Let us consider the z component of the spin representation $\mathrm{s}_{\mathbf{k}}{}^z$,

$$\mathrm{s}_{\mathbf{k}}{}^z=\begin{pmatrix} (a_{\mathbf{k}},a_{\mathbf{k}})-(b_{\mathbf{k}},b_{\mathbf{k}}) & -(a_{\mathbf{k}},b_{-\mathbf{k}}{}^*)+(b_{\mathbf{k}},a_{-\mathbf{k}}{}^*) \\ -(b_{-\mathbf{k}}{}^*,a_{\mathbf{k}})+(a_{-\mathbf{k}}{}^*,b_{\mathbf{k}}) & (b_{-\mathbf{k}}{}^*,b_{-\mathbf{k}}{}^*)-(a_{-\mathbf{k}}{}^*,a_{-\mathbf{k}}{}^*) \end{pmatrix}. \tag{A21}$$

Using the perturbed functions in Eqs. (A20), we see that $\mathrm{s}_{\mathbf{k}}{}^z$ is identical with the Pauli spin matrix $\mathrm{s}^z=\begin{pmatrix} \frac{1}{2} & \\ & -\frac{1}{2} \end{pmatrix}$ up to first order in $\mathcal{H}_{\mathrm{s-o}}$.

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g Factor and Donor Spin-Lattice Relaxation for Electrons in Germanium and Silicon*

LAURA M. ROTH
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts

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The g factors of electrons in Ge and Si are calculated on the basis of the effective mass approximation. The results are consistent with experimental spin resonance data. The effect is predicted to be anisotropic, with $g_{\parallel}$ less than $g_{\perp}$. This anisotropy introduces a strong interaction between the electron spin and shear waves, for the singlet donor ground state. This interaction can account in order of magnitude for the observed spin-lattice time τ_s for donor electrons in Si at low temperatures, including both a one-phonon process and a two-phonon Raman-type process. The temperature and magnetic-field dependence for the two processes are predicted to be $\tau_s{}^{-1}\propto TH^4$ and $\tau_s{}^{-1}\propto T^7H^2$, respectively. The temperature dependence agrees with experiment; however there are discrepancies in the magnetic-field dependence. τ_s is predicted to be anisotropic.

INTRODUCTION

THE g factors of electrons in semiconductors differ from two because of spin-orbit interaction. The effect can be calculated using the effective mass approximation, and can become large when there is a nearby band connected by momentum matrix elements and split by spin-orbit interaction. This is often the case when the effective masses are small. Results for indium antimonide and the $k=0$ electrons in germanium have been reported by Roth, Lax, and Zwerdling.[1] The effect has also been found to be large in bismuth by Blount and Cohen.[2] In the present paper estimates of g factors for the conduction electrons in germanium and silicon will be obtained. The result for germanium has been reported elsewhere.[3]

An interesting feature of the calculation is that the effect is anisotropic with $g_{\parallel}$ (parallel to the axis of the electron's ellipsoid) differing from two by considerably more than $g_{\perp}$. Since spin resonance experiments are usually carried out for electrons on donors, in the singlet state,[4] the observed g factor is isotropic. However, the anisotropic part of g is responsible for a large interaction of donor electron spins with shear waves. This apparently accounts for the small observed spin-lattice relaxation times of donor electrons in silicon, and the calculation is given in the second section of the paper. Both a direct and a Raman-type process are considered and compared with the experimental results of Honig and Stupp[5] and Feher and Gere.[6]

THE *g*-FACTOR

The g factor for a twofold degenerate band edge (including spin) can be obtained from the effective mass approximation for degenerate bands with spin-orbit interaction, as obtained by Luttinger and Kohn.[7] The effective mass Hamiltonian in the presence of a magnetic field is given by

$$\mathcal{H}_{ij}=\frac{p^2}{2m}\delta_{ij}+2\beta(\mathbf{s})_{ij}\cdot\mathbf{H}+\frac{1}{m^2}\sum_n{}'\frac{\mathbf{P}\cdot\boldsymbol{\pi}_{in}\boldsymbol{\pi}_{nj}\cdot\mathbf{P}}{\mathcal{E}_{0n}}. \tag{1}$$

Here

$$\mathbf{P}=\mathbf{p}+e\mathbf{A}/c, \tag{2}$$

where $\mathbf{p}$ is the momentum operator and $\mathbf{A}$ the vector potential, both acting upon envelope functions for the two degenerate band edges over which the indices i and j run. The second term of Eq. (1) is the electron spin interaction with the magnetic field $\mathbf{H}$, with β the Bohr magneton, and $(\mathbf{s})_{ij}$ the matrix element of the

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[1] L. M. Roth, B. Lax, and S. Zwerdling, Phys. Rev. **114**, 90 (1959).

[2] E. I. Blount and M. Cohen, Westinghouse Research Laboratory scientific paper (unpublished).

[3] L. M. Roth and B. Lax, Phys. Rev. Letters **3**, 217 (1959); L. M. Roth, Lincoln Laboratory Quarterly Progress Report on Solid-State Research, January, 1959 (unpublished), p. 45.

[4] W. Kohn, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 257.

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

[6] G. Feher and E. A. Gere, Phys. Rev. **114**, 1245 (1959).

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

electron spin between band edge wave functions. In the third term $\boldsymbol{\pi}$ is the modified momentum operator,

$$\boldsymbol{\pi}=\mathbf{p}+(\hbar\mathbf{s}\times\nabla V)/2mc^2, \tag{3}$$

and the matrix elements are between band edge wave functions, the prime on the sum indicating that the bands i, j are to be omitted. This term contributes both to the effective mass and the g factor. This can be seen by breaking up the expansion into two parts, one involving the vector components of $\mathbf{P}$ in a symmetric combination, and the other in an antisymmetric contribution. Using the relationship for the antisymmetric term,

$$\mathbf{P}\times\mathbf{P}=(e\hbar/ic)\mathbf{H}, \tag{4}$$

we have for the last term in Eq. (1),

$$\frac{1}{m^2}\sum_n \frac{\mathbf{P}\cdot\{\boldsymbol{\pi}_{in},\boldsymbol{\pi}_{nj}\}\cdot\mathbf{P}}{\mathcal{E}_{0n}}+\frac{1}{m^2}\frac{e\hbar}{2ic}\mathbf{H}\cdot{\sum_n}' \frac{\boldsymbol{\pi}_{in}\times\boldsymbol{\pi}_{nj}}{\mathcal{E}_{0n}}, \tag{5}$$

where the curly bracket indicates the symmetric product.

The 2×2 effective mass Hamiltonian, Eq. (1), can be expressed in terms of the 2×2 unit matrix and the three components of the Pauli spin vector $\boldsymbol{\sigma}$. The most general form which is Hermitian and is invariant under the combined operations of time reversal and reversal of the magnetic field is

$$H_{ij}=\tfrac{1}{2}\mathbf{P}\cdot[m^*]^{-1}\cdot\mathbf{P}\delta_{ij}+(\beta/2)\boldsymbol{\sigma}_{ij}\cdot\boldsymbol{g}\cdot\mathbf{H}, \tag{6}$$

where $[m^*]^{-1}$ is a real symmetric dyadic given from Eqs. (1) and (5) by

$$[m^*]^{-1}=\frac{1}{m}\boldsymbol{1}+\frac{2}{m^2}\sum_n \frac{\{\boldsymbol{\pi}_{in},\boldsymbol{\pi}_{ni}\}}{\mathcal{E}_{0n}}, \tag{7}$$

and $\boldsymbol{g}$ is a real dyadic, not necessarily symmetric, given by

$$\boldsymbol{\sigma}_{ij}\cdot\boldsymbol{g}=4(\mathbf{s})_{ij}+\frac{2}{im}\sum_n \frac{\boldsymbol{\pi}_{in}\times\boldsymbol{\pi}_{nj}}{\mathcal{E}_{0n}}. \tag{8}$$

In Eq. (8) the first term is equal to $2\boldsymbol{\sigma}_{ij}$ for the case of no spin-orbit interaction. This is not necessarily so otherwise. The second term vanishes in the absence of spin-orbit interaction. That the right-hand side is proportional to $\boldsymbol{\sigma}_{ij}$ follows from its time reversal properties: σ changes sign under the time reversal operator $-i\sigma_yC$, where C is the complex conjugation operator. $\mathbf{s}$, $\boldsymbol{\pi}$, and i also change sign, while the Hamiltonian corresponding to the energy denominator is invariant under this operation. The argument involving time reversal actually holds only for a band edge at the center of the Brillouin zone. Away from the center of the zone, a band edge of this type can occur if there is also inversion invariance, in which case the appropriate operator is $-i\sigma_yCI$, with I the inversion operator. The effect of time reversal is discussed in detail by Blount and Cohen.[2]

In evaluating Eq. (8) it is often the case that the band edge is s-like, with a nearby p-like band which makes the dominant contribution to the effective mass, Eq. (7). If the p-like band has a large spin-orbit splitting, the dominant contribution to the g factor is also from this band edge, and comes from the difference in energy denominators between the two split components. This was found to be the case for the direct electron in germanium, and for electrons in InSb, as calculated by Roth, Lax, and Zwerdling[1] in which the actual wave functions used were of zero order in the spin-orbit operator. The g factor in InSb was found to be very large (-50) because of the small band gap and large spin-orbit splitting. Even larger g values were found by Blount and Cohen[2] for Bi, again due to the combination of a small band gap and large spin-orbit splitting. Another interesting case is that of the split-off valence band in Ge or Si, in which the g factor was obtained by Luttinger[8] and can be related to what is essentially a g factor for the fourfold degenerate band.

For electrons in Ge or Si it is a good approximation to treat the spin-orbit interaction,

$$H_{so}=(\hbar/2m^2c^2)\mathbf{s}\cdot(\nabla V\times\mathbf{P})\equiv2\mathbf{s}\cdot\mathbf{h}, \tag{9}$$

as small, and introduce it to first order. We shall not restrict ourselves to a single connecting band edge, although we shall find that for both cases the dominant contribution to g is from one band edge. In Eq. (3) we shall neglect the second term; i.e., replace $\boldsymbol{\pi}$ by $\mathbf{p}$, as this can be shown to contribute a term of order $\langle p^2/2m\rangle/mc^2$ to the g factor, which is small compared to one. Through the use of perturbation theory, we can rewrite Eq. (8), factoring out $\boldsymbol{\sigma}=2\mathbf{s}$ from Eq. (9), to obtain

$$\boldsymbol{g}=2\boldsymbol{1}+\frac{2}{mi}{\sum_{\mu\nu}}'\frac{1}{\mathcal{E}_{0\mu}\mathcal{E}_{0\nu}}\{\mathbf{h}_{0\mu}\mathbf{p}_{\mu\nu}\times\mathbf{p}_{\nu0} \\ +\mathbf{h}_{\mu\nu}\mathbf{p}_{0\mu}\times\mathbf{p}_{\nu0}+\mathbf{h}_{\nu0}\mathbf{p}_{0\mu}\times\mathbf{p}_{\mu\nu}\}. \tag{10}$$

The conduction band edges for Ge and Si are away from the center of the zone but lie on symmetry axes so that the constant energy surfaces are ellipsoidal. From symmetry the g tensor has only the components $g_{zz}=g_{\parallel}$, $g_{xx}=g_{yy}=g_{\perp}$, where z is the axis of the ellipsoid. To find what terms contribute to Eq. (10), we specialize to the two cases.

Germanium

The conduction band edges in Ge are at the points L at the center of the hexagonal faces of the Brillouin zone, and according to Herman[9] belong to the repre-

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[8] J. M. Luttinger, Phys. Rev. **102**, 1030 (1956); Equation (b.9) is in error; the spin term should be $(e/6mc)(2Km-1)\boldsymbol{\sigma}\cdot\mathbf{H}$.

[9] F. Herman, Phys. Rev. **93**, 1214 (1954); Revs. Modern Phys. **30**, 102 (1958).

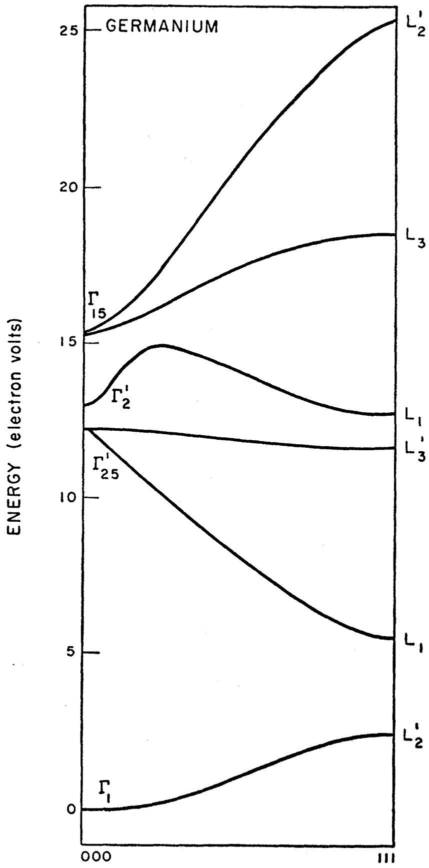

FIG. 1. Schematic diagram of the energy bands for Ge along a [111] axis of the Brillouin zone. After Herman (see reference 9) and Phillips (see reference 14).

sentation L_1 of the group of the wave vector.[10,11] A sketch of the energy bands along the [111] direction in germanium is shown in Fig. 1, showing nearby band edges which may contribute to the sums. To find which band edges are connected to L_1 by the perturbation $\mathbf{p}$, we use the fact that p_x, p_y transform as L_3', and p_z as L_2', where z is along the axis of the ellipsoid. Furthermore h_x, h_y transform as L_3 and h_z as L_2. From Eq. (10) we see that h_z appears in g_{11} and h_x in $g_{xx}=g_\perp$. Using group theory and Eq. (10), we find then that

$$\begin{aligned} g_{11}-2=&\mathrm{Re}\frac{4}{mi}\sum_{\mu\nu}\frac{1}{\mathcal{E}_{0\mu}\mathcal{E}_{0\nu}}(L_1|p_x|L_{3'}{}^{\mu x}) \\ &\times(L_{3'}{}^{\mu x}|h_z|L_{3'}{}^{\nu y})(L_{3'}{}^{\nu y}|p_y|L_1) \\ &+\mathrm{Re}\frac{8}{mi}\sum_{\mu\nu}\frac{1}{\mathcal{E}_{0\mu}\mathcal{E}_{0\nu}}(L_1|h_z|L_2{}^{\mu}) \\ &\times(L_2{}^{\mu}|p_x|L_{3'}{}^{\nu y})(L_{3'}{}^{\nu y}|p_y|L_1), \end{aligned} \tag{11}$$

$$\begin{aligned} g_\perp-2=&\mathrm{Re}\frac{4}{mi}\sum_{\mu\nu}\frac{1}{\mathcal{E}_{0\mu}\mathcal{E}_{0\nu}}(L_1|p_y|L_{3'}{}^{\mu y}) \\ &\times(L_{3'}{}^{\mu y}|h_x|L_{2'}{}^{\nu})(L_{2'}{}^{\nu}|p_z|L_1) \\ &+\mathrm{Re}\frac{4}{mi}\sum_{\mu\nu}\frac{1}{\mathcal{E}_{0\mu}\mathcal{E}_{0\nu}}(L_1|h_x|L_3{}^{\mu y}) \\ &\times(L_3{}^{\mu y}|p_y|L_{2'}{}^{\nu})(L_{2'}{}^{\nu}|p_z|L_1) \\ &+\mathrm{Re}\frac{4}{mi}\sum_{\mu\nu}\frac{1}{\mathcal{E}_{0\mu}\mathcal{E}_{0\nu}}(L_1|p_y|L_{3'}{}^{\mu y}) \\ &\times(L_{3'}{}^{\mu y}|p_z|L_3{}^{\nu x})(L_3{}^{\nu x}|h_x|L_1), \end{aligned} \tag{12}$$

where Re is "real part of." Here we have labeled the band edges by the representation to which they belong, and in addition the superscripts x and y distinguish the basis functions for the two-dimensional representations. These expressions can be compared with those for the effective masses,

$$\begin{aligned} \frac{m}{m_t}&=1+\frac{2}{m}\sum_{\mu}\frac{1}{\mathcal{E}_{0\mu}}|(L_1|p_x|L_{3'}{}^{\mu x})|^2, \\ \frac{m}{m_l}&=1+\frac{2}{m}\sum_{\mu}\frac{1}{\mathcal{E}_{0\mu}}|(L_1|p_z|L_{2'})|^2. \end{aligned} \tag{13}$$

In g_{11} the major contribution comes from the first term in Eq. (11) as in the second term L_2 appears, which is far away. If we assume that the major contribution to the first term and to m/m_t comes from one band edge (Fig. 1), we find

$$g_{11}-2=-(\delta/\mathcal{E}_{13'})(m/m_t-1), \tag{14}$$

where $\delta=2i(L_{3'}{}^{x}|h_z|L_{3'}{}^{y})$ is the spin orbit splitting of the $L_{3'}$ band. We can estimate δ by using the basis functions at the center of the zone, giving $\delta\sim(2/3)\Delta$ where $\Delta=0.3$ ev is the splitting of the valence band at $k=0$. The value of $\mathcal{E}_{13'}$, the energy separation between the L_1 and $L_{3'}$ bands, can be estimated from the experiments of Phillip and Taft[12] who found a strong absorption at $\sim$2 ev which is probably the vertical transition of electrons from the $L_{3'}$ band to the L_1 band.[3,13] Using these and the value of m/m_t of 12 from cyclotron resonance, we find

$$g_{11}\sim 0.9. \tag{15}$$

For $g_\perp$, the first term of Eq. (12) can be estimated in a similar way, if we assume that all the momentum matrix elements are the same, and that these and the matrix elements of $\mathbf{h}$ are the same as Eq. (11). This gives

$$g_\perp-2\cong-(\delta/\mathcal{E}_{13'})(m/m_l-1)+\Delta g_\perp. \tag{16}$$

From $m/m_l=0.6$, the first term of Eq. (16) is 0.04.

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[10] L. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).

[11] G. F. Koster, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 173.

[12] H. R. Philipp and E. A. Taft, Phys. Rev. **113**, 1002 (1959).

[13] J. C. Phillips, J. Chem. Phys. Solids **12**, 208 (1960).

This result is somewhat unreliable since there is some cancellation in the expression for m/m_l. The second term of Eq. (12) is small but the last term may contribute since the band edges L_3 and $L_{3'}$ appear. This is given in Eq. (16) as $\Delta g_\perp'$. If the matrix elements are the same order of magnitude as in the first term of Eq. (11) and the Γ_3 edge is 5 ev away,[14] this contributes 0.4 to $g_\perp$, with the sign uncertain. However, we expect the matrix element of h_x to be reduced since the Γ_1 band edge is s-like. An argument that can be used to estimate the reduction is to take as a measure of overlap contribution to Δ (in a tight binding approximation) the difference between Δ and the atomic spin-orbit splitting of 0.2 ev. Since the only contribution to our matrix element would be from overlap we would multiply by $\frac{1}{3}$, giving $|\Delta g_\perp'|\sim 0.1$. Phillips,[15] however, argues the matrix element of h_x depends on the amount of p character in the L_1 band obtained by projecting the plane waves on core functions, and that this is very small, making $\Delta g_\perp'$ almost negligible.

In any case we see that there should be considerable anisotropy in the g factor. The effective g factor for conduction electrons on a particular ellipsoid is given by

$$g^2 = g_{\shortparallel}^2 \cos^2\theta + g_\perp^2 \sin^2\theta, \tag{17}$$

where θ is the angle of the magnetic field with the axis of the ellipsoid. However, the spin resonance experiments are generally carried out on donors, and in this case the ellipsoids are mixed. For the donor singlet state[4] (see part 2) the effective g factor is given by

$$g = \tfrac{1}{3} g_{\shortparallel} + \tfrac{2}{3} g_\perp. \tag{18}$$

This is estimated to be $g \sim 1.7$ in good agreement with the result of 1.57 obtained by Feher, Wilson, and Gere.[16] One can also calculate the g values for the triplet donor state, using the Hamiltonian of Eq. (21) below.[3]

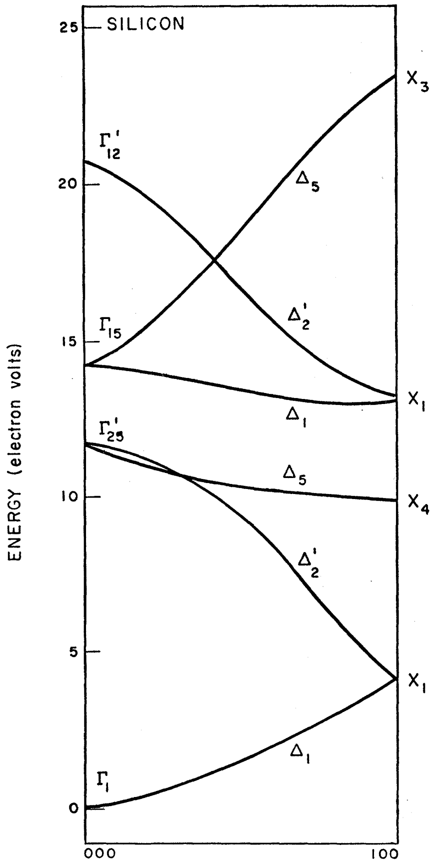

FIG. 2. Schematic diagram of the energy bands for Si along a [100] axis of the Brillouin zone. After Herman (see reference 9) and Phillips (see reference 14).

Silicon

Similar expressions can be obtained for Si, for which the conduction band minima are along the 100 axes in the Brillouin zone, as sketched in Fig. 2. Here we have:

$$\begin{aligned} g_{\shortparallel} - 2 = {} & \mathrm{Re}\frac{1}{mi}\sum_{\mu\nu}\frac{1}{\mathcal{E}_{0\mu}\mathcal{E}_{0\nu}}(\Delta_1|p_x|\Delta_5^{\mu x}) \\ & \times(\Delta_5^{\mu x}|h_z|\Delta_5^{\nu y})(\Delta_5^{\nu y}|p_y|\Delta_1) \\ & + \mathrm{Re}\frac{8}{mi}\sum_{\mu\nu}\frac{1}{\mathcal{E}_{0\mu}\mathcal{E}_{0\nu}}(\Delta_1|h_z|\Delta_{1'}) \\ & \times(\Delta_{1'}|p_x|\Delta_5^{\mu y})(\Delta_5^{\mu y}|p_y|\Delta_1), \end{aligned} \tag{19}$$

$$\begin{aligned} g_\perp - 2 = {} & \mathrm{Re}\frac{4}{mi}\sum_{\mu\nu}\frac{1}{\mathcal{E}_{0\mu}\mathcal{E}_{0\nu}}(\Delta_1|p_y|\Delta_5^{\mu y}) \\ & \times(\Delta_5^{\mu y}|h_x|\Delta_1^{\nu})(\Delta_1^{\nu}|p_z|\Delta_1) \\ & + \mathrm{Re}\frac{4}{mi}\sum_{\mu\nu}\frac{1}{\mathcal{E}_{0\mu}\mathcal{E}_{0\nu}}(\Delta_1|h_x|\Delta_5^{\mu y}) \\ & \times(\Delta_5^{\mu y}|p_y|\Delta_1^{\nu})(\Delta_1^{\nu}|p_z|\Delta_1) \\ & + \mathrm{Re}\frac{4}{mi}\sum_{\mu\nu}\frac{1}{\mathcal{E}_{0\mu}\mathcal{E}_{0\nu}}(\Delta_1|p_y|\Delta_5^{\mu y}) \\ & \times(\Delta_5^{\mu y}|p_z|\Delta_5^{\nu y})(\Delta_5^{\nu y}|h_x|\Delta_1). \end{aligned} \tag{20}$$

For $g_{\shortparallel}$, if we estimate the first term in Eq. (19) in a similar way as for Ge, and use $\Delta = 0.04$ ev, $m/m_t = 5$, $\mathcal{E}_{15} = 4$ ev,[9] we obtain -0.03 for this term. Assuming that this is the only term of importance the donor spin resonance would have $g-2 = -0.01$, as compared with the experimental value of -0.003. However, Elliot,[17] who has made a similar calculation, has pointed out that the spin-orbit splitting of the Δ_5 band vanishes at

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[14] J. C. Phillips, Phys. Rev. **112**, 685 (1958).

[15] J. C. Phillips (private communication).

[16] G. Feher, D. K. Wilson, and E. A. Gere, Phys. Rev. Letters **3**, 25 (1959). Recent spin resonance experiments with strained samples by Wilson and Feher [Bull. Am. Phys. Soc. Ser. II, **5**, 60 (1960)] give $g_{\shortparallel} = 0.87 \pm 0.05$, $g_\perp = 1.92 \pm 0.05$.

[17] R. J. Elliot (private communication).

the zone edge (the point X, Fig. 2) and is therefore probably smaller than $(\frac{2}{3})\Delta$ at the band edge, which is 85% of the way from Γ to X. A reduction by a factor of three would be reasonable and give agreement with experiment.

Another term which may be important is the third term in Eq. (20) for $g_\perp$. Here the matrix element of p_z vanishes at X, and is of the order of $\hbar(k_0-k_X)=0.15\hbar(2\pi/a)$ where k_0 and k_X are the wave vectors for the band minimum and the point X, and a is the lattice spacing. The matrix element of p_y is the same as in the first term of Eq. (19), as are the energy denominators. If the matrix element of h_x is the same as that of h_z in Eq. (19), one finds that this term would be about $\frac{1}{6}$ of Eq. (19) with the sign uncertain. The spin orbit matrix element is again reduced below an atomic spin orbit splitting, in this case because the wave function at Δ is mainly s-like. According to Phillips,[15] the amount of p-character is about 20%, giving a reduction by a factor of 5. Alternatively, a tight binding argument such as was employed in estimating $g_\perp$ for Ge would give a reduction of a factor of three. Thus, we can estimate that $g_\perp-2$ is something like $\frac{1}{6}$ of $g_\parallel-2$. This indicates that there is anisotropy in the g-tensor in Si as well as in Ge.

SPIN-LATTICE INTERACTION

The interaction of electron spins on donor impurities[5,6] with lattice waves has been found to be much larger than expected on the basis of calculations up to this time.[18,19] The following calculation, which is similar to the work of Van Vleck,[20] apparently accounts for the magnetic-field dependent part of the spin-lattice time τ_s observed by Honig and Stupp in phosphorus-doped silicon.[5] In addition a Raman-type process is considered. The result for the direct process is also applicable to acoustic spin resonance.

Of primary importance in the calculation is the fact that the ground donor level[4] is split into a singlet, doublet, and triplet for Si, and a singlet and triplet for Ge, due to the mixing of the various ellipsoids on the donor, with the singlet usually lowest. We shall call the states other than the singlet arising in this manner excited states. In the presence of a magnetic field we have found that an electron on a given ellipsoid has an anisotropic g tensor, with $g_\parallel$ less than $g_\perp$. For a general direction of the magnetic field, the $\boldsymbol{\sigma}\cdot\boldsymbol{g}\cdot\mathbf{H}$ interaction is different for different ellipsoids, and can therefore mix singlet and excited states, and, in particular, different spin states. There is therefore an interaction with lattice waves involving a spin flip. The usual "Van Vleck cancellation"[19] does not apply here—the latter is due to time reversal invariance which does not apply in an interaction involving a magnetic field. The spin-lattice interaction obtained is large because the energy denominator involved is a singlet-excited state splitting rather than an energy gap.

Direct Spin-Lattice Interaction

We consider a donor electron in the singlet state in Ge or Si. We can write the interaction of the electron spin with a magnetic field in the following form,

$$H_s=(\beta/2)\boldsymbol{\sigma}\cdot\boldsymbol{g}_{op}\cdot\mathbf{H}, \tag{21}$$

where

$$\boldsymbol{g}_{op}=g\boldsymbol{1}+(g_\parallel-g_\perp)\textstyle\sum_i|i)(i|\{\hat{n}_i\hat{n}_i-\frac{1}{3}\boldsymbol{1}\}. \tag{22}$$

In Eq. (22), g is given by Eq. (18) and is the observed g factor in the singlet donor state. In the second term $|i)(i|$ is a projection operator which selects out the ith ellipsoid, and $\hat{n}_i$ is a unit vector in the direction of the axis of the ellipsoid.

The second term in Eq. (22) mixes the singlet and excited states. If we denote the singlet state by $|0)$ and the rest of the states by $|n)$, the perturbed singlet state $|0')$ is given in Dirac notation by

$$|0')=|0)-\textstyle\sum_n|n)\dfrac{(n|(\beta/2)\boldsymbol{\sigma}\cdot\boldsymbol{g}_{op}\cdot\mathbf{H}|0)}{\mathcal{E}_n-\mathcal{E}_0}. \tag{23}$$

The electron-phonon interaction is given by

$$H_d=\boldsymbol{\varepsilon}:\mathbf{E}_{op}, \tag{24}$$

where $\boldsymbol{\varepsilon}$ is the strain tensor and where $\mathbf{E}_{op}$ is a deformation potential operator again involving projection operators:

$$\mathbf{E}_{op}=E_1\boldsymbol{1}+E_2\textstyle\sum_i|i)(i|\{\hat{n}_i\hat{n}_i-\frac{1}{3}\boldsymbol{1}\}. \tag{25}$$

E_1 and E_2 are the usual deformation potential parameters for electrons.[21] We now have, to first order in H_s,

$$\begin{aligned}(0'|H_d|0')&=(0|E_1\Delta|0)\\&\quad-(1/\delta)\textstyle\sum_n\{(0|\boldsymbol{\varepsilon}:\mathbf{E}_{op}|n)(n|(\beta/2)\boldsymbol{\sigma}\cdot\boldsymbol{g}_{op}\cdot\mathbf{H}|0)\\&\qquad+(0|(\beta/2)\boldsymbol{\sigma}\cdot\boldsymbol{g}_{op}\cdot\mathbf{H}|n)(n|\boldsymbol{\varepsilon}:\mathbf{E}_{op}|0\},\end{aligned} \tag{26}$$

where Δ is the dilitation, and δ is the singlet-triplet splitting for Ge, or the singlet-doublet splitting for Si. We are making use of the fact that there are no matrix elements connecting the singlet to the *triplet* in Si, as the latter involves antisymmetric combinations of pairs of opposite ellipsoids, while the singlet state as well as the perturbations involved are symmetric in opposite ellipsoids. From the completeness relation we can write,

$$\textstyle\sum_n|n)(n|=\sum_i|\bar{\imath})(\bar{\imath}|-|0)(0|, \tag{27}$$

where $|\bar{\imath})$ represents the lowest donor level on an ellipsoid (as distinguished from $|i)$ which just gives the ellipsoid. Using Eq. (27) and the orthogonality of states on different ellipsoids, we find for the second term in Eq. (26), denoted by H',

$$\begin{aligned}H'=&-[(g_\parallel-g_\perp)\beta H/\delta]\textstyle\sum_i|(0|\bar{\imath})|^2\\&\times(\bar{\imath}|\hat{n}_i\cdot\boldsymbol{\varepsilon}\cdot\hat{n}_i-(\Delta/3)|\bar{\imath})(\boldsymbol{\sigma}\cdot\hat{n}_i\hat{n}_i\cdot\mathbf{H}-\tfrac{1}{3}\boldsymbol{\sigma}\cdot\mathbf{H}).\end{aligned} \tag{28}$$

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[18] D. Pines, J. Bardeen, and C. P. Slichter, Phys. Rev. **106**, 489 (1957).

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

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

[21] C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).

The only spatial dependence of $\boldsymbol{\varepsilon}$ is in the plane wave $e^{i\mathbf{q}\cdot\mathbf{r}}$, for a phonon of wave vector $\mathbf{q}$. If we assume that $qr_0 \ll 1$, where r_0 is the radius of the donor state, we can replace the exponential by 1; i.e., we take $\boldsymbol{\varepsilon}$ to be constant. This is valid for phonons up to 15° in Si and 5° in Ge. Further, since the singlet involves a symmetric combination of wave functions from all the ellipsoids, the summation in Eq. (28) is just the average of the angular factors. Carrying out the averages, we find for the two cases,

$$\text{Si}: H'=\beta(g_{\parallel}-g_{\perp})(E_2/\delta)\times\tfrac{1}{3}[\sigma_x H_x\epsilon_{xx}+\sigma_y H_y\epsilon_{yy}+\sigma_z H_z\epsilon_{zz}-\boldsymbol{\sigma}\cdot\mathbf{H}\Delta/3], \quad (29)$$

$$\text{Ge}: H'=\beta(g_{\parallel}-g_{\perp})(E_2/\delta)\times(2/9)[(\sigma_x H_y+\sigma_y H_x)\epsilon_{xy}+\text{c.p.}], \quad (30)$$

where c.p. stands for "cyclic permutations."

Calculation of τ_s

The relaxation time τ_s is given by

$$\tau_s^{-1}=(2\pi/\hbar)\textstyle\sum_{\mathbf{q},t}\{|(N_{\mathbf{q}t},+|H'(\mathbf{q},t)|N_{\mathbf{q}t}+1,-)|^2+|(N_{\mathbf{q}t},-|H'(\mathbf{q},t)|N_{\mathbf{q}t}-1,+)|^2\}\,\delta(\hbar\omega_{\mathbf{q}}-g\beta H), \quad (31)$$

where the sum is over the phonon wave vector $\mathbf{q}$ and the polarization t. N refers to the occupation number for the phonons, and + and − refer to up and down spins. $H'(\mathbf{q},t)$ is given by Eq. (29) or (30) with the strain given by

$$\boldsymbol{\varepsilon}(q,t)=(\hbar/2\rho\omega_{\mathbf{q}t})^{\frac{1}{2}}(a_{\mathbf{q}t}+a_{\mathbf{q}t}^{+})i\{\mathbf{q},\boldsymbol{\eta}_{\mathbf{q}t}\}. \quad (32)$$

where a and a^{+} are annihilation and creation operators, $\boldsymbol{\eta}$ is the polarization vector, and ρ is the density. Since we expect transverse and longitudinal waves to give somewhat different results, we average Eq. (31) over the two types of modes, using an isotropic model for the elastic waves. This gives

$$\text{Si}: \tau_s^{-1}=\frac{1}{\pi}\left(\frac{E_2}{\delta}\frac{(g_{\parallel}-g_{\perp})}{3g}\right)^2\frac{\omega^4 kT}{\rho}\times\left(\frac{2}{5c_t^5}+\frac{4}{15c_l^5}\right)\left\{\frac{H_x^2H_y^2+\text{c.p.}}{H^4}\right\}, \quad (33)$$

$$\text{Ge}: \tau_s^{-1}=\frac{1}{\pi}\left(\frac{E_2}{\delta}\frac{(g_{\parallel}-g_{\perp})}{3g}\right)^2\frac{\omega^4 kT}{\rho}\times\left(\frac{2}{5c_t^5}+\frac{4}{15c_l^2}\right)\frac{4}{9}\left\{\frac{1}{2}-\frac{H_x^2H_y^2+\text{c.p.}}{H^4}\right\}. \quad (34)$$

The factor $1/c^5$ is an order of magnitude smaller for longitudinal than for transverse waves, so the latter dominate. We shall assume $g_{\perp}=2$, so that $(g_{\parallel}-g_{\perp})/3=g-2=\Delta g$, with g given by Eq. (18). This quantity can then be obtained from experiment. The only unknown is then δ, which we shall take as 10^{-2} ev for Si. Using $\Delta g/g=1.5\times10^{-3}$, $E_2=11$ ev, $c_t^5\sim5\times10^{28}$ cgs, we find for 1.2°K, 9000 Mc and an average direction for H, $\tau_s\sim1000$ sec. The result obtained by Honig and Stupp[5] was 420 minutes, so that our result represents an embarrassment of riches, but is certainly in better agreement than the 10^9 sec obtained by Abrahams.[19] For Ge, with $c_t^5\sim3\times10^{27}$ cgs, $\Delta g/g\sim0.3$, $E_2=15$ ev, and $\delta\sim4\times10^{-3}$ ev, we find similarly $\tau_s\sim10^{-3}$ sec.

It is interesting that τ_s^{-1} is predicted to depend on the direction of the magnetic field, and in particular to vanish for $\mathbf{H}\|[100]$ in Si. Such an anisotropy has not been observed thus far; however in Ge, there is anisotropy in the inhomogeneous broadening[16] which is evidently due to residual strains. It is evident from Eq. (30) that the change in g due to shear $[\propto(+|H'|+)]$ vanishes in the [100] direction, which is consistent with the narrowing observed by Feher, Wilson, and Gere[16] in this direction.

Raman-Type Process

We consider a two-step process in which a phonon of wave vector $\mathbf{q}$ is absorbed and a phonon of wave vector $\mathbf{q}'$ is emitted, the spin flipping in either step. In the intermediate state the electron is raised from the singlet to an excited state. The expression for the relaxation rate is

$$\tau_s^{-1}=(2\pi/\hbar)\textstyle\sum_{\mathbf{q},\mathbf{q}',t,t'}\{|(+|H'(\mathbf{q},\mathbf{q}',t,t')|-)|^2+|(-|H'(\mathbf{q}',\mathbf{q},t',t)|+)|^2\}\delta(\hbar\omega_{\mathbf{q}'}-\hbar\omega_{\mathbf{q}}-\hbar\omega), \quad (35)$$

where

$$H'(\mathbf{q},\mathbf{q}',t,t')=(0',N_{\mathbf{q}t}|H_d(\mathbf{q},t)|n',N_{\mathbf{q}t}-1)\times\frac{1}{\mathcal{E}_0'-\mathcal{E}_n'+\hbar\omega_{\mathbf{q}}}(n',N_{\mathbf{q}'t'}|H_d(\mathbf{q}',t')|0,N_{\mathbf{q}'t'}+1)+(0',N_{\mathbf{q}'t'}|H_d(\mathbf{q}',t')|n',N_{\mathbf{q}'t'}+1)\frac{1}{\mathcal{E}_0'-\mathcal{E}_n'-\hbar\omega_{\mathbf{q}'}}\times(n',N_{\mathbf{q}t}|H_d(\mathbf{q},t)|0',N_{\mathbf{q}t}-1), \quad (36)$$

with H_d given by Eq. (24), in which $\boldsymbol{\varepsilon}$ is given by Eq. (32). Here the primed electron states include H_s, Eq. (21) and we have assumed for simplicity that n' is diagonal in this interaction. We now evaluate this to first order in H_s, considering only the contribution due to E_2, Eq. (25), since we shall include only transverse waves. If we assume that $kT\ll\delta$, we can neglect the energy of the phonon in the denominators. The result is then

$$H'(\mathbf{q},\mathbf{q}',t,t')=(6/\delta^2)(g_{\parallel}-g_{\perp})^2E_2^2\textstyle\sum_i|(0|i)|^2\times(\boldsymbol{\sigma}\cdot\hat{n}_i\hat{n}_i\cdot\mathbf{H}-\tfrac{1}{3}\boldsymbol{\sigma}\cdot\mathbf{H})(N_{\mathbf{q}t}|\hat{n}_i\cdot\boldsymbol{\varepsilon}(\mathbf{q},t)\cdot\hat{n}_i-\tfrac{1}{3}\Delta(\mathbf{q},t)|N_{\mathbf{q}t}-1)(N_{\mathbf{q}'t}|\hat{n}_i\cdot\boldsymbol{\varepsilon}(\mathbf{q}'t')\cdot\hat{n}_i-\tfrac{1}{3}\Delta(\mathbf{q}',t')|N_{\mathbf{q}'t'}+1). \quad (37)$$

We now substitute this in Eq. (35). Averaging over transverse waves only, and neglecting $\hbar\omega$ compared to kT, we finally obtain for Si,

$$\tau_s^{-1}=\frac{9\pi^3}{175}\left(\frac{E_2}{\delta}\right)^4\left(\frac{\Delta g}{g}\right)^2\omega^2\frac{(kT)^7}{\hbar^5\rho^2c_t^{10}}\left(\frac{H_x^2H_y^2+\text{c.p.}}{H^4}\right). \qquad (38)$$

For the same parameters used with Eq. (33), and for 4.2°K, this gives 60 sec, as compared with Feher and Gere's[6] result of 25 sec for P-Si under the same conditions. The T^7 dependence agrees with their experimental results; however, Eq. (38) predicts a quadratic magnetic field dependence, whereas Feher and Gere[6] observed no field dependence between 3000 and 8000 gauss.

Discussion of τ_s

It is evident that the effects considered here can account in order of magnitude for the observed spin-lattice relaxation rate in n-Si as observed by Honig and Stupp and by Feher and Gere. This represents an improvement by a factor of 10^6 over previous calculations for the direct process, the factor being due to the appearance of the singlet-doublet or singlet-triplet splitting in an energy denominator, rather than an energy gap. In the details of the results, however, there are still some discrepancies. For the direct process, $\tau_s^{-1}\propto H^4T$, and while the quartic field dependence was observed by Honig and Stupp for sufficiently high magnetic fields, at lower fields (below 9000 gauss), there was an additional contribution independent of the magnetic field. In the calculation, one factor of H^2 arose from the H_s perturbation, and the other from the number of phonons "on speaking terms" with the spins.[20] It is difficult to see how either factor could be eliminated; thus our method fails to explain the magnetic-field dependence of τ_s^{-1}. The same applies to the Raman process.

A test of the validity of this mechanism would be the observation of the predicted anisotropy. In looking for this it would be best to select the high magnetic-field range in which the field dependence is predicted correctly.

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Note added in proof.—A similar calculation of τ_s for the direct process has been made by Dr. Hiroshi Hasegawa [Bull. Am. Phys. Soc. Ser. II, **5**, 159 (1960) and Phys. Rev. **118**, 1523 (1960)] with essentially the same result. The author wishes to thank Dr. Hasegawa for interesting discussions and for the correction of a numerical error.

Recent experimental work of G. Feher, E. A. Gere, and D. K. Wilson [Bull. Am. Phys. Soc. Ser. II, **5**, 264 (1960)] and of A. Honig (private communication) has shown that the anisotropy in τ_s for Si is smaller than predicted here and in Dr. Hasegawa's work. Therefore, another mechanism for relaxation must be present. This is evidently a one-valley process, essentially independent of the fact that the electron is bound to a donor, and a calculation of the effect will be presented in a future publication. The work of Feher *et al.*, also indicates that the anisotropy in the g-shift for Si electrons is smaller than estimated here, a fact which probably accounts for our overestimate of τ_s^{-1}.

According to A. Honig (private communication) the magnetic field independent contribution to the direct process is concentration dependent, so that the H^4 dependence now agrees with experiment. For the Raman-type process there is still a discrepancy. The existence of a field independent Raman-type process was pointed out to the author by Dr. Hasegawa and this is being currently investigated.