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A perturbed vacancy model for the R1 EPR centre in diamond*

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Abstract. Radiation damage produces many defects in diamond that are associated with lattice vacancies and interstitial atoms. EPR has proved to be a valuable tool in the characterization of such defects although often detailed models of the defect structure have not been attempted. It is shown that the R1 defect that is characterized using EPR as a defect having $S = 1$ can be interpreted in a highly strained vacancy model where a spin–orbit effect plays a key role. The inclusion of a Jahn–Teller interaction in the model is also discussed and it is shown that this could hold important significance for the **D** tensor associated with the defect.

1. Introduction

There are many defect complexes present in diamond that are thought to be associated with the lattice vacancy (V). Close to the vacancy, atomic nitrogen has been associated with defect structures as NV (the 1.945 eV optical band), N_2V (H3), N_3V (N3) or N_4V (the B aggregate) with the nitrogen occupying nearest-neighbour locations about the vacant lattice site. Each of these structures gives well defined optical features [1, 2] and often the defect exhibits strong Jahn–Teller interactions [2, 3, 4].

More recently the vacancy has been found to play an important role in the aggregation of the nitrogen [5, 6]. It can profoundly affect resulting defect structures and the rate at which these are formed very often plays a role in the formation of nitrogen aggregates. Nitrogen is an important impurity in diamond and arises in several forms. Defects that have been observed by EPR in diamonds containing single substitutional nitrogen atoms associated with some negative vacancies are a series of complexes W11–14 (the W centres). It has been suggested [7] that such complexes are associated with stressed negatively charged vacancies, perhaps with nitrogen also implicated. Similarly, correlation between a 1.685 eV optical line and the R2 EPR centre has been explained within a stressed neutral vacancy model [8].

Radiation damage gives a multitude of vacancy related centres that have been studied using EPR [9, 10, 11], some of which become rapidly mobile as the temperature changes and as such are highly unstable. The observed correlation between a 1.685 eV zero-phonon line in the optical spectrum of diamond and the R2 EPR centre has established for the first time the existence of a triplet multiplet lying above the ground state of the neutral vacancy. The ground state of the neutral vacancy is ^1E and so the multiplet was identified as $^3T_1$. Using available estimates of the stress interaction of the electronic states of the neutral

* This paper is dedicated to the memory of Professor J H N Loubser.

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lattice vacancy [12, 13], it was deduced that $^3T_1$ lay between 40 meV and 200 meV above ^1E. In this paper we shall now look at another characteristic EPR centre that is produced following radiation damage.

In diamonds containing very little nitrogen, it has been observed that many defects have an effective $S = 1$ [9, 10]. One centre in particular that has $S = 1$ and appears in most irradiated diamonds is the R1 centre. The centre has an extremely large zero-field splitting [9, 14] (almost four times larger than for the W centres) suggesting a high degeneracy in the ground state of the system. The centre has near $\langle 111 \rangle$ symmetry (like the W centres) and a **g** tensor with principal values that are very near two. In this paper we shall propose a model for the R1 centre that involves a stressed neutral vacancy.

2. Perturbed lattice vacancies with spin–orbit interaction

The electronic structure of the neutral vacancy is such that the ground state of the centre is $^1E(a_1^2t_2^2)$ with an excited vibronic state $^1A_2$ lying 8 meV above [12, 13, 15]. The $^3T_1(a_1^2t_2^2)$ is some 40–200 meV above ^1E. Associated with the neutral vacancy is the well known GR1 transition—$^1E(a_1^2t_2^2)$ to $^1T_2(a_1^2t_2^2)$. From group theory the effect of uniaxial stress perturbation, $V_{\langle 111 \rangle}$, along the $\langle 111 \rangle$ direction on the ^1E state is zero. In $^1T_2$ the stress can be represented in terms of a uniaxial stress coefficient C that is given by the following matrix element:

$$C = \langle {}^1T_2\xi | V_{\langle 111 \rangle} | {}^1T_2\zeta \rangle. \tag{1}$$

This can further be expressed in terms of one-electron states as

$$C = \langle {}^1T_2\xi | V_{\langle 111 \rangle} | {}^1T_2\zeta \rangle = \langle t_2\xi | V_{\langle 111 \rangle} | t_2\zeta \rangle K(T_2) \tag{2}$$

where $K(T_2)$ is a Jahn–Teller quenching factor. Similarly in the $^3T_1$ multiplet, group theory gives

$$C' = \langle {}^3T_1X | V_{\langle 111 \rangle} | {}^3T_1Z \rangle = -\langle t_2\xi | V_{\langle 111 \rangle} | t_2\zeta \rangle K'(T_2) \tag{3}$$

and where again the $K'(T_2)$ is a quenching factor. If we assume that $K(T_2) = K'(T_2)$ we see that

$$C = -C'. \tag{4}$$

There is also an isotropic component to the stress affecting the energy of each multiplet. We have used the measured value [12, 13] for the $^1T_2$ level to estimate this interaction in the $^3T_1$ multiplet. So far in the theory of the neutral vacancy the effects of a spin–orbit interaction as represented through an operator of the form

$$H = \sum_i \xi(r_i)(l \cdot s)_i \tag{5}$$

has been neglected. Although small (the spin–orbit constant for carbon is ~ 28 cm^{-1}) this interaction would have important implications for fine measurements on the system as obtained using EPR, for example. Spin–orbit coupling causes the $^3T_1$ state to split into E, T_1, T_2 and A_1 components, E of the $^3T_1$ multiplet interacting with the ^1E multiplet. The energies are given by

$$E(E, T_2) = +\lambda \qquad E(T_1) = -\lambda \qquad E(A_1) = -2\lambda \tag{6}$$

and for the two spin–orbit E states from eigenvalues of the matrix

$$\begin{pmatrix} \Delta + \lambda & \sqrt{2}\lambda' \\ \sqrt{2}\lambda' & 0 \end{pmatrix} \tag{7}$$

where the energy separation is $\Delta = E(^3T_1) - E(^1E)$ and we have taken

$$\lambda = \langle T_2(^3T_1)| \sum_i \xi(r_i)(l \cdot s)_i |T_2(^3T_1)\rangle \tag{8}$$

$$\lambda' = \langle E(^3T_1)| \sum_i \xi(r_i)(l \cdot s)_i |E(^1E)\rangle \tag{9}$$

to be the spin–orbit coupling parameters. Jahn–Teller quenching is quite strong in the ^1E state and so we would not expect $\lambda = \lambda'$. In the argument that follows we shall define this ratio as

$$k = \lambda'/\lambda. \tag{10}$$

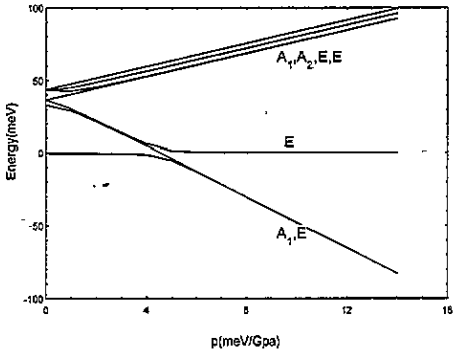

Figure 1. Energy levels of a neutral vacancy with ⟨111⟩ axial perturbation and inclusion of spin–orbit coupling. Values used for the uniaxial stress parameters are $C = -4.25$ meV GPa^{-1} with $\lambda = 28$ cm^{-1}. p is the stress.

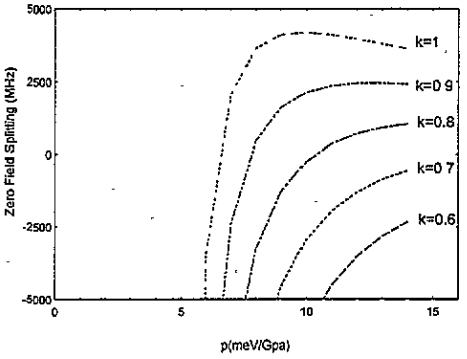

Figure 2. Splitting between the lower A_1 and E levels of figure 1. The measured value as determined using a spin Hamiltonian with $S = 1$ is 3200 MHz.

Proceeding with these definitions it is straightforward to set up interaction matrices involving both spin–orbit and trigonal perturbation and after that obtain from these, energies as a function of an applied stress p. The results are shown in figure 1, where the energy separation between the $^3T_1$ and ^1E states of the unperturbed vacancy has been taken as 40 meV, within the limits suggested in [8]. The A_2 vibronic state lying at 8 meV above ^1E has not been included. The effects of this state are relatively unimportant for ⟨111⟩ distortions especially when spin–orbit effects are included. It can be seen that there is rapid lowering in energy of the A_1 and E trigonal components of the spin–orbit $A_1(^3T_1)$ and $T_1(^3T_1)$ states, so that around a stress of $p = 4$ GPa they almost overlap with ^1E. Beyond $p = 4$ GPa, there is a near degeneracy of the A_1 and E states and collectively the states appear as an effective spin triplet. The very small splitting between these two states can be interpreted as the zero-field component of a spin = 1 Hamiltonian of the form

$$H = D_\perp \left(S_x^2 + S_y^2\right) + D_\parallel S_z^2 \tag{11}$$

such that the splitting, δ, between the degenerate $S_z = \pm 1$ and $S_z = 0$ of this spin Hamiltonian is

$$\delta = D_\parallel - D_\perp. \tag{12}$$

In the case of the R1 centre $\delta \sim 3200$ MHz [14], although the absolute sign of the zero-field splitting tensor has not yet been decided. Within the present model for the R1 centre this means that the order of the A_1 and E spin–orbit states is experimentally unknown.

2.1. Jahn–Teller effects

The Jahn–Teller quenching can greatly affect the size of δ and thus the zero-field splitting tensor **D** because of relative values of λ and λ'. Although a significant amount of information exists for the Jahn–Teller coupling in the ^{1}E state nothing is known about coupling in the $^3T_1$. The nature of the Jahn–Teller coupling in the excited state $^1T_2$ of GR1 is different to that in ^{1}E [4] and so it will be hardly unexpected if this were the case for $^3T_1$. To illustrate this point we have undertaken the calculation with different values of the parameter k (which was defined in equation (10)). These results are shown in figure 2. As shown, quite modest differences have a profound effect on the relative ordering of the lower E and A_1 levels and in turn this will affect the sign of the **D** tensor. An estimate of the stress at the R1 centre is therefore difficult to make without a detailed knowledge of the Jahn–Teller quenching, however as is clear from figure 2 the stress p is greater than about 6 GPa.

3. Conclusion

We have seen quite clearly that a model for the R1 EPR centre of a perturbed neutral vacancy, with the stress at the vacancy estimated to be more than 6 GPa, is consistent with the available experimental data. The source of the stress is not known, but may be a nearby interstitial, as was suggested for the R2 EPR centre [8]. The nature of the observed large zero-field splitting at the R1 defect arises because of a very near degeneracy in lower spin–orbit A_1 and E states. Ordering of these levels is profoundly affected by the Jahn–Teller interactions in the ^{1}E and $^3T_1$ multiplets that in turn will decide the absolute sign of the **D** tensor. Quenching will also affect the magnitude of any orbital contribution to the observed **g** factor. Further EPR work in finding the absolute sign of the **D** tensor of R1 will therefore contribute toward a further understanding of the Jahn–Teller interaction occurring at the neutral vacancy in diamond.

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