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# Electron paramagnetic resonance studies of native defects in diamond

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Abstract. Isolated substitutional nitrogen, the impurity characterising type Ib diamond, is unstable against distortion along the  $\langle 111 \rangle$  directions. Because of the trigonal site symmetry a four-fold orientational degeneracy of the impurity in the diamond crystal exists. By applying uniaxial stress this degeneracy is lifted and the nitrogen impurities are aligned. This stress-induced ordering was quantitatively monitored by means of the C-P1 electron paramagnetic resonance spectrum associated with these centres. The stress-induced ordering was annealed using isothermal procedures. When compared to results reported earlier, in the present experiments a significantly smaller dependence upon the temperature was found for the reorientation of centres. The relaxation times, in the temperature range from 78 to 197 K, do not obey an Arrhenius law. It is concluded that reorientation of impurities occurs by thermally activated tunnelling through the potential barriers separating the distorted configurations. A quantitative analysis of this process is presented.

In type IIb natural diamond a new EPR spectrum was found. The spectrum, which we labelled C-NL1, is tentatively associated with holes bound to the acceptor boron. A discussion is given of the dependence of the resonance on stress, temperature, and magnetic field orientation. Values for the spin-Hamiltonian parameters are derived.

## 1. Introduction

Natural diamonds are generally contaminated by dissolved impurity atoms, impurity clusters, and mineral inclusions. Nuclear probe studies (Sellschop 1979) have revealed the presence of many impurity elements, but nitrogen is the predominant impurity in diamond crystals. When it is present to high concentration (>50 PPM) the diamond is classified as type I. If the nitrogen is mainly accommodated on isolated lattice sites as substitutional impurity atoms, the diamond is of type Ib. Type II crystals are relatively free from nitrogen. In rare cases the predominant impurity is boron on substitutional lattice sites; these crystals are called type IIb (Walker 1979).

Various experimental techniques have been applied to study the physical properties of defects in diamond. Among these, the method of electron paramagnetic resonance (EPR) has provided the spectroscopic identification of a large number, about 50, of smallsized defects. In particular EPR has revealed the point group symmetry of defects and has been crucial in establishing atomic models. Loubser and Van Wijk (1978) recently reviewed the situation.

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This paper reports research by EPR on two defects in diamond. The defects are single substitutional nitrogen in type Ib and single substitutional boron in type IIb diamond. As mentioned above these impurities are present in natural diamonds without any man-made irradiations or heat-treatments, and for this reason we refer to them as native impurities or defects.

## 2. Nitrogen in type Ib diamond

## 2.1. Electronic structure

Nitrogen is the most common impurity of natural diamonds. In the great majority of crystals it is present in the form of nitrogen atom pairs or larger clusters: these diamonds are classified as type Ia. In relatively few cases, however, the nitrogen impurity atoms are dispersed throughout the crystal and occupy isolated substitutional lattice sites: such diamonds are called type Ib. Nitrogen in type Ib diamond, being a substitutional group V impurity in an elemental covalent solid, behaves as a donor. It introduces a deep level in the diamond bandgap at about 2.2 eV below the conduction band edge (Vermeulen and Farrer 1975). In the neutral charge state the donor electron is bound to the nitrogen atom. Because of the odd number of defect electrons the centre is paramagnetic. The associated EPR spectrum is labelled C-P1. Detailed studies of the centre by EPR and electron-nuclear double resonance were carried out by Smith et al (1959b), Loubser and Du Preez (1965), and by Cook and Whiffen (1966). The localisation of the donor electron can be determined from the observed hyperfine interactions with the central nitrogen atom and with surrounding <sup>13</sup>C atoms on nearby lattice sites. From this analysis it is deduced that the unpaired donor electron primarily resides in a region between the nitrogen atom and one of the four nearest-neighbour carbon atoms. The donor electron occupies an antibonding orbital. In order to minimise energy the relevant carbon-nitrogen bond will increase its length relative to the normal nearest-neighbour distance. This implies a distortion of the donor centre from undistorted cubic (point group  $\overline{4}3m$ ) to trigonal (point group 3 m). The threefold symmetry axis is along a  $\langle 111 \rangle$  crystallographic direction. The impurity model is illustrated in figure 1.



Figure 1. Model of substitutional nitrogen in diamond in the distortion orientation labelled c. Also shown are axes defining the coordinate system and compressive stress P along the  $[0\bar{1}1]$  direction.

Since its first observation in EPR by Smith *et al* (1959b) nitrogen in diamond has been considered as a Jahn-Teller system (Sturge 1967, Stoneham 1975, 1979). In this view the donor electron, when the nitrogen is thought to be constrained to the tetrahedral substitutional site, occupies a triply degenerate  $T_2$  level in the bandgap. Calculations using extended Hückel theory by Messmer and Watkins (1970, 1973) and the CNDO method by Mainwood (1979) corroborate this conception. Coupling to the  $T_2$  vibrational mode lifts the orbital degeneracy by lowering the symmetry and a stable distorted state is achieved. The experimentally observed trigonal symmetry is understood as a manifestation of the Jahn-Teller instability. Though this interpretation seemed to be well established, recent theoretical progress questions its validity. It is believed that the nitrogen donor electron is in an  $A_1$  gap-level. Since this state is orbitally nondegenerate, no Jahn-Teller distortion is to be expected. Nevertheless, as pseudopotential calculations by Brand and Jaros (1977) have shown, the centre is unstable against distortion along  $\langle 111 \rangle$  axes. This instability is due to interlevel coupling by the distortion, rather than to the intralevel effect of the Jahn-Teller mechanism.

## 2.2. Orientational degeneracy

For a given lattice site of the nitrogen atom four different  $\langle 111 \rangle$  directions for distortion are possible. For purposes of reference the resulting orientations of the defect are labelled by a, b, c and d, as indicated in figure 1. If no strains or impurity interactions are present the four defect orientations are equivalent in energy; in equilibrium they will therefore occur with equal probability. The energy minima in the  $\langle 111 \rangle$  directions are separated by potential barriers. Figure 2 illustrates the defect potential for the energy minima a and b in the  $[\bar{1}11]$  and  $[11\bar{1}]$  directions, respectively, and the maximum energy in the saddlepoint ab in the [010] direction. Position x represents the nitrogen atom coordinate along a lowest-energy trajectory connecting the minima a and b.



Figure 2. The defect potential V(x) as a function of the position x of the nitrogen atom along a path connecting the two minima a and b. No stress present.

The energy equivalence of the different defect orientations is destroyed when uniaxial stress is applied to the crystal. A compressive stress in the  $[0\bar{1}1]$  direction, shown as an example in figure 1, will compress the bond lengths in the b and c directions, while those in the a and d directions are stretched. As a consequence the energy of nitrogen centres in the b and c orientations is raised relative to the energy of the a and d orientations. Under suitable conditions reorientations of defects will occur. At high temperature, thermally activated jumps across the potential barrier will take place at a rate determined by the ratio of the thermal energy kT and the barrier height V(0). With external stress present a new distribution, according to the Boltzmann law, of nitrogen centres over the four available orientations will eventually be established. For the case considered, the concentrations  $n_i$  (i = a, b, c, d) of the four orientations will satisfy  $n_a = n_d > n_b = n_c$ . This effect is known as stress-induced ordering, or alignment (Nowick and Heller 1963, 1965; Nowick and Berry 1972). The degree of alignment increases with the applied stress. For nitrogen in diamond this was reported by Ammerlaan and Burgemeister (1980).

#### 2.3. Electron paramagnetic resonance

The effect of defect alignment is experimentally observable in the C-P1 EPR spectrum associated with neutral nitrogen (Loubser and Van Wijk 1978). The main isotope of nitrogen, i.e. <sup>14</sup>N with a natural abundance of 99.63%, has nuclear spin I = 1. Therefore, the EPR signal of the centre is split by hyperfine interaction into three components, corresponding to  $m_I = -1$ , 0, and +1 successively. The  $\langle 111 \rangle$  axial character of the defect electron distribution is reflected in the angular dependence of the hyperfine interaction of the  $m_I = \pm 1$  components. In these components the resonances associated with the four defect orientations are usually well resolved. Therefore, EPR can be used to monitor the nitrogen orientations a, b, c and d individually. The amplitudes of the resonance lines are assumed to be proportional to the number of centres in the corresponding orientation. From the ratios of the resonance amplitudes the relative populations of the orientations are derived.

The experimental result is illustrated by figure 3. Spectra recorded with and without stress applied to the sample are both shown. The two resonances at low magnetic field belong to  $m_I = +1$ , the resonances at high field are for  $m_I = -1$ . The central part of the spectrum, consisting of a single isotropic line corresponding to  $m_I = 0$ , is omitted. This part of the spectrum does not reveal the defect reorientations since the contributions from all orientations coincide. In the particular case shown in figure 3 the magnetic field was parallel to [011]. For this high-symmetry direction the resonances from defect orientations a and d, and those of b and c, coincide pairwise. The experimental result shows that with [011] compressive stress present the resonances corresponding to the a and d orientations are enhanced compared to the random strain-free distribution, while those corresponding to the b and c orientations are reduced. This demonstrates the stress-induced ordering.

Actual EPR measurements were performed in our K band superheterodyne spectrometer tuned to dispersion and with the sample between liquid nitrogen and room temperature. Details of the equipment are described by Sieverts (1978).

#### 2.4. Reorientation time constants

When stress is removed any defect alignment previously induced will anneal. Reorientations of defects will restore the random distribution of centres over the four possible



Figure 3. EPR spectrum of neutral substitutional nitrogen in natural diamond with and without compressive uniaxial stress of 1.97 GPa along the  $[0\bar{1}1]$ direction. The spectra were measured at the microwave frequency 22.789 GHz, with magnetic field **B** parallel to [011], and with the sample at the temperature 295.3 K. The central part of the spectrum, corresponding to  $m_I = 0$ , is omitted.

orientations. This process was studied as a function of anneal time using an isothermal annealing procedure. Because of the low concentration of nitrogen atoms, less than  $10^{19}$  cm<sup>-3</sup>, they behave as isolated independent impurities. One therefore expects first-order kinetics for the anneal process. The alignment  $|n_i(t) - n_i(\infty)|$  as a function of time, t, given by  $|n_i(0) - n_i(\infty)| \exp(-t/\tau)$  is determined by a relaxation time constant,  $\tau$ . Results of these isothermal experiments are shown in figure 4 for two temperatures.



Figure 4. The anneal of the alignment  $|n_i(t) - n_i(\infty)|$ , induced by a stress of 1.67 GPa in the [111] direction, as a function of time at constant temperature.

The straight lines are least squares adjustments to the experimental data points. From the results it appears that the reorientation time constant depends upon the temperature in the anneal process. These isothermal anneal experiments were performed at 10 temperatures in the range from 78 to 197 K: the relaxation times,  $\tau$ , as a function of reciprocal temperature are represented in figure 5. Obviously, the curvature in the line





connecting experimental data points indicates a large deviation from Arrhenius-type behaviour. Apparently, the reorientation of nitrogen centres is not a simple activated process. This conclusion becomes even more evident when results from high-temperature experiments are included. At high temperatures the reorientation frequencies of the centres become comparable to frequency differences associated with the hyperfine splittings. This will result in line broadening. At still higher temperatures, when reorientation frequencies near 1 GHz are much larger than those corresponding to differences in the hyperfine splitting, one resonance is observed at the average position of the previously separated components. Such studies of dynamical effects were carried out by Loubser and Van Ryneveld (1967) and by Shul'man *et al* (1967). These effects can be described in a way analogous to the hindered rotation of molecular complexes. Using the theory developed by Gutowski and Pake (1950) the reorientation rate can be obtained from an analysis of the observed lineshapes and positions. Both these high-temperature results and the present low-temperature results for the reorientation frequency are included in figure 6.

## 2.5. Tunnelling process

The high-temperature results were given by the authors as an Arrhenius-type expression  $v = v_0 \exp \left[-V(0)/kT\right]$  with an activation energy V(0), as given in table 1, of 0.7 and 0.76 eV. This is consistent with the physical notion of a thermally activated reorientation process over a potential barrier with that height. On extrapolating these results to the low-temperature region between 78 and 197 K a much lower reorientation rate is predicted than is actually observed. At low temperature the available thermal energy is insufficient



Figure 6. Experimentally observed reorientation frequencies, both from the dynamic process at high temperatures and from the static process at low temperatures, for nitrogen in diamond, compared to calculated values. See text for details of this figure.

ν <sub>o</sub>	V(0) (eV) 0.7 0.76 0.70	Temperature range	Reference	
(s <sup>-1</sup> )		(K)		
$     \begin{array}{r} 10^{13} \\       4 \times 10^{12} \\       1.3 \times 10^{13}     \end{array} $		600-750 600-1230 78-1230	Shul'man <i>et al</i> (1967) Loubser and Van Ryneveld (1967) This work	

 Table 1. Relaxation time parameters of substitutional nitrogen in diamond.

to surmount the potential barrier. The only possibility left is reorientation by quantum mechanical tunnelling through the barrier.

In the semiclassical WKB approximation the tunnelling frequency  $v_{t,n}$  is calculated as the product of an incidence frequency and a transmission factor for the barrier V(x)along the lowest-energy trajectory. For a particle with mass *m* and energy  $W_n$  it is given by (Townes and Schawlow 1955, Landau and Lifshitz 1965):

$$\nu_{t,n} = (\nu_0/\pi) \exp\left((-1/\hbar) \int_{V(x) > W_n} \{2m[V(x) - W_n]\}^{1/2} dx\right).$$

Assuming a parabolic potential barrier, as represented in figure 2, the tunnelling expression can be evaluated analytically. For a barrier of that shape the oscillation frequency,  $\nu_0$ , the barrier width, L, and the maximum barrier height, V(0), are related by  $\pi^2 m \nu_0^2 L^2 = 4V(0)$ . The reduced mass, m, is taken equal to the nitrogen atom mass. The integral must be evaluated over the region of tunnelling, between  $x = -x_n/2$  and  $x = +x_n/2$ , where the

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energy of the particle is less than the local barrier height. In an excited state with *n* vibrational quanta absorbed, the particle energy  $W_n$  equals  $(n + \frac{1}{2})hv_0$ . According to Boltzmann statistics the excited levels are occupied to the fraction  $f_n = f_0 \exp[(W_0 - W_n)/kT]$  $= f_0 \exp(-nhv_0/kT)$ . The normalisation condition  $\sum_n f_n = 1$  determines  $f_0$ . In this analysis we are taking into account transitions between the ground states  $W_0$  in the potential wells, as well as tunnelling transitions between excited states. The total frequency,  $v_t$ , is found by summation over all states with their corresponding occupancy factor. By solving rate equations one finds  $v_t = 4 \sum_n f_n v_{n,t}$ . The factor 4 emerges from the fact that four defect orientations exist. Thus, for a parabolic potential barrier, characterised by its two parameters, maximum height V(0) and oscillation frequency  $v_0$ , the tunnel frequency  $v_t$ can be calculated.

The results of such a calculation, with the parameters as given in table 1, are presented in figure 6. The reorientation frequencies between the single excited states are represented by the light curves labelled with the level index n. The total reorientation frequency, obtained by addition, is given by the heavy full curve extending from the lowest to the highest temperature. For comparison the experimental data are also included in figure 6. The short straight lines in the upper left corner represent the high-temperature results of Loubser and Van Ryneveld (1967) and Shul'man et al (1967). Our results are marked with the data points at the 10 measurement temperatures. With the simple set of two parameters a good general agreement between calculated and measured frequencies is found over the whole wide temperature range. We therefore conclude that the concept of tunnelling is adequate to explain the experimentally observed reorientation rates. At low temperature the dominant reorientation mechanism for the nitrogen centres is tunnelling through the potential barriers separating the distorted configurations. At high temperature, reorientations occur by thermally activated jumps over these barriers. For intermediate temperatures a mixed process of thermal activation and tunnelling between excited states is active.

## 2.6. Discussion

The calculated reorientation frequency in the tunnelling regime, i.e. for level n = 0 at low temperature, depends very sensitively on the parameter  $v_0$ . From the low-temperature match to the experimental data therefore an accurate determination of  $v_0$ , given in table 1, is obtained. However, the value obtained for  $v_0$  depends on the shape of the potential barrier, which we rather arbitrarily assumed to be parabolic. For any reasonable different choice of barrier shape a somewhat different value for  $v_0$  would have been obtained. On the other hand, values for the pre-exponential factor  $v_0$  derived from measurements in the thermally activated regime are often inaccurate. Usually these experiments are carried out in a limited temperature region and small errors in the activation energy are accompanied by large uncertainties in the pre-exponential factor. Our value for  $v_0$ corresponds to a vibration with wavelength  $\lambda = 23 \ \mu m$ . The experimentally observed optical absorptions in the infrared due to nitrogen in diamond are between  $\lambda = 7$  and 10  $\mu m$ (Dyer *et al* 1965, Chrenko *et al* 1971, Davies 1977).

Using the relation  $\pi^2 m \nu_0^2 L^2 = 4V(0)$ , valid for the parabolic barrier of figure 2, and our parameters of table 1, we calculate L = 0.11 nm. If we take the path of reorientation as part of a circle from one  $\langle 111 \rangle$  distorted orientation to a second  $\langle 111 \rangle$  orientation,

the barrier width L is related to the distortion magnitude  $\Delta d$  by  $L = 1.91 \Delta d$ . Thus we find a distortion of the nitrogen atom away from its tetrahedral substitutional site by  $\Delta d = 0.056$  nm. Compared to the carbon atom nearest-neighbour distance, d = 0.154 nm, this represents a distortion by 36%. Previous estimates of this distortion amount to 26% (Messmer and Watkins 1970, 1973), 5–10% (Mainwood 1979), up to 32% (Stoneham 1979), and 5–10% (Smith *et al* 1959b). Though more unanimity in this figure is desirable, it can safely be concluded from these data that the distortion of the nitrogen centre is large.

## 3. Boron in type IIb diamond

#### 3.1. Semiconducting diamond

Some 30 years ago Custers (1952, 1954) recognised that a very small proportion of type II diamonds exhibit special optical properties. Whereas diamonds are usually perfect insulators these particular specimens are extrinsic p-type semiconductors at room temperature. They were classified as type IIb. Initially aluminium was thought to be the acceptor impurity. However, ample evidence has now shown that the acceptor centre is substitutional boron (Lightowlers and Collins 1976, Collins and Lightowlers 1979). The boron impurity introduces a shallow gap-level at about 0.37 eV above the valence band edge (Williams *et al* 1970, Bourgoin *et al* 1979). The acceptor state is described by the effective mass theory (Kohn 1957, Rauch 1962). In the past attempts have been made to observe the paramagnetic resonance from free valence band holes or from holes bound to the acceptor. Though some positive results were reported (Smith *et al* 1959a, Bell and Leivo 1967, Bourgoin *et al* 1972) it remained difficult to provide conclusive evidence that the observed resonances were really associated with the acceptor.

Recently we have observed a resonance which we tentatively ascribe to acceptor-bound holes. For reference purposes the new resonance spectrum is labelled C-NL1. Some of its general characteristics are described in this section; the stress, temperature, and magnetic field dependence are discussed in the remainder of this paragraph. The resonance was detected in six samples cut from four type IIb stones. The EPR spectrum consists of one line of nearly gaussian shape without any resolved structure. Using our K band spectrometer the resonance field was in the range from 650 to 900 mT. Depending on conditions of the measurement, i.e. stress, temperature and magnetic field direction, the full width at half maximum is between 5 and 50 mT. In best cases the signal-to-noise ratio is as high as 1000.

#### 3.2. Stress dependence

Without exception in these six samples the resonance is only observable when stress, in our case uniaxial compressive stress, is applied to the crystal. Typically, starting from the nonstressed situation and increasing the stress the resonance appears rather suddenly at some value. At higher values of stress the increase of signal levels off and sometimes a slight decrease sets in. In some cases the saturation stress was not achieved. A characteristic example is shown in figure 7.

This stress dependence of the resonance is similar to the behaviour of acceptor resonances in silicon as reported and discussed by Feher *et al* (1960). In the effective mass theoretical approach (Kohn 1957) the acceptor ground state is fourfold degenerate



Figure 7. The amplitude of C-NL1 resonance as a function of compressive uniaxial stress parallel to the [100] direction. Measurements were made with the magnetic field parallel to [011] and with the sample at the temperature 4.2 K.

due to the degeneracy of the valence band edge. An effective spin J = 3/2 is assigned to it. Random internal strains split the ground state into two Kramers doublets. With a magnetic field applied six transitions are possible, but broadening by the random strain and short spin-lattice relaxation times make these resonances difficult to observe. With large external stress only the transition in the lowest-lying Kramers doublet will remain possible. To first order the g value of this transition is strain independent. Since silicon and diamond have the same valence band structure this applies to both materials. The required external strain must be sufficient to overcome the level splittings by the internal strains. This value may therefore be sample dependent, as is actually observed. Only recently it became possible to grow silicon crystals of such high crystalline perfection that the six acceptor state EPR transitions were observable at zero external stress (Neubrand 1978).

## 3.3. Temperature dependence

For observation of the resonance, temperatures in the liquid helium range are required. A typical example is given in figure 8. Again this behaviour is similar to that of acceptor resonances in silicon (Feher *et al* 1960, Neubrand 1978). It is a distinctive feature of the



Figure 8. The amplitude of the C-NL1 resonance as a function of sample temperature. Measurements were made with a uniaxial compressive stress of 0.68 GPa in the  $[0\bar{1}1]$  direction and with the magnetic field parallel to [100].

resonance. The necessity to operate at low temperature indicates strong spin-lattice coupling. This is related to the orbital angular momentum inherent in the J = 3/2 acceptor ground state. It contrasts sharply to other centres in diamond which have their orbital angular momentum quenched by crystal forces. For these centres the associated resonances are observable near room temperature and have spin-only g values close to the free electron g value 2.0023.

## 3.4. Magnetic field dependence

To obtain the spin-Hamiltonian parameters of the C-NL1 spectrum the angular dependence of the resonance field  $\mathbf{B}_{res}$  was studied. Because of instrumental limitations only measurements with the magnetic field  $\mathbf{B}$  in a plane perpendicular to the uniaxial stress  $\mathbf{P}$  were made. For  $\mathbf{B} \perp \mathbf{P} \parallel [100]$  no angular variation was observed. The isotropic effective g value,  $g_{eff} \equiv h\nu/\mu_{\rm B}\mathbf{B}_{res}$ , was found to be  $2.156 \pm 0.012$ . Similarly, for  $\mathbf{P} \parallel [111] \perp \mathbf{B}$ the resonance was isotropic, with  $g_{eff} = 2.168 \pm 0.023$ . Real angular dependence as shown in figure 9 was found for  $\mathbf{P} \parallel [0\overline{1}1]$ . A curve can be drawn through the experimental data points using the expression  $g_{eff}^2 = g_{100]}^2 \cos^2 \theta + g_{[011]}^2 \sin^2 \theta$ . For a reasonable fit suitable





values are  $g_{100]}^2 = 5.75 \pm 0.05$  and  $g_{011]}^2 = 3.7 \pm 0.1$ . The C-NL1 resonances observed in all samples fit into the above framework. Slight dependences of the resonance field upon the magnitude of the stress and upon the temperature cause large error limits.

The Hamiltonian  $\mathscr{H}$  appropriate to describe acceptors in uniform strain fields was given by Neubrand (1978). It consists of the magnetic-field-dependent part  $\mathscr{H}_{B}$  (Luttinger 1956) and the strain-dependent part  $\mathscr{H}_{\epsilon}$  (Kleiner and Roth 1959).

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_{B} + \mathcal{H}_{\epsilon} \\ \mathcal{H}_{B} &= g_{1}^{\prime} \mu_{B} \left( B_{x} J_{x} + B_{y} J_{y} + B_{z} J_{z} \right) + g_{2}^{\prime} \mu_{B} \left( B_{x} J_{x}^{3} + B_{y} J_{y}^{3} + B_{z} J_{z}^{3} \right) \\ \mathcal{H}_{\epsilon} &= b^{\prime} (\epsilon_{xx} J_{x}^{2} + \epsilon_{yy} J_{y}^{2} + \epsilon_{zz} J_{z}^{2}) \\ &+ (2/\sqrt{3}) d^{\prime} (\epsilon_{xy} \{J_{x} J_{y}\} + \epsilon_{yz} \{J_{y} J_{z}\} + \epsilon_{zx} \{J_{z} J_{x}\}) \end{aligned}$$

In this Hamiltonian  $\epsilon_{xx}$ , etc, are the strain tensor elements, and  $J_x J_y$  is the notation for the symmetrised Hermitian product  $\frac{1}{2}(J_x J_y + J_y J_x)$ . There are four spin-Hamiltonian constants to be determined. Two of these,  $g'_1$  and  $g'_2$ , are the g factors of the Zeeman splitting. The two deformation potentials b' and d' are related to the normal and shear components of the strain, respectively. These parameters are primed as they apply to bound holes. Analytical expressions for the eigenvalues of the Hamiltonian  $\mathcal{H}$  can be derived for the limit of high external stress. The effective g values of the transitions are then given as follows:

$$\mathbf{P} \parallel [100], \quad g_{\text{eff},\perp} = 2g'_1 + 5g'_2$$
  

$$\mathbf{P} \parallel [111], \quad g_{\text{eff},\perp} = 2g'_1 + (7/2)g'_2$$
  

$$\mathbf{P} \parallel [0\bar{1}1], \quad g^2_{\text{eff},\perp} = g^2_{[100]}\cos^2\theta + g^2_{[011]}\sin^2\theta$$

where

$$\begin{split} g^2_{[100]} &= [g'_1 + (13/4)g'_2] + 2[g'_1 + (7/4)g'_2]/(1 + S^2)^{1/2} \\ g^2_{[011]} &= (1 + S^2)^{-1} \left\{ (5/2) [g'_1{}^2 + (41/10)g'_1g'_2 + (73/16)g'_2{}^2] (1 + S^2) \\ &- 2[g'_2{}^2 + 5g'_1g'_2 + (91/16)g'_2{}^2] (1 + S^2)^{1/2} \\ &- (2\sqrt{3}) [g'_1{}^2 + (7/2)g'_1g'_2 + (49/16)g'_2{}^2] (1 + S^2)^{1/2}S \\ &- (1/2) [g'_1{}^2 + (1/2)g'_1g'_2 - (71/16)g'_2{}^2] \\ &+ (2\sqrt{3}) [g'_1{}^2 + 5g'_1g'_2 + (91/16)g'_2{}^2] S \\ &+ (3/2) [g'_1{}^2 + (5/2)g'_1g'_2 + (9/16)g'_2{}^2] S^2 \right\}. \end{split}$$

The parameter S, defined as  $S = -d'(c_{11} - c_{12})/2b'c_{44}$ , is related to  $\gamma$ , introduced by Pikus and Bir (1961), by  $S\gamma = -1$ . The elastic moduli  $c_{11}$ ,  $c_{12}$  and  $c_{44}$  are given by McSkimin and Andreatch (1972) and by the Grimsditch and Ramdas (1975).

Inspection of the formulae shows that only the ratio of the deformation potential constants can be determined by our experiments. The resulting values for the spin-Hamiltonian constants are given in table 2. For comparison, results for boron in silicon are included. The sign of  $g'_1$  is chosen negative according to Bir *et al* (1963). The upper line for silicon presents the *g* values obtained by Bir *et al* (1963) from an analysis of results under stress by Feher *et al* (1960). The lower line gives the results from Neubrand (1978) for the zero-stress experiment. Our results for diamond are to be considered as provisional since they are based on a small number of experiments and approximate methods of analysis. Nevertheless, the similarity between the diamond and silicon parameters supports the identification of the C-NL1 spectrum with holes bound to boron.

Table 2. Spin-Hamiltonian parameters of EPR spectrum C-NL1, and those of boron in silicon.

System	g'1	g'2	d'/b'	Reference
С:В	$-1.10 \pm 0.05$	$+0.01 \pm 0.02$	1.60	This work
Si:B	-1.21	+0.002		Bir et al (1963)
	$-1.071 \pm 0.004$	$-0.031 \pm 0.001$	2.61	Neubrand (1978)

## 4. Conclusions

At low temperature the reorientations of substitutional nitrogen atoms in type Ib diamond occur predominantly by tunnelling. In type IIb diamond an electron paramagnetic resonance spectrum is observed which is ascribed to holes bound to the substitutional acceptor boron.

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