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## Models for the di-nitrogen centres found in brown diamond

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**Abstract.** No new experiments are reported in this paper: the paper comprises a re-interpretation of published EPR data on the various di-nitrogen centres in brown diamond, including the new ENDOR results of our previous paper on the W7 centre. The new evidence about W7 provided by these measurements, particularly the identification of the site symmetry as  $C_1$ , together with other data about the centre, has enabled us to propose a definitive model for W7: a puckered ring structure (comprising four C atoms, one N atom and  $N^+$  ion). This model for the W7 centre is shown to lead, by comparison of the properties of the two centres, to a second neighbour,  $N-C-N^+$ , model for the N1 centre. This model for N1 is shown, in the appendix, to allow new information to be drawn from  $^{13}C$  hyperfine structure in the EPR spectrum of P1, the single substitutional nitrogen. A re-examination of published experimental EPR data of Welbourn for the N4 centre, showing that the two nitrogen atoms are equivalent, is used to propose a collinear  $N-C^+-C-N$  model for N4. The occurrence of only some of the possible orientations of W7 and N4 centres allowed by the symmetry operations of the N4 centre, are explained in terms of a model of the formation of these two centres by plastic deformation.

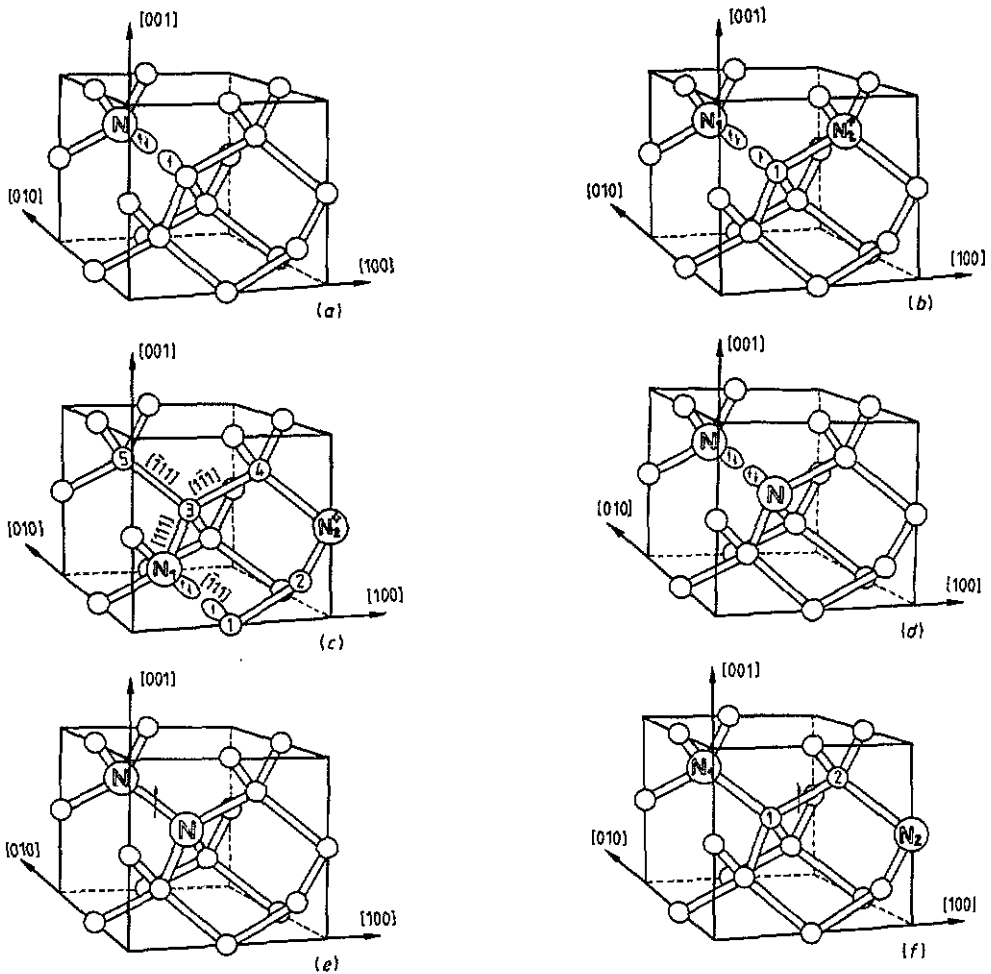
### 1. Introduction

This paper describes no new experiments; it discusses a clarification of the hitherto ambiguously characterized atomic models for several EPR centres in brown diamond, which is facilitated by the results of a previous paper, Newton and Baker (1991), hereafter referred to as I.

A brief review of the properties of brown diamond has been given in the introduction of I. Apart from the EPR centres, which we discuss below, the two main features of importance for this paper are (i) the presence of a large concentration of nitrogen, thought to be incorporated substitutionally, much of it in the form of A centres comprising two nearest-neighbour nitrogen atoms (figure 1(d)); and (ii) the presence of plastic deformation, high dislocation densities and (111) slip planes.

Several EPR centres have been found in brown diamond, some of which are peculiar to brown diamond. Many of the centres exhibit a hyperfine structure which suggests that they involve nitrogen atoms; several of them involve two nitrogen atoms. The N2 centre is found in all brown diamonds, without any reported exception (Scherbakova *et al*

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**Figure 1.** Structures of centres discussed in this paper. Carbon atoms C, are labelled just with the subscript  $i$ . (a) P1 centre, (b)  $N_1-C_1-N_2^+$  ( $N_1$ ), (c) non-coplanar  $N_1-C_1-C_2-N_2^+$  (puckered ring) (W7), (d) A centre, (e) W24 centre,  $N^+-N^-$ , and (f) coplanar  $N_1-C_1^+-C_2-N_2$ .

1975): this centre has been shown to involve nitrogen (Newton and Baker 1989), even though it has no resolved hyperfine structure. Some brown diamonds contain the N1 centre: a di-nitrogen centre in which the two nitrogen atoms are not equivalent (Shcherbakova *et al* 1969, Loubser and van Wyk 1985). The magnitudes of the hyperfine interactions are similar to those of the W7 centre, in which the two nitrogen atoms are not equivalent either. This is discussed in detail in I. The ubiquitous P1 centre (Smith *et al* 1959) is also found in brown diamonds in varying concentrations. Two centres, N4 (Welbourn 1978) and W7 appear to be found only in brown diamond. They are both di-nitrogen centres with  $S = \frac{1}{2}$  and they are not isotropically distributed throughout the possible sites in the diamond. All the W7 defects are found in a single (110) plane, and the observed N4 spectra arise from centres whose hyperfine interactions have axial symmetry about only one of the four possible  $\langle 111 \rangle$  directions. It is shown later in this paper that the two nitrogen atoms of the N4 centre are in fact equivalent, with identical

**Table 1.** Comparison of the spin Hamiltonian parameters and other properties of the four principal di-nitrogen centre in diamond.

Parameter or feature	W7 <sup>a</sup>	N1 <sup>b</sup>	N4	W24 <sup>c</sup>
<i>g</i> -value	2.0023	2.0024	2.002(1)	2.0025(5)
$A_{\parallel}^{(1)}/h$ MHz	121.39	130.0	91.3(3)	154.7(3)
$A_{\perp}^{(1)}/h$ MHz	86.00	90.2	65.6(3)	81.0(3)
Symmetry axis of major N	$\langle 111 \rangle$	$\langle 111 \rangle$	$\langle 111 \rangle$	$\langle 111 \rangle$
$A_1^{(2)}/h$ MHz	13.58	-8.3	$\mathbf{A}^{(2)} = \mathbf{A}^{(1)}$	$\mathbf{A}^{(2)} = \mathbf{A}^{(1)}$
$A_2^{(2)}/h$ MHz	16.01	-7.9		
$A_3^{(2)}/h$ MHz	14.00	-7.9		
Symmetry axis of minor N	low symmetry	$\langle 110 \rangle$		
Spatial anisotropy	$[111]$ and $[\bar{1}\bar{1}\bar{1}]$	none	$[111]$	none
Number of sites	2	12	1	4
Motional averaging	200–600 K	400–1100 K	none	none
Activation energy	0.24 eV	0.4 eV		
Special features				Produced by light <451 nm

<sup>a</sup> Newton and Baker (1991).<sup>b</sup> Loubser and van Wyk (1985).<sup>c</sup> van Wyk and Loubser (1983).**Table 2.** <sup>14</sup>N hyperfine parameters and calculated molecular orbital coefficients for P1, the major nitrogen of W7 and N1 centres, and for the W24 and N4 centres:  $p/s = \beta^2/\alpha^2$ .

Centre	$A_s/h$ (MHz)	$A_p/h$ (MHz)	$\alpha^2$	$\beta^2$	$\eta^2$	$p/s$
P1 <sup>a</sup>	92.22	10.88	0.206	0.794	0.247	3.85
W7	97.79	11.79	0.203	0.797	0.267	3.93
N1	103.5	13.3	0.193	0.807	0.30	4.2
N4	74.2	8.6	0.209	0.791	0.196	3.78
W24	105.6	24.6	0.116	0.884	0.502	7.59

<sup>a</sup> Cook and Whiffen (1966).

hyperfine interactions axially symmetric about the same  $\langle 111 \rangle$  direction. For some of these centres several models have been proposed but it has hitherto been difficult to obtain sufficient evidence for the unambiguous assignment of a definite atomic model.

There have been several examples where the addition of detailed information provided by ENDOR to that provided by EPR and other evidence has led to a definite characterization, e.g. for the single substitutional nitrogen atom, the P1 centre (figure 1(a)), (Cook and Whiffen 1966).

In I it has been shown by ENDOR of the W7 di-nitrogen centre that: (i) it has  $C_1$  symmetry, and (ii) the hyperfine and quadrupole interactions of the major nitrogen are very similar to those of P1 (table 2 and 3 of I). In this paper we wish to use this new ENDOR evidence to propose a model for the W7 centre and, as a consequence, to infer models for other centres; this includes a re-interpretation of EPR of the N4 centre, which enables us to establish a model for that centre.

There appear to be two different types of paramagnetic di-nitrogen defect found in diamond, those like W24 and N4 where the nitrogen hyperfine interactions are equal (these are discussed further in section 6), and those like W7 and N1 where the two nitrogen atoms are inequivalent, with one hyperfine interaction much larger than the other. The spin Hamiltonian for di-nitrogen centres is given in equation (1) in section 4.1 of I. Tables 1 and 2 compare the properties of these centres. Section 4.2 of I explains the significance of the coefficients  $\eta$ ,  $\alpha$  and  $\beta$ , and how they are deduced from the measured hyperfine parameters.

## 2. The W7 centre

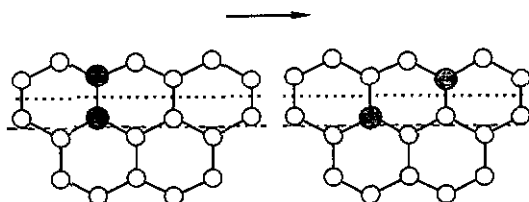
Two models have been previously proposed for the W7 centre: (i)  $N_1-C_1-N_2^+$  (figure 1(b)) by Loubser and Wright (1973), and (ii) non-coplanar  $N_1-C_1-C_2-N_2^+$  (figure 1(c)) by Shcherbakova *et al* (1975). Both models assume that one of the nitrogen atoms, say  $N_2$ , has lost an electron and that the unpaired electron on the other is primarily located in an antibonding orbital, say  $N_1-C_1$ , as in the P1 centre (figure 1(a)). Both models assume that  $N_2$  is in a nearby substitutional site, which is distorted only slightly from  $T_d$  symmetry. The expected quadrupole interaction for  $N_2$  for both models is therefore small, in agreement with our measurements on W7 (section 4.3 of I). For the full set of symmetry operations of the diamond structure, one would expect twelve symmetry-related  $C_v$  sites for  $N_1-C_1-N_2^+$ , and twenty four such symmetry-related  $C_1$  sites for  $N_1-C_1-C_2-N_2^+$ , but only two symmetry-related sites occur in the spectra. This sort of spatial anisotropy has also been found for N4 centres in brown diamonds (see section 6), and it seems to be associated with plastic deformation in these diamonds.

The motional averaging observed above 77 K is attributed by Loubser and Wright to the hopping of the unpaired electron between  $N_1-C_1$  and  $N_2-C_1$  antibonding orbitals in the  $N_1-C_1-N_2^+$  model, with the nitrogen atoms effectively exchanging roles, which would be expected if these two orbitals were lower in energy than any of the other N-C antibonding orbitals.

The model proposed by Shcherbakova *et al* (1975) correlates defect formation with plastic deformation and directly accounts for the spatial anisotropy of the defect, neither of which have been adequately explained in terms of the  $N_1-C_1-N_2^+$  model. They propose that the non-coplanar  $N_1-C_1-C_2-N_2^+$  structure is formed from the non-paramagnetic di-nitrogen A centre (figure 1(d)) by translational slip of dislocations caused by plastic deformation. Figure 2 shows how, for slip in a (111) plane, when a dislocation passes an A centre aligned along [111], one of the nitrogen atoms may be displaced relative to the other by the Burgers vector  $a/\sqrt{2}$  in a  $[1\bar{1}0]$  direction. If the displaced nitrogen is ionized in the slipping process, possibly because strain changes the energy levels of the site sufficiently to make ionization energetically favourable, the resulting structure models the measured properties of the W7 centre reasonably well. Motional averaging was explained by hopping of the unpaired electron from  $N_1-C_1$  to  $N_2-C_2$ .

## 3. The N1 centre

The hyperfine parameters for N1 are similar to those of W7 (table 1). Two models have been proposed that assume that since the major hyperfine interaction is similar to that



**Figure 2.** Projection of the diamond structure onto the  $(11\bar{2})$  plane showing the translational displacement along  $[1\bar{1}0]$  in the  $(111)$  so called shuffle plane shown dotted, proposed by Shcherbakova *et al* (1975), which converts  $N-N$  into a non-coplanar  $N_1-C_1-C_2-N_2$ . Also shown, broken line, is the parallel so-called glide plane in which slip is believed to occur (Hirsch 1985). The arrow shows the Burger's vector.

of the P1 centre; the unpaired electron is primarily located in a  $N-C$  antibonding orbital. This unpaired electron interacts weakly with the second nitrogen. The symmetry of  $A^{(2)}$  has been difficult to determine from EPR, because it is almost isotropic: Shcherbakova *et al* (1969) measured a different symmetry from Loubser and van Wyk (1985) who showed the hyperfine interaction to be axially symmetric about a  $\langle 110 \rangle$  direction. There should be 12 symmetry-related  $C_v$  sites with reflection symmetry in  $(110)$  planes. The four symmetry related  $\langle 111 \rangle$  axes for  $A^{(1)}$  are clearly evident in the spectra illustrated by both authors, but the anisotropy in  $A^{(2)}$ , which would cause the further threefold splitting of each of these spectra, is much smaller than the linewidth illustrated by Loubser and van Wyk (1985). It has been shown by these authors, using motional averaging, that  $A^{(2)}$  has the opposite sign to  $A^{(1)}$ .

Originally, Shcherbakova *et al* (1969) proposed a structure  $C_1-N_1-N_2^+$  for the N1 centre. This site for  $N_2$  was proposed as a result of comparing the magnitude of the  $^{14}N$  hyperfine interaction of the minor nitrogen with that of a  $^{13}C$  atom in the same geometrical position relative to the nitrogen in the P1 centre. However, as we discuss in the appendix, the assignment of  $^{13}C$  sites for P1 centres is not unambiguous. The defect was assumed to be formed by the ionization of a  $N-N$  pair (A centre) in such a way that the unpaired electron went into one of the six  $N-C$  bonds. However, van Wyk and Loubser (1983) have shown that in an ionized A centre (W24) the unpaired electron is in an  $N-N$  antibonding orbital (section 6). An improbable way of obtaining an unpaired electron in an  $N-C$  bond, in view of the expectation that  $N$ -containing centres would tend to be electron donors, is that  $N-N$  could be supposed to pick up an extra electron to form  $N-N-C^-$ . However, any model involving an unpaired electron in an  $N-C$  bond is inconsistent with the motional averaging observed by Loubser and van Wyk (1985), as for this model one would expect motional averaging with the unpaired electron jumping between any of the  $N-C$  bonds, which is not found experimentally.

Later, Shcherbakova *et al* (1972) proposed another model in which a vacancy was trapped by a  $N-N$  pair but the interpretation of the experimental evidence to justify such a structure has never been published.

Loubser and van Wyk (1985) proposed the same non-coplanar  $N_1-C_1-C_2-N_2^+$  structure for N1 as was proposed by Shcherbakova for W7 (see section 2).

#### 4. Models for the W7 and N1 centres

Although it does not appear to have been previously proposed, it is evident that the

$N_1-C_1-N_2^+$  model (discussed above in connection with W7 in section 2) is also consistent with the measured  $^{14}\text{N}$  hyperfine interaction of the N1 defect. An isotropic distribution of such defects correctly predicts the observed motional averaging of N1 if hopping of the unpaired electron between only the  $N_1-C_1$  and  $N_2-C_2$  antibonding orbitals is allowed.

Hence, it appears that the two structures  $N_1-C_1-N_2^+$  and  $N_1-C_1-C_2-N_2^+$  could be applicable to either W7 or N1 centres, so we need a satisfactory way to differentiate between them. To do this we consider both the evidence of other workers reviewed above, and the new information provided by our measurements discussed in I.

Since the hyperfine interaction with  $N_2$  in both models is assumed to be small, spin polarization must be considered. The only probable orbital on the second nitrogen is  $sp^n$ , which would give rise to a hyperfine interaction of the same sign as  $A^{(1)}$ . Hence, we believe that  $A^{(2)}$  in N1, which is of the opposite sign to  $A^{(1)}$ , must be predominantly indirect in origin. If we assume that the unpaired electron in the main  $N_1-C_1$  antibonding orbital is localized on the carbon atom, with a lone pair on  $N_1$ , we would expect spin polarization to contribute negatively to the hyperfine interaction of nitrogen  $N_2$  in  $N_1-C_1-N_2^+$  and positively for nitrogen  $N_2$  in  $N_1-C_1-C_2-N_2^+$ .

We expect the departures of the hyperfine and quadrupole interactions for the major nitrogen of  $N_1-C_1-C_2-N_2^+$  from those of P1 to be smaller than for  $N_1-C_1-N_2^+$  because for the former structure all nearest and next-nearest neighbours of  $N_1$  are carbon atoms. One would expect the quadrupole interaction with  $N_2$  to be greater for  $N_1-C_1-N_2^+$  than for  $N_1-C_1-C_2-N_2^+$  because in the former the nitrogen atom is closer to the  $N_1-C_1$  bond, which is distorted by the additional electron. The quadrupole interaction in N1 has not been measured but the very small  $P^{(2)}$  in W7 favours the assignment of  $N_1-C_1-C_2-N_2^+$  to this centre. However, the most significant new piece of evidence which favours the  $N_1-C_1-C_2-N_2^+$  model for W7 is the low symmetry of the  $A^{(2)}$  and  $P^{(2)}$  matrices, which would be expected as the site has no symmetry, whereas they would not be expected for the  $N_1-C_1-N_2^+$  site as it would have reflection symmetry in (110).

In fact, the  $N_1-C_1-N_2^+$  structure seems to account satisfactorily for all of the properties of N1 including the [110] symmetry of the site.

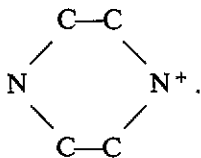
One feature which might be thought to favour  $N_1-C_1-N_2^+$  as the model of W7 is the larger magnitude of  $A^{(2)}$  compared with N1, because larger magnitude might be thought to indicate closer proximity to the unpaired electron in the  $N_1-C_1$  antibonding orbital. However, a larger magnitude is not necessarily evidence of greater localization, since we do not know the magnitudes of direct and indirect contributions to the interaction. As we believe that these contributions will have the same sign on  $N_2$  in  $N_1-C_1-C_2-N_2^+$  and the opposite sign in  $N_1-C_1-N_2^+$ , partial cancellation would account for the smaller magnitude in N1.

In spite of the different conclusions drawn by Shcherbakova *et al* (1969) from a comparison of their measurements of  $^{13}\text{C}$  hyperfine interactions for neighbouring sites in N1 with similar data for P1, we believe that the  $N_1-C_1-N_2^+$  model for N1 is supported by this comparison. This is discussed further in the Appendix, and the comparison between N1 and P1 is used to make firmer assignments for some of the ambiguous correlations between  $A$  parameters and neighbouring sites in P1.

Hence, we believe all this information indicates that W7 corresponds to a non-coplanar  $N-C-C-N^+$  site and N1 to a  $N-C-N^+$  site. This assignment for N1 could be confirmed by ENDOR measurements, particularly of the minor nitrogen, which would

(i) confirm the (110) symmetry of the site and (ii) should show a larger quadrupole interaction than W7.

A further feature of the model of W7 is evident in figure 1(c) that shows that what we have been calling a non-coplanar N—C—C—N<sup>+</sup> site should be thought of as a puckered ring with C<sub>2h</sub> symmetry



Jahn–Teller distortion causes the unpaired electron to go into one of the four N—C bonds, so lowering the symmetry of the site to C<sub>1</sub>. Of these four possible sites for one ring, only two are distinguishable because they are related in pairs by inversion. Hopping of the electron from one N to the other would average the A<sup>(1)</sup> and A<sup>(2)</sup> interaction for each site but would not average the two sites. The two different sites must correspond to occupation of differently oriented N—C bonds (N<sub>1</sub>—C<sub>1</sub> and N<sub>1</sub>—C<sub>3</sub> in figure 1(c)). So far as we understand the motional averaging reported by Loubser and Wright (1973), this has similar activation energy for hopping between these two orbitals and between the two nitrogen atoms. This activation energy is much lower than that for averaging in P1, presumably due to the presence of the neighbouring N<sup>+</sup>.

## 5. The mechanism for generating W7 centres

The centre illustrated in figure 1(c), generated by the process illustrated in figure 2, is sufficient to provide both of the symmetry-related W7 centres observed at low temperatures because it is possible for the lone pair on N<sub>1</sub> to be directed along two symmetry related directions [111] and  $\bar{1}\bar{1}\bar{1}$ . Hence the measurements suggest that there is only one of the twelve possible puckered ring structures formed in the crystal. Only one such ring would be formed by slip along  $[\bar{1}\bar{1}0]$  in (111) if the plane of slip is that indicated by a dotted line in figure 2 between the widely spaced planes of atoms (called the shuffle set by Hirth and Lothe (1968)) that intersects bonds directed along [111] as illustrated by Shcherbakova *et al.* To form the site illustrated in figure 1(c), the atom N<sub>2</sub> would have been displaced from the site labelled 3, slip occurring in the (111) plane intersecting the bond labelled [111]. However, it seems likely (Hirsch 1985) that slip occurs between the closely spaced planes of atoms (called the glide set by Hirth and Lothe), shown as a broken line in figure 2, which would disrupt A centres with three different orientations, producing three different types of site. To produce a puckered ring as illustrated in figure 1(c) requires slip in a different plane. For example, slip along  $[\bar{1}\bar{1}0]$  in (11 $\bar{1}$ ) would produce displacement in a plane between the site marked 3 and those marked 4, 5 and N<sub>1</sub>. Such slip would displace N<sub>2</sub> from the site labelled 3, disrupting A centres aligned along [111] (atom sites N<sub>1</sub>—3),  $\bar{1}\bar{1}\bar{1}$  (5—3) and  $[\bar{1}\bar{1}\bar{1}]$  (4—3), producing, respectively: the puckered ring oriented as in figure 1(c); a coplanar N<sub>1</sub>—C<sub>1</sub>—C<sub>2</sub>—N<sub>2</sub> centre oriented as in figure 1(f), which is not observed (but see section 6); and an A centre oriented along  $\bar{1}\bar{1}\bar{1}$  (4—N<sub>2</sub>), which would not be observable. In order that only one type of puckered ring should be formed, one requires that A centres should be aligned along [111] only; or together with  $[\bar{1}\bar{1}\bar{1}]$ , as that would not be disrupted by slip in the plane of closely spaced atoms.



One way in which a unique orientation of a centres might arise is as a result of uniaxial strain along  $[111]$  at a temperature at which the N atoms are mobile and tending to aggregate. This model for the production of a unique site is easy to conceive, but is probably not very plausible. It is known that the single lone pair in the the N—C bond of the P1 centre increases the bond length by at least 10% over the C—C bond length (section 6); and the bond length of a singly ionized N—N is even longer (section 6). As the two lone pairs in the a centre probably cause the bond length to be even greater, it is likely that compressive strain would inhibit the stabilization of N—N pairs along a single  $[111]$  direction and that extensive strain would be needed to form pairs along a unique axis.

There is another way in which unique puckered ring might be formed, which does not require extensive strain. A compressive strain along  $[1\bar{1}0]$  would tend to stabilize A centres in the  $(1\bar{1}0)$  plane, whose axes  $[111]$  and  $[11\bar{1}]$  are normal to the strain, relative to those whose axes lie out of the plane. If, now, these two sites are disrupted by slip in the  $[1\bar{1}0]$  direction in  $(11\bar{1})$ , the site directed along  $[111]$  produces the puckered ring site as described above, and the  $[11\bar{1}]$  site would not be disrupted as it does not lie in the plane of slip.

## 6. N4 and W24 centres

We have not made any new measurements on these centres, but we have reanalysed the interpretation of the data for N4. Furthermore, discussion of the properties of this other type of di-nitrogen centre is of interest in comparison with the properties of W7 and N1. The spin Hamiltonian parameters for these two centres with two equivalent nitrogen atoms have been determined by EPR (table 1).

Van Wyk and Loubser (1983) observed the W24 centre in type Ia diamond only while the sample was illuminated with light of wavelength less than 415 nm. Four symmetry-related sites were observed with hyperfine interactions of axial symmetry for the two nitrogen atoms about the same  $\langle 111 \rangle$  direction. Table 2 shows the hyperfine and bonding parameters as defined in section 4.2 of 1, deduced from the hyperfine parameters in table 1. Van Wyk and Loubser propose that W24 is formed by ionization of an A centre, so producing a  $N^{\pm}N$  centre with a single unpaired electron in an antibonding orbital (figure 1(e)). This is consistent with the 50% occupancy of orbitals on each of the two nitrogen atoms. The  $p/s$  ratio is greater than that required for  $sp^3$  bonding, and greater even than that found in the P1 centre (table 2) indicating that the nitrogen atoms repel one another to form a bond at least 10% longer than the normal C—C bond length.

The N4 centre is a very uncommon centre that has been found in only a few naturally occurring brown diamonds. It was first observed, but incorrectly interpreted, by Shcherbakova *et al* (1975); it was remeasured by Welbourn and Woods (1977) who interpreted it as arising from a centre with two nearly equivalent A matrices for the two nitrogen atoms, both axially symmetric about the same  $\langle 111 \rangle$  direction, say  $[111]$ . The centre is not isotropically distributed among the possible sites in the diamond: there was no evidence of centres oriented along other  $\langle 111 \rangle$  directions. The A matrices were thought to be different because of small splittings of the hyperfine lines. However, the analysis failed to take into account the fact that the coincidence of transitions such as those corresponding to  $M\{^1\} = +1$ ,  $M\{^2\} = 0$  and  $M\{^1\} = 0$ ,  $M\{^2\} = +1$  is removed by second-order terms of order  $A^2/g\mu_B B$ , corresponding to a line separation of  $\sim 50 \mu\text{T}$ . We have reinterpreted the data given by Welbourn (1978) on the assumption that the two A

matrices are identical with axial symmetry about  $[111]$ . The quadrupole interaction was assumed to be so small as to have negligible effect on the EPR spectrum. The parameters given in table 1 were determined by diagonalizing the  $18 \times 18$  matrix for the spin Hamiltonian (equation (1) in I), and using a least squares fitting procedure to fit 50 of Welbourn's data points corresponding to 18 different directions. There is excellent agreement between the calculated angular variation and the data, vindicating the assumption that the two nitrogen atoms are equivalent. Table 1 lists the parameters obtained in our fit and table 2 lists the bonding parameters deduced from the hyperfine parameters in table 1.

Welbourn proposed the  $N^+-N$  model, assigned above to W24, for the N4 centre. Three facts indicate that the  $N^+-N$  model is not correct for this centre: (i) that only about 40% of the unpaired electron would be located in the N—N antibonding orbital, (ii) that N4 is observed without illumination, and (iii) that the distribution of sites is spatially anisotropic.

Comparison with our proposed model for the W7 centre leads us to speculate about a similar model for N4: that is, a planar  $N_1-C_1^+-C_2-N_2$  structure (figure 1(f)). The hyperfine interaction for both nitrogen atoms in such a centre would be axially symmetrical about the same  $[111]$  axis, and the majority of the unpaired electron would be localized on  $C_1$  and  $C_2$ . This model is supported by the similarity of  $p/s$  and  $\eta^2$  to the values for P1: the proposed structure is like two parallel P1 centres but with somewhat smaller localization on each nitrogen, as the unpaired electron is shared between two N—C bonds. Such a centre could be formed for example by displacement of one of the nitrogen atoms in an A centre aligned along  $[111]$  by a dislocation with Burgers vector  $a/\sqrt{2}$  in the  $[1\bar{1}0]$  direction in the  $(11\bar{1})$  plane, combined with ionization of the centre. The difference from our model for the formation of W7 in strained diamond is only in the direction of alignment of the A centre relative to the direction of the Burger's vector. It is even possible to speculate about why the N4 centre is found in such small concentration, and why it is so much less common than the W7 centre. If the dislocations which give rise to these two centres result from the same compressive strain, say along  $[1\bar{1}0]$ , which causes the slip in the  $[1\bar{1}0]$  direction in  $(11\bar{1})$ , this compressive strain will be much more likely to produce A centres aligned along  $[111]$  and  $[1\bar{1}\bar{1}]$  than those aligned along  $[111]$  and  $[\bar{1}\bar{1}\bar{1}]$ . Hence W7, derived from A centres along  $[111]$  is much more likely to be produced than N4 from those along  $[\bar{1}\bar{1}\bar{1}]$ .

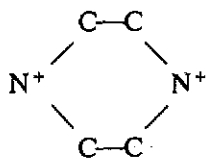
## 7. Discussion

Presumably a  $N^+$  ion would be incorporated into the diamond lattice, forming four  $sp^3$  orbitals, without lattice dilatation; indeed the extra positive charge might cause small local shrinkage by rendering  $N^+$  smaller than C.

It is the extra electrons needed to provide overall charge neutrality that cause the lattice dilation. It is interesting that the response of the lattice to this is different for the various centres we have discussed.

Several of them lower their symmetry by incorporating the additional electron into a specific antibonding orbital. So, when the electron is added to a single  $N^+$  with  $T_d$  symmetry, it goes into one of the four antibonding orbitals with a neighbouring C, so lowering the symmetry of P1 to  $C_{3v}$ . The site for  $N^+-C-N^+$ , lying in a  $(110)$  plane has  $C_{2v}$  symmetry, for which there would be six sites. When an electron is added it goes into one of the two N—C antibonding orbitals with the shared C, so lowering the symmetry

to  $C_v$  with twelve sites. A puckered ring



has  $C_{2h}$  symmetry. An added electron goes into one of the four N—C bonds in the ring, so lowering the symmetry to  $C_1$ : there are four possible sites, but only two are distinguishable because they are related in pairs by inversion.

In contrast, a single electron in  $N^+—N^+$  is equally shared in an antibonding orbital between the two N atoms and a single electron in coplanar  $N^+—C—C—N^+$  is equally shared by the two C atoms in the chain. Presumably, in these cases, no energy advantage is gained by Jahn–Teller distortion.

One interesting feature of these centres is that they all appear to have a hyperfine interaction with axial symmetry about  $\langle 111 \rangle$ . This is not required by the symmetry of the sites, except for P1 and W24. For the other sites with Jahn–Teller distortion it represents the fact that they can all be regarded as mildly perturbed P1 centres, so the presence of the nearby  $N^+$  does not noticeably distort the symmetry of the orbitals around the major nitrogen. For N4 it suggests that, as for P1, the major distortion of atomic positions is probably of the atoms  $C_1$  and  $C_2$  in figure 7(f), leaving the orbitals on the two N atoms still aligned about  $[111]$ .

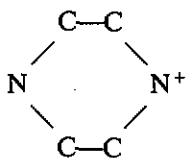
It is rather surprising that the di-nitrogen centres discussed in this paper exist in a paramagnetic, ionized form. That all of them except W24, which is excited by optical irradiation, occur in strained diamond suggests that there might be an electron trap associated with dislocations into which it is energetically favourable for an electron to move from these centres.

There seems to be no evidence of N4 or W7 centres, nor of N1 centres, in unstrained diamond either occurring naturally or produced by optical irradiation or in a state with  $S = 1$ . Although there are nitrogen-containing  $S = 1$  centres, none appears to have an atomic arrangement associated with N4, N1 or W7. This may not be surprising for W7 or N4, as it may represent the fact that when N atoms are so far apart, there is not a sufficient energetic advantage to cause them to associate rather than be statistically distributed. However, as N1 cannot be formed by a dislocation disrupting an A centre, it appears that N1 ought to be present even in unstrained crystals, so one might expect it to be produced by electron or optical irradiation of unstrained diamonds. The concentration of N1 in brown diamond was found to be increased by electron irradiation by Shcherbakova *et al* (1969).

## 8. Conclusion

ENDOR measurements on the W7 centre described in I have shown, although the magnetic hyperfine and electric-quadrupole interaction matrices for the nitrogen atom with the larger interaction have axial symmetry about a  $\langle 111 \rangle$  direction, that these matrices for the other nitrogen atom have no symmetry. This, together with other properties of the

centre, suggest that it is formed by a puckered ring structure,



with Jahn-Teller distortion such that the unpaired electron is in one of the two N—C antibonding orbitals.

As a consequence of this assignment, but also consistent with all other evidence about it, the N1 centre is shown to be N—C—N<sup>+</sup>.

A reanalysis of previously published data for N4 shows that its two nitrogen atoms are equivalent, contrary to what was previously reported, and that its properties are consistent with a planar structure N—C<sup>+</sup>—C—N.

The occurrence of only some of the possible symmetry related sites for W7 and N4 has been explained by a detailed extension of a previously proposed model involving plastic deformation of the diamond.

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### Appendix: N1 and P1 centres

It appears that the conclusions we have reached about the various centres discussed in this paper may enable us to resolve the question of associating hyperfine parameters measured for various <sup>13</sup>C neighbours of N in P1 with specific sites.

Table 3 lists the <sup>13</sup>C hyperfine parameters in decreasing order of isotropic contribution  $A_s$  for P1 and N1 centres, and figure 3 shows the sites of these possible atoms. The [111]

**Table 3.** <sup>13</sup>C hyperfine parameters in P1 and N1 centres.  $n$  is the number of symmetry-related sites of each type. For a P1 centre with axial symmetry about [111], all three sites of type-I neighbour have axis [111] and types II and III have one site each with axes  $[\bar{1}11]$ ,  $[1\bar{1}1]$  and  $[11\bar{1}]$ .

Neighbour	P1 <sup>a</sup>			N1 <sup>b</sup>		
	$A_s$ (MHz)	$A_p$ (MHz)	$n$	$A_s$ (MHz)	$A_p$ (MHz)	$n$
I	35.33	3.01	3	28.3	2.6	3
II	25.85	-1.18	3	21.3	0.6	3
III	12.35	1.11	3	16.7	1.1	2
IV	8.24		6			
V	4.15		3			
VI	2.75		6(9?)			

<sup>a</sup> Barklie and Guven (1981).

<sup>b</sup> Shcherbakova *et al* (1969).

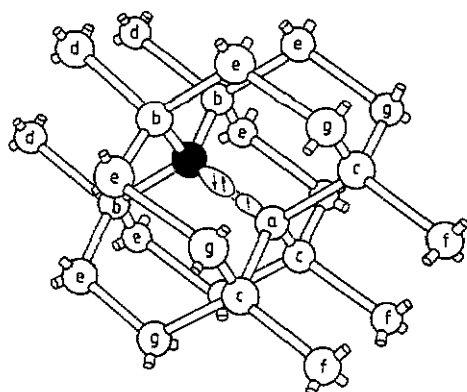


Figure 3. Carbon sites neighbouring nitrogen in the P1 centre. Atoms  $C_i$  are labelled only with the subscript  $i$ , and equivalent atoms have been given the same label.

symmetry of I indicates site  $C_d$  or  $C_f$ , and Bower and Symons (1966) argue that as the majority of the unpaired electron is situated on  $C_a$ , I should be associated with  $C_f$ . No opinion is offered about which of II or III should correspond to  $C_b$  and  $C_c$ .

The possibility, suggested by Shcherbakova *et al* (1969), that in N1 the minor nitrogen is situated on one of the  $C_b$  sites is discredited, as discussed in section 3, by (i) lack of motional narrowing, and (ii) the assignment of W24 to an ionized N—N centre. We have argued that the site of the minor nitrogen is  $C_c$ . This is supported by the fact that there is a set comprising only *two* equivalent  $^{13}\text{C}$  neighbours and also that the ratio of the values of  $A_s$  for these two carbon sites to that for the minor nitrogen is approximately equal to two, the value expected for identical admixture of 2s orbitals on the two atoms. This then appears to associate definitively site II with  $C_b$  and site III with  $C_c$ .

No  $^{13}\text{C}$  hyperfine structure has been observed in N1 associated with  $C_a$ . There is a 21% increase in the electron density on the major nitrogen relative to P1, and an increase on  $C_c$ , suggesting a decrease on  $C_a$ . The 40% increase on  $C_c$  compared with the 20% decrease on  $C_f$  and  $C_b$  is probably due to the fact that for  $C_c$  direct and indirect contributions tend to cancel, whereas for  $C_f$  and  $C_b$  they have the same sign.

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