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# THEORY OF PHOTOGALVANIC EFFECT IN FERROELECTRICS

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A summary of the author's basic results on the theory of the photogalvanic effect (PGE) is presented. This effect is the production of current in homogeneous crystals under homogeneous illumination, without an electric field.

Photocurrent connected with uniform illumination has been reported by different authors,[1,2,3] and was correctly interpreted by A. M. Glass *et al.*[1] The essence of this new phenomenon lies in the generation of a constant electric current by light due to the crystal symmetry (for instance the presence of polar axis).

Thus the PGE is completely different from a wide number of conventional effects caused by crystal inhomogeneity on non-uniform illumination etc., and also from the photon drag effect. As shown from Glass's experiments the PGE is of great magnitude. In particular the illumination of homogeneous crystals provides internal fields of about $10^4$ to $10^5$ V/CM.

Phenomenological expression for photogalvanic current is given by

$$j_l^p = \beta_{lkL}(\omega)\,(E_k E_L^* + c.c.) \tag{1}$$

where $\beta_{lkL}$ is photogalvanic tensor, $\omega$ is the light frequency.

The photogalvanic tensor $\beta_{lkL}$ is different from zero, for asymmetrical crystals.[4] In the case of crystal asymmetry it can be characterized by one polar axis $\beta_{lkL}$ and can be reduced to linear combination by three scalar functions

$$\beta_{lkL} = \alpha c_l \delta_{kL} + \beta c_l c_k c_L + \gamma(\delta_{lk} c_L + \delta_{iL} c_k) \tag{2}$$

where $c$ is the unit vector along the polar axis. The relations (1) and (2) show that $j^p$ the direction and magnitude of $j^p$ depend on polarization and light frequency.

The theory of PGE in semiconductors suggested in Ref. 4 is not correct since it does not respect the time reflection invariance.

Below we shall give a brief account of the main results of PGE theory partially published in previous papers.[5–9] It contains an explanation of the effect, the study of microscopic mechanism and the influence of PGE on macroscopic properties of the crystal.

The PGE theory is based on the kinetic equation for the electron (hole) distribution function

$$\partial f_k/\partial t = I_k^i - I_k^r + I_k^{coll} \tag{3}$$

where $I_k^{i,r,coll}$ are the velocity of the ionization, recombination and collision with impurities and phonons. Let the right part of (3) have the asymmetrical contribution $I_k^{as}(f_k)$ with the property expressed by

$$I_k^{as}(f_k^s) = -I_{-k}^{as}(f_k^s); f_k^s = f_{-k}^s \tag{4}$$

then the stationary solution (3) cannot be purely symmetrical, it should have the asymmetrical contribution $f_k^{as} = -f_{-k}^{as}$ leading to the current. It should be noted also that it is valid in the case of non-equilibrium situation. If the electron and phonon distribution functions are in equilibrium, $I_k^{as}(f_k)$ is always zero. The reason for $I_k^{as}(f_k)$ being zero at equilibrium is not trivial, since detailed balance of $I_k^{as}$ is not inherent and there is a compensating contribution to $I_k^{as}$. Different PGE mechanisms are correlated with different contributions to the asymmetrical collision integral. We have taken into account the asymmetry of the ionization and the recombination of the electrons, and that of the scattering at impurities and phonons. $I_k^{i,r}$ asymmetry is due to the distortion of the conduction electron Bloch function around the impurity. For dipole

impurities and small $k$ $I_k^{as}$ is simply expressed by the symmetrical collision member

$$(I_k^i)^{as} = lm(d \cdot k)/\pi k(I_k^i)^s \tag{5}$$

where $d$ is the dipole impurity moment, $m$ is the electron mass.

The equality $(I_k^i)^{as} = -(I_k^r)^{as}$, results from the invariance with respect to the time reflection. Therefore, asymmetrical contributions from ionization and recombination are not equal to zero at the thermodynamical equilibrium. Thus, models in which only ionization and recombinations are asymmetrical appears to be incorrect. They lead to a current in equilibrium. If we consider the asymmetry of ionization and recombination it is essential to take into account the asymmetry of the scattering at ionized impurities.

The effect of asymmetric scattering turns out to be equivalent to the sign change $(I_k^r)^{as}$ in Eq. (3)[6] otherwise there will be no thermodynamical equilibrium.

The current value can be expressed from (3) and (5). In the case of impurities in the $P$ state we have

$$j^p = \frac{2}{3\pi^2}\frac{l^2 k_0}{h\omega}\frac{\alpha J d}{\Gamma_l h}(1 - (8/\pi)^{1/2})\, c \tag{6}$$

where $\alpha$ is absorption coefficient, $J$ is the light intensity, $\omega$ is its frequency, $k_o$, $k_T$ are momentum of excitation and thermal momentum, $\Gamma_l^{-1}$ is the electronic isotropization time.

The contribution to the ionization and recombination current may be observed from the formula (6). A sign change of $j^p$ with light frequency was observed experimentally.[3] The low temperature photocurrent variation is determined by the temperature dependence of the $\Gamma_l^{-1} \sim a + \beta T^{+3}$. The $T^{-3}$ power law was observed experimentally.[10] For typical parameters Eq. (6) gives a current value of $j^p \sim (10^{-8}$ to $10^{-9})J$(A/Wcm).

For the shallow impurity centres the theory PGE was suggested in Ref. 7.

In undoped crystals the PGE may be connected to the asymmetrical electron–phonon interaction during band–band transitions.[8] Thus the current magnitude tends to differ from the calculated value in Eq. (6) by the factor $T/Mc_s^2$, where $M$ is the unit cell mass, $c_s$ is the sound velocity. The PGE seems to be due to the asymmetry of electron scattering at impurities and phonons.[6,8] However these contributions to the current are lower in Eq. (6) by the factor $Na^3k^2/m\Gamma_l$ and $(T/Mc_s^2)^2$, where $N$ and $a$ are concentration and size of the impurity.

In the case of large asymmetry, matrix element of dipole momentum for band–band transition, the Coulomb interaction between the electron and the hole is the basic effect which determined the asymmetry. The photocurrent has the same order of magnitude as in Eq. (6). This question was discussed in more detail by M. V. Entin *et al.*[11] The high photocurrent value was observed in undoped crystals in Ref. 10.

The influence of a magnetic field on PGE has also been investigated[9] and is characterized by supplementary contributions to $j^p$. One of them (the Hall contribution) has an order of magnitude $j^H \sim l(c \times H)/mc\Gamma_l$, the other is caused by the influence of magnetic field on ionization and recombination. Provided that impurities are paramagnetic and taking into account the spin dependence of the electron dispersion law $\varepsilon_k$,

$$\varepsilon_k = k^2/2m + \lambda[c \times k] \cdot s \tag{7}$$

The current contribution has the order of magnitude $j^s \sim (Z\alpha)^2(lH/mcT)$, where $\alpha$ is fine structure constant. At low temperature $j^s$ is greater than $j^H$.

Macroscopic properties of the crystals are greatly affected by the PGE. Its influence on optical damage has been studied before.[1] Another interesting effect is PGE influence on phase transitions. In fact with illuminated ferroelectric crystals the internal field $E^p$ induced by PGE is given by

$$j = j^p - \sigma E^p = 0 \tag{8}$$

where $\sigma$ is the crystal conductivity. Since $E^p$ is proportional to $P$, the PGE brings about an additional $\delta F \sim P^2$ to the free energy, which in turn results in additional shift of the phase transition point. This shift is estimated to be about a few degrees.

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