PHYSICAL REVIEW VOLUME 114, NUMBER 5 JUNE 1, 1959

Electron Spin Resonance Experiments on Donors in Silicon. II. Electron Spin Relaxation Effects

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(Received December 29, 1958)

The different relaxation processes that connect the four energy levels in phosphorus doped silicon have been investigated experimentally. The relaxation time T_s ($\Delta m_s=\pm 1$, $\Delta m_I=0$) was found to be independent of phosphorus concentration below $\sim 10^{16}$ P/cm^3. Its value at 3200 oersteds and 1.25°K was $\sim 3\times 10^{+3}$ seconds and varied as $1/T$ for $1.3°\text{K}<T<2°\text{K}$ and as $1/T^7$ for $2.5°\text{K}<T<4.2°\text{K}$. The magnetic field dependence in the $1/T$ region suggests a direct phonon process. In the $1/T^7$ region T_s was independent of the magnetic field between 3000 and 8000 oersteds. Above a concentration of 10^{16} P/cm^3 T_s varied rapidly with donor concentration, dropping to 10^{-4} seconds at 3×10^{17} P/cm^3. In this concentration dependent region T_s was independent of the magnetic field but depended on the number of acceptors present. None of the T_s mechanisms can at present be accounted for by the theories of Pines, Bardeen, and Slichter, and Abrahams. The relaxation time T_x ($\Delta m_s=\pm 1$, $\Delta m_I=\mp 1$) was $\sim$30 hours at 3000 oersteds and $\sim$5 hours at 8000 oersteds in fair agreement with the theory of PBS. The relaxation time T_N ($\Delta m_I=\pm 1$, $\Delta m_s=0$) at 1.25°K exceeded 10 hours.

The effect of light was investigated with a monochromator for $0.5\text{ ev}<h\nu<2\text{ ev}$. The number of carriers introduced by light was obtained from the Hall coefficient. In a sample with 7×10^{15} P/cm^3, T_s was reduced to 25 seconds by 2×10^6 electrons/cm^3. Under the same conditions the spin-spin time T_{ss} was reduced to 1 second. The bottleneck in the T_s-spin exchange mechanism suggested by PBS is the spin-lattice relaxation time of the free carriers. This bottleneck is absent in a double spin exchange mechanism suggested by Anderson and is responsible for the observed T_{ss} process.

A resonant spin-spin interaction was observed between the electron bound to an iron impurity and the phosphorus donor electron when the magnetic field at which the two resonance lines overlap was traversed. The application of this "mixing" effect to a nuclear polarization scheme is discussed. A complete mixing of two levels was also observed in phosphorus doped silicon at a magnetic field of 40 oersteds.

A spin diffusion process capable of transmitting a spin excitation to different parts of the resonance line was observed in arsenic doped silicon. This process proceeds in discrete steps with frequencies determined by the different Larmor frequencies of the Si^{29} nuclei situated at various lattice sites relative to the donor atom.

I. INTRODUCTION

THE first relaxation time measurements on donors in silicon were performed by Honig.[1] He found, what seemed then, unusually long relaxation times (tens of seconds at 4°K) and concluded that they were associated with a nuclear relaxation process. It was subsequently shown by him[2] and others[3,4] that one is dealing with long electron spin relaxation times. The work to be reported in this paper is essentially an outgrowth of these early experiments. In continuing them we were stimulated by the theoretical work of Pines, Bardeen, and Slichter,[5] and Abrahams,[6] and by the hope that with such a well understood system as donors in silicon[7] progress could be made towards a better understanding of electron spin relaxation processes.

After a few preliminary experiments it became evident that the problem was more complicated than had been originally anticipated. Different relaxation mechanisms were found to be effective at different temperatures, impurity concentrations, magnetic fields and numbers of free carriers. For this reason it was decided to concentrate mainly on the simplest impurity center namely phosphorus which has a nuclear spin of $\frac{1}{2}$. Even with this restriction imposed, the present work does not claim to be an exhaustive treatment of this very large subject. It is intended to point out several of the mechanisms that have been isolated, to give representative values of the observed relaxation times and to show how they are influenced by different external parameters. Only two of the observed mechanisms can at present be accounted for by the theory of PBS.[5] One involves a simultaneous electron-nuclear spin flip (T_x), and the other a spin exchange mechanism that occurs when carriers are introduced by light.

In addition to the spin lattice relaxation times, several types of spin-spin interactions were observed. One results from the interaction between an iron impurity and a phosphorus hyperfine line and provides an effective nuclear polarization scheme. Another type of spin interaction that involves the flipping of Si^{29} nuclei was observed. It results in a "discrete" spin diffusion process which connects spin packets within the resonance line.

Besides the fundamental interest in the relaxation mechanisms of the donor electrons there are several "practical" consequences which hinge on the presence or absence of specific relaxation processes. Among these are several nuclear polarization schemes,[3,5,8,9] the ability

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[1] A. Honig, Phys. Rev. **96**, 234 (1954).

[2] A. Honig and J. Combrisson, Phys. Rev. **102**, 917 (1956).

[3] A. Abragam and J. Combrisson, Compt. rend. **243**, 576 (1956).

[4] Feher, Fletcher, and Gere, Phys. Rev. **100**, 1784 (1955).

[5] Pines, Bardeen, and Slichter, Phys. Rev. **106**, 489 (1957).

[6] E. Abrahams, Phys. Rev. **107**, 491 (1957).

[7] For a review article on this subject see W. Kohn—*Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957), Vol. 5.

[8] G. Feher, Phys. Rev. **103**, 500 (1956).

[9] F. M. Pipkin and J. W. Culvahouse, Phys. Rev. **109**, 1423 (1958).

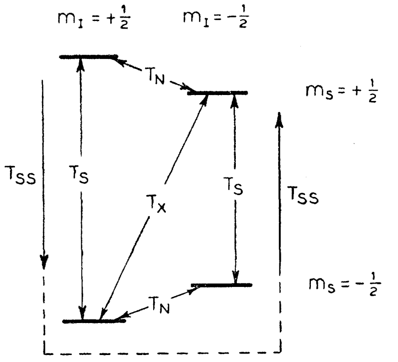

FIG. 1. Various relaxation processes indicated by arrows that connect the levels in a system with $I=\frac{1}{2}$, $S=\frac{1}{2}$. This corresponds to phosphorus doped silicon. The processes may be distinguished experimentally by disturbing the equilibrium population in different ways. The $(+\frac{1}{2}, +\frac{1}{2}) \leftrightarrow (-\frac{1}{2}, -\frac{1}{2})$ transition is forbidden and is therefore not indicated.

to apply the ENDOR technique to these centers (see Part I[10]) and their applications to masers.[11,12]

II. THE DIFFERENT RELAXATION PROCESS

Let us consider the simple system of an electron with $S=\frac{1}{2}$ coupled to a nucleus with $I=\frac{1}{2}$. This corresponds to the phosphorus donor and because of its simplicity was the center that was investigated in most detail. The energy levels of such a system are shown in Fig. 1 in which the various possible relaxation processes that are operative between the different levels are indicated by the arrows T_x, T_s, T_{ss}, T_N. (We shall use these symbols to identify the relaxation processes as well as the relaxation times which characterize them.) In any relaxation time measurement one has to disturb the thermal equilibrium that exists between two levels. The relaxation times are then obtained by either measuring the microwave power required to cause a deviation from the equilibrium or else by observing the rate at which the spin system returns to equilibrium after it has been disturbed. A convenient "disturbance" is accomplished by either completely saturating the spin system or reversing its direction by an adiabatic fast passage.[13] The latter approach is particularly advantageous when one deals with relatively long relaxation times and was used in all our experiments except when dealing with relaxation times below one second. The present system, as illustrated in Fig. 1, is complicated by the fact that we are dealing with a variety of relaxation processes. One has to devise, therefore, methods of disturbing the equilibrium population in *different* ways in order to disentangle the different processes. We will not enter at present into the details of the experimental procedures used to accomplish this but will present later several examples to illustrate the principles involved. In essence we measure the instantaneous population difference $A(t)$ between the "disturbed" levels by performing a paramagnetic resonance experiment on the donor electron. The relaxation time T is then obtained from an expression of the form $A(t) = A_0[1-\exp(-t/T)]$ where A_0 is the equilibrium population between the two levels under scrutiny. In those cases in which one observes a deviation from this exponential form the relaxation time is arbitrarily defined as the time taken for the magnetization to build up to $(1-1/e)$ of its final value. It should be noted that each process, designated by an arrow, may itself represent several different physical mechanisms that are capable of bringing the two corresponding levels into thermal equilibrium. Once the different processes have been separated experimentally, one is left with the more usual problem of trying to understand the relaxation mechanism (or mechanisms) responsible for a particular process.

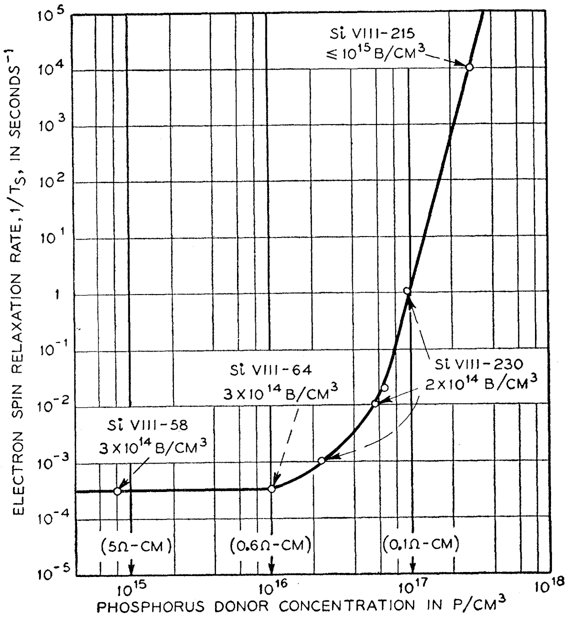

FIG. 2. Electron spin relaxation rate *vs* donor concentration in phosphorus doped silicon ($T=1.25$°K), $H\simeq3200$ oersteds). The donor and acceptor concentrations were obtained by measuring the Hall coefficient *vs* temperature. Sample VIII-215 exhibited impurity band conduction which prevented the accurate determination of the boron concentration.

III. CONCENTRATION DEPENDENCE OF T_s

When the silicon sample is placed into a magnetic field, the two spin-lattice[14] processes that can build up

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[10] G. Feher, preceding paper [Phys. Rev. **114**, 1219 (1959)].

[11] Combrisson, Honig, and Townes, Compt. rend. **242**, 2451 (1956).

[12] Feher, Gordon, Buehler, Gere, and Thurmond, Phys. Rev. **109**, 221 (1958).

[13] F. Bloch, Phys. Rev. **70**, 460 (1956).

[14] Strictly speaking one is really measuring spin-bath relaxation times, but because of the low concentrations of the paramagnetic centers used throughout our experiments the lattice-bath time does not enter. At higher concentration this need not be the case [see J. H. Van Vleck, Phys. Rev. **59**, 724 (1941); Gorter, Van der Marel, Bolger, Physica **21**, 103 (1955); Giordmaine, Alsop, Nash, and Townes, Phys. Rev. **109**, 302 (1958)].

an appreciable magnetization are T_s and T_x. In phosphorus doped silicon T_s was found to be predominant in all cases. A description of the experimental procedure used to distinguish between T_s and T_x is postponed till the end of the next section where the T_x mechanism is discussed. The values of T_s vary over a wide range and depend very strongly on the donor concentration.[4,15] Figure 2 illustrates the concentration dependence of T_s in phosphorus doped silicon at 1.25°K and $\sim$9000 Mc/sec. From this plot it is apparent that we are dealing with at least two distinct mechanisms. Below $\sim 10^{16}$ P/cm^3 a concentration independent and above $\sim 10^{16}$ P/cm^3 a concentration dependent T_s mechanism predominates. Accordingly we have divided our discussion into two sections, although it should be noted that this division is somewhat arbitrary and applies strictly only to T_s at 1.25°K and 3200 oersteds, at which the data of Fig. 2 were taken. The results of Fig. 2 were obtained on samples cut from single (pulled) crystals.* The donor (phosphorus) and acceptor (boron) concentrations were determined by measuring the Hall coefficient between room temperature and 20°K.[16] For this purpose standard six arm bridges[17] were cut from the same samples on which the relaxation time measurements were made.

The sample with 3×10^{17} P/cm^3 had a carrier concentration at 20°K of $\sim 10^{13}$ electrons/cm^3. This is approximately four orders of magnitude larger than one would expect for noninteracting centers. This behavior as well as the low mobility at 20°K of 50 cm^2/v sec indicates the presence of impurity band conduction.[16] The resistivity of this sample at 4°K was $\sim 10^7$ ohm-cm. The boron concentration in this sample is believed to be below 10^{15} B/cm^3, but because of the impurity band conduction process could not be measured accurately.

In measuring the long relaxation times encountered in this work great care had to be taken to prevent light and also room temperature radiation from reaching the sample. (See Sec. VI.) This was accomplished by wrapping the glass cavity in several layers of aluminum foil with carbon paper interposed. The inside of the waveguide leading to the cavity was filled with styrofoam and at one place a 1 mm glass window was inserted in the guide to absorb the room temperature radiation.

IV. RELAXATION TIMES IN THE CONCENTRATION INDEPENDENT REGION

A. The T_s Process

The experiments were performed on sample VIII-64 which had a donor concentration of 7×10^{15} P/cm^3 (see Fig. 2). The temperature dependence of T_s is illustrated in Fig. 3. In the temperature region between 1.25°K and 2°K the relaxation time is approximately inversely proportional to the first power of temperature. This dependence was also found by Honig and Stupp[18] and is consistent with a direct phonon process. Above 2°K the temperature dependence becomes more pronounced and between 3°K and 4.2°K T_s becomes inversely proportional to the seventh power of the temperature indicating that a new mechanism predominates. The strong dependence of T_s on temperature above 3°K suggests that we are dealing with a Raman type mechanism.[19]

It should be noted that the T^7 fit extends only over a narrow temperature region. As a consequence the experimental data can also be fitted fairly well with an exponential temperature dependence of the form $T_s \sim \exp(\Delta E/T)$ where $\Delta E \simeq 25$°K. Such an activation energy could, for instance, arise from the first excited donor state.[7] Since the position of this excited state is expected to depend on the chemical impurity the experiments were repeated on an arsenic doped silicon sample with 10^{16} As/cm^3. The relaxation rate in this sample at 4.2°K was found to be $1/T_s = 2.5\times10^{-2}$ sec^{-1} and again obeyed a T^7 law between $3°\mathrm{K} < T < 4.2°\mathrm{K}$.

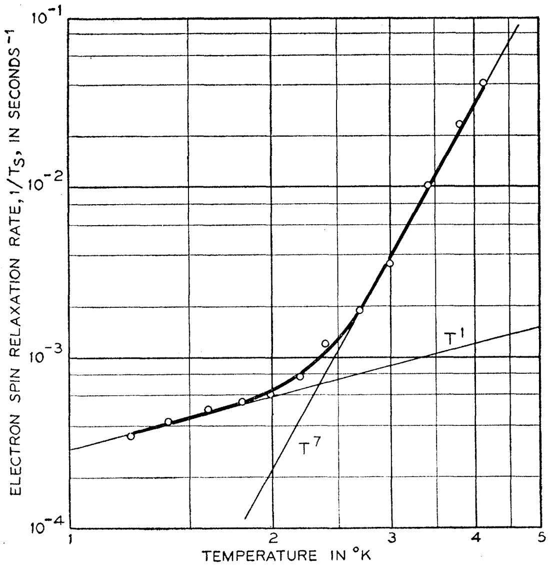

FIG. 3. Electron spin relaxation rate *vs* temperature in phosphorus doped silicon (7×10^{15} P/cm^3, $H\simeq3200$ oersteds, Sample: Si VIII-64). The break in the curve is presumably due to a transition from a direct phonon to a Raman type process.

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[15] G. Feher and E. A. Gere, Bull. Am. Phys. Soc. Ser. II, **3**, 415 (1958).

* *Note added in proof.*—An additional measurement was made on a zone refined crystal with 3×10^{15} P/cm^3. The relaxation rate at 1.25°K and 3200 oersteds was found to be $\sim 2\times10^{-4}$ sec^{-1}. When dealing with such extremely slow relaxation rates the presence of paramagnetic impurities which escape detection may be of importance. In view of the small number of measurements made in this concentration region, the *strict* concentration independence should be therefore taken with some reservations. Honig and Stupp [Bull. Am. Phys. Soc. Ser. II, 4, 261 (1959)] report for this region a concentration dependent relaxation mechanism superimposed on a concentration independent mechanism.

[16] F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).

[17] P. Debye and E. Conwell, Phys. Rev. **93**, 693 (1954).

[18] A. Honig and E. Stupp, Phys. Rev. Lett. **1**, 275 (1958).

[19] I. Waller, Z. Physik **79**, 370 (1932); R. De L. Kroenig, Physica **6**, 33 (1939); J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

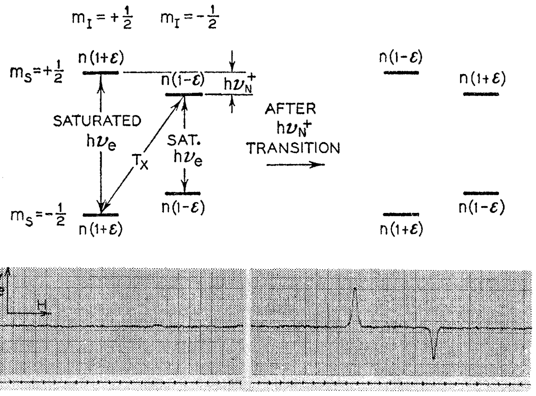

FIG. 4. Illustration of the method used to determine T_x in the presence of a much shorter T_s in phosphorus doped silicon (7×10^{15} P/cm³, $T=1.25$°K, $H\simeq3200$ oersteds, Sample: Si VIII-64). From the amplitudes of the lines and the time interval during which T_x was operative one obtains at 3200 oersteds a value of $T_x\cong30$ hours. Note that the saturation procedure results in a normal Overhauser effect and gives rise to the predicted nuclear polarization.

T_s was also measured at 20°K by the microwave saturation method.[20] $d\chi''/dH$ was found to drop to half its unsaturated value for a microwave field of $H_1=0.25$ oersteds. In order to obtain the relaxation time T_s one has to know the functional dependence of the microwave signal $d\chi''/dH$ on the saturation parameter $(1/4)(H_1)^2T_sT_2$. This dependence is well known for both homogeneously[20] and inhomogeneously[21] broadened lines. The saturation behavior of the phosphorus line at 20°K showed that it was inhomogeneously broadened (e.g., the line width did not increase, for large values of the saturation parameter) and had a relaxation rate of $1/T_s\simeq10^{+6}$ sec^{-1}. T_2 in the expression for the saturation parameter is obtained from the width of a single spin packet which in our case was assumed to be equal to the microwave field of 0.25 oersteds.[22] If one extrapolates the T^7 dependence from the 4.2°K data one obtains for the relaxation rate a value of $2\times10^{+3}$ sec^{-1}. The fact that one observes a much faster rate suggests that at 20°K another mechanism has taken over. It would be instructive to extend the temperature region above 4°K in order to establish the T^7 law more firmly and also find the transition to the other temperature dependence.

The magnetic field dependence was reported by Honig and Stupp.[18] They found that $1/T_s$ varied as H^4 above 8000 oersteds. Below this field they observed a slower variation indicating a contribution from a field independent relaxation mechanism. All of our experiments were performed at fields below 8000 oersteds and are in general agreement with their observations. At a temperature of 3.5°K at which the T^7 process predominates, T_s was found to be independent of the magnetic field (3000 oersteds$<H<$8000 oersteds). At the highest fields a small correction due to the contribution of the direct phonon process was applied.

The experimental procedure used to investigate the magnetic field dependence was as follows: After saturating the resonance lines at ~3200 oersteds, the magnetic field was set to any desired value and after different time intervals returned to the monitoring field of 3200 oersteds at which all our measurements were performed. Because of the long relaxation times involved one can safely neglect small changes in the magnetization that occur during the time interval in which the magnetic field is being changed and the resonance lines are being monitored.

A theoretical estimate of T_s was made by PBS[5] who assumed a modulation of the spin orbit coupling by lattice vibrations. At 9000 Mc/sec and 1.2°K they obtain a value of $T_s\geq4.5\times10^3$ sec which, as they point out, is an enormous overestimate of the effectiveness of the mechanism. Abrahams[6] reinvestigated the same mechanism taking into account certain cancellations in the matrix element that were neglected by PBS.[5] He arrives at a value of $T_s\sim10^9$ sec which, of course, could never be observed. Abrahams also investigated a Raman type process in which a phonon is scattered from one state into another while the electron spin flips. His result for this type of mechanism is $T_s\sim10^{15}T^{-13}$. Both the absolute value of the relaxation time and its temperature dependence are at variance with the observed relaxation times above 2.5°K, where one presumably might be dealing with a Raman type process. It must be concluded therefore that the origin of both T_s mechanisms remains at present unexplained.

B. The T_x Process

We proceed now to a discussion of the T_x process which involves a simultaneous electron-nuclear spin flip ($\Delta m_I=\pm1$, $\Delta m_s=\mp1$). This relaxation process is of importance in several nuclear alignment schemes and has been the subject of previous investigations.[3,5,23,24] In order to find experimentally the value of T_x in cases in which $T_x\gg T_s$, one has to eliminate first the short circuiting effect of T_s. This is conveniently done by saturating (i.e., equalizing populations) the two electronic transitions as indicated for phosphorus doped silicon in Fig. 4. After T_x has had time to establish an appreciable Boltzmann factor between the $(+\frac{1}{2},-\frac{1}{2})$ and $(-\frac{1}{2},+\frac{1}{2})$ levels,[25] the nuclear $h\nu_N^+$ (see Fig. 3) transition is induced by an adiabatic fast passage.[13]

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[20] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

[21] A. M. Portis, Phys. Rev. **91**, 1071 (1953).

[22] Note that for a homogeneously broadened line T_2 corresponds to the entire width of the line. This would result in a relaxation rate of $1/T_s\simeq10^{+5}$ sec^{-1}. In the presence of spin diffusion the relaxation rate assumes a value between the two extrema.

[23] J. W. Culvahouse and F. M. Pipkin, Phys. Rev. **109**, 319 (1958).

[24] G. Feher, *Proceedings of the Kamerlingh-Onnes Memorial Conference on Low-Temperature Physics, Leiden, Holland, 1958* [Suppl. Physica **24**, 80 (1958)].

[25] We use the (m_s,m_I) notation to identify the levels. Note that the transition between the $(+\frac{1}{2},+\frac{1}{2})$ and $(-\frac{1}{2},-\frac{1}{2})$ levels involves a $\Delta m=2$ change and is therefore forbidden.

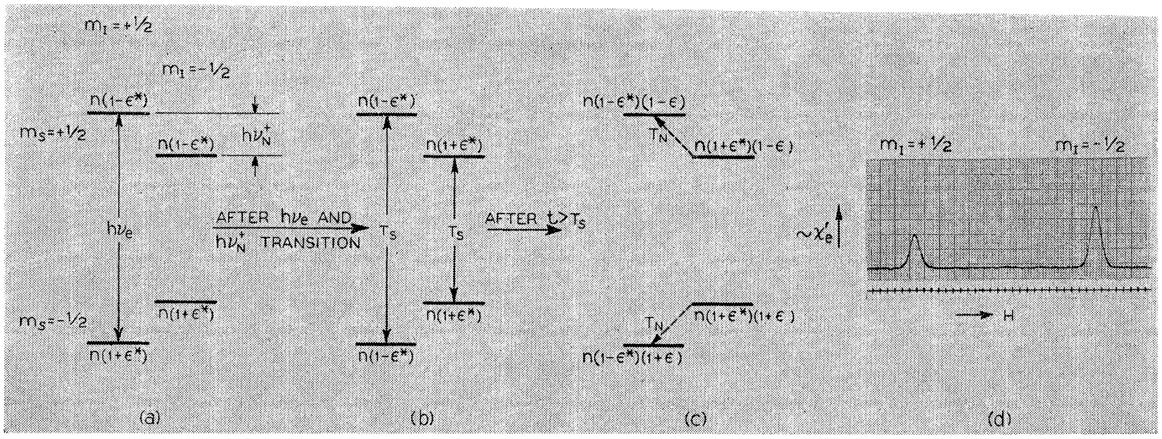

FIG. 5. Illustration of the method used to determine T_N in the presence of a shorter T_s (but longer T_x) in phosphorus doped silicon; (a) The magnetization is brought to thermal equilibrium at a high field. The corresponding Boltzmann factor is $2\epsilon^*$; (b) After a double adiabatic fast passage the m_I levels are preferentially occupied; (c) The populations after $t>T_s$; (d) The experimental trace from phosphorus doped silicon (7×10^{15} P/cm^3, $T=1.25$°K, $H=3200$ oersteds). The expected ratio of amplitudes is $\sim(1+\epsilon^*)/(1-\epsilon^*)$. From the rate at which the amplitudes of the two lines tend to equalize T_N may be obtained. Note the large nuclear polarization that is obtained during this procedure.

This exchanges the population between the two nuclear levels, and results in a population distribution as indicated in Fig. 4. If one sweeps now the magnetic field, one resonance line corresponding to an emission and one to an absorption is obtained. By varying the time interval during which the T_x transition is allowed to operate one finds a value of $T_x\simeq30$ hours for $H=3200$ oersteds, $T=1.25$°K and $T_x\simeq5$ hours for $H\simeq8000$ oersteds, $T=1.25$°K. The 30 hours relaxation time was calculated from the observed amplitude after a 6 hour saturation time and from the known equilibrium amplitude at 3200 oersteds. The saturation is accomplished by continuously sweeping through both resonance lines, but turning off the microwave power while the magnetic field sweeps through the value corresponding to the T_x transition. Note that the saturation procedure results in a normal Overhauser[26,5] effect and gives rise to the predicted nuclear polarization.

PBS[5] have investigated theoretically the relaxation mechanism that arises from the modulation of the hyperfine interaction by the lattice vibrations. They predict that T_x should be inversely proportioned to H^2, and for phosphorus doped silicon should have a value of $T_x\simeq10$ hours ($H=3000$ oersteds, $T=1.25$°K). This is in fair agreement with the experimental values and for low donor concentrations leaves little doubt as to the mechanism involved. At high phosphorus concentrations a much shorter T_x process was found,[27] but so far has not been investigated quantitatively.

For the As and Sb donors T_x was found to be shorter than T_s. Since the nuclear spins of these donors are larger than $\frac{1}{2}$, T_x may be determined from the time dependence of the amplitudes of the lines corresponding to different m_I values. These procedures as well as the experimental results on *As* are discussed in detail by Abragam[3] and Culvahouse and Pipkin.[23]

C. The T_N Process

The T_N relaxation process was measured at 1.25°K and 3200 oersteds on sample VIII-64 containing 7×10^{15} P/cm^3. The experimental procedure as illustrated in Fig. 5 was to populate preferentially the two $m_I=-\frac{1}{2}$ levels. This was accomplished by equilibrating the magnetization at a high field and subsequently performing two adiabatic fast passages.[8] The first involves the electronic transition $h\nu_e$ and the second the nuclear transition $h\nu_N{}^+$. The level populations after the two transitions are indicated in Fig. 5(b), where ϵ^* denotes the electronic Boltzman factor corresponding to the high equilibration field (in our case $\sim$8000 oersteds). After T_s has had time to establish a Boltzman factor corresponding to the monitoring field of 3200 oersteds, one expects the ratio of the amplitudes of the two resonance lines to be $(1+\epsilon^*)/(1-\epsilon^*)$. This is illustrated in Fig. 5(c) and the corresponding experimental trace in Fig. 5(d). The two relaxation processes that can equalize the amplitudes of the two lines are T_x and T_N. Since T_x has been found previously we were able to establish that $T_N>10$ hours. This relaxation process is of importance in connection with nuclear orientation schemes since it represents the minimum rate at which transient nuclear orientations are destroyed.

It should be noted that the T_N process does not necessarily involve the actual flipping of a donor nucleus. The transfer of the donor electron from one donor to another may accomplish such a process if the two donor nuclei in question are in a different m_I state. If during this process the electron spin also flips, a T_{ss} process results as discussed in the next paragraph. It is not too surprising that neither of the two mechanisms

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[26] A. W. Overhauser, Phys. Rev. **92**, 411 (1954).

[27] Feher, Fuller, and Gere, Phys. Rev. **107**, 1462 (1957).

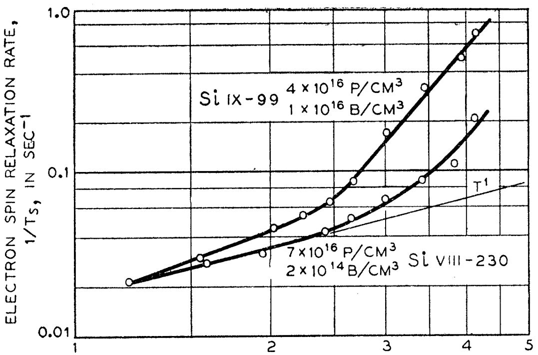

FIG. 6. Electron spin relaxation rate *vs* temperature in two samples with different amounts of compensation. Note the faster relaxation rate in the compensated sample in spite of its lower donor concentration. ($T=1.25°$K, $H\simeq3200$ oersteds.)

proved to be very effective at the low temperatures and low donor concentrations used.

D. The T_{ss} Process

The T_{ss} process was investigated at 1.25°K and 3200 oersteds on the previously discussed sample. The experimental procedure was to invert only one of the m_I lines by sweeping through it under adiabatic fast passage conditions. The T_{ss} process then aids the T_s process in relaxing this line. The amplitude of the line that was not inverted will be diminished by the T_{ss} process. (For an illustration of this effect see Sec. VI and Fig. 8.) No such effect was found in this sample which established a lower limit of $T_{ss}>5$ hours.

One of the possible physical mechanisms responsible for the T_{ss} process was already discussed in the previous section. Another possible mechanism involves a simultaneous electron spin-spin flip. This becomes possible if the exchange interaction between the two electrons is large enough.[28] If there are free carriers present in the sample a double exchange scattering[29] mechanism also provides an effective T_{ss} mechanism (see Sec. VI).

V. RELAXATION TIMES IN THE CONCENTRATION DEPENDENT REGION

For a donor concentration exceeding $\sim10^{16}$ P/cm^3, the relaxation time T_s is a strong function of the number of impurities as illustrated in Fig. 2. All the experimental points, except on the sample with the highest impurity concentration, were obtained by observing the amplitudes of the resonance lines at different time intervals after they were saturated. The relaxation time of sample VIII-215 containing 3×10^{17} P/cm^3 was obtained by the microwave saturation method.[20] The saturation behavior of the line indicated that it was homogeneously broadened (e.g., the line width increased with increasing microwave power).

The temperature dependence[30] of sample VIII-230 containing 7×10^{16} P/cm^3 is shown in Fig. 6. It does not show the sharp break that $1/T_s$ exhibited in the concentration independent region (see Fig. 3), although at the lowest temperatures $1/T_s$ seems to approach again a T^1 dependence.

The magnetic field dependence was investigated on the same sample. At 1.25°K T_s was found to be independent of field in the range between 3000 and 8000 oersteds. This indicates that, unlike in the concentration independent region, the observed relaxation mechanism does not proceed via a simple direct phonon process.

PBS[5] have calculated a concentration dependent relaxation time which arises from a modulation of the exchange coupling between neighboring impurities. Both the order of magnitude of this relaxation time and its dependence on temperature and field rule out the importance of their mechanism.

The effect of the acceptor concentration on T_s was investigated on a compensated sample (IX-99) containing 4×10^{16} phosphorus donors/cm^3 and 1×10^{16} boron acceptors/cm^3. The temperature dependence of $1/T_s$ is shown in Fig. 6 and deviates significantly from the uncompensated sample. The coincidence of the relaxation rates at 1.25°K of the two samples is fortuitous. The enhanced relaxation rate of the compensated sample is illustrated in Table I where its rate is compared with two uncompensated samples containing only 2×10^{14} B/cm^3. One of these has the same number of donor electrons (i.e., un-ionized donors) and the other the same total number of donors (both ionized and un-ionized) as the highly compensated sample. In each case the relaxation time is considerably longer than in the compensated sample. The effect of the acceptors is to empty an equal number of donors. This allows the "hopping" of an electron from an occupied to an unoccupied donor and is responsible for an impurity conduction process as postulated by Mott[31]

TABLE I. Effect of the acceptor concentration on the relaxation rate $1/T_s$ of the donor electrons ($T\cong1.25°$K, $\nu_e\sim9000$ Mc/sec). The data on the uncompensated sample were obtained from Fig. 2.

No. of phosphorus donors N_D	No. of boron acceptors N_A	No. of donor electrons N_D-N_A	$1/T_s$
4×10^{16} P/cm^3	1×10^{16} B/cm^3	3×10^{16}/cm^3	2×10^{-2} sec^{-1}
4×10^{16} P/cm^3	2×10^{14} B/cm^3	4×10^{16}/cm^3	3×10^{-3} sec
3×10^{16} P/cm^3	2×10^{14} B/cm^3	3×10^{16}/cm^3	1.5×10^{-3} sec

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[28] These exchange interactions have been calculated by A. Miller and E. Abrahams (to be published).

[29] This mechanism was suggested by P. W. Anderson (private communication).

[30] A temperature independence was previously reported for T_s in this sample (see reference 15). The origin of this discrepancy is possibly due to an incomplete shielding of the sample in the previous experiment (see Sec. VI).

[31] N. F. Mott, Can. J. Phys. 34, 1356 (1956).

and Anderson.[32] So far no successful theoretical estimates have been made on the effect of such a process on the electron spin relaxation time.

In concluding this section we wish to point out that there are a number of other imperfections which, unlike the number of acceptors, have not been kept under proper control. Notable among them are dislocations and dissolved oxygen which in a pulled rotated crystal is present in amounts of the order of 10^{18} O/cm^3.[33] In this connection it seems worthwhile to mention an experiment on a phosphorus doped silicon crystal ($\sim 5\times 10^{16}$ P/cm^3) which contained 1.3 atomic percent of germanium (see Part I, Sec. III-F). The relaxation time T_s on this sample was reduced by not more than about a factor of two or three over the relaxation time in pure silicon. In another experiment $\sim 10^{16}$ iron impurities/cm^3 (see Part I, Sec. III-D) were diffused into a sample with 10^{16} P/cm^3. The relaxation time of the phosphorus donor electron was not affected (except at a particular field as discussed in Sec. VII) and fell very near the curve of Fig. 2.

VI. EFFECT OF LIGHT ON THE RELAXATION TIME

In the early experiments performed in collaboration with Fletcher,[34] it was found that light had a pronounced effect on the observed relaxation time. Recently Honig[35] reported that wavelengths between 2 and 25 microns are principally responsible for the reduction in the relaxation times. In this section we wish to discuss several aspects of this effect.

A. Dependence of the Light Effect on the Photon Energy

The first question we wished to answer quantitatively was the wavelength dependence of the reduction in the relaxation time. The experiments were performed by shining light from a Gaertner quartz monochromator (Model L234-150) on the sample. For this purpose part of the silver coating was removed from the walls of the microwave cavity and Dewars with transparent windows were used. The absolute light intensity was obtained with a lead sulfide cell put inside the microwave cavity in place of the sample. The lead sulfide cell in turn was calibrated with a thermocouple.[36] The important quantity affecting the relaxation time is not the number of photons, but the number of free carriers (and the sign of charge) that they produce. Since no data on the photoionization of impurities and the electron-hole pair production in silicon at helium temperatures could be found, a separate set of experiments was performed in order to obtain these quantities. For this purpose a standard[17] six-arm Hall-bridge was cut from the same crystal from which the 7×10^{15} P/cm^3 sample for the relaxation time measurements was obtained. The Hall coefficient was obtained at $H=4000$ oersteds[37] and 1.25°K by shining light on the sample. A vibrating reed electrometer (Applied Physics Corporation, Model 31) was used to measure the current and the Hall voltage. The sign of the Hall coefficient corresponded to electrons throughout the spectral region investigated.

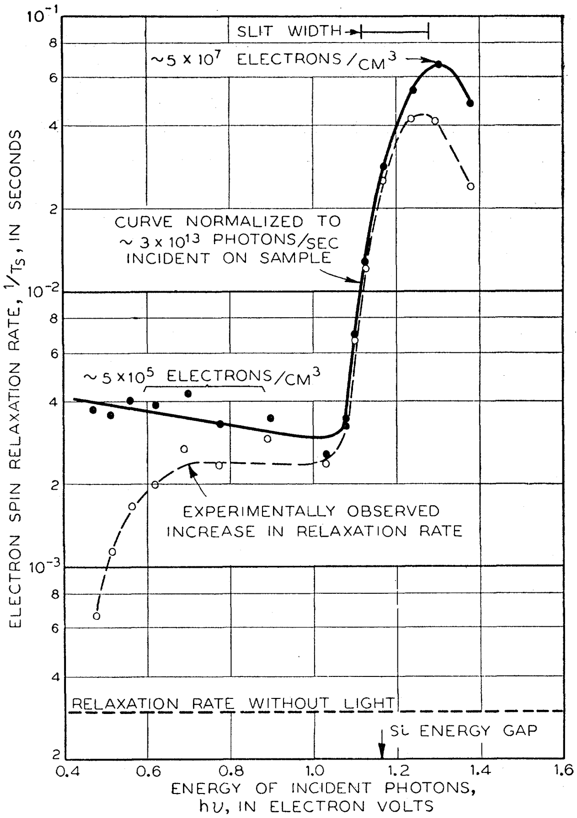

FIG. 7. The effect of light of different wavelengths on the relaxation rate in phosphorus doped silicon (7×10^{15} P/cm^3, $T=1.25$°K, $H\simeq 3200$ oersteds). The sharp increase in relaxation rate occurs at the band gap where electron-hole pairs are produced. The number of free carriers produced by the light was obtained from the Hall coefficient.

Figure 7 shows the results obtained on the phosphorus

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[32] This mechanism was independently suggested by P. W. Anderson (private communication) who worked on the theory in collaboration with D. Pines and E. Abrahams [see D. Pines, Can. J. Phys. **34**, 1367 (1956)].

[33] Kaiser, Keck, and Lange, Phys. Rev. **101**, 1264 (1956).

[34] G. Feher and R. C. Fletcher, Bull. Am. Phys. Soc. Ser. II, **1**, 125 (1956).

[35] A. Honig, *Proceedings of the Kamerlingh-Onnes Memorial Conference on Low-Temperature Physics, Leiden, Holland, 1958* [Suppl. Physica 24, Sept. (1958)].

[36] We would like to thank R. J. Collins for helping with the calibration of the thermocouple.

[37] If one assumes a unity quantum yield, one obtains from the number of incident photons/cm^2 and the number of carriers/cm^3 a recombination lifetime of the order of one microsecond. Some of the other properties of the silicon sample ($N_D=7\times 10^{15}$ P/cm^3, $N_A=5\times 10^{14}$ B/cm^3) that were investigated at 1.25°K with extrinsic light were as follows: The electronic mobility $\mu_e=12\,000$ cm^2/v sec. Ohm's law was satisfied up to the highest electric fields used ($E_{\text{MAX}}=5$ v/cm). The magnetoresistance $\Delta\rho/\rho$ between 1000 and 8000 oersteds was found to be proportional to $H^{+1.5}$. A deviation from the usual H^2 relationship is to be expected if impurity scattering is present (C. Herring, private communication).

doped silicon sample with 7×10^{15} P/cm^3. One curve represents the observed reduction in the relaxation time, the other curve has been normalized to a constant photon flux of $\sim3\times10^{13}$ photons/sec incident on the sample. (For a discussion of sample geometry see Part I, Sec. II B-3.) This curve was calculated by assuming that the reduction in relaxation time is proportional to the number of incident photons. This assumption was justified in detail for one wavelength only ($h\nu\simeq1.2$ ev). The number of electrons created by light follows approximately the normalized curve below $h\nu<1.15$ ev. For this region we find that $\sim5\times10^{15}$ electrons/cm^3 reduce T_s to about 300 sec. The large discontinuity in the relaxation time at the energy gap of ~1.15 ev corresponds to the production of electron-hole pairs. The measurements in this region are less reliable because the large absorption coefficient of the sample prevents a uniform distribution of free carriers through the sample. (Note that the diffusion length of the electrons at this temperature is of the order of 10^{-3} cm.) As a consequence different parts of the sample will have different relaxation times.[38] In the analysis of our experiments the longer times are weighted more heavily and may account for the drop in the observed effectiveness of the carriers (i.e., 5×10^7 electrons/cm^3 produced a T_s of ~15 sec). The predominant charge carriers in this region were found to be electrons with a mobility approximately equal to the carriers produced in the extrinsic region.[37] It should be noted at this point that there are several uncertainties involved in reproducing the same conditions for the sample used in the Hall effect measurement and the spin resonance experiment. For this reason no attempt was made to obtain the absolute values for the effectiveness of the carriers in producing a given relaxation time to better than about a factor of two.

In order to study the details of the relaxation mechanisms that are involved, the light intensity was increased by replacing the monochromator with filters. The extrinsic region was investigated with a germanium filter that transmits light with an energy of $h\nu<0.66$ ev. The lower limit was set by the glass Dewars which transmit $h\nu>0.5$ ev. The intrinsic region was studied by using a 3-cm thick water filter which transmits light with an energy of $h\nu>0.9$ ev.

B. The Spin Exchange Mechanism

In this section we wish to discuss the mechanisms that are responsible for the reduction of the relaxation times by free carriers. In order to distinguish between the T_s and T_{ss} process the magnetization of the sample was "prepared" in the following way: First the spin system was brought to thermal equilibrium at 3200 oersteds by illuminating the sample. Next the populations corresponding to either one or both of the hf lines were inverted by performing an adiabatic fast passage.[13] No light was allowed to fall on the sample during this process. The decay of the magnetization was subsequently observed by performing a spin resonance experiment after illuminating the sample for different periods of time. The results of this experimental procedure for light in the extrinsic region ($0.5\text{ ev}<h\nu<0.66$ ev) are illustrated in Fig. 8.

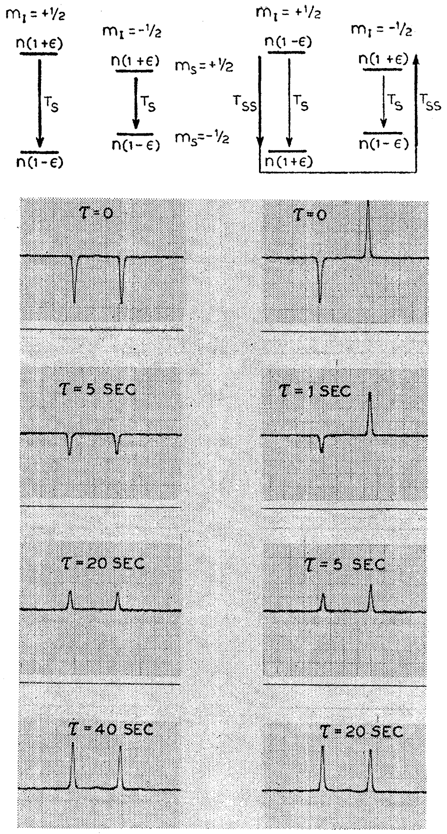

FIG. 8. The T_s and T_{ss} mechanisms in phosphorus doped silicon with $\simeq4\times10^{16}$ conduction electrons/cm^3 introduced by light ($0.5\text{ ev}<h\nu<0.66$ ev). When both lines are inverted by an adiabatic fast passage only the T_s mechanism is effective. With only one line inverted the T_{ss} mechanism is seen to be predominant. From the above traces one finds that $T_s\simeq25$ sec. $T_{ss}\simeq1$ sec. The large difference between T_s and T_{ss} indicates the polarization of conduction electrons by exchange scattering ($T=1.25$°K, $\sim7\times10^{15}$ P/cm^3, $H\simeq3200$ oersteds).

When *both* hf lines are inverted, T_s is the only relaxation time that can fully restore the magnetization to its thermal equilibrium value. The T_x mechanism under these conditions can at most equalize the populations in all the levels. By inducing the $h\nu_N{}^+(\Delta m_s=0,\ \Delta m_I=\pm1)$ transitions after the lines had partially relaxed the amplitudes of the two hyperfine lines remained the same. From this we conclude that $T_x\gg T_s$. The T_{ss} mechanism in this case is inoperative since the popula-

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[38] This effect could be used to determine diffusion lengths at these low temperatures. By shining light with a frequency $h\nu\gg1.15$ ev carriers will be produced only at the surface. They will be responsible for building up the magnetization to a value given approximately by $M_0\,\lambda/d$ where λ is the diffusion length, d the thickness of the sample and M_0 the maximum magnetization due to all the donors.

tion difference in both lines is the same at all times. The results for this case are shown on the left half of Fig. 8. The number of electrons $n_e \simeq 4\times 10^6/\text{cm}^3$ and the measured relaxation time $T_s \simeq 25$ sec.

A different situation is encountered if only *one* of the hf lines is inverted. In this case both the T_s and T_{ss} mechanism is effective. One can show that under those conditions the amplitudes of the resonance signals A and B corresponding to the two hf lines are given by:

$$A/A_0 = 1 - e^{-t/T_s}(1 + e^{-t/T_{ss}}), \tag{1}$$

$$B/B_0 = 1 - e^{-t/T_s}(1 - e^{-t/T_{ss}}), \tag{2}$$

where t is the time interval measured from the instant that line A was inverted. A_0 and B_0 are the equilibrium amplitudes of the two lines ($A_0 = B_0$). An inspection of Fig. 8 immediately reveals that T_{ss} is more effective than T_s. A quantitative analysis shows that for

$$n_e \simeq 4\times 10^6 \text{ electrons/cm}^3$$

one obtains

$$T_{ss} = 1 \text{ sec}, \quad T_s = 25 \text{ secs}.$$

A similar set of experiments was performed with intrinsic light ($h\nu > 1.15$ ev). The light intensity was cut down to obtain the same relaxation time T_s as was obtained with extrinsic light. Under those conditions, the ratio T_s/T_{ss} was approximately the same as that obtained before. In addition, however, an admixture of T_x was observed.

The fact that T_{ss} is more effective than T_s provides a clue as to the mechanism involved. PBS[5] proposed a spin exchange mechanism in which the conduction electron collides with the impurity and exchanges the spin in the process. The conduction electron in turn has to relax to the lattice. The relative ineffectiveness of this process arises from the fact that 7×10^{15} donor electrons have to be relaxed by only 4×10^6 free carriers. In order to reduce T_s to one second, the spin lattice relaxation time T_c of the conduction electrons has to be shorter than 10^{-9} sec, otherwise they will become polarized and ineffective. It was pointed out by Anderson[39] that a double spin exchange, i.e., a T_{ss} mechanism would leave the spin of the conduction electron unaltered, thereby remove the T_c bottleneck and result in an increase in the effectiveness of T_{ss}.

The cross section for the T_{ss} mechanism may be estimated as follows: The number of collisions that are effective in producing a double exchange is given by $(1/T_{ss}) = (1/4)\sigma v n_e$, where v is the velocity of the conduction electrons ($\sim 10^6$ cm/sec) and σ is the capture cross section. (The factor of four arises from the fact that in each collision the two electrons may have their spins in the same state.) Substituting the experimentally found values one arrives at $\sigma \simeq 2\times 10^{-12}$ in good agreement[40] with the estimate of PBS.[5]

In the extreme case in which the T_s mechanism is limited by T_c one may write[5] $T_s = T_c N_D/n_e$. Substituting the experimentally found values one obtains for $T_c \simeq 10^{-8}$ sec. This time is much shorter[41] than the relaxation time $T_c{}^*$ of unbound electrons in degenerate samples which have a value of $T_c{}^* \simeq 3\times 10^{-7}$ sec (see Part I, Sec. IIE). The star indicates that one is not dealing with the same kind of carriers in both cases. The electrons in the degenerate samples discussed in Part I move in an impurity band, whereas in the light experiments they are raised into the conduction band. Another difference between the two cases is the number of carriers participating in the conduction process. In the light experiments one is dealing with few carriers which may be effectively relaxed by a relatively small number of fast relaxing impurities. A possible source of such impurities may be for example clusters of phosphorus atoms.

C. Saturation of a Background Line During Illumination

Before concluding this section we would like to present some experimental results for which we have no adequate explanation at present. It was found that when the microwave power was turned on during the time the sample was illuminated ($0.5 \text{ ev} < h\nu < 0.66$ ev) the equilibrium magnetization acquired by the donor electrons was reduced. This reduction in magnetization was most pronounced when the magnetic field was set during the illumination period to a value corresponding to $g = 2.00 \pm 0.01$, i.e., between the two phosphorus hf lines. With the external dc magnetic field set to this position, a microwave field of $H \simeq 0.05$ oersted reduced the magnetization of the donor electrons to half their maximum value. With the dc magnetic field set at ±200 oersteds from the value corresponding to $g = 2.00$, the carriers created during the illumination were able to build up the magnetization of the donor electrons to 75% of their maximum value.

Phenomenologically such a behavior would be expected if one saturated paramagnetic centers that are in contact with the conduction electrons† and have a

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[39] P. W. Anderson (private communication).

[40] This agreement is better than expected in view of the simplifying assumptions made by PBS[5] and the experimental uncertainties in the determination of n_e as discussed in the text. It should be pointed out that in the experiments described one measures spin exchange cross sections at electron energies that are more than two orders of magnitude lower than the binding energy of the donor electron. In the analogous atomic experiments of scattering electrons from hydrogen, serious experimental difficulties are encountered when one tries to reduce the electron energies below about one tenth of the ionization energy of hydrogen. [See the experimental data of Bederson, Hammer, and Malamud quoted in the article by S. Borowitz and H. Greenberg, Phys. Rev. **108**, 716 (1957).]

[41] A. Honig [Bull. Am. Phys. Soc. Ser. II, 3, 377 (1958)] also finds that $T_c{}^* < T_c$.

† *Note added in proof.*—Additional evidence in support of the presence of such paramagnetic centers comes from the study of hot electrons in silicon (G. Feher, to be published). When conduction electrons were accelerated in an electric field and acquired a temperature in excess of the lattice temperature (i.e., were "hot"), their spin temperature remained relatively low indicating a cooling mechanism by the background impurities.

total width of 400 oersteds and a g-value of 2.00. The nature of these centers is at present not understood. They may be related to the centers discussed in connection with the T_c^* mechanism in the previous section.

A similar behavior was observed when light with an energy of $h\nu > 0.9$ ev was used. In this case, however, the T_x transitions were also partially saturated when the microwave field was turned on during the illumination period. We recall in this connection that with the microwaves turned off a T_x admixture in this region of light energies was found. This behavior indicates that the centers which are responsible for the T_s or T_x relaxation mechanism can be saturated by the microwave field, thereby reducing their effectiveness. The nature of the center responsible for the T_x mechanism is particularly puzzling. They promote the $(m_s=+\frac{1}{2}, m_I=-\frac{1}{2}) \leftrightarrow (-\frac{1}{2}, +\frac{1}{2})$ transitions (see Fig. 1) which involve no change in total angular momentum.[42]

VII. RESONANT SPIN-SPIN INTERACTIONS

In this section we wish to discuss processes in which the total magnetization of the sample remains unchanged. These take place when two spins perform a mutual spin flip without changing the total energy of the system. The T_{ss} mechanism described earlier does not fall into this category because the energies of the two lines corresponding to the two m_I values differ by the hf interaction energy. In order to make a resonant spin-spin-interaction possible the Zeeman levels must be equidistant.

A. Interaction Between Two Different Chemical Impurities

A system that satisfies the requirements of having equidistant energy levels is provided by silicon doped with both phosphorus and iron (see Part I, Sec. III D). Since the electronic g-values of the P and Fe centers are different, there exists a critical "mixing" field H_{MIX} at which one of the P lines overlaps with the Fe resonance line.[43] The value of this field is given approximately by

$$g(P)\mu_0 H_{\mathrm{MIX}}+\tfrac{1}{2}a(P)=g(\mathrm{Fe})\mu_0 H_{\mathrm{MIX}}, \qquad (3)$$

where a (P) is the hf interaction of the phosphorus donor electron (see Part I, Sec. II C-4). For the P and Fe centers $H_{\mathrm{MIX}} \simeq 600$ oersteds.

In order to observe the spin-spin interaction one must make the Boltzmann factor associated with the Fe levels different from the one corresponding to the phosphorus levels. This is easily accomplished since the relaxation time T_s (Fe) is several orders of magnitude shorter than T_s (P). Both centers were equilibrated at $H_{\mathrm{EQU}} \simeq 3000$ oersteds whereupon the field was reduced to the critical value at which the resonance lines overlapped. The electron system associated with the iron impurity relaxed in a fraction of a second and came to thermal equilibrium with the lattice at the field H_{MIX}. Since at this field one of the phosphorus lines $(m_I=+\frac{1}{2})$ was in thermal contact with the Fe line via a spin-spin interaction, it also acquired the Boltzmann factor corresponding to H_{MIX}. The other phosphorus line $(m_I=-\frac{1}{2})$ was unaltered since it could come to thermal equilibrium only via its own T_s which is long in comparison to the times involved in our measurement.

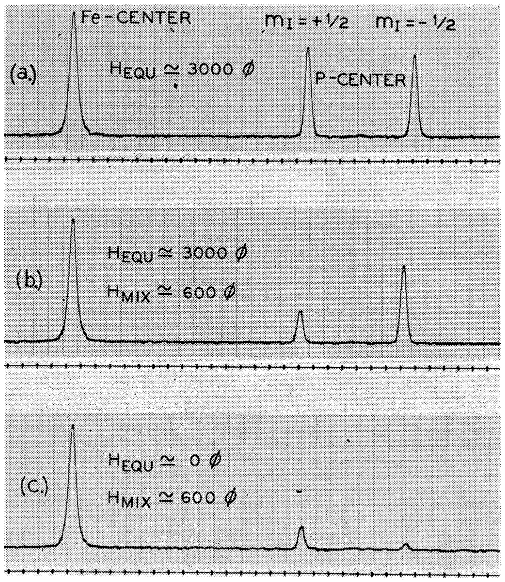

FIG. 9. Spin-spin interaction between the electron associated with the Fe impurity and the donor electron; (a) The spectrum without interactions after the magnetization had been equilibrated at $\sim$3000 oersteds; (b) The spins were brought to thermal equilibrium at 3000 oersteds. The trace shows the spectrum after the lines were made to overlap at the mixing field of $\sim$600 oersteds; (c) Same as (b) except that the sample was equilibrated in zero magnetic field. For complete mixing the $m_I=+\frac{1}{2}$ line in trace (b) and (c) should have the same amplitude. Note that this system may be used to polarize the phosphorus nuclei as discussed in the text ($\sim10^{16}$ P/cm^3, $\sim10^{16}$ Fe/cm^3, $T=1.25$°K, $\nu_e \cong 9000$ Mc/sec).

The experimental results are illustrated in Fig. 9. The upper trace shows the resonance signal when the sample was equilibrated at 3000 oersteds. Both P lines had approximately the same amplitude. Trace b in Fig. 9 indicates the effect of the spin-spin interaction when the magnetic field was reduced to the critical value $H_{\mathrm{MIX}} \simeq 600$ oersteds. The $m_I=+\frac{1}{2}$ phosphorus line which was made to overlap with the Fe line is clearly smaller although the reduction falls somewhat short of the theoretically predicted value indicating an incomplete spin-spin interaction. The effect can also be

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[42] M. Lax (private communication) has suggested that perhaps the annihilation of excitons may induce this transition. It is also interesting to note that the transition between the first excited donor state and its ground state[7] involves no change in total angular momentum.

[43] A similar interaction between two electron spin resonance lines has also been observed in Gadolinium Ethyl Sulfate [G. Feher and H. E. D. Scovil, Phys. Rev. **105**, 760 (1957)]. The interaction between different nuclear levels has been investigated in detail by A. Abragam and W. G. Proctor [Phys. Rev. **109**, 1441 (1957)].

demonstrated by reducing the magnetization due to the phosphorus donors to zero, either by saturating the line or by waiting for several relaxation times at $H=0$. After traversing the critical field $H_{\rm MIX}$, the amplitude of the $m_I=+\frac{1}{2}$ line exceeded the amplitude of the $m_I=-\frac{1}{2}$, the former having again acquired the Boltzmann factor via the Fe line [see Fig. 9(c)].

The spin-spin interaction described above may be used to polarize the donor nuclei without the necessity of a microwave source. After one of the donor levels has acquired the desired Boltzmann factor, the radio frequency transition $h\nu_N^+(m_s=+\frac{1}{2}, m_I=+\frac{1}{2})\leftrightarrow(+\frac{1}{2}, -\frac{1}{2})$ is induced. This results in a nuclear polarization η which for a donor with $I=\frac{1}{2}$ has the maximum value of

$$\eta=\frac{N_{-\frac{1}{2}}-N_{+\frac{1}{2}}}{N_{-\frac{1}{2}}+N_{+\frac{1}{2}}}=(1/2)\tanh\left(\frac{g\mu_0H}{2kT}\right)\simeq\frac{g\mu_0(H_{\rm EQU}-H_{\rm MIX})}{4kT}, \qquad (4)$$

where $H_{\rm EQU}$ is the field at which the centers are equilibrated, $H_{\rm MIX}$ is the critical field at which the two lines overlap and $N_{-\frac{1}{2}}$, $N_{+\frac{1}{2}}$ are the populations in the respective m_I levels.

Another possible use of this mixing technique is the indirect observation of a resonance line too weak or too broad to be observed directly. If its relaxation time is short enough, it may be studied by observing its effect on the relaxation time of the donor[44] at different magnetic fields.

B. Interactions Between the Same Species of Donors

A spin-spin interaction may also take place at a magnetic field at which one has equidistant energy levels belonging to the same donor. In trying to realize one of the polarization schemes in phosphorus doped silicon suggested by Abragam,[45] we found[46] that the population differences between the levels disagreed with the predicted values. Anderson[39] pointed out that a spin-spin interaction should occur at the critical field H_c given by

$$[(\mu_D/I_D)+g(P)\mu_0]H_c=a(P).$$

This interaction results in the population differences as indicated in the level diagram of Fig. 10. The experimental traces in Fig. 10 show the amplitudes of the resonance lines that result from this mixing. The experimentally observed ratio of amplitudes is 2.4 in good agreement with the predicted value of 7/3 corresponding to complete mixing at the critical field. This and similar effects are discussed in more detail by Abragam and Combrisson.[47] The nuclear polarization resulting from a complete mixing is given by:

$$\eta=\frac{N_{-\frac{1}{2}}-N_{+\frac{1}{2}}}{N_{-\frac{1}{2}}+N_{+\frac{1}{2}}}\simeq-\frac{g\mu_0H}{12kT}. \qquad (5)$$

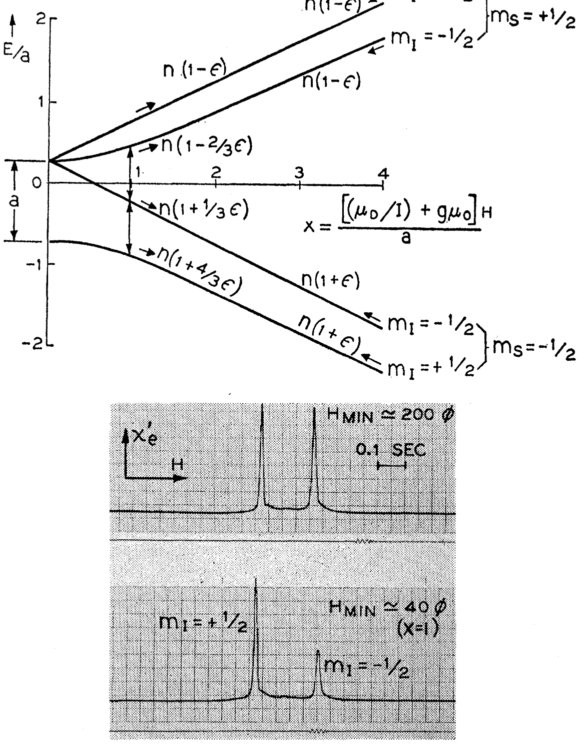

FIG. 10. Spin-spin interaction in phosphorus doped silicon at $x=1$ ($H\simeq 40$ oersteds). The magnetization was allowed to equilibrate at 8000 oersteds. The field was then reduced to different values of $H_{\rm MIN}$ in a time short compared to T_s and raised again in order to observe the signal (10^{16} P/cm^3, $T=1.25$°K, $\nu_e\simeq 9000$ Mc/sec). The theoretical ratio of amplitudes for complete mixing at $x=1$ is 7/3. This mixing results again in a nuclear polarization as given in the text.

VIII. SPIN DIFFUSION WITHIN THE LINE

In all our previous discussions it was assumed that no spin diffusion takes place from one part of the resonance line to another, i.e., that one deals with a truly inhomogeneously broadened line.[21] In this section it will be shown that this assumption is not rigorously justified and that a special kind of "discrete" spin diffusion is observed.

The experimental procedure used to observe the spin diffusion was as follows. The dc magnetic field was set to the center of the resonance line and the microwave field was turned on to saturate a narrow region of the

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[44] It is possible that at least part of the relaxation effects observed by Townes and co-workers [Giordmaine, Alsop, Nash, and Townes, Phys. Rev. **109**, 302 (1958)] may be due to such a "background" line [G. Feher, Bull. Am. Phys. Soc. Ser. II, **3**, 180 (1958)].

[45] A. Abragam, Compt. rend. **242**, 1720 (1956).

[46] G. Feher, Bull. Am. Phys. Soc. Ser. II, **1**, 384 (1956).

[47] A. Abragam and J. Combrisson, Suppl. Nuovo cimento **6**, No. 3, 1197 (1957).

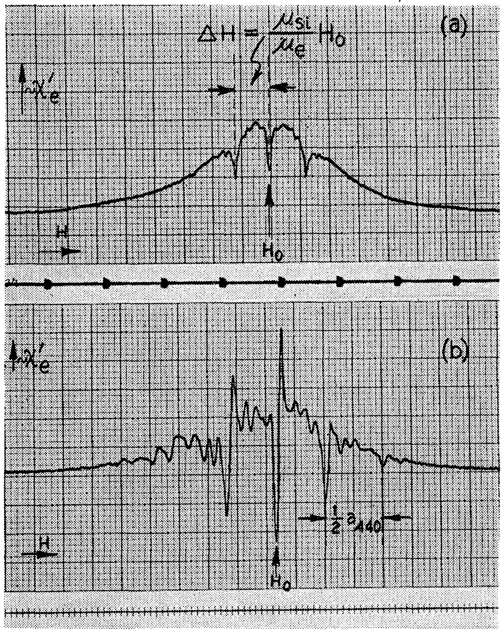

FIG. 11. "Discrete" spin diffusion in *As*-doped silicon ($\sim 2\times 10^{16}$ As/cm^3, $T=1.3$°K, $H\simeq 3200$ oersteds). The line was saturated by setting $H=H_0$ and then turning the microwave power on. ($H_1\simeq 10^{-2}$ oersteds for $\simeq 10$ sec.) The notches are displaced from H_0 by amounts corresponding to the Larmor frequencies of the Si^{29} nuclei at the different lattice points; (a) Direct detection without field modulation. (b) With magnetic field modulation.

line. In the absence of spin diffusion one would not expect the saturated region to diffuse and spread throughout the line. This indeed was found to be the case at 1.25°K both in As and P-doped silicon when the saturating microwave field was left on for a short time (of the order of a second). This is demonstrated in Fig. 2 of Part I where the steep sides of the saturated region and the undisturbed remaining part of the line indicate the absence of spin diffusion.[48] When the line was saturated for a longer period (of the order of 10–100 sec) it was found that although the "burned out hole" remained sharp, subsidiary holes appeared at frequencies which differed from that of the center of the line by an amount,

$$(\mu_{\mathrm{Si}}/I_{\mathrm{Si}})+\tfrac{1}{2}a_l, \tag{6}$$

where a_l is the hf interaction of the electron with the Si^{29} nucleus at the lth lattice site. (See Part I, Sec. II.) This is illustrated in Fig. 11 for As-doped silicon ($T=1.25$°K, $H\simeq 3200$ oersteds). The subsidiary holes indicate the presence of a "discrete" spin diffusion process that took place while the microwave field was inducing transitions between the electronic levels.

Equation (6) shows that the observed spin diffusion occurs in jumps corresponding to the Larmor frequencies of the different Si^{29} nuclei. This suggests that in this process Si^{29} nuclei flip and thereby change the resonant frequency of a given spin packet. One possible mechanism‡ by which this spin diffusion may take place has been proposed by Bloembergen.[49] It involves the simultaneous flip of *two* Si^{29} nuclei occupying similar position in neighboring donor orbits. This mechanism should result in a symmetric pattern around the saturating field H_0, since energy is conserved in each Si^{29} double flip.

A possible consequence of this discrete spin diffusion process is a reduction in the magnetization when the resonance line is traversed under adiabatic fast passage conditions. This is easily seen if one considers the distribution of spin packets after the line has been partially traversed. In this situation some spin packets point along and others point opposite the external magnetic field. A spin diffusion process therefore tends to connect spin packets pointing in opposite directions and thereby reduces the magnetization. This process may account for the observed anomalies discussed in Part I, Appendix A4.

It should be pointed out that—in principle at least—the discrete spin diffusion process may be used to obtain the hyperfine interaction constants a_l. Because of the reduced resolution and more complex nature of the spectrum, this method is, however, inferior to the ENDOR technique.

IX. ACKNOWLEDGMENTS

It is a pleasure to thank P. W. Anderson, E. Abrahams, and D. Pines for many valuable discussions throughout this work, R. J. Collins for helpful discussions on the light experiments, and the crystal growing group of the Bell Telephone Laboratories for supplying us with the samples used in this work.

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[48] P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

‡ *Note added in proof.*—Another mechanism which would account for the observed spectral diffusion arises in the following way. Because of the presence of the dipolar interactions, the microwave field can induce transitions in which both the electron and the Si^{29} nucleus flip [i.e. $(++\leftrightarrow --)$ and $(+-\leftrightarrow -+)$ transitions]. This would result in the saturation of spin packets at the observed frequencies.

[49] N. Bloembergen (private communication).

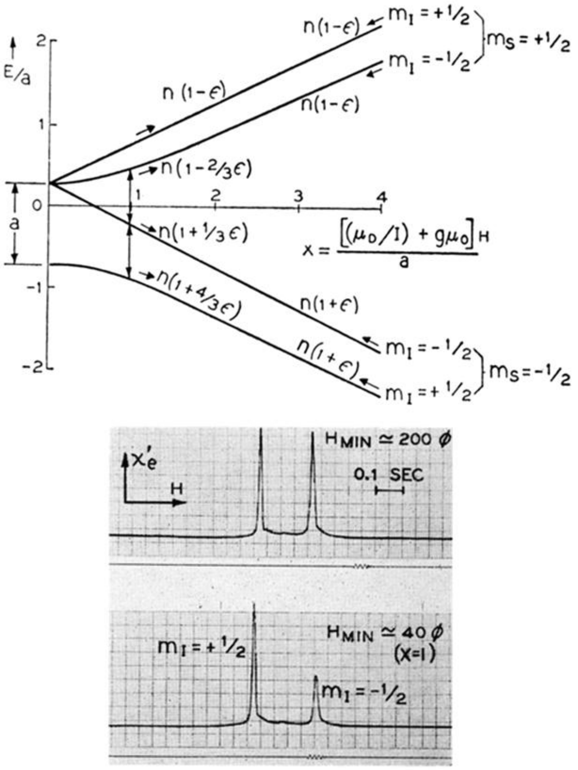

FIG. 10. Spin-spin interaction in phosphorus doped silicon at $x=1$ ($H \simeq 40$ oersteds). The magnetization was allowed to equilibrate at 8000 oersteds. The field was then reduced to different values of H_{MIN} in a time short compared to T_s and raised again in order to observe the signal (10^{16} P/cm^3, $T=1.25$°K, $\nu_e \simeq 9000$ Mc/sec). The theoretical ratio of amplitudes for complete mixing at $x=1$ is 7/3. This mixing results again in a nuclear polarization as given in the text.

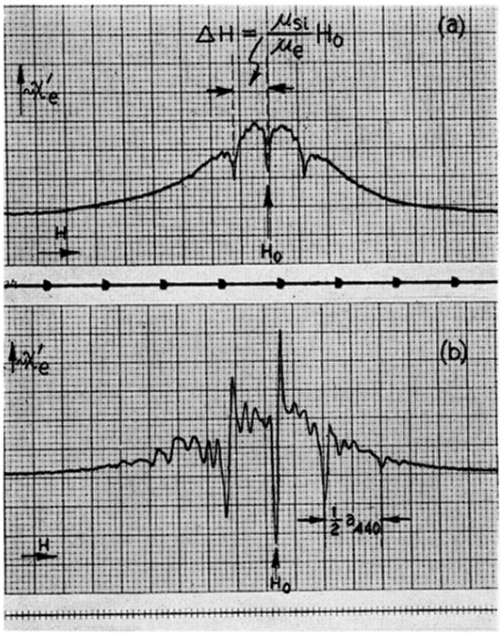

FIG. 11. "Discrete" spin diffusion in *As*-doped silicon ($\sim 2\times 10^{16}$ As/cm^3, $T=1.3$°K, $H\simeq 3200$ oersteds). The line was saturated by setting $H=H_0$ and then turning the microwave power on. ($H_1\simeq 10^{-2}$ oersteds for $\simeq 10$ sec.) The notches are displaced from H_0 by amounts corresponding to the Larmor frequencies of the Si^{29} nuclei at the different lattice points; (a) Direct detection without field modulation. (b) With magnetic field modulation.

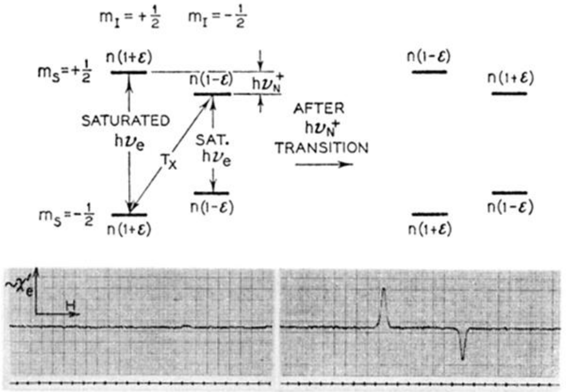

FIG. 4. Illustration of the method used to determine T_x in the presence of a much shorter T_s in phosphorus doped silicon (7×10^{15} P/cm^3, $T=1.25$°K, $H\simeq3200$ oersteds, Sample: Si VIII-64). From the amplitudes of the lines and the time interval during which T_x was operative one obtains at 3200 oersteds a value of $T_x\cong30$ hours. Note that the saturation procedure results in a normal Overhauser effect and gives rise to the predicted nuclear polarization.

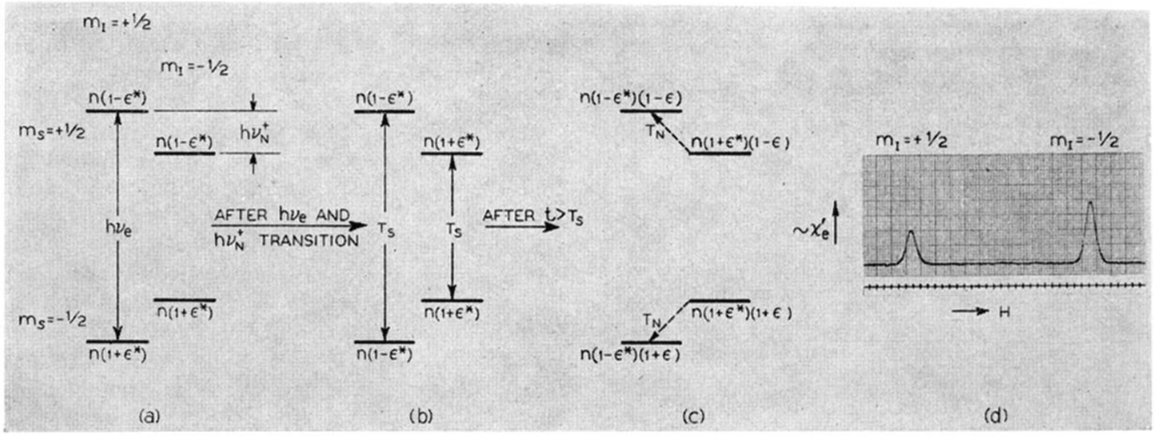

FIG. 5. Illustration of the method used to determine T_N in the presence of a shorter T_s (but longer T_x) in phosphorus doped silicon; (a) The magnetization is brought to thermal equilibrium at a high field. The corresponding Boltzmann factor is $2\epsilon^*$; (b) After a double adiabatic fast passage the m_I levels are preferentially occupied; (c) The populations after $t>T_s$; (d) The experimental trace from phosphorus doped silicon (7×10^{15} P/cm^3, $T=1.25$°K, $H=3200$ oersteds). The expected ratio of amplitudes is $\sim(1+\epsilon^*)/(1-\epsilon^*)$. From the rate at which the amplitudes of the two lines tend to equalize T_N may be obtained. Note the large nuclear polarization that is obtained during this procedure.

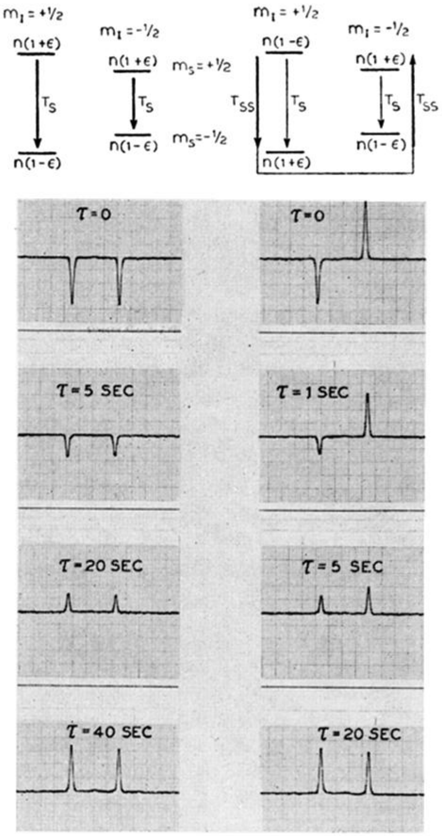

FIG. 8. The T_s and T_{ss} mechanisms in phosphorus doped silicon with $\simeq 4\times 10^{16}$ conduction electrons/cm^3 introduced by light (0.5 ev$<h\nu<$0.66 ev). When both lines are inverted by an adiabatic fast passage only the T_s mechanism is effective. With only one line inverted the T_{ss} mechanism is seen to be predominant. From the above traces one finds that $T_s \simeq 25$ sec. $T_{ss} \simeq 1$ sec. The large difference between T_s and T_{ss} indicates the polarization of conduction electrons by exchange scattering ($T = 1.25$°K, $\sim 7\times 10^{15}$ P/cm^3, $H \simeq 3200$ oersteds).

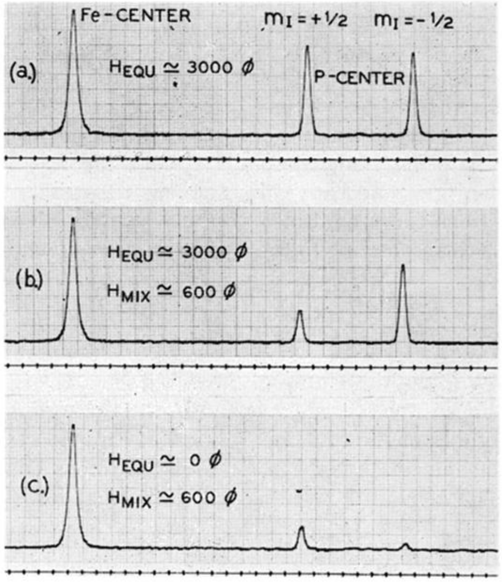

FIG. 9. Spin-spin interaction between the electron associated with the Fe impurity and the donor electron; (a) The spectrum without interactions after the magnetization had been equilibrated at ~3000 oersteds; (b) The spins were brought to thermal equilibrium at 3000 oersteds. The trace shows the spectrum after the lines were made to overlap at the mixing field of ~600 oersteds; (c) Same as (b) except that the sample was equilibrated in zero magnetic field. For complete mixing the $m_I=+\frac{1}{2}$ line in trace (b) and (c) should have the same amplitude. Note that this system may be used to polarize the phosphorus nuclei as discussed in the text (~10^{16} P/cm^3, ~10^{16} Fe/cm^3, $T=1.25$°K, $\nu_e \cong 9000$ Mc/sec).