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The R2 EPR centre and 1.685 eV absorption line in diamond

Alison Mainwood†, J E Lowther‡ and J A van Wyk‡

† Department of Physics, Kings College, Strand, London, UK

‡ Department of Physics, University of Witwatersrand, Wits 2050, South Africa

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Abstract. The R2 EPR centre and 1.685 eV zero-phonon line seen in the optical absorption spectrum of diamond, have been shown to correlate in intensity and are believed to be associated with the same defect. We propose that the defect responsible is a highly strained vacancy, the origin of strain possibly being a carbon interstitial. Existing stress parameters for the neutral vacancy are shown to predict an energy level structure in good agreement with those proposed for the R2 EPR and 1.685 eV centres. Furthermore, the model identifies the $^3T_1$ level of the unperturbed neutral vacancy (predicted theoretically but not observed previously) as being located up to 200 meV above the ^1E ground state.

1. Introduction

Point defects in diamond have been studied by optical and infra-red spectroscopy and EPR in particular, for many years [1, 2]. Most of them involve the most common impurities, nitrogen and boron.

However, there are many optical and paramagnetic features of diamond that are still not understood, including many created by radiation damage. Depending upon the level of damage, the defects formed may involve either carbon interstitials, vacancies or both [1]. Of these defects, work on type I diamond [2, 3] indicated that vacancies play an important role either in complexes with nitrogen or in unperturbed form.

In the neutral form the vacancy has been associated with the GR1 optical band which is a vibronic band with a strong zero-phonon line at 1.673 eV. It is known to have a ^1E ground state and a $^1T_2$ excited state which derive from the $a_1^2t_2^2$ configuration of the one-electron states a_1 near the top of the valence band and t_2 in the energy gap [4]. There is also a $^3T_1$ state, also derived from the $a_1^2t_2^2$ configuration, which has been predicted theoretically [5] to be close in energy to the ground state, but has not been observed. If it were as close to the ground state as has been predicted, EPR measurements should be able to detect it. Therefore, it must either be located 200 meV or more above the ^1E ground state of the vacancy, when even at high temperatures its population would be too low to detect, or the EPR signal coincides and is confused with other defect signals.

Vacancy-related complexes with nitrogen located adjacent to the vacancy are, in general, reasonably well understood [2]. However another class of vacancy-related defects, which has not been investigated, is those complexes where there is a separation of a few lattice spacings between vacancy and defect. In this case the defect acts to produce a strain field about the vacancy inducing perturbation of the vacancy levels. For example, the self-interstitial in diamond is thought to be in a ⟨100⟩ split configuration which will produce lattice strain and thereby cause compression along a 100 axis [6]. Even for a vacancy with

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an impurity in its immediate vicinity the Coulson–Kearsley model of the isolated vacancy [4] has been shown to have overall validity when understanding the behaviour of the defect [7]. Thus the Coulson–Kearsley model would play an even more important role when attempting to set up a model when the defect is remote from the vacancy.

Characteristic properties of the neutral vacancy (GR1) are its Jahn–Teller behaviour which varies from multiplet to multiplet [2]. Although the ground ^{1}E state of the neutral vacancy does not give rise to any EPR, a centre having a weak zero-phonon line at 1.685 eV has been reported with rather unique EPR behaviour. This centre, labelled R2 in EPR, has a ground state energy scheme in which the first and second energy levels have spin $S = 0$ and a third $S = 1$ [8, 9]. Optical spectroscopy has established that the centre has tetragonal symmetry and Walker [10] has suggested that the centre involves an interstitial complex together with some form of lattice impurity. The similar origin of the the optical 1.685 eV line and the R2 EPR centre is also evident as both signals anneal out at 700 K [11]. Walker [10] showed a strong correlation between the two signals, both being proportional to the electron radiation dose at low doses, with a saturation observed around 10^{22} electrons m^{-2}. Using his dose dependence, and the vacancy production rate [3], there are approximately a twentieth as many R2 centres as GR1 centres in the linear dose regime. Using the methods of [2] and observations that there is a 1 meV broadening of the GR1 zero-phonon line at this dose [12] we can estimate that the average lattice strains are about 2×10^{-5}.

Radiation damage displaces host atoms leaving vacancies, with the displaced interstitial atom possibly remaining a few lattice spacings away without immediately recombining. The strain about the vacancy may be a means by which the vacancy could trap an interstitial reducing the total strain energy of the complex. In this case annealing of the crystal would release the trapped interstitial which then migrates to recombine with the vacancy or some other defect on the crystal. When the lattice is strained by radiation damage, the trapping mechanism would become less effective, and a saturation at high dose would be observed. The 1.685 eV and R2 defects exhibit identical annealing behaviour [10], both annealing out at temperatures at which the vacancies are immobile [3]. Interstitials have been reported to be mobile at lower temperatures [13] and a migration energy of 1.3 eV has been quoted [14]. This is supported by annealing IIa diamonds at 600 °C showing a fast initial loss of the GR1 band due to vacancy–interstitial recombination [3]—completely distinct from the vacancy migration (which has an energy of some 2.3 eV).

Previous identification of EPR centres, in this case O1 and R5, with a vacancy–interstitial complex was somewhat undermined by calculations [15] showing a distance of 0.2 Å between the vacancy and interstitial—a result indicating problems with their calculations rather than a stable defect. We suggest that an interstitial–vacancy complex is unlikely to be stable unless the defects are separated by a few bond lengths.

The location of the 1.685 eV zero-phonon line, close to the 1.673 eV energy of GR1, suggests that the impurity involved in Walker's model may be a lattice vacancy. Owen [16] had considered a vacancy model, but was not aware of the tetragonal nature of the defect and thus an incorrect conclusion was made concerning the origin of the defect levels. Now that stress parameters are available for all the GR1 levels [11, 17] it seems appropriate to re-examine the model of the 1.685 eV centre and attempt to explain the origin of the R2 EPR signal. Although spin-Hamiltonian parameters are available for R2 [18], they are not useful in suggesting a structure for the defect, but are not inconsistent with the perturbed vacancy model proposed here.

Within the model proposed, it is possible that the EPR signal derives from a spin=1 level associated with the interstitial or the vacancy. A split interstitial has been calculated to have a mid-gap doubly degenerate one-electron state which is split with lattice relaxation, by a

Jahn–Teller distortion [19]. However, the energy levels show much too large a splitting to be associated with the R2 properties, especially the spin=1 configuration. In all the theoretical models of the vacancy, on the other hand, a $^3T_1$ level is predicted to be located near the ground state ^1E level, and we suggest that it is this electronic level associated with the stressed vacancy that gives rise to the R2 EPR signal.

2. Perturbed vacancy model

The GR1 system is well known to exhibit a variety of Jahn–Teller properties, most significantly a Jahn–Teller quenching in various stress related properties. The lowest energy transition allowed in such a centre when it is subject to ⟨100⟩ stress is from the $^1A_1$ level of the split ground ^1E state of the vacancy to the $^1B_2$ of the excited split $^1T_2$ [17]. In this case the quenching contribution to the various parameters, B, D and E [11, 17], used to quantify the stress can be estimated from expressions obtained for the various multiplet states involved. Using group theory and taking the ^1E ground and $^1T_2$ as arising within the $a_1^2t_2^2$ configuration of the Coulson–Kearsley model we obtain:

$$B = \langle {}^1E\epsilon \mid V_\epsilon \mid {}^1E\epsilon \rangle = \frac{-2\langle t_2\xi \mid V_\epsilon \mid t_2\xi \rangle}{\sqrt{3}} q \tag{1}$$

and

$$D = \langle {}^1T_2\xi \mid V_\epsilon \mid {}^1T_2\xi \rangle = -\langle t_2\xi \mid V_\epsilon \mid t_2\xi \rangle K(E) \tag{2}$$

where q and $K(E)$ are Jahn–Teller quenching factors which can take the values $0.5 < q < 1$ [20] and $0 < K(E) < 1.0$ [21] and the $\mid t_2\xi \rangle$ are Coulson and Kearsley's one-electron states [4].

Thus we obtain

$$\frac{B}{D} = \frac{2q}{\sqrt{3}K(E)} \tag{3}$$

which using experimental values for B and D [11, 17] gives $K(E) = 0.26$ for the neutral lattice vacancy using $q = 0.5$.

Similarly a ⟨100⟩ stress matrix element for the $^3T_1(a_1^2t_2^2)$ multiplet can be deduced as

$$\langle {}^3T_1\xi \mid V_\epsilon \mid {}^3T_1\xi \rangle = -\langle t_2\xi \mid V_\epsilon \mid t_2\xi \rangle K(E)'. \tag{4}$$

For this state we can specify the ⟨100⟩ stress splitting through parameters B'. We shall assume that there is no quenching in the $^3T_1$ state ($K(E)' = 1.0$), and propose that the $^3T_1$ level of the neutral vacancy is located *above* ^1E and that it is a component of this state that is associated with the $S = 1$ EPR signal. Furthermore, no spin-orbit interaction between the ^1E and $^3T_1$ states is assumed which, as pointed out by Stoneham and Lannoo [22], could lead to a lattice instability. The energy states have then been calculated from expressions that are given in table 2.

In figures 1(*a*) and (*b*) we show the predicted splittings of the ground state structure and table 2 lists in detail numerical values of the ground state splittings and also the calculated zero-phonon energy of the neutral vacancy system when subject to ⟨100⟩ uniaxial stress. As the stress parameters taken from Clark and Walker [11] and Davies and Penchina [17] were derived from experiments in which the maximum uniaxial stress was about 1.5 GPa [17], we would expect significant modification at the much higher stresses envisaged about

Table 1. Energy of the neutral vacancy under (100) stress, p, relative to the low-lying ground state ^{1}E of the neutral vacancy. Δ_2 is the energy difference beween the $^3T_1$ and ^{1}E levels.

State	Energy
$^1T_2\xi, \eta$	$W_T + A_T p - Bp$
$^1T_2\zeta$	$W_T + A_T p + 2Bp$
$^3T_1x, y$	$\Delta_2 + A'_T p - B'p$
^3T_1z	$\Delta_2 + A'_T p + 2B'p$
^1A	$\frac{1}{2}\{W_A + (A_E - 2D + A_A)p +$ $[(W_A + A_A p + A_E p - 2Dp)^2 - 4(W_A + A_A p)(A_E p - 2Dp) + 16E^2p^2]^{0.5}\}$
$^1E\theta$	$\frac{1}{2}\{W_A + (A_E - 2D + A_A)p -$ $[(W_A + A_A p + A_E p - 2Dp)^2 - 4(W_A + A_A p)(A_E p - 2Dp) + 16E^2p^2]^{0.5}\}$
$^1E\epsilon$	$A_E p + 2Dp$

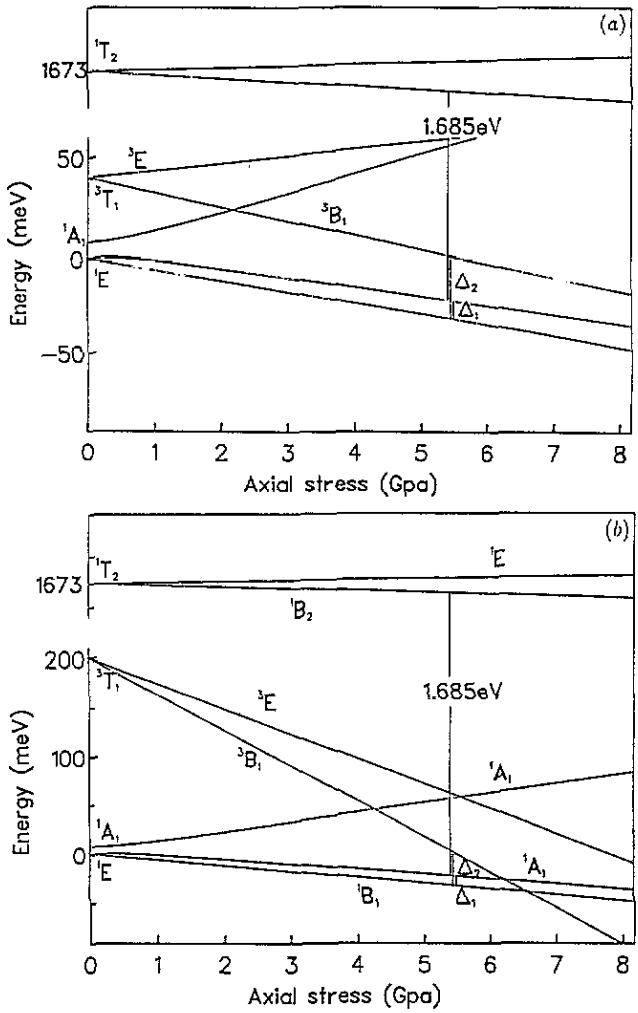

Figure 1. (100) stress on lower-lying states of the neutral vacancy where the $^3T_1$ level at zero stress lies (*a*) 40 meV and (*b*) 200 meV above the ground ^{1}E state.

the vacancy for the model of the R2 EPR centre we postulate here. First we employed the

measured stress parameters from Clark and Walker [11] together with $K(E)'$=1.0 and A_T'=0 for the $^3T_1$ state. This gave the results shown in figure 1(*a*) and labelled (*a*) in table 2. From this we deduce that the $^3T_1$ state of the unperturbed vacancy lies about 40 meV above the ^1E ground state. As can be seen at stresses in the region of 5.5 GPa agreement with experiment of the Δ_1 energy splitting and zero-phonon energy is already quite fair when the $^3T_1$ to ^1E splitting is 40 meV. The zero-phonon energy is sensitive to the magnitude of Jahn–Teller coupling in the $^1T_2$ state, and a small increase in the magnitude of this coupling over that for the perfect vacancy could significantly improve agreement with experiment. Such an increase in quenching could also explain why the 1.685 eV zero-phonon line is always observed to be relatively weak [1].

Table 2. Relative energy level splittings (as defined in figure 1) and zero-phonon energies. (*a*) $^3T_1$ energy of 40 meV (figures 1(*a*) and (*b*) $^3T_1$ energy of 200 meV and $A_T' = -29.2$ meV GPa^{-1} (figure 1(*b*)).

Stress (GPa)	Δ_1 (meV)	Δ_2 (meV) (*a*)	Δ_2 (meV) (*b*)	Zero phonon line (meV)
0.0	0.0	40.0	200.0	1673.0
1.0	4.9	38.7	169.4	1672.0
2.0	6.4	37.4	148.8	1674.6
3.0	7.4	36.1	118.2	1677.4
4.0	8.4	34.8	77.6	1680.6
5.0	9.3	33.5	46.6	1683.7
6.0	10.2	32.1	16.3	1686.8
exp.	6±2 [10]	33±5 [10],37 [16]		1685.

Alternatively, we have used a larger value of 200 meV for the $^3T_1$ state but now with a slightly larger value (but within an acceptable range [11, 17]) of the hydrostatic stress parameter A_T'. The energy level structure so deduced is then shown in figure 1(*b*) and labelled (*b*) in table 2. Of course both Δ_1 and the zero-phonon energy do not depend upon A_T' but we see that again the value of Δ_2 is in agreement with experiment for stresses around 5.5 GPa.

3. Conclusion

We have seen that results of quantitative analysis of the effect of a ⟨100⟩ stress at a neutral lattice vacancy are consistent with known properties of the R2 EPR centre and 1.685 eV optical spectrum. Calculations for two limiting ranges of stress parameters and $^3T_1$ to ^1E splitting were presented, both suggesting that the stress about the vacancy is about 5.5 GPa. Thus we suggest the R2 centre and the 1.685 eV zero-phonon line originate from a severely stressed neutral lattice vacancy. Furthermore, the analysis has placed an estimate of between 40 and 200 meV on the separation between the $^3T_1$ and ground ^1E states of the neutral lattice vacancy.

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