

heavily doped Ge and Si; however, their thermal conductivities are much lower so that alloys with very high figures of merit are attainable.

We have prepared *n*-type and *p*-type Ge-Si alloys with figures of merit as high as $0.95 \times 10^{-3} \text{ deg}^{-1}$ and $0.55 \times 10^{-3} \text{ deg}^{-1}$, respectively, averaged over a temperature range 700°–1200°K. We have measured 7.3% power conversion efficiency on a couple made up of bars of *n*-type and *p*-type alloys with dimensions $\frac{1}{2} \text{ in.} \times \frac{1}{4} \text{ in.} \times \frac{1}{2} \text{ in.}$ The cold junction temperature was 300°K and the hot junction temperature was 1140°K. The output current and voltage, into a matched load,

were 12 amp and 0.19v. The efficiency predicted from the material properties was 10%. The difference between the theoretical and measured efficiencies could be entirely accounted for by electrical contact resistance and radiation losses.

ACKNOWLEDGMENTS

We thank S. M. Christian for supplying several Ge-Si crystals, E. V. Fitzke and H. E. Temple for their assistance in the material preparation, R. J. Paff for the x-ray analysis and R. W. Cohen for the power conversion measurements.

Two-Phonon Transitions in the Impurity Conduction in Semiconductors

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(Received July 10, 1961)

The two-phonon transition rate for carrier transfer from an occupied impurity center to an empty one was calculated on the basis of the formalism given by Gummel and Lax for the multiphonon processes in the Born-Oppenheimer and deformation-potential approximations. The general formula for the two-phonon transition rate was investigated in detail in the case of simple parabolic band in two regions of temperature. Numerical data are given for *n*- and *p*-type Si and Ge. It is shown that two-phonon transitions can play a role in impurity conduction in materials with low mobility of carriers and low impurity concentration.

I. INTRODUCTION

IMPURITY conduction in semiconductors at low concentrations of impurities is due to tunnelling of carriers from the ground state of occupied impurity centers to the ground state of empty ones. Unoccupied majority centers are present because of compensation. The transition rate depends on the overlap of the wave functions of the carrier in the neighboring impurity centers and decreases rapidly with decreasing impurity concentration. The ionized majority and minority centers give an electrostatic potential which varies from center to center. Thus hopping of carriers from occupied impurity centers to empty ones can occur only with absorption or emission of phonons. In this way the observed activation energy of impurity conduction can be explained.^{1,2} The trapping of the carrier on an impurity center can occur also because of interaction with the deformed crystal lattice.³

The transition rate for phonon-accompanied carrier transfer from one center to another was obtained theoretically by the use of the resonance energy³ or the deformation potential^{1,2} as perturbation. The last method gave satisfactory agreement with the experimental data but only one-phonon processes were investigated in detail in this way.

The purpose of the present work is to obtain the ratio of the transition rates for two-phonon and one-phonon processes by the use of the deformation-potential approximation. As in references 1 and 2, only longitudinal acoustic phonons are taken into account. We use the general formalism for multiphonon transitions developed by Gummel and Lax⁴ (to be referred to in the following as GL) in the Born-Oppenheimer and deformation-potential approximations. This formalism is a first-order perturbation theory, so that we do not have here transitions through intermediate states, as was proposed in reference 1. The perturbing operator is linear in the elastic wave amplitudes, and the possibility of multiphonon transitions occurs because of the dependence of the equilibrium position of the lattice atoms on the state of the carrier.

Phonons may be visualized to be involved in a transition for two reasons: firstly, because of the failure of the carrier to adjust instantaneously to the atomic positions (so-called kinetic phonons, *K*), and secondly, as the result of the deformed lattice relaxation (lattice-relaxation phonons, *LR*). It is well known that the multiphonon processes can be obtained also by taking into account the nonlinear terms in the perturbing operator.⁵ This was not done here, because it is difficult

¹ T. Kasuya and S. Koide, *J. Phys. Soc. Japan* **13**, 1287 (1958).

² A. Miller and E. Abrahams, *Phys. Rev.* **120**, 745 (1960).

³ Y. Toyozawa, *Progr. Theoret. Phys. (Kyoto)* **23**, 378 (1960).

⁴ H. Gummel and M. Lax, *Ann. Phys.* **2**, 28 (1957).

⁵ S. Koshino, *Progr. Theoret. Phys. (Kyoto)* **18**, 23 (1957).

to obtain the coefficients of these terms. Thus our two-phonon transition rates will be rather underestimated.

In the GL formalism only the terms independent and linear in elastic wave amplitudes are taken into account in the wave functions of the carrier. In our case it is a rather crude approximation because the energy of interaction with the deformed crystal lattice can be of the order of the electrostatic energy difference between two impurity centers.³ This is one more reason why our two-phonon transition rates will be underestimated.⁴

II. TWO-PHONON TRANSITION RATES

We start from the formula (GL 3.34).⁴ The fundamental (i.e., proportional to the deformation potential constant squared) part of the one-phonon (K) transition rate from the carrier state a to the state b is

$$W_{ba}^{1I} = (2\pi/\hbar^2)h(\omega_0). \quad (1)$$

As one can see from the following, this is just the transition rate treated by Miller and Abrahams.² The fundamental (i.e., proportional to the deformation potential constant in the fourth power) part of the two-phonon (one phonon K and one LR) transition rate is

$$W_{ba}^{2I} = (2\pi/\hbar^2)\{Fh(\omega)\}_{\omega=\omega_0}. \quad (2)$$

The fundamental part of the two-phonon K transition rate is

$$W_{ba}^{2II} = (2\pi/\hbar^2)\{Gg(\omega)\}_{\omega=\omega_0}. \quad (3)$$

We are interested only in the ratios

$$W_{ba}^{2I}/W_{ba}^{1I} = \{Fh(\omega)\}_{\omega=\omega_0}/h(\omega_0), \quad (4)$$

$$W_{ba}^{2II}/W_{ba}^{1I} = \{Gg(\omega)\}_{\omega=\omega_0}/h(\omega_0). \quad (5)$$

From the formulas (GL 3.32, 3.33)

$$\{Fh(\omega)\}_{\omega=\omega_0} = \int_{-\infty}^{+\infty} f(\omega_0 - \omega)h(\omega)d\omega, \quad (6)$$

$$\{Gg(\omega)\}_{\omega=\omega_0} = \int_{-\infty}^{+\infty} g^*(\omega_0 - \omega)g(\omega)d\omega. \quad (7)$$

The functions $h(\omega)$ and $g(\omega)$ are the distribution functions for K phonons, and $f(\omega)$ for LR phonons. The positive argument in the function correspond to the emission, and negative to the absorption, of a phonon. Thus in the formulas (6) and (7), if ω is in the interval

$(0, \omega_0)$ we have absorption or emission of two phonons, and if ω is outside this frequency interval we have absorption and re-emission of phonons. If ω is beyond this interval we have always the emission of K phonons; if it is below this interval, absorption of K phonons.

We shall use the longitudinal acoustic modes in the complex form. The formulas (GL 3.28, 3.30, 3.31) and reference 7 of GL yield

$$f(\omega) = \langle (|\xi(\tau_j)|^2/\omega_j)\delta(|\omega| - \omega_j)\theta(\omega), \quad (8)$$

$$h(\omega) = \langle (|\lambda(\tau_j)|^2/\omega_j)\delta(|\omega| - \omega_j)\theta(\omega), \quad (9)$$

$$g(\omega) = \langle [(\xi(\tau_j)\lambda(-\tau_j) + \xi(-\tau_j)\lambda(\tau_j))/2\omega_j] \times \delta(|\omega| - \omega_j)\theta(\omega), \quad (10)$$

where following (GL 3.29)

$$\theta(\omega) = \omega \exp(\hbar\omega/2kT)[2 \sinh(\hbar\omega/2kT)]^{-1}. \quad (11)$$

We use the notation $(1/N)\sum_j a_j = \langle a_j \rangle$, N being the number of unit cells in the crystal and j , a longitudinal acoustic mode with the wave vector τ_j and frequency ω_j .

Following the formulas (GL 3.15, 3.16), we have

$$\xi(\tau_j) = (2M\hbar\omega_j^3)^{-1/2}[B_{bb}(\tau_j) - B_{aa}(\tau_j)], \quad (12)$$

$$\lambda(\tau_j) = (\hbar^3\omega_j/2M)^{1/2}[E_b(0) - E_a(0)]^{-1}B_{ba}(\tau_j). \quad (13)$$

M is the mass of the unit cell. $E_b(0) - E_a(0) = \Delta E_{ba}$ is the energy difference between the carrier states b and a in nondeformed crystal lattice.

We can neglect the difference of the lattice relaxation energies in the two carrier states when we deal with the ground states of two impurity centers of the same kind. Then from the formula (GL 3.17) we obtain

$$\omega_0 = -\Delta E_{ba}/\hbar. \quad (14)$$

Taking into account only the linear interaction with longitudinal acoustic phonons, we have from (GL 3.5, 3.1, 4.1) and in analogy with (GL 4.2)

$$B_{kl}(\tau_j) = iE_1\tau_j \int u_k^* \exp(i\tau_j \cdot \mathbf{r})u_l d\mathbf{r}, \quad (15)$$

where E_1 is the Bardeen-Shockley constant and u_k, u_l are the wave functions of the carrier in the states k, l in nondeformed crystal lattice.

If we assume a Debye spectrum for the longitudinal acoustic phonons, then the summation over modes in the formulas (8)–(10) can be easily performed. Using (12)–(14), the results are

$$\langle (|\xi(\tau_j)|^2/\omega_j)\delta(|\omega| - \omega_j) \rangle = (16\pi^3\hbar v^3\omega_0^2 d)^{-1} \int \left| B_{bb}\left(\frac{|\omega|}{v}\Omega\right) - B_{aa}\left(\frac{|\omega|}{v}\Omega\right) \right|^2 d\Omega, \quad (16)$$

$$\langle (|\lambda(\tau_j)|^2/\omega_j)\delta(|\omega| - \omega_j) \rangle = (\hbar\omega^2/16\pi^3 v^3\omega_0^2 d) \int \left| B_{ba}\left(\frac{|\omega|}{v}\Omega\right) \right|^2 d\Omega, \quad (17)$$

$$\begin{aligned} & \langle [(\xi(\tau_j)\lambda(-\tau_j) + \xi(-\tau_j)\lambda(\tau_j))/2\omega_j]\delta(|\omega| - \omega_j) \rangle \\ &= -(16\pi^3 v^3\omega_0^2 d)^{-1} \int \left[B_{bb}\left(\frac{|\omega|}{v}\Omega\right) - B_{aa}\left(\frac{|\omega|}{v}\Omega\right) \right] B_{ba}\left(-\frac{|\omega|}{v}\Omega\right) d\Omega, \end{aligned} \quad (18)$$

v being the velocity of sound, d the density of the crystal, and Ω a unit vector. Integrations are over all directions of Ω . From these formulas and from (4)–(11) we have

$$W_{ba}^{2I}/W_{ba}^1 = (32\pi^3 \hbar v^3 |\omega_0|^3 d)^{-1} \sinh(\hbar |\omega_0|/2kT) \left[\int \left| B_{ba} \left(\frac{|\omega_0|}{v} \Omega \right) \right|^2 d\Omega \right]^{-1} \\ \times \int_{-\infty}^{+\infty} \left[\int \left| B_{ba} \left(\frac{|\omega|}{v} \Omega \right) \right|^2 d\Omega \right] \left[\int \left| B_{bb} \left(\frac{|\omega_0 - \omega|}{v} \Omega \right) - B_{aa} \left(\frac{|\omega_0 - \omega|}{v} \Omega \right) \right|^2 d\Omega \right] \\ \times (|\omega|^3 / |\omega_0 - \omega|) [\sinh(\hbar |\omega|/2kT) \sinh(\hbar |\omega_0 - \omega|/2kT)]^{-1} d\omega, \quad (19)$$

$$W_{ba}^{2II}/W_{ba}^1 = (32\pi^3 \hbar v^3 |\omega_0|^3 d)^{-1} \sinh(\hbar |\omega_0|/2kT) \left[\int \left| B_{ba} \left(\frac{|\omega_0|}{v} \Omega \right) \right|^2 d\Omega \right]^{-1} \\ \times \int_{-\infty}^{+\infty} \left\{ \int \left[B_{bb} \left(\frac{|\omega|}{v} \Omega \right) - B_{aa} \left(\frac{|\omega|}{v} \Omega \right) \right] B_{ba} \left(-\frac{|\omega|}{v} \Omega \right) d\Omega \right\} \\ \times \left\{ \int \left[B_{bb}^* \left(\frac{|\omega_0 - \omega|}{v} \Omega \right) - B_{aa}^* \left(\frac{|\omega_0 - \omega|}{v} \Omega \right) \right] B_{ba}^* \left(-\frac{|\omega_0 - \omega|}{v} \Omega \right) d\Omega \right\} \\ \times |\omega| |\omega_0 - \omega| [\sinh(\hbar |\omega|/2kT) \sinh(\hbar |\omega_0 - \omega|/2kT)]^{-1} d\omega. \quad (20)$$

III. TRANSITION RATES FOR CARRIER TRANSFER

We shall use now the formulas derived in the preceding section to obtain the two-phonon transition rates for carrier transfer from occupied impurity centers to empty ones at low impurity concentrations.

Let us denote by \mathbf{R} the vector from the ion of the center a to the ion of the center b . The wave function of the ground state of the center a is $u(\mathbf{r})$ and of the center b is $u(\mathbf{r} - \mathbf{R})$. Now we have to obtain the wave functions of the two-center Hamiltonian in nondeformed crystal lattice. Let us suppose that the electrostatic energy of the carrier, given by the ionized majority and minority impurity centers and the external field, is greater at the center b than at the center a . We suppose also that the difference of this energy between centers a and b is much greater than the resonance energy, but smaller than the electrostatic energy at the center a given by the ion of the center b . Now we can take a normalized linear combination of the functions $u(\mathbf{r})$ and $u(\mathbf{r} - \mathbf{R})$ and, minimizing the mean energy of the two-center Hamiltonian, we obtain the ground-state wave function in the form^{1,2}

$$u_a(\mathbf{r}) \cong u(\mathbf{r}) + C u(\mathbf{r} - \mathbf{R}), \quad (21)$$

where

$$1 \gg |C|^2 \gg \left| \int u^*(\mathbf{r} - \mathbf{R}) u(\mathbf{r}) d\mathbf{r} \right|^2. \quad (22)$$

The wave function of the first-excited state of the two-center Hamiltonian is given as orthogonal to (21) and normalized (we neglect the terms proportional to first or higher powers of the overlap and second or higher powers of C)⁶:

$$u_b(\mathbf{r}) \cong u(\mathbf{r} - \mathbf{R}) - C^* u(\mathbf{r}). \quad (23)$$

We treat the functions (21) and (23) as the wave functions of the carrier localized in the nondeformed crystal lattice on the centers a and b , respectively. The energy difference ΔE_{ba} between these states is approximately equal to the difference of the electrostatic energy at the two centers. Of course, the form of the functions (21) and (23) holds also in the case when the smaller electrostatic energy is at the center b ; then (23) is the ground-state wave function of the two-center Hamiltonian and (21) is the wave function of the first excited state.

The formulas (21)–(23) yield

$$\int u_b^*(\mathbf{r}) \exp(i\tau \Omega \cdot \mathbf{r}) u_a(\mathbf{r}) d\mathbf{r} \\ \cong \int u^*(\mathbf{r} - \mathbf{R}) \exp(i\tau \Omega \cdot \mathbf{r}) u(\mathbf{r}) d\mathbf{r} + C [\exp(i\tau \Omega \cdot \mathbf{R}) - 1] \int u^*(\mathbf{r}) \exp(i\tau \Omega \cdot \mathbf{r}) u(\mathbf{r}) d\mathbf{r}, \quad (24)$$

$$\int u_b^*(\mathbf{r}) \exp(i\tau \Omega \cdot \mathbf{r}) u_b(\mathbf{r}) d\mathbf{r} - \int u_a^*(\mathbf{r}) \exp(i\tau \Omega \cdot \mathbf{r}) u_a(\mathbf{r}) d\mathbf{r} \cong [\exp(i\tau \Omega \cdot \mathbf{R}) - 1] \int u^*(\mathbf{r}) \exp(i\tau \Omega \cdot \mathbf{r}) u(\mathbf{r}) d\mathbf{r}. \quad (25)$$

⁶ In reference 2, Eqs. (II-9, 11, 13, 14), C was used erroneously instead of C^* , but this does not affect the following part of that paper.

We neglect the first term on the right side of the formula (24), as was also done by Miller and Abrahams, Eq. (II-11).² We are justified in doing this by the right part of the inequality (22) and because the function $u^*(\mathbf{r}-\mathbf{R})u(\mathbf{r})$ is much more spread out in space than the function $u^*(\mathbf{r})u(\mathbf{r})$. Then

$$\int \left| \int u_b^*(\mathbf{r}) \exp(i\tau\mathbf{\Omega} \cdot \mathbf{r}) u_a(\mathbf{r}) d\mathbf{r} \right|^2 d\mathbf{\Omega} = 2|C|^2 \int [1 - \cos(\tau\mathbf{\Omega} \cdot \mathbf{R})] \left| \int u^*(\mathbf{r}) \exp(i\tau\mathbf{\Omega} \cdot \mathbf{r}) u(\mathbf{r}) d\mathbf{r} \right|^2 d\mathbf{\Omega}, \quad (26)$$

$$\begin{aligned} \int \left| \int u_b^*(\mathbf{r}) \exp(i\tau\mathbf{\Omega} \cdot \mathbf{r}) u_b(\mathbf{r}) d\mathbf{r} - \int u_a^*(\mathbf{r}) \exp(i\tau\mathbf{\Omega} \cdot \mathbf{r}) u_a(\mathbf{r}) d\mathbf{r} \right|^2 d\mathbf{\Omega} \\ = 2 \int [1 - \cos(\tau\mathbf{\Omega} \cdot \mathbf{R})] \left| \int u^*(\mathbf{r}) \exp(i\tau\mathbf{\Omega} \cdot \mathbf{r}) u(\mathbf{r}) d\mathbf{r} \right|^2 d\mathbf{\Omega}, \quad (27) \end{aligned}$$

$$\begin{aligned} \int \left\{ \left[\int u_b^*(\mathbf{r}) \exp(i\tau\mathbf{\Omega} \cdot \mathbf{r}) u_b(\mathbf{r}) d\mathbf{r} - \int u_a^*(\mathbf{r}) \exp(i\tau\mathbf{\Omega} \cdot \mathbf{r}) u_a(\mathbf{r}) d\mathbf{r} \right] \int u_b^*(\mathbf{r}) \exp(-i\tau\mathbf{\Omega} \cdot \mathbf{r}) u_a(\mathbf{r}) d\mathbf{r} \right\} d\mathbf{\Omega} \\ = 2C \int [1 - \cos(\tau\mathbf{\Omega} \cdot \mathbf{R})] \left| \int u^*(\mathbf{r}) \exp(i\tau\mathbf{\Omega} \cdot \mathbf{r}) u(\mathbf{r}) d\mathbf{r} \right|^2 d\mathbf{\Omega}. \quad (28) \end{aligned}$$

We can neglect the oscillating function $\cos(\tau\mathbf{\Omega} \cdot \mathbf{R})$ in these three formulas, as was done in reference 2, Eq. (II-14), with respect to formula (26). Let us denote

$$U(\tau) = (4\pi)^{-1} \int \left| \int u^*(\mathbf{r}) \exp(i\tau\mathbf{\Omega} \cdot \mathbf{r}) u(\mathbf{r}) d\mathbf{r} \right|^2 d\mathbf{\Omega}, \quad (29)$$

and introduce a new variable

$$x = \omega/\omega_0. \quad (30)$$

From the formulas (19), (20), (15), (26)–(30), and (14) we obtain finally

$$\begin{aligned} W_{ba}^{2I}/W_{ba}^1 = (E_1^2 \Delta E_{ba}^2 / 4\pi^2 \hbar^3 v^5 d) \sinh(|\Delta E_{ba}|/2kT) \left[U\left(\frac{|\Delta E_{ba}|}{\hbar v}\right) \right]^{-1} \\ \times \int_{-\infty}^{+\infty} U\left(\frac{|\Delta E_{ba}|}{\hbar v} |x|\right) U\left(\frac{|\Delta E_{ba}|}{\hbar v} |1-x|\right) \\ \times |x|^5 |1-x| [\sinh(|\Delta E_{ba}| |x|/2kT) \sinh(|\Delta E_{ba}| |1-x|/2kT)]^{-1} dx, \quad (31) \end{aligned}$$

$$\begin{aligned} W_{ba}^{2II}/W_{ba}^1 = (E_1^2 \Delta E_{ba}^2 / 4\pi^2 \hbar^3 v^5 d) \sinh(|\Delta E_{ba}|/2kT) \left[U\left(\frac{|\Delta E_{ba}|}{\hbar v}\right) \right]^{-1} \\ \times \int_{-\infty}^{+\infty} U\left(\frac{|\Delta E_{ba}|}{\hbar v} |x|\right) U\left(\frac{|\Delta E_{ba}|}{\hbar v} |1-x|\right) \\ \times |x|^3 |1-x|^3 [\sinh(|\Delta E_{ba}| |x|/2kT) \sinh(|\Delta E_{ba}| |1-x|/2kT)]^{-1} dx. \quad (32) \end{aligned}$$

The x values from the interval (0,1) correspond to the emission or absorption of two phonons; if x is outside this interval there is an absorption and re-emission of phonon. If $\Delta E_{ba} < 0$, then for $x > 1$ there is always emission of K phonons and for $x < 0$, absorption of K phonons. If $\Delta E_{ba} > 0$, then for $x < 0$ there is always emission of K phonons and for $x > 1$, absorption of K phonons.

In the integral in the formula (31) the function is symmetrical with respect to the point $x = \frac{1}{2}$ except for the factor x^4 . Because of the fact that $x^4 < (1-x)^4$ if $x < \frac{1}{2}$, greater contributions come from $x > 1$ than from $x < 0$. This means that a process consisting in absorption of an LR phonon and emission of a K phonon is more

probable than the absorption of a K phonon and emission of an LR phonon in the case $\Delta E_{ba} < 0$, and less probable when $\Delta E_{ba} > 0$.

In the formulas (31) and (32), $|C|^2$ does not appear. W_{ba}^1 is proportional to $|C|^2$, which depends very strongly on the structure and spread of the wave function of the carrier at the impurity center. Because of that, the computation of W_{ba}^1 is difficult.^{1,2} The dependence of $U(\tau)$ on the structure and spread of the wave function is much weaker.

Low Temperatures

We shall investigate the formulas (31) and (32) in two limiting cases: for low and "high" temperatures.

First we treat the case $T \rightarrow 0$. Then

$$\begin{aligned} \lim_{T \rightarrow 0} [\sinh(|\Delta E_{ba}|/2kT) / \sinh(|\Delta E_{ba}| |x|/2kT) \\ \times \sinh(|\Delta E_{ba}| |1-x|/2kT)] \\ = \begin{cases} 2 & \text{if } 0 < x < 1, \\ 0 & \text{if } x < 0 \text{ or } x > 1. \end{cases} \end{aligned} \quad (33)$$

In the vicinity of the points 0 and 1 one has

$$\begin{aligned} \sinh(|\Delta E_{ba}|/2kT) / \sinh(|\Delta E_{ba}| |x|/2kT) \\ \times \sinh(|\Delta E_{ba}| |1-x|/2kT) \\ \cong \begin{cases} (2kT/|\Delta E_{ba}| |x|) & \text{if } x \cong 0, \\ (2kT/|\Delta E_{ba}| |1-x|) & \text{if } x \cong 1. \end{cases} \end{aligned} \quad (34)$$

In the formulas (31) and (32), $|x|$ and $|1-x|$ appear to at least the first power, so in the limit $T \rightarrow 0$ we can neglect the contributions to integrals from the singularities in (34) and use (33). The integrations are now over the interval (0,1), i.e., at low temperatures only the absorption or emission of two phonons are important for two-phonon processes. If $|\Delta E_{ba}|$ is small enough to yield $U(|\Delta E_{ba}|/\hbar v) \cong 1$, then from (31)–(33) we have

$$(W_{ba}^{2I}/W_{ba}^{1I})_{T \rightarrow 0} = E_I^2 \Delta E_{ba}^2 / 84\pi^2 \hbar^3 v^5 d, \quad (35)$$

$$(W_{ba}^{2II}/W_{ba}^{1I})_{T \rightarrow 0} = E_I^2 \Delta E_{ba}^2 / 280\pi^2 \hbar^3 v^5 d. \quad (36)$$

Thus the transition rate is higher for the process with one K phonon and one LR phonon. The total two-phonon transition rate at low temperatures is given by the formula

$$\begin{aligned} [(W_{ba}^{2I} + W_{ba}^{2II})/W_{ba}^{1I}]_{T \rightarrow 0} \\ = 13E_I^2 \Delta E_{ba}^2 / 840\pi^2 \hbar^3 v^5 d. \end{aligned} \quad (37)$$

In the case of a simple spherical and parabolic band and shallow, hydrogen-like impurity states, we have from (29)

$$U(\tau) = (1 + e^4 \tau^2 / 16\epsilon^2 E_I^2)^{-4}, \quad (38)$$

ϵ being the static dielectric constant and E_I , the ionization energy of the impurity center. If

$$e^2 |\Delta E_{ba}| / \hbar \epsilon v E_I < 1, \quad (39)$$

then $U(|\Delta E_{ba}|/\hbar v) \cong 1$ and the formulas (35)–(37) hold.

We want now to discuss the temperature T_c below which we can use (35)–(37). The relatively greatest contribution from the singularities in (34) is the contribution from the singularity at the point $x=1$ in the expression (31). This singularity is given by (34) approximately in the interval $(1-2kT/|\Delta E_{ba}|, 1+2kT/|\Delta E_{ba}|)$ and the relative contribution in (31) is about

$$\begin{aligned} \left[(2kT/|\Delta E_{ba}|) \int_{1-2kT/|\Delta E_{ba}|}^{1+2kT/|\Delta E_{ba}|} x^5 dx \right] / 2 \\ \times \int_0^1 x^5 (1-x) dx \cong 168 (kT/|\Delta E_{ba}|)^2. \end{aligned} \quad (40)$$

This is small, and so the formulas (35)–(37) are valid, if the temperature is below

$$T_0 = |\Delta E_{ba}| / 30k. \quad (41)$$

“High” Temperatures

Now we shall treat the case “ $T \rightarrow \infty$ ”. Then

$$\begin{aligned} \sinh(|\Delta E_{ba}|/2kT) / \sinh(|\Delta E_{ba}| |x|/2kT) \\ \times \sinh(|\Delta E_{ba}| |1-x|/2kT) \\ \cong 2kT / |\Delta E_{ba}| |x| |1-x|. \end{aligned} \quad (42)$$

As was pointed out earlier, the function $U(\tau)$ depends rather weakly on the structure and spatial extension of the wave function of carrier at the impurity center; hence we can use (38) as a reasonable approximation in many real cases. We assume again the inequality (39). The formulas (31), (32), (38), and (42) yield then, after integrations,

$$(W_{ba}^{2I}/W_{ba}^{1I})_{T \rightarrow \infty} = (W_{ba}^{2II}/W_{ba}^{1I})_{T \rightarrow \infty}, \quad (43)$$

$$\begin{aligned} [(W_{ba}^{2I} + W_{ba}^{2II})/W_{ba}^{1I}]_{T \rightarrow \infty} \\ = 9\hbar^2 k \epsilon^5 E_I^2 E_I^5 T / 2\pi e^{10} \Delta E_{ba}^4 d. \end{aligned} \quad (44)$$

The contributions to $(W_{ba}^{2I}/W_{ba}^{1I})_{T \rightarrow \infty}$ and $(W_{ba}^{2II}/W_{ba}^{1I})_{T \rightarrow \infty}$ from the processes consisting in emission or absorption of two phonons, i.e., from the integrations over the interval (0,1), are smaller than 1.4% and 0.24%, respectively. So at “high” temperatures only the two-phonon processes consisting in absorption and re-emission of phonons are important.

We want now to estimate the temperature T_∞ above which the formulas (43) and (44) hold. We can use the approximation (42) if it is valid at the point in which that maximum of the functions in (31) and (32) which is farthest from $x=\frac{1}{2}$ occurs. It is the point $x' < 0$ at which the function in (31) has the maximum. We can use (42) and so (43) and (44) if $|\Delta E_{ba}| |x'|/2kT < 1/\sqrt{3}$. Computing x' , we arrive at

$$T_\infty = 2\hbar \epsilon v E_I / e^2 k. \quad (45)$$

From the formulas (41) and (45) we see that the assumption (39) can be written as

$$T_\infty / T_0 > 60. \quad (46)$$

For deep impurity states $U(\tau)$ is greater than for the shallow ones, because the wave function in a deep state is less extended in space. Consequently, the two-phonon processes would be more probable in such states. From this point of view the expression (44), which rises with rising E_I , can be at least qualitatively valid also for deep states, but the GL formalism used here is not suitable in such cases.⁴

IV. DISCUSSION OF RESULTS

In Table I we summarize the experimental data and the values obtained from the formulas (41), (45), (37), and (44) for n - and p -type silicon and germanium. For

TABLE I. Ratio of the two-phonon to one-phonon transition rates for carrier transfer in *n*- and *p*-type Si and Ge.

Mate- rial	d (g/cm ³)	v (10 ⁵ cm/sec)	ϵ	$ E_1 $ (ev)	E_I (10 ⁻² ev)	ϵ_3 (10 ⁻³ ev)	T_I (°K)	T_0 (°K)	T_∞ (°K)	T_∞/T_0	$(W_{ba}^{2I} + W_{ba}^{2II})/W_{ba}^{1I}$ $T < T_0$	$T > T_\infty$
<i>n</i> -Si } <i>p</i> -Si }	2.3	8.3	11.7 ^a	{ 15 ^c 9 ^d	{ 3.9 ^{g,h} 4.5 ^{g,i}	{ 4.8 ^{m,n} 5.0 ^{m,o}	{ 15 ^{m,n} 20 ^{m,o}	{ 2 2	{ 40 50	{ 20 25	{ $\sim 10^{-2}$ $\sim 10^{-2}$	{ $\sim 10^{-3}T$ $\sim 10^{-3}T$
<i>n</i> -Ge } <i>p</i> -Ge }	5.4	4.9	16.0 ^b	{ 11.4 ^e 8 ^f	{ 0.98 ^{h,j} 1.08 ^{k,l}	{ 0.99 ^{p,q} 0.323 ^{r,s}	{ 3 ^{p,q} 4 ^{r,s}	{ 0.4 0.13	{ 9 9	{ 20 70	{ $\sim 10^{-3}$ 4×10^{-4}	{ $\sim 10^{-3}T$ 0.23 T

^a W. Dunlap and R. L. Watters, Phys. Rev. **92**, 1396 (1953).^b F. A. d'Alroy and H. Y. Fan, Phys. Rev. **103**, 1671 (1956).^c See reference 4.^d An approximate value computed from the mobility of holes at 150°K, the mobility being measured by M. B. Prince [Phys. Rev. **93**, 1204 (1954)].^e See reference 2.^f H. Brooks, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 85.^g J. A. Burton, Physica **20**, 845 (1954).^h Sb donors.ⁱ B acceptors.^j H. Y. Fan and P. Fisher, J. Phys. Chem. Solids **8**, 270 (1959).^k P. Fisher and H. Y. Fan, Phys. Rev. Letters **2**, 456 (1959).^l Ga acceptors.^m R. K. Ray and H. Y. Fan, Phys. Rev. **121**, 768 (1961).ⁿ Sb concentration 5.9×10^{16} cm⁻³, compensation of few percent.^o B concentration 8.94×10^{16} cm⁻³, compensation of few percent.^p H. Fritzsche, J. Phys. Chem. Solids **6**, 69 (1958).^q Sb concentration 1.6×10^{18} cm⁻³, compensation of few percent.^r H. Fritzsche and M. Cuevas, Phys. Rev. **119**, 1238 (1960).^s Ga concentration 7.47×10^{14} cm⁻³, compensation 40%.

$|\Delta E_{ba}|$ we take the observed activation energy of the conductivity, ϵ_3 . The temperature T_I about which the impurity conduction sets in, i.e., becomes greater than the band conductivity, is also given. In the cases in which the assumption (46) is not fulfilled, we give only the order of magnitude of the ratio of transition rates.

A fair agreement of the theoretical values of conductivity, obtained from the one-phonon transition rate only, with the experimental data was reached by Miller and Abrahams² for *n*-type germanium. From Table I we see that in this material, as well as in *n*- and *p*-type silicon, the two-phonon transition rate is very small. On the other hand, in *p*-type Ge the two-phonon transition rate at "high" temperatures is large enough to be of importance in calculation of the conductivity. As can be seen from formula (44) and the experimental data in

Table I, this is rather due to the effect of the low impurity concentration in the *p*-Ge sample used (i.e., small value of ϵ_3) than to the effect of the differences in the constants of the materials. For small $|\Delta E_{ba}|$ we shall have a fulfillment of the assumption (46), a low value of (37) and a high (44).

We conclude that the two-phonon transitions play a role in the impurity conduction in semiconductors with low mobility of carriers (high $|E_1|$, E_I , T_I) and low impurity concentration.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Professor L. Infeld for his kind interest in this work, to Docent M. Suffczyński for valuable suggestions and remarks, and to Dr. J. Kołodziejczak for discussions.