Nonlinear conductivity tensor in graded mixed semiconductors*

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A mixed semiconductor crystal with graded composition (i.e., a heterojunction) is characterized by a position-dependent effective mass, which leads to an additional force acting on free carriers. Taking this force into account, as well as the carrier-concentration gradient, the Boltzmann equation is solved in the presence of two oscillating electric fields of arbitrary frequencies, and a general expression for the second-order conductivity tensor is obtained. This tensor is linear in the effective-mass gradient and in the carrier-concentration gradient, and independent of carrier statistics. Limiting cases $\omega\tau \gg 1$ and $\omega\tau \ll 1$ are discussed in detail. For $\omega\tau \gg 1$, the expected second-harmonic generation associated with the mass gradient is at least comparable with that observed in homogeneous semiconductors. For $\omega\tau \ll 1$, nonlinear effects are much stronger than in a homogeneous material in this frequency range. Measurement of the nonlinear current offers a method of directly determining the effective-mass gradient.

I. INTRODUCTION

In recent years much theoretical and experimental work has been devoted to the investigation of the properties of mixed semiconductor crystals with a graded, slowly varying composition. Many mixed semiconducting alloys can be prepared with composition varying over a wide range. Typical examples are alloys whose two components have similar crystal structure and lattice constants, e.g., $Cd_xHg_{1-x}Te$. The properties of such alloys are usually described in terms of composition-dependent band structure. For mixed crystals with slowly varying composition, band parameters (energy gap, effective mass, etc.) are treated as position dependent.

There are several specific physical effects which can be observed in graded mixed semiconductors. In particular, two groups of effects seem to be of special interest: effects due to position dependence of the energy gap, and those produced by the effective-mass gradient.

Variation of the energy gap with position yields a difference between fields acting on electrons and holes (so-called "quasielectric" fields)[1] and seriously modifies effects such as, for example, the photovoltaic effect[2-6] and the photoelectromagnetic effect.[3,7-9] Energy-gap variation leads also to an anti-Stokes effect, i.e., to the electric field dependence of luminescent spectra in electron-hole recombination.[6,10,11]

Less attention has been paid so far to the effects produced by the effective-mass gradient, although this gradient may be large in narrow-gap graded mixed crystals because of the strong dependence of the effective mass on composition. Influence of the effective-mass gradient on the photovoltaic effect in $Cd_xHg_{1-x}Te$ was already recognized,[5] and this gradient was taken into account also in the calculation of the photocarrier distribution in graded mixed semiconductors.[12]

The classical Hamiltonian for a free particle with position-dependent mass $m^*(\vec{r})$ is

$$H=\vec{p}^2/2m^*(\vec{r})+\epsilon(\vec{r})+U(\vec{r},t)\,, \qquad (1)$$

where $\vec{p}$ is the particle momentum canonically conjugated with $\vec{r}$, and $\epsilon(\vec{r})+U(\vec{r},t)$ is the potential energy in external fields. For free carriers in graded mixed crystals expression (1) was written by Verié.[13] Here $U(\vec{r},t)$ is interpreted as the potential energy induced by a macroscopic external electric field and $\epsilon(\vec{r})$ as the position-dependent band edge in the absence of an external field (i.e., potential energy in the "quasielectric" and macroscopic internal fields for carriers under consideration). Expression (1) turns out to be the classical counterpart of the quantum-mechanical effective-mass Hamiltonian derived in the "virtual-crystal" approximation under the following assumptions[14-16]: The composition (and hence both band edge and effective mass) varies very slowly over the lattice constant; the energy-band extrema are parabolic and nondegenerate; and their locations in the Brillouin zone are independent of composition. If, moreover, the band extrema are spherical and the crystal symmetry is high (e.g., cubic),[16] we obtain expression (1) as the classical limit of the effective-mass Hamiltonian.

From the classical Hamiltonian (1) we obtain equations of motion

$$\dot{\vec{p}}=[\vec{p}^2/2m^{*2}(\vec{r})]\,\nabla_r m^*(\vec{r})-\nabla_r\epsilon(\vec{r})-\nabla_r U(\vec{r},t)\,, \qquad (2)$$

$$\dot{\vec{r}} = \vec{p}/m^*(\vec{r}) \ , \tag{3}$$

which can also be written in the form

$$m^*(\vec{r})\,\ddot{\vec{r}} = -\tfrac{1}{2}\dot{\vec{r}}[\dot{\vec{r}}\cdot\nabla_r m^*(\vec{r})] - \tfrac{1}{2}\dot{\vec{r}}\times[\dot{\vec{r}}\times\nabla_r m^*(\vec{r})] - \nabla_r\epsilon(\vec{r}) - \nabla_r U(\vec{r},t) \ . \tag{4}$$

Thus, the relation of velocity and momentum is similar to that for a particle with constant mass. However, an additional force appears in the equation of motion (2). This force is proportional to $\nabla_r m^*(\vec{r})$ and is independent of momentum direction. Two additional terms appear also in the expression for acceleration, Eq. (4). The first one is parallel (or antiparallel) to the velocity, and the second is perpendicular.

An important feature of the equations of motion (2) and (3) [or Eq. (4)] is that they are nonlinear even for a homogeneous field $-\nabla_r[\epsilon(\vec{r}) + U(\vec{r}, t)]$, in spite of parabolicity of the band. Hence for particles obeying these laws of motion, a nonlinear response to external electric fields may be expected. For an individual particle, this response depends on the initial velocity of the particle. Therefore the Drude approach is inapplicable to calculation of the nonlinear response of a system of particles.

Grinberg and Kastalskii have already suggested the possibility of nonlinear optical effects produced by an effective-mass gradient, and have estimated the nonlinear polarizability of the free-electron gas.[17] However, they used the Drude approach and incorrectly omitted the first term in the equation of motion (2) (see Note added in proof).

The purpose of the present paper is to solve the Boltzmann equation for free carriers obeying Eqs. (2) and (3) in the presence of two oscillating nonuniform electric fields of arbitrary polarizations and frequencies, and to calculate the second-order conductivity tensor for this system. In graded mixed semiconductors the effective-mass gradient is usually accompanied by a band-edge gradient and a carrier-concentration gradient (determined by the previous two). We therefore also take into account the band-edge gradient (as well as the carrier-concentration gradient) in the calculation. The case of several equivalent band extrema is also included.

In Sec. II we solve the Boltzmann equation up to terms of second order in the electric fields and linear in the effective-mass gradient, band-edge gradient, and nonuniformity of electric fields. In Sec. III the second-order conductivity tensor is calculated and discussed. The general results of that section are then applied to the specific cases of low and high frequencies of external electric fields in Sec. IV. As will be shown in Sec. V, the expected second-harmonic generation and combining of frequencies are at least comparable with those observed in homogeneous semiconductors at high frequencies, and significantly stronger at low frequencies.

II. BOLTZMANN EQUATION

In this section we consider a single band extremum. Obviously, if there are several equivalent band extrema, the distribution function, carrier density, current, etc. are the same for all of them.

Suppose two oscillating electric fields of arbitrary polarization and of angular frequency ω_1 and ω_2, respectively, are acting on the carriers, i.e.,

$$-\nabla_r U(\vec{r}, t) = q\,\mathrm{Re}[\vec{E}_1(\vec{r})\,e^{-i\omega_1 t} + \vec{E}_2(\vec{r})e^{-i\omega_2 t}] \ . \tag{5}$$

Here q is the carrier charge, and $\vec{E}_1(\vec{r})$ and $\vec{E}_2(\vec{r})$ are complex vectors. It is assumed that electric fields of the space charges induced by the external oscillating fields are already included in Eq. (5).

We assume that the charge density of ionized impurities (defects) is constant in time. This holds, for example, if ω_1 and ω_2 are much higher than the generation and recombination rates, or if all impurities (defects) are ionized. With this assumption, the sources of field (5) are only the changes in local carrier density.

In the collisionless case the motion of carriers is described by the classical Hamiltonian (1), and Liouville's theorem holds. Therefore, the left-hand side of our Boltzmann equation is

$$\frac{\partial}{\partial t} f + \dot{\vec{p}}\cdot\nabla_p f + \dot{\vec{r}}\cdot\nabla_r f \ , \tag{6}$$

where $f(\vec{p}, \vec{r}, t)$ is the distribution function, and $\dot{\vec{p}}$ and $\dot{\vec{r}}$ are given by Eqs. (2), (3), and (5).

The collision term in the Boltzmann equation will have the simplest form if we assume the existence of a relaxation time τ independent of position and energy (i.e., also of electric fields). However, one should take into account that the carrier density at a given point may oscillate. Then the relaxation process changes the distribution function towards the equilibrium distribution corresponding to the carrier density at a given point and time (see, e.g., Ref. 18). Thus, the right-hand side of the Boltzmann equation is

$$-[f(\vec{p}, \vec{r}, t) - f_0(\vec{p}^2/2m^*(\vec{r}) + \epsilon(\vec{r}) - \eta(\vec{r}, t))]/\tau \ , \tag{7}$$

where f_0 is the Fermi-Dirac distribution function and $\eta(\vec{r}, t)$ is defined by

$$n(\vec{r}, t) = \int f(\vec{p}, \vec{r}, t)\,d^3p = \int f_0(\vec{p}^2/2m^*(\vec{r}) + \epsilon(\vec{r}) - \eta(\vec{r}, t))\,d^3p \ . \tag{8}$$

Here $n(\vec{r}, t)$ denotes the carrier density at a given point and time. By definition, $\eta(\vec{r}, t)$ is the difference between the actual quasi-Fermi level and the Fermi level in the absence of external electric fields. For m^*, ϵ, $\vec{E}_1$, and $\vec{E}_2$ varying not too rapidly in space, it is justified to neglect all terms of the second and higher orders in first derivatives of m^*, ϵ, $\vec{E}_1$, and $\vec{E}_2$, as well as terms involving the second or higher derivatives of m^*, ϵ, $\vec{E}_1$, or $\vec{E}_2$. Also, we will neglect all terms of the third and higher orders in $\vec{E}_1$, $\vec{E}_2$, and their derivatives.

If $\nabla_r m^*(\vec{r}) \equiv 0$, $\nabla_r \epsilon(\vec{r}) \equiv 0$, and the fields $\vec{E}_1$ and $\vec{E}_2$ are uniform, then $\eta(\vec{r}, t) \equiv 0$ even in the presence of $\vec{E}_1$ and $\vec{E}_2$. Therefore $\eta(\vec{r}, t)$ is of at least first order in $\nabla_r m^*$, $\nabla_r \epsilon$, or first derivatives of $\vec{E}_1$ or $\vec{E}_2$, and we can expand

$$f_0(\vec{p}^2/2m^*(\vec{r}) + \epsilon(\vec{r}) - \eta(\vec{r}, t)) \cong f_0 - f_0'\eta(\vec{r}, t) . \quad (9)$$

In the right-hand side of Eq. (9) and everywhere in the following, the argument of f_0, f_0', f_0'', etc. is $(\vec{p}^2/2m^*(\vec{r}) + \epsilon(\vec{r}))$, and the single and double primes denote first and second derivatives with respect to the argument.

We have

$$\int f_0 d^3p = n_0(\vec{r}) , \quad (10)$$

$$\int f_0' d^3p = -\frac{1}{2} \int [2m^*(\vec{r})/\vec{p}^2] f_0 d^3p$$
$$= -\tfrac{1}{2} n_0(\vec{r}) \langle \mathcal{E}^{-1} \rangle , \quad (11)$$

where $n_0(\vec{r})$ and $\langle \mathcal{E}^{-1} \rangle$ (also depending on $\vec{r}$) denote the carrier concentration and the average reciprocal kinetic energy, respectively, in the absence of external electric fields. Integrating Eq. (9) and making use of Eqs. (8), (10), and (11), we obtain

$$\eta = 2\langle \mathcal{E}^{-1} \rangle^{-1} (n - n_0)/n_0 . \quad (12)$$

Of course, $n - n_0$ is of at least first order in $\nabla_r m^*$, $\nabla_r \epsilon$, or first derivatives of $\vec{E}_1$ or $\vec{E}_2$.

From Eqs. (9) and (12), the collision term (7) has the form

$$-[f - f_0 + 2\langle \mathcal{E}^{-1} \rangle^{-1} f_0'(n - n_0)/n_0]/\tau . \quad (13)$$

We shall calculate $n - n_0$ using the equation of continuity

$$-\frac{\partial}{\partial t}(n - n_0) = q^{-1} \nabla_r \cdot \vec{J} , \quad (14)$$

where $\vec{J}(\vec{r}, t)$ is the free-carrier current density. As was already mentioned, we perform all calculations keeping only terms independent of and linear in $\nabla_r m^*$, $\nabla_r \epsilon$, or first derivatives of $\vec{E}_1$ or $\vec{E}_2$. Thus, we neglect the contribution to $\nabla_r \cdot \vec{J}$ from the part of $\vec{J}$ linear in $\nabla_r m^*$, $\nabla_r \epsilon$, or first derivatives of $\vec{E}_1$ or $\vec{E}_2$. The part of $\vec{J}$ independent of $\nabla_r m^*$, $\nabla_r \epsilon$ and of first derivatives of $\vec{E}_1$ or $\vec{E}_2$ does not involve terms of the second order in $\vec{E}_1$ and/or $\vec{E}_2$ because of inversion symmetry. Therefore the only contribution to $\nabla_r \cdot \vec{J}$ is given by terms of $\vec{J}$ independent of $\nabla_r m^*$, $\nabla_r \epsilon$ and of first derivatives of $\vec{E}_1$ and $\vec{E}_2$, and linear in $\vec{E}_1$ or $\vec{E}_2$. These terms have the same form as for a homogeneous semiconductor in a uniform field but with the local values of m^*, n_0, $\vec{E}_1$, and $\vec{E}_2$:

$$\sigma^1(\omega_1, \vec{r}) \vec{E}_1(\vec{r}) e^{-i\omega_1 t} + \sigma^1(\omega_2, \vec{r}) \vec{E}_2(\vec{r}) e^{-i\omega_2 t} , \quad (15)$$

where

$$\sigma^1(\omega, \vec{r}) = q^2 n_0(\vec{r}) \tau_\omega / m^*(\vec{r}) , \quad (16)$$

$$\tau_\omega = \tau/(1 - i\omega\tau) . \quad (17)$$

In Eqs. (15)–(17) and everywhere in the following we use complex quantities; of course, only their real parts have physical meaning.

As was already mentioned, the sources of field (5) are only the changes in local carrier density:

$$\kappa(\omega_1) \nabla_r \cdot \vec{E}_1 e^{-i\omega_1 t} + \kappa(\omega_2) \nabla_r \cdot \vec{E}_2 e^{-i\omega_2 t} = 4\pi q (n - n_0) . \quad (18)$$

Here $\kappa(\omega)$ is the lattice dielectric constant at the frequency ω, assumed to be position-independent.

Inserting Eq. (15) into Eq. (14), using (18), and solving for $n - n_0$, we obtain

$$n - n_0 = \frac{q n_0 \tau^2}{m^*} \left(\frac{\nabla_r m^*}{m^*} - \frac{\nabla_r n_0}{n_0} \right)$$
$$\cdot \{ [(\Omega_{\omega_1}^2 - \omega_1^2)\tau^2 - i\omega_1\tau]^{-1} \vec{E}_1 e^{-i\omega_1 t}$$
$$+ [(\Omega_{\omega_2}^2 - \omega_2^2)\tau^2 - i\omega_2\tau]^{-1} \vec{E}_2 e^{-i\omega_2 t} \} , \quad (19)$$

where Ω_ω is the plasma frequency

$$\Omega_\omega^2 = 4\pi q^2 n_0 / \kappa(\omega) m^* . \quad (20)$$

Writing Eq. (18) [or, rather, writing Eq. (5)], we have assumed implicitly that there is no time-independent part $N(\vec{r})$ of $n - n_0$ (and no time-independent part of $\nabla_r U$). In fact, $N(\vec{r})$ vanishes, as can be seen from the following argument. $N(\vec{r})$ should be linear in $\nabla_r m^*$, $\nabla_r \epsilon$, or first derivatives of $\vec{E}_1$ or $\vec{E}_2$. Terms of the second order in and independent of $\vec{E}_1$ and $\vec{E}_2$ and linear in $\nabla_r m^*$ or $\nabla_r \epsilon$ vanish because of inversion symmetry. The same is true for terms of the first order in $\vec{E}_1$ or $\vec{E}_2$ and linear in first derivatives of $\vec{E}_1$ or $\vec{E}_2$. If we shift the origin of the time scale, $\vec{E}_1$, $\vec{E}_2$ and their derivatives are multiplied by phase factors. This will change the values of the remaining terms. On the other hand, $N(\vec{r})$ is independent of time and, consequently, of the choice of its origin. Therefore, $N(\vec{r})$ vanishes.

One can observe from Eq. (19) that in the particular case of $\vec{E}_1$, $\vec{E}_2$ perpendicular to $\nabla_r m^*$, $\nabla_r n_0$, the quantity $n - n_0 \equiv 0$ and the collision term is of the usual form $-(f-f_0)/\tau$. It can also be seen that $n-n_0$ is independent of carrier statistics and depends only on carrier concentration.

Expressions (10) and (11) yield

$$\nabla_r n_0 = \tfrac{3}{2} n_0 (\nabla_r m^*/m^*) - \tfrac{1}{2} n_0 \langle \mathcal{E}^{-1}\rangle \nabla_r \epsilon \,. \tag{21}$$

From Eqs. (2), (3), (5), (6), (13), (19), and (21) we finally obtain the Boltzmann equation in the form

$$\frac{\partial}{\partial t} f + [(\vec{p}^2/2m^{*2})\nabla_r m^* - \nabla_r\epsilon + q\,\mathrm{Re}(\vec{E}_1 e^{-i\omega_1 t} + \vec{E}_2 e^{-i\omega_2 t})]\cdot\nabla_p f + (\vec{p}/m^*)\cdot\nabla_r f$$
$$= -\left[f - f_0 + \left(\frac{q\tau^2}{m^*}\right) f_0'\left(\nabla_r\epsilon - \langle\mathcal{E}^{-1}\rangle^{-1}\frac{\nabla_r m^*}{m^*}\right)\cdot\{[(\Omega_{\omega_1}^2-\omega_1^2)\tau^2 - i\omega_1\tau]^{-1}\vec{E}_1 e^{-i\omega_1 t} + [(\Omega_{\omega_2}^2 - \omega_2^2)\tau^2 - i\omega_2\tau]^{-1}\vec{E}_2 e^{-i\omega_2 t}\}\right]\frac{1}{\tau}\,. \tag{22}$$

The distribution function f can be expanded in powers of $\vec{E}_1$, $\vec{E}_2$, and of first and higher derivatives of $\vec{E}_1$, $\vec{E}_2$, m^*, and ϵ. The coefficients of this expansion are functions of m^* and ϵ. We insert f in that form into Eq. (22) and then neglect all terms of the second and higher orders in first derivatives of m^*, ϵ, $\vec{E}_1$, and $\vec{E}_2$, and terms involving the second or higher derivatives of m^*, ϵ, $\vec{E}_1$, or $\vec{E}_2$. We neglect also all terms of the third and higher orders in $\vec{E}_1$, $\vec{E}_2$ and their derivatives. Comparing coefficients, we obtain a set of recurrent equations. Solving them, we find

$$f(\vec{p},\vec{r},t) = f_0 + \varphi^1(\omega_1)\vec{E}_1 e^{-i\omega_1 t} + \varphi^1(\omega_2)\vec{E}_2 e^{-i\omega_2 t} + \varphi^2(\omega_1,-\omega_1)\vec{E}_1\vec{E}_1^* + \varphi^2(\omega_2,-\omega_2)\vec{E}_2\vec{E}_2^* + \varphi^2(\omega_1,\omega_1)\vec{E}_1\vec{E}_1 e^{-2i\omega_1 t}$$
$$+ \varphi^2(\omega_2,\omega_2)\vec{E}_2\vec{E}_2 e^{-2i\omega_2 t} + 2\varphi^2(\omega_1,\omega_2)\vec{E}_1\vec{E}_2 e^{-i(\omega_1+\omega_2)t} + 2\varphi^2(\omega_1,-\omega_2)\vec{E}_1\vec{E}_2^* e^{-i(\omega_1-\omega_2)t}\,, \tag{23}$$

where φ^1 and φ^2 are tensors of first and second rank, respectively, defined by

$$\varphi^1(\omega)\vec{E} = -\left(q\frac{\tau_\omega}{m^*}\right) f_0'\left[\vec{E}\cdot\vec{p} + (\vec{E}\cdot\nabla_r\epsilon)\{\tau_\omega + \tau[(\Omega_\omega^2-\omega^2)\tau^2 - i\omega\tau]^{-1}\} - \left(\vec{E}\cdot\frac{\nabla_r m^*}{m^*}\right)\right.$$
$$\left.\times\left(\frac{\vec{p}^2\tau_\omega}{2m^*} + \tau[(\Omega_\omega^2-\omega^2)\tau^2 - i\omega\tau]^{-1}\langle\mathcal{E}^{-1}\rangle^{-1}\right) + \frac{\tau_\omega}{m^*}(\vec{E}\cdot\vec{p})\left(\vec{p}\cdot\frac{\nabla_r m^*}{m^*}\right) - \frac{\tau_\omega}{m^*}[\vec{p}\cdot\nabla_r(\vec{E}\cdot\vec{p})]\right]\,, \tag{24}$$

$$\varphi^2(\omega',\omega'')\vec{E}'\vec{E}'' = \frac{q^2\tau_{\omega'+\omega''}}{4m^*} f_0'\left[(\tau_{\omega'}+\tau_{\omega''})(\vec{E}'\cdot\vec{E}'') + (\tau_{\omega'}^2 - \tau_{\omega''}^2)m^{*-1}(\vec{E}'\cdot\vec{p})\left(\vec{E}''\cdot\frac{\nabla_r m^*}{m^*}\right)\right.$$
$$- (\tau_{\omega'}^2 - \tau_{\omega''}^2)m^{*-1}\left(\vec{E}'\cdot\frac{\nabla_r m^*}{m^*}\right)(\vec{E}''\cdot\vec{p}) + [\tau_{\omega'}^2 + \tau_{\omega''}^2 + \tau_{\omega'+\omega''}(\tau_{\omega'}+\tau_{\omega''})]$$
$$\times m^{*-1}(\vec{E}'\cdot\vec{E}'')\left(\vec{p}\cdot\frac{\nabla_r m^*}{m^*}\right) - \tau_{\omega'}^2 m^{*-1}[\vec{E}''\cdot\nabla_r(\vec{E}'\cdot\vec{p})] - \tau_{\omega''}^2 m^{*-1}[\vec{E}'\cdot\nabla_r(\vec{E}''\cdot\vec{p})]$$
$$\left. - [\tau_{\omega''}^2 + \tau_{\omega'+\omega''}(\tau_{\omega'}+\tau_{\omega''})]m^{*-1}\vec{E}'\cdot[(\vec{p}\cdot\nabla_r)\vec{E}''] - [\tau_{\omega'}^2 + \tau_{\omega'+\omega''}(\tau_{\omega'}+\tau_{\omega''})]m^{*-1}\vec{E}''\cdot[(\vec{p}\cdot\nabla_r)\vec{E}']\right]$$
$$+ \frac{q^2\tau_{\omega'+\omega''}}{4m^{*2}} f_0''\left[(\tau_{\omega'}+\tau_{\omega''})(\vec{E}'\cdot\vec{p})(\vec{E}''\cdot\vec{p}) + \{\tau_{\omega'}^2 + \tau_{\omega'+\omega''}(\tau_{\omega'}+\tau_{\omega''}) + \tau\tau_{\omega'}[(\Omega_{\omega'}^2 - \omega'^2)\tau^2 - i\omega'\tau]^{-1}\}\right.$$
$$\times(\vec{E}'\cdot\nabla_r\epsilon)(\vec{E}''\cdot\vec{p}) + \{\tau_{\omega''}^2 + \tau_{\omega'+\omega''}(\tau_{\omega'}+\tau_{\omega''}) + \tau\tau_{\omega''}[(\Omega_{\omega''}^2 - \omega''^2)\tau^2 - i\omega''\tau]^{-1}\}$$
$$\times(\vec{E}'\cdot\vec{p})(\vec{E}''\cdot\nabla_r\epsilon) - \left([\tau_{\omega'}^2 + \tau_{\omega'+\omega''}(\tau_{\omega'}+\tau_{\omega''})]\frac{\vec{p}^2}{2m^*} + \tau\tau_{\omega'}[(\Omega_{\omega'}^2 - \omega'^2)\tau^2 - i\omega'\tau]^{-1}\langle\mathcal{E}^{-1}\rangle^{-1}\right)$$
$$\times\left(\vec{E}'\cdot\frac{\nabla_r m^*}{m^*}\right)(\vec{E}''\cdot\vec{p}) - \left([\tau_{\omega''}^2 + \tau_{\omega'+\omega''}(\tau_{\omega'}+\tau_{\omega''})]\frac{\vec{p}^2}{2m^*} + \tau\tau_{\omega''}[(\Omega_{\omega''}^2 - \omega''^2)\tau^2 - i\omega''\tau]^{-1}\right.$$
$$\left.\times\langle\mathcal{E}^{-1}\rangle^{-1}\right)(\vec{E}'\cdot\vec{p})\left(\vec{E}''\cdot\frac{\nabla_r m^*}{m^*}\right) + [\tau_{\omega'}^2 + \tau_{\omega''}^2 + 2\tau_{\omega'+\omega''}(\tau_{\omega'}+\tau_{\omega''})]m^{*-1}\left(\vec{p}\cdot\frac{\nabla_r m^*}{m^*}\right)$$
$$\times(\vec{E}'\cdot\vec{p})(\vec{E}''\cdot\vec{p}) - [\tau_{\omega'}^2 + \tau_{\omega'+\omega''}(\tau_{\omega'}+\tau_{\omega''})]m^{*-1}[\vec{p}\cdot\nabla_r(\vec{E}'\cdot\vec{p})](\vec{E}''\cdot\vec{p})$$
$$\left. - [\tau_{\omega''}^2 + \tau_{\omega'+\omega''}(\tau_{\omega'}+\tau_{\omega''})]m^{*-1}(\vec{E}'\cdot\vec{p})[\vec{p}\cdot\nabla_r(\vec{E}''\cdot\vec{p})]\right]\,. \tag{25}$$

III. CONDUCTIVITY

Because of relation (3), the current density is given by

$$\vec{J}(\vec{r},t)=\frac{q}{m^*}\int \vec{p}f(\vec{p},\vec{r},t)\,d^3p\ .$$

Integrating Eqs. (23)–(25), expressing $\nabla_r\epsilon$ by $\nabla_r n_0$ [see Eq. (21)], and using Eq. (18) and (19) to eliminate $\nabla_r\cdot\vec{E}_1$ and $\nabla_r\cdot\vec{E}_2$, we obtain

$$\vec{J}(\vec{r},t)=\sigma^1(\omega_1)\vec{E}_1e^{-i\omega_1t}+\sigma^1(\omega_2)\vec{E}_2e^{-i\omega_2t}+\sigma^2(\omega_1,-\omega_1)\vec{E}_1\vec{E}_1^*+\sigma^2(\omega_2,-\omega_2)\vec{E}_2\vec{E}_2^*+\sigma^2(\omega_1,\omega_1)\vec{E}_1\vec{E}_1e^{-2i\omega_1t}$$
$$+\sigma^2(\omega_2,\omega_2)\vec{E}_2\vec{E}_2e^{-2i\omega_2t}+2\sigma^2(\omega_1,\omega_2)\vec{E}_1\vec{E}_2e^{-i(\omega_1+\omega_2)t}+2\sigma^2(\omega_1,-\omega_2)\vec{E}_1\vec{E}_2^*e^{-i(\omega_1-\omega_2)t}\ , \qquad (26)$$

where σ^1 is given by Eq. (16), and the third rank tensor σ^2, which determines the nonlinear contribution to the current, is defined by

$$\sigma^2(\omega',\omega'')\vec{E}'\vec{E}''=\left(q^3\,\frac{\tau^2_{\omega'+\omega''}(\tau_{\omega'}+\tau_{\omega''})n_0}{4m^{*2}}\right)\left\{\frac{\omega''\tau^2}{i\tau_{\omega''}[(\Omega^2_{\omega''}-\omega''^2)\tau^2-i\omega''\tau]}\left(1+\frac{i\tau_{\omega''}}{\omega''\tau_{\omega'+\omega''}(\tau_{\omega'}+\tau_{\omega''})}\right)\right.$$
$$\times\left[\vec{E}''\cdot\left(\frac{\nabla_rm^*}{m^*}-\frac{\nabla_rn_0}{n_0}\right)\right]\vec{E}'+\frac{\omega'\tau^2}{i\tau_{\omega'}[(\Omega^2_{\omega'}-\omega'^2)\tau^2-i\omega'\tau]}\left(1+\frac{i\tau_{\omega'}}{\omega'\tau_{\omega'+\omega''}(\tau_{\omega'}+\tau_{\omega''})}\right)$$
$$\left.\times\left[\vec{E}'\cdot\left(\frac{\nabla_rm^*}{m^*}-\frac{\nabla_rn_0}{n_0}\right)\right]\vec{E}''+(\vec{E}'\cdot\vec{E}'')\frac{\nabla_rm^*}{m^*}-(\vec{E}'\cdot\nabla_r)\vec{E}''-(\vec{E}''\cdot\nabla_r)\vec{E}'\right\}\ . \qquad (27)$$

Obviously,

$$\sigma^2(\omega',\omega'')\vec{E}'\vec{E}''=\sigma^2(\omega'',\omega')\vec{E}''\vec{E}'\ ,$$

$$\sigma^2(\omega',\omega'')\vec{E}'\vec{E}''=\sigma^{2*}(-\omega',-\omega'')\vec{E}'\vec{E}''.$$

Integrating Eqs. (23)–(25) one can calculate n and check Eq. (19) and continuity equation (14). One can also observe that the second-order terms in current are produced by both ∇_rm^* and ∇_rn_0, and also by nonuniformity of electric fields.

An important feature of the second-order conductivity tensor σ^2 given by Eq. (27) is that it is independent of carrier statistics and depends only on carrier density. The sign of σ^2 depends on the sign of the carrier charge.

It appears that the case of $\vec{E}_1$, $\vec{E}_2$ perpendicular to

$$\frac{\nabla_rm^*}{m^*}-\frac{\nabla_rn_0}{n_0}$$

is of particular interest. As was already mentioned, carrier density is then time independent. The electric fields may therefore be uniform. In that case only the third term in Eq. (27) does not vanish, and second-order components of the current density are parallel to the effective-mass gradient and do not depend on the carrier-density gradient.

For several equivalent band extrema the distribution function, carrier density and current density are the same for each extremum, and are given by Eqs. (16), (19), (20), and (23)–(27). One has only to remember that n_0 denotes the equilibrium carrier concentration in a single extremum, except for Eq. (20) where n_0 is the total carrier concentration. Summing up contributions from all extrema one obtains the total carrier and current densities expressed by the same expressions (16), (19), (20), (26), and (27), but with n_0 denoting everywhere the total carrier concentration.

IV. LIMITING CASES

In this section we will present approximate expressions for the second-order conductivity tensor in different ranges of frequencies ω' and ω''. There are four limiting cases which are all discussed in the following.

A. $|\omega'|,|\omega''|\ll 1/\tau$

Keeping only terms of the lowest order in $|\omega'|\tau$ and $|\omega''|\tau$ we obtain from Eq. (27)

$$\sigma^2(\omega',\omega'')\vec{E}'\vec{E}''\cong\left(\frac{q^3\tau^3n_0}{2m^{*2}}\right)\left\{\frac{1}{2}[(\Omega^2_{\omega''}-\omega''^2)\tau^2-i\omega''\tau]^{-1}\left[\vec{E}''\cdot\left(\frac{\nabla_rm^*}{m^*}-\frac{\nabla_rn_0}{n_0}\right)\right]\vec{E}'+\tfrac{1}{2}[(\Omega^2_{\omega'}-\omega'^2)\tau^2-i\omega'\tau]^{-1}\right.$$
$$\left.\times\left[\vec{E}'\cdot\left(\frac{\nabla_rm^*}{m^*}-\frac{\nabla_rn_0}{n_0}\right)\right]\vec{E}''+(\vec{E}'\cdot\vec{E}'')\frac{\nabla_rm^*}{m^*}-(\vec{E}'\cdot\nabla_r)\vec{E}''-(\vec{E}''\cdot\nabla_r)\vec{E}'\right\}\ . \qquad (28)$$

If $\vec{E}'$ and $\vec{E}''$ are perpendicular to

$$\frac{\nabla_r m^*}{m^*} - \frac{\nabla_r n_0}{n_0},$$

the second-order conductivity tensor does not depend on frequencies ω' and ω''.

B. $|\omega'| \ll 1/\tau \ll |\omega''|$

Here we keep only terms of the lowest order in $|\omega'|\tau$ and in $(|\omega''|\tau)^{-1}$, obtaining

$$\sigma^2(\omega', \omega'')\vec{E}'\vec{E}'' \cong -\left(\frac{q^3\tau n_0}{4m^{*2}\omega''^2}\right)\Bigg\{-\omega''^2\tau^2[(\Omega^2_{\omega''} - \omega''^2)\tau^2 - i\omega''\tau]^{-1}\left[\vec{E}''\cdot\left(\frac{\nabla_r m^*}{m^*} - \frac{\nabla_r n_0}{n_0}\right)\right]\vec{E}'$$
$$- i\omega''\tau[(\Omega^2_{\omega'} - \omega'^2)\tau^2 - i\omega'\tau]^{-1}\left[\vec{E}'\cdot\left(\frac{\nabla_r m^*}{m^*} - \frac{\nabla_r n_0}{n_0}\right)\right]\vec{E}'' + (\vec{E}'\cdot\vec{E}'')\frac{\nabla_r m^*}{m^*}$$
$$- (\vec{E}'\cdot\nabla_r)\vec{E}'' - (\vec{E}''\cdot\nabla_r)\vec{E}'\Bigg\}. \tag{29}$$

If $\vec{E}'$ and $\vec{E}''$ are perpendicular to

$$\frac{\nabla_r m^*}{m^*} - \frac{\nabla_r n_0}{n_0},$$

the second-order conductivity tensor depends only on the higher frequency ω''. We thus have a type of electro-optical effect.

C. $|\omega'|, |\omega''| \gg 1/\tau, |\omega' + \omega''| \ll 1/\tau$

In this case we retain only terms of the lowest order in $(|\omega'|\tau)^{-1}$, $(|\omega''|\tau)^{-1}$ and $|\omega' + \omega''|\tau$. This yields

$$\sigma^2(\omega', \omega'')\vec{E}'\vec{E}'' \cong \left(\frac{q^3\tau n_0}{2m^{*2}|\omega'\omega''|}\right)\Bigg\{-\tfrac{1}{2}\omega''^2\tau^2[(\Omega^2_{\omega''} - \omega''^2)\tau^2 - i\omega''\tau]^{-1}\left[\vec{E}''\cdot\left(\frac{\nabla_r m^*}{m^*} - \frac{\nabla_r n_0}{n_0}\right)\right]\vec{E}'$$
$$- \tfrac{1}{2}\omega'^2\tau^2[(\Omega^2_{\omega'} - \omega'^2)\tau^2 - i\omega'\tau]^{-1}\left[\vec{E}'\cdot\left(\frac{\nabla_r m^*}{m^*} - \frac{\nabla_r n_0}{n_0}\right)\right]\vec{E}'' + (\vec{E}'\cdot\vec{E}'')\frac{\nabla_r m^*}{m^*}$$
$$- (\vec{E}'\cdot\nabla_r)\vec{E}'' - (\vec{E}''\cdot\nabla_r)\vec{E}'\Bigg\}. \tag{30}$$

D. $|\omega'|, |\omega''|, |\omega' + \omega''| \gg 1/\tau$

Keeping only terms of the lowest order in $(|\omega'|\tau)^{-1}$, $(|\omega''|\tau)^{-1}$, and $(|\omega' + \omega''|\tau)^{-1}$, we obtain from Eq. (27)

$$\sigma^2(\omega', \omega'')\vec{E}'\vec{E}'' \cong -\left(\frac{iq^3 n_0}{4m^{*2}\omega'\omega''(\omega' + \omega'')}\right)\Bigg\{-\omega''(\omega' + \omega'')\tau^2[(\Omega^2_{\omega''} - \omega''^2)\tau^2 - i\omega''\tau]^{-1}\left[\vec{E}''\cdot\left(\frac{\nabla_r m^*}{m^*} - \frac{\nabla_r n_0}{n_0}\right)\right]\vec{E}'$$
$$- \omega'(\omega' + \omega'')\tau^2[(\Omega^2_{\omega'} - \omega'^2)\tau^2 - i\omega'\tau]^{-1}\left[\vec{E}'\cdot\left(\frac{\nabla_r m^*}{m^*} - \frac{\nabla_r n_0}{n_0}\right)\right]\vec{E}'' + (\vec{E}'\cdot\vec{E}'')\frac{\nabla_r m^*}{m^*}$$
$$- (\vec{E}'\cdot\nabla_r)\vec{E}'' - (\vec{E}''\cdot\nabla_r)\vec{E}'\Bigg\}. \tag{31}$$

If $\Omega_{\omega'}\tau \gg 1$ (or $\Omega_{\omega''}\tau \gg 1$), σ^2 has a resonancelike behavior in cases B, C, and D for $\omega' \sim \Omega_{\omega'}$ (or $\omega'' \sim \Omega_{\omega''}$).

V. DISCUSSION OF RESULTS

We shall not consider here the detailed behavior of the general expressions for the second-order conductivity tensor, Eqs. (26) and (27). In particular, combining of frequencies (heterodyning), and effects originating specifically from the carrier density gradient and from nonuniformity of electric fields are not discussed at this point. We shall restrict further consideration to the case of a single electric field (i.e., $\vec{E}_2 = 0$) perpendicular to

$$\frac{\nabla_r m^*}{m^*} - \frac{\nabla_r n_0}{n_0},$$

and we shall assume that this field is uniform. We shall present some semiquantitative estimates for both frequency regions $\omega_1 \ll 1/\tau$ and $\omega_1 \gg 1/\tau$. For simplicity the subscript 1 will be omitted in the following. This case appears to be the most interesting (and the most practical) from the experimental point of view.

A. $\omega \ll 1/\tau$

From Eqs. (16), (26), and (28) we have

$$\vec{J}(\vec{r}, t) \cong \left(\frac{q^2 \tau n_0}{m^*}\right)\vec{E}\, e^{-i\omega t} + \left(\frac{q^3 \tau^3 n_0}{2m^{*2}}\right)\frac{\nabla_r m^*}{m^*} \times (\vec{E}\cdot\vec{E}^* + \vec{E}\cdot\vec{E}\, e^{-2i\omega t}). \quad (32)$$

For a linearly polarized electric field, $\vec{E}$ is real, and

$$\mathrm{Re}\,\vec{J}(\vec{r}, t) \cong \left(\frac{q^2 \tau n_0}{m^*}\right)\vec{E}\cos\omega t + \left(\frac{q^3 \tau^3 n_0}{2m^{*2}}\right)\vec{E}^2 \times \frac{\nabla_r m^*}{m^*}(1+\cos 2\omega t)\ . \quad (33)$$

Thus, the uniform electric field of frequency ω perpendicular to the effective-mass and carrier-density gradients produces a current density parallel to the effective-mass gradient. This current density is proportional to $\cos^2\omega t$, i.e., it has a time-independent component and a component oscillating with the frequency 2ω.

Instead of measuring the oscillating component of current parallel to the effective-mass gradient one can measure the electric field $\vec{E}_{comp}\cos 2\omega t$ compensating this current. From Eqs. (16) and (33)

$$\vec{E}_{comp}/\vec{E}^2 = \tfrac{1}{2} q\tau^2 \nabla_r (m^{*-1}) = -(\mu^2/2q)\nabla_r m^*\ , \quad (34)$$

where $\mu(\vec{r}) = |q|\,\tau/m^*(\vec{r})$ is the carrier mobility. If $\mu(\vec{r})$ is approximately constant between the points $\vec{r}_1$ and $\vec{r}_2$, the compensating potential difference between these points is

$$U_{comp}(\vec{r}_2) - U_{comp}(\vec{r}_1) = (\mu^2/2q)[m^*(\vec{r}_2) - m^*(\vec{r}_1)]\,\vec{E}^2\ . \quad (35)$$

It can be noted that Eq. (34) may be derived in a less formal but simpler and more intuitive way without explicitly solving the Boltzmann equation up to terms linear in $\nabla_r m^*$ and $\nabla_r \epsilon$. From the solution of the standard Boltzmann equation for free carriers (in the case of $\nabla_r m^* \equiv 0$ and $\nabla_r \epsilon \equiv 0$) one finds that the oscillating part of average $\vec{p}^2$ is

$$m^{*2}\mu^2\vec{E}^2\cos 2\omega t\ ,$$

and this gives a contribution to the average $\dot{\vec{p}}$ [see Eq. (2)].

This contribution is to be canceled by the electric field $\vec{E}_{comp}\cos 2\omega t$. Thus from Eq. (2) one obtains

$$(m^{*2}\mu^2\vec{E}^2\cos 2\omega t/2m^{*2})\nabla_r m^* + q\vec{E}_{comp}\cos 2\omega t = 0$$

and, consequently, Eq. (34).

Let us put $|\nabla_r m^*| \approx 4m_0/\mathrm{cm}$ (m_0 is the free-electron mass) and $\mu \approx 10^5\ \mathrm{cm^2/V\,sec}$, which correspond roughly to n-type $Hg_{1-x}Cd_xTe$ with x changing from 0 to 1 in a distance of about one millimeter. Equation (34) then gives $\vec{E}_{comp}/\vec{E}^2 \approx 10^{-5}$ cm/V. For $E \approx 1$ V/cm, $E_{comp} \approx 10\ \mu$V/cm. If the sample is 0.2 mm thick, we have $|m^*(\vec{r}_2) - m^*(\vec{r}_1)| \approx 0.08 m_0$ and $|U_{comp}(\vec{r}_2) - U_{comp}(\vec{r}_1)| \approx 0.2\ \mu$V. It seems, therefore, that the effect considered may be used as a method of determining the effective-mass gradient.

In this paper we have not distinguished between the momentum- and energy-relaxation times. If the energy-relaxation time is much longer than the momentum-relaxation time (as it usually is), one may expect strong nonlinear effects from the increase of carrier temperature in the presence of $\nabla_r m^*$ and $\nabla_r n_0$. There is probably one more effect contributing to $\vec{E}_{comp}$, namely, the thermoelectric effect originating from an oscillating inhomogeneous temperature increase produced by the electric current. If the oscillation of lattice temperature is considered, it should decrease rapidly with increasing frequency ω. The carrier temperature oscillations will decrease only for ω higher than the inverse energy-relaxation time. It should also be noted that position dependence of the relaxation time τ, neglected in the present paper, may produce an additional nonlinear current contributing to $\vec{E}_{comp}$.

B. $\omega \gg 1/\tau$

From Eqs. (16), (26), (30), and (31)

$$\vec{J}(\vec{r}, t) = \left(\frac{iq^2 n_0}{m^*\omega}\right)\vec{E}\, e^{-i\omega t} + \left(\frac{q^3 \tau n_0}{8m^{*2}\omega^3}\right)\frac{\nabla_r m^*}{m^*} \times [4\omega\vec{E}\cdot\vec{E}^* - (i/\tau)\vec{E}\circ\vec{E}\, e^{-2i\omega t}]\ . \quad (36)$$

We therefore have here a second-order electric polarization $\vec{P}(\vec{r}, t)$ oscillating with frequency 2ω:

$$\vec{P}(\vec{r}, t) = \chi(\vec{r})\vec{E}\vec{E}\, e^{-2i\omega t}\ , \quad (37)$$

where

$$\chi(\vec{r})\vec{E}\vec{E} = \left(\frac{q^3 n_0}{16m^{*2}\omega^4}\right)\vec{E}^2\ \frac{\nabla_r m^*}{m^*}\ . \quad (38)$$

Let us put $n_0 \approx 3\times 10^{17}\ \mathrm{cm^{-3}}$, $m^* \approx 0.02 m_0$ and $|\nabla_r m^*|/m^* \approx 10^4\ \mathrm{cm^{-1}}$, corresponding roughly to n-type $Hg_{1-x}Cd_xTe$ with $x \approx \frac{1}{4}$ at the point in question but changing from 0 to 1 over a distance of about 20 μm. For the wavelength of the CO_2 laser (10.6 μm), χ is approximately 6×10^{-8} esu, i.e., of the order of nonlinear susceptibilities observed in homogeneous materials. For lower frequencies, the above effect will dominate other mechanisms of second-harmonic generation.

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Note added in proof. The Drude approach was also used by B. Lax [*Proceedings of the International Conference on the Physics and Chemistry of Semiconductor Heterojunctions and Layer Structures* (Akadémai Kaidó, Budapest, 1971), Vol. I, p. 63].

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