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Reduction factors for strongly coupled orbital triplet Jahn–Teller systems: II. $T \otimes (e + t_2)$ Jahn–Teller systems

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Abstract. A method of studying strongly coupled Jahn–Teller (JT) systems involving a unitary transformation and energy minimisation procedure developed in the preceding paper for $T \otimes e$ and $T \otimes t$ JT systems is used to obtain analytical expressions for the first- and second-order JT reduction factors of $T \otimes (e + t_2)$ JT systems. The effect of anisotropic corrections to the first-order reduction factors is also investigated.

1. Introduction

Many magnetic impurity ions in semiconducting crystals have orbital triplet states which are strongly coupled to both e - and t_2 -type cluster displacements. The vibronic states of such systems are combinations of states localised in potential energy wells which can lie along tetragonal, trigonal and orthorhombic axes of the crystals. It is difficult to determine good eigenstates of these systems in general, as states associated with all three sets of wells must be taken into account. However, if the energy gap between the lowest energy set of wells and the remaining wells is sufficiently large and the mixing between states in different wells small, it is a good approximation to consider the lowest energy wells only. This is most likely to occur in strong coupling (Dunn and Bates 1987).

In this paper, we investigate $T \otimes (e + t_2)$ Jahn–Teller (JT) systems which have orthorhombic wells as distinct energy minima. Most of the previous work on these systems was reviewed by the present authors in Bates *et al* (1987), so this will not be repeated here. It should, however, be noted that many approaches to $T \otimes (e + t_2)$ JT systems consider the special case of equal coupling to the e - and t_2 -type phonon modes, in which the three different types of energy wells coexist (e.g. Chancey 1987). Consequently, the results obtained using these methods are fundamentally different to those obtained in this paper.

The aim of this paper is to obtain analytical expressions for JT reduction factors in orthorhombic $T \otimes (e + t_2)$ JT systems using the unitary transformation approach of Bates *et al* (1987) and Dunn (1988). The methods used are similar to those applied to $T \otimes e$ and $T \otimes t$ JT systems in the preceding paper (Bates and Dunn 1989). Expressions for first-order reduction factors will be obtained using states which take account of anisotropic effects (Dunn and Bates 1988), and the results obtained compared to those of previous calculations. Approximate analytical expressions for second-order reduction factors of spin–orbit coupling will then be derived (neglecting the anisotropic perturbations). No previous calculations of these reduction factors appear to have been reported.

It is well known that it is necessary for either quadratic or anharmonic perturbations to be present for orthorhombic wells to exist (Muramatsu and Iida 1970, Bersuker and Polinger 1974, Bacci *et al* 1975, Lister and O'Brien 1984). For the calculations presented in this paper, it will be assumed that the orthorhombic wells are generated by the bilinear form of quadratic coupling (Sakamoto 1982, Bersuker and Polinger 1983). However, it is a simple matter to extend the calculations to cover other perturbations.

2. Background

A summary of the unitary transformation method of Bates *et al* (1987), Dunn (1988) and Dunn and Bates (1988) was given in Bates and Dunn (1989), so only a very brief summary will be given here. The results apply to a T_1 ion in T_d symmetry.

In the unitary transformation method, a transformation U of the form

$$U = \exp \left(i \sum_j \alpha_j P_j \right) \quad (2.1)$$

is applied to the basic JT Hamiltonian, where the α_j are free parameters covering the e-type phonon modes $j = \theta$ and ε and the t_2 -type modes $j = 4, 5$ and 6 . The α_j are then chosen to minimise the energy of approximate eigenstates of the transformed Hamiltonian $\tilde{\mathcal{H}}$. It is found that with quadratic couplings, six orthorhombic wells exist (labelled by $k = 1$ to 6) at positions $-\alpha_j^{(k)} \hbar$ in phonon-coordinate space, where

$$\alpha_j^{(k)} = (V_j / \hbar \mu \omega_j^2) n_j^{(k)} \quad (j = \theta, \varepsilon, 4, 5, 6) \quad (2.2)$$

and

$$\begin{aligned} n_\theta^{(1)} = n_\theta^{(2)} = \frac{1}{2} \varphi_e & & -n_\theta^{(1)} = n_\theta^{(2)} = (\sqrt{3}/2) \varphi_t \\ n_\theta^{(3)} = n_\theta^{(4)} = -\frac{1}{4} \varphi_e & & n_\varepsilon^{(3)} = n_\varepsilon^{(4)} = (\sqrt{3}/4) \varphi_e & & -n_\varepsilon^{(3)} = n_\varepsilon^{(4)} = (\sqrt{3}/2) \varphi_t \\ n_\theta^{(5)} = n_\theta^{(6)} = -\frac{1}{4} \varphi_e & & n_\varepsilon^{(5)} = n_\varepsilon^{(6)} = -(\sqrt{3}/4) \varphi_e & & -n_\varepsilon^{(5)} = n_\varepsilon^{(6)} = (\sqrt{3}/2) \varphi_t \end{aligned}$$

and all other $n_j^{(k)} = 0$, where

$$\varphi_e = \frac{(1-2C)}{(1-A^2)} \quad \text{and} \quad \varphi_t = \frac{(1-B/2)}{(1-A^2)} \quad (2.3)$$

with

$$A = -\frac{\sqrt{3}}{2} \frac{V_{BL}}{\mu \omega_E \omega_T} \quad B = -\frac{V_E V_{BL}}{V_T \mu \omega_E^2} \quad C = \frac{A^2}{B}$$

and V_{BL} is the bilinear coupling constant. The positions of the wells agree with the results of other procedures (e.g. Bersuker and Polinger 1974). The ground states localised in the six wells (in the transformed picture) will be written in the form $|X_0^{(k)}; 0\rangle$, where $X_0^{(k)}$ is the appropriate orbital state and the '0' indicates that there are no phonon excitations present in the transformed picture. In terms of states x, y and z of an orbital $l = 1$, it can be shown that $X_0^{(1)} = xy_+$, $X_0^{(2)} = xy_-$, $X_0^{(3)} = yz_+$, $X_0^{(4)} = yz_-$, $X_0^{(5)} = zx_+$ and $X_0^{(6)} = zx_-$, where $ab_\pm = (1/\sqrt{2})(a \pm b)$. The minimum of each well is at the energy $-E_{ET}$, where

$$E_{ET} = \frac{1}{4} E_E \varphi_e + \frac{3}{4} E_T \varphi_t \quad (2.4)$$

and E_E and E_T are the magnitudes of the JT energies of $T \otimes e$ and $T \otimes t$ JT systems,

respectively. These are defined in terms of the usual e- and t_2 -type coupling constants V_E and V_T (see Dunn and Bates 1988) by

$$E_E = 4K_E^2/\hbar\omega_E \quad \text{and} \quad E_T = 4K_T^2/3\hbar\omega_T \quad (2.5)$$

where

$$K_E = -\frac{\hbar^{1/2}V_E}{2(2\mu\omega_E)^{1/2}} \quad \text{and} \quad K_T = \frac{(3\hbar)^{1/2}V_T}{2(2\mu\omega_T)^{1/2}}.$$

Each ground state lies above the minimum of the well by the zero-point energy ($\hbar\omega_E + \frac{3}{2}\hbar\omega_T$). There are two orbital excited states in each well, with energies

$$\lambda_1 = 3E_T\varphi_1^2 \quad \text{and} \quad \lambda_2 = \frac{2}{3}(E_E\varphi_e + E_T\varphi_1^2) \quad (2.6)$$

with respect to the ground states. For wells $k = 1$ and 2 , the two excited states are $|X_1^{(1)}; 0\rangle = |xy_-; 0\rangle$, $|X_2^{(k)}; 0\rangle = |z; 0\rangle$, $|X_1^{(2)}; 0\rangle = |xy_+; 0\rangle$ and $|X_2^{(2)}; 0\rangle = |z; 0\rangle$, respectively. The states for the remaining four wells follow from direct permutation of the symmetry labels.

Each orbital state has a set of excited phonon states associated with it. These states will be written in the general form $|X_i^{(k)}; \theta^p \varepsilon^q 4^r 5^s 6^t\rangle$ ($i = 0, 1$ or 2), where θ^p indicates the presence of p θ -type phonon excitations, etc. These excited states have energy $[(p + q)\hbar\omega_E + (r + s + t)\hbar\omega_T]$ with respect to the 'zero-phonon' states.

The above states can be improved by the addition of a perturbation which takes account of anisotropy in the potential wells. The new states obtained will not be repeated explicitly in this paper owing to their cumbersome nature. All relevant results can be found in Dunn and Bates (1988).

The states obtained so far are all applicable to the transformed Hamiltonian $\tilde{\mathcal{H}}$. States applicable to the original untransformed system can be obtained by multiplying the transformed states by the unitary transformation appropriate to the well concerned. This specific form of U is called U_k , where

$$U_k = \exp\left(\sum_j C_j^{(k)}(b_j - b_j^\dagger)\right) \quad (2.7)$$

with

$$C_j^{(k)} = -(\frac{1}{2}\hbar\mu\omega_j)^{1/2}\alpha_j^{(k)}$$

where b_j^\dagger and b_j are the usual creation and annihilation operators for a mode symmetry j . Such states will be written in the form $|X_0^{(k)'}; 0\rangle (= U_k |X_0^{(k)}; 0\rangle)$. The untransformed states are not orthogonal to each other and do not have cubic symmetry, so are not good eigenstates of the system as a whole. However, cubic combinations of these states, constructed using projection operator techniques, can be shown to be good approximations to the eigenstates of \mathcal{H} (Bates *et al* 1987). The degeneracy of the six orthorhombic wells is then split, to produce a lower T_1 triplet and upper T_2 triplet, whose z -type components are

$$\begin{aligned} |T_{1\text{zet}}\rangle &= N_{T1\text{et}}(|zx'_+; 0\rangle + |zx'_-; 0\rangle + |yz'_+; 0\rangle - |yz'_-; 0\rangle) \\ |T_{2\text{zet}}\rangle &= N_{T2\text{et}}(|zx'_+; 0\rangle + |zx'_-; 0\rangle - |yz'_+; 0\rangle + |yz'_-; 0\rangle) \end{aligned} \quad (2.8)$$

where

$$4N_{T1\text{et}}^2(1 + S_{\text{et}}) = 1 \quad \text{and} \quad 4N_{T2\text{et}}^2(1 - S_{\text{et}}) = 1$$

and S_{et} is the oscillator overlap between, for example, $|xy'_+; 0\rangle$ and $|yz'_+; 0\rangle$. This overlap can be evaluated to

$$S_{\text{et}} = \exp[-\frac{3}{2}(K_E/\hbar\omega_E)^2\varphi_e^2 - (K_T/\hbar\omega_T)^2\varphi_t^2]. \quad (2.9)$$

The x - and y -type states of the triplets can be obtained from the z -states by cyclically interchanging x , y and z . The energies of the cubic T_1 and T_2 states were given in Bates *et al* (1987) and Dunn and Bates (1988) and so, as the expressions are somewhat complicated, they will not be repeated here.

It will be necessary in the following calculations to determine the oscillator overlap between, for example, the ground states $|xy'_+; 0\rangle$ and $|xy'_-; 0\rangle$ associated with wells 1 and 2. This overlap, which will be called \bar{S}_{et} , can be shown to take the value

$$\bar{S}_{\text{et}} = \exp[-2(K_T/\hbar\omega_T)^2\varphi_t^2]. \quad (2.10)$$

3. First-order reduction factors

First-order JT reduction factors for the T_1 and T_2 ground-state triplets have been calculated using both the simple isotropic states and the anisotropic states derived in Dunn and Bates (1988), using similar procedures to those used for $T \otimes e$ and $T \otimes t$ JT systems in the preceding paper (Bates and Dunn 1989).

Using the simple isotropic states, the reduction factors between the T_1 states are calculated to be

$$\begin{aligned} K_{11}^{\text{et}}(T_1) &= 2N_{T1\text{et}}^2(3S_{\text{et}} + \bar{S}_{\text{et}}) \\ K_{11}^{\text{et}}(T_2) &= 2N_{T1\text{et}}^2(1 + 3S_{\text{et}}) \\ K_{11}^{\text{et}}(E) &= N_{T1\text{et}}^2(1 + 4S_{\text{et}} + 3\bar{S}_{\text{et}}) \end{aligned} \quad (3.1)$$

where the labels '11' indicate that the reduction factors are between the T_1 states. These formula are identical to those obtained by Bersuker and Polinger (1974). (Note that the S and \bar{S} used by Bersuker and Polinger have values that are half those used here.) For the T_2 triplet, the reduction factors are

$$\begin{aligned} K_{22}^{\text{et}}(T_1) &= 2N_{T2\text{et}}^2(S_{\text{et}} - \bar{S}_{\text{et}}) \\ K_{22}^{\text{et}}(T_2) &= -\frac{1}{2} \\ K_{22}^{\text{et}}(E) &= N_{T2\text{et}}^2(1 - 4S_{\text{et}} + 3\bar{S}_{\text{et}}). \end{aligned} \quad (3.2)$$

Bersuker and Polinger (1974) state that the reduction factors between the T_2 states are the same as those between the T_1 states, which cannot be the case. Reduction factors can also be calculated between the T_1 and T_2 states. The two sets of states belong to different effective $l = 1$ manifolds, so operators must be chosen which reflect this. However, it can be shown that l_x (of $l = 1$) can be used as a suitable T_1 operator and $T_{xy} = (\sqrt{3}/4)(l_x l_y + l_y l_x)$ as a suitable T_2 operator if it is assumed that the states all belong to the same $l = 1$ manifold. $E_\theta = \frac{1}{2}[3l_z^2 - l(l+1)]$ can similarly be used as a suitable E -operator. However, it is incorrect to use $E_\epsilon = (\sqrt{3}/2)(l_x^2 - l_y^2)$. The appropriate operator for E_ϵ is

$$-(i/\sqrt{6})(l_x^{(1)} T_{yz}^{(2)} + l_y^{(1)} T_{zx}^{(2)} - 2l_z^{(1)} T_{xy}^{(2)})$$

(constructed using the tables of Koster *et al* (1963) for example), where $l_x^{(1)}$ operates on T_1 states and $T_{yz}^{(2)}$ on T_2 states, etc. It must be remembered that the reduction factors

have arbitrary signs, dependent upon the phase definitions of the T_1 and T_2 states. One consistent choice gives

$$\begin{aligned} K_{12}^{et}(T_1) &= 2N_{T1et}N_{T2et}(-S_{et} + \bar{S}_{et}) \\ K_{12}^{et}(T_2) &= 2N_{T1et}N_{T2et}(1 - S_{et}) \\ K_{12}^{et}(E) &= 3N_{T1et}N_{T2et}(1 - \bar{S}_{et}). \end{aligned} \quad (3.3)$$

If the anisotropic states of Dunn and Bates (1988) are used, the nine reduction factors are calculated to be

$$\begin{aligned} K_{11}^{et}(T_1) &= 2N_{T1et}^2(3PS_{et} + \bar{S}_{et}) \\ K_{11}^{et}(T_2) &= 2N_{T1et}^2(1 + 3QS_{et}) \\ K_{11}^{et}(E) &= N_{T1et}^2(1 + 4RS_{et} + 3\bar{S}_{et}) \\ K_{22}^{et}(T_1) &= 2N_{T2et}^2(PS_{et} - \bar{S}_{et}) \\ K_{22}^{et}(T_2) &= 2N_{T2et}^2(-1 + QS_{et}) \\ K_{22}^{et}(E) &= N_{T2et}^2(1 - 4RS_{et} + 3\bar{S}_{et}) \\ K_{12}^{et}(T_1) &= 2N_{T1et}N_{T2et}(-PS_{et} + \bar{S}_{et}) \\ K_{12}^{et}(T_2) &= 2N_{T1et}N_{T2et}(1 - QS_{et}) \\ K_{12}^{et}(E) &= 3N_{T1et}N_{T2et}(1 - \bar{S}_{et}) \end{aligned} \quad (3.4)$$

where

$$\begin{aligned} P &= 1 - \frac{3}{4}I\varphi_t + 3\varphi_e\varphi_t(K + 2M) \\ Q &= 1 + \frac{3}{4}I\varphi_t + 3\varphi_e\varphi_t(K + 2M) \\ R &= 1 + \frac{3}{4}J\varphi_e - \frac{3}{4}I\varphi_t - 3\varphi_e\varphi_t(K - 2M) \end{aligned} \quad (3.5)$$

with

$$\begin{aligned} I &= \frac{E_T}{\lambda_2 + \hbar\omega_T} \left(1 + \frac{B}{4}\varphi_e \right) & J &= \frac{E_E}{\lambda_1 + \hbar\omega_E} \\ K &= \frac{K_E^2}{\hbar\omega_E} \frac{K_T^2}{\hbar\omega_T} \frac{V_{BL}}{V_E V_T} \frac{1}{\lambda_2 + \hbar\omega_E + \hbar\omega_T} & M &= \frac{K_E^2}{\hbar\omega_E} \frac{K_T^2}{\hbar\omega_T} \frac{V_{BL}}{V_E V_T} \frac{1}{\hbar\omega_E + \hbar\omega_T}. \end{aligned}$$

Here N_{T1et} and N_{T2et} are the normalisation factors for the anisotropic T_1 and T_2 states (Dunn and Bates 1988).

The values of the reduction factors in the very-strong-coupling limit are identical to those of Lister and O'Brien (1984), except for the $K_{12}^{et}(E)$ reduction factor, which has a value twice that given in Lister and O'Brien (1984). To investigate the behaviour of the reduction factors for weaker couplings, the above formula for the reduction factors have been plotted as a function of the parameter $\eta = E_E/E_T$. This parameter is introduced to fix the relative strengths of the e- and t_2 -type couplings and so ensure that the orthorhombic wells remain minima throughout the range of the plot.

In figure 1, the reduction factors for the T_1 states have been plotted as functions of $K_T/\hbar\omega$, where $\omega_E = \omega_T = \omega$. The lower set of curves have $\eta = 1.2$ (which is equivalent to fixing $K_E = \pm 0.632 K_T$). For such values of K_E and K_T , the orthorhombic

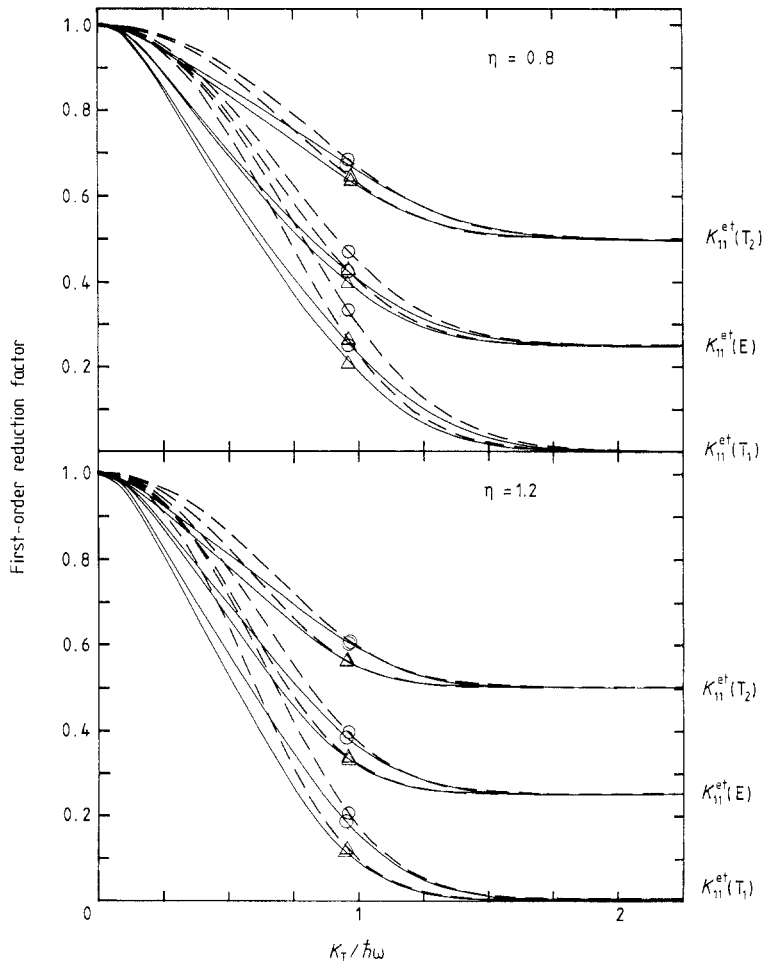


Figure 1. Variation of the first-order reduction factors $K_{ii}^{et}(E)$, $K_{ii}^{et}(T_1)$ and $K_{ii}^{et}(T_2)$ as a function of $K_T/\hbar\omega$, where $\omega_E = \omega_T = \omega$. The lower set of curves are for $\eta = 1.2$ and the upper set for $\eta = 0.8$. The broken curves are the results of the calculations without anisotropy and the full curves with anisotropy. For the lower set of curves, those marked with a circle have $F_{BL} = 0.065$ and those marked with a triangle have $F_{BL} = 0.105$. For the upper set, those marked with a circle have $F_{BL} = 0.035$ and those marked with a triangle have $F_{BL} = 0.075$.

wells will only be energy minima if (Bates *et al* 1987)

$$F_{BL} = \frac{K_T^2}{\hbar\omega_T} \frac{V_{BL}}{V_E V_T} > \frac{3(\eta - 1)}{8\eta} = 0.0625 \tag{3.6}$$

(in the absence of other quadratic couplings). Graphs have been plotted for $F_{BL} = 0.065$ and 0.105 . The upper set of curves have $\eta = 0.8$. This is equivalent to fixing $K_E = \pm 0.516 K_T$. For orthorhombic energy minima,

$$F_{BL} > \frac{(1 - \eta)}{8\eta} = 0.03125. \tag{3.7}$$

Graphs have been plotted for $F_{BL} = 0.035$ and 0.075 . It should be noted that the

bilinear coupling constant V_{BL} must always be positive to ensure orthorhombic energy minima (in the absence of other quadratic couplings).

Figure 1 shows that the anisotropic corrections to the reduction factors for the T_1 states are small for all coupling strengths. The corrections to the T_2 states can become very large at weak values of coupling because $S_{et} \rightarrow 1$, and so $N_{T_{2et}} \rightarrow \infty$ in this limit. Also, the limit of $K_{22}^{et}(E)$ as K_E and $K_T \rightarrow 0$ is path-dependent. Problems can be expected to arise with the T_2 states in weak coupling as the separation from the T_1 ground state becomes large.

The three reduction factors for the T_1 states are related by the condition

$$K_{11}^{et}(E) + \frac{3}{2}[K_{11}^{et}(T_2) - K_{11}^{et}(T_1)] = 1 - 3f_{11}^{et}(T_1) \quad (3.8)$$

where $f_{11}^{et}(T_1) = 0$ if the anisotropic corrections are neglected and

$$f_{11}^{et}(T_1) = 3N_{T_{1et}}^2 S_{et} \varphi_t(-\frac{1}{2}I + 4\varphi_e K) \quad (3.9)$$

when anisotropy is included. This relation was derived originally by Leung and Kleiner (1974) from the normalisation condition for a T_1 vibronic state. The equivalent result for a T_2 state is

$$K_{22}^{et}(E) + \frac{3}{2}[K_{22}^{et}(T_1) - K_{22}^{et}(T_2)] = 1 + 3f_{22}^{et}(T_2) \quad (3.10)$$

where $f_{22}^{et}(T_2) = 0$ without anisotropy and

$$f_{22}^{et}(T_2) = 3N_{T_{2et}}^2 S_{et} \varphi_t(\frac{1}{2}I + 4\varphi_e K) \quad (3.11)$$

with the anisotropic corrections. The reduction factors between the T_1 and T_2 states are constrained by the orthogonality of T_1 and T_2 states, such that

$$K_{12}^{et}(E) + \frac{3}{2}[K_{12}^{et}(T_1) - K_{12}^{et}(T_2)] = 3f_{12}^{et}(T_{12}) \quad (3.12)$$

where also $f_{12}^{et}(T_{12}) = 0$ without anisotropy and

$$f_{12}^{et}(T_{12}) = 3N_{T_{1et}} N_{T_{2et}} S_{et} \varphi_t(\frac{1}{2}I) \quad (3.13)$$

when anisotropy is included.

The values of the three functions $f_{11}^{et}(T_1)$, $f_{22}^{et}(T_2)$ and $f_{12}^{et}(T_{12})$ are all small, as predicted by Leung and Kleiner (1974). However, Leung and Kleiner predict that $f_{11}^{et}(T_1)$ should be positive, whereas the expression (3.9) can be either positive or negative.

4. Second-order reduction factors

Second-order reduction factors for spin-orbit coupling can be calculated in a manner analogous to that detailed in § 3.2 of the preceding paper for $T \otimes e$ and $T \otimes t$ JT systems. It is first necessary to obtain a set of phonon excited states which can be used as a basis for second-order perturbation theory. The isotropic cubic combinations of states (2.8) will be used for the zero-phonon states. However, the simple states with phonon excitations localised in the six orthorhombic wells will be used as excited states owing to the difficulties in obtaining a full set of cubic states. Although the states are not mutually orthogonal, and so only form an approximate basis set, the assumption is reasonable for a first approximation. The combinations of θ and ϵ phonons appearing in the true cubic combinations will be used (Dunn 1988) to minimise the overlaps between the excited states. Hence the states used are

$$|xy'_\pm; \theta_z^p \epsilon_x^q 4^r 5^s 6^t\rangle \quad |yz'_\pm; \theta_x^p \epsilon_x^q 4^r 5^s 6^t\rangle \quad |zx_\pm; \theta_y^p \epsilon_y^q 4^r 5^s 6^t\rangle \quad (4.1)$$

(summed over all $n = p + q + r + s + t \geq 1$), where $|\theta_x^p\rangle = (b_{\theta_x}^+)^p |0\rangle$ etc., with

$$\begin{aligned} b_{\theta_z}^+ &= b_{\theta}^+ & b_{\theta_x}^+ &= -(1/2)b_{\theta}^+ + (\sqrt{3}/2)b_{\epsilon}^+ & b_{\theta_y}^+ &= -(1/2)b_{\theta}^+ - (\sqrt{3}/2)b_{\epsilon}^+ \\ b_{\epsilon_z}^+ &= b_{\epsilon}^+ & b_{\epsilon_x}^+ &= -(\sqrt{3}/2)b_{\theta}^+ - (1/2)b_{\epsilon}^+ & b_{\epsilon_y}^+ &= (\sqrt{3}/2)b_{\theta}^+ - (1/2)b_{\epsilon}^+ \end{aligned} \quad (4.2)$$

(note that $\theta_x^p \neq (-(1/2)\theta + (\sqrt{3}/2)\epsilon)^p$, etc.). The excited states will be assumed to be of energy

$$E_n = (p + q)\hbar\omega_E + (r + s + t)\hbar\omega_T \quad (4.3)$$

relative to the ground state. Hence for the T_1 states $|T_{1x}\text{et}\rangle$, $|T_{1y}\text{et}\rangle$ and $|T_{1z}\text{et}\rangle$, the set of excited states used consists of the three states $|T_{2x}\text{et}\rangle$, $|T_{2y}\text{et}\rangle$ and $|T_{2z}\text{et}\rangle$ and the set of states (4.1) summed over all $n \neq 0$. The three T_1 states are formed into the projection operator P_0 and all excited states with n excitations into the projection operator P_n . In a similar manner, the set of states P_0 applicable to the T_2 triplet consists of the states $|T_{2x}\text{et}\rangle$, $|T_{2y}\text{et}\rangle$ and $|T_{2z}\text{et}\rangle$ and P_n consists of $|T_{1x}\text{et}\rangle$, $|T_{1y}\text{et}\rangle$ and $|T_{1z}\text{et}\rangle$ and the set (4.1).

The second-order reduction factors can then be calculated using the perturbation

$$V = - \sum_{n=1}^{\infty} P_0(\mathbf{l} \cdot \mathbf{S})P_n(\mathbf{l} \cdot \mathbf{S})P_0/E_n \quad (4.4)$$

This requires evaluating matrix elements between wells l and k , such as

$$\begin{aligned} \langle X_0^{(l)'}; 0 | \mathbf{l} \cdot \mathbf{S} | X_0^{(k)'}; \theta_z^p \epsilon_z^q 4^r 5^s 6^t \rangle \\ = \langle X_0^{(l)} | \mathbf{l} \cdot \mathbf{S} | X_0^{(k)} \rangle \langle 0 | U_l^+ U_k | \theta_z^p \epsilon_z^q 4^r 5^s 6^t \rangle. \end{aligned} \quad (4.5)$$

The oscillator matrix element can be evaluated using the identities of Dunn (1988), with the result that

$$\langle 0 | U_l^+ U_k | \theta_z^p \epsilon_z^q 4^r 5^s 6^t \rangle = S'(D_{\theta}^{(kl)})^p (D_{\epsilon}^{(kl)})^q (D_4^{(kl)})^r (D_5^{(kl)})^s (D_6^{(kl)})^t / (p!q!r!s!t!)^{1/2} \quad (4.6)$$

where

$$D_j^{(kl)} = C_j^{(k)} - C_j^{(l)}$$

and S' is the oscillator overlap between $|X_0^{(l)}\rangle$ and $|X_0^{(k)}\rangle$ (i.e. $S' = S_{\text{et}}$ or \bar{S}_{et}). The matrix elements must then be summed over all $n \neq 0$. To simplify the algebra, it is useful to define the functions

$$\begin{aligned} A(i, j, k, l) &= \frac{1}{(i!j!k!l!)^{1/2}} \left(\frac{3}{2} \frac{K_E}{\hbar\omega_E} \right)^i \left(\frac{\sqrt{3}}{2} \frac{K_E}{\hbar\omega_E} \right)^j \left(\frac{K_T}{\hbar\omega_T} \right)^k \left(\frac{K_T}{\hbar\omega_T} \right)^l \\ B(i, j, k) &= \frac{1}{(i!j!k!)^{1/2}} \left(\sqrt{3} \frac{K_E}{\hbar\omega_E} \right)^i \left(\frac{K_T}{\hbar\omega_T} \right)^j \left(\frac{K_T}{\hbar\omega_T} \right)^k \\ C(i) &= \frac{1}{(i!)^{1/2}} \left(\frac{2K_T}{\hbar\omega_T} \right)^i \end{aligned} \quad (4.7)$$

where i, j, k and l are integers. The matrix elements (4.5) can then be written in terms of these three functions by substituting the correct values for the $D_i^{(kl)}$. For example,

$$\begin{aligned} \langle xy'_-; 0 | \mathbf{l} \cdot \mathbf{S} | xy'_+; \theta_z^p \epsilon_z^q 4^r 5^s 6^t \rangle &= -i \bar{S}_{\text{et}} C(t) \delta_{0p} \delta_{0q} \delta_{0r} \delta_{0s} S_z \\ \langle yz'_+; 0 | \mathbf{l} \cdot \mathbf{S} | xy'_+; \theta_z^p \epsilon_z^q 4^r 5^s 6^t \rangle &= \frac{1}{2} -i S_{\text{et}} (-1)^{q+r} A(p, q, r, t) \delta_{0s} (S_x - S_y + S_z) \end{aligned} \quad (4.8)$$

$$\langle \sum x'_+; 0 | \mathbf{I} \cdot \mathbf{S} | y'_+; \theta_z^p \varepsilon_z^q 4^r 5^s 6^t \rangle = \frac{1}{2} i S_{\text{et}} (-1)^s B(q, r, s) \delta_{0p} \delta_{0r} (S_x + S_y - S_z)$$

where δ_{0i} is the Kronecker delta function (with one index = 0).

It is also necessary to evaluate the matrix elements

$$\langle X_0^{(l)'}; 0 | \mathbf{I} \cdot \mathbf{S} | X_0^{(k)'}; \theta_x^p \varepsilon_x^q 4^r 5^s 6^t \rangle$$

and

$$\langle X_0^{(l)'}; 0 | \mathbf{I} \cdot \mathbf{S} | X_0^{(k)'}; \theta_y^p \varepsilon_y^q 4^r 5^s 6^t \rangle.$$

These calculations are more complicated than those above owing to the nature of multiple x - and y -type θ and ε phonon excitations. For example, the vibronic component of the x -type matrix element is

$$\langle 0 | U_1^\dagger U_k | \theta_x^p \varepsilon_x^q 4^r 5^s 6^t \rangle = S' (D_4^{(kl)})^r (D_5^{(kl)})^s (D_6^{(kl)})^t (p!q!)^{1/2} F_{pq} / (r!s!t!)^{1/2} 2^{p+q} \quad (4.9)$$

where

$$F_{pq} = \sum_{\alpha=0}^p \sum_{\beta=0}^q \frac{(-1)^{p+q-\alpha} (\sqrt{3})^{\alpha+q-\beta} (D_\theta^{(kl)})^{p+q-\alpha-\beta} (D_\varepsilon^{(kl)})^{\alpha+\beta}}{\alpha! (p-\alpha)! \beta! (q-\beta)!}.$$

These matrix elements can be written in terms of the functions $A(i, j, k, l)$, $B(i, j, k)$ and $C(i)$, where the parameters i, j, k and l are functions of the summation indices.

Combinations of the above matrix elements must now be taken to form the matrix elements

$$\langle T_1 z e t | \mathbf{I} \cdot \mathbf{S} | X_0^{(k)'}; \theta_z^p \varepsilon_z^q 4^r 5^s 6^t \rangle$$

etc. These are then formed into the appropriate expressions to evaluate (4.4). This involves taking a sum over all p, q, r, s and t (excluding $p = q = r = s = t = 0$). Fortunately, when the indices are summed, the matrix elements involving x - and y -combinations of θ and ε can be greatly simplified. For example, the product

$$\sum_{\alpha=0}^p \sum_{\beta=0}^q (\sqrt{3})^{\alpha+q-\beta} [(p+q-\alpha-\beta)! (\alpha+\beta)!]^{1/2} A((p+q-\alpha-\beta), (\alpha+\beta), r, s)$$

which frequently appears in the calculations, simplifies to

$$\sum_{\alpha=0}^p \sum_{\beta=0}^q 3^{q-\beta} A(p, q, r, s) (p!q!)^{1/2}. \quad (4.10)$$

The resulting sums can be further simplified by noting that

$$\sum_{\alpha=0}^p \frac{p!}{\alpha! (p-\alpha)!} = 2^p \quad \text{and} \quad \sum_{\beta=0}^q \left(-\frac{1}{3}\right)^\beta \frac{q!}{\beta! (q-\beta)!} = \left(\frac{2}{3}\right)^q. \quad (4.11)$$

Finally, use is made of the identity

$$\sum_{u=0}^{\infty} \frac{(x+y)^u}{u! (u+\lambda)} = \sum_{v=0}^{\infty} \sum_{w=0}^{\infty} \frac{x^v y^w}{v! w! (v+w+\lambda)} \quad (4.12)$$

to reduce sums over multiple indices to sums in either one or two indices. It is found that the calculation results in the five independent sums $f_1^{\text{et}} - f_5^{\text{et}}$, where

$$f_1^{\text{et}} = S_{\text{et}}^2 [G(3X, 2Y) + H_T(2Y)]$$

$$f_2^{\text{et}} = \bar{S}_{\text{et}}^2 H_T(4Y)$$

$$\begin{aligned}
 f_3^{\text{et}} &= S_{\text{et}} \bar{S}_{\text{et}} H_{\text{T}}(2Y) \\
 f_4^{\text{et}} &= S_{\text{et}}^2 [G(\frac{3}{2}X, Y) + H_{\text{E}}(\frac{3}{2}X) + H_{\text{T}}(Y)] \\
 f_5^{\text{et}} &= S_{\text{et}}^2 [G(3X, 2Y) + 2H_{\text{E}}(3X) + H_{\text{T}}(2Y)]
 \end{aligned} \tag{4.13}$$

with

$$G(x, y) = \sum_{u, v=1}^{\infty} \frac{x^u y^v}{u! v! (u \hbar \omega_{\text{E}} + v \hbar \omega_{\text{T}})}$$

and

$$H_i(z) = \frac{1}{\hbar \omega_i} \sum_{j=1}^{\infty} \frac{z^j}{j!} \quad (i = \text{E or T})$$

and where

$$X = (K_{\text{E}}/\hbar \omega_{\text{E}})^2 \quad \text{and} \quad Y = (K_{\text{T}}/\hbar \omega_{\text{T}})^2.$$

The sums $f_1^{\text{et}} - f_5^{\text{et}}$ will be called the second-order reduction factors. It should be noted that $G(x, y)$ can only be reduced to a sum over one index in the special case $\omega_{\text{E}} = \omega_{\text{T}}$.

There is a further term that contributes to the reduction factors in this system. This term, which we call g^{et} , arises due to the coupling between the cubic T_1 and T_2 ground states. This has been evaluated to

$$g^{\text{et}} = L^2/\Delta \quad \text{where} \quad L = 2N_{T_1\text{et}} N_{T_2\text{et}} (S_{\text{et}} - \bar{S}_{\text{et}}) \tag{4.14}$$

and Δ is the inversion splitting between T_1 and T_2 ($\Delta = (E_{T_2\text{et}} - E_{T_1\text{et}})$ for the T_1 state and $(E_{T_1\text{et}} - E_{T_2\text{et}})$ for the T_2 state). It should be noted that the limit of g^{et} when $\Delta \rightarrow 0$ is well defined owing to the behaviour of L as $\Delta \rightarrow 0$.

The second-order factors $\hbar \omega N_{T_1\text{et}}^2 f_1^{\text{et}} - \hbar \omega N_{T_1\text{et}}^2 f_5^{\text{et}}$ and $\hbar \omega g^{\text{et}}$ have been plotted in figure 2 for $\eta = 0.8$ and 1.2 and with $\omega_{\text{E}} = \omega_{\text{T}} = \omega$ and neglecting V_{BL} in Δ . The figure shows that the second-order reduction factors are all significantly smaller than the first-order reduction factors over the full range of coupling strengths investigated. This is in contrast to the $T \otimes t JT$ system, in which the second-order reduction factors can dominate (Bates and Dunn 1989).

The effect of spin-orbit coupling to second order can be described by the effective Hamiltonian (in $l = 1$)

$$\mathcal{H}_{\text{so}} = \mathcal{H}_{\text{so}}^{(1)} + \mathcal{H}_{\text{so}}^{(2)} \tag{4.15}$$

where

$$\mathcal{H}_{\text{so}}^{(1)} = \gamma \lambda \mathbf{l} \cdot \mathbf{S}$$

$$\begin{aligned}
 \mathcal{H}_{\text{so}}^{(2)} &= \lambda^2 [b(\mathbf{l} \cdot \mathbf{S})^2 + c(E_{\theta} E_{\theta}^s + E_{\epsilon} E_{\epsilon}^s) \\
 &\quad + d(L_{yz} S_{yz} + L_{zx} S_{zx} + L_{xy} S_{xy}) + e l(l+1) S(S+1)]
 \end{aligned} \tag{4.16}$$

(with $E_{\epsilon} = -(\sqrt{3}/2)(l_x^2 - l_y^2)$), where $E_{\theta}^s = E_{\theta}$ with l replaced by S , etc., $L_{yz} = l_y l_z + l_z l_y$ and where γ is the first-order reduction factor $K_{11}^{\text{et}}(T_1)$. The second-order coefficients in (4.16) can be calculated in terms of $f_1^{\text{et}} - f_5^{\text{et}}$ and g_{et} by comparing the matrix elements of \mathcal{H}_{so} with those of the perturbation (4.4). It is then found that for the T_1 triplet,

$$b = 2N_{T_1\text{et}}^2 (f_1^{\text{et}} - 4f_3^{\text{et}} - 2f_4^{\text{et}} - f_5^{\text{et}}) + g^{\text{et}}$$

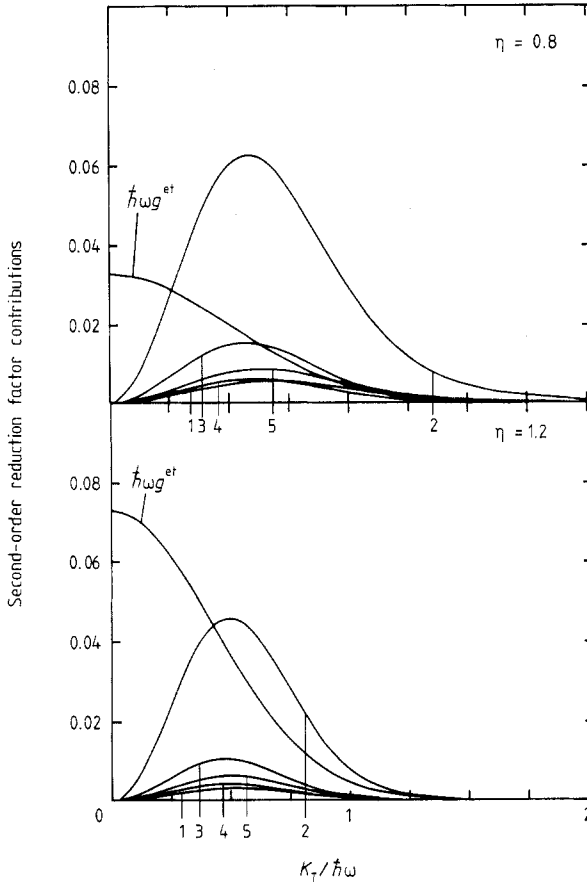


Figure 2. Variation of the factors $\hbar\omega N_{T1et}^2 f_1^{et}$ to $\hbar\omega N_{T1et}^2 f_5^{et}$ (labelled 1 to 5) and $\hbar\omega g^{et}$ as a function of $K_T/\hbar\omega$, where $\omega_E = \omega_T = \omega$. The lower set of curves have $\eta = 1.2$ and the upper set $\eta = 0.8$.

$$c = \frac{2}{3}N_{T1et}^2(f_1^{et} - 2f_2^{et} + 4f_3^{et} - f_5^{et}) - \frac{4}{3}g^{et} \tag{4.17}$$

$$d = -2N_{T1et}^2 f_1^{et}$$

$$e = \frac{1}{2}c + d.$$

Alternatively, it is possible to put $d = 0$ and redefine γ , b , c and e (as for $T \otimes t$ JT systems in Bates and Dunn (1989)) so that γ contains both first- and second-order contributions. It is then found that

$$\begin{aligned} \gamma &= K_{11}^{et}(T_1) - 2N_{T1et}^2 f_1^{et} \\ b &= -2N_{T1et}^2(f_1^{et} + 4f_3^{et} + 2f_4^{et} + f_5^{et}) + g^{et} \\ c &= \frac{2}{3}N_{T1et}^2(5f_1^{et} - 2f_2^{et} + 4f_3^{et} - f_5^{et}) - \frac{4}{3}g^{et} \\ e &= \frac{1}{2}c - 2N_{T1et}^2 f_1^{et}. \end{aligned} \tag{4.18}$$

The effective Hamiltonian (4.16) can also be used to describe spin-orbit coupling in the T_2 ground states. It is found that the same reduction factors apply, either with $\gamma = K_{22}^{et}(T_1)$ and

$$a = 0$$

$$\begin{aligned}
 b &= 2N_{T2et}^2(-f_1^{et} - 2f_4^{et} + f_5^{et}) - g^{et} \\
 c &= \frac{2}{3}N_{T2et}^2(5f_1^{et} - 2f_2^{et} + 4f_3^{et} + 8f_4^{et} - 5f_5^{et}) + \frac{4}{3}g^{et} \\
 d &= 2N_{T2et}^2 f_1^{et} \\
 e &= \frac{1}{2}c - d
 \end{aligned}
 \tag{4.19}$$

or with $\gamma = K_{22}^{et}(T_1) - 2N_{T2et}^2 f_1^{et}$ and

$$\begin{aligned}
 b &= 2N_{T2et}^2(f_1^{et} - 2f_4^{et} + f_5^{et}) - g^{et} \\
 c &= \frac{2}{3}N_{T2et}^2(f_1^{et} - 2f_2^{et} + 4f_3^{et} + 8f_4^{et} - 5f_5^{et}) + \frac{4}{3}g^{et} \\
 d &= 0 \\
 e &= \frac{1}{2}c - 2N_{T2et}^2 f_1^{et}.
 \end{aligned}
 \tag{4.20}$$

In all cases, the term in e is included to ensure that the trace of \mathcal{H}_{s_0} is zero.

As there are four parameters in the effective Hamiltonian (4.16) and six reduction factors, it is not possible to determine independently values for the reduction factors from experimental results without further information, such as uniaxial stress data.

It can be difficult to distinguish a $T \otimes (e + t_2)$ JT system from a $T \otimes e$ or a $T \otimes t$ JT system purely from the form of the effective Hamiltonian. For example, our calculations for $T \otimes (e + t_2)$ JT systems show that f_2^{et} is the largest of the six second-order reduction factors (figure 2) so that the second-order part of \mathcal{H}_{s_0} is dominated by the 'c' term ($E_\theta E_\theta^s + E_\epsilon E_\epsilon^s$). This can make the system appear very similar to a $T \otimes e$ JT system, in which the 'c' term can also dominate (Bates and Dunn 1989). However, for a given coupling strength, f_2^{et} is much smaller than the second-order $T \otimes e$ reduction factors f_a^e and f_b^e , allowing a possible distinction between the two systems to be made.

5. Conclusions

As in the case of $T \otimes t$ JT systems described in the previous paper, the transformation method of Bates *et al* (1987) has been successfully applied to $T \otimes (e + t_2)$ JT systems for the calculation of analytical expressions for both first- and second-order JT reduction factors. This would appear to be the first time that second-order reduction factors have been calculated for this system by any method. The first-order reduction factors have also been calculated incorporating so-called anisotropic corrections to the effective oscillator frequencies, again for the first time to our knowledge. Our first-order reduction factor results cannot be compared with the numerical results of Boldyrev *et al* (1981) and Sakamoto (1982) because such calculations relate to systems in which wells of all three symmetries coexist.

There are further improvements which can be made in the calculations of the second-order reduction factors. In particular, we are currently in the process of constructing a full set of cubic excited states for use in the calculations. Anisotropic and bilinear corrections are likely to be small compared to the above modifications.

It is important to apply the above theory to real $T \otimes (e + t_2)$ JT systems. Unfortunately, there are very few systems known which are of this type. One system that has been identified as $T \otimes (e + t_2)$ is GaAs:Cr³⁺ (Krebs and Stauss 1977) and our analysis of the original electron paramagnetic resonance and other experiments using the above theory will be reported separately (Parker *et al* 1989). Very recently, Sahraoui-Tahar *et al* (1989) and Butler *et al* (1989) have shown that the ground states

of Ni^{2+} ions in both GaAs and GaP may also undergo orthorhombic JT distortions.

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