

Magnetic resonance spectroscopy in semiconducting diamond†

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Abstract. In type-IIb semiconducting diamond an electron paramagnetic resonance spectrum, which is labelled C-NL1, is observed. For detection of the resonance low sample temperatures ($T < 4$ K) and the application of a large uniaxial stress ($P \approx 1$ GPa) are required. The spectrum can be analysed with an effective spin $J = \frac{3}{2}$ and a spin Hamiltonian including terms depending on the magnetic field and on the strain. From the angular dependence of the magnetic field at resonance the spectroscopic splitting factors are determined, $g'_1 = 1.10 (\pm 0.05)$, $g'_2 = +0.01 (\pm 0.02)$, and the ratio of the deformation potentials $d'/b' = 1.55 (\pm 0.05)$. By analogy to the corresponding characteristics of shallow acceptors in silicon, the resonance is associated with the neutral acceptor (boron) in p-type diamond. The width of the resonance can be explained as due to broadening by random internal strains.

1. Acceptor states in semiconducting diamond

Type-IIb diamonds, representing only a very small part of the natural crystals, form a well-defined category (Custers 1952, 1954, Walker 1979). Although they are among the purest diamonds, the presence of non-compensated acceptors gives them electrical conductivity (Collins and Lightowlers 1979). It was established by careful analysis that boron is the main acceptor impurity (Lightowlers and Collins 1976, Collins and Williams 1971) replacing the earlier supposition favouring aluminium (Dean *et al* 1965). Ionisation of the acceptors makes type-IIb diamond a p-type extrinsic semiconductor. Room-temperature resistivities as low as $100 \Omega \text{ cm}$ correspond to acceptor concentrations in the range of 10^{17} cm^{-3} . The electrical level of the acceptor at $E_{\text{vb}} + 0.3685 \text{ eV}$, as determined by the Hall effect (Collins and Williams 1971), is shallow with respect to the band gap, but is not easily thermally ionised. Therefore, even at room temperature, most acceptor impurities will be in the non-ionised state, with the hole bound to the acceptor.

The neutral acceptors have unpaired spins and consequently attempts to observe these centres by electron paramagnetic resonance (EPR) have been made (Loubser and van Wijk 1978). Smith *et al* (1959) reported a complicated spectrum, which became known as the 14-line spectrum but was later labelled as the P2 spectrum, as arising from aluminium acceptors. Shcherbakova *et al* (1971) re-examined the spectrum and

† This paper is dedicated to Dr Paul Dean. It was received too late to be included in the Special Issue.

interpreted the resonance as due to a nitrogen–aluminium donor–acceptor pair on neighbouring carbon sites (Dean 1965). Subsequent studies by Loubser and Wright (1973), Shcherbakova *et al* (1978) and van Wijk (1982), in which electron–nuclear double resonance was also used, have now established as the most likely model a three-nitrogen centre probably containing an additional lattice vacancy. Another resonance, consisting of a single isotropic line, was observed, also in natural semiconducting diamonds, by Bell and Leivo (1967). Similar to spectrum P2 this resonance is observable at room temperature, with a g -value very close to but slightly higher than the free-electron g -value, 2.0023. Using heavily boron-doped synthetic diamonds Bourgoin *et al* (1972) observed two EPR lines. It was argued that one of these is due to free holes in the valence band, whereas the other arises from holes bound to the boron atoms. The synthetic crystals have large grown-in axial strains. The resonances are observable over a wide temperature range, including room temperature. The g -factors vary from about 0.6 to 3 depending on the orientation of the magnetic field with respect to the crystal axes, and moreover are strongly temperature dependent. In all of these reports it was difficult to provide conclusive evidence that the observed resonances are really associated with the acceptor impurities.

In this paper still another resonance is reported which we ascribe to the neutral acceptor in semiconducting diamond. For reference purposes the spectrum is denoted by C-NL1. The identification of the spectrum with acceptor impurities is entirely based on the close analogy of the characteristics of the spectrum C-NL1 and those of the well-known shallow states in silicon. The shallow impurity states in semiconductors are successfully described by the effective-mass theory (Kohn 1957). The acceptor states are formed from states derived from the top of the valence band. The ground state has fourfold multiplicity due to a twofold orbital and the twofold spin degeneracy. The orbital p character of the ground-state wavefunctions will cause a strong spin–lattice coupling and large deviations of the Zeeman splitting g -factor from the spin-only value $g = 2.0023$. To analyse the EPR results an effective spin $J = \frac{3}{2}$ is associated with the isolated ground-state quartet. Between the four states six EPR transitions are possible. All of these are observed in high-quality silicon crystals with very low values of internal strains (Neubrand 1978). For diamond, inevitably, the presence of internal strains, random in magnitude and orientation, will cause splitting of the ground state into two Kramers doublets. The strain-induced splittings are comparable with the Zeeman splittings in the EPR experiment. Because of their random character the strains will broaden the resonances and consequently lower their intensities, below the detection limit. An external uniform stress can be applied to reduce the effect of internal strains. For sufficiently large stress the two Kramers doublets become effectively decoupled and one resonance transition, between the two levels of the lowest-energy doublet, becomes observable. Under these conditions one resonance, still strain broadened, will be detected. The application of external stress is a strict requirement for observation of this resonance. Also, low temperatures are necessary to obtain the appropriate spin–lattice relaxation rates. For silicon the acceptor state resonances for all column III impurities, B, Al, Ga and In, were observed and behave according to the expectations as outlined above. For the NL1 resonance in diamond an exactly identical dependence on strain and temperature is found experimentally. This was discussed in some detail in a previous conference paper (Ammerlaan 1981). The NL1 spectrum was observed in six samples cut from type-IIb stones, and only in these semiconducting diamonds. The measurements were performed in a K-band superheterodyne spectrometer tuned to observe the dispersion.

In the next section of this paper the angular dependence of the magnetic resonance is analysed, providing the spectroscopic characterisation of the spectrum. In §3 the broadening effect due to internal strains is discussed on a quantitative basis.

2. Spectroscopic characterisation

To analyse the angular variation of the resonance the spin Hamiltonian formalism is applied. To deal with the four levels in the ground state an effective spin $J = \frac{3}{2}$ is required. Substitutional acceptor impurities are in a crystalline environment of cubic symmetry. The most general spin Hamiltonian $\mathcal{H}$, allowed by spin and symmetry, taking into account the linear effects of the magnetic field by $\mathcal{H}_B$ and of the strain by $\mathcal{H}_\epsilon$ takes the form (Luttinger 1956, Kleiner and Roth 1959, Bir *et al* 1963, Neubrand 1978):

$$\mathcal{H} = \mathcal{H}_B + \mathcal{H}_\epsilon \quad (1)$$

with

$$\mathcal{H}_B = +g'_1 \mu_B (B_x J_x + B_y J_y + B_z J_z) + g'_2 \mu_B (B_x J_x^3 + B_y J_y^3 + B_z J_z^3) \quad (2)$$

$$\mathcal{H}_\epsilon = +b'(\epsilon_{xx} J_x^2 + \epsilon_{yy} J_y^2 + \epsilon_{zz} J_z^2) + \frac{1}{3}\sqrt{3}d'[\epsilon_{xy}(J_x J_y + J_y J_x) + \epsilon_{yz}(J_y J_z + J_z J_y) + \epsilon_{zx}(J_z J_x + J_x J_z)]. \quad (3)$$

The spin Hamiltonian constants, i.e. the Zeeman splitting factors g'_1 and g'_2 and the deformation potentials b' and d' , are accentuated to distinguish them from the corresponding parameters for free holes. The Cartesian components of the strain tensor are represented by ϵ_{xx} , etc. Due to instrumental limitations the magnetic field $\mathbf{B}$ was rotatable only in a plane perpendicular to the external stress $\mathbf{P}_e$. In the available samples the external stress could be applied parallel to a [100], [111] or [011] direction. In the limit of an infinitely large external stress, diagonalisation of the Hamiltonian matrix gives the following analytical expressions for the effective g -value, g'_{eff} , in these three cases:

$$\mathbf{P}_e \parallel [100], \mathbf{B} \perp \mathbf{P}_e : g'_{\text{eff}} = 2g'_1 + 5g'_2 \quad (4)$$

$$\mathbf{P}_e \parallel [111], \mathbf{B} \perp \mathbf{P}_e : g'_{\text{eff}} = 2g'_1 + \frac{7}{2}g'_2 \quad (5)$$

$$\mathbf{P}_e \parallel [0\bar{1}1], \mathbf{B} \perp \mathbf{P}_e : g'_{\text{eff}} = (g'_{100} \cos^2 \theta_{100} + g'_{011} \cos^2 \theta_{011})^{1/2} \quad (6)$$

with

$$g'_{100} = g'_1 + \frac{13}{4}g'_2 + 2(g'_1 + \frac{7}{4}g'_2)/(1 + S^2)^{1/2} \quad (7)$$

$$g'_{011} = g'_1 + \frac{7}{4}g'_2 - [(g'_1 + \frac{13}{4}g'_2) + (g'_1 + \frac{7}{4}g'_2)S\sqrt{3}]/(1 + S^2)^{1/2}. \quad (8)$$

The relative influences of the shear and normal components of the strain are accounted for by the strain parameter S , which is defined as $S = -d'S_{44}/2b'(S_{11} - S_{12})$. Values for the compliance constants S_{11} , S_{12} and S_{44} are reported in the literature (McSkimin and Andreatch 1972, Grimsditch and Ramdas 1975): $S_{11} - S_{12} = 1.05 \times 10^{-12} \text{ Pa}^{-1}$, $S_{44} = 1.727 \times 10^{-12} \text{ Pa}^{-1}$.

In agreement with the above predictions the resonance is isotropic when $\mathbf{B}$ is rotated perpendicular to $\mathbf{P}_e$ for $\mathbf{P}_e \parallel [100]$ and $\mathbf{P}_e \parallel [111]$, with $g'_{\text{eff}} = -2.156 (\pm 0.012)$ and $g'_{\text{eff}} = -2.168 (\pm 0.023)$, respectively. A non-zero angular variation is observed when $\mathbf{P}_e \parallel [0\bar{1}1]$, with extremal values $g'_{100} = -2.399 (\pm 0.01)$ for $\mathbf{B} \parallel [100]$ and $g'_{011} = -1.901 (\pm 0.04)$ for $\mathbf{B} \parallel [011]$. An illustration is given in figure 1. The spin Hamiltonian constants

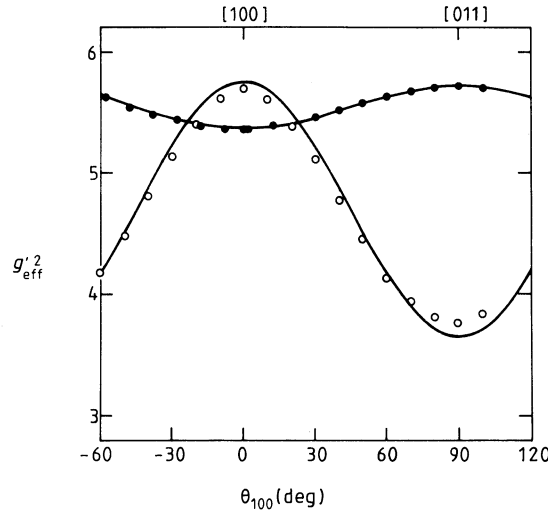


Figure 1. Angular dependence of the line position, represented by g'_{eff}^2 , for $P_e \parallel [011]$, B in the (011)-plane, for the resonances C:B ($P_e = 0.67$ GPa, $T = 1.4$ K) and Si:Ga ($P_e = 0.60$ GPa, $T = 1.4$ K). The experimental data points are: ●, Si:Ga; ○, C:B. The full curves are according to equation (6).

Table 1. The spin Hamiltonian parameters for EPR spectrum C-NL1, derived from the angular dependence of the line position at high external stress.

System	g'_1	g'_2	S	d'/b'
C:B	-1.10 ± 0.05	$+0.01 \pm 0.02$	-1.28 ± 0.04	$+1.55 \pm 0.05$
Si:Ga	-1.16 ± 0.01	-0.01 ± 0.01	-1.84 ± 0.02	$+2.88 \pm 0.03$

were derived yielding the results as specified in table 1. Since the formulae as applied are valid for infinitely large stress P_e , only the ratio d'/b' of the deformation potentials can be determined. The results obtained for the six samples behave in a consistent manner, although individual differences between the samples appear to be noticeable. To allow for these effects, the error margins quoted in table 1 are taken to be quite wide. The results indicate that $g'_2 \ll g'_1$. Therefore, to a good approximation one may put $g'_2 = 0$ and obtain the simplified expressions for (7) and (8):

$$g'_{100} = g'_1 [1 + 2/(1 + S^2)^{1/2}] \quad (9)$$

$$g'_{011} = g'_1 [1 - (1 + S\sqrt{3})/(1 + S^2)^{1/2}]. \quad (10)$$

This indicates that for $S = -\sqrt{3}$ also the angular variation for $B \perp P_e \parallel [011]$ will be isotropic. Depending on whether $S > -\sqrt{3}$ or $S < -\sqrt{3}$ the phase of the angular dependence will be opposite. To illustrate this point, results for Si:Ga (van Kemp and Ammerlaan 1985), contrasting with boron in diamond, are also included in figure 1 and table 1. The negative sign attached to g'_1 is not determined experimentally, but is based on theoretical considerations (Bir *et al* 1963).

In diamond more than sixty paramagnetic centres have so far been observed in EPR (Loubser and van Wijk 1978). With the exception of the resonance reported by Bourgoin *et al* (1972), all of these have g -tensor components close to $g = 2.0023$. This is the result of a general effective quenching of orbital contributions to the magnetic moment by the strong covalent crystal forces. The unusual g -factor established for resonance C-NL1 is therefore quite a significant piece of evidence as regards identification.

3. Strain broadening

The difficulty in observing shallow acceptor resonances is always related to line broadening due to strains. Obviously, strains do not lift the degeneracy of the Kramers doublet ground state. To first order the Zeeman splitting of the doublet will be strain independent, as indicated by the formulae (4) to (8). In higher order the g -factor of the Zeeman effect is affected by the strain. A quantitative confirmation of these notions is useful. Formulae (4) to (6) are applicable only for infinitely large external stress, by which the broadening action of internal stresses is entirely suppressed. To evaluate the effects of internal strain under more realistic conditions a formula was derived for the special case of $P_e \parallel [100]$ and $B \perp P_e$. The result obtained for the effective g -value is:

$$\begin{aligned}
 g'_{\text{eff}} = & +2g'_1 + 5g'_2 - \frac{3}{8}(g'_1 + \frac{5}{2}g'_2 - \frac{3}{4}g'_2 \cos 4\varphi_B) \\
 & \times [(g'_1 + \frac{7}{4}g'_2)\mu_B B/b'(S_{11} - S_{12})(P_e + P_i \cos \theta_P)]^2 \\
 & + \{-\frac{1}{8}S^2(g'_1{}^2 + \frac{19}{2}g'_1g'_2 + \frac{253}{16}g'_2{}^2)/(g'_1 + \frac{5}{2}g'_2) \\
 & + [\frac{1}{2}\sqrt{3}S(g'_1 + \frac{7}{4}g'_2) + \frac{3}{8}S^2(g'_1{}^2 + \frac{9}{2}g'_1g'_2 + \frac{89}{16}g'_2{}^2)/(g'_1 + \frac{5}{2}g'_2)] \\
 & \times \sin 2\varphi_P \sin 2\varphi_B \\
 & + [-\frac{3}{2}(g'_1 + \frac{7}{4}g'_2) + \frac{3}{8}S^2(g'_1{}^2 + \frac{5}{2}g'_1g'_2 + \frac{9}{16}g'_2{}^2)/(g'_1 + \frac{5}{2}g'_2)] \\
 & \times \cos 2\varphi_P \cos 2\varphi_B\}(P_i \sin \theta_P/P_e)^2. \quad (11)
 \end{aligned}$$

In this formula $P_i = |P_i|$ and $P_e = |P_e|$ represent the magnitude of the internal and external stresses, respectively. The angles θ_P , φ_P and φ_B are the polar angle (θ) with respect to $[100]$ and the azimuthal angle (φ) with reference to $[010]$ for the stress (P) and magnetic field (B). For the validity of expression (11) it is required that the energies $b'(S_{11} - S_{12})P_i$ and $d'S_{44}P_i$ associated with the internal strain are small compared with the splitting $b'(S_{11} - S_{12})P_e$ between the two doublets induced by the external stress. The Zeeman energies $g'_1\mu_B B$ and $g'_2\mu_B B$ also have to be small compared with this doublets separation. Expression (11) represents the perturbation in third order of the internal strains and the Zeeman effect on the doubly degenerate ground state.

The random nature of the internal stresses P_i may be described by distributions of magnitudes P_i and of directions θ_P and φ_P . The inclusion of these variable parameters in expression (11) will yield a distribution of values for g'_{eff} . The line broadening and shape effects may thus be estimated. Experimental observations on the linewidth for $P_e \parallel [100]$ and B in the (100)-plane are reproduced in figure 2. It is evident that the linewidth has a marked anisotropy.

For an understanding of this angular variation first the effect of the component of P_i parallel to $[100]$, i.e. parallel to P_e , is considered. In this case P_i merely adds to P_e . By

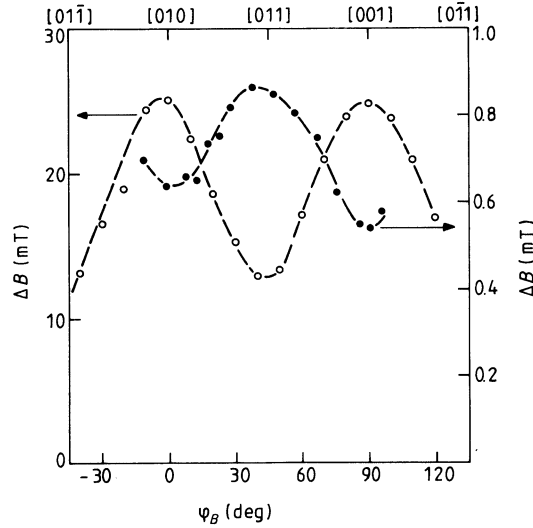


Figure 2. Angular dependence of the linewidth ΔB , for $P_e \parallel [100]$, B in the (100)-plane, for the resonances C:B ($P_e = 0.48$ GPa, $T = 1.4$ K) and Si:Ga ($P_e = 0.56$ GPa, $T = 1.4$ K). The broken curves merely connect the data points which are: $\circ$, C:B; $\bullet$, Si:Ga.

putting $\theta_p = 0^\circ$ in formula (11) and using $P_i \ll P_e$ the expression reduces to:

$$g'_{\text{eff}} = +2g'_1 + 5g'_2 - \frac{3}{8}(g'_1 + \frac{5}{2}g'_2 - \frac{3}{2}g'_2 \cos 4\varphi_B) \times [(g'_1 + \frac{7}{4}g'_2)\mu_B B/b'(S_{11} - S_{12})P_e]^2 (1 - 2P_i/P_e). \quad (12)$$

An angular variation of the linewidth with fourfold symmetry is predicted by formula (12). Although this is in agreement with the actual experimental observations, as shown in figure 2, the calculated effect is much too small. Next the components of P_i perpendicular to $P_e \parallel [100]$ are considered. Their effect is to produce a tilt of the total stress $P_e + P_i$ away from $[100]$. This has a larger effect as indicated by formula (11). For line broadening the relevant part of the formula are the terms on the five lower lines. To simplify matters the approximation $g'_2 = 0$, allowed since $g'_2 \ll g'_1$, is introduced, giving as a result for the P_i -dependent part:

$$g'_{\text{eff}} = +g'_1 [-\frac{1}{8}S^2 + (\frac{1}{2}\sqrt{3}S + \frac{3}{8}S^2) \sin 2\varphi_p \sin 2\varphi_B + (-\frac{3}{2} + \frac{3}{8}S^2) \cos 2\varphi_p \cos 2\varphi_B] (P_i/P_e)^2. \quad (13)$$

Depending on the values of S and φ_B this expression predicts lineshapes varying from rather symmetric to clearly asymmetric. The parameters put boron-doped diamond in the former case, in agreement with the observation of a single symmetric resonance. For Si:Ga both theory and experiment agree on asymmetric lineshapes. Again $S = -\sqrt{3}$ corresponds to isotropy; for this special value of S no angular variation of the linewidth is expected. For $S > -\sqrt{3}$ and $S < -\sqrt{3}$ the angular dependence of linewidth with B in the (100)-plane will be of opposite phase. The results for C:B and Si:Ga, as shown in figure 2, substantiate this conclusion.

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