AN EXPERIMENTAL STUDY OF
ELECTRON SPIN RESONANCE
IN SYNTHETIC DIAMOND

A thesis submitted to the University of Warwick
for the degree of Doctor of Philosophy
by Brian R. Angel, M.Sc.

The work described in this thesis was carried out in the School of Physics at the University of Warwick and in the Department of Physics at the College of Technology, Plymouth, during the period from September, 1965, to September, 1968.

This is to certify that, unless otherwise stated, the results presented here were obtained by B. R. Angel under my supervision.

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CONTENTS

ABSTRACT

This thesis is divided into five chapters. The first chapter begins with a discussion of the basic principles of electron spin resonance and concludes with a description of the theoretical interpretation of electron spin resonance spectra in terms of the Spin Hamiltonian.

The first part of the second chapter is a general discussion of the physical properties of diamond and includes reasons for the classification of diamond into various types. The second part of the chapter is devoted to a brief historical survey of the developments in the production of synthetic diamond. The final part of the chapter is an outline of the experiments which have led to the identification of nitrogen as a major impurity in natural and synthetic diamond.

The third chapter combines and describes some of the experimental studies which have been made on diamond using the technique of electron spin resonance. Particular emphasis is placed on theories which have been put forward to explain the electron spin resonance signals associated with substitutional nitrogen in natural diamond. Electron spin resonance associated with synthetic diamond is discussed under a separate heading.

The fourth chapter is devoted entirely to a description of the experiments carried out in this work and is concerned mainly with electron spin resonance from five different types of

commercially available synthetic diamond. Those resonances, which are due to the nitrogen and ferromagnetic impurities, are shown to depend markedly on the nature of the diamond as well as its temperature. Experiments on samples which have been treated either by heating or crushing or by a combination of both, are also described. In addition, results are presented which were obtained from visual examination of samples by optical microscopy and which supplement the information obtained from the electron spin resonance survey. Some of the results are discussed as they are presented. The chapter concludes with a summary of the main features of interest which were observed.

In the final chapter the results from a number of the experiments are discussed and correlated in an attempt to present a more complete description of the experimental observations. Some of the ways in which the electron resonance spectrum due to nitrogen impurity in synthetic diamond is affected by the conditions existing in the material are established. The nature of the ferromagnetic additive, the concentration of dispersed nitrogen, the formation of free radicals by carbonisation or mechanical damage, ^{13}C, ^{15}N and quadrapole effects and acceptor impurities such as aluminium or boron are all factors which it is suggested are important. In addition, a mechanism is proposed to explain the disappearance of the ferromagnetic resonance in heated synthetic diamond which is observed in conjunction with a narrowing of the line width from the nitrogen resonance. Finally, some practical applications of the results are discussed and future experimental work is suggested.

Copies of papers published by the author are bound into the thesis. An additional paper is included which was published by the author and his supervisor immediately preceding this work and which is directly related to it.

1. THE PRINCIPLES OF ELECTRON SPIN RESONANCE

Many of the results which are to be discussed have been obtained by the technique of electron spin resonance. For this reason the basic principles of this subject are presented together with a rather more detailed account of those interactions which are of importance in interpreting the subsequent experimental results. More generalised and detailed discussion of the theories of electron spin resonance are covered extensively in the available literature.[1-8]

1.1. The Resonance Condition

If an atomic system, which possesses a resultant spin angular momentum and, therefore, a magnetic moment, is placed in a magnetic field, the spin degeneracy is lifted and a splitting of the energy levels is produced. Transitions between the energy levels created by the magnetic field may then be induced by an oscillating magnetic field of suitable frequency and symmetry.

The simplest system consists of a single unpaired electron with an angular momentum of $sh/2\pi$ $(s = \pm\frac{1}{2})$ and a magnetic moment of $2\sqrt{s(s+1)}\beta$ where h is Planck's constant and β is the Bohr magneton. The magnetic field produces two levels with an energy separation $g\beta H$ where g is the spectroscopic splitting factor and H is the magnitude of the applied steady magnetic field. The two energy levels correspond to the electron precessing about the positive and negative directions of H. If an oscillating magnetic field of frequency ν is applied in a plane normal to the steady magnetic field, transitions can be induced between the levels when $h\nu = g\beta H$. For the single electron system the spin of the electron provides the only contribution to the angular momentum; g is equal to 2.0023 and the resonance condition is satisfied for a steady magnetic field of 3,400 Oe when ν is 9,500 M Hz. ν occurs, therefore, in the microwave region of the electromagnetic spectrum for magnetic fields above about 1,000 Oe.

In a sample which contains many unpaired electron systems, the thermal equilibrium distribution of the unpaired electrons between the energy levels created by the applied magnetic field is described by the Maxwell-Boltzmann expression. For the group of single electron systems, the ratio of the number of unpaired electrons in the higher energy state n_2 to the number in the lower energy state n_1 is given by $\frac{n_2}{n_1} = e^{-\left(\frac{h\nu}{kT}\right)}$ where k is Boltzmann's constant and T is the absolute temperature. At all but the lowest temperatures, $h\nu \ll kT$ and to a good approximation $\Delta n = \frac{n_0 h\nu}{2kT}$ where $\Delta n = n_1 - n_2$ and $n_0 = n_1 + n_2$. Transitions between the two energy levels are induced by the applied radiation and occur with equal probability in either direction. However, as the number changing state per second is proportional to the probability per second of a change and to the population of the state, there is a net migration of electron spins from the lower to the higher level.

It follows that if a sufficiently strong mechanism is available which will enable electrons in the higher level to lose energy and to relax to the lower level, the population difference will be maintained and a continuous absorption of power from the oscillating magnetic field will take place. A steady state resonance can be observed in this case if the level of the oscillating field at the sample is monitored. If the relaxation mechanism does not exist n_1 will become equal to n_2, the system will be saturated and a steady state resonance will not occur. Partial saturation will occur when the relaxation mechanism is present but is weak. A decrease in the amplitude of the central part of the resonance will then be observed together with an increase in the recorded line width.

1.2. Spin-Lattice Relaxation

Interactions between the electron spins and their surroundings can cause the spin orientation to change while the energy difference is transferred to the lattice. They can, therefore, provide the relaxation mechanism which is necessary to maintain the equilibrium population difference. Kronig[9] suggested that, for the case of a paramagnetic ion in particular, lattice phonons produce a vibration of the crystalline electric field at the ion which can modulate the energy levels of the ion. Although the phonons cannot interact directly with the spin but only with the orbital motion, the interaction can take place through spin-orbit coupling in which there is magnetic interaction between the spin and its orbital motion.

The spins can exchange energy with the phonons via the above mechanism in two ways. In the direct process a whole quantum corresponding to the energy level difference is exchanged directly with a phonon of the same frequency. In the indirect or Raman process energy is transferred by the inelastic scattering of a phonon when the spin changes orientation. Kronig[9] has derived expressions for the relaxation times which might be expected from these two mechanisms. For $s = \frac{1}{2}$ his expressions are of the form:

Direct Process $T_1 = \dfrac{10^4 \Delta^4}{\lambda^2 H^4 T}$ sec.

Indirect or Raman Process $T_1 = \dfrac{10^4 \Delta^6}{\lambda^2 H^2 T^7}$ sec.

where Δ = separation between the ground state and the next highest orbital level (in cm^{-1}), λ = spin-orbit coupling coefficient, T = absolute temperature. T_1 is the inverse of the transition rate and is a measure of the time taken for the interaction to restore thermal equilibrium. The broadening of the energy levels, $\Delta\nu$, produced by the interaction is of the order of $\frac{1}{T_1}$. The equations describing both mechanisms show that ions with small values of Δ should have wide absorption lines. A reduction in temperature will be necessary to increase the relaxation time and thus reduce the line width. A typical value of the cut-off frequency for the phonon spectrum of a crystal is 10^{13} Hz and at frequencies of 10^{10} Hz (X-Band microwave region) the intensity of the phonons is very weak. Since the higher frequency modes are more plentiful but are only excited at high temperatures it follows that the indirect process is more important than the direct process at high temperatures whereas at low temperatures the reverse is true.

1.3. Spin-Spin Relaxation

Additional relaxation processes, which occur through interactions between the spins, have the effect of varying the relative energies of the spin levels and can produce a line broadening (Dipolar broadening). The theory of the effect has been studied in detail by Van Vleck[10] and by Pryce and Stevens.[11]

If each ion is regarded as a dipole precessing in the applied magnetic field, (Larmor precession) its component in the direction of the applied field will have a steady value which will produce an extra magnetic field at the neighbouring paramagnetic ions. The total field value at any one ion is altered slightly and the energy levels are consequently shifted. This effect varies with the direction of the applied magnetic field and the contribution of each neighbouring dipole will have an angular dependence of the form $(1 - 3\cos^2\theta)$ where θ is the angle between the line joining the dipoles and the direction of the applied field.

The rotating component of the precession can also cause line broadening by inducing transitions between spins of the same

Larmor frequency thereby reducing the lifetimes of their energy states.

Line broadening caused by a relaxation process which limits the lifetime of an energy state is an example of homogeneous broadening. Homogeneous broadening applies only to line broadening caused by interactions within the spin system where a single relaxation process is involved. It is possible to saturate the whole of a homogeneously broadened line by applying an oscillating field of sufficient intensity anywhere within the frequency range determined by the line width. When saturation occurs the effect is to reduce the expected power absorption and to alter the line shape. (Section 1.1)

Inhomogeneously broadened lines occur either due to inhomogeneities in the megnetic field such as those produced by the steady field components of the dipolar interaction or by interactions which vary with a period which is long compared with the time of a spin transition. The lime shape in this case is produced by a distribution of individual lines each with their own characteristic relaxation times. Provided, therefore, that interactions involving cross relaxation processes (Section 1.5) are relatively weak, any additional broadening which occurs due to saturation takes place for the individual lines separately. The line shape and width does not change on saturation but the expected power absorption falls in the same proportion across the whole of the line shape.

From the foregoing discussion it is clear that dipolar broadening results from two line broadening effects, one of which is an inhomogeneous effect due to the steady field components and the other is a homogeneous effect due to the rotating field components. For interacting dipoles which are not identical it is possible that the gyromagnetic ratios of the nuclei involved may differ to such an extent that dipolar broadening is caused mainly by the inhomogeneous broadening effect.

Spin-spin or dipolar interaction is characterised by a relaxation time T_2 in a similar manner to spin lattice relaxation. In contrast to the spin lattice interaction, however, the spin-spin interaction is not temperature dependent. Moreover, spin-spin interaction falls off rapidly with increasing distance between the ions. If on the other hand the spins are brought closer together dipolar broadening does not necessarily increase as might be expected.

1.4. Exchange Interaction

If the ions are sufficiently close together the wave functions describing the spin states will overlap and a simple vector summation of the magnetic fields of the dipoles at neighbouring lattice sites does not lead to a satisfactory description of the behaviour of the system. It is necessary to consider interactions between a large number of strongly interacting ions. Van Vleck[10] studied this problem in 1948 and showed that the spins are coupled by exchange forces and the effect can modify the line width considerably.

When the neighbouring ions are similar exchange interaction narrows the observed line width at half-height and broadens it in the wings. In theoretical terms this means that the second moment of the lime shape remains constant but the fourth moment changes.[10] For dissimilar ions two different transitions may be brought together and one broader line may be produced. Exchange interaction is found in many undiluted paramagnetic salts and the expected dipolar broadening is often reduced by a large factor. An effect of this kind is observed in diamond with the resonance from high concentrations of dispersed nitrogen. (Section 3.3.3)

1.5. Cross Relaxation

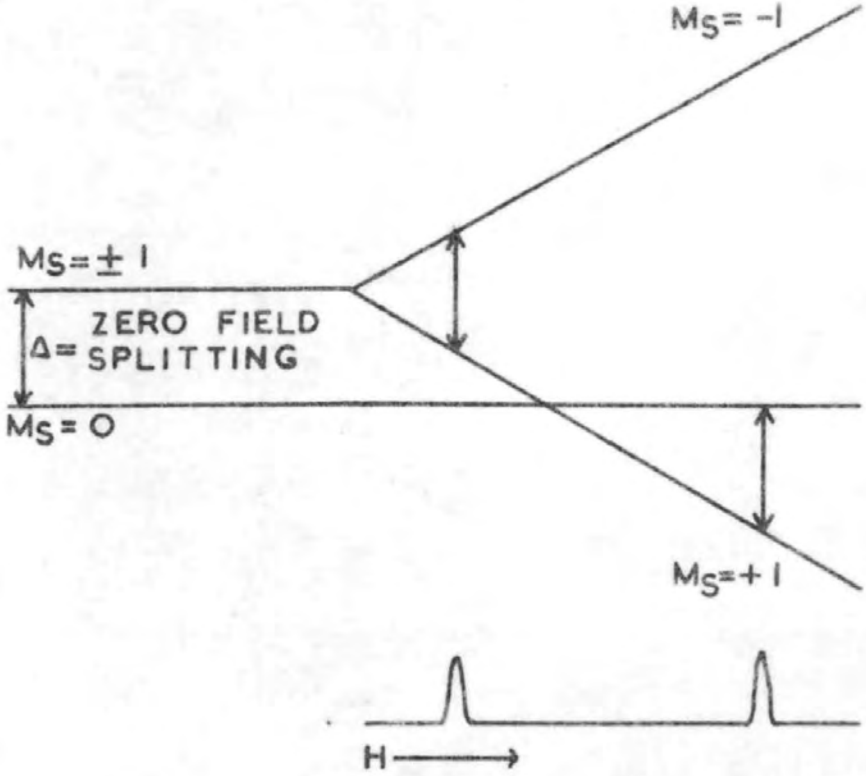
Results from past experimental studies have shown that it is not always possible to interpret magnetic resonance spectra satisfactorily with the aid of the relaxation processes so far described. Spin-lattice relaxation describes a mechanism whereby a spin system remains in thermal equilibrium with the lattice. In contrast, dipolar interaction describes how thermal equilibrium between the spins is achieved. It follows, therefore, that if spin lattice relaxation is reduced by lowering the temperature of the system so that $T_1 > T_2$, the equilibrium between the spins is obtained through dipolar interaction rather than through the lattice and the line width of a resonance is determined by the dipolar interaction. For many systems, in particular those in which adjacent resonance lines partially overlap, dipolar broadening does not provide a logical explanation of experimentally observed line widths. For example, the line width ΔH due to dipolar broadening is given approximately by the expression $\Delta H \sim N x 10^{-19}$ Oe where N is the number of unpaired electron spins per cc.[12] In many instances, including the case of diamond, the value of N is not high enough to account for observed line widths. Consequently, additional relaxation mechanisms have been proposed and investigated.[13]

For equal spacing of the energy levels of a spin system a Boltzmann distribution over the different spin levels is established in a time of the order of T_2. For unequal spacing the establishment of a Boltzmann distribution occurs relatively slowly[14, 15] and, therefore, the spins come into equilibrium with the lattice first with their respective relaxation times T_1. In the intermediate region of approximately equal spacing different parts of the spin system may come into internal equilibrium in an intermediate time T_{21} which is called the cross-relaxation time. Bloembergen et al[13] have shown that multiple flip-flop processes of neighbouring ions in which the Zeeman energy is almost conserved are responsible for this effect and the small balance of energy is taken up by the dipolar interaction. It is worth noting here that it is the higher order terms C, D, E, and F of the dipolar Spin Hamiltonian (Sections 1.7 and 1.11) which account for the multiple spin flip processes.

Cross relaxation effects have been observed by Sorokin et al[16] for the nitrogen centre in natural diamond. With the aid of a suitably designed microwave circuit they were able to disturb the distribution of electrons in the energy levels associated with one resonance line and at the same time to measure changes in the intensities of the remaining lines as the system returned to equilibrium via the cross relaxation processes. In this work similar effects were observed in one synthetic diamond. They are discussed in more detail in Section 4.13.3.

1.6. Fine Structure

The theory described at the beginning of this chapter referred to a single unpaired electron with a half integral spin. In a system, which might be for example a paramagnetic ion, where the ground state is an orbital singlet with a spin multiplicity of more than two ($S \geqslant 1$), the degeneracy of the spin levels is often lifted even in the absence of an applied magnetic field. Such a zero-field splitting is illustrated in Fig. 1 for the case of an ion with $S = 1$ in a crystal field with an axial component. The axial field splits the triplet into a singlet and doublet. The application of a magnetic field parallel to the axis of symmetry causes the



ZERO FIELD SPLITTING FOR AN ION WITH S=1
IN A CRYSTAL FIELD WITH AXIAL SYMMETRY

FIG.1

levels to diverge linearly with slopes proportional to the values of M_S. Allowed transitions between the levels are governed by the selection rule $\Delta M_S = \pm 1$ when the oscillating magnetic field is perpendicular to the applied magnetic field. Since these transitions occur at different field values the spectrum will have a fine structure consisting of 2S lines. In certain situations forbidden lines corresponding to $\Delta M_S = \pm 2$ can be observed.

When the zero field splitting is large, the application of a convenient magnetic field may never bring the levels close enough for transitions to be induced by an oscillating magnetic field in the microwave region. However, a theorem due to Kramers[17] states that if there is an odd number of unpaired electrons in the ion, then no electric field can completely remove the degeneracy and the bottom level is always at least two-fold degenerate in spin. Electron spin resonance is, therefore, always theoretically possible in such cases.

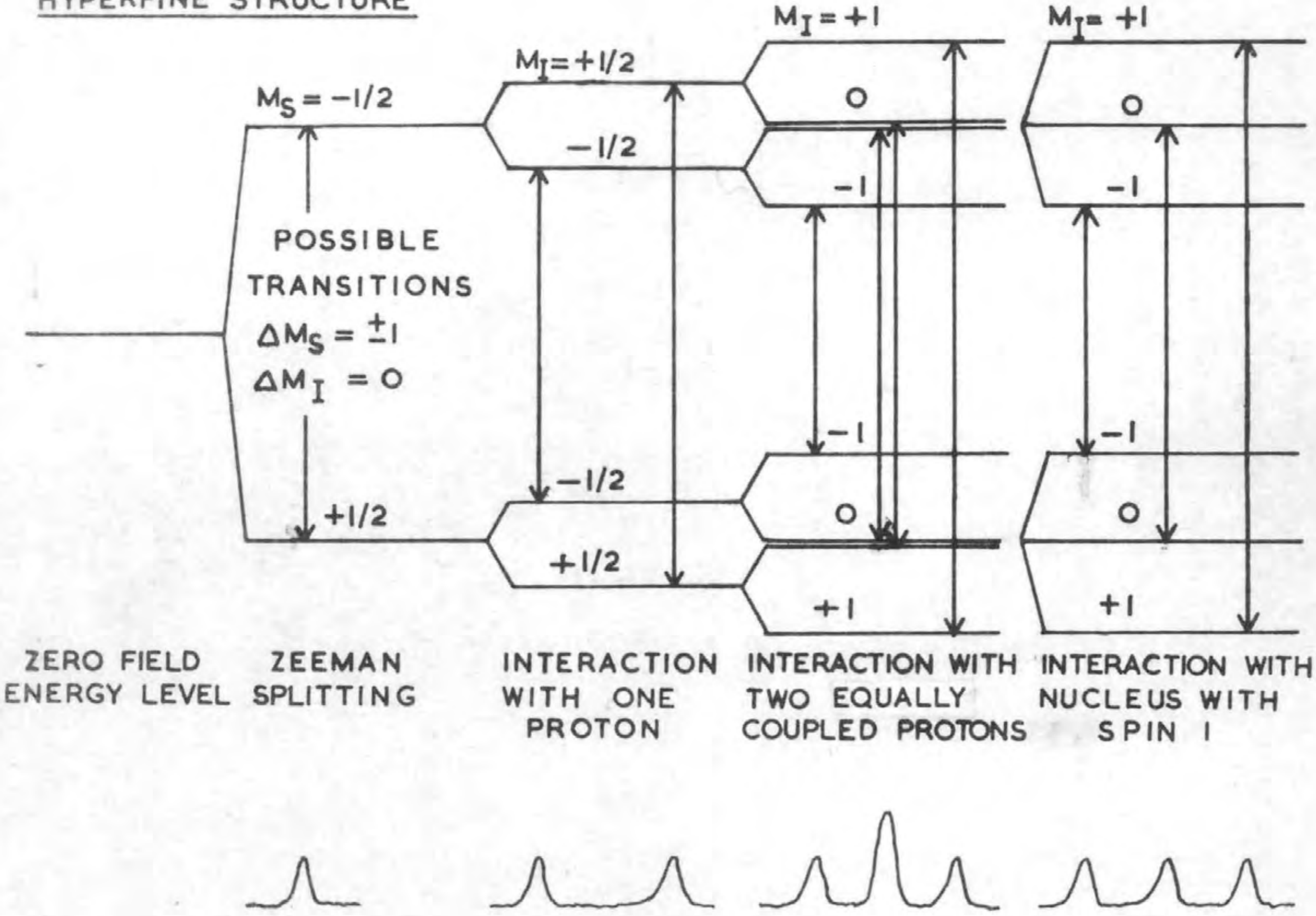
1.7. Hyperfine Structure

If the orbit of an unpaired electron embraces a nucleus which has a spin and, therefore, a magnetic moment, there is often a magnetic interaction between the electron and the nucleus which can split the electron energy levels. In the general case the interaction comprises an isotropic part and an anisotropic part. Isotropic splitting occurs when the orbital of the unpaired electron possesses s-character and the probability distribution of the electron density at the nucleus is finite. The nucleus is quantised in the magnetic field due to the electron and an additional magnetic field which will either add to or subtract from the external field is produced at the electron by the nucleus. If the nucleus has a magnetic quantum number M_I in the field of the electron, the allowed transitions between the energy levels which are split by this interaction are given by the selection rules $\Delta M = \pm 1$ and $\Delta M_I = 0$.

For an unpaired electron interacting with a single nucleus with a spin number I, (2I + 1) lines are possible. If the electron interacts with more than one nucleus the number of lines produced and their expected intensities depend on the spin numbers of the nuclei, their relative abundances, and the relative magnitudes of the hyperfine interactions. For example, if the electron spin interacts more strongly with a nucleus with spin number I_1 than it does with a second nucleus with spin number I_2, then $(2I_1 + 1)$ lines appear which are each split into $(2I_2 + 1)$ sub-components. Examples of the expected transitions are shown in Fig. 2 for the three cases of an electron spin interacting with one proton, equally with two protons, and with a nucleus with a spin number of 1. The third example is applicable to a substitutional nitrogen atom in diamond when the steady magnetic field is applied along a <100> direction.

FIG. 2

HYPERFINE STRUCTURE



It is necessary in the case of diamond to specify the direction of the steady magnetic field as the number of lines produced also depends on the symmetry of the probability distribution of the electron at the nucleus. Isotropic splitting only takes into account the effect of an unpaired spin probability density which is spherically distributed about a nucleus. For non-spherical symmetry in which the electron orbital may possess p-character as well as s-character, anisotropic splitting can occur and the spacing between the hyperfine lines depends on the angle between the steady magnetic field and the axis of symmetry. By measuring the magnitude of the spacings between the hyperfine lines for various known orientations of a crystal it is possible to assess the amount of s and p character associated with an unpaired electron orbital. As measurements of this type represent an important part of the work to be described a more detailed theoretical interpretation of hyperfine interaction is now presented.

The simple classical interaction energy E between two magnetic moments $\underline{\mu}_1$ and $\underline{\mu}_2$ is given by[18] $E = \frac{\underline{\mu}_1 . \underline{\mu}_2}{r^3} - \frac{3(\underline{\mu}_1 . \underline{r})\ (\underline{\mu}_2 \underline{r})}{r^5}$ where $\underline{r}$ is the vector joining the two magnetic dipoles. To obtain a quantum mechanical description of the interaction $\underline{\mu}_1$ and $\underline{\mu}_2$ are treated as operators and are defined as $\underline{\mu}_1 = \delta_1 \hbar \underline{I}_1$ and $\underline{\mu}_2 = \delta_2 \hbar \underline{I}_2$ where $\underline{I}_1$ and $\underline{I}_2$ are angular momentum operators and δ_1 and δ_2 are the gyromagnetic ratios of the two interacting nucleons. The

Hamiltonian (H_d) for the system then becomes

$$H_d = \frac{\delta_1 \delta_2}{r^3}\left(\underline{I}_1 . \underline{I}_2 - \frac{3}{r^2}(\underline{I}_1 . \underline{r})(\underline{I}_2 . \underline{r})\right)$$

By expanding this expression and using the raising and lowering operators $I^+ = I_x + iI_y$ and $I^- = I_x - iI_y$ the expression may be written

$$H_d = \frac{\delta_1 \delta_2 \hbar^2}{r^3}\left(A' + B' + C + D + E + F\right)$$

where $A' \propto I_{1z} \; I_{2z}$

$B' \propto (I_1^+ \; I_z^- + I_1^- \; I_z^+)$

$C \propto (I_1^+ \; I_{2z} + I_{1z} \; I_2^+)$

$D \propto (I_1^- \; I_{2z} + I_{1z} \; I_2^-)$

$E \propto I_1^+ \; I_2^+$

$F \propto I_1^- \; I_2^-$

The significance of the various terms A', B', C, D etc. are best visualised by considering which states are connected by them. Clearly, term A' is completely diagonal. On the other hand B' simultaneously flips one spin up and the other one down (A single flip-flop process). The remaining terms are off diagonal and either flip only one spin or both simultaneously up or down. Slichter has shown[2] that the net effect of the off diagonal terms is to produce very weak absorption peaks at 0 and $2\omega_0$ on either side of the resonant frequency ω_0. The relaxation processes involved for these peaks can be described under the general heading of cross-relaxation. If an accurate theoretical explanation of observed line width is required it may be necessary to consider the off diagonal terms and multiple flip-flop processes. (Sections 1.5 and 3.2.2.) In contrast, the terms A' and B' are the only two which have to be considered to provide a satisfactory explanation of anisotropic hyperfine splitting.

It is clear from the expression for H_d that as the distance between the two magnetic moments becomes increasingly small the interaction energy becomes infinite and, therefore, the classical interaction theory is no longer valid. A term (the Fermi Contact term) has to be included in the description of the interaction to allow for isotropic splitting which results from the s-character associated with an electron orbital. The fundamental derivation of this term is complicated and will not be included here. A simpler derivation has been suggested by Slichter[2] using classical theory. When the Fermi contact term is included in the description of the interaction the completed hyperfine interaction operator for an unpaired electron with an effective spin number S interacting with a nucleus with spin number I is then represented by the expression

$$H = \frac{\delta_1 \delta_2 \hbar^2}{r^3}\left[\frac{3(\underline{r}\cdot\underline{S})(\underline{r}\cdot\underline{I})}{r^2} - (\underline{S}\cdot\underline{I})\right]$$

$$+ \frac{\delta_1 \delta_2 \hbar^2}{r^3}\,\frac{8\pi}{3}\quad \delta(\underline{r})\,\underline{S}\cdot\underline{I}$$

where $\delta(\underline{r})$ is a Dirac - δ function.

To express the interaction as a function of spin co-ordinates only an integration over the spatial parts of the electronic wave function is performed and $\langle H \rangle = \int |\psi^2(r)| \, H \, d\tau$

For an axially symmetric wave function (as in the case of the nitrogen centre in diamond) $\langle x^2/r^5 \rangle = \langle y^2/r^5 \rangle$, while terms such as $\langle \frac{xy}{r^5} \rangle$ are zero. Therefore, if $\alpha = \langle \frac{1}{r^3} \rangle$ and $\beta = \langle x^2/r^5 \rangle$ then $\langle \frac{Z^2}{r^5} \rangle = \alpha - 2\beta$.

Collecting terms,

$$\langle H \rangle = \frac{\delta_1 \delta_2 \hbar^2}{r} \left\{ \left[\frac{8\pi}{3} \psi^2(0) + 2(\alpha - 3\beta) \right] I_z S_z \right.$$

$$\left. + \left[\frac{8\pi}{3} \psi^2(0) - (\alpha - 3\beta) \right] (I_z S_z + I_y S_y) \right\}$$

that is, $\langle H \rangle = A I_z S_z + B(I_x S_x + I_y S_y)$

where $A = \frac{\delta_1 \delta_2 \hbar^2}{r} (0 + 2P)$

$$B = \frac{\delta_1 \delta_2 \hbar^2}{r} (0 - P)$$

$$0 = \left(\frac{8\pi}{3}\right) |\psi(0)|^2 \qquad \text{(s character)}$$

$$P = \left\langle \frac{(Z^2 - \frac{1}{2}(x^2 + y^2))}{r^5} \right\rangle \text{(p character)}$$

The calculation shows how values of A and B appearing in the Spin Hamiltonian are related to the s and p character of the unpaired electron orbital.

1.8. Quadrapole Interaction

Many of the processes which occur in electron spin resonance involve magnetic interactions. However, small intensity transitions which are forbidden by the $\Delta M_I = 0$ selection rule sometimes arise as the result of an interaction between the gradient of an electric field at the nucleus and the quadrapole moment of the nucleus. The quadrapole moment is characterised by a parameter Q which is a measure of the charge distribution of the nucleus. For nuclei with a spin number greater than $\frac{1}{2}$ the charge distribution is non-spherical and Q is finite. The nucleus may be considered to be elongated in the direction of the electric field when Q is positive or flattened when Q is negative while still retaining its symmetry about the axis of spin. If the applied magnetic field is parallel to the symmetry axis of the electric field the interaction shifts all the hyperfine energy levels by an equal amount and hence produces no change in the observed transitions. If, however, the applied magnetic field is not parallel to the electric field the two types of interaction compete and try to quantise the nucleus along their respective axies. It is possible then for the selection rule $\Delta M_I = 0$ to be broken and for small intensity 'forbidden' transitions to occur. In addition, the shift of the energy levels is not the same for each hyperfine component as it depends on M_I^2. In this work effects of this kind were observed in one synthetic diamond. They are discussed in more detail in Section 4.13.1.

1.9. Line Width

The possibility that the line width of an electron resonance is determined either by homogeneous or by inhomogeneous broadening processes has been discussed in Section 1.3.

The uncertainty relationship $\Delta E \Delta t \sim 1$ suggests a line broadening due to spin-lattice interaction of the order of $\frac{1}{T_1}$. Interactions between the spins with which the characteristic time T_2 is associated also contribute to the width of the absorption line. In addition, cross relaxation processes characterised by T_{21} may occur. To a first approximation therefore, the total line width is given by $\frac{1}{T_1} + \frac{1}{T_2} + \frac{1}{T_{21}}$.

Line broadening due to the spin-lattice interaction can be reduced by lowering the temperature but clearly T_2 is not temperature dependent. Depending on the presence or absence of spin-lattice interaction within a cross relaxation process, T_{21} may or may not be temperature dependent.[3]

The effect of exchange interaction with respect to line width has been discussed in Section 1.4.

If the spin lattice interaction is weak (T_1 is long) partial saturation may occur. The degree of saturation depends on the value of T_1 relative to the level of microwave power incident on the sample. To avoid saturation broadening, superheterodyne detection systems are employed in which microwave power levels at the sample can be kept very low.

Additional line broadening may be caused by the experimental apparatus. Variations of the magnetic field value over the sample volume which are greater than the natural line width, produce a macroscopic distribution of local magnetic field and hence can cause line broadening (inhomogeneous broadening). The design and construction of the magnet may be responsible for this effect. In addition, sidebands produced by A.C. methods of detection, in particular by modulation of the steady magnetic field, can be the cause of an observed line broadening. Both the frequency and the amplitude of the modulation should be at least an order of magnitude less than the natural line width if accurate line shape measurements are required. This condition is partially relaxed if maximum sensitivity is the criterion.

In the case of synthetic diamond it will be shown that line broadening is due to a spread of local magnetic field caused by ferromagnetic impurities within the sample. Hereafter, this phenomena is referred to as ferromagnetic broadening.

1.10. Ferromagnetic Resonance

In general, theories applicable to electron spin resonance phenomena in paramagnetic systems are well developed and provide a satisfactory explanation of experimental observations. In direct contradistinction resonance from ferromagnetic materials is still not fully understood although it was discovered by Griffiths[19] in 1946.

A theory due to Kittell[20] is able to account for both the resonant field position and the shape of the absorption lines.

Although demagnetising fields and magnetic anisotropy are taken into account the theory can only yield quantitative results if samples have at least one dimension less than the skin depth ($\sim 1\mu$ at X-band frequencies). It is usual, therefore, to utilise samples which are either in the form of thin sheets with the microwave field applied tangential to the sheet and the steady magnetic field applied normal to the sheet, or which are in the form of small spheres. If a spherical specimen with a diameter less than the skin depth is used, the theory is considerably simplified as it is not then necessary to introduce demagnetising factors. However, isolated spheres with diameters less than the skin depth are particularly difficult to produce. Bagguley[21] has overcome the problem for some metals by producing colloidal suspensions in paraffin wax which contain spherical particles less than 100Å in diameter. The theory of ferromagnetic resonance has also been studied in detail by Polder[22]. However, there remain two outstanding points in which the theory and experimental observations are not reconciled. These are the experimentally observed high g-values and large line widths.

Theoretically, due to the close proximity of the spins in a ferromagnetic material, exchange narrowing effects should be greater than dipolar broadening effects and narrower lines are expected. Several authors[23-25] have postulated other interactions including spin-lattice interaction, skin effect, an interaction with conduction electrons and anisotropic exchange forces, but with little success so far.

In this work ferromagnetic resonances were observed with line widths between 500 and 1500 Oe and g-values between 3 and 4. These values are typical of those obtained in ferromagnetic resonance for which at the moment there is no satisfactory theory.

1.11. The Spin Hamiltonian

In order to distinguish between the various effects so far discussed and to ease the problem of interpreting resonance spectra, it is convenient to introduce the concept of the Spin Hamiltonian which was developed by Abragam and Pryce[26].

If a paramagnetic ion is taken as an example, the wave function which completely describes an electronic state is an admixture of the spin and orbital wave functions of the free ion suitably modified by the environment of the ion. The lowest state which experimentally is usually the most important, may be characterised by a single quantum number S', called the effective spin. S' is defined by equating the number of electronic transitions in the lowest state to $2S'$. At temperatures when only the lowest levels are appreciably populated, the paramagnetic ion can be treated as a magnetic dipole having $(2S' + 1)$ allowed orientations in an applied magnetic field, each energy level being associated with one orientation.

If, however, the energy levels have a zero field splitting energy terms must be added representing electrostatic interaction with the crystal field and magnetic interaction with other spins. The sum of all terms, written as a sum of the energy operators to be applied to the effective spin states is known as the Spin Hamiltonian. The actual energies are then the eigen values E which satisfy the operator equation $H\psi = E_0 \psi$ where ψ is the wave function of the spin state.

Abragam and Pryce[26] demonstrated that the splittings between the energy levels of a spin system may be calculated with a Spin Hamiltonian by first and second order perturbation theory. The result is precisely the same as if one ignored the orbital angular momentum explicitly and replaced its effect by an anisotropic coupling between the electron spin and the external magnetic field.

If the crystalline electric field has axial symmetry, the Spin Hamiltonian reduces to the form

$$H = D(S_z^2 - \tfrac{1}{3} S(S + 1)) + \beta(g_{\parallel} H_z S_z + g \ (H_x S_x + H_y S_y))$$
$$+ AI_z S_z + B(I_x S_x + I_y S_y) + Q' \ (I_z^2 - \tfrac{1}{3} I(I + 1))$$

where S is the effective electronic spin and I is the nuclear spin. D represents the splitting of the Zeeman levels when $H = 0$ (zero field splitting) in the absence of nuclear interaction and comes from the effect of the crystal field, spin-orbit coupling and the spin-spin interaction. $g_{\parallel}$ and $g_{\perp}$ are the g values when the applied magnetic field is respectively parallel, and perpendicular to, the crystalline field axis. The g-values are related to the spin-orbit coupling which mixes the ground and excited states and introduces a contribution to the electronic moment from the otherwise quenched orbital angular momentum. Values of A and B are related to the magnetic dipole interactions between electrons and nuclei which produce the hyperfine structure. Q' is the parameter which measures the small changes in the spectrum produced by the quadrapole interaction. The Spin Hamiltonian provides the essential link between theory and experiment and leaves the experimentalist with the task of measuring the various parameters A, B, g, D, etc.

Other terms may be included in the Spin Hamiltonian to allow for magnetic interactions between electrons and for magnetic interactions between the applied field and the nuclear magnetic moments. In electron spin resonance studies energies associated with these interactions are usually sufficiently small to be neglected. Clearly, the form of the Spin Hamiltonian for a particular case depends largely on the symmetry of the surroundings of the paramagnetic ion.

Experiments show that for substitutional nitrogen donors in diamond the g-value is isotropic and $D = 0$.

In addition lines due to quadrapole interaction are very weak. It is possible, therefore, because of the axial symmetry of the system, to interpret the main spectrum by using a Spin Hamiltonian of the form

$$(g\beta\ H.S) + (AI_zS_z + B(I_xS_x + I_yS_y))$$

The way in which A and B are related to the symmetry properties of the unpaired electron orbital has been demonstrated in Section 1.7.

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2. DIAMONDS

2.1. General Considerations

Diamonds have been the subject of a considerable amount of scientific investigation as they possess some interesting physical properties apart from their well known aesthetic appeal.

The most striking feature to arise from early experiments[1] on natural diamond was the marked specimen dependence of the physical properties. For this reason it is usual, when investigating diamonds experimentally, to consider a number of stones and to identify the physical properties which are common to particular groups of diamonds. Experimental data may then be correlated with easily identifiable parameters such as shape, size and colour.

Although synthetic diamonds were first produced in 1953, it has not been possible as yet to produce a crystal of gem-stone quality. The exact nature of the process of diamond growth, whether natural or synthetic, is still not fully understood. Two theories have been proposed for natural diamond which is known to have a volcanic origin. The first theory suggests that the diamond is crystallised at great depths and is released when the volcanic eruption occurs. The second theory suggests that crystallisation takes place as the molten material cools after the eruption. The successful synthesis of diamond at high temperatures and pressures supports the first theory. However, in order to achieve diamond synthesis in the laboratory, temperatures of at least 1700°C are necessary together with pressures of 50,000 atmospheres in contrast with temperatures of 1200°C and pressures of 1,000 atmospheres which are found in volcanic action at great depths[2]. The conditions for the growth of diamond crystals in the laboratory are not, therefore, an exact reproduction of those which occur naturally. In addition to high pressures and temperatures, the production of synthetic diamond also requires the introduction of a metal catalyst into the reaction mixture with the result that relatively large amounts of the metal remain as an impurity in the finished product. Some care has, therefore, to be exercised when analysing results from synthetic diamond if the conclusions drawn are to be applied in the general sense to natural stones. Although it is clearly important to compare results for natural and synthetic diamond, most published work refers specifically to one type or the other. An important part of this work is concerned with a determination of some of the differences which exist between natural and synthetic diamond.

It should be pointed out that the unquestionable existence of synthetic diamond is founded on three basic properties which are common to both natural and synthetic diamond. These are an identical structure as determined by X-ray analysis, an equal hardness and a comparable resistance to corrosion by very strong acid solutions. However, upon closer examination of synthetic diamond, although many of the characteristics of natural diamonds are retained, other new features appear. For example, amongst natural diamonds the most common faces which appear are usually octahedral or dodecahedral. Cube faces are relatively rare and are always rough and pitted. In direct contradistinction cube faces are common in synthetic diamond and are often surprisingly smooth and perfect.

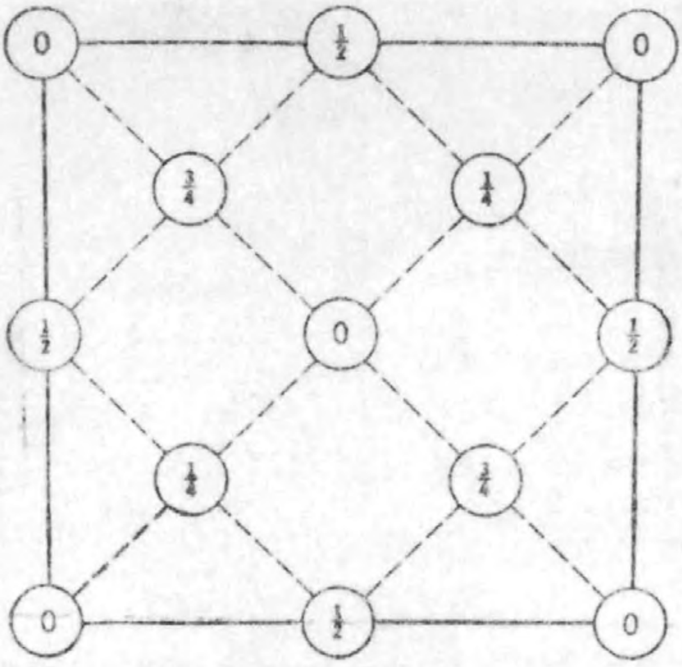
Many of the results published on synthetic diamond have been presented by scientists who have had a full knowledge of the method of specimen preparation and who, in addition, were able to produce crystals with controlled impurity concentrations. The need for industrial security has meant that certain information of this kind was not available for this work.

2.2. The Physical Properties of Diamonds

2.2.1. Structure

A perfect crystal of diamond contains carbon atoms only. Each atom lies at the centre of a regular tetrahedron and is joined to four others which lie at the corners of the tetrahedron.

The space lattice is face centred cubic with a basis of two atoms at 0, 0, 0; $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$, associated with each lattice point as shown diagrammatically in Fig. 3. The diagram shows the atomic positions in the unit cell projected on to a cube face. Fractions denote height above the base in units of a cube edge. The points at 0 and $\frac{1}{2}$ are on a face centred cubic lattice and those at $\frac{1}{4}$ and $\frac{3}{4}$ are on a



ATOMIC POSITIONS IN THE UNIT CELL OF DIAMOND STRUCTURE PROJECTED ON A CUBE FACE

FIG.3

similar lattice which is displaced along the body diagonal by one quarter of its length. There are eight atoms in a unit cell and each atom has four nearest neighbours and twelve next nearest neighbours. The edge length of the unit cell is 3.567Å and the distance between nearest neighbours is 1.544Å. The density of diamond is 3.52 $gm.cm.^{-3}$

Most natural diamonds exist either in the form of octahedra whose faces are (111) planes or as dodecahedra whose faces are (110) planes. The simple cube with (100) faces is often found in synthetic diamond but rarely occurs in natural stones. In addition, natural diamonds in the form of flat triangular plates are found and are commonly referred to as 'macles'. The plates are bounded by (111) faces with a twin passing through the centre and parallel to the large faces. A large amount of natural diamond is found to exist as agglomerates of small poorly formed crystals and is known as boart.

2.2.2. Optical Properties and Classification

Diamond has a high refractive index of 2.417 at 5890Å which makes internal reflections possible from rear facets. It is this property combined with a high dispersive power that gives rise to the natural brilliance.

The classification of diamond into two types; Type I and Type II, was first proposed by Robertson et al[1] as a result of a comprehensive survey on a large number of natural stones. Their experiments illustrated marked differences in a wide variety of physical properties. Type I diamonds have an absorption peak at a wave number of 1290 cm^{-1} in the infra-red and absorb strongly below 3000Å in the ultra-violet. They show little photoconductivity and are birefringent. In contrast Type II diamonds have no 1290 cm^{-1} absorption and are transparent down to 2250Å. They are photoconductive and optically isotropic. Most diamonds show characteristics that lie between these extremes of classification. However, in general this approximate method of classification is directly related to the types of impurities present in the crystals. It can be shown that Type I diamonds contain relatively large concentrations of nitrogen impurity which do not exist in Type II diamonds[3].

A sub-classification of Type II diamonds into Type IIa and Type IIb was proposed by Custers[4] in 1952. He found that some Type II diamonds exhibited semi-conducting properties and these were classified as Type IIb. A similar classification for Type I diamonds was proposed by Dyer et al[5] in 1965 and was based on the configuration and constitution of the nitrogen impurity in Type I specimens. Diamonds classified as Type Ib are discussed in more detail in Section 3.2.5.

2.2.3. Thermal Properties

Diamonds of gem quality have thermal conductivities at room temperature greater than any other substance. A Type IIa diamond has a thermal conductivity which is five times greater than that of copper at 0°C increasing to twenty five times at -175°C.

At high temperatures a diamond will burn or be transformed into other allotropic forms of carbon. The rate and degree of the transformation depends on the temperature and duration of the heating as well as on the environment in which the heating is carried out.[6,7]

In the presence of oxygen a diamond will begin to burn at about 600°C. When the oxygen content is reduced to correspond to a partial pressure of 0.4 Torr diamond will graphitize at temperatures above 700°C. When the oxygen content is further reduced to 10^{-3} Torr, no thermal transformations take place even at 1600°C. At temperatures above 1800°C diamond becomes fully graphitized even in a high vacuum.

2.2.4. Hardness and Strength

Diamond is the hardest material known to exist in the natural state and, therefore, has the highest number (10) on the Mohs' scale of hardness. However, the term hardness when applied to diamond may refer to its resistance to wear when used as the cutting edge of a machine tool, to its resistance to wear when used as a die, or to its resistance to grinding and polishing. In each case the rate of wear depends on the particular circumstances in which the diamond is employed. Regardless of the technique used to determine a hardness factor, it is found that hardness varies between different directions on the same face, and between different faces. Although conflicting explanations have been given, all theories agree that the hardness variations must exhibit the same symmetry as the diamond itself. It is beyond the scope of this thesis to discuss hardness effects in detail. A paper published recently by E. M. and J. Wilks[8] reviews the situation and provides many references on this topic.

Diamond has a compressive strength of 200 kg mm^{-2}, a bending strength of 30 kg mm^{-2}, and a modulus of elasticity between 72,000 and 93,000 kg mm^{-2}. As the compressive strength and particularly the bending strength are comparatively low, diamond is brittle. The modulus of elasticity is higher than that of all other materials.

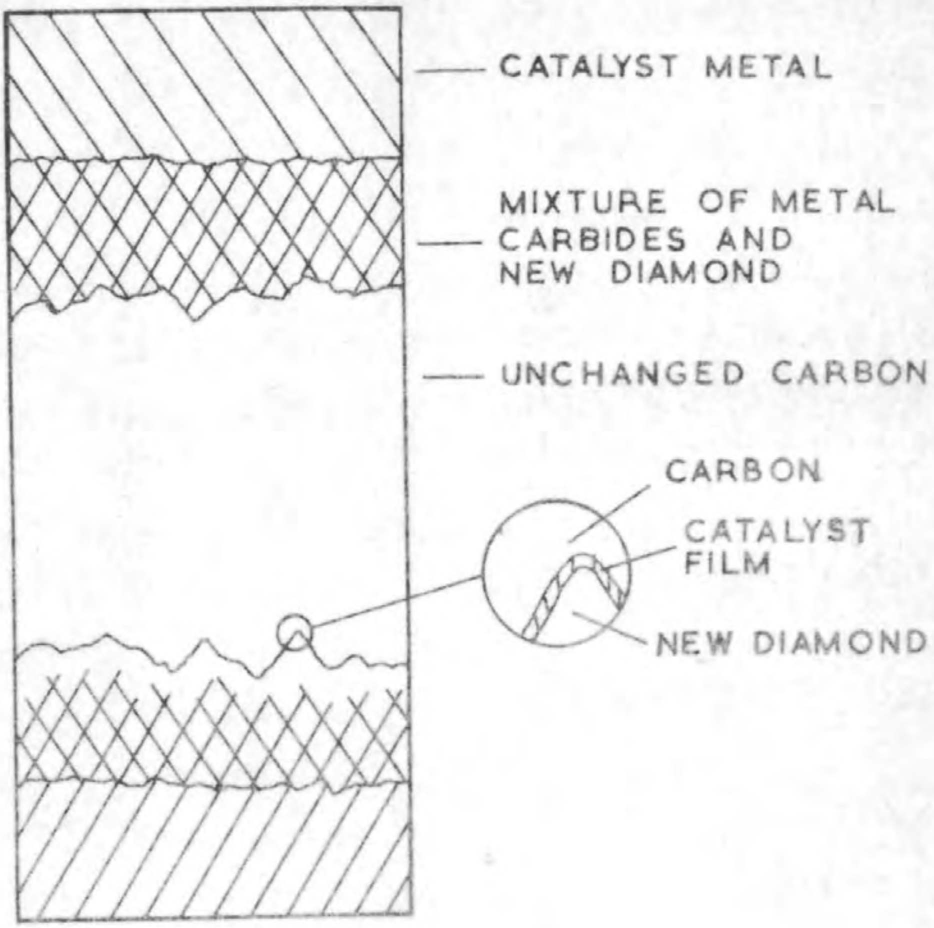
2.3. Synthetic Diamond

The physical properties of synthetic diamond are probably more varied than those observed in natural stones as synthetic diamond can be grown under fairly well controlled conditions. Only a limited variety of synthetic stones are available commercially. In many cases, only specimens which lend themselves to a particular type of examination have been selected for study. This is particularly so for examination by optical transmission spectroscopy as the diamonds are in general coloured and contain many imperfections and impurities.

The first confirmed synthesis of diamond was achieved in 1953 by A.S.A.E. (Allmana Svenska Elektriska Aktiebolaget) in Sweden. However, claims had been made earlier by Hannay[9] in 1880 and

Moissan[10,11] in 1896 although these were inconclusive. The diamonds produced in Sweden were less than 1 mm in size and it was thought that such small stones did not warrant publicity.

In 1947, Bridgman[12] performed a series of experiments using new high pressure techniques. The results, combined with theoretical considerations of the diamond-graphite thermodynamic equilibrium curve, led to a successful synthesis of diamond at the General Electric Company in 1955. Bundy et al[13] showed that diamonds could be synthesised somewhere in the pressure region 30,000-100,000 Atm at temperatures between 1200°C and 3200°C. At this stage little information on the reaction mixture had been released, although it was stated that a metallic caralyst had to be included in the reaction mixture and also that the pressure and temperature of the system had to be controlled to ensure that diamond was thermodynamically stable. In 1959 Bovenkork et al[14] published a full account of this research. The actual transformation from carbon to diamond occurred across a thin film of catalytic material approximately 0.1 mm thick which separated the carbon from the diamond. The situation is illustrated in Fig. 4. It was noted that the crystal habit varied with the temperature of formation. At the lowest temperatures used, cubes were predominant, whereas at intermediate temperatures cubes, cubo-octahedra, or dodecahedra were formed. Only at the highest temperatures were octahedra formed. No tetrahedra were ever observed.



DIAMOND GROWTH FROM GRAPHITIC CARBON

FIG. 4

In 1959 the De Beers group[15,16] in South Africa announced a successful synthesis of diamond and by 1963 had opened a synthetic diamond plant which yielded an output provisionally estimated at 750,000 carats (1 carat = 200 mgm) per annum. Although details have never been released, the process used for the manufacture of these stones appears to be very similar to that of the General Electric Company. The three most commonly used catalysts are now known to be iron, nickel, and cobalt.

Since 1959 a number of different methods have been employed in the synthesis of diamond. They include contributions from the Dutch[17] and the Japanese[18]. However, large quantities of different types of synthetic diamond are available only from De Beers or the General Electric Company.

It is worth noting that the direct transformation of graphite to diamond without the aid of a metallic catalyst was finally achieved by Bundy[19,20] in 1962. As a result of his work it was possible to locate the diamond-graphite-liquid triple point and, therefore, to complete the phase diagram for carbon. This is shown in Fig. 5.

Although the details of specimen preparation had not been made available, the scientific investigation of synthetic diamond began soon after the announcement of successful synthesis. X-ray studies on two types of synthetic diamond manufactured by the General Electric Company and A.S.A.E., Sweden, were made by

Londsdale et al[21] in 1959. They found that specimens supplied by the General Electric Company always contained single crystal inclusions of nickel or of a nickel-rich face centred compound. Results from a spectrographic analysis illustrated that many metallic impurities were present in the diamond. Concentrations of nickel were as high as 0.2%.

The Swedish specimens, which were not available commercially, did not appear to contain nickel but platinum was identified. However, a private communication from the supplier indicated that platinum was not used intentionally as a catalyst.

In 1961 Charette[22] reported the infra-red spectra of eight synthetic diamonds made at the Adamant Research Laboratory at Johannesburg. Optical measurements were made by Raal[20] in the ultra violet but only tentative suggestions were made on the subject of their classification. As a result of observations made on twenty-six specially selected stones by the same laboratory in 1962, Charette[23] stated definitely that both Type I and Type II synthetic diamonds exist.

In 1959 and 1960 Tolansky[24,25] studied the surface microstructure of synthetic stones supplied by the General Electric Company and the De Beers group. Precise optical and interferometric techniques revealed features which had not been observed on natural diamonds. They were as follows:-

1. Octahedral faces with a hopper or skeletal character.
2. Remarkably smooth plane cubic faces.
3. Dendritic growth characteristics.
4. Well defined growth spirals on the highly perfect cube faces.

A mechanism to describe the growth of cube faces was proposed by Kamiya and Lang[26] in 1964 after detailed X-ray diffraction and absorption topographic measurements were made on two selected synthetic diamonds manufactured by the General Electric Company. It was shown theoretically that cube faces can form if fluctuations occur in the growth rate and nickel is present.

2.4. Nitrogen in Diamond

The first indication that nitrogen exists as a major impurity in many diamonds emerged from a study made by Kaiser and Bond[3] in 1959. Specimens were heated to a temperature of 2000°C in a carbon crucible and the gases released during graphitisation were analysed with a mass spectrometer. In some cases concentrations of nitrogen as high as 0.23% were found. Furthermore, a correlation between the nitrogen content and the intensity of absorption in the infra-red at 1290 cm^{-1} was observed.

Precise X-ray determinations of lattice parameters and density measurements on specimens with different nitrogen concentrations led Kaiser and Bond[3] to suggest that the impurity existed in the form of substitutional and not as interstitial atoms. This conclusion was supported by the fact that nitrogen is a Group V element and lies next to and above carbon in the periodic table, and could possibly be present as a substitutional donor in the diamond lattice. Electron spin resonance measurements made by Smith et al[27] in 1959 demonstrated that this was indeed the case.

Perhaps one of the most interesting features of this work concerned the concentration and environment of the nitrogen impurity. Concentrations in the range 10^{15} - 10^{17} /cc were measured and were several orders of magnitude less than those reported by Kaiser and Bond[3]. As a result of this work most of the nitrogen impurity in diamond was thought to be present in a non paramagnetic form and hence would not be expected to give rise to an electron resonance signal.

Substitutional pairs of nitrogen atoms were suggested by Smith et al[27] as an example of non paramagnetic arrangements of the nitrogen impurity. Unfortunately, at the time at which they reported their experiments Smith et al[27] did not describe in detail the type of diamonds which gave rise to the electron spin resonance spectra. This information has since been shown to be of considerable significance and its implication will be discussed later in the thesis. In 1960 Kemmey and Mitchell[28] suggested that the substitutional nitrogen may be compensated electronically by aluminium acceptors or alternatively may exist in diamond in an aggregated form.

Anomolous X-ray spikes projecting from the Laue spots for certain diamonds observed by Raman and Nilakanton[29] led Frank[30] in 1956 to suggest that this phenomena could be explained by the presence of platelets of impurity atoms substitutionally placed in the cube planes. He considered silicon to be the relevant impurity. However, in 1958 Caticha-Ellis and Cochran,[31] although agreeing in principle with Frank's proposal, showed that the concentration of silicon found in diamond is too small to account for the spike intensities.

Following the discovery of high concentrations of nitrogen in diamonds, Elliot[32] in 1960 proposed the presence of platelets of nitrogen impurity atoms lying in the cube planes.

There was now sufficient evidence to suggest that the absorption at 1290 cm^{-1} in the infra-red would not arise from isolated substitutional nitrogen but might well do so in the presence of nitrogen platelets.[32,33] Clearly, a large amount of information had been accumulated which suggested that the nitrogen impurity in diamond exists in two different forms. A direct observation of the nitrogen platelets had yet to be achieved.

In 1961 Evans and Phaal[34] examined the kinetics of the diamond-oxygen reaction and applied their results in the following year[35] to produce specimens which were sufficiently thin for examination by transmission electron microscopy. They showed that Type I diamonds do contain nitrogen platelets on (100) planes and that these defects are absent in Type II diamonds.

In order to compute the total nitrogen content of diamond and hence to substantiate the results of Kaiser and Bond[3] which had been obtained from only five specimens, Lightowlers and Dean[36] in 1964 used the technique of photon activation analysis. Their method depended on the reaction $^{14}N\ (\gamma\ ,\ n)\,^{13}N$. Specimens were irradiated with high energy gamma rays obtained as bremsstrahlung from an electron linear accelerator. The isotope ^{13}N which is produced by the reation decays by positron emission with a half life of 10.5 minutes. The results obtained from the positron-count confirmed those of Kaiser and Bond[3] and also demonstrated the non-uniform distribution of the impurity. However, this method only lends itself to the determination of total nitrogen content and does not provide information on the environment of the nitrogen in the crystal lattice.

Further evidence for the non-uniform distribution of nitrogen platelets in Type I diamonds was provided by the ultra-violet transmission topographs produced by Takagi and Lang[37] in 1964.

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3. ELECTRON SPIN RESONANCE IN DIAMOND

3.1. Natural Diamond

3.1.1. Irradiation Damage

Electron spin resonance was first observed in diamond by Griffiths et al[1] in 1954. Their measurements were concerned exclusively with the paramagnetic centres produced in natural stones by irradiation with fast neutrons. Subsequently, irradiation damage in diamond has been studied extensively[2-4] although in general, the spectra obtained are complicated and difficult to interpret.

3.1.2. Aluminium Acceptors

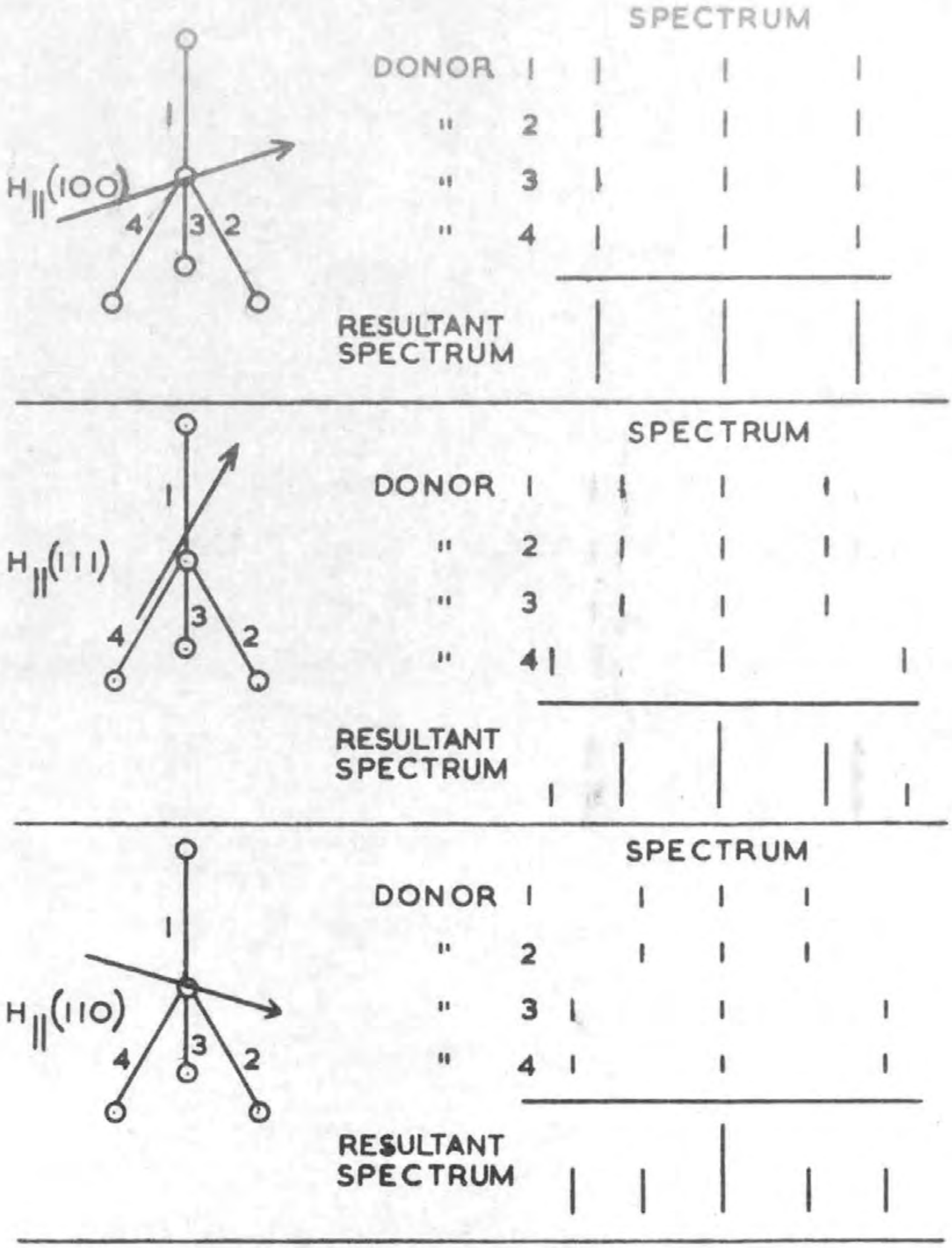
In 1958 Smith et al[5] reported a weak electron spin resonance spectrum in unirradiated natural diamond. A complicated spectrum of up to thirty lines covering a magnetic field range of approximately 30 Oe was observed. The spectrum varied with the orientation of the steady magnetic field to the crystallographic axis and the hyperfine structure corresponded to interaction between an electron spin and a nucleus with a spin of $\frac{5}{2}$. The spectrum was attributed to aluminium ions constituting bound acceptors. At the time of this work spectrographic studies[6] had established that aluminium was one of the elements most frequently found in diamond.

3.2. Substitutional Nitrogen

3.2.1. Hyperfine Interaction

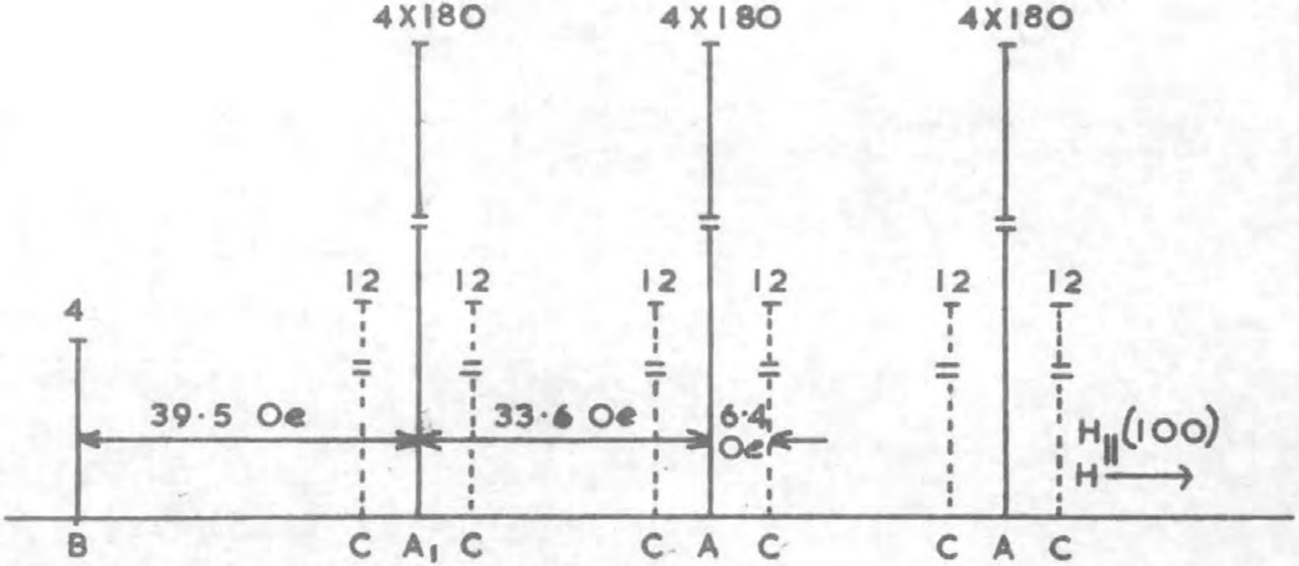
Electron spin resonance from dispersed substitutional nitrogen in diamond was first reported by Smith et al[7] in 1959. For a given nitrogen donor one of the carbon-nitrogen bond directions is a hyperfine axis and gives rise to four similar types of equally abundant donors. For each primitive cell containing a nitrogen donor there is an equal probability that the donor electron will be confined to any one of the four bond directions since the jump time of the electron between the four bond directions is relatively slow for this system below 930°C.[17] For the nitrogen nucleus I = 1 and, therefore, if the unpaired electron orbital on the nitrogen atom only possesses s-character three lines (2I + 1) would appear in the spectrum regardless of the orientation of the magnetic field. However, the orbital also possesses p-character and hence an anisotropic splitting occurs (Fig. 6). If the magnetic field is applied along a $\langle 100 \rangle$ direction so that it makes an equal angle with all four bond directions, the hyperfine splitting will be the same for each of the donors. In contrast, for the field applied in a $\langle 111 \rangle$ direction (along one of the bonds) the spacing between the three lines for donors in bonds parallel to $\langle 111 \rangle$ directions will be greater than that for each of the three remaining bonds all of which make an equal angle with the steady magnetic field. Fig. 6 shows how for this orientation, five lines are produced with intensities in the ratios 1 : 3 : 4 : 3 : 1.

Fig. 7 is a diagrammatic representation of the spectrum obtained by Smith et al[7]. A labelled diagram showing the positions



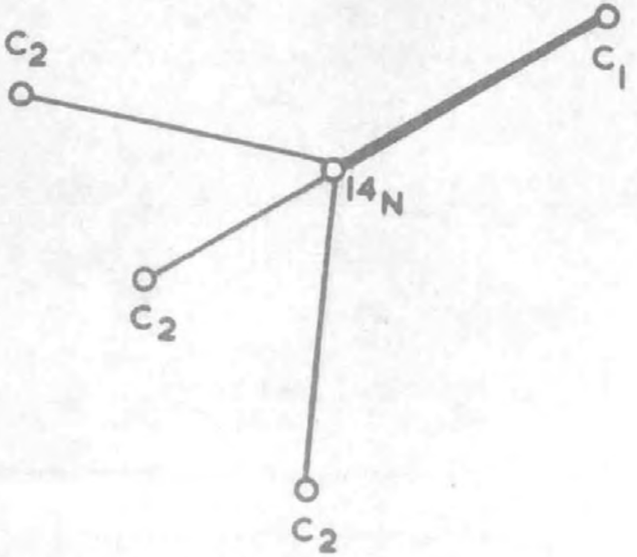
ANISOTROPIC HYPERFINE STRUCTURE DUE TO ^{14}N IN DIAMOND

FIG.6



SCHEMATIC REPRESENTATION OF THE E.S.R. SPECTRUM OF SUBSTITUTIONAL NITROGEN IN DIAMOND. NUMBERS REPRESENT RELATIVE INTENSITIES OF LINES. CLASSIFICATION OF LINES INTO THREE GROUPS A, B, AND C IS DISCUSSED IN THE TEXT.

FIG.7



IDENTIFICATION OF ^{13}C CENTRES WHICH PRODUCE LINES OF GROUPS B AND C (FIG.7)

FIG. 8

of the ^{13}C atoms in the diamond lattice which are responsible for the groups B and C lines, is given in Fig. 8.

Donors of ^{14}N interacting with ^{13}C nuclei (nuclear spin $I = \frac{1}{2}$; C_1 in Fig. 8) were shown to exist by the appearance of a weak additional hyperfine spectrum (B). In order to make quantitative measurements of the relative intensities of the resonance lines the gain of the detecting system had to be reduced as the low field satellite (A_1) of the main nitrogen triplet was approached. As a result of the reduction in gain and the overlap of lines due to their finite width, it was not possible to observe all the B lines and therefore they are not reproduced in Fig. 7. The intensity of this spectrum (4 in Fig. 7) was correlated quantitatively with the 1.1% natural abundance of ^{13}C within the diamond lattice. Similar results were obtained for the group C lines (Intensity 12) which were observed in the wings of the main lines and which were attributed to the donor electron density on the basal ^{13}C nearest neighbour atoms. (C_2 in Fig. 8).

The results are best described by the Spin Hamiltonian

$$H = g\beta H.S + As_zI_z + B(S_xI_x + S_yI_y)$$

$$+ A'S_zI'_z + B'\ (S_xI'_x + S_yI'_y)$$

where $S = \frac{1}{2}$ $g = 2.0024$ (isotropic); $I = 1$

$I = \frac{1}{2}$ is the nuclear spin of C.

Measured values of the hyperfine constants were as follows:

A = 40.8 Oe., B = 29.2 Oe.
A = 60.8 Oe., B = 25.3 Oe.

The results were interpreted by assuming that the unpaired electron donated by the nitrogen is in an antibonding orbital between the carbon and nitrogen atoms. The orbital is of the form $\psi = \frac{1}{\sqrt{2}}(\phi_N - \phi_C)$ (Neglecting overlap) where ϕ_N and ϕ_C are hybrid orbits each consisting of 2s and 2p atomic orbitals. Thus ϕ is of the form $\phi \simeq s + \lambda p$. From the expressions derived for A and B (Section 1.7) it is possible to calculate the relative amounts of s and p orbit associated with the antibonding orbital. The values of the unpaired electron probability densities (0 and P) deduced from the experimental results are shown in Fig. 9. They are compared with values computed for a model in which the unpaired electron is assumed to be in a regular sp^3 type antibonding orbital between the carbon and nitrogen atoms and also for a similar model in which the bond is stretched by 10%. The stretched bond model corresponds to $\lambda = \sqrt{7}$ and therefore the probabilities of finding the electron in an s or a p orbit are $\frac{1}{8}$ and $\frac{7}{8}$ respectively. The results show that reasonable agreement is obtained in the case of the stretched bond model.

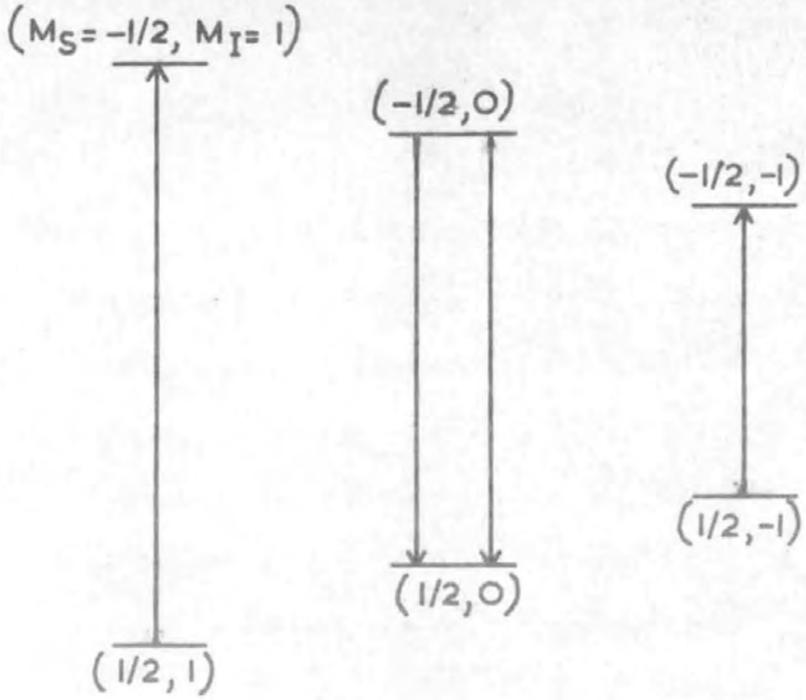
3.2.2. Cross-Relaxation

The shape and width of the nitrogen resonance in diamond are not satisfactorily explained if only the relaxation processes characterised by T_1 and T_2 are considered. Multiple spin flip processes and cross relaxation effects which are characterised by T_{21} (Section 1.5) also have to be considered.

	EXPERIMENTAL	CALCULATED SP^3 ORBITAL	CALCULATED 10% ELONGATION
O_N	2·41	4·8	2·37
P_N	0·28	0·38	0·44
O_C	0·78	3·1	1·53
P_C	0·25	0·18	0·21

FIG.9

The cross relaxation effects reported by Bloembergen et al[8] suggested that, for the nitrogen resonance in diamond, two spins of the centre line can make a downward transition while a spin belonging to each satellite line makes an upward transition (Fig. 10). Simple considerations of the rate at which these processes could occur were made by Sorokin et al[9] in 1960. They showed that if a saturating microwave field is suddenly applied to one of the three lines of the nitrogen spectrum, a weak probing microwave signal at either of the two other lines should register a change in absorption in a time T_{21}. Theoretical arguments showed that by saturating the centre line, the absorption at either satellite should drop to zero provided that T_{21} is much less than T_1 and T_2. Alternatively, if either of the satellite lines are saturated the intensities of the centre lines and the remaining satellite lines should be reduced by $\frac{3}{4}$ and $\frac{2}{6}$ of their thermal equilibrium values respectively. These predictions were verified experimentally. In addition, it was shown both theoretically and experimentally that for certain cases the four spin flip mechanism may be used to invert the population of one of the satellite lines and to establish continuous wave maser operation. A similar effect has been observed in this work from one synthetic diamond. It is discussed in more detail in Section 4.13.3.



ENERGY LEVEL DIAGRAM FOR SUBSTITUTIONAL NITROGEN IN DIAMOND $H_{\parallel}(100)$ SHOWING THE FOUR SPIN FLIP MECHANISM THROUGH WHICH CROSS RELAXATION PROCEEDS

FIG.10

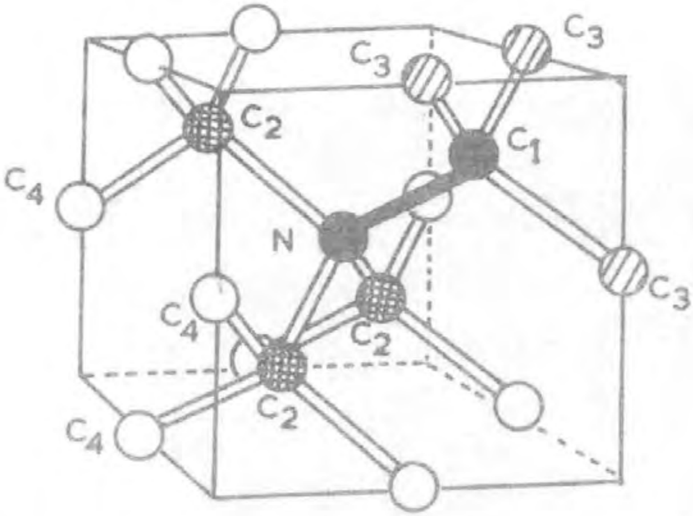
3.2.3. Distribution of Substitutional Nitrogen

The distribution of substitutional nitrogen donors in diamond was investigated in 1964 by Samsenenko.[10] He considered line shape changes in different specimens and used the method of linear superposition to show that the wings of the line profiles fitted a Gaussian distribution while the central portion had a Lorentz form. He concluded that the concentration of paramagnetic centres in a certain volume of the crystal had attained a value such that exchange interaction was important. Further calculations showed that the regions of elevated nitrogen content represented about 2% of the total crystal volume. He was unable, however, to suggest the exact nature of the distribution.

3.2.4. The Effect of ^{13}C and ^{15}N

In 1964 Loubser and Du Preez[11] re-examined the electron spin resonance spectra of natural diamonds. Carefully selected stones, which gave rise to narrow spectrum lines, were used. The spectrometer was operated at very low energy densities in the microwave cavity in order to avoid saturation effects and the smallest possible 100 kH$_z$ magnetic field modulation was used to avoid broadening the lines. A typical spectrum is shown in Fig. 11 together with a diagram of the diamond lattice to aid explanation of the results. Apart from the lines which are spaced symmetrically on either side of the main triplet and which were attributed by Smith et al[27] to nearest neighbours (denoted C_I), additional lines (A) were found

E.S.R. SPECTRUM OF NITROGEN DONORS IN DIAMOND. GROUP A LINES DUE TO ^{13}C (CENTRES II, III, AND IV,); GROUP B LINES DUE TO NITROGEN QUADRAPOLE MOMENT; GROUP C LINES DUE TO ^{15}N.



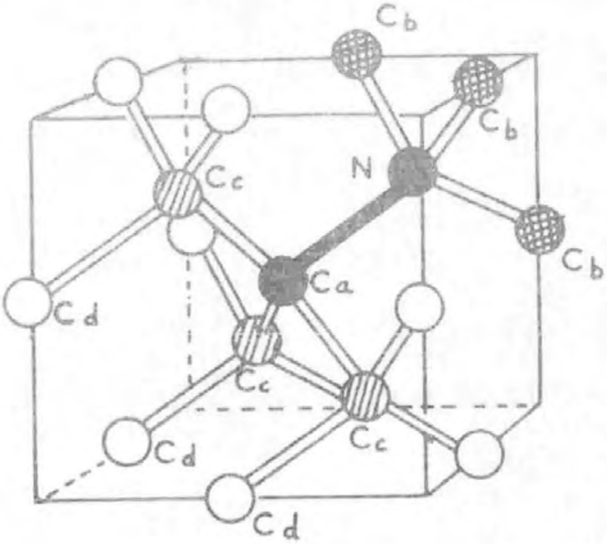
IDENTIFICATION OF ^{13}C CENTRES PRODUCING THE LINES OF GROUP A. (LOUBSER 1964)

FIG.11

which were close to the main lines. These were attributed to the interaction of the impaired electron with ^{13}C at other lattice sites (Centres II, III and IV). In addition, lines (B) were found and were shown to be due to the interaction of the quadrapole moment of the nitrogen nucleus with the electric field-gradient at the nucleus. Finally, lines (C) due to the isotope ^{15}N with a nuclear spin $I = \frac{1}{2}$ were also identified.

The lines (A) have since been considered by other authors[12,13] in more detail and a more precise theoretical approach to the problem has been developed. Group (A) lines were attributed by Loubser and Du Preez[11] to three different types of defect which were designated centres II, III and IV in decreasing order of hyperfine splitting. As in the work of Smith et al[7], the centre II lines were associated with ^{13}C in one of the three basal carbon positions (C_2 in Fig. 11). Loubser and Du Preez[11] made the assumption that the unpaired electron spent most of its time on the nitrogen atom but the calculations of Bower and Symons[12] demonstrated that this was not so. However, Loubser and Du Preez also pointed out that if the lines of centre III were attributed to ^{13}C in one of the carbon positions basal to the carbon in the N-C bond (C_3 in Fig. 11) and if the antibonding orbital gave a greater density on the C_1 carbon than on the nitrogen, the association of the lines of the C_2 and C_3 carbons would be reversed. In either case the centres II and III lines would have three times the intensity of the centre I lines in agreement with experiment. The probable position of the ^{13}C atoms which gave rise to the lines of centre IV, was given as C_4. The lines due to C_3 and C_4 were found to be isotropic and therefore it was assumed that only the contact part of the hyperfine interaction had a finite value at these more distant nuclei. This model suffered one serious drawback. If it was correct, it was difficult to explain the direction of the hyperfine axis of the ^{13}C atom of centre II which would have been expected to be along the C_2-N direction. This was not the case.

The contradiction led Bower and Symons[12] to propose a slightly different configuration for the centre. Their model is shown in Fig. 12. In this case it was assumed that the unpaired electron was located predominantly on the carbon atom. Lines due to centres III and IV were assigned to C_c and C_b. A finite unpaired electron density on the carbon atoms C_d was proposed as the reason for the lines of centre II. In this case the hyperfine axis was parallel to the C_a-N bond direction and produced a closer agreement with experimental results. Further theoretical evidence in support of Bower's results was published in 1965 by Every and Schonland.[13] A molecular orbital treatment was given for the nitrogen centre in diamond. It accounted satisfactorily for the quadrapole and main hyperfine constants associated with centres I and II.



IDENTIFICATION OF ^{13}C CENTRES (C_a, C_b, C_c, AND C_d REFERRED TO IN TEXT) PRODUCING THE LINES OF GROUP A. (FIG. 11) (BOWER 1966)

FIG. 12

3.2.5. Type Ib Classification

The interpretation of electron spin resonance spectra in natural diamonds was now more fully understood and it appeared that there was little further information to be gained from similar experimental investigations. However, in the same year, Dyer et al[14] studied the combined optical and paramagnetic properties of a large number of diamonds and the results (summarised in Fig. 13) had far reaching consequences. The most surprising observation was that only approximately 0.1% of the total number of natural stones examined produced the electron spin resonance spectra characteristic of dispersed substitutional nitrogen donors. In addition, they observed an optical absorption spectrum which had not been previously reported. It was suggested that diamonds which possessed these characteristics should be classified as Type Ib. Although natural stones of this type were found to be extremely rare it was shown that the synthetic diamonds which were also examined in this survey, could invariably be classified as Type Ib.

3.2.6. Coated Stones

The reason why Smith et al[7] did not point out that electron spin resonance could be observed only in a very small number of natural diamonds was probably due to the fact that they had examined a relatively common form of stone known as 'coated diamond'. These stones consist of a clear diamond core with an opaque overgrowth of imperfectly grown diamond or coat which is often very thick.

Type	Characteristic defect centres	Characteristic ultra-violet and visible features	Characteristic infra-red features	Characteristic E.S.R. features
I a	Nitrogen in platelet form (Elliott 1960)	Secondary absorption edge (Clark et al. 1956 a)	A bands (Sutherland et al. 1954)	None
I b	Nitrogen in dispersed form (Smith et al. 1959)	I b system	I b bands	I b spectrum (Smith et al. 1959)
II a	No nitrogen structural defects (Clark et al. 1956 b)	Absorption continuum between 2.0 ev and 5.4 ev (Clark et al. 1956 b)	None, only intrinsic bands of diamond (Lax and Burnstein 1955)	Single isotropic line (Duncan 1963)
II b	No nitrogen; acceptor centres (Wedepohl 1957)	Absorption Continuum between 1.0 ev and 2.0 ev (Wedepohl 1957)	II b bands (Wedepohl 1957)	None

Characteristic absorption properties of the diamond types. (After Dyer et al.[14]).

Fig. 13.

Clearly, a composite crystal of this type should not be used if the characteristics so determined are presented as typical of a single crystal. It is likely that the diamonds examined by Samsenenko[10] were also of the coated variety and were not Type I as specified. These suggestions are supported by the results of experiments performed by Faulkner[15] in which he demonstrated that the electron spin resonance spectra in coated diamonds arises from dispersed substitutional nitrogen in the coat. The spectrum was not observed in the core which remained after the coat had been removed.

More recent work which is connected directly with the nitrogen centre, was reported by Cook and Whiffen[16] in 1966. An Endor study of a Type Ib natural diamond enabled more accurate values of the hyperfine constants A and B to be quoted. These were given as $A = 40.723$ Oe and $B = 29.062$ Oe.

The above review represents work carried out on natural diamond up to and including the period during which the results presented here were obtained. However, since that time, further experimental work has followed. More recently Loubser and Van Ryneveld[17] have reported electron spin resonance measurements of Type Ib natural diamond in the temperature range from 330°C to 960°C. It was shown that at temperatures of 930°C the reorientation of the Jahn-Teller distortion of the substitutional nitrogen centre was sufficiently rapid to produce isotropic lines of equal intensity regardless of crystal orientation.

3.3. Synthetic Diamond

3.3.1. General Considerations

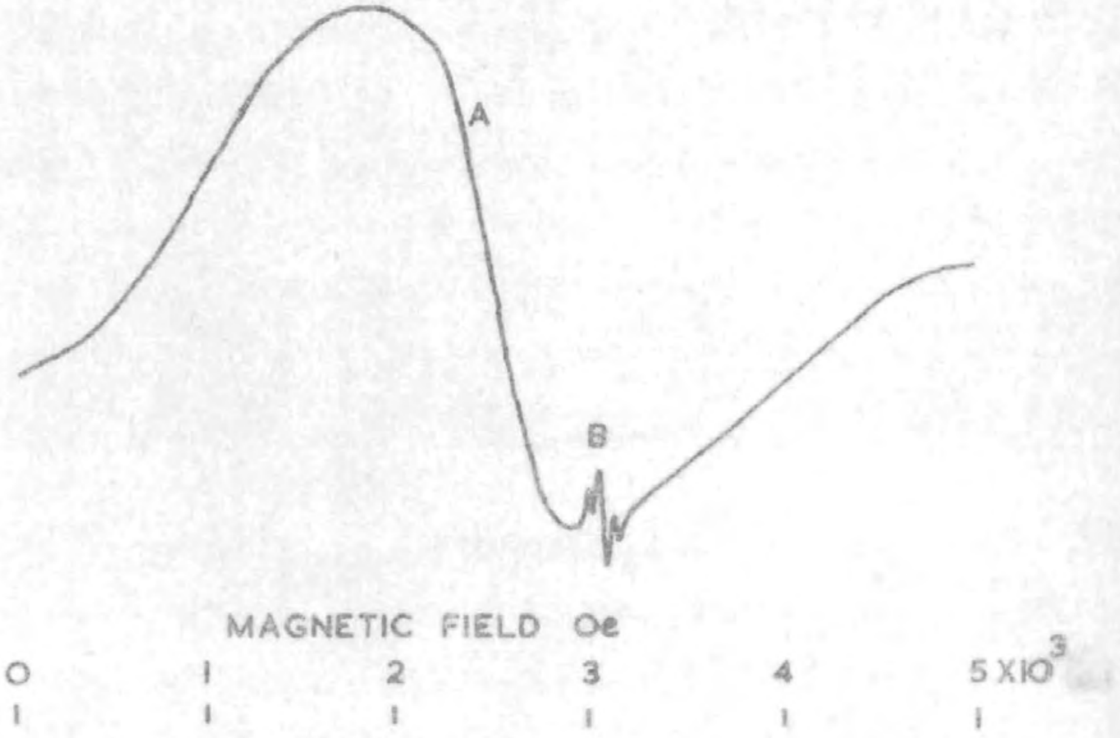
Manufacturers of synthetic diamond describe their products with the aid of a system of letters and numbers. The letters describe the suitability of the product for bonding by a resin or a metal. The relative merits of the various types in this respect are not directly relevant and will not be discussed further. The numbers relate to the size in terms of the dimensions of the sieves through which the diamond will pass (mesh range). The table in Fig. 14 relates mesh numbers and size.

Electron spin resonance in synthetic stones was first reported by Huggins and Canon[18] in 1962. Only the R.V.G. type of the three which they examined is available commercially and is prepared with a nickel catalyst. The electron spin resonance spectrum from R.V.G. diamond is shown in Fig. 15. The broad band (A) is attributed to transition metal impurities (mainly nickel). The resonance (B) which is attributed to dispersed substitutional nitrogen atoms is superimposed on the broad band and is centred very close to the free spin g - value.

Two other spectra were reported which were obtained from specially prepared crystals. One specimen was produced with an aluminium : 2 nickel catalyst and the other was produced with a boron catalyst. The wide band (A) was no longer present in the

MESH NUMBER	DIMENSIONS IN mm	MESH NUMBER	DIMENSIONS IN mm
30	0·59	100	0·149
35	0·50	120	0·125
40	0·42	140	0·105
45	0·35	170	0·088
50	0·297	200	0·074
60	0·250	230	0·062
70	0·210	270	0·053
80	0·177	325	0·044

FIG.14



E.S.R. SPECTRUM OF A BULK SAMPLE OF R.V.G. DIAMOND (HUGGINS 1962)

FIG.15

aluminium : 2 nickel doped specimen and the detail at $g = 2$ was reduced to the extent that it was impossible to define the structure. In the boron doped specimen no spectrum occurred at $g = 2$ but a broad resonance centred about $g = 3$ was observed. Hyperfine structure was not observed when this specimen was cooled to -173°C, but the band at $g = 3$ decreased im intensity and a structure of unresolved detail began to appear at $g = 2$. No explanations for these phenomena were offered.

3.3.2. Lime Width of the Nitrogen Resonance

For synthetic diamond, the electron spin resonance spectrum from the substitutional nitrogen donors is often incompletely resolved as the lines are considerably inhomogeneously broadened by the spread of local magnetic field produced by the ferromagnetic impurities which remain in the crystals after manufacture. In 1965 Dyer et al[14] grew diamond crystals with a non-ferromagnetic catalyst Brightray - S (78 Ni, 21 Cr, 1 Fe) and examined the electron spin resonance spectrum. Their results are shown in Fig. 16. Although the central isotropic line was much narrower (3.9 Oe) than in the commercially available samples (8.0 Oe), the random orientation with respect to the magnetic field of many small crystals produced broad satellite lines. Using the same type of theory developed by Sands[19] the maximum and minimum values of the spacing between hyperfine lines, A and B were deduced.

It should be emphasised that at this time there had been no reports of electron spin resonance investigations of single crystals of synthetic diamond. In addition, the line width of the nitrogen resonance in crystals grown with Brightray - S was still an order of magnitude greater than that observed in natural Type Ib diamond.

3.3.3. Previous Work by the Author

Finally work which was carried out by the author[20] shortly before the present survey was undertaken and which was confirmed during it, is now described. Collective samples of three different types of synthetic diamond manufactured by the General Electric Company were examined. Each sample contained the same mass of diamond but differed in the sizes of the individual stones. The variations in intensity of the nitrogen resonance between the three samples indicated that the distribution of the substitutional nitrogen donors in single stones was non-uniform. As in all previous reports the conclusions drawn with respect to a single stone were extrapolated from results obtained with bulk samples.

The line shape of the nitrogen resonance for specimens consisting of the smaller stones was also observed to differ noticeably from the line shape for specimens of the larger stones. The narrowing of the central peak in the case of smaller stones which contained a high concentration of nitrogen ($> 10^{19}$/cc), was attributed to exchange interaction between the nitrogen centres. Results subsequently published by Loubser et al[21] have supported this suggestion.

3.4. Summary

This section has summarised briefly the published work on diamomd which is most relevant to this thesis. In the case of synthetic stones the majority of the specimens described were manufactured either by the General Electric Company or the De Beers group. Although some authors used stones which they described as typical of those available commercially, the majority were specially selected or grown to a known specification. Apart from the work presented in this thesis on three types of synthetic diamond only one other publication[18] related directly to a type of diamond (R.V.G.) which is known to be commercially available.

Although detailed information regarding the manufacture of synthetic diamond is not disclosed, it is felt that investigations can nevertheless make an important contribution to a more complete understanding of the properties of this material. It is inevitable that wide variations in physical properties will be observed if specimens are prepared under different conditions and, therefore, in order that the results obtained in this work may be compared with those of future investigations, particular attention has been given to synthetic diamond which is commercially available.

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4. AN EXPERIMENTAL STUDY OF SYNTHETIC DIAMOND

4.1. Introduction

An experimental study was made of five different types of synthetic diamond all of which are commercially available. The method of preparation is different for each type and consequently variations are observed in their physical properties. For a given type variations were also observed amongst diamonds of different shape and size. Many of the experiments involved diamonds which had been subjected to heat treatment. The nature of the diamonds was modified by this treatment to the extent that significant changes in physical properties were detected. Two resonance lines not previously reported for synthetic diamond were observed. One was due to carbonisation of heated samples and the other occurred only at liquid nitrogen temperatures. The numerous variations in physical properties are clearly reflected in the results which illustrate that in many cases they are typical of all five types of synthetic diamond. In contrast, certain properties are characteristic only of a particular species. As the combination of so many variables can lead to confusion the results of each set of experiments are discussed in turn. Discussion at some points is limited until results from further experiments involving different techniques have been presented.

4.2. Experimental Apparatus

Preliminary electron spin resonance investigations of samples of synthetic diamond were made with an X-band spectrometer which was constructed by the author. A simple transmission cavity was used with magnetic field modulation at 50 kHz produced by a coil mounted inside the cavity. The magnet system comprised a Newport 4" magnet energised by an Advance power supply. This spectrometer gave results which provided the basis of this work but it was not sufficiently sensitive (approximately 10^{13} spins Oe^{-1} line width) to detect a resonance from a single synthetic diamond. In addition, the magnetic field produced by the 4" magnet was not sufficiently uniform over a typical sample volume (approximately 0.5 cc for a bulk sample of synthetic diamond) to resolve lines less than 3 Oe wide.

The electron spin resonance spectra presented in this thesis were obtained from a Decca XI spectrometer which operates at 9270 MHz (X-Band) with 100 kHz magnetic field modulation. The modulation coils are mounted in the walls of a rectangular cavity (TE_{102}) which is used in a reflection mode. The klystron is phase locked to a harmonic of a low noise crystal controlled oscillator. In addition the effects of cavity drift can be minimised by locking the klystron to the cavity. With 1 m.W. microwave power at the cavity and for a time constant of 1 second, the sensitivity is 4×10^{11} spins Oe^{-1} line width. The sample temperature is continuously variable from

-175°C to $+300^{\circ}$C. The magnet which was kindly loaned by Dr. E. F. W. Seymour of the School of Physics, University of Warwick, had flat pole pieces of 6" diameter and was not a commercial design.

The optical micrographs were obtained with a Zeiss Ultraphot II. Facilities were available which permitted observation either by transmission or reflection. The micrographs were recorded on standard Ilford plates (9 x 12 cm). Observations at elevated temperatures were made with a Griffin-Teller hot stage microscope. The sample temperature could be varied from room temperature to 1800°C in an atmosphere of argon.

Spectrographic analysis was carried out on a Hilger Large Quartz Spectrograph.

Single crystal faces were ground and polished with a two bearing scaife incorporating a spindle mounted in blocks of Lignum Vitae. A device was constructed whose working principles were similar to those of a conventional sand-blasting machine in order to reduce the overall dimensions of diamonds as uniformly as possible. A diagram of the machine is shown in Fig. 17. By increasing the rate of air flow it was possible to produce air turbulence which in turn caused the diamonds to collide and so to produce abrasion.

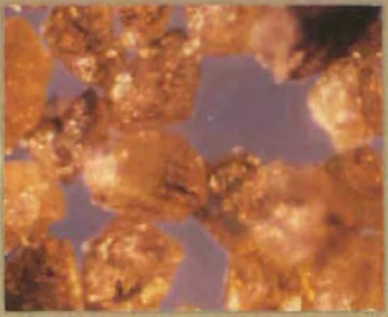
The vacuum furnace which was used for the heat treatment was not a commercial design. The heating process was by radio frequency induction in a cylindrical tantalum susceptor. Specimens were contained in a thoria crucible which was suspended inside the susceptor with tantalum wire. The water cooled induction coil was powered by an oscillator at 400 kH_z with a maximum output of 30 kW. The coil was mounted inside an inverted water cooled bell-jar in which glass ports were situated to enable temperature measurements to be made with an optical pyrometer.

X-ray microprobe analysis was carried out by Dr. D. Burr of International Nickel Ltd. on an electron microprobe analyser manufactured by Cambridge Instruments Ltd. Both line and spot analysis were carried out with the probe operated at 15 kV.

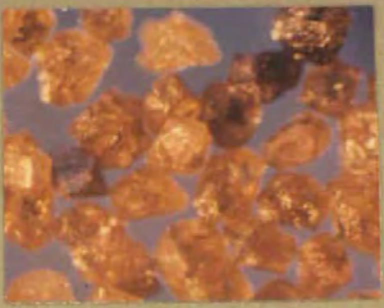
Infra-red spectra were recorded by Professor J. J. Charette of the University of Lovanium, Congo, using a Perkin-Elmer 112G spectrometer with the microscope attachment model 85.

4.3. Sample Specification

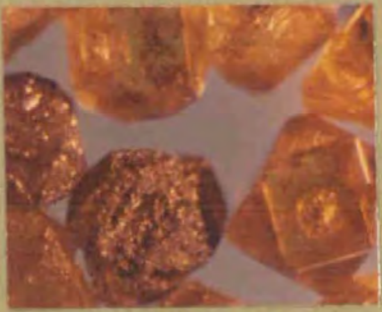
Of the five different types of synthetic diamond used in this work three were manufactured by the General Electric Company of the U.S.A. and are described as M.B.G. (Metal Bond Grinding), M.B.S. (Metal Bonding Saw), and R.V.G. (Resinous Vitrified Grinding). The other two types were produced by the De-Beers Organisation and are designated M.D.A. (Metal Diamond Abrasive) and R.D.A. (Resin Diamond Abrasive). The general appearance of all five types of diamond is illustrated in Fig. 18.



R.V.G. 40/60

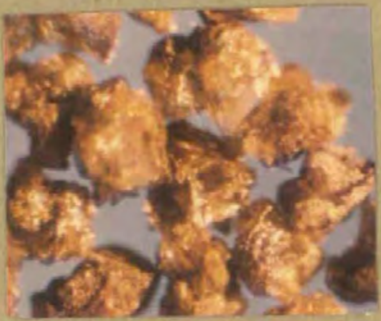


M.B.G. 60/80



M.B.S. 35/40

U.S. GENERAL ELECTRIC



M.D.A. 40/60

R.D.A. 40/60

DE BEERS

FIG.18

4.4. Electron Spin Resonance Survey of Bulk Samples

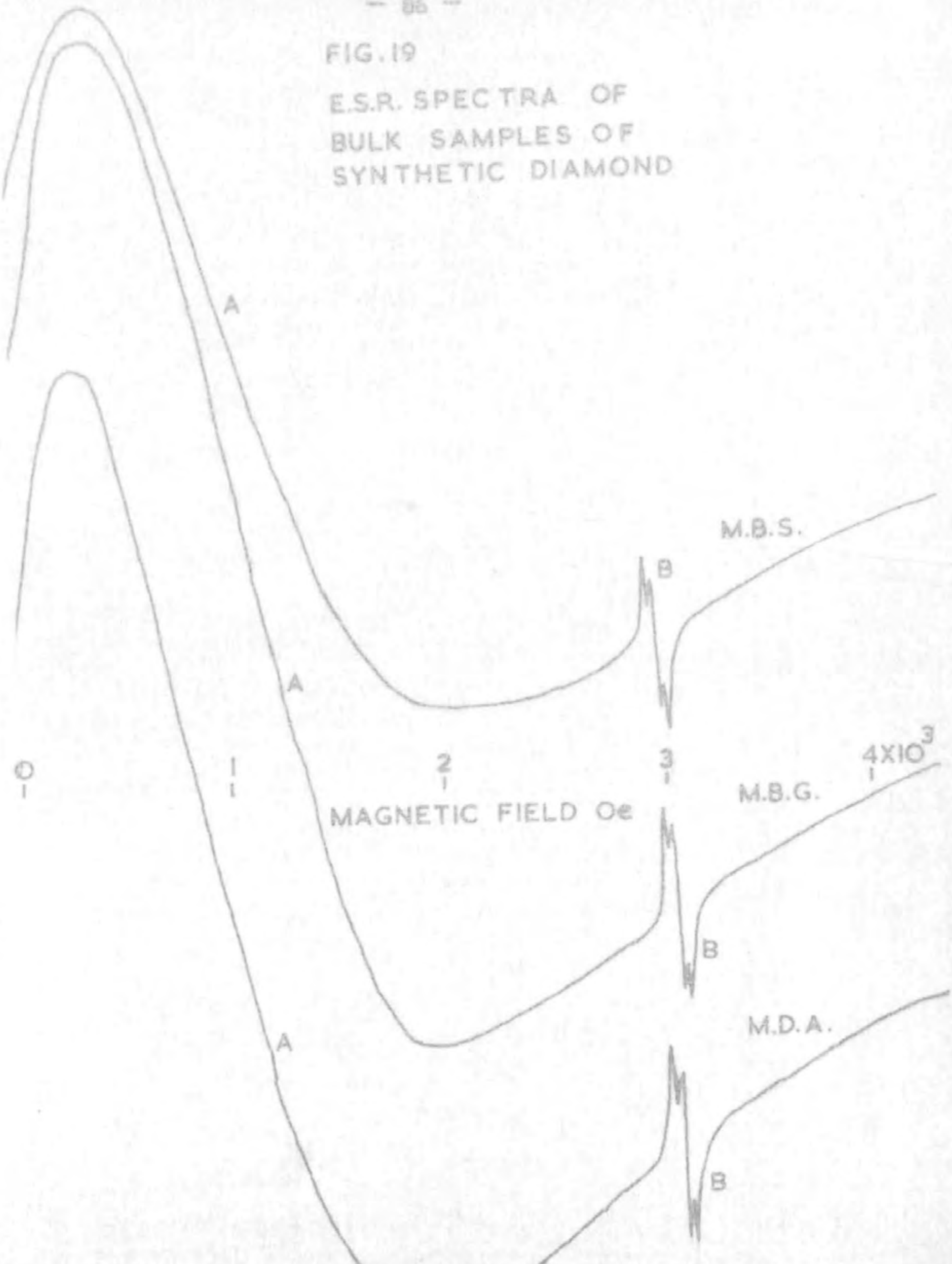
Typical electron spin resonance spectra associated with synthetic diamond at room temperature are shown in Fig. 19. Hereafter, that part of the spectrum (A) which is attributed to ferromagnetic impurities will be referred to as the broad resonance and the triplet spectrum (B) due to substitutional nitrogen atoms as the nitrogen resonance. Other resonances will be referred to explicitly as they are discussed.

The investigation was started by recording the spectra from 0.1 gms of each of the five types of diamond. (Figs. 19 and 20). The similarity between the broad resonances from the metal bonding diamonds is clearly indicated together with a marked difference between both the resin bonding types and between the metal and resin bonding types. It was likely, therefore, that although different catalyst may have been used in the preparation of resin bonding types, a common catalyst was involved in the case of metal bonding diamonds. The variation in line width of the nitrogen resonance supported this suggestion.

The widest variations in the width and intensity of the nitrogen resonance occurred in the resin bonding samples. Two distinct features were apparent. First of all both the broad resonance and the nitrogen resonance from the R.V.G. diamond appeared to be more intense than was the case for the R.D.A. Secondly, the three lines of the nitrogen resonance of the R.D.A. sample appeared

FIG. 19

E.S.R. SPECTRA OF BULK SAMPLES OF SYNTHETIC DIAMOND



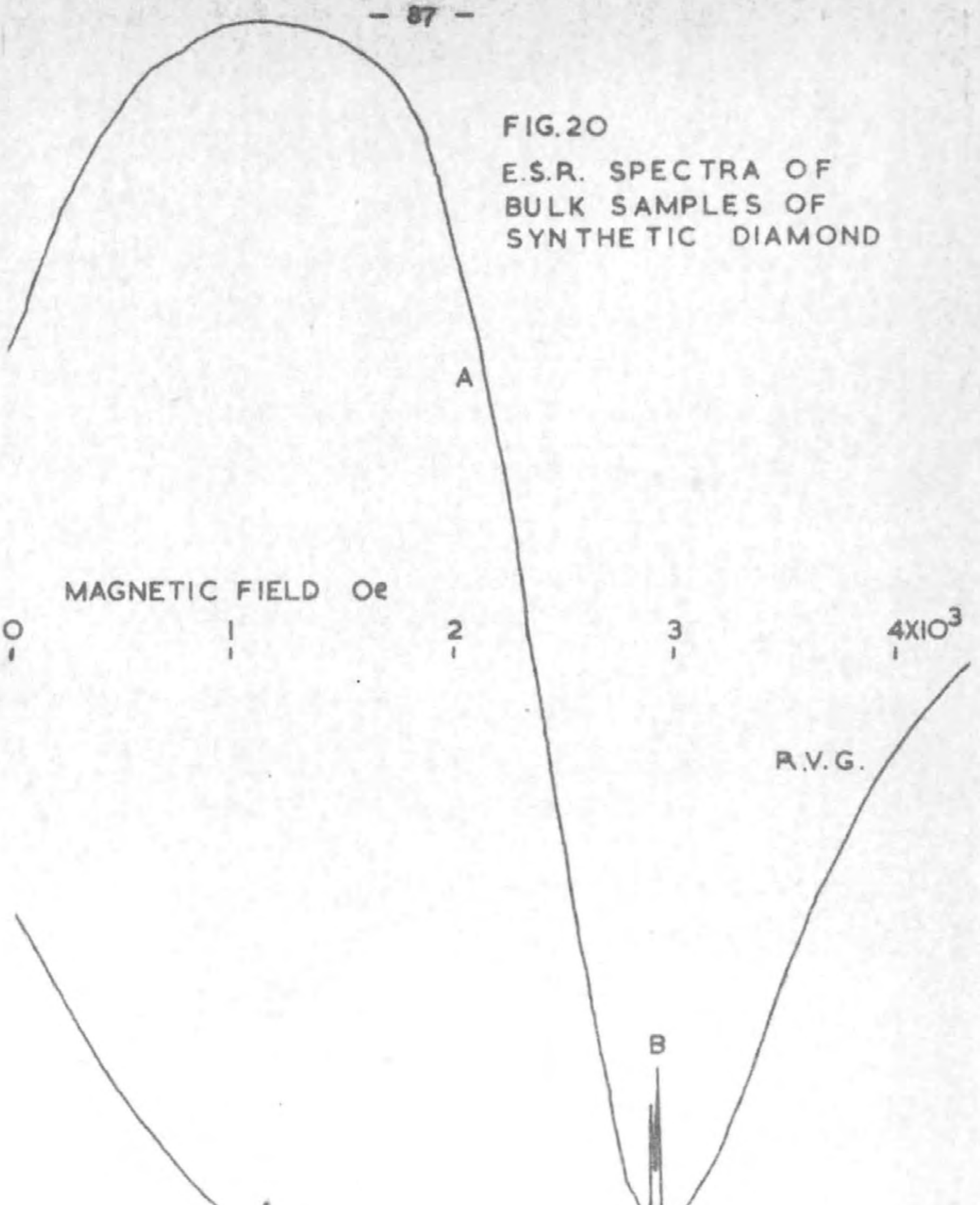


FIG. 20

E.S.R. SPECTRA OF BULK SAMPLES OF SYNTHETIC DIAMOND to be broadened to the extent that they appeared as a single isotropic line. Experiments with heated samples which are discussed in Section 4.7 verified that this was so. It is also important to note that the lines from the R.V.G. sample were the narrowest of all five types.

As far as the author is aware, no steps were taken by the manufacturers to exclude nitrogen from the reaction mixture in the preparation of R.D.A. diamond. There was no reason to suppose, therefore, that the mean concentration of nitrogen impurity in these crystals should be less than that in the four other types. However, the intensity of the nitrogen resonances indicated that this might have been the case. Previous work[1] had demonstrated the variation in amplitude of electron spin resonance signals with size of specimen. In this case, however, the spectra were representative of stones whose dimensions were within the mesh ranges 35/80 (177μ to 350μ) and, therefore, the appearance of the suppressed resonance due to this effect was not expected. The R.D.A. sample possibly contained aluminium or boron which can cause a reduction in the intensity of the nitrogen resonance.[2]

The spectra also illustrated that the intensity of the broad resonance could not be correlated with the broadening effect on the nitrogen lines. For example, the broad resonance was very intense for the R.V.G. diamond but the nitrogen lines were sharp. The reverse was true for R.D.A. diamond. These results suggested that it was unlikely that a defect occurred in the diamond which was jointly responsible for the broad resonance and the broadening effect of the nitrogen lines.

4.5. The Nature of the Ferromagnetic Additives

Variations in the broad resonance suggested that different types of ferromagnetic catalyst were used in the manufacture of each of the five different types of synthetic diamond. However, with the exception of R.V.G. diamond which was known to contain nickel,[2] the nature of the additives was unknown. An attempt was made, therefore, to determine the composition of the diamonds using the technique of X-ray microanalysis.

The intensity of the broad resonance suggested that concentrations of ferromagnetic impurity might have been as high as 10^{20} atoms cm^{-3}. In addition, experiments carried out by Kamiya and Lang[3] in 1964 demonstrated the presence of nickel rich surface films and Ni-rich globules in some synthetic diamonds. Although the equipment required to carry out the X-ray microanalysis was not readily available, Dr. D. Burr of International Nickel Ltd., kindly agreed to assist. A copy of his report on the work is included overleaf where it can be seen that neither iron nor nickel could be identified. Unsuccessful attempts were made to identify other metallic substances which may have been present. After further discussion with Dr. Burr and his colleagues it was clear that the results could not lead to any positive conclusions.

INTERNATIONAL NICKEL LIMITED
Development and Research Department

D. 5024 REPORT NO. 1

MICROANALYSIS OF SYNTHETIC DIAMOND

HISTORY

Electron spin resonance studies of the structure of synthetic diamonds at the University of Warwick have led to the suggestion that the surface layer may contain nickel, which is present in the catalyst used in the manufacturing process.

SAMPLES

Synthetic diamond particles were supplied and microanalysis was requested for nickel and iron at the surface.

EXPERIMENTAL PROCEDURE

Particles were inserted in aluminium discs by pressing onto clean glass or tantalum sheet, and examined in the microprobe analyser at 15 kV. Line and spot analyses were performed.

RESULTS

No indication of the presence of nickel could be obtained. Several records showed very small intensity maxima at the wavelength appropriate to iron, but the effect was not reproducible and could not be definitely distinguished from background radiation.

CONCLUSIONS

No nickel or iron was detectable in the samples. The limit of detection in a relatively large volume is $\sim$0.01 wt.%, but if the elements are present only in a volume small compared with probe dimensions, the limit is correspondingly higher.

DJB/PMMo
August, 1966.

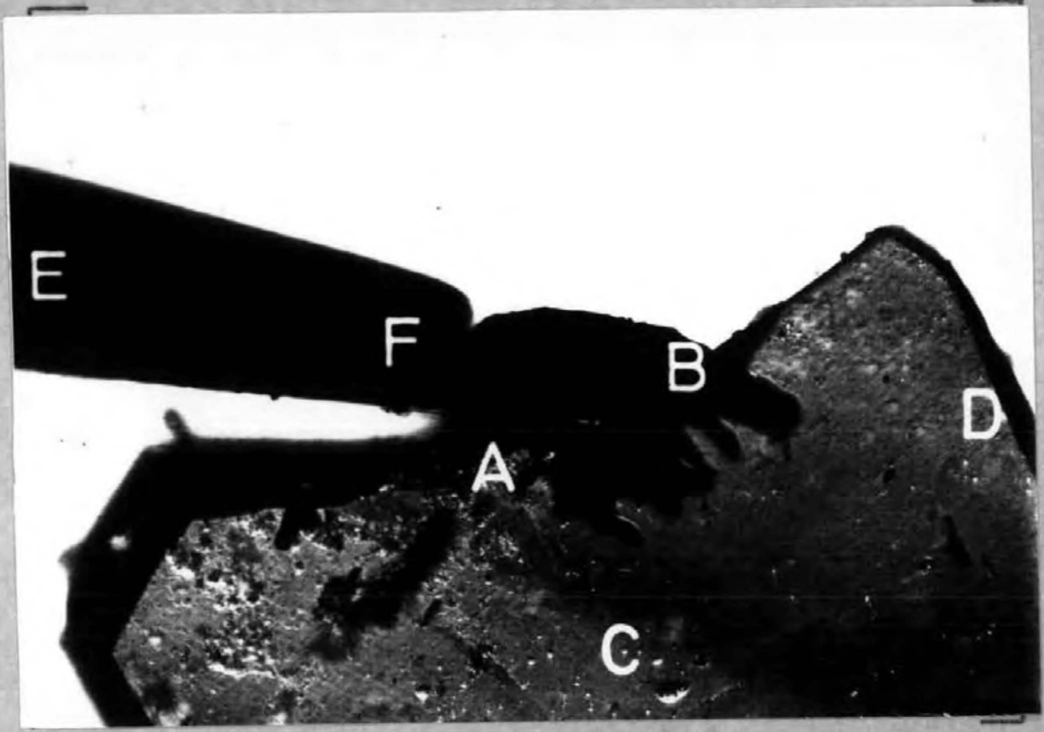
4.6. Visible Inclusions

The coloured photographs (Fig. 18 Page 84) show that many dark inclusions are visible in synthetic diamond. As the majority of the synthetic diamonds examined in this work were ferromagnetic it was thought that the inclusions comprised aggregates of ferromagnetic impurity. The results of the X-ray microanalysis did not support this suggestion. In addition similar inclusions which were not ferromagnetic were readily visible in natural diamond. The true nature of dark inclusions in synthetic diamond was not therefore obvious. A simple but convincing experiment demonstrated beyond reasonable doubt that the visible inclusions were ferromagnetic.

To provide a means of examining the inclusions a diamond containing a dark inclusion which was clearly visible, was ground on a scaife to expose parallel dodecahedral faces. To produce such a specimen the scaife was charged with natural diamond powder of dimensions less than 1μ. Although a single polished face proved to be extremely difficult to obtain, the problem was partly eased as a result of advice kindly given by experts at Culver Diamonds Ltd., Lichfield. However, no information was available on methods of producing the second parallel face on such small stones ($\sim 420\mu$). The first face was ground using a conventional soldered dop to hold the diamond. It was not possible using this device to reverse the crystal and so to preserve the correct orientation. As an alternative method, the crystal was cemented with the ground face adjacent to the flat end of a brass rod which was then lowered on to the scaife so that the principle axis of the diamond was perpendicular to the face of the scaife. Great care had to be exercised to ensure that grinding was allowed to continue at short intervals so that the heat produced did not crack the stone.

Fig. 21 shows an optical micrograph taken with transmitted light. The sketch illustrates the experimental arrangement. The dark inclusion is visible and extends into the crystal as shown by the boundary AB. During the grinding process, the crystal broke around the inclusion in a direction parallel to the grinding lines CD which accounts for the extension of the inclusion above the crystal surface. The strong attraction of the inclusion to a pair of magnetised tweezers EF indicated that it was ferromagnetic. As can be seen from the sketch, the attraction was sufficiently strong to allow the specimen to be held in a horizontal plane without further support. Apart from the inclusion, no other region of the crystal was attracted to the tweezers. The dark perimeter on the micrograph was caused by the edges of the crystal.

The inclusion was dissolved in concentrated hydrochloric acid but due to the small concentration of metallic ions in the solution, it was not possible to identify the ions by chemical



TRANSMISSION OPTICAL MICROGRAPH OF MBS 35/40 DIAMOND AS SUPPLIED, WITH GROUND OPPOSITE DODECAHEDRAL FACES.

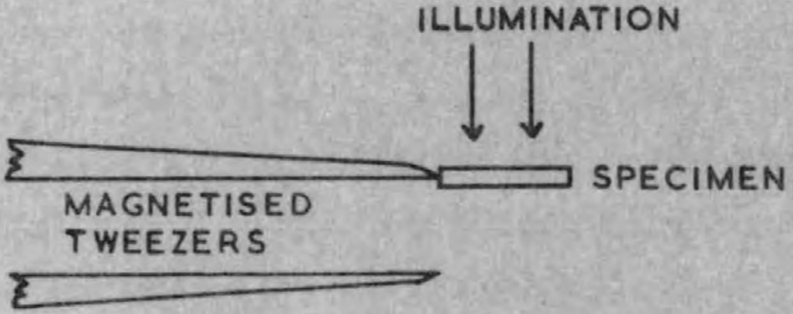


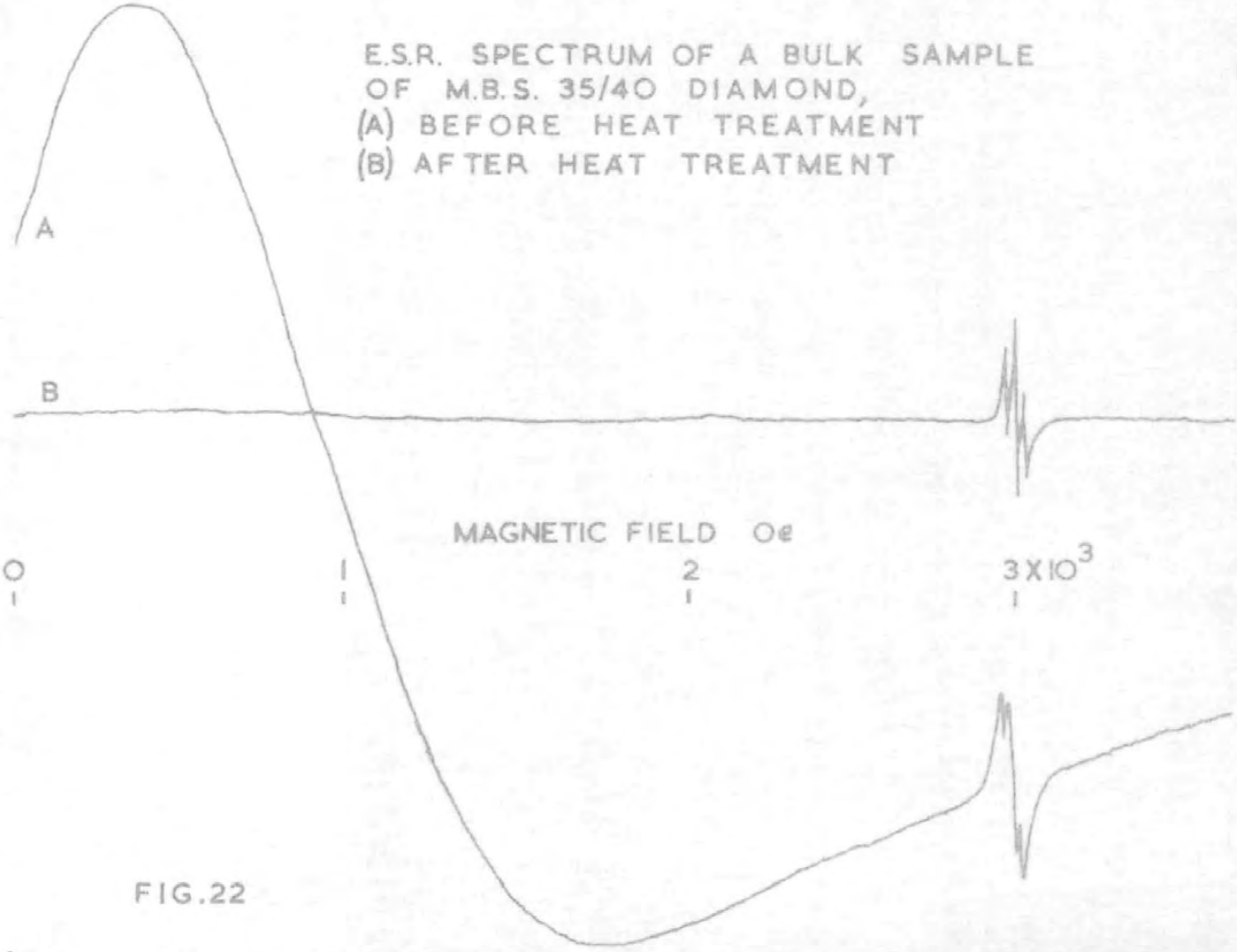
FIG. 21

analysis. There was no longer any doubt that the dark inclusions were aggregates of ferromagnetic impurity although their composition was unknown.

4.7. The Effect of Heat Treatment

Lonsdale et al[4] in 1959 showed that the anomalous X-ray spikes which occur on the Laue spots from synthetic diamond can be removed by heating the diamond at 1500°C in vacuo. They suggested that the metallic inclusions melted and were dispersed. It was possible, therefore, that similar treatment might give rise to significant changes in the electron spin resonance spectra, and at the same time could possibly provide a means of identifying the chemical composition of the evaporated metallic impurities by allowing them to recondense in a more concentrated form. With the aid of a vacuum furnace samples were heated for a few minutes at a temperature of approximately 1500°C and a pressure of 5×10^{-5} Torr. The effect on the electron spin resonance spectra was very pronounced and is shown in Fig. 22 for a bulk sample of M.B.S. 35/40 diamond.

Two distinct features are apparent. The broad resonance was removed and the nitrogen lines appeared to be much charper. Similar results were obtained with all five types of synthetic diamond. The effect of heat treatment was, therefore, to either remove the ferromagnetic additive from the crystals or to reduce it to a form which no longer produced a broad resonance. The



E.S.R. SPECTRUM OF A BULK SAMPLE OF M.B.S. 35/40 DIAMOND,
(A) BEFORE HEAT TREATMENT
(B) AFTER HEAT TREATMENT

FIG.22

first alternative seemed more likely as a significant loss in weight occurred after heating. In addition, discolourations which were characteristic of the type of diamond appeared on the crucibles. For R.V.G. and the three M-type diamonds the colour observed was green but for R.D.A. it was a very dark blue. The residue on the crucibles was dissolved in concentrated hydrochloric acid and the resulting solutions were subjected to chemical analysis. Although the concentrations of metal ions were small positive results were obtained. The residue from R.D.A. samples was found to contain cobalt unlike the residue from R.V.G. diamond which, as expected, contained nickel. The metal from all three M-type diamonds was identified as a mixture of iron and nickel. No other elements were detected.

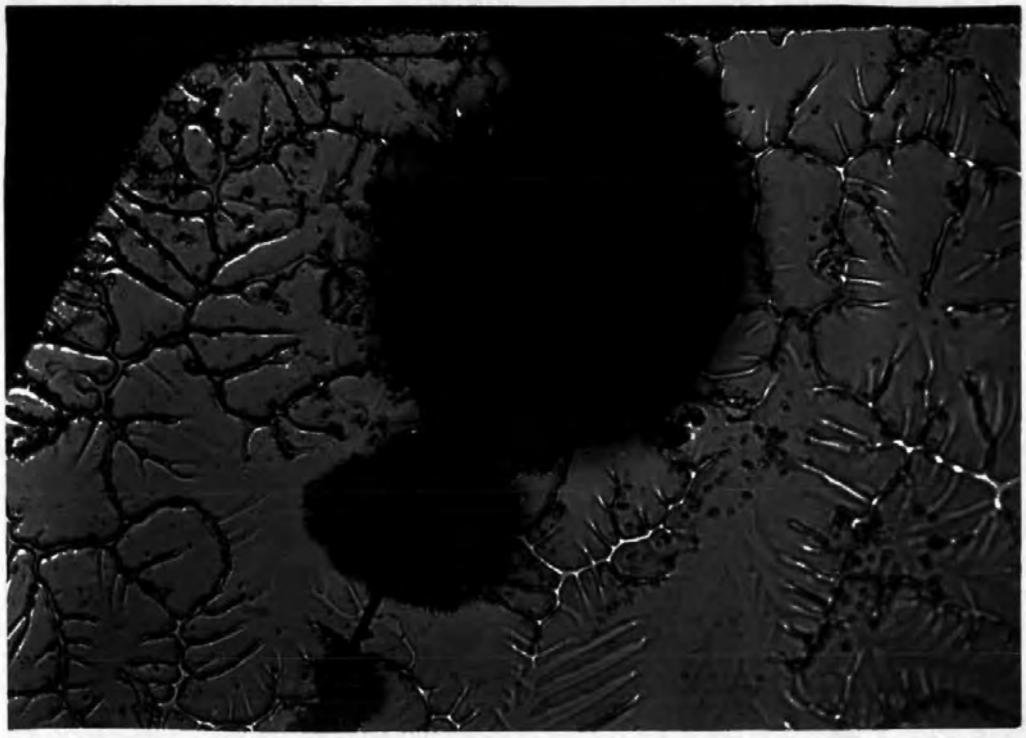
At this point the investigation had established that the effect of heat treatment at 1500°C was to remove either part or all of the ferromagnetic additive. However, neither the mechanisms involved in the process nor the effect of temperatures less than 1500°C were known. This being so, crystals which had been heated at various temperatures between 800°C and 1500°C were examined with an optical microscope.

Although it was not possible to make detailed observations of specimens as they were being heated, the results of an exmination of a crystal after its temperature had been raised to approximately 1200°C for a few minutes, were found to be particularly significant. The optical micrographs in Fig. 23 which were all recorded with reflected light, show the main features of interest. The first photograph is one of a typical (111) face prior to any heat treatment. The dendritic nature of the surface is clearly visible. The same face, after the crystal had been heated in the manner described, is shown in the second micrograph. The appearance of dark regions can be seen superimposed on two lines which are parallel to the edges of the crystal face and which were caused by cracks at the crystal face. The remaining dark regions were of particular interest and therefore were studied in more detail. The results are best described by referring to micrographs 3 and 4 which were recorded with increased magnification. By focussing the microscope alternately on the crystal surface and the top surface of the dark regions the majority of them were found to be hillocks which extended at least 75μ from the crystal face. Although the tops of the hillocks showed a definite pattern it could not be identified with a known crystal symmetry.

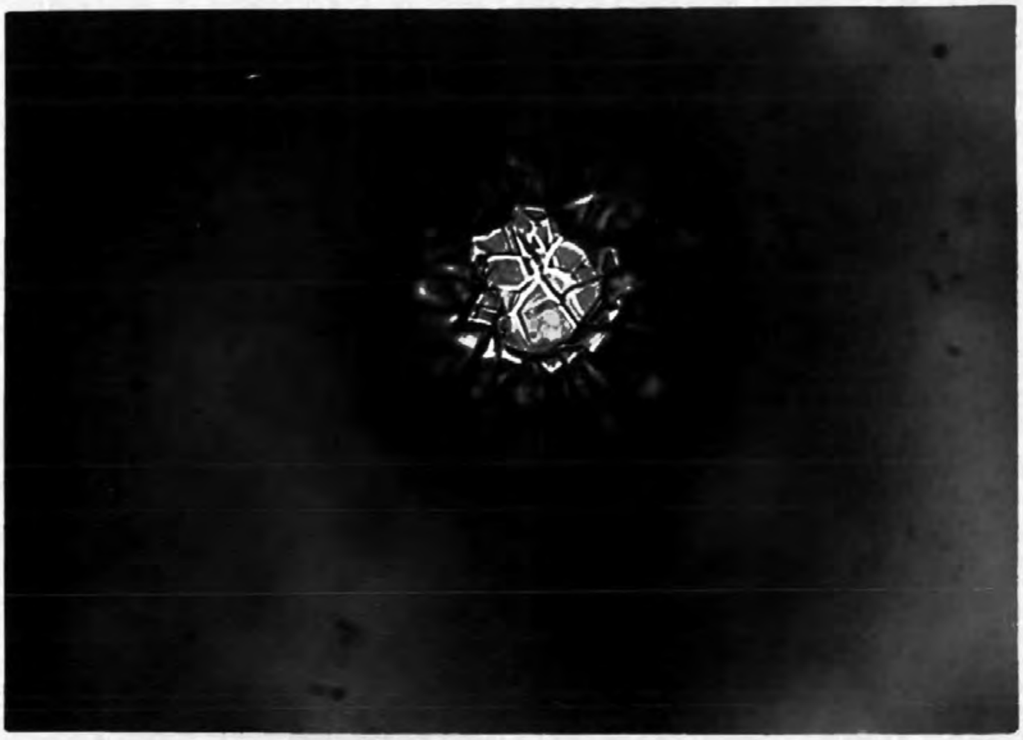
A series of experiments were carried out to investigate the nature of the hillocks and their associated patterns. The experiments showed that the hillocks adhered to magnetised tweezers in a manner similar to that previously described for inclusions inside the diamond. In addition, it was found that

1. ×20.

2. FIG. 23 ×20.

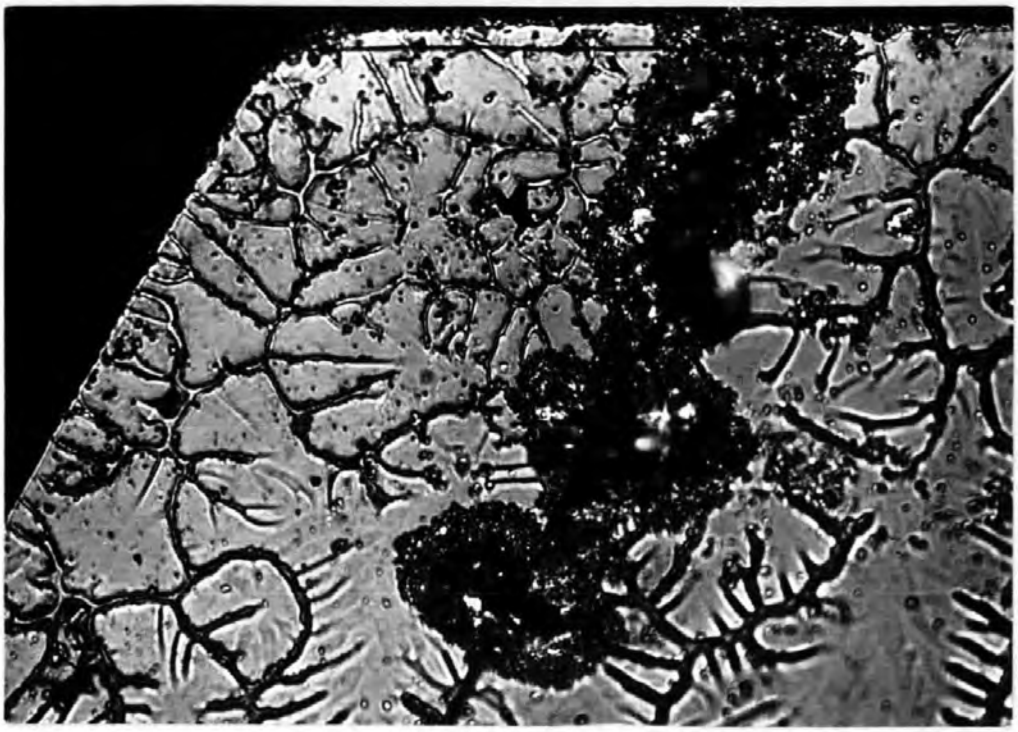


3. × 80.



4. × 80.

FIG. 23



5. ×80.

FIG.23

the hillocks could be dissolved in boiling aqua-regia. The surface which remained (micrograph No. 5) appeared rough and pitted. It was concluded, therefore, that the hillocks comprised ferromagnetic material which prior to the heating process existed inside the diamond probably as dark visible inclusions.

The electron spin resonance lines of the nitrogen resonance remained broadened after this treatment and the broad resonance was present. Only when the diamond was heated to 1500°C in vacuo did the width of the nitrogen resonance decrease and the broad resonance disappear.

It was possible with the aid of a hot stage microscope to control the temperature more accurately and to observe the extrusion of the metal as the temperature of the specimen was increased. The diamond was contained in an atmosphere of argon for the examination as the windows of the cell in which the diamond was situated were not sufficiently rigid to withstand the excess pressure caused by evacuation. The design of the optical system restricted the thickness of the windows. This technique had the advantage that more than one crystal face could be observed at the same time. Conclusive evidence was obtained to show that in the majority of cases the diamonds cracked to expose (111) faces. In addition the extrustion process took place in two distinct stages.

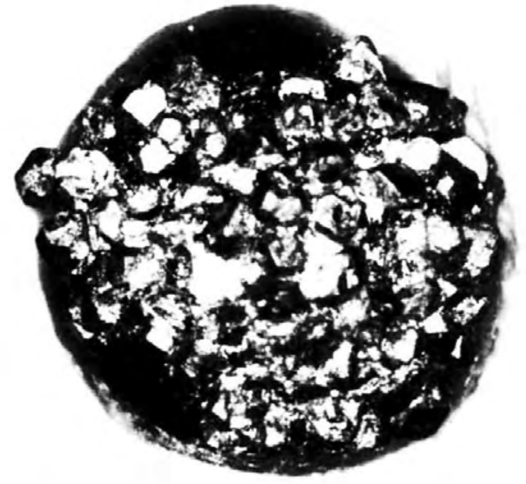
At temperatures of approximately 800°C migration of material through the crystal occurred and it became opaque. As natural diamond remains transparent under the same conditions the observation is attributed to graphitisation and the formation and migration of ferromagnetic globules. At this stage no metal appeared at the surface. A further increase in temperature was required to release the metal to the surface. The production of a crack which immediately preceded the release of metal in some cases produced sufficient disturbance to make movement of the whole diamond clearly visible. The release of strain energy stored in the stone as a result of the growth of the metallic inclusions provides an acceptable explanation. Both processes occurred very rapidly and it was not possible to study the mechanisms involved in more detail.

As it was suspected that the sudden cleavage of a diamond due to expansion of the metallic inclusions produced small fragments of diamond which might be responsible for the observed patterns on the hillocks, mixtures of diamond and metal were heated in vacuo at a temperature of 1200°C. It was found that for either iron or nickel or for a mixture of both, the metals melted to form a globule and the diamonds floated to the surface where they remained approximately half immersed. The result was to produce a piece of metal which tended to be hemispherical in shape with the majority of the curved surface encrusted with diamonds. (Fig. 24) The process of heating the metals alone, produced very smooth surfaces and patterns on the hillocks could not be reproduced. The patterns were most probably due to small fragments of diamond which had floated to the surface of the molten metal. The fragments probably resulted from the heating process which caused cleavage of the crystal. Additional evidence for this conclusion was obtained by performing scratch tests on plate glass. The metal failed to make any impression on the glass but an inverted hillock produced a scratch with comparative ease.

4.8. Experiments with oxidised samples

An alternative and somewhat more quantitative investigation of the composition of the ferromagnetic additives was carried out by oxidising known weights of each type of diamond. Larger quantities of residue were obtained by this method and consequently a more detailed chemical analysis was possible.

The weights of the residues obtained from complete oxidation of equal weights of two samples were compared. One of the samples consisted of stones as supplied by the manufacturer and the other of stones which had received the heat treatment. It was found that approximately 70% of the ferromagnetic additive in a bulk sample of synthetic diamond could be removed by heating the stones in vacuo at 1500°C for 15 minutes.



X15.

REFLECTION OPTICAL MICROGRAPH OF A HEMISPHERE OF METAL (IRON OR NICKEL OR A MIXTURE OF BOTH) ENCRUSTED WITH DIAMONDS WHICH WAS PRODUCED BY HEATING A MIXTURE OF DIAMOND AND METAL IN VACUO AT 1200°C

FIG. 24

With the exception of the R.V.G. residue, the electron spin resonance spectrum associated with the residues obtained after complete oxidation was found to be identical with the appropriate broad spectrum from unheated stones. No signal was obtained from the R.V.G. residue. A negative result was also obtained from a powdered sample of nickel oxide. In the process of oxidation, the diamond residue had probably been oxidised to form a similar compound.

Although no further information concerning the nature of the additives was obtained by oxidising diamonds manufactured by the General Electric Company a significant result was obtained from the R.D.A. and M.D.A. diamond. A small number of white crystallites appeared in both the residues. The largest quantity was obtained from the R.D.A. sample. At first the crystallites were thought to have come from the roof of the furnace in which the diamond had been heated or possibly from the alumina boats which were used as containers. By repeated trial both these possibilities were eliminated. It should be pointed out that relatively large quantities of diamond had to be destroyed in order to obtain correspondingly small amounts of residue. For this reason it was not possible to obtain a sufficient quantity of crystallites for chemical analysis. A more detailed qualitative analysis was carried out by spectrographic analysis on all five types of diamond before and after oxidation.

4.9. Spectrographic Analysis

A Hilger quartz spectrograph was used in the analysis. The spectral region from 2600Å to 5000Å was covered and was selected because it included the major portion of the sensitive lines of the elements which preliminary examination had shown were present. Each sample was ignited at a current of 7 amps with an electrode separation of 3mm.

For the majority of samples, copper electrodes were used in preference to carbon electrodes as the latter would have given rise to strong cyanogen bands and would have tended to obscure the principal lines associated with some of the expected trace elements. Separate tests were made with carbon electrodes to determine if copper was present. The arc method was used as the exitation process was sufficiently energetic to give detectable spectra for most elements.

The method also had the advantage that the sample did not need to be treated chemically with the associated risk of contamination. An attempt was made to detect the thirty elements listed in Fig. 25. The most sensitive lines and the appropriate checking lines for each element are also given in Fig. 25. A spectrum of each element was recorded on a separate plate and compared with the spectra obtained from each type of diamond and its

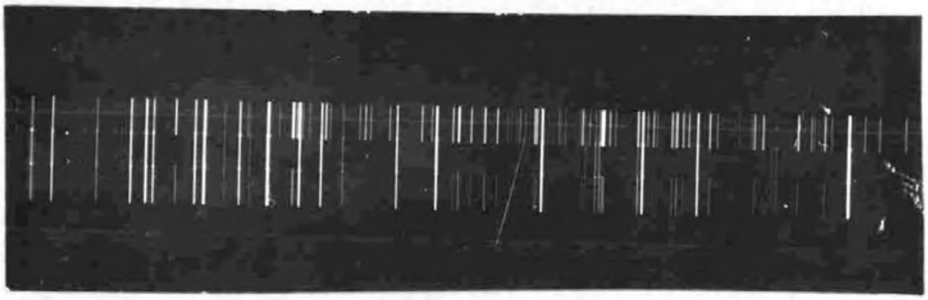
Element	Most Sensitive Line (Å)	Check Line (Å)
Aluminium	3961.53	3944.03
Antimony	3267.48	3232.52
Arsenic	2860.46	2898.73
Barium	4554.04	
Beryllium	3130.42	3131.06
Bismuth	3067.73	2897.98
Calcium	4226.73	2899.78
Chromium	4254.34	4274.80
Cobalt	3453.51	3405.12
Copper	3247.55	3273.96
Germanium	3039.08	3269.50
Gold	3122.8	
Iron	3719.94	3734.14
Lead	4057.83	3683.47
Lithium	4602.99	3232.67
Magnesium	2852.13	3096.92
Manganese	4030.76	4033.07
Nickel	3414.77	3524.54
Potassium	4047.22	4044.16
Rubidium	4215.58	4201.81
Scandium	4246.85	3613.8
Silicon	2881.59	3905.52
Silver	3280.67	3382.89
Sodium	3302.94	3302.34
Strontium	4607.34	4077.71
Tin	3262.33	3034.12
Titanium	3349.41	3371.46
Tungsten	4008.76	4294.62
Zinc	3345.51	3302.56
Zirconium	3391.98	3438.23

Fig. 25.

associated residue on a Hilger comparator. The analysis was semi-quantitative and no attempt was made to determine the absolute quantities of the impurities present in the samples. Part of a typical spectrum showing predominately Iron and Nickel lines is shown in Fig. 26 together with the results of the analysis. The results were the same both for the diamonds and their associated residues.

The intensities of the spectral lines suggest that those elements classified as major constituents were introduced intentionally by the manufacturer into the reaction mixture. It has been mentioned previously that R.D.A. samples probably contained aluminium or boron. (Page 88). The analysis established the existence of aluminium but in addition suggested that silicon was present. It is likely that silicon might have arisen from the pyrophilite used in the diamond presses. If this is so, it is difficult to understand why it should not have been present in the samples manufactured by the General Electric Company. A logical explanation is clearly not possible without more details of the manufacturing process.

The results also suggest that chromium is the only addition to iron and nickel required as a major constituent to produce the larger M.B.S. diamond rather than the M.B.G. diamond.



AN ARC SPECTRUM OF M.B.G. DIAMOND IN THE RANGE 3197–2943 Å. SHOWING IRON AND NICKEL LINES

RESULTS OF SPECTROGRAPHIC ANALYSIS

Type of Diamond or Residue	Major Constituents	Trace Elements
M.B.S. 35/40	Iron, Nickel, Chromium	Magnesium, Manganese
M.B.G. 60/80	Iron, Nickel	Chromium, Magnesium, Manganese
R.V.G. 40/60	Nickel	Iron, Magnesium, Manganese
M.D.A. 40/60	Aluminium, Silicon, Nickel, Iron	Magnesium, Manganese, Chromium
R.D.A. 40/60	Aluminium, Silicon, Cobalt	Manganese, Magnesium, Iron

FIG. 26

4.10. Single Crystal Studies

4.10.1. The correlation between electron spin resonance phenomena and crystal habit

The intensity of the nitrogen and the broad resonances from bulk samples indicated the possibility of observing these resonances in single diamonds. Spectra were easily detected in almost all of the M.B.S. 35/40 diamonds, although for these stones the spectra showed marked variations. Each crystal without exception gave rise to a broad resonance, but in some cases no nitrogen resonance could be detected and some correlation between electron spin resonance phenomena and general appearance was anticipated. Only a very small number of the four remaining types of diamond gave detectable resonances and therefore the M.B.S. diamond was selected for special consideration.

With the aid of a small magnifying glass (x10) it was possible to divide a bulk sample into four main groups A, B, C, and D. The stones in group A had a pale greenish-yellow colour and only a few dark inclusions were visible. Group B contained stones with a large number of inclusions and appeared either black or very dark green. Group C was intermediate between groups A and B. The stones in group D were a sub-section of C but with an almost perfect octahedral habit. They were comparatively rare and only 20 were obtained. The stones of all groups were attracted to a permanent magnet. Spectra were recorded individually for samples of 50 stones from each of the groups A, B and C and for the 20 stones of group D.

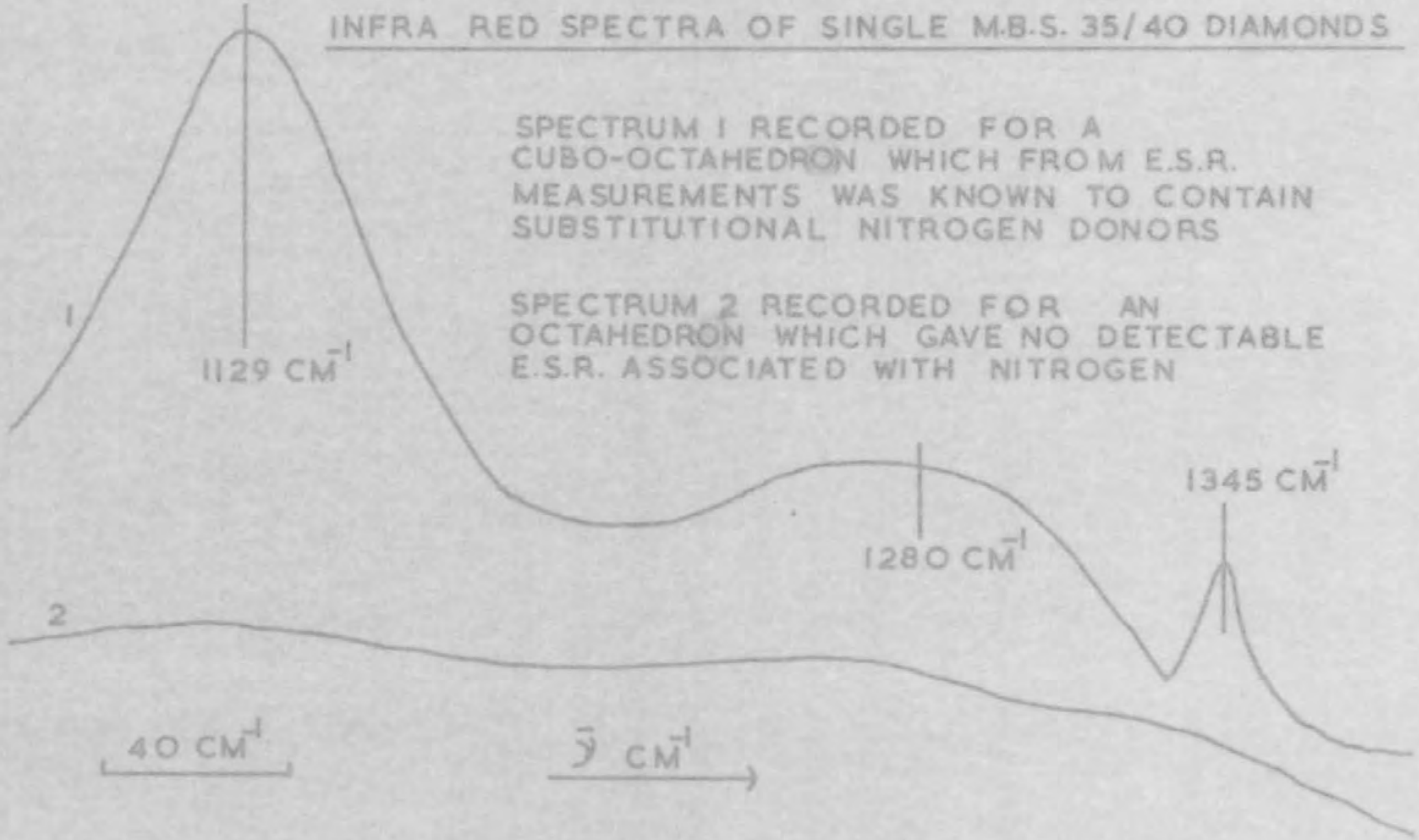
All samples gave a broad resonance with an apparently anisotropic g-value and a variable intensity. No correlations were detected between the samples.

Each stone from groups A, B, and C gave a nitrogen resonance with an isotropic g-value, a line width of 8 Oe, and a shape which was more nearly Gaussian than Lorentzian. The intensity varied between stones by a factor of approximately 5 but a direct correlation with the group to which it belonged did not appear to exist.

For the octahedra no trace of a nitrogen resonance could be found. Furthermore, a bulk sample comprising the whole group failed to produce a resonance in the region of $g = 2$. These crystals were, therefore, the only type in which any noticeable correlation existed between an electron spin resonance and the general appearance.

The absence of an electron resonance from the octahedra suggested that the number of substitutional nitrogen atoms in these stones was at least 2 orders of magnitude smaller than the number in the common cubo-octahedra. As far as the author is aware a common catalyst is used in the manufacture of M.B.S. diamond and therefore it seems unlikely that the octahedra contained sufficiently large amounts of boron or aluminium to completely suppress the nitrogen resonance. (Section 3.3). Alternatively, these diamonds may have been formed at temperatures which were sufficiently high to allow the formation of non-paramagnetic nitrogen platelets by diffusion. If this were the case it should be possible to identify the nitrogen impurity by an absorption peak in the infra red at 1280 cm^{-1} as this technique would respond to the total number of nitrogen atoms. Due to the small size of the crystals, the specialised equipment required to take advantage of this method was not readily available. In this respect the author is grateful to Professor J. J. Charette of the University of Lovanium, Congo, who made infra-red measurements on the octahedra. He found that only two diamonds were sufficiently transparent to be investigated. The spectra were compared with a reference spectrum from a cubo-octahedron which had previously been examined by electron spin resonance and was known to contain detectable amounts of substitutional nitrogen. The results of the investigation are shown in Fig. 27.

Earlier experiments had led Dyer et al[6] to suggest that peaks at 1129 cm^{-1} and 1345 cm^{-1} together with a broad saddle between the peaks were probably produced by isolated nitrogen donors. In addition they showed that a peak at 1280 cm^{-1} within the broad saddle is associated with a non-paramagnetic form of nitrogen. In the case of the octahedra, but not for the cubo-octahedra, the peaks at 1129 cm^{-1} and 1345 cm^{-1} were likely to be absent. Fig. 27 shows that the expected behaviour is observed. In neither case was a peak at 1280 cm^{-1} detected. It seems, therefore, that only



INFRA RED SPECTRA OF SINGLE M.B.S. 35/40 DIAMONDS

SPECTRUM 1 RECORDED FOR A CUBO-OCTAHEDRON WHICH FROM E.S.R. MEASUREMENTS WAS KNOWN TO CONTAIN SUBSTITUTIONAL NITROGEN DONORS

SPECTRUM 2 RECORDED FOR AN OCTAHEDRON WHICH GAVE NO DETECTABLE E.S.R. ASSOCIATED WITH NITROGEN

FIG. 27

substitutional nitrogen is present in the cubo-octahedra as the electron spin resonance measurements suggest and that no significant amount of nitrogen in any form is present in the octahedra.

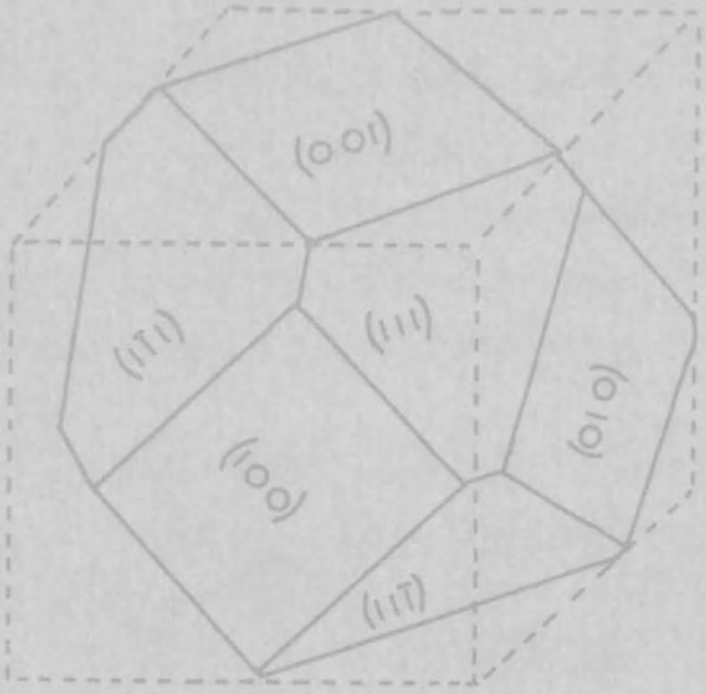
These results provide strong additional evidence for assigning the absorption peaks in the infra-red at 1129 cm^{-1} and 1345 cm^{-1} to isolated substitutional nitrogen donors. In addition, they suggest that for substitutional nitrogen in M.B.S. diamonds there is a direct correlation between electron spin resonance and infra-red spectra. Perhaps the most interesting result is the definite correlation which seems to exist between the nitrogen content and the crystal habit. A comparison of the amounts of nitrogen in the octahedra and cubo-octahedra suggests that nitrogen impurity in diamond probably encourages the growth of cube faces. The source of nitrogen and its distribution in the reaction mixture remains unknown. The explanation for production of octahedra may be that they are formed in regions of the reaction mixture where the concentration of nitrogen is relatively low. A non uniform distribution of nitrogen might occur if the temperature is sufficiently high in some regions of the mixture to enable nitrogen to diffuse out of the diamond at a higher rate than the growth process is taking place. In order to clarify the problem experiments would have to be performed with crystals grown in a controlled environment.

4.10.2. Orientation Effects

The ability to detect an electron resonance from a single synthetic diamond leads directly to an investigation of the variation of the spectra with orientation in the steady magnetic field. Experiments of this kind have been performed by Loubser and Du Preez[5] on the nitrogen centre in large natural Type Ib diamond but not on a single synthetic diamond. Dyer et al[6] quoted values of the hyperfine constants for synthetic diamond by examining bulk samples and applying the theory developed by Sands[7] to evaluate the constants for a large number of crystals in random orientation. The results were obtained from crystals which had been produced with a non-ferromagnetic additive Brightray-S (78 Ni, 21 Cr, 1 Fe). The resulting reduction in line width provided greater resolution and enabled more accurate quantitative measurements to be made. In this work single diamonds were used and a larger reduction in line width was obtained.

It is clearly important to determine if the angular variation of the nitrogen resonance is the same for synthetic and natural diamond and also if any angular correlations are associated with the additional resonances in synthetic diamond. The main difficulties involved in determining these properties arise due to the small size of available specimens. The largest synthetic diamond available for this work (M.B.S. 35/40) in which the average concentration of nitrogen donors is approximately 10^{18} cm^{-3} contains only 10^{14} unpaired spins. As the nitrogen lines are broadened by the ferromagnetic impurity the resonance lies within a magnetic field spread of approximately 100 Oe, the sensitivity of the spectrometer must be, therefore, at least 10^{12} spins Oe^{-1} line width in order to detect a resonance. Difficulties are also encountered in the controlled manipulation of small diamonds.

To study orientation effects in a single diamond the most convenient axis of rotation is a line passing through the centre of a diamond perpendicular to (110) planes. It is then possible to rotate the crystal about this axis and to align the magnetic field parallel to the three principal planes (100, 110, 111) in turn. The diamond should be mounted with a (110) face adjacent to the flat base of a sample tube. However, this was not possible with the M.B.S. diamonds unless they were ground to expose a (110) face. A diagram which illustrates the form of the cubo-octahedra is given in Fig. 28. It can be seen that the (110) faces are not visible. The (100) faces are bounded by edges which are in <110> directions and the (111) faces are bounded by six edges. If the diamonds are ground to provide a convenient axis of rotation they are reduced in volume to the extent that the total number of spins becomes too small to detect. As an alternative



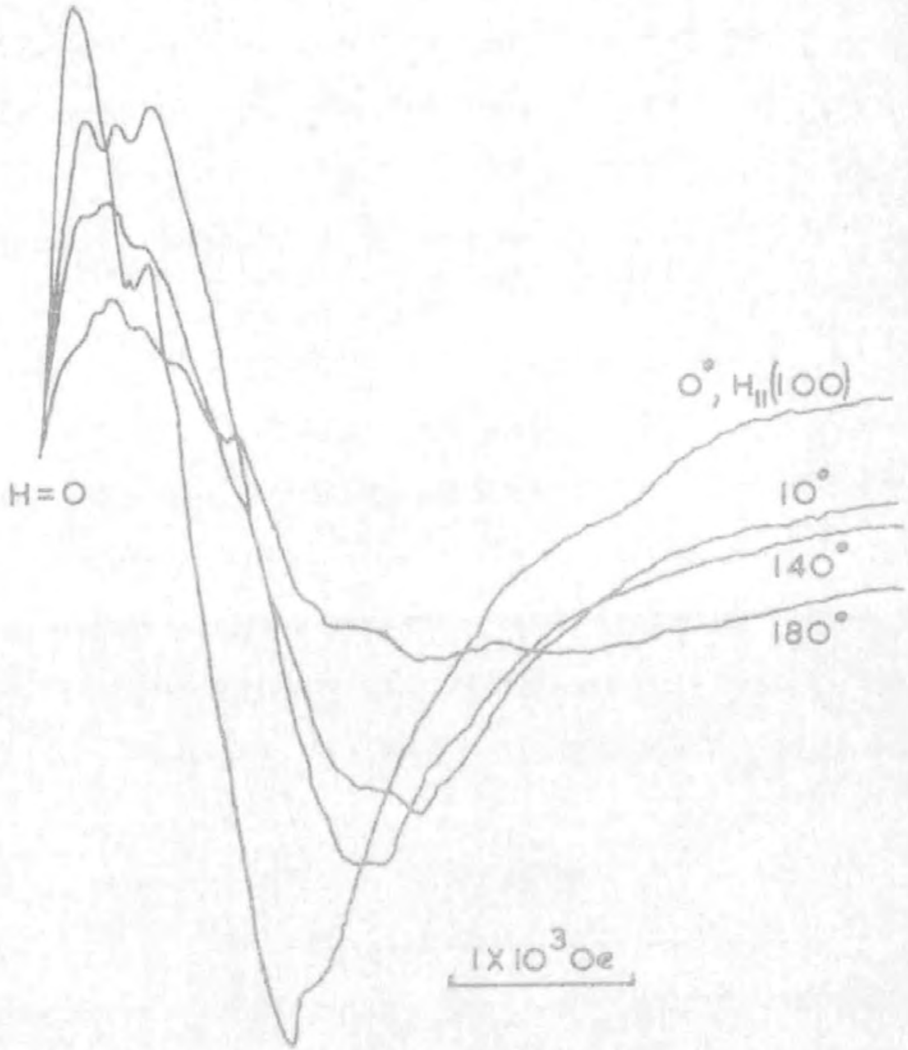
IDENTIFICATION OF CRYSTAL FACES OF A CUBO OCTAHEDRAL DIAMOND (M.B.S.)

FIG.28

the base of a sample tube was ground at 45° and a diamond was cemented with a cube face in contact with the ground surface. Although controlled manipulation of such small specimens (~ 0.5 mm diameter) proved extremely difficult, electron spin resonance spectra were recorded for a large number of diamonds at known orientations.

In general Type Ib natural diamonds have no preferred shape and it is necessary to orientate specimens by X-ray methods. For the regularly shaped M.B.S. diamond correct orientation was possible by visual examination. The broad resonance was investigated by aligning a diamond with the magnetic field parallel to a [100] direction and by recording the electron resonance spectra for 10° rotations from this orientation. The intensity, shape and apparent g-value varied with the rotation but it was not possible to associate the variation with crystal symmetry. Additional tests on a number of single crystals established that wide variations occur but that coincidence is not necessarily obtained at the same orientation. Extremes in the variations of the spectrum for a single diamond are illustrated in Fig. 29. It seemed unlikely that the centres responsible for the broad resonance had a preferential shape and lay in any particular plane.

The nitrogen resonance was recorded for three orientations corresponding to the steady magnetic field aligned parallel to the



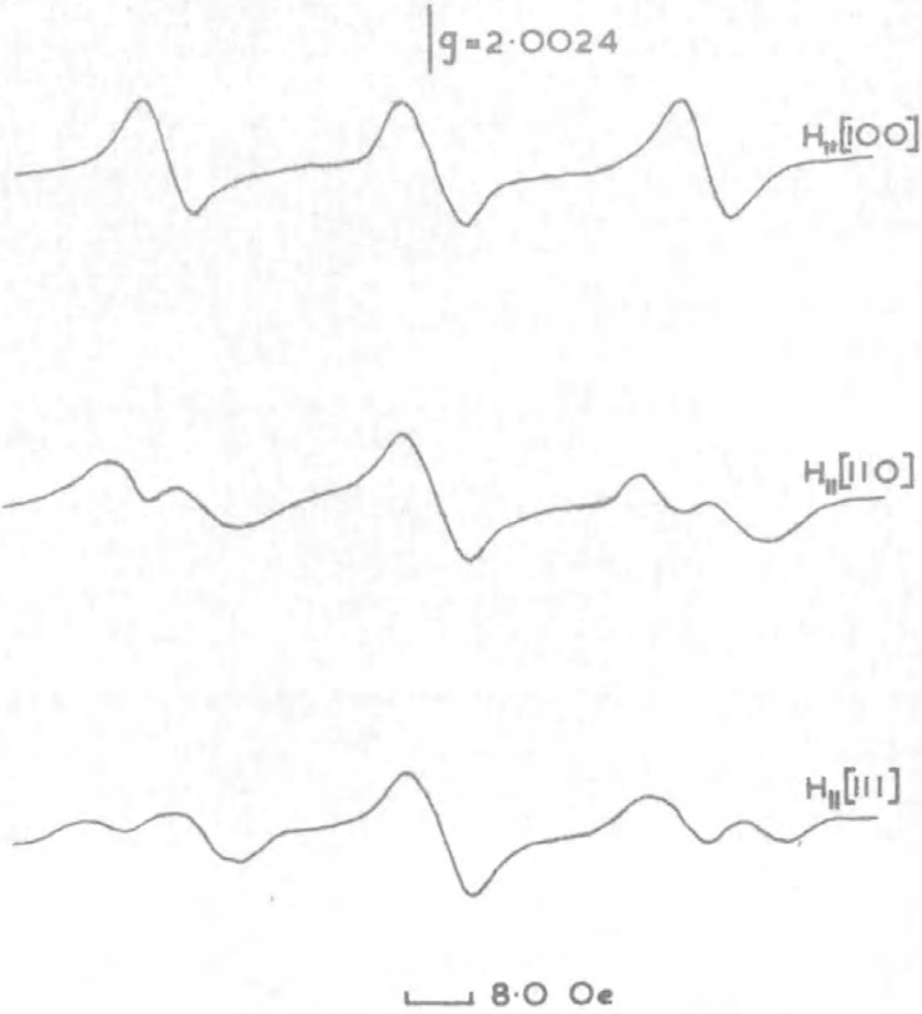
EXTREMES IN THE VARIATION OF THE BROAD RESONANCE OF A M.B.S. DIAMOND AT DIFFERENT ORIENTATIONS WITH RESPECT TO THE STEADY MAGNETIC FIELD

FIG. 29

three principal crystal planes. Although the expected anisotropic splitting occurred the lines were broadened by ferromagnetic inclusions to such an extent that they were not clearly resolved and, therefore, it was not possible to measure the hyperfine constants accurately. This problem was overcome by using heat treated samples. (Section 4.7)

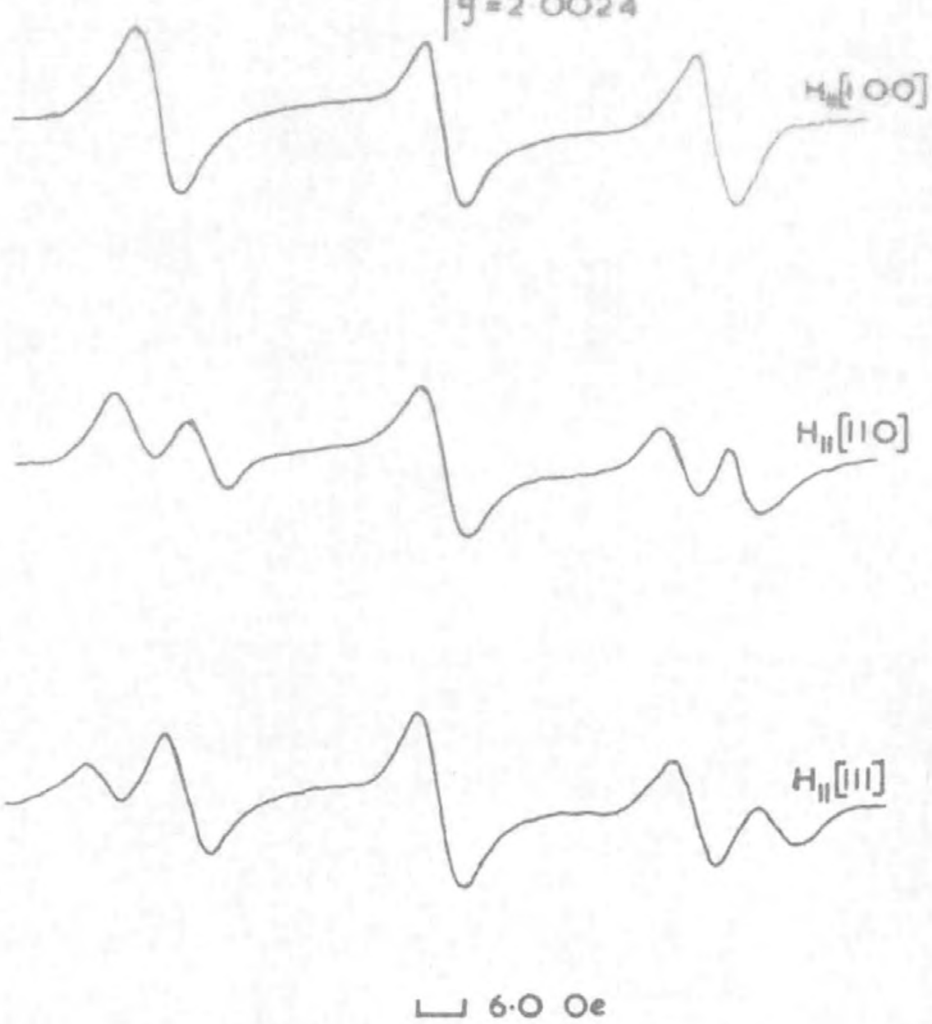
After heating at 1500°C in vacuo the stones of groups A, B, and C (Section 4.10.1) were reclassified into two groups. Group 1 contained stones which were still attracted to a permanent magnet whereas those in group 2 were not so attracted. In all cases the intensity of the nitrogen resonance remained unchanged but the line width from group 2 had been reduced from 8.0 ± 0.5 Oe to 3.0 ± 0.5 Oe. Group 1 gave a width which was slightly less at 6.0 ± 0.4 Oe.

Having reduced the width of the nitrogen lines it was now possible to measure the hyperfine constants more accurately with a stone from group 2. Figs. 30, 31, and 32 show nitrogen spectra obtained from three crystals. One of these had not received the heat treatment whilst the other two were from groups 1 and 2. The g-value in each case was 2.0024 ± 0.0005 (isotropic) and the hyperfine constants were $A = 41.0 \pm 0.4$ Oe and $B = 28.9 \pm 0.4$ Oe. These values are consistent with those obtained from natural diamond.



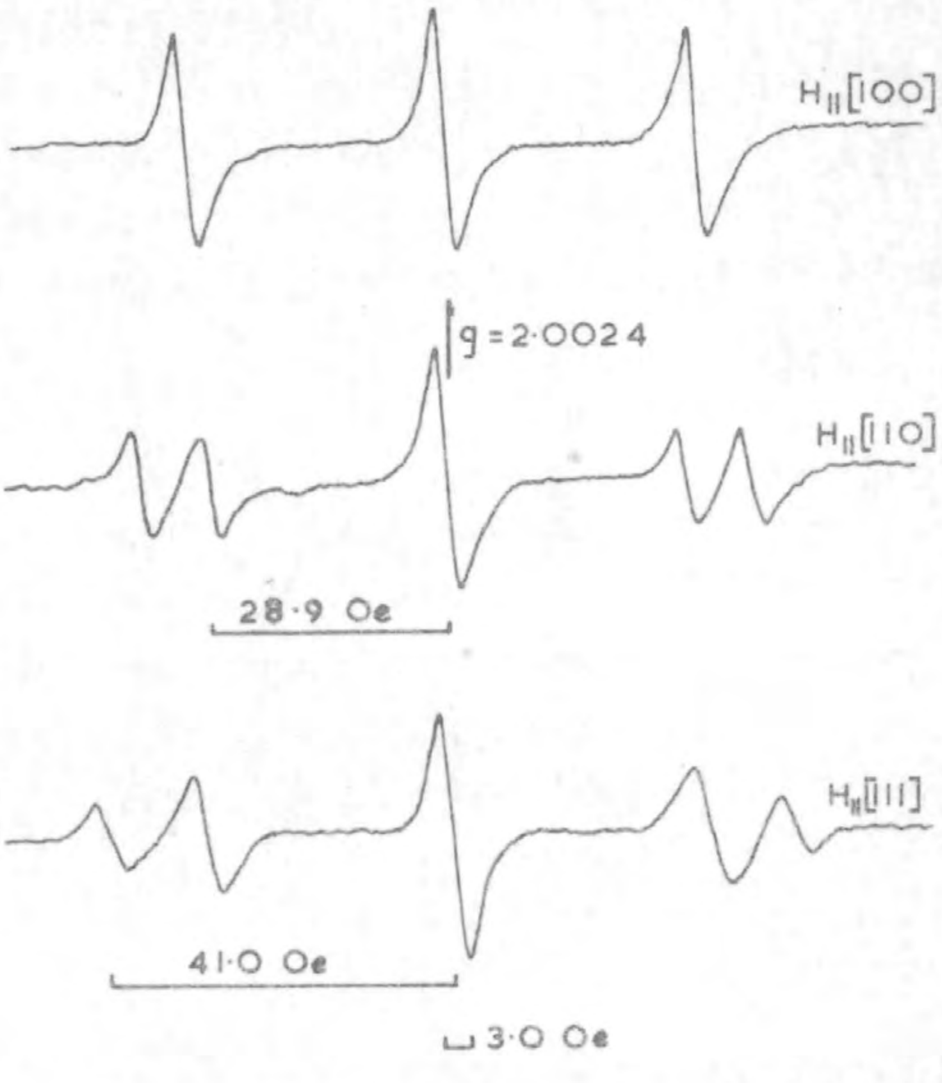
E.S.R. SPECTRA OF THE SUBSTITUTIONAL NITROGEN IN A SINGLE M.B.S. 35/40 DIAMOND OF GROUP 2, AT FIXED ORIENTATIONS TO THE APPLIED MAGNETIC FIELD, BEFORE HEAT TREATMENT

FIG.30



E.S.R. SPECTRA OF THE SUBSTITUTIONAL NITROGEN IN A SINGLE MBS 35/40 DIAMOND OF GROUP I, AT FIXED ORIENTATIONS TO THE APPLIED MAGNETIC FIELD, AFTER HEAT TREATMENT IN VACUO AT 1500°C

FIG. 31



E.S.R. SPECTRA OF THE SUBSTITUTIONAL NITROGEN IN A SINGLE M.B.S. 35/40 DIAMOND OF GROUP 2, AT FIXED ORIENTATIONS TO THE APPLIED MAGNETIC FIELD, AFTER HEAT TREATMENT IN VACUO AT 1500°C

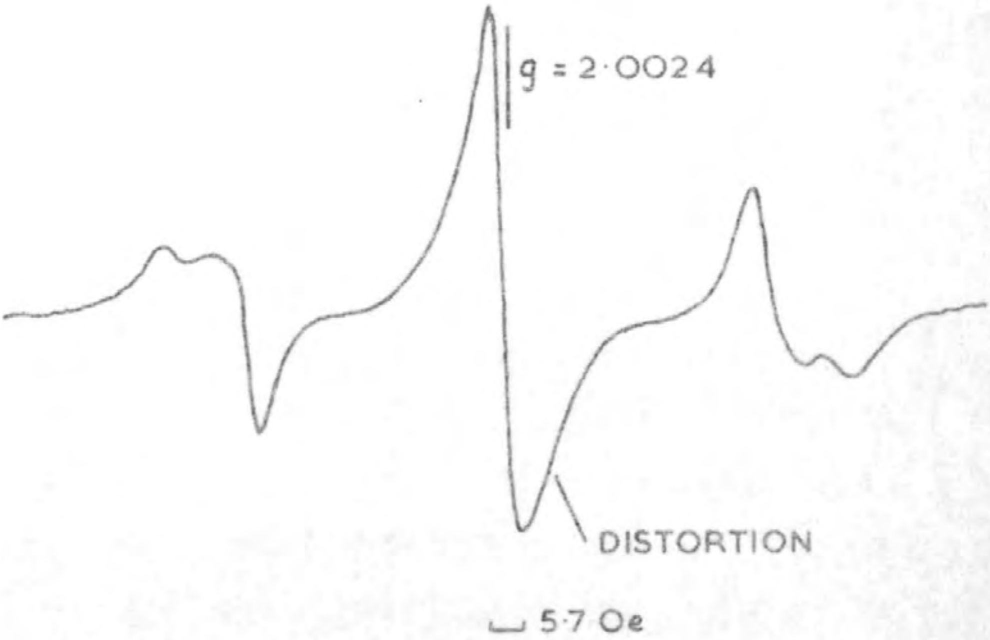
FIG. 32

4.11. Surface Carbonisation

Dyer et al[6] have suggested that the nitrogen spectrum from a bulk sample of synthetic diamond which does not contain ferromagnetic additive has the shape which is expected from a large number of crystals in random orientation. It is interesting and possible to verify that this is the case by using the heated stones from group 2.

The nitrogen resonance from a single stone was recorded and by successive addition of further stones it was established that the shape of the satellite lines in a bulk specimen was due to their random orientation. During this experiment a distortion was noticed on the high field side of the central peak of the nitrogen triplet (Fig. 33) which can be attributed to a second resonance occurring at a g-value slightly greater than that of the nitrogen resonance. The effect was small and not easily detectable in single crystals but arose as a direct result of the heating process.

In order to investigate the effect in more detail, five stones which were slightly imperfect octahedra with small visible cube faces were examined before and after heat treatment. The distortion from perfect octahedral habit resulted in only a small nitrogen resonance which was used as a convenient reference. After heat treatment the additional line was clearly visible and



E.S.R. SPECTRUM OF A BULK SAMPLE OF M.B.S. 35/40 DIAMOND AFTER HEAT TREATMENT IN VACUO AT 1500°C

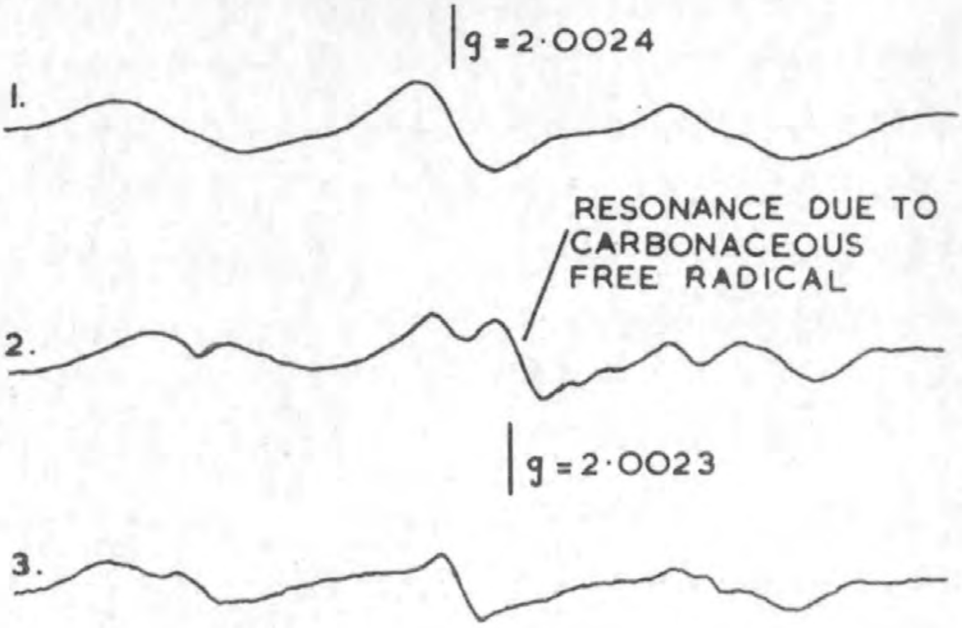
FIG. 33

had approximately the same intensity as the nitrogen resonance. It occurred at a g-value of 2.0023 and had a width of 5.8 ± 0.5 Oe. Consideration of the heating conditions and of the previous work on the subject[8,9] suggested that the resonance could be attributed to the usual free radical produced by carbonisation. Prolonged boiling in aqua-regia did not remove the resonance but it did disappear when a small amount of the surface was removed by uniform abrasion with natural diamond powder contained in an air blast. Spectra to illustrate the effect are given in Fig. 34. The origin of the carbon which provided the free radical was most probably the diamond itself. An alternative explanation would require carbon enriched aggregates of additive.

4.12. Spatial Variation of concentration of substitutional nitrogen

Immediately preceding this work the author[1] predicted that the concentration of substitutional nitrogen in synthetic diamond varies inversely with the mean radius of the sample. In order to verify this prediction by more precise methods than had been previously employed an attempt was made to reduce uniformly the size of a bulk sample. The machine previously described was used. (Section 4.2)

A preliminary investigation was disappointing. The stones became coated very quickly with metal from the walls of the enclosure and a prolonged air blast produced no further grinding action. It was necessary to remove the diamonds after intervals



E.S.R. SPECTRA OF A SAMPLE OF M.B.S. 35/40 DIAMOND CONSISTING OF FIVE SLIGHTLY IMPERFECT OCTAHEDRA

1. BEFORE HEAT TREATMENT
2. AFTER HEAT TREATMENT IN VACUO AT 1500°C
3. AFTER HEAT TREATMENT BUT WITH SURFACE LAYERS REMOVED

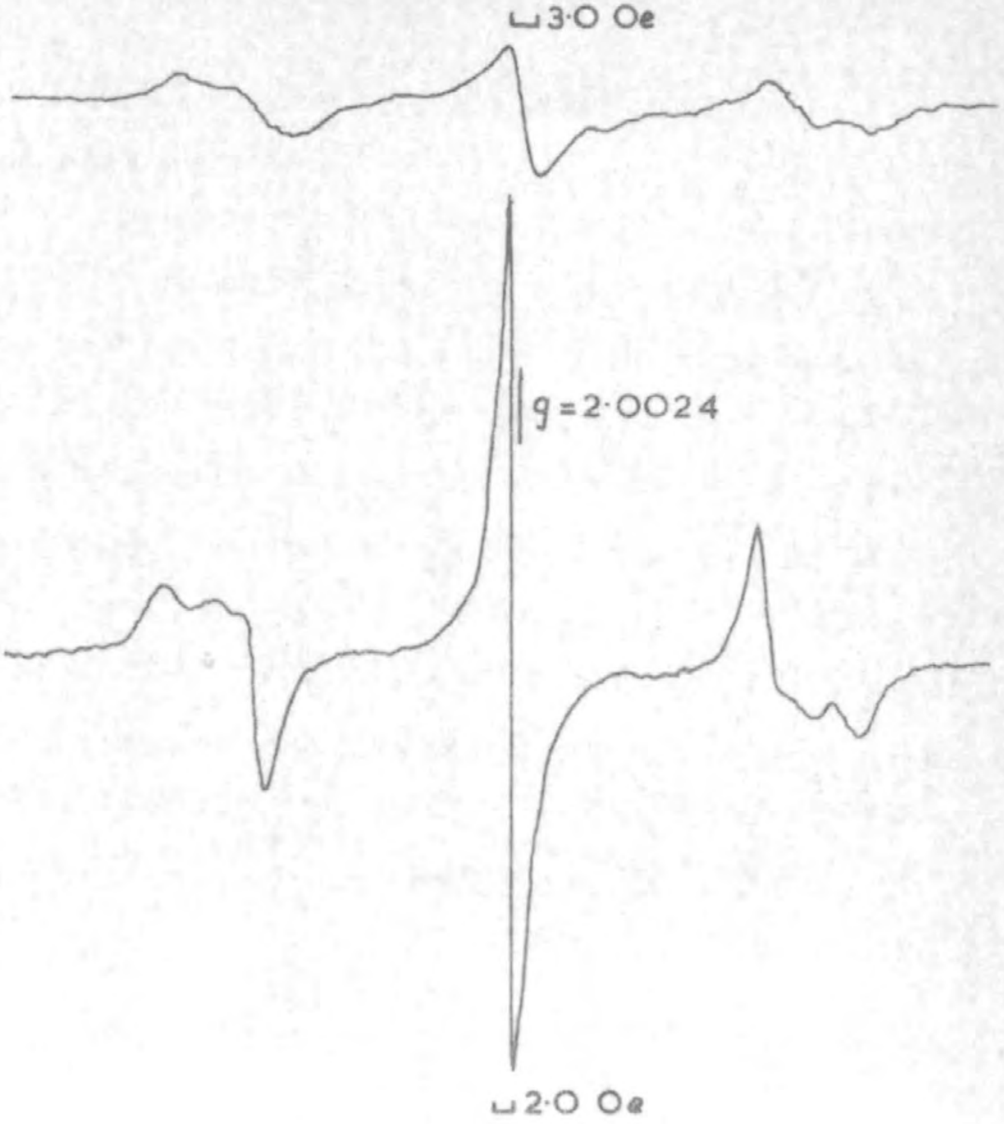
FIG.34

of a few minutes and to dissolve the metal coating in aqua-regia. After repeated trials the stones became almost spherical (Fig. 35). However, the reduction in mean diameter was too small to produce a significant change in the intensity of the nitrogen resonance. The resistance of spherical diamonds to abrasion seemed to increase markedly and further reduction in size was not possible.

Visual examination of the heated samples from group 2 revealed that some of the stones had become friable in their outer regions and these were, therefore, subjected to the grinding technique. 3 mgm of diamond with a mean diameter of 90μ was obtained from approximately 1 gm of M.B.S. 35/40 diamond (mean diameter 460μ). The intensities of the nitrogen resonance from the two samples of ground and unground diamond of equal mass were expected to vary by at least a factor of 3 if the distribution of the donors previously proposed by the author[1] was correct. The results, shown in Fig. 36 confirmed the expected behaviour. The line width was reduced to 2.0 ± 0.3 Oe and the shape of the satellite resonances was more peaked which suggested narrower component lines. It is also of interest to note that the central peak was symmetrical due to the removal of the crystal surface and therefore of the free radical mentioned in the preceding section. The narrowing of the central peak was expected due to exchange interaction. (Section 1.4).

REFLECTION OPTICAL MICROGRAPH OF A SAMPLE OF MBS 35/40 DIAMOND WHICH HAS BEEN GROUND TO PRODUCE ALMOST COMPLETELY SPHERICAL STONES

FIG. 35



E.S.R. SPECTRA OF EQUAL WEIGHTS OF M.B.S.35/40 DIAMOND, 1. BEFORE GRINDING (MEAN DIAMETER 460 μ) 2. AFTER GRINDING (MEAN DIAMETER 90 μ)

FIG. 36

4.13. Electron Spin Resonance at Low Temperatures

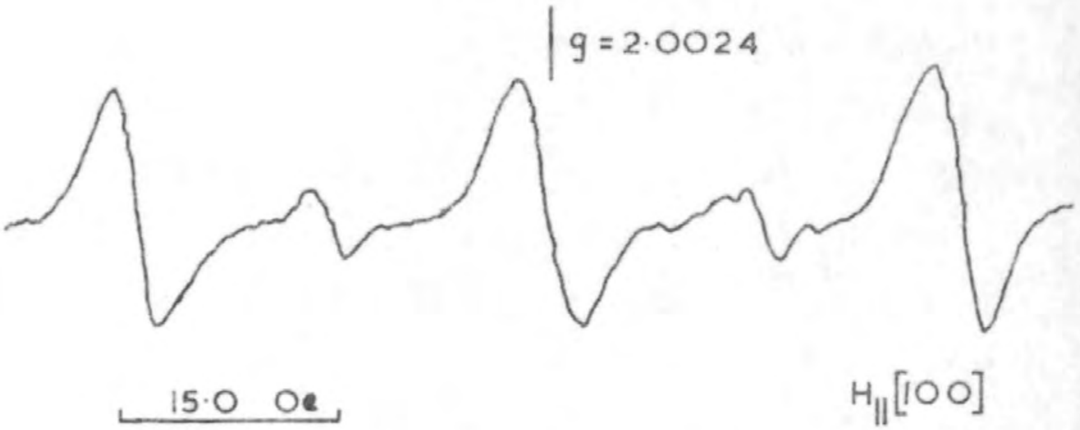
4.13.1. Quadrapole Effects

Although the nitrogen lines were easily saturated at liquid nitrogen temperatures it was possible under these conditions to observe hyperfine lines mid-way between the outer lines and the central isotropic line. (Fig. 37) These were very weak and could only be observed when a diamond was aligned with the magnetic field parallel to (100) planes. Similar lines have been observed in natural diamond[5] and have been attributed to quadrapole interaction.

Unsuccessful attempts were made to observe additional lines due to ^{15}N which also have been detected in natural diamond[5]. Two additional effects which had not been reported and which are of particular interest, were also observed at liquid nitrogen temperatures.

4.13.2. A New Resonance Line

An additional resonance was observed in all types of synthetic diamond with the exception of the octahedra of group D. Below -53°C a single isotropic line with a width of 6 Oe appeared at $g = 2.0310$. At this time there had been no reports of such a resonance and, therefore, the electron spin resonance spectra of all four types of natural diamond were re-examined. In order to increase the probability of detecting the new line bulk samples were used wherever possible. It was established that as the

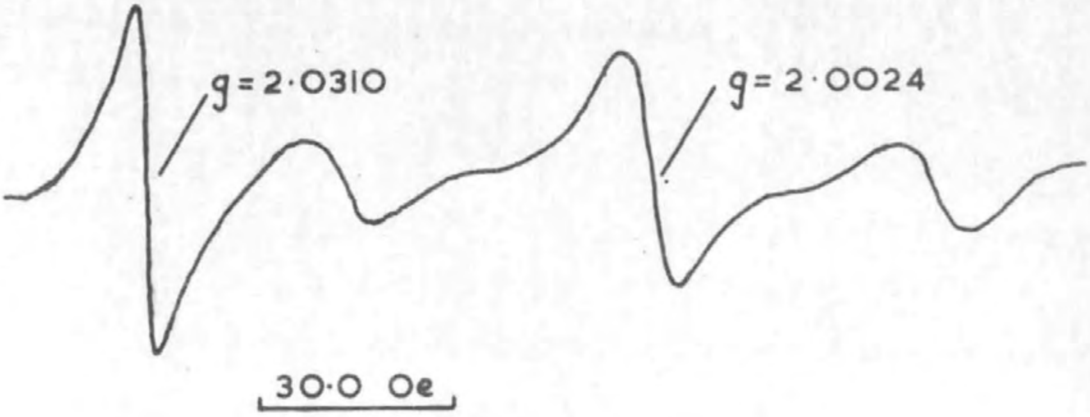


E.S.R. SPECTRUM OF SUBSTITUTIONAL NITROGEN IN A M.B.S. DIAMOND AT −175°C. LINES OF THE MAIN TRIPLET ARE PARTIALLY SATURATED; LINES MID-WAY BETWEEN THE MAIN TRIPLET ARE DUE TO THE QUADRAPOLE MOMENT OF ^{14}N.

FIG.37

resonance could only be observed in synthetic and not natural diamond it was associated with the ferromagnetic additive. The change in intensity of the resonance was particularly rapid in the region of $-73^{\circ}C$ but approximated to the usual $\frac{1}{T}$ dependence at lower temperatures. In heated samples the intensity remained unchanged but the line width was reduced by the same amount as the nitrogen lines and suggests that the broadening mechanism is the same for both resonances. A distribution of local magnetic field by aggregates of additive which are removed by the heating process provides a logical mechanism. A typical resonance is shown in Fig. 38.

Loubser and van Ryneveld[10] observed the same resonance independently at approximately the same time and reported their work. As a result of measurements on diamond grown with and without nickel additive they attributed the line to the presence of dispersed nickel although its form was not certain. If these results are combined with the work reported here a number of interesting problems arise. In diamonds which were grown with additives other than nickel the intensity of the resonance would be expected to be relatively small or even non existent. For example, the R.D.A. diamond was found to contain large amounts of cobalt but no nickel. In contrast, the R.V.G. diamond contained nickel only. However, the intensity of the resonance was approximately the same for both types of diamond. Clearly, if nickel is



E.S.R. SPECTRUM OF A BULK SAMPLE OF M.B.S. 35/40 DIAMOND (AS SUPPLIED) AT −175°C

FIG.38

present, the amount which gives rise to the resonance is in all cases very small and therefore may only be a part of the total nickel content.

The resonance could not be observed from the octahedra of group D (M.B.S. diamond containing iron and nickel). Furthermore, the absence of a nitrogen resonance in these stones suggested that in order to produce the isotropic resonance both nitrogen donors and dispersed nickel may need to coexist. The possibility that the concentrations of both impurities in the octahedra might have been sufficiently low to prevent detection by electron spin resonance should be noted. Clearly, further experiments to resolve these problems satisfactorily would require diamonds with known impurity concentrations and as these were not available no further progress was made.

4.13.3. Cross Relaxation Effects: Inversion

It has been mentioned in Section 3.2.2. that in special cases it is possible to invert the population of one of the satellite lines of the nitrogen resonance and to establish continuous wave maser operation. Sorokin et al[11] in 1960 showed that the effect can only be observed in diamonds which give additional resonance lines due to impurities. For these diamonds inversion of the low field satellite was obtained with a specially designed microwave circuit in which it was possible to saturate only the central line and at the same time observe either of the satellite lines. In this work using a conventional electron spin resonance spectrometer in which each resonance line is individually recorded as the magnetic field is swept through the resonant value it was not possible to observe the three nitrogen lines simultaneously and at the same time to saturate any one line. Nevertheless an inversion effect was observed. The spectrum is shown in Fig. 39. Unlike Sorokin's results in which the low field satellite inverted whilst the high field satellite remained unchanged, the central line appeared to invert whilst the low field satellite remained unchanged. In addition the high field satellite appeared to be saturated. Unfortunately, the effect was not reproducible and after many repeated trials it was observed only three times in one synthetic diamond which had been heated at 1500°C in vacuo. Consequently, the effect could not be examined in detail.

4.14. Experiments with Crushed Samples

Line widths narrower than any previously reported in synthetic diamond were observed in heated samples of group 2. Although line widths of 3.9 Oe were reported by Dyer et al[6] in samples of synthetic diamond grown with a non-ferromagnetic catalyst Brightray-S this value is at least an order of magnitude greater than the lower limit of 0.3 Oe which is observed in natural diamond. It should be noted that to date no satisfactory explanation has been offered to explain line width variations in natural coated stones. No details of spin concentrations were

AN INVERSION EFFECT IN THE E.S.R. SPECTRUM OF SUBSTITUTIONAL NITROGEN IN A M.B.S. 35/40 DIAMOND (PREVIOUSLY HEATED IN VACUO AT 1500°C) AT −175°C. THE CENTRAL LINE IS INVERTED WHILE THE HIGH FIELD SATELLITE LINE IS ALMOST COMPLETELY SATURATED.

FIG.39

given by Dyer et al[6] but it is unlikely that in the case of diamonds grown with the Brightray-S, the concentration exceeded 10^{19} spins cm^{-3}. For spin concentrations less than approximately 10^{19} cm^{-3} dipolar broadening would not be significant and it is difficult to see why the lines should not have been narrower.

Experiments carried out in the present investigation on samples of synthetic diamond of mean diameter 460μ which had been crushed past a 240 mesh sieve (66μ) and heated in vacuo at a temperature of 1600°C have shown that line widths can be reduced to 0.5 Oe. In samples which had been crushed, cleaned in aqua-regia, but not heated, line widths of 1 Oe were observed. It is reasonable to suppose that if the sample is crushed to smaller dimensions, the width may be reduced even further.

These results suggest that if synthetic diamond is crushed in addition to being heated, the aggregates of ferromagnetic additive which would otherwise melt and remain in the diamond, will be able to gain access to a surface and so be able to evaporate. The larger amount of additive extracted would produce a reduction in the spread of local magnetic field within the diamond with a consequent reduction in the observed width of any inherently narrow resonance. It seems reasonable to suggest, therefore, that in samples grown with Brightray-S ferromagnetic compounds were formed which caused the lines to be broadened. The same may be true for some natural coated stones.

As the broadening effect of the ferromagnetic additive was not confined to the nitrogen resonance but extended to the resonance associated with dispersed metallic ions, the variation of the line width of this resonance with temperature could be investigated more precisely by using the crushed samples. The width varied from 5.7 ± 0.4 Oe to 1.2 ± 0.1 Oe over the range -60°C to -100°C and appeared to be a linear function of inverse temperature over this range. Below -100°C and as the temperature approached -177°C, the line width tended towards a constant value determined by the small amount of additive still present in the diamond.

4.15. Summary

All available types of synthetic diamond were ferromagnetic. The characteristics of the broad electron spin resonance spectrum and the width of the nitrogen resonance seemed to be determined largely by the nature of the ferromagnetic additives.

The effect of heat treatment in vacuo was to remove the broad resonance completely and to narrow the nitrogen lines to varying extents. There was, however, no correlation between the extent of the narrowing and the retention of ferromagnetic properties. By heating alone, line widths were reduced to 3.0 Oe. Although this value was greater than that observed in natural Ib diamond, it was possible to make fairly accurate measurements on a single crystal and so to obtain values for the hyperfine constants which were in agreement with those previously obtained for natural diamond.

Line widths approaching the smallest values observed in natural diamond were obtained by crushing and heating synthetic diamond. However, further measurements on single crystals with the improved resolution of lines were not possible due to the reduced size of the stones.

As well as removing the broad resonance the heat treatment also gave rise to free radicals on or near the surface of the diamonds. In addition, some stones became more friable and consequently their size could be reduced and the variation of concentration of substitutional nitrogen with mean radius of sample could be studied in a most direct way.

A resonance not previously reported was observed at liquid nitrogen temperatures.

4.16. References

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5. FINAL DISCUSSION AND CONCLUSIONS

5.1. Discussion and Conclusions

Unlike natural diamonds, which may or may not contain nitrogen impurity in detectable quantities, each type of synthetic diamond contained detectable amounts of nitrogen with the exception of the octahedra. The origin of the nitrogen impurity remains undetermined and it is not possible to explain the affinity of diamond for nitrogen. As the nitrogen is substitutional and not interstitial in form it is unlikely that it diffuses into the diamonds after they have been formed. In this respect an investigation into the possibility of forcing nitrogen into natural Type Ib diamonds at high pressure would be interesting.

In order to investigate the existence of nitrogen in the octahedra, experiments are being developed to determine the total nitrogen content of synthetic diamond samples. Unlike natural stones which may contain 100 times as much nitrogen in platelet form compared with the substitutional nitrogen content, synthetic diamond appears to either contain very small undetectable amounts of nitrogen (as in the case of the octahedra) or fairly large concentrations (as high as 0.01%) most of which is in the substitutional form. Present methods of synthesis do, therefore, almost certainly differ from the natural processes in at least some respects.

The nitrogen resonance has been shown to be influenced by the nature of the ferromagnetic additive, the concentration of the nitrogen impurity, free radicals produced by carbonisation or mechanical damage, the presence of ^{13}C and ^{15}N, quadrapole interaction, and acceptor impurities such as aluminium. The most noticeable differences in spectra from the different types of synthetic diamond arise as a result of the various types of ferromagnetic additive used in manufacture. As well as producing a characteristic broad resonance the effect of the additives is to broaden the nitrogen lines to varying extents. The results show that in the case of a nickel additive the line widths are similar to those obtained from natural coated stones. The effect of iron and chromium is to increase the line widths considerably. Diamonds containing aluminium and cobalt were found to exhibit spectra whose lines were broadened to such an extent that they could no longer be resolved. In order to provide a satisfactory explanation of the ferromagnetic broadening effects a detailed knowledge of the ferromagnetic complexes within the crystals is necessary. As far as the author is aware, little or no information is available which describes the possible formations of metallic compounds at the pressures and temperatures used in the diamond reaction. Furthermore, it has not been possible to determine the nature of dispersed metallic ions in the diamond lattice. It is hoped that future investigations will clarify the situation. However, the present work has suggested that relatively small amounts of ferromagnetic impurities might easily give rise to significant broadening of the nitrogen lines. The variation in line width observed in coated natural diamond is probably due in part to the presence of very small quantities of metallic impurities whose nature remains undetermined.

The narrowest lines so far observed occur in natural Type Ib diamond. It would be interesting, therefore, to use the technique of spectrographic analysis to determine the relative impurity concentrations in natural Type Ib and coated stones. As natural Type Ib stones are rare, it was not possible to carry out such an experiment in this work.

When the nitrogen lines become broadened to such an extent that they tend to merge, any additional resonance which occurs in the region of $g = 2$ will clearly affect the shape of the spectrum as a whole. The effect may be small but could limit the accuracy with which the hyperfine constants of the nitrogen resonance are determined.

The production of a free radical which gave rise to a resonance at $g = 2.0023$ is of particular interest. Its existence can be identified by the assymetry it produces in the central peak of the nitrogen resonance. However, the concentration of the free radicals may be just sufficient to produce an apparent g-shift of the nitrogen resonance without necessarily giving rise to a noticeable distortion.

The resonance associated with the free radical is almost identical to that observed in natural Type IIa diamond for which no explanation has as yet been offered. Natural Type IIa diamonds may, therefore, contain similar centres. The results of a spectrographic analysis of a natural Type IIa diamond are not inconsistent with this suggestion in that impurities were not detected apart from those found in the majority of synthetic diamonds. Nevertheless, the possibility of an alternative centre being responsible for a similar resonance cannot be excluded. The enhancement of the central peak obtained with crushed specimens clearly indicates an alternative mechanism for the production of a free radical. However, in the case of crushed specimens the free radicals decay and it is unlikely that the surface effects in Type IIa diamonds are responsible for the isotropic line at $g = 2$ (Fig. 13).

Secondary effects due to exchange interaction are more noticeable in small stones. Additional evidence has been obtained in this work to support the suggestion that the concentration of substitutional nitrogen varies inversely with the mean radius of a stone although the average concentration over a sample remains approximately constant for all sizes. For smaller stones the contribution to exchange interaction increases and produces a detectable narrowing of the central peak. It should be pointed out that in general the smaller synthetic diamonds supplied by manufacturers comprise mixtures of crushed stones. The diamonds used in this work had not been subjected to any treatment by the manufacturers apart from the usual cleaning processes.

Previous electron spin resonance investigations have shown that mechanisms other than those so far mentioned give rise to additional lines in the nitrogen spectrum. Isotopic variation of carbon and nitrogen provides an example[1] although unless the lines are narrow and the concentration of substitutional nitrogen is high, the lines cannot be resolved on account of the low natural abundances. A further example is illustrated by the spectrum in Fig. 37 which shows quadrapole lines obtained from a synthetic diamond. In this case a high microwave power level is used so that the main lines are reduced by saturation, and the quadrapole lines are more easily detected. It has not been possible to resolve lines from $C_{13} - N_{14}$ pairs in synthetic diamond. The intensities of the lines are small and are expected to occur very close to the main lines. The line width in synthetic diamond is larger than the expected splitting and the effect cannot be detected.

For samples in which aluminium is present a spectrum due to bound aluminium acceptors is expected in the region $g = 2$. Previous work[2] has shown that in natural diamond the spectrum comprises between 14 and 30 lines in a total magnetic field spread of approximately 30 Oe. The number of lines depends on the orientation of the diamond to the steady magnetic field. If a spectrum of this type is superimposed on the nitrogen spectrum and is of a lower intensity than the nitrogen resonance the shape of the central peak would be altered to a greater extent than that of the satellite lines. Furthermore, the g-value of the aluminium resonance would be slightly shifted relative to that of the nitrogen resonance (Al. $g = 2.0023$, N. $g = 2.0024$). A combination of the two spectra could easily lead to a base line shift on either side of the central peak of the nitrogen triplet. An effect of this kind is noticeable when bulk samples are used. In addition a displacement of the base line of the nitrogen spectrum can be produced by the tail of the broad resonance. The degree of shift is determined by the type of additive used. For example, in the case of R.V.G. diamond the base line of the nitrogen spectrum is situated on a fairly horizontal portion of the broad resonance and therefore only small shifts are observed (Fig. 20). In contrast, all M-type diamonds give rise to significant shifts (Fig. 19).

The most interesting and significant results have probably been obtained from heated samples. Any mechanism which is proposed as an explanation of the observed effects of heat treatment must account for the variable extent of the narrowing of the nitrogen lines and also for the disappearance of the broad resonance together with a reduction or loss of the gross ferromagnetic property. The following mechanism accounts for the experimental observations.

X-ray measurements by Kamiya and Lang[3] provide evidence that synthetic diamonds which have been produced with a nickel catalyst, contain nickel rich surface films with particle diameters less than 1μ. With the exception of the gross inclusions previously discussed, the catalyst was found to exist primarily in the form of aggregates of varying sizes which are located preferentially in the outer regions of the diamond. If the broad resonance is attributed to aggregates or particles which have at least one dimension of the order of or less than the microwave skin depth (1μ), the contribution from the larger aggregates and inclusions is expected to be small as only their outer regions are effective. In contrast, it has been shown that the attraction of diamonds to a permanent magnet is determined mainly by gross inclusions.

After heating in vacuo at 1200°C the larger aggregates are able to melt and exert pressure on the diamond so that a distribution of cracks is produced along $\{111\}$ cleavage planes through which the additive may escape. The formation of spherically shaped globules of molten catalyst is most probably due to surface tension effects. The inability to wet diamonds with any type of material is a well known hinderance in the diamond tool industry. Although the melting points of Ni, Co, and Fe metals lie in the range from 1455°C to

1535°C, the required depression of the melting point can be obtained if the aggregates are enriched with carbon. At this stage the broad resonance would not be expected to change significantly.

Two processes occur if the temperature is raised to 1600°C. In the first process, aggregates of molten additive which have reached the surface of the crystal, evaporate. The results indicate that on average approximately 70% of the total amount of additive is removed by this process. In the second process it is suggested that the smaller particles coalesce locally but remain trapped within the diamomd. There is no longer a sufficient number of particles present whose dimensions are small enough to produce an observable broad resonance. Diamonds which still contain aggregates of catalyst remain attracted to a permanent magnet and the nitrogen resonance may still be significantly broadened although less so than in the unheated crystals. The experiments involving crushed specimens have illustrated quite clearly that the majority of broadening is due to gross inclusions which can be removed by heating. For the stones of Group 2 which are not noticeably attracted to a permanent magnet, most of the aggregated catalyst probably gains access to the surface by any of a number of extensions of the proposed mechanisms. The magnitude of the broadening and the gross ferromagnetic effects are, therefore, correspondingly less.

For reasons given previously (Section 4.13.2) it is not possible to explain in detail the existence of the additional electron resonance which appears at lower temperatures. However, it is clear that some of the additive also exists in the diamond both before and after heat treatment in a more dispersed form which has quite different properties from the aggregated additive. Attempts were made to anneal this type of defect but even when the temperature was raised to approximately 2000°C and the diamond began to graphitise very rapidly no change was observed.

5.2. Practical Applications

The results of this work might easily lead to some practical applications in the diamond manufacturing and tool industry. Past reports[4,5] have indicated that diamonds can be produced which are free of nitrogen impurity. Unfortunately, no details of the catalyst or of the diamond were given. It would seem from the work reported here that in the case of M.B.S. diamond the absence of nitrogen favours the growth of octahedral crystals. Clearly, it is advantageous to be able to control the shape of synthetic diamond.

In most practical applications of diamond in grinding tools, the stones have to be securely fixed within the host medium. For this reason, manufacturers provide different types of synthetic diamond which because of their shape and mechanical properties lend themselves to different types of bonding systems. The efficiency of a particular bond is determined primarily by the nature of the diamond surface. It has been shown that metal may be displaced from synthetic diamonds and may exist in the formation of an improved bond to the host medium. The experiments involving heat treatment of mixtures of metal and diamond (Fig. 24) illustrate the feasibility of this suggestion.

A second method of treating the surfaces of a diamond in order to make them more chemically suitable for bonding might well be achieved with crushed specimens. In this case, immediately after crushing, the surfaces are likely to contain free radicals due to broken bonds and are consequently chemically very active. Before the free radicals decay they may be used to form a strong bond to a material which in turn would lend itself to bonding to the host medium in a way which is superior to normal direct bonding between the diamond and the host medium.

The degree of friability of a synthetic diamond sample is determined by the method of manufacture. This property is desirable for industrial use and samples are available which have a range of friability indices. Heat treatment similar to that described in this work might easily lead to a convenient method of producing diamonds with these characteristics.

The gross inclusions which have been shown to contain ferromagnetic material tend to weaken the crystals and in this respect they assist in producing a more friable type of diamond. This characteristic might however be more directly and usefully employed.

The variation in the hardness of diamond with crystal direction is well known and an appropriate crystal alignment within a diamond grinding wheel would lead to greater efficiency. As a result of the large number of diamonds employed and their small size, no attempts to orientate the crystals have been made. However, if diamonds could be produced which contained aggregates of ferromagnetic material arranged as laminae in preferred planes, the application of a magnetic field might well provide a means of controlling their orientation within the grinding wheel.

5.3. Future work

The results presented here suggest that metallic impurities in synthetic diamond can exist either as large visible inclusions or as dispersed metallic ions. In both cases, however, knowledge of the physical properties of the impurity is limited and experiments to investigate the defects in more detail would therefore be important. Preliminary experiments with cleaved crystals have demonstrated that gross inclusions can be extracted for closer examination.

The dispersed metallic ions present a more challenging problem both from the experimental and the theoretical viewpoints. The intensity of the resonance which occurs at liquid nitrogen temperatures and which has been attributed to the dispersed ions, indicates that the concentration may be as low as one part per million. Consequently experimental methods of detection are limited. In this respect, it is hoped that further electron spin resonance investigations combined with additional non-destructive techniques such as X-ray fluorescence analysis, will provide a clearer understanding of the physics of synthetic diamond.

Ludwig and Woodbury[6] reported an electron resonance from dispersed nickel ions in germanium which is similar to that observed in synthetic diamond but which shows hyperfine structure at -271°C. Provision is being made to examine heated synthetic diamonds at similar temperatures.

In order to establish that the amount of substitutional nitrogen in natural diamonds is often several orders of magnitude less than the total nitrogen content, the total nitrogen content was determined by gas fusion analysis.[7] Similar measurements on synthetic diamond would be of interest particularly on the octahedra which would seem to be Type IIa.

5.4. References

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DISTRIBUTION OF SUBSTITUTIONAL NITROGEN DONORS IN SYNTHETIC DIAMONDS

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CONSIDERABLE attention has been devoted to the study of nitrogen impurity in natural diamonds using the technique of electron spin resonance[1-3]. The spectrum obtained is due to the unpaired electron provided by the substitutional nitrogen atom and the main feature is a triplet at $g = 2{\cdot}0024$ caused by interaction with the nitrogen nucleus which has a spin of unity. The distribution of nitrogen is variable and would seem to depend on the method by which the diamond was formed.

In the majority of natural diamonds nitrogen exists substitutionally in the form of non-paramagnetic platelets and such diamonds have recently been classified as Type 1*a* (ref. 4).

Type I*b* diamonds contain nitrogen atoms which are not linked in platelet form. The electron spin resonance spectrum is usually narrow (0·3 oersted) and depends on the orientation of the static magnetic field to the diamond lattice. It has hyperfine constants $A = 40{\cdot}8$ oersteds and $B = 29{\cdot}2$ oersteds and typical concentrations lie in the range 10^{14}–10^{17} atoms cm^{-3}. A theory of the interaction for the nitrogen centre has been developed[1,3].

Samsonenko[2] observed electron spin resonance from nitrogen in natural diamonds and obtained two sets of superimposed lines of different widths. Line shape measurements indicated that the broad resonance was probably caused by dipolar interaction between nitrogen centres in regions of elevated concentration. He concluded that pairing of spins takes place and platelets are formed at concentrations of the order of 10^{20} atoms cm^{-3}. Exchange interaction should precede such pairing and evidence for this is provided by the Lorentz form of the central peak.

Huggins and Cannon[5] studied 'RVG'-type ('resinous vitrified grinding'-type) synthetic diamond and obtained the nitrogen spectrum superimposed on a broad resonance

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due to the transition metal catalyst used during preparation. The nitrogen resonance is considerably broader than is observed with natural diamonds and the three lines overlap considerably. More recent results by Dyer *et al.*[4] using samples of mean diameter 400μ strongly suggest that the major contribution to the line-width is produced by a spread in the local field due to ferromagnetic inclusions. For the nitrogen concentrations present, the satellite lines are broadened owing to the angular variation of the hyperfine coupling and the random distribution of the diamonds which form the sample. Evidence that nitrogen exists in platelet form is not obtained and synthetic diamond is thought to be wholly Type 1*b*. The nitrogen content can be controlled during formation and can have a value up to about 10^{20} atoms cm^{-3}.

In the work presented here the electron spin resonance spectra have been recorded for a range of 'MBG'-type ('metal bonding grinding'-type) synthetic diamonds of different sizes. The diamonds are passed through sieves of known mesh and groups of the same mean diameter are isolated. Each diamond is assumed to be spherical and the diameter of a group is quoted as the mean mesh size of two consecutive sieves. A sample of constant weight, equal to 48 mg, is taken from the appropriate group and consists of between 6,000 and 130,000 single diamonds depending on the group diameter.

A typical spectrum is shown in Fig. 1. For the samples investigated, the concentration of paramagnetic transition metal impurity remains constant at approximately 10^{21} spins cm^{-3}. This is also true for specimens of 'MBS'- ('metal bonding saw') and 'RVG'-type synthetic diamonds which were studied, although *g*-value variations suggest a different catalyst. Ferromagnetic inclusions can clearly be expected.

Table 1 summarizes the results obtained for the nitrogen resonance. The spectrometer was calibrated against diphenyl picryl hydrazyl to obtain the concentration of paramagnetic centres and against methyl methacrylate monomer treated with nitric oxide[6] to define the magnetic field axis. The *g*-value of the central nitrogen resonance is $2{\cdot}0024 \pm 0{\cdot}0007$ and is in agreement with other published results. The splitting between the satellite lines (*a*) is

Table 1

r_d (μ)	N_{sec} Spins $cm^{-3} \times 10^{19}$	ΔH Oersteds	$\left[\dfrac{N_d\Big\|_{11\cdot7\mu}^{r_d}}{N_d\Big\|_{0}^{11\cdot7\mu}}\right]$ Calculated
81·5	2·43	14·0	53
68·5	3·00	12·4	36
48·5	3·68	12·1	18
40·5	4·35	7·8	12
29·0	6·55	6·2	5

60 ± 2 oersteds and the width of each satellite (2b) is 20 ± 2 oersteds measured as shown in Fig. 1. These three parameters remain constant within the deviations quoted.

The concentration of paramagnetic nitrogen, N_{scc}, in the sample is given in the second column of Table 1 and is obtained by dividing the observed intensity by the total volume of diamond. It is clear that the concentration is not the same for diamonds of all sizes taken from the same batch and increases as they become smaller. One way in which the variation may be expressed is by plotting the concentrations in Table 1 against $1/r_d$, where r_d is the mean radius of the diamonds in a given sample. The graph obtained is linear (Fig. 2) and suggests that over the range investigated the number of paramagnetic nitrogen centres per cm^{-3} at a radius r cm within an individual diamond can be represented by the equation:

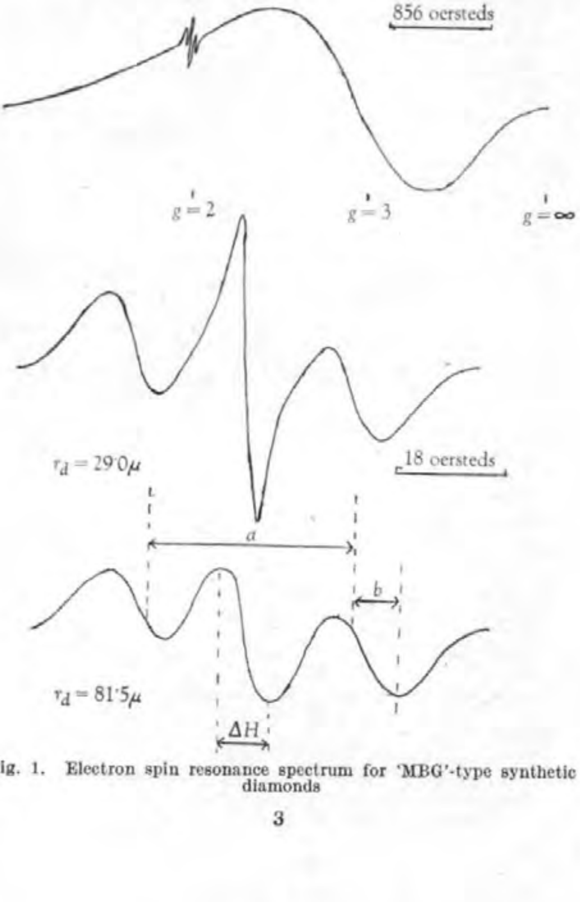

Fig. 1. Electron spin resonance spectrum for 'MBG'-type synthetic diamonds

$$N_{cc} = \frac{K_1}{r} + K_2 \qquad \begin{array}{l} K_1 = 1{\cdot}2 \times 10^{17} \\ K_2 = 1{\cdot}8 \times 10^{18} \end{array}$$

A similar relationship is obtained for 'MBS'- but not for 'RVG'-type diamonds. The latter inconsistency is believed to be caused by the irregular and elongated shape of 'RVG'-type diamonds for which the present experimental method is not suited.

Although the curve of Fig. 2 can equally well be fitted by an expression for N_{cc} involving exponentials, the foregoing expression is preferred since it provides at least as good an agreement with experiment, and is more convenient mathematically.

The observed spectra are made up of contributions from continuously varying concentrations of paramagnetic nitrogen, each element of which will have an associated line width. The surface values of N_{cc} are approximately equal to $0{\cdot}7\ N_{scc}$. Using the foregoing expression for N_{cc} it is now possible to calculate the position within a diamond at which the paramagnetic nitrogen concentration has reached 10^{20} atoms cm^{-3}. The value obtained is $11{\cdot}7\mu$. Exchange interaction and possible pairing of spins should be observed in this region.

The reduction of width of the central resonance (ΔH in Fig. 1) may be explained if it is assumed that an exchange narrowed resonance is obtained from nitrogen in the inner regions of a diamond at a radius less than $11{\cdot}7\mu$. There are approximately 10^{12} paramagnetic centres per cm^3 within the $11{\cdot}7\mu$ radius sphere, and the mean concentration is $1{\cdot}5 \times 10^{20}$ cm^{-3}. The expression for N_{cc} used to fit the experimental results cannot be assumed to hold below $11{\cdot}7\mu$ but it is assumed to be valid down to this value. The fourth column in Table 1 lists calculated values of the ratio of the number of paramagnetic nitrogen centres contained within the inner sphere of radius

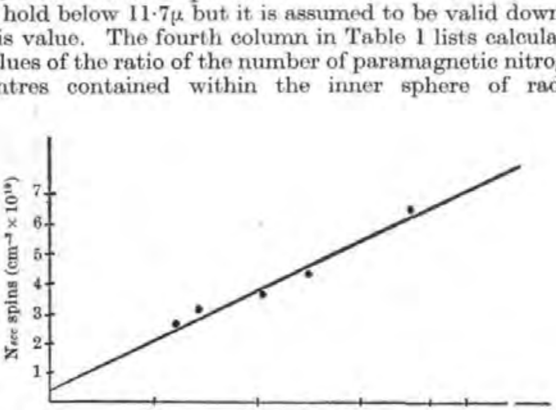

Fig. 2. Graph of N_{scc} against $1/r_d$ for 'MBG'-type synthetic diamonds

$11{\cdot}7\mu$ to the number of such centres contained within the shell defined by the inner sphere and the surface:

$$\mathrm{N}_d\Big|_{11\cdot7\mu}^{r_d} = 4\pi\int_{11\cdot7\mu}^{r_d} \mathrm{N}_{cc}r^2\mathrm{d}r$$

and:

$$\mathrm{N}_d\Big|_{0}^{11\cdot7\mu} = \frac{4\pi}{3}\, r_d^3\mathrm{N}_{scc} - \mathrm{N}_d\Big|_{11\cdot7\mu}^{r_d}$$

$\mathrm{N}_d\Big|_{0}^{11\cdot7\mu}$ is constant for all samples and is of the order 10^{12}. These ratios indicate, as observed, that the contribution of an exchange narrowed signal to the total resonance is small for diamonds of $r_d = 81{\cdot}5\mu$ but has become important for $r_d = 29{\cdot}0\mu$.

For the concentrations present, the line-widths are too large to be accounted for by dipolar interactions between nitrogen centres distributed randomly throughout the lattice, using the relationship $\Delta H \sim \mathrm{N}_{cc} \times 10^{-19}$ oersteds[7]. Ferromagnetic inclusions appear to offer a proven explanation[4].

Random orientation of a large number of diamonds will produce an asymmetrical broadening of the satellite resonances but not of the central peak. The effect, although present, is not very marked in these experiments owing to the broadening produced by the ferromagnetic inclusions which affects all three lines.

Further experiments are in progress to reduce the size of synthetic diamonds by etching and preliminary results are in agreement with the foregoing conclusions. It should be of interest to investigate small synthetic diamonds.

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Correlation between the Nitrogen Impurity Content and the Crystal Habit of Synthetic Diamond

THE presence of nitrogen in diamond has provided an explanation for some of the variations which are observed in the physical properties of this material[1–3]. The nitrogen impurity can exist either as dispersed substitutional donors, in which case electron spin resonance is observed[2], or as non-paramagnetic aggregates of atoms[3]. Absorption peaks in the infrared can be obtained from nitrogen in either form[4]. Peaks at 1,129 cm^{-1} and 1,345 cm^{-1}, coupled by a broad saddle which is peaked at 1,290 cm^{-1}, are characteristic of the paramagnetic centres. In contrast, aggregates of nitrogen give a single peak at 1,280 cm^{-1}. Dyer *et al.*[4] have shown that the two forms of nitrogen can be distinguished even if they co-exist in a particular specimen. In most cases, however, the nitrogen exists predominantly in one form and the diamond is classified either as type 1*a* or as type 1*b*. In type 1*a* diamond, the aggregates of nitrogen are in a majority and in type 1*b* diamond the concentration of dispersed nitrogen is the larger.

In a recent survey of *MBS* 35/40 synthetic diamond (mean size 480μ) (manufactured by the General Electric Company) by electron spin resonance, we[5] found that, unlike most stones which exhibited the electron resonance associated with dispersed substitutional nitrogen (type 1*b*), a small number of stones gave no detectable resonance. Diamonds of this type were invariably almost perfect octahedra whereas the usual habit for *MBS* 35/40 diamond is cubo-octahedral. The octahedra have now been examined both by electron spin resonance and by infrared spectroscopy.

Of the small number of octahedra which were available, only two were sufficiently free from inclusions to be investigated. The stones gave no observable electron resonance signal characteristic of dispersed nitrogen, while the infrared peaks associated with either the dispersed or aggregated nitrogen were scarcely detectable.

Cubo-octahedral diamonds which had previously been examined by electron spin resonance and were known to contain approximately 10^{17} nitrogen donors/cm^3 gave infrared peaks at 1,129 cm^{-1} and1,345 cm^{-1}, the amplitudes of which were several times greater than the noise level.

For *MBS* 35/40 diamond at least, there seems to be a correlation between the nitrogen impurity content and the crystal habit. The correlation suggests that the presence of nitrogen probably encourages the growth of cube faces.

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Some Electron Spin Resonance Properties of Heat Treated Synthetic Diamond

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ABSTRACT

Three distinct and known E.S.R. spectra, which are obtained from five commercially available types of synthetic diamond, are discussed. The resonances are due to dispersed substitutional nitrogen, small aggregates and dispersions of ferromagnetic additive.

Heat treatment *in vacuo* at 1200°C causes the migration of a significant amount of the additive from the interior to the surface but does not markedly affect the E.S.R. properties.

Heat treatment *in vacuo* at 1500°C removes larger quantities of the additive and also that resonance which may reasonably be attributed to the small aggregates of additive. An additional line is observed at the free-spin g-value. In a certain selection of heated stones the line width of the nitrogen resonance is narrowed to 3 oe and the symmetry properties of the resonance may be studied more precisely.

The behaviour of perfect octahedral stones does not appear to correspond in all respects to that of the common cubo-octahedral diamond. The appearance and mechanical properties of heated stones are also discussed.

§ 1. INTRODUCTION

THE paramagnetism of unirradiated natural and synthetic diamond has been studied extensively using the technique of electron spin resonance. A particularly fruitful aspect of the work has been the identification and investigation of dispersed substitutional nitrogen donors in natural stones which are classified as Type Ib. The paramagnetism arises from the unpaired electron provided by the nitrogen atom which can be considered as localized predominantly in an anti-bonding orbital along one of the four C–N bond directions (Smith *et al.* 1959). The main feature of the spectrum is a hyperfine triplet due to interaction with the nitrogen nucleus which has a spin of unity. The g-value for the central line is 2·0024 and the interaction is partly anisotropic with hyperfine constants $A = 40{\cdot}8$ oe and $B = 29{\cdot}2$ oe (Smith *et al.* 1959). The separation between the central peak and each satellite line varies as $(A^2 \cos^2 \theta + B^2 \sin^2 \theta)^{1/2}$ oe, where θ is the angle between the C–N bond direction and the applied static magnetic field. The spectrum for a single stone containing many such donors can be deduced if it is accepted that each bond direction is occupied

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with equal probability. Only when the applied field is parallel to a [100] direction and every bond in the diamond is at the same angle to the field, are three symmetrical lines of equal intensity and separation observed.

The line width for homogeneous Type Ib natural diamond can be as small as 0·3 oe. These stones are rare compared with coated diamonds in which the substitutional nitrogen exists only in the coat and line widths vary from 2 to 6 oe. The narrowness of the lines combined with a sufficiently high concentration of nitrogen has enabled the above model for the donor to be further tested by permitting measurements in the regions between the main triplet. Resonances attributed to interactions with the nuclei of $^{15}N(I=\frac{1}{2})$ and nearby $^{13}C(I=\frac{1}{2})$ in their natural abundances have been detected and discussed by Loubser and du Preez (1965). The existence of quadrupole interaction (Loubser and du Preez 1965), dipolar (Samsonenko 1965) and exchange effects (Loubser *et al.* 1965, Smith *et al.* 1966) has also been demonstrated. The basic model for the dispersed substitutional nitrogen donor seems to rest on a firm experimental basis although the complete distribution of the unpaired spin density over the nearby carbon atoms is the subject of further discussion at the present time (Every and Schonland 1965, Bower and Symons 1966). It is now realized that the spin density is greater on the carbon atom of the C–N bond than on the nitrogen atom.

In the case of synthetic diamond, such detailed and direct measurements have not, to our knowledge, been made, although most commercially available stones are Type Ib with averaged concentrations of paramagnetic nitrogen which can be as high as 10^{20} per cm^3. One important reason for this is the generally greater line width which may obscure both variations in the hyperfine interaction and any intermediate lines. Although the small size of the stones is a factor, it is not as important as might be supposed owing to the apparent linear variation of nitrogen concentration with the reciprocal of the radius which has been reported by Smith *et al.* (1966). For very small stones (usually less than 100 μ diameter for commercially available specimens) exchange effects will begin to affect the shape of the recorded spectrum.

The increased width has been attributed to variations of local magnetic field produced by the presence of ferromagnetic additive used in the manufacturing process. Direct evidence for the effect was presented by Dyer *et al.* (1965) who recorded the nitrogen resonance from a bulk sample of diamond grown with the non-ferromagnetic additive Brightray-S, which contains Ni, Cr and Fe in the proportions 78 : 21 : 1. They found a width approximately the same as that obtained from natural coated stones (3·9 oe). The shape of the satellite resonances and the enhancement of the central isotropic line agreed with the theoretical predictions of Sands (1955) which apply to a large number of randomly orientated stones. We shall show that it is possible to obtain reduced line widths of 3 oe by suitable heat treatment and selection of commercially available samples. The symmetry properties of the nitrogen resonance may then be studied directly in the larger single stones where the signal to noise ratio is a maximum. A further reduction in width to 2 oe can be achieved by grinding the heated stones.

Perfect octahedral MBS 35/40 stones do not appear to contain detectable paramagnetic nitrogen nor do they give the isotropic resonance at low temperatures reported by Loubser and Ryneveld (1966).

In addition to the nitrogen resonance, a broad resonance is observed in synthetic diamond at room temperature which can extend from zero field to below the free spin g-value. The effect has been reported previously for bulk samples by Huggins and Cannon (1962). They showed that the characteristics of the spectrum depend on the nature of the ferromagnetic additive used. It is of interest to study a single stone to establish if a relationship exists between this resonance and a particular crystallographic axis.

The heat treatment referred to above has the effect of removing the broad resonance for each of the five types of commercially available diamond which we have investigated. The resonance may reasonably be attributed to additive in the surface and near surface regions where it exists in high concentration and from which a majority is extracted by the heat treatment. As the width of the nitrogen resonance is reduced significantly in only a limited number of stones, it appears that the form of the ferromagnetic additive which produces the broad resonance is either not the major cause of the broadening or, if it is, only a proportion is effective.

A further effect of the heat treatment, certainly in the largest MBS stones, is to produce a single isotropic line at $g = 2{\cdot}0023$.

§ 2. EXPERIMENTAL APPARATUS

A Decca X1 spectrometer operating at 9270 Mc/s with 100 kc/s field modulation was used to record the electron resonance spectra. The sample temperature could be varied continuously down to 87°K. The magnet had flat pole faces of 6 in. diameter and was not a commercial design.

The optical micrographs were obtained with a Zeiss Ultraphot II.

§ 3. OBSERVATIONS

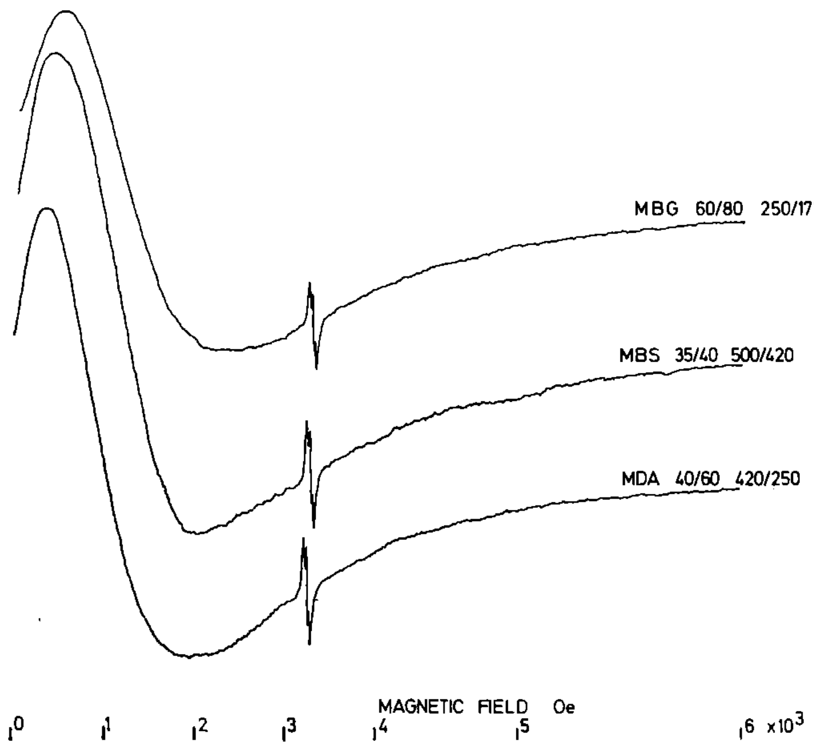
3.1. *Ferromagnetic Additive*

Figures 1 and 2 show typical electron resonance spectra of bulk samples of the same weight of MBS, MBG, MDA, RVG and RDA type synthetic diamond as supplied. The MBS, MBG and RVG is manufactured by the General Electric Company and the MDA and RDA by the De Beers Organization. The numbers after the type letters refer to the size range in terms of mesh number and in microns. The largest stones of each type were used in order that any contribution to the nitrogen resonance from exchange effects in the central cores was kept to a minimum (Smith *et al.*

1966). In each case a sufficient number of stones were present to ensure that the spectra did not change when the sample was rotated.

The characteristics of the broad resonance and the intensity and width of the nitrogen lines are similar for MBS, MBG and MDA diamond (fig. 1). The ferromagnetic additives are, therefore, expected to be similar for each type.

Fig. 1



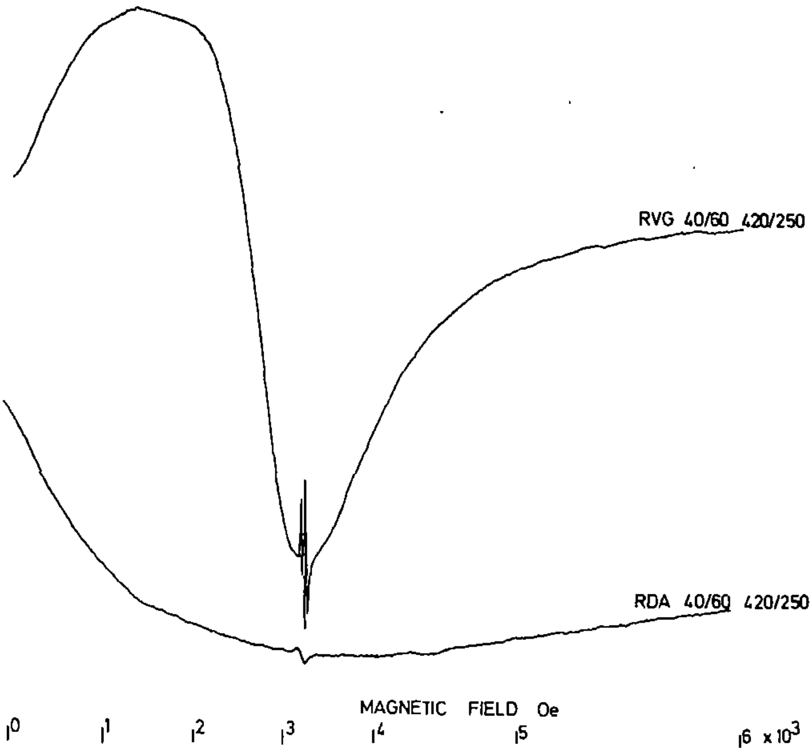
Typical E.S.R. spectra of bulk samples of MBG, MBS and MDA synthetic diamond as supplied.

A qualitative indication of the identity of the additive was obtained by heating the samples *in vacuo* at 1500°C for a few minutes. A sufficient amount of the additive was extracted from the diamond in this way and was analysed. An alternative and somewhat more quantitative indication was obtained by oxidizing known weights of each type in air and analysing the residue.

The results of these tests suggest, as expected, that nickel and iron are present in MBS, MBG and MDA diamond. In addition a very small number of white crystallites appeared in the residue from the MDA sample. A spectrographic analysis indicated that they contained aluminium and silicon as the major constituents.

The characteristics of the spectra from RVG and RDA diamond (fig. 2) are clearly different from each other and from the MBS–MBG–MDA group. The RVG stones are known to contain predominantly nickel additive (Huggins and Cannon 1962) in similar concentrations and as the nitrogen lines at $g=2$ are narrow, it seems that the 8 oe width of the MBS–MBG–MDA group is not due to nickel.

Fig. 2



Typical E.S.R. spectra of bulk samples of RVG and RDA synthetic diamond as supplied.

The residue from the RDA diamond contained a relatively high concentration of cobalt. A larger number of the same white crystallites were also obtained. We attribute the single line at $g=2$ to a resonance from dispersed substitutional nitrogen which is broadened by the additive to the extent that the component lines are not visible. Evidence for the identification was obtained from observations on smaller RDA specimens and also from the effect on the larger specimens of heat treatment *in vacuo* at 1500°c. In the latter case a proportion of the additive was removed and three lines appeared. The intensity of the resonance at $g=2$ was less than for the other samples which contained between 10^{18} and 10^{19} nitrogen atoms per cc averaged over the sample volume. The aluminium probably causes a suppression of the nitrogen resonance. In the case of MDA diamond the concentration of aluminium is not so large that the nitrogen resonance is affected in a significant way.

For single MBS 35/40 stones it is possible to observe both the nitrogen and the broad resonances. These diamonds have well-developed faces and permit unambiguous orientation by visual examination. A single cubo-octahedral stone was aligned with a [100] direction parallel to the applied magnetic field and the broad resonance was recorded for 10° rotations from this orientation. The intensity, shape and apparent g-value varied with the rotation. It has not been possible to associate the variation with the crystal symmetry. Additional tests on a number of single stones established that wide variations occur but that coincidence is not necessarily obtained at the same orientation. It seems unlikely that the centres responsible for the broad resonance have a preferential shape and lie in any particular plane.

3.2. *Substitutional Nitrogen in Single Stones*

The nitrogen resonance was recorded individually for 170 MBS 35/40 stones which had been divided into four groups according to their appearance. The stones in Group A had a pale greenish yellow colour and only a few dark inclusions were visible. Group B were very dark, being either black or very deep green, and contained a large number of inclusions. Group C were intermediate between Group A and Group B. Group D were a sub-selection of C but with an almost perfect octahedral habit ({111} faces visible). There were 50 stones in Groups A, B and C but only 20 in Group D as these are comparatively rare. The stones of all groups were attracted to a permanent magnet.

Each stone in Groups A, B and C gave a three line resonance having an isotropic g-value, a line width of 8 oe and a shape which was more nearly Gaussian than Lorentzian. These parameters do not, therefore, depend on the criteria adopted for the classification of the stones. The effect of variations in orientation is not easy to measure directly with a width of this order. The intensity varied between samples by a factor of approximately 5, but a direct correlation with the group to which it belonged did not appear to exist. The broad resonance was present in each stone but again no correlations between the groups were detected.

For Group D the broad resonance appeared on each occasion but no trace of a nitrogen resonance could be found. A sample of the 20 octahedra also failed to produce a resonance in the region of $g = 2$. The number of dispersed substitutional nitrogen atoms which are paramagnetic is, therefore, at least two orders of magnitude smaller than the number in the common cubo-octahedral diamonds taken from the same batch, assuming a line width of 8 oe.

An additional resonance, which has none of the characteristics of the broad resonance, can be obtained from most synthetic but not natural diamond. A single isotropic line with a width of 6 oe appears at $g = 2$ at temperatures below about 220°K. The resonance was observed recently by Loubser and Ryneveld (1966) and independently by ourselves. The change in intensity is particularly rapid in the region of 200°K but approximates to the usual $1/T$ dependence near liquid nitrogen temperature. As a result of their measurements on stones grown with and without nickel additive, Loubser and Ryneveld (1966) attributed the line to the presence of dispersed nickel, although its form is not certain. We find that the line is present in each of the five types of commercially available diamond used in this work, with the exception of the octahedra of Group D. Although the measured width is 6 oe, the line has probably been broadened by the same mechanism which broadens the nitrogen lines, and the inherent width is less. Smaller widths have been observed in stones which have received the heat treatment referred to below.

It is possible that both nitrogen donors and dispersed nickel must co-exist to produce the isotropic resonance. Alternative speculation would be that these stones contain nitrogen in either platelet form or bound to an acceptor-like impurity, which may be dispersed nickel, or that the nitrogen concentration, as well as the concentration of dispersed nickel, is so low that they are Type IIa. At the present time we are not able to make significant measurements on the octahedra other than by electron spin resonance.

3.3. *Some Effects of Heat Treatment*

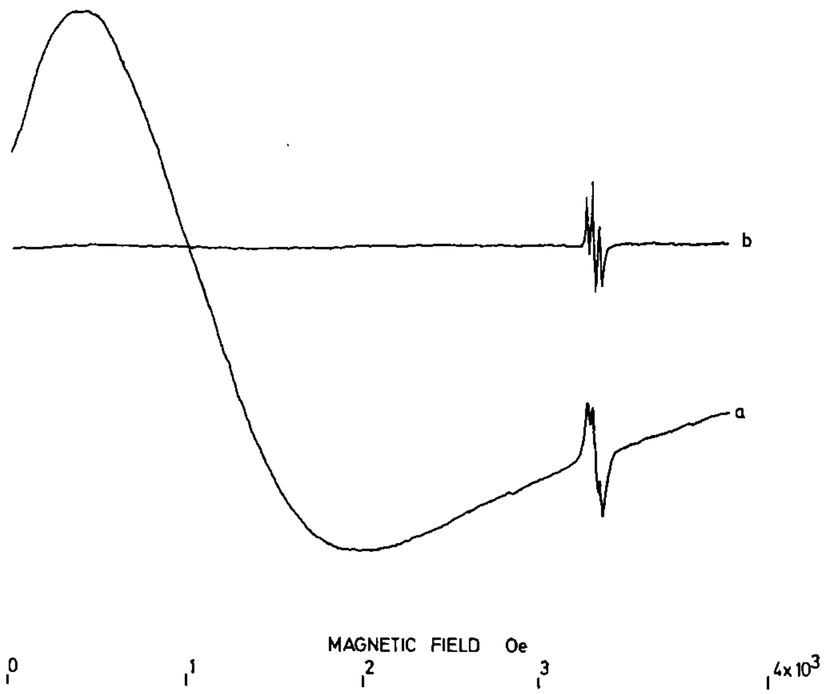
Approximately 70% of the ferromagnetic additive in synthetic diamond may be removed by heating the stones *in vacuo* (5×10^{-5} torr) at 1500°C for 15 min. The percentage estimate was made by comparing the weights of the residues obtained from complete oxidation of equal weights of two samples. One sample consisted of stones as supplied and the other of stones which had received the heat treatment.

The broad resonance was removed by the heat treatment for each of the five types of commercially available diamond. The effect is illustrated for a bulk sample of MBS 35/40 in fig. 3.

After the heat treatment the stones of Groups A, B and C were reclassified into Group 1 and Group 2. Group 1 contained stones which were still attracted to a permanent magnet whereas those in Group 2 were not so attracted. In all cases the intensity of the nitrogen resonance had not changed but the line width from Group 2 had been reduced from $8{\cdot}0 \pm 0{\cdot}5$ oe to $3{\cdot}0 \pm 0{\cdot}3$ oe. Group 1 gave a width which was slightly less at $6{\cdot}0 \pm 0{\cdot}4$ oe. Prolonged heat treatment *in vacuo* at 1500°C did not reduce the width of either group further nor did it affect the behaviour of the stones towards a permanent magnet.

Clearly any mechanism which is proposed to explain the effects of heat treatment should account for the difference in the width of the nitrogen resonance and in the attraction to a permanent magnet, between the stones of Group 1 and Group 2. At the same time it should explain the absence of the broad resonance in all heated stones.

Fig. 3

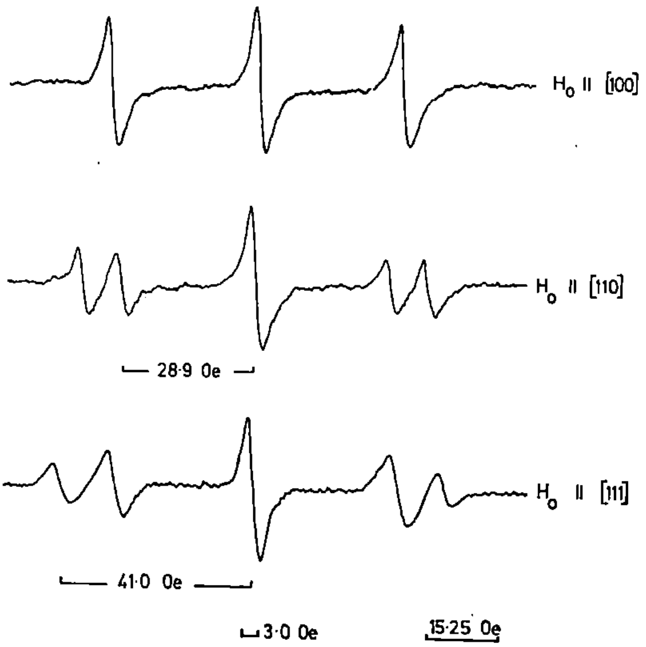


The effect of heat treatment *in vacuo* at 1500°c on the E.S.R. spectrum of a bulk sample of MBS 35/40 diamond, (*a*) before heat treatment and (*b*) after heat treatment.

Figure 4 shows a typical spectrum from a stone of Group 2 for three orientations with respect to the applied magnetic field. The g-value is $2{\cdot}0024 \pm 0{\cdot}0005$ and the hyperfine constants are $A = 41{\cdot}0 \pm 0{\cdot}4$ oe and $B = 28{\cdot}9 \pm 0{\cdot}4$ oe. These parameters are consistent with those obtained for natural Ib diamond.

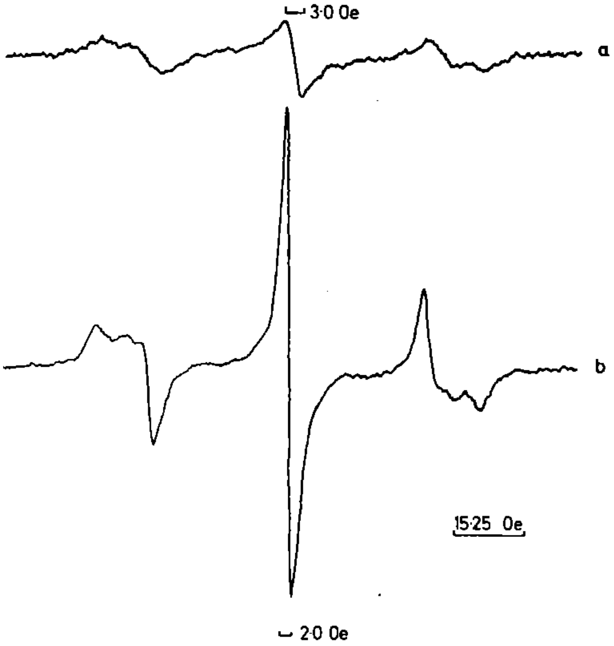
A bulk sample of stones of Group 2 was ground by diamond powder contained in an air blast. Approximately 1% of the stones were uniformly reduced in size such that their mean diameter lay between $80\,\mu$ and $100\,\mu$. Figure 5 shows the nitrogen resonance obtained from 3 mg of the sample before and after grinding. The width is reduced to $2{\cdot}0 \pm 0{\cdot}3$ oe and the shape of the satellite resonances is more peaked which suggests narrower component lines. The intensity is increased after grinding owing to the increase in concentration which occurs towards the centres of the stones. The concentration of nitrogen is not sufficiently large that exchange effects are expected to modify the spectrum in a significant way. Detailed orientation checks have not been possible with these stones.

Fig. 4



E.S.R. spectra of the substitutional nitrogen in a single crystal of MBS 35/40 diamond of Group 2, at fixed orientations to the applied magnetic field, after heat treatment *in vacuo* at 1500°c.

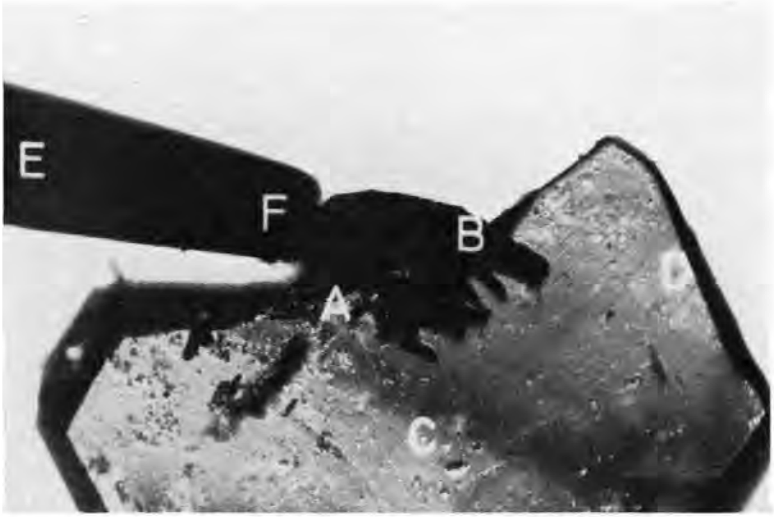
Fig. 5



E.S.R. spectra of equal weights of heated MBS 35/40 diamond (*a*) before grinding (size range 420 μ to 500 μ) and (*b*) after grinding (size range 80 μ to 150 μ).

Careful examination of the nitrogen resonance in stones of Group 2 revealed a distortion on the high field side of the central peak. In order to provide better separation, five stones, which were imperfect octahedra with visible cube faces, were examined before and after heat treatment. The departure from perfect octahedral habit resulted in only a small nitrogen resonance which was used as a convenient reference. The results of the measurements show an additional line of approximately the same intensity as the nitrogen resonance. It occurs at a g-value which is the same as that for a standard carbon sample and has a width of $5{\cdot}8 \pm 0{\cdot}5$ oe. It is likely that this width is close to the true width as it is greater than that of the nitrogen lines, and therefore, exceeds any gross broadening effects which exist. Prolonged boiling in aqua regia did not remove the resonance but it did disappear when a small amount of the surface was removed by uniform abrasion with natural diamond powder contained in an air blast. We conclude, after paying due regard to the conditions of temperature and pressure under which the effect appeared and to the previous work on the subject (for example, Evans and Sauter 1961, Seal 1963, Evans and James 1964), that the line is a surface or near surface effect and is probably due to the usual free radical produced by carbonization. The origin of the carbon is not certain as two sources are possible. They are the diamond itself and any carbon-enriched aggregates of additive. The resonance exhibited none of the features which would be expected from graphite.

Fig. 6



Transmission optical micrograph of MBS 35/40 diamond as supplied, with ground opposite dodecahedral faces.

3.4. *Optical Micrographs*

It is interesting to observe the appearance of the MBS 35/40 stones. Figure 6 shows a transmission optical micrograph of a typical stone which had been ground to produce two opposite dodecahedral faces. A dark inclusion is visible which extends into the crystal as shown by the boundary AB. During the grinding process the crystal broke around the inclusion in a direction parallel to the grinding lines CD which accounts for the extension of the inclusion above the crystal surface. The micrograph also shows the adhesion of a pair of magnetized tweezers EF to the inclusion and indicates that it is ferromagnetic. There is no noticeable strong attraction between the tweezers and the inner regions of the crystal. The dark perimeter on the micrograph is shadow.

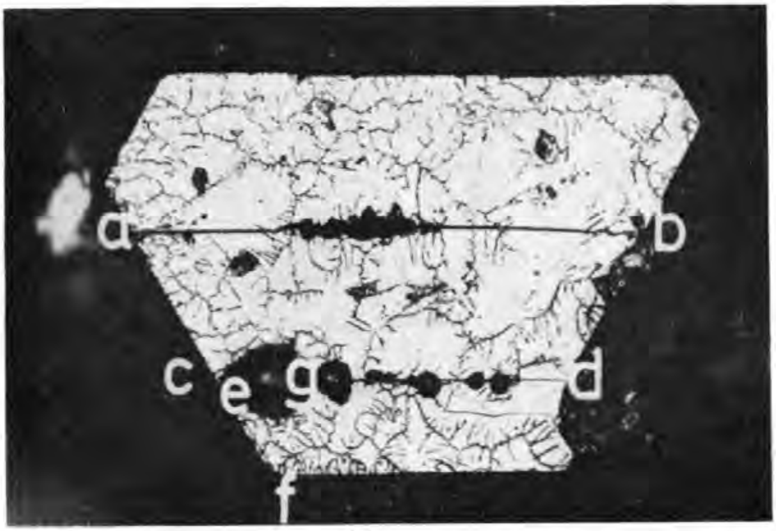
A number of similar stones, which had not been ground, were observed by reflected light. Figure 7 is an optical micrograph of a (111) face and is typical of all the stones observed. The dendritic structure characteristic of the solidification of the surrounding additive during manufacture, is visible. Trigons, both negatively and positively orientated, could be observed on some {111} faces. Their significance has been discussed by Tolansky (1955), Frank *et al.* (1958), Lang (1964) and others. Figure 8 shows the same face as fig. 7 after the specimen had been heated *in vacuo* at 1200°c for a few minutes. Under these conditions some of the ferromagnetic additive is able to arrive at the surface but does not evaporate.

Fig. 7

Reflection optical micrograph of a (111) face of a typical MBS 35/40 diamond as supplied.

The dark lines *ab*, *cd* and *ef* in fig. 8 are consistent with the suggestion that the extracted material appears where {111} octahedral faces meet the (111) face. The line *ef* is at an angle of 60° to *ab*. Observations with a hot-stage microscope on a number of stones show that the diamond cracks to expose {111} faces in nearly every case. We conclude that when additive melts, the internal stresses can cause the diamond to crack along the preferred {111} planes and in this way the additive is able to gain access to the surface. It is unlikely that diffusion through the lattice can explain the observed facts. The top of the hillock *g*, which is 75 μ above the crystal surface, shows a pattern which we are not able to identify.

Fig. 8



Reflection optical micrograph of the same (111) face as fig. 7 but after heat treatment *in vacuo* (5×10^{-5} torr) at 1200°c

When the stone was boiled in aqua regia, the ferromagnetic additive was removed from the surface which appeared rough and pitted. The electron resonance spectrum from the dispersed substitutional nitrogen remained broadened up to this point and the broad resonance was present. Further heating in vacuo at 1500°c was necessary to reduce the line width to the minimum observed in similar stones and to remove the broad resonance.

Heated stones are difficult to grind on a scaife as they break easily. They can, however, be ground uniformly by diamond powder contained in an air blast, in contrast with stones which have not received the heat treatment. They are clearer than before and in many ways they have the appearance of natural grit. Such behaviour is consistent with the existence of many cracks and the products of carbonization.

§ 4. Discussion

The behaviour of the broad resonance, and the variation in width of the nitrogen resonance after heat treatment, in synthetic diamond which contains ferromagnetic additive, may be accounted for in the following way.

The additive would seem to exist primarily in the form of aggregates of varying size which, with the exception of a number of gross inclusions, are located preferentially in the outer regions of the diamond. If the broad resonance is attributed to those aggregates or particles which have at least one dimension of the order of or less than the microwave skin depth ($1\,\mu$), the contribution from the larger particles and inclusions is expected to be small, as only their outer regions are effective. The attraction of the diamond to a permanent magnet and the near random distribution of the local field over all the nitrogen centres contributing to the resonance, is, therefore, a necessary consequence. The x-ray topographic measurements of Kamiya and Lang (1965) on synthetic diamond containing nickel provide evidence that the surface metal is in the form of particles less than approximately $1/100\,\mu$ diameter.

In addition it is interesting to note that the width of the nitrogen resonance is greater for those diamonds which show a high effective g-value for the broad resonance. The variation in magnitude of the effects under discussion amongst the five types of commercially available synthetic diamond may be explained to a large extent if the concentration and identity of the ferromagnetic additive which they contain is considered in conjunction with any previous heat treatment.

After heating *in vacuo* at 1200°c, the larger aggregates are able to melt and to exert pressure on the diamond so that a distribution of cracks is produced along $\{111\}$ cleavage planes through which the additive may escape. It is important to note that although the melting points of Ni, Co and Fe metals lie in the range 1455°c to 1535°c, the required depression of melting point can be obtained if the aggregates are enriched with carbon. The broad resonance from the small particles would not be expected to change significantly with the treatment, nor by the subsequent removal of additive from the surface. Heat treatment at 1500°c may be supposed to extend the above process in a restricted form to the small particles, which probably coalesce locally and produce microcracks containing additive. It is clearly not possible to suggest a detailed mechanism on the basis of the present results.

The broad resonance would not be expected to occur after heat treatment at the higher temperature due to the increased dimensions or possibly the different shape of the aggregates, but the stones may still be attracted to a permanent magnet and the nitrogen resonance may still be broadened. Such behaviour is pronounced for the majority of stones (Group 1). For the stones of Group 2 we presume that most of the aggregated additive has been able to gain access to the surface by any of a number of straightforward extensions of the proposed mechanism. The magnitude of the broadening of the nitrogen resonance, or indeed any other resonance, is, therefore, correspondingly less and the stones are not noticeably attracted to a permanent magnet. Some of the additive also exists in the diamond in a more dispersed form which has quite different properties.

The apparently anomalous behaviour of perfect octahedral MBS 35/40 diamond would seem to warrant further investigation particularly as a large number of these rare stones was not available for this work.

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The reduction of electron-spin-resonance linewidths in synthetic diamond

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Abstract. An improved method for the removal of aggregates of ferromagnetic additive from synthetic diamond is presented. Electron-spin-resonance linewidths are reduced as a consequence and may approach 0·5 Oe.

Electron spin resonance from substitutional nitrogen in diamond (type Ib) has been extensively reported (see, for example, Smith *et al.* 1959, Loubser and du Preez 1965). The principal feature of the resonance is a three-line spectrum due to a hyperfine interaction between the unpaired electron donated by the nitrogen atom and the nitrogen nucleus ($I=1$). The linewidth varies from specimen to specimen and has a lower limit of about 0·3 Oe in the case of natural diamond which does not contain regions with unusually high concentrations of nitrogen donors.

Synthetic diamond, in contrast to the natural material, is invariably type Ib. Metallic inclusions are present and arise from the additives (iron, cobalt, nickel, etc.) used in the manufacturing process. The structure of the inclusions and their effect on the diamond lattice have been studied by x-ray methods (see, for example, Phaal and Woods 1966). As well as producing anomalous x-ray spikes projecting from the reciprocal lattice points of the synthetic diamond, the inclusions, on account of their ferromagnetic properties, give rise to a spread of local magnetic field and hence to a broadening of the nitrogen electron-spin-resonance lines. For commerically available specimens, which have not been heated in any way except for the cleaning processes used after manufacture, the linewidths vary between approximately 5 Oe and 30 Oe, depending on the type of additive used. Dyer *et al.* (1965) reported linewidths of 3·9 Oe in synthetic diamond powder which had been grown with the non-ferromagnetic additive Brightray-S (78% Ni, 21% Cr, 1% Fe). It is unlikely that this width was caused by dipolar broadening, but rather by a significant ferromagnetic effect from aggregates of additive in the grown diamond which did not reflect the original composition of the Brightray-S. Smith and Angel (1967) obtained a reduction from 8·0 to 3·0 Oe in MBS 35/40 synthetic diamond† by heating the specimen *in vacuo* to 1500°c. Under these conditions the larger aggregates melted and exerted sufficient pressure on the surrounding diamond to produce a distribution of small cracks along the $\{111\}$ cleavage planes through which the metal could evaporate. It was shown that, for a bulk specimen, approximately 70% of the ferromagnetic additive was removed by the heating process and that the residual width could reasonably be attributed to aggregates of additive which remained in the diamond after the heat treatment.

In recent experiments it has been possible to reduce the width to 0·5 Oe, and so to approach closely to the narrowest lines obtained from natural diamond. The reduction was achieved by crushing a bulk sample of synthetic diamond, which consisted of stones with a mean diameter of 460 μm, past a 240 mesh sieve (66 μm). The sample was then heated *in vacuo* (50 μtorr) to about 1500°c and cleaned in boiling aqua regia. Intermediate linewidths of about 1 Oe were observed in specimens which had been crushed, sieved and cleaned in aqua regia but not heated. It is reasonable to suppose that if the sample were crushed to smaller dimensions the width might be reduced even further.

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† Synthetic diamond with dimensions in the range 420–500 μm manufactured by the General Electric Company, U.S.A., for use in saw blades using a metallic bond.

As the broadening effect of the ferromagnetic additive is not confined to the nitrogen resonance, but extends to all other resonances, more precise electron-spin-resonance measurements can be made on synthetic diamond using the treated samples, provided that the limitation of small stones is acceptable. It has been possible, for example, to observe a variation with temperature of the linewidth of the single isotropic resonance at $g=2{\cdot}0310$ which was first reported by Loubser and van Ryneveld (1966) and which they attributed to dispersed nickel. The width between maxima on the derivative of the absorption varied from $5{\cdot}7 \pm 0{\cdot}4$ to $1{\cdot}2 \pm 0{\cdot}1$ Oe over the range 213–133°K, and appeared to be a linear function of inverse temperature over this range. Above 213°K the intensity was nearly two orders of magnitude less than its value at 96°K, and the resonance could not be detected with certainty. In addition the low-field satellite of the nitrogen resonance tended to interfere with the measurement at the higher temperature, although its effect could be reduced by using higher values of microwave power so that the nitrogen lines were preferentially saturated. Below 133°K and as the temperature approached 96°K the linewidth tended towards a constant value determined by the small amount of additive still present in the diamond.

The success of the method presented here in reducing the widths of the nitrogen and nickel resonances in synthetic diamond provides further support for the suggestion that aggregates of ferromagnetic additive are responsible for the broadening. The results of semi-quantitative measurements by spectroscopic analysis on a range of the treated samples also agree with this conclusion. It would now be interesting to enquire if the variation in linewidth between various natural stones containing substitutional nitrogen is due to ferromagnetic impurities.

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