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Strong Jahn–Teller effects in the excited $^3T_1$ state of V^{3+} ions in III–V materials

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Abstract. Previous studies of the optical absorption bands attributed to the $^3A_2 \rightarrow {}^3T_1(F)$ internal transitions of V^{3+} ions in GaP, GaAs and InP have shown that a very strong $T \otimes t_2$ Jahn–Teller effect is active in the $^3T_1(F)$ state. An analysis is presented for the GaP:V^{3+} system which reconciles the structure of the accompanying zero-phonon line in terms of second-order Jahn–Teller spin–orbit coupling contributions, with the strength of the coupling deduced from the properties of the band. In the cases of GaAs:V^{3+} and InP:V^{3+}, it is proposed that strong coupling to e modes is also present.

1. Introduction

Optical spectroscopy is a powerful technique for the characterisation and identification of magnetic impurity ions in semiconductors. With these experiments, the shape and structure of an optical absorption or photoluminescence band and the structure of the accompanying zero-phonon line (ZPL), if present, are known to depend upon both the type and strength of the coupling of the states of the ion concerned to the lattice. In many cases, both the band and the ZPL can be satisfactorily modelled by standard procedures. However, the orbital triplet states of many substitutional 3d ions in III–V semiconductors are exceptionally strongly coupled to vibrations of the lattice, and in particular to those of t_2 type. Until very recently, a theory of the structure of the ZPL for such Jahn–Teller (JT) systems had not been developed in sufficient detail to give consistent results in the simultaneous modelling of the ZPL and the band. Particular examples of systems for which both the ZPL and band have been observed and which cannot be modelled with the simple theories are V^{3+} ions in GaP, GaAs and InP. For these ions, simple theory predicts that the ZPL should have four components whereas in GaP, two components only are observed, and in GaAs and InP only one component is observed. This paper describes how to use recently published calculations of the second-order JT reduction factors involved in spin–orbit coupling to obtain unified models for the three examples cited above.

2. The GaP:V^{3+} system

In their optical studies of several vanadium-doped GaP crystals, Ulrici *et al* (1987) identified a triple-peaked absorption band with a central maximum at $\simeq 9600\,cm^{-1}$.

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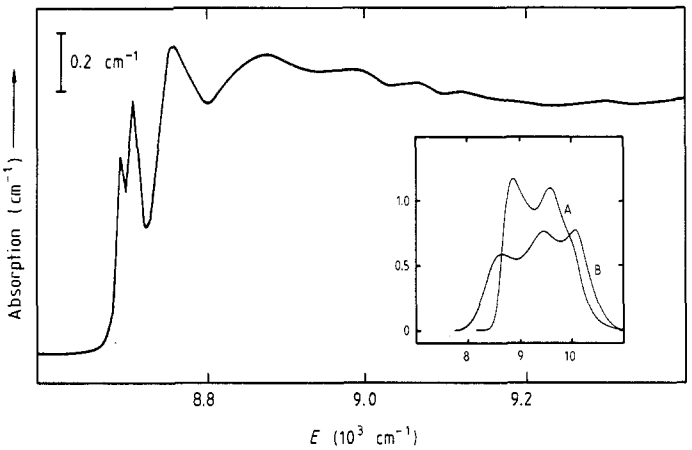

Figure 1. Part of the optical absorption spectrum of the internal $^3A_2 \rightarrow {}^3T_1(F)$ transition of V^{3+} ions in GaP measured at $T = 5$ K. The inset shows the entire broad-band absorption spectrum of this transition measured at $T = 78$ K (A) and 300 K (B).

Superimposed on this were three sharp lines at 8698.7, 8713.1 and 8762.7 cm^{-1}, with half-widths 5.6, 9.7 and 40 cm^{-1} respectively. These features are all illustrated in figure 1. From measurements of the increase of the separation between the side peaks and central peak with increasing temperature, they deduced (using the theory of Cho 1968) that a very strong $T \otimes t_2$ JT effect is operating within the $^3T_1(F)$ state and that the Huang–Rhys factor $(S_t = E_T/\hbar\omega_T) = 7 \pm 2$ where E_T is the JT energy and $\hbar\omega_T$ the phonon quantum energy. They also proposed that the three sharp lines were associated with the components of the $^3A_2 \rightarrow {}^3T_1(F)$ ZPL transitions of V^{3+}. However, the large value of S_t would result in very small spin–orbit splittings in the $^3T_1(F)$ states (due to large JT quenching terms). As the A-state cannot be split, it would therefore be difficult to produce three lines separated by $\simeq 65$ cm^{-1}.

We believe that an alternative interpretation is preferable in which only the first two sharp peaks are associated with a ZPL and the third peak, which is much broader and distinct, is either a phonon replica or is associated with an excited vibronic state. We will now re-examine the structure of the ZPL ignoring the third broad peak.

The $^3T_1(F)$ states can be modelled by an isomorphic $\ell = 1$ operator, and spin–orbit coupling described by an effective Hamiltonian:

$$\mathcal{H}_{\text{eff}} = a\boldsymbol{\ell}\cdot\boldsymbol{S} + b(\boldsymbol{\ell}\cdot\boldsymbol{S})^2 + c(E^{\ell}_{\theta}E^{S}_{\theta} + E^{\ell}_{\varepsilon}E^{S}_{\varepsilon}) \tag{1}$$

where

$$E^{\ell}_{\theta} = \tfrac{1}{2}[3\ell_z^2 - \ell(\ell+1)] \qquad E^{\ell}_{\varepsilon} = (\sqrt{3}/4)(\ell_+^2 + \ell_-^2) \tag{2}$$

are orbital operators and $E^S_\theta \equiv E^\ell_\theta$ with ℓ replaced by S. For a strong $T \otimes t_2$ JT effect and neglecting anisotropy, the parameters a, b and c are given by (Bates and Dunn 1989)

$$\begin{aligned} a &= k_1^{T_1}K_t(T_1)\lambda + \lambda^2 N_{Tt}^2 (k_1^{T_1})^2 (f_a^t - f_b^t) \\ b &= -2N_{Tt}^2 (k_1^{T_1})^2 (f_a^t + f_b^t)\lambda^2 \\ c &= -\tfrac{4}{3}N_{Tt}^2 (k_1^{T_1})^2 (f_\alpha^t - f_b^t)\lambda^2 \end{aligned} \tag{3}$$

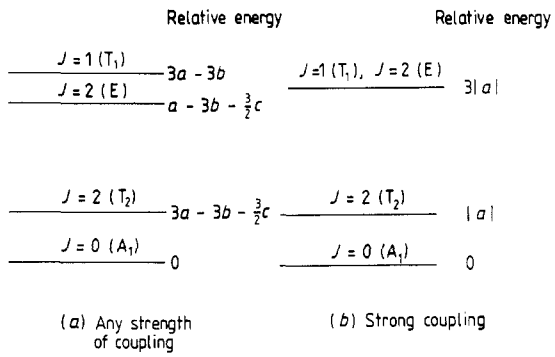

Figure 2. The energy level diagram and energies of the excited $^3T_1(F)$ state of V^{3+} ions in GaP showing the splitting caused by the second-order JT spin–orbit coupling.

where $k_1^{T_1}(=-3/2)$ is the isomorphic constant, $K_t(T_1)$ is the first-order reduction factor for a T_1 operator, f_a^t and f_b^t are the second-order reduction factors and N_{Tt} is the normalising constant for the cubic tunnelling states.

An analysis of the eigenvalues of $\mathcal{H}_{\text{eff}}$ shows that the $^3T_1(F)$ state splits into four components, which may be labelled by their J $(=\ell + S)$ value. Taking the $J = 0$ (A_1) state as the energy zero, the other states are $J = 2$ (T_2), $J = 2$ (E) and $J = 1$ (T_1) with relative energies of $(3a - 3b - \frac{3}{2}c)$, $(a - 3b - \frac{3}{2}c)$ and $(3a - 3b)$ respectively (figure 2(*a*)). Obviously, these energies depend upon the values of the reduction factors, which in turn depend upon the magnitude of the coupling strength. The reduction factors were plotted as a function of $K_T/\hbar\omega_T\,(=(3E_T/4\hbar\omega_T)^{1/2})$ in Bates and Dunn (1989). The broad-band analysis indicated that $S_t = 7 \pm 2$, and hence $K_T/\hbar\omega_T = 2.3 \pm 0.3$. For this range of coupling strengths, it is more appropriate to redraw the curves of Bates and Dunn (1989) on an expanded scale. These values are shown in figure 3. It is clear that for all values of $K_T/\hbar\omega_T > 2.0$, the term f_b^t dominates. When the terms in $K_T(T_1)$ and f_a^t are neglected, it is found that the $J = 1$ and $J = 2$ (E) states are degenerate, with energy $-3a$, and the $J = 2$ (T_2) state has energy $-a$ (figure 2(*b*)). For $K_T/\hbar\omega_T = 2.3$, it can be seen that $N_{Tt}^2 f_b^t = 0.025$. Taking $\lambda = 100\,\text{cm}^{-1}$ and $\hbar\omega_T = 100\,\text{cm}^{-1}$ from the experiments of Ulrici *et al* (1987), we find

$$a = -5.6 \pm 1.0\,\text{cm}^{-1}.$$

We therefore suggest that the ZPL observed in GaP: V^{3+} shows transitions from the $^3A_2$ ground state to the two lowest of the excited states which are unresolved (their calculated separation of $5.6 \pm 1.0\,\text{cm}^{-1}$ is about the same as the measured line width) and to the pair of upper degenerate states (the calculated separation of $16.8 \pm 3\,\text{cm}^{-1}$ is consistent with the experimental separation of $14.4\,\text{cm}^{-1}$). This thus consistently explains both the sharp ZPL structure and the value of S_t obtained from the band.

3. The GaAs: V^{3+} and InP: V^{3+} systems

Absorption measurements on the GaAs: V^{3+} system have been reported (e.g. Ulrici *et al* 1985). The spectrum shows a triple-peaked band, similar to that observed in GaP: V^{3+}, but with a ZPL (at $8132\,\text{cm}^{-1}$) that shows no structure, and a half-width of $3\,\text{cm}^{-1}$. From measurements on the triple-peaked band, it was deduced that a $T \otimes t_2$ JT effect dominates in this system with $S_t \simeq 10$. A similar analysis to that for GaP: V^{3+} gives a value for a of

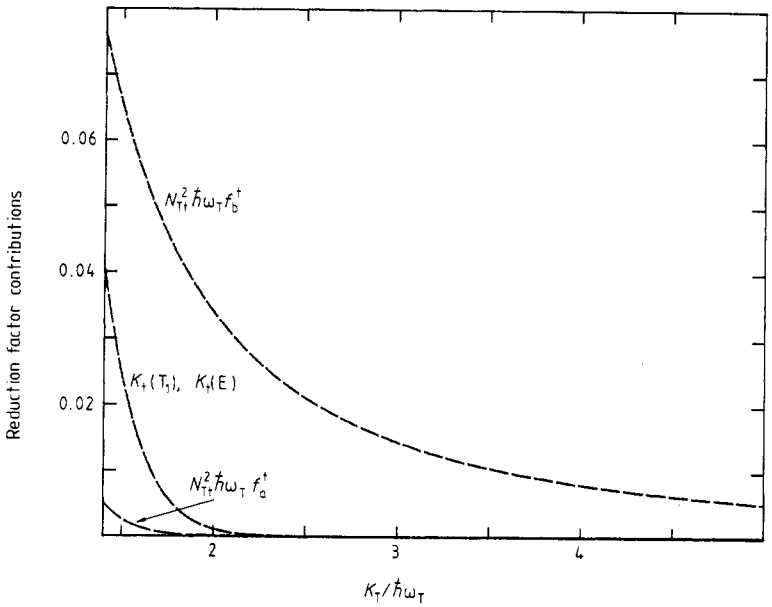

Figure 3. The first-order JT reduction factors $K_t(T_1)$ and $K_t(E)$ and second-order factors $N_{T_1}^2\hbar\omega_T f_a^t$ and $N_{T_1}^2\hbar\omega_T f_b^t$.

3.8 cm^{-1}, which predicts a ZPL with two components, at 3.8 cm^{-1} and 11.4 cm^{-1}. In order for the second-order spin–orbit splitting in the $^3T_1(F)$ state to be less than 3 cm^{-1} (so that the structure in the ZPL would not be resolved) $S_t \simeq 40$ is required. This value is very unrealistic as it would imply an extremely large value for E_T and the ZPL should not be observable at all. This clearly shows that the JT effect cannot be pure $T \otimes t_2$ in the case of GaAs: V^{3+}.

We suggest that a more complicated JT system is present in which the trigonal wells are the absolute minima in Q-space consistent with a $T \otimes t_2$ JT system but that a significant amount of coupling to the e modes is also present. This implies that the orthorhombic wells have energies slightly higher than the trigonal wells, and so the effective second-order reduction factors from $T \otimes t_2$ contain significant $T \otimes (e + t_2)$ character. Unfortunately, the theory of $T \otimes t_2$ JT systems has not yet been extended to include mixed systems of this type, so a quantitative analysis cannot be undertaken at present. However, Dunn and Bates (1989) have shown that for a pure $T \otimes (e + t_2)$ JT system, the second-order reduction factors are significantly smaller than they are for a pure $T \otimes t_2$ JT system. We therefore expect the e coupling to decrease the $T \otimes t_2$ second-order spin–orbit coupling splitting. This would allow the ZPL results to be described with a much smaller value of S_t. This result would also be consistent with the uniaxial stress experiments in OA on the ZPL (Côte and Clerjaud 1990), which show a large effect from t_2-type stresses.

The absorption spectrum from InP: V^{3+} is very similar to that from GaAs: V^{3+} in that the shape of the line indicates a dominant $T \otimes t_2$ JT effect and the ZPL has only one component (Clerjaud *et al* 1987). Also the uniaxial stress experiments on the ZPL (Nash *et al* 1984) give results very similar to those of GaAs: V^{3+}. Thus the interpretation given above for GaAs: V^{3+} is also applicable to InP: V^{3+}.

4. Discussion

The nature of the JT effect operating in the three V^{3+} systems is not yet fully clarified from the above discussion alone. However, according to the original analysis by Ulrici *et al* (1985) for GaAs : V^{3+}, the existence of triple-peaked line shapes together with the characteristic temperature dependence shows unequivocally that the $T \otimes t_2$ JT effect operates on the $^3T_1(F)$ excited state in all three cases. Within both the semi-classical approximation and more sophisticated models (i.e. the independent ordering approximation), only strong $T \otimes t_2$ coupling creates a triple-peaked line shape. Various additional $T \otimes e$ and $T \otimes a$ couplings lead to a broadening or a smearing out of the triple-peaked structure (Cho 1968). A further complication arises from the fact that spin–orbit coupling can also affect the line shapes (see the discussion of the ΔE_1 values in Ulrici *et al* 1985, 1987).

Further support of a dominant $T \otimes t_2$ interaction comes from the temperature dependence of the skewness of the band. The evidence points to the presence of some quadratic $T \otimes t_2$ coupling for the GaAs : V^{3+} system which implies therefore that the linear coupling of the same symmetry is likely to dominate other couplings (Nasu and Kojima 1974).

Additional evidence for this assignment can be obtained by two other measurements on the spectra.

(i) If the ground state is an orbital singlet and the excited state is either of a pure linear $E \otimes e$ or a pure linear $T \otimes t_2$ type, then the separation δ in energy between the ZPL and the centre of the band very approximately equals E_{JT}, the JT energy. E_{JT} can be derived from the temperature dependence of the band. Ulrici *et al* (1985, 1987) have measured E_{JT} and these values together with those of δ are as follows:

	δ (cm^{-1})	E_{JT} (cm^{-1})
GaAs	740	780
GaP	680	710

It is seen that in both GaP and GaAs the values of E_{JT} and δ agree. As a pure $E \otimes e$ is inappropriate, the above simple calculations are not in contradiction with a dominant $T \otimes t_2$ JT effect for both systems.

(ii) For a pure and linear $T \otimes t_2$ system, the ratio R of the intensity I_{ZPL} of the ZPL and the intensity I_{bb} of the broad band is given by the approximate simple relation

$$R = I_{ZPL}/I_{bb} = \exp(-S_t).$$

This expression is only approximate because a more accurate calculation of I_{ZPL} should include a factor f to describe both the electronic overlap and the effect of the construction of the symmetry-adapted vibronic states as well as the overlap between the displaced oscillators (M C M O'Brien 1989). It is expected that f will be in the range $0.3 < f < 2$. Now I_{ZPL} and I_{bb} are directly proportional to the areas under the ZPL and the broad band spectra respectively, so, neglecting the electronic overlap:

for GaAs:V^{3+}: $R = 3.3 \times 10^{-4}$ which gives $S_t = 8.0 \pm 1$

for GaP:V^{3+}: $R = 4.4 \times 10^{-3}$ which gives $S_t = 5.4 \pm 2$.

These values are very close to 10 ± 2 and 7 ± 2 respectively, deduced from the temperature dependence of the line shapes. Thus these additional measurements are also not in contradiction with a pure $T \otimes t_2$ system.

Theoretical complications in the analyses of the ZPLs are also present. The formulae (3) for the reduction factors are based on a cluster model. If a more realistic multi-mode model were to be used (Bates 1978), the effective values for ω and E_{JT} would be different from those appearing in calculations from the band shapes. Also, simplifications in the form of the excited vibronic states were used in the derivation of the second-order reduction factors (Dunn 1989).

Obviously it would be most helpful if further independent experimental evidence were available to confirm our proposals about the nature of the JT coupling and the ZPL splittings. We have already referred to the uni-axial stress data of Côte and Clerjaud (1990) for GaAs: V^{3+} and Nash *et al* (1984) for InP: V^{3+}. However, it is not possible to deduce values for the coupling constants from these measurements as no information is available on the effective compliance tensor for the V^{3+} ligand molecule. This could be significantly different from that for the perfect crystal. We suggest further experiments such as magnetic circular dichroism and optically detected magnetic resonance should be undertaken in order to test our suggestion that a linear $T \otimes t_2$ JT effect is dominant in the excited $^3T_1(F)$ states for all three systems.

In conclusion, we have provided an explanation of the optical data concerning the $^3A_2 \rightarrow {}^3T_1(F)$ transition in V^{3+} in GaP in terms of a strong $T \otimes t_2$ JT effect and including second-order JT-generated spin–orbit coupling terms. The corresponding data for V^{3+} ions in both GaAs and InP again suggest a $T \otimes t_2$ coupling but with a significant additional e coupling.

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