

## Theory of Absorption of Electromagnetic Radiation by Hopping in *n*-Type Silicon and Germanium. II

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In a previous paper the absorption of electromagnetic radiation at 0°K in the wavelength region from 100 to 800  $\mu$  and from 500  $\mu$  to 2.5 cm in *n*-type silicon and germanium, respectively, has been investigated theoretically. The model used was that of photon-induced hopping of an electron between the ground states of donors without phonon participation. The results obtained are compared in the present paper with the theory of Tanaka *et al.* It is shown that at the short wavelengths the main contribution to the absorption is given by the "polar pairs" neglected in the treatment of Tanaka *et al.* In Sec. 3 of this paper the contribution to the absorption given by the photon-induced hopping accompanied by the emission of a phonon is investigated. This contribution is rather small in *n*-Ge but important in *n*-Si at short wavelengths. The range of validity of our results is also discussed.

### 1. INTRODUCTION

THE phonon-induced hopping of a carrier from a neutral majority impurity center to an ionized one in compensated semiconductors has been studied in the impurity conduction range, both experimentally and theoretically, in ac electric fields up to frequencies of about  $10^{10}$  cps.<sup>1-5</sup> The energy differences for these transitions are given by the Coulomb potential of the nearest ionized minority center and the external electric field.

To explain a part of their experimental results concerning microwave absorption in *p*-type Si, Tanaka and Fan<sup>4</sup> proposed another hopping mechanism, namely photon-induced hopping without phonon participation ("direct absorption process"). This mechanism of absorption was studied experimentally and theoretically in the microwave range by Tanaka *et al.*<sup>5</sup> It was also used in the paper of the present authors<sup>6</sup> (denoted hereafter by I) to compute the absorption at shorter wavelengths in *n*-type Si and Ge at 0°K. We were interested in the wavelength region from 100 to 800  $\mu$  and from 500  $\mu$  to 2.5 cm in Si and Ge, respectively. In these wavelength regions at 0°K the photon-induced hopping is the only possible mechanism of absorption; other absorption mechanisms, such as lattice vibrations, excitations of neutral impurity centers, and free carriers, are, in principle, absent here. Also the absorption by phonon-induced hopping vanishes at 0°K.<sup>2</sup>

In the first part of the present paper we adapt the theoretical results of Tanaka *et al.* to our case of *n*-type Si and Ge at 0°K and compare the formula obtained with the results of paper I. This comparison gives an estimate of the range of validity of the approximations used by Tanaka *et al.* which are not used in I. In particular it is shown that at short wavelengths the main

contribution to the absorption is given by the "polar pairs" of donors. The contribution from these pairs was neglected by Tanaka *et al.*; therefore we obtained a higher absorption coefficient in I.

In Sec. 3 we calculate the contribution to the absorption coefficient given by photon-induced hopping accompanied by the emission of a longitudinal acoustic phonon. These transitions must not be confused with the simultaneous absorption of a photon and emission of a phonon which takes place in the phonon-induced hopping because in our case the energy of the photon is higher than that of the phonon. The possibility of photon-induced hopping accompanied by the emission of phonons occurs in our case because of the dependence of the equilibrium position of the lattice atoms on the state of the carrier. It is shown that the contribution given by photon-induced hopping accompanied by the emission of one phonon becomes important at shorter wavelengths and has a quantitative, but not qualitative, effect on the wavelength dependence of the absorption coefficient. This effect is rather unimportant in Ge but important in Si. In both materials the contribution given by photon-induced hopping accompanied by the emission of more than one phonon is unimportant.

Unfortunately our results cannot be compared with experiment at the present time because, as far as we know, no appropriate experimental data are available.

### 2. DIRECT ABSORPTION

In their paper Tanaka *et al.*<sup>5</sup> investigate theoretically the absorption of electromagnetic radiation by direct absorption processes. They compare the formula obtained for the real part of the conductivity with their experimental results for microwave absorption in Si at the frequency 9 Gc/sec. This comparison seems to be unjustified because the relaxation energy  $E_{LR}$  of the lattice deformed by interaction with a carrier localized on an isolated majority center is larger in *n*- and *p*-type Si than the energy difference  $\hbar\omega$  for transition at the frequency used. In such cases the carrier-phonon inter-

<sup>1</sup> M. Pollak and T. H. Geballe, Phys. Rev. **122**, 1742 (1961).

<sup>2</sup> M. Pollak, Phys. Rev. **133**, A564 (1964).

<sup>3</sup> S. Golin, Phys. Rev. **132**, 178 (1963).

<sup>4</sup> S. Tanaka and H. Y. Fan, Phys. Rev. **132**, 1516 (1963).

<sup>5</sup> S. Tanaka, M. Kobayashi, E. Hanamura, and K. Uchinokura, Phys. Rev. **134**, A256 (1964).

<sup>6</sup> J. Blinowski and J. Mycielski, Phys. Rev. **136**, A266 (1964).

action cannot be treated as a weak one,<sup>7</sup> as was done by Tanaka *et al.* and also in our paper I and in the present paper.

On the other hand the upper limit for the concentration  $N$  of the majority impurities given by Tanaka *et al.* seems to be too low. They consider that the localized-pair model is applicable if the average distance  $R^* = (4\pi N/3)^{-1/3}$  between majority impurities is much larger than the separations in the pairs giving the main contribution to the absorption. This assumption means that in the immediate neighborhood of a pair there is no other majority center. It seems, however, that the localized-pair model is valid in the theory of photon-induced hopping even in the case of the existence of such a center if the Coulomb potential of the ionized minority impurity at the position of this center is different from the potentials at the positions of the two impurities of the pair. Therefore the restriction (20) used by us (for other reasons) in paper I, which means that the separations in the pairs giving the main contribution to the absorption must be smaller than  $2.2R^*$ , should probably justify the use of the localized-pair model.

In their paper Tanaka *et al.* obtained the formula for the real part of the conductivity due to the direct absorption processes in the case of  $kT \gg \hbar\omega$  and a single spherical parabolic energy band. To compare their results with ours we must, first of all, adapt their formula to the case  $kT \ll \hbar\omega$ . This introduces the factor  $2kT/\hbar\omega$ . In our range of concentration  $N$ , compensation  $K$ , and wavelength  $\lambda$  we have  $\lambda\alpha/\epsilon^{1/2} < 4$  and thus we can obtain from the real part of the conductivity the absorption coefficient  $\alpha$  in the form

$$\frac{\alpha}{K} = \frac{\pi^2 \Gamma(5/3) \epsilon^{1/2} \omega}{2c} N \frac{a R^3(\omega)}{R^*}. \quad (1)$$

$K$  is the compensation, i.e., the ratio of minority- to majority-center concentration.  $\epsilon$  and  $c$  denote the static dielectric constant and the velocity of light, respectively.  $a$  is the radius of the orbit—for the time being, in the hydrogen-like ground state—of the carrier at the majority impurity center.  $R(\omega)$  is the larger of the two solutions of the equation

$$2|W_R| = \hbar\omega,$$

where  $W_R$ , the resonance energy, is given in the case of hydrogen-like centers by the formula

$$|W_R| = (2e^2/3\epsilon a^2) R \exp(-R/a).$$

$R$  denotes the distance between the two centers of the pair.

In Fig. 1 we give the dependence of the absorption coefficient per unit compensation on the wavelength of radiation for  $n$ -type Ge at various concentrations of donors computed in paper I (solid curves). Curve A

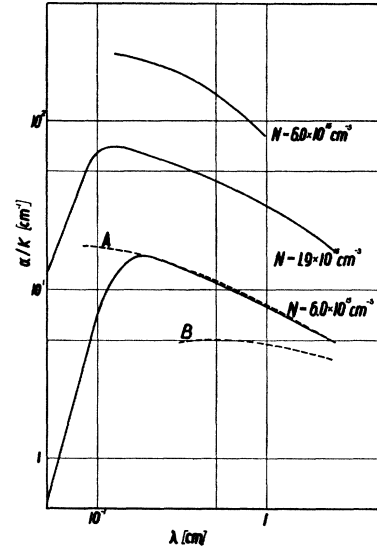


FIG. 1. The dependence of the absorption coefficient given by direct absorption processes, per unit compensation, on the wavelength of radiation for  $n$ -Ge at various concentrations of donors. The solid curves are taken from I; the curves A and B are computed for  $T=0^\circ\text{K}$  on the basis of Tanaka *et al.*'s considerations (see Ref. 5) for the spherical parabolic and many-valley band structures, respectively. The curve A is fitted by the choice of the donor orbit radius.

was computed for  $N=6.0 \times 10^{15} \text{ cm}^{-3}$  from Eq. (1) ( $\epsilon=16.0$ ) with  $a=58 \text{ \AA}$  chosen to obtain the best fit to the corresponding solid curve. The agreement between the two curves seems to be excellent, except for the short wavelengths, but this is accidental because in our calculations for  $n$ -type Ge we used another form of the resonance energy  $W_R$ .

To adapt the results of Tanaka *et al.* to the case of  $n$ -type Ge (or  $n$ -type Si) we must take  $W_R$  in the form given by Miller and Abrahams<sup>8</sup> and used by us in I:

$$\langle W_R^2 \rangle_{\text{av}} = (2\pi^{1/2} e^4 / 9 \epsilon^2 a^2 n \eta^{1/2}) (R/a)^{3/2} \exp(-2R/a). \quad (2)$$

$\langle \rangle_{\text{av}}$  denotes the average over all directions of the vector  $\mathbf{R}$ .  $n$  is the number of conduction-band minima (6 and 4 for Si and Ge, respectively) and  $\eta$  denotes

$$\eta = (a/b)^2 - 1.$$

Here (and in the following)  $a$  is the transverse orbit radius of the donor ground state;  $b$  is the longitudinal radius.

Equation (1) holds in  $n$ -type Ge (or  $n$ -type Si) band structures with the sole modification that  $a$  is the transverse orbit radius and  $R(\omega)$  is the larger of the two solutions of the equation

$$2(\langle W_R^2 \rangle_{\text{av}})^{1/2} = \hbar\omega, \quad (3)$$

where  $\langle W_R^2 \rangle_{\text{av}}$  is given by Eq. (2).

Curve B in Fig. 1 gives the dependence of the ratio  $\alpha/K$  on the wavelength of radiation computed from the

<sup>7</sup> J. Mycielski, Phys. Rev. **125**, 1975 (1962).

<sup>8</sup> A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).

modified Eq. (1) for  $n$ -type Ge at  $N=6.0 \times 10^{15} \text{ cm}^{-3}$  ( $a=70.8 \text{ \AA}$ ,  $\eta=18.8$ ). The agreement with the corresponding solid curve is rather poor, especially at the shorter wavelengths—the absorption computed by us is much higher. The dependence of  $\alpha$  on  $N$  given by Eq. (1) is that  $\alpha$  is proportional to  $N^{4/3}$  and the position of the maximum on the  $\alpha$ -versus- $\lambda$  curve given by this formula does not depend on  $N$ . On the contrary, at  $\lambda=3 \times 10^{-1} \text{ cm}$  the dependence of  $\alpha$  on  $N$  in our results is rather that  $\alpha$  is proportional to about  $N^{8/7}$ ; the position of the maximum shifts to shorter wavelengths with increasing  $N$ .

In their theory, Tanaka *et al.* take into account only the homopolar impurity pairs, i.e., the pairs for which the difference  $\Delta$  of the Coulomb potential of the ionized minority impurity at the positions of the two centers of the pair is smaller than  $2|W_R|$ . It must be observed also that the calculations are done (both in Tanaka *et al.*'s paper and in our paper I) under the assumption that the overlap integral is small enough. This restriction is not fulfilled for the homopolar pair in  $n$ -type Ge if  $2|W_R|$  equals the photon energy with  $\lambda$  smaller than about  $3 \times 10^{-1} \text{ cm}$ .

The discrepancy between Eq. (1) and the results of our theory, in which all the pairs were taken into account, shows that at the short wavelengths the main contribution to the direct absorption is given by the pairs for which  $\Delta > 2|W_R|$  (the so-called polar pairs). At a given energy difference between the two states of the carrier, the separation  $R$  in the polar pair is larger than in the homopolar one. Because of this, at least one-half of the total absorption coefficient is given throughout the whole range of  $\lambda$ 's in our calculations (see paper I) by the pairs with small overlap integrals.

In the range of the shortest wavelengths, in which we have a sharp drop of the absorption coefficient (at  $N=6.0 \times 10^{15} \text{ cm}^{-3}$  in  $n$ -type Ge  $\alpha$  is proportional to about  $\lambda^{3.7}$ ), Eq. (1) cannot be used for still another reason, namely, that in the derivation of this formula there is involved an essential assumption that  $R(\omega) \gg \epsilon R^* \hbar \omega / e^2$ , and this is not fulfilled at our shortest wavelengths. At these wavelengths the absorption drops mainly because the number of polar pairs with small separations  $R$  and high potential difference  $\Delta$  is low.

Equation (1) also cannot be used to explain the drop of the absorption coefficient at long wavelengths on the two upper curves in Fig. 1 because the assumption  $R(\omega) \ll 2R^*$  used by Tanaka *et al.* is not fulfilled there and the number of appropriate homopolar pairs is overestimated.

In their paper<sup>4</sup> Tanaka and Fan pay attention to the fact that the pairs of majority impurities with exceptionally small  $R$  and large  $|W_R|$  act as traps (so-called molecule-ion traps). Even at 0°K these traps will be ionized and a part of the majority centers nearest to the minority impurities will be neutral. This

effect was not taken into account in our calculations nor in the derivation of Eq. (1). The estimate of the concentration of molecule-ion traps given by Tanaka and Fan [we have introduced into their Eq. (27) the factor  $\frac{1}{2}$  which was there erroneously omitted] shows that at our highest donor concentrations ( $2.0 \times 10^{18} \text{ cm}^{-3}$  and  $6.0 \times 10^{16} \text{ cm}^{-3}$  in Si and Ge, respectively) the trapping effect can be important even at the highest compensations ( $K=0.2$ ). At lower donor concentrations the trapping effect can limit the validity of our results to not too small compensations.

### 3. PHOTON-INDUCED HOPPING WITH PHONON EMISSION

The equilibrium position of the lattice atoms depends on the state of the carrier and this gives the possibility of photon-induced hopping accompanied by the emission of a phonon, the phonon energy being smaller than the energy of the photon. We shall now investigate the contribution to the absorption coefficient given by such processes taking into account only the longitudinal acoustic phonons. A single deformation-potential constant and a Debye spectrum of phonons will be assumed. The transition rate at 0°K from an arbitrary electron bound state  $b$  to the electron bound state  $a$  with the simultaneous absorption of a photon and emission of a phonon is, according to the formalism developed for weak electron-phonon interaction by Lax, Burstein, and Gummel<sup>9,10</sup>

$$W_{ab}^1 = (4\pi^2 e^2 / c \hbar^2 \epsilon^{1/2}) \exp(-\beta) |\langle a | \mathbf{r} | b \rangle \cdot \mathbf{n}|^2 \times \int_0^\infty f(\omega + \omega_0) I(\omega) d\omega. \quad (4)$$

We denote by  $\mathbf{n}$  the unit vector parallel to the electric vector of radiation and by  $I(\omega)$  the intensity of the radiation per unit interval of the angular frequency  $\omega$ .  $-\hbar\omega_0$  represents the electronic energy difference between the states  $a$  and  $b$  (in a nondeformed crystal lattice) plus the difference of the lattice relaxation energies in the two electronic states. At 0°K

$$\beta = \int_0^\infty f(\omega') d\omega',$$

and  $f(\omega')$  is the distribution function of the lattice relaxation phonons.

Let us now consider the states  $a$  and  $b$  as the lowest two states of the electron at the ionized donor pair (for the wave functions of these states see I). As was shown in I, if the overlap integral  $S$  for this pair is small,

$$S < 0.03, \quad (5)$$

<sup>9</sup> M. Lax and E. Burstein, Phys. Rev. **100**, 592 (1955).

<sup>10</sup> H. Gummel and M. Lax, Ann. Phys. (N. Y.) **2**, 28 (1957).

we have

$$\beta \cong (\Delta^2 + 4S^2W^2)(\Delta^2 + 4W^2)^{-1}\beta_0, \quad (6)$$

$$\beta_0 = \frac{E_1^2}{2\pi^2\hbar v^3 d} \int_0^\infty U(\tau) \tau d\tau. \quad (7)$$

$\Delta$  is as before the potential difference at the pair and  $W$  denotes

$$W = W_R - \frac{1}{2}S\Delta + Z. \quad (8)$$

$Z$  originates from the inhomogeneity of the field of the ionized acceptor in the region of the two donors of the pair.  $E_1$  is the deformation-potential constant and  $v$  and  $d$  denote the sound velocity and the density of the crystal, respectively.  $U(\tau)$  is by definition

$$U(\tau) = (4\pi)^{-1} \int |\langle u(\mathbf{r}) | \exp(i\tau \mathbf{\Omega} \cdot \mathbf{r}) | u(\mathbf{r}) \rangle|^2 d\Omega.$$

$u(\mathbf{r})$  is the wave function of the electron in the ground singlet state of an isolated donor. The integration is over all directions of the unit vector  $\mathbf{\Omega}$ .

As was shown in I, if (5) holds and

$$\omega' R/v > 3, \quad (9)$$

$\mathbf{R}$  being as before the vector connecting the two donors of the pair, then at 0°K

$$f(\omega') \cong (E_1^2 \omega' / 2\pi^2 \hbar v^5 d) (\Delta^2 + 4S^2W^2) (\Delta^2 + 4W^2)^{-1} \times U(\omega'/v) \theta(\omega'). \quad (10)$$

$\theta(\omega')$  is by definition

$$\theta(\omega') = \begin{cases} 1 & \text{if } \omega' > 0, \\ 0 & \text{if } \omega' < 0. \end{cases}$$

We shall denote by  $E_{LR}$  the relaxation energy of the lattice deformed by interaction with an electron localized on an isolated donor. This energy is<sup>7</sup>

$$E_{LR} = \frac{E_1^2}{4\pi^2 v^2 d} \int_0^\infty U(\tau) \tau^2 d\tau.$$

We can use the formalism of Lax, Burstein, and Gummel (i.e., treat the electron-phonon interaction as a weak one) if the energy of lattice relaxation  $E_{LR}$  is small compared with the positive energy difference  $\Delta E$  between the two states of the electron at the pair (in a nondeformed crystal lattice). Accordingly, we shall assume that

$$\Delta E > 2E_{LR}. \quad (11)$$

As was shown in I, if (11) and (5) hold, we have

$$\omega_0 \cong -\Delta E/\hbar, \quad \Delta E \cong (\Delta^2 + 4W^2)^{1/2}, \quad (12)$$

and the assumption (11) can be rewritten in the form

$$(\Delta^2 + 4W^2)^{1/2} > 2E_{LR}. \quad (13)$$

It was also shown in I that under the assumption (5)

$$|\langle a | \mathbf{r} | b \rangle \cdot \mathbf{n}|^2 = (\mathbf{R} \cdot \mathbf{n})^2 (W + \frac{1}{2}S\Delta)^2 (\Delta^2 + 4W^2)^{-1}. \quad (14)$$

We use  $I(\omega)$  in the form of a  $\delta$  function. Because of Eq. (12), the assumption (9) must then hold in the form

$$[\hbar\omega - (\Delta^2 + 4W^2)^{1/2}]R/\hbar v > 3, \quad (15)$$

where  $\omega$  is the angular frequency of the monochromatic electromagnetic radiation.

Summarizing, under the assumptions (5), (13), and (15) we have, from Eqs. (4), (6), (10), (12), and (14),

$$\begin{aligned} W_{ab}^1 &= (2e^2 E_1^2 / c \hbar^4 \epsilon^{1/2} v^5 d) \\ &\times \exp[-\beta_0 (\Delta^2 + 4S^2W^2) (\Delta^2 + 4W^2)^{-1}] \\ &\times (W + \frac{1}{2}S\Delta)^2 (\Delta^2 + 4S^2W^2) (\Delta^2 + 4W^2)^{-2} \\ &\times [\hbar\omega - (\Delta^2 + 4W^2)^{1/2}] U\{[\hbar\omega - (\Delta^2 + 4W^2)^{1/2}]/\hbar v\} \\ &\times \theta[\hbar\omega - (\Delta^2 + 4W^2)^{1/2}] (\mathbf{R} \cdot \mathbf{n})^2 I, \end{aligned} \quad (16)$$

where  $I$  is the intensity of the radiation. One can see that in the case  $\Delta < 2|W_R|$  (i.e., in the case of the homopolar pair) the approximation  $\Delta=0$  cannot be used here.

We shall investigate the case of small compensation,

$$K < 0.2. \quad (17)$$

We neglect the dipole potentials given by the ionized-acceptor-ionized-donor pairs present in the crystal and we assume that in the region of the donor pair the field of the nearest acceptor is homogeneous enough to neglect  $Z$  in Eq. (8). These two assumptions will be discussed later. We have

$$\Delta \cong (e^2/\epsilon)(1/R_a - 1/R_b),$$

where  $\mathbf{R}_a$  and  $\mathbf{R}_b$  are the positions of the two donors of the pair relative to that of the acceptor ( $\mathbf{R} = \mathbf{R}_b - \mathbf{R}_a$  and  $R_a < R_b$ ). Following I we obtain the absorption coefficient given by photon-induced hopping with photon emission

$$\alpha^1 = \hbar\omega K N^3 \int dv_a \exp \frac{-4\pi N R_a^3}{3} \int_{R_b > R_a} dv_b W_{ab}^1. \quad (18)$$

$W_{ab}^1$  is given by Eq. (16) where  $I$  is replaced by 1. If  $\beta_0$  is not much larger than unity, we can, using (5), replace  $\Delta^2 + 4S^2W^2$  in the exponent in Eq. (16) by  $\Delta^2$ .

Now we introduce, as in I, the following approximation: in Eq. (18) we replace  $W_R^2$  and  $S^2$  by  $\langle W_R^2 \rangle_{av}$  and  $\langle S^2 \rangle_{av}$ . According to Miller and Abrahams,<sup>8</sup> for  $n$ -type Si and Ge,  $\langle W_R^2 \rangle_{av}$  is given by Eq. (2) and

$$\langle S^2 \rangle_{av} = (\pi^{1/2}/18n\eta^{1/2})(R/a)^{7/2} \exp(-2R/a). \quad (19)$$

These equations are correct, if (5) holds in the form

$$\langle S^2 \rangle_{av}^{1/2} < 0.03. \quad (20)$$

Because of (20) the assumptions (13) and (15) now have the form

$$(\Delta^2 + 4\langle W_R^2 \rangle_{av})^{1/2} > 2E_{LR}, \quad (21)$$

$$[\hbar\omega - (\Delta^2 + 4\langle W_R^2 \rangle_{av})^{1/2}]R/\hbar v > 3. \quad (22)$$

Using (20), changing the variables in Eq. (18) and integrating over three of them we obtain finally ( $R$ ,  $R_a$ , and  $\Delta$  have the same meaning as before)

$$\alpha^1 = \frac{16\pi^2 \epsilon^{1/2} E_1^2 K N^3 \omega}{3ch^3 v^5 d} \int_{R(\omega)}^{\infty} dR R^3 \langle W_R^2 \rangle_{av} \int_0^{(\hbar^2 \omega^2 - 4\langle W_R^2 \rangle_{av})^{1/2}} d\Delta (\Delta^2 + 4\langle S^2 \rangle_{av} \langle W_R^2 \rangle_{av}) (\Delta^2 + 4\langle W_R^2 \rangle_{av})^{-2} \\ \times [\hbar\omega - (\Delta^2 + 4\langle W_R^2 \rangle_{av})^{1/2}] \exp[-\beta_0 \Delta^2 (\Delta^2 + 4\langle W_R^2 \rangle_{av})^{-1}] U\{[\hbar\omega - (\Delta^2 + 4\langle W_R^2 \rangle_{av})^{1/2}]/\hbar v\} l(R, \Delta), \quad (23)$$

with

$$l(R, \Delta) = \int_{R_{a1}}^{R_{a2}} R_a^4 \left(1 - \frac{\epsilon R_a \Delta}{\epsilon^2}\right)^{-3} \exp\left[-\frac{4\pi N R_a^3}{3}\right] dR_a, \quad (24)$$

where

$$R_{a1} = \epsilon^2 / \epsilon \Delta + \frac{1}{2} R - (\epsilon^4 / \epsilon^2 \Delta^2 + \frac{1}{4} R^2)^{1/2}, \\ R_{a2} = (\epsilon^2 R / \epsilon \Delta + \frac{1}{4} R^2)^{1/2} - \frac{1}{2} R.$$

$R(\omega)$  is as before the larger of the two solutions of Eq. (3). If these solutions do not exist or if the larger of them is smaller than  $a$ , then  $R(\omega) = a$ .

The assumptions (20)–(22) were essential for the derivation of Eq. (23). Therefore, we can use this formula only if the contribution from the range of  $R$  and  $\Delta$  in which (20)–(22) are not fulfilled does not play the main role in the absorption.  $\hbar\omega$  must be much smaller than the ionization energy of a donor and the

intensity of radiation must be small enough to avoid the “saturation effect,” i.e., a serious change of electron-state occupation.

In Eq. (23) we neglected, for the same reasons as in Eq. (18) in paper I, the contribution from the pairs for which the distance between donors is smaller than  $a$ .

Because  $\langle W_R^2 \rangle_{av}$  decreases rapidly with increasing  $R$ , the main contribution to the absorption coefficient of Eq. (23) is given by  $R$ 's within a few  $a$  from  $R(\omega)$ , i.e., by the pairs for which  $|W_R|$  is of the order of  $\hbar\omega$ . From this and from the first term in the second integral in Eq. (23) one can observe that the main contribution is given by the pairs for which  $\Delta$  is of the order of  $2(\langle W_R^2 \rangle_{av})^{1/2}$ . Because of a sharp drop<sup>11</sup> of the function  $\omega' U(\omega'/v)$  at  $\omega' > \omega_{\max}'$  [ $\omega_{\max}'$  being the position of the maximum of  $\omega' U(\omega'/v)$ ], the contribution from the pairs at which  $\Delta E \ll \hbar\omega - \hbar\omega_{\max}'$  is small (also because at such pairs  $|W_R| \ll \hbar\omega$ ).

We assumed before that the field of the acceptor is homogeneous so that we can neglect  $Z$  in Eq. (8). This, as well as the whole procedure of obtaining the two-center electronic states, cannot be justified in the case of jumps “through” the acceptor ( $|Z|$  is then of the order of  $|W_R|$ ). The same reasoning as in paper I leads to the conclusion that the contribution from the jumps “through” the acceptor can be neglected if

$$N < 8/\pi R^3(\omega). \quad (25)$$

As in paper I we can show that under our assumptions the main contribution to the absorption is given by  $R_a \lesssim (\pi N)^{-1/3}$  and by the electron jumps within the volume including one acceptor.

#### 4. NUMERICAL RESULTS AND DISCUSSION

In Table I we present the values of the material constants used by us. The values of  $\beta_0$  and  $E_{LR}$  were taken from the paper by Myszkowski and Gómułka<sup>11</sup> and  $\hbar\omega_{\max}'$  was computed from the formulas for the function  $U(\tau)$  in  $n$ -type Si and Ge given in the same paper.

The numerical computations of the ratio  $\alpha^1/K$  given by Eq. (23) were performed for the concentrations of donors  $2.0 \times 10^{17}$  and  $6.2 \times 10^{17} \text{ cm}^{-3}$  in Si and  $6.0 \times 10^{15}$  and  $1.9 \times 10^{16} \text{ cm}^{-3}$  in Ge. The results are given

<sup>11</sup> A. Myszkowski and S. Gómułka, Phys. Rev. 134, A1102 (1964).

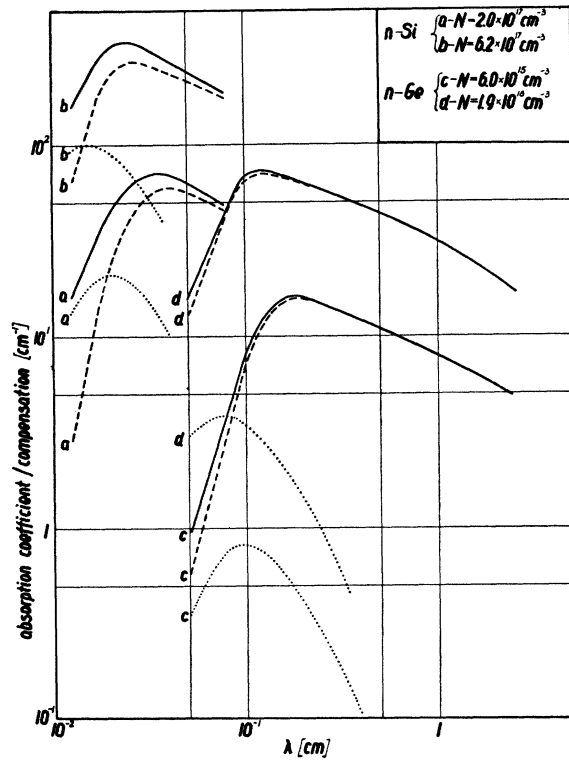


FIG. 2. The dependence of the absorption coefficient per unit compensation on the wavelength of radiation for  $n$ -Si and  $n$ -Ge at various concentrations of donors. Broken curves correspond to direct absorption, dotted curves to absorption with the emission of one phonon. Solid curves give the sum of these two absorptions.

TABLE I. Values of the material constants.

Material	$\epsilon$	$v$ ( $10^5$ cm/sec)	$d$ (g/cm <sup>3</sup> )	$a$ (Å)	$\eta$	$\hbar\omega_{\max}'$ (eV)	$ E_1 $ (eV)	$\beta_0$	$E_{LR}$ (eV)
<i>n</i> -Si	11.7	8.3	2.3	22.1	4.2	$2.2 \times 10^{-3}$	15	0.43	$8.0 \times 10^{-4}$
<i>n</i> -Ge	16.0	4.9	5.4	70.8	18.8	$4.4 \times 10^{-4}$	11.4	0.059	$2.5 \times 10^{-5}$

in Fig. 2 (dotted curves) together with the corresponding direct-absorption curves taken from paper I. The sum of the two absorptions is also plotted. As in paper I, we are interested in  $\hbar\omega$  smaller than one-fourth of the ionization energy of a donor. In the ranges of the maxima of the  $\alpha^1$  curves and at shorter wavelengths, the contribution given by  $R$ 's and  $\Delta$ 's fulfilling (20)–(22) is not smaller than about one-half of  $\alpha^1$ . The curves are plotted up to values of  $\lambda$  such that this contribution is about 10% of  $\alpha^1$ . Our results, especially at long wavelengths, are, therefore, semiquantitative. In both materials in the ranges investigated, of  $\omega$  and  $N$  the assumption (25) is fulfilled.

The effect of  $\alpha^1$  on the total absorption coefficient is important at short wavelengths in Si. Instead of approximate proportionality of the absorption coefficient to  $\lambda^{5.0}$ , given for  $N = 2.0 \times 10^{17}$  cm<sup>-3</sup> by the direct absorption processes, we have the total-absorption coefficient approximately proportional to  $\lambda^{2.3}$ . In Ge the contribution of  $\alpha^1$  to the total absorption coefficient is small.

As mentioned above, the main contribution to  $\alpha^1$  in the ranges of the maxima of the  $\alpha^1$  curves and at shorter wavelengths is given by pairs with  $R$  fulfilling (20), i.e.,  $R \gtrsim 3a$ , and by the phonons with energies fulfilling (22). At these wavelengths  $R(\omega) < 3a$ . As stated before,  $R$ 's outside the region of a few  $a$  from  $R(\omega)$  do not give an important contribution to  $\alpha^1$ . Thus the main contribution is given by  $R$ 's about  $3a$ – $5a$ . Taking  $R = 4a$  and combining this with (22), we estimate that the phonon energies are higher than about  $1.9 \times 10^{-3}$  eV and  $3.4 \times 10^{-4}$  eV in Si and Ge, respectively. As mentioned above, the contribution from the transitions with phonon energy higher than  $\hbar\omega_{\max}'$ , i.e.,  $2.2 \times 10^{-3}$  eV in Si and  $4.4 \times 10^{-4}$  eV in Ge, is rather small. Thus in the ranges of the maxima of the  $\alpha^1$  curves and at shorter wavelengths the phonon energies are about  $\hbar\omega_{\max}'$ . It is interesting to observe that this is similar to the differences between the positions of the maxima on  $\alpha^1$  and  $\alpha$  curves which in both materials and at all concentrations are equal to about  $1.4\hbar\omega_{\max}'$ .

In deriving the formula for the absorption coefficient  $\alpha^1$ , we neglected the dipole potentials of ionized-acceptor-ionized-donor pairs present in the crystal. Because in the ranges of the maxima of the  $\alpha^1$  curves and at shorter wavelengths the main contribution to  $\alpha^1$  is given by the pairs at which  $\Delta E \approx \hbar\omega - \hbar\omega_{\max}'$ , and because  $\Delta$  is of the order of  $2(\langle W_R^2 \rangle_{av})^{1/2}$  and  $R$  is about  $4a$ , we can show by reasoning similar to that given in paper I that we can neglect the dipole poten-

tials in the derivation of  $\alpha^1$  if

$$K < [\epsilon(\hbar\omega - \hbar\omega_{\max}')/4ae^2]N^{-2/3}.$$

In the ranges of the maxima of all our  $\alpha^1$  curves and at shorter wavelengths this restriction is weaker than the restriction (17) used by us; a similar situation occurred also with respect to the restriction (21) of paper I for direct absorption at these wavelengths and concentrations.

The compensation  $K$  must be not too small, in order to avoid the effect of molecule-ion traps.

The assumption  $T = 0^\circ\text{K}$  should be interpreted to mean that  $kT$  is much smaller than both  $\Delta E$  and the phonon energy. Because in the ranges of the maxima of the  $\alpha^1$  curves and at shorter wavelengths these two energies are of the same order, it is sufficient to assume  $kT \ll \hbar\omega$ , as for the direct absorption.

We shall now estimate the contribution to the absorption coefficient given by the processes consisting of simultaneous absorption of a photon and emission of two phonons. If we take into account at  $0^\circ\text{K}$  both one-phonon and two-phonon processes then according to Lax, Burstein and Gummel<sup>9,10</sup> we must replace the function  $f(\omega_e)$  in Eq. (4) ( $\hbar\omega_e = \hbar\omega + \hbar\omega_0$  being the energy of the emitted phonon) by

$$f(\omega_e) + \frac{1}{2} \int_0^{\omega_e} f(\omega_e - \omega') f(\omega') d\omega'. \quad (26)$$

In the second term, corresponding to the two-phonon processes,  $\hbar\omega_e$  is the sum of the energies  $\hbar\omega_e - \hbar\omega'$  and  $\hbar\omega'$  of the two emitted phonons. Using the function  $f$  in the form of Eq. (10) and taking into account that

$$(\Delta^2 + 4S^2W^2)(\Delta^2 + 4W^2)^{-1} < 1,$$

we obtain that the ratio of the second to the first term

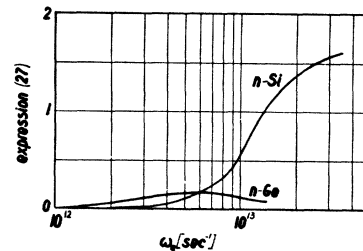


FIG. 3. Expression (27) estimating the ratio of the transition rates with two-phonon and one-phonon emission as the function of the sum of the angular frequencies of the emitted phonons in *n*-Si and *n*-Ge.

in (26) is smaller than

$$[E_1^2/4\pi^2\hbar v^5 d\omega_e U(\omega_e/v)] \times \int_0^{\omega_e} (\omega_e - \omega') \omega' U[(\omega_e - \omega')/v] U(\omega'/v) d\omega'. \quad (27)$$

The results of the numerical computations of (27) are given in Fig. 3. One can see from this figure that in *n*-Ge the two-phonon processes are unimportant as compared with the one-phonon processes. In *n*-Si the second term in (26) has the maximum at  $\omega_e \approx 8 \times 10^{12} \text{ sec}^{-1}$  (about  $2\omega_{\text{max}}$ ). Thus the main contribution to the absorption with two-phonon emission will be given by the pairs at which  $\omega_e \approx 8 \times 10^{12} \text{ sec}^{-1}$ . One can see

from Fig. 3 that at such values of  $\omega_e$  the one-phonon process is about three times more frequent. Therefore, in *n*-Si also we can neglect the two-phonon processes as compared with the one-phonon processes.

It seems that the processes consisting of simultaneous absorption of a photon and emission of more than two phonons can also be neglected in both materials.

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### Isotope Shift of a Low-Lying Lattice Resonant Mode\*

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A sharp and very low-frequency lattice absorption due to a lithium resonant mode has been found in KBr:LiBr. A large frequency shift with lithium isotopes has been observed. The experimental results can be understood with a simplified lattice model in which both nearest-neighbor force constants and the mass of the impurity are varied. It is concluded that the resonant mode comes from a remarkable softening of the forces between the impurity and the surrounding lattice.

THE dynamics of a heavy substitutional isotopic impurity in a lattice has been approximately described in terms of two kinds of lattice modes, namely, approximate phonon modes and resonant modes.<sup>1-3</sup> The phonon modes are similar to modes in a pure crystal, while the resonant modes are localized around the impurity position. For an alkali halide lattice with the appropriate substitutional impurity, a resonant mode in which the impurity vibrates with a markedly different amplitude than does the corresponding atom in the host crystal is expected to be strongly infrared-active. The absorption of far-infrared radiation by a lattice mode activated by a heavy substitutional impurity has been reported.<sup>4</sup> Recently, a surprisingly low-frequency lattice absorption has been identified with the very light impurity  $\text{Li}^+$  in KBr.<sup>5</sup>

In this note, we wish to report the observation and

interpretation of a large frequency shift with lithium isotope of the resonant mode in KBr. The experimental results can be understood with a simplified lattice model in which both nearest-neighbor (n.n.) force constants and the mass of the impurity atom are varied. A fit gives n.n. force constants which are about 0.6% of the host-lattice force constants. Finally, for such large force-constant changes, the expression for the resonant-mode frequency simplifies to an Einstein oscillator form.

High-purity single crystals of KBr doped with small concentrations of  $\text{Li}^6\text{Br}$  and  $\text{Li}^7\text{Br}$  have been grown in an argon atmosphere by the Kyropoulos technique.<sup>6</sup> From thermal-conductivity measurements on both quenched and annealed crystals, the substitutional impurity centers appear to consist of individual lithium ions.<sup>7</sup> Far-infrared transmission measurements from a frequency of 90 to  $12 \text{ cm}^{-1}$  have been made on these doped crystals. The apparatus for these measurements has been described elsewhere.<sup>4</sup> The samples were maintained at  $1.5^\circ\text{K}$  by helium exchange gas in contact with the sample and with a liquid-helium reservoir.

The impurity-induced absorption coefficient has been

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