

Possible evidence of a copper-related electron paramagnetic resonance centre in diamond

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 2053

(<http://iopscience.iop.org/0953-8984/13/10/302>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 08:46

Please note that [terms and conditions apply](#).

Possible evidence of a copper-related electron paramagnetic resonance centre in diamond

J M Baker

Oxford Physics, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK

E-mail: m.baker1@physics.oxford.ac.uk

Received 5 September 2000

Abstract

The EPR centre W36, found in natural type IIb diamond, has been previously attributed to a boron-related point defect, largely on account of its four line hyperfine structure attributed to ^{11}B . The attribution has been re-examined, and no simple boron-related site has been found capable of accounting for the measured parameters. It is concluded that W36 is much more likely to be related to copper, probably at a semi-vacancy site $(\text{C}_3\text{VCuVC}_3)^+$. An unusual feature of this centre is the very small value of the fine structure parameter D . Two other centres, W10 and W32, with similarly small values of D , which may also be associated with 3d ions, are briefly discussed.

1. Introduction

There has been interest in impurity atoms incorporated in the diamond lattice as point defects, since they profoundly modify optical, electrical, thermal and mechanical properties [1]. Nearly all the elements of the periodic table have been found in natural diamond [2], but only a few have been shown to be incorporated at sites in the diamond lattice [3]. The most common of these is nitrogen, and diamond is classified as type I if nitrogen is detectable by infrared absorption (> 1 ppm), and otherwise as type II. Diamond with an excess of boron is semiconducting, and is classified as type IIb. The interest in boron-related defects stems from the acceptor level of B_S^0 between 0.35 and 0.40 eV above the valence band [4], which gives rise to the semiconduction. There is also interest in transition metal impurities because of their range of possible charge states. So far, only Ni [5] and Co [6] have been shown to occupy sites in the lattice. This much more limited range of 3d ions than is observed in substitutional or interstitial sites in silicon [7] presumably reflects the much smaller space than in the silicon lattice, because of the 35% smaller lattice constant. As the 3d ions become smaller as the atomic number Z increases, slowly for constant charge state, and rapidly for fixed $3d^n$ configuration, it is not unexpected that the observed EPR centres correspond to elements at the high Z end of the group

The principal techniques which have been used to study such defects have been optical (absorption and luminescence) [8] and electron paramagnetic resonance (EPR) [9]. The atomic species involved in the defect is clear from characteristic hyperfine structure (hfs) in the EPR:

the EPR centre W8 was confirmed as Ni_5^- by ^{61}Ni hfs [10] and the participation of Co in O4 was confirmed by ^{59}Co hfs [6].

This paper focuses on the EPR centre W36, found in natural type IIb diamond, which has previously been attributed to a boron-related point defect [11]. This paper re-examines that attribution, and concludes that it is more likely that the centre is related to copper.

2. Previous measurements in diamond

2.1. Previous measurements on 3d ions in diamond

A large number (~ 20) of probably nickel-related sites have been described in diamond [12]. Those for which models have been confirmed are related to single nickel atoms in substitutional [5], T_d interstitial [13] or the so-called semi-vacancy site [14], the latter being at a bond centre midway between two vacancies. 3d ions at interstitial sites form no bonds, and are subject to a crystal field with the symmetry of the surrounding atoms: as next-nearest neighbours dominate the crystal field at the T_d interstitial site, this has octahedral symmetry. In the substitutional or the semi-vacancy sites the 3d ion forms four or six bonds respectively with its neighbours. The unpaired electron wavefunction is an admixture of 3d orbitals and linear combinations of ligand orbitals of the appropriate symmetry. Whether the bonding orbital is principally on the 3d ion or the ligands depends upon the tightness of the binding of the 3d and carbon orbitals. If the 3d electrons are more tightly bound, the 3d shell is filled, and the unpaired electrons are primarily on the dangling bonds of the surrounding atoms: this is the so-called 'vacancy' model [15], as the properties of the defect depend upon the orbitals of the vacancy. If the 3d electrons are less tightly bound, the unpaired electrons are primarily in the 3d shell, and the properties are more like those of 3d ion salts: this is known as the Ludwig–Woodbury (LW) model [7, 16]. These models are extreme descriptions, and the true situation lies between them. Not enough is known about 3d atoms in diamond for a full understanding of the situation.

The orbital angular momentum associated with 3d electrons gives the potential for g -values to differ from g_e . For most nickel-related centres in diamond the g -value is sufficiently close to g_e for the orbital angular momentum to be regarded as quenched, in first order. The spin–orbit coupling $\lambda \mathbf{L} \cdot \mathbf{S}$ admixes orbitals at energy Δ to give $\delta g = (g - g_e) \sim \lambda / \Delta$ [17]. For 3d ions, δg can be moderately large, e.g. ~ 0.2 for Ni^{2+} and Cu^{2+} ions in hydrated salts [17], but for defects in diamond involving dangling orbitals it is generally small, e.g. for the negatively charged vacancy, V^- , $\delta g = 0.0004$ [18]. This difference arises from different values of λ (typically ~ 100 MeV for Cu^{2+} and ~ 3.5 MeV for C) and of Δ (typically 1 eV for 3d ions and 5 eV for diamond). For mixed wavefunctions, the effects of spin–orbit coupling are intermediate, as is the resultant δg . At the extreme of the *vacancy* model one expects δg to be small, and at the extreme of the LW model δg will be large. For the T_d substitutional site, Ni^- , $3d^7$, has $\delta g = 0.0296$ [5].

2.2. Previous measurements on boron-related sites

In contrast to single substitutional nitrogen, N_5^0 , which displays EPR (P1 centre [19]) because its extra electron is sited in one of the four N–C anti-bonding orbitals, single substitutional B_5^0 has not been observed in EPR. Shallow acceptors, such as boron, have been difficult to observe by EPR in silicon, because of the peculiarities of the valance band; they have become visible as a wide line only after application of uniaxial stress [20]. Similar EPR lines have been found in the same way in type IIb diamond (NL1 EPR centre [21]); but, as with many EPR defects

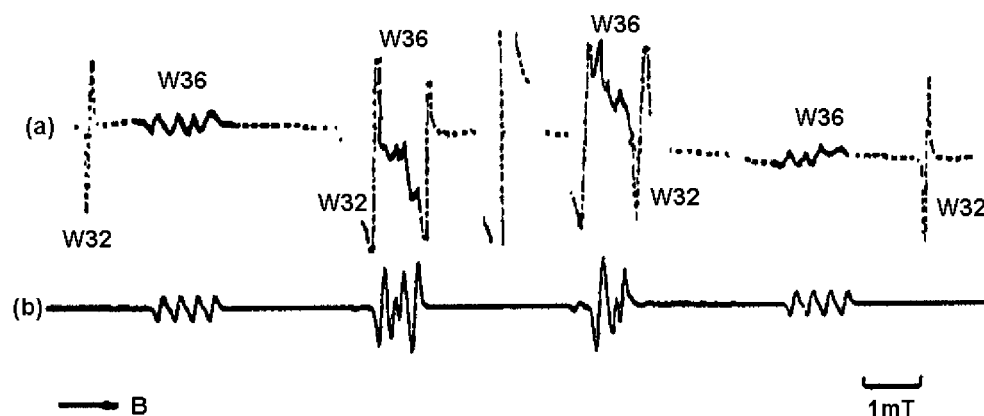


Figure 1. (a) The observed EPR spectrum of W36 (solid curve) (and of W32 (dotted curve)) at ~ 9.6 GHz for B parallel to $\langle 111 \rangle$, and (b) the calculated spectrum for W36 using the parameters in table 1 (the figure is taken from [11]).

Table 1. Spin Hamiltonian parameters for the EPR centres discussed, with $S = 1$.

Centre (model)	Reference	D (MHz)	g	A_S (MHz)	A_P (MHz)	P (MHz)
W36	[11]	155.4	2.002	6.9	0.9	-5.4
W32	[11]	204.9	2.002			
W15 (N-V) ⁻	[24]	2874	2.0028	2.2	0.07	-5.04
R4/W6 (V-V) ⁰	[28]	390 ^a	2.002 ^a			

^a This value is extrapolated to $T = 400$ K, where the normally C_{2h} symmetry approximates to axial about $\langle 111 \rangle$.

which are found only in type IIb material, there is no hfs characteristic of the isotopes of B to confirm whether the structure of the defect actually involves B, or whether it is the acceptor nature of B_S which has allowed donor sites to become EPR active by transfer of an electron to B_S . Only two EPR centres have been found which do appear to have this hfs, NIRIM-4 [22] and W36 [11].

There is no ambiguity about the structure of NIRIM-4 as a $\langle 100 \rangle$ split interstitial $(B-N)^+$. The $(B-N)$ split interstitial site has C_{2v} symmetry about $\langle 100 \rangle$ (rare in diamond), the N and B atoms each being sp^2 bonded to two C atoms and to one another. The N and B atoms also each have a non-bonding p_π orbital normal to the N-B direction. For $(N-B)^0$ that on N is full and that on B is empty, so the ground state is diamagnetic with $S = 0$. That the principal hfs of NIRIM-4 is of ^{14}N shows that the centre is $(B-N)^+$, with a single unpaired p_π orbital centred on ^{14}N . There is a small density of unpaired electron on B, which gives rise to a characteristic four line hfs of ^{11}B (81.2% natural abundance). The seven line hfs was also observed from the less abundant (18.8%) ^{10}B , even though its lines are only 13% of the intensity of those of the more abundant ^{11}B . NIRIM-4 has so far been found only in synthetic B-doped diamond after electron irradiation. It seems unlikely that electron irradiation at nominally room temperature would induce mobility of N or B, but it is known to induce mobility of self-interstitials (I) under conditions of irradiation [23], as evidenced by the formation of the EPR centre R1 (I-I)⁰. This suggests that NIRIM-4 might be produced from $(B_S-N_S)^0$ pairs formed during the growth process, by reaction with mobile self-interstitials.

W36 has $S = 1$, and a much smaller hfs than NIRIM-4. Figure 1 [11] shows that the line width is similar to the line separation, so it is impossible to detect the hfs of ^{10}B , which would

lie within the four lines of ^{11}B . The site has axial symmetry about $\langle 111 \rangle$, described the spin Hamiltonian (1) with parameters given in table 1.

$$H = g\mu_B \mathbf{S} \cdot \mathbf{B} + D[S_z^2 - (1/3)S(S+1)] + A_S \mathbf{S} \cdot \mathbf{I} + A_P[3S_z I_z - \mathbf{S} \cdot \mathbf{I}] + P[I_z^2 - (1/3)I(I+1)]. \quad (1)$$

When the external magnetic field \mathbf{B} is applied along $\langle 111 \rangle$, it is parallel to the axis of one site which gives the simple four line hfs seen in figure 1, but makes an angle of $\cos^{-1}(1/\sqrt{3})$ with the axis of the other three sites which gives a much more complex hfs showing the effect of a nuclear quadrupole interaction. Figure 1 shows a reconstruction of the spectrum with spin Hamiltonian (1) and the parameters given in table 1.

3. Possible boron-related models for W36

The principal reasons for attributing the spectrum of W36 to boron are: (a) that the diamond is of type IIb, and (b) the four line hfs, consistent with ^{11}B . However, to confirm this assignment, it is necessary to invent a model capable of having the unusually small D , very small A_S , very small A_P and quite large quadrupole interaction.

The value of A_S corresponds to 0.22% of an unpaired 2s electron on B; and A_P corresponds either to 0.57% of an unpaired 2p electron, or to magnetic dipole–dipole interaction between the boron nucleus and an unpaired electron at a distance of about 0.3 nm along $\langle 111 \rangle$. The quadrupole interaction indicates an electric field gradient at the nucleus which is similar to that at ^{14}N in P1 [19]. This suggests either a partly filled B–C bond, or a lone pair in B–V. The electric field gradient set up by an external charge, even at a nearest neighbour site at 0.154 nm, would produce only $P \sim 0.1$ MHz. The centre cannot be an electron in a B–C bond, as that would give $S = \frac{1}{2}$ and large hfs like P1 ($A_S = 92$ MHz, $A_P = 11$ MHz). Also, it cannot be a simple $(\text{B–V})^-$ centre, as that would be analogous to W15 [24], $(\text{N–V})^-$, which has very large D (2900 MHz), because of spin–spin interaction between the unpaired electrons in the dangling orbitals of the vacancy. The other three parameters are remarkably analogous to those for ^{14}N in W15.

There are two ways in which one might have a very small D : (a) two $S = \frac{1}{2}$ systems, ~ 0.5 nm apart along $\langle 111 \rangle$ coupled by magnetic dipole–dipole interaction; (b) two (or more) electrons in a complex with quenched orbital angular momentum with basically cubic symmetry, but with a small trigonal distortion. Possibility (a) is not consistent with one of the electrons being associated with B, because that would have a large hfs, also it is difficult to understand why two centres so related by translation along $\langle 111 \rangle$ should be any more stable than the many other possible sites with two centres at the same separation. Possibility (b) might be a vacancy, but it would have to be in a ^3A state, which is calculated to be far from the ground state [25], or it could be a 3d ion with quenched angular momentum and a singlet ground state, which could be only $3d^2$ in the tetrahedral symmetry of a substitutional site or $3d^8$ in the octahedral symmetry of an interstitial site. A substitutional site could not be the nearest neighbour of B^- , as that would both set up a huge trigonal crystal field at the 3d ion, and would have large B hfs. A more distant neighbour along $\langle 111 \rangle$ would not set up the electric field gradient for the quadrupole interaction. An interstitial site for Ni^{2+} , $3d^8$, is not an unreasonable possibility in type IIb diamond, as Ni_i^{2+} is known to occur as NIRIM-1 at a cubic site, so Ni_i^{2+} might occur in association with B_s^- at a site beyond the nearest neighbour on a $\langle 111 \rangle$ axis. This would be exactly the correct position to produce the observed A_P due to magnetic dipolar interaction between the ^{10}B nucleus and the 3d electrons, but it would still give too small a quadrupole interaction and too large a value of D .

If one could account for the constraints of the spin Hamiltonian parameters by a complex centre with several constituents placed at different positions to account for different parameters, it would require an extremely improbable combination. The similarity of all parameters except D to those for $(N-V)^-$ suggest B–V associated with a trigonal cluster of vacancies, like $(BV_4)^-$ or larger, which might separate the unpaired electrons sufficiently to give a small value of D . However, if such a centre could be formed associated with B, one would expect its analogue with N to exist, and no such centre has been found.

It therefore seems that, plausible though the attribution to boron might seem, there is no simple model centre which could give rise to the observed combination of spin-Hamiltonian parameters.

Another counter-indication about this site is that W36 is not observed in B-doped diamonds grown from nickel solvent catalyst, which ought to be ideal for the production of the boron-related site if it exists,

4. Alternative models

If boron is a doubtful contender, what other possible elements have nearly 100% isotope with $I = \frac{3}{2}$? Lithium, sodium and potassium seem unlikely, because lithium is the only alkali metal to be found in a defect site in the larger lattice of silicon [26], so even that would probably not fit in the smaller diamond lattice. Copper has two isotopes with $I = \frac{3}{2}$ and such closely similar nuclear moments that the hfs of the two isotopes would not be resolved in the observed hfs of W36. Could the hfs of W36 correspond to Cu? We know that NIRIM-1 [13] corresponds to interstitial Ni^+ , $3d^9$, $t_2^6e^3$, $S = \frac{1}{2}$, so in p-type diamond one might find Ni^{2+} and Cu^{3+} , $t_2^6e_2$, $S = 1$. This configuration is not subject to Jahn–Teller distortion, so the weak axial distortion would have to arise from some on-axis defect, such as V^0 beyond the nn site. The other possibility is that for the different 3d ion there might be a real spontaneous trigonal distortion as predicted by the local spin density model [27] for Ni_i^+ . It has been proposed that the EPR centre NE4 [14] corresponds to Ni at a semi-vacancy site: $(C_3VNiVC_3)^-$. If Cu were incorporated as $(C_3VCuVC_3)^+$, corresponding to Cu^+ , $3d^{10}$, in $(V_2)^0$, the ‘vacancy’ model, which is known to be a better approximation towards the heavy end of the 3d group [15], it would have $S = 1$ and possibly smaller D than for R4/W6 [28] (table 1). The spherically symmetrical 3d ion could have very small hfs, and the axial symmetry of the site could lead to a small anisotropy of hfs and the quadrupole interaction (the quadrupole moments of the isotopes of Cu are much larger than that of ^{11}B , so require a much smaller electric field gradient to provide the observed quadrupole interaction). The small δg would correspond to the majority of the unpaired electron being on the C dangling bonds, as expected for the vacancy model. Furthermore, the large concentration of the acceptor B might encourage Cu to be in the Cu^+ charge state. The very small hfs is consistent with the very small hfs found for odd isotopes of Sn in the EPR of Sn^0 at the semi-vacancy site in silicon [29].

It therefore seems much more likely that W36 is a copper-related centre than a boron-related centre. Although W36 has so far been found only in natural diamond, this assignment could be checked by trying to form W36 in a synthetic type IIb diamond by heavily doping, with boron, diamond prepared so as to give high concentration of NIRIM-1, in a solvent catalyst containing copper. So far, diamonds grown this way do not exhibit W36 as grown, but it would be of interest to anneal such crystals to look for aggregation of B and Ni, analogous to the aggregation of N and Ni in type Ib crystals.

If this model for W36 is correct, one might wonder whether the closely similar site corresponding to Ni^0 , $3d^{10}$, in $(V_2)^0$, $(C_3VNiVC_3)^0$ might exist with similar spin Hamiltonian

parameters, but no hyperfine structure (^{61}Ni is the only isotope of Ni with non-zero nuclear spin, and it has only 1.4% natural abundance). There is only one other centre, also found in type IIb diamond with very similar parameters to W36, which is W32 (the spectrum is also shown in figure 1, and the spin Hamiltonian parameters are given in table 1).

Is the very small δg for these two centres consistent with the much larger δg found for NE4, for which the likely but unconfirmed model is $(\text{C}_3\text{VNiVC}_3)^-$, $3d^{10}$, in $(\text{V}_2)^-$ if the vacancy model is appropriate? This shows that for NE4 the unpaired electron wavefunction has a much larger amplitude on the 3d ion, leading to larger effect of spin-orbit coupling, which is responsible for δg . This trend is in the right direction, as the smaller nuclear charge on Ni would bind $3d^{10}$ less tightly, leading to greater admixture with the ligand wavefunctions. The negatively charged site occurs because NE4 is observed in synthetic type Ib diamond where there is abundant donor nitrogen.

The association of W32 with $(\text{C}_3\text{VNiVC}_3)^0$ would be much more difficult to confirm, as synthetic diamonds grown from nickel solvent catalyst show a large variety of nickel-related defects [3].

5. Conclusion

A re-examination of the properties of the EPR centre W36 found in a natural type IIb diamond suggests that it is more likely to be related to copper, probably Cu^+ in the semi-vacancy form $(\text{C}_3\text{VCuVC}_3)^+$, than to boron as originally proposed. If this is correct, W36 is the first copper-related centre to be suggested in diamond.

Appendix. Another trigonal centre with a small value of D

The discussion above has illustrated the difficulty of finding models for centres with more than one electron, an unusually small value of D and trigonal symmetry, within the limitations imposed by the crystal structure of diamond.

In addition to W36 and W32, the EPR centre W10 also has trigonal symmetry about $\langle 111 \rangle$ and a small value of D (154.4 MHz), and $g = 2.001$, but it differs from them in that $S = 2$ [9].

W10 has been attributed to Cr^0 , $3d^6$, at a strongly axially distorted interstitial site [11]. The case is made that the strong trigonal crystal field separates the 3d levels into a lowest a_1 state containing two paired electrons, and single occupancy of each of the two excited e states, for which Hund's rule coupling gives $S = 2$. The system of six electrons corresponds to a D state which is split by the crystal field into a singlet ground state and a doublet state at energy K , of the order of the trigonal component of the crystal field, and another doublet at much higher energy Δ , corresponding to the cubic component of the crystal field. The orbital angular momentum is quenched, but spin-orbit coupling mixes the two excited states. The admixture with the lower doublet dominates as $K \ll \Delta$. This leads to $\delta g \sim \lambda/K$ and $D \sim \lambda^2/K$. The measured δg is very small, showing that the orbital angular momentum is highly quenched. This then appears to account for the very small observed value of D .

However, this analysis ignores the fact that the wavefunction for this lowest orbital singlet state does not have cubic symmetry, so there is a contribution to D from spin-spin interaction, which would be large. For Fe^{2+} , $3d^6$, which ought to be similar to Cr^0 , $3d^6$, the spin-spin coupling parameter $\rho \sim 0.9 \text{ cm}^{-1}$ [30]. Hence for Cr^0 as envisaged by [11] $D \sim (\rho + \lambda^2/K)$, which should be large, and there is not even the possibility that the two terms cancel as they have the same sign. The model of W10 as Cr^0 , $3d^6$, in a trigonally distorted interstitial site cannot therefore be correct.

The alternative is to seek a weakly perturbed cubic site where the wavefunction of the ground state does have cubic symmetry. To construct a state with $S = 2$ poses a problem. One requires at least four orbitals, which means at least d electrons on a single atom, four dangling orbitals, or a composite. Systems with $S = 2$ are very rare among 3d salts, and small trigonal perturbations do not produce the characteristics observed in W10. In silicon there are two types of site with $S = 2$, one for $3d^6$ where because of orbital degeneracy the g -value is very different from g_e [7], and one for a strange site involving a tetrahedral arrangement of four Mn_i^0 ($3d^7$) [31]. The latter has cubic symmetry and must correspond to a ferromagnetic coupling of four spins of $\frac{1}{2}$. Apart from W10, the only other $S = 2$ system observed in diamond [32] is the 5A_2 excited state of the neutral vacancy V^0 . If the ‘vacancy’ model were appropriate to a substitutional defect in diamond, it might be possible that a $3d^{10}$ substitutional system could sufficiently change the order of the energy levels of the neutral vacancy to make 5A_2 the ground state. For a spectrum without hfs this would have to be either Fe_S^{2-} , Ni_S^0 or Zn_S^{2+} . Other evidence [33] suggests that Ni_S^0 has $S = 0$.

A more complex centre could be involved like $[(Mn_i)_4]^0$ in silicon [32]. This, with no hfs, would have to be $[(Fe_i)_4]^{4+}$ or $[(Cr_i)_4]^{4-}$, with a small axial distortion. A ferromagnetically coupled system of two $S = 1$ defects lying along a $\langle 111 \rangle$ axis, separated by ~ 0.6 – 0.7 nm, does not seem any more probable than systems with similar separation but aligned along other directions, which are not observed.

Another possibility is that Ni^0 or Zn^{2+} , $3d^{10}$, at the centre of a semi-vacancy site $(V_2)^{2-}$, i.e. $(C_3VNiVC_3)^{2-}$ or $(C_3VZnVC_3)^0$, might have a ground state for the vacancy model of the form $a_{1g}^2 a_{1u}^2 e_g^2 e_u^2$, $S = 2$. Such a state is probably of quite high energy for $(V_2)^{2-}$ itself, but that might be pulled down by the central $3d^{10}$ ion. Brown diamonds have previously shown positively charged impurity centres (N1, N–C–N⁺ [34], N4 [35] and OK1 [36], N–C–C–N⁺), suggesting that the dislocations responsible for the colour are effective electron traps, which indicates that the Zn-related site is more likely than the Ni-related site; however, Zn does not appear to have been found in diamond in appreciable concentration [2].

References

- [1] Field J E (ed) 1979 *The Properties of Diamond* (London: Academic) part I
- [2] Sellschop J P F 1992 *The Properties of Natural and Synthetic Diamond* (London: Academic) p 81
- [3] See references [1]–[6] in Nadolinny V A, Yeliseyev A P, Baker J M, Newton M E, Twitchen D J, Lawson S C, Yuryeva O P and Feigelson B N 1999 *J. Phys.: Condens. Matter* **11** 7357
- [4] Collins A T 1994 *Properties and Growth of Diamond* ed G Davies (INSPEC) p 265
- [5] Isoya J, Kanda H, Norris J R, Tang J and Bowman M K 1990 *Phys. Rev. B* **41** 3905
- [6] Twitchen J D, Baker J M, Newton M E and Johnston K 2000 *Phys. Rev. B* **61** 9
- [7] Ludwig G W and Woodbury H H 1962 *Solid State Phys.* **13** 223
- [8] Clark C D, Collins A T and Woods G S 1992 *The Properties of Natural and Synthetic Diamond* (London: Academic) p 35
- [9] Loubser J H N and van Wyk J A 1978 *Rep. Prog. Phys.* **41** 1201
- [10] Samoilovich M I, Bezrukov G N and Butuzov V P 1971 *JETP Lett.* **14** 379
- [11] Loubser J H N and van Wyk J A 1987 *S. Afr. J. Phys.* **10** 165
- [12] Ammerlaan C A J *Paramagnetic Centres in Diamond* (Landolt–Börnstein) at press
- [13] Isoya J, Kanda H and Uchida Y 1990 *Phys. Rev. B* **42** 9843
- [14] Nadolinny V A, Yeliseyev A P, Yuryeva O P and Feigelson B N 1997 *Appl. Magn. Reson.* **12** 543
- [15] Watkins G D 1983 *Physica B + C* **117B–118B** 9
- [16] Ludwig G W and Woodbury H H 1960 *Phys. Rev. Lett.* **5** 98
- [17] Abragam A and Bleaney B 1970 *Paramagnetic Resonance of Transition Metal Ions* (Oxford: Clarendon)
- [18] Isoya J, Kanda H, Uchida Y, Lawson S C, Yamasaki S, Itoh H and Morita Y 1992 *Phys. Rev. B* **45** 1436
- [19] Smith V V, Sorokin P P, Gelles I L and Lasher G J 1959 *Phys. Rev.* **115** 1546
- [20] Feher G, Hensel J C and Gere E A 1960 *Phys. Rev. Lett.* **5** 309

-
- [21] Ammerlaan C A J and van Kemp R 1985 *J. Phys. C: Solid State Phys.* **18** 2623
- [22] Isoya J, Kanda H and Morita Y 1997 *Phys. Rev. B* **56** 6392
- [23] Hunt D C, Twitchen D J, Newton M E, Baker J M, Anthony T R, Banholzer W F and Vagralsi S S 2000 *Phys. Rev. B* **61** 3863
- [24] Davies G and Hamer M F 1976 *Proc. R. Soc.* **348** 285
- [25] Mainwood A, Lowther J E and van Wyk J A 1993 *J. Phys.: Condens. Matter* **5** 7929
- [26] Amerlaan C J A *Paramagnetic Centres in Silicon* ed M Schultz (Landolt-Börnstein) at press
- [27] Lowther J E 1995 *Phys. Rev. B* **51** 91
- [28] Twitchen D J, Newton M E, Baker J M, Anthony T R and Banholzer W F 1999 *Phys. Rev. B* **59** 12900
- [29] Watkins G D 1975 *Phys. Rev. B* **12** 4383
- [30] Pryce M H L 1950 *Phys. Rev.* **80** 1107
- [31] Ludwig G W, Woodbury H H and Carlson R O 1959 *J. Chem. Phys. Solids* **8** 490
- [32] van Wyk J A, Tucker O D, Newton M E, Baker J M, Woods G S and Spear P 1995 *Phys. Rev. B* **52** 12657
- [33] Nadolinny V A, Yelisseyev A P, Yuriyeva O P and Feigelson B N 1977 *Appl. Magn. Reson.* **12** 543
- [34] Newton M E and Baker J M 1992 *J. Phys.: Condens. Matter* **4** 8119
- [35] Newton M E and Baker J M 1991 *J. Phys.: Condens. Matter* **3** 3605
- [36] Newton M E and Baker J M 1991 *J. Phys.: Condens. Matter* **3** 3591