THE LOW-LYING LEVELS OF THE GR 1 CENTRE IN DIAMOND

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The structure of the satellite lines of the GR 1 band in diamond is analysed. It is shown to arise from a vibronic splitting, as in the model of Lannoo and Stoneham. Sufficient data are available to extract values of the Jahn-Teller energy, the effective phonon frequency and certain higher order terms characterising the Jahn-Teller behaviour.

The GR 1 band in diamond is one of the few tetragonal stresses were measured, both within the E state, giving \( G_E \), and between the A and E states, giving \( G_A \). The ratio of the coefficients, \( G_X/G_E \), is actually of special importance. By combining these data with the theory of O'Brien, one can show the vibronic origin of the GR 1 structure.

1. One or Two Electronic States?

The first stage is to show that both the A and E states derive from a single electronic state coupled to lattice vibrations of E symmetry, and not from two distinct A and E electronic states. The argument is this. If there is a single electronic state coupled to the lattice, then there are strong bounds on the ratio \( G_X/G_E \). This ratio must lie between 1 and \( \frac{1}{2} \), values which satisfactorily bracket the two experimental values of 1.17 and 1.36. However, if two electronic states are involved, \( G_X/G_E \) should be very small, far less than the observed values. The reason here is that the E electronic state will have a Jahn-Teller distortion and the A electronic state will not, so that \( G_A/G_E \) involves a ratio of the stress coupling coefficients. Thus the ratio of the inter- and intra-level coupling coefficient fits nicely with the assumption of vibronic structure associated with an electronic E state and is not consistent with the assumption of two distinct electronic states.

The vibronic model can be tested much more stringently. In doing so, values of parameters characterising the Jahn-Teller coupling can be extracted in a way which avoids many of the assumptions often used.

2. Vibronic Analysis

The basic model involves an electronic E state coupled to modes of E symmetry. As is customary, but not entirely necessary, the E modes are assumed to have a single energy \( \hbar\omega \) only. The coupling leads to a Jahn-Teller distortion which lowers the total potential energy by \( E_{JT} \) and which removes the electronic
degeneracy. However, a further degeneracy remains. If the two independent tetragonal distortions are \( \theta \) and \( \epsilon \), then the potential energy surface depends only on \( \sqrt{\epsilon^2 + \theta^2} \), giving the so-called "Mexican hat" form. This situation has been discussed in detail by Longuet-Higgins et al. A number of interactions can break the extra degeneracy for constant \( \sqrt{\epsilon^2 + \theta^2} \). These extra interactions are the ones which tend to stabilize a tetragonal distortion along one or other of the cubic crystal axes, rather than giving some general orthorhombic distortion. When the extra interactions are weak (as here, where the barrier 28 between two minima is much less than \( E^T \)) one can use an approach analogous to treatments of the hindered rotor to examine the effects on the energy levels. This is the basis of the O'Brien's treatment, and we shall use her analysis together with some extra results of Englman. It will also become clear that \( E^T \gg 28 \) and that \( RX \) is very small, so that the basic assumptions of our model are satisfied.

Given the \( E-A \) separation \( \Delta \) and \( GX/GE \), the work of O'Brien and of Englman allows one to calculate (i) the barrier 28, (ii) the frequency \( \nu_0 \) of the relatively-soft mode associated with reorientation at constant \( \sqrt{\epsilon^2 + \theta^2} \), (iii) the energies of higher vibronic states, and (iv) the energy \( \alpha \equiv (\nu_0)^2/4E^T \). If an estimate of the change in local elastic constants is added (a source of uncertainty), then the value of \( GX \) separately permits an estimate of (v) \( \alpha \equiv (\nu_0)^2/4E^T \). Clearly \( \alpha \) and \( \lambda \) are not independent, but \( GX \) will allow one to estimate \( \lambda \). If a small estimate of \( E^T \) is made and \( RG \) is estimated from this, then the approximation is not necessary. The main uncertainty is in the effects of the defect on the local elastic constants. Here it is assumed that the effects are intermediate between none at all and those estimated in the detailed model calculations of Larkins and Stoneham.

3. Results

The results are summarised in Figure 1. Since there is some experimental uncertainty in \( GX/GE \), the results are given for a range of values. It is simplest to begin with a specific choice, so the Davis-Penchina results will be chosen and used with the Larkins-Stoneham estimate of the change in local elastic constants. The following figures emerge:

(a) There is a large Jahn-Teller energy of 0.63 eV, actually one of the largest recorded;
(b) The phonon energy \( \nu_0 \) is 0.131 eV, close to the value estimated by Lidiard and Stoneham's simple calculations but larger than the Larkins-Stoneham prediction. As one hoped the energy is less than the Raman energy of 0.165 eV and so lies within the range of phonons in the perfect diamond lattice;
(c) The barrier height for motion at constant \( \sqrt{\epsilon^2 + \theta^2} \) is a mere 0.026 eV. This is a factor of about 25 less than \( E^T \), and verifies that the O'Brien theory is appropriate. The energy of the low-frequency mode corresponding to vibrations at constant \( \sqrt{\epsilon^2 + \theta^2} \) is correspondingly low, being about 0.036 eV, and much less than \( \nu_0 \);
(d) The Ham reduction factor \( RX \equiv \exp(-\frac{3}{2}E^T/\nu_0) \), which would be a measure of \( Gx/GE \) if two distinct electronic states were involved, is of order \( 10^{-3} \), far less than the 1.17 observed;
(e) The next higher vibronic levels are about 12 meV higher in energy. This is probably enough to explain why they are not observed, for they will be about 20 meV above the ground state and probably not populated at the temperatures of interest.

Thus, with this specific choice a consistent set of parameters emerges which satisfy very strong constraints. The same is true (as can be seen from the figure) for most of the possible values of choices. An exception occurs if the Clark-Walker value of \( Gx/GE \) is used, when rather large phonon energies result. But even here, modest charges within the experimental errors suffice to give an alternative and acceptable set of parameters.

4. Final comments

Two important features have emerged. First, the vibronic origin of the satellite line to the GR 1 band has been established. Secondly, the Jahn-Teller parameters have been extracted subject to strong constraints and without major assumptions. However, the present results do not identify the Jahn-Teller distortion as tetragonal (\( Q \)) or orthorhombic (\( c \)), nor the A state as \( A_1 \) or \( A_2 \).

It remains to relate the present conclusions to other work. Lowther has recently discussed the intensities of the GR 1 line and of its vibrational sidebands in terms of a very similar model, with encouraging agreement with observation. Like both the experimental analyses and the earlier theory, Lowther's treatment involves vibronic coupling both in the \( E \) state discussed here and the weaker coupling in the \( T \) state excited optically. The main consequences of the present work and of Lowther's analysis has been to confirm the model proposed by Lannoo and Stoneham in giving a vibronic origin to the satellite lines. It is also of interest to note the existence of systems other than the GR 1 band which show analogous structure and whose behaviour can be understood with a similar analysis.

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Fig. 1. Summary of vibronic results for an E electronic state coupled to E modes, with small higher-order terms. The energies are scaled to give the observed splitting \( \Delta \) between the lowest (E) and first excited (A) vibronic states; other parameters are expressed in terms of a ratio of coupling coefficients. The shaded areas encompass values obtained if the local elastic constants are varied from their perfect crystal values (case I) to the softer values suggested by Larkins and Stoneham (case II). Experimental values of \( G_x \) and \( G_e \) from refs. 4 and 5 are indicated.

REFERENCES
7. F.S. HAM, Phys. Rev. A138, 1727 (1965); see also ref.9, and §8.4.4. of ref.1.