

fields is given by

$$a = -g\mu_0(H_{mI=\frac{1}{2}} - H_{mI=-\frac{1}{2}}), \quad (G5)$$

i.e., no corrections are necessary.

From the average of the two fields $H_{mI=\frac{1}{2}}$ and $H_{mI=-\frac{1}{2}}$ we can define a measured g value, g_m , given by

$$h\nu = \frac{1}{2}g_m\mu_0(H_{mI=\frac{1}{2}} + H_{mI=-\frac{1}{2}}). \quad (G6)$$

Comparing this expression with (G3), we obtain for the true g value

$$g = g_m\{1 - \frac{1}{2}(a/g\mu H)^2[I(I+1) - \frac{1}{4}]\}. \quad (G7)$$

If we subject the sample to a compressive stress changing the hyperfine splitting a , then the differential correction to g is given by

$$\Delta g = 2(g_m - g)(\Delta a/a). \quad (G8)$$

Electron Spin Resonance Studies in SiC

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Electron spin resonance studies have been made on boron and nitrogen as impurities in 6H silicon carbide. It is concluded that both impurities substitute for carbon and that they occupy the three nonequivalent carbon sites with equal probability. Hyperfine structure is well resolved for both species. The pattern for boron occupying one site is unusual in that the hyperfine splitting vanishes when the applied field is about 50° from the hexagonal axis of the crystal. The nitrogen hyperfine structure is interpretable in terms of some s character for the unpaired electron, while the boron hyperfine structure indicates predominantly p character.

I. INTRODUCTION

THE basic arrangement of atoms in Column IV semiconductors such as Ge, Si, and SiC is tetrahedral. An atom of a Column V element normally acts as a donor in such semiconductors since it has one valence electron left over after completing the normal tetrahedral bonding. At sufficiently low temperatures this electron is localized near the donor atom; at high temperatures it can ionize and give rise to n -type conduction. Similarly, an atom of a Column III element acts as an acceptor and gives rise to p -type conduction.

Most semiconductors, including silicon carbide, are intrinsically diamagnetic; the perfect crystal has no unpaired electrons and does not show spin resonance absorption. However, many impurities introduced into such semiconductors are paramagnetic and result in spin resonance absorption. The Column III and Column V elements act as such impurities in the Column IV semiconductors. The Column V elements, P, As, Sb, and Bi, have been extensively studied by spin resonance in Si.¹ Resonance of the first three donors has recently been reported in Ge^{2,3}; the Column V element nitrogen has been studied in diamond.⁴

Column III elements have recently been observed in Si subjected to uniaxial stress.⁵

Spin resonance of Column V and Column III elements in SiC has been reported by van Wieringen.⁶ He attributed a three-line spectrum in n -type material to nitrogen and a single-line spectrum in p -type material to Column III acceptors. This was the first report of resonances due to N and Column III acceptors in a Column IV semiconductor. In this paper we report on further studies of N- and B-doped SiC. A preliminary account of our experiments has already been given.⁷

The spin resonance spectrometer used to study SiC operates at a microwave frequency ν of about 14 kMc/sec. Thus the magnetic field H for resonance is of order 5000 gauss for systems (including N and B in SiC) with g factors near that of the free electron. Some measurements were made at 20 kMc/sec with a correspondingly higher field. The electron-nuclear double resonance technique¹ has also been employed. Details of the experimental equipment have been given elsewhere.⁸

The SiC crystals studied were small hexagonal single

¹ G. Feher, J. C. Hensel, and E. A. Gere, *Phys. Rev. Letters* **5**, 309 (1960).

² G. Feher, D. K. Wilson, and E. A. Gere, *Phys. Rev. Letters* **3**, 25 (1959).

³ R. E. Pontinen and T. M. Sanders, Jr., *Phys. Rev. Letters* **5**, 311 (1960).

⁴ W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, *Phys. Rev.* **115**, 1546 (1959).

⁵ J. S. van Wieringen, in *Semiconductors and Phosphors*, edited by M. Schön and H. Welker (Interscience Publishers, Inc., New York, 1958), p. 367.

⁷ H. H. Woodbury and G. W. Ludwig, *Bull. Am. Phys. Soc.* **4**, 144 (1959).

⁸ G. W. Ludwig and H. H. Woodbury, *Phys. Rev.* **113**, 1014 (1959); H. H. Woodbury and G. W. Ludwig, *ibid.* **117**, 102 (1960).

crystals believed to be of the high-temperature form, $6H$.⁹ Some crystals containing nitrogen were selected from material obtained from the Carborundum Company or from the Norton Company. Samples intentionally doped with nitrogen or boron were grown by Scace.¹⁰

II. THEORY

A phenomenological spin Hamiltonian will be used to describe the observed spectra. The significance of some of the interaction constants is discussed in Sec. IV.

The spin Hamiltonian of an impurity having an electron spin $S=\frac{1}{2}$, a nuclear magnetic moment, and a nuclear electric quadrupole moment is¹¹

$$\mathcal{H} = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} + \mathbf{I} \cdot \mathbf{P} \cdot \mathbf{I} - \beta_N \mathbf{I} \cdot \mathbf{g}_N \cdot \mathbf{H}. \quad (1)$$

The first term describes the direct interaction of the applied magnetic field with the electron spin; the second term gives the interaction between the electron spin and the nuclear spin I ; the third term describes the interaction of the nuclear quadrupole moment with the electric field gradient; and the last term describes the interaction of the nuclear spin with the applied magnetic field. In general, there will be several different nuclei interacting with the electron spin. In SiC, these would include Si^{29} and C^{13} nuclei of the host lattice as well as the nucleus of the impurity atom; here only the interaction with the impurity atom is included.

Each substitutional site in hexagonal SiC has threefold symmetry about the hexagonal axis. For this symmetry (1) can be written

$$\begin{aligned} \mathcal{H} = & \beta [g_{11} S_z H_z + g_{\perp} (S_z H_x + S_y H_y)] \\ & + A S_z I_z + B (S_x I_x + S_y I_y) \\ & + P [I_z^2 - \frac{1}{3} I(I+1)] - \gamma \beta_N \mathbf{H} \cdot \mathbf{I}. \end{aligned} \quad (2)$$

Here A and B denote the components of the magnetic hyperfine interaction tensor parallel to and perpendicular to the z (hexagonal) axis, respectively, and other parameters are defined similarly. Only one parameter, the scalar P , is required to describe the quadrupolar interaction. For simplicity we have assumed that the effective nuclear g tensor \mathbf{g}_N is equal to the nuclear g factor γ times the unit dyadic. Neglecting all hyperfine interaction, the $M=+1/2$ to $-1/2$ spin resonance transition is given by

$$\begin{aligned} h\nu &= g\beta H; \\ g^2 &= g_{11}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta, \end{aligned} \quad (3)$$

⁹ See H. Jagodzinski and H. Arnold in *Silicon Carbide*, edited by J. R. O'Connor and J. Smiltens (Pergamon Press, New York, 1960), p. 136, and accompanying articles and references therein for a description of the various forms of SiC.

¹⁰ For a description of the furnace used see R. I. Scace and G. A. Slack, *J. Chem. Phys.* **30**, 1551 (1959).

¹¹ For a discussion of the spin Hamiltonian, the reader is referred to A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **205**, 135 (1951). See also W. Low, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1960), Suppl. 2, Part II.

where θ is the angle between the z axis and the applied magnetic field.

In most resonant systems the magnetic interaction between the nucleus and the electron spin is large compared with the direct interaction between the nucleus and the applied field, i.e., $|A, B| \gg |\gamma \beta_N H|$. However, $|\gamma \beta_N H|$ ($\sim 2.3 \times 10^{-4} \text{ cm}^{-1}$ for B^{11}) is somewhat larger than $|A|$ and $|B|$ for boron in SiC under our experimental conditions and the usual method of treating the hyperfine interactions in (2) does not apply. Ham has treated the hyperfine interaction placing no restriction on the relative magnitudes of $\beta_N \mathbf{H} \cdot \mathbf{g}_N \cdot \mathbf{I}$ and $\mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$ of (1). His results are given in the Appendix. Three cases of particular interest to SiC are discussed at this point.

Case A. $|A, B| \gg |\gamma \beta_N H, P|$. For $|A|$ and $|B|$ sufficiently large the nucleus is quantized along the direction of the field of the electron spin. Substituting (A3), (A5), (A6), (A8), and (A12) into (A9), and assuming $S=1/2$ and $(g_N)_{11} = (g_N)_{\perp} = \gamma$, the energy levels are

$$\begin{aligned} W(M, m) = & g\beta H M + K M m - \gamma \beta_N H m \\ & \times (A g_{11} \cos^2\theta + B g_{\perp} \sin^2\theta) / K g \\ & + (1/2) P m^2 [3(A g_{11} / K g)^2 \cos^2\theta - 1], \end{aligned} \quad (4)$$

where

$$K^2 g^2 = A^2 g_{11}^2 \cos^2\theta + B^2 g_{\perp}^2 \sin^2\theta,$$

and g is given by (3). The constant term in P has been dropped.

The allowed ($M=+1/2$ to $-1/2$; $\Delta m=0$) transitions are given by

$$h\nu = g\beta H + K m, \quad (5)$$

while the electron-nuclear double resonance transitions

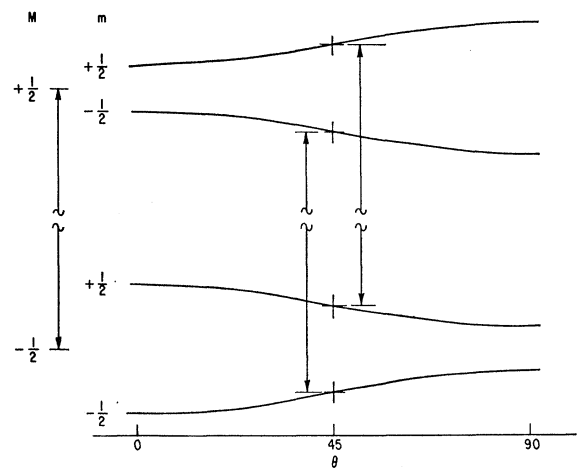


FIG. 1. Energy levels for the case $|\gamma \beta_N H| > |A, B|$ as a function of the angle between the applied magnetic field and the axis of symmetry, as given by (7). For simplicity, we have chosen $A = -B = \gamma \beta_N H = 2$ (all in arbitrary units), $g_{11} = g_{\perp}$, and $S = I = \frac{1}{2}$. At an angle such that $\tan^2\theta = g_{11} A / g_{\perp} B$, the two allowed transitions are equal in energy and no hyperfine splitting is observed.

TABLE I. Resonance parameters for N-doped SiC.

	g_{11}	g_1	$ A $ (10^{-4} cm^{-1})
Larger signal	2.0036	2.0030	11.08
Smaller signal	2.0040	2.0026	11.20

($\Delta M=0$, $\Delta m \pm 1$) are

$$hf = |KM + (m-1/2)P[3(Ag_{11}/Kg)^2 \cos^2\theta - 1] - \gamma\beta_N H(Ag_{11} \cos^2\theta + Bg_1 \sin^2\theta)/(Kg)|, \quad (6)$$

where f is the double resonance frequency.

Case B. $|\gamma\beta_N H| \gg |A, B|$; $P=0$. Here the axis of quantization of the nucleus is the applied field rather than the field generated at the nucleus by the unpaired electrons. Substituting (A3), (A5), and (A13) into (A9), and again assuming $(g_N)_{11} = (g_N)_1 = \gamma$,

$$W(M, m) = g\beta H M + m\gamma\beta_N H - M m \times [(g_{11}/g)A \cos^2\theta + (g_1/g)B \sin^2\theta]. \quad (7)$$

The allowed ($M = +1/2$ to $-1/2$; $\Delta m = 0$) transitions are given by

$$h\nu = g\beta H - m[(g_{11}/g)A \cos^2\theta + (g_1/g)B \sin^2\theta]. \quad (8)$$

It is noted that at $\theta=0^\circ$ and 90° , (8) and (5) are identical except for an arbitrariness in the sign of m . However, (8) and (5) give different results at intermediate angles. The difference becomes marked if A and B have opposite signs; in particular, if (8) applies the hyperfine splitting vanishes at an intermediate angle (see Fig. 1).

For $|\gamma\beta_N H|$ comparable to $|A|$ and $|B|$, m is no longer a good quantum number and forbidden transitions occur. If A and B are of opposite signs and comparable in magnitude, (8) is a good first approximation as long as $|\gamma\beta_N H| > |A|$.

Case C. $|P| \gg |A, B, \gamma\beta_N H|$. If the quadrupolar interaction is large compared to other hyperfine interaction terms, the axis of quantization of the nucleus is the z axis regardless of the direction of the applied magnetic field. This problem is similar to that of the Zeeman splitting in nuclear quadrupole resonance,¹² and to electron spin resonance in the case of a strong axial field.¹³ For \mathbf{H} along the z axis the normal hyperfine pattern is seen, while for \mathbf{H} perpendicular to the z axis the hyperfine splitting vanishes for $m \pm \frac{1}{2}$. For example, if $I = \frac{3}{2}$ the pattern for \mathbf{H} perpendicular to z is composed of three lines of intensity 1:2:1.

For intermediate cases ($|A, B|$ or $|\gamma\beta_N H|$ comparable to $|P|$) forbidden transitions occur except for \mathbf{H} parallel to z . An unequal spacing of lines occurs for \mathbf{H} perpendicular to z .

III. EXPERIMENTAL RESULTS. N-DOPED SiC

The spin of the dominant N isotope (N^{14}) is 1. Thus, one normally expects the spectrum of atomically dispersed N to be composed of one or more sets of 3 equally intense hyperfine lines. Figure 2 shows such a spectrum in SiC where two overlapping sets of three lines are observed. Both sets can be described by (5) and (6); the parameters are summarized in Table I. In each case the value for the hyperfine interaction parameter was obtained from double resonance measurements, which also showed the hyperfine interaction to be isotropic within the accuracy of the measurements ($\pm 0.01 \times 10^{-4} \text{ cm}^{-1}$). The double resonance measurements also indicated that the quadrupolar interaction constant $P \leq 0.01 \times 10^{-4} \text{ cm}^{-1}$. A value 0.404 ± 0.003 was measured for γ in agreement with the known nuclear g factor for N^{14} . This is definitive evidence that the spectrum is produced by N.

Both the double resonance experiments and the spectrum of Fig. 2 indicate that the stronger signal arises from about twice as many centers as the weaker signal. Attempts to resolve the stronger signal into (presumably two) components were unsuccessful. Weak double resonance signals, tentatively attributed to Si^{29} , were also observed. These were not analyzed because of their low intensity.

The crystal whose spectrum is shown in Fig. 2 was a piece weighing 31 mg broken out of a larger mass of undoped SiC obtained from the Norton Company. It was very slightly colored. From the intensity of the spin

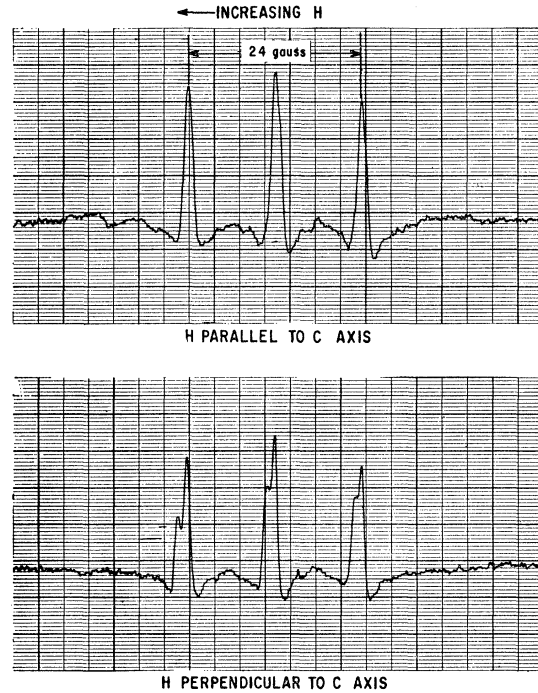


FIG. 2. Spectrum of N in SiC at 20.4°K. The derivative of the dispersion signal has been recorded.

¹² T. P. Das and E. L. Hahn, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Suppl. 1, pp. 7-11.

¹³ G. W. Ludwig, H. H. Woodbury, and F. S. Ham (to be published).

resonance pattern, it was estimated to contain $\sim 3 \times 10^{16}/\text{cm}^3$ uncompensated N. It is noted that most samples contained much more N than this. At higher concentrations there are interactions between closely situated N impurity atoms and additional weak lines are observed between the main lines. At sufficiently high N concentrations a single broad line is observed.⁶

IV. EXPERIMENTAL RESULTS. B-DOPED SiC

Boron has two stable isotopes, B^{10} and B^{11} , having nuclear spins of 3 and $\frac{3}{2}$, respectively. Since B^{11} is about 80% abundant, one normally expects a spectrum consisting of one or more sets of four equally intense lines. The B^{10} will produce a background of seven weaker lines. Figure 3 shows the spectrum that is observed in B-doped SiC when H is along the hexagonal axis. It can be resolved into three sets of four lines, designated I, II, and III in Fig. 3. The sets appear to be equally intense although there is a marked difference in line-width between I and II or III at the higher temperature. Several crystal growing runs were doped with boron enriched to 92% or 96% in B^{10} . Crystals from such runs showed many poorly resolved lines instead of the pattern seen in Fig. 3. The number and position of the lines were consistent with the spin and moment of B^{10} and the resonance parameters measured in samples containing boron of normal isotopic abundance (i.e., for B^{11}).

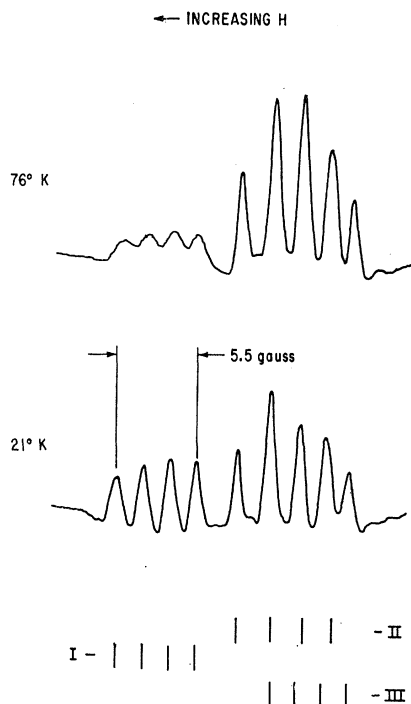


FIG. 3. Spectrum of B in SiC with H parallel to the hexagonal axis and with $\nu = 14$ kMc/sec. The derivative of the dispersion signal has been recorded.

The boron spectrum is anisotropic and as H is rotated away from the hexagonal axis it is less easily separated into components. Spectrum I has been traced as a function of angle. It consists of four hyperfine lines whose spacing is slightly nonuniform at intermediate angles. The angular dependence of the average hyperfine splitting is plotted in Fig. 4; it is in good agreement with (8), indicating that A and B have opposite signs.

Except for H parallel to the hexagonal axis, the spectra II and III have not been analyzed with complete success. They consist of more than four hyperfine lines; the forbidden transitions presumably arise because several hyperfine terms are comparable in magnitude. The spectra are isotropic for H in the plane perpendicular to the hexagonal axis.

The boron spectrum as observed at 20 kMc/sec for H at angles of 0° , 50° , and 90° with respect to the hexagonal axis is shown in Fig. 5. At 50° the I spec-

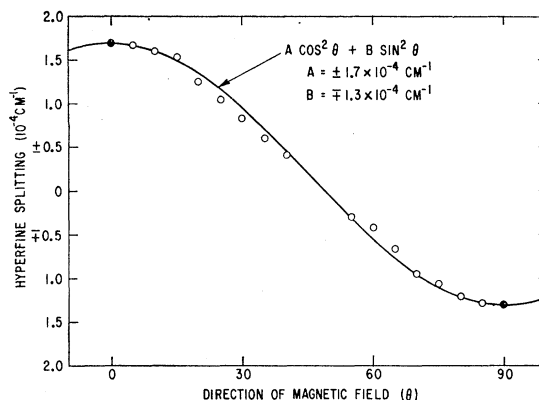


FIG. 4. Plot of the hyperfine splitting of the boron I resonance pattern as a function of the direction of the magnetic field with respect to the hexagonal axis. The curve represents (8) normalized at $\theta = 0^\circ$ and 90° .

trum has collapsed into a single intense line as predicted by (8). The I spectrum at 90° consists of four hyperfine lines (no forbidden transitions) showing that $|P| \ll |B|$. The other two spectra are more complicated at 90° , indicating that $|P| \gtrsim |B|$. The resolution of spectra of different g increases with increasing spectrometer frequency; still higher frequency operation would aid in the analysis of spectra II and III.

With H parallel to the hexagonal axis, additional hyperfine lines have been observed. The intensity is approximately what one expects if the 4.7% abundant isotope Si^{29} is randomly distributed in four equivalent positions about each B site. This implies that B substitutes for C in SiC, since each C atom has four Si nearest neighbors, while each Si atom has twelve Si nearest neighbors.

Table II summarizes the resonance parameters for the boron I, II, and III spectra. The Si^{29} hyperfine interaction parameter is designated T .

The sample whose spectrum is shown in Figs. 3 and 5 is a dark (but not opaque) platelet weighing 4.2 mg grown by Scace. The furnace charge was doped to a level of 3×10^{19} B/cm³. However, the intensity of the resonant absorption indicates that this sample contains only 5×10^{17} /cm³ uncompensated B. It is believed that most of the boron was lost in the furnace and that the crystals were not highly compensated.

Electron-nuclear double resonance was not detected for B, presumably because the spin-lattice relaxation time was short. It might prove possible to detect double resonance using a less heavily doped sample since dipole-dipole interactions probably influence the relaxation time at the concentration employed. At still higher boron concentrations the hyperfine structure is not resolved and a single resonance line of anisotropic width is observed, as reported previously by van Wieringen.⁶

V. DISCUSSION

The features of the observed spectra that one would like to explain can conveniently be divided into two parts: the qualitative character and the quantitative

TABLE II. Resonance parameters for B-doped SiC. The values of g_{\parallel} for spectra II and III are considered tentative. The Si²⁹ hyperfine interaction (T) was measured for H parallel to the hexagonal axis.

Site	g_{\parallel}	g_{\perp}	A (10^{-4} cm ⁻¹)	B (10^{-4} cm ⁻¹)	$ T $ (10^{-4} cm ⁻¹)
I	2.0020	2.0068	± 1.70	∓ 1.30	5
II	2.0056	(2.003)	± 2.1		3
III	2.0062	(2.005)	± 1.7		4

values of the parameters. The first gives information about the geometry of the sites in which the impurity is located; the second pertains to the nature of the wave functions which describe the electrons involved in the resonance absorption. We will now consider the first of these problems.

A basic characteristic of all forms of SiC is the tetrahedral arrangement of the nearest neighbors, i.e., each C is surrounded by a tetrahedron of Si and vice versa. However, the tetrahedral arrangement can be built up in a variety of ways, leading to a variety of crystalline forms which differ in over-all symmetry and in the positions of distant neighbors. The form $6H$ (or α -SiC, type II) has over-all hexagonal symmetry. When one views a model of the $6H$ lattice it is apparent that there are three distinct and equally abundant sites for both C and Si. The C sites, for example, can be distinguished by noting the distances to the nearest Si sites along the hexagonal axis. One such Si site is always in a nearest neighbor position to the C site. If $3d$ is the nearest neighbor distance, then the distance to the other Si site along the hexagonal axis is $5d$, $9d$, or $11d$, depending upon the type of site from which one starts.

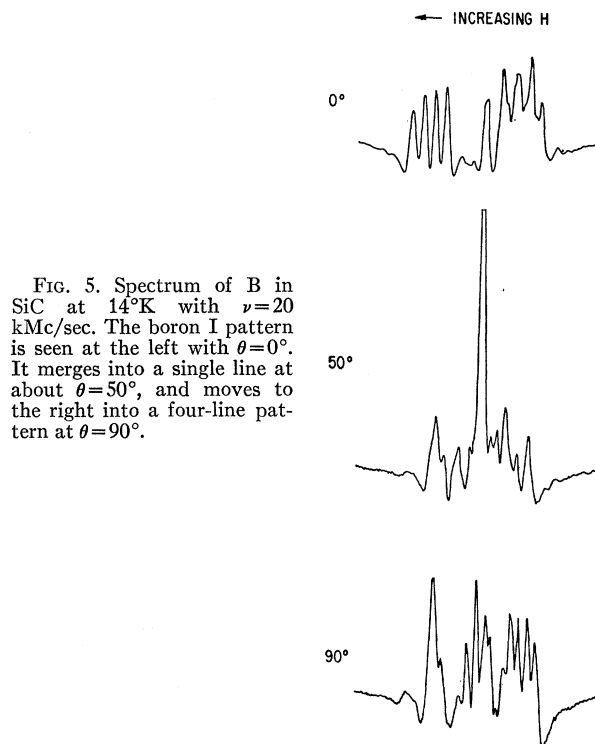


FIG. 5. Spectrum of B in SiC at 14°K with $\nu = 20$ kMc/sec. The boron I pattern is seen at the left with $\theta = 0^\circ$. It merges into a single line at about $\theta = 50^\circ$, and moves to the right into a four-line pattern at $\theta = 90^\circ$.

The Si²⁹ interaction observed on the B spectrum indicates that the B is substituting for C. Thus, it would appear reasonable to identify the boron I, II, and III spectra with the three different C sites. X-ray data taken with electrical measurements have indicated that N also substitutes for C.¹⁴ The N spectrum we observe can be explained by assuming that N enters into two different sites in a ratio of about 2:1 or equally into three sites, two of which give very similar spin resonance behavior. The latter seems the more plausible. Thus, we conclude that both N and B substitute uniformly into the three C sites in SiC. It also seems reasonable that the largest asymmetries occur for an impurity occupying the C site with the nearest Si neighbors along the hexagonal axis; the other two sites differ in more distant neighbor arrangements and show similar properties. On this basis the "smaller" nitrogen resonance pattern and the boron I resonance pattern would correspond to N and B, respectively, situated in the carbon site with the nearest Si neighbors along the hexagonal axis.

The second problem pertains to the character of the wave functions describing the impurity. The features of the hyperfine interaction give considerable information about this. Consider first the N impurity. The isotropic character of the hyperfine interaction indicates a predominantly contact (s -electron) interaction of the

¹⁴ J. A. Lely, *Ber. deut. keram. Ges.* **32**, 229 (1955); J. A. Lely and F. A. Kröger, in *Semiconductors and Phosphors*, edited by M. Schön and H. Welker (Interscience Publishers, Inc. New York, 1958), p. 525.

usual Fermi-Segrè form given by

$$a = (16\pi/3)\gamma\beta_N\beta|\psi(0)|^2, \quad (9)$$

where $|\psi(0)|^2$ is the amplitude of the wave function at the N nucleus. Equating (9) to the observed hyperfine interaction, one finds that $|\psi(0)|^2 = 0.34 \times 10^{24} \text{ cm}^{-3}$. It is noted that this value of $|\psi(0)|^2$ for N in SiC is comparable to the value¹ $0.43 \times 10^{24} \text{ cm}^{-3}$ for P in Si, but much smaller than the value $\sim 50 \times 10^{24} \text{ cm}^{-3}$ estimated¹⁵ for a 2s electron on a free N atom. The small value of $|\psi(0)|^2$ is consistent⁶ with a hydrogenic model in which the wave function is spread out in a relatively large orbit about the nitrogen impurity.¹⁶

N has been observed by spin resonance in one other Column IV semiconductor, diamond.⁴ The hyperfine structure in diamond is anisotropic, the interaction constant being $38.2 \times 10^{-4} \text{ cm}^{-1}$ along a N—C bond axis and $27.4 \times 10^{-4} \text{ cm}^{-1}$ perpendicular to it. The interpretation given for this anisotropy is that the unpaired electron is partially localized in an antibonding orbital. The electron is tightly bound and the hydrogenic approximation does not apply.

The situation for B in SiC is quite different from that for N. The relatively large ionization energy, 0.25 eV as compared with 0.08 eV for the N donor, indicates that the hole is bound relatively close to the impurity (the hydrogenic model is not a good approximation).¹⁶ However, the small value for the hyperfine interaction constant indicates that the wave function amplitude at the nucleus is small. This, as well as the anisotropy, can be qualitatively understood by assuming that the wave function has predominantly *p* character.⁶

An alternative description of the magnetic hyperfine interaction to that in (2) is

$$a\mathbf{S} \cdot \mathbf{I} + b(3S_z I_z - \mathbf{S} \cdot \mathbf{I}), \quad (10)$$

where

$$a = (A + 2B)/3; \quad b = (A - B)/3. \quad (11)$$

The first term in (10) is the contact term while the second is the dipole-dipole term. One would expect *a* to be given by (9) and *b* to be given by

$$b = \frac{4}{3}\gamma\beta_N\beta\langle r^{-3} \rangle. \quad (12)$$

From (9) and (12) one anticipates that *a* and *b* will both have the sign of γ . (For B¹¹, $\gamma = -1.79$). However, from (11) and Table II one finds for the boron I spectrum

$$a = \pm 0.3 \times 10^{-4} \text{ cm}^{-1}; \quad b = \mp 1.0 \times 10^{-4} \text{ cm}^{-1}.$$

The fact that *a* and *b* have opposite signs is not understood. A reversal of sign for the contact term has been observed in other spectra and explained on the basis

¹⁵ This estimate was made in the manner described by W. Kohn and J. M. Luttinger, Phys. Rev. **97**, 883 (1955).

¹⁶ See, for example, the discussion by R. W. Keyes in *Silicon Carbide*, edited by J. R. O'Connor and J. Smiltens (Pergamon Press, New York, 1960), p. 395.

of polarization of inner shells¹⁷; a similar mechanism may apply here.

The shift of the *g* factor of shallow donors in semiconductors from the free-electron value has been related to band parameters by Roth and Lax.¹⁸ The small *g* shift for nitrogen in SiC implies a small spin-orbit interaction, as expected since N, Si, and C are light elements. The small *g* shift for boron implies that the ground state of this acceptor is orbitally nondegenerate. Thus, one presumes that the hexagonal field has split any degeneracy of the valence band (such as exists in Si and Ge) by an amount large compared to the spin-orbit interaction. A study of B in cubic SiC would show whether the acceptor ground state is degenerate in the absence of the hexagonal field.

ACKNOWLEDGMENTS

The authors are indebted to R. I. Scace for his close cooperation in preparing crystals doped with various impurities. They thank F. S. Ham for pointing out the $[(g_{11}/g)A \cos^2\theta + (g_1/g)B \sin^2\theta]$ term describing the boron I hyperfine interaction and for preparing the Appendix. They also acknowledge many helpful discussions with F. S. Ham, G. A. Slack, and others of the General Electric Research Laboratory. G. D. Watkins performed the experiments on B-doped SiC crystals at 20 kMc/sec. C. R. Trzaskos assisted in all phases of the measurements.

Note added in proof. The authors thank Dr. L. Patrick for pointing out an algebraic error in the neighbor distances along the hexagonal axis, and for communicating an analysis he has made of the different sites in the 6H lattice.

APPENDIX

The purpose of this Appendix is to derive an expression for the angular variation of the hyperfine splitting of an ion when the nuclear Zeeman energy is as large as the hyperfine interaction, and any nuclear quadrupole interaction is small. Thus we consider the Hamiltonian¹¹

$$\begin{aligned} \mathcal{H} = & \beta[g_{11}H_zS_z + g_1(H_xS_x + H_yS_y)] \\ & + D[S_z^2 - \frac{1}{3}S(S+1)] \\ & + AS_zI_z + B(S_xI_x + S_yI_y) \\ & + P[I_z^2 - \frac{1}{3}I(I+1)] \\ & - \beta_N[(g_N)_{11}H_zI_z + (g_N)_1(H_xI_x + H_yI_y)]. \quad (A1) \end{aligned}$$

Equation (A1) is somewhat more general than (2) of the text: *S* is no longer assumed equal to $\frac{1}{2}$; a crystalline field (*D*) term is included; and the interaction between the nucleus and the applied field is described by an effective nuclear *g* factor having components $(g_N)_{11}$ and $(g_N)_1$ parallel to and perpendicular to the axis of

¹⁷ J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957); V. Heine, *ibid.* **107**, 1002 (1957).

¹⁸ L. M. Roth and B. Lax, Phys. Rev. Letters **3**, 217 (1959); L. M. Roth, Phys. Rev. **118**, 1534 (1960).

symmetry, respectively. We introduce a new coordinate system to diagonalize the ordinary Zeeman interaction which is assumed to be larger than other terms in \mathcal{H} . The part of \mathcal{H} diagonal in the eigenstates of the ordinary Zeeman interaction then provides a sub-Hamiltonian $\mathcal{H}_N(M)$ for the nuclear levels going with $S_z' = M$. (Off-diagonal parts of \mathcal{H} have been treated by Bleaney¹⁹ by perturbation theory and will be ignored here.) We obtain

$$\mathcal{H}_N(M) = W(M) + R(M)I_z' + S(M)I_x' + P[(I_z'\cos\varphi - I_x'\sin\varphi)^2 - \frac{1}{3}I(I+1)], \quad (\text{A2})$$

where

$$W(M) = \beta g H M + \frac{1}{2}D[M^2(3\cos^2\varphi - 1) + S(S+1)(\sin^2\varphi - \frac{2}{3})], \quad (\text{A3})$$

$$g = (g_{11}^2 \cos^2\theta + g_{12}^2 \sin^2\theta)^{\frac{1}{2}}, \quad (\text{A4})$$

$$\begin{aligned} \cos\varphi &= (g_{11}/g) \cos\theta, \\ \sin\varphi &= (g_{12}/g) \sin\theta, \end{aligned} \quad (\text{A5})$$

and θ is the angle between the magnetic field H and the axis of symmetry. Also

$$\begin{aligned} R(M) &= (A \cos^2\varphi + B \sin^2\varphi)M \\ &\quad - (\beta_N H/g)[(g_N)_{11}g_{11} \cos^2\theta + (g_N)_{12}g_{12} \sin^2\theta], \\ S(M) &= (B-A)M \sin\varphi \cos\varphi \\ &\quad + (\beta_N H/g)[(g_N)_{11}g_{12} - (g_N)_{12}g_{11}] \sin\theta \cos\theta. \end{aligned} \quad (\text{A6})$$

Making a second coordinate transformation to diagonalize the part of $\mathcal{H}_N(M)$ linear in I , we obtain

$$\begin{aligned} \mathcal{H}_N(M) &= W(M) + [R^2(M) + S^2(M)]^{\frac{1}{2}}I_z'' \\ &\quad + P[I_z''^2 \cos^2(x+\varphi) + I_x''^2 \sin^2(x+\varphi) \\ &\quad - (I_z''I_x'' + I_x''I_z'')\cos(x+\varphi)\sin(x+\varphi) \\ &\quad - \frac{1}{3}I(I+1)], \end{aligned} \quad (\text{A7})$$

where

$$\begin{aligned} \cos x &= R(M)/[R^2(M) + S^2(M)]^{\frac{1}{2}}, \\ \sin x &= S(M)/[R^2(M) + S^2(M)]^{\frac{1}{2}}. \end{aligned} \quad (\text{A8})$$

If P is small, the eigenvalues are

$$\begin{aligned} W(M, m) &= W(M) + [R^2(M) + S^2(M)]^{\frac{1}{2}}m \\ &\quad + P\{m^2[\frac{3}{2}\cos^2(x+\varphi) - \frac{1}{2}] + \frac{1}{2}I(I+1) \\ &\quad \times [\sin^2(x+\varphi) - \frac{2}{3}]\}. \end{aligned} \quad (\text{A9})$$

¹⁹ B. Bleaney, *Phil. Mag.* 42, 441 (1951).

This neglects terms of order $P^2/(R^2 + S^2)^{\frac{1}{2}}$ arising from off-diagonal parts of the quadrupole interaction.

From (A6) we find

$$\begin{aligned} [R^2(M) + S^2(M)] &= K^2M^2 + (g_N\beta_N H)^2 - 2M\beta_N H \\ &\quad \times [A(g_N)_{11} \cos\theta \cos\varphi + B(g_N)_{12} \sin\theta \sin\varphi], \end{aligned} \quad (\text{A10})$$

with

$$\begin{aligned} K^2 &= A^2 \cos^2\varphi + B^2 \sin^2\varphi, \\ g_N^2 &= (g_N)_{11}^2 \cos^2\theta + (g_N)_{12}^2 \sin^2\theta. \end{aligned} \quad (\text{A11})$$

Usually $|g_N\beta_N H/KM| < 1$; by expanding (A10) in powers of $(g_N\beta_N H/KM)$ we obtain the usual result,^{19,20}

$$\begin{aligned} [R^2(M) + S^2(M)]^{\frac{1}{2}} &= KM - \beta_N H[(A/K)(g_N)_{11} \\ &\quad \times \cos\theta \cos\varphi + (B/K)(g_N)_{12} \sin\theta \sin\varphi] \\ &\quad + O((g_N\beta_N H)^2/K). \end{aligned} \quad (\text{A12})$$

If, however, $|g_N\beta_N H/KM| > 1$ we expand in $(KM/g_N\beta_N H)$ to obtain

$$\begin{aligned} [R^2(M) + S^2(M)]^{\frac{1}{2}} &= g_N\beta_N H - M\{[A(g_N)_{11}/g_N] \\ &\quad \times \cos\theta \cos\varphi + [B(g_N)_{12}/g_N] \sin\theta \sin\varphi\} \\ &\quad + O(K^2M^2/g_N\beta_N H). \end{aligned} \quad (\text{A13})$$

"Allowed" electron spin resonance transitions are given by

$$\begin{aligned} h\nu &= W(M, m) - W(M-1, m) \\ &= g\beta H + D(M - \frac{1}{2})(3\cos^2\varphi - 1) \\ &\quad + m\{[R^2(M) + S^2(M)]^{\frac{1}{2}} \\ &\quad - [R^2(M-1) + S^2(M-1)]^{\frac{1}{2}}\}. \end{aligned} \quad (\text{A14})$$

Thus for $|g_N\beta_N H/KM| < 1$ the hyperfine splitting is proportional to K and is of the same sign for all angles regardless of the relative signs of A and B [see (A12)]. However when $|g_N\beta_N H/KM| > 1$ the hyperfine splitting as given by (A13) can change sign as a function of angle if $A(g_N)_{11}$ and $B(g_N)_{12}$ have opposite signs.

If $P/[R^2 + S^2]^{\frac{1}{2}}$ is not small the off-diagonal terms in P may not be neglected in evaluating the eigenvalues,¹⁹ and the spectrum is distorted from that given by (A14) except for $\theta=0$. Forbidden lines may occur for $\theta \neq 0$ because of the nuclear quadrupole interaction¹⁹ and also because the coordinate transformation leading to (A7) is somewhat different for different M .

²⁰ W. Low, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Suppl. 2, p. 61.