Scattering of Phonons by Bound Donor Electrons in Doped Germanium*

ANIL KUMAR AND ARUN KUMAR SRIVASTAVA
Physics Department, Allahabad University, Allahabad, India
AND
G. S. VERMA
Physics Department, Banaras Hindu University, Varanasi, India

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In the present work the scattering of phonons by bound donor electrons is calculated for resonance and nonresonance frequencies using Kwok's approach, and the results are applied to explain the phonon conductivity of doped Ge.

I. INTRODUCTION

The scattering of phonons by bound donor electrons has long been an interesting problem.[1] Previously Keyes[2] initiated this scattering mechanism to explain the thermal resistance of n-Ge. He observed that the scattering depends on the number of occupied donor electrons rather than on the total impurity concentration. Later Griffin and Carruthers[3] discussed the elastic scattering of phonons by bound electrons in n-Ge in great detail. Recently Kwok[4] has extended the problem to include other inelastic scattering processes to explain the attenuation of phonons by neutral donor electrons at low temperatures in n-Ge.

Kwok[4] has studied the attenuation for frequencies $\hbar\omega_{q\lambda}\ll 4\Delta$. He observed that the elastic scattering of phonons off the singlet state is proportional to the phonon frequency to the fourth power, the elastic scattering of phonons off the triplet state is proportional to the square of the phonon frequency, and inelastic phonon scattering processes are independent of the phonon frequency. The aim of the present paper is to simplify the expressions of the phonon attenuation obtained by Kwok for the situations $\hbar\omega_{q\lambda}\gg 4\Delta$, $K_BT\gg 4\Delta$, and $\hbar\omega_{q\lambda}\ll 4\Delta$, $K_BT\ll 4\Delta$, in suitable forms which can be used to explain the phonon conductivity results of doped Ge in the off-resonance situations, where other phonon scattering processes are also relevant.

II. THEORY

Phonons in doped germanium in the low-temperature range are scattered as a result of electronic transitions between the different donor-electron states. The ground state in the doped Ge is fourfold degenerate. This degeneracy is partly lifted due to intervalley interaction and the ground state splits into two states, singlet and triplet states. The energy separation between the singlet and the triplet state is known as "chemical shift" and is denoted by 4Δ. The scattering of phonons by donor electrons is relevant below 50°K. At higher temperatures this scattering of phonons due to donors is negligible and other scattering mechanisms make a major contribution. The well-known deformation-potential matrix elements describing electronic transitions between the different levels can be written as

$$\Xi_{n'n}{}^{\lambda}(\mathbf{q})=\epsilon_i(\mathbf{q},\lambda)q_j(E_d\delta_{ij}\delta_{n'n}+\tfrac{1}{3}E_uD_{n'n}{}^{ij})F(q)$$
$$(n',\ n;\ \text{triplet, singlet}),$$

where $\epsilon_i(\mathbf{q},\lambda)$ is the polarization vector, q is the unit vector along $\mathbf{q}$, and E_d and E_u are the deformation potentials. D_r are the angular matrices and depend on the geometrical structure of the conduction band.

Since the dilation term vanishes, when we consider the matrix elements between the singlet and the triplet states, one can write the deformation-potential matrix elements as

$$\Xi_{n'n}{}^{\lambda}(\mathbf{q})=\tfrac{1}{3}E_uD_{n'n}{}^{\lambda}F(q)$$
$$=\Xi_{n'n}{}^{\lambda}(q)F(q). \quad (1)$$

Hasegawa[5] and Kwok[4] have studied these angular matrices in great detail. Here $F(q)$ is a form factor and is defined as

$$F(q)\cong(1+\tfrac{1}{4}a^{*\,2}q^2)^{-2}, \quad (2)$$

where a^* is the effective Bohr radius.

A. Scattering of Phonons

The electronic transitions between the singlet and the triplet states in the first-order approximation can be written as

$$\hbar\omega_{q\lambda}+(\text{singlet})\rightleftharpoons(\text{triplet}).$$

In the off-resonance situation, $\hbar\omega_{q\lambda}\neq 4\Delta$, the energy is not conserved for this process; the first-order contribution to the attenuation of phonons is negligible.

1. Resonant Scattering

a. Elastic processes ($\hbar\omega_{q\lambda}\cong 4\Delta$). The effective scattering processes can be symbolically written as

$$\hbar\omega_{q\lambda}+(\text{singlet})\rightleftharpoons(\text{int.})\rightleftharpoons\hbar\omega_{q'\lambda'}+(\text{singlet}),$$
$$\hbar\omega_{q}+(\text{triplet})\rightleftharpoons(\text{int.})\rightleftharpoons\hbar\omega_{q'\lambda'}+(\text{triplet}).$$

One can write the expression for τ_q^{-1}, as obtained by

Kwok:

$$\tau_q^{-1}=(\pi/2\rho C_\lambda^2)\omega_{q\lambda}\sum_n f_n(T)\times\sum_{q'\lambda'}(\omega_{q'\lambda'}/\rho C_{\lambda'}^2)\delta(\omega_{q\lambda}-\omega_{q'\lambda'})\times\sum_{n'\,(\epsilon_{n'}=\epsilon_n)}\left|\sum_m\left(\frac{\Xi_{n'm}^{\lambda'}(\mathbf{q})\Xi_{mn}^{\lambda}(\mathbf{q})}{\epsilon_m-\epsilon_n-\hbar\omega_{q\lambda}}+\frac{\Xi_{n'm}^{\lambda}(\mathbf{q})\Xi_{mn}^{\lambda'}(\mathbf{q})}{\epsilon_m-\epsilon_n+\hbar\omega_{q\lambda}}\right)\right|^2, \quad (3)$$

where n, m, and n' refer to the initial, intermediate, and final electronic states, respectively. Equation (3) can be simplified easily by substituting the values of the deformation-potential matrix elements. The simplified expressions can be written as

$$\tau_q^{-1}=\frac{E_{ui}{}^4 4(4\Delta)^2}{4\pi\rho 3^4 C_\lambda^2}F^2(q)\frac{\omega_{q\lambda}{}^4}{[(\hbar\omega_{q\lambda})^2-(4\Delta)^2]^2}\langle\langle D_s^{\lambda 1'}\rangle\rangle\times\left\{f_0(T)+f(T)\left[2+\left(\frac{\hbar\omega_{q\lambda}}{4\Delta}\right)^2\right]\right\}\left(\frac{F_1^2(q)}{C_1^5}+\frac{3}{2}\frac{F_2^2(q)}{C_2^5}\right). \quad (4)$$

where $\epsilon_T-\epsilon_S=4\Delta$, C_1=longitudinal velocity, $C_2=C_3$= transverse velocity, and the angular integration over $d\Omega$ is being considered. Equation (4) is the same as that obtained by Griffin and Carruthers for resonant scattering phonons.

b. Inelastic scattering. The inelastic phonon scattering processes can be symbolically expressed as

$$\hbar\omega_{q\lambda}+(\text{triplet})\rightleftharpoons(\text{int.})\rightleftharpoons\hbar\omega_{q'\lambda'}+(\text{singlet}).$$

The expression for the relaxation time for inelastic phonon scattering processes when an electron jumps down from the triplet to the singlet state can be defined as

$$\tau_q^{-1}=\frac{\pi}{2\rho C_\lambda^2}\omega_{q\lambda}\left[1-\exp\left(-\frac{\hbar\omega_{q\lambda}}{K_BT}\right)\right]f(T)F^2(q)\sum_{q'\lambda'}\frac{\omega_{q'\lambda'}}{\rho C_{\lambda'}{}^2}\delta\left(\omega_{q'\lambda'}-\frac{4\Delta}{\hbar}-\omega_{q\lambda}\right)F^2(q')\times\sum_{n=1}^{3}\left|\sum_{m=1}\left(\frac{\tilde{\Xi}_{om}^{\lambda'}(q')\tilde{\Xi}_{mn}^{\lambda}(q)}{\epsilon_m-\epsilon_n-\hbar\omega_{q\lambda}}+\frac{\tilde{\Xi}_{om}^{\lambda}(q)\tilde{\Xi}_{mn}^{\lambda'}(q')}{\epsilon_m-\epsilon_0+\hbar\omega_{q\lambda}}\right)\right|^2. \quad (5)$$

Using Hasegawa's[5] matrix elements, one can simplify Eq. (5), and the simplified expression can be written

$$\tau_q^{-1}=\frac{f(T)}{4\pi\rho^2C_\lambda^2}\frac{\omega_{q\lambda}(\omega_{q\lambda}+4\Delta/\hbar)^3}{(\hbar\omega_{q\lambda})^2}F^2(q)\left\{\frac{F_1^2(q)}{C_1^5}\langle\langle\sum_n|\sum_m(\tilde{\Xi}_{om}{}^{1'}\tilde{\Xi}_{mn}{}^{\lambda}-\tilde{\Xi}_{oo}{}^{\lambda}\tilde{\Xi}_{on}{}^{1'})|^2\rangle\rangle+\frac{F_2^2(q)}{C_2^5}\times[\langle\langle\sum_n|\sum_m(\tilde{\Xi}_{om}{}^{2'}\tilde{\Xi}_{mn}{}^{\lambda}-\tilde{\Xi}_{oo}{}^{\lambda}\tilde{\Xi}_{on}{}^{2'})|^2\rangle\rangle+\langle\langle\sum_n|\sum_m(\tilde{\Xi}_{om}{}^{3'}\tilde{\Xi}_{mn}{}^{\lambda}-\tilde{\Xi}_{oo}{}^{\lambda}\tilde{\Xi}_{on}{}^{3'})|^2\rangle\rangle]\right\}. \quad (6)$$

These angular matrices have been simplified for $\lambda=1, 2, 3$ in Appendix B. It has been shown by Kwok that the magnitudes of the inelastic phonon scattering processes and thermally assisted phonon absorption processes are effectively the same. One can, therefore, include the effect of the thermally assisted phonon absorption processes by considering only twice the value of inelastic phonon scattering processes given by Eq. (6).

2. *Off-Resonance Situations* ($\hbar\omega_{q\lambda}\neq 4\Delta$)

a. Elastic scattering processes for frequencies $\hbar\omega_{q\lambda}\ll 4\Delta$. Kwok has simplified his Eq. (3) [Eq. (15) of Ref. 4] for low frequencies such that $\hbar\omega_{q\lambda}\ll 4\Delta$. The expression can be written as

$$\tau_q^{-1}=\frac{f_0(T)}{4\pi\rho C_\lambda^2}\omega_{q\lambda}{}^2\frac{1}{\hbar^2}\left(\frac{\hbar\omega_{q\lambda}}{4\Delta}\right)^2F^2(q)\sum_{\lambda'}\frac{4}{\rho C_{\lambda'}{}^5}F^2\left(q\frac{C_\lambda}{C_{\lambda'}}\right)\langle\langle|\sum_{m=1}\tilde{\Xi}_{om}{}^{\lambda'}\tilde{\Xi}_{mo}{}^{\lambda}|^2\rangle\rangle+\frac{f(T)}{4\pi\rho C_\lambda^2}\omega_{q\lambda}{}^2\frac{1}{\hbar^2}F^2(q)\sum_{\lambda'}\frac{1}{\rho C_{\lambda'}{}^5}F^2\left(q\frac{C_\lambda}{C_{\lambda'}}\right)\langle\langle\sum_{n,n'}|\sum_m(\tilde{\Xi}_{n'm'}{}^{\lambda'}\tilde{\Xi}_{mn}{}^{\lambda}-\tilde{\Xi}_{n'm}{}^{\lambda}\tilde{\Xi}_{mn}{}^{\lambda'})|^2\rangle\rangle. \quad (7)$$

Using Hasegawa's and Griffin and Carruther's matrix elements [see Eq. (3.14) of Ref. 3], one can simplify Eq. (7) for τ_q^{-1} as

$$\tau_q^{-1}=\frac{f_0(T)}{4\pi\rho C_\lambda^2}\omega_{q\lambda}{}^2\frac{1}{\hbar^2}\left(\frac{\hbar\omega_{q\lambda}}{4\Delta}\right)^2F^2(q)\sum_{\lambda'}\frac{4}{\rho C_{\lambda'}{}^5}F^2\left(q\frac{C_\lambda}{C_{\lambda'}}\right)(\tfrac{1}{3}E_u)^4\langle\langle D_s^{\lambda\lambda'}\rangle\rangle+\frac{f(T)}{4\pi\rho C_\lambda^2}\omega_{q\lambda}{}^2F^2(q)\sum_{\lambda'}(\rho C_{\lambda'}{}^5)^{-1}\times F^2\left(q\frac{C_\lambda}{C_{\lambda'}}\right)(\tfrac{1}{3}E_u)^4 2\langle\langle(D_T^{\lambda\lambda'}-D_S^{\lambda\lambda'})\rangle\rangle. \quad (8)$$

It can be further simplified by expanding the summation $\sum_{\lambda'}$ where $\lambda'=1, 2, 3$. The final expression can be written as

$$\tau_q^{-1}=\frac{E_u^4}{3^4\pi\rho^2 C_\lambda^2\hbar^2}F^2(q)\langle\langle D_S^{\lambda\lambda'}\rangle\rangle\left(\frac{F_1^2(q)}{C_1^5}+\frac{3}{2}\frac{F_2^2(q)}{C_2^5}\right)\omega_{q\lambda}^2\left[f_0(T)\left(\frac{\hbar\omega_{q\lambda}}{4\Delta}\right)^2+f(T)\right]. \quad (9)$$

Here, λ is the polarization index of the phonons. One can also calculate the contribution of the longitudinal and transverse phonons separately. $\langle\langle D_S^{\lambda\lambda'}\rangle\rangle$ depends upon the geometrical structure of the conduction band (see Table I).

b. Inelastic processes ($\hbar\omega_{q\lambda}\ll 4\Delta$). The expression for τ_q^{-1} for inelastic phonon scattering processes, for frequencies such that $\hbar\omega_{q\lambda}\ll 4\Delta$, can be written as [see Eq. (22)]

$$\tau_q^{-1}\frac{f(T)}{4\pi\rho C_\lambda^2}(\hbar K_B T)^{-1}F^2(q)\sum_{\lambda'}(\rho C_{\lambda'}{}^5)^{-1}\left(\frac{4\Delta}{\hbar}\right)^3 F^2\left(\frac{4\Delta}{\hbar C_{\lambda'}}\right)\langle\langle\sum_n|\sum_m(\tilde{\Xi}_{om}{}^{\lambda\lambda'}\tilde{\Xi}_{mn}{}^{\lambda}-\tilde{\Xi}_{oo}{}^{\lambda}\tilde{\Xi}_{on}{}^{\lambda'})|^2\rangle\rangle. \quad (10)$$

Using Hasegawa's matrix elements and expanding the summation $\sum_{\lambda'}$, one can write the simplified expression as

$$\tau_q^{-1}=\frac{f(T)}{4\pi\rho^2 C_\lambda^2}(\hbar K_B T)^{-1}F^2(q)\left(\frac{4\Delta}{\hbar}\right)^3\left\{F^2\left(\frac{4\Delta}{\hbar C_1}\right)\langle\langle\sum_n|\sum_m(\tilde{\Xi}_{om}{}^{1'}\tilde{\Xi}_{mn}{}^{\lambda}-\tilde{\Xi}_{oo}{}^{\lambda}\tilde{\Xi}_{on}{}^{1'})|^2\rangle\rangle+F^2\left(\frac{4\Delta}{\hbar C_2}\right)\right.$$
$$\left.\times[\langle\langle\sum_n|\sum_m(\tilde{\Xi}_{om}{}^{2'}\tilde{\Xi}_{mn}{}^{\lambda}-\tilde{\Xi}_{oo}{}^{\lambda}\tilde{\Xi}_{on}{}^{2'})|^2\rangle\rangle+\langle\langle\sum_n|\sum_m(\tilde{\Xi}_{om}{}^{3'}\tilde{\Xi}_{mn}{}^{\lambda}-\tilde{\Xi}_{oo}{}^{\lambda}\tilde{\Xi}_{on}{}^{3'})|^2\rangle\rangle]\right\}. \quad (11)$$

The calculations of the angular matrices are given in Appendix A.

We observe that for frequencies such that $\hbar\omega_{q\lambda}\ll 4\Delta$, the elastic phonon scattering off the singlet state is proportional to the phonon frequency to its fourth power and population of the singlet state, elastic phonon scattering off the triplet state is proportional to the square of phonon frequency and population of the triplet state, and inelastic phonon scattering is proportional to the population of the triplet state divided by the temperature.

c. Elastic scattering ($\hbar\omega_{q\lambda}\gg 4\Delta$). It is observed that for some system the experimental data correspond to the frequencies such that $\hbar\omega_{q\lambda}\gg 4\Delta$. We also consider this case and try to obtain the simplified expressions for τ_q^{-1} for both elastic and inelastic phonon scattering processes, for frequencies $\hbar\omega_{q\lambda}\gg 4\Delta$.

The inverse of the relaxation time for the elastic phonon scattering off the singlet state can be written as

$$\tau_q^{-1}=(\pi/2\rho C_\lambda^2)\omega_{q\lambda}[F^2(q)/(\hbar\omega_{q\lambda})^2]f_0(T)\times\sum_{q'\lambda'}(\omega_{q'\lambda'}/\rho C_{\lambda'}{}^2)\delta(\omega_{q'\lambda'}-\omega_{q\lambda})$$
$$\times F^2(q')\langle\langle|\sum_m(\tilde{\Xi}_{om}{}^{\lambda'}\tilde{\Xi}_{mo}{}^{\lambda}-\tilde{\Xi}_{om}{}^{\lambda}\tilde{\Xi}_{mo}{}^{\lambda'})|^2\rangle\rangle. \quad (12)$$

Substituting the values of the deformation-potential matrix elements and simplifying one can show that the angular matrices vanish (see Appendix B). It therefore shows that there is no scattering of phonons off the singlet state, for frequencies $\hbar\omega_{q\lambda}\gg 4\Delta$.

Following the procedure of Kwok, we can write an expression for τ_q^{-1} for elastic phonon scattering off the triplet state as follows:

$$\tau_q^{-1}=\frac{f(T)}{4\pi\rho C_\lambda^2}\omega_{q\lambda}^2\frac{1}{\hbar^2}F^2(q)\sum_{\lambda'}(\rho C_{\lambda'}{}^5)^{-1}F^2\left(q\frac{C_\lambda}{C_{\lambda'}}\right)\times\langle\langle\sum_{n,n'}|\sum_m(\tilde{\Xi}_{n'm}{}^{\lambda'}\tilde{\Xi}_{mn}{}^{\lambda}-\tilde{\Xi}_{n'm}{}^{\lambda}\tilde{\Xi}_{mn}{}^{\lambda'})|^2\rangle\rangle. \quad (13)$$

Substituting the values of the deformation-potential matrix elements and simplifying (see Appendix B), we obtain the final expression as

$$\tau_q^{-1}=3\frac{f(T)}{4\pi\rho C_\lambda^2\hbar^2}\frac{E_u^4}{3^4}F^2(q)\langle\langle D_S^{\lambda\lambda'}\rangle\rangle\omega_{q\lambda}{}^2 4\left(\frac{F_1^2(q)}{C_1^5}+\frac{3}{2}\frac{F_2^2(q)}{C_2^5}\right). \quad (14)$$

d. Inelastic scattering ($\hbar\omega_{q\lambda}\gg 4\Delta$). The relaxation time for inelastic phonon scattering processes for frequen-

TABLE I. Values of tensors $\ll D_S^{\lambda\lambda'}\gg$ and $\ll\cdots\gg$ Eq. (B9) $\lambda\lambda'$ for $\lambda=1, 2, 3$ and $\lambda'=1, 2, 3$.

λ \ λ'	$\ll D_S^{\lambda\lambda'}\gg$[a]	$\ll\cdots\gg_{Eq.\ (B9)}$ $\lambda'=1$	$\ll\cdots\gg_{Eq.\ (B9)}$ $\lambda'=2$	$\ll\cdots\gg_{Eq.\ (B9)}$ $\lambda'=3$
1	48/225	128/315	70/315	90/315
2	32/225	34/315	20/315	58.5/315
3	40/225	126/315	106.5/315	84/315

[a] Reference 3.

cies $\hbar\omega_{q\lambda}\gg 4\Delta$ can be defined as

$$\tau_q^{-1}=\frac{\pi}{2\rho C_\lambda^2}\omega_{q\lambda}\left[1-\exp\left(\frac{-\hbar\omega_{q\lambda}}{K_BT}\right)\right]f(T)F^2(q)$$
$$\times\sum_{q'\lambda'}\frac{\omega_{q'\lambda'}}{\rho C_{\lambda'}^2}(1+n_{q'\lambda'})\delta(\omega_{q'\lambda'}-\omega_{q\lambda})F^2\left(q\frac{C_\lambda}{C_{\lambda'}}\right)$$
$$\times\frac{1}{(\hbar\omega_{q\lambda})^2}\langle\langle\sum_n|\sum_m(\tilde{\Xi}_{om}{}^{\lambda'}\tilde{\Xi}_{mn}{}^{\lambda}-\tilde{\Xi}_{oo}{}^{\lambda}\tilde{\Xi}_{on}{}^{\lambda'})|^2\rangle\rangle. \quad (15)$$

Equation (15) can be simplified by substituting the values of the matrix elements; the expression given by Eq. (15) modifies to

$$\tau_q^{-1}=\frac{f(T)}{4\pi\rho^2C_\lambda^2\hbar^2}\omega_{q\lambda}^2F^2(q)\left\{\frac{F_1^2(q)}{C_1^5}\right.$$
$$\times\langle\langle\sum_n|\sum_m(\tilde{\Xi}_{om}{}^{1'}\tilde{\Xi}_{mn}{}^{\lambda}-\tilde{\Xi}_{oo}{}^{\lambda}\tilde{\Xi}_{on}{}^{1'})|^2\rangle\rangle$$
$$+\frac{F_2^2(q)}{C_2^5}[\langle\langle\sum_n|\sum_m(\tilde{\Xi}_{om}{}^{2'}\tilde{\Xi}_{mn}{}^{\lambda}-\tilde{\Xi}_{oo}{}^{\lambda}\tilde{\Xi}_{on}{}^{2'})|^2\rangle\rangle$$
$$\left.+\langle\langle\sum_n|\sum_m(\tilde{\Xi}_{om}{}^{3'}\tilde{\Xi}_{mn}{}^{\lambda}-\tilde{\Xi}_{oo}\tilde{\Xi}_{on}{}^{3'})|^2\rangle\rangle]\right\}. \quad (16)$$

The angular matrices have been simplified in Appendix B. It is here observed that there is no scattering of phonons off the singlet state. The scattering of phonons in the rest of the processes is proportional to the population of the triplet state and the square of the phonon frequency.

The above calculations show that the scattering of phonons by donors depends on the phonon frequency, the population of the state, and the matrices $D_{n'n}{}^{\lambda}$ which depend on the geometrical structure of the conduction band. The conduction-band structures for Ge and Si have been studied in great detail. One can, therefore, calculate the exact relations for the relaxation times for elastic and inelastic scattering of phonons by donors. Hasegawa and later Kwok have calculated the angular integrations of these matrices. We have used these values to calculate the values of τ_q^{-1} from Eqs. (3)–(16).

It is also observed that the values of the angular integrations of the matrices $D_{n'n}{}^{\lambda}$ are a constant factor. One can, therefore, lump these deformation-potential matrix elements into an adjustable parameter H. The expressions given by Eqs. (3)–(16) modify to

I. $\tau_q^{-1}=HF^4(q)\omega_{q\lambda}{}^2[f_0(T)(\hbar\omega_{q\lambda}/4\Delta)^2+f(T)]$
for $\hbar\omega_{q\lambda}\ll 4\Delta$, elastic processes (17)

II. $\tau_q^{-1}=H_1F^4(q)(4\Delta/K_BT)(4\Delta/\hbar)^2f(T)$
for $\hbar\omega_{q\lambda}\ll 4\Delta$, inelastic processes (18)

III. $\tau_q^{-1}=HF^4(q)\omega_{q\lambda}{}^2f(T)$
for $\hbar\omega_{q\lambda}\gg 4\Delta$, elastic processes (19)

IV. $\tau_q^{-1}=H_1F^4(q)\omega_{q\lambda}{}^2f(T)$
for $\hbar\omega_{q\lambda}\gg 4\Delta$, inelastic processes. (20)

Here,

$$H=(E_u{}^4/3^4\pi\rho^2C_\lambda{}^2\hbar^2)F,$$
$$F=\langle\langle D_S{}^{\lambda 1'}\rangle\rangle \quad (21)$$
$$H_1=(E_u{}^4/3^4\pi\rho^2C_\lambda{}^2\hbar^2)F_1,$$
$$F_1=\langle\langle[\text{Eq. (B9), Appendix B}]\rangle\rangle_{\lambda\lambda'} \quad (22)$$

where F and F_1 depend on the geometrical structure of the conduction band.

III. SCATTERING OF PHONONS BY BOUND ELECTRONS AND PHONON CONDUCTIVITY OF DOPED Ge

It has been observed in Ge that the introduction of impurities[6–10] drastically reduces the value of lattice thermal conductivity (by about two orders of magnitude at temperatures below 4°K). This reduction bears direct proportion to the increase in the donor concentration. The above effects on the phonon conductivity of Ge are explained on the basis of the resonant scattering of phonons by bound donor electrons. In the presence of other phonon scattering processes,[11,12] the additivity of reciprocal relaxation times is used to incorporate the resonance scattering relaxation rate. Callaway's formalism is then used to study the phonon conductivity of doped Ge at different temperatures in the range 1.3–50°K. In the Debye approximation, κ_{ph} is given by[13]

$$\kappa_{ph}=(2\pi^2\bar{v})^{-1}\int_0^{\omega_D}\frac{\tau(T,\omega)}{K_BT^2}\frac{\hbar^2\omega^4\exp(\hbar\omega/K_BT)d\omega}{[\exp(\hbar\omega/K_BT)-1]^2}, \quad (23)$$

where $\bar{v}$ is the average sound velocity, $\tau^{-1}(T,\omega)=\sum_j\tau_j^{-1}(T,\omega)$, and τ_j^{-1} is the relaxation rate of the jth scattering mechanism. For the present problem, $\tau^{-1}=\tau_p^{-1}+\tau_q^{-1}$, where τ_p^{-1} refers to pure Ge (where the only defects which one has to consider are isotopes) and τ_q^{-1} is the relaxation rate for the scattering of phonons by donors. For τ_p^{-1}, we have taken

$$\tau_p^{-1}=(C/L)+A\omega^4+B_1\omega^2T^3+B_2\omega^2T^3, \quad (24)$$

where for a pure specimen $C/L=7.622\times10^5$ sec^{-1}, $C=3.5\times10^5$ cm/sec, $L=1.12(S)^{1/2}=1.12(4.4\times4.4)^{1/2}$ mm$=0.459$ cm, $A=2.57\times10^{-44}$ sec^3, $(B_1+B_2)=2.77\times10^{-23}$ sec/°K^3. These values were obtained by Callaway[13] for the pure-Ge case and have been utilized here since they give best agreement between theory and experiment for the pure-Ge case. The first term denotes boundary scattering, the second denotes point-defect scattering, and the third and fourth terms represent scattering due to normal and umklapp processes. In terms of the dimensionless variable $x=\hbar\omega/K_BT$ one can write

$$\tau_p^{-1}=7.622\times10^5+7.5224T^4x^4+0.4739x^2T^5. \quad (25)$$

The corrections to the phonon conductivity due to normal phonon processes has been shown to be negli-

TABLE II. Values of the adjustable parameter H and the corresponding shear deformation potential for different Sb-doped and compensated Ge samples.

Samples	Concentration N_{ex} (10^{17} cm^{-3})	H (10^6 sec^{-1} deg^{-2})	Calculated[a] E_u (eV) deformation potential	Expt E_u (eV)
Sb 172	0.061	1.0	16.03	
Sb 207	0.24	2.0	11.91	
SbGa 204	0.26	4.0	19.14	(15–19)
SbGa 170	0.54	3.0	13.63	
SbGa 183	1.44	2.0	8.65	

[a] Calculated from the relation $E_u^4(\text{eV}) \cong 4.030 \times 10^{13}\, H/N_{ex}$.

gible in the case of Ge. Similar expressions can also be written if one considers momentum-conserving electron-phonon collisions, and it has been shown by Gaur and Verma[10] that such corrections also make negligible contributions to the phonon conductivity. Hence, in the present calculations, the corrections to the phonon conductivity due to momentum-conserving scattering processes are not considered.

A. Sb-Doped Ge

Since the resonance in the phonon conductivity of Sb-doped Ge occurs at about 0.7°K, the present range of temperature (1.3–50°K) in which we are interested corresponds to the case where $\hbar\omega \gg 4\Delta$ and $K_BT \gg 4\Delta$. The elastic scattering part of τ_q^{-1} for the above situation is given by

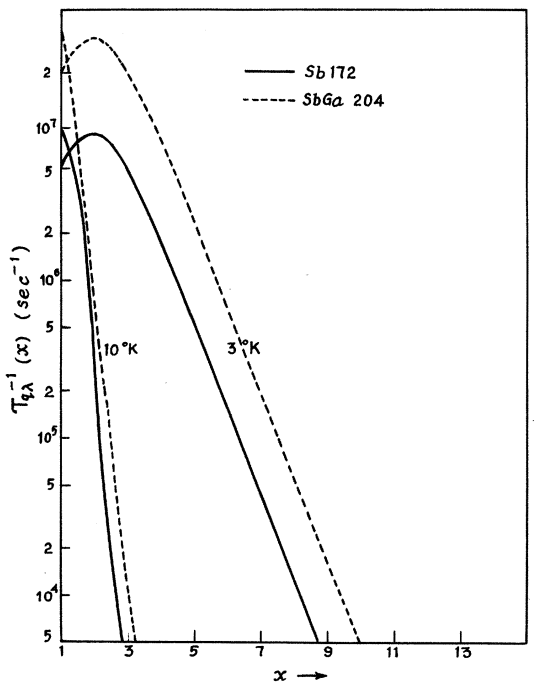

FIG. 1. Plot of (τ_q^{-1}) Eq. (8) versus x for Sb-doped Ge sample Sb 172 for temperatures 3 and 10°K.

$$\tau_q^{-1}(\text{elastic}, \hbar\omega \gg 4\Delta;\ K_BT \gg 4\Delta) = 10\,\frac{40}{225}\,\frac{f(T)}{4\pi\rho^2C^7\hbar^2}\,\frac{E_u^4}{3^4}\,F^4(q)\omega_{q\lambda}^2. \quad (26)$$

It has been found that the scattering off the singlet vanishes. Here ρ is the mass density of the system, E_u is the shear deformation potential, C is the average phonon velocity, and $F(q)$ is the form factor which is defined as

$$F^2(q) \cong (1+\tfrac{1}{4}a^{*\,2}q^2)^{-4}, \quad (27)$$

where a^* is the effective Bohr radius and under Debye approximation $\omega_{q\lambda} = Cq$. $f(T)$ is the thermal equilibrium population of the triplet state and is related to the thermal equilibrium population of the ground state $f_0(T)$, as $f_0(T)+3f(T)=1$ and $f_0(T)=A\exp(-E_0/K_BT)$, where E_0 is the ground-state energy. The scattering of phonons, in this case, is proportional to the square of the phonon frequency and the population of the triplet state.

The inelastic part of τ_q^{-1} for $\hbar\omega_{q\lambda} \gg 4\Delta$ and $K_BT \gg 4\Delta$ is given by

$$\tau_q^{-1}(\text{inelastic}, \hbar\omega \gg 4\Delta;\ K_BT \gg 4\Delta) = \frac{239}{325}\,\frac{f(T)}{4\pi\rho^2C^7\hbar^2}\,\frac{E_u^4}{3^4}\,F^4(q)\omega_{q\lambda}^2. \quad (28)$$

We again observe that the inelastic phonon scattering is proportional to the square of the phonon frequency and the population of the triplet state. One can include the effect of the thermally assisted phonon absorption process by considering twice the value of the inelastic phonon scattering processes. This we have done in our present calculations.

The total effective relaxation time for phonon scattering by bound donor electrons for $\hbar\omega_{q\lambda} \gg 4\Delta$ and $K_BT \gg 4\Delta$ may be defined as

$$\tau_q^{-1} = \tau_q^{-1}(\text{elastic}) + \tau_q^{-1}(\text{inelastic}) = 3.295\left[f(T)/4\pi\rho^2C^7\hbar^2\right](E_u^4/3^4)F^4(q)\omega_{q\lambda}^2. \quad (29)$$

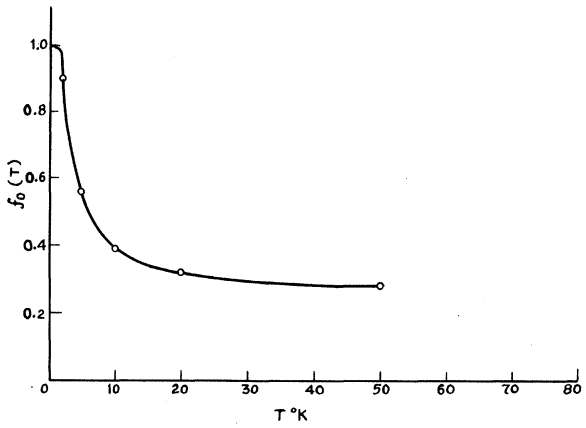

FIG. 2. Temperature dependence of the occupation probability $f_0(T)$ for the singlet state against temperature.

We have to multiply the above expression for τ_q^{-1} by the donor concentration N_{ex} to obtain the total effective scattering of phonons by donors.

The combined relaxation τ_c^{-1} can be expressed as

$$\tau^{-1}=\tau_c^{-1}=7.622\times10^5+7.5224T^4x^4+0.4739x^2T^5 +HF^4(x)f(T)T^2x^2, \quad (30)$$

where

$$H=3.295(K_B^2E_u^4/4\pi\rho^2C^7\hbar^43^4)N_{ex} \quad (31)$$

and N_{ex} is the donor concentration. The coefficient H is treated as an adjustable parameter. This adjustable parameter is also a measure of the electron-phonon coupling. This expression for τ^{-1} [Eq. (30)] is used to calculate the phonon conductivity at different temperatures.

We have examined the phonon conductivity of the various Sb-doped Ge samples[9] Sb 172, Sb 207, SbGa 170, SbGa 183, and SbGa 204 in the temperature range 1.3–50°K, which corresponds to the off-resonance situation $\hbar\omega_{q\lambda}\gg4\Delta$ and $K_BT\gg4\Delta$. The last three samples are the compensated samples. τ_q^{-1} versus x has been plotted for the above samples at different temperatures and the results for two samples Sb 172 and SbGa 204 are shown in Fig. 1 at two temperatures 3 and 10°K. Figure 2 shows the plot of $f_0(T)$ versus T. The phonon conductivity plots with respect to temperature for the same two typical samples are shown in Figs. 3 and 4. From these figures it is observed that the theoretically calculated values of the phonon conductivity on the basis of additivity of reciprocal relaxation times, which incorporates τ_q^{-1} [Eq. (29)] and Callaway model, agree remarkably well with the experimental values, for the whole temperature range. The adjusted value of the parameter H, which gives the best fit for the experimental curves, has been used to calculate the value of the deformation potential, which occurs in fourth power in the expression for H. The adjusted values of the parameter H as well as the deformation potential derived therefrom for the different samples are given in Table II. It may be observed from this table that the use of τ_q^{-1} [Eq. (29)] gives good agreement between the adjusted and experimentally observed values of the deformation potential for the sam-

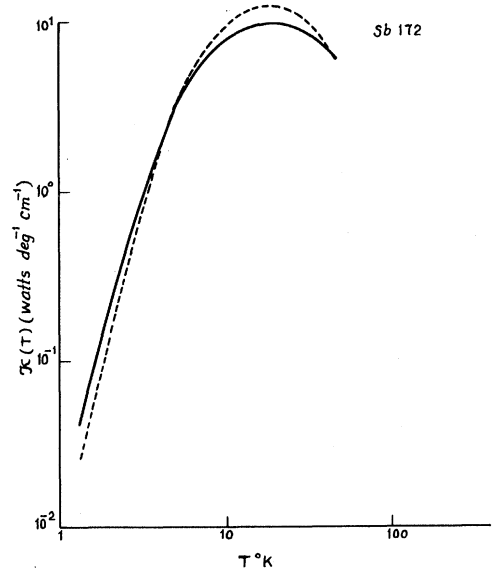

FIG. 3. Phonon conductivity of Sb 172 sample ($N_{ex}=0.061\times10^{17}$ cm^{-3}). The solid line is the experimental results of Goff and Pearlman (Ref. 4) and the dotted line is the theoretical curve. The values of τ_q^{-1} are calculated from Eq. (29).

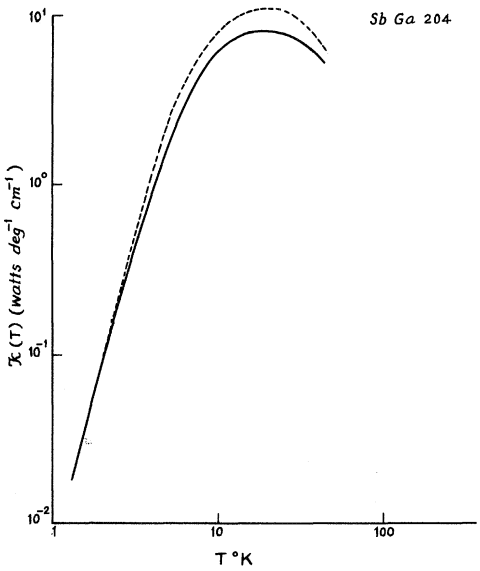

FIG. 4. Phonon conductivity of SbGe 204 sample ($N_{ex}=0.12\times10^{17}$ cm^{-3}). The solid line is the experimental results of Goff and Pearlman and the dotted line is the theoretical curve. The values of τ_q^{-1} are calculated from the Eq. (29).

ples Sb 172 and SbGa 204. For other samples Sb 207, SbGa 170, and SbGa 183 the values of the shear deformation potential are lower than the experimentally accepted values, 15–19 eV, as shown in Table II.

B. As-Doped Ge

For As-doped Ge samples, $4\Delta=4.15\times10^{-3}$ eV and $4\Delta/K_B=T_R=49°$K. The resonance at $\omega_R\sim K_BT_R/\hbar$ would have its strongest effect somewhere between $T_M\sim\frac{1}{6}T_R$ and $T_M\sim\frac{1}{5}T_R$. Thus T_M for As-doped Ge samples lies at about 8°K. However, no marked resonance dip in the phonon conductivity at about 8°K is observed in As-doped Ge samples. (There is, however, one exception, namely, sample As 223I,[9] where a dip occurs at about 7°K.) According to Griffin and Carruthers, the true resonance energy lies at a frequency such that qr_0 is substantially greater than unity, where r_0 is the effective Bohr radius and is 37 Å for As. When $q>1/r_0$, the scattering dies off very quickly and the result is that this cutoff suppresses the effect of the resonance. Kwok has used the method of thermodynamic Green's functions, which is more suitable in dealing with phonons close to the resonance frequency where simple perturbation techniques fail owing to divergence difficulties. The simplified expression for

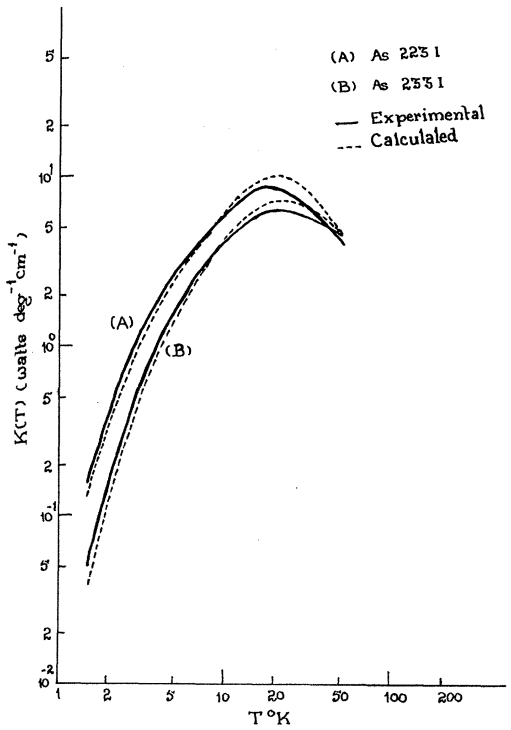

FIG. 5. Phonon conductivity of As-doped Ge samples As 223I ($N_{ex}=0.2\times10^{17}$ cm^{-3}) and As 233I ($N_{ex}=1.1\times10^{17}$ cm^{-3}). The dotted line is the experimental curve and the solid is the theoretical curve with τ_q^{-1} calculated on the basis of Kwok's perturbation theory.

TABLE III. Values of the adjustable parameter H and the corresponding shear deformation potential for different As-doped Ge samples.

Sample	Concentration N_{ex} (10^{17} cm^{-3})	H (10^6 sec^{-1} deg^{-2})	Calculated[a] E_u (eV)
As 223I	0.21	3.0	6.5
As 233I	1.1	6.0	5.1

[a] Calculated from the relation $E_u^4(\text{eV})\cong1.2\times10^{13}\ H/N_{ex}$.

the resonance scattering relaxation time obtained on the basis of thermodynamic Green's function can be expressed as

$$\tau_r^{-1}=H'\frac{xT(1-e^{-x})f_0(T)}{[1-(K_B/4\Delta)xT]^2[1-\exp(-4\Delta/K_BT)]}N_{ex}, \tag{32}$$

where $x=\hbar\omega_{q\lambda}/K_BT$ and

$$H'=F(\tfrac{1}{3}E_u)^4\frac{F^2(4\Delta/\hbar c)(4\Delta)}{2\pi\hbar^4\rho^2C^25}\left(\frac{2}{3\bar{v}_1{}^5}+\frac{1}{\bar{v}_2{}^5}\right). \tag{33}$$

Here F is a constant which depends on the geometrical structure of the conduction band.

Because of the narrow width of the resonance, the application of the above expression to explain the phonon conductivity in the off-resonance situations is not proper. However, if one wants to explain the magnitude of phonon conductivity at about the resonance temperature $T_M(=8°\text{K})$, one needs large values of the shear deformation potential of the order of 200–250 eV. This suggests that one needs damping term in the resonance denominator.

We have used second-Born-perturbation results for τ_q^{-1} to explain the phonon conductivity of As-doped Ge samples in the temperature range 1.3–50°K. Since the resonance effect is expected to be maximum at about 8°K, we have used Eq. (29) for the resonance scattering relaxation rate in the temperature range 10–50°K, which holds good for $\hbar\omega_{q\lambda}\gg4\Delta$ and $K_BT\gg4\Delta$. In the temperature range 1.3–5°K, we have used Eqs. (17) and (18) for τ_q^{-1}, which holds good for $\hbar\omega_{q\lambda}\ll4\Delta$ and $K_BT\ll4\Delta$. The simplified expression for τ_q^{-1} is as follows:

$$\tau_q^{-1}(\hbar\omega\ll4\Delta;\ K_BT\ll4\Delta)=HF^4(x)\times\left\{\frac{400}{225}(Tx)^2\left[f_0(T)\left(\frac{K_BTx}{4\Delta}\right)^2+f(T)\right]+\frac{478}{315}\left(\frac{4\Delta}{K_B}\right)^2\left(\frac{4\Delta}{K_BT}\right)f(T)\right\}, \tag{34}$$

where

$$H=E_u{}^4K_B{}^2/4\pi\rho^2\hbar^43^4C^7. \tag{35}$$

For the resonance range 5–10°K, we have extrapolated the results both from above and below the resonance

region. The results of calculation of phonon conductivity for the samples As 223I and As 233I [9] are shown in Fig. 5. The solid lines represent the experimental curves and dotted lines denote the theoretical curves. The values of the parameters used in the analysis of phonon conductivity are given in Table III. The values of the shear deformation potential which one obtains from the adjustable parameter H on the basis of second Born perturbation results are 6.5 and 5.1 eV for As 223I and As 233I, respectively. These values may be compared with the experimental values which lie in the range 15–19 eV.

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APPENDIX A

The matrix elements obtained to explain electronic transitions can be calculated by using Hasegawa's $D_{n'n}{}^{\lambda}$. These matrices are obtainable by considering the symmetry of the system. Griffin and Carruthers have given relations for combined matrices with

$$D_S{}^{\lambda\lambda'}=(\sum_m D_{om}{}^{\lambda}D_{mo}{}^{\lambda'})^2, \tag{A1}$$

$$D_T{}^{\lambda\lambda'}=\sum_{n'}\sum_{n}(D_{n'm}{}^{\lambda}D_{mn}{}^{\lambda'})^2. \tag{A2}$$

They have also shown that

$$\langle\langle D_T{}^{\lambda 1'}\rangle\rangle=3\langle\langle D_S{}^{\lambda 1'}\rangle\rangle,$$
$$2[\langle\langle D_S{}^{\lambda 2'}\rangle\rangle+\langle\langle D_S{}^{\lambda 3'}\rangle\rangle]=3\langle\langle D_S{}^{\lambda 1'}\rangle\rangle,$$
$$[\langle\langle D_T{}^{\lambda 2'}\rangle\rangle+\langle\langle D_T{}^{\lambda 3'}\rangle\rangle]=3[\langle\langle D_S{}^{\lambda 2'}\rangle\rangle+\langle\langle D_S{}^{\lambda 3'}\rangle\rangle].$$

One can now find the values of the matrix elements describing electronic transitions by using these relations.

APPENDIX B

To calculate the value of $\tau_q{}^{-1}$ for frequencies $\hbar\omega_{q\lambda}\ll 4\Delta$ (elastic processes), one find that the scattering of phonons off the singlet state is given by

$$\tau_q{}^{-1}\alpha\langle\langle\,|\sum_m \tilde{\Xi}_{om}{}^{\lambda'}\tilde{\Xi}_{mo}{}^{\lambda}\,|^2\rangle\rangle=(\tfrac{1}{3}E_u)^4\langle\langle\,|\sum_m D_{om}{}^{\lambda'}D_{mo}{}^{\lambda}\,|^2\rangle\rangle$$
$$=(\tfrac{1}{3}E_u)^4\langle\langle D_S{}^{\lambda'\lambda}\rangle\rangle. \tag{B1}$$

Similarly, the scattering of phonons off the triplet state is given by

$$\tau_q{}^{-1}\alpha\langle\langle\sum_{n,n'}|\,(\tilde{\Xi}_{n'o}{}^{\lambda'}\tilde{\Xi}_{on}{}^{\lambda}-\tilde{\Xi}_{n'o}{}^{\lambda}\tilde{\Xi}_{on}{}^{\lambda'}\,|^2\rangle\rangle$$
$$=(\tfrac{1}{3}E_u)^4\langle\langle\sum_{n,n'}|\,(D_{n'o}{}^{\lambda'}D_{on}{}^{\lambda}-D_{n'o}{}^{\lambda}D_{on}{}^{\lambda'}\,|^2\rangle\rangle$$
$$=(\tfrac{1}{3}E_u)^4\langle\langle\sum_{n,n'}|\,(D_{n'o}{}^{\lambda'}D_{on}{}^{\lambda})^2-2(D_{n'o}{}^{\lambda'}D_{on}{}^{\lambda}D_{n'o}{}^{\lambda}D_{on}{}^{\lambda'})$$
$$+(D_{n'o}{}^{\lambda}D_{on}{}^{\lambda'})^2\,|\,\rangle\rangle$$
$$=(\tfrac{1}{3}E_u)^4 2(\langle\langle D_T{}^{\lambda\lambda'}\rangle\rangle-\langle\langle D_S{}^{\lambda\lambda'}\rangle\rangle), \tag{B2}$$

where Eqs. (A1)–(A3) have been used. Equation (B2) remains effectively the same for other elastic processes.

The elastic scattering of phonons off the singlet state, for frequencies $\hbar\omega_{q\lambda}\gg 4\Delta$, can be defined as [see Eq. (12)]

$$\tau_q{}^{-1}\alpha\langle\langle\,|\sum_m(\tilde{\Xi}_{om}{}^{\lambda'}\tilde{\Xi}_{mo}{}^{\lambda}-\tilde{\Xi}_{om}{}^{\lambda}\tilde{\Xi}_{mo}{}^{\lambda'})\,|^2\rangle\rangle$$
$$=(\tfrac{1}{3}E_u)^4\langle\langle\,|\sum_m(D_{om}{}^{\lambda'}D_{mo}{}^{\lambda}-D_{om}{}^{\lambda}D_{mo}{}^{\lambda'})\,|^2\rangle\rangle. \tag{B3}$$

Considering the symmetry of the matrices one can say that

$$\tau_q{}^{-1}\longrightarrow\text{negligible quantity.}$$

Finally, we come to the matrix elements describing the electronic processes for inelastic phonon scattering processes. One finds for this case

$$\tau_q{}^{-1}\alpha\langle\langle\sum_n|\sum_m(D_{om}{}^{\lambda'}D_{mn}{}^{\lambda}-D_{oo}{}^{\lambda}D_{on}{}^{\lambda'})\,|^2\rangle\rangle. \tag{B4}$$

Using Kwok's table for matrices $D_{n'n}{}^{\lambda}$, we find

$$\langle\langle\sum_n|\sum_m(D_{om}{}^{\lambda'}D_{mn}{}^{\lambda}-D_{oo}{}^{\lambda}D_{on}{}^{\lambda'})\,|^2\rangle\rangle$$
$$=\langle\langle\sum_n|\sum_m(D_m{}^{\lambda'}D_{mn}{}^{\lambda}-D^{\lambda}D_n{}^{\lambda'})\,|^2\rangle\rangle \tag{B5}$$
$$=\langle\langle\sum_n|\,D_1{}^{\lambda'}D_{1n}{}^{\lambda}-D_o{}^{\lambda}D_n{}^{\lambda'}+D_2{}^{\lambda'}D_{2n}{}^{\lambda}+D_3{}^{\lambda'}D_{3n}{}^{\lambda}\,|^2\rangle\rangle, \tag{B6}$$

where

$$\sum_n D_1{}^{\lambda'}D_{1n}{}^{\lambda}=D_1{}^{\lambda'}D_o{}^{\lambda}+D_1{}^{\lambda'}D_3{}^{\lambda}+D_1{}^{\lambda'}D_1{}^{\lambda},$$
$$\sum_n D_2{}^{\lambda'}D_{2n}{}^{\lambda}=D_2{}^{\lambda'}D_o{}^{\lambda}-(D_2{}^{\lambda'}D_3{}^{\lambda}+D_2{}^{\lambda'}D_2{}^{\lambda}), \tag{B7}$$
$$\sum_n D_3{}^{\lambda'}D_{3n}{}^{\lambda}=D_3{}^{\lambda'}D_1{}^{\lambda}-D_3{}^{\lambda'}D_2{}^{\lambda}+D_3{}^{\lambda'}D_o{}^{\lambda}.$$

Substituting Eqs. (6) and (7) into Eq. (5), we find

$$\tau_q{}^{-1}\alpha\langle\langle\,|\,D_1{}^{\lambda'}D_3{}^{\lambda}+D_1{}^{\lambda'}D_1{}^{\lambda}+D_3{}^{\lambda'}D_1{}^{\lambda}-D_2{}^{\lambda'}D_3{}^{\lambda}$$
$$-D_2{}^{\lambda'}D_2{}^{\lambda}-D_3{}^{\lambda'}D_2{}^{\lambda}\,|^2\rangle\rangle \tag{B8}$$
$$=\langle\langle\,|\,(D_2{}^{\lambda'}D_3{}^{\lambda})^2+(D_1{}^{\lambda'}D_1{}^{\lambda})^2+(D_3{}^{\lambda'}D_1{}^{\lambda})^2$$
$$+(D_2{}^{\lambda'}D_3{}^{\lambda})^2+(D_2{}^{\lambda'}D_2{}^{\lambda})^2+(D_3{}^{\lambda'}D_2{}^{\lambda})^2$$
$$+2(D_1{}^{\lambda'}D_3{}^{\lambda}D_3{}^{\lambda'}D_1{}^{\lambda})-2(D_1{}^{\lambda'}D_1{}^{\lambda}D_2{}^{\lambda'}D_2{}^{\lambda})$$
$$+2(D_2{}^{\lambda'}D_3{}^{\lambda}D_3{}^{\lambda'}D_2{}^{\lambda})\,|\,\rangle\rangle. \tag{B9}$$

The angular integration of these matrices can be obtained with the help of Hasegawa's Table III. We have calculated these angular matrices and, with reference to polarization, we have given the important values in Table I.

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[1] W. Kohn, in *Solid States Phys.*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 5, p. 257.
[2] R. W. Keyes, Phys. Rev. **122,** 1171 (1961).
[3] A. Griffin and P. Carruthers, Phys. Rev. **131,** 1976 (1963).
[4] P. C. Kwok, Phys. Rev. **149,** 666 (1966).
[5] H. Hasegawa, Phys. Rev. **118,** 1526 (1961).
[6] J. P. Dismukes, L. Ekstrom, E. F. Steigmeier, K. Kudman, and D. S. Beers, J. Appl. Phys. **35,** 2899 (1964).
[7] E. F. Steigmeier and B. Abeles, Phys. Rev. **136,** A1149 (1964).
[8] N. K. S. Gaur, C. M. Bhandari, and G. S. Verma, Phys. Rev. **144,** 628 (1965).
[9] J. F. Goff and N. Pearlman, Phys. Rev. **140,** A2151 (1965).
[10] N. K. S. Gaur and G. S. Verma, Phys. Rev. **159,** 610 (1967).
[11] P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 7.
[12] P. Carruthers, Rev. Mod. Phys. **33,** 92 (1961).
[13] J. Callaway, Phys. Rev. **113,** 1046 (1959).

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Configuration Mixing of Subsidiary Minima: Corrections to the Ground-State Wave Function for Donors in Silicon*

T. G. CASTNER, JR.†
Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627

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The introduction of wave-function components from the region of the L_1, K_1, and U_1 points of the lowest conduction band into the ground-state wave function of the shallow donors As, P, and Sb is shown to improve substantially the agreement between the calculated Fermi contact constants for identified ENDOR shells and the experimental Fermi contact constants measured by Hale and Mieher. This wave-function admixture is the band-structure analogy to configuration mixing in atomic physics, and is calculated here employing first-order perturbation theory, the total impurity potential being the perturbing interaction. If one considers the low-energy L_1, K_1, and U_1 regions as subsidiary minima (strictly correct only for the L_1 region), this approach represents a logical extension of the Kohn-Luttinger formalism. This admixture of subsidiary minima is donor dependent (largest for As, intermediate for P, smallest for Sb) and is able to explain satisfactorily the numerous observed donor anomalies, even including the inverted-order cases. The calculated results indicate the positive identification of two new ENDOR shells, shell C as site (5, 5, 5) and shell F as site (2, 2, 0), and suggest the tentative identification of nine other ENDOR shells with lattice sites. Matching experimental Fermi contact constants and calculated values versus $k_0/k_{\max}$ for positively and tentatively identified ENDOR shells yields $k_0/k_{\max}=0.87\pm0.01$. A noninversion component of wave function has been introduced, resulting from the tetrahedral potential admixing $4f$-nf wave function (satisfying A_1 symmetry) into the solution of the single-valley Schrödinger equation. This addition makes only a slight improvement in the over-all agreement. The subsidiary-minima-admixture approach has also been attempted for the deep donor S^+, yielding an improved qualitative agreement between theory and experiment. The admixture of subsidiary minima has a number of other physical consequences: (1) The donor-nucleus hyperfine interaction can be reasonably accounted for, including the donor dependence, without employing the sharply peaked Whittaker function and a cutoff radius; (2) the "shear" deformation potential Ξ_u determined by ESR or optical experiments using the $1s$-A_1 donor ground state may not yield the true "shear" deformation potential of the Δ_1 minima; (3) the energy of the $1s$-A_1 state contains an important second-order correction from the subsidiary minima which can account for between 25% and 50% of the energy correction to the effective-mass value. It is shown the valley-valley coupling terms account for nearly all the energy correction of the $1s$-A_1 state, and that the single-valley correction is very small, contrary to previous work. Analysis of the location of the lattice sites positively and tentatively identified with ENDOR shells yields evidence that the three-dimensional appearance of the wave-function density of the $1s$-A_1 state significantly reflects the tetrahedral symmetry of the atoms surrounding the donor.

I. INTRODUCTION

The generally accepted treatment of the energy levels and wave functions of shallow donors and acceptors in semiconductors has been that developed by Kohn and Luttinger.[1] This elegant theory has been very successful when applied to the excited states of donors and acceptors; however, marked deviations have been observed[2] for the $1s$ states (particularly in silicon), most notably for the $1s$-A_1 ground state. These deviations have been attributed to central-cell corrections[3] and a number of attempts of several different types[4–9] have been made to calculate the corrected energy of the ground state. Efforts to correct the wave function have been made by Kohn and Luttinger[4] and also Muller[8] in an effort to explain the much larger wave-function density at the donor nucleus obtained from the hyperfine interaction with the donor nucleus.[10] Recently, a substantial amount of remarkable experimental data concerning the shallow donors As, P, and Sb in silicon has been reported by Hale and Mieher[11] (hereafter designated as HM I) using the ENDOR