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Donor Electron Spin Relaxation in Silicon*

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A study of donor electron spin relaxation which can occur due to the presence of spin-orbit coupling is carried out. It is found that at helium temperatures both the direct and Raman processes are too weak to be observed, but that at 14°K the Raman process yields a relaxation time of 1 sec.

Several mechanisms of relaxation due to the interaction with conduction electrons are also discussed. It is found that none of them can compete with the exchange-scattering process considered by Pines, Bardeen, and Slichter.

I. INTRODUCTION

THE recent work of Feher, Fletcher, and coworkers[1] on the electron spin resonance of donor states in silicon has led to extensive discussion of the properties of these states. Kohn and Luttinger have developed the effective-mass formalism[2] for impurity states in semiconductors[3] and have been able to give approximate wave functions which account for the experimentally observed hyperfine splitting of the donor electron resonance.[4]

The relaxation time of the donor electron spin turns out to be quite long at low concentrations, of the order of minutes and longer. At concentrations greater than 4×10^{16} per cc, the relaxation times shorten to seconds and are highly concentration-dependent.[5] Furthermore, a marked decrease of the relaxation time has been observed when light is incident upon the sample.[6] Pines, Bardeen, and Slichter[7] have proposed several methods for producing nuclear polarization in the case where the electron spin relaxation time is very long. In the course of this work, they investigated some of the mechanisms of relaxation of the donor electron spins.

In relatively pure samples there are two important types of relaxation processes. In one, the electron spin and the donor-nucleus spin flip simultaneously by way of the hyperfine interaction. The relaxation time T_x for this process has been calculated in PBS and gives good agreement with experiment. The second type of relaxation involves the electron spin only. There are several interactions which lead to a process of this sort and two of these have been discussed by PBS: the vibrational modulation of the electron spin-orbit coupling and the vibrational modulation of the hyperfine interaction of the electron spin with Si^{29} nuclei. The relaxation time T_s for electron-spin-only processes as calculated by PBS is much longer than that which is observed and they conclude that the observed T_s must be due to a concentration-dependent mechanism as yet unknown.

In the case that there are electrons present in the conduction band of the semiconductor, one is led to consider the interaction between the conduction electrons and the bound donor electron. An exchange-scattering process which flips the spins of both electrons has been considered by PBS and they find that if there are as many as 10^8 conduction electrons per cc, the relaxation time will be in the neighborhood of the experimental values of reference 6. One would, of course, expect a much smaller concentration of thermally ionized electrons in the conduction band at the temperatures at which the experiments are carried out, 4°K and below, so that this process is only of interest in relation to those experiments in which light is incident upon the sample.

In this report, we propose to discuss two topics: first, how the effects of spin-orbit coupling lead to a relaxation time T_s and second, several conduction-electron mechanisms not considered by PBS.

II. SPIN-ORBIT COUPLING

As a result of the work of Kohn and Luttinger[3,4] we now have a good picture of the nature of the wave function of the bound donor electron. In a region outside the atomic cell in which the impurity is located, the effective-mass approximation is valid and the wave function for the ground state may be written

$$\Psi(\mathbf{r})=\frac{1}{\sqrt{6}}\sum_{i=1}^{6} F_i(\mathbf{r})\psi_i(\mathbf{r}), \tag{1}$$

where i labels the six equivalent conduction-band energy minima at $\mathbf{k}_i$ in (100) directions in the wave vector space of the silicon crystal. The Bloch function in the perfect crystal associated with the ith minimum is ψ_i and F_i is a slowly varying function which is a solution of a Schrödinger equation for the potential due to the impurity but with the ordinary mass replaced by the anisotropic effective mass appropriate to the ith minimum. There are two ways in which this wave function must be modified if we take account of the

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[1] Fletcher, Yager, Pearson, Holden, Read, and Merritt, Phys. Rev. 94, 1392 (1954); Fletcher, Yager, Pearson, and Merritt 95, 844 (1954); Feher, Fletcher, and Gere, Phys. Rev. 100, 1784 (1955).

[2] J. M. Luttinger and W. Kohn, Phys. Rev. 97, 869 (1955).

[3] W. Kohn and J. M. Luttinger, Phys. Rev. 98, 915 (1955).

[4] W. Kohn and J. M. Luttinger, Phys. Rev. 97, 883 (1955).

[5] Reference 1 and private communication from G. Feher.

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

[7] Pines, Bardeen, and Slichter, Phys. Rev. 106, 489 (1957), hereafter referred to as PBS.

spin-orbit coupling. As is well known,[8] the Bloch function in the presence of spin-orbit coupling must be modified. For the nondegenerate conduction band, this modification is quite simple. The effect of spin-orbit coupling is to mix into ψ_i a small admixture of opposite spin. One must also consider modifications of the F_i due to the fact that there will be a spin-orbit interaction associated with the impurity atom. Actually, because of the short range of the spin-orbit interaction, the effect takes place quite close to the impurity, in a region where the effective-mass approximation breaks down. However, one can estimate the importance of the spin-orbit coupling associated with the impurity. Experiments[5] have been carried out using impurities (Li, P, As, Sb) which in the free atom have spin-orbit coupling constants covering a range characterized by a factor of almost 100. In each case, the observed shift, Δg, of the electron spin resonance g factor from the free-electron value has been the same and about equal to the Δg observed for the conduction electron resonance in silicon.[9] We may therefore expect the contribution to Δg from the impurity spin-orbit coupling to be not greater than 0.01 of that due to the spin-orbit coupling associated with the silicon atoms. If one were to set out to calculate the spin-orbit coupling due to the impurity one would abandon the effective-mass approximation in favor of an atomic approximation in the central atomic cell. Because the wave function is primarily of s-character,[4] one would find the effect to be small, as the experimental results indicate. Let us for the moment assume, then, that in the relaxation effects also, the effects of impurity spin-orbit coupling are small compared to the spin-orbit interaction with the atoms of the host silicon crystal.

A. Direct Relaxation Process

We now turn to a consideration of the spin-lattice relaxation associated with the spin-orbit coupling due to the silicon atoms. This coupling will occur at some distance from the impurity and we expect that the effective-mass wave function of Eq. (1) will be quite good. Of course, we modify the Bloch functions to account for the spin-orbit coupling in the perfect lattice.

As shown by PBS, the matrix element for donor electron spin flip induced by variations in the electrostatic potential can be written, in the deformation-potential approximation,[10]

$$(\Psi_0{}^+,\delta V\Psi_0{}^-)=(\Psi_0{}^+,E_1\Delta\Psi_0{}^-). \tag{2}$$

Here δV and E_1 are the change in potential and total energy associated with a dilation $\Delta(\mathbf{r})$, and $\Psi_0{}^+$ for example, is the ground state wave function [Eq. (1)] for spin up. The matrix element on the right does not vanish since there is a small admixture of opposite spin in each wave function due to the spin-orbit coupling. We have ignored another term on the right which arises because the dilation produces a modulation of the amount of admixture of spin down in $\Psi_0{}^+$. This term has been discussed by PBS and they show that it must be small due to the adiabatic response of the bound-electron wave function to variations of the electrostatic potential. When their result is corrected for "Van Vleck cancellation" (see below), the relaxation time arising from this term is of order 10^8 sec.

For longitudinal waves, we have

$$\Delta=\boldsymbol{\nabla}\cdot\delta\mathbf{R}(\mathbf{r})=i(\hbar/2\rho Vs)^{\frac{1}{2}}q^{\frac{1}{2}}[b_qe^{i\mathbf{q}\cdot\mathbf{r}}-b_q{}^*e^{-i\mathbf{q}\cdot\mathbf{r}}],$$

where ρ is the density of the silicon crystal whose volume is V, s is the velocity of sound, and b_q, $b_q{}^*$ are destruction and creation operators for phonons of wave vector $\mathbf{q}$. The interaction, Eq. (2), represents the absorption or emission of a phonon with the simultaneous flip of the bound-electron spin and is called a "direct process."

The matrix element for the direct process has been estimated very roughly by PBS to lead to a relaxation time of the order of 100 minutes. We shall now show that this is a serious underestimate of the relaxation time.

We wish to calculate a matrix element $\langle H'\rangle=(\Psi_0{}^+,H'\Psi_0{}^-)$ where the initial state has n_q+1 phonons of wave vector $\mathbf{q}$ and the final state has one less. H' is the matrix element for absorption of a phonon:

$$H'=iE_1(\hbar/2\rho Vs)^{\frac{1}{2}}q^{\frac{1}{2}}(n_q+1)^{\frac{1}{2}}e^{i\mathbf{q}\cdot\mathbf{r}}. \tag{3}$$

The ground state wave functions, including the spin-orbit coupling in the Bloch functions, may be written

$$\begin{aligned}\Psi_0{}^\pm&=A\,|\pm\rangle+M^\pm B^\pm|\mp\rangle,\\ A&=\frac{1}{\sqrt{6}}\sum_{i=1}^{6}F_i\psi_i,\\ B^\pm&=\frac{1}{\sqrt{6}}\sum_{i=1}^{6}F_i\varphi_i{}^\pm,\end{aligned} \tag{4}$$

where ψ_i in the Bloch function for the ith minimum in the absence of spin-orbit coupling and $M^+\varphi_i{}^+$, for example, is the amount of admixture of *down* spin into the Bloch function of *up* spin due to the spin-orbit coupling. If one calculates this admixture by perturbation theory,[8] $M^\pm$ is a matrix element of the order of $\lambda/(-\Delta\pm g\beta H)$, where λ is a spin-orbit coupling constant and Δ is the energy separation to the next excited conduction-band state which is mixed in by the spin-orbit interaction. The Bloch function for the excited state mixed into an unperturbed Bloch function with spin up from the ith minimum is $\varphi_i{}^+$. The spin-orbit perturbation is periodic in the crystal and therefore $\varphi_i{}^\pm$

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

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

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

has the same wave vector as ψ_i. The wave functions involved here have a symmetry such that the matrix element $M^{\pm}$ is real and independent of the minimum for which we are calculating the wave function.

The matrix element for the direct process takes the form

$$\langle H'\rangle = G(n_q+1)^{\frac{1}{2}}q^{\frac{1}{2}}[M^-(A,e^{i\mathbf{q}\cdot\mathbf{r}}B^-)+M^+(B^+,e^{i\mathbf{q}\cdot\mathbf{r}}A)],$$

where G represents the numerical factors in Eq. (3). As Van Vleck has previously pointed out,[11] a matrix element of this sort vanishes if $M^-=M^+$ due to the fact that $(B^-)^*=-B^+$. This "Van Vleck cancellation," which is a consequence of Kramers' theorem, leads to a reduction of the matrix element by a factor $2g\beta H/\Delta$. We then have

$$\langle H'\rangle = G(2g\beta H/\Delta)(n_q+1)^{\frac{1}{2}}q^{\frac{1}{2}}M(B^+,e^{i\mathbf{q}\cdot\mathbf{r}}A), \tag{5}$$

where M is of order λ/Δ; λ/Δ maybe estimated as just the g-shift Δg for the electron spin resonance.

We now estimate the matrix element appearing in Eq. (5). Our first approximation is to neglect the anisotropy in the effective mass. In this case,[3] the F_i are the same for each minimum and have the form of a hydrogenic $1s$ function with an effective Bohr radius $a=\hbar^2\kappa/m^*e^2\simeq 20$ A, where κ is the dielectric constant and m^* is an average effective mass $\sim 0.3m$. Our matrix element becomes

$$(B^+,e^{i\mathbf{q}\cdot\mathbf{r}}A)=\tfrac{1}{6}\sum_{ij}\int F^2(\mathbf{r})\varphi_i^{+*}e^{i\mathbf{q}\cdot\mathbf{r}}\psi_j d\mathbf{r}. \tag{6}$$

We now expand $F^2(\mathbf{r})$ in a Fourier series; its Fourier coefficients are $f(\boldsymbol{\lambda})$. We introduce $\varphi_i^+=v_i^+\exp(i\mathbf{k}_i\cdot\mathbf{r})$, $\psi_j=u_j\exp(i\mathbf{k}_j\cdot\mathbf{r})$. With this notation, (6) becomes

$$\tfrac{1}{6}\sum_{ij\lambda} f(\boldsymbol{\lambda})(v_i^+,u_je^{-i(\mathbf{k}_i-\mathbf{k}_j+\boldsymbol{\lambda}-\mathbf{q})\cdot\mathbf{r}}). \tag{7}$$

Now $v_i^{+*}u_j$ is periodic so that $\mathbf{k}_i-\mathbf{k}_j+\boldsymbol{\lambda}-\mathbf{q}=\mathbf{K}$, where $\mathbf{K}$ is a reciprocal lattice vector or zero. We next observe that $F^2(\mathbf{r})$ varies slowly with respect to the lattice parameter so that

$$f(\boldsymbol{\lambda})=(1/V)(1+\tfrac{1}{4}a^2\lambda^2)^{-2} \tag{8}$$

is small for λ's of the order of a reciprocal lattice vector since $Ka\sim 15$. Furthermore, the magnitude of the resonant phonon wave vector $q=g\beta H/\hbar s$ is only of the order of 10^5 cm^{-1}, so that the leading term in the matrix element comes from $i=j$, $\mathbf{K}=0$ and is

$$\tfrac{1}{6}\textstyle\sum_i f(\mathbf{q})(v_i^+,u_i).$$

This is zero because of the orthogonality of Bloch functions of the same wave vector from different bands. This result already reduces the matrix element as compared with that calculated by PBS. The next term comes from $i\neq j$, $\mathbf{K}=0$ and is

$$\tfrac{1}{6}\textstyle\sum_{ij} f(\mathbf{k}_i-\mathbf{k}_j-\mathbf{q})(v_i^+,u_j).$$

An investigation of the symmetry properties[12] of the ψ_i and $\varphi_i^{\pm}$ reveals that $(v_i^+,u_j)=S_{i,j}=-S_{-i,j}=-S_{i,-j}=-S_{j,i}=S_{-i,-j}$ and $S_{i,-i}=0$. This, together with the fact that $q\ll|\mathbf{k}_i-\mathbf{k}_j|$, which allows a convergent Taylor-series expansion of $f(\mathbf{k}_i-\mathbf{k}_j-\mathbf{q})$, yields zero for this term also. This means that the first nonzero terms involve λ's of the order of a reciprocal lattice vector, leading to a further reduction in the matrix element by a factor $\sim(2/Ka)^4\sim 4\times 10^{-4}$. The origin of this reduction is in the nature of the wave function for the bound donor states which are linear combinations of rapidly oscillating Bloch functions with slowly varying envelopes F_i. It is just the fact that the F_i are slowly varying which makes the term in the matrix element which connects the same minima essentially zero. The Bloch functions entering the ground state wave function have phase factors $\exp(i\mathbf{k}_i\cdot\mathbf{r})$ whose wave vectors $\mathbf{k}_i$ are symmetrically disposed in the six equivalent (100) directions and we find that the terms in the matrix element which connect unlike minima vanish due to a destructive interference between the Bloch functions. This result holds even if we do not neglect the anisotropy in the effective mass.

We conclude then that the Van Vleck cancellation and the phase cancellation increase the relaxation time estimated by PBS (75 min) to such an extent that it never can be observed. The estimate of PBS for the relaxation time due to impurity spin-orbit coupling, when corrected for Van Vleck cancellation and with the assumption that the fraction of Δg due to the impurity is about 0.01, gives $T_s\sim 10^9$ sec which is also out of reach.

B. Raman Processes

If we treat the interaction between the phonons and the donor electron in second order, we obtain Raman-type processes in which a phonon is scattered from a state q to a state p while the electron spin flips. The effective matrix element contains transitions to an excited orbital state with the emission or absorption of a phonon and then transitions back to the ground state with the absorption or emission of a phonon. The spin may flip either in the first transition or the second.

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

[12] The group of the wave vector for one of the minima in (100) directions is the group Δ [see C. Herring, J. Franklin Inst. **233**, 525 (1942)]. ψ_i transforms according to the identity representation Δ_1 of this group and $\varphi_i^{\pm}$ transforms according to one of the rows of the two-dimensional representation Δ_5. We select $\varphi_i^{\pm}$ to be that function belonging to Δ_5 which is connected to ψ_i by the spin-orbit perturbation $(\nabla V\times\mathbf{p})^{\pm}$. For example, for the (100) minimum, in an LCAO (localized combination of atomic orbitals) representation of the Bloch functions, the atomic orbitals entering ψ_i would be s and p_x functions and the atomic orbital in $\varphi_i^{\pm}$ would be a p_z function.

The matrix element is

$$\langle H'\rangle = G^2(pq)^{\frac{1}{2}}[n_q(n_p+1)]^{\frac{1}{2}}\sum_a \left\{\frac{1}{-\Delta_a-\hbar sq}\times[H_{p,-q}^{+}+H_{p,-q}^{-}] + \frac{1}{-\Delta_a+\hbar sp}[H_{-q,p}^{+}+H_{-q,p}^{-}]\right\}, \quad (9)$$

$$H_{p,q}^{\pm} = (\Psi_0^{+}, e^{i\mathbf{p}\cdot\mathbf{r}}\Psi_a^{\pm})(\Psi_a^{\pm}, e^{i\mathbf{q}\cdot\mathbf{r}}\Psi_0^{-}),$$

where Δ_a is the energy separation to the excited state whose wave function for spin up, say, is Ψ_a^{+}. We have neglected the Zeeman energy in the denominators since it is small and a Van Vleck cancellation does not occur here.

The lowest-lying excited state which enters the matrix element is the "1s state"[3] which transforms according to the polar vector representation T_1 of the symmetry group of the donor state, i.e., the tetrahedral group. However, the matrix elements for these states will be small due to the fact that only different minima will be connected even in those parts of the matrix element where the spin does not flip (see $H_{pq}^{\pm}$ above) and therefore a phase cancellation of the type discussed previously will reduce the matrix element. It is for this reason that there are no appreciable optical transitions to these states.[13] The states which make the largest contribute to our matrix element, as in the optical case, are the $2p$, $m=0$, ± 1 states. These states must be considered together since there is some interference in their contributions to the total matrix element. The $2p$ states are specified more precisely in the Appendix. The wave function for the ground state is the same as (4), where we may neglect the difference between M^{+} and M^{-}. The excited state wave functions may be written

$$\Psi_a^{\pm} = E_a|\pm\rangle + MF_a^{\pm}|\mp\rangle,$$

where E_a and $F_a^{\pm}$ are defined in the Appendix. The details of the calculation of the matrix element appear there also. We find

$$\langle H'\rangle = 2G^2M(pq)^{\frac{1}{2}}[n_q(n_p+1)]^{\frac{1}{2}}\hbar s(p+q) \times\sum\nolimits_a (h_{p,-q}^{a}-h_{-q,p}^{a}),$$

$$h_{p,-q}^{a} = (A, e^{i\mathbf{p}\cdot\mathbf{r}}E_a)(B^{+}, e^{-i\mathbf{q}\cdot\mathbf{r}}E_a), \quad (10)$$

where the sum is over the three $m=0$ states and three of the $m=\pm 1$ states. A typical result for one of these states is

$$h_{p,-q}^{1} = -i(2\Delta g/a^2k^4M)p_xq_z, \quad (11)$$

where k is the magnitude of the electron wave vector at a minimum. If $k_{\max}$ is the wave vector at the edge of the first zone, then $k\sim(3k_{\max}/4)$.[14] The terms for the other excited states have a similar structure. We combine our results and find

$$\langle H'\rangle = 16G^2(\Delta g/a^2k^4)[\hbar s(p+q)\delta/\Delta^3](pq)^{\frac{1}{2}} \times[n_q(n_p+1)]^{\frac{1}{2}}[(\mathbf{q}\times\mathbf{p})_x - i(\mathbf{q}\times\mathbf{p})_y],$$

where Δ is the mean energy separation to the $2p$ states and δ is the splitting between the $2p$, $m=0$ and $2p$, $m=\pm 1$ states.[12]

The relaxation time due to Raman processes is obtained from the usual expression

$$1/T_s = (2\pi/\hbar)\sum\nolimits_{p,q}|\langle H'\rangle|^2\delta[\hbar s(p-q)-g\beta H] = (8/\pi)^3[(12)!/9](E_1^4\delta^2/\Delta^6) \times[(\Delta g)^2/\hbar^{11}\rho^2 s^{14}a^4k^8](kT)^{13}. \quad (12)$$

In performing the integral over p, we have neglected $g\beta H$ in comparison to $\hbar sp$ and have used a low-temperature approximation such that $n_p(n_q+1)\simeq\exp(-\hbar sp/kT)$. An evaluation of T_s gives

$$T_s\sim 10^{15}T^{-13}.$$

The Raman process is clearly ineffective at helium temperatures, but because of its very rapid temperature dependence it will be of the order of 1 sec at 14°K and will begin to wash out the resonance at temperatures well below that of liquid air. A very rapid variation of relaxation time with temperature should be observed in the liquid hydrogen region.

III. INTERACTION WITH CONDUCTION ELECTRONS

In this section we treat the case where there may be electrons present in the conduction band of the semiconductor, either because of excitation by light or because of a very high concentration of impurities. Interactions between these electrons and the bound donor electrons can produce a spin flip of the donor electron and lead to a relaxation effect. In what follows we treat the electrons as free particles.

A. Coulomb Scattering

The Coulomb scattering of conduction electrons and bound electrons can produce a flip of the bound electron spin only, if we account for the spin-orbit admixture in the donor state. This process may be disposed of immediately since the matrix element involved is of the same sort as that considered in Sec. II-A for direct phonon absorption. We find an interaction operator similar to (3):

$$H' = (4\pi e^2/V)q^{-2}e^{i\mathbf{q}\cdot\mathbf{r}},$$

where $(4\pi e^2/Vq^2)$ is the Fourier transform of the Coulomb interaction and $\mathbf{q}$ is the momentum transfer to the conduction electron. The calculation becomes identical to that for direct phonon processes and suffers from both Van Vleck and phase cancellations.

B. Spin-Current Interaction

In this process, the bound electron spin experiences the magnetic field of a passing conduction electron and

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[13] W. Kohn, Phys. Rev. **98**, 1856 (1955).

[14] W. Kohn (private communication). This is a very tentative estimate.

flips its spin. The spin-orbit coupling is not involved. The calculation is straightforward, although somewhat lengthy. The matrix element involved describes a transition from a state $(1/V)^{\frac{1}{2}}\Psi_0^{+}(\mathbf{r}_1)e^{i\mathbf{p}\cdot\mathbf{r}_2}$ to a state $(1/V)^{\frac{1}{2}}\Psi_0^{-}(\mathbf{r}_1)e^{i\mathbf{q}\cdot\mathbf{r}_2}$ through an interaction

$$H_{\text{int}}=(\beta e/mc)\boldsymbol{\sigma}\cdot\mathbf{r}\times\mathbf{p}/r^3,$$

where $\boldsymbol{\sigma}$ is the spin operator for the bound electron, $\mathbf{p}$ is the momentum operator for the conduction electron whose wave function is $(1/V)^{\frac{1}{2}}e^{i\mathbf{p}\cdot\mathbf{r}}$ and $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$ is the relative coordinate. The matrix element is easily evaluated in the effective-mass approximation and the result inserted into the expression for the relaxation time (12). The integrals are quite tedious and the result is equivalent to one which may be obtained by a simple argument[15] which uses the technique discussed by Slichter and Pines.[16] The interaction energy is of order

$$\Delta E\sim(\beta e/mc)(mv/r^2),$$

where v is the velocity of the conduction electron. We have

$$\delta\omega=\Delta E/\hbar\sim(\tfrac{1}{2}r_0)(v/r^2),$$

where r_0 is the classical electron radius $=e^2/mc^2$. The correlation time is just the separation of the two electrons divided by the velocity v, so that

$$(\delta\omega)^2\tau_c=(\tfrac{1}{2}r_0)^2(v/r^3).$$

To get the relaxation time, we must sum this expression over r. If there are n_v conduction electrons per cc with velocity v, we have

$$1/T=(\tfrac{1}{2}r_0)^2n_vv\int_a^b\frac{4\pi r^2}{r^3}dr=\pi r_0^2n_vv\ln(b/a).$$

Here b is the maximum value of r and may be determined roughly by the requirement that energy be conserved in the scattering process:

$$b\sim1/\Delta k_{\min};\quad(\hbar^2k/m)\Delta k_{\min}=g\beta H.$$

The minimum value of r is just $a\sim1/k=\hbar/mv$ so that $b/a\sim E/\beta H$, where E is the conduction electron energy and we have taken $g=2$. The relaxation time is then

$$1/T=\pi r_0^2n_vv\ln(E/\beta H).$$

At 3000 gauss, for electrons of thermal energies at 4°K, we have $T\sim10^{18}/n$ sec and for electrons of 1-ev energy, we have $T\sim10^{16}/n$ sec. This mechanism is clearly ineffective compared to the exchange-scattering mechanism discussed by PBS since we can never expect n to be as large as 10^{12} per cc.

C. Spin-Spin Interaction

We treat now the dipole-dipole interaction between the conduction electron and the bound donor electron. In this process both spins flip and one must concern oneself with the relaxation rate of the conduction electrons as well. This has already been discussed by PBS and it is sufficient to compare the value for the transition probability U for the dipole-dipole flip with their U for the exchange scattering. We have

$$\begin{aligned}\delta\omega&\sim(1/\hbar)(\beta^2/r^3)\langle\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2\rangle\\&=(2/\hbar)\beta^2/r^3.\end{aligned}$$

As before, we have $\tau_c=r/v$ and $r_{\min}\sim\hbar/mv$. This gives

$$n_vU=n_v\int(\delta\omega)^2\tau_cd\mathbf{r}=(\tfrac{1}{2}\pi r_0^2)n_vv.$$

Our result is $U\sim10^{-25}v$ as compared with $U\sim6\times10^{-12}v$ for the exchange process. The dipole-dipole mechanism is also ineffective.

IV. CONCLUSION

We have discussed the effects of spin-orbit coupling on the relaxation time for donor electron spins in silicon. We find that at helium temperatures and below, the relaxation time T_s is much longer than that experimentally observed and that it is only at liquid hydrogen temperatures that the Raman process can be important. This result, when compared the considerations of PBS reinforces their conclusion that the observed T_s must be due to a concentration-dependent process of unknown origin. Feher's work[17] so far gives no evidence that the observed T_s at concentrations of 10^{16} donors/cc is concentration-independent; T_s is definitely concentration-dependent above 4×10^{16}.

We have considered also several mechanisms which can cause relaxation because of interactions between donor electrons and conduction electrons. In each case, the relaxation effects are much smaller than the exchange scattering discussed by Pines, Bardeen, and Slichter.

V. ACKNOWLEDGMENTS

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APPENDIX

We consider here some of the details of the Raman calculation of Sec. II B of the text. First, we specify the $2p$ donor states. The wave functions for these states may be written[3] $\sum_i\alpha_a^{(i)}F_i\psi_i$. If we number the minima in the (100), ($\bar{1}$00), (010), $\cdots$ directions $i=1,2,\cdots,6,$

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[15] The author is indebted to C. P. Slichter for pointing this out.

[16] D. Pines and C. P. Slichter, Phys. Rev. **100**, 1014 (1955).

[17] G. Feher (private communication).

respectively, then the $\alpha_a^{(i)}$ are

$$\left.\begin{aligned}\alpha_1^{(i)}&=(\tfrac{3}{2})^{\frac{1}{2}}(x,x,0,0,0,0)\\ \alpha_2^{(i)}&=(\tfrac{3}{2})^{\frac{1}{2}}(0,0,y,y,0,0)\\ \alpha_3^{(i)}&=(\tfrac{3}{2})^{\frac{1}{2}}(0,0,0,0,z,z)\end{aligned}\right\}2p,\ m=0,$$

$$\left.\begin{aligned}\alpha_4^{(i)}&=\tfrac{1}{2}\sqrt{3}(0,0,x,x,x,x)\\ \alpha_5^{(i)}&=\tfrac{1}{2}\sqrt{3}(y,y,0,0,y,y)\\ \alpha_6^{(i)}&=\tfrac{1}{2}\sqrt{3}(z,z,z,z,0,0)\\ \alpha_7^{(i)}&=\tfrac{1}{2}\sqrt{3}(0,0,z,-z,y,-y)\\ \alpha_8^{(i)}&=\tfrac{1}{2}\sqrt{3}(z,-z,0,0,x,-x)\\ \alpha_9^{(i)}&=\tfrac{1}{2}\sqrt{3}(y,-y,x,-x,0,0)\end{aligned}\right\}2p,\ m=\pm 1. \tag{A-1}$$

We have included here only excited states $a=1, 2, \cdots, 9$, which transform according to T_1. The reason is that in a matrix element of the form $(\Psi_a{}^+, e^{i\mathbf{q}\cdot\mathbf{r}}\Psi_0{}^+)$ [see Eq. (9)] no other states will contribute in a dipole approximation $\exp(i\mathbf{q}\cdot\mathbf{r})\sim 1+i(\mathbf{q}\cdot\mathbf{r})$ since $\mathbf{r}$ transforms according to T_1 and Ψ_0 transforms according to the identity representation A_1. Higher terms in the expansion of $\exp(i\mathbf{q}\cdot\mathbf{r})$ will be small because of the slow variation of the F_i.

With the $\alpha_a^{(i)}$ denoted above, the excited state wave functions may be written

$$\begin{aligned}\Psi_a{}^\pm&=E_a|\pm\rangle+MF_a{}^\pm|\mp\rangle,\\ E_a&=\sum\alpha_a{}^{(i)}F_i\psi_i,\\ F_a{}^\pm&=\sum\alpha_a{}^{(i)}F_i\varphi_i{}^\pm,\end{aligned}$$

where M is the matrix element defined in connection with Eq. (4). With this notation, a typical term of the matrix element (9) is

$$H_{p,-q}{}^+=M(A,e^{i\mathbf{p}\cdot\mathbf{r}}E_a)[(E_a,e^{-i\mathbf{q}\cdot\mathbf{r}}B^-)+(F_a{}^+,e^{-i\mathbf{q}\cdot\mathbf{r}}A)].$$

The term $[A, \exp(i\mathbf{p}\cdot\mathbf{r})E]$ may be evaluated approximately by a procedure similar to that used for the direct process. We expand $\alpha_a^{(i)}F^2(\mathbf{r})$ in a Fourier series, with Fourier coefficients $f_a^{(i)}(\boldsymbol{\lambda})=\frac{1}{2}iaf(\boldsymbol{\lambda})\lambda_a^{(i)}$ where $f(\boldsymbol{\lambda})$ is defined in (8) and $\lambda_a^{(i)}$ is the component of $\boldsymbol{\lambda}$ defined by $\alpha_a^{(i)}$. For example, $\lambda_5^{(2)}=\frac{1}{2}\sqrt{3}\lambda_y$ [see (A-1)]. With the same approximation used to treat Eq. (9), we find the leading term, for $i=j$,

$$(A,e^{i\mathbf{p}\cdot\mathbf{r}}E_a)=(V/\sqrt{6})\textstyle\sum_i f_a{}^{(i)}(\mathbf{p}). \tag{A-2}$$

The phonon wave vectors $\mathbf{p}$ which are of importance at helium temperatures have magnitude 10^6 cm^{-1} so that $pa\ll 1$ and an approximate expression for $f_a^{(i)}(\mathbf{p})$ is $(ia/2V)p_a^{(i)}$. In this approximation, the states $a=7, 8, 9$ give no contribution since for these $p_a^{(i)}=-p_a^{(-i)}$. Our result is then, for example,

$$(A,e^{i\mathbf{p}\cdot\mathbf{r}}E_1)=-\tfrac{1}{2}iap_x. \tag{A-3}$$

Using the fact that the states 7, 8, 9 do not contribute, we can combine the terms in (9) with the use of relations which can be established by investigating the symmetry properties of the Bloch functions ψ_i and $\varphi_i^\pm$: $A^*=A$, $(B^\pm)^*=-B^\pm$, $E^*=E$, $(F^\pm)^*=-F^\pm$. We obtain Eq. (10) of the text, and we must evaluate

$$h_{p,-q}{}^a=(A,e^{i\mathbf{p}\cdot\mathbf{r}}E_a)(B^+,e^{-i\mathbf{q}\cdot\mathbf{r}}E_a).$$

The first factor in $h_{p,-q}$ has already been evaluated in Eqs. (A-2) and (A-3). The second factor may be estimated in a similar manner. The result is

$$(B^+,e^{-i\mathbf{q}\cdot\mathbf{r}}E_a)=-(\tfrac{1}{6})^{\frac{1}{2}}\textstyle\sum_{ij}f_a{}^{(j)}(\mathbf{q}+\mathbf{k}_i-\mathbf{k}_j)S_{ij}. \tag{A-4}$$

We now expand $f_a^{(i)}(\mathbf{q}+\mathbf{k}_i-\mathbf{k}_j)$ in powers of $(q/|\mathbf{k}_i-\mathbf{k}_j|)$ and keep only the first term. The zeroth-order term makes no contribution by the orthogonality condition and we have, for (A-4),

$$(8/Va^3\sqrt{6})\textstyle\sum_{ij}[q_a{}^{(i)}-4\mathbf{q}\cdot(\mathbf{k}_i-\mathbf{k}_j)\times(k_i-k_j)_a{}^{(i)}/|\mathbf{k}_i-\mathbf{k}_j|^2]S_{ij},$$

where we have taken $|\mathbf{k}_i-\mathbf{k}_j|a\gg 1$ ($\mathbf{k}_i\neq\mathbf{k}_j$ since $S_{ii}=0$) and the meaning of $q_a^{(i)}$ is the same as that for $\lambda_a^{(i)}$. Recognition is again made of the symmetry properties of S_{ij} whose absolute magnitude we estimate by $(V\Delta g/M)$. The result, for example, is

$$(B^+,e^{-i\mathbf{q}\cdot\mathbf{r}}E_i)=(4\Delta g/a^3k^4M)q_z,$$

where k is defined in the text following Eq. (11).