

Contribution of Lattice Scattering between Nonequivalent Valleys to Free-Carrier Infrared Absorption in Semiconductors

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In a multivalley band-structure like that of the conduction band of germanium, a contribution to the absorption of infrared radiation by free carriers is made by a scattering process which does not play a role in normal transport processes but which may be of importance for hot-electron phenomena; this is the scattering between nonequivalent valleys of the conduction band. The absorption induced by this extra scattering process results in a transfer of the electrons from the $\langle 111 \rangle$ valleys to the $\langle 100 \rangle$ valleys or the $[000]$ valley. A quantum-mechanical calculation was made of the partial absorption constant μ_i^* due to this scattering on the basis of a deformation-potential type theory. The final formula obtained for μ_i^* is similar to that derived previously for the partial absorption constant μ^{opt} due to optical intravalley scattering. The physical significance of some limiting forms of μ_i^* at low temperatures is discussed.

THE process of absorption of infrared radiation by free charge carriers in semiconductors is governed mainly by the same scattering processes which also are of importance in the determination of transport phenomena^{1,2}; these are intravalley lattice-scattering by acoustical and optical modes, impurity scattering, and intervalley scattering. However, in those cases, like, e.g., germanium, where several conduction bands lie relatively closely together so that "the" conduction band has subsidiary minima of slightly higher energies than the main minima, a contribution to the absorption of light is made by a scattering process which does not play a role in normal transport phenomena but which could actually play a role in hot-electron problems: this is the scattering between the absolute minima of the conduction band (in germanium the $\langle 111 \rangle$ minima) and the higher lying subsidiary minima (in germanium the $\langle 100 \rangle$ minima and the $[000]$ minimum). That this scattering between nonequivalent valleys of the conduction band should play a role in determining the absorption constant at photon energies of sufficient magnitude to bridge the distance between the minima was already pointed out by Rosenberg and Lax.³ Since then more detailed experimental evidence has been collected⁴ which points to the necessity of having a theoretical description of the contribution of these processes to the absorption constant in *n*-type germanium at wavelengths shorter than approximately 14μ .

The calculations which lead to the partial absorption constant μ_i^* due to lattice scattering between nonequivalent valleys (henceforth shortly called nonequivalent intervalley scattering) are very similar to those given rather explicitly in reference 1 (henceforth indicated by I). Therefore, after a short description of the

model on which the present calculations were based, we shall content ourselves with giving the final results and a short discussion of their significance.

Since, in germanium, the energy difference ΔE between the bottom of a $\langle 111 \rangle$ valley and a $\langle 100 \rangle$ valley or the $[000]$ valley is about 0.18 eV, at all temperatures not much higher than room temperature nearly all electrons are in the $\langle 111 \rangle$ valleys at equilibrium. Therefore the initial state \mathbf{k} of an electron before the absorption process of a photon of frequency ν may be considered to belong to one of the $\langle 111 \rangle$ valleys, say the $[111]$ valley. The energy in this valley is given by

$$E_{\mathbf{k}} = (\hbar^2/2m)(\mathbf{k} - \mathbf{k}_0)\tilde{\alpha}(\mathbf{k} - \mathbf{k}_0), \quad (1)$$

where \mathbf{k}_0 is the vector belonging to the minimum of this valley and $\tilde{\alpha}$ is the reciprocal effective-mass tensor multiplied by the normal electron mass m , $\tilde{\alpha} = \|m/m_{i\langle 111 \rangle}\|$. The final state of the electron \mathbf{k}' belongs to one of the $\langle 100 \rangle$ valleys or the $[000]$ valley, say the $[100]$ valley. The energy in this valley is given by

$$E_{\mathbf{k}'} = (\hbar^2/2m)(\mathbf{k}' - \mathbf{k}_1)\tilde{\beta}(\mathbf{k}' - \mathbf{k}_1) + \Delta E, \quad (2)$$

where \mathbf{k}_1 is the vector belonging to the minimum of the $[100]$ valley and $\tilde{\beta}$ is given by

$$\tilde{\beta} = \|m/m_{i[100]}\|. \quad (3)$$

We now assume that the interaction with the lattice vibrations which is effective in inducing the transitions considered here has the same form as the interaction with the optical modes if described in the deformation-potential model; this was first introduced by Harrison⁵ and treated in detail in I. We then find, in complete analogy with the calculations in I, for the absorption constant due to the transition from the $[111]$ valley to

¹ H. J. G. Meyer, Phys. Rev. **112**, 298 (1958).

² H. J. G. Meyer, J. Phys. Chem. Solids **8**, 264 (1959).

³ R. Rosenberg and M. Lax, Phys. Rev. **112**, 843 (1958).

⁴ S. M. de Veer (unpublished results).

⁵ W. A. Harrison, Phys. Rev. **104**, 1281 (1956).

the [100] valley:

$$\begin{aligned} \mu_{[111] \rightarrow [100]} &= \frac{n}{4} \frac{1}{3 \times 8^2 \pi^4} (\det \bar{\alpha})^{\frac{1}{2}} \frac{\hbar^2 v}{m^2 M c \epsilon^{\frac{3}{2}}} \left[\frac{\hbar^2}{2 \pi m k T} \right]^{\frac{3}{2}} \frac{1}{\nu^3} \frac{D_i'^2}{\omega_i'} \\ &\times \int d\mathbf{k}' \int d\mathbf{k} \exp[-E_{\mathbf{k}}/kT] \\ &\times |\bar{\alpha}(\mathbf{k} - \mathbf{k}_0) - \bar{\beta}(\mathbf{k}' - \mathbf{k}_1)|^2 \\ &\times \{n_i' \delta[E_{\mathbf{k}'} - (E_{\mathbf{k}} + \hbar\nu + \hbar\omega_i')] \\ &+ (n_i' + 1) \delta[E_{\mathbf{k}'} - (E_{\mathbf{k}} + \hbar\nu - \hbar\omega_i')]\}. \quad (4) \end{aligned}$$

This formula differs from the corresponding expression (3.6) of I⁶ if written down explicitly for optical scattering in that a new deformation potential constant D_i' is introduced describing the interaction with the modes of frequency ω_i' and occupation number n_i' responsible for the scattering between nonequivalent valleys; furthermore, a factor $|\bar{\alpha}(\mathbf{k} - \mathbf{k}_0) - \bar{\beta}(\mathbf{k}' - \mathbf{k}_1)|^2$ is introduced instead of the factor $|\bar{\alpha}(\mathbf{k} - \mathbf{k}')|^2$ while $E_{\mathbf{k}}$ and $E_{\mathbf{k}'}$ are now given by (1) and (2), respectively. Furthermore, just as in I, n is the density of the electrons in the conduction band, v is the volume of a unit cell of the crystal, M is the mass of a germanium atom and ϵ is the dielectric constant, while all the other symbols have their conventional meaning. If now $\bar{\alpha}^{\frac{1}{2}} \mathbf{k}$ and $\bar{\beta}^{\frac{1}{2}} \mathbf{k}'$ are introduced as new integration variables, the integrations in (4) can be performed without much difficulty if the usual assumption is made that the frequency of the high-energy phonons, involved in the scattering process considered here, does not depend on its wave vector. The final result does not depend explicitly on the angle between the two valleys considered, so that the contribution of the various $\langle 100 \rangle$ valleys can be added. If the sum of the squares of the corresponding deformation potential constants is called $D_i'^2$ and if the contributions of the electrons which are initially in the various $\langle 111 \rangle$ valleys are added, we finally get for the partial absorption constant μ_i^* due to the scattering between nonequivalent valleys in the conduction band:

$$\begin{aligned} \mu_i^* &= n \frac{e^2 k^{\frac{3}{2}} m^{\frac{1}{2}} v}{6 \pi^{7/2} \hbar^4 c M \omega_0 \epsilon^{\frac{3}{2}}} D_i'^2 \frac{\bar{\alpha}}{(\det \bar{\alpha})^{\frac{1}{2}}} \left(\frac{D_i'^2}{D} \right)^2 \frac{\omega_0}{\omega_i^*} \frac{1}{2} \left(1 + \frac{\bar{\beta}}{\bar{\alpha}} \right) \\ &\times \frac{\det \bar{\alpha}^{\frac{1}{2}}}{\det \bar{\beta}^{\frac{1}{2}}} \frac{T^{\frac{3}{2}} \nu^{-3}}{\exp(\hbar\omega_i^*/kT) - 1} \exp \zeta_{\pm} \\ &\times \left\{ \zeta_{+}^2 K_2(|\zeta_{+}|) + \frac{\zeta_{+}^3}{|\zeta_{+}|} \frac{\bar{\beta} - \bar{\alpha}}{\bar{\beta} + \bar{\alpha}} K_1(|\zeta_{+}|) \right. \\ &\left. + \zeta_{-}^2 K_2(|\zeta_{-}|) + \frac{\zeta_{-}^3}{|\zeta_{-}|} \frac{\bar{\beta} - \bar{\alpha}}{\bar{\beta} + \bar{\alpha}} K_1(|\zeta_{-}|) \right\}. \quad (5) \end{aligned}$$

⁶ In that formula a factor $|\bar{\alpha}(\mathbf{k}' - \mathbf{k})|^2$ was omitted which, however, was rightly taken into account in the actual calculations.

Here ω_i^* is the effective angular frequency ascribed to the phonons responsible for the scattering considered here, $\bar{\beta}$ and $\bar{\alpha}$ are the arithmetic averages of the corresponding diagonalized tensors, e.g.,

$$\bar{\beta} = \frac{1}{3}(\beta_1 + \beta_2 + \beta_3); \quad (6)$$

the important parameters ζ_{+} and ζ_{-} occurring in (5) are defined by

$$\zeta_{\pm} = (\hbar\nu - \Delta E \pm \hbar\omega_i^*)/2kT. \quad (7)$$

Furthermore, just as in I, ω_0 is the frequency of the optical modes, D is the optical deformation potential constant, $z = \hbar\nu/2kT$ and K_1 , K_2 are modified Bessel functions. Finally we have made use of the equality $\{1 - [(\gamma - 1)/3\gamma]\} \alpha_2^{-\frac{1}{2}} = \bar{\alpha}/(\det \bar{\alpha})^{\frac{1}{2}}$, where $\gamma = \alpha_1/\alpha_2$.

It should be noted that our expression (5) is very similar to the corresponding expression (5.3) of I, valid for optical intravalley scattering and for normal inter-valley scattering between equivalent valleys. The only more or less qualitative difference is the occurrence of the first modified Bessel function K_1 . It is easily verified that our expression (5) becomes indeed identical with (5.3) of I if the following substitutions are made: $D_i'^2 \rightarrow D$, $\omega_i^* \rightarrow \omega_0$, $\bar{\beta} \rightarrow \bar{\alpha}$, $\Delta E \rightarrow 0$, which corresponds to the substitution of the process of scattering between equivalent valleys instead of the process of scattering between nonequivalent valleys.

A detailed discussion of the various limiting cases can be omitted as it would be very similar to the discussions given in Sec. 5.2 of I. However, some additional remarks regarding the physical interpretation of the special cases which occur if $\zeta \gg 1$, $\zeta \ll -1$, or if $\zeta \approx 0$ can be made. In fact, from the limiting behavior of the two relevant modified Bessel functions for very small and very large ζ , viz.

$$K_1(\zeta) \rightarrow 1/\zeta; \quad K_2(\zeta) \rightarrow 2/\zeta^2, \quad (\zeta \rightarrow 0) \quad (8)$$

and

$$K_1(\zeta) \sim K_2(\zeta) \rightarrow (\pi/2\zeta)^{\frac{1}{2}} e^{-\zeta}, \quad (\zeta \rightarrow \infty)$$

it follows that

$$\text{for } \zeta \gg 1, \quad \mu_i^* \propto \bar{\beta} (\pi/2)^{\frac{1}{2}} |\zeta|^{\frac{3}{2}} e^{-|\zeta|} \sim \bar{\beta} \zeta^2 K_2(|\zeta|), \quad (9a)$$

$$\text{for } \zeta \ll -1, \quad \mu_i^* \propto \bar{\alpha} (\pi/2)^{\frac{1}{2}} |\zeta|^{\frac{3}{2}} e^{-|\zeta|} \sim \bar{\alpha} \zeta^2 K_2(|\zeta|), \quad (9b)$$

$$\text{for } \zeta \approx 0, \quad \mu_i^* \propto \frac{1}{2} (\bar{\alpha} + \bar{\beta}) \times 2 \sim \frac{1}{2} (\bar{\alpha} + \bar{\beta}) \zeta^2 K_2(|\zeta|). \quad (9c)$$

Now the occurrence of the respective factors $\bar{\beta}$, $\bar{\alpha}$, and $\frac{1}{2}(\bar{\alpha} + \bar{\beta})$ at the right-hand side of (9) is easily understood as follows:

(a) For $\hbar\nu \gg \Delta E$ and low temperature ($\zeta \gg 1$), practically all electrons contributing to μ_i^* have initially the same low-energy kT whereas the final energy is much higher than the minimum energy of the $\langle 100 \rangle$ valleys. Therefore, in the squared matrix element of (4) the term containing $(\mathbf{k}' - \mathbf{k}_1)^2$ is predominant and yields the factor $\bar{\beta}$ in (9a).

(b) For $\hbar\nu \ll \Delta E$ and low temperature, only those

few electrons in the $\langle 111 \rangle$ valleys contribute to μ_i^* which have a thermal energy ϵ_{th} which obeys the equation $h\nu + \epsilon_{th} \approx \Delta E$. This energy is much higher than the minimum energy of these valleys while the final energy is nearly equal to the minimum energy of the $\langle 100 \rangle$ valleys. Now the term proportional to $(\mathbf{k} - \mathbf{k}_0)^2$ in (4) is predominant, yielding the factor $\bar{\alpha}$ in (9b).

(c) If $h\nu \approx \Delta E$, both terms in the squared matrix element of (4) are of equal importance, yielding the factor $\frac{1}{2}(\bar{\alpha} + \bar{\beta})$ of (8c).

Furthermore, it can be seen from (5) that μ_i^*

becomes very small for sufficiently low temperatures and sufficiently long wavelengths such that $[\Delta E - (h\nu + \hbar\omega_i^*)]/kT \gg 1$. With $\Delta E/k = 2030^\circ\text{K}$, $\hbar\omega_i^*/k = 316^\circ\text{K}$, and $T = 300^\circ\text{K}$, we therefore find that the effect of nonequivalent intervalley scattering on the absorption constant becomes rapidly negligible at room temperature if the wavelength λ becomes larger than about 14μ .

⁷This corresponds, rather arbitrarily, to a value found by Weinreich and quoted by Brockhouse, *J. Phys. Chem. Solids* **8**, 400 (1959).

Single-Crystal and Polycrystal Resistivity Relationships for Yttrium*

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Different proposals for calculating polycrystal resistivities from single-crystal values are applied to yttrium metal. It is shown that a simple average yielding $\rho_{\text{poly}} = \frac{1}{3}(2\rho_{\perp} + \rho_{\parallel})$ gives the best fit to experimental data.

INTRODUCTION

IT is reasonable to expect that a general relation exists between the principal resistivities of a single crystal and the isotropic resistivity of a polycrystalline sample of the same substance. There is, however, little agreement in the literature as to the form of this relation; several methods of calculating the polycrystal resistivity have been proposed. Voigt¹ suggests

$$\sigma_{\text{poly}} = \frac{1}{3}(2\sigma_{\perp} + \sigma_{\parallel}),$$

which is the same as

$$\rho_{\text{poly}} = 3\rho_{\perp}\rho_{\parallel}/2\rho_{\perp} + \rho_{\perp}, \quad (1)$$

where ρ_{\parallel} and ρ_{\perp} are the principal resistivities of a hexagonal crystal measured parallel and perpendicular to the axis of symmetry, and where $\rho_{\perp} = 1/\sigma_{\perp}$, $\rho_{\parallel} = 1/\sigma_{\parallel}$, $\rho_{\text{poly}} = 1/\sigma_{\text{poly}}$. Andrade and Chalmers² obtain

$$\rho_{\text{poly}} = \frac{[\rho_{\perp}(\rho_{\parallel} - \rho_{\perp})]^{\frac{1}{2}}}{\tan^{-1}\{[(\rho_{\parallel} - \rho_{\perp})/\rho_{\perp}]^{\frac{1}{2}}\}}$$

for the case $\rho_{\parallel} > \rho_{\perp}$. This is equivalent to

$$\rho_{\text{poly}} = \frac{[\rho_{\perp}(\rho_{\parallel} - \rho_{\perp})]^{\frac{1}{2}}}{\tanh^{-1}\{[(\rho_{\parallel} - \rho_{\perp})/\rho_{\perp}]^{\frac{1}{2}}\}} \quad (2)$$

for $\rho_{\perp} > \rho_{\parallel}$. Bruggeman³ proposes

$$\rho_{\text{poly}} = \frac{1}{4}\{\sigma_{\perp} + [\sigma_{\perp}(8\sigma_{\parallel} + \sigma_{\perp})]^{\frac{1}{2}}\},$$

or

$$\rho_{\text{poly}} = 4 / \left\{ \frac{1}{\rho_{\perp}} + \left[\frac{1}{\rho_{\perp}} \left(\frac{8}{\rho_{\parallel}} + \frac{1}{\rho_{\perp}} \right) \right]^{\frac{1}{2}} \right\}. \quad (3)$$

Another method,⁴ which has been proposed more recently, yields

$$\rho_{\text{poly}} = \frac{1}{3}(2\rho_{\perp} + \rho_{\parallel}). \quad (4)$$

This relation is the result of an average over the total solid angle of the well-known expression,

$$\rho(\theta) = \rho_{\parallel} \cos^2\theta + \rho_{\perp} \sin^2\theta,$$

for the resistivity along an arbitrary direction of current flow in a hexagonal crystal.⁵

Several attempts^{2,3} to resolve this question experimentally have been indecisive; if the anisotropy ratio, $\rho_{\perp}/\rho_{\parallel}$, is very near unity, the small difference between values given by any of Eqs. (1)–(4) is masked by the probable error of the experiment. Recently Hall *et al.*⁶ have reported the principal single-crystal resistivities of yttrium (see Table I). Their values at 300°K lead to the exceptionally high anisotropy ratio of

$$\rho_{\perp}/\rho_{\parallel} = 2.07,$$

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⁵ W. Boas and J. K. Mackenzie, *Progress in Metal Physics*, edited by B. Chalmers (Interscience Publishers, Inc., New York, 1950), Vol. II, p. 90.

⁶ P. M. Hall, S. Legvold, and F. H. Spedding, *Phys. Rev.* **116**, 1446 (1959).