Interaction of Electron on the Donor Center with the Crystal Lattice in Germanium and Silicon

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(Received 8 July 1963)

The diagonal matrix element of interaction of the bound electron with longitudinal acoustic phonon, squared and averaged over all directions of the phonon wave vector, was calculated for n-type Ge and Si assuming a single-deformation-potential constant. The donor wave functions have been taken in the elipsoidal form. Some simple integrals containing the squared and averaged matrix element are given and are used, as an example, to get the one-phonon transition rate in the impurity conduction by "hopping" and the relaxation energy of the lattice deformed by interaction with the donor electron. Appreciable differences are found between the case of elipsoidal and spherical donor wave functions.

INTRODUCTION

THE electron bound to the donor center in the homopolar crystal produces a deformation (a change of the equilibrium positions of the crystal atoms) in the vicinity of the center because of the interaction with acoustic phonons. This deformation influences several physical processes in the crystal. It changes the one-phonon transition probability and gives the possibility of the multiphonon processes in the case of the impurity conduction by "hopping."[1-4] A similar effect occurs in the case of the thermal recombination of donors and electrons.[5] The deformation of the crystal lattice gives also the difference between the energies of thermoionization and photoionization of donors.[6] In the process of absorption of the electromagnetic wave by the bound electron this deformation gives the possibility of the simultaneous absorption of photon and emission of phonons and so has an influence on the shape of the absorption lines.[7] In all papers referred to above[1-7] taking into account lattice-deformation effects requires computation of the diagonal matrix element of deformation potential of the phonon in the ground state of the electron on the isolated donor. This matrix element squared must then be averaged over all directions of the wave vector $\boldsymbol{\tau}$ of the phonon. The result in the case of the isotropic sound velocity is proportional to the function $U(\tau)$ which is by definition

$$U(\tau)=(\tfrac{1}{4}\pi)\int\left|\int u^*(\mathbf{r})\exp(i\tau\boldsymbol{\Omega}\mathbf{r})u(\mathbf{r})d^3x\right|^2 d\Omega, \quad (1)$$

if we assume a single deformation-potential constant and we are interested only in the interaction of electron with longitudinal acoustic phonons. By $u(\mathbf{r})$ we denote the ground-state wave function of electron on impurity center in nondeformed crystal lattice and we define $\boldsymbol{\tau}=\tau\boldsymbol{\Omega}$.

The function $U(\tau)$ was obtained in the referred papers[1-7] assuming in most cases the isotropic conduction band (the hydrogen-like donors). The purpose of the present work is to obtain the function $U(\tau)$ in the case of donors in Ge and Si. We simplify the problem assuming a single, isotropic deformation-potential constant and the isotropic velocity of the sound and taking into account only longitudinal acoustic phonons. The results of this paper can be easily used in another materials with similar shape of the conduction-band minima. The paper contains also same simple integrals with the function $U(\tau)$ for Ge and Si. We used them, as an example, to get the corrections to the results of the Ref. 2 which deal with the one-phonon transition rate in the impurityc onduction by "hopping." We obtain also corrections to the lattice relaxation energy.

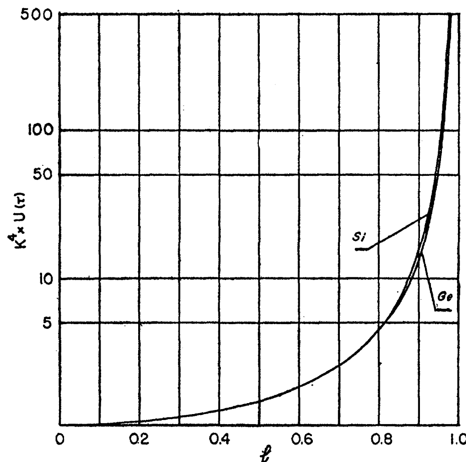

FIG. 1. The dependence of the function $U(\tau)$ on $l=[\alpha/(\alpha+1)]^{1/2}\times[1+(4/a^2\tau^2)]^{-1/2}$. For $l\rightarrow 1$ the asymptotic behavior is $(1-l^2)^{-3}/24$ and $(1-l^2)^{-3}/18$ for Ge and Si, respectively.

CALCULATION OF THE FUNCTION $U(\boldsymbol{\tau})$

In Ge and Si we have in the presence of the chemical shift the donor ground-state wave functions of the

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form[8]

$$u(\mathbf{r})=n^{-1/2}\sum_{q=1}^{n}F_q(\mathbf{r})\phi_q(\mathbf{r}). \qquad (2)$$

The sum is performed over the n minima of the conduction band (n equals 4 and 6 in Ge and Si, respectively). ϕ_q is the Bloch function for the qth minimum and F_q is of the form

$$F_q(x,y,z)=(\pi a^2 b)^{-1/2} \times\exp\{-[(x^2+y^2)/a^2+z^2/b^2]^{1/2}\}, \qquad (3)$$

where the z axis is parallel to the axis containing the qth minimum. The constants a and b are the transverse and longitudinal radii of the orbit, respectively.

With (2) we have

$$\int u^*(\mathbf{r})\exp(i\tau\mathbf{\Omega}\mathbf{r})u(\mathbf{r})d^3x =n^{-1}\int\sum_{p,q=1}^{n}F_pF_q\phi_p{}^*\phi_q\exp(i\tau\mathbf{\Omega}\mathbf{r})d^3x. \qquad (4)$$

Neglecting terms with $p\neq q$ because of the rapid oscillation of $\exp[i\mathbf{r}(\boldsymbol{\kappa}_q-\boldsymbol{\kappa}_p)]$, where $\boldsymbol{\kappa}_q$ is the wave vector for the qth minimum, and performing the integration we obtain

$$\int u(\mathbf{r})\exp(i\tau\mathbf{\Omega}\mathbf{r})u(\mathbf{r})d^3x=n^{-1}\sum_{q=1}^{n}f_q, \qquad (5)$$

where

$$f_q=K^{-2}[1-l^2(\mathbf{\Omega}\mathbf{p}_q)^2]^{-2}. \qquad (6)$$

We denoted here $\boldsymbol{\kappa}_q=\kappa_q\mathbf{p}_q$ and

$$K=1+\tfrac{1}{4}a^2\tau^2, \qquad (7)$$

$$l^2=[\alpha/(\alpha+1)][1+(4/a^2\tau^2)]^{-1}, \qquad (8)$$

$$\alpha=(a/b)^2-1. \qquad (9)$$

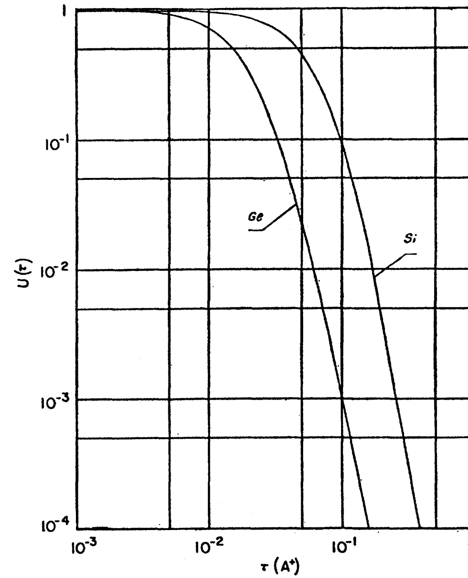

FIG. 2. The function $U(\tau)$ versus wave number τ of the phonon. For $\tau\to\infty$ the asymptotic behavior is $367.4\times K^{-4}$ and $14.81\times K^{-4}$ for Ge and Si, respectively.

For arbitrary τ we have $0\leq l^2<1$.

From (1) and (5) we obtain

$$U(\tau)=n^{-2}\sum_{p,q=1}^{n}u_{pq}(\tau), \qquad (10)$$

where

$$u_{pq}(\tau)=(4\pi)^{-1}\int f_pf_qd\Omega. \qquad (11)$$

Performing the integral in (11) and denoting $\mathbf{p}_p\mathbf{p}_q=(p,q)$ we obtain

$$u_{pq}=(4\pi K^4)^{-1}\{M[l,(p,q)]+M[l,-(p,q)]\}, \qquad (12)$$

where

$$M[l,(p,q)]=(\pi/2)\frac{[(2-l^2)^2-l^4(p,q)^2]\{(7-l^2)[1-(p,q)^2]-2\}+6l^4(p,q)^2[1-(p,q)^2]}{[1-(p,q)^2](1-l^2)[(2-l^2)^2-l^4(p,q)^2]^2}$$
$$+(\pi/16)\frac{\{[18-l^2-l^2(p,q)][1-(p,q)]+4\}[2-l^2-l^2(p,q)]+3l^4[1-(p,q)][1+(p,q)]^2}{[1-(p,q)]^{3/2}[2-l^2-l^2(p,q)]^{5/2}}$$
$$\times\ln\frac{(1+l)\{[1-l(p,q)]\{[2-l^2-l^2(p,q)]^{1/2}+l[1-(p,q)]^{1/2}\}+\{(1-l^2)[1-(p,q)]^{1/2}\}\}}{(1-l)\{[1+l(p,q)]\{[2-l^2-l^2(p,q)]^{1/2}-l[1-(p,q)]^{1/2}\}+\{(1-l^2)[1-(p,q)]^{1/2}\}\}}. \qquad (13)$$

In the case of $(p,q)=\pm1$, u_{pq} reduces to

$$\frac{33-40l^2+15l^4}{48(1-l^2)^3}+\frac{5}{32l}\ln\frac{1+l}{1-l}=F(4,\tfrac{1}{2};\tfrac{3}{2};l^2). \qquad (14)$$

[8] W. Kohn, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 257.

For $\tau=0(l=0)$, we have from (12) and (13) $u_{pq}=1$ for all p and q and so $U(\tau)=1$. For $\tau\to\infty$, $(l\to[\alpha/(\alpha+1)]^{1/2})$ we have $u_{pq}\to 0$ and $U(\tau)\to 0$.

In the isotropic case ($a=b$, $\alpha=0$, $l=0$) we have simply $u_{pq}=K^{-4}$ and $U(\tau)=K^{-4}$.

If we expand f_p and f_q in powers of l^2 and perform the integral in (11) we get instead of (12)

$$u_{pq}=K^{-4}\sum_{r=0}^{\infty} l^{2r}\frac{1}{(2r+1)!!}\sum_{s=0}^{r}(r-s+1)(s+1)\times\sum_{t=0}^{s}\binom{2s}{2t}(p,q)^{2t}[1-(p,q)^2]^{s-t}(2r-2s+2t-1)!!(2s-2t-1)!!. \quad (15)$$

GERMANIUM AND SILICON

In the case of germanium $n=4$, $(p,q)=+1$, $\pm\frac{1}{3}$. From (10), (12) and (13) we obtain

$$U_{\mathrm{Ge}}(\tau)=2^{-8}K^{-4}\left\{\frac{4(33-40l^2+15l^4)}{3(1-l^2)^3}+\frac{10}{l}\ln\frac{1+l}{1-l}+\frac{27[(3-2l^2)(3-l^2)(19-4l^2)+6l^4]}{(1-l^2)(3-2l^2)^2(3-l^2)^2}\right.$$
$$+\frac{9[(18-l^2)(3-2l^2)+6l^4]}{l(3-2l^2)^{5/2}}\ln\frac{(1+l)\{(3-l)[(3-2l^2)^{1/2}+l]+3(1-l^2)\}}{(1-l)\{(3+l)[(3-2l^2)^{1/2}-l]+3(1-l^2)\}}$$
$$\left.+\frac{9[(63-2l^2)(3-l^2)+6l^4]}{2^{5/2}l(3-l^2)^{5/2}}\ln\frac{(1+l)\{(3+l)[2^{1/2}(3-l^2)^{1/2}+2l]+6(1-l^2)\}}{(1-l)\{(3-l)[2^{1/2}(3-l^2)^{1/2}-2l]+6(1-l^2)\}}\right\} \quad (16)$$

or from (10) and (15)

$$U_{\mathrm{Ge}}(\tau)=K^{-4}(1.000+1.333l^2+1.644l^4+1.943l^6+2.247l^8+2.567l^{10}+3.191l^{12}+3.285l^{14}+3.608l^{16}+\cdots). \quad (17)$$

In the case of silicon $n=6$, $(p,q)=\pm1$, 0. From (10), (12) and (13) we obtain

$$U_{\mathrm{Si}}(\tau)=2^{-4}3^{-2}K^{-4}\left\{\frac{33-40l^2+15l^4}{(1-l^2)^3}+\frac{15}{2l}\ln\frac{1+l}{1-l}+\frac{24(5-l^2)}{(1-l^2)(2-l^2)^2}\right.$$
$$\left.+\frac{3[(22-l^2)(2-l^2)+3l^4]}{l(2-l^2)^{5/2}}\ln\frac{(1+l)[(2-l^2)^{1/2}+l+1-l^2]}{(1-l)[(2-l^2)^{1/2}-l+1-l^2]}\right\}, \quad (18)$$

or from (10) and (15)

$$U_{\mathrm{Si}}(\tau)=K^{-4}(1.000+1.333l^2+1.644l^4+1.943l^6+2.263l^8+2.628l^{10}+3.048l^{12}+3.528l^{14}+4.069l^{16}+\cdots). \quad (19)$$

Dependence of $K^4U(\tau)$ on l for Ge- and Si-type materials is plotted on the Fig. 1. Taking $\alpha=18.8$, $a=70.8$ Å for Ge and $\alpha=4.2$, $a=22.1$ Å for Si we obtain the dependences of $U(\tau)$ on τ given on the Fig. 2.

PARTICULAR INTEGRALS

We calculate here the integrals of the type $\int_0^\infty U(\tau)\tau^\kappa d\tau$ for $\kappa=0$, 1, 2, 3. We use formula (10) and u_{pq} in the form (14) for $(p,q)=\pm1$ or in the form (15) for $(p,q)\neq\pm1$.

In the case of germanium we obtain

$$\int_0^\infty U_{\mathrm{Ge}}(\tau)d\tau=\frac{15\pi}{64a}\left\{\frac{1}{3}\left[\frac{\alpha}{\alpha+1}\right]^{-1/2}\arcsin\left[\frac{\alpha}{\alpha+1}\right]^{1/2}+1.000+0.1667\frac{\alpha}{\alpha+1}+0.05722\left[\frac{\alpha}{\alpha+1}\right]^2\right.$$
$$+0.02560[\alpha/(\alpha+1)]^3+0.01327[\alpha/(\alpha+1)]^4+0.007581[\alpha/(\alpha+1)]^5$$
$$\left.+0.005640[\alpha/(\alpha+1)]^6+0.002991[\alpha/(\alpha+1)]^7+\cdots\right\}, \quad (20)$$

$$\int_0^\infty U_{\mathrm{Ge}}(\tau)\tau d\tau=\frac{1}{2a^2}\left\{\frac{1}{6}\left[\frac{\alpha}{\alpha+1}\right]^{-1/2}\ln\frac{1+[\alpha/(\alpha+1)]^{1/2}}{1-[\alpha/(\alpha+1)]^{1/2}}+1.000+0.3333\frac{\alpha}{\alpha+1}+0.1526\left[\frac{\alpha}{\alpha+1}\right]^2\right.$$
$$+0.08190[\alpha/(\alpha+1)]^3+0.04855[\alpha/(\alpha+1)]^4+0.03081[\alpha/(\alpha+1)]^5$$
$$\left.+0.02500[\alpha/(\alpha+1)]^6+0.01428[\alpha/(\alpha+1)]^7+\cdots\right\}, \quad (21)$$

$$\int_0^\infty U_{\mathrm{Ge}}(\tau)\tau^2 d\tau=\frac{3\pi}{16a^3}\left\{\frac{1}{3}(\alpha+1)^{1/2}+1.000+0.5000\frac{\alpha}{\alpha+1}+0.2861\left[\frac{\alpha}{\alpha+1}\right]^2+0.1792\left[\frac{\alpha}{\alpha+1}\right]^3\right.$$
$$+0.1195[\alpha/(\alpha+1)]^4+0.08340[\alpha/(\alpha+1)]^5+0.07332[\alpha/(\alpha+1)]^6$$
$$\left.+0.04487[\alpha/(\alpha+1)]^7+0.03187[\alpha/(\alpha+1)]^8+\cdots\right\}, \quad (22)$$

$$\int_0^\infty U_{\mathrm{Ge}}(\tau)\tau^3 d\tau=a^{-4}\left\{\frac{1}{6}(\alpha+1)+\frac{1}{12}\left[\frac{\alpha}{\alpha+1}\right]^{-1/2}\ln\frac{1+[\alpha/(\alpha+1)]^{1/2}}{1-[\alpha/(\alpha+1)]^{1/2}}+1.000+0.6667\frac{\alpha}{\alpha+1}+0.4578\left[\frac{\alpha}{\alpha+1}\right]^2\right.$$
$$+0.3276[\alpha/(\alpha+1)]^3+0.2427[\alpha/(\alpha+1)]^4+0.1848[\alpha/(\alpha+1)]^5+0.1750[\alpha/(\alpha+1)]^6$$
$$\left.+0.1142[\alpha/(\alpha+1)]^7+0.08591[\alpha/(\alpha+1)]^8+\cdots\right\}. \quad (23)$$

In the case of silicon we obtain

$$\int_0^\infty U_{\mathrm{Si}}(\tau)d\tau=\frac{5\pi}{24a}\left\{\frac{1}{2}\left[\frac{\alpha}{\alpha+1}\right]^{-1/2}\arcsin\left[\frac{\alpha}{\alpha+1}\right]^{1/2}+1.000+0.1667\frac{\alpha}{\alpha+1}+0.05500\left[\frac{\alpha}{\alpha+1}\right]^2+0.02321\left[\frac{\alpha}{\alpha+1}\right]^3\right.$$
$$\left.+0.01133[\alpha/(\alpha+1)]^4+0.006138[\alpha/(\alpha+1)]^5+0.003602[\alpha/(\alpha+1)]^6+\cdots\right\}, \quad (24)$$

$$\int_0^\infty U_{\mathrm{Si}}(\tau)\tau d\tau=\frac{4}{9a^2}\left\{\frac{1}{4}\left[\frac{\alpha}{\alpha+1}\right]^{-1/2}\ln\frac{1+[\alpha/(\alpha+1)]^{1/2}}{1-[\alpha/(\alpha+1)]^{1/2}}+1.000+0.3333\frac{\alpha}{\alpha+1}+0.1467\left[\frac{\alpha}{\alpha+1}\right]^2\right.$$
$$\left.+0.07429[\alpha/(\alpha+1)]^3+0.04145[\alpha/(\alpha+1)]^4+0.02494[\alpha/(\alpha+1)]^5+0.01597[\alpha/(\alpha+1)]^6+\cdots\right\}, \quad (25)$$

$$\int_0^\infty U_{\mathrm{Si}}(\tau)\tau^2 d\tau=\frac{\pi}{6a^3}\left\{\tfrac{1}{2}(\alpha+1)^{1/2}+1.000+0.5000\frac{\alpha}{\alpha+1}+0.2750\left[\frac{\alpha}{\alpha+1}\right]^2+0.1625\left[\frac{\alpha}{\alpha+1}\right]^3\right.$$
$$\left.+0.1019[\alpha/(\alpha+1)]^4+0.06752[\alpha/(\alpha+1)]^5+0.04683[\alpha/(\alpha+1)]^6+\cdots\right\}, \quad (26)$$

$$\int_0^\infty U_{\mathrm{Si}}(\tau)\tau^3 d\tau=\frac{8}{9a^4}\left\{\tfrac{1}{4}(\alpha+1)+\frac{1}{8}\left[\frac{\alpha}{\alpha+1}\right]^{-1/2}\ln\frac{1+[\alpha/(\alpha+1)]^{1/2}}{1-[\alpha/(\alpha+1)]^{1/2}}+1.000+0.6667\frac{\alpha}{\alpha+1}+0.4400\left[\frac{\alpha}{\alpha+1}\right]^2\right.$$
$$\left.+0.2971[\alpha/(\alpha+1)]^3+0.2073[\alpha/(\alpha+1)]^4+0.1497[\alpha/(\alpha+1)]^5+0.1118[\alpha/(\alpha+1)]^6+\cdots\right\}. \quad (27)$$

Taking $\alpha=18.8$, $a=70.8$ Å for Ge and $\alpha=4.2$, $a=22.1$ Å for Si we obtain values given in the Table I.

CORRECTIONS TO THE ONE-PHONON "HOPPING" PROBABILITY AND LATTICE RELAXATION ENERGY

According to Ref. 2 the total one-phonon transition rate for the electron transfer from the donor a to the donor b is

$$W_{ba}^{1\mathrm{tot}}=W_{ba}^{1}(1-A)^2\exp(-\alpha), \quad (28)$$

where W_{ba}^1 is the one-phonon transition rate if we neglect the dependence of the equilibrium positions of the lattice atoms on the state of the carrier. α and A are the quantities described in Ref. 2. In particular for low absolute temperature T

$$\alpha_{T\to 0}=\frac{E_1^2}{\pi h v^3 d}\int_0^\infty U(\tau)\tau d\tau, \quad (29)$$

$$A_{T\to 0}=\frac{hE_1^2}{4\pi^3 v\Delta E_{ba}^2 d}\int_0^\infty U(\tau)\tau^3 d\tau. \quad (30)$$

E_1 is the deformation-potential constant, ΔE_{ba} the

TABLE I. Values of the integrals of the form $\int_0^\infty U(\tau)\tau^\kappa d\tau$ for n-type Ge and Si.

Material	$k=0$ (cm^{-1})	$k=1$ (cm^{-2})	$k=2$ (cm^{-3})	$k=3$ (cm^{-4})
n-Ge	1.78×10^6	2.4×10^{12}	6.1×10^{18}	2.5×10^{25}
n-Si	5.36×10^6	2.05×10^{13}	1.4×10^{20}	1.4×10^{27}

TABLE II. Corrections to the one-phonon "hopping" probability and lattice relaxation energy for n-type Ge and Si.

Material	$\alpha_{T\to 0}$	$A_{T\to 0}$	$(W_{ba}{}^{1\text{tot}}/W_{ba}{}^{1})_{T\to 0}$	E_{LR} (eV)
n–Ge	0.059(0.08)	0.067(0.08)	0.82(0.78)	$2.5\times10^{-5}(3.3\times10^{-5})$
n–Si	0.43(0.56)	0.39(0.59)	0.24(0.10)	$0.80\times10^{-3}(1.1\times10^{-3})$

difference of the electrostatic energy of the carrier in the two donors, v the velocity of sound in the crystal, and d the density of the crystal.

In the Table II we give the values of $\alpha_{T\to 0}$, $A_{T\to 0}$ and $(W_{ba}{}^{1\text{tot}}/W_{ba}{}^{1})_{T\to 0}$ obtained from (28)–(30) and from data given in Table I for n-type Ge and Si samples studied in Ref. 2. We give also the values of relaxation energy E_{LR} of the lattice deformed by interaction with the donor electron, which is[2]

$$E_{\text{LR}}=\frac{E_1{}^2}{4\pi v^2 d}\int_0^\infty U(\tau)\tau^2 d\tau\,. \tag{31}$$

In Table II we give in brackets for comparison the values obtained previously[2] in approximation of hydrogen-like, spherical donor.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Professor M. Suffczyński for his interest in this work and to Dr. J. Mycielski for suggesting the problem and for valuable suggestions and remarks.

PHYSICAL REVIEW VOLUME 134, NUMBER 4A 18 MAY 1964

Measurement of the Conductivity Effective Mass in Semiconductors Using Infrared Reflection

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(Received 21 November 1963; revised manuscript received 7 February 1964)

There exist various approximate relationships between the conductivity effective mass of free carriers m_c and the angular frequency ω_0 of the reflectivity minimum in the infrared arising from the free-carrier dispersion. A detailed analysis of the reflectivity equation shows that it is possible to obtain a relationship between m_c and ω_0 when in addition one has a knowledge of the free-carrier concentration, the drift mobility, and the dielectric constant of the semiconductor at very high frequencies. This relationship is shown to yield a value of $m_c{}^*=0.145$ for n-type germanium at room temperature using data presented in the literature. This value compares well with the value of $m_c{}^*=0.15$ obtained using a combination of reflection and transmission measurements. The experimental work required to obtain accurate values for m_c using this relationship is considerably less than that required by other techniques, such as cyclotron resonance, magnetoplasma, and combined infrared reflection and transmission measurements, which are presently used. Moreover, this procedure can be applied over very broad ranges of temperature and of free-carrier concentration.

INTRODUCTION

IN this paper[1] we are concerned with the determination of the conductivity effective mass, which is understood to be the effective mass entering in the free-carrier mobility

$$\mu=(e/m_c)\langle\tau\rangle\,, \tag{1}$$

where e is the electronic charge, m_c is the conductivity effective mass, and $\langle\tau\rangle$ is the relaxation time averaged over all of the free current carriers. The determination of this parameter has received increasing attention in recent years. The earliest and the most extensive investigations to date have utilized cyclotron resonance techniques. For example, the conductivity effective mass has been measured at liquid-helium temperature, where the relaxation time of free carriers is sufficiently long for both germanium and silicon.[2,3] Recently infrared techniques also have been employed for this determination. In one instance, the conductivity effective masses in germanium, silicon, and indium antimonide were obtained from a combination of reflection and transmission measurements conducted at room temperature.[4] In another instance only reflection measurements were required, in conjunction with varying intensities of magnetic field, to determine the conductivity effective masses of mercury selenide and indium antimonide.[5]

We are proposing in this paper that it is possible to determine m_c very accurately simply from a measure-

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[1] This paper is based upon a dissertation by the author submitted in partial fulfillment of the degree of Doctor of Science to the Electrical Engineering Department of the Massachusetts Institute of Technology and published as Scientific Report No. 7 under Contract No. AF 19(604)-4153 (Jan. 1962). Air Force Cambridge Research Laboratory document number AFCRL-62-129.

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