Bulk electroluminescence related to the photovoltaic effect

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An analysis is made of the phenomena related to the photovoltaic effect by universal thermodynamic relationships. It is shown that the inverse photovoltaic effect represents nonequilibrium generation (or absorption) of photons proportional to an external electric field. The contribution of these phenomena to the static conductivity is discussed.

The photovoltaic effect,[1] representing the appearance of a constant electric current in homogeneous crystals under the influence of homogeneous illumination, has been observed and investigated on many occasions.[1–3] Satisfactory microscopic models of this effect have been proposed. However, the phenomena linked to the photovoltaic effect by universal thermodynamic relationships have not hitherto been considered and they will be discussed below.

Nonlinear responses of a quantum system to an external force, changes in mean-square fluctuations in the first order in respect of the external force, and irreducible averages of three quantities in a thermodynamic equilibrium state of a system are not independent quantities. In particular, a change in the correlation function of the current under the action of an alternating electric field can be expressed in terms of the corresponding nonlinear susceptibilities:

$$\delta\langle[j^\beta(\omega_2)j^\gamma(\omega_3)]_+\rangle=K^{\beta\gamma,\alpha}(\omega_2,\omega_3)E^\alpha(\omega_2+\omega_3),$$
$$\delta j^\alpha(\omega_2+\omega_3)=X^{\alpha,\beta\gamma}(\omega_2,\omega_3)E^\beta(\omega_2)E^\gamma(\omega_3)(-\omega_2\omega_3)^{-1},$$
$$K^{\beta\gamma,\alpha}(\omega_2,\omega_3)=(\omega_2+\omega_3)^{-1}\Big\{\mathrm{cth}\frac{\omega_3\hbar}{2T}X^{\beta,\alpha\gamma}(-\omega_2-\omega_3,\omega_3)$$
$$+\mathrm{cth}\frac{\omega_2\hbar}{2T}X^{\gamma,\beta\alpha}(\omega_2,-\omega_2-\omega_3)$$
$$-\left(\mathrm{cth}\frac{\omega_2\hbar}{2T}+\mathrm{cth}\frac{\omega_3\hbar}{2T}\right)X^{\alpha,\beta\gamma}(-\omega_2,-\omega_3)\Big\},\tag{1}$$
$$\omega_1+\omega_2+\omega_3=0.$$

The validity of the above relationships can be demonstrated by a direct comparison of the expressions for these quantities in terms of the matrix elements of the current operator and energy levels of a quantum system, as well as by analytic continuation of the appropriate relationships obtained by the Matsubara diagram technique. Going to the limit $\omega_1\to0$, we obtain the change in the correlation function of the currents proportional to a static external electric field:

$$K^{\beta\gamma,\alpha}=\frac{i\hbar\omega^2}{4\pi}\mathrm{cth}\frac{\omega\hbar}{2T}\left[\frac{\partial}{\partial E^\alpha}(\varepsilon^{\beta\gamma}-\varepsilon^{\gamma\beta*})\right]$$
$$-\frac{\hbar^2\omega^2}{2T}\beta^{\alpha,\beta\gamma}(\omega)\,\mathrm{sh}^{-2}\frac{\omega\hbar}{2T}.\tag{2}$$

The first two terms in the above expression appear because of a change in the permittivity in an electric field (electrooptic effect), whereas the third is related directly to the photovoltaic effect coefficient[1]:

$$j^\alpha=\beta^{\alpha,\beta\gamma}(\omega)E^\beta(\omega)E^{\gamma*}(\omega).$$

If the absorption coefficient of light of a given material is less than the reciprocal of the wavelength, it is possible to use the kinetic equation for photons. Expressing the change in the number of photons per unit time in terms of the correlation function of the currents, we obtain

$$\frac{\partial N_k}{\partial t}=\frac{1}{\tau_k}(N_k{}^0-N_k)+\left(\frac{\partial N_k}{\partial t}\right)_0,$$
$$\left(\frac{\partial N_k}{\partial t}\right)_0=-2\pi\frac{\hbar\omega_k}{T}\mathrm{sh}^{-2}\frac{\omega_k\hbar}{2T}\beta^{\gamma,\alpha\beta}(\omega_k)e_k{}^\alpha e_k{}^{\beta*}E^\gamma,\tag{3}$$

where e_k^α is the photon polarization vector. The first two terms in Eq. (2) are included in $\tau_k^{-1}\sim\mathrm{Im}\varepsilon$. An allowance for these terms gives rise to a correction to the absorption coefficient and this correction is proportional to the field and not to the photon distribution function. The third term in Eq. (2) describes nonequilibrium generation and absorption of photons under the influence of a static electric field. It should be stressed that this effect is due to the absence of an equilibrium in a sample, i.e., it is connected with the flow of an electric current. If in the presence of an electric field an equilibrium is established in a sample and an inhomogeneous distribution of the charge density creates diffusion currents compensating the ohmic current, this results in compensation of nonequilibrium generation (absorption) referred to above. Usually electroluminescence is the term used for the generation of photons of visible light when a current is flowing through a sample and such generation is attributed to the presence of inhomogeneities.[4] The effect described by the system (3) can be called electroluminescence, bearing in mind however the arbitrary nature of the sign of $(\delta N/\delta t)_0$ and the circumstance that the generation and absorption occur in a homogeneous sample. If before the application of a field the sample is in equilibrium with external thermal radiation and there are no photon fluxes, then steady-state radiation fluxes appear in the sample and in the surrounding space after the application of the field; the directions of these fluxes are reversed on reversal of the sign of the field. A radiation detector with the same temperature as the sample reacts only to these fluxes.

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Unfortunately, the characteristics of such electroluminescence cannot be determined from the currently available experimental data because measurements of the photovoltaic effect are carried out at photon energies which are at least an order of magnitude higher than the thermal energy and the contribution of such frequencies to the integral electroluminescence is exponentially small. Therefore, in our estimates we shall use a specific theoretical model of the photovoltaic effect.

Let us assume that in the case of an intrinsic semiconductor we have $\omega_{pl} \ll 1/\tau \ll T$, where τ is the carrier momentum relaxation time. The dominant mechanism of the photovoltaic effect at frequencies $\omega \lesssim T$ is naturally the intraband effect.[1,5] In this case the photovoltaic current appears because of asymmetric scattering of carriers with a distribution function which is perturbed by an alternating electric field. An estimate of the photovoltaic tensor given in Ref. 1

$$\beta \sim \xi e^3 n_0 v_T^{-1} m^{-2} \omega^{-2}$$

(n_0, m, and v_T are, respectively, the density, mass, and typical velocity of carriers; $\xi < 1$ is a dimensionless parameter representing the ratio of the probabilities of asymmetric and symmetric scattering) is valid in the frequency range $1/\tau \ll \omega \ll T$ and is independent of the specific symmetry of a noncentrosymmetric crystal. We shall estimate the energy flux from an opaque sample, i.e., a sample with the smallest size much greater than the reciprocal of the absorption coefficient. We shall then assume that the absorption is mainly due to carriers:

$$J \sim J_0 (v_{\mathrm{dr}}/v_T) \varepsilon^{-2}, \quad J_0 = \sigma_0 T^4, \quad \xi \sim 1, \tag{4}$$

where σ_0 is the Stefan-Boltzmann constant and v_{dr} is the drift velocity of carriers. A flux of this intensity should be readily detectable in experiments.

We shall briefly consider characteristic symmetric realizations of the effect. In a material with the pyroelectric symmetry we have

$$\partial N/\partial t \sim \mathbf{PE}$$

(**P** is a selected vector) and the total number of photons generated per unti volume differs from zero. In the case of nonpyroelectric piezoelectrics we have

$$\partial N/\partial t \sim k^\alpha k^\beta \varkappa^{\alpha\beta\gamma} E^\gamma, \quad \varkappa^{\alpha\alpha\gamma} \equiv 0$$

and the total number of photons generated by unit volume is zero. The magnitude and the sign of the flux which appears on any face of a crystal depends considerably on the orientation of this face relative to the symmetry axis of a crystal. The sum of the flux intensities from three mutually perpendicular faces of a crystal is zero. In the case of a crystal of class O, we find that

$$\partial N/\partial t \sim \mathbf{kE}$$

and the sign of $\delta N/\delta t$ is different for right- and left-hand polarized waves. The energy flux across the crystal surface differs from zero only because of the natural optical activity of the crystal and it is small in terms of $Ta_B/\hbar c$ compared with Eq. (4), but its compensation is due to the addition of two oppositely directed fluxes with different polarizations.

The density of the photovoltaic current is expressed in terms of the occupation numbers of the photon states N_k:

$$j^\gamma = \int \frac{d^3k}{(2\pi)^3} \beta^{\gamma,\alpha\beta}(\omega) \cdot 2\pi\hbar\omega_k e_k^\alpha e_k^{*\beta} (N_k - N_k^0). \tag{5}$$

In this expression in addition to the terms proportional to N_k describing the photovoltaic effect and appearing because of the asymmetry of the photon absorption processes there is a term independent of N_k, which is due to the asymmetry of the emission processes. The magnitude of this term can be found noting that Eq. (5) represents an expression for the second-order response of the current to an electromagnetic field, i.e., it should contain only terms of the first and zeroth power in N_k, and in a state of equilibrium of the electron system with thermal radiation there should be no current. Therefore, in the case of ferroelectric crystals we can expect an effect similar to the pyroelectric effect and also related directly to the photovoltaic effect. If we abruptly change the temperature of external thermal radiation, then the temperature of a crystal transparent at frequencies $\sim T/\hbar$ changes slowly under the influence of such radiation, whereas the photon distribution corresponding to the temperature of the external radiation is established much faster. Therefore, according to Eq. (5), a current flows through the sample. Estimating it subject to the above assumptions, we obtain

$$j \sim \frac{C}{T}(T_{\mathrm{ext}} - T), \quad \frac{C}{T} \sim \frac{e n_0 v_T}{T}\left(\frac{e^2}{\hbar c}\right)\left(\frac{T}{mc^2}\right)\varepsilon^{3/2},$$

$$\frac{C}{\sigma T} \sim \frac{v_T}{\mu T}\frac{e^2}{\hbar c}\frac{T}{mc^2}\varepsilon^{3/2} \sim 10^{-13} \quad \frac{\mathrm{V}}{\mathrm{cm}\cdot\mathrm{K}},$$

where T_{ext} is the temperature of the external radiation. It should be pointed out that knowing the dependence of j on the temperature of the external radiation, we can find the frequency dependence of the photovoltaic effect in the infrared range. In the limit $T \to T_{\mathrm{ext}}$ the current j and the change in the energy ε per unit volume are related very simply:

$$\frac{\partial \varepsilon}{\partial t} = -T\big|_{T_{\mathrm{ext}} \to T} \frac{\partial \mathbf{j}}{\partial T_{\mathrm{ext}}} \mathbf{E}.$$

This relationship can be obtained directly from thermodynamics and the analysis is similar to a thermodynamic analysis of the Peltier effect.

The photons emitted in the electroluminescence process also create a current, in accordance with Eq. (5). This mechanism contributes to the static conductivity. We find from Eqs. (5) and (3) that

$$\Delta\sigma^{\alpha\beta} = \int \frac{d^3k}{2\pi} \beta^{\alpha,\gamma\delta}(\omega_k) \beta^{\beta,\varepsilon,\zeta}(\omega_k) e^\gamma e^\varepsilon e^{\delta*} e^{\zeta*} \frac{(\hbar\omega_k)^2}{T}$$

$$\times \operatorname{sh}^{-2}\left(\frac{\omega_k \hbar}{2T}\right) \tau_k.$$

Estimating this expression under the assumptions made above, we obtain

$$\Delta\sigma/\sigma \sim \xi^2 (e^2/\hbar c)(v_T/c)^2 \varepsilon^{5/2}.$$

The mechanism of the photovoltaic effect associated with the asymmetry of the impurity-band transitions[6] gives rise to a correction of the conductivity of the same order of magnitude. Then, the activation factor in Eq. (3) cancels out to a factor which occurs in the conductivity via the density of carriers in a band.

This contribution to the conductivity is characterized by a strong spatial dispersion at distances of the order of the reciprocal of the absorption coefficient of thermal photons. At these distances we can observe size effects in the conductivity of such conductors. This contribution makes the conductivity dependent on whether the conductor is surrounded by reflecting or absorbing surfaces. If two noncentrosymmetric conductors are separate and insulated, but radiation can be exchanged between them, then the application of an *emf* to one of the conductors gives rise to a current in the other conductor. These effects make it possible to identify the above contribution against the background of the conventional conductivity, in spite of the smallness of the latter.

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