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# Tunnelling splitting and relaxation in the multimode $T \otimes t_2$ Jahn–Teller system

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**Abstract.** The complex problem of the multimode  $T \otimes t_2$  Jahn–Teller effect for an impurity ion at a cubic site is studied in terms of tunnelling of oscillator states localized in trigonal minima on the lowest sheet of the adiabatic potential energy surface. The low-symmetry trigonal wells are interpreted in terms of the Jahn–Teller polaron. Its similarity to and difference from the traditional polaron in ionic crystals is discussed. The harmonic approximation at the bottom of the wells is used in the infinite-coupling limit. Phonon Green functions are introduced in order to solve the infinite set of linear equations for the corresponding Fourier transforms. From the solutions, an expression is derived for the tunnelling splitting energy gap. It is also shown that the results obtained coincide with the exact calculation reported in the literature in the particular case of no phonon dispersion (when all the frequencies coincide). The effect of relaxation broadening of the tunnelling splitting energy levels is also discussed together with an analysis of the relation between coherent and incoherent tunnelling. It is shown that the tunnelling splitting is not smoothed by the relaxation broadening and therefore is observable if the Jahn–Teller stabilization energy is bigger than  $\sim 1.5\hbar\omega_m$ , where  $\omega_m$  is the Debye frequency of the vibrations of the crystal lattice. Relaxation effects for a Jahn–Teller impurity ion are compared with the so-called ohmic-dissipative effect for tunnelling in a two-level system.

## 1. Introduction

Multimode phenomena in Jahn–Teller (JT) systems, where the electron-vibrational coupling is to an infinitely large number of crystal lattice modes, present long-standing and important problems in the theory of vibronic interactions (for a general review see Bersuker and Polinger 1989). The most interesting applications in the fields of physics and chemistry occur for impurity centres in crystals. Many of the available experimental data demonstrate clearly a resolved vibronic structure in the impurity spectra. Numerous attempts to interpret the vibronic structure of such multimode systems in terms of a one-mode theory have been made but they are very speculative and usually fail. In particular, an impressive demonstration of the essential inapplicability of the one-mode model to the problem of fine vibronic structure in the energy spectrum of multimode JT systems can be found in Köppel *et al* (1984). Thus an improved and more accurate theory is required. Here we focus attention on one important part of the theory, namely that of the tunnelling splitting (Bersuker (1962); some more recent references are given in Polinger *et al* (1993)).

Among the important features of multimode systems introduced by the continuous energy spectrum is relaxation of the tunnelling excitation into the phonon continuum. At

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a temperature  $T = 0$  K, this is due to resonance between one of the excited tunnelling levels and the phonon excited states adjacent to the ground energy level. At  $T \neq 0$ , in addition to the dissipation of the tunnelling energy into the phonon bath, there is so-called phonon-assisted tunnelling via excited phonon states that results in additional inhomogeneous broadening of the tunnelling energy levels. Relaxation is a major problem for tunnelling effects in multimode systems. In particular, in cases when the dephasing effect of the dissipative system is strong, the tunnelling can become incoherent, and then the corresponding broadening of the tunnelling energy levels is comparable to or larger than the tunnelling splitting energy gap itself. As a result, the vibronic structure can be swamped and the tunnelling splitting will not be observed at all. Therefore, in order to establish whether the vibrational relaxation has such a drastic effect and to estimate limits of the effect, it is important to compare the tunnelling splitting energy gap with the relaxation broadening of the tunnelling energy levels for a relatively simple case such as a JT impurity centre.

Generally, the problem of tunnelling in a (pseudo-) spin system linearly coupled to a phonon bath has been given special attention in the last decade because of its importance in the problem of macroscopic quantum tunnelling and macroscopic quantum coherence. (For a general review, see the book of Benderskii *et al* (1994) and the series of papers by Dekker (1991a, b, c, d).) In contrast to the present work, most of these papers consider the so-called pseudo-JT system with two quasi-degenerate singlet terms, or a double-well potential, resulting from linear coupling of the two electronic terms to the phonon bath. Surprisingly, from the point of view of the number of free parameters involved, this two-level model is somewhat more complicated than the case of a cubic-symmetry threefold-degenerate T term linearly coupled to threefold-degenerate  $t_2$ -type vibrations (the so-called  $T \otimes t_2$  case). In addition to the electron-phonon coupling constant, the former includes the bare energy gap separating the singlet electronic energy levels. This is not an additional parameter in the  $T \otimes t_2$  case. (If the energy gap is equal to zero, tunnelling in the two-level case is forbidden by symmetry.) Tunnelling is also possible in the so-called  $E \otimes e$  problem, when two degenerate electronic states are coupled to twofold-degenerate vibrations. However, second-order warping terms with the corresponding second-order vibronic constant must be included, so again there are more parameters. In this sense, the linear  $T_1 \otimes t_2$  system is the simplest non-trivial tunnelling case containing the minimum number of free parameters. Moreover, application of the JT model to an impurity T term adds some specific information about the phonon spectral density. The realistic character of the model provides a unique opportunity for an experimental check on the approximations used. They can then be applied correctly to more complicated systems in the future.

In contrast to the pseudo-JT two-level case and single-mode models, the quantitative multimode JT theory for the  $T \otimes t_2$  systems remains in a poor state of development. The only model of general importance for the tunnelling splitting problem in the multimode case originates from the 'simple approach' of O'Brien (1972). (See also the review by Engelman and Halperin (1978).) Another approach to the problem of tunnelling in JT systems, including multimode cases, was proposed by Polinger (1974) (see also Bersuker and Polinger (1989) and Polinger *et al* (1993)). It is based upon the fact that tunnelling takes place along a stationary path connecting minimum points via a saddle point forming the potential barrier separating the minima. Finally, the paper of Bersuker and Polinger (1981) on tunnelling splitting in the multimode  $E \otimes e$  case should be mentioned in this context. In that work, the warping effect is assumed to be weak compared to the JT stabilization energy but, at the same time, of sufficient strength to allow tunnelling.

In the present paper, an alternative approach is used in which the multimode  $T_1 \otimes t_2$

system is described in terms of vibronic states localized in multi-dimensional minima. It follows that developed originally by Bersuker (1962) for the single-mode case. The tunnelling splitting energy gap is expressed in terms of off-diagonal matrix elements of the original Hamiltonian and the corresponding overlap integral (section 2). In section 3, the adiabatic potential energy surface (APES) of the multimode system is studied in terms of the harmonic approximation and the concept of a JT polaron is introduced and compared to the usual meaning of this term in solid-state physics. The corresponding states are presented as displaced harmonic oscillators localized at the bottom of the minima. These oscillator states are then used in section 4 to express the tunnelling splitting energy gap in terms of the phonon density of the host lattice. The imaginary part of the second-order energy correction mixing the zero-phonon tunnelling state with excited phonon states adjacent to the ground state gives the probability of multi-phonon relaxation (section 5). The implications of these results are discussed in section 6.

## 2. The multimode Hamiltonian of the Jahn–Teller $T \otimes t_2$ system and the tunnelling splitting energy gap

We consider a small-radius ion substituting for a host-lattice ion at an octahedral site in an infinite crystal and take the case in which the impurity ion is in a threefold-degenerate electronic state. To be more specific, we consider the case of a  $T_{1u}$  term. (Other cases of different environments (tetrahedral or cubal) and/or different threefold-degenerate electronic terms ( $T_{1g}$ ,  $T_{2g}$  and  $T_{2u}$ ) are either similar to the case under consideration or require only a minor generalization.) In accordance with perturbation theory for degenerate terms, it is necessary to limit the analysis to the three electronic basis functions  $\psi_x(r) = |x\rangle$ ,  $\psi_y(r) = |y\rangle$  and  $\psi_z(r) = |z\rangle$  of the  $T_{1u}$  term. The Hamiltonian of the system can then be presented as a  $3 \times 3$  matrix such that its elements are operators of the nuclear coordinates. In particular, the electron–phonon interaction involving only linear coupling to the nuclear displacements of the nearest-neighbouring atoms has the matrix form

$$\mathcal{H}_{int} = V_T(Q_\xi T_\xi + Q_\eta T_\eta + Q_\zeta T_\zeta) \quad (2.1)$$

where  $V_T$  is the linear vibronic coupling constant, and the  $Q_\gamma$  and  $T_\gamma$  are  $T_{2g}$ -type symmetrized displacement coordinates of the neighbours and orbital operators respectively, having transformation properties  $\xi \sim yz$ ,  $\eta \sim zx$  and  $\zeta \sim xy$ . More precisely, the orbital operators  $T_\gamma$  can be defined as  $3 \times 3$  matrices acting within the  $\ell = 1$  orbital triplet states  $|x\rangle$ ,  $|y\rangle$  and  $|z\rangle$ , so  $T_\xi = \frac{1}{2}\sqrt{3}(\ell_x \ell_y + \ell_y \ell_x)$  etc. It is important to distinguish the displacement coordinates of the nearest-neighbour atoms  $Q_\gamma$  from the normal modes  $Q_{kj}$  of the host crystal lattice. The former are wave packets of the normal modes which are localized at the first coordination sphere of the impurity ion. They can be expressed in terms of the normal modes as

$$Q_\gamma = \sum_{\kappa} a_\kappa (T_2 \gamma) Q_\kappa. \quad (2.2)$$

The sum over  $\kappa$  ( $=k, j$ ) includes both different phonon wavenumbers  $k$  and different dispersion curve branches  $j$  and  $a_\kappa (T_2 \gamma)$  are the Van Vleck (1940) expansion coefficients. Adding in the Hamiltonian of the crystal lattice vibrations, the Hamiltonian for this  $T_{1u} \otimes t_{2g}$  multimode system can be written in the form

$$\mathcal{H} = \frac{1}{2} \sum_{\kappa} P_\kappa^2 + \frac{1}{2} \sum_{\kappa} \omega_\kappa^2 Q_\kappa^2 + V_T(Q_\xi T_\xi + Q_\eta T_\eta + Q_\zeta T_\zeta) \quad (2.3)$$

where  $P_\kappa$  is the linear momentum conjugate to the normal coordinate  $Q_\kappa$  and  $\omega_\kappa$  is the corresponding phonon frequency. For simplicity, we assume that the vibrational problem of the defect of mass and force constant is automatically included in definitions of  $P_\kappa$ ,  $Q_\kappa$  and  $\omega_\kappa$ .

In the present paper, our attention is focused on the case of strong vibronic coupling. In this case the adiabatic approximation can be used in which the two upper sheets of the three-sheet APES can be neglected. According to the Jahn–Teller theorem, in the lowest APES the high-symmetry nuclear configuration is unstable and several low-symmetry equivalent minima occur. In the particular case of linear  $T_{1u} \otimes t_{2g}$  coupling under consideration, the lowest APES has four absolute minimum points,  $a$ ,  $b$ ,  $c$  and  $d$ . They correspond to four trigonally distorted nuclear configurations of the lattice transforming readily into each other under the relevant symmetry group operations. As will be shown below, in the multimode case the number of minimum points and their symmetry is determined by the number of relevant symmetry operations as in the single-mode case, and is not related to the number of Jahn–Teller-active modes (Bersuker and Polinger 1989).

The depth of the potential wells and the heights and widths of the potential barriers separating the wells depend primarily on the magnitude of the linear coupling constant. In the limiting case of infinitely strong coupling, the impurity system is locked into one of the wells and hence the system retains this distortion for infinite time. The ground state of the system then is fourfold degenerate, with its multiplicity being equal to the number of equivalent minima. The wave functions in a particular well in the ‘crude adiabatic approximation’ (Longuet-Higgins 1961) can be presented as a simple product of an orbital state  $|i\rangle$  ( $i = a, b, c, d$ ) and an oscillator function  $|m\rangle_i$  where  $m$  denotes the phonon occupation number. For the ground state in well  $d$ , for example, we can write the wave function as  $|d, 0\rangle \equiv |d\rangle|0\rangle_d$ , where the orbital state

$$|d\rangle = c_x|x\rangle + c_y|y\rangle + c_z|z\rangle \quad (2.4)$$

is the adiabatic electronic wave function at the minimum point  $d$  of the lower APES with coefficients  $c_r$  ( $r = x, y, z$ ) which are to be determined.

It is convenient here to use the crude adiabatic approximation (Longuet-Higgins 1961) rather than the full adiabatic (or Born–Oppenheimer) approximation. In the latter, the electronic factor in the product wave function is allowed to vary continuously as a function of the vibrational coordinates  $Q$ . This approximation was discussed in detail by O’Brien (1989) and Ham (1990) in relation to the rôle played by the geometric (Berry) phase in the simple  $T \otimes t$  JT system. These authors pointed out that the use of the crude adiabatic approximation instead of the full approximation can lead to erroneous results in some cases (e.g. in calculations of the reduction factors in strong coupling). However, the authors have shown previously (see, e.g., Bates *et al* 1987, Dunn 1988) that their crude adiabatic approximation involving transformations in which the electronic function is fixed by the form that it assumes at the minimum point of the well has been very successful in accounting for many of the properties of strongly coupled JT systems. Whereas this approach only poorly represents the wave function in the barrier regions between the wells, it does take into account fully the spread of the wave functions throughout the potential wells. It also has the considerable advantage that the calculations undertaken can be entirely analytical rather than computational. Thus the same approximation will be used here.

If the vibronic coupling is not infinite but still very strong, the system tunnels through the potential barriers and the ground fourfold-degenerate energy level splits. This splitting is referred to as the ‘tunnelling splitting’ or ‘inversion splitting’ (Bersuker 1962). Only a single tunnelling path is relevant in all cases and this is independent of the number of

modes involved. The latter circumstance determines the discrete character of the energy spectrum associated with the tunnelling splitting. According to the general approach of Bersuker (1962), tunnelling energy levels  $A_{2u}$  and  $T_{1u}$  can be obtained by solving the eigenvalue problem using localized vibronic states which form the non-orthogonal basis set of the infinite-coupling limit. Bersuker and Polinger (1989) and Polinger *et al* (1993) give further discussions on the approximations used in the various approaches. Tunnelling lifts the fourfold degeneracy of the ground state into a  $T_1$  ground state and an  $A_2$  excited state that are linear combinations of the original well states. For example,

$$|A_2\rangle = \frac{1}{2\sqrt{1+3s}}(|a, 0\rangle + |b, 0\rangle + |c, 0\rangle + |d, 0\rangle). \quad (2.5)$$

The energies of the  $T_{1u}$  and  $A_{2u}$  states are given by

$$E(A_2) = \frac{H_{11} + 3H_{12}}{1 + 3s} \quad \text{and} \quad E(T_1) = \frac{H_{11} - H_{12}}{1 - s} \quad (2.6)$$

where, for example,  $H_{12} = \langle c, 0|\mathcal{H}|d, 0\rangle$ ,  $H_{11} = \langle c, 0|\mathcal{H}|c, 0\rangle$  and  $s = \langle c, 0|d, 0\rangle$ . (The values of  $s$ ,  $H_{11}$  and  $H_{12}$  are independent of the actual wells chosen.) The corresponding tunnelling splitting  $\delta$  is thus given by

$$\delta = E(A_2) - E(T_1) = 4 \frac{H_{12} - sH_{11}}{1 + 2s - 3s^2} = 4\Gamma. \quad (2.7)$$

In terms of  $\Gamma$ ,  $E(A_2) \approx H_{11} + 3\Gamma$  and  $E(T_1) \approx H_{11} - \Gamma$ . This result has a clear physical meaning:  $H_{11} = -E_{JT} + \frac{1}{2} \sum_{\kappa} \hbar \tilde{\omega}_{\kappa}$ , so  $E(A_2)$  and  $E(T_1)$  contain the usual three contributions from the adiabatic theory of the separation of the motion. This is the well-known hierarchy of energy gaps. For a typical order of magnitude of  $E_{JT}$ , the energy of the system in the average field of all electrons is  $1000 \text{ cm}^{-1}$  to  $3000 \text{ cm}^{-1}$ . For the energy of the vibrational system in its ground states ( $\frac{1}{2} \sum_{\kappa} \hbar \tilde{\omega}_{\kappa}$ ), a typical order of magnitude is  $100 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$ . The terms  $3\Gamma$  and  $-\Gamma$  in the expressions for  $E(A_2)$  and  $E(T_1)$  represent the energy contributions due to hindered rotations of the system when it passes from one minimum to another through the potential barriers. Their corresponding order of magnitude is expected to be  $1 \text{ cm}^{-1}$  to  $50 \text{ cm}^{-1}$  (see below).

### 3. The Jahn–Teller polaron in the infinite-coupling limit

If the normal coordinates  $\tilde{q}_{\kappa}$  and the corresponding normal frequencies  $\tilde{\omega}_{\kappa}$  in the well  $d$ , for example, were known, the ground oscillator state  $|0\rangle_d$  would be written in the form

$$|0\rangle_d = N \exp \left\{ -\frac{1}{2\hbar} \sum_{\kappa} \tilde{\omega}_{\kappa} [\tilde{q}_{\kappa}^{(d)}]^2 \right\} \quad (3.1)$$

where  $N$  is the normalization constant which may be found from the relation  $N^4 = \prod_{\kappa} [\tilde{\omega}_{\kappa}/(\pi\hbar)]$ . However, as the normal frequencies and normal nuclear coordinates of the distorted JT system are unknown, equation (3.1) must be replaced by

$$|0\rangle_d = N \exp \left\{ -\frac{1}{2\hbar} \sum_{\kappa\lambda} q_{\kappa}^{(d)} \omega_{\kappa\lambda}^{(d)} q_{\lambda}^{(d)} \right\} = N \exp \left\{ -\frac{1}{2\hbar} \mathbf{q}_d^{\dagger} \boldsymbol{\omega}_d \mathbf{q}_d \right\} \quad (3.2)$$

where  $q_{\kappa}^{(d)} = Q_{\kappa} - Q_{\kappa}^{(d)}$  are atomic displacements from the minimum point  $d$  and  $\omega_{\kappa\lambda}^{(d)}$  are second derivatives of the lowest APES at the minimum point  $d$ . Matrix notation is introduced such that  $\mathbf{q}_d$  is an  $n$ -component vector with components  $q_{\kappa}^{(d)}$ , and  $\boldsymbol{\omega}_d$  is an  $n \times n$  matrix with elements  $\omega_{\kappa\lambda}^{(d)}$ . The above definition of  $N$  is then replaced with the relation

$N^4 = \det(\omega_d)/(\pi\hbar)^n$ . In equations (3.1) and (3.2),  $n$  is equal to the number of degrees of freedom (which approaches infinity in this case). The label  $d$  of the particular well in the right-hand side is necessary because the frequency matrix is different for different wells as the principal axes in the  $n$ -dimensional space are oriented differently. However, its determinant is the same for different wells, so  $N$  does not need to have the label  $d$  associated with it.

According to Öpik and Pryce (1957), for an extremum point on the lowest APES we can use the Hellmann–Feynman theorem and write  $(\psi|\partial\mathcal{H}/\partial Q_\kappa|\psi) = 0$ , where the orbital state  $|\psi\rangle$  is expressed in the form (2.4). It follows from this equation that, in terms of the coefficients  $c$ , the equilibrium coordinates of the crystal lattice modes are given by

$$Q_\kappa = -\frac{V_T}{\omega_\kappa^2} [a_\kappa(T_2\xi)\langle T_\xi \rangle + a_\kappa(T_2\eta)\langle T_\eta \rangle + a_\kappa(T_2\zeta)\langle T_\zeta \rangle] \quad (3.3)$$

where  $\langle T_\gamma \rangle = (\psi|T_\gamma|\psi)$ , such that  $\langle T_\xi \rangle = -2c_y c_z$ ,  $\langle T_\eta \rangle = -2c_z c_x$  and  $\langle T_\zeta \rangle = -2c_x c_y$ . Substituting these expressions into the electronic Schrödinger equation of the adiabatic approximation, solutions for  $c_x$ ,  $c_y$  and  $c_z$  can be found.

For the single-mode  $T_1 \otimes t_2$  case, the lowest sheet of the APES is well known to have four trigonal minima, with six orthorhombic saddle points separating them (Öpik and Pryce 1957). For the multimode case, the lowest sheet has qualitatively the same shape but with the important difference that it has an infinite number of dimensions. The values of the  $c$ s are the same in the multimode case as in the single-mode one. These numerical values are well known and may be found in different reviews and papers (e.g. Öpik and Pryce 1957). The coefficients  $\{c_x, c_y, c_z\}$  for the trigonal wells are  $(1, 1, -1)/\sqrt{3}$ ,  $(1, -1, 1)/\sqrt{3}$ ,  $(-1, 1, 1)/\sqrt{3}$  and  $(-1, -1, -1)/\sqrt{3}$  which are labelled  $a$ ,  $b$ ,  $c$  and  $d$  respectively. The corresponding JT energy is given by the same expression as in the single-mode case, namely  $E_{JT} = 2V_T^2/(3\omega_T^2)$ . However, as distinct from the one-mode case where  $\omega_T$  is known at the outset, in the multimode case a value for  $\omega_T$  must be found by solving

$$\omega_T^{-2} = \langle \omega^{-2} \rangle \quad \text{where} \quad \langle \omega^{-m} \rangle = \sum_\kappa a_\kappa^2(T_2\gamma)\omega_\kappa^{-m} = \int \rho_T(\omega)\omega^{-m} d\omega. \quad (3.4)$$

Here the phonon density of the  $T_2$  modes,  $\rho_T(\omega) = \sum_\kappa a_\kappa^2(T_2\gamma)\delta(\omega - \omega_\kappa)$ , is introduced. The nuclear displacements (3.3) and the corresponding lowering of energy by  $E_{JT}$  can be interpreted as resulting from the formation of the so-called Jahn–Teller polaron localized at the impurity centre on one of its four trigonal axes (Polinger 1979, Bersuker and Polinger 1989). In general, it differs from the polaron described in traditional textbooks on solid-state physics in the following two ways. Firstly, the JT polaron has a multi-electron nature indicating that the corresponding impurity electronic wave function (2.5) can be expressed in terms of a Slater determinant (or a linear combination of such determinants); it is not therefore a one-electron state. Secondly, the effects of lattice distortions are due not only to the Coulomb interaction of the impurity electrons with ions of the crystal lattice (the ionic component of chemical bonding) but also to the covalent contribution to the electron–phonon interaction. Indeed, the JT effect is known frequently to be important also in the case of covalent crystals.

The special feature of the strong-coupling case under consideration is that the small-radius impurity electron wave function, localized mostly within the first coordination sphere, produces a polaron of relatively large radius which can extend over several elementary cells. The first coordination sphere is distorted by the low-symmetry impurity electron wave function whilst the second sphere is elastically pushed by the distortion of the first sphere; similarly, the third sphere is pushed by the second sphere, and so on. As the

strength of the vibronic coupling increases, the radius of the resulting JT polaron also increases. It follows from (3.3) that this arises from the factor  $\omega_\kappa^{-2}$  which describes the elastic correlation of local distortions. In the Debye model for acoustic phonons,  $\omega_\kappa \sim k$  and therefore  $\omega_\kappa^{-2} \sim k^{-2}$ . This  $k^{-2}$ -dependence in the reciprocal space of wave vectors corresponds to a relatively smooth  $r^{-1}$ -dependence in real space describing Coulomb-like long-range correlation of nuclear displacements. In the particular case of one impurity electron in an ionic crystal lattice, the JT polaron reduces to the usual polaron which is localized at one of the degenerate impurity orbitals.

There is a further consequence of the JT effect. The low symmetry of the Jahn–Teller polaron produces anisotropy within the trigonal wells, so, at the bottom of each trigonal well, the high-symmetry threefold-degenerate  $T_2$  modes of the cubic lattice each split into a twofold-degenerate E mode and a non-degenerate  $A_1$  mode. Let us consider one of the wells ( $d$ ) in more detail. The curvature of the adiabatic potential energy surface at the bottom of the trigonal minimum is different from the non-JT case. In the harmonic approximation, the curvature can be obtained by a perturbation theory approach with displacements  $q_\kappa^{(d)} = Q_\kappa - Q_\kappa^{(d)}$  taken as small parameters of the theory. The second-order Hamiltonian describing nuclear vibrations at the bottom of the well  $d$  can be written in the form

$$\mathcal{H}_d = -E_{JT} + \frac{1}{2} \sum_\kappa p_\kappa^2 + \frac{1}{2} \sum_\kappa \omega_\kappa^2 q_\kappa^2 - \frac{1}{6} \omega_T^2 (Q_u^{(d)2} + Q_v^{(d)2}) \quad (3.5)$$

where  $Q_u^{(d)}$  and  $Q_v^{(d)}$  are symmetrized nuclear displacements of the nearest neighbours, transforming as the irreducible representation  $E_g$  of the trigonal symmetry group such that

$$Q_u^{(d)} = \frac{1}{\sqrt{2}} (Q_\eta^{(d)} - Q_\zeta^{(d)}) \quad \text{and} \quad Q_v^{(d)} = \frac{1}{\sqrt{6}} (-2Q_\xi^{(d)} + Q_\eta^{(d)} + Q_\zeta^{(d)}) \quad (3.6)$$

where the  $Q_\gamma^{(d)}$  are given by (2.2) but with displaced coordinates  $q_\kappa^{(d)}$  instead of  $Q_\kappa$ . Related forms for the other wells may be derived in a similar way.

The Hamiltonian (3.5) no longer possesses cubic symmetry but instead it has the trigonal symmetry of the well. This causes anisotropy which is described by the last two terms in (3.5), by virtue of the JT effect itself. We note also that these last two terms are off-diagonal in the sense that the  $Q_\kappa^{(d)}$  are no longer normal coordinates. As the perturbation expressed by these terms is composed of displacements of the nearest-neighbour atoms only, the corresponding vibrational problem is local and can be easily solved.

In order to determine the vibrational spectrum of the localized motion at the bottom of the wells, we introduce the phonon Green function

$$D_{\kappa\lambda}^{(d)}(t) = \langle\langle q_\kappa^{(d)} | q_\lambda^{(d)} \rangle\rangle = -\frac{i}{\hbar} \theta(t) \langle [q_\kappa^{(d)}(t), q_\lambda^{(d)}] \rangle \quad (3.7)$$

where the time dependence in  $q_\kappa^{(d)}(t)$  is given within the Heisenberg representation of the Hamiltonian  $\mathcal{H}_d$  such that

$$q_\kappa^{(d)}(t) = \exp(i\mathcal{H}_d t / \hbar) q_\kappa^{(d)} \exp(-i\mathcal{H}_d t / \hbar).$$

Using standard techniques, the infinite system of linear equations for the Fourier transform of the Green function involving the new variable  $\omega$  may be solved. The solution can be expressed in the matrix form

$$\mathbf{D}_d(\omega) = \mathbf{D}_0(\omega) - K(\omega) \mathbf{D}_0(\omega) \mathbf{W}_d \mathbf{D}_0(\omega) \quad (3.8)$$

where the matrices  $\mathbf{D}_d$ ,  $\mathbf{D}_0$  and  $\mathbf{W}_d$  act in the multi-dimensional space of phonon modes. The number of rows and columns is equal to the number of vibrational degrees of freedom,



which approaches infinity in this case.  $\mathbf{D}_0(\omega)$  has matrix elements given by

$$D_{\kappa\lambda}^0(\omega) = \frac{1}{2\pi} \frac{\delta_{\kappa\lambda}}{\omega^2 - \omega_\kappa^2}. \quad (3.9)$$

Also,

$$K(\omega) = \frac{2\pi\omega_T^2}{3 + 2\pi\omega_T^2 G_0(\omega)} \quad (3.10)$$

where  $G_0(\omega)$  is the zeroth-order Green function for the  $T_2$  modes. This can be determined from the general definition

$$G_m(\omega) = \frac{1}{2\pi} \sum_{\kappa} \frac{a_\kappa^2(T_2\gamma)}{\omega_\kappa^m (\omega^2 - \omega_\kappa^2)} \quad (3.11)$$

with  $m = 0$ . The matrix  $\mathbf{W}_d$  is given by

$$\mathbf{W}_d = \mathbf{u}_d \mathbf{u}_d^\dagger + \mathbf{v}_d \mathbf{v}_d^\dagger \quad (3.12)$$

where  $\mathbf{u}_d = (\mathbf{a}_\eta - \mathbf{a}_\zeta)/\sqrt{2}$  and  $\mathbf{v}_d = (-2\mathbf{a}_\xi + \mathbf{a}_\eta + \mathbf{a}_\zeta)/\sqrt{6}$ . Here  $\mathbf{a}_\xi$ ,  $\mathbf{a}_\eta$  and  $\mathbf{a}_\zeta$  are  $n$ -component vectors with elements  $a_\kappa(T_2\xi)$ ,  $a_\kappa(T_2\eta)$  and  $a_\kappa(T_2\zeta)$  respectively. As the four wells are symmetry related, the above equations can also be made to apply to the remaining three wells simply by redefining  $\mathbf{u}_d$  and  $\mathbf{v}_d$ .

#### 4. Calculation of the tunnelling splitting

To find  $N$ , it is necessary to calculate the determinant of the frequency matrix  $\omega_d$ . This can be expressed in terms of the Green function (3.8) in the form

$$\omega_d = -4 \int_0^\infty v^2 \Im[\mathbf{D}_d(v + i\epsilon)] dv \quad (4.1)$$

where  $\Im$  denotes the imaginary part. The argument of  $\mathbf{D}_d$  indicates that the poles are evaluated by replacing  $\omega$  with  $\omega + i\epsilon$  and letting  $\epsilon \rightarrow 0$ . Again, similar results can be obtained for the other wells by appropriate interchange of labels. The determinant  $\det(\omega_d)$  can be written in the form  $\exp\{\ln[\det(\omega_d)]\}$  and the exponent may be evaluated by using the integral expression

$$\ln[\det(\omega_d)] = \int_0^\infty \ln(v) \rho(v) dv \quad (4.2)$$

where  $\rho(v) = -2\{\text{Sp}[\mathbf{D}_d(v + i\epsilon)]\}$  is the phonon density at the bottom of the well  $d$  and  $\mathbf{D}_d$  is given in (3.8). This results in the following expression for  $\det(\omega_d)$ :

$$\det(\omega_d) = \exp\left\{\frac{4}{\pi} \int_0^\infty \ln(v) \Im[K(v + i\epsilon) R_0(v + i\epsilon)] dv\right\} \prod_{\kappa} (\omega_\kappa) \quad (4.3)$$

where  $R_0(v)$  can be obtained from the general definition

$$R_m(v) = \frac{1}{2\pi} \sum_{\kappa} \frac{a_\kappa^2(T_2\gamma)}{\omega_\kappa^m (v^2 - \omega_\kappa^2)^2} \quad (4.4)$$

with  $m = 0$ . This expression has a similar form to that for  $G_m(v)$  introduced in (3.11) except that, in equation (4.4),  $v^2 - \omega_\kappa^2$  is squared.

From the wave functions given by equation (3.1) or (3.2), it is possible to evaluate the matrix elements and overlap integrals of (2.6) and (2.7). The overlap integral is then given by  $s = \langle c, 0|d, 0 \rangle = (c|d)\{0|0\}_{cd} = (-\frac{1}{3})\{0|0\}_{cd}$ . The phonon overlap is given by a

multi-dimensional integral over the components of the vector  $\mathbf{q} = \{\dots, q_\kappa, \dots\}$  in phonon space and is such that

$$\langle 0|0 \rangle_{cd} = N^2 \exp \left[ -\frac{4V_T^2}{3\hbar} \langle \omega^{-3} \rangle \right] \int \exp \left( -\frac{1}{\hbar} \mathbf{q}^\dagger \mathbf{A}_{cd} \mathbf{q} + \mathbf{f}^\dagger \mathbf{q} \right) d\mathbf{q} \quad (4.5)$$

where  $\mathbf{f} = (4V_T/3)(\omega_0)^{-1} \mathbf{a}_\xi$  and  $\omega_0$  is a diagonal matrix with original frequencies  $\omega_\kappa$  on the main diagonal,  $(\omega_0)_{\kappa\lambda} = \omega_\kappa \delta_{\kappa\lambda}$ . The elements of the matrix  $\mathbf{A}_{cd}$  operating in the same multi-dimensional space can be written in the matrix form  $\mathbf{A}_{cd} = \omega_0 + \Omega_{cd}$ , where

$$\Omega_{cd} = 2 \int_0^\infty v^2 \Im \{ K(v + i\epsilon) \mathbf{D}_0(v + i\epsilon) [\mathbf{W}_c + \mathbf{W}_d] \mathbf{D}_0(v + i\epsilon) \} dv \quad (4.6)$$

with  $\mathbf{D}_0(v)$ ,  $K(v)$  and  $\mathbf{W}_d$  given in (3.9), (3.10) and (3.12) respectively.

In contrast to the matrices  $\mathbf{W}_c$  and  $\mathbf{W}_d$ , the matrix  $\Omega_{cd}$  introduced above is not local because of the presence of the Green functions  $\mathbf{D}_0(v)$  in (4.6). The latter matrix describes elastic correlations of the Cartesian displacements of different nuclei in the crystal lattice and therefore, as discussed in section 3, they can include long-range correlations. Physically, the non-local character of the matrix  $\mathbf{A}_{cd}$  is due to the large radius of the JT polarons of which one is along the threefold (trigonal)  $c$ -axis and the other is along another threefold axis, the  $d$ -axis. Therefore, the overlap region of the corresponding wave functions is larger than one elementary cell. Although it is larger than the first coordination sphere, all of the effects under consideration in the present paper take place in a relatively small neighbourhood of the impurity centre. In this sense the effects remain local.

Using multi-dimensional Gaussian quadrature, we find

$$\langle 0|0 \rangle_{cd} = N_{cd} \exp \left\{ -\frac{4V_T^2}{3\hbar} \langle \omega^{-3} \rangle + \frac{4V_T^2}{9\hbar} \boldsymbol{\xi}^\dagger (\omega_0)^{-1} (\mathbf{A}_{cd})^{-1} (\omega_0)^{-1} \boldsymbol{\xi} \right\} \quad (4.7)$$

where  $N_{cd} = [\det(\omega_d)/\det(\mathbf{A}_{cd})]^{1/2}$  and  $\langle \omega^{-3} \rangle$  is  $\langle \omega^{-m} \rangle$  from (3.4) with  $m = 3$ . In contrast to the results above, which are accurate within the approximations used, both the inverse matrix  $(\mathbf{A}_{cd})^{-1}$  in the exponent of (4.7) and  $\det(\mathbf{A}_{cd})$  cannot be calculated exactly because of the non-local character of  $\Omega_{cd}$  discussed above. The matrix  $(\mathbf{A}_{cd})^{-1} = (\omega_0 + \Omega_{cd})^{-1}$  can be presented as a power series of the matrix  $\Omega_{cd}$  but, unfortunately, the matrix elements of this series cannot be expressed in terms of powers of a non-matrix algebraic expression. (We call this effect the JT-induced inter-mode correlation and such a correlation is an important part of the multimode JT effect.) The ascending terms of the series in  $\Omega_{cd}$  are non-multiplicative functionals of the phonon density of states. Therefore the power series cannot be convoluted back into a concise function of the parameters of the problem.

The approximation to be used in the following is to replace the second- and higher-order terms of the series by the corresponding powers of the linear term. In order to calculate  $\det(\mathbf{A}_{cd})$ , the same integral expression as in (3.9) is used once more with the one difference that  $\rho(v)$  in this case denotes the density of eigenvalues of the matrix  $\mathbf{A}_{cd}$  and  $\rho(v) = -2 \Im \{ \text{Sp}[\mathbf{P}(v + i\epsilon)] \}$ , where the matrix Green function  $\mathbf{P}(v) = [2\pi(v\mathbf{I} - \mathbf{A}_{cd})]^{-1}$  has been introduced. Presenting  $\mathbf{P}$  as a power series of the matrix  $\Omega_{cd}$  and replacing the third- and higher-order terms in the corresponding expansion of  $\rho(v)$  by powers of the second-order term we find that

$$N_{cd} = \exp \left\{ \frac{2}{\pi} \int_0^\infty \ln(v) \Im [vK(v + i\epsilon)R_0(v + i\epsilon) - M(v + i\epsilon)] dv \right\} \quad (4.8)$$

where  $K(v)$  is given in (3.10),

$$M(v) \approx U(v) \left[ \frac{U(v)}{6U(v) + W(v)} + \frac{U(v)}{12U(v) + W(v)} + \frac{U(v)}{4U(v) + W(v)} \right] \quad (4.9)$$

and where

$$W(v) \approx 4 \left(1 - \sqrt{\frac{2}{3}}\right)^2 \sum_{\kappa} \frac{\omega_{\kappa}^2 a_{\kappa}^2 (\mathbb{T}_2 \gamma)}{(v - \omega_{\kappa})^3} \quad U(v) \approx \left(1 - \sqrt{\frac{2}{3}}\right) \sum_{\kappa} \frac{\omega_{\kappa} a_{\kappa}^2 (\mathbb{T}_2 \gamma)}{(v - \omega_{\kappa})^2}.$$

Thus we can rewrite (4.7) in the form

$$\{0|0\}_{cd} = N_{cd} \exp \left\{ \frac{-\alpha E_{JT}}{\hbar \omega_T} \right\} \quad (4.10)$$

with

$$\begin{aligned} \alpha &= 2 \langle \omega^{-3} \rangle \omega_T^3 \left(1 - \frac{\langle \omega^{-3} \rangle}{Z}\right) \\ Z &= 3 \langle \omega^{-3} \rangle + 8 \int_0^{\infty} v^2 \Im [K(v + i\epsilon) G_2^2(v + i\epsilon)] dv \end{aligned} \quad (4.11)$$

where  $G_2(v)$  is  $G_m(v)$  from (3.11) with  $m = 2$ .

In order to obtain an expression for  $\delta$  (equation (2.7)), we must evaluate the matrix elements  $H_{11}$  and  $H_{12}$ . As discussed above, the former is readily obtained and is simply equal to  $-E_{JT} + \frac{1}{2} \sum \hbar \omega_{\kappa}$  which, in the strong-coupling limit, can be approximated to  $-E_{JT}$ . The off-diagonal matrix element  $H_{12}$  can be expressed as

$$H_{12} = \left( -E_{JT} + \frac{1}{2} \sum_{\kappa} \hbar \omega_{\kappa} \right) s + \langle c, 0 | \Delta H_d | d, 0 \rangle \quad (4.12)$$

where  $\Delta H_d$  is the difference between the original Hamiltonian (2.3) and the vibrational Hamiltonian (3.5) at the bottom of the well  $d$ . The wave functions in the matrix elements are the same as those given in (2.4), (2.5) and (3.2). A shift transformation  $\mathbf{q} = \mathbf{q}_1 + \mathbf{Q}$  to the point  $\mathbf{q}_1 = \frac{1}{2} \mathbf{A}^{-1} \mathbf{f}$  results in an exponential function in the integrand which is invariant with respect to inversion in  $Q$ -space. As a result of this shift transformation, terms linear in  $Q$  vanish but terms remain which are quadratic in  $Q$ . The non-zero contributions to the off-diagonal matrix elements  $H_{12}$  come from constant terms of the type  $\Lambda = \Delta H_d(\mathbf{q}_1)$ . In the limiting case of strong vibronic coupling, the terms remaining which are quadratic in  $Q$  may be neglected in comparison to contributions from the orbital operator  $\Lambda$ . Thus we have  $H_{12} = H_{11}s - \beta E_{JT}s$  with

$$\beta = \frac{12B - 2}{3B^2} \quad \text{and} \quad B = 3 + 8\omega_T^2 \int_0^{\infty} v^2 \Im [K(v + i\epsilon) G_1(v + i\epsilon) G_2(v + i\epsilon)] dv \quad (4.13)$$

and  $G_m$  as defined by (3.11). On substituting for the various expressions contained in (2.7), we obtain the final result

$$\delta = \frac{4}{3} N_{cd} \beta E_{JT} \exp \left\{ -\frac{\alpha E_{JT}}{\hbar \omega_T} \right\} \quad (4.14)$$

where  $\alpha$  is given in (4.11),  $\beta$  in (4.13) and  $N_{cd}$  in (4.8). It is worthwhile to note that the approximate result (4.14) for  $\delta$  has the same form as the result of the exact calculation (without the approximations introduced above to solve the multimode problem) of Bersuker (Bersuker 1962, Bersuker and Polinger 1989) obtained for the particular case of no phonon dispersion (i.e. when all of the phonon frequencies coincide, so all  $\omega_{\kappa} = \omega_T$ ). In this case, it is a simple matter to evaluate  $\alpha$  and  $\beta$ , and it is found that identical values are obtained.

### 5. Multi-phonon relaxation of the tunnelling energy levels

In the calculations so far, the perturbation approach was limited to the four zeroth-order wave functions,  $|i, 0\rangle = |i\rangle|0\rangle_i$ ,  $i = a, b, c, d$ , and in this respect it remains the same as in the single-mode molecular case. The only modification introduced by the multimode character of the vibronic coupling is in the magnitude of the corresponding matrix elements and, consequently, in the magnitude of the tunnelling splitting energy gap. However, in the case of a JT impurity centre, each of the four degenerate ground states in the wells has a *continuous spectrum* of phonon excited states,  $|i\rangle|n\rangle_i$ ,  $n \neq 0$ , associated with this ground state. The corresponding energy levels, the phonon replicas,  $E_n^{(0)}$ , are the same for different wells. It is important to note that, in the multimode case, as distinct from the JT effect in a molecule, the phonon replicas represent a superposition of an *infinite* number of oscillator-type equidistant energy spectra with phonon frequencies filling continuously several acoustic and optical phonon bands.

Also, it is important that the lower edge of the phonon frequencies of the three acoustic bands equals zero. The corresponding one- and many-phonon excitations of the acoustic phonons can be infinitely small, filling and overlapping the tunnelling splitting energy gap. The first excited tunnelling energy level  $A_2$  and the corresponding tunnelling state (given by (2.5)) is therefore submerged in the continuous spectrum of multi-phonon excitations associated with the ground state. The latter circumstance provides resonant relaxation of the excited vibronic state  $A_2$  and corresponding relaxation broadening of the vibronic singlet term  $A_2$ . The relaxation in this case implies that the vibronic excitation  $4\Gamma$  of the impurity centre, when the vibronic singlet  $A_2$  is populated, can be transformed into one or several phonon quanta of the non-coupled crystal lattice which are spread over the crystal with no chance to return back to the impurity centre.

The next step is to include second-order effects resulting from the admixture of the four ground-state zeroth-order wave functions  $|i\rangle|0\rangle_i$  to the rest of the unperturbed states  $|j\rangle|n\rangle_j$ ,  $n_j \neq 0$ . The corresponding second-order correction for the excited  $A_2$  term is described by

$$E_{A_2}^{(2)} = \sum_{j,n} \frac{|\langle j, n | \mathcal{H} | A_2 \rangle|^2}{E_{A_2}^{(1)} - E_n^{(0)} + i\epsilon} \quad (5.1)$$

where  $j = a, b, c, d$ ;  $n \neq 0$ , and  $i\epsilon$  is added to pass around the point of divergence at  $E_n^{(0)} = E_{A_2}^{(1)}$ . As is well known from perturbation theory for a continuous spectrum, the expression

$$\gamma = -2 \Im E_{A_2}^{(2)} = \frac{2\pi}{\hbar} \sum_{j,n} |\langle j, n | \mathcal{H} | A_2 \rangle|^2 \delta\left(\frac{E_{A_2}^{(1)} - E_n^{(0)}}{\hbar}\right) \quad (5.2)$$

gives the relaxation broadening of the energy level  $A_2$  due to transitions of the  $A_2$  excitation into the bath of oscillator states associated with the ground  $T_2$  term. Here  $\delta[(E_{A_2}^{(1)} - E_n^{(0)})/\hbar]$  is the  $\delta$ -function expressing the Fermi golden rule, and  $n$  ( $\neq 0$ ) is the combined phonon quantum number of the excited oscillator states. Substituting  $\mathcal{H}|A_2\rangle = E_{A_2}^{(1)}|A_2\rangle$  and using (2.7) and (5.2), the above expression for  $\gamma$  can be transformed into

$$\gamma = \frac{\pi}{2\hbar} E_{JT}^2 \sum_{k,l} \sum_j \sum_{n \neq 0} \langle k, 0 | j, n \rangle \langle j, n | l, 0 \rangle \delta\left(\frac{E_0^{(0)} + 4\Gamma - E_n^{(0)}}{\hbar}\right). \quad (5.3)$$

In the first sum, terms with  $k = j$  and  $l = j$  vanish due to orthogonality of the corresponding oscillator states ( $\langle 0|n\rangle = \langle n|0\rangle = 0$ , when  $n \neq 0$ ). The remaining nine terms with  $k \neq j$ ,

$l \neq j$ , are all equal to each other because the wells transform into one another under symmetry operations of the impurity site. Therefore

$$\gamma = \frac{9\pi E_{JT}^2}{2\hbar} \sum_{n \neq 0} |\langle c, 0 | d, n \rangle|^2 \delta \left[ \frac{1}{\hbar} (E_0^{(0)} + 4\Gamma - E_n^{(0)}) \right]. \quad (5.4)$$

The sum over  $n$  in (5.4) is equivalent to the well-known expression

$$F(\Omega) = \sum_n |\langle c, 0 | d, n \rangle|^2 \delta \left[ \Omega - \frac{1}{\hbar} (E_n^{(0)} - E_0^{(0)}) \right] \quad (5.5)$$

for the form factor of the absorption band for an electron transition  $c \rightarrow d$  at  $T = 0$  K when the energy separation of the singlet electronic terms  $c$  and  $d$  equals zero and the frequency  $\Omega$  of the incident light equals  $4\Gamma/\hbar$ . The multi-phonon band for such a singlet–singlet transition in the limiting case of strong linear coupling is often modelled by the well-known bell-shaped function.

Although all of the mathematics necessary to work out (5.4) is well known (e.g. see Perlin and Tsukerblatt 1974), the exact expression for (5.4) as a function of  $\Omega$  in the multimode case cannot be obtained in analytical form. The case under consideration is even more complicated because of the so-called Dushinski effect: the orientations of normal modes at the bottoms of the wells  $c$  and  $d$  are different whilst the corresponding normal frequencies are the same. Since the problem cannot be solved analytically, an approximate representation of the bell-shaped function  $F(\Omega)$  by a Gaussian curve seems reasonable. We shall use the advantage that moments of  $F(\Omega)$  can be calculated exactly without any additional approximations.

The moments of a spectral distribution  $F(\Omega)$  are defined as follows. The zeroth moment (intensity of the band) is

$$\bar{\Omega}^0 = \int_{-\infty}^{\infty} F(\Omega) d\Omega. \quad (5.6)$$

The first moment, the centre of gravity of the band, is defined as

$$\bar{\Omega} = (\bar{\Omega}^0)^{-1} \int_{-\infty}^{\infty} \Omega F(\Omega) d\Omega \quad (5.7)$$

and the second central moment is defined as

$$\sigma_2 = (\bar{\Omega}^0)^{-1} \int_{-\infty}^{\infty} (\Omega - \bar{\Omega})^2 F(\Omega) d\Omega. \quad (5.8)$$

Substituting (5.5) into (5.6) and taking into consideration that (5.4) does not include terms with  $n = 0$ , we find that the zeroth moment equals  $(1/9)(1 - s^2) \approx 1/9$ , where  $s$  is the overlap integral considered in section 3.

Substituting (5.5) into (5.7) and taking into consideration that the integral with the delta function replaces  $\Omega$  by  $(E_n^{(0)} - E_0^{(0)})/\hbar$  and that  $E_n^{(0)}|d, n\rangle = \mathcal{H}_d|d, n\rangle$  and  $E_n^{(0)}|c, n\rangle = \mathcal{H}_c|c, n\rangle$ , the first moment is given by  $(1/\hbar)_c \langle 0 | \mathcal{H}_d - \mathcal{H}_c | 0 \rangle_c$ . Here  $\mathcal{H}_d$  is the harmonic Hamiltonian (3.5) for the well  $d$ ,  $\mathcal{H}_c$  is analogous to  $\mathcal{H}_d$  but for the minimum  $c$ , and  $|0_c\rangle$  is the ground-state oscillator wave function localized at the well  $c$ . It follows that

$$\bar{\Omega} = \frac{64 E_{JT}}{27 \hbar} \approx 2.37 \frac{E_{JT}}{\hbar}. \quad (5.9)$$

Note that the centre of gravity of the bell-shaped distribution is close to the frequency of its maximum,  $\Omega = 3E_{JT}/\hbar$ , which corresponds to the Franck–Condon transition. The difference is due to some asymmetry in  $F(\Omega)$  which makes it slightly different from the Gaussian curve.

On substituting the above results and (5.4) into (5.8), the second moment can be expressed in the equivalent form

$$\sigma_2 = -(\bar{\Omega})^2 + \frac{1}{\hbar^2} \{0_c | (\mathcal{H}_d - \mathcal{H}_c)^2 | 0_c\}. \quad (5.10)$$

This gives

$$\sigma_2 \approx 2.173 \omega_T^2 \langle \omega^{-1} \rangle \frac{E_{JT}}{\hbar} \quad (5.11)$$

where  $\omega_T$  is given in (3.4) and  $\langle \omega^{-1} \rangle = \sum_{\kappa} a_{\kappa}^2 / \omega_{\kappa}$ .

The Gaussian curve with the first three moments given is

$$F(\Omega) = \frac{\bar{\Omega}^0}{\sqrt{2\pi\sigma_2}} \exp \left[ -\frac{(\Omega - \bar{\Omega})^2}{2\sigma_2} \right]. \quad (5.12)$$

Substituting (5.10) and (5.12), and also 1/9 for the zeroth moment into (5.13) we get

$$F(\Omega) \approx 0.03 \sqrt{\frac{\hbar}{\omega_T^2 \langle \omega^{-1} \rangle E_{JT}}} \exp \left[ -\frac{0.23(\hbar\Omega - 2.37E_{JT})^2}{E_{JT} \hbar \omega_T^2 \langle \omega^{-1} \rangle} \right]. \quad (5.13)$$

In our case  $\hbar\Omega = 4\Gamma \ll E_{JT}$ , so  $\hbar\Omega$  in the exponent of (5.14) can be neglected compared with  $2.37E_{JT}$ . Substituting this result into (5.4) and (5.5) finally gives

$$\gamma \approx 0.425 E_{JT} \sqrt{\frac{E_{JT}}{\hbar \omega_T^2 \langle \omega^{-1} \rangle}} \exp \left[ -1.29 \frac{E_{JT}}{\hbar \omega_T^2 \langle \omega^{-1} \rangle} \right]. \quad (5.14)$$

The Gaussian approximation for  $F(\Omega)$  of (5.5) gives an envelope of the actual spectral curve. The latter is known to have complicated vibrational fine structure at  $T = 0$  K which is mostly pronounced in the low-frequency spectral range close to the zero-phonon line. It is just the spectral range, the so-called one-phonon side band, which is important for the present consideration because, in our case,  $\Omega = 4\Gamma/\hbar$  and  $\Gamma$  is very small compared to the average phonon frequency. At the same time, in the strong-coupling case, the frequency dependence of  $F(\Omega)$  has essentially a multi-phonon character and even in the one-phonon spectral region it includes important multi-phonon contributions. Usually in this spectral range, very close to the zero-phonon line, the absorption intensity has a trough. This is due to the well-known circumstance that the phonon density of long-wavelength acoustic vibrations is close to zero. Therefore, at small frequencies the actual magnitude of  $F(\Omega)$  is smaller than the value of the envelope, and the relaxation broadening  $\gamma$  can be an order of magnitude less than the estimated value given by (5.14). In other words, (5.14) can serve as the upper bound for  $\gamma$ .

A lower bound for  $\gamma$  can be obtained by neglecting the multi-phonon contributions in  $F(\Omega)$ . In this case, the vibrational relaxation of the tunnelling states has a one-phonon resonant nature. It is proportional to the phonon density at the resonant frequency  $3\Gamma/\hbar$  and also to the square of the transition matrix element. In this respect, the one-phonon relaxation for the pseudo-spin JT system is very similar to the spin-lattice relaxation in the traditional theory of spin resonance (see, e.g., Stevens 1967). Taking into consideration that  $\Gamma$  is proportional to the overlap integral  $s = (-\frac{1}{3})\{0|0\}_{cd}$ , that the phonon density in the long-wavelength spectral region is proportional to  $\omega^4$  (see (6.1) below) and that the square of the transition matrix element is proportional to  $s^2$ , we can deduce that the resultant value of  $\gamma$  is of the order of  $s^6$ . This means that the lower bound for  $\gamma$  is not critical with respect to the coherent tunnelling in the limiting case of strong vibronic coupling.

## 6. Application using the Debye model

It is interesting to compare the magnitude of the tunnelling splitting energy gap  $4\Gamma$  given by (4.14) with the relaxation broadening  $\gamma$  expressed by (5.14). To estimate  $4\Gamma$  and  $\gamma$ , we consider first the case of the predominant coupling to one acoustic phonon band. For long-wavelength acoustic phonons, we can use the Debye model for which  $\omega_\kappa = c_s k$ , where  $c_s$  is the average speed of sound in the crystal and  $k$  is the phonon wavenumber. The phonon density for the interacting  $T_2$  vibrations

$$\rho(\omega) = \sum_{\kappa} a_{\kappa}^2 (T_2 \gamma) \delta(\omega - \omega_{\kappa})$$

can be approximated by

$$\rho(\omega) = \begin{cases} \frac{5\omega^4}{\omega_m^5} & \text{if } 0 \leq \omega \leq \omega_m \\ 0 & \text{if } \omega < 0 \text{ or } \omega > \omega_m. \end{cases} \quad (6.1)$$

Here  $\omega_m$  is the Debye frequency of the crystal. Substituting (6.1) into (4.8)–(4.11) and into (5.14) we find

$$\delta = 4\Gamma \approx 0.2 E_{JT} \exp \left[ -0.96 \frac{E_{JT}}{\hbar\omega_m} \right] \quad \gamma \approx 0.5 E_{JT} \sqrt{\frac{E_{JT}}{\hbar\omega_m}} \exp \left[ -1.72 \frac{E_{JT}}{\hbar\omega_m} \right]. \quad (6.2)$$

As can be seen from (6.2), both  $\delta$  and  $\gamma$  decrease exponentially with  $E_{JT}/\hbar\omega_m$ . Typical values for  $\hbar\omega_m$  are  $100 \text{ cm}^{-1}$  to  $800 \text{ cm}^{-1}$ . In the strong-coupling case typical values of  $E_{JT}$  are  $1000 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$ . This gives the following estimated intervals for the tunnelling splitting energy gap and the relaxation broadening:  $0 < \delta \lesssim 60 \text{ cm}^{-1}$  and  $0 < \gamma \lesssim 65 \text{ cm}^{-1}$  which correspond to experimental results (Bersuker and Polinger 1989). The tunnelling splitting can be observed only if the energy gap  $\delta$  is bigger than the relaxation broadening  $\gamma$  of the tunnelling splitting energy levels. According to the above results in the Debye model, this can happen if  $E_{JT} > 1.4 \hbar\omega_m$ . In other words, in the limiting case of very strong coupling, the relaxation broadening of the tunnelling energy level decreases faster with  $E_{JT}$  and becomes even smaller than  $\delta$  when the vibronic coupling constant increases and  $\delta$  gets smaller. Most of the tunnelling is coherent in this case and the incoherent contribution may be neglected.

## 7. Discussion and conclusion

In respect of coherence, the JT tunnelling for impurity centres is different compared with the so-called ohmic-dissipative effect of the environment on tunnelling in a two-level system (Chakravarty and Leggett 1984, Leggett *et al* 1987). In this case, when the phonon density  $\rho(\omega)$  is assumed to be proportional to the phonon frequency, the vibrational relaxation is known to quench tunnelling, resulting in localization of the system in one of the minimum configurations (Tanaka and Sakurai 1986). The latter is known to result in a discontinuous change from tunnelling to localized states when the tunnelling splitting energy gap gets smaller. This happens on account of the divergency associated with the exponent in (4.8) in the ohmic-dissipative case. As it is negative, the infinite exponent results in a zero value of the overlap integral  $s$  which implies no tunnelling, and the ensemble of impurity centres in a crystal would represent a spin-glass-like disordered system of differently localized JT polarons. The above-mentioned divergence is due to an overestimate of the contribution of the long-wavelength phonons to the exponent in  $s$  if the phonon density is assumed to

be proportional to the phonon frequency. In the case of a JT impurity centre, the long-wavelength frequency dependence of the phonon density is  $\omega^4$  from (6.1). This determines a natural lower cut-off for phonon excitations with no divergency in the exponent of  $s$ , and the spin-glass-like disordered phase should not appear. (In this consideration we neglect such an alternative mechanism of localization as random strain, always present in any crystal, with its inhomogeneous broadening of vibronic energy levels and the consequent possibility of localization of the impurity centres in the JT wells.)

It looks tempting to consider the case of predominant coupling to one narrow optical phonon band. In this case phonon dispersion can be neglected at the final step and some simple expressions for both  $\delta$  and  $\gamma$  can be obtained. While the former has the clear physical meaning of single-mode (molecular) tunnelling, no resonant relaxation of the tunnelling excitation into the bath of optical phonons is possible, and the above expression for  $\gamma$  is meaningless. This is because  $\delta$  is much less than the smallest of the optical phonon quanta  $\hbar\omega$  and the vibronic singlet energy level  $A_2$  is not submerged into the continuous energy spectrum of phonon excitations in this case. Mathematically, this is because all delta functions in the right-hand side of (5.2) equal zero and therefore  $\gamma = 0$ . However, this does not mean that there is no relaxation broadening at all in this case but that it has a different nature and should be calculated in a different way.

The above theory is applicable for a temperature of 0 K only, as several additional effects arise at finite temperatures. One of these is the anharmonicity in the potential energy surface. If this is included (in the present consideration, anharmonicity is neglected; cf. section 3), the vibrational frequencies become temperature dependent and, in particular, the E modes in the trigonal minima, which are oriented towards the barriers (the tunnelling modes), soften. The corresponding frequency decreases with temperature and this results in a lowering of the effective potential barriers separating the minima. In this way,  $\delta$  appears to be temperature dependent and increases with temperature. With larger  $\delta$ , the vibronic structure may be more readily resolved. However, the increasing broadening transforms the coherent tunnelling into an incoherent one and the tunnelling vibronic structure of the energy levels should disappear at higher temperatures.

It seems reasonable to use and compare different approaches to the problem of tunnelling and relaxation for multimode systems treating the JT-induced intermode correlation in a different way. As a possible alternative we mention the WKB approach in which the tunnelling mode is separated from all of the remaining degrees of freedom with the latter serving as a bath (see, e.g., Polinger *et al* 1993). Preliminary results of the method developed in this paper were published by Polinger *et al* (1997).

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