The role of the Jahn–Teller effect and of the intermediate ligand field in the optical spectra of Cr³⁺-doped GaP and GaAs

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Abstract. The Jahn–Teller coupling constants for the ground state ($^4T_1$) and first excited state ($^4T_2$) of Cr³⁺-doped GaP and GaAs were evaluated by the angular overlap model. Our calculation could provide quantitative justification for the recent proposal of Dunn and Bates according to which the Jahn–Teller effect is responsible for the differences observed in the optical spectra of these systems. The importance of configuration mixing in the ground state is discussed.

In recent years, Cr-doped GaP and GaAs crystals have been the subject of much experimental and theoretical work (for a review see Clerjaud (1985)). In spite of the apparent similarity between the two systems, significant differences in their spectroscopic behaviour have been reported. Particularly striking is the fact that, while a very strong $^4T_1 \to {}^4T_2$ zero-phonon line (ZPL) is observed for GaP (Williams *et al* 1982, Eaves *et al* 1985, Thomas *et al* 1987), no such line is observed for GaAs. Very recently Dunn and Bates (1987) have proposed a mechanism based on the Jahn–Teller effect (JTE) to explain this difference. More precisely, since the intensity of the ZPL is proportional to the vibrational overlap between the ground-state vibrational wavefunctions relative to the two electronic states, the presence of the ZPL depends on the relative displacement of the potential minima; this displacement is expected to be small if both electronic states are Jahn–Teller (JT) coupled to the same kind of vibrational mode, provided that the coupling constants have the same sign.

Even though in the literature we have not found clear evidence that Cr³⁺ optical transitions (either ZPLs or vibronic bands) have been observed in GaAs:Cr³⁺ (see, however, Koschel *et al* (1976) and Deveaud *et al* (1984)), the JT mechanism proposed by Dunn and Bates for the absence of a ZPL is attractive in itself for its simplicity, and in this paper we shall put it on a more quantitative basis and shall show that the mixing between different electronic states does play a fundamental role in determining the spectroscopic properties.

Since Cr^{3+} substitutes for Ga in both crystals, the system can be schematised as a tetrahedral cluster of the CrX_4 type. In T_d symmetry the two low-lying quartets of the free Cr^{3+} ion, ^4F and ^4P, span the following irreducible representations:

$$^4P \rightarrow {}^4T_1(e^2t_2)$$
$$^4F \rightarrow {}^4T_1(et_2^2) + {}^4T_2(et_2^2) + {}^4A_2(t_2^3)$$

where we indicate the strong-field electronic configurations in parentheses.

The wavefunction of the $^4T_1$ ground state is actually a mixture of the two $^4T_1$ levels which arise from the (e^2t_2) and (et_2^2) configurations owing to an intermediate ligand field (Lever 1984):

$$\Psi_{gs} = (1 - \alpha^2)^{1/2} \, {}^4T_1(e^2t_2) + \alpha {}^4T_1(et_2^2). \tag{1}$$

The expression of α is obtained by diagonalising the following energy matrix:

$$\begin{vmatrix} -12B + 8Dq & 6B \\ 6B & -3B - 2Dq \end{vmatrix}$$

where Dq is the crystal-field splitting and B is the Racah parameter for inter-electronic repulsion; diagonalisation yields (Landau and Lifshitz 1966):

$$\alpha(Dq/B) = -[\tfrac{1}{2}\{1 + (10Dq/B - 9)/[(10Dq/B - 9)^2 + 144)]^{1/2}\}]^{1/2}.$$

The ZPL in Cr-doped GaP was attributed (Eaves *et al* 1985, Halliday *et al* 1986, Thomas *et al* 1987) to the $^4T_1 \rightarrow {}^4T_2$ internal transition of Cr^{3+}. The $^4T_2$ excited state can safely be considered as being pure $^4T_2(et_2^2)$ arising from the ^4F term of the free ion. It is clear that both $^4T_1$ and $^4T_2$ levels can undergo a JT effect, and there seems to be indication that both ε and τ_2 modes are active (Clerjaud 1985, Dunn and Bates 1987).

The evaluation of the JT coupling constants is not a simple task; however, some years ago one of us (Bacci 1978, 1979) proposed a semi-quantitative method, based on the angular overlap model (i.e. a simplified LCAO MO theory), and was able to obtain simple relationships for the coupling constants of a cluster containing a metal ion. According to this method, the following expressions can be obtained for the ground $^4T_1$ state of Cr^{3+} in T_d symmetry:

$$b = -(2\sqrt{6}/3R)(e_\sigma - e_\pi/3)[1 - \alpha^2(6e_\sigma + e_\pi)/(3e_\sigma - e_\pi)] \tag{2a}$$
$$c = -(2\sqrt{2}/3R)(e_\sigma - \tfrac{7}{3}e_\pi)(1 - \alpha^2/2) \tag{2b}$$
$$c' = \tfrac{2}{3}(\partial e_\sigma/\partial R - \tfrac{1}{3}\partial e_\pi/\partial R)(1 - \alpha^2/2) \tag{2c}$$

where b is the JT coupling constant to tetragonal (bending) modes, c to trigonal bending modes and c' to trigonal stretching modes; R is the metal–ligand bond distance, while e_σ and e_π are the energy changes of the metal orbitals due to the σ and π interactions with the ligand orbitals (Bacci 1978, 1979). From equation (2a) it is evident that the sign of b critically depends on the mixing coefficient α; for example, in the case $e_\pi = 0$, b reverses its sign according to whether α is larger or smaller than $1/\sqrt{2}$, i.e. according to whether the $^4T_1(et_2^2)$ or the $^4T_1(e^2t_2)$ character is dominant in the ground state.
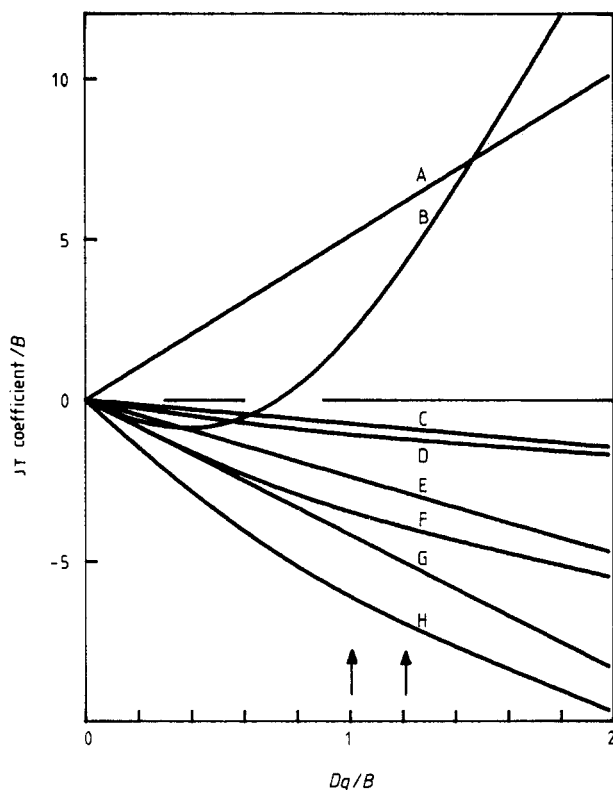
By the same method, we find for the $^4T_2(et_2^2)$ excited state

$$b = (2\sqrt{6}/3R)(e_\sigma - \tfrac{4}{3}e_\pi) \tag{3a}$$
$$c = -(\sqrt{2}/3R)(e_\sigma - \tfrac{7}{3}e_\pi) \tag{3b}$$
$$c' = \tfrac{1}{3}(\partial e_\sigma/\partial R - \tfrac{1}{3}\partial e_\pi/\partial R). \tag{3c}$$

The order of magnitude of the JT coupling constants for both systems $GaP:Cr^{3+}$ and $GaAs:Cr^{3+}$ can be obtained from equations (2) and (3) provided that some assumptions

Figure 1. JT coupling coefficients normalised to B as a function of Dq/B: curve A, $b(^4T_2)$; curve B, $b(^4T_1)$; curve C, $c(^4T_2)$; curve D, $c(^4T_1)$; curve E, $c'(^4T_2,$ GaP); curve F, $c'(^4T_1,$ GaP); curve G, $c'(^4T_2,$ GaAs); curve H, $c'(^4T_1,$ GaAs). Curves A–D are relative to bending modes and are almost coincident for GaP and GaAs, so that only one line has been drawn, while curves E–H are relative to stretching modes. The arrows indicate the position of GaP $(Dq/B \simeq 1.2)$ and of GaAs $(Dq/B \simeq 1)$, as discussed in the text.

are made. The same value of the nephelauxetic ratio ($\beta = B/B_0 = 0.86$, where $B_0 = 918\ \mathrm{cm}^{-1}$ is the free-ion value for Cr^{3+}) was taken for Cr^{3+} in both crystals (Hemstreet and Dimmock 1979). Since in the angular overlap model the ligand-field splitting in a tetrahedral complex is given by (Lever 1984)

$$10Dq = 4e_\sigma/3 - 16e_\pi/9 \tag{4}$$

and since in general $e_\pi/e_\sigma \simeq 0.1$–$0.3$, it is possible to estimate e_σ and e_π as a function of Dq. The derivatives of these quantities were evaluated as described by Bacci (1979); the metal–ligand bond length R was taken as in the host crystal: $R = 2.35$ Å for GaP and $R = 2.44$ Å for GaAs.

In figure 1 we give the B-normalised JT coupling constants as a function of Dq/B for $e_\pi/e_\sigma = 0.3$, which is the most appropriate value for ligands such as P and As. GaP:Cr is easily located in the figure at $Dq/B = 1.2$ since $Dq = 942\ \mathrm{cm}^{-1}$ as it results from the ZPL energy and from the value of the reduced parameter B:

$$Dq = (E_{\mathrm{ZPL}}^2 + 15E_{\mathrm{ZPL}}B)/(120B + 10E_{\mathrm{ZPL}}) \tag{5}$$

with $E_{\mathrm{ZPL}} = 8308\ \mathrm{cm}^{-1}$ (strictly speaking, equation (5) is only valid with no JTE, but owing to the smallness of the latter with respect to $10Dq$ it can be used in this case as well). For GaAs the determination of Dq is not trivial, since contradictory indications exist. A theoretical evaluation by the X_α scattered-wave cluster method (Hemstreet and Dimmock 1979) gives the rather low Dq-value of $403\ \mathrm{cm}^{-1}$. A different way of estimating Dq is to use empirical laws (Liro *et al* 1987); by using the observed proportionality

between the product DqE_I and R^{-7} (where E_I is the ionisation energy of the impurity and R the nearest-neighbour distance) and using the known Dq data for GaP, we find for GaAs the remarkably high Dq-value of about 1340 cm^{-1}. Another empirical relation (Liro *et al* 1987) states that Dq and Phillips' ionicity are proportional; this gives, for GaAs, $Dq \simeq 980$ cm^{-1}. From the experimental point of view, as mentioned, the situation is not very clear. Claims have been made about the observation of Cr^{3+} transitions in GaAs (Koschel *et al* 1976, Deveaud *et al* 1984); in particular the onset of the 0.8 eV absorption was tentatively attributed to the $^4T_1 \rightarrow {}^4T_2$ transition, which from equation (5) gives Dq of the order of 740 cm^{-1}.

Thus the indications for Dq are quite scattered. However, if we used a simple scaling relation involving GaP, GaAs:V^{2+} (Kaufmann *et al* 1982), for Cr^{3+} we would obtain $Dq(\text{GaAs})/Dq(\text{GaP}) \simeq 0.9$, in reasonable agreement with the experimental indication, i.e. $Dq/B \simeq 1$.

Let us now discuss the role of the JTE as it emerges from the coupling constants in figure 1.

If we consider only the linear JTE, the symmetry of the minima in the ground state ($^4T_1$) and excited state ($^4T_2$) is determined by the following conditions (Öpik and Pryce 1957):

$$b^2/K_\varepsilon > c^2/K_\tau \qquad \text{tetragonal minima}$$

$$b^2/K_\varepsilon < c^2/K_\tau \qquad \text{trigonal minima}$$

where the K-values are the elastic constants. Although it is difficult to obtain a reliable evaluation of these latter quantities by the present method, the value of K for bending modes may be expected to be much smaller (up to an order of magnitude) than for stretching modes. Considering the fact that in these systems the tetragonal modes are bending modes, from figure 1 we can safely say that, for GaP:Cr^{3+}, tetragonal minima are expected both in the ground state and in the excited state, confirming the proposal of Dunn and Bates (1987); note also that, since b is positive in both states, the tetragonal minima correspond to the same kind of distortions, thus resulting in larger overlap between the ground vibrational states. The fact that $b(^4T_1) < b(^4T_2)$ is also qualitatively consistent with the fact that the effect of a (111) trigonal stress is completely quenched in the $^4T_2$ state and not quenched in the $^4T_1$ state (Thomas *et al* 1987), and with the level scheme obtained by Thomas *et al* from high-resolution luminescence spectra. In fact, the A and B levels in figure 2 of Thomas *et al* (1987), in the limit of strong JTE, would be simply the spin–orbit components of the $^4A_2$ level which results from the static JT splitting of $^4T_2$ into $^4A_2$ and ^4E, while the 1–6 lower levels would be the six Kramers doublets of $^4T_1$, whose spin–orbit splitting is quenched by the Ham effect. Darcha *et al* (1987) also found evidence by EPR measurements of a moderate tetragonal JTE in the ground state.

For GaAs:Cr^{3+}, our calculation indicates that when $Dq/B \simeq 0.9$–1 in the $^4T_1$ state the b and c coupling coefficients are not very different in value, and both are three to five times smaller than c' (which relates to a stretching mode), thus putting the three kinds of mode on the same level as concerns the possibility of generating stable JT distortions; this is a necessary condition (Bacci *et al* 1975a, b) because a higher-order JTE and/or random static strain can stabilise orthorhombic distortions (orthorhombic minima were actually proposed for the ground state of GaAs:Cr by Stauss and Krebs (1980) and Challis and de Goer (1984)). On the contrary, in $^4T_2$ (as in the case of GaP), tetragonal modes are clearly expected to dominate.

These results perfectly match the hypotheses of Dunn and Bates (1987) and, in our opinion, could support the mechanism which they have proposed for explaining the

different optical behaviour of Cr-doped GaP and GaAs. One should not forget, however, that an obvious alternative reason why GaAs:Cr shows no ZPL might be that (as mentioned at the beginning of this paper) *no emission at all* takes place in this material, possibly because the corresponding absorption transition might end within the conduction band (Langer and Heinrich 1985).

In any case, our calculation provides a quantitative explanation of GaP:Cr^{3+} phenomenology. Furthermore, it should be stressed that, owing to the closeness of the two low-lying $^4T_1$ levels in a tetrahedral arrangement, configuration mixing cannot be overlooked in an analysis of the JT distortions, because flattening or elongation of the tetrahedron does depend on the value of α.

The role of higher-order effects in determining the topology of the adiabatic potential surfaces has not been investigated because the linear JTE itself does not appear to be very strong. Moreover, such a study would introduce several further JT coupling coefficients and/or anharmonic constants which, most probably, would have to be treated as fitting quantities, and this would be contrary to the spirit of the present paper.

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