In conclusion it should be emphasized again that the two basic assumptions of the theory presented here, namely the form of $p(H,T)$ and the use of the Ising approximation have not been rigorously proved valid but are put forward as extremely plausible assumptions which explain the experimental results.

Spin-Lattice Relaxation of Shallow Donor States in Ge and Si through a Direct Phonon Process*

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The many-valley character of the conduction band edge of germanium and silicon causes an anisotropy of the g shift and of the deformation potential for the conduction electrons. It is shown that the combination of these two effects provides a mechanism for spin-lattice relaxations of the donor spins in germanium and silicon that yields $1/T_s$ proportional to the temperature T and to the fourth power of the static magnetic field H. Using known data about the deformation potential constant, the g shift, the energy of the intervalley splitting, and the elastic constants, the magnitude of T_s is found to be approximately 2×10^{-3} sec for phosphorus donors in germanium, and 1×10^4 sec for phosphorus donors in silicon. These values refer to $T = 1.25°K$, $H = 3000$ gauss, with the field applied along the [111] axis. Our mechanism fails to give a finite T_s for donors in silicon, when the field is applied along the [100] axis.

1. INTRODUCTION

THE present investigation is concerned with a mechanism which may be responsible for spin-lattice relaxations of shallow donor spins in Ge and Si. We restrict our considerations to direct phonon processes, i.e., to processes which involve the absorption or emission of only one phonon.

The interaction of an electron with lattice vibrations in such a nonpolar crystal has been treated by many authors from the deformation-potential point of view.[1] In particular, a generalized theory of the deformation potential for many-valley semiconductors has been developed by Herring and Vogt.[2,3] According to these authors, the shift of the electronic energy of the ith valley due to a strain $\mathfrak{U}$ is given by

$$\epsilon^{(i)} = \sum_{\alpha,\beta} U_{\alpha\beta}(\Xi_d\delta_{\alpha\beta} + \Xi_u K_\alpha^{(i)}K_\beta^{(i)}), \qquad (1.1)$$

where $U_{\alpha\beta}$ is the (α,β) component of the strain tensor $\mathfrak{U}$, $\mathbf{K}^{(i)}$ is the unit vector pointing from the origin to the bottom of the ith valley in the first Brillouin zone, and Ξ_d and Ξ_u are energy constants whose magnitudes are several ev. If one writes the displacement of the lattice at a position $\mathbf{r}$ due to the lattice vibration as a

Fourier series:

$$\mathbf{Q}(\mathbf{r}) = \sum_q \mathbf{Q}(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{r}}, \qquad (1.2)$$

then, using Eq. (1.1), the corresponding Fourier component of the energy shift is given by

$$\epsilon_q^{(i)} = \Xi_d(i\mathbf{Q}_q\cdot\mathbf{q}) + \Xi_u(i\mathbf{Q}_q\cdot\mathbf{K}^{(i)})(\mathbf{K}^{(i)}\cdot\mathbf{q}). \qquad (1.3)$$

The first and the second terms in the right-hand side of Eq. (1.3) represent the interaction of the electron with the lattice wave of a wave vector $\mathbf{q}$ through the volume dilation, and the shearing strain, respectively.

In the present paper, we wish to show the importance of the second term of the expression (1.3) in the mechanism of spin-lattice relaxations of shallow donor states in Ge and Si. The effect of shearing strains on the ground state of donors has been discussed by Price[4] and by Kohn.[5] One interesting feature of these states, first pointed out by Kohn and Luttinger,[6] is a splitting of the degenerate ground state through the intervalley interaction due to the impurity potential. The recent experiments on acoustoelectric effect (Ge),[7] piezoresistance (Ge),[8] Hall effect (Si),[9] and spin resonance (Si,Ge)[10,11] have confirmed this feature, and have

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provided some numerical data on the energy interval between the ground state and the split-off excited states. Since any kind of static strain mixes these excited states with the ground state, we may expect a similar mixing effect from the electron-lattice interaction given by Eq. (1.3).

The mathematical procedure used here is a simple perturbation treatment which assumes that the intervalley splitting is large enough for the interaction with lattice vibrations to be regarded as a small perturbation. This treatment may not be legitimate in the case of very shallow donors such as Li in Si or Sb in Ge, for which the simple picture of a singlet ground state might not be appropriate.

The present mechanism interprets the resulting interaction between electron spins and lattice vibrations as a modulation of the g shift by lattice vibrations. Although we are concerned with the particular cases of donor states in Ge and Si, the present mechanism may also apply to the spin-lattice relaxations through direct phonon processes in other cases, e.g., paramagnetic salts, provided that the electronic state under consideration is orbitally nondegenerate.

Calculations of the spin-lattice relaxation time T_s of donors in Si due to direct phonon processes have been made by several authors,[12,13] and a large discrepancy has been found between the experimental values[14,15] and the theoretical predictions. The essential difference between the previous calculations and the present one consists in the following two points:

1. The only part of the electron-phonon interaction previously taken into account was that due to the isotropic dilation; i.e., the interaction corresponding to the first term of the expression (1.3).

2. The amplitude of the excited states with reversed spin which is mixed into the ground state by a static magnetic field H is given approximately by $g\mu_B H/\Delta E \times \Delta g/g$. The quantity ΔE was taken previously to be the difference between the energies of the conduction band and an adjacent band, in order of magnitude 1 ev. In our treatment, however, ΔE is the energy of the intervalley splitting whose order of magnitude is $10^{-3} \sim 10^{-2}$ ev.

This second point results in a rather large difference in the numerical estimate of T_s, and modifies greatly the previous results. Section 2 and Sec. 3 together with Appendix are devoted to explaining this point. The explicit formula for the spin-lattice relaxation rate $1/T_s$ is presented in Sec. 4. Discussions concerning its field dependence and order of magnitudes are given in Sec. 5. One interesting prediction of the theory is that $1/T_s$ will be anisotropic, i.e., $1/T_s$ will depend on the direc-

tion of the static magnetic field with respect to the crystallographic axes, especially in the case of Si. In fact, for Si, our mechanism gives $1/T_s = 0$, when the field is applied along $\langle 100 \rangle$ directions. This is essentially due to the geometrical structure of the conduction band edge in Si. The question of what mechanism is responsible for relaxation in this special case remains open.

After this work was completed, there appeared an abstract[16] by L. M. Roth stating almost the same conclusion as that obtained in the present paper.

2. PERTURBATION FORMULA

Let $\bar{\Psi}_n(\mathbf{r})$ be a complete set of normalized wave functions for a donor electron in a Ge or Si crystal, and write the ground state as $\bar{\Psi}(\mathbf{r})$, dropping the subscript $n=0$. The function $\bar{\Psi}_n(\mathbf{r})$ satisfies the Schrödinger equation

$$\mathcal{H}_e \bar{\Psi}_n = E_n \bar{\Psi}_n, \tag{2.1}$$

where the Hamiltonian $\mathcal{H}_e$ for the donor electron is given by

$$\mathcal{H}_e = \mathbf{p}^2/2m + V(\mathbf{r}) + \mathcal{H}_{s-o}. \tag{2.2}$$

The potential $V(\mathbf{r})$ is the sum of the periodic potential V_{period} and the impurity potential V_{imp}, and $\mathcal{H}_{s-o}$ represents the spin-orbit interaction given by

$$\mathcal{H}_{s-o} = (\hbar/2m^2 c^2)(\mathbf{s} \times \text{grad} V) \cdot \mathbf{p}. \tag{2.3}$$

We shall consider the interactions of the electron with a static magnetic field and with lattice vibrations as small perturbations. The Hamiltonians of these interactions will be denoted by $\mathcal{H}_z$, and $\mathcal{H}_{e-L}$, respectively. The Zeeman energy $\mathcal{H}_z$, up to first order in the static magnetic field $\mathbf{H}$, can be written as

$$\mathcal{H}_z = \mu_B \mathbf{H} \cdot (\boldsymbol{\ell} + g_s \mathbf{s}), \tag{2.4}$$

where μ_B is the Bohr magnetron, $g_s = 2.0023$, the free-electron g-value, and $\boldsymbol{\ell}$ and $\mathbf{s}$ are the orbital and spin angular-momentum vectors, respectively. The three components of $\mathbf{s}$ are the Pauli spin matrices, and $\boldsymbol{\ell}$ is defined by

$$\boldsymbol{\ell} = (1/\hbar)\mathbf{r} \times \boldsymbol{\pi}, \quad \boldsymbol{\pi} = \mathbf{p} + (\hbar/2mc^2)(\mathbf{s} \times \text{grad} V). \tag{2.5}$$

It follows from Kramers' theorem that every donor level is at least doubly degenerate in the absence of the magnetic field, and in what follows the symbol $\bar{\Psi}_n(\mathbf{r})$ represents two eigenfunctions $\Psi_n(\mathbf{r})$ and $\Phi_n(\mathbf{r})$ with a

TABLE I. Classification of "$1-s$" like donor states in Ge and Si according to irreducible representation of T_d and $\bar{T}_d$.

	T_d	$\bar{T}_d$
Ground state Ge, Si	Γ_1 (A_1)[a]	$\Gamma_6 \times \Gamma_1 = \Gamma_6$
1st excited states Ge, Si	Γ_4 (T_1)[a]	$\Gamma_6 \times \Gamma_4 = \Gamma_7 + \Gamma_8$
2nd excited states Si	Γ_3 (E)[a]	$\Gamma_6 \times \Gamma_3 = \Gamma_8$

[a] The notations A_1, T_1, and E in the brackets are used by Kohn and Luttinger.[6]

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

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common energy E_n. Accordingly, the matrix element of an operator X between two functions $\bar\Psi_1(\mathbf{r})$ and $\bar\Psi_2(\mathbf{r})$ is represented by a 2×2 matrix, which we write simply as $(\bar\Psi_1, X\bar\Psi_2)$. Therefore, assuming that the ground state is orbitally nondegenerate, the shift of the energy of the ground state to the lowest order in $\mathfrak{K}_z$ and $\mathfrak{K}_{e-L}$ can be expressed by a 2×2 matrix as follows:

$$\Delta\mathfrak{K}=(\bar\Psi,\mathfrak{K}_z\bar\Psi)+(\bar\Psi,\mathfrak{K}_{e-L}\bar\Psi)$$

$$+\sum_n{}'\frac{1}{E-E_n}[(\bar\Psi,\mathfrak{K}_z\bar\Psi_n)(\bar\Psi_n,\mathfrak{K}_{e-L}\bar\Psi)$$

$$+(\bar\Psi,\mathfrak{K}_{e-L}\bar\Psi_n)(\bar\Psi_n,\mathfrak{K}_z\bar\Psi)].\quad(2.6)$$

As was pointed out by Abrahams,[13] the first-order effect of the electron-lattice interaction given by the second term $(\bar\Psi,\mathfrak{K}_{e-L}\bar\Psi)$ of the above expression does not yield any spin-lattice interaction, because the relations

$$(\bar\Psi,\mathfrak{K}_{e-L}\bar\Psi)=(\Phi,\mathfrak{K}_{e-L}\Phi),$$
$$(\bar\Psi,\mathfrak{K}_{e-L}\Phi)=(\Phi,\mathfrak{K}_{e-L}\bar\Psi)=0\quad(2.7)$$

are satisfied (Van Vleck cancellation). Thus the spin-lattice interaction responsible for the relaxation effects is represented by the third term in Eq. (2.6). In this term the summation runs over all excited states, but we shall consider only those low-lying excited states which are split off from the ground state by the intervalley interaction due to the impurity potential. A discussion of this point will be given in Sec. 5.

It has been shown by Kohn and Luttinger[6] that the wave functions of the ground state and of these excited states can be written as

$$\Psi(\mathbf{r})=\sum_{(i)}\alpha^{(i)}\Psi^{(i)}(\mathbf{r}),$$

and
$$\quad(2.8)$$

$$\Psi_r(\mathbf{r})=\sum_{(i)}\alpha_r^{(i)}\Psi^{(i)}(\mathbf{r}),$$

respectively, where the superscript i represents the location of an energy valley in the conduction band, and runs from 1 to 4 for Ge and from 1 to 6 for Si. In the absence of spin these wave functions belong to irreducible representations of the full tetrahedral group T_d, and the corresponding sets of amplitudes $\alpha_r^{(i)}$ are determined by symmetry alone. The classification of these states according to irreducible representations of T_d is given in Kohn and Luttinger's paper.[6] In the presence of spin the wave functions belong to irreducible representations of the tetrahedral double-group $\bar T_d$. Table I gives a classification of the states according to these irreducible representations.

Since the angular momentum vector ℓ and the spin $\mathbf{s}$ are axial vectors and transform like Γ_5,[17] the only states

which have nonvanishing matrix elements of ℓ and $\mathbf{s}$ with the ground state, whose symmetry is $\Gamma_6\times\Gamma_1=\Gamma_6$, are those which appear in the decomposition of $\Gamma_6\times\Gamma_5$. The latter is equal to $\Gamma_6+\Gamma_8$. As is seen from Table I, the representation Γ_8 occurs among the relevant low-lying excited states of donors in both Ge and Si. In the following section we shall derive explicit expressions for the matrix elements of ℓ between the ground state and some of these excited states.

The spin-orbit interaction may both shift levels and also remove the degeneracy of the states Γ_4. However, these changes are generally small compared to the intervalley splitting, and may be neglected. Making this assumption, we attribute the admixture of spin functions entirely to the effect of the spin-orbit interaction on the conduction band, and write

$$\Psi^{(i)}(\mathbf{r})=\int A^{(i)}(\mathbf{k})\bar\psi_\mathbf{k}(\mathbf{r})\frac{d\mathbf{k}}{(2\pi)^3},\quad(2.9)$$

where $A^{(i)}(\mathbf{k})$ satisfies

$$A^{(i)}(\mathbf{k})=0,\quad|\mathbf{k}-\mathbf{k}_i|\gg1/a^*,\quad(2.10)$$

a^* being the effective Bohr radius of the ground state of the donor, and a measure of the size of the orbit. Since $1/a^*$ is generally small compared to the length of a reciprocal lattice vector, $\Psi^{(i)}(\mathbf{r})$ is usually approximated by a product of $\bar\psi_{\mathbf{k}i}(\mathbf{r})$, the Bloch function at the bottom of the ith valley, and the envelope function

$$F^{(i)}(\mathbf{r})=\int A^{(i)}(\mathbf{k})e^{i(\mathbf{k}-\mathbf{k}i)\cdot\mathbf{r}}\frac{d\mathbf{k}}{(2\pi)^3}.\quad(2.11)$$

We shall use $\bar\psi_\mathbf{k}(\mathbf{r})$ to denote the pair of Bloch functions

$$\psi_\mathbf{k}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_\mathbf{k}(\mathbf{r}),\quad\phi_\mathbf{k}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}v_\mathbf{k}(\mathbf{r}),\quad(2.12)$$

which forms Kramers' doublet. These functions satisfy the Schrödinger equation for the perfect crystal:

$$\mathfrak{K}_{\text{crystal}}\bar\psi_\mathbf{k}\equiv\left[\frac{p^2}{2m}+V_{\text{period}}+\frac{\hbar}{2m^2c^2}(\mathbf{s}\times\operatorname{grad}V_{\text{period}})\cdot\mathbf{p}\right]\bar\psi_\mathbf{k}$$

$$=E(\mathbf{k})\bar\psi_\mathbf{k}.\quad(2.13)$$

They are normalized as follows:

$$(\bar\psi_\mathbf{k},\bar\psi_{\mathbf{k}'})_{\text{crystal}}=(2\pi)^3\delta(\mathbf{k}-\mathbf{k}'),\quad(\bar\psi_\mathbf{k},\bar\psi_\mathbf{k})_{\text{cell}}=\Omega.\quad(2.14)$$

where Ω is the volume of the unit cell. Under these conditions, a donor function

$$\Psi(\mathbf{r})=\int_{\text{1st zone}}A(\mathbf{k})\bar\psi_\mathbf{k}(\mathbf{r})\frac{d\mathbf{k}}{(2\pi)^3}$$

is then normalized if $A(\mathbf{k})$ satisfies the equation

$$\int_{\text{1st zone}}A^*(\mathbf{k})A(\mathbf{k})\frac{d\mathbf{k}}{(2\pi)^3}=1.\quad(2.15)$$

[17] The notations Γ of irreducible representations of T_d and $\bar T_d$ are same as those given by H. Bethe, Ann. Physik 3, 133 (1929), and by R. J. Elliott, Phys. Rev. 96, 280 (1954). See also G. Dresselhaus, Phys. Rev. 100, 580 (1955).

Finally, we note that the matrix element of an operator X between two donor states $\bar{\Psi}_1(\mathbf{r})$ and $\bar{\Psi}_2(\mathbf{r})$ can be expressed in terms of the matrix elements of X between Bloch states. The relation is

$$(\bar{\Psi}_1, X\bar{\Psi}_2) = \int\int A_1^*(\mathbf{k})(\bar{\psi}_k, X\bar{\psi}_{k'}) A_2(\mathbf{k}') \frac{d\mathbf{k}d\mathbf{k}'}{(2\pi)^6}. \quad (2.16)$$

3. MATRIX ELEMENTS OF PERTURBING INTERACTIONS

A. Zeeman Energy: $\mathfrak{IC}_z = \mu_B H \cdot (l + g_s s)$

The matrix elements of $\mathfrak{IC}_z$ between the Bloch functions $\bar{\psi}_k(\mathbf{r})$ and $\bar{\psi}_{k'}(\mathbf{r})$ are

$$(\bar{\psi}_k, \mathfrak{IC}_z \bar{\psi}_{k'})$$

$$= \mu_B H \cdot \begin{pmatrix} (\psi_k,(\ell+g_s\mathbf{s})\psi_{k'}) & (\psi_k,(\ell+g_s\mathbf{s})\phi_{k'}) \\ (\phi_k,(\ell+g_s\mathbf{s})\psi_{k'}) & (\phi_k,(\ell+g_s\mathbf{s})\phi_{k'}) \end{pmatrix}. \quad (3.1)$$

Since the spin-orbit interaction is present in the periodic potential, the electronic spin $\mathbf{s}$ is not a constant of motion and its $\bar{\psi}_k$ representation will not in general be identical with the Pauli spin matrices, but of the form

$$(\bar{\psi}_k, \mathbf{s}\bar{\psi}_{k'}) = \mathbf{s}_k(2\pi)^3\delta(\mathbf{k}-\mathbf{k}'), \quad (3.2)$$

where each component of the vector $\mathbf{s}_k$ is a 2×2 matrix

$$\mathbf{s}_k = \begin{pmatrix} \delta_k & \gamma_k^* \\ \gamma_k & -\delta_{-k} \end{pmatrix}, \quad \delta_k, \delta_{-k} = \text{real}, \quad (3.3)$$

in which the constants δ_k and γ_k are even functions of $\mathbf{k}$, so that

$$\mathbf{s}_{-k} = \mathbf{s}_k. \quad (3.4)$$

However, when the conduction band under consideration is orbitally nondegenerate, so that the spin-orbit interaction $\mathfrak{IC}_{s-o}$ may be treated as a perturbation in determining $\bar{\psi}_k(\mathbf{r})$ and $E(\mathbf{k})$, the spin representation (3.3) is identical with the Pauli matrices up to first order in $\mathfrak{IC}_{s-o}$. Deviations from the Pauli matrices are at least of second order in $\mathfrak{IC}_{s-o}$. Rigorous arguments concerning this are presented in the Appendix.

It is shown in the Appendix that the matrix (3.1) can be written in the following simple form:

$$(\bar{\psi}_k, \mathfrak{IC}_z\bar{\psi}_{k'}) = \mu_B H \cdot [\ell_k\mathbf{1} + \mathbf{g}_k \cdot \mathbf{s}_k](2\pi)^3\delta(\mathbf{k}-\mathbf{k}'), \quad (3.5)$$

provided that the conduction band is orbitally non-degenerate and the crystal has a center of inversion. The first term of this expression is $\mu_B H \cdot \ell_k$ times the 2×2 unit matrix $\mathbf{1}$, and is spin independent. Here ℓ_k is the angular momentum vector in $\mathbf{k}$ space defined by

$$\ell_k = (m/\hbar^2)[i\nabla_k \times \nabla_k E(\mathbf{k})], \quad (3.6)$$

∇_k being a gradient operator operating on a function of $\mathbf{k}$ in the first Brillouin zone. The second term of the expression (3.5) is a linear combination of the three "Pauli-like" matrices $\mathbf{s}_k$ ($\mathbf{s}_k^\alpha$, $\alpha = x, y, z$), and is spin

dependent. The quantity $\mathbf{g}_k$ is a 3×3 tensor which connects the components of the magnetic field $\mathbf{H}$ with the components of the spin $\mathbf{s}_k$. This tensor $\mathbf{g}_k$ may be interpreted as the g tensor of the conduction electron spins.

The quantity $\mathbf{g}_k \cdot \mathbf{s}_k$ can be expressed in terms of the matrix elements of the operators $\pi = \mathbf{p} + (\hbar/2mc^2)(\mathbf{s} \times \text{grad}V_{\text{period}})$, and $i\nabla_k$ between Bloch functions of the conduction band and those of other bands. Writing

$$\mathbf{g}_k \cdot \mathbf{s}_k = (g_s\mathbf{1} + \mathbf{\Delta}_k + \mathbf{\Delta}_{1k}) \cdot \mathbf{s}_k, \quad (3.7)$$

the tensors $\mathbf{\Delta}_k$ and $\mathbf{\Delta}_{1k}$ are defined by the following equations:

$$\mathbf{\Delta}_k \cdot \mathbf{s}_k = \frac{1}{im\Omega^2}\sum_n{}' \frac{1}{E(\mathbf{k})-E_n(\mathbf{k})}(\bar{\psi}_k, \pi\bar{\psi}_{nk})_{\text{cell}}$$

$$\times (\bar{\psi}_{nk}, \pi\bar{\psi}_k)_{\text{cell}}, \quad (3.8)$$

$$\mathbf{\Delta}_{1k} \cdot \mathbf{s}_k = -(mi/\hbar^2\Omega)(\nabla_k\bar{u}_k, \bar{u}_k)_{\text{cell}} \times \nabla_k E(\mathbf{k}). \quad (3.9)$$

In the expression (3.8), $\bar{\psi}_{nk}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\bar{u}_{nk}(\mathbf{r})$ is a set of Bloch functions belonging to the nth band, and the summation runs over all bands except the conduction band under consideration. The right-hand sides of Eqs. (3.8) and (3.9) are 2×2 matrices, which are discussed in the Appendix on the basis of Kramers' theorem, and shown to be of the form given in Eq. (3.3). Since any matrix of the form (3.3) can be written as a linear combination of three independent matrices of the same form, the right-hand sides of Eqs. (3.8) and (3.9) must be linear combinations of the three matrices $\mathbf{s}_k^\alpha$ ($\alpha = x, y, z$), as we have indicated by using the notation $\mathbf{\Delta}_k \cdot \mathbf{s}_k$ and $\mathbf{\Delta}_{1k} \cdot \mathbf{s}_k$, respectively. By way of example let us consider the z component of $\mathbf{\Delta}_k \cdot \mathbf{s}_k$. We have

$$(\mathbf{\Delta}_k \cdot \mathbf{s}_k)^z = \frac{1}{mi}\sum_n{}' \frac{1}{E(\mathbf{k})-E_n(\mathbf{k})}$$

$$\times \begin{bmatrix} \pi_{\psi n}^x\pi_{n\psi}^y - \pi_{\psi n}^y\pi_{n\psi}^x, & \pi_{\psi n}^x\pi_{n\phi}^y - \pi_{\psi n}^y\pi_{n\phi}^x \\ \pi_{\phi n}^x\pi_{n\psi}^y - \pi_{\phi n}^y\pi_{n\psi}^x, & \pi_{\phi n}^x\pi_{n\phi}^y - \pi_{\phi n}^y\pi_{n\phi}^x \end{bmatrix}, \quad (3.10)$$

where

$$\pi_{\psi n}^x = (1/\Omega)(\psi, \pi^x\psi_n)_{\text{cell}},$$
$$\pi_{n\phi}^y = (1/\Omega)(\psi_n, \pi^y\phi)_{\text{cell}}, \text{ etc.} \quad (3.11)$$

The diagonal element of this matrix multiplied by μ_B is just equal to Roth, Lax, and Zwerdling's expression[18] for the effective Bohr magneton [when Eq. (3.10) is applied to $\mathbf{k}=0$]. The off-diagonal elements of the matrix will vanish at $\mathbf{k}=0$, but will not vanish at general points in the first Brillouin zone.

The tensors $\mathbf{\Delta}_k$ and $\mathbf{\Delta}_{1k}$ are generally slowly varying functions of $\mathbf{k}$, and are replaced by their values at each point of the conduction band minima, where $\mathbf{\Delta}_{1k}$

[18] L. M. Roth, B. Lax, and S. Zwerdling, Phys. Rev. 114, 91 (1951), Appendix A.

vanishes because $\mathbf{A}_{1k}$ is proportional to $\nabla_k E(\mathbf{k})$. Thus, near the point $\mathbf{k}=\mathbf{k}_i$, the ith minimum of the conduction band, the Zeeman energy is represented by

$$(\bar{\psi}_k, \mathcal{3C}_z \bar{\psi}_{k'})_{k, \, k' \approx k_i} = \mu_B \mathbf{H} \cdot \boldsymbol{\ell}_k (2\pi)^3 \delta(\mathbf{k}-\mathbf{k}')$$
$$+ \mu_B \mathbf{H} \cdot (g_s \mathbf{1} + \mathbf{A}^{(i)}) \cdot \mathbf{s}_{ki} (2\pi)^3 \delta(\mathbf{k}-\mathbf{k}'), \quad (3.12)$$

where

$$\mathbf{A}^{(i)} = \mathbf{A}_{k_i}, \quad (3.13)$$

and, up to first order in the spin-orbit interaction $\mathcal{3C}_{s-o}$, $\mathbf{s}_{ki}$ may be replaced by the Pauli matrices $\mathbf{s}$. The first correction to the expression (3.12) is

$$(\bar{\psi}_k, \mathcal{3C}_z \bar{\psi}_{k'})_{k, \, k' \approx k_i}^{(1)}$$
$$= \mu_B \mathbf{H} \cdot \mathbf{A}_1^{(1)} (\mathbf{k}-\mathbf{k}_i) \cdot \mathbf{s} (2\pi)^3 \delta(\mathbf{k}-\mathbf{k}'), \quad (3.14)$$

where

$$\mathbf{A}_1^{(i)}(\mathbf{k}-\mathbf{k}_i) \cdot \mathbf{s}$$
$$= -(mi/\hbar^2\Omega)(\nabla_k \bar{u}, \nabla_k \bar{u})_{\text{cell}} (\mathbf{k}-\mathbf{k}_i) \times \nabla_k E(\mathbf{k}). \quad (3.15)$$

Since $\mathbf{A}_k$ and $\mathbf{A}_{1k}$ are even functions, the tensors for a particular valley (i) and its inverse $(-i)$ are related by

$$\mathbf{A}^{(-i)} = \mathbf{A}^{(i)}, \quad \mathbf{A}^{(-i)}(-\mathbf{k}+\mathbf{k}_i) = \mathbf{A}^{(i)}(\mathbf{k}-\mathbf{k}_i). \quad (3.16)$$

These relations simplify the calculation in Si.

We now write the matrix element of $\mathcal{3C}_z$ between two donor functions.

$$(\bar{\psi}_1, \mathcal{3C}_z \bar{\psi}_2) = \mu_B \mathbf{H} \cdot \int\!\!\int_{\text{1st zone}} A_1^*(\mathbf{k})[\boldsymbol{\ell}_k + \mathbf{g}_k \cdot \mathbf{s}_k]$$

$$\times A_2(\mathbf{k}')\delta(\mathbf{k}-\mathbf{k}')\frac{d\mathbf{k}d\mathbf{k}'}{(2\pi)^3}$$

$$= \mu_B \mathbf{H} \cdot \int_{\text{1st zone}} A_1^*(\mathbf{k}) \left[\frac{mi}{\hbar^2} \nabla_k \times \nabla_k E(\mathbf{k}) \right.$$

$$\left. + (g_s \mathbf{1} + \mathbf{A}_k + \mathbf{A}_{1k}) \cdot \mathbf{s}_k \right] A_2(\mathbf{k}) \frac{d\mathbf{k}}{(2\pi)^3}. \quad (3.17)$$

For the ith valley donor function $\bar{\Psi}^{(i)}(\mathbf{r})$ with the property indicated by Eq. (2.10), we may use the approximate expressions (3.12) and (3.14), and write

$$(\bar{\Psi}^{(i)}, \mathcal{3C}_z \bar{\psi}^{(i)}) = \mu_B \mathbf{H} \cdot (g_s \mathbf{1} + \mathbf{A}^{(i)} + \mathbf{A}_1^{(i)}) \cdot \mathbf{s}, \quad (3.18)$$

where

$$\mathbf{A}_1^{(i)} = \int |A^{(i)}(\mathbf{k})|^2 \mathbf{A}^{(i)}(\mathbf{k}-\mathbf{k}_i) \frac{d\mathbf{k}}{(2\pi)^3}. \quad (3.19)$$

We note that the expectation value of the angular momentum $\boldsymbol{\ell}_k$ must vanish, since the envelope function $F^{(i)}(\mathbf{r})$ can be taken to be real.

The anisotropy of the g tensor at the conduction band edge of Ge has been discussed by Roth and Lax.[19] The crystal symmetry requires that the tensor has the

following form:

$$\mathbf{g}^{(i)} = g_s\mathbf{1} + \mathbf{A}^{(i)} + \mathbf{A}_1^{(i)} = \begin{vmatrix} g_t & & \\ & g_t & \\ & & g_l \end{vmatrix}, \quad (3.20)$$

where the principal axes of this tensor coincide with those of the effective mass tensor for the valley. For convenience we rewrite this equation in the form

$$\mathbf{g}^{(i)} = g_t\mathbf{1} + g'3\mathbf{U}^{(i)}, \quad (3.21)$$

where

$$g' = \tfrac{1}{3}(g_l - g_t), \quad \mathbf{U}^{(i)} = \begin{vmatrix} 0 & & \\ & 0 & \\ & & 1 \end{vmatrix}. \quad (3.22)$$

The expectation value of $\mathcal{3C}_z$ in the ground state and the off-diagonal element of $\mathcal{3C}_z$ between the ground state and a low-lying excited state defined by Eq. (2.8) are given by

$$(\bar{\Psi}, \mathcal{3C}_z\bar{\Psi}) = \mu_B\mathbf{H} \cdot \sum_i \alpha^{(i)2}(g_t\mathbf{1} + g'3\mathbf{U}^{(i)}) \cdot \mathbf{s}$$
$$= g\mu_B\mathbf{H} \cdot \mathbf{s}, \quad g = \tfrac{1}{3}(2g_t + g_l), \quad (3.23)$$

$$(\bar{\Psi}, \mathcal{3C}_z\bar{\Psi}_r) = \mu_B\mathbf{H} \cdot \sum_{(i)} \alpha^{(i)}\alpha_r^{(i)}(g_t\mathbf{1} + g'3\mathbf{U}^{(i)}) \cdot \mathbf{s}$$
$$= g'\mu_B\mathbf{H} \cdot D_r \cdot \mathbf{s}, \quad (3.24)$$

respectively. The tensor D_r is defined by

$$D_r = 3\sum_{(i)} \alpha^{(i)}\alpha_r^{(i)}\mathbf{U}^{(i)}. \quad (3.25)$$

We note that in Eq. (3.24) the unit tensor $\mathbf{1}$ does not contribute to the summation because of the orthogonality condition $\sum_{(i)} \alpha^{(i)}\alpha_r^{(i)} = 0$. The tensor D_r depends only on the geometrical structure of the conduction band edge.

B. Electron-Lattice Interaction:

$$\mathcal{3C}_{e-L} = -Q(\mathbf{r}) \cdot \mathbf{grad}\, V_{\text{period}}$$

For the displacement $Q(\mathbf{r})$ decomposed into modes of the lattice vibrations, we shall only consider the contribution of acoustic modes of vibration to the displacement $Q(\mathbf{r})$, so that

$$Q(\mathbf{r}) = \sum_{q,t} [\mathbf{e}_t(\mathbf{q})a_{qt}e^{i\mathbf{q}\cdot\mathbf{r}} + \mathbf{e}_t^*(\mathbf{q})a_{qt}^* e^{-i\mathbf{q}\cdot\mathbf{r}}], \quad (3.26)$$

where

$$\mathbf{e}_t(\mathbf{q}) = \mathbf{e}_t^*(-\mathbf{q}), \quad t = 1, 2, 3 \quad (3.27)$$

is a polarization vector, and the amplitudes a_{qt} and a_{qt}^* satisfy

$$[a_{qt}, a_{qt}^*] = \hbar/2NM\omega_{qt}. \quad (3.28)$$

Here M is the mass of the unit cell, and N is the number of unit cells in the crystal. Neglecting umklapp processes, we find that the matrix element of the interaction $\mathcal{3C}_{e-L}$ for a process involving the phonon $(\mathbf{q}, t)$ is

$$(\bar{\psi}_k, \mathcal{3C}_{e-L}\bar{\psi}_{k'})_{qt;\, k,\, k' \approx k_i}$$
$$= a_{qt}[ie_t(\mathbf{q}) \cdot (\Xi_d\mathbf{1} + \Xi_u\mathbf{U}^{(i)}) \cdot \mathbf{q}(2\pi)^3\delta(\mathbf{k}-\mathbf{k}'-\mathbf{q})]$$
$$+ a_{qt}^*[\text{same term as above except } \mathbf{q}$$
$$\text{being replaced by } -\mathbf{q}]. \quad (3.29)$$

[19] L. M. Roth and B. Lax, Phys. Rev. Letters 3, 217 (1959).

In the above expression, $\mathbf{1}$ is the unit tensor, $\mathbf{U}^{(i)}$ is the tensor defined in Eq. (3.22), and Ξ_d and Ξ_u are Herring's deformation-potential constants with the dimension of energy, which measure the strength of the interaction with isotropic dilations and uniaxial strains, respectively. If we make use of the Sommerfeld-Bethe approximation,[20] then

$$(\Xi_d\mathbf{1}+\Xi_u\mathbf{U}^{(i)})_{\alpha\beta}$$

$$=\frac{\hbar^2}{m\Omega}\int_{\text{cell}}(\text{grad}u_{\mathbf{k}_i}{}^*)_\alpha(\text{grad}u_{\mathbf{k}_i})_\beta d\mathbf{r}. \quad (3.30)$$

It will be noted that this type of coupling is spin independent, and that there must be another term depending on spin, whose magnitude will be approximately Δg times smaller than the term given in Eq. (3.30). However, the corresponding term of the effective spin-lattice interaction turns out to be at least of second order in $\mathcal{3C}_{\text{s-o}}$, so that it may be neglected here.

For the ith valley donor function $\Psi^{(i)}(\mathbf{r})$ given in Eq. (2.10), we have

$$(\bar\Psi^{(i)},\mathcal{3C}_{\text{e-L}}\Psi^{(i)})_{\mathbf{q}t}$$

$$=\int\int A^{*(i)}(\mathbf{k})(\bar\psi_{\mathbf{k}},\mathcal{3C}_{\text{e-L}}\psi_{\mathbf{k}'})A^{(i)}(\mathbf{k}')\frac{d\mathbf{k}d\mathbf{k}'}{(2\pi)^6}$$

$$=a_{\mathbf{q}t}[i\mathbf{e}_t(\mathbf{q})\cdot(\Xi_d\mathbf{1}+\Xi_u\mathbf{U}^{(i)})\cdot\mathbf{q}]f^{(i)}(\mathbf{q})+\text{c.c.}, \quad (3.31)$$

where

$$f^{(i)}(\mathbf{q})=\int\int A^{*(i)}(\mathbf{k})A^{(i)}(\mathbf{k}')\delta(\mathbf{k}-\mathbf{k}'-\mathbf{q})\frac{d\mathbf{k}d\mathbf{k}'}{(2\pi)^3}$$

$$=\int A^{*(i)}(\mathbf{k}+\mathbf{q})A^{(i)}(\mathbf{k})\frac{d\mathbf{k}}{(2\pi)^3}$$

$$=\int F^{(i)}(\mathbf{r})^2 e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r}, \quad f^{(i)*}(\mathbf{q})=f^{(i)}(-\mathbf{q}). \quad (3.32)$$

We see that in the limit of long-wave phonons, i.e.,

$$q\rightarrow 0, \quad f^{(i)}(\mathbf{q})\rightarrow 1. \quad (3.33)$$

The function $f^{(i)}(\mathbf{q})$ may be set equal to 1 when $a^*q\ll1$. In that case the expression (3.31) reduces to Eq. (1.3) of the Introduction. A rough approximation to $f^{(i)}(\mathbf{q})$ can be obtained as follows. If we assume an envelope function of the form $F^{(i)}(\mathbf{r})=(\pi a^2 b)^{-\frac{1}{2}}\exp-\{[(x^2+y^2)/a^2]+z^2/b^2\}^{\frac{1}{2}}$, then, $f^{(i)}(\mathbf{q})=$ real $=1/\{1+\frac{1}{4}[(q_x{}^2+q_y{}^2)a^2+q_z{}^2b^2]\}^2$. We now make further approximation of replacing the constants a and b by a single effective Bohr radius a^* in a proper way,[5] so that

$$f^{(i)}(\mathbf{q})\approx 1/[1+\tfrac{1}{4}a^{*2}q^2]^2=f(q). \quad (3.34)$$

We now have approximate expressions for the matrix

[20] A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 2, p. 509.

elements $(\bar\Psi,\mathcal{3C}_{\text{e-L}}\Psi)$, and $(\bar\Psi,\mathcal{3C}_{\text{e-L}}\Psi_r)$:

$$(\bar\Psi,\mathcal{3C}_{\text{e-L}}\Psi)_{\mathbf{q}t}$$

$$=(\Xi_d+\tfrac{1}{3}\Xi_u)f(q)q(a_{\mathbf{q}1}+a_{\mathbf{q}1}{}^*) \quad (3.35)$$

for longitudinal phonons, $t=1$,

$$=0 \quad \text{for transverse phonons}, \quad t=2, 3, \quad (3.36)$$

$$(\bar\Psi,\mathcal{3C}_{\text{e-L}}\Psi_r)_{\mathbf{q}t}$$

$$=(\Xi_u/3)f(q)\{[i\mathbf{e}_t(\mathbf{q})\cdot D_r\cdot\mathbf{q}]a_{\mathbf{q}t}+\text{c.c.}\}, \quad (3.37)$$

where the tensor D_r is that defined by Eqs. (3.23) and (3.20).

Thus the off-diagonal elements of the interactions $\mathcal{3C}_z$ and $\mathcal{3C}_{\text{e-L}}$ can both be expressed in terms of a common tensor D_r. The tensors D_r for different substances and for different states are tabulated in Table II. We label there the states by representations of the single group T_d, since the small splitting between the levels corresponding to the extra representations Γ_7 and Γ_8 of the double group $\bar T_d$ is consistently neglected in this calculation. For Ge, $r(=1, 2, 3)$ denotes the three states belonging to Γ_4, and for Si, $r(=1, 2)$ denotes the two states belonging to Γ_3. The states belonging to Γ_4 in Si are discarded, since in that case $\mathbf{U}^{(-i)}=\mathbf{U}^{(i)}$, $\alpha_r{}^{(-i)}=-\alpha_r{}^{(i)}$, and consequently $D_r=0$.

C. Perturbation Energy

For discussing the Zeeman energy, Eq. (3.24), it is convenient to specify the tensor D_r in a Cartesian coordinate system with axes parallel and perpendicular to the static magnetic field $\mathbf{H}$. If H ($\sin\theta\cos\phi$, $\sin\theta\sin\phi$, $\cos\theta$) are the polar coordinates of $\mathbf{H}$ referred to the $\langle 100\rangle$ axes in the crystal, θ being the angle between $\mathbf{H}$ and one of these axes, then a suitable set of orthogonal axes are defined by the vectors

$$u^{(1)}(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta),$$

$$u^{(2)}(\cos\theta\cos\phi, \cos\theta\sin\phi, -\sin\theta), \quad (3.38)$$

$$u^{(3)}(-\sin\phi, \cos\phi, 0).$$

In this representation the expression (3.24) becomes

$$(\bar\Psi,\mathcal{3C}_z\Psi_r)=g'\mu_B H(D_r{}^{(t')}s_{t'})$$

$$=g'\mu_B H(D_r{}^{(1)}s_1+D_r{}^{(2)}s_2+D_r{}^{(3)}s_3), \quad (3.39)$$

TABLE II. Expressions for tensors D_r in the Cartesian coordinate system with orthogonal axes $\langle 100\rangle$ for donor states Γ_4 in Ge and for donor states Γ_3 in Si. The constants $\alpha_r{}^{(i)}$ entering D_r defined by Eq. (3.25) are those given by Kohn and Luttinger,[a] which are modified so that they are orthogonal to each other.

Γ_4			
Ge	$D_1=1/\sqrt2\begin{vmatrix}0 & 1 \\ & 1 \\ 1 & 1 & 0\end{vmatrix}$,	$D_2=1/\sqrt2\begin{vmatrix}0 & -1 \\ & 1 \\ -1 & 1 & 0\end{vmatrix}$,	$D_3=\begin{vmatrix}1 \\ 1 & 1 \\ & 0\end{vmatrix}$
Γ_3			
Si	$D_1=1/\sqrt2\begin{vmatrix}1 \\ & 1 \\ & & -2\end{vmatrix}$,	$D_2=-\sqrt3/\sqrt2\begin{vmatrix}1 \\ & -1 \\ & & 0\end{vmatrix}$	

[a] See reference 6.

TABLE III. Expressions for the components of D_r in the Cartesian coordinate system with orthogonal axes $u^{(1)}$, $u^{(2)}$, $u^{(3)}$, defined in Eq. (3.38).

		r	$D_r^{(1)}$	$D_r^{(2)}$	$D_r^{(3)}$
Ge	Γ_4	1	$(1/\sqrt{2}) \sin 2\theta (\cos\phi + \sin\phi)$	$(1/\sqrt{2}) \cos 2\theta (\cos\phi + \sin\phi)$	$(1/\sqrt{2}) \cos\theta (\cos\phi - \sin\phi)$
		2	$(-1/\sqrt{2}) \sin 2\theta (\cos\phi - \sin\phi)$	$(-1/\sqrt{2}) \cos 2\theta (\cos\phi - \sin\phi)$	$(1/\sqrt{2}) \cos\theta (\cos\phi + \sin\phi)$
		3	$\sin^2\theta \sin 2\phi$	$\sin\theta \cos\theta \sin 2\phi$	$\sin\theta \cos 2\phi$
Si	Γ_3	1	$(1/\sqrt{2}) \sin^2\theta - 2 \cos^2\theta)$	$(1/\sqrt{2}) 3 \sin\theta \cos\theta$	0
		2	$(\frac{3}{2})^{\frac{1}{2}} \sin^2\theta \cos 2\phi$	$-(\frac{3}{2})^{\frac{1}{2}} \sin\theta \cos\theta \cos 2\phi$	$(\frac{3}{2})^{\frac{1}{2}} \sin\theta \sin 2\phi$

where s_1, s_2, and s_3 are the components of the spin parallel and perpendicular to $\mathbf{H}$, respectively. The coefficients $D_r^{(t')}$ as functions of θ and ϕ are also given in Table III.

Similarly, for discussing the electron-lattice interaction, Eq. (3.37), it is convenient to introduce another Cartesian coordinate system with axes parallel and perpendicular to the wave vector $\mathbf{q}$. Three polarization vectors $i\mathbf{e}_t(\mathbf{q})$, ($t = 1, 2, 3$), form a suitable set of the axes if the spectrum of the lattice vibration is characterized by pure longitudinal and transverse modes. In this case we have

$$(\bar{\Psi}, \mathcal{H}_{e-L}\bar{\Psi}_r)_q = (\Xi_u/3) f(q) q (D_r^{(t)} a_{qt} + \text{c.c.}). \quad (3.40)$$

If the polar coordinates of $\mathbf{q}$ with respect to the $\langle 100 \rangle$ axes in the crystal are (ϑ, ψ), then the coefficients $D_r^{(t)}$ in Eq. (3.40) may be obtained by replacing (θ, ϕ) by (ϑ, ψ) in the corresponding term in Table III.

Finally, inserting the expressions (3.39) and (3.40) into the third term of Eq. (2.6), we obtain an effective coupling between a donor spin and the lattice wave of wave vector $\mathbf{q}$:

$$\Delta\mathcal{H}_{s-Lq} = \frac{2g'\mu_B H\Xi_u}{-3\Delta E} f(q) q (a_{qt} \sum_r D_r^{(t)} D_r^{(t')}$$
$$+ \text{c.c.})s_{t'}, \quad (3.41)$$

where

$$\Delta E = E(\Gamma_4) - E(\Gamma_1) \quad \text{for Ge,}$$
$$\Delta E = E(\Gamma_3) - E(\Gamma_1) \quad \text{for Si.} \quad (3.42)$$

4. CALCULATION OF SPIN-LATTICE RELAXATION RATE

The transition probabilities $W_{-\to+}$ and $W_{+\to-}$ per unit time that the donor spin be flipped from down to up and from up to down due to the effective interaction in Eq. (3.41) are given by

$$W_{-\to+} = \frac{2\pi}{\hbar} \left(\frac{g'\mu_B H\Xi_u}{3\Delta E} \right)^2 \frac{\hbar}{2NM}$$

$$\times \sum_{qt} \frac{q^2}{\omega_{qt}} f^2(q) [(\sum_r D_r^{(t)} D_r^{(2)})^2$$

$$+ (\sum_r D_r^{(t)} D_r^{(3)})^2] n_{qt} \delta(g\mu_B H - \hbar\omega_{qt}), \quad (4.1)$$

$$W_{+\to-} = \frac{2\pi}{\hbar} \left(\frac{g'\mu_B H\Xi_u}{3\Delta E} \right)^2 \frac{\hbar}{2NM}$$

$$\times \sum_{qt} \frac{q^2}{\omega_{qt}} f^2(q) [(\sum_r D_r^{(t)} D_r^{(2)})^2$$

$$+ (\sum_r D_r^{(t)} D_r^{(3)})^2] (n_{qt}+1) \delta(g\mu_B H - \hbar\omega_{qt}), \quad (4.2)$$

respectively, where $n_{qt} = 1/[\exp(\hbar\omega_{qt}/kT) - 1]$ represents the number of $(\mathbf{q}, t)$ phonons in thermal equilibrium. The corresponding spin-lattice relaxation time is obtained from the relation

$$1/T_s = W_{-\to+} + W_{+\to-}. \quad (4.3)$$

Because of energy conservation, the frequency of the relevant phonons absorbed and emitted in these processes is $g\mu_B H/\hbar$ which is quite low compared to the Debye frequency. It is even lower than the frequency corresponding to the energy kT in typical relaxation experiments (for $T = 2°K$, $H = 3000$ gauss: $\hbar\omega/kT = 0.1$), so that we may approximate the number of phonons by

$$n_{qt} \approx n_{qt} + 1 \approx kT/\hbar\omega_{qt}, \quad (4.4)$$

and take

$$f(q) \approx 1. \quad (4.5)$$

The theory of elastic waves in lattices provides a relation between ω_{qt} and $\mathbf{q}$ in terms of the elastic constants. For Ge or Si, the three frequencies ω_{qt}, ($t = 1, 2, 3$), are obtained by solving a secular equation of the Shockley type,[21] and are of the form

$$\omega_{qt} = v_t(\vartheta, \psi) q, \quad (4.6)$$

where $v_t(\vartheta, \psi)$ contains four constants, namely $\rho = M/\Omega$, the density, and three elastic constants c_{11}, c_{12}, and c_{44}. The velocity generally depends on the direction of the wave vector $\mathbf{q}$, but not on its magnitude. If, however, the relation

$$c^* \equiv c_{11} - c_{12} - 2c_{44} = 0 \quad (4.7)$$

is satisfied, the frequency spectrum of the lattice vibration is completely isotropic, and is characterized exactly by one longitudinal and two transverse modes.

[21] W. Shockley, Phys. Rev. 78, 173 (1950). See also Helen M. Smith, Phil. Trans. Roy. Soc. (London) A241, 105 (1948).

TABLE IV. Mean values $\langle (\sum_r D_r^{(t)} D_r^{(t')})^2 \rangle_{\vartheta\psi}$ as functions of the orientation of the magnetic field **H**.

	t'	Longitudinal mode $t=1$ $\langle (\sum_r D_r^{(1)} D_r^{(t')})^2 \rangle$	Transverse modes $t=2, 3$ $\langle (\sum_r D_r^{(2)} D_r^{(t')})^2 \rangle + \langle (\sum D_r^{(3)} D_r^{(t')})^2 \rangle$
Ge	1	$(4/15)(\sin^4 2\theta + \sin^4\theta \sin^2 2\phi)$	$(2/5)(\sin^2 2\theta + \sin^4\theta \sin^2 2\phi)$
	2	$(1/15)(4\cos^2 2\theta + \sin^2 2\theta \sin^2 2\phi)$	$(1/10)(4\cos^2 2\theta + \sin^2 2\theta \sin^2 2\phi)$
	3	$(4/15)(\cos^2\theta + \sin^2\theta \cos^2 2\phi)$	$(2/5)(\cos^2\theta + \sin^2\theta \cos^2 2\phi)$
Si	1	$(1/5)[(3\cos^2\theta - 1)^2 + 3\sin^4\theta \cos^2 2\phi]$	$(3/10)[(3\cos^4\theta - 1)^2 + 3\sin^4\theta \cos^2 2\phi]$
	2	$(3/5)\sin^2\theta \cos^2\theta (3 + \cos^2 2\phi)$	$(9/10)\sin^2\theta \cos^2\theta (3 + \cos^2 2\phi)$
	3	$(3/5)\sin^2\theta \sin^2 2\phi$	$(9/10)\sin^2\theta \sin^2 2\phi$

The corresponding eigenvectors of the secular equation, i.e., the polarization vectors, are identical with those defined in Eqs. (3.36), with (θ,ϕ) replaced by (ϑ,ψ). Up to the first order in c^*, the frequency ω_{q1} of the longitudinal mode is calculated based on the first-order perturbation treatment, obtaining

$$\rho v_1^2(\vartheta,\psi)$$
$$= c_{11} + c^*[-1 + \sin^4\vartheta(\cos^4\psi + \sin^4\psi) + \cos^4\vartheta], \quad (4.8)$$

together with Eq. (4.6).

Inserting Eq. (4.6) into Eqs. (4.1), (4.2), and (4.3), we have

$$\frac{1}{T_s} = 2\pi \left(\frac{g'\Xi_u}{3g\Delta E}\right)^2 \sum_t [\omega^2 G_t(\omega)]_{\omega=(1/\hbar)g\mu_B H} \frac{kT}{\Omega}$$
$$\times \left\langle \frac{1}{\rho v_t^2} [(\sum_r D_r^{(t)} D_r^{(2)})^2 + (\sum_r D_r^{(t)} D_r^{(3)})^2] \right\rangle_{\vartheta\psi}. \quad (4.9)$$

In this expression $G_t(\omega)$ denotes the density of states in the spectrum of the tth vibrational mode,

$$G_t(\omega) = \frac{\Omega}{(2\pi)^3} \int_S \frac{\sin\vartheta d\vartheta d\psi}{v_t^3(\vartheta\psi)} \omega^2, \quad (4.10)$$

and the $\langle F \rangle_{t\vartheta\psi}$ denotes the mean value of a function $F(\vartheta,\psi)$ of the angles (ϑ,ψ), i.e.,

$$\langle F \rangle_{t\vartheta\psi} = \left(1 \Big/ \int \frac{\sin\vartheta d\vartheta d\psi}{v_t^3(\vartheta\psi)}\right) \int_S \frac{\sin\vartheta d\vartheta d\psi}{v_t^3(\vartheta\psi)} F(\vartheta,\psi), \quad (4.11)$$

where the range of the integration is the surface of the unit sphere. We do not, however, attempt to carry out the integration exactly. For the purpose of an order-of-magnitude estimate it is sufficient to replace $v_t^2(\vartheta,\psi)$ by its mean value, obtaining

$$\frac{1}{T_s} = \frac{1}{\pi}\left(\frac{g'\Xi_u}{3g\Delta E}\right)^2 \left(\frac{g\mu_B H}{\hbar}\right)^4 kT \sum_t \frac{1}{\rho \bar{v}_t^5}$$
$$\times \langle [(\sum_r D_r^{(t)} D_r^{(2)})^2 + (\sum_r D_r^{(t)} D_r^{(3)})^2] \rangle_{\vartheta\psi}, \quad (4.12)$$

where

$$\rho \bar{v}_t^2 = c_{11} - \tfrac{2}{5}c^*, \quad t=1$$
$$= c_{44} + \tfrac{1}{5}c^*, \quad t=2, 3. \quad (4.13)$$

The mean value

$$\langle (\sum D_r^{(t)} D_r^{(t')})^2 \rangle_{\vartheta\psi}$$
$$= \frac{1}{4\pi} \int_S \sin\vartheta d\vartheta d\psi (\sum_r D_r^{(t)} D_r^{(t')})^2 \quad (4.14)$$

is calculated by making use of the explicit form of $D_r^{(t)}$ given in Tables II and III. The results are shown in Table IV as functions of the polar coordinates (θ,ϕ), the direction of the static magnetic field **H** referred to the crystallographic axis [100]. For Ge, we have

$$\frac{1}{T_s} = \frac{4}{5\pi}\left(\frac{g'\Xi_u}{3g\Delta E}\right)^2 \left(\frac{1}{\rho\bar{v}_2^5} + \frac{2}{3\rho\bar{v}_1^5}\right)\left(\frac{g\mu_B H}{\hbar}\right)^4$$
$$\times kT f_{Ge}(\theta,\phi), \quad (4.15)$$

where

$$f_{Ge}(\theta,\phi) = \tfrac{1}{2}[\cos^2 2\theta + \cos^2\theta$$
$$+ \sin^2\theta(\cos^2\theta \sin^2 2\phi + \cos^2 2\phi)]; \quad (4.16)$$

and for Si,

$$\frac{1}{T_s} = \frac{6}{5\pi}\left(\frac{g'\Xi_u}{3g\Delta E}\right)^2 \left(\frac{1}{\rho\bar{v}_2^5} + \frac{2}{3\rho\bar{v}_1^5}\right)\left(\frac{g\mu_B H}{\hbar}\right)^4$$
$$\times kT f_{Si}(\theta,\phi), \quad (4.17)$$

where

$$f_{Si}(\theta,\phi) = \tfrac{3}{4}\sin^2\theta(4\cos^2\theta + \sin^2\theta \sin^2 2\phi). \quad (4.18)$$

5. DISCUSSION

The predicted dependence of $1/T_s$ on the temperature T and on the field strength H is seen readily in the expressions (4.9) or (4.12). The linear dependence on T and the fourth-power dependence on H are due to the facts that, (1) the square of the matrix element of $\Delta\mathcal{H}_{s-L}$ is proportional to H^2, (2) the main term in the density of states $G(\omega)$ for acoustical phonons is proportional to ω^2, and (3) the mean value of the square of the dynamical strain is proportional to kT, and is independent of H.

To evaluate $1/T_s$ numerically, it is necessary to know the magnitudes of the constants entering the formulas. For P and As donors in Ge and Si, most of these constants are now known from experiments on donor-spin resonance, acoustoelectric effect, piezoelectric

effect, Hall effect, and the velocity of sound.[22] These constants are summarized in Tables V and VI. Some of the values are not quite certain, since discrepancies are found between the data from different types of experiment.

For P and As donors in Ge, the spin-resonance experiments made by Feher, Wilson, and Gere[11] have revealed a large g shift, and also a marked anisotropy of the linewidth with respect to the direction of **H**. These authors have proposed a mechanism for this anisotropic linewidth assuming a modulation of the g shift due to local strains. The mechanism proposed in the present paper is essentially the same as theirs, except that here the origin of the strain is a dynamical one due to the electron-lattice interaction. A further experiment has been carried out[23] by the same authors to investigate the change in the g shift due to an external strain, and they have succeeded in measuring directly g' and the ratio $\Xi_u/\Delta E$. The numerical values they obtained are included in Table V, and used in the estimation of $1/T_s$.[24]

For donors in Si, no data from direct measurement of g' or $\Xi_u/\Delta E$ is available at present. However, the recent experiment on the Hall effect in P-doped Si made by Long and Myers[9] has provided a value of $\Delta E = 9 \sim 12 \times 10^{-3}$ ev. Also an estimate made by Herring and Vogt[3] gives the value $\Xi_u = -7$ ev. The mean anisotropy g' is still unknown. Here, we assume tentatively that $|g_t - g_t|$ is equal to $|\Delta g| = |g - g_s|$, the difference between the g-value defined in Eq. (3.23) and the free electron g-value, the latter being equal to 2.0023. Using these values

TABLE V. Experimental values of the g shift, the anisotropy of the g shift, the deformation-potential constants, and the inter-valley splitting for P and As donors in Ge and Si.

	Ge	Donor	Si	Donor
$g = \frac{1}{3}(2g_t + g_l)$	1.5631 ±0.0003[a]	P	1.99850 ±0.0001[b]	P
	1.5701 ±0.0003[a]	As	1.99837 ±0.0001[b]	As
$g' = \frac{1}{3}(g_l - g_t)$	−0.37[c]	P		
	−0.36[c]	As		
Ξ_u ev	16[d,e], 19[f]		−7[e]	
ΔE ev	(4.10 ±0.15) ×10⁻³	As	1 ×10⁻² [g]	P
$\Xi_u/\Delta E$	(6.1 ±0.9) ×10³ [c]	P	−7 ×10²	P
	(4.5 ±0.9) ×10³ [c]	As		
$(g'\Xi_u/3g\Delta E)^2$	2.3 ×10⁵	P	(2 ×10⁻²)	P
	1.2 ×10⁵	As		

[a] See reference 11.   See reference 3.
[b] See reference 10, 11.   [f] See reference 8.
[c] See reference 24.   [g] See reference 9.
[d] See reference 7.

[22] H. J. McSkimin, J. Appl. Phys. **24**, 988 (1953).
[23] D. K. Wilson and G. Feher, Bull. Am. Phys. Soc. **5**, 60 (1960).
[24] The author would like to thank D. K. Wilson and Dr. G. Feher for making their experimental data available to him before publication.

TABLE VI. Experimental values of the density and the elastic constants from McSkimin.[a] For definitions of c^*, $\bar{v}_1$, and $\bar{v}_2$, see Eqs. (4.7) and (4.13).

	Ge	Si
ρ g cm⁻³	5.35	2.33
c_{11} 10¹² d cm⁻²	1.316	1.675
c_{12}	0.495	0.650
c_{44}	0.684	0.800
c^*	−0.547	−0.575
$\bar{v}_1$ cm sec⁻¹	5.37×10⁵	9.33×10⁵
$\bar{v}_2$	3.28×10⁵	5.42×10⁵

[a] See reference 22.

$$1/T_s = 1.3 \times 10 H^4 T f_{Ge}(\theta,\phi) \text{ sec}^{-1}$$
$$\text{for P in Ge,} \qquad (5.1)$$

$$= 7.2 H^4 T f_{Ge}(\theta,\phi) \text{ sec}^{-1} \quad \text{for As in Ge, and} \quad (5.2)$$

$$= 9.3 \times 10^{-7} H^4 T f_{Si}(\theta,\phi) \text{ sec}^{-1}$$
$$\text{for P in Si,} \qquad (5.3)$$

where H is in kilogauss and T in degrees K.

We now consider the angular factors $f_{Ge}(\theta,\phi)$ and $f_{Si}(\theta,\phi)$. When the field **H** is applied in (110) plane, these factors reduce to

$$f_{Ge}(\theta) = \cos^4\theta + \frac{1}{2} \sin^4\theta,$$
$$f_{Si}(\theta) = \frac{3}{4} \sin^2\theta(1 + 3 \cos^2\theta). \qquad (5.4)$$

The values of f_{Ge} and f_{Si} in three important cases, corresponding to **H** in [100], [111], and [110] directions, are shown in Table VII. Using these values our estimates of $1/T_s$ for **H** in the [111] directions under the conditions $H = 3$ kilogauss and $T = 1.25°$K are

$$1/T_s = 4.4 \times 10^2 \text{ sec}^{-1} \quad \text{for P in Ge}$$
$$= 2.4 \times 10^2 \text{ sec}^{-1} \quad \text{for As in Ge, and}$$
$$= 9 \times 10^{-5} \text{ sec}^{-1} \quad \text{for P in Si.} \qquad (5.5)$$

In the case of Ge, these are the minimum values of $1/T_s$ with respect to field direction. The maximum value of $1/T_s$ in Ge occurs when the field is in the [100] directions, and then $1/T_s = 1.3 \times 10^3$ sec⁻¹ (P), and 7.3×10^2 sec⁻¹ (As). In the case of Si, on the other hand, the above value corresponds to the maximum of $1/T_s$. Our mechanism gives $1/T_s = 0$ in Si when the field is in the [100] direction. These anisotropic properties are essentially due to the geometrical structures of the conduction band edges.

The angular dependence expressed by the factors f_{Ge} and f_{Si} in Eqs. (4.16) and (4.17) must be regarded as only qualitatively correct, since we have used a simple model of the frequency spectrum of lattice vibrations, and neglected elastic anisotropy in the integration in Eq. (4.11). However, the conclusion that $1/T_s = 0$ for H in the [100] direction in Si would not be modified by any refinement of that integration. Since this is a crucial feature of the present theory, we will note here the approximations which have been made in deriving this result.

TABLE VII. Values of the angular factors f_{Ge}, and f_{Si}.

	[100]	[111]	[110]
$f_{Ge}(\theta,\phi)$	1	$\frac{1}{3}$	$\frac{1}{2}$
$f_{Si}(\theta,\phi)$	0	1	$\frac{3}{4}$

1. We have made use of Kohn and Luttinger's effective-mass functions $\Psi_r(\mathbf{r}) = \sum \alpha_r{}^{(i)}\Psi^{(i)}(\mathbf{r})$. In Si when the field is in the [100] direction the matrix element of $\mathbf{H \cdot l}$ between two such approximate functions with different spins vanishes, leading to $1/T_s = 0$.

2. We have neglected the spin-orbit interactions due to the impurity potential which, if included, might yield an additional splitting and admixture of different spins, although the effect would be small.

3. We have neglected the contribution from excited states other than the low-lying intervalley excited states.

We wish to discuss briefly the contribution from higher excited states mentioned in the item 3. Using Kohn and Luttinger's approach, every donor wave function $\bar\Psi_n(\mathbf{r})$ may be written as a single (or linear combination of) ith valley donor function (s),

$$\Psi_n{}^{(i)}(\mathbf{r}) = \int A_n{}^{(i)}(\mathbf{k})\bar\psi_k(\mathbf{r})\frac{d\mathbf{k}}{(2\pi)^3},$$

similar in form to the lowest few states [see Eq. (2.11)]. We can write the matrix elements of $\mathcal{H}_{e-L}$ with these states in the form given in Eq. (3.31), obtaining

$$(\bar\Psi^{(i)}, \mathcal{H}_{e-L}\Psi_n{}^{(i)})_{qt}$$
$$= a_{qt}[ie_t(\mathbf{q}) \cdot (\Xi_d\mathbf{1} + \Xi_u\mathbf{U}^{(i)}) \cdot \mathbf{q}f_n{}^{(i)}(\mathbf{q})] + \text{c.c.}, \quad (5.6)$$

where

$$f_n{}^{(i)}(\mathbf{q}) = \int A^{*(i)}(\mathbf{k}+\mathbf{q})A_n{}^{(i)}(\mathbf{k})\frac{d\mathbf{k}}{(2\pi)^3}$$

$$= \int F^{*(i)}(\mathbf{r})F_n{}^{(i)}(\mathbf{r})e^{i\mathbf{q}\mathbf{r}}d\mathbf{r}. \quad (5.7)$$

Kohn and Luttinger show that every $A_n{}^{(i)}(\mathbf{k})$ satisfies, to the first approximation, a common effective mass equation, so that $A^{(i)}(\mathbf{k})$ and $A_n{}^{(i)}(\mathbf{k})$ are orthogonal to each other. Therefore, the factor $f_n{}^{(i)}(\mathbf{q})$, in contrast to the factor $f^{(i)}(\mathbf{q})$ in Eq. (3.32), tends to zero at the limit of long wave phonons, and in fact

$$f_n{}^{(i)}(\mathbf{q}) = 0(a^*q), \quad q \to 0. \quad (5.8)$$

Accordingly, the contribution to the transition probabilities $W_{-\to+}$, and $W_{+\to-}$ from these states must involve a higher power of q than the contribution already treated, so that the corresponding rate $1/T_s$ will be proportional to a power of H higher than the fourth.

This argument leads us to the conclusion that of all the excited states of shallow donors only the low-lying

intervalley excited states can be responsible for the dependence of $1/T_s$ on the fourth power of the field strength H.

CONCLUSION

We have calculated the spin-lattice relaxation rate of certain donors in Ge and Si due to the modulation of the g shift by lattice vibrations. The characteristic features of the rate obtained are that (1) it is proportional to kT, and to H^4, and that (2) it is anisotropic with respect to the field direction. These properties make it feasible to check the theory against experimental results.

The spin-lattice relaxation time of P donors in Si has been measured by several authors. Although the results obtained are quite complicated, depending on both the donor concentration and the temperature, the first feature has been confirmed at very low temperatures in the case of very low donor concentrations. The experimental study of the relaxation properties of donors in Ge is also promising. In the circumstances it would be desirable to carry out experiments on the anisotropy of $1/T_s$.

APPENDIX. DERIVATION OF EQS. (3.3)–(3.9)

We use the symbol $\mathcal{J}$ to denote an operator acting on the two spin functions α, and β, which satisfies the relations

$$\mathcal{J}\alpha = \beta, \quad \mathcal{J}\beta = -\alpha. \quad (A1)$$

Starting with a Bloch function $\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_k(\mathbf{r})$ with wave vector $\mathbf{k}$, we may define another Bloch function $\phi_{-k}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}}v_{-k}(\mathbf{r})$ with wave vector $-\mathbf{k}$ by the relations

$$\phi_k = \mathcal{J}\psi_{-k}{}^*, \quad \psi_k = -\mathcal{J}\phi_{-k}{}^*. \quad (A2)$$

Kramers' theorem for these Bloch functions can be stated as follows[25]: If $\psi_k(\mathbf{r})$ satisfies the Schrödinger equation for the crystal with energy $E(\mathbf{k})$, then $\phi_{-k}(\mathbf{r})$ satisfies the same equation with energy $\bar E(-\mathbf{k})$, and

$$\bar E(-\mathbf{k}) = E(\mathbf{k}). \quad (A3)$$

When the crystal has a center of inversion, it is possible to choose the phase of $\phi_k(\mathbf{r})$ so that

$$\phi_k(\mathbf{r}) = \phi_{-k}(-\mathbf{r}). \quad (A4)$$

In this case the two Bloch functions $\psi_k(\mathbf{r})$ and $\phi_k(\mathbf{r})$ are taken to be orthogonal to each other, and belong

[25] H. A. Kramers, Proc. Acad. Sci. Amsterdam 33, 959 (1930). See also E. O. Kane, J. Phys. Chem. Solids 1, 82 (1956).

to a common energy band $E(\mathbf{k})$, so that

$$E(\mathbf{k}) = \bar{E}(-\mathbf{k}) = \bar{E}(\mathbf{k}). \tag{A5}$$

We now consider the matrix of the spin $\mathbf{s}$,

$$\mathbf{s}_\mathbf{k} = (\bar{\psi}_\mathbf{k}, \mathbf{s}\bar{\psi}_\mathbf{k}) = \begin{pmatrix} (\psi_\mathbf{k}, \mathbf{s}\psi_\mathbf{k}) & (\psi_\mathbf{k}, \mathbf{s}\phi_\mathbf{k}) \\ (\phi_\mathbf{k}, \mathbf{s}\psi_\mathbf{k}) & (\phi_\mathbf{k}, \mathbf{s}\phi_\mathbf{k}) \end{pmatrix}. \tag{A6}$$

Symmetry relations between the four elements of this matrix can be stated as follows:

I $\qquad (\psi_\mathbf{k}, \mathbf{s}\psi_\mathbf{k}), (\phi_\mathbf{k}, \mathbf{s}\phi_\mathbf{k}) = \text{real}, \tag{A7}$

$$(\psi_\mathbf{k}, \mathbf{s}\phi_\mathbf{k}) = (\phi_\mathbf{k}, \mathbf{s}\psi_\mathbf{k})^*, \tag{A8}$$

because the operator $\mathbf{s}$ is Hermitian.

II $\qquad (\phi_\mathbf{k}, \mathbf{s}\phi_\mathbf{k}) = -(\psi_{-\mathbf{k}}, \mathbf{s}\psi_{-\mathbf{k}}), \tag{A9}$

$$(\psi_\mathbf{k}, \mathbf{s}\phi_\mathbf{k}) = (\phi_{-\mathbf{k}}, \mathbf{s}\psi_{-\mathbf{k}})^*. \tag{A10}$$

These equations can be proved by using Eqs. (A2), and the relation

$$\mathcal{J}\mathbf{s}^*\mathcal{J}^{-1} = -\mathbf{s}. \tag{A11}$$

III Combining Eqs. (A8) and (A10), we see that the off-diagonal elements $(\psi_\mathbf{k}, \mathbf{s}\phi_\mathbf{k})$ and $(\phi_\mathbf{k}, \mathbf{s}\psi_\mathbf{k})$ are even functions of $\mathbf{k}$. Furthermore, if the crystal has a center of inversion, the diagonal elements $(\psi_\mathbf{k}, \mathbf{s}\psi_\mathbf{k})$ and $(\phi_\mathbf{k}, \mathbf{s}\phi_\mathbf{k})$ must also be even, since Eq. (A4) is satisfied, and consequently $\mathbf{s}_{-\mathbf{k}} = \mathbf{s}_\mathbf{k}$.

Next we consider the matrix elements of the angular momentum

$$\boldsymbol{\ell} = (1/\hbar)\mathbf{r} \times \boldsymbol{\pi}, \quad \boldsymbol{\pi} = \mathbf{p} + (\hbar/2mc^2)(\mathbf{s} \times \mathrm{grad} V_{\text{period}}).$$

$$(\bar{\psi}_\mathbf{k}, \boldsymbol{\ell}\bar{\psi}_{\mathbf{k}'}) = \int e^{-i\mathbf{k}\cdot\mathbf{r}} \bar{u}_\mathbf{k}^*(\mathbf{r}) \boldsymbol{\ell} e^{i\mathbf{k}'\cdot\mathbf{r}} \bar{u}_{\mathbf{k}'}(\mathbf{r}) d\mathbf{r}$$

$$= \frac{i}{\hbar}\nabla_\mathbf{k} \times \int e^{-i\mathbf{k}\cdot\mathbf{r}} \bar{u}_\mathbf{k}^*(\mathbf{r}) \boldsymbol{\pi} e^{i\mathbf{k}'\cdot\mathbf{r}} \bar{u}_{\mathbf{k}'}(\mathbf{r}) d\mathbf{r}$$

$$- \frac{i}{\hbar}\int e^{-i\mathbf{k}\cdot\mathbf{r}} \nabla_\mathbf{k} \bar{u}_\mathbf{k}^*(\mathbf{r}) \times \boldsymbol{\pi} e^{i\mathbf{k}'\cdot\mathbf{r}} \bar{u}_{\mathbf{k}'}(\mathbf{r}) d\mathbf{r}. \tag{A12}$$

The first and the second terms represent the nonperiodic and the periodic parts of the angular momentum, respectively. For further reduction we shall use the explicit form of the matrix elements of the operator $\boldsymbol{\pi}$, and a sum rule. In the case of crystals with a center of inversion, we have

$$(\psi_\mathbf{k}, \boldsymbol{\pi}\psi_{\mathbf{k}'}) = (\phi_\mathbf{k}, \boldsymbol{\pi}\phi_{\mathbf{k}'})$$
$$= (m/\hbar)\nabla_\mathbf{k} E(\mathbf{k})(2\pi)^3\delta(\mathbf{k}-\mathbf{k}'), \tag{A13}$$

$$(\psi_\mathbf{k}, \boldsymbol{\pi}\phi_{\mathbf{k}'}) = (\phi_\mathbf{k}, \boldsymbol{\pi}\psi_{\mathbf{k}'}) = 0. \tag{A14}$$

The sum rule is

$$(e^{i\mathbf{k}\mathbf{r}}\nabla_\mathbf{k}\bar{u}_\mathbf{k}, \boldsymbol{\pi}\bar{\psi}_\mathbf{k})_{\text{cell}}$$

$$= \frac{\hbar}{m\Omega}\sum_n{}' \frac{1}{E(\mathbf{k})-E_n(\mathbf{k})} (\bar{\psi}_\mathbf{k}, \boldsymbol{\pi}\bar{\psi}_{n\mathbf{k}})_{\text{cell}}(\bar{\psi}_{n\mathbf{k}}, \boldsymbol{\pi}\bar{\psi}_\mathbf{k})_{\text{cell}}$$

$$+ (m/\hbar)(\nabla_\mathbf{k}\bar{u}_\mathbf{k}, \bar{u}_\mathbf{k})_{\text{cell}}\nabla_\mathbf{k} E.^{26} \tag{A15}$$

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[26] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955). It is stated there that the term $(\nabla_\mathbf{k}\bar{u}_\mathbf{k}, \bar{u}_\mathbf{k})$ vanishes, when the crystal

Inserting Eqs. (A13), (A14), and (A15) into Eq. (A12), we obtain

$$(\bar{\psi}_\mathbf{k}, \boldsymbol{\ell}\bar{\psi}_{\mathbf{k}'}) = [(m/\hbar^2)i\nabla_\mathbf{k} \times \nabla_\mathbf{k} E(\mathbf{k})$$
$$+ \boldsymbol{\Delta}_\mathbf{k}\cdot\mathbf{s}_\mathbf{k} + \boldsymbol{\Delta}_{1\mathbf{k}}\cdot\mathbf{s}_\mathbf{k}](2\pi)^3\delta(\mathbf{k}-\mathbf{k}'), \tag{A16}$$

where

$$\boldsymbol{\Delta}_\mathbf{k}\cdot\mathbf{s}_\mathbf{k} = \frac{1}{im\Omega^2}\sum_n{}' \frac{1}{E(\mathbf{k})-E_n(\mathbf{k})}(\bar{\psi}_\mathbf{k}, \boldsymbol{\pi}\bar{\psi}_{n\mathbf{k}})_{\text{cell}}$$

$$\times (\bar{\psi}_{n\mathbf{k}}, \boldsymbol{\pi}\bar{\psi}_\mathbf{k})_{\text{cell}},$$

$$\boldsymbol{\Delta}_{1\mathbf{k}}\cdot\mathbf{s}_\mathbf{k} = -(mi/\hbar^2\Omega)(\nabla_\mathbf{k}\bar{u}_\mathbf{k}, \bar{u}_\mathbf{k})_{\text{cell}} \times \nabla_\mathbf{k} E(\mathbf{k}). \tag{A17}$$

The right-hand sides of these equations are represented by 2×2 matrices, and it can be proved that they satisfy the same symmetry relations as the matrix of the spin, $\mathbf{s}_\mathbf{k}$, except that the diagonal components of $\boldsymbol{\Delta}_{1\mathbf{k}}\cdot\mathbf{s}_\mathbf{k}$ do not necessarily satisfy the relation III. The matrix $\boldsymbol{\Delta}_{1\mathbf{k}}\cdot\mathbf{s}_\mathbf{k}$ satisfy the relations I, and II, so that it is of the form

$$\boldsymbol{\Delta}_{1\mathbf{k}}\cdot s_\mathbf{k} = \begin{pmatrix} \delta_\mathbf{k} & \gamma_\mathbf{k}^* \\ \gamma_\mathbf{k} & -\delta_{-\mathbf{k}} \end{pmatrix}, \quad \delta_\mathbf{k}, \delta_{-\mathbf{k}} = \text{real},$$
$$\text{and} \quad \gamma_{-\mathbf{k}} = \gamma_\mathbf{k}. \tag{A18}$$

However, the change of the phase of $\psi_\mathbf{k}(\mathbf{r})$ and $\phi_\mathbf{k}(\mathbf{r})$ will generally cause an additional term of the form $\frac{1}{2}(\delta_\mathbf{k}-\delta_{-\mathbf{k}})\mathbf{1}$, which cannot be determined by symmetry alone. It is noted that this term is spin independent, and antisymmetric with respect to $\mathbf{k}$. The expectation value of this quantity in a donor wave function must vanish, and therefore would not modify the results.

Finally, we present a perturbation treatment of the spin-orbit interaction $\mathcal{3C}_{\text{s-o}}$ for the Bloch functions. Let $\{e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}^0(\mathbf{r})\}$ be a complete set of the Bloch functions unperturbed by $\mathcal{3C}_{\text{s-o}}$, and construct the Bloch functions, up to first order in $\mathcal{3C}_{\text{s-o}}$,

$$\psi_\mathbf{k}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}[a_\mathbf{k}(\mathbf{r})\alpha + b_\mathbf{k}(\mathbf{r})\beta],$$
$$\phi_\mathbf{k}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}[-b_{-\mathbf{k}}^*(\mathbf{r})\alpha + a_{-\mathbf{k}}^*(\mathbf{r})\beta] \tag{A19}$$

for a particular band $n = 0$.

$$a_\mathbf{k}(\mathbf{r}) = u_\mathbf{k}^0(\mathbf{r}) + \sum_n{}' \frac{(n\alpha|\mathcal{3C}_{\text{s-o}}|\alpha)}{E(\mathbf{k})-E_n(\mathbf{k})}u_{n\mathbf{k}}^0(\mathbf{r}),$$

$$b_\mathbf{k}(\mathbf{r}) = \sum_n{}' \frac{(n\beta|\mathcal{3C}_{\text{s-o}}|\alpha)}{E(\mathbf{k})-E_n(\mathbf{k})}u_{n\mathbf{k}}^0(\mathbf{r}),$$

$$-b_{-\mathbf{k}}^*(\mathbf{r}) = \sum_n{}' \frac{(n\alpha|\mathcal{3C}_{\text{s-o}}|\beta)}{E(\mathbf{k})-E_n(\mathbf{k})}u_{n\mathbf{k}}^0(\mathbf{r}),$$

$$a_{-\mathbf{k}}^*(\mathbf{r}) = u_\mathbf{k}^0(\mathbf{r}) + \sum_n{}' \frac{(n\beta|\mathcal{3C}_{\text{s-o}}|\beta)}{E(\mathbf{k})-E_n(\mathbf{k})}u_{n\mathbf{k}}^0(\mathbf{r}). \tag{A20}$$

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has a center of inversion. This is not necessarily the case when spin-orbit interactions are present. This fact was pointed out by Y. Yafet (private communication).

Let us consider the z component of the spin representation $s_k{}^z$,

$$s_k{}^z = \begin{pmatrix} (a_k,a_k)-(b_k,b_k) & -(a_k,b_{-k}{}^*)+(b_k,a_{-k}{}^*) \\ -(b_{-k}{}^*,a_k)+(a_{-k}{}^*,b_k) & (b_{-k}{}^*,b_{-k}{}^*)-(a_{-k}{}^*,a_{-k}{}^*) \end{pmatrix}.$$ (A21)

Using the perturbed functions in Eqs. (A20), we see that $s_k{}^z$ is identical with the Pauli spin matrix $s^z = \begin{pmatrix} \frac{1}{2} & \\ & -\frac{1}{2} \end{pmatrix}$

up to first order in $\mathcal{H}_{s-o}$.

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

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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 $g_{||}$ 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 $\tau_s{}^{-1} \propto T^7 H^2$, 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 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

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

Here

$$\mathbf{P} = \mathbf{p} + e\mathbf{A}/c,$$ (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.

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[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).