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The Jahn–Teller effect in the $^5T_2$ state of Fe^{2+} in III–V materials

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Abstract. Estimates of the first-order Jahn–Teller reduction factor (γ) of the $^5T_2$ state of Fe^{2+} in III–V materials are made from an examination of FTIR studies. Values of γ between 0.01 and 0.2 are deduced.

1. Introduction

Relatively few works are devoted to the Jahn–Teller effect (JTE) in Fe^{2+} in III–V materials. The JTE in the $^5T_2$ state of Fe^{2+} ion has been studied by Slack *et al* (1966) and Ham and Slack (1971) in the case of ZnS. The former reported a reduction factor of 0.02 for ZnS. From Zeeman (photoluminescence) measurements, West *et al* (1980) have deduced a reduction factor equal to 0.2 for the $^5T_2$ state of Fe^{2+} in GaP. More recently, Vogel *et al* (1991) have indicated that the JTE in the $^5T_2$ state of Fe^{2+} is weaker in III–V than in II–VI materials. They have calculated an upper limit ($\approx$ 150 cm^{-1}) for the Jahn–Teller energy in InP, GaAs and GaP. The JTE within the ^5E state of Fe^{2+} ion is much smaller in all materials. The unequal separations between the photoluminescence lines, in agreement with the third-order spin–orbit coupling, clearly lead West *et al* (1980) to this conclusion. They have determined a reduction factor of 0.9998 for the ^5E state of Fe^{2+} in GaP.

The main purpose of the present article is to estimate the JTE in the $^5T_2$ state of Fe^{2+} in III–V materials. A model is resolved algebraically. From analysis of experimental information given by Pressel (1992), values of the first-order Jahn–Teller reduction factor are obtained.

2. Theoretical model

The six d electrons of the doubly ionized iron atom couple to form a ^5D atomic ground multiplet. The T_d symmetry crystal field lifts the orbital degeneracy producing an orbital triplet $^5T_2$ and an orbital doublet ^5E at energies -4 Dq and $+6$ Dq respectively relative to the free-ion value (Low and Weger 1960, Slack *et al* 1969). Dq is negative. The ^5E level lies lowest and spin–orbit effects, to the third order, produce five unequally spaced levels Γ_1, Γ_4, Γ_3, Γ_5 and Γ_2 in increasing order of energy (West *et al* 1980). The upper $^5T_2$ multiplet is split by static spin–orbit coupling into three branches: Γ_5 alone, Γ_4 and Γ_3 in the second one and Γ_5^*, Γ_4^* and Γ_1 in the last one (Low and Weger 1960, Slack *et al* 1966).

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It is considered here that the $^5T_2$ state can be split by a dynamic spin–orbit coupling described by the following effective Hamiltonian:

$$\mathcal{H}_{eff} = -A\boldsymbol{L}\cdot\boldsymbol{S} - B(\boldsymbol{L}\cdot\boldsymbol{S})^2 - \tfrac{3}{2}C(L_x^2S_x^2 + L_y^2S_y^2 + L_z^2S_z^2) \tag{1}$$

with $L = 1$ and $S = 2$. This is similar to the $\mathcal{H}_{eff}$ summarized by Abhvani *et al* (1983, 1984) and reviewed by Bates (1978) in zero magnetic field and zero strain for the cluster model. In the case when the coupling $T \otimes e$ dominates, they obtained

$$\begin{aligned} -A &= -\lambda(\gamma + 2\lambda f_1') \\ -B &= -\lambda^2(F_a + 2f_1') \\ -\tfrac{3}{2}C &= \lambda^2(4f_D' - F_b) + B \end{aligned} \tag{2}$$

where λ is the spin–orbit coupling constant, γ is the first-order Jahn–Teller reduction factor, F_a and F_b are the second-order Jahn–Teller reduction factors, $f_D' = k_1/\Delta$ and $f_1' = \gamma k_1/\Delta$ are the second-order spin–orbit factors with $k_1 = 1$ if there is no covalency effect and $\Delta = 10$ Dq. $\mathcal{H}_{eff}$ is written in the $\langle m_1, m_s|$ basis, then in the $\langle J, m_J|$ basis. An exact diagonalization of $\mathcal{H}_{eff}$ leads to the exact algebraic eigenvalues given in table 1.

Table 1. Exact algebraic eigenvalues of $\mathcal{H}_{eff}$.

Level label	Energy
Γ_3	$-2A - 4B - 3C$
Γ_4^*	$\frac{1}{4}\left[-2A - 10B - 21C + 3\sqrt{4(A+B)(A+B+C) + 9C^2}\right]$
Γ_5^*	$\frac{1}{4}\left[2A - 26B - 33C + \sqrt{100(A-B)(A-B+0.12C) + 9C^2}\right]$
Γ_3	$A - B - 3C$
Γ_4	$\frac{1}{4}\left[-2A - 10B - 21C - 3\sqrt{4(A+B)(A+B+C) + 9C^2}\right]$
Γ_5	$\frac{1}{4}\left[2A - 26B - 33C - \sqrt{100(A-B)(A-B+0.12C) + 9C^2}\right]$

3. Determination of parameters

3.1. Method

For Fe^{2+} in the three materials (InP, GaAs and GaP), the A, B and C parameters are determined by fitting the algebraic difference between energy levels and the experimental difference between energy levels deduced from the experimental results of Pressel (1992) and Thonke and Pressel (1991) as obtained by Fourier transform of infrared (FTIR) absorption studies. Then, the Jahn–Teller parameters are calculated using relations (2) and the values of λ and Δ as estimated by Pressel (1992). For his estimation, Pressel has used the full Hamiltonian of the $3d^6$ ion and the photoluminescence data ($\Gamma_5(^5T_2) \rightarrow {}^5E$). These latter values are given in table 2. West *et al* (1980) have obtained similar values for GaP. They are also given in table 2 for comparison. Furthermore, considering that the JTE has little incidence on the ^5E state a calculation of differences of energy levels within the ^5E state using the formulae of West *et al* (1980) obtained with spin–orbit coupling taken to third order has given values which agree with the experimental differences observed by Pressel.

Pressel's experiments show many lines. Some can be explained by transitions between energy levels of the ^5E state and energy levels of the $^5T_2$ state. However, among those

Table 2. Values of λ and Δ as determined by Pressel (1992) for Fe^{2+} in InP, GaAs and GaP and by West *et al* (1980) in GaP†.

Sample	λ (cm^{-1})	Δ (cm^{-1})
InP	−86.0	−3038
GaAs	−90.3	−3206
GaP	−92.7	−3552
	−93.5†	−3554†

transitions only four, occurring between the same energy level of $^5E(\Gamma_4)$ and four energy levels of $^5T_2$, make it possible to calculate three differences needed for fitting. Their positions determined to the nearest 0.1 cm^{-1} are given in table 3. Therefore, they alone have been retained to be examined in this paper.

Table 3. Experimental positions (cm^{-1}) of lines recorded by Pressel (1992) and corresponding transitions proposed here according to three hypotheses (i), (ii) and (iii).

Transitions					
(i)	(ii)	(iii)	InP	GaAs	GaP
$\Gamma_4(^5E) \rightarrow \Gamma_5(^5T_2)$	$\Gamma_4(^5E) \rightarrow \Gamma_5(^5T_2)$	$\Gamma_4(^5E) \rightarrow \Gamma_5(^5T_2)$	2830.2	2988	3329.5
$\Gamma_4(^5E) \rightarrow \Gamma_3(^5T_2)$	$\Gamma_4(^5E) \rightarrow \Gamma_4(^5T_2)$	$\Gamma_4(^5E) \rightarrow \Gamma_4(^5T_2)$	2874	3025	3378
$\Gamma_4(^5E) \rightarrow \Gamma_4(^5T_2)$	$\Gamma_4(^5E) \rightarrow \Gamma_3(^5T_2)$	$\Gamma_4(^5E) \rightarrow \Gamma_5^*(^5T_2)$	2949	3069.3	3417
$\Gamma_4(^5E) \rightarrow \Gamma_5^*(^5T_2)$	$\Gamma_4(^5E) \rightarrow \Gamma_5^*(^5T_2)$	$\Gamma_4(^5E) \rightarrow \Gamma_4^*(^5T_2)$	3103	3239.9	3632

As in the case of a JTE an inversion of energy levels of the $^5T_2$ state may appear, so that as many hypotheses as possible regarding their respective positions have been considered. Only two hypotheses give a convenient fit.

Three analyses are presented here.

(i) There is a change in the order of $\Gamma_4(^5T_2)$ and $\Gamma_3(^5T_2)$ as proposed by Thonke and Pressel (1991). The transitions considered occur between Γ_4 of the ^5E state and successively Γ_5, Γ_3, Γ_4 and Γ_5^* of the $^5T_2$ state.

(ii) The order of $^5T_2$ energy levels is the same as obtained with static spin–orbit coupling. The transitions considered occur between Γ_4 of the ^5E state and successively Γ_5, Γ_4, Γ_3 and Γ_5^* of the $^5T_2$ state.

(iii) There is a change in the order of $\Gamma_5^*(^5T_2)$ and $\Gamma_3(^5T_2)$ with regard to disposition of energy levels with static spin–orbit coupling. The transitions considered occur between Γ_4 of the ^5E state and successively Γ_5, Γ_4, Γ_5^* and Γ_4^* of the $^5T_2$ state.

All three points are taken up in the table 3.

3.2. Results and comments

For each case the results obtained and some comments are given.

(i) There is no possible fitting. It seems that inversion $\Gamma_3(^5T_2) \leftrightarrow \Gamma_4(^5T_2)$ does not work.

(ii) A fitting is possible to within 0.01 cm^{-1} at most. Table 4 indicates the obtained values for *A*, *B* and *C* parameters and the calculated values for the first-order Jahn–Teller

Table 4. The values of A, B and C parameters and the calculated values of γ and positions of energy levels in the hypothesis (ii). Their calculated positions, without JTE, are given in brackets.

Sample	InP	GaAs	GaP
A (cm^{-1})	−86.34	−74.98	−85.75
B (cm^{-1})	−30.65	−23.67	−24.29
C (cm^{-1})	36.98	23.43	21.47
γ	0.950	0.786	0.879
Γ_1 (cm^{-1})	184.3 (230.4)	174.3 (241.6)	204.2 (243.5)
Γ_4^* (cm^{-1})	92.9 (201.2)	113.2 (211.1)	146.6 (214.4)
Γ_5^* (cm^{-1})	−12.6 (177.8)	49.0 (186.7)	89.1 (191.2)
Γ_3 (cm^{-1})	−166.6 (−56.8)	−121.6 (−59.8)	−125.9 (−63.7)
Γ_4 (cm^{-1})	−241.6 (−71.4)	−165.9 (−75.0)	−164.9 (−78.2)
Γ_5 (cm^{-1})	−285.4 (−249.2)	−202.9 (−261.7)	−213.4 (−269.4)

reduction factor γ. Furthermore, the energy level values of the $^5T_2$ state are calculated with the formulae in table 1. For comparison, table 4 gives in brackets the calculated values of energy levels with formulae of Low and Weger (1960) established approximately in the case of static spin–orbit coupling. In both cases the −4 Dq term is omitted. These formulae are as follows (with Dq < 0):

$$\Gamma_1 : -4\ \mathrm{Dq} - 2\lambda - 24\lambda^2/10\ \mathrm{Dq}$$
$$\Gamma_4^* : -4\ \mathrm{Dq} - 2\lambda - 12\lambda^2/10\ \mathrm{Dq}$$
$$\Gamma_5^* : -4\ \mathrm{Dq} - 2\lambda - 2.4\lambda^2/10\ \mathrm{Dq}$$
$$\Gamma_3 : -4\ \mathrm{Dq} + \lambda - 12\lambda^2/10\ \mathrm{Dq}$$
$$\Gamma_4 : -4\ \mathrm{Dq} + \lambda - 6\lambda^2/10\ \mathrm{Dq}$$
$$\Gamma_5 : -4\ \mathrm{Dq} + 3\lambda - 3.6\lambda^2/10\ \mathrm{Dq}.$$

The values of γ shows that the JTE is weak for the $^5T_2$ state. The JTE is slightly greater than obtained for the ^5E state of Fe^{2+} in GaP (West *et al* 1980). Besides, there appears a drop in of energy levels specially in InP and a smaller range of energy levels in GaAs and GaP with regard to static spin–orbit coupling. However, if the JTE is weak, then the parameters B and C should be about one order of magnitude smaller than A (Slack *et al* 1966). This is not the case.

(iii) A fitting is possible to within 0.01 cm^{-1} at most. Table 5 indicates the values obtained for A, B and C parameters. The deduced Jahn–Teller parameters are given. The energies of levels of the $^5T_2$ state are calculated and can be compared with corresponding values, in brackets (without the JTE), given in table 4. There appears, for the three materials, a sharper drop and even smaller range of energy levels than in case (ii) corresponding to a higher JTE. There is a mixing of states. Furthermore, table 5 shows that

$$\gamma_{InP} < \gamma_{GaAs} < \gamma_{GaP}.$$

Therefore, the JTE is smaller in GaP than in InP. Let us note that the value of γ obtained here for the $^5T_2$ state of Fe^{2+} in GaP is the same as the value (0.2) of the orbital reduction factor obtained by West *et al* (1980) using photoluminescence studies. Here, the order of energy levels considered corresponds to the order of energy levels of the $^5T_2$ state for Cr^{2+} in GaAs (Abhvani *et al* 1982) from the lowest to the highest for Fe^{2+} and from the highest to the lowest for Cr^{2+}, keeping in mind that the $^5T_2$ state is lower than the ^5E state for Cr^{2+} (Dq > 0). A comparison of the obtained value γ for Fe^{2+} in GaAs with that for Cr^{2+}

Table 5. The values of A, B and C parameters and calculated values of first- and second-order Jahn–Teller reduction factors and positions of energy levels in the hypothesis (iii).

Sample	InP	GaAs	GaP
A (cm^{-1})	−1.08	−11.38	−20.76
B (cm^{-1})	−15.68	−14.88	−16.96
C (cm^{-1})	53.51	50.65	59.61
γ	0.012	0.123	0.213
F_a $(cm^{-1})^{-1}$	$-0.002\approx 0$	$-0.002\approx 0$	$-0.002\approx 0$
F_b $(cm^{-1})^{-1}$	0.008	0.007	0.008
Γ_1 (cm^{-1})	−95.7	−69.7	−69.5
Γ_4^* (cm^{-1})	−126.7	−115.6	−133.2
Γ_3 (cm^{-1})	−145.9	−148.4	−182.6
Γ_5^* (cm^{-1})	−280.7	−286.2	−348.1
Γ_4 (cm^{-1})	−355.7	−330.5	−387.2
Γ_5 (cm^{-1})	−399.5	−367.5	−435.8

in the same material ($\gamma \approx 0.003$, Bates *et al* 1988) shows that it is about two orders of magnitude greater for Fe^{2+} than for Cr^{2+}.

For the three materials concerned and the transitions studied in cases (ii) and (iii) the theoretical model proposed and submitted for calculation gives differences between energy levels which are more precise by about one order of magnitude than the experimental results. Consequently the parameters deduced can be considered as reasonably accurate.

4. Conclusion

Taking into account the above comments, in the $^5T_2$ state of Fe^{2+} there appears an inversion of energy levels Γ_3 and Γ_5^* with regard to static spin–orbit coupling. In this condition, the comparison of experimental results of Pressel with the theoretical model proposed leads to

(i) a confirmation of the result of West *et al* concerning the first-order reduction factor in GaP and

(ii) a first evaluation of this factor in InP and GaAs

showing that the JTE is about two orders of magnitude smaller than for Cr^{2+} in GaAs.

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