"Hole Burning" in Phosphorus-Doped Silicon†

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"Hole burning" within the inhomogeneously broadened electron-paramagnetic-resonance line associated with isolated shallow donor inpurities in silicon is shown to arise principally from forbidden transitions involving electron-Si^{29} dipolar coupling, rather than from a discrete spectral diffusion process. Additional holes due to scalar hyperfine-coupled forbidden transitions on impurity pair states are also identified. Hole-fading phenomena occurring after successive microwave irradiations and spin-lattice relaxations are attributed to long-lasting nuclear polarization of the Si^{29} spins.

I. INTRODUCTION

EARLY experiments[1,2] involving "hole burning" on electron-paramagnetic-resonance (EPR) lines in silicon were based on the inhomogeneous line broadening[3] of the shallow donor resonances. The resonances are composed of many "spin packets," each of which has its own particular resonance frequency and is itself a homogeneously broadened line whose width is determined primarily by the dipolar field of neighboring electrons. For donors in silicon, the packet frequency is determined by the hyperfine and dipolar interactions between the unpaired donor electron and the nuclear moments of the 4.8% abundant Si^{29} nuclei encompassed within the region where the electron's wave function is appreciable. Since this region extends over thousands of silicon lattice sites, the resultant hyperfine interaction is governed by a Poisson distribution, which results in an approximately Gaussian line shape. For phosphorus donors,[2] the linewidth is independent of external magnetic field and is approximately equal to 8 MHz, in frequency units.

In the presence of inhomogeneous broadening, a given portion of a resonance line can be saturated by a microwave field at its resonant frequency ν, while the remaining portion of the line is unaffected for long times generally characteristic of spectral diffusion. After such a saturation, the line appears normal except for a narrow "hole" at the saturation frequency, which accounts for the term "hole burning." Hole-related phenomena can be investigated via the ENDOR technique,[1] or by direct observation. The present study is confined to the latter method.

Feher and Gere[2] found auxiliary holes displaced from the microwave frequency ν by $\pm\nu(Si^{29})\pm\frac{1}{2}a_l$, where $\nu(Si^{29})$ is the Zeeman resonance frequency of a Si^{29} nucleus in the external magnetic field and a_l is the hyperfine constant in frequency units describing the interaction between the donor electron and the Si^{29} nucleus at the lth site relative to the donor nucleus. The a_l's have been measured through ENDOR techniques by Feher,[1] and more recently by Hale and Mieher.[4] These satellite holes were observed at a given power level to appear less rapidly than the "direct" hole at ν, and attained smaller amplitude. It was suggested[2] that these satellites were due either to a "discrete spin diffusion" mechanism or to forbidden transitions involving spin flips of both electrons and Si^{29} nuclei. Recently, Bekouri *et al.*[5] have observed similar effects in a number of other materials and have concluded that discrete spin diffusion is not responsible for the effect in their cases.

In the present work, the holes in phosphorus-doped silicon were reexamined and their origins were ascertained. In addition, several new types of satellite holes were observed and interpreted.

II. PHOSPHORUS-DOPED SILICON ENERGY LEVELS AND TRANSITIONS

The magnetic Hamiltonian of a phosphorus donor in silicon at high magnetic fields can be expressed to first order as follows:

$$\mathcal{H}=g_S\mu_BHm_S+hAm_Pm_S-\frac{\mu(P^{31})}{I(P^{31})}Hm_P+\sum_l\left[ha_lm_Sm_l-\frac{\mu(Si^{29})}{I(Si^{29})}Hm_l\right]+\sum_l hb_lm_Sm_l(1-3\cos^2\theta_l)\,, \quad (1)$$

where g_S is the electronic spectroscopic splitting factor, A is the P^{31} hyperfine constant in frequency units, a_l and b_l are, respectively, the contact and dipolar hyperfine constants of the Si^{29} nuclei at the lth site, μ_B, $\mu(P^{31})$, and $\mu(Si^{29})$ are the Bohr magneton and the magnetic moments of the P^{31} and Si^{29} nuclei, respectively, θ_l is the angle between the position vector (with respect to the P^{31} nucleus) of the lth Si^{29} site and the external magnetic field **H**, and m_S, m_P, and m_l are the high-field projections of the electronic, P^{31} and lth site Si^{29} spins, respectively, along **H**.

The allowed transitions correspond to the selection rule $\Delta m_S=\pm1$, $\Delta m_P=\Delta m_l=0$. These occur at the

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[1] G. Feher, Phys. Rev. **114**, 1219 (1959).
[2] G. Feher and E. A. Gere, Phys. Rev. **114**, 1245 (1959).
[3] A. M. Portis, Phys. Rev. **91**, 1071 (1953).
[4] E. B. Hale and R. L. Mieher, Bull. Am. Phys. Soc. **12**, 297 (1967).
[5] P. J. Bekouri, B. G. Berulava, O. G. Khakhanashvili, and T. I. Sanadze, Phys. Letters **24A**, 156 (1967).

frequencies

$$\nu=\nu_e+Am_P+\sum_l\left[a_lm_l+b_lm_l(1-3\cos^2\theta_l)\right],\quad (2)$$

where $\nu_e=g_S\mu_BH/h$, namely, the electron Zeeman frequency in the absence of hyperfine and dipolar interactions. If the third term in Eq. (2) were ignored, the resonance spectrum would consist of two narrow lines at $\nu_e\pm\frac{1}{2}A$, with homogeneous line widths given by the dipolar field [not included in the Hamiltonian of Eq. (1)] of the neighboring donor electrons. The third term, however, gives rise to the inhomogeneous broadening. It is the diagonal term of the electron $-Si^{29}$ magnetic interaction, whose off-diagonal elements are responsible for the transition processes associated with the satellite holes.

In the following discussion of such transitions, it is convenient to assume a particular value for the spin state of the phosphorus donor nucleus, say $m_P=+\frac{1}{2}$. This arbitrary choice is justified since changes in m_P will not be discussed in this section and hence the sole effect of the electron-donor nucleus interaction is to add a constant Am_P to the energy of the transitions considered. Thus in Fig. 1, we represent the energy levels of electrons in three different spin packets (each electron having $m_P=\frac{1}{2}$) and a Si^{29} spin at the lth lattice site. The b_l term of Eq. (2) is neglected in these energy levels and the effects of the other Si^{29} spins are lumped together so that the central resonance frequency (that which would result if the hyperfine interactions with the donor and lth-site Si^{29} nuclear spins were neglected) can be written as

$$\nu_0=\nu_e+\sum_k{}'\,a_km_k,\quad (3)$$

where the prime denotes the omission from the sum of the particular lth lattice site under consideration. The center frequencies of the three spin packets of Fig. 1, ν_0, ν_0', and ν_0'' have been chosen to satisfy the conditions

$$\nu_0'=\nu_0-\nu(Si^{29})+\tfrac{1}{2}a_l$$
and
$$\nu_0''=\nu_0+\nu(Si^{29})+\tfrac{1}{2}a_l.\quad (4)$$

It can be seen from Fig. 1 that in this case the energy difference between states 1 and 2 is equal to that between 1′ and 4′ and 2″ and 3″. Thus if microwave power of frequency $\nu=\nu_0+\frac{1}{2}A+\frac{1}{2}a_l$ is present, it can produce not only the "allowed" transition $2\rightarrow1$ and the resultant "direct" hole at ν, but also the weaker transitions $4'\rightarrow1'$ and $2''\rightarrow3''$ which result in holes at $\nu\pm\nu(Si^{29})\pm\frac{1}{2}a_l$. A nonzero probability for such "forbidden" transitions results from the mixing of states which is a consequence of the dipolar and hyperfine coupling of the electron and the Si^{29} nuclei.

The most prominent source of such mixing is the anisotropic interaction due to the dipolar coupling between the donor electron and the Si^{29} spins. We can select the portion $\mathcal{H}_d'$, out of the usual expansion for this dipolar interaction, which gives the required

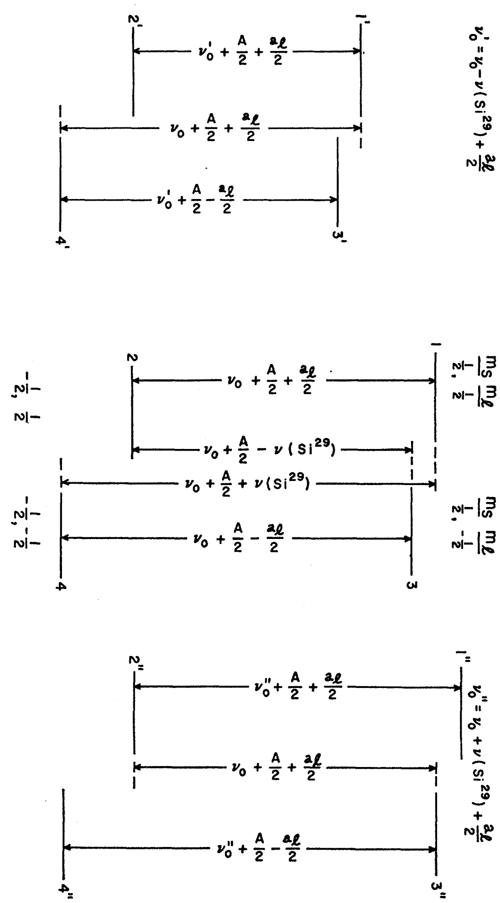

FIG. 1. Energy-level diagram indicating transition frequencies for three spin packets of an isolated phosphorus donor in silicon. The P^{31} nuclear spin quantum number m_P is arbitrarily chosen to be $+\frac{1}{2}$ for these packets, and $|\frac{1}{2}a_l|>\nu(Si^{29})$ is assumed.

mixing:

$$\mathcal{H}_d'=\left[-\tfrac{3}{2}\gamma_e\gamma_l(\hbar^2/r^3)\right]\sin\theta_l\cos\theta_le^{\mp i\phi_l}S_zI_{l,\pm}$$
$$=b_l''\sin\theta_l\cos\theta_le^{\mp i\phi_l}S_zI_{l,\pm},\quad (5)$$

where θ_l and ϕ_l are the angular coordinates of the lth Si^{29} site relative to an axis along $\mathbf{H}$, and γ_e and γ_l are the electronic and Si^{29} gyromagnetic ratio, respectively. We have replaced the factor in brackets by b_l'', which is related[6] to the dipolar hyperfine constant b_l defined and measured by Feher.[1] The first-order expansion of the state functions is then

$$|m_S,m_P,m_l\rangle'=|m_S,m_P,m_l\rangle+\frac{1}{2}\frac{b_l''\sin\theta_l\cos\theta_le^{\mp i\phi_l}}{[E(m_S,m_P,m_l)-E(m_S,m_P,m_l\pm1)]}\times|m_S,m_P,m_l\pm1\rangle,\quad (6)$$

[6] b_l'' is expected to be of the same order of magnitude as b_l. For example, under an assumption of spherical symmetry for the angle ϕ defined by Feher (Ref. 1), $b_l''=-3/2b_l$. Substitution of b_l for b_l'', even in those cases where the b_l term used alone is an oversimplification, should be adequate for the approximate calculation of relative transition probabilities, which is our intent here.

where $E(m_S,m_P,m_l)$, etc., are the energies of the unperturbed states. Because of this mixing, the microwave magnetic field component perpendicular to **H** will induce, in addition to the "allowed" transitions ($\Delta m_S=\pm1$, $\Delta m_P=\Delta m_l=0$) of probability W_0, the forbidden transitions, of the type $1\rightarrow4$, $2\rightarrow3$. The probability for such forbidden transitions W_F is obtained from Eq. (6):

$$W_F[|m_S,m_P,m_l\rangle\rightarrow|m_S+1,\,m_P,\,m_l\pm1\rangle]$$
$$=\tfrac{1}{4}(b_l'')^2\sin^2\theta_l\cos^2\theta_l\bigg\{\frac{1}{[E(m_S,m_P,m_l)-E(m_S,\,m_P,\,m_l\pm1)]^2}+\frac{1}{[E(m_S+1,\,m_P,\,m_l\pm1)-E(m_S+1,\,m_P,\,m_l)]^2}$$
$$+\frac{2\sin2\phi_l}{[E(m_S+1,\,m_P,\,m_l\pm1)-E(m_S+1,\,m_P,\,m_l)][E(m_S,m_P,m_l)-E(m_S,\,m_P,\,m_l\pm1)]}\bigg\}W_0. \quad (7)$$

Another type of mixing is possible due to the terms $\frac{1}{2}a_lS_\pm I_{l,\mp}$ in the donor electron $-Si^{29}$ contact hyperfine interaction. In this case, the first-order mixing of the state functions can be written

$$|m_S,m_P,m_l\rangle'=|m_S,m_P,m_l\rangle+\frac{\langle m_S\pm1,\,m_P,\,m_l\mp1|\frac{1}{2}a_lS_\pm I_{l,\mp}|m_S,m_P,m_l\rangle}{[E(m_S,m_P,m_l)-E(m_S\pm1,\,m_P,\,m_l\mp1)]}\times|m_S\pm1,\,m_P,\,m_l\mp1\rangle. \quad (8)$$

As shown by Jeffries,[7] this mixing allows forbidden transitions of the type $2\rightarrow3$, in which the component of the total spin along the field **H** is conserved. These transitions are thus driven by the microwave magnetic field component parallel to **H**.

The mixing of states through both contact hyperfine and dipolar coupling can also result in discrete spin-diffusion, via cross-relaxation. This can be seen from Fig. 1, where in addition to the mutual electron spin flip-flops which constitute the usual "T_2" or transverse spin-relaxation processes, there is now a finite probability for some electron spin flips to involve a Si^{29} flip also. The fraction of all electron flips which involve changes in nuclear spin should be proportional to the square of the state mixing fraction. Thus a given electron belonging to a packet of central resonant frequency ν_0 (see Fig. 1) could make a transition such as $3\rightarrow2$, which for energy conservation would be accompanied by an allowed transition like $4'\rightarrow3'$ of frequency $\nu_0'+\frac{1}{2}A-\frac{1}{2}a_l=\nu_0+\frac{1}{2}A-\nu(Si^{29})$. It is easily seen that such cross-relaxation processes will also produce "holes" at $[\pm\nu(Si^{29})\pm\frac{1}{2}a_l]$ displacement from the saturation frequency ν, as well as lumps (increased signal intensity) at $\nu\pm a_l$.

III. EXPERIMENTS AND DISCUSSION

A. Experimental

To determine the relative strengths of discrete spin diffusion and forbidden transitions in producing the observed satellite holes, saturation experiments similar to those of Feher and Gere[2] at X band (9.4 GHz) were carried out at both X band and K band (24.1 GHz). The advantage of the experiments at K band derives from the higher nuclear Zeeman frequency, $\nu(Si^{29})$, which equals 7.0 MHz at the magnetic field of about 8.7 kOe corresponding to the K-band electronic resonance. Since in this case $\nu(Si^{29})$ is comparable to the approximate 8 MHz width of the EPR line, it becomes possible to apply microwave power at a frequency *outside* the EPR line while still permitting some of the $[\pm\nu(Si^{29})\pm\frac{1}{2}a_l]$ satellites to fall within the line.

The experiments at both frequencies were carried out at 1.1°K with a standard spectrometer incorporating, for signal-to-noise considerations, field modulation and lock-in detection. Signal observation was confined to the dispersive mode. The procedure consisted of adjusting the magnetic field to the resonant value corresponding to a narrow portion of the EPR spectrum. Microwave radiation of adjustable power level at frequency ν was then applied for a time t, after which the power was readjusted to a fixed "measuring" level prior to field sweeping and signal observation. The magnetic field modulation employed was $\sim$0.25 Oe and the modulation frequency was about 850 Hz.

The samples consisted of both compensated and uncompensated phosphorus-doped silicon in the concentration range $5\times10^{15}/cm^3$ to $4\times10^{16}/cm^3$.

B. Holes at $\nu\pm\nu(Si^{29})$

When the K-band microwave frequency ν was positioned just off either of the two hyperfine resonances associated with isolated phosphorus impurities, a hole appeared on the line at a frequency separation $\nu(Si^{29})$ from ν. The result of such a saturation is shown in Fig. 2, where in this particular case the hole appears at $\nu+\nu(Si^{29})$. A similar hole appears at $\nu-\nu(Si^{29})$ when ν is positioned above the line. The intensity of these $\pm\nu(Si^{29})$ satellites was observed to be essentially independent of the position of the saturating frequency ν relative to the EPR line. This indicates that, at least at the power levels used here ($\sim$0.1 mW), forbidden

[7] C. D. Jeffries, Phys. Rev. **106**, 164 (1957).

transitions dominate any discrete spin-diffusion processes. If this were not the case, one would expect the hole intensity to be proportional to the number of directly saturated spins and hence to be a function of the position of ν relative to the EPR line.

At the powers available at K-band frequencies, only the holes at $\nu\pm\nu(\mathrm{Si}^{29})$ were observed for ν close to the hyperfine resonance frequencies of the isolated impurities. This is consistent with our experiments at X band as well as those of Feher and Gere[2] in which such holes are much more easily produced than those appearing at $\nu\pm\nu(\mathrm{Si}^{29})\pm\frac{1}{2}a_l$, where $a_l\neq 0$. Inasmuch as the energy denominators in Eq. (7) are expected to increase with increasing field, the corresponding forbidden transition probabilities are expected to decrease going from X- to K-band frequencies.

At X band, the holes corresponding to $a_l\neq 0$ were seen at higher microwave powers. If we substitute into Eq. (7) the values obtained[1,4] for a_l and b_l'' (Ref. 6) as well as the energies obtained from Ref. 1, we obtain for the forbidden transition probability involving the (111)Si^{29} site $W_F(111)/W_0\simeq 2.5\times 10^{-3}$ at $H=3.4$ kOe, where we have averaged over the angle variables since our experimental accuracy did not justify angular dependence measurements.

Similarly, for the (400)Si^{29} site we obtain $W_F(400)/W_0\simeq 1.5\times 10^{-3}$. The (440) holes are approximately a factor of 5 more forbidden than the (400) holes. These transition probabilities are roughly in accord with the experimentally determined values of the minimum microwave power required to produce the different holes.

In both our X- and K-band experiments, the very small hyperfine interaction for the (111) site ($a_{111}=0.54$ MHz) made it difficult to resolve satellites at $\nu\pm\nu(\mathrm{Si}^{29})\pm\frac{1}{2}a_{111}$ from the very intense ones appearing at $\nu\pm\nu(\mathrm{Si}^{29})$. However, inspection of the earlier results[2] of similar saturation in As-doped Si in which the (111) hyperfine interaction is much larger ($a_{111}=1.3$ MHz) indicates that the (111) satellites are distinct from and weaker than the holes at $\nu\pm\nu(\mathrm{Si}^{29})$. Inasmuch as the transition probability calculations in As-Si give similar results to those in P-Si, we must conclude that these very intense $\nu\pm\nu(\mathrm{Si}^{29})$ satellites arise from transitions involving sites other than those close to the phosphorus impurity such as are considered in the above calculations. The strength of these transitions could be attributed to the large number of sites with $a_l\simeq 0$. However, on the basis of the existing picture of the wave function, the dipolar coupling b_l is so small for distant sites as to make the total transition probability for such sites, at best, comparable to that of the very close sites. It is possible that at the relatively high concentrations used, distortions of the electronic wave function by the presence of close neighboring donors produce long-range anisotropic hyperfine interactions of the required magnitude. This would be in agreement with an observed decrease in the degree of "forbiddenness"

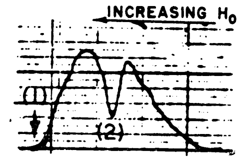

FIG. 2. Low-frequency EPR hyperfine line of phosphorus donor in silicon after a 0-sec application of $\sim$1-mW microwave power at $\sim$24 GHz. $T=1.1$°K. The magnetic field setting corresponds to a donor electron resonance frequency which, in the absence of Si^{29} interactions, would occur at point (1). The hole at (2) is displaced $\nu(\mathrm{Si}^{29})$, or 7.0 MHz, below (1). Amplitude of the hole at (2) is independent of the position (1).

of such satellite producing transitions with increasing concentration, as well as with other evidence for such distortions (see Sec. III).

It should be emphasized here that identification of the satellite holes with forbidden transitions at moderate power levels does not preclude the possibility of discrete spin diffusion causing holes at very low powers where the forbidden transition probability becomes negligible. However, no conclusive evidence of such processes was found.

C. Other Holes

When a more complete study of the discrete saturation spectrum in the region of the EPR lines was made at K-band frequencies, two additional phenomena were observed. A hole appeared on the hyperfine lines when the saturation frequency ν was positioned on the high frequency side of either line. This hole appeared at resonant frequency $\nu-\nu(\mathrm{P}^{31})$; at 8.7 kOe, $\nu(\mathrm{P}^{31})$ is 16.75 MHz. There is no forbidden transition corresponding to such a frequency $[\nu=\nu_0\pm\frac{1}{2}A+\nu(\mathrm{P}^{31})]$ in the energy-level diagram of an isolated donor. We believe these holes are due to transitions in close exchange-coupled pairs of donor atoms which act as an $S=1$ electronic spin system.[8,9] The energy levels for such a pair are represented in Fig. 3, where the transitions $1a$, b; $2a$, b; $3a$, b correspond, respectively, to the three pair lines at $\nu_0\pm\frac{1}{2}A$ and ν_0 and where the symbols $T_{\pm 1,0}$, $t_{\pm 1,0}$, and s denote the z substates for the triplet $S=1$ electronic pair spin, the triplet $I=1$ nuclear pair spin, and the singlet $I=0$ nuclear pair spin, respectively. From this diagram, it can be seen that transition ($4b$) will produce a hole, as observed, on the high frequency ($\nu_0+\frac{1}{2}A$) line when $\nu=\nu_0+\frac{1}{2}A+\nu(\mathrm{P}^{31})$, while transition ($4a$) similarly affects the low frequency ($\nu_0-\frac{1}{2}A$) line when $\nu=\nu_0-\frac{1}{2}A+\nu(\mathrm{P}^{31})$. Holes at $\nu+\nu(\mathrm{P}^{31})$ do not appear when the frequency ν of the applied microwave power is positioned on the low-frequency side of either line. Thus, we conclude that the observed holes arise from transitions of the scalar hyperfine mixed type which are driven by the unavoidably remanent component of the microwave magnetic field parallel to $\mathbf{H}$. If the mixing were due to dipolar interaction, the transi-

[8] C. P. Slichter, Phys. Rev. **99**, 479 (1955).
[9] D. Jerome and J. M. Winter, Phys. Rev. **134**, A1001 (1964).

tions (5*a*) and (5*b*) (Fig. 3) would be as probable as the (4*a*) and (4*b*) transitions, producing holes at $\nu+\nu(P^{31})$. This dominance of the scalar hyperfine mixing is not unexpected since the tetrahedral symmetry of the donor wavefunction results in a zero dipolar magnetic field at an isolated donor nucleus. The breakdown of this symmetry by the presence of a nearby donor allows a nonzero field and a resultant dipolar mixing of states. It is estimated later on that the dipolar interaction is small ($\sim$1 MHz) in comparison to the hyperfine interaction A (118 MHz).

These hole producing transitions occur only among the small fraction of spins ($\sim$5% for a sample with donor concentration of $\sim10^{16}/cm^3$) which act as $S=1$ pairs. Since transitions 1*a*, *b* and 2*a*, *b* (Fig. 3) of the pair coincide with the two resonances of the isolated donors, the holes in the pair donors are transferred via cross-relaxation to the isolated donor resonances. However, in the over-all process, the population of the (T_0,t_0) state of the pair is driven away from its equilibrium value. Since the pairs are much less numerous than the isolated donors, relaxation of the (T_0,t_0) state with respect to $(T_0, t_{\pm1})$ must occur for significant sized holes to appear in the observed isolated donor resonances. This relaxation might occur via cross-relaxation with forbidden transitions ($\Delta m_S=\pm1$, $\Delta m_P=\mp1$) of isolated donors, or by other nuclear spin relaxation mechanisms. An observed growth of the intensity of these holes with increasing duration of applied

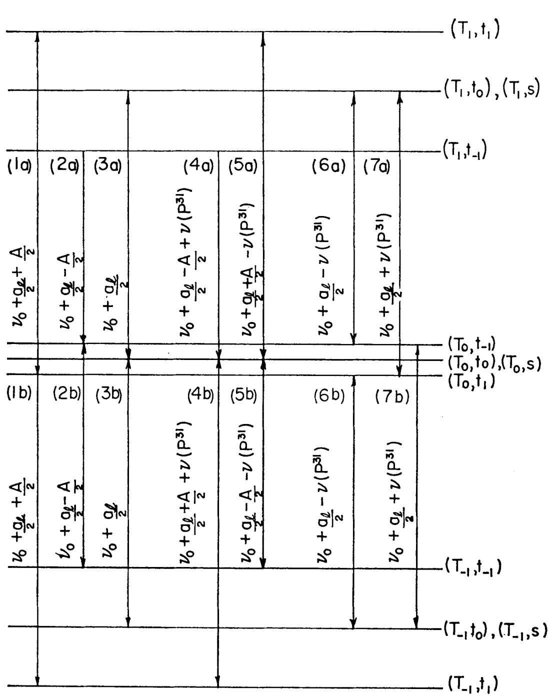

FIG. 3. Energy-level diagram indicating transition frequencies for a spin packet of the electronic triplet state of an exchange coupled pair of phosphorus impurities in Si.

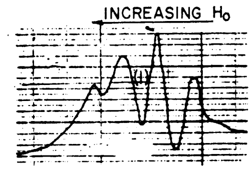

FIG. 4. Low-frequency EPR hyperfine line of phosphorus donor in silicon after a 10-sec application of $\sim$10 mW microwave power at $\sim$9 GHz. $T=1.1$°K. The magnetic field setting corresponds to a donor electron resonance frequency which, in the absence of Si^{29} interactions, would occur at a frequency of $[\frac{1}{2}A+\nu(P^{31})]$, or 65.5 MHz, above point (1).

microwave power for times up to 4 min on a $4\times10^{16}/cm^3$-doped sample is attributed both to the diluteness of the active electronic pair states and the bottleneck associated with this nuclear relaxation rate. Effects related to growth of holes under conditions of nuclear polarization are discussed in Sec. III D.

K-band microwave irradiation at frequencies just above the central pair line at ν_0 also produced a hole on each hyperfine line at separations $+[\frac{1}{2}A-\nu(P^{31})]$ and $-[\frac{1}{2}A+\nu(P^{31})]$ from the applied microwave frequency ν. These holes correspond to the transitions (7*a*, *b*) in Fig. 3, as well as to transitions in the isolated donor analogous to $2\rightarrow3$ (Fig. 1) involving a donor electron spin flip plus a P^{31} (not Si^{29}) nuclear spin flip. As in the previous case, the absence of holes at $\{\nu+[\frac{1}{2}A+\nu(P^{31})]\}$ and $\{\nu-[\frac{1}{2}A-\nu(P^{31})]\}$ which would correspond to (6*a*, *b*) (Fig. 3) and the analog of $(1\rightarrow4)$ in Fig. 1, indicates that these hole producing transitions are not due to dipolar coupling and must be of the scalar hyperfine mixed type.

At *X*-band frequencies where $H=3.4$ kOe and greater microwave power is available, not only holes corresponding to the transitions (7*a*, *b*) but also a weaker set of holes apparently corresponding to transitions (6*a*, *b*) are obtained. Furthermore, the resulting disturbance on the EPR line is no longer interpretable as a single hole but is a more complicated structure as shown in Fig. 4. In general, this disturbance suggests a central hole at the position predicted by the transitions (6*a*, *b*; 7*a*, *b*), surrounded by satellites at $\pm\nu(Si^{29})$ separation, although this is difficult to ascertain since the structure is distorted by the field modulation and sweep conditions, as has been discussed by Weger.[10] Since the principal holes observed here occur at $\nu\pm\frac{1}{2}A\pm\nu(P^{31})$, and therefore result from forbidden transitions on either side of ν_0, we must ascribe at least part of their origin to a dipolar mixing of states. As discussed previously, this mixing arises only in donors having a sufficiently close neighboring donor to destroy the tetrahedral symmetry and produce a nonzero magnetic dipolar field at the donor nucleus. These transitions are driven by the usual perpendicular (to **H**) component of the microwave magnetic field, and have a transition probability analogous to that given by Eq. (7). Since the

[10] M. Weger, Bell System Tech. J. **39**, 1013 (1960).

minimum power for these dipolar mixed transitions exceeds that required for "allowed" hole burning by $\sim 10^9$, we can conclude from the forbidden transition probability expression that the electron $-P^{31}$ dipolar interaction energy is ~ 1MHz. These dipolar mixed holes were not seen in our K-band experiments presumably because of the lower power available in that frequency region and the ν_0^{-2} dependence of the forbidden transition probability. The holes at $\nu + A/2 - \nu(P^{31})$ and $\nu - \frac{1}{2}A - \nu(P^{31})$ arise from both the above dipolar mixed and the hyperfine mixed forbidden transitions in donor pairs. Indeed, these holes appear at lower microwave power than those due solely to the dipolar mixing, because the hyperfine interaction is much stronger than the dipolar interaction.

The structure surrounding these holes, suggested to be $\pm\nu(\mathrm{Si}^{29})$ satellites, could be ascribed to doubly forbidden P^{31} and Si^{29} flips, with the unexpected apparent strength related to the unusually strong $\nu \pm \nu(\mathrm{Si}^{29})$ holes discussed in Sec. III B.

D. Nuclear Polarization Effects

A characteristic of the phenomena described here is the fading, or the decrease in amplitude, of the holes under certain conditions. One of these conditions is when the microwave radiation is applied to a narrow portion of a resonance line for a time t such that T_1 (electronic) $< t < T_1$ (nuclear). If we refer to Fig. 1 and consider the transition $4' \rightarrow 1'$ involving an electron and Si^{29} site for the case where $a_l = 0$, it is apparent that in the absence of any electronic spin-lattice relaxation, a hole occurs at $\nu - \nu(\mathrm{Si}^{29})$. However, when t is within the time range specified above, the state populations are such that $n_4' = n_1'$, and n_4'/n_3' and n_2'/n_1' approach the appropriate Boltzmann factor. Under these conditions, it is evident that the observed signal from the packet at $\nu - \nu(\mathrm{Si}^{29})$ is almost equal to its value in the absence of saturation. Fading of this type was observed for the holes arising from microwave irradiation near the central line also. For example, the central line holes disappeared for saturation times greater than about 8 min in a weakly compensated sample (1.7×10^{16} P/cm^3, 0.35×10^{16} Al/cm^3) whose electronic T_1 was about 5 min. In these cases, it is believed that the large difference in electronic and nuclear relaxation times rather than spectral diffusion is responsible for the fading since the holes are continuously being generated by the applied microwave power.

Another type of hole fading occurs after a repeated series of discrete saturations and subsequent spin-lattice relaxations. The amplitude of the holes produced was found to decrease steadily with the number of such saturation-relaxation cycles, even though the microwave irradiation time $t \ll T_1$ (electronic), in contrast to the case described above. This phenomenon is attributed to a build-up of a sizable Si^{29} nuclear polarization through successive forbidden transition saturations. Under such conditions, allowing a time between successive application of microwaves which exceeds T_1 (electronic) but is less than T_1 (nuclear), the population difference between two levels (e.g., n_4' and n_1' of Fig. 1) involved in the forbidden transition is reduced by at least a factor of 2 for a maximally polarized nuclear spin system attainable under this type of forbidden transition process. Thus, less power is absorbed through forbidden transitions and the holes produced are of smaller amplitude.

The "fading" phenomena and the general time dependence of the various types of holes may yield useful information concerning the nuclear relaxation processes of the centers involved. This might be particularly useful in the case of holes arising solely from close pairs, in that the relaxation processes and other properties of such pairs could be studied, to a certain degree, independently of those of the more numerous isolated spins.