# Electron-Spin Resonance of Nitrogen Donors in Diamond

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Electron-spin resonance of bound substitutional nitrogen donors in diamond is observed and discussed. The g factor is isotropic at  $2.0024 \pm 0.0005$ . For a given donor, one of the C-N bond directions is a hyperfine axis with constants A = 40.8 oersteds, B = 29.2 oersteds. There are thus four types of donors, equally abundant. A model for the donor wave function is proposed which puts the donor electron principally into an antibonding orbital located on a nitrogen atom and on one of its nearest-neighbor carbon atoms. A C-N bond distortion results which can be regarded as a manifestation of the Jahn-Teller effect. A careful search reveals the presence of an additional weak spectrum due to donors on N14-C13 pairs. (The isotope C13 which has a nuclear spin of  $\frac{1}{2}$  has a natural abundance of 1.1%.) The hyperfine constants measured for a C<sup>13</sup> atom of an N-C pair are A' = 60.8 oersteds, B' = 25.3 oersteds. The s and p contributions to all 4 measured hyperfine constants are separated to give the values

> $O_{\rm N} = (8\pi/3) |\psi(0)|^2 = 2.41$  atomic units,  $P_{\rm N} = \langle [z^2 - \frac{1}{2}(x^2 + y^2)]/r^5 \rangle_{\rm N} = 0.28$  atomic unit,  $O_{\rm C} = (8\pi/3) |\psi(0)|^2_{\rm C} = 0.78$  atomic unit,  $P_{\rm C} = \langle [z^2 - \frac{1}{2}(x^2 + y^2)]/r^5 \rangle_{\rm C} = 0.25$  atomic unit.

These are compared with theoretical values obtained by assuming a simple antibonding wave function composed of nitrogen and carbon tetrahedral orbitals. An increase of several percent in the N-C separation along the hyperfine axis is strongly implied by the comparison.

### I. INTRODUCTION

**P**REVIOUS work<sup>1,2</sup> reporting electron-spin resonance in diamond has been concerned exclusively with paramagnetic centers produced by irradiation with fast neutrons. Fairly specific models such as carbon vacancies and interstitials, C2 molecules, etc., were proposed to account for the spectra observed in diamonds treated in an atomic pile for times varying from 10 hours to 1850 hours. The spectra of these defects are characterized by electronic spin values S=1 and S=2, by line widths ranging from 5 oersteds to 70 oersteds, and by various irreversible changes brought about by temperature annealing.

Recently<sup>3,4</sup> room-temperature paramagnetic resonance spectra have been observed in natural, unirradiated diamonds. These spectra are characterized by isotropic g values differing very little from the freeelectron g value, by line widths typically about 0.3 oersted, by characteristic hyperfine structures arising from the interaction of an unpaired electron spin with the spin of the impurity nucleus to which the electron is bound, and by long spin-lattice relaxation times.

The minor element content in natural diamond had been determined by a number of spectrographic studies.<sup>5,6</sup> Si, Ca, Mg, Al, Fe, Ti, Cu, and B were generally found to be the most abundant nongaseous impurities. Recently<sup>7,8</sup> considerable amounts of gases have been found in natural diamonds by Kaiser and his co-workers. Nitrogen is the predominant gas and a concentration as large as 0.1% was reported. The same investigators measured the infrared absorption coefficient at  $7.8 \mu$  and showed its proportionality to the amount of nitrogen present in the stone. Thus a fairly complete explanation seems to have been provided regarding the question of the real difference between type I and type II diamonds.9 Type I diamonds have infrared absorption bands in the 7-13  $\mu$  range while type II diamonds are transparent in this range. Another property which distinguishes type I from type II diamonds is the ultraviolet absorption cutoff frequency. For type I's this frequency is approximately 3000 A (4.15 ev). For type II's it is 2250 A (5.5 ev). The value 5.5 ev is, of course, the band gap energy for diamond. Kaiser's group<sup>10</sup> has now shown that the shift of the ultraviolet absorption curve in type I diamonds is also proportional to the nitrogen content.

A survey of the paramagnetic resonance spectra of approximately 100 natural diamonds11,12 has independently shown us that nitrogen is present as a common impurity in diamond. It is certainly the most abundant paramagnetic impurity in natural diamond. Nitrogen being a group V element, and being next to

4, 27 (1959). <sup>8</sup> W. K. Kaiser and W. L. Bond, Phys. Rev. **115**, 857 (1959). <sup>9</sup> See M. Lax and E. Burstein, Phys. Rev. **97**, 39 (1955), where

W. K. Kaiser (private communication).

<sup>&</sup>lt;sup>1</sup> Griffiths, Owen, and Ward, in Defects in Crystalline Solids Grinnins, Owen, and Ward, in Dejects in Crystalline Solids (The Physical Society, London, 1955), p. 81.
<sup>a</sup> M. C. M. O'Brien and M. H. L. Pryce, in Defects in Crystalline Solids (The Physical Society, London, 1955), p. 88.
<sup>a</sup> Smith, Gelles, and Sorokin, Phys. Rev. Letters 2, 39 (1959).
<sup>4</sup> Smith, Gelles, and Sorokin, Bull. Am. Phys. Soc. Ser. II, 4, 144 (1959).
<sup>5</sup> F. C. Checker, Am. Mixed and 27, 22 (1042).

 <sup>&</sup>lt;sup>6</sup> F. G. Chesley, Am. Mineralogist 27, 20 (1942).
 <sup>6</sup> F. A. Raal, Am. Mineralogist 42, 354 (1957); E. N. Bunting

and A. Van Valkenburg, Am. Mineralogist 43, 102 (1958).

<sup>&</sup>lt;sup>7</sup> Kaiser, Bond, and Tanenbaum, Bull. Am. Phys. Soc. Ser. II,

<sup>&</sup>lt;sup>11</sup> Most of the diamonds were kindly made available to us by Mr. Bart van Berg of the Rough Diamond Company, New York, New York.

<sup>&</sup>lt;sup>12</sup> A type I, a type II(a), and a type II(b) were provided us by Dr. J. F. H. Custers of the Diamond Research Laboratory.



dc MAGNETIC FIELD Ho (OERSTEDS)

FIG. 1. Electron-spin resonance of nitrogen in diamond (temp= $295^{\circ}$ K). The dc magnetic field is parallel to the crystal axis indicated. This spectrum is referred to in the text as spectrum A.

carbon in the periodic table, should be present as a substitutional donor in the diamond lattice. One could expect a large fraction of the nitrogen donor electrons to be bound at room temperature. Furthermore, one might expect the structure of the donor wave function in diamond to be quite different from that of donors in silicon.<sup>13</sup> In this paper a specific model is suggested for the wave function of the bound nitrogen donor electron and experimental evidence is presented with which the model can be tested.

# **II. PARAMAGNETIC RESONANCE SURVEY**

Using standard X-band resonance techniques, one hundred and twenty natural diamonds were individually surveyed at room temperature. Almost all of the samples were good single crystals ranging in size from 0.25 to 1.0 carat. Many of the stones were perfect octahedrons; generally these were the more lightly colored South African specimens. X-ray analysis revealed that a few of the more densely colored stones, opaque greenish colored diamonds from the Belgian Congo and Sierra-Leone regions, were twinned, but others selected of this type were perfect crystals. The Belgian Congo and Sierra-Leone stones appear to have the greatest concentration of nitrogen impurities, as judged by the strength of the microwave resonance absorption. The spectrum due to nitrogen is reproduced in Fig. 1. This resonance was strongly observed in roughly half of the

samples. As indicated by Fig. 1, the signal-to-noise ratio for the nitrogen resonance in these samples is large.

In about thirty samples a spectrum which we had previously<sup>3</sup> attributed to bound aluminum acceptors was observed. We recently measured the g value of this resonance to be  $g=2.0027\pm0.0005$ . Further work appears to be needed to make the identity of this center more certain. Two distinct other types of spectra with g values  $\approx 2.00$  were seen. These are not as yet understood by us. Paramagnetic resonance was detected in every sample.

Angular studies were made for each of the above distinct spectra, orientation of samples being accomplished by x-ray techniques and also by referring to the known scheme of plane indices for the macroscopic crystal faces. A few runs were made at liquid nitrogen and liquid helium temperatures which indicated a pronounced increase in the tendency for the lines to be saturated at these temperatures. No quantitative results for the relaxation times have been obtained as yet. g values were measured by placing a small amount of the free radical DPPH ( $g=2.0036\pm0.0003$ ) in the cavity together with a diamond sample. Values of the magnetic field were measured by proton resonance.

#### III. INTERPRETATION OF THE NITROGEN SPECTRUM

From Fig. 1 one observes that the g factor of the resonance is isotropic and that for  $H_0||[100]$  there is a triplet of equally spaced, equally intense lines. As the hyperfine splitting multiplicity is 2I+1, this suggested that the impurity producing the resonance is nitrogen

<sup>&</sup>lt;sup>13</sup> W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 257; H. Brooks, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. VII, p. 85.

which is practically the only element with nuclear spin 1. The appearance of the spectra for the two other orientations shown is explained by considering the possibilities of more than one type of center. The simplest assumption is that a nitrogen atom is substitutional and that one of the C-N bond directions is a hyperfine axis. The resonance spectrum from a given nitrogen would then consist of 3 equal-intensity hyperfine lines whose spacing |K| depends on the angle  $\theta$ that the hyperfine axis makes with the direction of the external magnetic field  $\mathbf{H}_0$ . The spacing |K| should vary as  $K^2 = A^2 \cos^2\theta + B^2 \sin^2\theta$ .<sup>14</sup> It does follow this variation. The constants are A = 40.8 oersteds, B = 29.2oersteds. The nearest-neighbor configuration in diamond is tetrahedral, with bonds along [111] directions. Therefore, when  $H_0$  is parallel to a [111] crystal direction, 25% of the donor centers will have their axes parallel to  $\mathbf{H}_0$ . This is the relative orientation for which |K| is a maximum. The remaining 75% of the donor centers make an angle  $\theta = \cos^{-1}(-\frac{1}{3})$  with  $\mathbf{H}_0$ . The expected 3:1 ratio of the satellite intensities is clearly seen in Fig. 1. Similar considerations apply to the two other orientations. That there are 4 types of impurity centers equally abundant is also shown by the fact that for arbitrary orientations the outer satellites are resolved into as many as four lines. No effects due to an interaction with the nuclear quadrupole moment of nitrogen are seen, presumably because of its small value  $(Q = +0.02 \times 10^{-24} \text{ cm}^2).$ 

If the nitrogen donor electron occupied a hydrogenlike orbit of predominantly s character the hyperfine interaction would be isotropic, with A = B. As this is not the case experimentally one must therefore conclude that there is a large admixture of p or higher type orbit to the donor wave function. In the model we propose, the electron with unpaired spin occupies principally an antibonding<sup>15</sup> orbital between the nitrogen impurity atom in a substitutional site and one of its carbon nearest neighbors. Schmid<sup>16</sup> has shown that bonding orbitals of the Hund-Mulliken type give a better account of the cohesive energy of diamond than those of a simple Heitler-London type. These orbitals are of the form

$$\psi_{B,A} = (1/\sqrt{2})(\phi_{\mathrm{N}} \pm \phi_{\mathrm{C}}),$$

where  $\phi_N$ ,  $\phi_C$  are hybridized  $sp^3$  orbitals of tetrahedral type which point towards the appropriate nearest neighbor. The + and - signs are for the bonding and antibonding orbitals. It should be noted that if one assumes that the valence electron states are made up of bonding electrons of this type, one is forced to make up conduction band states from antibonding orbitals of the same type.

The model assumes that the repulsive force exerted

on the nitrogen-carbon pair distorts the lattice sufficiently to localize the electron principally on a simple antibonding orbital. The situation may be viewed as a manifestation of the Jahn-Teller effect.<sup>17</sup> The orbital degeneracy is that associated with the possibility of locating the electron on any one of the four equivalent antibonding orbitals about the nitrogen atom. The frequency of reorientation of the Jahn-Teller distortion must be less than one Mc/sec at room temperature in order not to conflict with the observed line width.

Comparison is invited between the model proposed here and that which is known to predict rather well the properties of donors in silicon and germanium. For the latter one considers the excess electron subject to a Coulomb potential e/er of the impurity ion. The orbits are large (25 A) compared to the distance between atoms and the time needed for the electron to pass an atom is greater than the time required for the inner bound electrons of the atom to readjust and polarize the medium, thus reducing the Coulomb force by a factor  $1/\epsilon$ . In the case of nitrogen in diamond, on the other hand, the much more tightly bound donor electron orbits at a much greater frequency so that electronic polarization is not allowed to develop, the Coulomb potential then remaining approximately e/r. Thus the "radius" of the nitrogen donor is more or less consistent with the free hydrogen Bohr radius; the donor ionization energy is likewise probably closer to the value for a hydrogen atom than it is to the 0.4-ev value predicted for a potential  $V = e/\epsilon r$  with  $\epsilon = 5.7$ , the value of the dielectric constant of diamond. Being thus confined to the immediate vicinity of the donor ion where it can essentially exist in any one of four available antibonding orbitals, the electron falls into a selected one, the corresponding N-C bond is weakened and distorted, and the electron is trapped in the given antibonding orbital.

Consideration of this model suggested the following experimental check. As there is a small natural abundance (1.1%) of C<sup>13</sup>, and as this isotope has a nuclear spin of  $\frac{1}{2}$ , there should exist a weak additional spectrum arising from donor electrons in antibonding orbits on N<sup>14</sup>-C<sup>13</sup> pairs. The C<sup>13</sup> nuclear spin splits the nitrogen triplet so that the weak additional spectrum should consist of pairs symmetrically disposed about each of the main nitrogen absorptions. Each line would be roughly 180 times smaller than the corresponding line of the main spectrum. A careful search revealed this set of C<sup>13</sup> lines; portions of this spectrum which will hereafter be called B are reproduced authentically in Fig. 2 and schematically in Fig. 3. In the traces shown in Fig. 2 the recorder zero adjustment was changed several times to keep the pen on scale as the low-field satellites of the main spectrum were approached. These traces show clearly why we are able to see only those portions of the spectrum B which lie outside the outer

 <sup>&</sup>lt;sup>14</sup> B. Bleaney, Phil. Mag. 42, 441 (1951).
 <sup>15</sup> See, for example, C. A. Coulson, *Valence* (Oxford University Press, Oxford, 1952), p. 88.
 <sup>16</sup> L. A. Schmid, Phys. Rev. 92, 1373 (1953).

<sup>&</sup>lt;sup>17</sup> H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) A161, 220 (1937).





LINE SEPARATIONS (OERSTEDS)

Fig. 3. Schematic representation of the microwave absorption spectrum of bound nitrogen donors in diamond. Relevant portions of the spectra A, B, C discussed in the text are shown.

satellites of the main spectrum A. Other runs made by reducing the spectrometer gain by 100 at the positions of the main satellites enabled relative intensities to be measured. The measured intensity of the B spectrum relative to that of the main nitrogen spectrum is in approximate agreement with the factor 1/180. From the data the C<sup>13</sup> hyperfine constants are at once deduced to be |A'| = 60.8 oersteds, |B'| = 25.3 oersteds. The three other observed line positions may then be compared with the predicted values obtained from  $K'^2 = A'^2 \cos^2\theta + B'^2 \sin^2\theta$ . None of the 3 comparisons for |K'| is off by more than 1 oersted. The hyperfine axis for the C<sup>13</sup> spectrum is again the C-N bond direction. Besides this well-defined set of lines B, some weak structure was observed on the wings of the main nitrogen satellites (dashed lines in Fig. 3). Only for the case  $H_0 || [100]$  could these latter lines, hereafter called spectrum  $\vec{C}$ , be clearly distinguished. For this particular orientation the complete spectrum C consists of three groups of 2 lines, the latter being symmetrically located on each side of a main nitrogen absorption and separated from it by 6.4 oersteds. The measured intensity of these lines C relative to the main nitrogen lines A is approximately consistent with the factor 1/60. The C splitting is a rough measure of the donor electron density on the basal carbon nearestneighbor atoms. From these data it appears that the donor electron is indeed mainly confined to the nitrogen atom and one of the nearest neighbor carbon atoms.

In the Appendix it is shown that if the wave function for the unpaired electron is axially symmetric, the hyperfine constants are given by

$$A = 2\mu_{0}\mu_{I}g_{I}\{O+2P\},$$
  

$$B = 2\mu_{0}\mu_{I}g_{I}\{O-P\},$$
where
$$O = (8\pi/3) |\psi(0)|^{2},$$

$$P = \langle [z^{2} - \frac{1}{2}(x^{2} + y^{2})]/r^{5} \rangle.$$
(1)

The quantity P, which vanishes for a pure s orbital, would be a positive quantity for an antibonding orbital of the type proposed. Solving for O and P, and using the experimental values for A, B:

$$A = (40.8)\gamma_{\rm el}\hbar,$$
$$B = (29.2)\gamma_{\rm el}\hbar,$$

one has

$$O_{\rm N} = 16.3 \times 10^{24} \text{ cm}^{-3} = 2.41$$
 atomic units,

$$P_{\rm N} = 1.9 \times 10^{24} \text{ cm}^{-3} = 0.28 \text{ atomic unit.}$$

The value for  $O_N$  implies a density of the donor wave function at the nitrogen nucleus:  $|\psi(0)|^2_N = 1.95 \times 10^{24}$  cm<sup>-3</sup>. Likewise one obtains from the C<sup>13</sup> data the experimental values

$$O_{\rm C} = 5.24 \times 10^{24} \text{ cm}^{-3} = 0.78$$
 atomic unit,  
 $P_{\rm C} = 1.67 \times 10^{24} \text{ cm}^{-3} = 0.248$  atomic unit,

 $|\psi(0)|^2 = 0.63 \times 10^{24} \text{ cm}^{-3}$ .

To compare theory and experiment, the values which are predicted from the N-C antibonding orbital assumption will now be considered. From the Hartree solutions for the free atoms<sup>18,19</sup> and from  $\langle 1/r^3 \rangle$  averages computed from spectroscopic data,<sup>20</sup> one obtains

$$O_{\rm N}{}^{A} = \frac{8\pi}{3} |\psi(0)|^{2} = 38.0 \text{ atomic units,}$$
$$P_{\rm N}{}^{A} = \left\langle \frac{z^{2} - \frac{1}{2}(x^{2} + y^{2})}{r^{5}} \right\rangle_{2P_{z}} = \frac{2}{5} \left\langle \frac{1}{r^{3}} \right\rangle_{2P}$$

=1.01 atomic units,

 $O_{\rm C}^{A} = 24.6$  atomic units,  $P_{\rm C}{}^{\rm A} = 0.48$  atomic unit.

Neglecting overlap integrals entirely, the following values are obtained for the case of a simple antibonding orbital  $\psi = (1/\sqrt{2})(\phi_{\rm N} - \phi_{\rm C})$ :

> $O_{\rm N}{}^{AB} \cong 4.75$  atomic units.  $P_{\rm N}{}^{AB} \cong 0.38$  atomic unit,  $O_{\rm C}{}^{AB} \cong 3.08$  atomic units,  $P_{\rm C}{}^{AB} \cong 0.18$  atomic unit.

It is clear that this simple approximation predicts a greater density of the donor wave function at the nitrogen and carbon nuclei than is experimentally observed. The discrepancy is enhanced if the overlap integral  $S = \int \phi_N \phi_C d\mathbf{r}$  is taken into account, for the above quantities are then increased by a factor  $\eta = 1/2$  $(1-S)\cong 3$ . The situation improves markedly if one assumes an axial displacement of both nitrogen and carbon atoms away from one another. This process reduces the amount of *s* character in the antibonding wave function. The overlap integral  $\int \phi_N \phi_C d\mathbf{r}$  is also reduced, due both to the above mentioned change in hybridization and to the increase in internuclear distance. For an orbital  $\phi \sim (s + \lambda p)$  directed along the axis of a distorted tetrahedral set of bonds, the amount of hybridization is determined by the formula<sup>21</sup>  $tan\phi$  $=-\lceil 2(1+\lambda)\rceil^{\frac{1}{2}}, \phi$  being the angle between the axial and basal bonds. If the nitrogen or carbon atom is displaced far enough, the hybridized orbital which contributes to the donor wave function becomes a pure  $P_z$  orbital. In this case the three basal bonds are

TABLE I. Comparison of observed atomic constants with values obtained from models discussed in the text.  $\eta'$  is the value of the overlap integral for a 10% increase in the C-N bond distance.

	Observed	Atomic	Model predicted (no dis- tortion)	Model predicted (10% dis- tortion)
$O_{ m N}$ $P_{ m N}$ $O_{ m C}$ $P_{ m C}$	2.41 0.28 0.78 0.248	38.0 1.01 24.6 0.48	$\begin{array}{c} 4.8\eta \\ 0.38\eta \\ 3.1\eta \\ 0.18\eta \end{array}$	$\begin{array}{c} 2.37\eta' \\ 0.44\eta' \\ 1.53\eta' \\ 0.21\eta' \end{array}$

trigonal,  $sp^2$ . Clearly, this represents an extreme situation, and an intermediate displacement probably occurs which reduces  $O_N^{AB}$  and  $O_C^{AB}$  sufficiently. A guess at what might be a maximum tolerable displacement for the nitrogen atom could reasonably be put at 5% of the normal C-C bond length. This would change the hybridization of the orbital used in the antibonding wave function to approximately 12.5% s character, 87.5% p character ( $\lambda = \sqrt{7}$ ). In this estimate, the connection is made between the displacement of the nitrogen atom and the angle  $\phi$  between the axial and basal orbitals of the nitrogen atom by requiring the axes of the nitrogen basal orbitals to pass through the midpoints of the undistorted C-N basal bonds. The tetrahedral orbitals on the basal carbon atoms remain fixed, and "bent" bonds are thus formed. This constraint is approximately consistent with the requirement that maximum overlap of the basal bonds be established for a given nitrogen displacement. The 5%distortion reduces  $O_N^{AB}$  to 2.37 atomic units while  $P_N^{AB}$ becomes 0.44 atomic unit. The same displacement applied to the carbon atom results in values for  $O_{\rm C}^{AB}$ ,  $P_{C}^{AB}$  of 1.53, 0.21 atomic units, respectively. Table I summarizes the comparisons discussed above. While the above estimate of a net increase of 10% in the C-N bond length due to the presence of the extra antibonding electron may be too high, an increase of several percent is certainly reasonable. Localization of the donor electron in one antibonding orbital argues for a fairly severe atomic distortion. Furthermore, not too much energy may actually be lost in the "bent" bonds which are formed between a displaced nitrogen or carbon atom and the three basal carbon atoms. A relatively large increase in the separation of an N-C pair may be responsible for the anomalous x-ray spots<sup>22</sup> which characterize type I diamonds.

Actually, while it is clear from the experimental data that the bound donor electron spends by far the greatest time per atom on the nitrogen and on one of the nearestneighbor carbon atoms, one sees from Fig. 3 (dashed lines) that the wave function density is not entirely negligible on all other carbon atoms. The resolvable weak lines (C) on either side of the main satellites for the case  $H_0 || [100]$  seem to indicate that the wave function density on each of the basal carbon atoms is about

 <sup>&</sup>lt;sup>18</sup> Brown, Bartlett, and Dunn, Phys. Rev. 44, 296 (1933).
 <sup>19</sup> C. C. Torrance, Phys. Rev. 46, 388 (1934).
 <sup>20</sup> R. G. Barnes and W. V. Smith, Phys. Rev. 93, 95 (1954).
 <sup>21</sup> See, for example, reference 15, p. 194.

<sup>&</sup>lt;sup>22</sup> K. Lonsdale, Proc. Roy. Soc. (London) A179, 315 (1942).

one-sixth that on the axial carbon atom. Calculation shows that this density cannot be attributed to the extension of the principal antibonding orbital at these points. The true wave function is, therefore, a linear combination of antibonding orbitals, with a predominant contribution from one of them. A more detailed consideration of the donor wave function is unwarranted until better data are obtained for the distribution of the wave function on atoms other than the N-C pair. It is clear that this could be done by using the doubleresonance technique of Feher.

# IV. REMARKS ON SPIN CONCENTRATIONS

In the majority of our samples the line width  $\Delta H$  of the nitrogen resonance was measured to be about 0.3 oersted between the points of maximum slope. This limiting line width may represent inhomogeneous broadening caused by the presence of C13 atoms on second-nearest-neighbor sites. Some variation of  $\Delta H$ towards greater values was observed in a few stones, but the cause of this is unknown. For spin-spin broadening to become important a nitrogen concentration  $\geq 10^{19}/cc$  is required. (For N electrons per cc which are randomly distributed in the lattice,  $\Delta H \cong N \times 10^{-19}$ oersteds.23) Our estimates of the spin concentrations of our various samples fall more in the range  $10^{15}$ - $10^{17}$ /cc. Since this is several orders of magnitude less than the amount of substitutional nitrogen Kaiser observes in diamonds, it is probable that most of the nitrogen may be present in a nonparamagnetic form, for example, in adjacent substitutional pairs. The isolated donors which produce the microwave resonance we see therefore represent only a small fraction of the nitrogen present.

No exchange effects<sup>24,25</sup> due to overlapping donor wave functions such as occur in the case of donors in silicon were observed. This seems reasonable because the bound donors in diamond are much more compact structures.

### V. ACKNOWLEDGMENT

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The cooperation of Mr. Bart van Berg of the Rough Diamond Company who made a large number of diamonds available to us for our microwave measurements is greatly appreciated. Through the efforts of Dr. J. F. H. Custers, Director of Research at the Diamond Research Laboratory, Industrial Distributors (1946) Ltd., we received a number of diamond blocks together with the results of optical measurements done on the samples by that laboratory. Their interest in our research is stimulating.

#### APPENDIX

The hyperfine interaction between an unpaired electron and a nucleus is represented by the operator

$$\Im \mathcal{C}_{int} = 2\mu_0 \mu_I g_I \left\{ \frac{\Im (\mathbf{r} \cdot \mathbf{S}) (\mathbf{r} \cdot \mathbf{I})}{r^5} - \frac{(\mathbf{S} \cdot \mathbf{I})}{r^3} \right\} + 2\mu_0 \mu_I g_I \frac{8\pi}{3} \delta(\mathbf{r}) \mathbf{S} \cdot \mathbf{I}.$$

To express this interaction as a function of spin coordinates only, an integration over the spatial coordinates is performed:

$$W = \int |\psi^{2}(\mathbf{r})| \Im C_{\text{int}} d\mathbf{r} = \langle \Im C_{\text{int}} \rangle$$
  
=  $2\mu_{0}\mu_{I}g_{I} \left\{ \frac{8\pi}{3} \psi^{2}(0) \mathbf{S} \cdot \mathbf{I} + \int \left[ \frac{\Im (\mathbf{S} \cdot \mathbf{r}) (\mathbf{r} \cdot \mathbf{I})}{r^{5}} - \frac{\mathbf{S} \cdot \mathbf{I}}{r^{3}} \right] |\psi^{2}(\mathbf{r})| d\mathbf{r} \right\}.$ 

For an axially symmetric electron wave function  $\langle x^2/r^5 \rangle$  $=\langle y^2/r^5\rangle$ , while terms such as  $\langle xy/r^5\rangle$  are zero. Collecting terms, one easily finds

$$W = 2\mu_0\mu_I g_I \left[ \left\{ \frac{8\pi}{3} \psi^2(0) + 2(\alpha - 3\beta) \right\} I_z S_z + \left\{ \frac{8\pi}{3} \psi^2(0) - (\alpha - 3\beta) \right\} (I_z S_z + I_y S_y) \right],$$
  
where  
$$\alpha = \langle 1/r^3 \rangle, \quad \beta = \langle x^2/r^5 \rangle.$$

That is,

$$W = AI_z S_z + B(I_x S_x + I_y S_y), \tag{A1}$$

with A and B as given in Eqs. (1). It can be shown<sup>14</sup> that the Hamiltonian (A1) implies an angular variation of the hfs given by  $K^2 = A^2 \cos^2\theta + B^2 \sin^2\theta$  when the g factor is isotropic.

 <sup>&</sup>lt;sup>28</sup> C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).
 <sup>24</sup> Feher, Fletcher, and Gere, Phys. Rev. **100**, 1784 (1955).
 <sup>25</sup> C. P. Slichter, Phys. Rev. **99**, 479 (1955).



FIG. 2. Arrows indicate a portion of the weak resonance spectrum B due to donor electrons on N<sup>14</sup>-C<sup>13</sup> pairs. The sign of the recorder input voltage is reversed from that of Fig. 1.