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Jahn–Teller impurity ion complexes in III–V semiconductors

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Abstract. A method of studying strongly coupled orbital triplet ions forming part of a trigonal tetrahedral complex is presented. It is based on the unitary transformation and energy minimization method described previously by Dunn and Bates for regular tetrahedral clusters, and it is assumed that the ion is coupled to the e-modes and to one set of the t_2 -modes of the trigonal cluster. The coordinates of the 13 minima in the potential surface are found and they are related to the tetragonal, trigonal and orthorhombic minima of the regular cluster. Results are presented for both the radial and transverse t_2 -modes. The ground states located in each of the minima are also deduced. These calculations form the basis for the evaluation of Jahn–Teller reduction factors for orbital triplet ions in such environments, which will be reported shortly.

1. Introduction

The technology used in the manufacturing of semiconducting materials has progressed much during the last decade, particularly with the fabrication of low-dimensional structures and superlattices. Although such materials have reached a high degree of purity, they nevertheless are still not entirely free of donors and acceptors. Defects are well known to have a pronounced effect on the properties of these materials and their identification and/or possible elimination are often vital for their use as device materials. It is also very clear that many latent defects are not simply substitutional (or interstitial). They can involve the replacement of at least two standard adjacent ions or atoms by different ions or atoms to form what is termed a complex or an associate.

In bulk semiconductors, it was realized that many of the unwanted conducting properties could be removed by intentionally doping the material with small concentrations of transition metal ions (e.g. chromium in GaAs). Such impurities can generate deep levels in the band gap of the semiconductor which act as traps for the excess donor electrons or acceptor holes so that the material changes from being semiconducting to semi-insulating. It is also very clear that many of such transition metal impurity ions do not enter the lattice as isolated, substitutional impurities but rather as part of a more complicated complex. For example, a significant fraction of the chromium impurity in GaAs occupies a Ga site which itself is adjacent to an As vacancy or, alternatively, is adjacent to another impurity (such as tellurium) which has substituted for the nearest-neighbour As atom.

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The existence of impurity-ion complexes greatly complicates the interpretation of experimental data on magnetic impurity systems. Clerjaud (1985) summarized the data known at that time for both isolated ions and for those forming part of a complex in GaAs, GaP and InP bulk crystals. Since then, numerous examples of other complexes in both bulk and LDS semiconductors have been found but their basic structure often remains uncertain. It appears that many of the ions which are part of a complex are very strongly coupled to the surrounding lattice and are frequently termed Jahn–Teller (JT) ions. An example of this is the $\text{Cr}^{2+}-\text{V}_{\text{As}}$ complex (where V_{As} is a vacancy at an adjacent As site) in GaAs which gives very strong acoustic paramagnetic resonance (APR) spectra (Bates *et al* 1984). The arsenic vacancy generates a sizeable trigonal field at the chromium site so that the resultant spectra has trigonal symmetry. (It should be noted that not all complexes contain magnetic ions.)

The simplest procedure for modelling the impurity-ion complex is to treat the magnetic ion in the same way as an isolated ion with an additional but purely static trigonal field acting as a perturbation. The vibronic coupling is treated in T_d symmetry. An alternative procedure is to solve the vibronic problem in C_{3v} symmetry so that the trigonal field is not regarded as just a static perturbation. The latter approach was the one used by Jäger (1968) for the study of sites of symmetry D_{3d} in spinels, and by Abou-Ghantous *et al* (1974) and Lacroix *et al* (1979) for transition metal ions in corundum. The method was extended to the $\text{Cr}^{2+}:\text{GaAs}$ system by Picoli *et al* (1983a, b). In this work, coupling to all the e-modes was included (derived from both the cubic e- and t_2 -modes).

The aim of this paper is to develop a more general model for a strongly-coupled ion at the centre of a trigonal cluster which is applicable to many of the complexes found in III–V semiconductors. The method to be used is based on the unitary transformation and energy minimization approach developed for ions at sites of T_d symmetry by Bates *et al* (1987, to be referred to as BDS), Dunn (1988, to be referred to as D) and by Dunn and Bates (1989) for orbital triplet systems. In a later paper (Simpson *et al* 1991), the JT reduction factors for the trigonal complex are derived so that they can be used to model the experimental data existing on many systems.

It would appear that the method proposed here is an improvement on those methods cited above because it is especially applicable for strongly-coupled ions. It is hoped that it will assist in the identification of such magnetic-ion complexes in both bulk and LDS semiconducting materials.

2. The model

The trigonal cluster consists of a magnetic ion at the origin surrounded by four non-magnetic ligands at sites i ($i = 1-4$) in a tetrahedral configuration, in which the ligand at site 1 (chosen to lie in the [111] direction), is different from the other three. The ligand 1 could be either tellurium or selenium, for example, or a vacancy. Its effective mass and charge will be different from that of the other ligands. Even though the cluster is embedded in and in direct contact with the rest of the crystal, the cluster will be distorted from the regular tetrahedral shape as the length of the bond in the [111] direction will be different from that in the other directions. Both the distortion and the charge difference generate a trigonal field within the cluster with the trigonal axis along [111]. They will also modify the ion-lattice coupling and consequently the Jahn–Teller modelling of such systems.

In order to analyse the effect of such changes, it is necessary to define various parameters for the trigonal cluster. Let us suppose that the effective charge on the impurity ligand is q_1 and that its distance from the origin is d_1 . Thus

$$q_1 = (1 + \delta)q \quad d_1 = (1 + \sigma)d \quad (2.1)$$

where q is the effective charge on the other three ligands which are at a distance d from the origin.

The Coulomb potential experienced by a single impurity electron at a point \mathbf{r} due to the surrounding four ligand charges q_i at equilibrium positions $\mathbf{R}_i^{(0)}$ is given by

$$V(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^4 \frac{q_i}{|\mathbf{R}_i^{(0)} - \mathbf{r}|} \quad (2.2)$$

where $q_i = q$ and $|\mathbf{R}_i^{(0)}| = d$ for ligands 2–4 and $q_i = q_1$ and $|\mathbf{R}_i^{(0)}| = d_1$ for ligand 1.

The ion–lattice coupling can be calculated by considering the effect that each of the collective modes of the cluster has on the ligands. In order to do this, local cartesian coordinates axes are set up at each ligand site in the usual way. The collective displacements Q_j , defined in exactly the same way as for the perfect tetrahedral cluster (Bates 1978) are then decomposed into components along the trigonal axes (X_i, Y_i, Z_i) at each site. It is necessary to consider the e-type displacements (Q_θ, Q_ϵ) and both of the sets of t_2 -type displacements (Q_4, Q_5, Q_6) and (Q_7, Q_8, Q_9), as all three modes of vibration are coupled to a T($l=1$) ion. The first set of t_2 modes (Q_4, Q_5, Q_6) involve radial displacements (Z_i) only and the other t_2 -modes involve transverse displacements only. Although they have identical transformation properties, their net effects will differ.

As a result of the collective displacements Q_j , the ligand at site i occupies a new point in space with a position vector

$$\mathbf{R}_i^{(j)} = \mathbf{R}_i^{(0)} + \mathbf{Q}_i^{(j)} \quad (2.3)$$

where $\mathbf{Q}_i^{(j)}$ is the displacement of the ion at site i . The potential $V(\mathbf{r})$ is then obtained by substituting $\mathbf{R}_i^{(j)}$ for $\mathbf{R}_i^{(0)}$ in (2.2). A binomial expansion in terms of cartesian coordinates x, y, z for the electronic potential energy can be made in the usual way (see, for example, Hutchings 1964). The terms without the Q_j produce the tetrahedral and trigonal fields. The terms involving the Q_j generate the ion–lattice coupling terms which may be further sub-divided, such that the main part (without both σ and δ) gives the ion–lattice interaction Hamiltonian H_{int} for the regular tetrahedral cluster. The remaining terms give the contribution ΔH_{int} to the ion–lattice coupling due to the change of ligand at site 1. It can be further sub-divided into that which arises from the change in the charge involving δ and that which arises from the static displacement involving σ .

3. The Hamiltonian for the ion–lattice coupling

3.1. The contribution from the regular tetrahedral cluster

The linear ion–lattice interaction Hamiltonian for the regular tetrahedral cluster is given by (BDS, equation (3.1))

$$H_{\text{int}} = V_E(Q_\theta E_\theta + Q_\epsilon E_\epsilon) + V_T(Q_4 T_{yz} + Q_5 T_{zx} + Q_6 T_{xy}) \\ + V_2(Q_7 T_{yz} + Q_8 T_{zx} + Q_9 T_{xy}) \quad (3.1)$$

where V_E, V_T and V_2 are the coupling constants for the e- and two t_2 -modes respectively.

The orbital operators are

$$E_\theta = \frac{1}{2}(3l_z^2 - 2) \quad E_\varepsilon = \frac{1}{4}\sqrt{3}(l_+^2 + l_-^2) \quad T_{xy} = \frac{1}{2}\sqrt{3}(l_x l_y + l_y l_x) \quad (3.2)$$

etc. H_{int} can be written in second quantized form (D, equation (5))

$$H_{\text{int}} = \sum_j K_j r_j (b_j^\dagger + b_j) \quad (j = \theta, \varepsilon; 4, 5, 6; 7, 8, 9) \quad (3.3)$$

where

$$\begin{aligned} r_\theta &= c_1^\dagger c_1 + c_2^\dagger c_2 - 2c_3^\dagger c_3 & r_\varepsilon &= -\sqrt{3}(c_1^\dagger c_1 - c_2^\dagger c_2) \\ r_4 = r_7 &= c_2^\dagger c_3 + c_3^\dagger c_2 & r_5 = r_8 &= c_3^\dagger c_1 + c_1^\dagger c_3 & r_6 = r_9 &= c_1^\dagger c_2 + c_2^\dagger c_1 \\ K_\theta = K_\varepsilon = K_E &= -\sqrt{\hbar} V_E / 2(2\mu\omega_E)^{1/2} & & & & \\ K_4 = K_5 = K_6 = K_T &= (3\hbar)^{1/2} V_T / 2(2\mu\omega_T)^{1/2} & & & & \\ K_7 = K_8 = K_9 = K_2 &= (3\hbar)^{1/2} V_2 / 2(2\mu\omega_2)^{1/2}. & & & & \end{aligned} \quad (3.4)$$

It has been assumed that each phonon mode has mass μ and frequency ω_j , where $\omega_\theta = \omega_\varepsilon = \omega_E$, $\omega_4 = \omega_5 = \omega_6 = \omega_T$ and $\omega_7 = \omega_8 = \omega_9 = \omega_2$. The c_i and c_i^\dagger are second-quantized orbital operators and b_j and b_j^\dagger are the second-quantized phonon operators, defined in the usual way.

Quadratic coupling contributions to the interaction Hamiltonian should also be included. The most important of these is the bi-linear term which involves one E-type and one T_2 -type displacement (Sakamoto 1982). By an appropriate choice of the sign and size of this term, saddle points in the potential energy surface can be converted into minima of orthorhombic symmetry. It has the form (D, equation (7))

$$H_{\text{int}}^{\text{BL}} = K_{\text{BL}} \sum_m \sum_n k_{mn} (b_m^\dagger b_n + b_n^\dagger b_m + b_m^\dagger b_n^\dagger + b_m b_n) r_n \quad \begin{matrix} (m = \theta, \varepsilon \\ n = 4, 5, 6, 7, 8, 9) \end{matrix} \quad (3.5)$$

where K_{BL} is the bilinear coupling constant, and the k_{mn} are defined by

$$\begin{aligned} k_{\theta 4} = k_{\theta 7} &= -\frac{1}{2} & k_{\varepsilon 4} = k_{\varepsilon 7} &= +\frac{1}{2}\sqrt{3} \\ k_{\theta 5} = k_{\theta 8} &= -\frac{1}{2} & k_{\varepsilon 5} = k_{\varepsilon 8} &= -\frac{1}{2}\sqrt{3} \\ k_{\theta 6} = k_{\theta 9} &= +1 & k_{\varepsilon 6} = k_{\varepsilon 9} &= 0. \end{aligned} \quad (3.6)$$

Finally, the vibronic Hamiltonian is

$$H_{\text{vib}} = \sum_j \hbar\omega_j (b_j^\dagger b_j + \frac{1}{2}). \quad (3.7)$$

Hence, the total Hamiltonian is

$$H = H_{\text{int}} + H_{\text{int}}^{\text{BL}} + H_{\text{vib}}. \quad (3.8)$$

In their analysis, BDS and D considered coupling to only one of the t_2 -modes (namely that involving Q_4, Q_5, Q_6). The result of coupling to the other t_2 mode would have been identical provided the labels 4–6 were changed to 7–9, V_T to V_2 and ω_T to ω_2 . It is not clear which of the t_2 modes dominate as calculations based on an idealized point charge model are very unreliable (e.g. Zunger 1986) and the effects of inner elasticity should be included (e.g. Cousins 1989). Unfortunately, the two types of t_2 modes affect the calculations differently so that both possibilities must be considered. (The problem of a T ion coupled to both t_2 modes simultaneously in a regular tetrahedral environment has

not yet been analysed in detail. It is impossible therefore to analyse further the cross-interaction between the two t_2 -modes which occurs via, for example, inner elasticity for the trigonal cluster).

3.2. The additional contribution from the trigonal cluster

For a T-ion coupled to the e- and radial t_2 -modes of the trigonal cluster, the method described in section 2.2 gives an additional contribution to H_{int} of

$$\Delta H_{\text{int}} = \frac{1}{4}\delta\{V_E(Q_\theta E_\theta + Q_\epsilon E_\epsilon) + V_T(Q_4 + Q_5 + Q_6)(T_{yz} + T_{zx} + T_{xy}) - \frac{1}{2}V_2[(Q_\theta - \sqrt{3}Q_\epsilon)T_{yz} + (Q_\theta + \sqrt{3}Q_\epsilon)T_{zx} - 2Q_\theta T_{xy}]\} \quad (3.9)$$

to the ion–lattice Hamiltonian from the charge asymmetry. The contributions arising from the ligand displacement are more complicated but follow an identical pattern to that given by (3.9) with δ replaced by -4σ but with the coupling constants V_E , V_T and V_2 replaced by V'_E , V'_T and V'_2 where

$$V'_L = V_L^{(2)} + \frac{3}{2}V_L^{(4)} \quad (L = E, 2) \quad (3.10)$$

$$V'_T = V_T^{(2)} + \frac{3}{2}V_T^{(4)}$$

Here $V_E^{(2)}$ and $V_E^{(4)}$ etc. are the second- and fourth-order contributions respectively to the coupling constants V_E etc. for a pure tetrahedral cluster (see, for example, Bates 1978). The regular coupling constants are defined by

$$V_M = V_M^{(2)} + V_M^{(4)} \quad (M = E, T, 2). \quad (3.11)$$

In a real trigonal cluster, the total additional contribution to the ion–lattice interaction is the sum of that part due to the change δ in charge, as given in (3.9) plus that part due to the charge σ in position of the ligand as summarized above.

For a T-ion coupled to the transverse t_2 -modes, ΔH_{int} is given by

$$\Delta H_{\text{int}} = \frac{1}{4}\delta\{V_E E_\theta [Q_\theta + \frac{1}{2}(2Q_9 - Q_8 - Q_7)] + V_E E_\epsilon [Q_\epsilon + \frac{1}{2}\sqrt{3}(Q_7 - Q_8)] + V_2(T_{yz} + T_{zx} + T_{xy})(Q_7 + Q_8 + Q_9) - \frac{1}{2}V_2[T_{yz}(Q_\theta - \sqrt{3}Q_\epsilon + 3Q_8 + 3Q_9) + T_{zx}(Q_\theta + \sqrt{3}Q_\epsilon + 3Q_7 + 3Q_9) + T_{xy}(-2Q_\theta + 3Q_8 + 3Q_7)]\} \quad (3.12)$$

for charge asymmetry. As with the radial modes, the corresponding Hamiltonian for the ligand displacement is obtained by replacing δ by -4σ , and V_M by V'_M ($M = E, L, 2$) and the total interaction is again the sum of the two components.

Although the expressions written above for ΔH_{int} appear to have cubic symmetry, trigonal symmetry can be displayed by taking combinations of the Q_j modes such as

$$(Q_4 + Q_5 + Q_6)/\sqrt{3} \quad \text{or} \quad (Q_7 + Q_8 + Q_9)/\sqrt{3}$$

which each have A_1 symmetry in the trigonal group.

Detailed calculations readily show that the above trigonal a_1 -modes have different coupling constants from the two other orthogonal trigonal e-modes derived from Q_4 , Q_5 , Q_6 .

Equations (3.9) and (3.12) can also be written in second quantized form with the result

$$\Delta H_{\text{int}} = \frac{1}{4}\delta \sum_j K_j R_j (b_j^\dagger + b_j) \quad (3.13)$$

for $j = \theta, \varepsilon, 4, 5, 6$ or $j = \theta, \varepsilon, 7, 8, 9$ where

$$\begin{aligned} R_\theta &= r_{\theta x} & R_7 &= (V_E/V_2)(r_{\theta x} - \sqrt{3}r_{\varepsilon y})/2\sqrt{3} \\ R_\varepsilon &= r_{\varepsilon y} & R_8 &= (V_E/V_2)(r_{\theta x} + \sqrt{3}r_{\varepsilon y})/2\sqrt{3} \\ R_4 &= R_5 = R_6 = r_z & R_9 &= -(V_E/V_2)r_{\theta x}/2\sqrt{3} \end{aligned} \quad (3.14)$$

with

$$\begin{aligned} r_{\theta x} &= r_\theta - (\sqrt{3}/2)r_x V_2/V_E & r_{\varepsilon y} &= r_\varepsilon - 3r_y V_2/V_E \\ r_z &= (r_4 + r_5 + r_6) & r_x &= (2r_6 - r_5 - r_4) & r_y &= (r_4 - r_5). \end{aligned} \quad (3.15)$$

As before, it is necessary to add to (3.13) that part due to the change in ligand position. The latter is obtained from (3.13) by replacing δ by -4σ , K_j by K'_j and R_j by R'_j where K'_j and R'_j are obtained directly from (3.4) and (3.14) by replacing V_M with V'_M ($M = E, T, 2$).

We neglect the effect of the trigonal perturbation on the bi-linear term as the changes will be small. The total Hamiltonian allowing for distortions is thus $H' = H_{\text{int}} + \Delta H_{\text{int}} + H_{\text{int}}^{\text{BL}} + H_{\text{vib}}$.

4. The unitary transformation

In the strong coupling limit, the system is frozen into one of the minima in the potential energy surface. To obtain these minima we follow the method of BDS and D and apply a transformation:

$$U' = \exp\left(i \sum_j \alpha'_j P_j\right) \quad (4.1)$$

where α'_j are free parameters for the trigonal cluster and P'_j are the conjugate momenta. Applying the transformation U' to Q_j has the effect of displacing the origin of each oscillator by $-\alpha'_j \hbar$. When the transformation is applied to the total Hamiltonian H' , it gives

$$\tilde{H}' = (U')^{-1} H' U' = \tilde{H}'_1 + \tilde{H}'_2 + \tilde{H}'_3 \quad (4.2)$$

where H'_1 does not contain any coupling to excited phonon states and is given by

$$\begin{aligned} \tilde{H}'_1 &= -r_\theta B_\theta - r_\varepsilon B_\varepsilon + \sqrt{3}(r_4 B_4 + r_5 B_5 + r_6 B_6) \\ &+ \frac{1}{2} \sum_j \hbar \omega_j + \frac{1}{2} \sum_j \mu_j \hbar^2 \omega_j^2 (\alpha'_j)^2 + H_{\text{int}}^{\text{BL}}(\alpha'_j) \end{aligned} \quad (4.3)$$

where $H_{\text{int}}^{\text{BL}}(\alpha'_j)$ is obtained from the original $H_{\text{int}}^{\text{BL}}$ with Q_j replaced by α'_j .

Now H'_2 and H'_3 contain terms that couple the system to excited phonon states, so

$$\tilde{H}'_2 = H_{\text{int}} + \Delta H_{\text{int}} - \sum_j \mu_j \hbar \omega_j^2 Q_j \alpha'_j \quad (4.4)$$

$$\tilde{H}'_3 = \sum_j \hbar \omega_j b_j^\dagger b_j. \quad (4.5)$$

Now

$$B_j = \frac{1}{2} \hbar V_j \beta_j \quad (4.6)$$

where, for the change in ligand charge, the β_j parameters are linear combinations of the α'_j parameters as listed below for the radial t_2 modes:

$$\begin{aligned}\beta_\theta &= (1 + \frac{1}{4}\delta)\alpha'_\theta & \beta_\varepsilon &= (1 + \frac{1}{4}\delta)\alpha'_\varepsilon \\ \beta_4 &= \alpha'_4 + \frac{1}{4}\delta(\alpha'_4 + \alpha'_5 + \alpha'_6) - (\delta V_2/8V_T)(\alpha'_\theta - \sqrt{3}\alpha'_\varepsilon) \\ \beta_5 &= \alpha'_5 + \frac{1}{4}\delta(\alpha'_4 + \alpha'_5 + \alpha'_6) - (\delta V_2/8V_T)(\alpha'_\theta + \sqrt{3}\alpha'_\varepsilon) \\ \beta_6 &= \alpha'_6 + \frac{1}{4}\delta(\alpha'_4 + \alpha'_5 + \alpha'_6) - (\delta V_2/8V_T)(-2\alpha'_\theta).\end{aligned}\quad (4.7)$$

When the system is coupled to transverse t_2 -modes the parameters are

$$\begin{aligned}\beta_\theta &= \alpha'_\theta + (\delta/8)(2\alpha'_\theta - \alpha'_7 - \alpha'_8 + 2\alpha'_9) \\ \beta_\varepsilon &= \alpha'_\varepsilon + (\delta/8)(2\alpha'_\varepsilon + \sqrt{3}\alpha'_7 - \sqrt{3}\alpha'_8) \\ \beta_7 &= \alpha'_7 + (\delta/8)(-\alpha'_\theta + \sqrt{3}\alpha'_\varepsilon + 2\alpha'_7 - \alpha'_8 - \alpha'_9) \\ \beta_8 &= \alpha'_8 + (\delta/8)(-\alpha'_\theta - \sqrt{3}\alpha'_\varepsilon - \alpha'_7 + 2\alpha'_8 - \alpha'_9) \\ \beta_9 &= \alpha'_9 + (\delta/8)(2\alpha'_\theta - \alpha'_7 - \alpha'_8 + 2\alpha'_9).\end{aligned}\quad (4.8)$$

The values of the oscillator displacement parameters α'_j needed to freeze the system into the potential minima in strong coupling are found by minimizing the total energy of the system with respect to the α'_j . As H'_1 is independent of the Q_s , it is a good Hamiltonian for determining approximate eigenstates of H . Also, as the β_j parameters are linear combinations of the α'_j parameters, an alternative procedure is to minimize with respect to the β_j . This means that the minima may be determined by finding those values of β_j (and hence of the α'_j) for which

$$\partial\langle H' \rangle / \partial \beta_j = 0 \quad (j = \theta, \varepsilon, 4, 5, 6 \text{ or } \theta, \varepsilon, 7, 8, 9). \quad (4.9)$$

Equivalent formulae can be derived for the problem of a change in ligand position. However, the derivation is even more complicated as V'_M is in general not equal to V_M . However, in point charge crystal field calculations, the coupling constants are dominated by the second order terms so that V'_M is approximately equal to V_M . With this simplifying assumption, the resulting equations are the same as (4.7)–(4.9) with δ replaced by -4σ . In the following discussions therefore, we take account of both effects by using the trigonal parameter δ' where $\delta' = \delta - 4\sigma$.

5. The potential minima in linear coupling

The analysis follows from that given in BDS, equations (5.1) to (5.6) with A_j replaced by B_j in all expressions. The minima are found with respect to the β_j instead of the α'_j . Again five simultaneous equations are formed namely:

$$\begin{aligned}2C'_\theta + 4X'B_\theta + (p' + 4(X')^2)[\gamma_E(1 - \frac{1}{2}\delta')B_\theta + \frac{1}{8}\delta C''_\theta] &= 0 \\ 2C'_\varepsilon + 4X'B_\varepsilon + (p' + 4(X')^2)[\gamma_E(1 - \frac{1}{2}\delta')B_\varepsilon + \frac{1}{8}\delta C''_\varepsilon] &= 0 \\ 2C'_4 + 4X'B_4 + (p' + 4(X')^2)[\gamma_T C_{T1} + \frac{1}{8}\delta' C'_{T1}] &= 0 \\ 2C'_5 + 4X'B_5 + (p' + 4(X')^2)[\gamma_T C_{T2} + \frac{1}{8}\delta' C'_{T2}] &= 0 \\ 2C'_6 + 4X'B_6 + (p' + 4(X')^2)[\gamma_T C_{T3} + \frac{1}{8}\delta' C'_{T3}] &= 0\end{aligned}\quad (5.1)$$

For coupling to the e- and transverse t_2 -modes, the labels 4, 5 and 6 are replaced by 7, 8 and 9 respectively. Similarly, the parameters γ_T and γ_{ET} are replaced by γ_2 and γ_{E2} respectively where

$$\begin{aligned}
 C'_\theta &= B_\theta^2 - B_\epsilon^2 + \frac{1}{2}(B_4^2 + B_5^2 - 2B_6^2) & C_{T1} &= B_4 - \frac{1}{2}\delta(B_4 + B_5 + B_6) \\
 C'_\epsilon &= -2B_\epsilon B_\theta - \frac{1}{2}\sqrt{3}(B_4^2 - B_5^2) & C_{T2} &= B_5 - \frac{1}{2}\delta(B_4 + B_5 + B_6) \\
 C'_4 &= B_4(B_\theta - \sqrt{3}B_\epsilon) + \sqrt{3}B_5B_6 & C_{T3} &= B_6 - \frac{1}{2}\delta(B_4 + B_5 + B_6) \\
 C'_5 &= B_5(B_\theta + \sqrt{3}B_\epsilon) + \sqrt{3}B_6B_4 & C'_{T1} &= \gamma_{ET}(B_\theta - \sqrt{3}B_\epsilon) \\
 C'_6 &= B_6(-2B_\theta) + \sqrt{3}B_4B_5 & C'_{T2} &= \gamma_{ET}(B_\theta + \sqrt{3}B_\epsilon) \\
 C''_\theta &= \gamma_{ET}(B_4 + B_5 - 2B_6) & C'_{T3} &= \gamma_{ET}(-2B_\theta) \\
 C''_\epsilon &= -\sqrt{3}\gamma_{ET}(B_4 - B_5) \\
 \gamma_L &= 4\mu\omega_L^2/V_L^2 \quad (L = E, T \text{ or } 2) & \gamma_T &= (V_2/V_E)
 \end{aligned} \tag{5.2}$$

where, for coupling to e- and radial t_2 -modes ($M = T$)

$$\gamma_{E2} = \gamma_E(V_E/V_2) + \gamma_2(V_2/V_E).$$

More substantial changes occur in the other terms in (5.1), namely

$$\begin{aligned}
 C_{T1} &= B_7 - \frac{1}{4}\delta'(2B_7 - B_8 - B_9) \\
 C_{T2} &= B_8 - \frac{1}{4}\delta'(2B_8 - B_9 - B_7) \\
 C_{T3} &= B_9 - \frac{1}{4}\delta'(2B_9 - B_7 - B_8).
 \end{aligned} \tag{5.3}$$

The two independent problems, one involving the radial t_2 -modes and the other the transverse t_2 -modes, both display the same form of equations as those found in the original work of BDS and D. They differ only in detail.

In seeking solutions to equations (5.1), it is necessary to make some approximations as the equations are considerably more complicated than the corresponding equations in BDS. We assume that δ is small so that, for each minimum k , the values of the $\alpha_j^{(k)'$ are close to the values $\alpha_j^{(k)}$ for the regular tetrahedral cluster. This implies that the parameters $\beta_j^{(k)}$ only differ from the parameters $\alpha_j^{(k)}$ by small amounts and that the energies of the wells differ by only small amounts from those calculated for the regular tetrahedral cluster. The new parameters are then expanded in a Taylor's series about the value obtained for the regular tetrahedral system retaining only terms which are first order in δ . After much manipulation (Simpson 1989), the values of $\alpha_j^{(k)'$ and the corresponding energies can be obtained, assuming that the effective masses are the same. The coordinates of the 13 minima ($k = 1-13$) are given in terms of the parameters $n_j^{(k)}$ and $\lambda_j^{(k)}$, where $\lambda_j^{(k)} = 0$ in the regular case (compare to equation (11) of D):

$$\alpha_j^{(k)'} = (V_j/\hbar\mu\omega_j)(n_j^{(k)} + \frac{1}{4}\delta'\lambda_j^{(k)}). \tag{5.4}$$

The values of the $n_j^{(k)}$ and the $\lambda_j^{(k)}$ are given in table 1 for the 13 minima for both cases (radial and transverse modes) of a T-ion coupled to one e-mode and one t_2 -mode.

The new energies and original orbital states are given in table 2. In deriving these results, it has been assumed that the frequencies ω_j are comparable in magnitude and that the relative values of the coupling constants K_E and either K_T or K_2 can be chosen to reproduce the tetragonal $[T \otimes e]$, trigonal $[T \otimes t]$ and orthorhombic $[T \otimes (e + t_2)]$

Table 1. The values of $n_i^{(k)}$ and $\lambda_i^{(k)}$. The definitions of the various terms are also given.

Well type	k	Number	$n_1^{(k)}$	$n_2^{(k)}$	$n_3^{(k)}, n_4^{(k)}$	$n_5^{(k)}, n_6^{(k)}$	$n_7^{(k)}, n_8^{(k)}$	$n_9^{(k)}, n_{10}^{(k)}$	$\lambda_1^{(k)}$	$\lambda_2^{(k)}$	$\lambda_3^{(k)}$	$\lambda_4^{(k)}$	$\lambda_5^{(k)}$	$\lambda_6^{(k)}$	$\lambda_7^{(k)}$	$\lambda_8^{(k)}$	$\lambda_9^{(k)}$	
Tetragonal	1	1	0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
	2	$\frac{1}{2}$	$\frac{1}{2}\sqrt{3}$	—	—	—	—	—	$\frac{1}{2}$	$\frac{1}{2}\sqrt{3}$	—	—	—	—	—	—	—	
	3	$\frac{1}{2}$	$-\frac{1}{2}\sqrt{3}$	—	—	—	—	—	$\frac{1}{2}$	$-\frac{1}{2}\sqrt{3}$	—	—	—	—	—	—	—	
Trigonal	4	—	—	$\frac{1}{3}\sqrt{3}$	$\frac{1}{3}\sqrt{3}$	$-\frac{1}{3}\sqrt{3}$	$-\frac{1}{3}\sqrt{3}$	—	5	5	7	2	2	—	—	—	-8	
	5	—	—	$\frac{1}{3}\sqrt{3}$	$-\frac{1}{3}\sqrt{3}$	$\frac{1}{3}\sqrt{3}$	$-\frac{1}{3}\sqrt{3}$	—	5	7	5	2	2	—	—	—	-8	
	6	—	—	$-\frac{1}{3}\sqrt{3}$	$\frac{1}{3}\sqrt{3}$	$-\frac{1}{3}\sqrt{3}$	$\frac{1}{3}\sqrt{3}$	—	7	5	2	2	-8	—	—	—	2	
	7	—	—	$-\frac{1}{3}\sqrt{3}$	$-\frac{1}{3}\sqrt{3}$	$-\frac{1}{3}\sqrt{3}$	$-\frac{1}{3}\sqrt{3}$	—	-9	-9	-9	0	0	—	—	—	0	
	Orthorhombic	8	$\frac{1}{2}$	0	0	0	$-\frac{1}{2}\sqrt{3}$	$\frac{1}{2}\sqrt{3}$	0	b	b	$-\frac{1}{2}\sqrt{3}$	c	c	—	—	—	$-\frac{1}{2}\sqrt{3}d_+$
		9	$\frac{1}{2}$	0	0	0	$\frac{1}{2}\sqrt{3}$	$-\frac{1}{2}\sqrt{3}$	0	1	1	$\frac{1}{2}\sqrt{3}$	$\frac{1}{2}d_+$	$\frac{1}{2}d_+$	—	—	—	$\frac{1}{2}\sqrt{3}d_+$
		10	$-\frac{1}{4}$	$\frac{1}{4}\sqrt{3}$	$-\frac{1}{4}\sqrt{3}$	0	0	$-\frac{1}{4}a_+$	$\frac{1}{4}\sqrt{3}a_+$	$-\frac{1}{4}\sqrt{3}$	b	b	$-\frac{1}{2}\sqrt{3}d_+$	c	—	—	—	c
11		$-\frac{1}{4}$	$\frac{1}{4}\sqrt{3}$	$\frac{1}{4}\sqrt{3}$	0	0	$-\frac{1}{4}a_+$	$\frac{1}{4}\sqrt{3}a_+$	$\frac{1}{4}\sqrt{3}$	1	1	$\frac{1}{2}\sqrt{3}d_+$	$\frac{1}{2}d_+$	—	—	—	c	
12		$-\frac{1}{4}$	$-\frac{1}{4}\sqrt{3}$	0	$-\frac{1}{4}\sqrt{3}$	0	$-\frac{1}{4}a_+$	$-\frac{1}{4}\sqrt{3}a_+$	b	$-\frac{1}{2}\sqrt{3}$	b	c	c	—	—	—	$-\frac{1}{2}\sqrt{3}d_+$	
13		$-\frac{1}{4}$	$-\frac{1}{4}\sqrt{3}$	0	$\frac{1}{4}\sqrt{3}$	0	$-\frac{1}{4}a_+$	$-\frac{1}{4}\sqrt{3}a_+$	1	$\frac{1}{2}\sqrt{3}$	1	$\frac{1}{2}d_+$	$\frac{1}{2}d_+$	—	—	—	$\frac{1}{2}\sqrt{3}d_+$	

$a_+ = \left(1 \pm \sqrt{3} \frac{V_2}{V_E}\right)$	$c = \left[-2E_{E2} + 2\sqrt{3} \left(\frac{2E_E + E_2}{V_E} + \frac{V_2}{V_2}\right)\right] / (E_E - E_2)$	$E_E = \frac{4K_E^2}{\hbar\omega_E}$
$b = \left(4E_{E1} + \sqrt{3} \frac{V_2}{V_E} - E_{E1}\right) / (E_E - E_{E1})$	$d_+ = \left(1 \pm \sqrt{3} \frac{V_2}{V_E}\right)$	$E_{E1} = \frac{4K_1^2}{3\hbar\omega_{E1}}$
	$e = \frac{1}{2}\sqrt{3}$	$E_{E2} = \frac{4K_2^2}{3\hbar\omega_{E2}}$
		$E_{E12} = \frac{K_E^2}{\hbar\omega_E} + \frac{K_2^2}{\hbar\omega_{E2}}$

Table 2. The corrections to the energies of the wells for the impurity cluster and the corresponding original orbital states.

Well type	<i>k</i>	T ₂ -mode	Energy of well	Orbital state
Tetragonal	1-3	—	$-\frac{1}{2}\delta'E_E$	<i>x, y, z</i>
Trigonal	4-6	Radial	$-\frac{1}{6}\delta'E_T$	<i>a, b, c</i>
	7		$-\frac{2}{3}\delta'E_T$	<i>d</i>
Trigonal	4-6	Transverse	$-\frac{2}{3}\delta'E_2$	<i>a, b, c</i>
	7		0	<i>d</i>
Orthorhombic	8, 10, 12	Radial	$-(\frac{1}{2}E_{ET} - AE_E)\delta'$	<i>xy₊, yz₊, zx₊</i>
	9, 11, 13		$-(\frac{1}{2}E_{ET} + AE_E)\delta'$	<i>xy₋, yz₋, zx₋</i>
Orthorhombic	8, 10, 12	Transverse	$-(\frac{1}{2}E_{E2} + AE_E + BE_2)\delta'$	<i>xy₊, yz₊, zx₊</i>
	9, 11, 13		$-(\frac{1}{2}E_{E2} - AE_E - BE_2)\delta'$	<i>xy₋, yz₋, zx₋</i>

The definitions of the ground vibronic states for the original cluster are as follows:

<i>Tetragonal</i>	<i>Trigonal</i>	<i>Orthorhombic</i>
$ z; 0\rangle$	$ a; 0\rangle = \frac{1}{3}\sqrt{3}(x; 0\rangle + y; 0\rangle - z; 0\rangle)$	$ xy_+; 0\rangle = \frac{1}{2}\sqrt{2}(x; 0\rangle + y; 0\rangle)$
$ y; 0\rangle$	$ b; 0\rangle = \frac{1}{3}\sqrt{3}(x; 0\rangle - y; 0\rangle + z; 0\rangle)$	$ xy_-; 0\rangle = \frac{1}{2}\sqrt{2}(x; 0\rangle - y; 0\rangle)$
$ x; 0\rangle$	$ c; 0\rangle = \frac{1}{3}\sqrt{3}(- x; 0\rangle + y; 0\rangle + z; 0\rangle)$	$ yz_+; 0\rangle = \frac{1}{2}\sqrt{2}(y; 0\rangle + z; 0\rangle)$
	$ d; 0\rangle = \frac{1}{3}\sqrt{3}(- x; 0\rangle - y; 0\rangle - z; 0\rangle)$	$ yz_-; 0\rangle = \frac{1}{2}\sqrt{2}(y; 0\rangle - z; 0\rangle)$
		$ zx_+; 0\rangle = \frac{1}{2}\sqrt{2}(z; 0\rangle + x; 0\rangle)$
		$ zx_-; 0\rangle = \frac{1}{2}\sqrt{2}(z; 0\rangle - x; 0\rangle)$

Also
 $A = (\sqrt{3}/2)V_2/V_E$ $B = (\sqrt{3}/2)V_E/V_2$

solutions. (Note that K_{BL} must have a value such that the orthorhombic solutions are true minima; see BDS and Dunn and Bates 1989.)

It can be seen from table 2 that, although the solutions of the impurity complex problem fall into the three coupling regions identified originally in the solution to the regular problem, the orbital degeneracies of the trigonal and orthorhombic systems are lifted (in agreement with the trigonal symmetry) although, to a first approximation, the states are unchanged. Also, although the radial and transverse trigonal systems behave in the same way as far as symmetry is concerned, the solutions differ in detail.

6. Improvements in the eigenstates within a well

For the regular cluster, the transformed states without any phonon excitations are, for well *k*, $|X_r^{(k)}; 0\rangle$ where $X_r^{(k)}$ is the orbital state. The orbital ground state has *r* = 0; the two excited states have *r* = 1 and 2. The ground state of the impurity cluster can be related to that of the regular cluster by the general equation

$$\overline{|X_0^{(k)}; 0\rangle} = |X_0^{(k)}; 0\rangle + \sum_{r=1,2} \gamma_r^{(k)} |X_r^{(k)}; 0\rangle \tag{6.1}$$

where

$$\gamma_r^{(k)} = \langle X_r^{(k)}; 0 | (\tilde{H}'_1 - \tilde{H}_1) | X_0^{(k)}; 0 \rangle / (E_0^{(k)} - E_r^{(k)}) \tag{6.2}$$

As $(\hat{H}'_1 - \hat{H}_1)$ does not contain any phonon operators, the $\gamma_j^{(k)}$ involve the matrix elements of orbital operators only. Now

$$(\hat{H}'_1 - \hat{H}_1) = -\frac{1}{4}\delta' \sum_j k_j r_j E_j \kappa_j^{(k)} \tag{6.3}$$

where r_j is defined in (3.4), $E_j = V_j^2/2\mu\omega_j^2$ and where $\kappa_j^{(k)}$ is defined by $\gamma_j^{(k)} - \alpha_j^{(k)} = \frac{1}{4}\delta' V_j \kappa_j^{(k)} / \hbar\mu\omega_j^2$. Also

$$\begin{aligned} k_j &= 1 && (j = \theta, \epsilon) \\ k_j &= -\sqrt{3} && (j = 4, 5, 6 \text{ or } 7, 8, 9). \end{aligned} \tag{6.4}$$

Detailed calculations show that in both cases

$$\begin{aligned} \gamma_1^{(k)} &= 0 && \text{for all } k \\ \gamma_2^{(k)} &= 0 && \text{for } k = 1, 2, 3, 7, 9, 11, 13. \end{aligned} \tag{6.5}$$

For the radial t_2 -modes,

$$\begin{aligned} \gamma_2^{(k)} &= -\sqrt{2}\delta'/6 && \text{for } k = 4, 5, 6 \\ \gamma_2^{(k)} &= \frac{\sqrt{2}\delta' E_T}{E_E - E_T} \left(\frac{1}{2} \frac{V_2}{V_E} \frac{E_E}{E_T} \right) && \text{for } k = 8, 10, 12 \end{aligned} \tag{6.6}$$

and for the transverse t_2 -modes,

$$\begin{aligned} \gamma_2^{(k)} &= +\sqrt{2}\delta'/12 && \text{for } k = 4, 5, 6 \\ \gamma_2^{(k)} &= \frac{-\sqrt{2}\delta' E_2}{E_E - E_2} \left[\frac{1}{4} - \frac{\sqrt{3}}{24} \left(\frac{V_2}{V_E} \frac{E_E}{E_2} - \frac{V_E}{V_2} \right) \right] && \text{for } k = 8, 10 \text{ and } 12. \end{aligned} \tag{6.7}$$

Thus it can be seen that the perturbation introduced by the impurity ligand affects only three (namely a , b and c) of the four trigonal ground states and also three (namely xy_+ , yz_+ and zx_+) of the six orthorhombic ground states.

7. Discussion

The aim of this paper has been to obtain the solution to the Jahn-Teller problem of an orbital triplet ion coupled strongly to its surroundings consisting of a trigonally distorted tetrahedral cluster. The distortion is due to one of the ligands being displaced along the bond or being a different ion or, as is more likely, to both changes occurring simultaneously. The calculations described are specifically for a change in charge but it is trivial to amend the details of the analysis for the other situation or when both cases occur simultaneously (see section 3.2).

The analysis has concentrated on the ion-lattice coupling which has been limited to the e-modes and to one of the t_2 -modes of the distorted cluster. The coordinates of the minima in the potential energy surface have been found by approximation methods by relating the analysis to that undertaken previously for the regular tetrahedral cluster. The situation which we have modelled is thought to be fairly common particularly as complexes are well known to exist in many semiconductors.

It is clear from table 1 that the minima in the potential energy surface for an ion in a complex are displaced from their position for the regular tetrahedron by varying

amounts. The number of minima is unchanged. In order to estimate the possible magnitudes of these shifts, we take the simple case of a vacancy. The most important effect is the removal of the ligand charge so that $\delta = -1$ in equation (2.1). This in turn would produce a shift of up to 25% in the positions of some of the minima (see equation (5.4) and table 1). However, in many complexes the shift is likely to be much less than this.

Previous attempts, such as those cited in the introduction, have concentrated on the modifications needed in defining the appropriate Q s and ion–lattice coupling constants for the reduced symmetry. Such results are contained within equations (3.8) to (3.12) in the analysis presented here. There do not appear to be any previous calculations which have been reported concerning the accurate positions of the minima in Q -space for the distorted complex. Neither the corrections to the results for anisotropy (Dunn and Bates 1989) nor the effect of the static trigonal field have been discussed in detail here. However, in obtaining the effective Hamiltonian for a real system a full account of these corrections must be included.

The main aim of this work was to provide an accurate base for the modelling and identification of JT impurities located at the centre of a complex. The calculations have been based on the unitary transformation and energy minimization method devised by two of the authors because from it accurate expressions for the minima can be obtained for strongly coupled JT systems. This is needed because, in order to model real systems, it is necessary to derive an accurate effective Hamiltonian to model the physical properties of the ion. This in turn demands that accurate values for the JT reduction factors must be obtained. It is possible to do this by the transformation method because good eigenstates can be obtained particularly for moderately and strongly coupled systems as described in sections 5 and 6 and in tables 1 and 2. The calculation of such reduction factors will form the basis of a second paper (Simpson *et al* 1991) to be published shortly.

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