Theoretical description of intervalence-band photoconductivity of p-Ge at 10.6 μm

R. B. James and D. L. Smith
California Institute of Technology, Pasadena, California 91125
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The absorption of CO_2 laser radiation alters the distribution of free holes in p-Ge due to optical transitions between the heavy- and light-hole bands. The modification of the hole distribution function leads to a change in the conductivity. We present a calculation of the linear photoconductive response at 10.6 μm as a function of hole density at room temperature and as a function of temperature for fixed hole density. We also describe the photoconductivity for high light intensities for which the effects of saturation of the intervalence-band transitions are important.

I. INTRODUCTION

The absorption of light in the 10-μm region by p-type germanium is determined by direct intervalence-band transitions in which a free hole in the heavy-hole band absorbs a photon and is excited to the light-hole band.[1] Since the absorption of light modifies the distribution of free holes, one expects a change in the sample conductivity upon illumination. Because the density of states in the heavy-hole band is much greater than that in the light-hole band, the photoexcited holes primarily scatter into high-energy states in the heavy-hole band. Thus the dominant change in the distribution function is an increase in the average energy of occupied states in this band. For temperatures and doping levels for which phonon scattering dominates the momentum relaxation, the conductivity decreases upon illumination because the rate of phonon scattering increases with increasing hole energy. For lower temperatures or higher doping levels where ionized-impurity scattering dominates the momentum relaxation, the conductivity increases with illumination because ionized-impurity scattering decreases with increasing hole energy. These photoconductive effects have been observed experimentally[2-7] and have been shown to influence the performance of p-Ge photon drag detectors.[8-10] In this paper we present a calculation of the photoconductive response of p-Ge upon illumination by 10.6-μm light as a function of doping level, temperature, and intensity.

Previous calculations of this photoconductive response have been based on idealized models in which the Ge valence bands have been replaced by a set of discrete energy levels, each characterized by an effective mobility.[6,7] In addition, the effects of saturation of the intervalence-band transitions were not included, so that the results could only be applied for low intensities. Here we describe the Ge valence band using degenerate $\vec{k}\cdot\vec{p}$ perturbation theory. We calculate the hole distribution as a function of the laser intensity in both the linear and nonlinear regimes. Using the calculated hole distribution, we determine the photoconductive response. We find reasonable agreement with experimental results. There are no adjustable parameters in the theory.

The paper is organized in the following way: In Sec. II we present our theoretical approach, in Sec. III we give our results for the change in the conductivity, and in Sec. IV we summarize our conclusions.

II. THEORETICAL APPROACH

The valence bands of Ge consist of three twofold degenerate bands: the heavy-hole, the light-hole, and the split-off hole bands. In thermal equilibrium the occupied hole states are in the heavy- and light-hole bands only. We consider the intervalence-band photoconductivity of p-Ge when the sample is pumped by a CO_2 laser. Since the laser does not couple free holes to states in the split-off hole band, only the heavy- and light-hole bands need to be considered. The dc current density owing to free holes is given by

$$\vec{J}=\left(\frac{1}{2\pi}\right)^3 N_h e \sum_b \int f_b(\vec{k})\vec{v}_{b\vec{k}}\,d^3k\,, \tag{1}$$

where N_h is the density of holes, b labels the band index, $\vec{k}$ is the wave vector, $f_b(\vec{k})$ is the one-hole distribution function, and $\vec{v}_{b\vec{k}}$ is the group velocity of the carrier with wave vector $\vec{k}$ in band b.

In order to calculate the current density and thus determine the conductivity, it is necessary to find the distribution function in the presence of the exciting laser and a small applied dc electric field. The distribution functions in the heavy- and light-hole bands are determined by solving the following equations[11,12]:

$$\beta(\vec{k})[f_h(\vec{k})-f_l(\vec{k})]+\frac{e}{\hbar}\vec{E}\cdot\nabla_{\vec{k}}f_h(\vec{k})$$

$$=-\sum_{c\vec{k}'}[R_{h\vec{k}\to c\vec{k}'}f_h(\vec{k})-R_{c\vec{k}'\to h\vec{k}}f_c(\vec{k}')]\,, \tag{2a}$$

and

$$\beta(\vec{k})[f_h(\vec{k})-f_l(\vec{k})]-\frac{e}{\hbar}\vec{E}\cdot\nabla_{\vec{k}}f_l(\vec{k})$$

$$=\sum_{c\vec{k}'}[R_{l\vec{k}\to c\vec{k}'}f_l(\vec{k})-R_{c\vec{k}'\to l\vec{k}}f_c(\vec{k}')], \quad (2b)$$

where $\beta(\vec{k})$ is given by

$$\beta(\vec{k})=\frac{2\pi^2}{\sqrt{\epsilon}\,m^2\omega c}\frac{e^2I}{3\hbar\omega}|\vec{P}_{hl}(\vec{k})|^2\frac{1/\pi\hbar T_2(\vec{k})}{[\Omega(\vec{k})-\omega]^2+[1/T_2(\vec{k})]^2}, \quad (3)$$

and

$$\frac{2}{T_2(\vec{k})}=\sum_{c\vec{k}'}(R_{h\vec{k}\to c\vec{k}'}+R_{l\vec{k}\to c\vec{k}'}). \quad (4)$$

Here, I is the light intensity, $\hbar\omega$ is the photon energy, $|\vec{P}_{hl}(\vec{k})|^2$ is the squared momentum matrix element between the Bloch states in the heavy- and light-hole bands (summed over the two degenerate states in each band), $R_{a\vec{k}\to b\vec{k}'}$ is the rate in which a hole in band a with wave vector $\vec{k}$ is scattered into band b with wave vector $\vec{k}'$, and $\Omega(\vec{k})$ is the angular frequency associated with the energy difference $[\epsilon_h(\vec{k})-\epsilon_l(\vec{k})]$, where $\epsilon_i(\vec{k})$ is the energy of the hole in band i with wave vector $\vec{k}$. The proportional to β in Eqs. (2a) and (2b) describes the change in the distribution due to optical excitation, the term proportional to E describes the acceleration of the holes by the electric field, and the terms proportional to R describe the scattering of the holes. The one-hole energies and momentum matrix elements in Eq. (3) are determined by degenerate $\vec{k}\cdot\vec{p}$ perturbation theory.[13] The cyclotron resonance parameters of Ref. 14 are used in the calculation. The hole-phonon contribution to the scattering rates appearing in Eqs. (2a) and (2b) are treated in the manner of Ref. 11. The hole-hole and hole-ionized-impurity scattering rates are included following Ref. 15.

In small dc electric fields, the distribution of carriers can be described by the sum of a small drift term and the distribution function without an electric field. Thus in small electric fields, we write

$$f_b(\vec{k})=f_b^0(\vec{k})+g_b(\vec{k}), \quad (5)$$

where $f_b^0(\vec{k})$ is the distribution function subject to the high-intensity laser but with no external electric field, and $g_b(\vec{k})$ is the modification of $f_b(\vec{k})$ due to the presence of the electric field. Here, it is assumed that $g_b(\vec{k})\ll f_b^0(\vec{k})$. The function $f_b^0(\vec{k})$ is computed as in Ref. 11. Using Eq. (5), we write Eqs. (2) to first order in the electric field

$$\beta(\vec{k})[g_h(\vec{k})-g_l(\vec{k})]+\frac{e}{\hbar}\vec{E}\cdot\nabla_{\vec{k}}f_h^0(\vec{k})$$

$$=-\sum_{c\vec{k}'}[R_{h\vec{k}\to c\vec{k}'}g_h(\vec{k})-R_{c\vec{k}'\to h\vec{k}}g_c(\vec{k}')], \quad (6a)$$

and

$$\beta(\vec{k})[g_h(\vec{k})-g_l(\vec{k})]-\frac{e}{\hbar}\vec{E}\cdot\nabla_{\vec{k}}f_l^0(\vec{k})$$

$$=\sum_{c\vec{k}'}[R_{l\vec{k}\to c\vec{k}'}g_l(\vec{k})-R_{c\vec{k}'\to l\vec{k}}g_c(\vec{k}')]. \quad (6b)$$

We assume that a relaxation time approximation can be made for the low dc field; that is, the rate of change of $g_h(\vec{k})$ due to collisions can be approximated by

$$\sum_{c\vec{k}'}[R_{h\vec{k}\to c\vec{k}'}g_h(\vec{k})-R_{c\vec{k}'\to h\vec{k}}g_c(\vec{k}')]=\frac{g_h(\vec{k})}{\tau_h(\vec{k})}, \quad (7)$$

and a similar expression for the effect of collisions on $g_l(\vec{k})$. Here, $\tau_h(\vec{k})$ $[\tau_l(\vec{k})]$ is the momentum relaxation time due to scattering of holes with wave vector $\vec{k}$ in the heavy- (light-) hole band by phonons and ionized impurities.[16]

Using Eqs. (6) and the relaxation time approximation, we write expressions for $g_b(\vec{k})$ in terms of the functions $f_b^0(\vec{k})$. Taking the dc electric field to be in the z direction, we have

$$g_h(\vec{k})=\frac{-e}{\hbar}\tau_h|E|\frac{\partial f_h^0}{\partial k_z}\left(\frac{1+\beta\tau_l[(\partial f_l^0/\partial k_z)/(\partial f_h^0/\partial k_z)+1]}{1+\beta(\tau_h+\tau_l)}\right), \quad (8a)$$

$$g_h(\vec{k})=\frac{-e}{\hbar}\tau_l|E|\frac{\partial f_l^0}{\partial k_z}\left(\frac{1+\beta\tau_h[(\partial f_h^0/\partial k_z)/(\partial f_l^0/\partial k_z)+1]}{1+\beta(\tau_h+\tau_l)}\right). \quad (8b)$$

Since $\vec{v}_b(\vec{k})=-\vec{v}_b(-\vec{k})$ and $f_b^0(\vec{k})=f_b^0(-\vec{k})$, we can write

$$J_z=2\left(\frac{1}{2\pi}\right)^3eN_h\sum_b\int g_b(\vec{k})v_{bz}(\vec{k})d^3k. \quad (9)$$

Integrating Eq. (9) by parts the conductivity is given by

$$\sigma=2\left(\frac{1}{2\pi}\right)^3\frac{e^2}{\hbar}N_h\int d^3k f_h^0(\vec{k})\frac{\partial}{\partial k_z}\left[\tau_h v_{hz}\left(\frac{1+\beta\tau_l[(\partial f_l^0/\partial k_z)/(\partial f_h^0/\partial k_z)+1]}{1+\beta(\tau_h+\tau_l)}\right)\right]$$

$$+2\left(\frac{1}{2\pi}\right)^3\frac{e^2}{\hbar}N_h\int d^3k f_l^0(\vec{k})\frac{\partial}{\partial k_z}\left[\tau_l v_{lz}\left(\frac{1+\beta\tau_h[(\partial f_h^0/\partial k_z)/(\partial f_l^0/\partial k_z)+1]}{1+\beta(\tau_h+\tau_l)}\right)\right]. \quad (10)$$

The factor

$$Z_h=\frac{1+\beta\tau_l[(\partial f_l^0/\partial k_z)/(\partial f_h^0/\partial k_z)+1]}{1+\beta(\tau_h+\tau_l)} \tag{11}$$

appearing in the heavy-hole band contribution to the conductivity, and the analogous factor Z_l present some numerical difficulties owing to the peaked nature of the terms involved. This factor differs significantly from unity only if $\beta\tau_h \gtrsim 1$.[17] We note that β is sharply peaked in the resonant region of the optical transition and negligibly small outside of this region. Thus we need only evaluate $\partial f^0/\partial k_z$ in the vicinity of the resonant region. At low light intensities where saturation of the optical transitions does not occur ($I \leq 1$ MW/cm^2), $\beta\tau_h$ is small compared to unity even in the resonant region, and Z_h is essentially one. At high intensities where saturation does occur, Z_h differs from unity in the resonant region. However, for the range of intensities considered in this paper ($I \leq 10$ MW/cm^2), this difference still does not make a large contribution to the integral in Eq. (10) because of limited range over which it occurs.

To estimate the value of Z_h, we only need to know the distribution function in the resonant region. We have previously found that these functions can be reasonably approximated by a simple analytical form for states in the resonant region[11]

$$f_h^0(\vec{k}) \approx f_h^e(\vec{k}) - \frac{\beta(\vec{k})T_h^{op}[f_h^e(\vec{k})-f_l^e(\vec{k})]}{1+\beta(\vec{k})(T_h^{op}+T_l)} \tag{12a}$$

and

$$f_l^0(\vec{k}) \approx f_l^e(\vec{k}) + \frac{\beta(\vec{k})T_l(\vec{k})[f_h^e(\vec{k})-f_l^e(\vec{k})]}{1+\beta(\vec{k})(T_h^{op}+T_l)}, \tag{12b}$$

where $f^e(\vec{k})$ is the equilibrium distribution,

$$\frac{1}{T_l(\vec{k})}=\sum_{b\vec{k}'} R_{l\vec{k}\to b\vec{k}'}, \tag{13}$$

and T_h^{op} is defined for the heavy-hole band analogous to Eq. (13) except that only optical-phonon scattering is included.

In the resonant region, the distribution functions in Eqs. (12a) and (12b) have a peaked structure owing to the Lorentzian factor contained in β. Taking the other factors in Eqs. (12) to be slowly varying in the resonant region, we approximate

$$\frac{\partial f^0}{\partial k_z} \approx \frac{\partial f^0}{\partial \beta}\frac{\partial \beta}{\partial k_z}. \tag{14}$$

With this approximation we have

$$\frac{\partial f_l^0/\partial k_z}{\partial f_h^0/\partial k_z} \approx \frac{T_l}{T_h^{op}}, \tag{15}$$

and thus a simple analytical expression for Z_h. To calculate the conductivity we must also evaluate the derivative of Z_h with respect to k_z. In evaluating this derivative, we take the factors other than β to be slowly varying in the resonant region and take the change in β to occur primarily through the Lorentzian factor which depends on $\Omega(\vec{k})$; that is, we approximate

$$\frac{\partial Z_h}{\partial k_z} \approx \frac{\partial Z_h}{\partial \beta}\frac{\partial \beta}{\partial \Omega}\frac{d\Omega}{dk_z}. \tag{16}$$

With this approximation, we have

$$\frac{\partial Z_h}{\partial k_z} = \left[\tau_h+\tau_l\left(\frac{T_l}{T_h^{op}}\right)\right]\frac{d\Omega}{dk_z}\frac{2\beta}{[1+\beta(\tau_h+\tau_l)]^2} \times \frac{\Omega-\omega}{(\Omega-\omega)^2+(1/T_2)^2}. \tag{17}$$

We treat the factor Z_l, which appears in the light-hole contribution to the conductivity in a similar way. We note that the expression in Eq. (17) is vanishingly small outside of the resonant region and changes sign as $\Omega(\vec{k})$ crosses ω. As a result this term tends to cancel in the $\vec{k}$-space integration. The inclusion of the terms containing $\partial Z_h/\partial k_z$ and $\partial Z_l/\partial k_z$ makes a contribution of less than 20% to the calculation of the photoinduced change in the conductivity at the highest intensities we consider.

III. RESULTS OF $\Delta\sigma(I)$

We compute the conductivity due to free holes by numerically integrating Eq. (10). For very lightly doped (near intrinsic) samples, we also include a term due to free electrons. We assume that the electron contribution is not much modified by illumination because the absorption cross section for electrons is nearly 2 orders of magnitude smaller than that for holes.[18]

In Fig. 1 we show the calculated results for $(-\Delta\sigma/\sigma I)$ vs N_h in the low-intensity regime where $\Delta\sigma$ is proportional to I. The calculation was done for room-temperature Ge illuminated by $\lambda = 10.6$ μm light. The conductivity has decreased upon illumination. The primary effect of illumination on the hole distribution is to increase the population of high-energy holes in the heavy-hole band. At room temperature and for the doping levels considered here, hole-phonon scattering limits the conductivity. Since hole-phonon scattering rates increase with increasing hole energy, the conductivity decreases with illumination. For hole densities between about 10^{14} and 4×10^{15} cm^{-3}, $(-\Delta\sigma/\sigma I)$ is essentially independent of N_h. In this region hole-impurity scattering makes a negligible contribution to the scattering rates. For hole densities greater than about 4×10^{15} cm^{-3}, $(-\Delta\sigma/\sigma I)$ decreases with increasing N_h. In this regime, hole-impurity scattering begins to play a role in limiting the mobility. Hole-impurity scattering

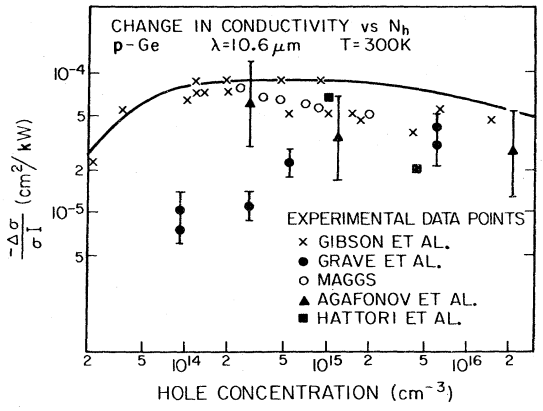

FIG. 1. Values of $(-\Delta\sigma/\sigma I)$ versus the hole concentration in p-Ge for CO_2 laser excitation at 10.6 μm, room temperature, and low light intensities. The calculated values of $(-\Delta\sigma/\sigma I)$ are shown by the solid curve. The experimental data are taken from ×, Ref. 4; ▲, Ref. 5; ■, Ref. 6; ●, Ref. 7; and o, Ref. 9. Error bars are reported only in Refs. 5 and 7.

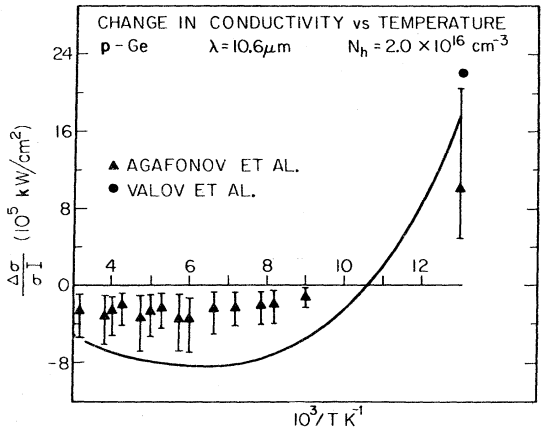

FIG. 2. Calculated values of the normalized change in the conductivity of p-Ge versus temperature for light at 10.6 μm, a hole concentration of 2.0×10^{16} cm^{-3}, and low-intensity excitation. The experimental data are taken from: ▲, Ref. 5 and ●, Ref. 3. Error bars are only reported in Ref. 5.

rates decrease with increasing hole energy. As a result the fractional increase in the total scattering rate (hole-phonon plus hole-impurity) does not increase as much with increasing hole energy in the more heavily doped samples. In addition, the hole distribution is not as strongly modified by illumination of a given intensity in the more heavily doped samples due to the increase in hole-ionized-impurity and hole-hole scattering which tends to maintain the equilibrium distribution. For hole densities less than about 10^{14} cm^{-3}, $(-\Delta\sigma/\sigma I)$ decreases with decreasing hole density. This decrease is due to the increased contribution to the conductivity of free electrons whose distribution is not strongly modified by illumination. (In Ge at 300 K, the intrinsic density is about 2×10^{13} cm^{-3}.)

Also shown in Fig. 1 are the available experimental results. There is considerable variation in the results reported by the various authors. Our calculated values are in fairly good agreement with the data of Gibson *et al.*[4] and those of Maggs.[9]

In Fig. 2 we present our results for the temperature dependence of $(\Delta\sigma/\sigma I)$ for a hole concentration of 2×10^{16} cm^{-3}. We choose this value for the hole density since experimental measurements exist and the change in the conductivity was observed to change sign over the temperature range that was reported.[5] We note that the change in the conducitivity is negative for temperatures greater than about 100 K and becomes positive for lower temperatures. In the higher-temperature regime, hole-phonon scattering plays a greater role in determining the momentum relaxation than hole-impurity scattering, and thus the conductivity decreases upon illumination. In the lower-temperature regime hole-ionized-impurity scattering dominates the momentum relaxation and the conducitivity increases upon illumination. The temperature at which $\Delta\sigma$ changes sign depends on the doping level. At lower doping levels, the sign change in $\Delta\sigma$ occurs at lower temperatures. This effect has been observed experimentally.[5] In addition, we note that the magnitude of $|\Delta\sigma/\sigma I|$ decreases as the temperature increases from about 150K. This decrease is due to an increase in the rate of phonon scattering at the higher temperatures. As a result of the increased scattering rate, the hole distribution is less strongly modified by a given light intensity at the higher temperatures. The experimental results of Refs. 3 and 5 are included in Fig. 2. The data show the same qualitative features as the calculated results. The calculation gives somewhat larger values for $|\Delta\sigma/\sigma I|$ than were observed in Ref. 5. From Fig. 1 we note that the room-temperature results reported in Ref. 5 are systematicallly smaller than those of Refs. 4 and 9.

Because of interest in the performance of photon-drag detectors at high laser intensities,[8-10] we also examine the photoconductive response of p-Ge at intensities for which saturation effects are important. In Fig. 3 we present the results of our calculation of $(-\Delta\sigma/\sigma I)$ as a function of N_h for different light intensities. The curve for 0.05 MW/cm^2 is in the linear regime. At the higher intensities, $(-\Delta\sigma/\sigma)$ increases with increasing intensity at a rate which is slower than

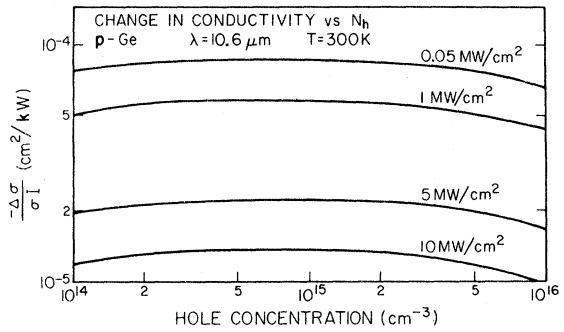

FIG. 3. Values of $(-\Delta\sigma/\sigma I)$ versus the hole concentration in p-Ge for $\lambda = 10.6$ μm and $T = 300$ K. The solid curves are our calculated values for intensities of 0.05 (linear regime), 1, 5, and 10 MW/cm^2.

linear. The nonlinear behavior is due to saturation of the intervalence-band transitions. The shapes of the curves at any given intensity are similar. We are not aware of any direct measurements of $(\Delta\sigma/\sigma I)$ at these high intensities; however, both saturable absorption[19,20] and nonlinear photon-drag voltages[9,10] have been seen experimentally. It is possible that this saturation effect could account for some of the variation in the experimental results shown in Fig. 1.

IV. SUMMARY AND CONCLUSIONS

We have presented a theory of the photoconductive response of p-Ge for light with a wavelength of 10.6 μm. Values of $(\Delta\sigma/\sigma I)$ are calculated as a function of doping level in the low-intensity regime at room temperature. We have also reported the temperature dependence of $(\Delta\sigma/\sigma I)$ at a fixed hole concentration in the low-intensity regime. The effect of saturation at high light intensities was investigated. The theory presented can be applied to other p-type semiconductors with a valence-band structure similar to that of Ge.

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[1]W. Kaiser, R. J. Collins, and H. Y. Fan, Phys. Rev. 91, 1342 (1953).
[2]A. M. Danishevskii, A. A. Kastal'skii, B. S. Ryvkin, S. M. Ryvkin, and I. D. Yaroshetskii, Zh. Eksp. Teor. Fiz. Pis'ma Red. 10, 470 (1969) [JETP Lett. 10, 302 (1969)].
[3]P. M. Valov, I. D. Yaroshetskii, and I. N. Yassievich, Zh. Eksp. Teor. Fiz. Pis'ma Red. 20, 448 (1974) [JETP Lett. 20, 204 (1974)].
[4]A. F. Gibson and P. N. D. Maggs, J. Phys. D 7, 292 (1974).
[5]V. G. Agafonov, P. M. Valov, B. S. Ryvkin, and I. D. Yarosketskii, Sov. Phys. Semicond. 9, 571 (1975).
[6]H. Hattori, O. Fujitani, and M. Umeno, J. Phys. Soc. Jpn. 36, 485 (1974).
[7]T. Grave and F. Keilmann, Z. Phys. B 32, 347 (1979).
[8]A. F. Gibson, M. F. Kimmitt, P. N. D. Maggs, and B. Norris, J. Appl. Phys. 46, 1413 (1975).
[9]P. J. Bishop, A. F. Gibson, and M. F. Kimmitt, IEEE J. Quantum Electron. QE-9, 1007 (1973). Values of $\Delta\sigma/\sigma I$ quoted in this paper were measured by P. Maggs.
[10]T. Kamibayashi, S. Yonemochi, and T. Miyakawa, Appl. Phys. Lett. 22, 119 (1973).
[11]R. B. James and D. L. Smith, Phys. Rev. B 21, 3502 (1980).
[12]We have assumed that there exist no impact ionization processes in which a hole is sufficiently energetic ($\gtrsim$ the band gap) to relax by an electron-hole pair production. This energy relaxation mechanism may be important at very high intensities; however, the experiments of Ref. 19 indicate that this process is negligible over the range of intensities presented in this paper.
[13]E. O. Kane, J. Phys. Chem. Solids 1, 82 (1956).
[14]J. C. Hensel and K. Suzuki, Phys. Rev. B 9, 4219 (1974).
[15]R. B. James and D. L. Smith, Solid State Commun. 33, 395 (1980).
[16]Hole-hole scattering is included in the calculation of the distribution f^0, but it is not included in the momentum relaxation rates. For hole-hole scattering, the total momentum is not changed; thus, it has little influence on the mobility.
[17]For p-Ge and hole states in the resonant region, τ_h is much greater than τ_l.
[18]P. J. Bishop and A. F. Gibson, Appl. Opt. 12, 2549 (1973).
[19]C. R. Phipps, Jr. and S. J. Thomas, Opt. Lett. 1, 93 (1977).
[20]A. F. Gibson, C. A. Rosito, C. A. Raffo, and M. F. Kimmitt, Appl. Phys. Lett. 21, 356 (1972).