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Studies of the GaP:Cr^{2+} Jahn–Teller system

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Abstract. Estimates of the first- and second-order Jahn–Teller reduction factors of the $^5T_2$ state of isolated substitutional Cr^{2+} in GaP are made from an examination of thermally detected EPR studies and a strain-stabilized strongly coupled $T \otimes e$ Jahn–Teller model.

1. Introduction

The substitutional Cr^{2+} ion in GaAs and InP has been detected by electron paramagnetic resonance (EPR) (Krebs and Stauss 1977, Stauss *et al* 1977) and later by thermally detected (TD) EPR experiments (Bates *et al* 1988, Handley *et al* 1990). Their analysis revealed that the Cr^{2+} ions are on strain-stabilized sites of tetragonal symmetry due to $T \otimes e$ Jahn–Teller (JT) coupling. The problem of GaP:Cr has been mentioned by Vasson *et al* (1994) and Ulrici and Kreissl (1996). But, in the above mentioned articles, the values of spin Hamiltonian parameters have been estimated for isolated Cr^{2+} in GaP, tetragonal symmetry fourth order terms being left aside. The parameter F was taken as equal to zero.

The main purpose of the present article is to estimate the JT effect in the $^5T_2$ state of isolated Cr^{2+} in GaP. Firstly, the accurate values of the five parameters of spin Hamiltonian are determined from TD-EPR experiments (El Metoui 1994, Vasson *et al* 1994). Secondly, with zero magnetic field and zero strain the $^5T_2$ state can be described by an effective Hamiltonian. This model is resolved algebraically. Thirdly, with the strain-stabilization hypothesis an analysis of the results obtained with both the spin and effective Hamiltonians, with zero magnetic field, allows the evaluation of the first and second order JT reduction factors.

2. The spin Hamiltonian

The $^5T_2$ ground states of the isolated substitutional Cr^{2+} ion in GaP can be described by the same spin Hamiltonian H_{spin} as used for the same ion in GaAs (Bates *et al* 1988) and InP (Handley *et al* 1990):

$$H_{spin} = g_{\parallel}\mu_B B_z S_z + g_{\perp}\mu_B(B_x S_x + B_y S_y) + DS_z^2 + \frac{a}{6}(S_x^4 + S_y^4 + S_z^4) + \frac{F}{180}\{35S_z^4 - [30S(S+1) - 25]S_z^2\} \quad (1)$$

with $S = S' = 2$ and where Oz, the tetragonal distortion axis, is along [001], [010] and [100] successively.

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The values of the parameters $g_\parallel$, $g_\perp$, a, D and F are obtained by the minimization technique fitting with theory (1) a set of TD-EPR lines attributed to isolated Cr^{2+} ion. These data points ($\times$), corresponding to 1–2 and 3–4 transitions (El Metoui 1994, Vasson *et al* 1994), are shown in figure 1, at 9.3 GHz, for the magnetic field B rotating in the (001) plane. The best fit with the model is obtained with the values given in table 1.

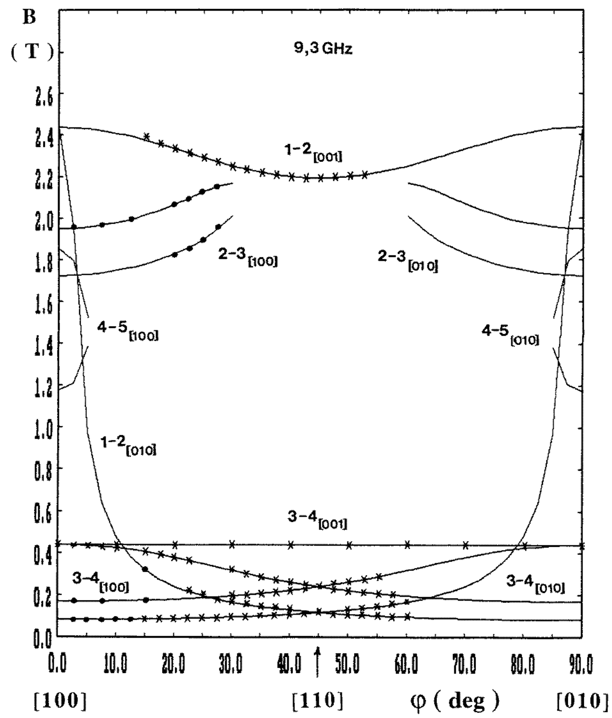

Figure 1. Comparison of the experimental points ($\times$, ●) with isofrequency calculated curves (1–2, 3–4, and 2–3 transitions) using the spin Hamiltonian at 9.3 GHz for B in the (001) plane.

Table 1. The computed values for the parameters of the spin Hamiltonian that give the best fit to all the data.

$g_\parallel$	$g_\perp$	a (GHz)	D (GHz)	F (GHz)
1.966	2.030	1.97	−49.3	−14.3

The isofrequency curves deduced from these parameters are also drawn, in solid lines, in figure 1. The theoretical curves agree with the experimental points to within the experimental error (0.002 T at most). Consequently the parameters obtained can be considered as reasonably accurate. Besides, some resonances (●) corresponding to theoretical curves can be identified: $(2–3)_{[100]}$ transition.

3. The effective Hamiltonian

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

$$H'_{eff} = -A\boldsymbol{L}\cdot\boldsymbol{S} - B(\boldsymbol{L}\cdot\boldsymbol{S})^2 - \frac{3}{2}\mathrm{C}(L_x^2S_x^2 + L_y^2S_y^2 + L_z^2S_z^2) + \frac{a}{6}(S_x^4 + S_y^4 + S_z^4) + \frac{F}{180}\{35S_z^4 - [30S(S+1) - 25]S_z^2\} \qquad (2)$$

with $L = 1$ and $S = 2$. Thus two additional terms have been added to H_{eff} summarized by Abhvani *et al* (1983, 1984), Bates *et al* (1988) and reviewed by Bates (1978) in zero magnetic field and zero strain for the cluster model. These two terms are the same terms in a and F of fourth order in spin as defined in equation (1).

In the case when the coupling $\mathrm{T}\otimes\mathrm{e}$ dominates, they obtained

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

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.

H'_{eff} is written in the $\langle m_1, m_s|$ basis, then in the $\langle J, m_J|$ basis. An exact diagonalization of H'_{eff} leads to the exact algebraic eigenvalues given in table 2.

Table 2. Exact algebraic eigenvalues of effective Hamiltonian.

Level label	Energy
Γ_5^*	$\frac{1}{4}\left\{2A - 26B - 33C + 14a - \frac{4}{3}F + \sqrt{\beta}\right\}$
Γ_4^*	$\frac{1}{4}\left\{-2A - 10B - 21C + 14a - \frac{4}{3}F + \sqrt{\alpha}\right\}$
Γ_3	$A - B - 3C + 3a - \frac{2}{3}F$
Γ_5	$\frac{1}{4}\left\{2A - 26B - 33C + 14a - \frac{4}{3}F - \sqrt{\beta}\right\}$
Γ_4	$\frac{1}{4}\left\{-2A - 10B - 21C + 14a - \frac{4}{3}F - \sqrt{\alpha}\right\}$
Γ_1	$-2A - 4B - 3C + 3a - \frac{2}{3}F$
$\alpha = 9[4(A+B)(A+B+C) + 9C^2] + 4(2A+2B+9C)\left(a + \frac{2}{3}F\right) + 4a^2$	
$\beta = 100(A-B)(A-B+0.12C) + 9C^2 + 4\left(-2A+2B-3C+a+\frac{2}{3}F\right)\left(a+\frac{2}{3}F\right)$	

For instance, in table 2, the order of energy levels is the same in decreasing order as the order deduced from static spin–orbit coupling (Low and Weger 1960, Slack *et al* 1966) from the highest to the lowest.

4. Estimation of the Jahn–Teller reduction factors

In the case of Cr^{2+} in GaAs, Abhvani *et al* (1982a) studying the effects of strain from their H_{eff}, have shown that positive strain isolates a lower set of one near doublet, one exact doublet and a singlet with energies decreasing at the same rate linearly with strain. Their separations are the same as those given by spin Hamiltonian with zero magnetic field.

Consequently, taking into account the strain stabilization and the linear decrease with strain of the energy levels, these separations are also the separations between energy levels with zero strain.

In that case the parameters A, B, C are determined here by fitting the algebraic difference between energy levels corresponding to H'_{eff} (2) and the calculated difference between energy levels deduced of H_{spin} (1) with zero magnetic field and the values of a, D, F given in table 1. As in the case of a JT effect 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 one hypothesis gives a convenient fit within 0.02 GHz at most. Table 3 indicates the obtained values for A, B and C parameters.

Table 3. 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. Their calculated positions, without JT effect, are given in brackets.

Sample	$GaP:Cr^{2+}$
A (GHz)	6.83
B (GHz)	5.89
C (GHz)	−33.31
γ	4.00×10^{-3}
f'_D (GHz^{-1})	4.74×10^{-6}
f'_1 (GHz^{-1})	1.90×10^{-8}
F_a (GHz^{-1})	2.05×10^{-6}
F_b (GHz^{-1})	3.33×10^{-6}
Γ_5^* (GHz)	272.5 (4992)
Γ_5 (GHz)	230.8 (−3392)
Γ_4^* (GHz)	229.1 (1600)
Γ_3 (GHz)	116.3 (1520)
Γ_4 (GHz)	80.14 (−3520)
Γ_1 (GHz)	78.17 (−3681)

Then, the first- and second-order JT reduction factors are calculated from the values of A, B, C by using relations (3) and taking $\lambda = 1680$ GHz (Handley 1989) and $\Delta \simeq 211$ THz (7041 cm^{-1}, Zunger 1986, or 7031.4 cm^{-1}, Ulrici and Kreissl 1996). The values obtained for γ, f'_D, f'_1, F_a and F_b are given in table 3.

Furthermore, the energy level values of the $^5T_2$ state are calculated with the formulae in table 2. As a comparison, table 3 gives in brackets the calculated values of energy levels with formulae of Low and Weger (1960) established approximatively 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 and $\lambda > 0$):

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

The value of γ (4.00×10^{-3}) shows that the JT effect is important for the $^5T_2$ state of isolated substitutional Cr^{2+} in GaP. This value is near that (2.93×10^{-3}) obtained by Bates *et al* (1988) for the same ion in GaAs.

However, it appears that $\gamma_{GaP} > \gamma_{GaAs}$. The same observation has been made for Fe^{2+} ion respectively present in GaP and GaAs (Gavaix 1996).

Besides, with regard to static spin–orbit coupling there are

(i) a very important narrowing of energy levels,

(ii) an inversion of energy levels Γ_3 and Γ_5 (with Γ_5 very near but above Γ_4^*). This disposition (Γ_5^*, Γ_5, Γ_4^*, Γ_3, Γ_4, Γ_1) from the highest to the lowest is the same as the disposition obtained by Abhvani *et al* (1982a, b) for substitutional Cr^{2+} in GaAs. But for a weaker JT effect, as in the case of the $^5T_2$ state of Fe^{2+} in InP, GaAs and GaP (Gavaix 1996) there was only an inversion of energy levels Γ_3 and Γ_5^*. Then, the order became Γ_5, Γ_4, Γ_5^*, Γ_3, Γ_4^*, Γ_1 from the lowest to the highest, keeping in mind that the $^5T_2$ state is higher than ^5E state for Fe^{2+} ($Dq < 0$ and $\lambda < 0$).

5. Conclusion

From a set of lines attributed to the isolated Cr^{2+} ion in GaP in TD-EPR spectra it has been possible to determine with accuracy the five parameters of the spin Hamiltonian and chiefly the parameter F which so far had been considered as zero.

Next, in zero magnetic field, the comparison of results with the theoretical model proposed leads to a first evaluation of the first- and second-order JT reduction factors for the Cr^{2+} ion in GaP. The value of the γ factor shows that the JT effect is of the same order of magnitude in GaP as in GaAs.

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