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⁴ J.-P. Jan and J. M. Gijssman, *Physica* **18**, 339 (1952).

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Hyperfine Splitting in Spin Resonance of Group V Donors in Silicon

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ADDITIONAL observations of the electron spin resonance absorption in *n*-type silicon¹ at 4.2°K have (1) confirmed the interpretation of hyperfine splitting by the donor nucleus, (2) shown that the hyperfine lines are replaced by a single line at high donor concentrations, (3) indicated that the line breadth of the hyperfine lines is of the inhomogeneous type, suggesting residual hyperfine broadening, and (4) revealed the existence of weak satellite lines attributable to forbidden transitions. These observations were made by the same method as described previously¹ on undeformed single crystal bars of silicon.

Fourteen clearly resolved resonance lines (Fig. 1) have been found in antimony-doped silicon (4×10^{21} atoms/cc). These lines naturally fall into two groups, each with lines of about equal intensity and separation. The six lines of the first group have an intensity 1.70 ± 0.05 times and an overall separation 1.32 ± 0.01 times the eight lines of the second group. The number of lines, their relative intensities, and their relative separations appear to be conclusive evidence that the six lines are attributable to interaction with the Sb^{121} nucleus ($I=5/2$, $\mu=3.360$,² abundance=56 percent) and the eight lines to the Sb^{123} nucleus ($I=7/2$, $\mu=2.547$,² abundance=44 percent).

A variety of samples with different concentrations of three donor materials, phosphorus, arsenic, and antimony, have been measured (Fig. 1). With all three it is found that if the concentration exceeds a certain amount (*ca.* 1×10^{18}) the multiplicity of lines disappears, being replaced by a single narrow line (<3 oersteds).

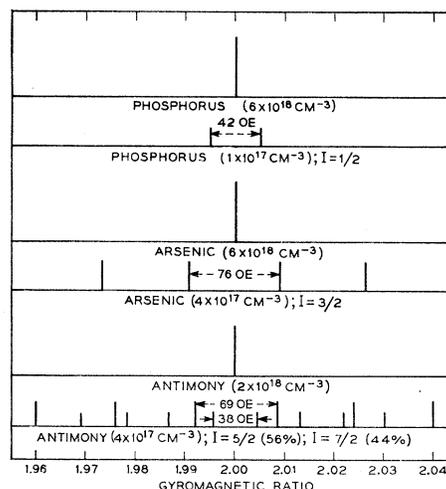


FIG. 1. A schematic representation of the absorption lines observed in silicon doped with various amounts of phosphorus, arsenic, and antimony.

This line has the same *g* factor and apparently is the same line which Portis *et al.*³ have attributed to conduction electrons.

In our experiments there is an as yet unexplained shift (≈ 25 oersteds) in the resonance lines with respect to the calibration line (diphenyl picryl hydrazyl) when the magnetic field is rotated around the cavity containing the sample. This effect accounts for the difference between the *g* factor of the arsenic-doped silicon of Fig. 1 and the previously quoted value.¹ All the samples of Fig. 1 were taken in the same orientation with the dc magnetic field parallel to the transverse rf magnetic field and along the $\langle 100 \rangle$ crystal direction. In this orientation all the lines have the same center of gravity at $g=2.0004 \pm 0.0005$.

An investigation of the saturation behavior with rf field of the hyperfine lines of an arsenic-doped sample reveals it to be of the inhomogeneous type described by Portis.⁴ This suggests that the remaining line breadth of the hyperfine lines is still caused by hyperfine interactions, presumably with the nuclei of Si^{29} (5

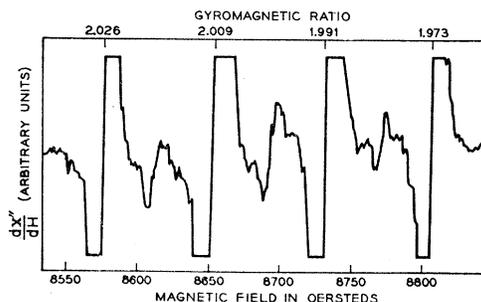


FIG. 2. A reproduction of the observed derivative of the resonance absorption lines of arsenic-doped silicon ($4 \times 10^{17} \text{ cm}^{-3}$) showing three satellite lines between the four principal hyperfine lines.

percent relative abundance). All the lines previously reported¹ as well as those in Fig. 1 were measured at rf levels comparable to those which completely saturated the one sample investigated.

As the rf level was decreased, the signal to noise ratio improved enough to show up three satellite lines in the arsenic-doped silicon. A reproduction of the actual trace is shown in Fig. 2. These lines are located midway between the four principal lines with the middle line of the three about $1\frac{1}{2}$ times as large as the side lines. A natural source for such lines is the almost forbidden transitions in which the donor nucleus flips at the same time the electron does. These transitions will produce lines precisely midway between the main lines as observed.

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² W. G. Proctor and F. C. Yu, *Phys. Rev.* **78**, 471 (1950).

³ Portis, Kip, Kittel, and Brattain, *Phys. Rev.* **90**, 988 (1953).

⁴ A. M. Portis, *Phys. Rev.* **91**, 1071 (1953).

Phosphorescence of Atoms and Molecules of Solid Nitrogen at 4.2°K

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WHILE investigating the possibility of freezing out free radicals at liquid helium temperatures, a phosphorescent glow was observed in the solid products from an electrodeless discharge through nitrogen gas at low pressure. It is possible, therefore, that constituents of the discharge, such as atomic nitrogen, are produced in solid form. This material is observed visually as a thin layer of substance frozen on the inner surface of a single-walled vessel submerged in liquid helium. Presence of an active species on or within the solid is apparent from a visible green glow.

The apparatus is illustrated in Fig. 1. Nitrogen gas is introduced through a control stopcock from a cylinder of nitrogen and traverses the discharge region (A) at low pressure, between 0.1 and 3 mm Hg. The discharge is excited by means of a microwave (2450 Mc/sec) voltage induced by antenna (C). The single-wall lower extremity (B) immersed in liquid helium (F) acts as a trap by freezing out all gases, and thus constitutes effectively a high-speed vacuum pump for maintaining the flow of nitrogen. In order to prevent solidification of discharge products at temperatures above 4.2°K, the flow is carried to the cold walls within a passageway kept nearly at room temperature. This relatively high temperature is maintained by forcing warm helium

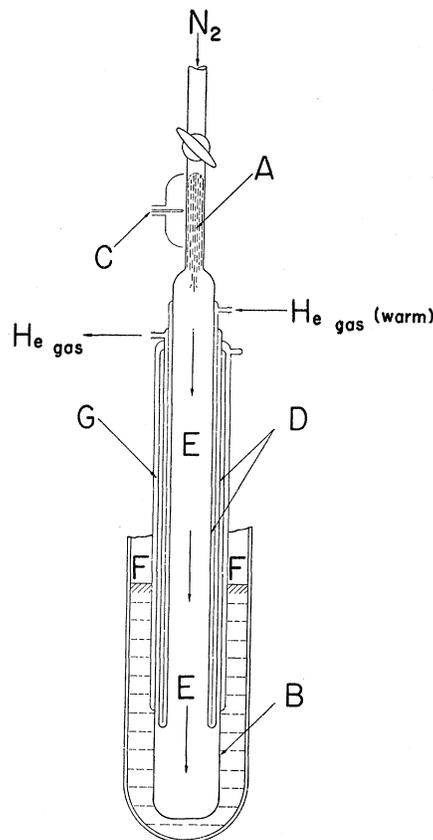


FIG. 1. Diagram of apparatus.

gas between compound walls (D) surrounding the channel (E) through which the discharge products pass. A vacuum region (G) surrounds the entire assembly above chamber (B).

While the discharge (A) is maintained, the walls of the collecting chamber (B) emit a strong green glow. This glow definitely originates from the inner surface where the deposition is occurring; this is verified by observing the interior of the chamber from above. Another characteristic of the surface glow is the random occurrence of local bright spots. After the discharge has been on for several minutes, brilliant flashes of blue appearance are observed spreading as much as two or three centimeters. These flashes are restricted to the surface (not volume effects within the chamber) and appear to be explosive reactions spreading within the deposited material.

After the discharge is extinguished and the flow of nitrogen is stopped, the green glow persists for more than two minutes. During this time the glow intensity diminishes steadily, with no spontaneous flashing. Admission of warm gas (nitrogen or helium) results in increased rate of disappearance and a blue glow before extinction. Removal of the vessel from liquid helium without adding warm gas has a similar result. Once, after the disappearance of both the green and blue