The Anomalous Photovoltaic Effect in Ferro and Piezoelectric Semiconductors and its Application for Optical Storage by Holography

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1. Introduction

The effect of nonequilibrium conductivity on the birefringence of ferro and piezoelectric semiconductors is referred to as photorefractive effect (PR effect) in the literature and has been widely used for recording volume holograms. In practice, the PR effect consists in the following. As a result of local illumination of a ferroelectric or piezoelectric crystal with an intense transient light (focused laser beam) a reversible change in birefringence occurs in the crystal volume inside the light beam. The extent of this change may be as great as $10^{-4} - 10^{-3}$ for some pyroelectrics (LiNbO$_3$, LiTaO$_3$) and the storage time of the effect varies over a very wide range, from milliseconds for BaTiO$_3$ to months for LiNbO$_3$. Hologram recording is accomplished by means of volume modulation corresponding to that of the recording beams. The recording resolution is extremely high $10^3 - 10^4$ lines/mm, which allows to reach the theoretical limits of three-dimensional storage density ($10^{12}$ bits/cm$^3$). On the contrary to the photographic layers the major advantage of this method of optical storage is the parallel processing, which includes write-in, read-out and erasure.

2. Photorefractive Effect in Ferroelectric Crystals

It may be shown that for ferro and piezoelectric materials the PR effect is mainly caused by anomalous photovoltaic effect (AP effect). When a homogeneous short-circuited ferroelectric or piezoelectric crystal is uniformly illuminated a stationary current $J$ passes through it. The photovoltaic current is directly proportional to the light intensity. The direction, the value and the sign of this photovoltaic current $J$ depend on the crystal symmetry and polarization of the light.

The photovoltaic current leads to the generation of the anomalously high photovoltages in the same direction. When measuring the photovoltage (in open circuit), a transitional photocurrent

$$ J^* = J + (\sigma_d + \sigma_{ph}) \frac{E}{l} $$

(1)

passes throughout the crystal in the definite direction. In (1) $E$ is the macroscopic electric field formed due to the charging of the crystal capacitance with the photovoltaic current $J$; $\sigma_d$ and $\sigma_{ph}$ are, respectively, the conductivity in darkness and under illumination. The photovoltage $V$ that appears in the crystal in this direction during Maxwellian relaxation time $\tau_{max}(J^* = 0)$ is

$$ V = E \frac{J}{\sigma_d + \sigma_{ph}} l $$

(2)

where $l$ is the distance between the electrodes.
According to (2) $V$ is directly proportional to the interelectrode distance and is not limited by the energy gap. Thus a macroscopic field $\vec{E}$ is induced in the crystal within the exposure time $t \geq \tau_{\text{max}}$. Because of the linear electro-optic effect the field $\vec{E}$ leads to a PR effect

$$\Delta n_i = \frac{1}{2} n_i^2 r_{ij} \vec{E}$$

where $r_{ij}$ are the electrooptic coefficients, $n_i$ are the refractive indices of the ordinary ($n_o$) and extraordinary ($n_e$) beams. The electrooptic equation (3) is recorded in the main crystallographic axes. After illumination the field $\vec{E}$ exists in the crystal for a long time due to the trapping of nonequilibrium electrons and holes. This trapping mechanism is responsible for the optical storage. For example LiNbO$_3$: Fe has localized Fe$^{3+}$ and Fe$^{2+}$ levels with Fe$^{2+}$ being a donor, while Fe$^{3+}$ is a trap. The PR effect in LiNbO$_3$: Fe is attributed to the photoexcitation of electrons from Fe$^{2+}$ levels into the conduction band, after which the electrons are captured by Fe$^{3+}$ traps. The erasure may be performed by annealing of the crystal at 170°C. There are the other methods of erasure (see below).

With AP effect in LiNbO$_3$: Fe, KDP and other high-resistance ferroelectrics the field $\vec{E}$ may reach values $\sim 10^4 \text{V cm}^{-1}$ (see below). The values of the fields $\vec{E}$ are in good agreement with the saturation values of $\Delta n_i$ and the electrooptic coefficients. The temperature dependence of $\Delta n_i$ correlates with that of the field $\vec{E}$ (2), caused mainly by the temperature dependence of $\sigma_{ph}$. The kinetics of the PR effect (including the dark relaxation) and the dependence of $\Delta n_i$ on the light intensity $I$ are determined by the Maxwellian relaxation and the dependence $\vec{E} = \vec{E}(I)$. At high intensities, when $\sigma_{ph} \gg \sigma_d$, $\vec{E}$ is independent of the light intensity (because $J, \sigma_{ph} \sim I$), which corresponds to the saturation of PR effect, when $\Delta n_i$ no longer varies with $I$. Fig. 1 shows the AP effect in LiNbO$_3$: Fe at illumination in Fe$^{3+}$ band ($\lambda = 488 \text{nm}$). The dependence of $\Delta (n_e - n_o)$ as a function of light intensity reveals the saturation at $\Delta n \approx 10^{-2}$. Substituting in (3) the values of $\Delta n \approx 10^{-2}$, $n_o \approx 2.28$, $n_e \approx 2.22$, $r_{33} \approx 8.6 \times 10^{-10} \text{cm V}^{-1}$, $r_{33} \approx 31 \times 10^{-10} \text{cm V}^{-1}$, we obtain $\vec{E} \approx 10^4 \text{V cm}^{-1}$, which is in a good agreement with the independent measurement of $\vec{E}$ in LiNbO$_3$: Fe (Fig. 4). The PR effect is observed in a large number of ferro and piezoelectric materials, including the ferroelectric ceramics.

3. The Anomalous Photovoltaic Effect in Ferro and Piezoelectric Crystals

The anomalous photovoltaic effect in the crystals and materials without the symmetry center is described by the photovoltaic tensor $\alpha_{ijk}$ of the third rank.40
where \( J_i \) is anomalous photovoltaic current and \( E_j, E_k \) are the projections of the light polarization vector (for the linear polarized light). The photovoltaic tensor \( \alpha_{ijk} \) is different from zero in crystals and textures without symmetry center. The AP effect was first observed for \( \text{LiNbO}_3 : \text{Fe} \) and a ferroelectric solid solution \( \text{Ba}_x\text{Sr}_{1-x}\text{Nb}_2\text{O}_6 \)\(^4,5\). Now AP effect is investigated in a great number of ferro and piezoelectrics\(^3\).

Fig. 2 shows for \( \text{LiNbO}_3 : \text{Fe} \) the experimental dependence of the photovoltaic current \( J \) on the direction of the light polarization plane and the light. Let us denote by \( J_z, J_y, J_x \) (\( z \) is the direction of the spontaneous polarization) the projections of the photovoltaic current and by \( \beta \) the angle between the light polarization plane and the corresponding crystal axis (Fig. 2). Taking into account the point group of \( \text{LiNbO}_3 \) (3m) and the different from zero components of the photovoltaic tensor \( \alpha_{ijk} \), we obtain from (4) the expressions for \( J_z, J_y, J_x \) (the direction of the linear polarized light propagation is shown in Fig. 2a, b, c)

\[
J_z = \alpha_{311} + (\alpha_{33} - \alpha_{31}) I \cos^2 \beta \\
J_y = -\alpha_{211} I \cos 2\beta \\
J_x = \alpha_{151} I \sin 2\beta
\]

where \( I \) is light intensity. The experimental dependences \( J_z(\beta), J_y(\beta) \) and \( J_x(\beta) \) are in good agreement with (5)—(7). The amplitude of the field \( \vec{E}_y = \frac{J_y}{\sigma_d + \sigma_{ph}} = 200 \text{ V cm}^{-1} \) was in Ref. 7 by one order of magnitude less than \( \vec{E}_z = \frac{J_z}{\sigma_d + \sigma_{ph}} \).

This transverse field \( \vec{E}_y \) leads to the PR effect in \( z \) direction \( \Delta n \approx 10^{-6} \), which sign depends on \( \beta \). The comparison of the experimental curves of Fig. 2 with (5)—(7) gives the photovoltaic coefficient values \( \kappa_{ijk} = \frac{1}{\alpha^*} \alpha_{ijk} \), where \( \alpha^* \) is absorption coefficient (in \( \text{LiNbO}_3 : \text{Fe} \) \( \alpha^* \approx 4.5 \text{ cm}^{-1} \) at \( \lambda = 500 \text{ nm} \)). Thus were obtained in Ref. 7

\[
k_{31} \approx 1.4 \times 10^{-9} \; ; \; k_{33} \approx 1.5 \times 10^{-9} \; ; \; k_{22} \approx 0.5 \times 10^{-10} \text{ A cm}^{-1} \text{ (w)}^{-1}.
\]

For all ferroelectrics there is a component in photovoltaic current \( J_z \), which does not depend on light polarization (see (5)). On the contrary in piezoelectrics AP effect can be observed only in polarized light. For example cubic piezoelectric \( \text{ZnS} \) (the point group 3/2) possesses of only one different from zero component of photovoltaic tensor \( \alpha_{14} \). The photovoltaic current \( J_z \) in the direction of the axes of the fourth order is given by the relation

\[
J_z = \frac{1}{2} \alpha^* k_{141} I \sin 2\beta
\]

Fig. 3 shows the experimental dependence of \( J_z \) on \( \beta \), which coincides with (8) for \( k_{14} \approx 5 \times 10^{-9} \text{ A cm}^{-1} \text{ (w)}^{-1} \). The corresponding field \( \vec{E}_z = \frac{J_z}{\sigma_d + \sigma_{ph}} = 40 \text{ V cm}^{-1} \). Therefore in high-resistance \( \text{ZnS} \) crystals we can observe PR effect, which sign and amplitude depend on the orientation of the light polarization plane.
The anomalous photovoltaic effect in ferro and piezoelectric semiconductors

The photovoltaic field $\vec{E}$ can be obtained from current-voltage characteristics of ferro or piezoelectrics. Fig. 4 gives the current-voltage characteristics of the photocurrent in LiNbO$_3$:Fe in $z$-direction. From (1) and (2), the steady state component of the photovoltaic current $J_z$ is measured by intercepts on the current axis, and the photovoltage $V$ or the field $\vec{E}$ by intercepts on the voltage axis. It can be seen from Fig. 4 that for light intensities $I$ in the range $10^{-1}$ to $10^{-10}$ W cm$^{-2}$, the photovoltaic current $J_z$ varies between $10^{-8}$ and $10^{-10}$ A cm$^{-2}$, which introduces a photovoltage $10^3$ to $10^4$ volts in a crystal of length $l=1$ cm.

Fig. 5 exhibits the spectral distribution of the steady state component of the photovoltaic current $J_z$ in LiNbO$_3$:Fe (curve 1) obtained in Ref. 5 and later confirmed in Ref. 9 (curve 2, Fig. 5). The AP effect in ferro or piezoelectrics may reveal intrinsic or extrinsic nature. Here we shall only note that for LiNbO$_3$:Fe this distribution shows a maximum near $\lambda=400$ nm, which corresponds to the Fe$^{2+}$ band and is not visible (or only slightly visible) in the photoconduction spectrum (curve 3, Fig. 5).

The common microscopic theory of AP effect photoferroelectrics was developed in Ref. 10. It was shown in Ref. 10 that a photovoltaic current is induced in a photoferroelectric not only by asymmetry of the impurity centers responsible for the generation and recombination of nonequilibrium carriers, but also by asymmetry of scattering on impurities and phonons. Asymmetry of elementary electron processes in a photoferrolectric is, in turn, associated with the asymmetric shape of the potential of impurity centers and their identical orientation in the lattice with respect to the direction of the spontaneous polarization. The variation in the concentration and distribution of nonequilibrium electrons in the conduction band is described by the kinetic equation for the distribution function $f_k$:

$$f_k = f_k(\lambda, T)$$
where $I_\text{ex}$ and $I_\text{rec}$ are the electron excitation and recombination rates, respectively, and $I_{\text{imp}}$ and $I_{\text{phon}}$ are the numbers of collisions of an electron with impurities and phonons, respectively, per unit time. If the distribution function is symmetric and satisfied the condition $f_k = f_{-k}$, there is no current in the crystal. If the right-hand side of the kinetic equation contains an asymmetric term satisfying the condition $l_k = -l_{-k}$, then the stationary solution of the equation also contains an asymmetric term, i.e. the asymmetric part of the distribution function $f_{a} = -f_{-a}$. The presence of the asymmetric distribution function results in a stationary current of

$$J = 2 \frac{q}{h} \int f_{a} d\epsilon.$$

Not only excitation and recombination, but also scattering on a dipole center with an asymmetric potential is asymmetric and, hence, leads to the appearance of an asymmetric part in the distribution function, i.e. to a stationary current. It is important to recall that up to now we have always dealt with the nonequilibrium distribution function. In Ref. 10 it was shown rigorously that for equilibrium electrons $f_{a} = 0$ and, consequently, the equilibrium (dark) current is equal to zero. This corresponds to the fact that in the equilibrium case the current associated with the excitation of electrons from asymmetric centers is fully offset by the current due to electron recombination and scattering. This theory thus leads both to an extrinsic and intrinsic photovoltaic current.

4. Photorefractive Holographic Recording

Let us consider here the recording of an elementary hologram on the basis of the PR effect. Suppose the recording medium is a photosensitive ferro or piezoelectric crystal, which is placed in the plane of intersection of two coherent light beams (the recording and the reference one), as shown in Fig. 6. Let the bisector of both beams be perpendicular to the crystal surface. The photovoltaic current $J_z$ generates the field $E_z$ in the direction of the polar axes $z$. Assuming the light intensity $I_0$ in the two beams to be equal, let us write down the intensity distribution along $z$ axis as

$$I(z) = 2I_0(1 + \cos k z),$$

where the spatial frequency of the interference strips is

$$k = 2 \frac{2\pi}{\lambda} \sin \theta.$$

Here $\lambda$ is the light wavelength in the crystal, and $\theta$ is the half-angle between the beams. The light absorption results in the generation of the photovoltaic current $J_z(\epsilon)$ and corresponding field $E_z(\epsilon)$, which is given by (2). Assuming that the light intensity $I_0$ is low, i.e. $\sigma_{ph} \ll \sigma_d$, we write down the distribution of the field $E_z$ along $z$ axis in the form

$$E_z = 2 \frac{\alpha_z}{\sigma_d} I_0(1 + \cos k z)$$

where $\alpha_z$ is the component of the photovoltaic tensor (4). The distribution of the PR effect in the $z$ direction is determined by (11) by electrooptic equation (3). For instance, for LiNbO3,
when the optical axis coincides with the \( z \) axis, we have, according to (3),

\[
\Delta n_i = (n_e^2 r_{33} - n_e^2 r_{31}) \frac{\alpha_z}{\sigma_d} I_0 (1 + \cos k |z|) \tag{12}
\]

where \( \Delta n_i = \Delta (n_e - n_0) \). Thus, there is the PR effect distribution in the \( z \) direction which reproduces the initial light intensity distribution and represent a recorded elementary phase hologram. The wave signal recorded on the basis of the PR effect can be reconstructed from the elementary hologram by illuminating the crystal with a uniform light beam of wavelength of \( \lambda_1 \) at an angle of \( \theta_1 \). The diffraction maximum takes place with \( \theta_1 \) and \( \lambda \) satisfy the Bragg condition

\[
\lambda_1 = \frac{2\pi}{|k| \sin \theta_1} \tag{13}
\]

A comparison of (13) and (10) shows that if the recording and reconstruction of a hologram is accomplished with light of the same wavelength, then \( \theta = \theta_1 \).

We have considered the recording of an elementary hologram corresponding to a single plane wave. But PR effect can be used for recording an arbitrary hologram corresponding to an arbitrary wave front.

Until now we have considered the PR effect and holographic recording of an extrinsic or intrinsic nature, when electron excitation occurred on absorbtion of a single photon.

Photorefractive recording by multiphoton excitation has a number of advantages over the case of single-photon absorption. Firstly, the sensitivity of the photorefractive material shifts into the long-wave region of the spectrum. Secondly, investigation into the mechanism of the intrinsic PR effect in broad-band photoferroelectrics is facilitated. Thirdly—and this is particularly important for the application of the PR effect in holography—the reconstruction of holograms in multiphoton photorefractive recording does not result in their degradation. We illustrate this last feature by the diagram in Fig. 7. Figure 7a reproduces recording of an elementary hologram with the aid of two coherent light beams of frequency \( \omega_1 \), as shown earlier in Fig. 6. The frequency \( \omega_1 \), however, is selected so that the energy \( h \omega_1 \) is insufficient for ionizing the impurity centers in a photoferroelectric (the impurity PR effect is considered for definiteness). Therefore, the surface of the photoferroelectric is illuminated simultaneously and uniformly with a light of frequency \( \omega_2 \) so that the twophoton absorption could lead to the ionization of the centers and hence to the PR effect. Since the illumination of the surface with a light of frequency \( \omega_2 \) is uniform, the elementary hologram reproduces the interference of the light beams of frequency \( \omega_1 \), as in Fig. 6. It can be seen from Fig. 7b that the reconstruction of the recorded hologram is achieved by illuminating the crystal with a coherent light beam of frequency \( \omega_1 \) at the Bragg angle (13). But this single-photon reconstruction does not result in ionization of the centers and in the degradation of the hologram. Therefore, the reconstruction of a hologram recorded in a photoferroelectric on two-photon excitation may be repeated many times without any perceptible damage. The erasure of a recorded hologram is achieved by uniform illumination of the surface with two light beams of frequencies \( \omega_1 \) and \( \omega_2 \), i.e. on uniform two-photon excitation (Fig. 7c).

The same advantage gives the application of the photopiezoelectrics. In this case the recording is performed by two coherent light beams with

\[
\text{Fig. 7 Multiphoton photorefractive recording. } \tag{11)}
\]

\begin{itemize}
  \item (a) recording of elementary hologram
  \item (b) reconstruction
  \item (c) erasure
\end{itemize}

\[\omega_1\]

\[\omega_2\]
polarization, which corresponds to the photovoltaic current \( J_z \) and field \( E_z \) in \( z \) direction. The reconstruction of the recorded hologram is achieved by illuminating the crystal with a coherent light beam of the same frequency. The polarization of the beam, however, is chosen so that the illumination does not generate the photovoltaic current in \( z \) direction. The erasure of a recorded hologram is achieved by uniform illumination of the surface with the light beam of the previous polarization. Thus the processing, which includes the combination of the light beams with different polarization, permits to reconstruct a hologram recorded in a photopiezoelectric without any damage.

The sensitivity of the photorefractive recording can be defined as \( \frac{dn_i}{dw} \) where \( w \) is entire absorbed light energy\(^{12}\). For photoferroelectrics

\[
\frac{dn_i}{dw} = 2gP_0k
\]

where \( P_0 \) is the spontaneous polarization, \( k \) is the effective photovoltaic constant and \( g \) is electrooptic constant (\( g \approx 1 \text{ cm}^4 \text{ C}^{-2} \) for oxygen-octahedral ferroelectrics). Substituting in (14) the values of \( P_0 \approx 0.7 \text{ C} \cdot \text{m}^{-2} \), \( k \approx 1.0 \times 10^{-9} \text{ Acm(W)}^{-1} \) for 

LiNbO\(_3\): Fe, we find \( \frac{dn_i}{dw} \approx 7 \times 10^{-5} \text{ cm}^3 \text{ J}^{-1} \).

5. Conclusion

The AP effect in ferro and piezoelectrics determines the photorefractive effect in these materials. The photorefractive effect has been applied to three-dimensional phase holography, where some of these materials compete with silver halides and nonconventional photographic materials in resolution. The AP effect in ferro and piezoelectrics is capable of producing imagewise distributions of voltages sufficiently high to allow for conventional xerographic development. This application of AP effect was considered in Ref. 13.

References