in which the two

phonon modes have equal coupling strengths and frequencies. Four different quadratic couplings were included in the analysis in turn. A different approach was used by Lister and O'Brien (1984), based on earlier work of O'Brien (1969) for the strong-coupling regime. By introducing an effective adiabatic potential surface, they deduced specific properties of the system by studying its shape. O'Brien (1971, 1990) published numerical results for the first- and second-order reduction factors for the $T \otimes (e + t_2)$ system in the special case of equal coupling, but the results did not include the effect of the quadratic terms in the Hamiltonian and therefore the symmetry of this system is higher than cubic.

In this paper, we will adopt the unitary transformation method used by Bates *et al* (1987), Dunn (1988, 1989) and Dunn and Bates (1989) to study the strongly coupled JT system in the equal-coupling case. In our discussion, the bilinear quadratic coupling term will be added into the vibronic Hamiltonian (and thus the system retains its cubic symmetry). It will be shown that for certain ranges of magnitude and sign of the bilinear coupling constant, the tetragonal and trigonal minima coexist. Subsequently, the ground vibronic states localized in these minima (or wells) are mixed to construct a new set of ground vibronic states by diagonalization of the full vibronic Hamiltonian (including the bilinear term). Finally, the results obtained will be used to calculate first- and second-order reduction factors for the coexisting system. The calculation of second-order reduction factors is performed using a modified version of the method of Polinger *et al* (1991) in which the general expressions derived for the reduction factors are improved. It is only necessary then to evaluate a few reduced matrix elements of vibronic states instead of summing over a large number of overlaps of phonon states. Also, as a good approximation in strong coupling, the symmetry-adapted excited vibronic states for the separate $T \otimes e$ and $T \otimes t_2$ JT systems are used as basis states for the calculations here.

2. The Hamiltonian and unitary transformation

The Hamiltonian for a $T_1 (l = 1)$ ion that is coupled both linearly and bilinearly to e modes (Q_θ, Q_ϵ) and t_2 modes (Q_4, Q_5, Q_6) of a cluster of cubic (T_d) symmetry is (Bates *et al* 1987)

$$\mathcal{H} = \mathcal{H}_{\text{vib}} + \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{int}}^{\text{BL}} \quad (2.1)$$

where

$$\begin{aligned} \mathcal{H}_{\text{vib}} &= (2\mu)^{-1}(P_\theta^2 + P_\epsilon^2 + P_4^2 + P_5^2 + P_6^2)\mathbf{1} \\ &\quad + (\mu/2)[\omega_E^2(Q_\theta^2 + Q_\epsilon^2) + \omega_T^2(Q_4^2 + Q_5^2 + Q_6^2)] \\ \mathcal{H}_{\text{int}} &= \frac{1}{2}V_E(\rho_\theta Q_\theta - 3^{1/2}\rho_\epsilon Q_\epsilon) - (3^{1/2}/2)V_T(\tau_4 Q_4 + \tau_5 Q_5 + \tau_6 Q_6) \\ \mathcal{H}_{\text{int}}^{\text{BL}} &= (3^{1/2}/2)V_{\text{BL}}\{Q_4[-\frac{1}{2}Q_\theta + (3^{1/2}/2)Q_\epsilon]\tau_4 \\ &\quad + Q_5[-\frac{1}{2}Q_\theta - (3^{1/2}/2)Q_\epsilon]\tau_5 + Q_6 Q_\theta \tau_6\} \end{aligned} \quad (2.2)$$

with respect to a set of T_1 electronic triplet states $|x\rangle, |y\rangle$ and $|z\rangle$, where, in matrix form,

$$\begin{aligned} \mathbf{1} &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \rho_\theta &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{bmatrix} & \rho_\epsilon &= \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \\ \tau_4 &= \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} & \tau_5 &= \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} & \tau_6 &= \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \end{aligned} \quad (2.3)$$

\mathcal{H}_{vib} represents the elastic energy of the cluster, \mathcal{H}_{int} the linear couplings and $\mathcal{H}_{\text{int}}^{\text{BL}}$ describes the bilinear coupling to one e-type and one t_2 -type mode. P_j is the momentum conjugate to Q_j , V_E is the linear coupling constant for the e modes, V_T that for t_2 modes and V_{BL} is the bilinear coupling constant. μ is the mass and ω_E and ω_T are the frequencies of e modes and t_2 modes respectively.

For strongly coupled JT systems, the transformation approach of Bates *et al* (1987) and Dunn (1988) may be adopted in which a transformation of the form

$$U = \exp\left(i \sum_{j=1}^5 \alpha_j P_j\right) \tag{2.4}$$

is applied to \mathcal{H} in (2.1), where the α_j are free parameters. This produces a transformed Hamiltonian

$$\tilde{\mathcal{H}} = U^\dagger \mathcal{H} U = \tilde{\mathcal{H}}_1 + \tilde{\mathcal{H}}_2 \tag{2.5}$$

such that $\tilde{\mathcal{H}}_2$ contains terms representing coupling to excited phonon states while $\tilde{\mathcal{H}}_1$ contains only electronic operators. Consequently when the ground states of the system are required, only $\tilde{\mathcal{H}}_1$ needs to be considered. To obtain the ground states and their energies, $\tilde{\mathcal{H}}_1$ should be minimized with respect to the α_j as in the method of Öpik and Pryce (1957). This gives values of α_j which define the positions of extrema points of tetragonal, trigonal and orthorhombic symmetry in the five-dimensional Q -space.

Comparing the results obtained here with those obtained in linear coupling by Bates *et al* (1987), it was found that the inclusion of the bilinear term in the Hamiltonian has no effect on the positions of extrema points, eigenstates and energies in the tetragonal and trigonal cases, but that the values of $\alpha_j^{(k)}$ for the orthorhombic extrema are multiplied by ϕ_E for $j = \theta$ and ϵ and by ϕ_T for $j = 4, 5$ and 6 , where

$$\begin{aligned} \phi_E &= \left(1 - 4 \frac{K_{\text{BL}}^2}{\hbar \omega_E \hbar \omega_T}\right)^{-1} \left(1 - 2 \frac{K_{\text{BL}} K_T}{\hbar \omega_T K_E}\right) \\ \phi_T &= \left(1 - 4 \frac{K_{\text{BL}}^2}{\hbar \omega_E \hbar \omega_T}\right)^{-1} \left(1 - 2 \frac{K_{\text{BL}} K_E}{\hbar \omega_E K_T}\right) \end{aligned} \tag{2.6}$$

in which the constants K_E , K_T and K_{BL} are defined by

$$K_E = -\frac{1}{2} \left(\frac{\hbar}{2\mu\omega_E}\right)^{1/2} V_E \quad K_T = \frac{1}{2} \left(\frac{3\hbar}{2\mu\omega_T}\right)^{1/2} V_T \quad K_{\text{BL}} = -2 \frac{V_{\text{BL}}}{V_E V_T} K_E K_T. \tag{2.7}$$

The energies of the orthorhombic extrema become (Dunn and Bates 1989)

$$E_{\text{ET}} = \left(1 - 4 \frac{K_{\text{BL}}^2}{\hbar \omega_E \hbar \omega_T}\right)^{-1} \left(-\frac{K_E^2}{\hbar \omega_E} - \frac{K_T^2}{\hbar \omega_T} + 4 K_{\text{BL}} \frac{K_E K_T}{\hbar \omega_E \hbar \omega_T}\right). \tag{2.8}$$

However, the corresponding eigenstates are still unchanged. We note that the expression for the energy E_{ET} of orthorhombic wells given in equation (6.2) of Bates *et al* (1987) was approximate because the factor $[1 - 4 K_{\text{BL}}^2 / (\hbar^2 \omega_E \omega_T)]^{-1}$ appearing in (2.8) was taken to be unity. It is important to use the exact result here as this factor is very important in the subsequent discussion for the case of equal coupling in which the tetragonal and trigonal minima coexist.

3. Equal coupling and the coexistence of tetragonal and trigonal minima

In terms of the parameters defined in (2.7), the expressions for E_E (the JT energy at the tetragonal extrema) and E_T (the JT energy at the trigonal extrema) are

$$E_E = -4K_E^2/(\hbar\omega_E) \quad E_T = -4K_T^2/(3\hbar\omega_T). \quad (3.1)$$

For the equal-coupling case, we take $E_E = E_T = E$ and $\omega_E = \omega_T = \omega$. It follows then that $\sqrt{3}K_E = K_T = K$ and (2.8) thus becomes

$$E_{ET} = E \left(1 - 4 \frac{K_{BL}^2}{(\hbar\omega)^2} \right)^{-1} \left(1 - \sqrt{3} \frac{K_{BL}}{\hbar\omega} \right). \quad (3.2)$$

The values of K_{BL} for which the tetragonal and trigonal minima coexist can be obtained by setting

$$E_{ET} > E \quad (3.3)$$

to push the tetragonal and trigonal extrema below the orthorhombic extrema. This occurs if

$$0 < K_{BL}/(\hbar\omega) < \sqrt{3}/4. \quad (3.4)$$

It is possible to determine whether these lowered extrema are absolute minima or saddle points by applying the method described by Bersuker and Polinger (1989). It is well known that in each of these extrema, the e and t_2 vibration modes labelled according to the cubic T_d group, are reduced to a set of new modes belonging to a group of lowered symmetry. In fact, at tetragonal extrema the symmetry is reduced to D_{2d} and we have $E \rightarrow A_1 \oplus B_1$ and $T_2 \rightarrow B_2 \oplus E$. At the trigonal extrema, the symmetry is lowered to C_{3v} and we have $E \rightarrow E$ and $T_2 \rightarrow A_1 \oplus E$. By applying ordinary perturbation theory, it is found that the curvatures κ (defined as the second derivative of the potential function with respect to Q_j) at the tetragonal extrema are

$$\begin{aligned} \kappa_{A_1} = \kappa_{B_1} &= \mu\hbar^2\omega^2 & \kappa_{B_2} &= \mu\hbar^2\omega^2 \\ \kappa_E &= \mu\hbar^2\omega^2 \frac{4K_{BL}}{\sqrt{3}\hbar\omega} \left(1 - \frac{K_{BL}}{\sqrt{3}\hbar\omega} \right). \end{aligned} \quad (3.5)$$

At the trigonal extrema, the curvature $\kappa_{A_1} = \mu\hbar^2\omega^2$, and κ_E (which has two different components in this case) is obtained from diagonalizing the matrix

$$\mu\hbar^2\omega^2 \frac{1}{3} \begin{bmatrix} 1 + \frac{8K_{BL}}{\sqrt{3}\hbar\omega} - \frac{8K_{BL}^2}{3\hbar^2\omega^2} & \sqrt{2} - \frac{8\sqrt{2}K_{BL}}{\sqrt{3}\hbar\omega} \\ \sqrt{2} - \frac{8\sqrt{2}K_{BL}}{\sqrt{3}\hbar\omega} & 2 \end{bmatrix}. \quad (3.6)$$

With (3.5) and (3.6), one can easily show that the curvatures at tetragonal and trigonal extrema are all positive (in the trigonal case, the determinant of the matrix in (3.6) is positive) for the ranges of the sign and magnitude of K_{BL} shown in (3.4). Therefore these extrema are absolute minima or 'wells'. The eigenstates localized in these wells can be transformed back and linearly combined using projection operator techniques (Dunn 1989) to obtain symmetry-adapted cubic vibronic ground states. Thus we have

$$|T_1xe\rangle = |x'; 0\rangle \quad |T_1ye\rangle = |y'; 0\rangle \quad |T_1ze\rangle = |z'; 0\rangle \quad (3.7)$$

for the tetragonal case of $T_1 \otimes e$ system, and

$$\begin{aligned} |T_1xt\rangle &= N_t(-|a'; 0\rangle - |b'; 0\rangle + |c'; 0\rangle + |d'; 0\rangle) \\ |T_1yt\rangle &= N_t(-|a'; 0\rangle + |b'; 0\rangle - |c'; 0\rangle + |d'; 0\rangle) \\ |T_1zt\rangle &= N_t(|a'; 0\rangle - |b'; 0\rangle - |c'; 0\rangle + |d'; 0\rangle) \end{aligned} \tag{3.8}$$

with

$$\begin{aligned} a &= \left(1/\sqrt{3}\right)(x + y - z) & b &= \left(1/\sqrt{3}\right)(x - y + z) \\ c &= \left(1/\sqrt{3}\right)(-x + y + z) & d &= \left(1/\sqrt{3}\right)(-x - y - z) \end{aligned} \tag{3.9}$$

for the trigonal case of $T_1 \otimes t_2$ system. $N_t = (\frac{1}{2})[1 + S_t/3]^{-1/2}$ is the normalizing factor in which $S_t = \exp[-(\frac{16}{9})(K/\hbar\omega)^2]$ is the oscillator overlap between two trigonal wells. In the above equations, $|\xi'; 0\rangle \equiv U_\xi|\xi; 0\rangle$ ($\xi = x, y, z, a, b, c, d$), where ξ labels the well and '0' denotes that there are no phonon excitations with respect to the transformed picture, and U_ξ is the value of the unitary transformation U evaluated at the ξ minimum.

It should be noted that, in deriving the above cubic ground states using the transformation method, $\tilde{\mathcal{H}}_2$ is neglected (section 2). Thus to take into account the effect of the bilinear term, better approximations to the exact eigenstates are obtained by diagonalizing the full vibronic Hamiltonian introduced in (2.1) with the symmetry-adapted states in (3.7) and (3.8) as bases. Since the Hamiltonian is a scalar of the cubic group and $|T_1\gamma e\rangle, |T_1\gamma t\rangle$ ($\gamma = x, y, z$) transform according to the row γ of the irreducible representation T_1 of the same cubic group, there are only three unique matrix elements of the Hamiltonian. These can be written as follows:

$$\begin{aligned} \langle T_1\gamma' e | \mathcal{H} | T_1\gamma e \rangle &= H_{11}\delta_{\gamma\gamma'} & \langle T_1\gamma' t | \mathcal{H} | T_1\gamma t \rangle &= H_{22}\delta_{\gamma\gamma'} \\ \langle T_1\gamma' e | \mathcal{H} | T_1\gamma t \rangle &= H_{12}\delta_{\gamma\gamma'} & \langle T_1\gamma' t | \mathcal{H} | T_1\gamma e \rangle &= H_{21}\delta_{\gamma\gamma'} \end{aligned} \tag{3.10}$$

where

$$\begin{aligned} H_{11} &= \left(\frac{5}{2}\hbar\omega - \frac{4K^2}{3\hbar\omega}\right) \\ H_{22} &= \left(\frac{5}{2}\hbar\omega - \frac{4K^2}{3\hbar\omega} \frac{9 + 7S_t}{3(3 + S_t)}\right) \\ H_{12} = H_{21} &= -\frac{4}{\sqrt{3}}N_tS_{et} \left(\frac{5}{2}\hbar\omega - \frac{8K^2}{3\hbar\omega} + \frac{4K_{BL}}{3\sqrt{3}} \frac{K^2}{(\hbar\omega)^2}\right). \end{aligned} \tag{3.11}$$

In the above, $S_{et} (= \exp[-(\frac{4}{3})(K/\hbar\omega)^2])$ is the oscillator overlap between tetragonal and trigonal wells in the equal-coupling base. Also (3.10) implies that \mathcal{H} can only mix states which have the same symmetry transformation properties. Thus the calculation of the eigenvalue problem for the ground states can be carried out within a two-dimensional subspace so that the problem can be reduced to solving the simple matrix equation

$$\begin{pmatrix} H_{11} - E & H_{12} - ES \\ H_{12} - ES & H_{22} - E \end{pmatrix} \begin{pmatrix} \zeta_e \\ \zeta_t \end{pmatrix} = 0 \tag{3.12}$$

where $S = \langle T_1 \gamma e | T_1 \gamma t \rangle = \langle T_1 \gamma t | T_1 \gamma e \rangle = -(4/\sqrt{3})N_t S_{et}$. The new ground vibronic states are then written in the form

$$|T_1 \gamma e t\rangle = \zeta_e |T_1 \gamma e\rangle + \zeta_t |T_1 \gamma t\rangle \quad (\gamma = x, y, z) \quad (3.13)$$

where ζ_e and ζ_t are combination coefficients. Solving (3.12), it is found that

$$\zeta_e = 1/(1 + 2\rho S + \rho^2)^{1/2} \quad \zeta_t = \rho/(1 + 2\rho S + \rho^2)^{1/2} \quad (3.14)$$

where

$$\rho = (E_{T_1}^{(0)} - H_{11})/(H_{12} - E_{T_1}^{(0)} S) \quad (3.15)$$

and where the energy of the ground vibronic state is

$$E_{T_1}^{(0)} = \frac{1}{2}(1 - S^2)^{-1}(H_{11} + H_{22} - 2H_{12}S - \Delta) \quad (3.16)$$

with

$$\Delta = [(H_{11} + H_{22} - 2H_{12}S)^2 - 4(1 - S^2)(H_{11}H_{22} - H_{12}^2)]^{1/2}. \quad (3.17)$$

(In the strong-coupling limit, the above expressions simplify such that $\zeta_t = \pm\zeta_e$ with the ground state taking the negative sign.)

4. First-order reduction factors

It is well known that, in spectroscopic studies, an ion in a crystal can often be conveniently described by an effective Hamiltonian in which the electronic terms are multiplied by parameters frequently referred to as reduction factors. An analysis of the reduction factors appearing in such effective Hamiltonians is one of the best ways of observing and identifying JT effects in solids (e.g. Ham 1965, O'Brien 1969, Bates 1978). In fact, in many real systems, the importance of JT effects is reflected by the size of the reduction factors and thus their calculation is fundamental to JT theory. In this section, we will extend our discussions to the calculations of both the first- and second-order reduction factors using the new ground vibronic states and the energy obtained above. ('First-order' reduction factors arise when a perturbation V is used in a first-order perturbation theory calculation and 'second-order' reduction factors when V is used twice in a second-order perturbation theory calculation.)

4.1. The general result

The basic definition of a first-order reduction factor is that it is the ratio of the diagonal matrix element of an orbital operator within a vibronic state to that of the diagonal matrix element of the same orbital operator within the corresponding orbital states. Thus the first-order reduction factor $K^{(1)}(\Gamma)$ is defined in general terms by

$$K^{(1)}(\Gamma) = \langle 0\Sigma\sigma_i | L_{\Gamma\gamma} | 0\Sigma\sigma_j \rangle / \langle \Sigma\sigma_i | L_{\Gamma\gamma} | \Sigma\sigma_j \rangle. \quad (4.1)$$

In the above, $|0\Sigma\sigma\rangle$ are the ground vibronic states, $|\Sigma\sigma\rangle$ the orbital states and $L_{\Gamma\gamma}$ the symmetrized orbital operators, where $\Sigma\sigma$, $\Gamma\gamma$ label the transformation properties according to the appropriate point group. (For example, ρ_θ , as defined in (2.3), could be the orbital

operator $L_{\Gamma\gamma}$, $|\Gamma_{1xe}\rangle$, as defined in (3.7), could be a vibronic state $|0\Sigma\sigma\rangle$ of x -type symmetry, and $|x\rangle$ the corresponding orbital state $|\Sigma\sigma\rangle$). If we define

$$(\Sigma\sigma_i|L_{\Gamma\gamma}|\Sigma\sigma_j) = \langle \Gamma\gamma \Sigma\sigma_j | \Sigma\sigma_i \rangle \tag{4.2}$$

where $\langle \Gamma\gamma \Sigma\sigma_j | \Sigma\sigma_i \rangle$ are the Clebsch-Gordan (CG) coefficients, then the definition of first-order reduction factors in (4.1) is simplified to

$$K^{(1)}(\Gamma) = \langle 0\Sigma || L_{\Gamma} || 0\Sigma \rangle. \tag{4.3}$$

The specific form of the $L_{\Gamma\gamma}$ which have E, T_1 and T_2 symmetries and which satisfy the definition (4.2), are given by

$$\begin{aligned} L_{E\theta} &= (\frac{1}{2})(C_1^\dagger C_1 + C_2^\dagger C_2 - 2C_3^\dagger C_3) & L_{E\epsilon} &= -(\sqrt{3}/2)(C_1^\dagger C_1 - C_2^\dagger C_2) \\ L_{T_1x} &= (1/\sqrt{2})(C_2^\dagger C_3 - C_3^\dagger C_2) & L_{T_1y} &= (1/\sqrt{2})(C_3^\dagger C_1 - C_1^\dagger C_3) \\ L_{T_1z} &= (1/\sqrt{2})(C_1^\dagger C_2 - C_2^\dagger C_1) & L_{T_2x} &= -(1/\sqrt{2})(C_2^\dagger C_3 + C_3^\dagger C_2) \\ L_{T_2y} &= -(1/\sqrt{2})(C_3^\dagger C_1 + C_1^\dagger C_3) & L_{T_2z} &= -(1/\sqrt{2})(C_1^\dagger C_2 - C_2^\dagger C_1). \end{aligned} \tag{4.4}$$

C_i^\dagger are the orbital creation operators, which are defined in terms of the orbital vacuum states $|0\rangle$ such that $C_1^\dagger|0\rangle = |x\rangle$, $C_2^\dagger|0\rangle = |y\rangle$ and $C_3^\dagger|0\rangle = |z\rangle$. C_i are the orbital annihilation operators corresponding to C_i^\dagger . In many cases, the above expressions for the orbital operators are not important since the definition (4.2) suffices for calculation purposes if the CG coefficients are available.

With the new ground vibronic states derived in section 3, the first-order reduction factors are given by

$$\begin{aligned} K^{(1)}(T_1) &= \zeta_e^2 S_e + \zeta_t^2 (\frac{16}{3}) N_t^2 S_t + 2\zeta_e \zeta_t S \\ K^{(1)}(T_2) &= \zeta_e^2 S_e + \zeta_t^2 (\frac{8}{3}) N_t^2 (1 + S_t) + 2\zeta_e \zeta_t S \\ K^{(1)}(E) &= \zeta_e^2 + \zeta_t^2 (\frac{16}{3}) N_t^2 S_t + 2\zeta_e \zeta_t S. \end{aligned} \tag{4.5}$$

Figure 1 shows the variations of $K^{(1)}(T_1)$, $K^{(1)}(T_2)$ and $K^{(1)}(E)$ as functions of $K/\hbar\omega$ with $K_{BL} = 0.3$. It is seen that $K^{(1)}(T_1) \rightarrow 0$, $K^{(1)}(T_2) \rightarrow \frac{1}{3}$ and $K^{(1)}(E) \rightarrow \frac{1}{2}$ (approaching the value of 0.5 from below) in the strong-coupling limit.

4.2. The linear equal coupling limit

Our results are different to those of O'Brien (1971) for the linear equal-coupling case (when the bilinear term is zero) because the Hamiltonian she used has 'accidentally' a higher symmetry (of the rotation group $SO(3)$). The inclusion of the bilinear term reduces the symmetry of the JT system to cubic. In fact, if the linear terms of the vibronic interaction are considered only, then the ground vibronic states in (3.7) and (3.8) can be combined to form a new set of ground vibronic states of which the corresponding phonon states transform according to the irreducible representation $l = 2$ of the $SO(3)$ group. The appropriate

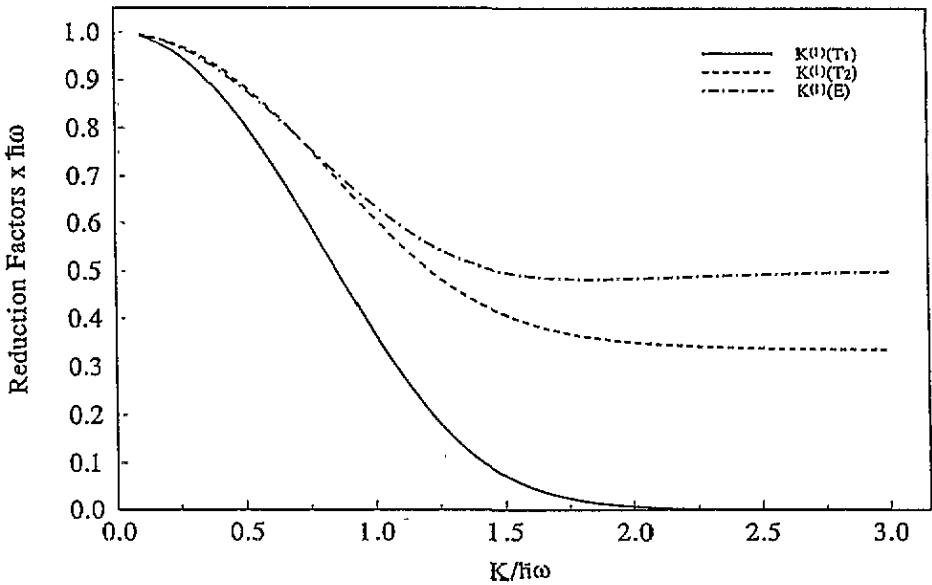


Figure 1. The first-order reduction factors $K^{(1)}(T_1)$, $K^{(1)}(T_2)$ and $K^{(1)}(E)$ plotted as functions of $K/\hbar\omega$ with $K_{BL} = 0.3$.

combination coefficients ζ'_e and ζ'_t can be found by using the condition that the symmetry-adapted phonon states satisfy the relation (Bersuker and Polinger 1989)

$$\{0(T_1)T_2\|0(T_1)T_2\} = \left(\frac{3}{2}\right)\{0(T_1)E\|0(T_1)E\}. \tag{4.6}$$

The phonon states are written in the form $|0(\Gamma)\Lambda\lambda\rangle$ and can be obtained by comparing (3.13) with the general expression for the ground vibronic states (Polinger *et al* 1991):

$$|0\Gamma\gamma\rangle = \sum_{\sigma\Lambda\lambda} |\Sigma\sigma\rangle|0(\Gamma)\Lambda\lambda\rangle\langle\Sigma\sigma\Lambda\lambda|\Gamma\gamma\rangle. \tag{4.7}$$

Therefore using (4.6) together with the normalization condition, we obtain

$$\zeta'_e = 1/(1 - 2\rho'S + \rho'^2)^{1/2} \quad \zeta'_t = -\rho'/(1 - 2\rho'S + \rho'^2)^{1/2} \tag{4.8}$$

with

$$\rho^2 = \left(\frac{3}{8}\right)(1 - S_e)/[N_t^2(1 - S_t)] \quad S = -\left(4/\sqrt{3}\right)N_tS_{et}. \tag{4.9}$$

Replacing ζ_e and ζ_t in (4.5) by ζ'_e and ζ'_t and replotting the first-order reduction factors, we find that now $K^{(1)}(T_2) \rightarrow K^{(1)}(E)$ which is not the case in cubic symmetry. We also find that, in the strong-coupling limit, $K^{(1)}(T_1) \rightarrow 0$ as before, but that $K^{(1)}(T_2)$ and $K^{(1)}(E)$ tend to the value $\frac{2}{3}$ as shown in figure 2. In figure 3, our results are compared to those of O'Brien (1990); they agree in the strong- and zero-coupling limits but differ for other values of the coupling constant. This is not surprising as our states are constructed from functions based on potential wells.

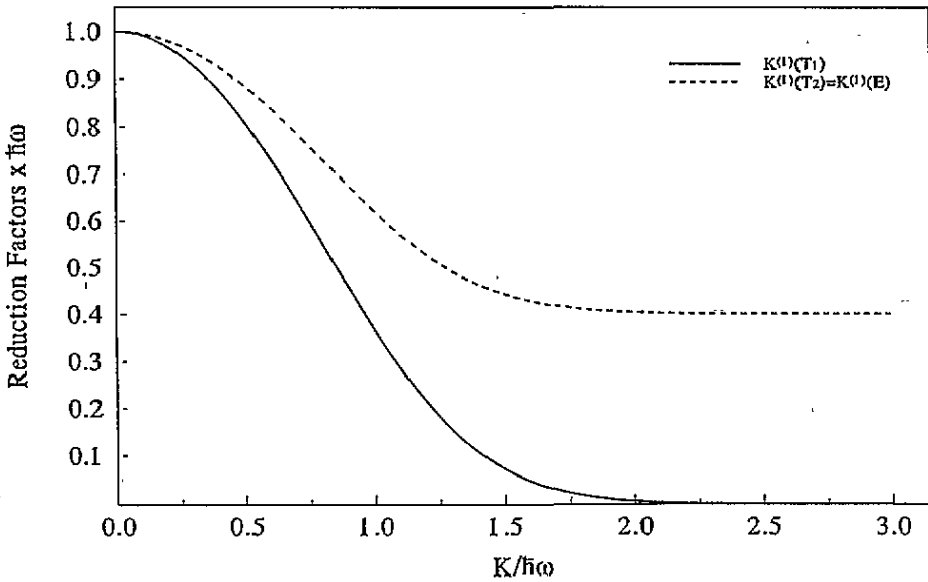


Figure 2. The first-order reduction factors $K^{(1)}(T_1)$, $K^{(1)}(T_2)$ and $K^{(1)}(E)$ plotted as a function of $K/\hbar\omega$ when only linear coupling terms are considered and states appropriate to $SO(3)$ are constructed.

In the equal-coupling case without the bilinear term, there is a continuous equipotential surface connecting together the 13 extrema which occurs when the quadratic coupling is included. Consequently, our transformation method should not be applicable. In producing the results shown in figure 2, we have constructed wave functions centred on the seven 'minima' in Q -space and added the condition which makes the phonon states given in (4.6) appropriate to $SO(3)$ symmetry. However, we have *not* included the bilinear term in this calculation, and thus the seven 'minima' are not true minima at all. Nevertheless, our transformation method has given sensible results at the two limits and in between the differences are not too large. Presumably, this is because the wells in the strong-coupling limit are infinitely sharp and the points chosen are sufficient in number to map accurately the $T \otimes d$ system. Figure 1 should give an accurate picture of the reduction factors when bilinear coupling is included (as the symmetry is cubic), when there is no reason why $K^{(1)}(T_2)$ should be equal to $K^{(1)}(E)$. The symmetry in figure 2 is moving towards $SO(3)$ and the results from O'Brien (1971) in figure 3 are of symmetry $SO(3)$ exactly.

5. Second-order reduction factors

In strong coupling, second-order reduction factors become particularly important as in many cases the first-order factors are small. They arise from non-zero matrix elements of V between the ground vibronic state and all the excited vibronic states as deduced in the usual perturbation theory summation. They satisfy the usual requirement that the matrix elements of the effective Hamiltonian within the purely *electronic* basis states are identical to those of V within the ground *vibronic* states (e.g. Bates *et al* 1987, Dunn and Bates 1989, Bersuker and Polinger 1989).

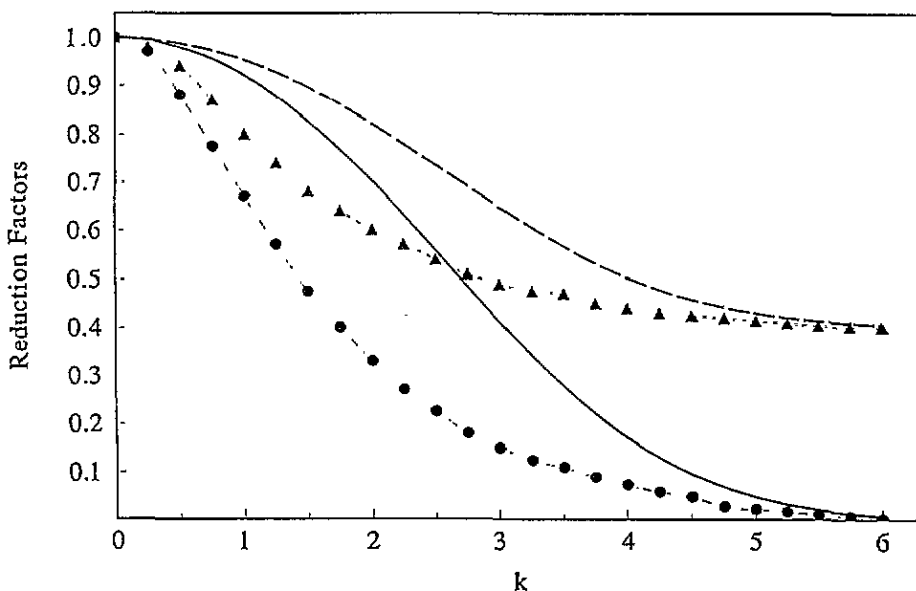


Figure 3. The first-order reduction factors calculated in this work compared to the numerical results of O'Brien (1971). (Note that the relation between our K and the k of O'Brien is $k = \sqrt{10K}$). The dashed line refers to our results for $K^{(1)}(T_2) = K^{(1)}(E)$ and the solid line to our results for $K^{(1)}(T_1)$. The triangles (▲▲▲▲) give the results for $K^{(1)}(T_2) = K^{(1)}(E)$ from O'Brien (1971) and the solid circles (●●●●) similar results for $K^{(1)}(T_1)$.

5.1. Definitions

From these basic definitions, Polinger *et al* (1991) derived a general expression for the second-order JT reduction factors in the form

$$K_M^{(2)}(\Gamma_k \otimes \Gamma_l) = (-1)^{j(\Gamma)} [\Gamma] \begin{bmatrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Gamma \end{bmatrix}^{-1} \sum_{\Lambda} (-1)^{j(\Lambda)} [\Lambda] \begin{bmatrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Lambda \end{bmatrix} R_{\Lambda}(\Gamma_k \Gamma_l) \quad (5.1)$$

with

$$R_{\Lambda}(\Gamma_k \Gamma_l) = \sum_n (E_{\Gamma}^{(0)} - E_{\Lambda}^{(n)})^{-1} S_n(\Gamma_k \Lambda \Gamma) S_n(\Gamma_l \Lambda \Gamma) \quad (5.2)$$

and where

$$S_n(\Sigma \Lambda \Gamma) = \sum_M (-1)^{j(M)+j(\Sigma)} \{0(\Gamma)M || n(\Lambda)M\} \begin{bmatrix} \Gamma & \Gamma & \Sigma \\ \Gamma & \Lambda & M \end{bmatrix} \quad (\Sigma = \Gamma_k, \Gamma_l) \quad (5.3)$$

In the above, Γ_k and Γ_l denote the symmetry components of the perturbation V and $j(\Gamma)$ are the fictitious angular momenta (see, e.g., Griffiths 1962). Also the 6Γ symbols are written with large square brackets and dimension of a representation with small square brackets. The oscillator overlap integrals are $\{0(\Gamma)M || n(\Lambda)M\}$. As can be seen from (5.3), in order to calculate second-order vibronic reduction factors for any real JT system, it is necessary to evaluate matrix elements involving the oscillator parts of the vibronic states. In the transformation method, this is done by comparing the vibronic states obtained with those in a general Clebsch–Gordan convolution form.

5.2. *An alternative procedure*

The problem with this approach is that we have to handle a greater number of oscillator states than vibronic states. Thus a more convenient way, which we introduce here, is to use the vibronic states directly for the calculations. The introduction of the symmetrized orbit operators $L_{\Gamma\gamma}$ defined in (4.4) has made this possible. Thus it is found that, in terms of the reduced matrix elements of $L_{\Gamma\gamma}$ between the vibronic ground and excited states, the function S_n , introduced in (5.3), can be expressed either in the form

$$S_n(\Sigma\Lambda\Gamma) = [\Gamma]^{-1}(-1)^{j(\Lambda)+j(\Gamma)} \langle n\Lambda \| L_{\Sigma} \| 0\Gamma \rangle \tag{5.4}$$

or in the form

$$S_n(\Sigma\Lambda\Gamma) = ([\Gamma][\Lambda])^{-1/2} \langle 0\Gamma \| L_{\Sigma} \| n\Lambda \rangle. \tag{5.5}$$

Thus either (5.4) or (5.5) can be used to replace (5.3) for the derivation of the S_n function. We will use (5.4) for the following calculations. In the case when $\Gamma_k = \Gamma_l$ we have

$$R_{\Lambda} \equiv R_{\Lambda}(\Gamma_k\Gamma_k) = \sum_n (E_{\Gamma}^{(0)} - E_{\Lambda}^{(n)})^{-1} S_n(\Gamma_k\Lambda\Gamma)^2 \tag{5.6}$$

with

$$S_n(\Gamma_k\Lambda\Gamma)^2 = [\Gamma]^{-2} \langle n\Lambda \| L_{\Gamma_k} \| 0\Gamma \rangle^2. \tag{5.7}$$

We consider a T_1 ion at a T_d site and take spin-orbit coupling as an example. In this case, $\Gamma = \Gamma_k = \Gamma_l = T_1$. On substituting appropriate values for the 6Γ symbols into (5.1), we obtain

$$\begin{aligned} R_{A_1}^{(2)}(T_1 \otimes T_1) &= 3R_{A_1} + 6R_E + 9R_{T_1} + 9R_{T_2} \\ R_E^{(2)}(T_1 \otimes T_1) &= -6R_{A_1} - 12R_E + 9R_{T_1} + 9R_{T_2} \\ R_{T_1}^{(2)}(T_1 \otimes T_1) &= 6R_{A_1} - 6R_E + 9R_{T_1} - 9R_{T_2} \\ R_{T_2}^{(2)}(T_1 \otimes T_1) &= -6R_{A_1} + 6R_E + 9R_{T_1} - 9R_{T_2} \end{aligned} \tag{5.8}$$

where

$$\begin{aligned} R_{A_1} &= \left(\frac{1}{9}\right) \sum_{ni} (E_{T_1}^{(0)} - E_{A_1^i}^{(n)})^{-1} \langle nA_1^i \| L_{T_1} \| 0T_1 \rangle^2 \\ R_E &= \left(\frac{1}{9}\right) \sum_{ni} (E_{T_1}^{(0)} - E_{E^i}^{(n)})^{-1} \langle nE^i \| L_{T_1} \| 0T_1 \rangle^2 \\ R_{T_1} &= \left(\frac{1}{9}\right) \sum_{ni} (E_{T_1}^{(0)} - E_{T_1^i}^{(n)})^{-1} \langle nT_1^i \| L_{T_1} \| 0T_1 \rangle^2 \\ R_{T_2} &= \left(\frac{1}{9}\right) \sum_{ni} (E_{T_1}^{(0)} - E_{T_2^i}^{(n)})^{-1} \langle nT_2^i \| L_{T_1} \| 0T_1 \rangle^2. \end{aligned} \tag{5.9}$$

In the above, the sums are over both $n(= p + q + r + s + t)$ and i , where the index i is used to distinguish between states of the same symmetry but different energy. The expression (5.8) for the reduction factors is exactly the same as that given earlier (Polinger

et al 1991, equation (2.27)) for the case of a $T \otimes t_2$ JT system but the definitions of the R_Λ in (5.9) are completely different.

In order to calculate R_Λ for this case, expressions for the energies $E_{T_1}^{(0)}$, $E_{T_1}^{(n)}$ are required together with the reduced matrix elements $\langle n\Gamma^i\gamma \| L_{T_1} \| 0T_1 \rangle$. The ground vibronic states $|0T_1\gamma\rangle$ and energy $E_{T_1}^{(0)}$ have been given by (3.13) and (3.16) respectively (note that $|0T_1\gamma\rangle \equiv |T_1\gamma e t\rangle$, $\gamma = x, y, z$) and the symmetrized orbit operators L_{T_1} by (4.4). Here we will use symmetry-adapted excited states of the $T \otimes t_2$ and the $T \otimes e$ systems and their energies for the calculations. As in the case of the ground vibronic states (section 3), the excited vibronic T_1 and T_2 states of the $T \otimes e$ system should be combined with those of the same symmetry for the $T \otimes t_2$ system to form the new sets of excited vibronic states. However, this calculation is complicated and may not have much effect on the final results so will not be attempted here.

Instead, we start with the excited vibronic states for $T \otimes t_2$ JT systems constructed by Dunn (1989) using projection operator techniques. They are written in the form

$$|n\Gamma_\gamma^i\rangle = N_j(l, m, n)|\phi_j(l, m, n)\rangle \quad (5.10)$$

where N_j are normalizing factors, given in equations (4.8)–(4.10) of Dunn (1989), and the states $|\phi_j\rangle$ are given in table 2 and equation (4.10) of Dunn (1989). The states with $j = 1$ –3 form one set of T_1 states ($\Gamma^i = T_1^{(1)}$), and the states with $j = 4$ –6 another set ($\Gamma^i = T_1^{(2)}$). A set of T_2 states is formed with $j = 7$ –9 ($\Gamma^i = T_2^{(1)}$), and pairs of E-type states with $j = 10$ and 11, $j = 12$ and 14 and $j = 13$ and 15 ($\Gamma^i = E^{(1)}$, $E^{(2)}$ and $E^{(3)}$). The A_1 states are formed with $j = 16$ and the A_2 states with $j = 17, 18$ and 19 ($\Gamma^i = A_2^{(1)}$, $A_2^{(2)}$ and $A_2^{(3)}$). Their energies $E_\Gamma^{(n)} = E_j(l, m, n)$ are given in equation (5.8) of Dunn (1989). (In order to take into account the extra coupling to the e mode, we must add $\hbar\omega$ to the latter energy).

For $T \otimes e$ JT systems, there are no vibronic states of A_1 , A_2 or E symmetry. Those excited states which transform as T_1 and T_2 can be written as

$$\begin{aligned} |nT_1^{(3)}\gamma\rangle &= U_\gamma|\gamma; \theta_\gamma^p \epsilon_\gamma^q\rangle && \text{for } q \text{ even} \\ |nT_2^{(2)}\gamma\rangle &= U_\gamma|\gamma; \theta_\gamma^p \epsilon_\gamma^q\rangle && \text{for } q \text{ odd} \quad (\gamma = x, y, z) \end{aligned} \quad (5.11)$$

where θ_γ^p denotes the presence of p excitations of the θ_γ -type oscillator, etc. The corresponding energies are given by

$$E_{T_i}^{(n)} = -4K^2/(3\hbar\omega) + (p + q + \frac{5}{2})\hbar\omega \quad (5.12)$$

in which $i = 3$ for q even and $i = 2$ for q odd.

As the excited vibronic states located in the two kinds of wells are given above, the reduced matrix elements needed in (5.9) can be calculated. The result is

$$\begin{aligned}
 \langle nA_1 || L_{T_1} || 0T_1 \rangle &= 0 \\
 \langle nE^{(1)} || L_{T_1} || 0T_1 \rangle &= 2\sqrt{6}N_{11}(r, s, t)g_1(r, s, s) \\
 \langle nE^{(2)} || L_{T_1} || 0T_1 \rangle &= \sqrt{6}N_{13}(r, s, t)[g_1(r, s, t) + g_1(s, r, t)] \\
 \langle nE^{(3)} || L_{T_1} || 0T_1 \rangle &= 0 \\
 \langle nT_1^{(1)} || L_{T_1} || 0T_1 \rangle &= -\sqrt{2}N_1(r, s, t)g_2(r, s, s) \\
 \langle nT_1^{(2)} || L_{T_1} || 0T_1 \rangle &= -\sqrt{2}N_4(r, s, t)[g_2(r, s, t) + g_1(r, t, s)] \\
 \langle nT_1^{(3)} || L_{T_1} || 0T_1 \rangle &= -\sqrt{2}g_3(p, q) \\
 \langle nT_2^{(1)} || L_{T_1} || 0T_1 \rangle &= -\sqrt{2}N_7(r, s, t)[g_2(r, s, t) - g_2(r, t, s)] \\
 \langle nT_2^{(2)} || L_{T_1} || 0T_1 \rangle &= -\sqrt{2}g_3(p, q)
 \end{aligned}
 \tag{5.13}$$

where

$$\begin{aligned}
 g_1(r, s, t) &= -\zeta_t Q (-1)^{r+s} (\delta_{0r} - \delta_{0t}) \\
 g_2(r, s, t) &= (-1)^{s+t} [\zeta_e P - \zeta_t Q (\delta_{0r} + \delta_{0t})] \\
 g_3(p, q) &= -(-1)^{p+q} (\zeta_e R - \zeta_t T \delta_{0q})
 \end{aligned}
 \tag{5.14}$$

and where

$$\begin{aligned}
 P &= \left(4/\sqrt{6}\right) S_{et} (2A/3)^{r+s+t} / (r!s!t!)^{1/2} \\
 Q &= \left(4\sqrt{2}/3\right) N_t S_t (4A/3)^{r+s+t} / (r!s!t!)^{1/2} \\
 R &= S_e \left(\sqrt{3}A\right)^p (A)^q / (2p!q!)^{1/2} \\
 T &= \left(4/\sqrt{6}\right) N_t S_{et} \left(2A/\sqrt{3}\right)^p / (p!)^{1/2}.
 \end{aligned}
 \tag{5.15}$$

In (5.15), $S_e = \exp[-2A^2]$ is the oscillator overlap between the ground states located in any two of the tetragonal wells where $A = K/\hbar\omega$.

The reduction factors may be written in the form (Polinger *et al* 1991, O'Brien 1990)

$$C = K_{A_1}^{(2)}/3 \quad B_E = K_E^{(2)} \quad A = -K_{T_1}^{(2)}/2 \quad B_T = K_{T_2}^{(2)}. \tag{5.16}$$

They are illustrated in figure 4 for $K_{BL} = 0.3$. This figure clearly show that B_T is not exactly equal to B_E in the strong-coupling region as was obtained in the numerical results of O'Brien (1990), although the same qualitative behaviour is observed. The origin of this difference can presumably again be attributed to the addition of the bilinear term into the basic Hamiltonian as discussed in section 4, so that the symmetry is cubic rather than SO(3).

6. Conclusions

The transformation method developed by Bates *et al* (1987) and Dunn (1988, 1989) has been applied to the case when the seven tetragonal and trigonal wells all have the same energy.

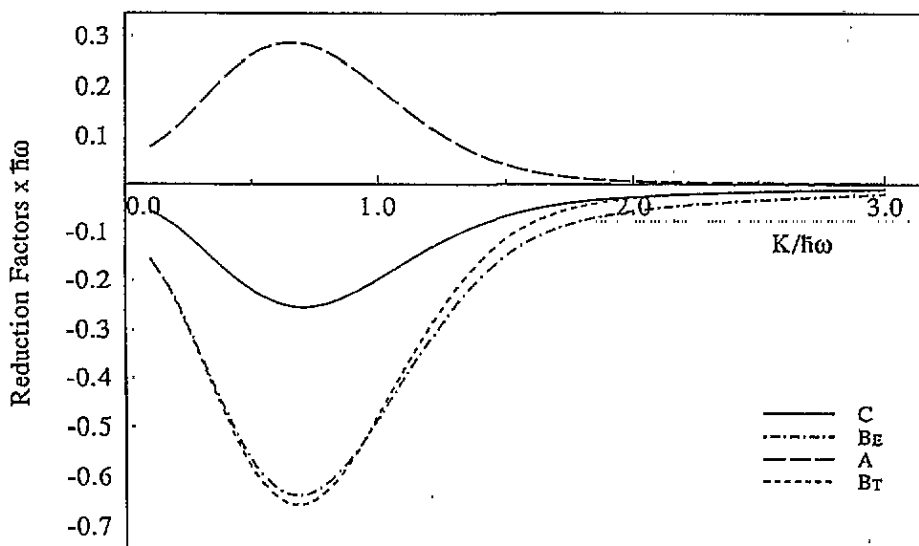


Figure 4. The second-order reduction factors A , B_E , B_T and C plotted as a function of $K/\hbar\omega$ with $K_{BL} = 0.3$. (Note that the reduction factors do not exactly go through the origin because the K_{BL} term remains finite.)

The inclusion of the bilinear coupling term in the Hamiltonian means that the trigonal and tetragonal wells can be pushed below the orthorhombic extrema by choosing a specific range of values for the constant K_{BL} and that the system retains its cubic symmetry. The ground vibronic states localized in the tetragonal and trigonal wells are combined linearly using projection operators (Dunn 1989) to obtain vibronic states of cubic symmetry. However, this technique cannot mix the basis states in trigonal wells with those in the tetragonal wells. Therefore, a better approximation to the exact eigenstates for the problem is obtained by diagonalizing the full vibronic Hamiltonian (2.1) with the above-mentioned symmetry-adapted states as basis states.

Within these new ground vibronic states, first-order reduction factors $K^{(1)}(T_1)$, $K^{(1)}(T_2)$ and $K^{(1)}(E)$ have been calculated. We find that, in our results, $K^{(1)}(T_2) \neq K^{(1)}(E)$ in strong coupling. This result is different from that obtained in the $T \otimes d$ case considered by O'Brien (1990). The 'splitting' observed here is attributed to the inclusion of the bilinear term which has lowered the symmetry of the vibronic Hamiltonian from $SO(3)$ to cubic. We have also shown that, if the ground vibronic states of $T \otimes e$ and $T \otimes t_2$ systems are combined appropriately to form new ground vibronic states of which the corresponding phonon states transform like the irreducible representation $l = 2$ of the rotation group $SO(3)$, then we find that $K^{(1)}(T_2) = K^{(1)}(E) \rightarrow \frac{2}{3}$ in the strong-coupling limit which is in agreement with the O'Brien result for the $T \otimes d$ case (O'Brien 1990).

Finally, we have improved the general expression for the calculation of second-order reduction factors. By introducing a set of symmetrized orbital operators, results can be obtained by evaluating a few reduced matrix elements of vibronic states only instead of summing over many phonon overlaps, thus simplifying the calculations. It is necessary to point out that the general expression (5.1) for second-order reduction factors is suitable for the triplet case only. A further improvement is needed when applying (5.1) to the doublet system (Liu et al 1994). We have calculated the second-order reduction factors for the specific example of spin-orbit coupling. It is interesting to see that in strong coupling B_E

is not exactly equal to B_T . This is in contrast to the $T \otimes d$ case for which $B_E = B_T$. The discrepancy is again likely to be caused by inclusion of the bilinear term.

One real example to which the above theory may apply is that of GaP:Ti³⁺. In optical-absorption experiments on this system in which the 2E -to- 2T_2 transition is studied, Al-Shaikh *et al* (1994) have found significant splittings of many lines when uniaxial stress is applied along the $\langle 001 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$ directions of the crystal, which cannot be explained by an orthorhombic model. However, further work is needed to verify that the model of co-existing tetragonal and trigonal wells applies to this case. In contrast, electron paramagnetic resonance (EPR) experiments on GaAs:Cr³⁺ have clearly shown that, in that system, an orthorhombic $T \otimes (e + t_2)$ JT model is needed especially because the angular dependence of the EPR spectrum displays orthorhombic symmetry (e.g. Parker *et al* 1990, Krebs and Stauss 1977). Another possible candidate for a coexisting system is GaP:Cr³⁺; although this system was supposed initially to be an example of a $T \otimes e$ JT system, on account of the E-type strain-stabilized EPR spectra observed (Darcha *et al* 1987), there are problems which have still to be resolved.

The need for a comprehensive JT theory in which the possibility that tetragonal and trigonal wells coexist has clearly been established. It is hoped that our calculations above will provide a realistic basis for future modelling.

Acknowledgment

One of us (YML) wishes to thank the UK committee of Vice-Chancellors and Principals for support from the Overseas Research Students Award Scheme during the course of this work.

References

- Al-Shaikh A M, Roura P, Ulrici W, Clerjoud B, Bates C A and Dunn J L 1994 *J. Phys.: Condens. Matter* to be submitted
- Bates C A 1978 *Phys. Rev.* **35** 187–304
- Bates C A, Dunn J L and Sigmund E 1987 *J. Phys. C: Solid State Phys.* **20** 1965–83
- Bersuker I B and Polinger V Z 1989 *Vibronic Interactions in Molecules and Crystals* (Berlin: Springer)
- Darcha M, Vasson A, Vasson A-M, Bates C A and Dunn J L 1987 *J. Phys. C: Solid State Phys.* **20** 2261–9
- Dunn J L 1988 *J. Phys. C: Solid State Phys.* **21** 383–99
- 1989 *J. Phys.: Condens. Matter* **1** 7861–81
- Dunn J L and Bates C A 1989 *J. Phys.: Condens. Matter* **1** 375–94
- Griffiths J S 1962 *The Irreducible Tensor Method for Molecular Symmetry Groups* (London: Prentice-Hall)
- Ham F S 1965 *Phys. Rev. A* **138** 1727–40
- Krebs J and Stauss G H 1977 *Phys. Rev. B* **15** 17–22
- Lister G M S and O'Brien M C M 1984 *J. Phys. C: Solid State Phys.* **17** 3975–86
- Liu Y M, Dunn J L and Bates C A 1994 *J. Phys.: Condens. Matter* **6** 859–72
- Öpik U and Pryce M H L 1957 *Proc. R. Soc. A* **238** 425–47
- O'Brien M C M 1969 *Phys. Rev.* **187** 407–18
- 1971 *J. Phys. C: Solid State Phys.* **4** 2524–36
- 1990 *J. Phys.: Condens. Matter* **2** 5539–53
- Parker L W, Bates C A, Dunn J L, Vasson A and Vasson A-M 1990 *J. Phys.: Condens. Matter* **2** 2841–56
- Polinger V Z, Bates C A and Dunn J L 1991 *J. Phys.: Condens. Matter* **3** 513–27
- Sakamoto N 1982 *Phys. Rev. B* **26** 6438–43