Further second-order reduction factors for the orthorhombic T(X)(e+t$_2$) Jahn-Teller systems

Further second-order reduction factors for the orthorhombic $T \otimes (e + t_2)$ Jahn–Teller systems

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Abstract. Second-order Jahn–Teller reduction factors have been calculated for the orthorhombic $T \otimes (e + t_2)$ Jahn–Teller system for orbital operators that have symmetries $E \otimes E$, $T_2 \otimes T_2$ and $T_2 \otimes E$. The calculations are based on the recently formulated symmetry-related method involving the calculation of oscillator overlaps. They are extracted from the symmetry-adapted cubic vibronic states derived analytically by Hallam *et al*. The results obtained are useful in the modelling of strongly coupled impurities in semiconductors when uniaxial stresses are applied to the system.

1. Introduction

In spectroscopic studies of a vibronic system, it is well known that Jahn–Teller (JT) reduction factors are very useful when an effective Hamiltonian is introduced to express the effects of perturbations within the degenerate levels in a compact manner. These reduction factors are called 'first-order' or 'second-order' according to the order in perturbation theory in which the perturbation V appears (Ham 1965). In some strongly coupled systems, second-order terms can have a greater influence than first-order terms, particularly in orbital triplet systems. Hence it is important to be able to calculate second-order reduction factors for such systems. The basic ideas of the problem are given in the books by Perlin and Wagner (1984) and Bersuker and Polinger (1989).

Reduction factors may be calculated numerically or analytically. In the former category, we cite the recent work of O'Brien (1990) for the second-order JT reduction factors involving the major perturbation of spin–orbit coupling for the $T \otimes t_2$ system. In the latter category, the Nottingham group has developed an analytical method for the calculation of the second-order reduction factors for both orbital triplet and orbital doublet systems. Two approaches to the problem have been used. One is the method described in Bates and Dunn (1989) and Dunn and Bates (1989) in which the reduction factors are obtained by comparing the matrix elements of the second-order perturbation involving V twice within the ground vibronic states to those of the effective Hamiltonian within a purely electronic basis by direct calculations. The other method uses the symmetry-related formalism developed by Polinger *et al* (1991) and Bates *et al* (1991). Here, the sums of overlaps between the appropriate oscillator ground states and the symmetry-adapted oscillator excited states are evaluated in order to obtain expressions for the second-order reduction factors.

Many papers have been published calculating second-order reduction factors by these two methods for spin–orbit coupling ($\lambda l \cdot s$) (e.g. Bates and Dunn 1989, Dunn and Bates 1989, Dunn *et al* 1990, Polinger *et al* 1991, Bates *et al* 1991) and Hallam *et al* (1992b) have considered in particular the $T \otimes (e + t_2)$ JT system. However, very recently Jamila *et al*

(1992) have calculated second-order reduction factors for the $T_2 \otimes t_2$ system for perturbations relating to uniaxial stress which have symmetries $E \otimes E$, $T_2 \otimes T_2$ and $T_2 \otimes E$. The aim of this paper is to extend the calculations to the $T \otimes (e + t_2)$ system for the same combinations of uniaxial stress based on the symmetry-related method. This is an obvious extension of the original calculations of Hallam *et al* (1992b). To do this, it is essential to have a complete set of symmetry-adapted vibronic states for the strongly coupled orthorhombic $T \otimes (e + t_2)$ *system. Such states are available now in Hallam et al (1992a).*

Apart from the modelling of data obtained from uniaxial stress experiments in systems that are already characterized, the theory described below can be used to help determine the nature of the coupling in an unclassified JT system and/or also assist in the identification of an unknown impurity. From a theoretical point of view, it is very interesting to see how the various systems and symmetries of the different perturbations are inter-related. Analytical calculations based particularly on the method of Polinger *et al* (1991) are ideal for this purpose in contrast to numerical methods where the symmetry properties are generally obscured.

The mathematical background to the method used for the derivation of the effective Hamiltonian for uniaxial stress is given in detail in section 2. This section also gives the general expressions for second-order reduction factors derived originally by Polinger *et al* (1991), Hallam (1991) and Kirk (1992). In section 3, second-order reduction factors for the perturbations described as $E \otimes E$, $T_2 \otimes T_2$ and $T_2 \otimes E$ for an orbital T_1 triplet at a T_d site are derived. A brief discussion of the ground–inversion-level coupling is given in section 4.

2. Mathematical background

2.1. Effective Hamiltonian

We consider an isolated orbital triplet that is strongly coupled to the vibration of its surroundings. The electronic orbital states may be written in the form $|\Gamma\gamma\rangle$; the eigenstates of the system are vibronic states that are written in the form $|N\Gamma\gamma\rangle$. The labels $\Gamma\gamma$ give the irreducible representation (IR) and the component of the state while N labels the repeated IR of the vibronic state such that their energies $E_\Gamma^{(N)}$ increase with increasing N. In Polinger *et al* (1991), vibronic eigenstates were written as

$$|N\Gamma\gamma\rangle = \sum_{\sigma\Lambda\lambda} |\Sigma\sigma\rangle |N(\Gamma)\Lambda\lambda\} \langle \Sigma\sigma\Lambda\lambda|\Gamma\gamma\rangle \tag{2.1}$$

where $\langle \Sigma\sigma\Lambda\lambda|\Gamma\gamma\rangle$ are the Clebsch–Gordan (CG) coefficients and $|N(\Gamma)\Lambda\lambda\}$ are functions of the nuclear coordinates Q and hence represent the phonon states. A perturbation V can cause a splitting of the ground vibronic state $|0\Gamma\gamma\rangle$. In second order, the additional splitting can be described by

$$\mathcal{H}^{(2)} = V G(\Gamma) V \tag{2.2}$$

where

$$G(\Gamma) = \sum_N \sum_{\Sigma\sigma} \frac{|N\Sigma\sigma\rangle\langle N\Sigma\sigma|}{E_\Gamma^{(0)} - E_\Sigma^{(N)}}. \tag{2.3}$$

As $G(\Gamma)$ is a scalar, the symmetry of $\mathcal{H}^{(2)}$ depends only on the symmetry within $V \otimes V$. In this way, the effective Hamiltonian $\mathcal{H}_{\text{eff}}^{(2)}$ used to describe the vibronic system can be obtained.

Now consider the effect of strain as the perturbation on the ground states. A perturbation Hamiltonian generated by the strain can be written in the general form

$$V = \sum_{\Gamma_k \gamma_k} V_{\Gamma_k} \bar{Q}_{\Gamma_k \gamma_k} L_{\Gamma_k \gamma_k} \qquad (2.4)$$

where V_{Γ_k} are coupling constants, $\bar{Q}_{\Gamma_k \gamma_k}$ is the static contribution to $Q_{\Gamma_k \gamma_k}$ from the strains of $\Gamma_k \gamma_k$ symmetry and $L_{\Gamma_k \gamma_k}$ are orbital operators. The latter may be identified by the CG coefficients from the relation

$$\langle \Gamma \gamma_i | L_{\Gamma_k \gamma_k} | \Gamma \gamma_j \rangle = \langle \Gamma_k \gamma_k \Gamma \gamma_j | \Gamma \gamma_i \rangle. \qquad (2.5)$$

On substituting (2.4) into (2.2) and defining appropriate second-order vibronic reduction factors $K_M^{(2)}(\Gamma_k \otimes \Gamma_k)$, we obtain a general expression for the effective Hamiltonian:

$$\mathcal{H}_{\text{eff}}^{(2)} = \sum_{M \mu} \sum_{\Gamma_k \gamma_k} \sum_{\Gamma_l \gamma_l} V_{\Gamma_k} V_{\Gamma_l} Q_{\Gamma_k \gamma_k} Q_{\Gamma_l \gamma_l} \langle \Gamma_k \gamma_k \Gamma_l \gamma_l | M \mu \rangle K_M^{(2)}(\Gamma_k \otimes \Gamma_l) P_{M \mu}(\Gamma_k \otimes \Gamma_l) \qquad (2.6)$$

where the second order reduction factors are defined as

$$K_M^{(2)}(\Gamma_k \otimes \Gamma_l) = \langle 0 \Gamma \gamma_i | \mathcal{P}_{M \mu}(\Gamma_k \otimes \Gamma_l) | 0 \Gamma \gamma_j \rangle / \langle \Gamma \gamma_i | P_{M \mu}(\Gamma_k \otimes \Gamma_l) | \Gamma \gamma_j \rangle \quad (2.7)$$

and the irreducible tensors are given by

$$\mathcal{P}_{M \mu}(\Gamma_k \otimes \Gamma_l) = \sum_{\gamma_k \gamma_l} L_{\Gamma_k \gamma_k} G(\Gamma) L_{\Gamma_l \gamma_l} \langle \Gamma_k \gamma_k \Gamma_l \gamma_l | M \mu \rangle$$

$$P_{M \mu}(\Gamma_k \otimes \Gamma_l) = \sum_{\gamma_k \gamma_l} L_{\Gamma_k \gamma_k} L_{\Gamma_l \gamma_l} \langle \Gamma_k \gamma_k \Gamma_l \gamma_l | M \mu \rangle. \qquad (2.8)$$

As an example, let us consider strains of E and T_2 symmetries. In this case, V is given by (Dunn and Bates 1988)

$$V = V_E (\bar{Q}_\theta E_\theta + \bar{Q}_\epsilon E_\epsilon) + V_T (\bar{Q}_4 T_{yz} + \bar{Q}_5 T_{zx} + \bar{Q}_6 T_{xy}) \qquad (2.9)$$

where V_E and V_T are first-order coupling constants, $\bar{Q}_\theta$ is the static contribution to Q_θ from strains of E_θ-type symmetry etc and E_θ, E_ϵ, T_{yz}, T_{zx} and T_{xy} are orbital operators having the symmetry indicated.

The magnitude of the strain energies $V_i \bar{Q}_i$ will be much less than the JT energy, so the effect of the strain can be treated as a perturbation on the vibronic states. After substituting (2.8) into (2.6), we obtain the following effective Hamiltonian to describe these strains:

$$\mathcal{H}_{\text{eff}}^{(2)} = \mathcal{H}_{\text{eff}}^{E \otimes E} + 2 \mathcal{H}_{\text{eff}}^{E \otimes T_2} + \mathcal{H}_{\text{eff}}^{T_2 \otimes T_2} \qquad (2.10)$$

where

$$\mathcal{H}_{\text{eff}}^{E \otimes E} = V_E^2 \{ \tfrac{1}{4} l(l+1) K_{A_1}^{(2)}(E \otimes E)(\bar{Q}_\theta^2 + \bar{Q}_\epsilon^2)$$
$$+ \tfrac{1}{2} K_E^{(2)}(E \otimes E)[E_\theta(\bar{Q}_\epsilon^2 - \bar{Q}_\theta^2) + E_\epsilon 2 \bar{Q}_\theta \bar{Q}_\epsilon] \} \qquad (2.11)$$

$$\mathcal{H}_{\text{eff}}^{E \otimes T_2} = V_E V_T \{ \tfrac{1}{4} \sqrt{3} K_{T_1}^{(2)}(E \otimes T_2)[\bar{Q}_4(\sqrt{3} \bar{Q}_\theta + \bar{Q}_\epsilon) T_{yz} + \bar{Q}_5(-\sqrt{3} \bar{Q}_\theta + \bar{Q}_\epsilon) T_{zx}$$
$$- 2 \bar{Q}_6 \bar{Q}_\epsilon T_{xy}] - \tfrac{1}{4} K_{T_2}^{(2)}(E \otimes T_2)$$
$$\times [\bar{Q}_4(\bar{Q}_\theta - \sqrt{3} \bar{Q}_\epsilon) T_{yz} + \bar{Q}_5(\bar{Q}_\theta + \sqrt{3} \bar{Q}_\epsilon) T_{zx} - 2 \bar{Q}_6 \bar{Q}_\theta T_{xy}] \} \qquad (2.12)$$

$$\mathcal{H}_{\text{eff}}^{T_2 \otimes T_2} = V_T^2 \{ \tfrac{1}{4} l(l+1) K_{A_1}^{(2)}(T_2 \otimes T_2)(\bar{Q}_4^2 + \bar{Q}_5^2 + \bar{Q}_6^2)$$
$$- \tfrac{1}{4} K_E^{(2)}(T_2 \otimes T_2)[E_\theta(\bar{Q}_4^2 + \bar{Q}_5^2 - 2 \bar{Q}_6^2) - E_\epsilon \sqrt{3}(\bar{Q}_4^2 - \bar{Q}_5^2)]$$
$$- \tfrac{1}{2} \sqrt{3} K_{T_2}^{(2)}(T_2 \otimes T_2)[T_{yz} \bar{Q}_5 \bar{Q}_6 + T_{zx} \bar{Q}_6 \bar{Q}_4 + T_{xy} \bar{Q}_4 \bar{Q}_5] \}. \qquad (2.13)$$

In fact, all real crystals will incorporate a wide range of different strains, which can be modelled by varying the values of the $\bar{Q}_i$s. Consider the uniaxial stress cases in which a stress is applied externally along a known axis of the crystal. A tetragonal strain along the [001] axis is generated when all the $\bar{Q}_i$ are zero except $\bar{Q}_\theta$. In this case, we have

$$\mathcal{H}_{\text{eff}}^{(2)} = V_E^2[\tfrac{1}{4}l(l+1)K_{A_1}^{(2)}(E \otimes E)\bar{Q}_\theta - \tfrac{1}{2}K_E^{(2)}(E \otimes E)E_\theta \bar{Q}_\theta^2]. \tag{2.14}$$

For a triagonal strain along the [111] axis of the cluster, we have $\bar{Q}_\theta = \bar{Q}_\epsilon = 0$ and $\bar{Q}_4 = \bar{Q}_5 = \bar{Q}_6 = \bar{Q}_T$. Therefore, the effective Hamiltonian is

$$\mathcal{H}_{\text{eff}}^{(2)} = V_T^2[\tfrac{1}{4}3l(l+1)K_{A_1}^{(2)}(T_2 \otimes T_2)\bar{Q}_T^2 - \tfrac{1}{2}\sqrt{3}K_{T_2}^{(2)}(T_2 \otimes T_2)\bar{Q}_T^2(T_{yz} + T_{zx} + T_{xy})]. \tag{2.15}$$

Finally, for an orthorhombic strain along the [110] axis of the crystal, $\bar{Q}_\epsilon = \bar{Q}_4 = \bar{Q}_5 = 0$, so we obtain

$$\begin{aligned}
\mathcal{H}_{\text{eff}}^{(2)} &= V_E^2[\tfrac{1}{4}l(l+1)K_{A_1}^{(2)}(E \otimes E)\bar{Q}_\theta^2 - \tfrac{1}{2}K_E^{(2)}(E \otimes E)E_\theta \bar{Q}_\theta^2] \\
&\quad + V_T^2[\tfrac{1}{4}l(l+1)K_{A_1}^{(2)}(T_2 \otimes T_2)\bar{Q}_6^2 + \tfrac{1}{2}K_E^{(2)}(T_2 \otimes T_2)E_\theta \bar{Q}_6^2] \\
&\quad + V_E V_T K_{T_2}^{(2)}(E \otimes T_2)\bar{Q}_6\bar{Q}_\theta T_{xy}
\end{aligned} \tag{2.16}$$

for the effective Hamiltonian.

2.2. Reduction factors

As we can see from the above, $\mathcal{H}_{\text{eff}}^{(2)}$ describes the effect of strains expressed in terms of second-order reduction factors which multiply the original electronic perturbations. Hence it is important to be able to calculate these reduction factors. Polinger *et al* (1991) developed a general expression for the derivation of second-order reduction factors, which is given by

$$\begin{aligned}
K_M^{(2)}(\Gamma_k \otimes \Gamma_l) = &\left((-1)^{j(\Gamma)}[\Gamma] \Big/ \begin{bmatrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Gamma \end{bmatrix} \right) \\
&\times \sum_\Lambda (-1)^{j(\Lambda)}[\Lambda] \begin{bmatrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Lambda \end{bmatrix} R_\Lambda(\Gamma_k \Gamma_l)
\end{aligned} \tag{2.17}$$

with

$$\begin{aligned}
R_\Lambda(\Gamma_k \Gamma_l) &= \sum_n \frac{S_n(\Gamma_k \Lambda \Gamma)S_n(\Gamma_l \Lambda \Gamma)}{E_\Gamma^{(0)} - E_\Lambda^{(n)}} \\
S_n(\Sigma \Lambda \Gamma) &= \sum_M (-1)^{j(M)+j(\Sigma)} \{0(\Gamma)M\|n(\Lambda)M\} \begin{bmatrix} \Gamma & \Gamma & \Sigma \\ \Gamma & \Lambda & M \end{bmatrix}.
\end{aligned} \tag{2.18}$$

In the above, the 6Γ symbols are written with large square brackets, the fictitious angular momentum operator as $j(\Gamma)$ and the dimension of a representation with small brackets (see, e.g., Griffiths 1962), Γ_k and Γ_l denote the symmetry components of the Vs and $\{0(\Gamma)M\|n(\Lambda)M\}$ are the oscillator overlap integrals.

To be able to use the formulation above, it is necessary to obtain expressions for the ground and excited vibronic states in symmetry-adapted form. This is generally a difficult problem. However, for the $T \otimes (e + t_2)$ system, these vibronic states have been calculated by Hallam *et al* (1992a). In order to extract the required oscillator parts of the vibronic states and thus calculate the reduction factors, the procedures given in the appendix must be used.

3. Calculations of the reduction factors

3.1. The reduction factors contained within $\mathcal{H}_{\text{eff}}^{\text{E} \otimes \text{E}}$

In this case, we have $\Gamma_k = \Gamma_l = \text{E}$. Substituting into (2.17), we obtain

$$K_{A_1}^{(2)}(\text{E} \otimes \text{E}) = 9[R_{T_1} + R_{T_2}] \qquad K_{E}^{(2)}(\text{E} \otimes \text{E}) = 9[R_{T_1} - R_{T_2}]. \qquad (3.1)$$

These expressions are exactly the same as those deduced by Jamila *et al* (1992) for the $T \otimes t_2$ JT system. This is because the general expression (2.17) for second-order reduction factors is valid for any type of vibronic system. The differences between the different systems are contained entirely within the overlap factors R_Λ. These in turn depend upon the details of the ground and all the excited vibronic states (Hallam *et al* 1992a). On comparing these symmetry states with the general form given in (2.1), simultaneous equations are obtained (see the appendix) which can be solved easily to give the phonon states required in the calculation of the second-order reduction factors. After a great deal of algebra, we obtain

$$R_{T_1} = \tfrac{1}{9}(G_1 + G_2) \qquad R_{T_2} = \tfrac{1}{3}(G_3 + G_4) \qquad (3.2)$$

where

$$G_1 = -\sum_N \Gamma_7(p, q, r, s, t)[4g_1(p, q, t, r, s) + g_2(p, q, r, s, t)]^2$$

$$G_2 = -4\sum_N \Gamma_{10}(p, q, r, s, t)g_1^2(p, q, r, s, t)$$

$$G_3 = -\sum_N \Gamma_{15}(p, q, r, s, t)g_2^2(p, q, r, s, t)$$

$$G_4 = -4\sum_N \Gamma_{16}(p, q, r, s, t)g_1^2(p, q, r, s, t) \qquad (3.3)$$

and where

$$\Gamma_i = N_7^2(0)N_i^2(p, q, r, s, t)/(E_i^{(N)} - E_7^{(0)})$$

$$g_1(p, q, r, s, t) = S_{\text{et}}H(p, q)A(r)A(s)\delta_{0,t}$$

$$g_2(p, q, r, s, t) = \bar{S}_{\text{et}}\delta_{0,p}\delta_{0,q}\delta_{0,r}\delta_{0,s}B(t)$$

$$A(i) = \frac{1}{\sqrt{i!}}\left(\frac{K_T}{\hbar\omega_T}\right)^i \qquad B(i) = \frac{1}{\sqrt{i!}}\left(\frac{2K_T}{\hbar\omega_T}\right)^i$$

$$H(p, q) = \frac{1}{\sqrt{p!q!}}\left(\frac{3K_E}{2\hbar\omega_E}\right)^p\left(\frac{\sqrt{3}K_E}{2\hbar\omega_E}\right)^q. \qquad (3.4)$$

In the above, p, q, r, s and t denote the numbers of phonon excitations, N_i are normalizing factors, S_{et} and $\bar{S}_{\text{et}}$ are the overlaps of the oscillator ground states (see Hallam *et al* (1992a) for more details).

Plots of $K_{A_1}^{(2)}$ and $K_{E}^{(2)}$ as a function of $K_T/\hbar\omega_T$ are shown in figure 1 with the simplifying assumption that $\omega_E = \omega_T = \omega$. Also, the ratio η of the JT energies for e to t_2 couplings is chosen to be 0.8 and the bi-linear constant $K_{BL} = -0.036$. (The reasons for this choice of parameter values are given in detail in Hallam *et al* (1992b).) A total of 25 phonons were used in the computations for figure 1 (that is, $p+q+r+s+t = 25$). Note that the formulae given in (3.4) are entirely general for *any* choice of parameter values and appropriate graphs can be obtained just as easily as the specific choice used above for display purposes.
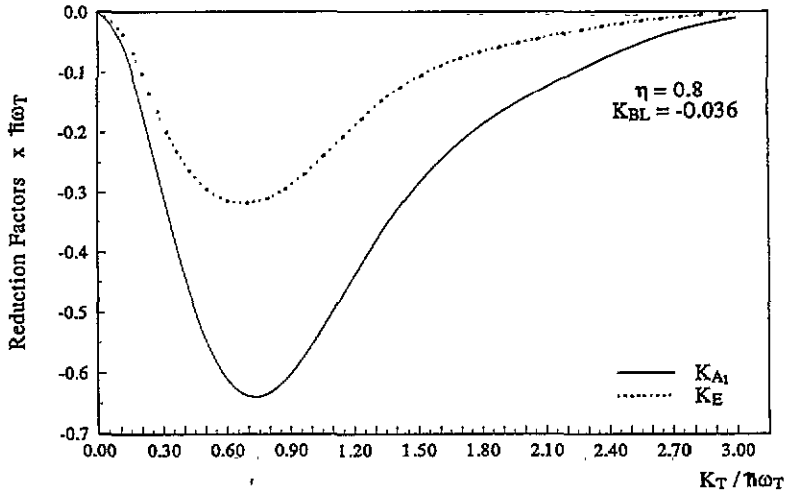
Figure 1. Second-order reduction factors for perturbations of the form E ⊗ E plotted as a function of $K_T/\hbar\omega$ for the orthorhombic T ⊗ (e + t$_2$) JT system with $\omega_E = \omega_T = \omega$ and with $\eta = 0.8$ and $K_{BL} = -0.036$.

3.2. The reduction factors contained in $\mathcal{H}_{\text{eff}}^{T_2 \otimes T_2}$

In this case, $\Gamma_k = \Gamma_l = T_2$. Because $T_2 \otimes T_2 = A_1 + E + T_1 + T_2$, we can obtain from (2.17) the four non-zero reduction factors

$$K_{A_1}^{(2)}(T_2 \otimes T_2) = 3R_{A_2} + 6R_E + 9R_{T_1} + 9R_{T_2}$$

$$K_E^{(2)}(T_2 \otimes T_2) = -6R_{A_2} - 12R_E + 9R_{T_1} + 9R_{T_2}$$

$$K_{T_1}^{(2)}(T_2 \otimes T_2) = -6R_{A_2} + 6R_E + 9R_{T_1} - 9R_{T_2}$$

$$K_{T_2}^{(2)}(T_2 \otimes T_2) = 6R_{A_2} - 6R_E + 9R_{T_1} - 9R_{T_2}. \tag{3.5}$$

On comparing the results given in equation (3.5) with the equivalent results for $T_1 \otimes T_1$ given in equation (2.27) of Polinger *et al* (1991), we see that R_{A_1} has become R_{A_2}. This is because for orbital states of T_1 symmetry, the direct product $T_1 \otimes T_1$ involves A_1 but not A_2 (the latter is contained within direct product $T_1 \otimes T_2$). After inserting the appropriate overlap integrals into (2.18), the R_As are given by

$$R_{A_2} = \tfrac{1}{3}G_1 \qquad R_E = \tfrac{1}{3}(G_2 + G_3)$$

$$R_{T_1} = \tfrac{1}{9}(G_4 + G_5) \qquad R_{T_2} = \tfrac{1}{9}(G_6 + G_7) \tag{3.6}$$

where

$$G_1 = -32 \sum_N \Gamma_2(p, q, r, s, t)[g_1(p, q, t, s, r) + (-1)^q g_1(p, q, t, r, s)]^2$$

$$G_2 = -4 \sum_N \Gamma_4(p, q, r, s, t)g_1^2(p, q, t, r, s)$$

$$G_3 = -4 \sum_N \Gamma_6(p, q, r, s, t)g_1^2(p, q, t, r, s)$$

$$G_4 = -4 \sum_N \Gamma_7(p,q,r,s,t)[g_1(p,q,t,r,s) + 2(-1)^q g_1(p,q,t,s,r)]^2$$

$$G_5 = -4 \sum_N \Gamma_{10}(p,q,r,s,t) g_1^2(p,q,r,s,t)$$

$$G_6 = -4 \sum_N \Gamma_{15}(p,q,r,s,t) g_1^2(p,q,t,r,s)$$

$$G_7 = -4 \sum_N \Gamma_{16}(p,q,r,s,t) g_1^2(p,q,r,s,t). \tag{3.7}$$

Plots of the reduction factors are shown in figure 2. The comments relating to figure 1 are also applicable to figure 2.
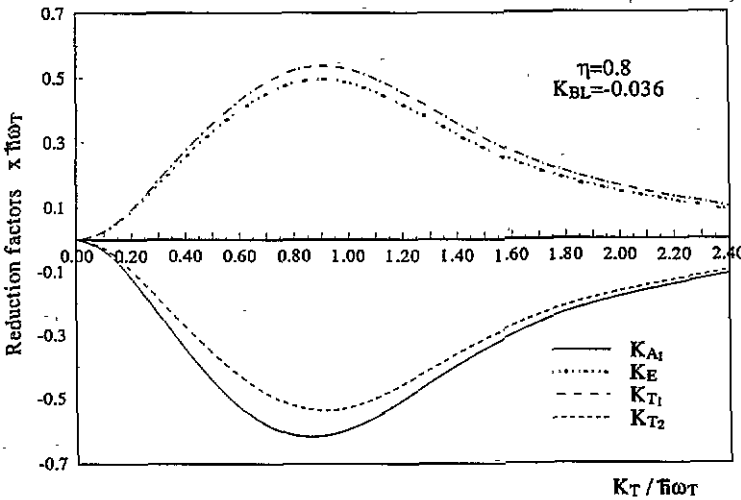

Figure 2. As for figure 1 but for perturbations of the form $T_2 \otimes T_2$.

3.3. The reduction factors contained in $\mathcal{H}_{eff}^{T_2 \otimes E}$

In this third case, $\Gamma_k = T_2$ and $\Gamma_l = E$. As in the case of the perturbation of $E \otimes E$ symmetry, some of the factors are zero. There are no second-order reduction factors that have the labels A_1, A_2 and E since only T_1 and T_2 are involved in the direct product $T_2 \otimes E$. The two non-zero factors are

$$K_{T_2}^{(2)}(T_2 \otimes E) = 3(3R_{T_1} - \sqrt{3}R_{T_2}) \qquad K_{T_2}^{(2)}(T_2 \otimes E) = 9(R_{T_1} + \sqrt{3}R_{T_2}) \tag{3.8}$$

where the R_Λ are given by

$$R_{T_1} = \tfrac{1}{9}(G_1 - G_2) \qquad R_{T_2} = \tfrac{1}{9}(G_3 + G_4) \tag{3.9}$$

where

$$G_1 = -2 \sum_N \Gamma_7(p,q,r,s,t)[g_1(p,q,t,r,s) + 2(-1)^q g_1(p,q,t,s,r)]$$
$$\times [4g_1(p,q,t,r,s) + g_2(p,q,r,s,t)]$$

$$G_2 = -4 \sum_N \Gamma_{10}(p,q,r,s,t) g_1^2(p,q,r,s,t)$$

$$G_3 = -2\sqrt{3} \sum_N \Gamma_{15}(p,q,r,s,t) g_1(p,q,t,r,s) g_2(p,q,r,s,t)$$

$$G_4 = -4\sqrt{3} \sum_N \Gamma_{16}(p,q,r,s,t) g_1^2(p,q,r,s,t). \tag{3.10}$$
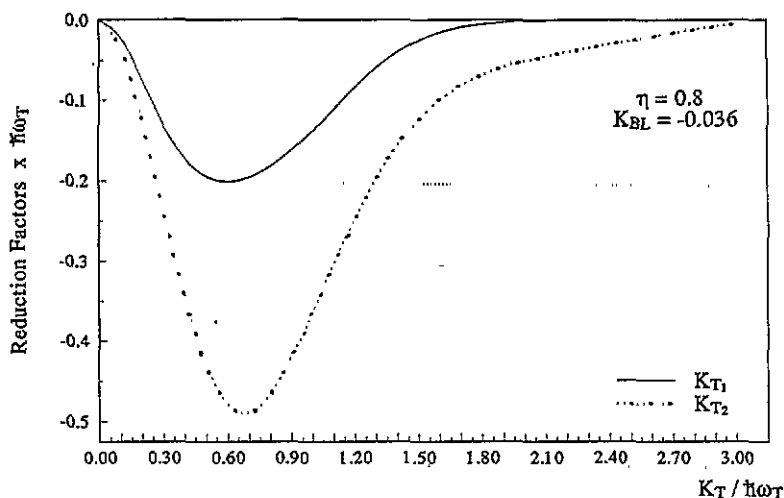
The results are shown in figure 3.

Figure 3. As for figure 1 but with perturbations of the form $E \otimes T_2$.

4. Discussion and conclusions

We discuss first the accuracy of the calculations. It is well known that, for a T_1 ion, the $T \otimes (e + t_2)$ JT system has a vibronic ground state of T_1 symmetry and an inversion level of T_2 symmetry. As these vibronic states are coupled by the E and T_2 strains studied here, a question arises concerning the convergence of the sums in our perturbation calculations of the reduction factors as the energy denominator tends to zero in the infinite-coupling limit. In order to investigate this limiting behaviour, new vibronic states have been obtained in which the strain has only diagonal elements by taking appropriate combinations of the vibronic ground and inversion states used above. Using these new states, it is found that the corrections to the reduction factors given above are proportional to $\bar{Q}_i^3$ and thus they are very small. We conclude therefore that the above analysis, which excluded coupling to the inversion level, is accurate.

This paper has described analytical calculations of the second-order reduction factors for the orthorhombic $T \otimes (e + t_2)$ JT system for perturbations which have symmetries $E \otimes E$, $T_2 \otimes T_2$ and $T_2 \otimes E$. As far as we are aware, these reduction factors have not previously been calculated by any method. The only other calculations for such perturbations appear to be those for the $T \otimes e$ (Ham 1965) and $T \otimes t_2$ (Jamila *et al* 1992) JT systems. In this paper, the second-order reduction factors have been calculated by following the symmetry-related method of Polinger *et al* (1991) and using the symmetry-adapted cubic vibronic states obtained previously by Hallam *et al* (1992a). The results obtained have the same general form as those derived earlier by Hallam *et al* (1992b) for the spin–orbit coupling which refer to $T_1 \otimes T_1$ perturbations. The positions of the peaks shown in figures 1–3 occur at similar values of $K_T/\hbar\omega_T$ as those shown in figure 1 of Hallam *et al* (1992b) for the spin–orbit coupling. Also their maximum values are approximately the same. (Note that different quantities have been plotted in our figures; the relation between the different quantities is given in equation (4.2) of Hallam *et al* (1992b).)

From a theoretical point of view, it is interesting to observe the various differences and similarities that exist among the results obtained for the different symmetries of the second-order perturbations for the $T \otimes (e + t_2)$ JT system alone as shown by equations (3.1)–(3.3) and (3.5). It is also of interest to compare the results of the same symmetries of perturbations between the different JT systems. Such comparisons are possible because the calculations are analytical and they have all used a method based on powerful symmetry arguments.

The results obtained here are primarily used to determine the effective Hamiltonians for the modelling of strongly coupled impurities in semiconductors when uniaxial stresses are applied to the system. A particular system of current interest to us is that of GaP:Ti^{3+}. Uniaxial stress experiments are being carried out on the optical absorption zero-phonon line where departures from a linear stress dependence have been observed (Al-Shaikh *et al* 1993). It is also apparent that both E- and T$_2$-type stresses affect the spectra. This leads to the question as to the nature of the JT effect in the upper T$_2$ vibronic state that best describes the system. Jamila *et al* (1992) gives the relevant results for T $\otimes$ t$_2$ systems, Ham (1965) for T $\otimes$ e systems and here we have the results for the T $\otimes$ (e + t$_2$) system. Work is currently in progress to try to establish the most likely type of JT effect operating in the excited state and the results described here will be significant in this analysis.

Acknowledgments

Appendix

In order to use equation (2.17) to calculate second-order reduction factors, we require expressions for the phonon states $|n(\Lambda)M\rangle$ which can be extracted from the vibronic states. A complete set of symmetry-adapted vibronic states for strongly coupled T$\otimes$(e+t$_2$) systems have been derived in Hallam *et al* (1992a) and can be written in the form

$$|n\Gamma\gamma\rangle = N^{\Gamma\gamma} \sum_k |X^{(k)'}; Y^{(k)}; Z_{\Gamma\gamma}^{(k)}\rangle \tag{A1}$$

with

$$|X^{(k)'}\rangle = \sqrt{\tfrac{1}{2}} \sum_\sigma \alpha_\sigma^{(k)} U_k |\Sigma\sigma\rangle$$

$$|Y^{(1)}\rangle = |\theta_z^p \epsilon_z^q\rangle \qquad \text{etc} \tag{A2}$$

$$|Z_{\Gamma\gamma}^{(1)}\rangle = c_1^{\Gamma\gamma} |4^r 5^s 6^t\rangle + c_3^{\Gamma\gamma} (-1)^q |4^s 5^r 6^t\rangle \qquad \text{etc}$$

where $|X^{(k)'}\rangle$ represents the electronic part of the state and $|Y^{(k)}\rangle$ and $|Z_{\Gamma\gamma}^{(k)}\rangle$ the e-type phonon and t$_2$-type phonon components respectively and the $N^{\Gamma\gamma}$s are normalizing factors. For details of these definitions see Hallam *et al* (1992a). By substitution, we have

$$|n\Gamma\gamma\rangle = \sqrt{\tfrac{1}{2}} N^{\Gamma\gamma} \sum_{\sigma k} a_\sigma^{(k)} |\Sigma\sigma\rangle U_k |Y^{(k)}; Z_{\Gamma\gamma}^{(k)}\rangle. \tag{A3}$$

Comparing (A3) with the general expression

$$|n\Gamma\gamma\rangle = \sum_{\sigma\Lambda\lambda} |\Sigma\sigma\rangle |n(\Gamma)\Lambda\lambda\rangle \langle\Sigma\sigma\Lambda\lambda|\Gamma\gamma\rangle \tag{A4}$$

we obtain a set of simultaneous equations:

$$\sum_{\Lambda\lambda} |n(\Gamma)\Lambda\lambda\}\langle\Sigma\sigma\Lambda\lambda|\Gamma\gamma\rangle = \sqrt{\tfrac{1}{2}}N^{\Gamma\gamma}\sum_k \alpha_\sigma^{(k)}U_k|Y^{(k)}; Z_{\Gamma\gamma}^{(k)}\rangle \tag{A5}$$

where $\sigma = x, y, z$. Solving these equations gives the phonon states required. In some cases, symmetry considerations may be of help in deriving the results. For example, when an orbital triplet of T_1 symmetry at a T_d site is considered, we have $\Sigma = T_1$ in the expression (A5). Suppose $\Gamma = A_2$; then since A_2 is only involved in the direct product $T_1 \otimes T_2$, there will be only one term with $\Lambda = T_2$ remaining on the left-hand side of the equation (A5). This can also be seen easily from the symmetry properties of CG coefficients. Thus we obtain directly the result

$$|n(A_2)T_2z\} = \tfrac{1}{2}\sqrt{6}N^{A_2}\sum_k \alpha_z^{(k)}U_k|Y^{(k)}; Z_{A_2}^{(k)}\rangle$$

$$= \tfrac{1}{2}\sqrt{6}N^{A_2}[U_3|\theta_x^p\epsilon_x^q 4^t 5^r 6^s\rangle + (-1)^q U_3|\theta_x^p\epsilon_x^q 4^t 5^s 6^r\rangle$$

$$- (-1)^{s+t}U_4|\theta_x^p\epsilon_x^q 4^t 5^r 6^s\rangle + (-1)^{q+s+t}U_4|\theta_x^p\epsilon_x^q 4^t 5^s 6^r\rangle$$

$$+ U_5|\theta_y^q\epsilon_y^q 4^r 5^t 6^s\rangle + (-1)^q U_5|\theta_y^p\epsilon_y^q 4^s 5^t 6^r\rangle + (-1)^{s+t}U_6|\theta_y^p\epsilon_y^q 4^r 5^t 6^r\rangle$$

$$- (-1)^{q+s+t}U_6|\theta_y^p\epsilon_y^q 4^r 5^t 6^s\rangle]. \tag{A6}$$

References

Al-Shaikh *et al* 1993 in preparation
Bates C A and Dunn J L 1989 *J. Phys.: Condens. Matter* **1** 2605–16
Bates C A, Dunn J L, Hallam L D, Kirk P J and Polinger V Z 1991 *J. Phys.: Condens. Matter* **3** 3441–53
Bersuker I B and Polinger V Z 1989 *Vibronic Interaction in Molecules and Crystal* (Berlin: Springer)
Dunn J L and Bates C A 1988 *J. Phys. C: Solid State Phys.* **21** 2495–509
—— 1989 *J. Phys.: Condens. Matter* **1** 2617–29
Dunn J L, Bates C A and Kirk P J 1990 *J. Phys.: Condens. Matter* **2** 10379–89
Griffiths J S 1962 *The Irreducible Tensor Method for Molecular Symmetry Groups* (London: Prentice-Hall)
Hallam L D 1991 *Thesis* University of Nottingham
Hallam L D, Bates C A and Dunn J L 1992a *J. Phys.: Condens. Matter* **4** 6775–95
—— 1992b *J. Phys.: Condens. Matter* **4** 6797–810
Ham F S 1965 *Phys. Rev.* A **138** 1727–40
Jamila S, Dunn J L and Bates C A 1992 *J. Phys.: Condens. Matter* **4** 4945–58
Kirk P J 1992 *Thesis* University of Nottingham
O'Brien M C M 1990 *J. Phys.: Condens. Matter* **2** 5539–53
Perlin Yu E and Wagner M 1984 *The Dynamical Jahn–Teller Effect in Localised Systems* (Amsterdam: North-Holland)
Polinger V Z, Bates C A and Dunn J L 1991 *J. Phys.: Condens. Matter* **3** 513–27