PHYSICAL REVIEW VOLUME 106, NUMBER 3 MAY 1, 1957

Nuclear Polarization and Impurity-State Spin Relaxation Processes in Silicon

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(Received January 31, 1957)

Two proposals are made for producing nuclear polarization by a transient analog of the Overhauser effect in the impurity-state electron spin resonance in silicon. The success of the proposal polarization schemes requires that the electron spin relaxation process in which the impurity nucleus and the electron simultaneously flip their spins be faster than those relaxation processes in which an electron alone changes its spin. A detailed study of many electron spin relaxation processes is carried out. It is found that for sufficiently low concentrations of P, As, and Sb impurities in silicon transient nuclear polarization should occur; for Li impurities it should not. The foregoing theoretical predictions have been verified for As by the recent experiments of Abragam and Combrisson, and of Feher.

I. INTRODUCTION

THE electron spin resonance of impurity states in silicon is of particular interest because of the very long relaxation times observed for extremely pure samples, and the much shorter, highly concentration-dependent, times found as the impurity concentration is increased.[1] In samples where the relaxation time is very long (of the order of minutes to hours), a number of interesting transient effects may be observable. In this paper we propose the existence, under suitable experimental conditions, of a transient nuclear analog of the Overhauser effect.[2] It should occur whenever the relaxation process in which the electron and the impurity nucleus simultaneously flip their spins is faster than those in which an electron alone changes its spin. The effect thus depends sensitively on the various possible electron relaxation processes, so that an experimental and theoretical investigation of these times is required before the feasibility of establishing nuclear polarization by the above scheme may be established. We were thus led to a theoretical investigation of a number of possible electron spin relaxation mechanisms.

We were originally stimulated in the investigation of such effects by the experiments of Honig[3] and the theoretical explanation proposed for them by Kaplan.[4] Honig studied the impurity spin resonance of As-doped Si, for which one finds four lines, separated by the hyperfine interaction of the impurity electron with the As nucleus. He observed that passage through one of the lines enhanced the neighboring lines, and on this basis Honig and Kaplan concluded that nearly 100% nuclear polarization occurred as a consequence of such passage through the first line. Our first conclusion was that Kaplan's proposed polarization scheme is, in fact, lacking in validity. On the other hand, we found that effects somewhat similar to those observed by Honig may be associated with a transient nuclear polarization; however, the order of magnitude of the polarization associated with such effects is considerably less than 100% and is of the order of that obtainable in a steady-state Overhauser polarization.

Our calculations of spin-lattice relaxation times for a number of possible mechanisms have led us to the conclusion that at helium temperatures all relaxation times for very pure samples are quite long (of the order of minutes), essentially because the electron is bound to a given impurity site in such a way that it tends to respond adiabatically to changes in its environment. As a result the matrix elements for bound electron spin flip are considerably reduced over those one would calculate neglecting the adiabaticity of the electron response. We furthermore find that the simultaneous spin-flip mechanism should be more effective in producing relaxation than the electron-spin-only mechanism for extremely pure samples of P-, As-, or Sb-doped silicon. Whether such conditions actually obtain in a given sample is difficult to decide in principle. First of all, Honig's experiment does not provide any evidence for the existence of a transient nuclear polarization. For, as Feher[5] was the first to point out, the experimental results obtained by Honig can be explained in terms of fast-passage theory.[6] Second, Feher *et al.*[1] find that the spin-lattice relaxation time is quite sensitive to impurity concentration, and is reduced from a time of the order of seconds for a concentration of $\sim 10^{17}$ phosphorous impurities in silicon to less than 10^{-5} second for a concentration of 4×10^{17}. This concentration-dependent time is undoubtedly caused by an an electron spin-flip-only mechanism. Under what conditions it is the fastest time of interest in a given sample we are not able to predict. We have investigated several possible causes for a highly concentration-dependent relaxation time, but thus far have not been able to invent a mechanism which yields sufficiently

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[1] Feher, Fletcher, and Gere, Phys. Rev. **100**, 1784 (1955); G. Feher (private communication).

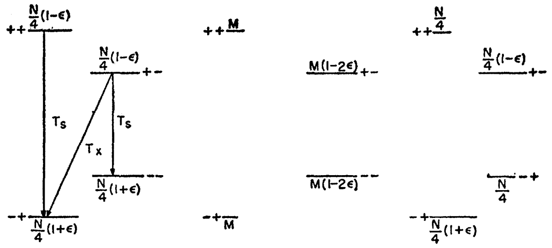
[2] A. W. Overhauser, Phys. Rev. **92**, 411 (1953).

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

[4] J. Kaplan, Phys. Rev. **96**, 238 (1954).

[5] G. Feher (private communication). See also A. Honig and J. Combrisson, Phys. Rev. **102**, 917 (1956).

[6] F. Bloch, Phys. Rev. **70**, 460 (1946).



A. THERMAL EQUILIBRIUM. B. SIMULTANEOUS SATURATION OF BOTH RESONANCE: $M=\frac{N}{4}(1+\epsilon)$. C. FIRST TRANSIENT EFFECT.

FIG. 1. Energy levels and their populations for a nucleus of spin $\frac{1}{2}$ and an electron of spin $\frac{1}{2}$ under various circumstances.

fast relaxation times to give agreement with experiment.

Recently Abragam and Combrisson[7] and Feher[8] have carried out experiments on samples of As-doped silicon which show that the simultaneous spin-flip mechanism is the most efficient relaxation process for the impurity electron, so that transient nuclear polarization should occur in these samples. Furthermore, the relaxation times they observe are in good accord with our theoretical prediction.

In the following section we consider the possibility of producing a transient Overhauser effect, and the ways in which it may be detected experimentally. We discuss two different kinds of transient effects which may be used to detect the polarization. In Sec. III we report our calculations on spin-lattice relaxation times for a number of possible mechanisms. In Sec. IV we compare our calculations with experiment, and in the appendix we analyze Kaplan's proposed explanation of the Honig experiments.

We wish to take this opportunity to call the reader's attention to a paper by Pound[9] which contains, we believe, the first description of a double-resonance effect. In an ingenious study of nuclear resonances with resolved quadrupole splittings, Pound applied the double-resonance technique to unravel the various relaxation mechanisms. The analysis we present below is essentially the same, although arrived at independently. It gives us particular pleasure to call the attention of the reader to Pound's pioneering work, since one of us (CPS) has omitted this important reference in earlier publications on the Overhauser effect.

II. TRANSIENT OVERHAUSER EFFECT

Let us consider an impurity with nuclear spin and electron spin both $\frac{1}{2}$ (as in the case of phosphorus) in a very strong magnetic field. We can then characterize the energy levels by M_S and M_I. We introduce the notion $(+\,-)$, $(+\,+)$, etc., for the various levels, where $(+\,-)$ means $M_S=+\frac{1}{2}$, $M_I=-\frac{1}{2}$, etc. The energy levels are shown schematically in Fig. 1. Possible spin-lattice relaxation processes are those indicated by the arrows, the corresponding relaxation times being T_X and T_S. The process which gives rise to T_X results from modulation of the hyperfine coupling by the lattice vibrations. A process which gives rise to T_S might result from modulation of the electron spin-orbit coupling by lattice vibrations, or perhaps by coupling with conduction electrons. We further assume that times for processes in which the nucleus alone flips are much longer than either T_X or T_S.[10] If there are N atoms, we have the populations at thermal equilibrium indicated in Fig. 1. Here $2\epsilon=\gamma_e H_0/kT$ represents the electron Boltzmann factor, and in calculating the relative populations we have neglected the nuclear gyromagnetic ratio γ_n with respect to the electron gyromagnetic ratio γ_e, and have neglected the hyperfine interaction constant relative to $\gamma_e H_0$. Prior to turning on the field we have equally populated levels.

We now consider three different ways in which nuclear polarization may be achieved, namely Overhauser's steady-state method and two transient methods.

(1) Normal Overhauser Effect

If we saturate both electron resonances simultaneously (i.e., the resonances associated with $M_I=+\frac{1}{2}$ and $M_I=-\frac{1}{2}$), we produce the normal Overhauser effect. We show how this comes about to illustrate the general type of calculation we carry out. The fact that the electron resonances are saturated means that the population $(+\,+)$ and $(-\,+)$ are equal, and likewise for $(+\,-)$ and $(-\,-)$. However, the relaxation process T_X maintains thermal equilibrium between the relative populations of $(+\,-)$ and $(-\,+)$. We have therefore the situation shown in Fig. 1, where M is to be determined. The condition on M is that the total population must be N, and hence that

$$M+M+M(1-2\epsilon)+M(1-2\epsilon)=N.$$

We find therefore that $M=\frac{1}{4}N(1+\epsilon)$. The total number of nuclei of spin up, n_+, is therefore $\frac{1}{2}N(1+\epsilon)$ and the total number with spin down, n_-, is $\frac{1}{2}N(1-\epsilon)$, giving a ratio

$$n_+/n_-=(1+\epsilon)/(1-\epsilon)\cong 1+2\epsilon.$$

Therefore, the nuclear population difference corresponds to an effective nuclear gyromagnetic ratio of $(\gamma_n)_{\text{eff}}=\gamma_e$. This is just Overhauser's result.

(2) First Transient Effect

The first transient polarization can be seen very simply. Let us assume that $T_X \ll T_S$. If we turn on the magnet and wait a time longer than T_X but less than T_S, we have thermal equilibrium established between

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

[8] G. Feher (private communication).

[9] R. V. Pound, Phys. Rev. **79**, 685 (1950).

[10] That nuclear times are long compared to the electronic times of interest may be deduced from the recent experiments of R. G. Shulman and B. J. Wyluda [Phys. Rev. **103**, 1127 (1956)]. Their experiments indicate a nuclear relaxation time in the very pure samples ($<10^{17}$ impurity atoms/cc) of at least 200 minutes.

the two levels $(+\,-)$ and $(-\,+)$, but no change in the populations of the $(+\,+)$ or $(-\,-)$ states. Therefore we have the readjustment of populations indicated on the righthand side of Fig. 1. The number of nuclei of spin up, n_+, is $\frac{1}{4}N+\frac{1}{4}(1+\epsilon)N$, whereas the number with spin down, n_-, is $\frac{1}{4}N+\frac{1}{4}(1-\epsilon)N$ so that

$$n_+/n_- = (2+\epsilon)/(2-\epsilon) = 1+\epsilon.$$

Thus *the nuclei are polarized to the same extent they would be if the nucleus had a gyromagnetic ratio of* $\frac{1}{2}\gamma_e$. This transient polarization will last for a time $\sim T_S$.

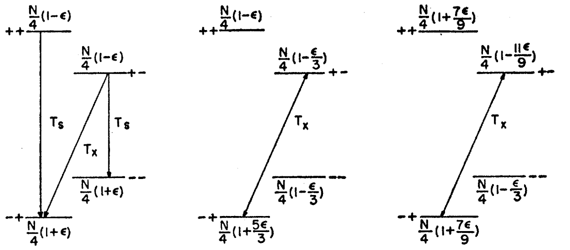
We could observe the presence of a polarization of this type by watching the intensity of the microwave electron spin resonance, which would reach its full value in a time T_S, but half its full value in the shorter time T_X. The presence of a pair of relaxation times T_X and T_S should also show up in a measurement of the magnetic susceptibility as a function of frequency using an alternating magnetic field *parallel* to H_0. For low frequencies the susceptibility should be $N\gamma_e^2\hbar^2I(I+1)/3kT$. At an angular frequency of about $1/T_S$, the susceptibility should drop to $\frac{1}{2}$; it should become zero for angular frequencies above $1/T_X$.

(3) Second Transient Effect

The second transient effect was invented by us to explain experimental results of the type described by Honig in which saturating one electron line enhanced the second line. Bloembergen[11] has independently suggested the same effect. As we have said, however, it appears that it is more likely that Honig's results can be best understood in terms of the rate of passage through the resonance, that is, as a fast-passage effect.

There are of course various experimental conditions that might prevail as far as a microwave resonance is concerned. The speed of passage through the line may be fast or slow compared to the relaxation times or the rate of transition induced by the external field, and additional parameters enter if one is modulating the magnetic field. For simplicity we shall consider a case in which $T_X \ll T_S$ and in which we can forget about the peculiar coherence effects of fast passage. We shall assume that we go through the resonance in a time long compared to T_X, and that the power level is high enough to produce complete saturation.

The populations under various experimental conditions are those shown in Fig. 2. *A* represents the situation before observation of the electron spin resonance. *B* gives the population changes produced when we saturate the $M_I=-\frac{1}{2}$ electron spin resonance line and wait a time short compared to T_S but long compared to T_X, so that the $(+\,-)$ and $(-\,+)$ states are in thermal equilibrium. *C* gives the level populations which result after we then proceed to saturate the $M_I=+\frac{1}{2}$ line in a time which is short compared to T_S.



A. THERMAL EQUILIBRIUM. B. AFTER SATURATING $M_I=-\frac{1}{2}$ ELECTRON RESONANCE. C. AFTER NEXT SATURATING $M_I=+\frac{1}{2}$ ELECTRON RES.

FIG. 2. Energy levels and their populations for a nucleus of spin $\frac{1}{2}$ and an electron of spin $\frac{1}{2}$ under various circumstances.

We first note that the $m_I=+\frac{1}{2}$ is enhanced relative to the $m_I=-\frac{1}{2}$ line. To show this, we need a criterion for intensity. Clearly there is a problem in how we define this since we have assumed complete saturation. However, a net amount of energy is absorbed from the microwave field, and we could use this as a measure of the intensity. An alternative measure, which is equivalent, is to take the population difference before passage. The latter criterion is based on the fact that the initial signal intensity (before the line is saturated) is proportional to the initial population difference. With these definitions, we note that the intensity of the $m_I=-\frac{1}{2}$ line which we observe first is proportional to 2ϵ. On the other hand, the intensity of the $m_I=+\frac{1}{2}$ line is proportional to $(5\epsilon/3)+\epsilon=(8\epsilon/3)$. The second line is therefore enhanced by the ratio 4/3 relative to the first line.

The degree of nuclear polarization produced at each stage of the process is as follows:

After passage through the $m_I=-\frac{1}{2}$ line:

$$\frac{n_+}{n_-}=\frac{2+5\epsilon/3-\epsilon}{2-2\epsilon/3}=1+2\epsilon/3,$$

which is equivalent to $(\gamma n)_{\text{eff}}=\gamma_e/3$.

After passage through the $m_I=+\frac{1}{2}$ line:

$$\frac{n_+}{n_-}=\frac{2(1+7\epsilon/9)}{2-11\epsilon/9-\epsilon/3}=1+14\epsilon/9,$$

which is equivalent to $(\gamma_n)_{\text{eff}}=7\gamma_e/9$. It is evident that a sizeable nuclear polarization has resulted. We should like to emphasize that *although the* $m_I=+\frac{1}{2}$ *electron line has increased 30% in intensity, it is not true that the nuclear polarization is correspondingly large.* That is, the intensity of the electron lines only tells us the degree of nuclear polarization when we have a theory of the detailed processes which take place.

The experimental situation in silicon is often that of adiabatic fast passage. In this case it is a simple matter to revise our calculations, the result being that (a) passage through a line inverts the population and (b) no changes in population are seen until relaxation has

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[11] N. Bloembergen (private communication).

taken place. Calculations along the lines we have indicated can then be carried out simply, but we shall omit them from our discussion. It is clear that one can get larger effective polarizations in this manner. Feher[12] has explored the theoretical ramifications extensively.

III. RELAXATION TIMES FOR THE SPIN RESONANCE OF GROUP V DONORS IN SILICON

We here wish to estimate the spin-lattice relaxation time due to the hyperfine interaction of the electron with the impurity nucleus, and to compare this with its relaxation time due to any other cause. The phonon-induced relaxation processes will only go if the spin flip of the electron is accompanied by the emission of phonon of energy $\hbar\omega_0$ (or inelastic scattering, if we are considering a Raman process), where ω_0 is the resonance frequency for the electron. Since $\hbar\omega_0$ is small compared to the binding energy of the electron, we may expect that the electron will tend to respond adiabatically to any change in its enrivonment which takes place with a frequency ω_0. As we shall see, this has the effect of reducing considerably the matrix elements for the spin flip of the bound electron. It also enables us to apply with some confidence the deformation potential concept of Bardeen and Shockley[13] to the calculation of our matrix elements.

As will be seen, we can obtain only an order of magnitude estimate of the relaxation times. For this reason, we shall not consider in detail the rather complicated wave function which describes the bound electron correctly, but instead think of a simplified wave function which corresponds to a single energy minimum with an average effective mass of $m^*=0.31m$. We have consistently dropped all angular dependences, spin-dependence of the matrix elements and the like, as essentially leading to factors of order unity. We also consider only longitudinal phonons in our explicit calculations, although for some of the processes we consider the transverse phonons may play an important role.

Using the deformation potential, it is quite straightforward to show that the matrix element for a transition from spin up to spin down induced by a change in the electrostatic potential V and spin-orbit interaction or hyperfine interaction H_I may be written

$$\begin{aligned}(\psi_{0-},\,(\delta V+\delta H_I)\psi_{0+})\\ =(\psi_{0-},\,E_{1+}\Delta\psi_{0+})+(E_{0+}-E_{0-})(\psi_{0-},\delta\psi_+).\quad(1)\end{aligned}$$

Here δV and δH_I are the change in potential, and $E_{1+}\Delta$ and $\delta\psi_+$ are the change in total energy and wave function for a spin up electron, all associated with a dilation Δ. For longitudinal waves we have

$$\Delta=\mathrm{div}\,\delta R(\mathbf{r})=\sum_k\left(\frac{ikq_k}{\sqrt{\rho}}\right)e^{i\mathbf{k}\cdot\mathbf{r}},\qquad(2)$$

where ρ is the density of Si. E_{0-} and E_{0+} are the energies of the spin down and spin up electron in the undilated lattice, and we have $E_{0+}-E_{0-}=\hbar\omega_0$.

(1) Electron-Nuclear Hyperfine Interaction

Let us first consider the matrix element (1) for the hyperfine interaction between the bound electron and the impurity nucleus. In this case $(\psi_{0-},E_{1+}\Delta\psi_{0+})$ vanishes because the spin parts of the spin-up and spin-down wave functions are orthogonal. We may calculate $\delta\psi_+$ directly. The wave functions in the absence of dilation are

$$\psi_{0+}=\varphi_1(\mathbf{r})\chi(+)+\tfrac{1}{2}a\varphi_1(\mathbf{r})\chi(-),\qquad(3)$$

where $a=A/(E_{0+}-E_{0-})$, A is the hyperfine splitting, and we have separated space and spin wave functions. The change associated with dilation is

$$\delta\psi_{0+}=\delta\varphi_1(\mathbf{r})\chi(+)+\tfrac{1}{2}(\delta a)\varphi_1(\mathbf{r})\chi(-)+\tfrac{1}{2}(a\delta\varphi_1)(\mathbf{r})\chi(-),$$

and we find

$$(E_{0+}-E_{0-})(\psi_{0-},\delta\psi_+)=\tfrac{1}{2}\delta A,$$

where δA is the change in the hyperfine splitting with dilation. Writing this as

$$\delta A=\gamma A\Delta(0),$$

where γ is a multiplicative factor of order 10 to 100, we may readily calculate our desired matrix element. The transition rate, and hence relaxation time T_X, is given by

$$\frac{1}{T_X}=\frac{2\pi}{\hbar}\int\frac{d\mathbf{k}}{(2\pi)^3}\delta(\hbar sk-\hbar\omega_0)(N_k+1|\tfrac{1}{2}\delta A|N_k)^2,\qquad(4)$$

and we find

$$T_X=(8\pi\hbar^2s^5\rho)/(\omega_0^2kT\gamma^2A^2).\qquad(5)$$

For the case where the nuclear spin is not $\frac{1}{2}$, the relaxation rates for the electron in the spin-up state will differ slightly with different nuclear spin orientations. Let us define T_X as the inverse relaxation rate for the electron with spin up, and the nucleus with spin state $-I$. We then find the general expression

$$T_X=\frac{4\pi\hbar^2s^5\rho}{\omega_0^2kT\gamma^2IA^2},\qquad(6)$$

where A is the hyperfine splitting of two adjacent lines in the spectrum. In Table I we give the calculated values for T_X for various impurity states in silicon, under the assumption that $\gamma=50$, $(\omega_0/2\pi)=9000$ Mc/sec and $T=1.2°$ K.

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[12] G. Feher, Phys. Rev. **103**, 500 (1956) and private communication.

[13] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

It is perhaps worth indicating briefly the reasoning which has led us to estimate γ as being of order 10 to 100. The change in A with dilation is a change in $|\psi(0)|^2$ with dilation, where $\psi(r)$ is the simplified impurity electron wave function. We have

$$\psi(r)=F(r)\varphi(r), \tag{7}$$

where $F(r)$ is a modulating function corresponding to the solution of the effective mass equation for the bound electron, and $\varphi(r)$ is a Bloch-function appropriate to the energy minimum under consideration. $F(r)$ is given by

$$F(r)=\frac{1}{(\pi a^{*3})^{\frac{1}{2}}}\exp(-r/a^*), \tag{8}$$

where a^* is the effective radius of the impurity atom and is $\sim$20 A. If we consider only $|F(0)|^2$, we underestimate A considerably since $|\varphi(0)|^2$ introduces a multiplicative factor of order 100 and the breakdown of the effective-mass approximation in the central cell may introduce another factor of order 2. However, in calculating changes in $|\psi(0)|^2$ with dilation it is probably a good first approximation to consider only the changes in $|F(0)|^2$ (and hence in the radius of the electronic orbit), since the adiabatic response of the electrons to the dilation will tend to smooth out the changes taking place over the region of a cell. In any case we underestimate γ by this procedure. The change in the Bohr orbit is due to a change in the dielectric constant, κ_0, and in the effective mass, m^*, with dilation. These changes are in turn closely related to the change in the energy bands on dilation, and for Si such changes may be considerable. Thus a 10% dilation might easily lead to a 100% change in the dielectric constant and a 50% change in the effective mass. For Si, these changes add up, so that the figures we have quoted would lead us to estimate $\gamma\sim 45$. In general we should be surprised if γ were greater than 100 or less than 10.

(2) Modulation of Electron Spin-Orbit Coupling by Lattice Vibrations

We now consider T_1 for the electron due to spin-orbit coupling. One might expect that this would be an important relaxation mechanism. For the conduction electron spin resonance in semiconductors it is the dominant relaxation mechanism, according to the work of Elliott.[14] As we shall see, for the bound electron this mechanism is, in fact, singularly ineffective. We go into the calculation in some detail, because a comparison of the bound and conduction electron matrix elements for this process shows the important role adiabaticity plays in reducing the bound electron matrix elements. We first calculate $(\psi_{0-},E_{1+}\Delta\psi_{0+})$. This matrix will be nonvanishing because of the admixture in ψ_{0+} of excited states ψ_{n-} due to the spin-orbit coupling. Actually this admixture will be of two kinds—that associated with the spin-orbit coupling with the Si atoms and that associated with the impurity. The amount of admixture may be roughly characterized by a Δg due to each mechanism. At first sight it would appear that the contribution to Δg from each of these mechanisms should be roughly comparable, for although the electron sees many more Si atoms, it is somewhat pulled in toward the impurity atom in the cell surrounding that atom, and the energy differences to the excited impurity levels are only $\sim$1/100 those of the excited conduction-type levels. This hypothesis is easily subject to experimental verification, for if the sample is allowed to warm up, so that the impurity levels are ionized, it should be possible to observe a shift in the central value for Δg as one goes from an impurity resonance to a conduction electron resonance, the impurity atom being relatively ineffective in this latter case. Recent experimental indications[8] are that the contribution to Δg from the impurity atoms is at least an order of magnitude smaller than that arising from the Si atoms.

TABLE I. T_X for the impurity state spin resonance in silicon. I is the nuclear spin, A is the hyperfine splitting (in ergs) of two adjacent lines, and T_X is the calculated value in minutes assuming $(\omega_0/2\pi)=9000$ Mc/sec, $\gamma=50$, and $T=1.2°$ K.

Impurity	I	A	T_X
Li^7	3/2	0.056×10^{-19}	3.64×10^6
P^{31}	1/2	7.8×10^{-19}	560
As^{75}	3/2	14×10^{-19}	56
Sb^{121}	5/2	13×10^{-19}	41
Sb^{123}	7/2	7.0×10^{-19}	97

We carry out a much simplified calculation of the matrix elements and associated relaxation times. We first note that for constant dilation Δ, the matrix element will vanish. Expanding the dilation associated with the resonance phonon wave vector k_0, we find that

$$\Delta\cong k_0 q_k \mathbf{k}_0\cdot\mathbf{r} \tag{9}$$

gives the first nonvanishing contribution. For the spin-orbit coupling associated with the Si atoms, the excited state wave functions will be Bloch type, and

$$(\psi_{0-},E_{1+}\Delta\psi_{0+})\approx\Delta g_{\mathrm{Si}}E_{1+}k_0^2q_k(3a_0), \tag{10}$$

since the integral may be carried out over each cell and yields just the cell size for $\langle r\rangle_{\mathrm{Av}}$. Note that if we are here considering the conduction electron case, the term will still be about this size.

On the other hand, for the spin-orbit admixture associated with the impurity atom, the excited state wave functions are spread out over a distance of the size of the Bohr orbit, $\kappa_0(m/m^*)a_0$, and we may write:

$$(\psi_{0-},E_{1+}\Delta\psi_{0+})\approx\Delta g_{\mathrm{imp}}E_{1+}k_0^2q_kr_{n0} \tag{11}$$

for an excited atomic state n, where r_{n0} is the dipole matrix element for a transition from this state to the

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[14] R. J. Elliott, Phys. Rev. 96, 266 (1954).

ground state. We thus find, for the relaxation time associated with this mechanism,

$$\left(\frac{1}{T_1}\right)_{\mathrm{s.o.}}=\frac{E_{1+}{}^2\omega_0{}^4kT}{2\pi\hbar^2\rho s^7}\{(\Delta g)^2{}_{\mathrm{imp}}\langle r_{n0}\rangle^2+(\Delta g)^2S_i9a_0{}^2)\}. \quad (12)$$

For a frequency of 9000 Mc/sec, $E_1\sim 14$ ev, $\langle r\rangle_{n0}\sim 2.4\times 10^{-7}$ cm, and $T=1.2°$ K, we find

$$T_{\mathrm{s.o.}}\cong\frac{1.5}{\alpha^2+0.009}\ \mathrm{min}, \quad (13)$$

where α is the portion of Δg associated with the impurity atom, and we have assumed that $\alpha<1$. The maximum value of α is probably about $\frac{1}{10}$, so that $T_{\mathrm{s.o.}}\gtrsim 75$ min under the above conditions.

Actually our time, given by (12), represents an enormous overestimate of the effectiveness of this relaxation mechanism. For, as is shown in detail by Abrahams,[15] there is a "Van Vleck"[16] cancellation which occurs in the matrix elements (10) and (11). The left-hand side of Eq. (10), for instance, may be written as

$$([\psi_{0-}+C_+\psi_+{}']E_{1+}\Delta[\psi_{0+}-C_-\psi_-{}']).$$

Here $C_-\sim\lambda/(\Delta E-\hbar\omega_0)$, $C_+\sim\lambda/(\Delta E+\hbar\omega_0)$, λ is the spin-orbit splitting, and ΔE is of the order of the energy differences between the ground state and the levels which are admixed by spin-orbit coupling. Because C_- and C_+ are nearly equal, the matrix element is reduced by a factor of $(C_--C_+)/C_+\sim(\hbar\omega_0/\Delta E)$. For the most favorable case, given by Eq. (11), this reduction amounts to multiplying the relaxation time by a factor of $\sim 10^4$, so that this relaxation mechanism may be completely ruled out *vis-à-vis* the hyperfine interaction discussed above.[17]

We now consider the contribution of the matrix element, $(E_{0+}-E_{0-})(\psi_{0-},\delta\psi_+)$ for this process, and show that it will generally be quite a bit smaller than that we discuss above. Because of the applicability of the adiabatic approximation we here assume that the wave functions are also deformable. This will underestimate the matrix element somewhat, but almost certainly by not more than a factor of 10. If we use the deformable wave function hypothesis, we have

$$\delta\psi_+=-\delta\mathbf{R}\cdot\nabla\psi_{0+},$$

so that our matrix element is

$$(E_{0+}-E_{0-})(\psi_{0-}\delta\mathbf{R}\cdot\nabla\psi_{0+}).$$

It is instructive to compare this with that we should obtain for this matrix element in the conduction electron case. Here it is more reasonable to calculate $\delta\psi$ by perturbation-theoretic methods, although this will tend to overestimate the matrix element somewhat. If we used perturbation theory for $\delta\psi$, we would have

$$(\psi_{0-},\delta\psi_+)\approx\frac{(\psi_{0-},\delta V\psi_{0+})}{E_{0+}-E_{0-}}\approx\frac{(\psi_{0-},\delta\mathbf{R}\cdot\nabla V\psi_{0+})}{E_{0+}-E_{0-}},$$

where we have applied the deformable potential idea of Bloch to obtain a very rough estimate. Thus, for the conduction electron we have

$$(E_{0+}-E_{0-})(\psi_{0-},\delta\psi_+)\approx(\psi_{0-},\delta\mathbf{R}\cdot\nabla V\psi_{0+}).$$

This estimate of the matrix element leads to order of magnitude agreement with experiment[14] and corresponds to a relaxation time $T_1\sim 10^{-5}$ sec at helium temperatures for the conduction electron resonance. The ratio of the bound electron matrix element to the conduction electron matrix element is $\sim\hbar\omega_0/\mathrm{ev}\sim 10^{-5}$, so that even increasing the bound electron matrix element by a factor of 10 leads us to a relaxation time of at least 1000 sec. The estimate does not include an additional effect which acts to increase the time by a factor of ~ 30; this comes from the difference in the effective density of states for the two cases, and has its origin in the fact that only one phonon can contribute to the bound electron case. Thus, the mechanism is clearly ineffective. The physical origin of the disparity between the conduction electron matrix element and the bound-electron term lies in the fact that the matrix element can only be appreciable when there are considerable variations in the effective potential acting on the electron within a given unit cell. This may occur for the conduction electron. However, because the bound electron responds so nearly adiabatically, effects of this sort are enormously reduced by about the order of magnitude discussed.

(3) Modulation of the Hyperfine Coupling with Si^{29} Nuclei by Lattice Vibrations

The modulation by lattice vibrations of the hyperfine interaction between the impurity electron and the Si^{29} nuclei in the sample (natural abundance 4.68%) can also lead to spin-lattice relaxation of the electron spin-flip-only type.[18] The matrix element for the interaction

TABLE II. (T_{Si}/T_X) for impurity states in silicon. The values for the lattice sum, $S^{\frac{1}{2}}(k_0)$, are estimated from the work of Kohn.[19]

Impurity	I	g	$\lvert\psi(0)\rvert^2$	$S^{\frac{1}{2}}(k_0)$	T_{Si}/T_X
Li^7	3/2	2.17	0.055×10^{25}	4.7×10^{21}	0.1
P^{31}	1/2	2.26	0.44×10^{24}	10×10^{21}	150
As^{75}	3/2	0.957	1.80×10^{24}	12×10^{21}	1000
Sb^{121}	5/2	1.37	1.20×10^{24}	10×10^{21}	2000
Sb^{123}	7/2	0.724	1.20×10^{24}	10×10^{21}	820

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[15] E. Abrahams (to be published).

[16] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

[17] A similar cancellation does not occur for the conduction electron case because C_- and C_+ there have quite different angular dependences.

[18] We should like to thank Dr. George Feher for suggesting that this mechanism might be important.

with a Si^{29} atom on the ith lattice site may be written as

$$\delta A_i = \gamma_i A_i \Delta(0)/2.$$

δA_i is the change in the hyperfine interaction of the electron with the ith Si^{29} atom as a consequency of the dilation Δ and γ_i is the appropriate multiplicative factor. We have

$$A_i = \frac{32\pi}{3}|\psi(r_i)|^2 \mu_{\mathrm{Si}}\mu_B \cong \frac{32\pi}{3}\left(\frac{1}{\pi a^{*3}}\right)\exp\left(\frac{-2r_i}{a^*}\right)|\varphi(0)|^2\mu_{\mathrm{Si}}\mu_B,$$

where r_i is the distance of the ith Si^{29} atom from the impurity nucleus. Again neglecting the change in $|\varphi(0)|^2$ with dilation, we find

$$\gamma_i \sim [2r_i/(a^*)^2 - 3/a^*]\partial a^*/\partial\Delta.$$

We neglect $2r_i/(a^*)^2$ with respect to $3/a^*$, an approximation which will lead us to overestimate γ_i for all the lattice sites of interest (where $2r_i/a^* \gg 3$, A_i is so far reduced as to be essentially ineffective). We then have $\gamma_i = \gamma$, i.e., the multiplicative factor is just what we found for the change in the electron-impurity hyperfine interaction with dilation. One may then easily show that the ratio of the relaxation time for the process we are considering, T_{Si}, to T_X for a given impurity nucleus, is

$$T_{\mathrm{Si}}/T_X = [2Ig^2|\psi(0)|^4]/[fg_{\mathrm{Si}}^2 \textstyle\sum_i \psi^4(r_i)],$$

where I and g are the spin and g value for the impurity nucleus, and f is the fraction of Si^{29} atoms in the sample (4.68% natural abundance).

Kohn[19] has calculated $\sum_i|\psi^4(r_i)|$ for various impurity atoms in Si. He finds that it may be well approximated by

$$\textstyle\sum_i \psi^4(r_i) = (1/36)[\eta S^{\frac{1}{2}}(k_0)]^2,$$

where η represents the extent to which the Bloch function is pulled in at the center of each silicon cell, and is ~ 200,[10] while $S^{\frac{1}{2}}(k_0)$ is a lattice sum which depends on the exact position, k_0, of the six energy minima in silicon.

In Table II we list estimated values of $S^{\frac{1}{2}}(k_0)$, and the ratio of T_{Si} to T_X for various impurity centers. We see that T_{Si} is faster than T_X for Li, but that it is considerably slower for the other impurity centers. There is some uncertainty in this calculation, because we do not yet know with certainty the value of k_0. However, even if we take the maximum values for $S^{\frac{1}{2}}(k_0)$ which Kohn calculates (a factor of four higher than the quoted values, found for $k_0 = 0$), we still do not find that T_{Si} competes with T_X for P, As, or Sb.

(4) Modulation of the Exchange Coupling between Neighboring Impurities

The hyperfine relaxation mechanism may well be the most effective one in extremely pure samples for all but Li-doped samples. However, the great reduction in relaxation times (from a few seconds to $\sim 10^{-5}$ sec) observed by Feher *et al.* as the impurity concentration is increased from 10^{17} to 4×10^{17} in P-doped silicon clearly cannot be explained on this mechanism. Because of the strong concentration dependence, we decided to investigate whether the fast relaxation time could be associated with the presence of a cluster of impurity atoms. We first consider the mutual flip of *two* impurity centers in which a net transfer of energy to or from the lattice results. This transition comes from a modulation of the exchange coupling between the two impurity electrons.

The calculation may be carried out in directly analogous fashion to that for the hyperfine interaction. If the exchange interaction is $J\mathbf{S}_1\cdot\mathbf{S}_2$, the matrix element for spin flip is given by

$$\delta J = \tfrac{1}{2}CJ\Delta(0), \tag{14}$$

where C is a suitable multiplicative factor. The transition rate is

$$\frac{1}{T} = \frac{2\pi}{\hbar}\int\frac{d\mathbf{k}}{(2\pi)^3}\delta(\hbar sk - \hbar\omega)|(n_k,\delta J,n_{k+1})|^2, \tag{15}$$

where ω is the difference in hyperfine splitting frequency for the two electrons. We find for the relaxation time,

$$T_{\mathrm{exch}} = 8\pi\hbar^2 s^5\rho/(\omega^2 kTC^2J^2), \tag{16}$$

and the ratio of T_{exch} and T_X may be written as

$$T_X/T_{\mathrm{exch}} = C^2J^2\omega^2/(\gamma^2A^2\omega_0^2). \tag{17}$$

J will be proportional to $\exp(-2r/a^*)$, where r is the distance between the impurities and a^* is the "dielectric Bohr radius." We have

$$\frac{1}{J}\frac{dJ}{d\Delta} = \frac{d}{d\Delta}\ln J = -\frac{d}{d\Delta}\frac{2r}{a^*} = \frac{2r}{a^*}\left(\frac{1}{a^*}\frac{da^*}{d\Delta}\right).$$

By way of comparison, we know that $A \cong \mathrm{const}/(a^*)^3$ (from the F function of Kohn and Luttinger) and

$$\frac{1}{A}\frac{dA}{d\Delta} = -\frac{3}{a^*}\frac{da^*}{d\Delta}.$$

Hence $C/\gamma \cong 2r/3a^*$ and

$$\frac{T_X}{T_{\mathrm{exch}}} = \left(\frac{2r}{3a^*}\right)^2\left(\frac{J}{A}\right)^2\left(\frac{\omega^2}{\omega_0^2}\right).$$

But $\omega = A/\hbar$, so that we finally obtain

$$T_X/T_{\mathrm{exch}} = (2r/3a^*)^2(J/\hbar\omega_0)^2. \tag{18}$$

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[19] W. Kohn, Phys. Rev. **105**, 509 (1957).

For a concentration of 3×10^{16} impurity atoms per cc, we estimate r, the most likely nearest neighboring spacing, as $\sim$87 A, for which value the exchange integral J is $\sim$0.88 gauss. Hence for an applied field of 3000 gauss, we have $T_{\text{exch}}\sim 4\times 10^5 T_X$. For a concentration of 10^{17} impurity atoms/cc, we find $T_{\text{exch}}\sim 225 T_X$. Hence we may rule out this mechanism.

(5) Exchange Scattering

In the case that there are electrons in the conduction band, we may encounter additional relaxation mechanisms for the bound electron. Two such mechanisms are the magnetic interaction of the bound spin with that of a conduction electron and the bound spin with the field of the moving change of a conduction electron. The calculation of these processes is given in the forthcoming paper by Abrahams.[15]

Another process that may occur when conduction electrons are present is the exchange scattering in which the impurity and conduction electrons change places. The conduction electron then relaxes presumably via a spin-orbit mechanism which could be fairly rapid.

The analysis of the exchange scattering is interesting, representing another case of coupled spins. We define the following quantities: n_+, $n_-\equiv$number of conduction electrons with spins up and down, respectively; N_+, N_-=number of impurity electrons with spins up and down. Then we can write differential equations for N_+ and n_+ as functions of time:

$$dN_+/dt=(N_-n_+-N_+n_-)U \tag{19a}$$

and

$$dn_+/dt=(N_+n_--N_-n_+)U+(W_{12}n_--W_{21}n_+). \tag{19b}$$

The quantity U is a probability of transition by exchange. The first equation represents the fact that mutual flips are required for an exchange process to change the impurity atom spin population. In the second equation the quantities W_{12} and W_{21} are probabilities of the conduction electron undergoing a spin flip due to a relaxation process. W_{12} and W_{21} differ slightly since at thermal equilibrium $n_-\neq n_+$. These equations can be solved readily. In particular, if we define the quantities x and y which characterize the population difference in + and − states by $N_+=\frac{1}{2}N(1+x)$ and $n_+=\frac{1}{2}n(1+y)$, we have two equations for x and y:

$$dx/dt=nU(y-x) \tag{20a}$$

and

$$dy/dt=NU(x-y)+W^--W^+y, \tag{20b}$$

where $W^-=W_{12}-W_{21}$ and $W^+=W_{12}+W_{21}$. By noting the form of the differential equation for dy/dt, we see that $1/W^+$ is the spin-lattice relaxation time for conduction electrons alone. Moreover, if the exchange term were missing, we see that in the steady state, $y=W^-/W^+$. Therefore W^-/W^+ must represent the thermal equilibrium value of y, the fractional spin excess in the lower state. The steady state solution of the pair of equations is $x=y$, $y=W^-/W^+$. In other words, both spin distributions for impurity and for bound electron are in thermal equilibrium.

If the spins are disturbed from thermal equilibrium, they will return, the rate of return being described by *two* characteristics times or their inverse, the relaxation rates. The relaxation rates are given by

$$\frac{\alpha_\pm}{nU}=\left(\frac{N}{n}+\frac{W^+}{nU}+1\right)\pm\left[\left(\frac{N}{n}+\frac{W^+}{nU}+1\right)^2-\frac{4W^+}{nU}\right]^{\frac{1}{2}}. \tag{21}$$

The slower rate, which will control the relaxation, is approximately $W^+/[1+(N/n)+(W^+/nU)]$ and hence is always slower than W^+ alone. We see that if W^+ is very large, so that the conduction electrons are in thermal equilibrium, our rate becomes nU, which is essentially the rate at which an impurity atom experiences collisions. We can estimate this time because $\frac{1}{2}U=\sigma V$, where σ is the cross section for spin exchange, and V the velocity of conduction electrons. The cross section can be estimated from the approximate formula for exchange scattering of electrons from hydrogen[20]: $\sigma=144\pi\hbar^4/m^2e^4$. The cross section in silicon can then be computed by assuming a dielectric constant, giving $\sigma=3\times 10^{-12}$ cm^2. If we take V as 10^6 cm/sec, $U=6\times 10^{-6}$/sec, and $nU=6\times 10^{-6}n$. For $n=10^8$ this gives a relaxation rate of 6×10^2/sec (or a time of 1.6×10^{-3} sec) provided the relaxation rate of conduction electrons is sufficiently rapid. Actually, however, it would be very difficult to achieve this situation because this requires $W^+\gg NU$. For 10^{16} impurity atoms/cm^3 we required W^+ large compared to $6\times 10^{-6}\times 10^{16}=6\times 10^{10}$. At room temperatures W^+ is probably only 10^9, and at He temperatures it is considerably less, so that we find that our relaxation rate is given approximately by W^+n/N. That is, the conduction electrons are so few that they gain energy from exchange collisions faster than they can give it up. In the helium range the conduction electron line width reported by Portis *et al.*[21] is about 2 gauss, indicating a relaxation rate of 4×10^7/sec for W^+. Hence, if $n/N=10^{-12}$ we would have a relaxation time of about 400 minutes. Such large values of n/N are unlikely as a result of thermal ionization in the low-temperature range, although presumably at 20°K or above the excitation could readily occur.

IV. DISCUSSION OF RESULTS AND COMPARISON WITH EXPERIMENT

Although in the preceding section we have estimated the various relaxation times in somewhat cavalier fashion, our results should be useful as an indication of what relaxation mechanisms are likely to be most effective in very pure samples. They should also provide

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[20] J. R. Oppenheimer, Phys. Rev. **32**, 361 (1928).

[21] Portis, Kip, Kittel, and Brattain, Phys. Rev. **90**, 988 (1953).

a qualitative estimate of the relaxation times one expects to encounter in such pure samples. In what follows, we shall define a pure sample as one in which concentration-dependent mechanisms are unimportant. This is a convenient definition because thus far we have not been able to invent an efficient concentration-dependent relaxation mechanism. We shall consider below whether experiments on "pure" samples (by the above definition) has thus far been carried out.

Our principle conclusion is that in "pure" samples at helium temperatures the relaxation times are all very long. We find that T_S is shorter than T_X for Li-doped samples, but even here T_S is 3.64×10^5 minutes at 1.2° K and 9000 Mc/sec. For P-, As-, and Sb-doped samples we find that T_X should be faster than T_S, so that nuclear polarization via the first or second transient effects we have discussed above should occur for sufficiently pure samples. Furthermore, the purity required for As or Sb samples will be less than that required for a P-doped sample, since the T_X for the foregoing samples is an order of magnitude faster.

Abragam and Combrisson[7] and Feher[8] have recently verified the foregoing theoretical predictions for As-doped silicon. Abragam and Combrisson worked with a sample with a concentration of $\sim10^{17}$ As atoms/cc. They observed the first transient effect described above. By measuring the relative rate at which the extreme and median lines of the hyperfine multiplet grow, they found a ratio of $T_X/T_S=\frac{1}{2}$. By measuring the growth of an extreme line with time, they obtain $T_S\sim20$ min, so that T_X was ~10 min in their sample. Our theoretical prediction (for their experimental arrangement of 9000 Mc/sec and 2° K) is $T_X=34$ min. Feher worked with a sample containing 3.5×10^{16} As atoms/cc. He used a technique similar to that of Abragam and Combrisson. At 1.2° K and 9000 Mc/sec, he finds $(T_X/T_S)=\frac{1}{2}$, $T_S=80$ min and $T_X=40$ min, while our predicted value of T_X is 56 min. In view of our rough estimate of γ, we regard the agreement between the theoretical and experimental values of γ as quite satisfactory.

The situation with regard to T_S is somewhat puzzling. The value found by Abragam and Combrisson of 20 min is considerably less than any T_S we have calculated thus far. Furthermore, they do not find a quadratic field dependence for T_S, as one would expect for any first order phonon-induced transition. Instead they find that T_S is independent of field between 1000 and 10 000 gauss. Furthermore, they find for T_S a temperature variation much stronger than $1/T$; T_S is ~1 min at 4° K and ~1 sec at 8° K. We are inclined to believe that this rapid temperature variation and lack of field dependence is produced by a concentration-dependent mechanism whose origin is at present uncertain, rather than to any of the mechanisms discussed in this paper.

We are in part led to this conclusion by Feher's results with P-doped Si. There even in the purest samples he has investigated (2.5×10^{16} P atoms/cc), T_X appears to be slow compared to T_S. Further, T_S is of the order of minutes at 1.2° K and varies much more rapidly with temperature than a $1/T$ law. And, as we have mentioned, T_S is strongly concentration-dependent, when the P concentration is increased above this value. Thus we would classify even 2.5×10^{16}/cc P-doped silicon as "impure" in the sense of our discussion above.

Finally we might mention that certain of Feher's experiments may be explained by the exchange scattering with free electrons that we discussed in the preceding section. Feher finds that shining light on a sample acts to reduce the relaxation time markedly.[22] For instance, he finds that shining light on a P-doped sample (2.5×10^{16}/cc) at 4° K reduces the relaxation time from 20 to 2.6 sec. Such a reduction would be accomplished provided the light produced 2.5×10^{8} conduction electrons, a not unreasonable assumption.

The research described in this paper was begun while all three authors were at the University of Illinois. One of us (D.P.) has continued work on the problem while a summer visitor at Bell Telephone Laboratories, Murray Hill, New Jersey; his work carried out there was notably aided by the stimulating atmosphere provided by the staff and management. We should like to acknowledge with pleasure helpful conversations on these and related topics with Dr. E. Abrahams, Dr. P. W. Anderson, Dr. G. Feher, Dr. R. C. Fletcher, and Dr. W. Kohn.

APPENDIX

Kaplan[4] has proposed an explanation of Honig's[3] postulated 100% nuclear polarization. Although the original experimental interpretation has proved incorrect, the question still remains whether Kaplan's theory might not apply to some cases. We wish to discuss briefly some objections to Kaplan's proposal.

The usual difficulty in aligning spins by application of an alternating magnetic field as a spin pump is that the field induces transitions in both directions. There is no preferred sense of spin flips. Kaplan does not discuss reverse transitions, and thus we are led to conclude that the polarization results from a unidirectional flipping mechanism. The physical basis seems to be that the nuclear transition removes the paramagnetic center from resonance so that no reverse transition occurs. It was this unidirectional feature that originally bothered us most about Kaplan's theory. We believe that his proposal is in error for the following reasons.

Kaplan gives two justifications of his formula—one semiclassical, the other quantum-mechanical. In the former he solves the hyperfine interaction to first order, neglecting the x-y components of the interaction. He

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

then considers that as a result of the electron spin flips, the *x-y* components behave randomly, possessing frequency components which induce nuclear transitions. We believe that the basic error in this approach is to consider the *x-y* coupling to be random. One can solve the hyperfine interaction exactly. In fact, inclusion of the *x-y* terms produces energy shifts which are much bigger than the line widths or alternating fields. One might say that coherent effects dominate. There is no transverse field "left over" to fluctuate.

The quantum-mechanical treatment is a second-order perturbation theory modified to include the effect of electron spin transitions. We point out to begin with that the calculation is second order simply because the first-order solution does not solve the hyperfine problem exactly. If one starts with the exact solution of the hyperfine problem, one has matrix elements of the alternating field between Kaplan's initial and final states. Of course, the energy difference is wrong, and one gets transitions only if the level widths are wide enough to satisfy the energy conservation. Clearly such a process is not unidirectional because the matrix elements are Hermitian.

Kaplan's calculation is not quite equivalent to this, however, because he modifies the second-order perturbation theory to include the effect of induced electron transitions. His modification consists of an assumed time dependence of the probability amplitude, a_i, of the initial state. Ordinarily one assumes that $a_i=1$. Following Weisskopf and Wigner, Kaplan assumes an exponential time dependence, the decay being $T_{\mathrm{rf}}{}^{\mathrm{el}}$ in Kaplan's notation, the inverse of the electron transition probability in the alternating field. We feel this approach is incorrect, because once again it overlooks other effects which surely dominate. To compute $T_{\mathrm{rf}}{}^{\mathrm{el}}$, Kaplan assumes a level broadening characterized by a T_2. As he points out, we do not wish to include static broadening in T_2, but only the natural breadth of an individual impurity level. He attributes the breadth to spin coupling with other impurities. In order to avoid the complication of including two impurity atoms, let us assume instead that the natural breadth is due to electron spin-lattice relaxation. Then we see two effects result. In the first place, the energy denominators are no longer so sharply resonant. In the second place, the lifetime of the initial state is not $T_{\mathrm{rf}}{}^{\mathrm{el}}$ but T_1, presumed shorter. If T_1 is *not* shorter, we cannot assume an exponential decay of a_i since the microwave field will carry the electron back and forth up and down as in a molecular beam experiment. If we do not assume that $T_1=T_2$, similar considerations apply.

We believe, therefore, that the correct method of computing the transition rate involves first order perturbation between the exact states of the hyperfine interaction. The transition probability becomes very small since it is nonresonant, and moreover the transitions are no longer unidirectional. No large polarization results.