

Second-order vibronic reduction factors for $T(X)(e+t_2)$ Jahn-Teller systems

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

1992 J. Phys.: Condens. Matter 4 6797

(<http://iopscience.iop.org/0953-8984/4/32/015>)

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

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 12:28

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

Second-order vibronic reduction factors for $T \otimes (e + t_2)$ Jahn–Teller systems

L D Hallam†, J L Dunn and C A Bates

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

Received

Abstract. Second-order vibronic reduction factors for spin–orbit coupling are derived for the strongly coupled orthorhombic $T \otimes (e + t_2)$ Jahn–Teller system. The method adopted is based on symmetry arguments as described by the authors in earlier papers. The symmetry-adapted cubic vibronic states, which are derived analytically in the companion paper, are used in the calculations. This approach gives a significant improvement in the accuracy compared to earlier calculations. The relevance of such calculations in the modelling of impurity T_1 ions occupying substitutional sites of T_d symmetry in III–V semiconductors is also discussed, with the orthorhombic GaAs:Cr³⁺ Jahn–Teller system considered as an example.

1. Introduction

It is well known that the coupling between an impurity ion and the vibrations of the surrounding lattice can greatly affect both the sizes and the number of terms appearing in the effective Hamiltonian used to describe a perturbation. This shows up through the introduction of reduction factors for which the labels ‘first-order’ or second-order’ denote the order in perturbation theory in which the perturbation appears (see, e.g., Ham 1965). However, it is also clear that there are numerous examples in which the second-order terms are much more important than first-order terms. This arises because the first-order terms decay exponentially with the strength of the ion–lattice coupling constant in contrast to some of the second-order terms which decay according to the reciprocal of the Jahn–Teller (JT) energy.

As discussed in the preceding paper (Hallam *et al* 1992), very little work has been undertaken previously to calculate the second-order reduction factors from basic JT theories for the $T \otimes t_2$ Jahn–Teller (JT) system and only one calculation for the orthorhombic $T \otimes (e + t_2)$ JT system has been reported. The latter was undertaken by two of the present authors (Dunn and Bates 1989b). However, in that work only the ground vibronic states were put into a symmetry-adapted form while the excited states used were the much simpler set appropriate to the infinite-coupling limit only. Now that a complete set of symmetry-adapted excited states is available in Hallam *et al* (1992), the calculations of Dunn and Bates (1989b) have been repeated to give a more accurate set of results. The object of this paper is to describe these calculations and give the results obtained.

† Now at: Department of Physics, The University, Leicester LE1 7RH, UK.

The paper begins with a summary of the general theory of second-order reduction factors using the symmetry arguments developed by Polinger *et al* (1991) and Bates *et al* (1991a, b). This requires the calculation of the sums of overlaps between symmetrized oscillator states. As described in Hallam *et al* (1992), the states used are derived from the transformation method introduced in a series of papers by Bates *et al* (1987), Dunn (1988, 1989) and Dunn and Bates (1989a). Spin-orbit coupling is then considered in detail as it is the most important perturbation present. Expressions for the four reduction factors are obtained using the symmetry-adapted excited states of Hallam *et al* (1992). These results are compared with the earlier results of Dunn and Bates (1989b) noting in passing that their graphs need correcting as they differ by numerical scaling factors from the (correct) formulae quoted there. Second-order off-diagonal reduction factors will also be calculated that allow for the mixing via the spin-orbit coupling between the ground vibronic and inversion states. Finally, the results are used in a new analysis of data obtained previously for the GaAs:Cr³⁺ system.

2. Mathematical background for orbital triplets with spin-orbit coupling

As in Polinger *et al* (1991) and Bates *et al* (1991a), we consider an isolated orbital T₁ triplet that is strongly coupled to the vibrations of its surroundings. The electronic orbital states may be written in the form $|\Gamma\gamma\rangle$; the eigenstates of the system are vibronic states which 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 . The vibronic eigenstates are written as a sum of products of electronic and vibrational states by using a Clebsch-Gordan convolution form (see, e.g., Griffiths 1962):

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

where $\langle\Sigma\sigma\Lambda\lambda|\Gamma\gamma\rangle$ are the Clebsch-Gordan coefficients and $|N(\Gamma)\Lambda\lambda\rangle$ are functions of the nuclear coordinates Q and thus represent the phonon states.

An alternative presentation is given in Hallam (1991) where V -coefficients are used instead of Clebsch-Gordan (CG) coefficients. With V -coefficients, the symmetry properties are more explicit than with CG coefficients and have the added advantage that permutations of the columns merely affect the overall sign of the coefficients. Nevertheless, we continue here to use the CG formalism in line with our earlier work.

A perturbation V can cause a splitting of the ground vibronic state $|0\Gamma\gamma\rangle$ in first order. In second order, the additional splitting can be described by the effective Hamiltonian:

$$\mathcal{H}^{(2)} = \sum_N \sum_{\Sigma\sigma} V \frac{|N\Sigma\sigma\rangle \langle N\Sigma\sigma|}{E_{\Gamma}^{(0)} - E_{\Sigma}^{(N)}} V. \quad (2.2)$$

$\mathcal{H}^{(2)}$ depends upon the nuclear as well as the space coordinates. However, as the contributions from the summation in (2.2) form a scalar, the symmetry of $\mathcal{H}^{(2)}$ depends only on the symmetry within $V \otimes V$. This means that the effective

Hamiltonian used to describe the vibronic system can be obtained from the purely electronic Hamiltonian by multiplying ($V \otimes V$) by the second-order reduction factor $K_M^{(2)}(\Gamma_k \otimes \Gamma_l)$ where (Polinger *et al* 1991)

$$K_M^{(2)}(\Gamma_k \otimes \Gamma_l) = \frac{(-1)^{j(\Gamma)}[\Gamma]}{\left[\begin{matrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Gamma \end{matrix} \right]} \times \sum_{\Lambda} (-1)^{j(\Lambda)}[\Lambda] \left[\begin{matrix} \Gamma_k & \Gamma_l & M \\ \Gamma & \Gamma & \Lambda \end{matrix} \right] \sum_N \left(\frac{S_N(\Gamma_k \Lambda \Gamma) S_N(\Gamma_l \Lambda \Gamma)}{E_{\Gamma}^{(0)} - E_{\Lambda}^{(N)}} \right) \quad (2.3)$$

with

$$S_N(\Sigma \Lambda \Omega) = \sum_{\Phi} (-1)^{j(\Phi)+j(\Sigma)} \{0(\Omega)\Phi || N(\Lambda)\Phi\} \left[\begin{matrix} \Gamma & \Gamma & \Sigma \\ \Omega & \Lambda & \Phi \end{matrix} \right]. \quad (2.4)$$

In the above, Γ_k and Γ_l denote the symmetry components of the V s, and the oscillator overlap integrals are $\{0(\Omega)\Phi || N(\Lambda)\Phi\}$ while the remaining terms give numerical factors. Also 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 square brackets (see, e.g., Griffiths 1962).

For spin-orbit coupling acting as a perturbation within a T_1 ion ($l = 1$), we take $V = \lambda l \cdot S$ so that $\Gamma_k = \Gamma_l = T_1$ and also $\Gamma = T_1$. The second-order spin-orbit coupling can be written as an effective Hamiltonian in the form (Polinger *et al* 1991, Bates *et al* 1991a)

$$\mathcal{H}_{\text{eff}}^{\text{so-so}} = \lambda^2 \sum_{M\mu} K_M^{(2)}(T_1 \otimes T_1) L_{M\mu}^{(2)} S_{M\mu}^{(2)} \quad (2.5)$$

where $L_{M\mu}^{(2)}$ and $S_{M\mu}^{(2)}$ are the second-order orbit and spin operators respectively which transform as $M\mu$. (For example, $L_{E0}^{(2)} = (1/\sqrt{6})(3l_z^2 - 2)$.) From group theory, we find that only reduction factors for which $M = A_1, E, T_1, T_2$ occur in this problem.

The $K_M^{(2)}$ may be obtained directly from (2.3) with the result (Polinger *et al* 1991)

$$\begin{aligned} K_{A_1}^{(2)}(T_1 \otimes T_1) &= +3R_{A_1} + 6R_E + 9R_{T_1} + 9R_{T_2} \\ K_E^{(2)}(T_1 \otimes T_1) &= -6R_{A_1} - 12R_E + 9R_{T_1} + 9R_{T_2} \\ K_{T_1}^{(2)}(T_1 \otimes T_1) &= +6R_{A_1} - 6R_E + 9R_{T_1} - 9R_{T_2} \\ K_{T_2}^{(2)}(T_1 \otimes T_1) &= -6R_{A_1} + 6R_E + 9R_{T_1} - 9R_{T_2} \end{aligned} \quad (2.6)$$

where the parameters R_{Λ} involve sums of terms involving overlap integrals (such as $\{0(T_1)T_1 || N(A_1)T_1\}$) divided by an energy. Expressions for the R_{Λ} are given in Polinger *et al* ((1991), equation (2.28)).

The above general formulae for the second-order reduction factors for the spin-orbit coupling acting within a T_1 orbital triplet are valid for *any* type of vibronic system. The differences between the different systems are contained entirely within the R_{Λ} and these in turn depend upon the details of the ground and all the excited vibronic states. We apply now these general results to the $T \otimes (e + t_2)$ JT system.

3. Calculation of the second-order reduction factors for $T \otimes (e + t_2)$ systems

3.1. Contributions from within the vibronic triplet only

In the above formulation, we require expressions for the ground and all the excited vibronic states. This is generally a difficult problem for all JT systems except $T \otimes e$ and the only method available appears to be that based on the transformation method developed by two of the authors. The preceding paper (table 1 of Hallam *et al* (1992)) gives the required vibronic states for the $T \otimes (e + t_2)$ system. From these vibronic states it is necessary to project out a phonon part of the required symmetry so that the reduced matrix elements of the phonon overlaps can be obtained. From these results the relevant R_Λ can then be calculated.

The phonon state $|N(\Gamma)\Phi\rangle$ has overall symmetry Φ and is derived from the excited vibronic state labelled by N of symmetry Γ . In order to derive the phonon state with the required symmetry, the appropriate vibronic state is expanded using (2.1). Thus in general we have

$$|N\Gamma\gamma\rangle = |x\rangle \left(\sum_{\Omega\omega} |N(\Gamma)\Omega\omega\rangle \langle T_1 x \Omega\omega | \Gamma\gamma \rangle \right) + |y\rangle \left(\sum_{\Omega\omega} |N(\Gamma)\Omega\omega\rangle \langle T_1 y \Omega\omega | \Gamma\gamma \rangle \right) + |z\rangle \left(\sum_{\Omega\omega} |N(\Gamma)\Omega\omega\rangle \langle T_1 z \Omega\omega | \Gamma\gamma \rangle \right). \quad (3.1)$$

The vibronic states given in Hallam *et al* (1992) contain phonon excitations via the unitary transformation operators U_i . They may thus also be expanded in the form of (3.1) above. For example, from table 1 of Hallam *et al* (1992), we have, for the vibronic state $|\psi_{14}^{T_2^y}\rangle$ the comparable relation

$$|\psi_{14}^{T_2^y}\rangle = (N_{14}/\sqrt{2}) \{ |x\rangle [-(-1)^q U_1 |\theta_x^p \epsilon_x^q 4^r 5^s 6^t\rangle + (-1)^{q+s+t} U_2 |\theta_x^p \epsilon_x^q 4^r 5^s 6^t\rangle] + |y\rangle [+U_3 |\theta_x^p \epsilon_x^q 4^t 5^s 6^r\rangle + (-1)^{s+t} U_4 |\theta_x^p \epsilon_x^q 4^t 5^s 6^r\rangle - (-1)^q U_1 |\theta_x^p \epsilon_x^q 4^r 5^s 6^t\rangle - (-1)^{q+s+t} U_2 |\theta_x^p \epsilon_x^q 4^r 5^s 6^t\rangle] + |z\rangle [+U_3 |\theta_x^p \epsilon_x^q 4^t 5^s 6^r\rangle - (-1)^{s+t} U_4 |\theta_x^p \epsilon_x^q 4^t 5^s 6^r\rangle] \}. \quad (3.2)$$

Comparing (3.2) with (3.1) gives simultaneous equations which can be solved to give phonon states of the required symmetry properties (Hallam 1991). Care must be taken to distinguish between phonon states that derive from vibronic states having the same symmetry but different energies. For example, there will be two phonon states of the form $|N(T_1)\Omega\omega\rangle$ since there are two sets of T_1 vibronic states having different energies.

The reduced matrix elements between phonon states are summarized in table 1. These results show that the reduced matrix element $\langle 0(T_1)T_1 | N(A_1)T_1 \rangle$ vanishes and, as a result, $R_{A_1}(T_1) = 0$. Substituting the reduced matrix elements into the expressions for the remaining R_Λ gives

$$R_E = -\frac{1}{9}(f_{et}^4 + f_{et}^6) \quad R_{T_1} = -\frac{1}{9}(f_{et}^9 + f_{et}^{10}) \quad R_{T_2} = -\frac{1}{9}(f_{et}^{15} + f_{et}^{16}) \quad (3.3)$$

Table 1. Non-zero reduced matrix elements of the phonon overlaps. Superscripts on the symmetry labels (e.g. T_1^2) distinguish between states of the same symmetry but different energy. The functions g_1 and g_2 are given in (3.6) and the normalizing factors in table 3 of Hallam *et al* (1992).

$$\begin{aligned}
 \langle 0(T_1)T_2 || N(E^1)T_2 \rangle &= -12N_7(0)N_4(p, q, r, s, t)(-1)^q g_1(p, q, t, r, s) \\
 \langle 0(T_1)T_2 || N(E^2)T_2 \rangle &= -12N_7(0)N_6(p, q, r, s, t)(-1)^q g_1(p, q, t, r, s) \\
 \langle 0(T_1)A_1 || N(T_1^1)A_1 \rangle &= \frac{4}{3}N_7(0)N_7(p, q, r, s, t)\{2g_1(p, q, t, r, s) + 2(-1)^q g_1(p, q, t, s, r) \\
 &\quad + g_2(p, q, r, s, t)\} \\
 \langle 0(T_1)E || N(T_1^1)E \rangle &= (2\sqrt{2}/3)N_7(0)N_7(p, q, r, s, t)\{2g_1(p, q, t, r, s) \\
 &\quad - 4(-1)^q g_1(p, q, t, s, r) + g_2(p, q, r, s, t)\} \\
 \langle 0(T_1)T_2 || N(T_1^1)T_2 \rangle &= -2\sqrt{3}N_7(0)N_7(p, q, r, s, t)g_2(p, q, r, s, t) \\
 \langle 0(T_1)T_2 || N(T_1^2)T_2 \rangle &= -4\sqrt{3}N_7(0)N_{10}(p, q, r, s, t)g_1(p, q, r, s, t) \\
 \langle 0(T_1)E || N(T_1^2)E \rangle &= (2\sqrt{2}/3)N_7(0)N_{15}(p, q, r, s, t)\{-2g_1(p, q, t, r, s) + g_2(p, q, r, s, t)\} \\
 \langle 0(T_1)T_2 || N(T_2^1)T_2 \rangle &= -2\sqrt{3}N_7(0)N_{15}(p, q, r, s, t)g_2(p, q, r, s, t) \\
 \langle 0(T_1)T_2 || N(T_2^2)T_2 \rangle &= -4\sqrt{3}N_7(0)N_{16}(p, q, r, s, t)g_1(p, q, r, s, t)
 \end{aligned}$$

so the second-order reduction factors are

$$\begin{aligned}
 K_{A_1}^{(2)}(T_1 \otimes T_1) &= -\frac{2}{3}(f_{et}^4 + f_{et}^6) - (f_{et}^9 + f_{et}^{10}) - (f_{et}^{15} + f_{et}^{16}) \\
 K_E^{(2)}(T_1 \otimes T_1) &= \frac{4}{3}(f_{et}^4 + f_{et}^6) - (f_{et}^9 + f_{et}^{10}) - (f_{et}^{15} + f_{et}^{16}) \\
 K_{T_1}^{(2)}(T_1 \otimes T_1) &= \frac{2}{3}(f_{et}^4 + f_{et}^6) - (f_{et}^9 + f_{et}^{10}) + (f_{et}^{15} + f_{et}^{16}) \\
 K_{T_2}^{(2)}(T_1 \otimes T_1) &= -\frac{2}{3}(f_{et}^4 + f_{et}^6) - (f_{et}^9 + f_{et}^{10}) + (f_{et}^{15} + f_{et}^{16})
 \end{aligned} \tag{3.4}$$

where

$$\begin{aligned}
 f_{et}^4 &= 36 \sum_N \Gamma_{49} g_1^2(p, q, t, r, s) & f_{et}^6 &= 36 \sum_N \Gamma_{69} g_1^2(p, q, t, s, r) \\
 f_{et}^9 &= 4 \sum_N \Gamma_9 [g_1(p, q, t, r, s) + 2(-1)^q (p, q, t, s, r) + g_2(p, q, r, s, t)]^2 \\
 f_{et}^{10} &= 4 \sum_N \Gamma_{10} g_1^2(p, q, r, s, t) & f_{et}^{16} &= 4 \sum_N \Gamma_{16} g_1^2(p, q, r, s, t) \\
 f_{et}^{15} &= 4 \sum_N \Gamma_{15} [g_1(p, q, t, r, s) - g_2(p, q, r, s, t)]^2
 \end{aligned} \tag{3.5}$$

and where

$$\begin{aligned}
 \Gamma_i &= N_{T_{1E}}^2 N_i^2(p, q, r, s, t) / (E_i^{(N)} - E_{T_{1E}}) \\
 g_1(p, q, r, s, t) &= S_{et} H(p, q) A(r) A(s) \delta_{0,t} \\
 g_2(p, q, r, s, t) &= \overline{S}_{et} B(t) \delta_{0,p} \delta_{0,q} \delta_{0,r} \delta_{0,s} \\
 A(i) &= [1/\sqrt{(i!)}] (K_T/\hbar\omega_T)^i & B(i) &= [1/\sqrt{(i!)}] (2K_T/\hbar\omega_T)^i \\
 H(p, q) &= [1/\sqrt{p!q!}] (3K_E/2\hbar\omega_E)^p (\sqrt{3}K_E/2\hbar\omega_E)^q.
 \end{aligned} \tag{3.6}$$

The overlaps are defined by

$$S_{\text{et}} = \exp[-\frac{3}{2}(K_E/\hbar\omega_E)^2 - (K_T/\hbar\omega_T)^2] \quad \overline{S}_{\text{et}} = \exp[-2(K_T/\hbar\omega_T)^2] \quad (3.7)$$

and the energies are given in table 4 of Hallam *et al* (1992).

3.2. Coupling to the inversion level

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. So far, only coupling between the ground and excited vibronic states has been included in the calculation of second-order reduction factors. The contribution from the ground-inversion-level coupling for the spin-orbit coupling perturbation $(\lambda l \cdot S)$ has the form

$$-\sum_{k=1}^{\infty} \langle 0(T_1) | (\lambda l \cdot S) | 0(T_2) k \rangle \langle 0(T_2) k | (\lambda l \cdot S) | 0(T_1) j \rangle / \delta$$

where the inversion splitting $\delta = E_{T_2}^{(0)} - E_{T_1}^{(0)}$. From Hallam *et al* (1992), the T_1 ground states are given by

$$|0(T_1)x\rangle = N_7(0) \left(|xy'_+\rangle + |xy'_-\rangle + |zx'_+\rangle - |zx'_-\rangle \right) \quad (3.8)$$

and the T_2 inversion level states by

$$|0(T_2)x\rangle = N_{13}(0) \left(|xy'_+\rangle + |xy'_-\rangle - |zx'_+\rangle + |zx'_-\rangle \right). \quad (3.9)$$

This results in an additional contribution of $-g_{\text{et}}/9$ to the value of R_{T_2} and so

$$R_{T_2}(T_1) = -\frac{1}{9}(f_{\text{et}}^{15} + f_{\text{et}}^{16} + g_{\text{et}}) \quad (3.10)$$

where

$$g_{\text{et}} = 2N_7(0)N_{13}(0)(S_{\text{et}} - \overline{S}_{\text{et}})/\delta.$$

Consequently all the second-order reduction factors given in (3.4) should be corrected by replacing the original $R_{T_2}(T_1)$ by the expression given in (3.10) above.

4. The results

O'Brien (1990) writes the effective Hamiltonian for an orbital triplet JT system in the symmetry-adapted form:

$$\mathcal{H}_{\text{eff}} = \lambda^2 \{ A(l \cdot S) + \frac{2}{3} B_E E(l) E(S) + \frac{2}{3} B_T T(l) T(S) + Cl(l+1) \} \quad (4.1)$$

where the coefficients A , B_E , B_T and C are related to the second-order reduction factors defined in (2.5) by

$$A = -\frac{1}{2} K_{T_1}^{(2)} \quad B_E = K_E^{(2)} \quad B_T = K_{T_2}^{(2)} \quad C = -\frac{1}{3} K_{A_1}^{(2)} \quad (4.2)$$

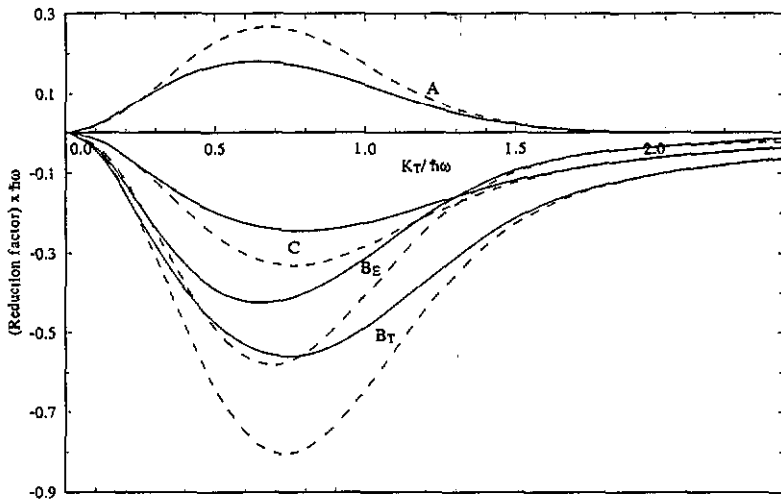


Figure 1. The reduction factors A , B_E , B_T and C plotted as a function of $K_T/\hbar\omega$ for the $T \otimes (e + t_2)$ JT system with $\eta = 0.8$ and $K_{BL} = -0.036$. The full curves give the new results calculated using the symmetry-adapted excited states and the broken curves show the results of Dunn and Bates (1989b) obtained using simple excited states.

and where $E(l)$, $T(l)$ are orbital operators of the stated symmetry. Plots of A , B_E , B_T and C as a function of K_T are shown in figures 1 and 2 taking the ratio η of the JT energies for e to t_2 couplings to be 0.8 and 1.2 respectively and the bilinear coupling constant $K_{BL} = -0.036$ and -0.082 respectively. These values of K_{BL} are chosen to ensure that the orthorhombic minima lie lowest in energy. (A full discussion about these parameters is given, for example, in Dunn and Bates (1989b).) For small values of K_T , the reduction factors were found to converge rapidly with only a few phonon excitations. More excitations were needed for larger values of K_T . However, it was found that no difference could be distinguished between graphs produced by summing up to $L (= M + N) = 20$ and $L = 25$ phonon excitations over the range of couplings displayed.

Also shown in the figures for comparison purposes are the results obtained from the equivalent formulae given in Dunn and Bates (1989b). These simple excited states were used that belong to the infinite-coupling limit and that are thus localized in the orthorhombic potential energy minima in Q -space. (It is necessary to point out that there is an error in the plots of the factors $f_1^{et} - f_5^{et}$ in figure 2 of Dunn and Bates (1989b). The formulae given in the paper are correct but the plots themselves involve $f_1/8$, f_2 , $f_3/2$, $f_4/4$ and $f_5/8$ instead of f_1 , f_2 , f_3 , f_4 and f_5 respectively. Thus four of the factors are much larger than those shown.)

As in the case of $T \otimes t_2$ JT systems described in Dunn *et al* (1990), the magnitudes of the reduction factors obtained from the symmetry-adapted cubic states are smaller than the equivalent factors obtained with the simple states. This occurs because of the greater amount of non-orthogonality between the simple states in moderate coupling. O'Brien (1990) has recently published numerical results for the $T \otimes (e + t_2)$ system. Unfortunately, the results are not directly comparable with those obtained here as they are calculated in the special case of equal coupling, although the same qualitative

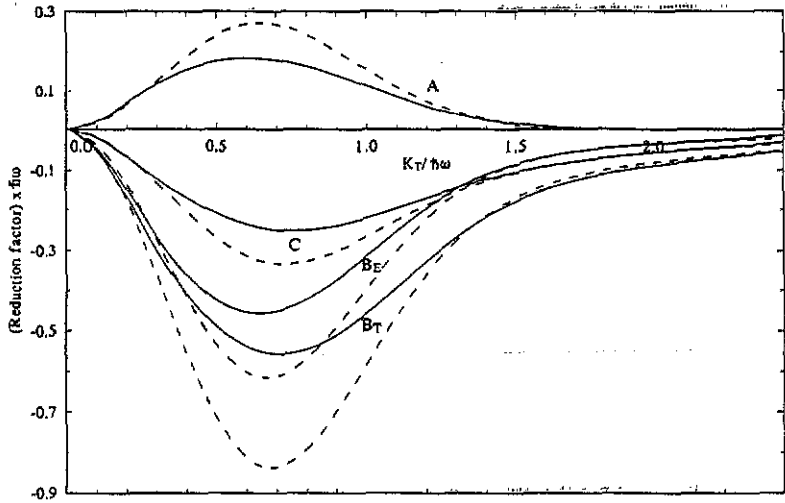


Figure 2. The same as figure 1 except that $\eta = 1.2$ and $K_{BL} = -0.082$.

behaviour is observed. Although the second-order reduction factors obtained using the improved symmetry-adapted states are reduced in magnitude compared with those obtained using simple states, they still dominate the first-order factors (Dunn and Bates 1989b) for $K_T > 1.0$.

It is clear that the dependence of the reduction factors on K_T for the orthorhombic $T \otimes (e + t_2)$ JT system are very similar to those of $T \otimes t_2$. On comparing figures 1 and 2 with figure 1(b) of Bates *et al* (1991a), we see that A is always positive and peaks at about $K_T/\hbar\omega_T = 0.7$ while B_E , B_T and C are all negative. For both systems, $|B_T| > |B_E| > |C|$. Also, the values of all four reduction factors are approximately the same for the two JT systems.

It is not possible to derive analytical expressions for the asymptotic behaviour of the reduction factors in strong coupling even though the simple excited states may be used. There are a number of reasons for this. Among them are that the factors φ_e and φ_t , arising from the very important bilinear term, cannot be sensibly replaced by unity because the concept of wells will disappear. Also, both K_E and K_T appear in different combinations in the relevant polynomials and the exponents and the use of the parameter η does not help.

For the $T \otimes t_2$ system, anisotropy corrections were introduced by Bates *et al* (1991a) in an approximate way, with the result (shown in their figure 1(a)) that there was better agreement between the analytical calculations and the numerical results of O'Brien (1990). Unfortunately, anisotropy is much more complicated in the $T \otimes (e + t_2)$ system and we have consequently been unable to add such corrections here.

5. Off-diagonal reduction factors

In many strongly coupled vibronic systems, there is an inversion level very close to the ground state and certain perturbations can cause significant admixtures of the

inversion states into the ground states of the system. Off-diagonal factors become significant when the difference between the inversion and ground levels (the inversion splitting) becomes comparable in magnitude with the second-order terms such as spin-orbit coupling.

Formulae to calculate the second-order off-diagonal reduction factors for any symmetry of perturbation are also given in Polinger *et al* ((1991), equation (2.30)). For the example of spin-orbit coupling, the result for the $T \otimes t_2$ problem is given in Bates *et al* ((1991a), equation (5.6)). Again, spin-orbit coupling is the dominant perturbation in the $T \otimes (e + t_2)$ problem. Thus with a T_1 vibronic ground state and a T_2 vibronic inversion state we have $\Gamma = T_1$, $\Omega = T_2$ and $\Gamma_l = \Gamma_k = T_1$ and the second-order off-diagonal reduction factor $K_M^{(2)}(\Gamma | (\Gamma_k \otimes \Gamma_l) | \Omega)$ for spin-orbit coupling becomes

$$K_M^{(2)}(T_1 | (T_1 \otimes T_1) | T_2) = -\frac{3}{2} \begin{bmatrix} T_1 & T_1 & M \\ T_1 & T_1 & T_1 \end{bmatrix}^{-1} \sum_{\Lambda} (-1)^{j(\Lambda)} [\Lambda] \begin{bmatrix} T_1 & T_2 & M \\ T_1 & T_1 & \Lambda \end{bmatrix} \times \sum_N \left[(E_{T_1}^{(0)} - E_{\Lambda}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{\Lambda}^{(N)})^{-1} \right] f(\Lambda) \tag{5.1}$$

where $f(\Lambda) = X_{T_1}(\Lambda) X_{T_2}(\Lambda)$ and

$$X_{\Delta}(\Lambda) = \sum_M (-1)^{j(M)} [M]^{-1/2} \{0(\Delta)M || N(\Lambda)M\} \begin{bmatrix} \Lambda & T_1 & \Delta \\ T_1 & M & T_1 \end{bmatrix}.$$

Also, the 6Γ coefficient is

$$\begin{bmatrix} T_1 & T_1 & M \\ T_1 & T_1 & T_1 \end{bmatrix} = 0 \quad \text{for} \quad M = A_1, A_2.$$

Thus only second-order off-diagonal reduction factors with $M = E, T_1$ and T_2 are non-zero.

After substituting specific values for the remaining CG coefficients, they are given by

$$K_E^{(2)}(T_1 | (T_1 \otimes T_1) | T_2) = -\frac{9\sqrt{3}}{2} \left(\sum_N \left[(E_{T_1}^{(0)} - E_{T_1}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{T_1}^{(N)})^{-1} \right] f(T_1^1) + \sum_N \left[(E_{T_1}^{(0)} - E_{T_1}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{T_1}^{(N)})^{-1} \right] f(T_1^2) + \sum_N \left[(E_{T_1}^{(0)} - E_{T_2}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{T_2}^{(N)})^{-1} \right] f(T_2^1) + \sum_N \left[(E_{T_1}^{(0)} - E_{T_2}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{T_2}^{(N)})^{-1} \right] f(T_2^2) \right)$$

$$K_{T_1}^{(2)}(T_1 | (T_1 \otimes T_1) | T_2) = -9 \left(-\frac{1}{\sqrt{3}} \sum_N \left[(E_{T_1}^{(0)} - E_{E^1}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{E^1}^{(N)})^{-1} \right] f(E^1) - \frac{1}{\sqrt{3}} \sum_N \left[(E_{T_1}^{(0)} - E_{E^2}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{E^2}^{(N)})^{-1} \right] f(E^2) \right)$$

$$\begin{aligned}
& -\frac{1}{2} \sum_N \left[(E_{T_1}^{(0)} - E_{T_1}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{T_1}^{(N)})^{-1} \right] f(T_1^1) \\
& -\frac{1}{2} \sum_N \left[(E_{T_1}^{(0)} - E_{T_1}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{T_1}^{(N)})^{-1} \right] f(T_1^2) \\
& +\frac{1}{2} \sum_N \left[(E_{T_1}^{(0)} - E_{T_2}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{T_2}^{(N)})^{-1} \right] f(T_2^1) \\
& +\frac{1}{2} \sum_N \left[(E_{T_1}^{(0)} - E_{T_2}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{T_2}^{(N)})^{-1} \right] f(T_2^2) \\
K_{T_2}^{(2)}(T_1|(T_1 \otimes T_1)|T_2) = & -9 \left(\frac{1}{\sqrt{3}} \sum_N \left[(E_{T_1}^{(0)} - E_{E^1}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{E^1}^{(N)})^{-1} \right] f(E^1) \right. \\
& +\frac{1}{\sqrt{3}} \sum_N \left[(E_{T_1}^{(0)} - E_{E^2}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{E^2}^{(N)})^{-1} \right] f(E^2) \\
& -\frac{1}{2} \sum_N \left[(E_{T_1}^{(0)} - E_{T_1}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{T_1}^{(N)})^{-1} \right] f(T_1^1) \\
& -\frac{1}{2} \sum_N \left[(E_{T_1}^{(0)} - E_{T_1}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{T_1}^{(N)})^{-1} \right] f(T_1^2) \\
& +\frac{1}{2} \sum_N \left[(E_{T_1}^{(0)} - E_{T_2}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{T_2}^{(N)})^{-1} \right] f(T_2^1) \\
& \left. +\frac{1}{2} \sum_N \left[(E_{T_1}^{(0)} - E_{T_2}^{(N)})^{-1} + (E_{T_2}^{(0)} - E_{T_2}^{(N)})^{-1} \right] f(T_2^2) \right) \quad (5.2)
\end{aligned}$$

where the $f(\Lambda)$ are given in table 2. The calculation of the second-order reduction factors proceeds in exactly the same way as that for $T \otimes t_2$. Similarly, the dependence of these factors on K_T and η may be computed after the relevant overlaps $X_\Delta(\Lambda)$ have been deduced. As much algebra is needed, no explicit results are given here.

Table 2. The functions $f(\Lambda)$ appearing in the off-diagonal second-order reduction factors where the $N_i(p, q, r, s, t)$ are the normalizing factors (Hallam *et al* (1992), table 3) and g_1 and g_2 are given in (3.6).

$$\begin{aligned}
f(E^1) &= (4/\sqrt{3}) N_7(0) N_{15}(0) N_4(p, q, r, s, t)^2 g_1(p, q, t, r, s)^2 \\
f(E^2) &= (4/\sqrt{3}) N_7(0) N_{15}(0) N_6(p, q, r, s, t)^2 g_1(p, q, t, r, s)^2 \\
f(T_1^1) &= \frac{4}{9} N_7(0) N_{15}(0) N_7(p, q, r, s, t)^2 \{ g_1(p, q, t, r, s) + 2(-1)^q g_1(p, q, t, s, r) + g_2(p, q, r, s, t) \} \\
&\quad \times \{ g_1(p, q, t, r, s) - 2(-1)^q g_1(p, q, t, s, r) + g_2(p, q, r, s, t) \} \\
f(T_1^2) &= \frac{4}{9} N_7(0) N_{15}(0) N_{10}(p, q, r, s, t)^2 g_1(p, q, r, s, t)^2 \\
f(T_2^1) &= \frac{4}{9} N_7(0) N_{15}(0) N_{15}(p, q, r, s, t)^2 \{ g_2(p, q, r, s, t) - g_1(p, q, t, r, s) \}^2 \\
f(T_2^2) &= \frac{4}{9} N_7(0) N_{15}(0) N_{16}(p, q, r, s, t)^2 g_1(p, q, r, s, t)^2
\end{aligned}$$

As in the case of the other reduction factors, no simple expressions for the asymptotic limit of the off-diagonal reduction factors can be obtained for the strong-coupling limit. They are likely to become important whenever the tunnelling level

approaches the ground vibronic state such that the energy gap δ is of the same size as the perturbation under consideration. Referring to figures 1 and 2 in Hallam *et al* (1992), this is likely to arise for K_T , K_E greater than about $1.75\hbar\omega$ in some cases for a relatively large perturbation such as spin-orbit coupling.

6. Application to the GaAs:Cr³⁺ system

The best known example of a strongly coupled orthorhombic JT system is probably that of GaAs:Cr³⁺ which has a 4T_1 ground state in tetrahedral symmetry. It was first identified by Krebs and Stauss (1977) from their electron paramagnetic resonance (EPR) experiments. Thermally detected (TD) EPR experiments were undertaken later from which further data related to the centre were obtained (Parker *et al* 1990). It was supposed that the 4T_2 inversion level had a sufficiently high energy that its effect on the ground vibronic state could be ignored in these experiments. Thus from the frequency dependence of the resonances and the isofrequency curves, it was shown that all the EPR data could be accounted for by an effective Hamiltonian for the 4T_1 vibronic ground state and written in the form (Parker *et al* 1990)

$$\begin{aligned} \mathcal{H}_{\text{eff}} = & a(\mathbf{l} \cdot \mathbf{S}) + b(\mathbf{l} \cdot \mathbf{S})^2 + c(E_\theta^l E_\theta^S + E_\epsilon^l E_\epsilon^S) + \mathcal{H}_{\text{strain}} \\ & + \mu_B \{ (g_e + f)(\mathbf{B} \cdot \mathbf{S}) + d(\mathbf{l} \cdot \mathbf{B}) + e[(\mathbf{l} \cdot \mathbf{S})(\mathbf{l} \cdot \mathbf{B}) + (\mathbf{l} \cdot \mathbf{B})(\mathbf{l} \cdot \mathbf{S})] \\ & + f(E_\theta^l E_\theta^{SB} + E_\epsilon^l E_\epsilon^{SB}) \} \end{aligned} \quad (6.1)$$

where a , b and c are the coefficients of the terms that describe first- and second-order spin-orbit coupling and d , e and f are the coefficients of the Zeeman terms and $g_e = 2.0023$. Also the operators are given by

$$E_\theta^l = \frac{1}{2}[3l_z^2 - l(l+1)] \quad E_\theta^{SB} = \frac{1}{2}[3B_x S_x - \mathbf{B} \cdot \mathbf{S}] \quad \text{etc.} \quad (6.2)$$

The fourth term in (6.1) represents the strain that pushes one of the six orthorhombic wells below all the others. For the [110] well we have

$$\mathcal{H}_{\text{strain}} = V[(\sin \gamma) E_\theta^l + \frac{1}{2}\sqrt{3}(\cos \gamma)(l_x l_y + l_y l_x)] \quad (6.3)$$

where V is the effective coupling constant and γ is the angle of the strain in the $Q_\theta - Q_\epsilon$ strain plane.

All the EPR spectra arise from transitions within the Zeeman-split levels of the lowest Kramers doublet from \mathcal{H}_{eff} . The values of the parameters that fitted the EPR data were found to be

$$\begin{aligned} a &= 6.55 \pm 0.3 \text{ cm}^{-1} & b &= -(2.05 \pm 0.3) \times 10^{-1} \text{ cm}^{-1} \\ c &= -(8 \pm 3) \times 10^{-1} \text{ cm}^{-1} & d &= (1.6 \pm 0.4) \times 10^{-2} \text{ cm}^{-1} \\ e &= (3.5 \pm 1.0) \times 10^{-4} \text{ cm}^{-1} & f &= (1.35 \pm 0.3) \times 10^{-3} \text{ cm}^{-1} \\ \gamma &= 1.23 \pm 0.01. \end{aligned} \quad (6.4)$$

The orthorhombic nature of the EPR spectra was explained by assuming that random strains stabilize the system into one of the six orthorhombic wells. The resultant spectrum is then a superposition of spectra from all six sets of sites such that

the isofrequency curves each display orthorhombic symmetry corresponding to one particular site. This occurs if $|V| > 45 \text{ cm}^{-1}$ and negative.

Parker *et al* (1990) showed that there were two main contributors to each of the non-Zeeman terms in \mathcal{H}_{eff} . One arises from the coupling of the excited 2E orbital state, at an energy E , to the ground 4T_1 state via the one-electron spin-orbit coupling (of parameter ξ' but modified by the JT effect through the introduction of first-order reduction factors). The second comes from the second-order JT reduction factors from the spin-orbit coupling which is the main theme of this paper. However, equation (6.1) has a different form from that of (4.1) and thus the second-order JT reduction factors given in (4.1) must be cast into the form of equation (6.1). Taking these points into consideration, and ignoring the Zeeman parameters which are known only rather poorly, we arrive at the relations

$$A_1 + C_1\lambda = 6.55 \quad A_2 + C_2\lambda = -0.21 \quad A_3 + C_3\lambda = -0.08$$

where

$$\begin{aligned} 6A_1 &= [K_{11}^{\text{et}}(T_2) - 2K_{11}^{\text{et}}(T_1)]\mathcal{P} & C_1 &= k^2(A + \frac{1}{2}B_T\lambda + kK_{11}^{\text{et}}(T_1)) \\ 3A_2 &= K_{11}^{\text{et}}(T_2)\mathcal{P} & C_2 &= k^2B_T\lambda \\ 9A_3 &= -2[2K_{11}^{\text{et}}(E) + K_{11}^{\text{et}}(T_2)]\mathcal{P} & C_3 &= k^2(B_E - B_T)\lambda \end{aligned} \quad (6.5)$$

and where $K_{11}^{\text{et}}(T_2)$ is the first-order reduction factor of T_2 symmetry etc (Dunn and Bates 1989b), $\mathcal{P} = \xi'^2/E$ and $k (= -3/2)$ is the isomorphic constant. (Note that a factor of $-2/9$ was omitted from the expression for A_3 given in Parker *et al* (1990) although the factor was included in the subsequent analysis.)

In principle, from a computer analysis of the values of the first-order reduction factors as a function of $K_T/\hbar\omega_T$ as given in Dunn and Bates (1989b) and of the second-order reduction factors given here in figures 1 and 2, it should be possible to find a value for $K_T/\hbar\omega_T$ which simultaneously satisfies all of equations (6.5). Unfortunately the equations are ill-conditioned in that small changes in the parameter values quoted above and/or the constants generate instabilities in the solutions. We know from other calculations that, for example, anisotropy has marked effects on the second-order reduction factors particularly in the region of $K_T/\hbar\omega_T$ where we expect a solution. Thus both our formulae and our data are not sufficiently accurate for a unique value of $K_T/\hbar\omega_T$ to be obtained in this way even allowing for variations in the λ , η and K_{BL} values. However, solutions to the problem are clearly possible for $K_T/\hbar\omega_T$ in the range 1.2–1.7 for $\eta = 1.2$ or 0.8 and $K_{\text{BL}} = -0.04$ that are physically acceptable but $K_T/\hbar\omega_T$ cannot be determined more precisely. Thus our calculations of second-order reduction factors with the cubic combinations of the excited states has still not enabled us to obtain a real fit to the data for this system without the availability of further experimental data.

It is apparent that, with this range of values of $K_T/\hbar\omega_T$, the main contributions come from the second-order terms as the first-order factors $K_{11}^{\text{et}}(T_2)$, $K_{11}^{\text{et}}(E)$ and $K_{11}^{\text{et}}(T_1)$ are very close to their limiting values of 0.5, 0.25 and 0 respectively. Also, this range of values for $K_T/\hbar\omega_T$ strongly supports the statement in Parker *et al* (1990) that, for the GaAs:Cr³⁺ system, the JT effect is orthorhombic and in the 'strong-coupling' regime and that the main magnetic properties of this virtually unique system arise from the close proximity of the 2E state to the 4T_1 ground state.

It is interesting to note also that reference was made in Parker *et al* (1990) to an estimate of K_T from a value for the inversion splitting ($\delta = 23 \text{ cm}^{-1}$) obtained from the phonon scattering experiments of Challis *et al* (1982), Ramdane *et al* (1983) and Hamdache *et al* (1982). A value of $K_T/\hbar\omega_T = 1.5$ was given which is at the centre of the range found here. Unfortunately, it is not possible to combine the data for δ with those from EPR to determine $K_T/\hbar\omega_T$ uniquely because additional approximate formulae would be added to the problem!

Finally, the range of values for $K_T/\hbar\omega_T$ deduced above are consistent with the neglect of the T_2 inversion level in writing down the effective Hamiltonian (6.1) in terms of an $l = 1$ orbital operator only. If this latter condition had not been met, it would have further complicated the analysis which emphasizes again the uniqueness of the GaAs:Cr³⁺ JT system.

7. Summary

An analytical method of calculating the second-order reduction factors for the strongly coupled $T \otimes (e + t_2)$ JT system has been described. It gives results that are more accurate than those given previously by Dunn and Bates (1989b) because the excited states have cubic symmetry and they are thus more nearly orthogonal to each other. It is found that the use of symmetry-adapted states gives smaller maximum and minimum values than the corresponding reduction factors obtained using the simple excited states localized in the wells. This system represents another important JT system after those of $T \otimes e$ and $T \otimes t_2$ but it is much more complicated than either and especially $T \otimes e$. Such orthorhombic systems are more common in tetrahedral symmetry because the coupling to t_2 modes for T_1 orbital states is often as large as the coupling to the e modes. It is interesting to note that, even in T_d symmetry, a T_2 orbital state is invariably more strongly coupled to e than to t_2 modes. Expressions have also been obtained for the off-diagonal reduction factors for $T \otimes (e + t_2)$ which, although not used specifically here, may be important in describing the mixing between the vibronic ground and excited states by perturbations additional to those of spin-orbit coupling. The example of GaAs:Cr³⁺ has been chosen to illustrate the importance of second-order JT reduction factors in obtaining an accurate effective Hamiltonian for orthorhombic systems.

Acknowledgments

We wish to acknowledge the many helpful discussions we have had on different aspects of this work with Professors V Z Polinger and F S Ham and with Drs M C M O'Brien, P J Kirk, A Vasson and A-M Vasson. One of us (LDH) also wishes to thank the SERC for a research studentship during the course of this work.

References

- Bates C A, Dunn J L, Hallam L D, Kirk P J and Polinger V Z 1991a *J. Phys. C: Solid State Phys.* **20** 1965-33
- Bates C A, Dunn J L, Polinger V Z, Hallam L D, Kirk P J and Jamila S 1991b *Mater. Sci. Forum* **83-87** 487-92

- Bates C A, Dunn J L and Sigmund E 1987 *J. Phys. C: Solid State Phys.* **20** 1965–83 (Corrigendum **20** 4013)
- Challis L J, Locatelli M, Ramdane A and Salce B 1982 *J. Phys. C: Solid State Phys.* **15** 1419–32
- 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 1989a *J. Phys.: Condens. Matter* **1** 375–94
- 1989b *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 *PhD Thesis* University of Nottingham
- Hallam L D, Bates C A and Dunn J L 1992 *J. Phys.: Condens. Matter* **4** 6775–96
- Hamdache M, King P J, Murphy D T and Rampton V W 1982 *J. Phys. C: Solid State Phys.* **15** 5559–80
- Ham F S 1965 *Phys. Rev. A* **138** 1727–40
- Krebs J J and Stauss G H 1977 *Phys. Rev. B* **15** 17–22
- O'Brien M C M 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
- Ramdane A, Salce B and Challis L J 1983 *Phys. Rev. B* **27** 2554–7