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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 observed which appears to be associated with a simple intrinsic defect. The isolated vacancy in one of its charge states appears to be a likely source (for a discussion see refs[1,2]), but precise identification is lacking. The GR 1 band has a zero phonon line associated with it, and it is the structure of this line which is the main concern of this note. The feature of special interest is that there is an additional sharp satellite line whose position and temperature dependence correspond to a state lying about 64 cm^{-1} above the vibronic ground state.

Several systems in diamond show low-lying states[1], others including the 300 cm^{-1} splitting of the so-called c-system, with spin 1, and the 550 cm^{-1} splitting in the so-called d-system. In the present paper the GR 1 system alone is discussed, and the origin of the 64 cm^{-1} structure analysed. There are two obvious types of explanation of the GR 1 structure. One possibility is that the low-lying excited state corresponds to a distinct electronic state and that there is an accidental near-degeneracy. The well-known results of Coulson and Kearsley[3] are often invoked in this case. The second possibility is that the splitting is vibronic in origin, coming from the interaction of the defect electrons with lattice vibrations. This second explanation, proposed some years ago by Lannoo and Stoneham[2], proves to be the case and, in consequence, new information about the GR 1 centre can be derived.

Analysis of the GR 1 system has been made possible by the recent experimental work of Davies and Penchina[4] and of Clark and Walker[5]. These authors have made piezo-spectroscopic measurements which determine the symmetry of the GR 1 centre almost completely and which give the (linear) electron-lattice coupling coefficients among the low-lying states.

The important experimental results are these. First, the main zero phonon transition is from an E state to a T state (T_1 or T_2). The low-lying excited state has A symmetry, so the satellite transition is $A_2 \rightarrow T_1$ or $A_1 \rightarrow T_2$. Secondly, the low-lying A excited state is at energy $\Delta = 64$ cm^{-1} above the ground E state. Thirdly, the stress-coupling coefficients to tetragonal stresses were measured, both within the E state, giving G_E, and between the A and E states, giving G_X. The ratio of the coefficients, G_X/G_E, is actually of special importance. By combining these data with the theory of O'Brien[6] 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 E 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 $\sqrt{2}$, 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_X involves a Ham reduction factor[7]. In consequence, G_X/G_E would be of order $R_X = \exp(-\frac{3}{2} E_{JT}/\hbar\omega)$, a factor which can be estimated and which is far too small to agree with the observed 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 θ and ε, then the potential energy surface depends only on $\sqrt{\varepsilon^2+\theta^2}$, giving the so-called "Mexican hat" form. This situation has been discussed in detail by Longuet-Higgins et al[8]. A number of interactions can break the extra degeneracy for constant $\sqrt{\varepsilon^2+\theta^2}$. 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 2β between two minima is much less than E_{JT}) 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[6] treatment, and we shall use her analysis together with some extra results of Englman[9]. It will also become clear that $E_{JT} >> 2\beta$ and that R_X is very small, so that the basic assumptions of our model are satisfied.

Given the E-A separation Δ and G_X/G_E, the work of O'Brien and of Englman allows one to calculate (i) the barrier 2β, (ii) the frequency $\hbar\Omega$ of the relatively-soft mode associated with reorientation at constant $\sqrt{\varepsilon^2+\theta^2}$, (iii) the energies of higher vibronic states, and (iv) the energy $\alpha \equiv (\hbar\omega)^2/4E_{JT}$. If an estimate of the change in local elastic constants is added (a source of uncertainty), then the value of G_E separately permits an estimate of $(v)\lambda\equiv(\hbar\omega)^2E_{JT}$. Clearly α and λ allow one to estimate $\hbar\omega$ and E_{JT} separately. Normally some guess is used for $\hbar\omega$ in estimating E_{JT}; here this is not necessary, for the parameters are fixed self-consistently. 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[9].

3. Results

The results are summarised in Figure 1. Since there is some experimental uncertainty in G_X/G_E, the results are given for a range of values. It is simplest to begin with a specific choice, so the Davis-Penchina[4] 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 $\hbar\omega$ is 0.131 eV, close to the value estimated by Lidiard and Stoneham's[11] 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 $\sqrt{\varepsilon^2+\theta^2}$ is a mere 0.026 eV. This is a factor of about 25 less than E_{JT}, and verifies that the O'Brien theory is appropriate. The energy of the low-frequency mode corresponding to vibrations at constant $\sqrt{\varepsilon^2+\theta^2}$ is correspondingly low, being about 0.036 eV, and much less than $\hbar\omega$;

(d) The Ham reduction factor $R_X \equiv \exp(-\frac{3}{2}E_{JT}/\hbar\omega)$, which would be a measure of G_X/G_E 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 G_X/G_E 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 (θ) or orthohombic (ε), nor the A state as A_1 or A_2.

It remains to relate the present conclusions to other work. Lowther[12] 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[4,5] and the earlier theory[2], 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[13].

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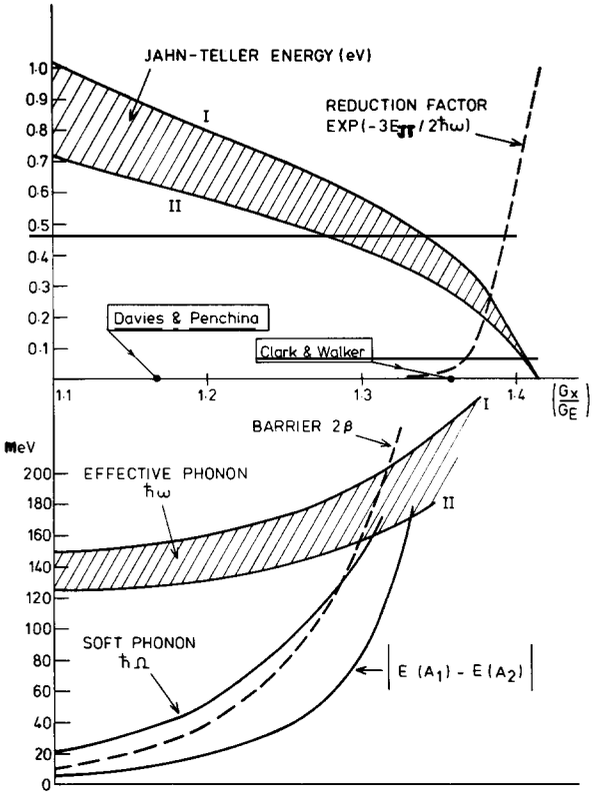

Fig. 1. Summary of vibronic results for an E electronic state coupled to E modes, with small higher-order terms. The energies are scaled to give the observed splitting Δ between the lowest (E) and first excited (A) vibronic states; other parameters are expressed in terms of a ratio of coupling coefficients. 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.

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