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EFFECT OF TRIGONAL STRESS ON THE OPTICAL ABSORPTION SPECTRA OF GaP:Ti^{3+}

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Abstract: Applying the theory developed for strongly coupled ions, the GaP:Ti^{3+} Jahn-Teller system has been modeled under a trigonal uniaxial stress in the [111] direction, since previous models have been found to be inappropriate. In this model second order stress terms have been incorporated and the results obtained are compared to the earlier linear model.

Keywords: Optical absorption spectra, strongly coupled ions, trigonal stress.

INTRODUCTION

Nowadays there is an interest in the study of impurity ions, in different lattice surroundings, due to the discovery of new type of materials. Coupling between the different modes of vibration of a fullerene molecule may play an important role in the high temperature superconductivity that some of them exhibit [Piekara-Sadi *et al* 2004, Abou-Ghantous *et al* 2002].

When intentional impurity addition in the semiconductors is done, the ion may enter in the lattice not as a simple, substitutional ion, but as a part of a complex system. In these cases the ions are strongly coupled to the lattice vibrations of the surroundings, complicating the interpretation of the properties of that system. This strong coupling between the lattice and the electronic motion is referred as the Jahn Teller effect. If a uniaxial stress is applied on that system, further complexity appears in the optical properties of the system. In order to model the optical properties of such systems an effective Hamiltonian is needed and the corresponding reduction factors need to be calculated.

The details presented will help in a better understanding of the effects of uniaxial stress in deep level impurity systems as the uniaxial stress is used increasingly as an additional technique in optical and other experiments. The computational fitting technique is explained briefly in the next section. The details of the effective Hamiltonian for the first and second order approximations are given in the subsequent sections, along with the graphs for each order. The theoretical calculations for different types of coupling constants are presented before discussion section. The last sections deals with the discussion and conclusion of the results obtained.

FITTING TECHNIQUE

The modeling of deep level impurities in a perfect lattice is done by constructing an effective Hamiltonian from the Jahn-Teller theory. The

effects of strain are incorporated as a small perturbation in this Hamiltonian as free parameters. The values of these free parameters are so chosen that they fit the energy transitions between the excited triplet and the ground doublet states of the impurity atom.

To obtain these free parameters the total Hamiltonians for the excited and ground states were diagonalised using a NAG (Nottingham Algorithm Group) routine for real and/ or complex symmetric matrices and the theoretical values for the transitions were found. Then the residues between each theoretical transition energy and corresponding experimental transition energy were obtained. These were summed up and the resulting function was minimized. The fit was terminated as soon as the values of the residues were within the experimental error. Not all the parameters used were independent from each other certain restrictions were used on them based on experimental observations.

The optical absorption measurements in zero magnetic field were performed by measuring the transmission of monochromatic light through the sample and the effect of uniaxial stress on the optical absorption of the monochromatic light was undertaken by Roura [Halliday *et al.* 1987, Roura *et al.* 1993].

FIRST ORDER TERMS IN EFFECTIVE HAMILTONIAN

The effective Hamiltonian for a degenerate ion must include terms representing first and second order spin-orbit coupling and random and uniaxial strain.

The effective Hamiltonian for the trigonal strain is [Al-Shaikh 1991]

$$\mathcal{H}_{eff}^{[111]} = a'\lambda\ell.S + \lambda\,[c(E_\theta^{\,l} E_\theta^{\,S} + E_\varepsilon^{\,l} E_\varepsilon^{\,S}) + b(\ell.S)^2] + A_2P + \alpha\ell_z^{\,2} - \eta'P(3\ell_z^{\,2}-2) + \tfrac{1}{3}\gamma P[(\ell_x\ell_y + \ell_y\ell_x) + (\ell_y\ell_z + \ell_z\ell_y) + (\ell_z\ell_x + \ell_x\ell_z)] \quad (1)$$

$$\mathcal{H}_{eff}^{[111]} = (\alpha' + \sigma P)\, T_1 \quad (2)$$

for the triplet and the doublet respectively. With $a' = K(T_1)\, k_1^{T1} + a$, with $K(T_1)$ being the first order reduction factor of T_1 symmetry, $k_1^{T1} = -1$ is an isomorphic constant, $\lambda = 159\ cm^{-1}$ is the spin-orbit coupling constant for a free Ti^{3+} ion, T_1 and T_2 are the components of the fictitious angular momentum operator $T = ½$ [Badran *et al.* 1993]

$$T_1 = ½(|\theta\rangle\langle\theta| - |\varepsilon\rangle\langle\varepsilon|)$$
$$T_2 = -½(|\theta\rangle\langle\varepsilon| + |\varepsilon\rangle\langle\theta|) \quad (3)$$

and the spin and orbital operators of symmetry E_θ and E_ε for the triplet are defined as

$$E_\theta^{\,l} = ½\,[3\ell_z^{\,2} - \ell(\ell+1)] \qquad E_\varepsilon^{\,l} = ¼\sqrt{3}\,(\ell_+^{\,2} + \ell_-^{\,2})$$
$$E_\theta^{\,S} = ½\,[3S_z^{\,2} - S(S+1)] \qquad E_\varepsilon^{\,S} = ¼\sqrt{3}\,(S_+^{\,2} + S_-^{\,2}) \quad (4)$$

A_2 is the term denoting hydrostatic pressure for trigonal type of strain, α and α' are the random strains, η', γ and σ are the trigonal stress coefficients for the triplet and the doublet respectively [Al-Shaikh 1991].
Operating with the states given by Bates *et al.* [1992], matrices for orbital doublet and triplets are given in Tables 1 and 2 respectively.
The parameter *b* is subjected to the condition obtained experimentally [Halliday *et al.* 1987]:

$$-¾\,\lambda\,(2a' - b) = 3.3\ \text{cm}^{-1} \qquad (5)$$

Table 1: Matrix Elements of the Effective Hamiltonian for the Doublet.

$\mathcal{H}_{eff}$	$\lvert\theta,\ ½\rangle$	$\lvert\theta,\ -½\rangle$	$\lvert\varepsilon,\ ½\rangle$	$\lvert\varepsilon,\ -½\rangle$
$\langle\theta,\ ½\rvert$	$½\,(\alpha' + \sigma P)$	0	0	0
$\langle\theta,\ -½\rvert$	0	$½\,(\alpha' + \sigma P)$	0	0
$\langle\varepsilon,\ ½\rvert$	0	0	$-½\,(\alpha' + \sigma P)$	0
$\langle\varepsilon,\ -½\rvert$	0	0	0	$-½\,(\alpha' + \sigma P)$

Table 3: Values of the Free Parameters.

	P [111]
b (cm^{-1})	-0.002
α (cm^{-1})	0.4
α' (cm^{-1})	-0.4
A_2 ($cm^{-1}\ MPa^{-1}$)	-0.024
η' ($cm^{-1}\ MPa^{-1}$)	-0.007
γ ($cm^{-1}\ MPa^{-1}$)	-0.06
σ ($cm^{-1}\ MPa^{-1}$)	-0.005

The values obtained for the parameters for the best fit are given in Table 3. The graph obtained using this data for the [111] direction of strain is given in Fig. 1.

SECOND ORDER TERMS IN THE EFFECTIVE HAMILTONIAN

Introducing the second order uniaxial stress terms into the Hamiltonian (1) an improvement can be made to the model discussed above.

$$\mathcal{H}_{eff}^{[111]} = a'\lambda\ell.S + \lambda\,[c(E_\theta^{\,l} E_\theta^{\,S} + E_\varepsilon^{\,l} E_\varepsilon^{\,S}) + b(\ell.S)^2] + A_2P + \alpha\ell_z^{\,2} - \eta' P(3\ell_z^{\,2} - 2)$$
$$+ ⅓\gamma\,P[(\ell_x\ell_y + \ell_y\ell_x) + (\ell_y\ell_z + \ell_z\ell_y) + (\ell_z\ell_x + \ell_x\ell_z)] + ¼9\,\xi_2\ell(\ell+1)\,P^2$$
$$+ ¾\,\zeta_2\,[(c_1^{+}c_2 + c_2^{+}c_1) + (c_1^{+}c_3 + c_3^{+}c_1) + (c_2^{+}c_3 + c_3^{+}c_2)]P^2 \qquad (6)$$

$$\mathcal{H}_{eff}^{[111]} = (\alpha' + \sigma P)\,T_1 \qquad (7)$$

Where ξ_2 and ζ_2 are stress coefficients and T_1 is the fictional orbital operator for the doublet.
Operating with the same states on this Hamiltonian of the system the matrices for the doublet and triplet are obtained.

Table 2: Matrix Elements of the Linear Effective Hamiltonian for the Triplet.

$\mathcal{H}_{eff}^{[111]}$	$-\cos\theta \mid 1, \frac{1}{2}\rangle + -\sin\theta \mid 0, \frac{1}{2}\rangle$	$-\cos\theta \mid 1, \frac{1}{2}\rangle + -\sin\theta \mid 0, -\frac{1}{2}\rangle$	$\sin\theta \mid 1, -\frac{1}{2}\rangle + -\cos\theta \mid 0, \frac{1}{2}\rangle$	$\sin\theta \mid 1, -\frac{1}{2}\rangle + -\cos\theta \mid 0, -\frac{1}{2}\rangle$	$\mid -1, -\frac{1}{2}\rangle$	$\mid 1, \frac{1}{2}\rangle$
$-\cos\theta < 1, -\frac{1}{2} \mid +- \sin\theta < 0, \frac{1}{2} \mid$	$-\frac{3}{4}\lambda(2a'-b)+(A_2+3\eta')P-\frac{1}{3}\alpha$	0	$\sqrt{2}\,(\eta' P-\frac{1}{3}\alpha)$	$-\frac{1}{3}\sqrt{\frac{1}{2}}\gamma P(1-i)$	$\sqrt{\frac{1}{3}}\sqrt{\frac{2}{3}}\gamma P i$	$\frac{1}{3}\sqrt{\frac{1}{3}}\sqrt{\frac{1}{2}}\gamma P(1+i)$
$-\cos\theta < -1, \frac{1}{2} \mid +- \sin\theta < 0, -\frac{1}{2} \mid$	0	$-\frac{3}{4}\lambda(2a'-b)+(A_2+3\eta')P-\frac{1}{3}\alpha$	$-\frac{1}{3}\sqrt{\frac{1}{2}}\gamma P(1+i)$	$\sqrt{2}\,(\eta' P-\frac{1}{3}\alpha)$	$-\frac{1}{3}\sqrt{\frac{1}{3}}\sqrt{\frac{1}{2}}\gamma P(1-i)$	$-\sqrt{\frac{1}{3}}\sqrt{\frac{2}{3}}\gamma P i$
$\sin\theta < 1, -\frac{1}{2} \mid +- \cos\theta < 0, \frac{1}{2} \mid$	$\sqrt{2}\,(\eta' P-\frac{1}{3}\alpha)$	$-\frac{1}{3}\sqrt{\frac{1}{2}}\gamma P(1-i)$	$(A_2+4\eta')P-\frac{2}{3}\alpha$	0	$-\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P i$	$\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P(1+i)$
$\sin\theta < -1, \frac{1}{2} \mid +- \cos\theta < 0, -\frac{1}{2} \mid$	$-\frac{1}{3}\sqrt{\frac{1}{2}}\gamma P(1+i)$	$\sqrt{2}\,(\eta' P-\frac{1}{3}\alpha)$	0	$(A_2+4\eta')P-\frac{2}{3}\alpha$	$-\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P(1-i)$	$\sqrt{\frac{1}{3}}\sqrt{\frac{1}{3}}\gamma P i$
$< -1, -\frac{1}{2} \mid$	$-\frac{1}{3}\sqrt{\frac{2}{3}}\gamma P i$	$-\frac{1}{3}\sqrt{\frac{1}{3}}\sqrt{\frac{1}{2}}\gamma P(1+i)$	$\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P i$	$-\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P(1+i)$	$(A_2-2\eta')P$	0
$< 1, \frac{1}{2} \mid$	$-\frac{1}{3}\sqrt{\frac{1}{3}}\sqrt{\frac{1}{2}}\gamma P(1-i)$	$\sqrt{\frac{1}{3}}\sqrt{\frac{1}{2}}\gamma P i$	$\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P(1-i)$	$-\sqrt{\frac{1}{3}}\sqrt{\frac{1}{3}}\gamma P i$	0	$(A_2-2\eta')P$

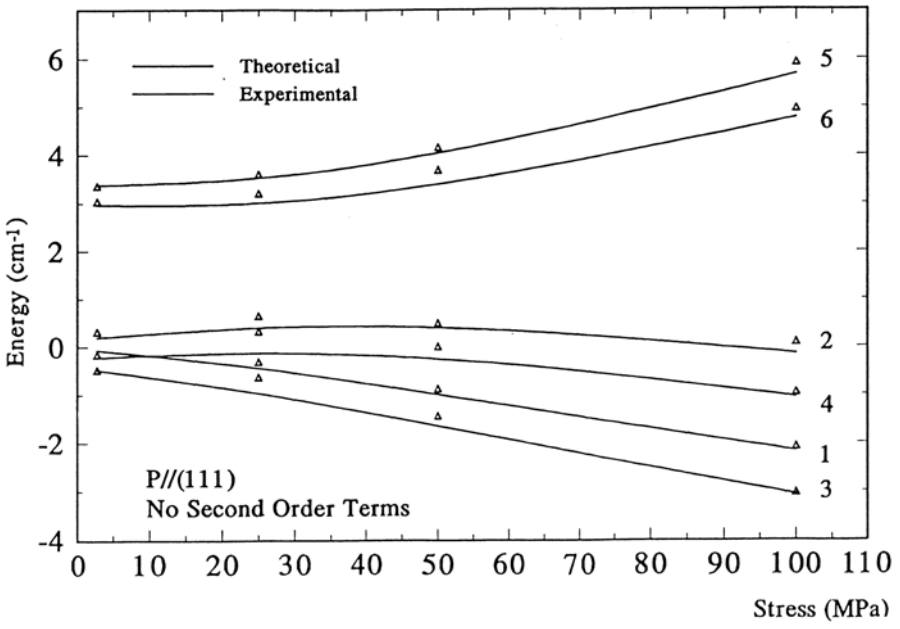

Fig.1: Energies of optical absorption lines with first order terms.

The matrix elements for the doublet and the triplet under trigonal strain are given in Tables 4 and 5, respectively, and the new values for the free parameters are given in Table 6.

Table 4: Effective Hamiltonian for the Doublet.

$\mathcal{H}_{eff}$	$\lvert\theta, \frac{1}{2}\rangle$	$\lvert\theta, -\frac{1}{2}\rangle$	$\lvert\varepsilon, \frac{1}{2}\rangle$	$\lvert\varepsilon, -\frac{1}{2}\rangle$
$\langle\theta, \frac{1}{2}\rvert$	$\frac{1}{2}(\alpha' + \sigma P) +$	0	0	0
$\langle\theta, -\frac{1}{2}\rvert$	0	$\frac{1}{2}(\alpha' + \sigma P) +$	0	0
$\langle\varepsilon, \frac{1}{2}\rvert$	0	0	$-\frac{1}{2}(\alpha' + \sigma P) +$	0
$\langle\varepsilon, -\frac{1}{2}\rvert$	0	0	0	$-\frac{1}{2}(\alpha' + \sigma P) +$

Table 6: Values of the Free Parameters

	P [111]
b (cm^{-1})	-0.20×10^{-2}
α (cm^{-1})	-0.23×10^{-1}
α' (cm^{-1})	-0.22
A_2 ($cm^{-1}\ MPa^{-1}$)	0.12×10^{-1}
η' ($cm^{-1}\ MPa^{-1}$)	-0.43×10^{-2}
γ ($cm^{-1}\ MPa^{-1}$)	-0.64×10^{-1}
σ ($cm^{-1}\ MPa^{-1}$)	-0.71×10^{-2}
ζ_2 ($cm^{-1}\ MPa^{-2}$)	-0.15×10^{-4}
ξ_2 ($cm^{-1}\ MPa^{-2}$)	-0.39×10^{-5}

Table 5: Matrix Elements of the Quadratic Effective Hamiltonian for the Triplet.

$\mathcal{H}_{eff}^{[111]}$	$-\cos\theta \mid 1, \frac{1}{2}\rangle + \sin\theta \mid 0, \frac{1}{2}\rangle$	$-\cos\theta \mid 1, \frac{1}{2}\rangle + \sin\theta \mid 0, -\frac{1}{2}\rangle$	$\sin\theta \mid 1, -\frac{1}{2}\rangle - \cos\theta \mid 0, \frac{1}{2}\rangle$	$\sin\theta \mid 1, -\frac{1}{2}\rangle + \cos\theta \mid 0, -\frac{1}{2}\rangle$	$\mid -1, -\frac{1}{2}\rangle$	$\mid 1, \frac{1}{2}\rangle$
$-\cos\theta < 1, -\frac{1}{2} \mid + \sin\theta < 0, \frac{1}{2} \mid$	$-\frac{3}{4}\lambda(2a'-b)+(A_2+3\eta')P-\frac{1}{3}\alpha+\frac{1}{2}(9\xi_2+\zeta_2)P^2$	0	$\sqrt{2}\,(\eta'P-\frac{1}{3}\alpha)+\frac{1}{4}\sqrt{\frac{1}{2}}(1-3i)\,\zeta_2P^2$	$-\frac{1}{3}\sqrt{\frac{1}{2}}\gamma P(1-i)$	$\sqrt{\frac{1}{3}}\sqrt{\frac{2}{3}}\gamma P i + \frac{3}{8}\sqrt{\frac{2}{3}}\,(1-3i)\zeta_2P^2$	$\frac{1}{3}\sqrt{\frac{1}{3}}\sqrt{\frac{1}{2}}\gamma P(1+i)$
$-\cos\theta < -1, \frac{1}{2} \mid + \sin\theta < 0, -\frac{1}{2} \mid$	0	$-\frac{3}{4}\lambda(2a'-b)+(A_2+3\eta')P-\frac{1}{3}\alpha+\frac{1}{2}(9\xi_2+\zeta_2)P^2$	$-\frac{1}{3}\sqrt{\frac{1}{2}}\gamma P(1+i)$	$\sqrt{2}\,(\eta'P-\frac{1}{3}\alpha)-\frac{1}{4}\sqrt{\frac{1}{2}}(1+3i)\,\zeta_2P^2$	$-\frac{1}{3}\sqrt{\frac{1}{3}}\sqrt{\frac{1}{2}}\gamma P(1-i)$	$-\sqrt{\frac{1}{3}}\sqrt{\frac{2}{3}}\gamma P i - \frac{3}{8}\sqrt{\frac{2}{3}}\,(1-2i)\zeta_2P^2$
$\sin\theta < 1, -\frac{1}{2} \mid + \cos\theta < 0, \frac{1}{2} \mid$	$\sqrt{2}\,(\eta'P-\frac{1}{3}\alpha)+\frac{1}{4}\sqrt{\frac{1}{2}}(1+3i)\,\zeta_2P^2$	$-\frac{1}{3}\sqrt{\frac{1}{2}}\gamma P(1-i)$	$(A_2+4\eta')P-\frac{2}{3}\alpha+\frac{1}{2}(9\xi_2-\zeta_2)P^2$	0	$\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P i + \frac{1}{4}\sqrt{3}\zeta_2P^2$	$\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P(1+i)$
$\sin\theta < -1, \frac{1}{2} \mid + \cos\theta < 0, -\frac{1}{2} \mid$	$-\frac{1}{3}\sqrt{\frac{1}{2}}\gamma P(1+i)$	$\sqrt{2}\,(\eta'P-\frac{1}{3}\alpha)-\frac{1}{4}\sqrt{\frac{1}{2}}(1-3i)\,\zeta_2P^2$	0	$(A_2+4\eta')P-\frac{2}{3}\alpha+\frac{1}{2}(9\xi_2-\zeta_2)P^2$	$-\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P(1-i)$	$\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P i - \frac{1}{4}\sqrt{3}\,(1+2i)\zeta_2P^2$
$< -1, -\frac{1}{2} \mid$	$-\sqrt{\frac{1}{3}}\sqrt{\frac{2}{3}}\gamma P i + \frac{3}{8}\sqrt{\frac{2}{3}}\,(1+3i)\zeta_2P^2$	$-\frac{1}{3}\sqrt{\frac{1}{3}}\sqrt{\frac{1}{2}}\gamma P(1+i)$	$\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P i + \frac{1}{4}\sqrt{3}\zeta_2P^2$	$-\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P(1+i)$	$(A_2+2\eta')P-\frac{2}{3}\alpha+\frac{1}{2}9\xi_2P^2$	0
$< 1, \frac{1}{2} \mid$	$\frac{1}{3}\sqrt{\frac{1}{3}}\sqrt{\frac{1}{2}}\gamma P(1-i)$	$\sqrt{\frac{1}{3}}\sqrt{\frac{2}{3}}\gamma P i - \frac{3}{8}\sqrt{\frac{2}{3}}\,(1+2i)\zeta_2P^2$	$\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P(1-i)$	$-\frac{1}{3}\sqrt{\frac{1}{3}}\gamma P i - \frac{1}{4}\sqrt{3}\,(1-2i)\zeta_2P^2$	0	$(A_2+2\eta')P-\frac{2}{3}\alpha+\frac{1}{2}9\xi_2P^2$

Plotting the graph for the different values of pressure, using the data in Table 6 we get a better fit as shown in Fig. 2 for this type of strain.

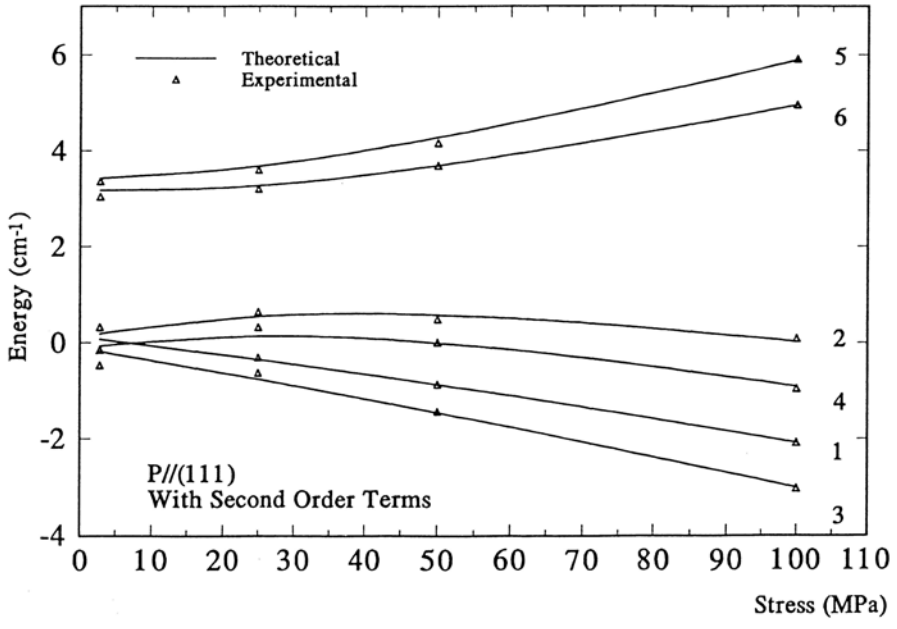

Fig.2: Energies of optical absorption lines with second order terms.

VIBRONIC HAMILTONIAN

The first order effective strain Hamiltonian is given by

$$\mathcal{H}_{eff}^{(1)} = \underline{V}_E(\underline{Q}_\theta E_\theta + \underline{Q}_\varepsilon E_\varepsilon) + \underline{V}_T(\underline{Q}_4 r_4 + \underline{Q}_5 r_5 + \underline{Q}_6 r_6) \quad (8)$$

where $\underline{V}_E$ and $\underline{V}_T$ are the coupling constants V_E and V_T multiplied by the appropriate first order reduction factor, and E_θ, E_ε r_4, r_5 and r_6 are the orbital operators defined by

$$r_4 = -\tfrac{1}{2}\sqrt{3}\,(c_2^+ c_3 + c_3^+ c_2) \qquad E_\theta = \tfrac{1}{2}\,(c_1^+ c_1 + c_2^+ c_2 - 2c_3^+ c_3)$$

$$r_5 = -\tfrac{1}{2}\sqrt{3}\,(c_3^+ c_1 + c_1^+ c_3) \qquad E_\varepsilon = -\tfrac{1}{2}\sqrt{3}\,(c_1^+ c_1 + c_2^+ c_2)$$

$$r_6 = -\tfrac{1}{2}\sqrt{3}\,(c_1^+ c_2 + c_2^+ c_1) \quad (9)$$

with c_i^+ and c_i are the orbital creation and annihilation operators [Bates *et al.* 1989].

Using (1) and (8) and the fact that for trigonal strain $\underline{Q}_E = \underline{Q}_\theta = \underline{Q}_\varepsilon$ and $\underline{Q}_T = \underline{Q}_4 = \underline{Q}_5 = \underline{Q}_6$, the relation between the fundamental parameters V_E and V_T and the stress coefficients η' and γ are found to be

$$K(E)\, V_E\, \underline{Q}_E = -2\eta' P \text{ and } K(T_2) V_T\, \underline{Q}_T = \tfrac{2}{3}\sqrt{\tfrac{1}{3}}\,\gamma P \quad (10)$$

where $K(E)$ and $K(T_2)$ are the appropriate reduction factors.

From Cousins [1981], Yoğurtçu *et al.* [1981] and Dunn and Bates [1988] we have

$$\underline{Q}_E = (1/\sqrt{6})\, Pa\, (S_{11}-S_{12}) \text{ and } \underline{Q}_T = -(6/\sqrt{6})\, PaS_{44}\,(1 - 8\underline{A}) \quad (11)$$

And

$$K(E)\, V_E\, a = -0.23 \times 10^5 \text{ cm}^{-1}$$
$$K(T_2)\, V_T\, a = 0.12 \times 10^5 \text{ cm}^{-1}$$
$$K(E')\, V_{E'}\, a = -0.35 \times 10^5 \text{ cm}^{-1} \quad (12)$$

where $K(E')$ is the appropriate first order reduction factor, $a = 5.45 \times 10^{-10}$ m is the unit cell size for GaP, the inner elasticity $\underline{A} = -0.13 \pm 0.01$, S_{ij} are the ith and jth components of the compliance tensor) with $S_{11}-S_{12} = (12.74 \pm 0.06)\times 10^{-12}$ m^{2}N^{-1} and $S_{44} = (14.22 \pm 0.02)\times 10^{-12}$ m^{2}N^{-1} at room temperature.

Using (10) with the new values of the parameters from Table 6 the first order terms are

$$K(E)\, V_E\, a = -0.23 \times 10^5 \text{ cm}^{-1}$$
$$K(T_2)\, V_T\, a = 0.12 \times 10^5 \text{ cm}^{-1}$$
$$K(E')\, V_{E'}\, a = -0.29 \times 10^5 \text{ cm}^{-1} \quad (13)$$

And the second order terms are obtained by comparing the quadratic terms in (6) and (7) with the effective Hamiltonian for the triplet and doublet, respectively [Dunn 1988]

$$\mathcal{H}_{eff} = V_T^2 \{ \kappa C [\underline{Q}_4^2 + \underline{Q}_5^2 + \underline{Q}_6^2]\, \ell(\ell+1) + \mu B_T [\underline{Q}_4 \underline{Q}_5 (c_1^+ c_2 + c_2^+ c_1) + \underline{Q}_4 \underline{Q}_6 (c_1^+ c_3 + c_3^+ c_1) + \underline{Q}_5 \underline{Q}_6 (c_2^+ c_3 + c_3^+ c_2)] + \nu B_E [(\underline{Q}_4^2 + \underline{Q}_5^2 + \underline{Q}_6^2)(c_1^+ c_1 + c_2^+ c_2 - 2c_3^+ c_3) + 3(\underline{Q}_4^2 - \underline{Q}_5^2)(c_1^+ c_1 - c_2^+ c_2)]$$

$$\mathcal{H}_{eff} = V_E^2 \{ C [\underline{Q}_\varepsilon^2 + \underline{Q}_\theta^2]\, T(T+1) + B_E [(\underline{Q}_\varepsilon^2 - \underline{Q}_\theta^2)\, T_1 + 2\, \underline{Q}_\varepsilon \underline{Q}_\theta T_2] \} \quad (14)$$

where C, B_T and B_E are the second order reduction factors, $\kappa = ¾$, $\mu = ¾$ and $\nu = -⅛$ are the trigonal stress coefficients, $\underline{Q}$ are the displacement coordinates under the stress, V_E is the lattice ion coupling coefficient, T_1 and T_2 are the components of the fictitious angular momentum operator T. Since for trigonal strain $\underline{Q}_4 = \underline{Q}_5 = \underline{Q}_6$, and using results from the Table 6 and (11) we have for the triplet under the trigonal strain

$$V_T^2 B_T \underline{Q}_T^2 = \zeta_2 P^2, \qquad B_T (V_T a)^2 = -0.39 \times 10^7 \text{ cm}^{-1}$$
$$V_T^2 C\, \underline{Q}_T^2 = \xi_2 P^2, \qquad C (V_T a)^2 = -0.1 \times 10^7 \text{ cm}^{-1} \quad (15)$$

DISCUSSION

The incorporation of second order uniaxial stress has improved the fit to experimental data from that given previously [Al-Shaikh 1991]. Unfortunately no quantitative analysis from the obtained result can be given as insufficient experimental data is available to fit the values of coupling

constants $K_E/\hbar\omega_E$ and $K_T/\hbar\omega_T$. From (15) we find that C and B_T are negative, in agreement to the calculated values [Bates *et al*. 1992, Jamila *et al*. 1992]. Also the addition of second order terms in the trigonal strain Hamiltonian does not affect the orbital doublet, as we can see by comparing the Tables 1 and 4.

To account for zero field zero stress splitting observed the parameters α and α' were introduced into the model. The origin of these terms is related to slight misorientation of the various tetrahedral clusters within GaP crystal and to the fact that the magnetic impurity ion does not occupy a pure T_d site.

CONCLUSIONS

We have further developed the work done by Al-Shaikh [1991] by including the second order terms in the analysis. It has also been shown that a satisfactory fit to the calculated JT parameter has been obtained in virtually every case.

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