above 3×10^3 V/cm, all the trapped electrons will be excited into the conduction band, and carrier densities will be constant. Therefore, the linear dependence of current on electric field suggests that the trap-free electron mobility will be independent of electric field between 3×10^3 and 1×10^4 V/cm. Among several possible mechanisms for the constant mobility, we will consider here the effect of the hot-electron-caused disturbance of the phonon distribution. Because of the high rate of phonon generation by hot electrons, and the weak phonon-phonon interaction at 4.2 K, it is expected that significant deviations from the thermal-equilibrium phonon distribution might be found at 4.2 K. This idea was presented theoretically by Paranjape[11] and Conwell,[12] and demonstrated in the case of covalent semiconductor such as n-type germanium.[13] In polar semiconductors, the same mechanism as that in covalent semiconductors is assumed for simplicity. According to Paranjape, when the scattering due to acoustical phonons prevails over other scattering mechanisms, the electric field dependence of the electron mobility is described by the relation $\mu_d \propto E^{-2(1-\beta)/(4-\beta)}$, where β is a constant depending on the phonon scattering mechanism, in which the lifetime of phonons $\tau(q)$ is expressed by $\tau(q)=\tau(q_0)\cdot(q_0/q)^\beta$. When $\beta=1$, it follows from this relation that the electron mobility should be independent of electric field. It is estimated that $\beta=0$ for the boundary scattering, and $\beta=1$ for phonons with energies in excess of thermal energies. The former is not important here because the time of sound propagation is much longer than the duration time of voltage pulse. Therefore, the observed linear relation of the current-vs-field curve between 3×10^3 and 1×10^4 V/cm is well understood by putting $\beta=1$ as far as the field dependence is concerned. Paranjape also suggests that when the electron temperature becomes sufficiently large, the effect of such a field-enhanced lattice scattering would gradually decrease. The observed $E^{-1/2}$ dependence above 1×10^4 V/cm suggests the appearence of the normal acoustical-phonon scattering effect.

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Low-Temperature Thermal Conductivity of p-Type Ge and Si

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The thermal conductivity of lightly doped p-type Ge and Si at low temperatures is calculated in terms of a single-mode phonon relaxation time due to elastic scattering by holes in the fourfold degenerate ground state together with boundary and isotopic scattering. Good agreement between the theory and experiment is obtained except at very low temperatures. The relation between the present theory and the mechanism responsible for the heat pulse and ultrasonic attenuation is briefly discussed.

I. INTRODUCTION

Large decreases of the thermal conductivity of lightly doped n-type Ge at low temperatures are caused by the phonon scattering by donor electrons.[1–4] Keyes[1] and Griffin and Carruthers[2] have

calculated the thermal conductivity taking account of the elastic scattering of phonons by the virtual transition of electrons between the singlet and the triplet of the donor ground state. Griffin and Carruthers[2] have also considered the resonance scattering of phonons between the singlet and the triplet. The results of their calculations, in particular Griffin and Carruthers's,[2] are in good agreement with the experimental data.[3,4] Recently, Pomerantz[5] and Pearlman and Goff[6] discussed a rather large contribution to the thermal conductivity from the inelastic scattering of phonons by donor electrons in Sb-doped Ge.

The effect similar to that observed in n-type Ge has also been observed in lightly doped p-type Ge and Si by Carruthers *et al.*[7] and by Holland and Neuringer,[8] respectively. Pyle[9] attempted to explain this effect by taking account of the phonon scattering by impurity molecule ions, but failed to give a quantitative explanation. Griffin and Carruthers[2] gave a qualitative discussion based on resonance phonon scattering. They assumed that the splitting of the quartet in the acceptor ground state arises from the central cell correction. However, the quartet does not split unless static fields of lower symmetry such as strains or magnetic fields exist. Shimizu[10] considered the splitting of the quartet by random internal strains due to dislocations and calculated the low-temperature thermal conductivity of p-Ge by taking account of the phonon scattering due to the virtual transition of acceptor holes between the split levels. The process considered by Shimizu[10] is the same as that considered by Keyes[1] and by Griffin and Carruthers[2] in n-Ge. Shimizu[10] showed that such a mechanism does not explain the experimental data.

The purpose of this paper is to show that the elastic phonon scattering by holes in the quartet, which has not been considered so far,[11] gives the thermal conductivity in good agreement with the experimental data in p-Ge and p-Si except at very low temperatures. The neglect of the small splitting of the quartet in our treatment is justified as long as the energy of phonons, which makes the main contribution to the thermal conductivity, is much larger than the splitting. A brief discussion is given on the scattering mechanism of low-frequency phonons at very low temperatures. The relation between our theory and the mechanism responsible for the heat pulse and ultrasonic attenuation is also briefly discussed.

II. PHONON RELAXATION RATE CAUSED BY ACCEPTOR-HOLE-PHONON INTERACTION

In Ge and Si, the valence-band edge and the ground state of shallow acceptors have fourfold degeneracy and Γ_8 symmetry.[12] Accordingly, the acceptor-hole-lattice interaction Hamiltonian is of the same form as that for free holes near the valence-band edge,[13,14] i.e.,

$$\mathcal{H}_{h-l} = \tfrac{2}{3} D_u^a[(J_x^2 - \tfrac{1}{3}J^2)e_{xx} + \text{cp}] + \tfrac{1}{3} D_{u'}^a [(J_x J_y + J_y J_x)e_{xy} + \text{cp}], \qquad (2.1)$$

where J_α is the αth component of the angular momentum operator for $J=\frac{3}{2}$, $e_{\alpha\beta}$ is the conventional strain component,[15] and cp denotes the cyclic permutation with respect to the indices x, y, z. The deformation potential constants D_u^a and $D_{u'}^a$ are, in general, not the same as those for free holes because the wave function of the acceptor ground state has a d-like part as well as an s-like part.[14]

We assume that the four levels of the ground state are identified by the quantum number M_J $(=\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2})$. The corresponding envelope functions are given by

$$\Psi_{M_J} = [(\pi a^{*3})^{-1/2} e^{-r/a^*}]\Phi_{M_J}, \qquad (2.2)$$

where Φ_{M_J} is the eigenfunction of M_J and the small amount of the d-like part is neglected in the orbital function. Expanding $e_{\alpha\beta}$ in phonon operators, we find that the matrix elements of the hole-lattice interaction between two acceptor states $|n\rangle$ and $|n'\rangle$ are given by

$$\langle n|\mathcal{H}_{h-l}|n'\rangle = \sum_{q,t}\left(\frac{\hbar\omega_{qt}}{2Mv_t^2}\right)^{1/2} f(q)(\tfrac{2}{3}D_{u'}^a)C_{qt}^{nn'}(a_{qt}+a_{qt}^\dagger), \qquad (2.3)$$

where

$$\begin{aligned} C_{qt}^{11} &= C_{qt}^{44} = -C_{qt}^{22} = -C_{qt}^{33} = \tfrac{1}{2}D(2\hat{q}_z e_{tz} - \hat{q}_x e_{tx} - \hat{q}_y e_{ty}),\\ C_{qt}^{12} &= -C_{qt}^{34} = \tfrac{1}{2}\sqrt{3}[(\hat{q}_z e_{tx} + \hat{q}_x e_{tz}) - i(\hat{q}_z e_{ty} + \hat{q}_y e_{tz})],\\ C_{qt}^{13} &= C_{qt}^{24} = \tfrac{1}{2}\sqrt{3}\,D(\hat{q}_x e_{tx} - \hat{q}_y e_{ty}) - i\tfrac{1}{2}\sqrt{3}(\hat{q}_x e_{ty} + \hat{q}_y e_{tx}),\\ C_{qt}^{14} &= C_{qt}^{23} = 0, \end{aligned} \qquad (2.4)$$

and

$$D = D_u^a/D_{u'}^a, \quad f(q) = (1 + \tfrac{1}{4}a^{*2}q^2)^{-2}. \qquad (2.5)$$

Here, the superscripts 1–4 stand for $M_J = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$, respectively, M is the mass of the crystal, a_{qt} and $a_{qt}^\dagger$ are the annihilation and creation operators for the phonon with wave vector $\vec{q}$ in the t branch, ω_{qt} is the angular frequency, v_t is the velocity of sound, a^* is the effective Bohr radius of the acceptor hole, $\hat{q}$ is the unit vector along $\vec{q}$, and $\vec{e}_t$ is the polarization vector of the phonon. If $\hat{q}$ $(\sin\theta\cos\phi,\ \sin\theta\sin\phi,\ \cos\theta)$ are the polar coordinates of $\hat{q}$ referred to the $\langle 100\rangle$ axes, then a convenient set of orthogonal axes for $\vec{e}_t$ is given by

$\vec{e}_1(\sin\theta\cos\phi,\ \sin\theta\sin\phi,\ \cos\theta)$,

$\vec{e}_2(-\cos\theta\cos\phi,\ -\cos\theta\sin\phi,\ \sin\theta)$,

$$\vec{e}_3(\sin\phi,\ -\cos\phi, 0), \tag{2.6}$$

where the subscripts 1–3 stand for the longitudinal and two transverse modes, respectively.

We shall now calculate the scattering rate of a phonon $(\vec{q}, t)$ into all other modes $(\vec{q}\,', t')$ by the hole-phonon interaction. The single-mode relaxation time τ_{qt} is defined by[2]

$$1/\tau_{qt} = \sum_{q't'} W(qt \to q't'), \tag{2.7}$$

where $W(qt \to q't')$ for the elastic phonon scattering in the second Born approximation is given by

$$W(qt \to q't')n_{qt}(n_{q't'}+1) = \frac{2\pi}{\hbar}\sum_n N_n(T) \times \sum_{n'}\left|\sum_m\left(\frac{\langle n'|\mathcal{H}_{h\text{-}l}(q't')|m\rangle\langle m|\mathcal{H}_{h\text{-}l}(qt)|n\rangle}{E_m - E_n - \hbar\omega_{qt}} + \frac{\langle n'|\mathcal{H}_{h\text{-}l}(qt)|m\rangle\langle m|\mathcal{H}_{h\text{-}l}(q't')|n\rangle}{E_m - E_n + \hbar\omega_{q't'}}\right)\right|^2_{(E_n=E_{n'})} \times \delta(\hbar\omega_{q't'} - \hbar\omega_{qt}). \tag{2.8}$$

Here n_{qt} is the occupation number of the phonon (q, t), E_α is the energy of the hole in the αth state, $N_\alpha(T)$ is the number of the acceptor holes per unit volume in the αth state, n, m, and n' stand for the initial, intermediate, and final states, respectively. The matrix element $\langle m|\mathcal{H}_{h\text{-}l}(qt)|n\rangle$ denotes the (q, t) component of $\langle m|\mathcal{H}_{h\text{-}l}|n\rangle$. Using Eqs. (2.3), (2.7), and (2.8), we obtain

$$\frac{1}{\tau_{qt}} = \frac{\pi\omega_{qt}}{\rho v_t^2} f^2(q) \quad (\tfrac{2}{3}D_{u'}^a)^4 \sum_n N_n(T)\sum_{n'}\sum_{q't'}\frac{\hbar\omega_{q't'}}{2\rho v_{t'}^2} f^2(q') \times\left|\sum_m\left(\frac{C_{q't'}^{n'm}C_{qt}^{mn}}{E_m - E_n - \hbar\omega_{qt}} + \frac{C_{qt}^{n'm}C_{q't'}^{mn}}{E_m - E_n + \hbar\omega_{q't'}}\right)\right|^2_{(E_n=E_{n'})} \times\delta(\hbar\omega_{q't'} - \hbar\omega_{qt}), \tag{2.9}$$

where ρ is the mass density.

The excited states of the acceptor in Ge and Si are about 7 meV ($\cong 80\,^\circ$K) and 30 meV ($\cong 330\,^\circ$K) above the ground state, respectively, so that the transition process involving these excited states hardly contributes to $1/\tau_{qt}$ and is neglected in this paper. The angular frequency of typical phonons which carry the heat at a temperature T is about $4kT/\hbar$. If we assume that the splitting of the quartet caused by various perturbations is much smaller than $4kT$, then Eq. (2.9) can be written as

$$\frac{1}{\tau_{qt}} = \frac{\omega_{qt}^2}{16\pi^2\rho^2 v_t^2\hbar^2} f^2\left(\frac{\omega_{qt}}{v_t}\right)(\tfrac{2}{3}D_{u'}^a)^4\sum_n N_n(T)\sum_{n'}\sum_{t'}\iint\sin\theta'\,d\theta'\,d\phi'\,\frac{1}{v_{t'}^5} f^2\left(\frac{\omega_{q't'}}{v_{t'}}\right)\left|\sum_m\left(C_{q't'}^{n'm}C_{qt}^{mn} - C_{qt}^{n'm}C_{q't'}^{mn}\right)\right|^2 \tag{2.10}$$

by putting $E_n = E_{n'} = E_m$.

In the calculation of the thermal conductivity $K(T)$, the angular average of $1/\tau_{qt}$, i.e.,

$$\frac{1}{\bar{\tau}_{qt}} = \frac{1}{4\pi}\iint\sin\theta\,d\theta\,d\phi\,\frac{1}{\tau_{qt}},$$

is required. From Eqs. (2.4), (2.6), and (2.10), we obtain

$$\frac{1}{\bar{\tau}_{qt}} = \frac{N\omega_{qt}^2}{100\pi\rho^2\hbar^2 v_t^2}(\tfrac{2}{3}D_{u'}^a)^4 f^2\left(\frac{\omega_{qt}}{v_t}\right)\times\left[\frac{1}{v_1^5}f^2\left(\frac{\omega_{qt}}{v_1}\right) + \frac{3}{2}\frac{1}{v_2^5}f^2\left(\frac{\omega_{qt}}{v_2}\right)\right]w_t, \tag{2.11}$$

where

$$w_1 = 24 + 48D^2 + 8D^4,$$
$$w_2 = 16 + 37D^2 + 7D^4, \tag{2.12}$$
$$w_3 = 20 + 35D^2 + 5D^4.$$

Here, N is the number of acceptor holes per unit volume, and v_1 and v_2 (equal to v_3) are the average velocities[2] of sound for the longitudinal and transverse modes of the phonon, respectively.

III. CALCULATION OF THERMAL CONDUCTIVITY AND COMPARISON WITH EXPERIMENT

Taking into account the boundary and isotopic scattering as well as the phonon scattering by acceptor holes, we shall evaluate $K(T)$ in lightly doped p-Ge and p-Si at low temperatures. The thermal conductivity is given by[2,16]

$$K(T) = \frac{k^4T^3}{6\pi^2\hbar^3}\sum_t\frac{1}{v_t}\int_0^\infty\frac{x^4e^x}{(e^x-1)^2}\tau\,dx, \tag{3.1}$$

where

$$1/\tau = 1/\tau_B + 1/\tau_I + 1/\bar{\tau}_{qt},$$
$$1/\tau_B = v_t/L, \tag{3.2}$$
$$1/\tau_I = A\omega_{qt}^4 = A(kT/\hbar)^4x^4.$$

TABLE I. Values of physical parameters used in the calculation of the thermal conductivity.

	Ge	Si
ρ(g cm^{-3})	5.35	2.33
v_1(cm sec^{-1})	5.37×10^5	9.33×10^5
v_2(cm sec^{-1})	3.28×10^5	5.42×10^5
N(cm^{-3})	2.3×10^{16} [a]	4.0×10^{16} [b]
L(cm)	0.3 [a]	0.7 [b]
A(sec^{-3})	2.40×10^{-44} [c]	1.32×10^{-45} [b]
a^*(Å)	37 [d]	15 [d]
D_u^a(eV)	4.2	3.2
$D_{u'}^a$ (eV)	4.9	3.8

[a]Reference 7. [c]Reference 2.
[b]Reference 8. [d]Reference 14.

Here, $x \equiv \hbar\omega_{qt}/kT$, $1/\tau_B$, and $1/\tau_I$ are the relaxation rate of the phonon by the boundary and isotopic scattering, respectively, and L is the Casimir length.[8] The numerical values of physical parameters used in the calculation of $K(T)$ are listed in Table I. The theoretical curves of $K(T)$ of p-Ge and p-Si are shown together with the experimental data by Carruthers *et al.*[7] and by Holland and Neuringer[8] in Figs. 1 and 2, respectively. It is seen that the agreement between theory and experiment is satisfactory except at very low temperatures.

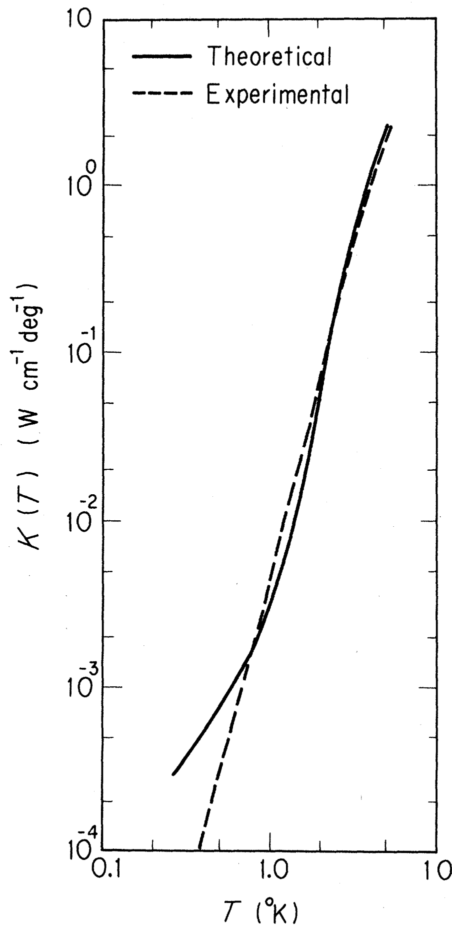

FIG. 1. Theoretical and experimental (Ref. 7) curves of the thermal conductivity in In-doped Ge as a function of temperature.

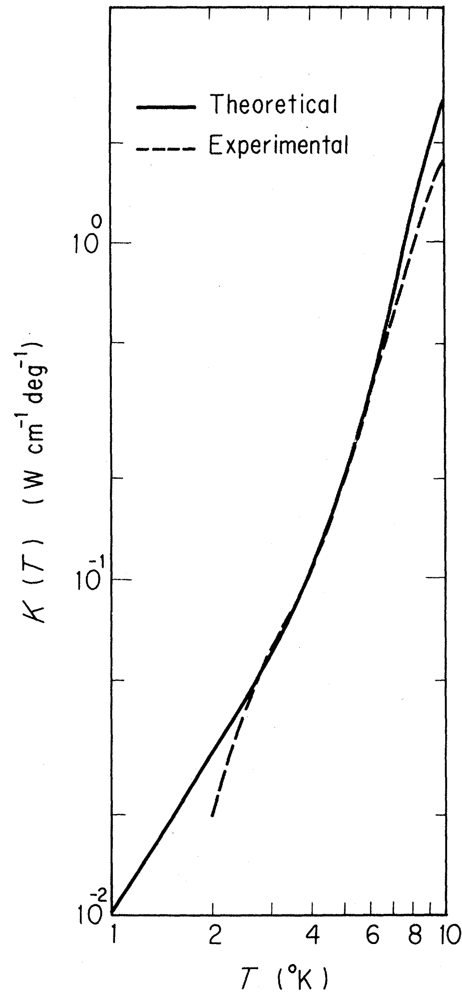

FIG. 2. Theoretical and experimental (Ref. 8) curves of the thermal conductivity in B-doped Si as a function of temperature.

We would like to remark on the values of the deformation potential constants D_u^a and $D_{u'}^a$ used in our evaluation of $K(T)$. As is seen from Eq. (2.9), the single-mode relaxation rate depends strongly on the values of D_u^a and $D_{u'}^a$. As far as we know, the values of D_u^a and $D_{u'}^a$ for the acceptor state have not been directly measured in experiments. According to the effective-mass theory,[14] these constants are somewhat smaller than the deformation potential constants D_u and $D_{u'}$ at the valence-band edge. However, such a conclusion is not very convincing because of limitations of the effective-mass theory. The experimental values of D_u and $D_{u'}$ at

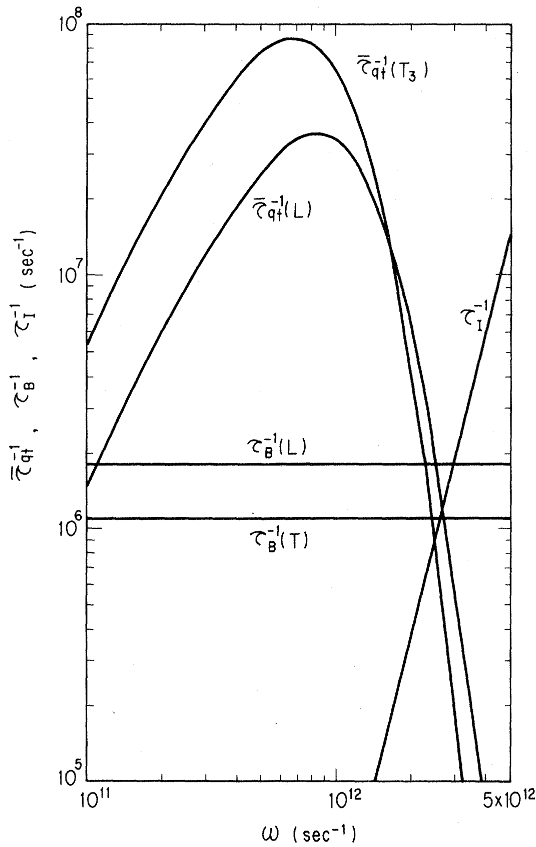

FIG. 3. Relaxation rate of phonons by the scattering by holes ($1/\bar{\tau}_{qt}$), by the isotopic scattering ($1/\tau_I$), and by the boundary scattering ($1/\tau_B$) in In-doped Ge (see Ref. 7) as a function of the angular frequency ω_{qt}. L stands for longitudinal phonons, while T_3 denotes the transverse phonons in the angular average corresponding to w_3 in Eq. (2.12) in the text.

the valence-band edge in Ge and Si have been obtained by several authors:

$D_u = 3.2$ eV, $D_{u'} = 6.1$ eV (Ref. 17);

$D_{u'} = 5.2$ eV (Ref. 18);

$D_u = 4.2$ eV, $D_{u'} = 4.9$ eV (Ref. 19)

in Ge; and

$D_u = 2.0$ eV, $D_{u'} = 2.7$ eV (Ref. 20)

in Si. The values of D_u^a and $D_{u'}^a$ listed in Table I have been tentatively chosen so as to give a good agreement with the experimental data.

IV. DISCUSSION

As is seen from Figs. 1 and 2, the hole-phonon interaction discussed in Sec. II becomes ineffective at very low temperatures, i.e., $T \lesssim 0.6$ °K in Ge and $T \lesssim 2$ °K in Si. In order to make this point clear, we have plotted the relaxation rates $1/\bar{\tau}_{qt}$, $1/\tau_I$, and $1/\tau_B$ against ω_{qt} for Ge and Si in Figs. 3 and 4, respectively. The factor $x^4 e^x (e^x - 1)^{-2}$ in the integrand in Eq. (3.1) is also plotted as a function of x in Fig. 5. Remark that $x = 1$ for $\omega_{qt} \cong 1.3 \times 10^{11}$ sec^{-1} at $T = 1$ °K. From Figs. 3–5, we can see that the relaxation rate due to the hole-phonon interaction for low-frequency phonons, which makes the main contribution to $K(T)$ at very low temperatures, decreases proportionally to ω_{qt}^2 with decreasing frequency. Let us consider the process by which low-frequency phonons are strongly scattered. As shown by Shimizu,[10] low-frequency phonons may be strongly scattered if small splittings exist in the acceptor ground state. Besides random internal strains due to dislocations, the Jahn-Teller effect may give rise to such a small splitting. In this paper we shall not calculate $K(T)$ at very low temperatures.

At higher temperatures, $1/\bar{\tau}_{qt}$ becomes also ineffective as is seen from Figs. 3 and 4. In this case, it should be remarked that for phonons satisfying the condition $a^*(\omega_{qt}/v_t) \geq 2$, $1/\bar{\tau}_{qt}$ depends strongly on the effective Bohr radius a^* of the acceptor holes. It is also noted that the value of a^* determined by the effective-mass theory is, in

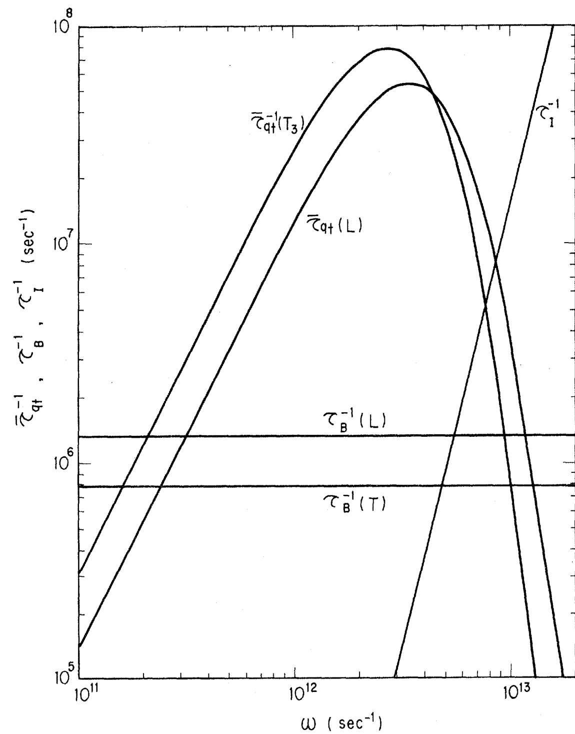

FIG. 4. Relaxation rate of phonons by the scattering by holes ($1/\bar{\tau}_{qt}$), by the isotopic scattering ($1/\tau_I$), and by the boundary scattering ($1/\tau_B$) in B-doped Si (see Ref. 8) as a function of the angular frequency ω_{qt}. L stands for longitudinal phonons, while T_3 denotes the transverse phonons in the angular average corresponding to w_3 in Eq. (2.12) in the text.

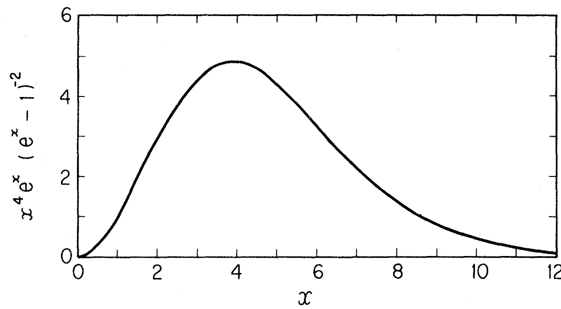

FIG. 5. The factor $x^4e^x(e^x-1)^{-2}$ in the integrand of Eq. (3.1) in the text as a function of $x \equiv \hbar\omega_{qt}/kT$.

general, larger than the true spread of the ground-state wave function. Therefore, the discrepancy between theory and experiment at higher temperatures in Figs. 1 and 2 could be removed by choosing a somewhat smaller value of a^* than that given in Table I.

V. OTHER ASPECTS

Pomerantz and von Gutfeld[21] have investigated the scattering of phonons with typical frequency $\omega_{qt} \cong 2\times10^{12}$ sec^{-1} by acceptors in In-doped Ge and In-doped Si by the heat-pulse method. They found two interesting phenomena: namely, that (i) longitudinal phonons are more strongly scattered than transverse phonons in Ge, while in Si transverse phonons are more strongly scattered, and (ii) the phonon scattering in Ge decreases with increasing phonon frequency, while in Si the scattering increases with frequency. As can be seen from Figs. 3 and 4, $\bar{\tau}_{qt}^{-1}(L) > \bar{\tau}_{qt}^{-1}(T_3)$ for $\omega \gtrsim 1.5\times10^{12}$ sec^{-1} in Ge, while $\bar{\tau}_{qt}^{-1}(T_3) > \bar{\tau}_{qt}^{-1}(L)$ at $\omega \simeq 2\times10^{12}$ sec^{-1} in Si. Thus the phenomenon (i) can be qualitatively explained by our theory. For the explanation of phenomenon (ii), let us note the following fact. Atoms in Si have an ionization energy of 0.16 eV which is about four times the effective-mass value, so that a^* is smaller than the effective-mass value of 15 Å. Therefore, the frequency at which the maximum of $1/\bar{\tau}_{qt}$ occurs shifts to higher frequency in Fig. 4. Figures 3 and 4 with above considerations give a reasonable explanation of phenomenon (ii).

Finally, we shall make a brief comment on the ultrasonic attenuation by acceptor holes. Preliminary results for the attenuation of 9-GHz shear waves measured by Pomerantz[22] show that the attenuation is typically about 10 dB/cm for $N=10^{16}$ cm^{-3} in p-Ge and p-Si. The attenuation coefficient α_{qt} for shear waves propagating along $\langle 100\rangle$, for example, by the elastic process discussed in Sec. II is given by

$$\alpha_{qt} = \frac{1}{\tau_{qt}\, v_t} = \frac{(3+3D^2)N\omega_{qt}^2}{10\pi\rho^2 v_t^3 \hbar^2} f^2\left(\frac{\omega_{qt}}{v_t}\right)\left(\tfrac{2}{3}D_{u'}^a\right)^4 \times\left[\frac{1}{v_1^5}f^2\left(\frac{\omega_{qt}}{v_1}\right)+\frac{3}{2}\frac{1}{v_2^5}f^2\left(\frac{\omega_{qt}}{v_2}\right)\right] , \quad (5.1)$$

with the help of Eq. (2.10). Inserting the values of parameters given in Table I and $N=10^{16}$ cm^{-3}, $\omega_{qt}=5.65\times10^{10}$ sec^{-1}, and $v_t=3.57\times10^5$ cm/sec (Ge) and 5.86×10^5 cm/sec (Si) into Eq. (5.1), we obtain $\alpha_{qt}=5$ db/cm (Ge) and 0.2 dB/cm (Si). Thus, the attenuation due to the elastic scattering by the quartet is smaller than the observed one, particularly in Si. This shows that the inelastic scattering and the resonant absorption as well as the elastic scattering by the ground-state split at random by strains may be responsible for the observed attenuation. Detailed discussion of the ultrasonic attenuation in p-type Ge and Si will be given in a separate paper.

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Electronic Structure of the Single Vacancy in Silicon*

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A technique based on the use of Wannier functions is employed to investigate the electronic structure of the isolated neutral vacancy in silicon. The change in crystal potential produced by the defect is represented as the negative of an atomic pseudopotential. Scattering phase shifts are calculated for states within the valence band. These phase shifts are used to estimate one major contribution to the formation energy of the vacancy; the change in the total one-electron energy, which can be expressed as an integral of the phase shifts over the occupied states. This quantity is computed and found to be equal to 23 eV.

I. INTRODUCTION

The object of this paper is to apply the techniques of solid-state scattering theory[1] to the study of the electronic structure of the single vacancy in silicon. In a previous paper, the formation of localized states in the band gap by both the single vacancy and the divacancy have been studied by similar techniques.[2] In this paper, we will focus attention on the changes produced in the one-electron wave functions of the occupied states, and on the consequent changes in the total energy of the system.

Because the present approach is different from that which many other workers have employed, it is useful to begin with a brief survey of a previous paper. Most of the existing studies of the vacancy in covalently bonded semiconductors have been based on molecular-orbital theory, whose applicability was initially proposed by Coulson and Kearsley.[3] The original calculations concerned vacancies in diamond. Their work has been extended[4,5] and recently applied to silicon.[6]

The essential idea of the molecular-orbital method as it has been applied to this problem is to separate conceptually the atoms in the immediate neighborhood of the defect from the rest of the crystal. These atoms, together with the defect, are regarded as forming a defect molecule. The energy levels of this molecule are then calculated. Although the concept of atoms in the immediate neighborhood of the defect is ambiguous to some extent, the usual practice has been to consider just the four atoms which are nearest neighbors of the vacancy. The four tetrahedral bonds which were ruptured when the central atom was removed are employed as basis states for the computation. The orbitals are hybrid sp^3 combinations directed toward the center of the defect. Combinations of these orbitals are constructed which belong to the Γ_1 and Γ_4 representations of the tetrahedral group. Let these combinations be denoted v and t, respectively. A configuration of the defect molecule may be described in terms of occupation of v and t functions, as $v^a t^{n-a}$, where $a = 0$, 1, or 2, and n is the number of electrons in the vacancy molecule ($n=4$ for the neutral vacancy; $n=5$ if there is a net negative charge of unity, etc.). For a given configuration, one now constructs wave functions of proper symmetry (eigenfunctions of S^2 and S_z, where S is the total spin), which transform according to the irreducible representations of the tetrahedral group.

The Hamiltonian used in the molecular-orbital calculation of the structure of the vacancy includes the interaction of each of the n vacancy electrons with the nuclei and other electrons of the atoms which are nearest neighbors of the vacancy, plus the Coulomb repulsion of the valence electrons.[6] The energies of states coming from a single configuration are determined as the expectation of this Hamiltonian using the wave functions constructed above. If states of the same symmetry occur in different configurations, configuration mixing can be introduced by calculating matrix elements of the Hamiltonian between these states and solving the resulting secular equation. The result is a set of (n-electron) energy states for the system.

The principal objection which can be brought against this procedure involves the concept of a